

Variational determination of the two-particle density matrix: the case of doubly-occupied space

Variationele bepaling van de tweedeeltjesdichtheidsmatrix in het geval van de dubbel-bezette ruimte

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Dissertation submitted in fulfillment of the requirements for the degree of
Doctor (Ph.D.) in Science: Physics

Department of Physics and Astronomy
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Ghent University
Academic year 2014-2015





The computational resources (Stevin Supercomputer Infrastructure) and services used in this work were provided by the VSC (Flemish Supercomputer Center), funded by Ghent University, the Hercules Foundation and the Flemish Government - department EWI.



This research was conducted at the Center for Molecular Modeling.

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Samenvatting

Alle materie is opgebouwd uit atomen. Democritus had dit al in de 5^{de} eeuw v.Chr. gepostuleerd, maar hij kon dit natuurlijk niet bewijzen. De wereld van het atoom bleek echter moeilijk te doorgronden. Pas vanaf de 19^{de} eeuw kwam er echt schot in de zaak. Men ontdekte dat atomen niet ondeelbaar waren en vond het deeltje dat wij tegenwoordig kennen als het elektron. In het begin van de 20^{ste} eeuw schakelde de ontdekkingstocht een versnelling hoger. Men kwam tot de conclusie dat een atoom grotendeels leeg is maar wel een harde kern heeft waarrond er elektronen bewegen. Verschillende nieuwe modellen om het atoom te beschrijven werden ingevoerd en verbeterd. Een belangrijk doorbraak kwam toen men de deeltje-golf dualiteit ontdekte: een elektron kan zich zowel als een golf en als een deeltje gedragen. Via het golfkarakter kunnen typische golf fenomenen zoals diffractie en constructieve interferentie verklaard worden, terwijl het deeltjeskarakter de meer intuïtieve beschrijving van het elektron toelaat. Het hoogtepunt kwam met de formulering van de Schrödinger vergelijking: deze beschrijft een systeem van deeltjes die interageren met elkaar. In het geval van elektronen heb je paarsgewijze interactie via de Coulombkracht: elk elektron wordt afgestoten van alle andere elektronen maar aangetrokken door de kern. Via de Schrödinger vergelijking kun je bepalen wat de meest optimale toestand (de toestand met de laagste energie) is van het systeem.

Het Heisenberg onzekerheidsprincipe veranderde de interpretatie van de wereld van het atoom fundamenteel: de absolute zekerheden verdwenen en men werkt nu met kansen. Op elke meting die men doet zit er een onbepaalde factor die fundamenteel is en niet veroorzaakt wordt door het meettoestel. Enkel met herhaalde metingen kun je terug een vorm van zekerheid krijgen. Dit alles is wat nu gekend staat onder de naam kwantummechanica. Deze tak van de wetenschap beschrijft de wereld op kleine schaal: de effecten ervan zijn pas belangrijk op de nanoschaal maar kunnen toch macroscopisch gezien worden. De toestand van een systeem wordt beschreven door een golf functie en de bijhorende energie. De golf functie met de laagste energie geeft het meest stabiele systeem. De golf functie bevat alle informatie over het systeem. De energie kun je bijvoorbeeld gebruiken om te voorspellen of een chemische reactie zal doorgaan of niet (verlaagt de reactie de energie of niet?). Helaas kan enkel voor het meest simpele systeem, een waterstof atoom, de golf functie en bijhorende energie exact worden neergeschreven. Voor andere systemen nemen we onze toevlucht tot numerieke methoden en benaderingen. Het probleem is dat de golf functie slecht schaalt met de grootte van het systeem: de hoeveel rekenkracht die nodig is om de golf functie te bepalen stijgt heel erg sterk met de grootte van het systeem. Dit maakt dat het enkel voor kleine systemen mogelijk is om

de volledige oplossing te bepalen binnen een redelijke tijd. Om rond dit euvel te werken zijn vele mogelijke oplossingen bedacht.

In dit werk bespreken we een van de methoden. Indien we werken in een kwantumsysteem waar de deeltjes paarsgewijs interageren, dan bevat de tweede orde dichtheidsmatrix van dit systeem alle belangrijke informatie. Dit is een handiger object om te gebruiken dan de golffunctie, omdat het veel compacter is en een strikte ondergrens geeft voor de energie. Dit laatste is handig omdat de meeste andere methoden een bovengrens geven op de energie. De moeilijkheid is echter dat bij het zoeken naar de optimale dichtheidsmatrix de zoektocht beperkt moet worden tot een bepaalde klasse: de dichtheidsmatrix moet N -representeerbaar zijn. Dit betekent dat er een ensemble van golffuncties moet bestaan waaruit de dichtheidsmatrix afleidbaar is. Het is helaas bewezen dat dit een ontzettend moeilijk probleem is. Er is een theorema dat de criteria voor N -representeerbaarheid bepaalt, maar dit is niet bruikbaar als een praktische test. Wat we wel kunnen doen is dit theorema gebruiken om een set nodige voorwaarden op te stellen: dit betekent dat we een aantal condities opleggen waaraan de dichtheidsmatrix minimaal moet voldoen. In het algemeen zijn deze condities niet voldoende om een N -representeerbare dichtheidsmatrix te vinden maar we kunnen het nu wel benaderen. De meeste simpele voorwaarden leiden tot de zogenaamde twee-index en drie-index condities. Dit zijn dan ook de condities die we gebruiken in dit werk.

Daarnaast bevatten de meeste quantum mechanische systemen een vorm van symmetrie: je kunt bepaalde operaties uitvoeren op het systeem zonder dat dit de golffunctie of dichtheidsmatrix verandert. Deze vrijheidsgraden kunnen gebruikt worden om de voorwaarden te vereenvoudigen.

De condities die we hebben afgeleid zijn algemeen: ze gelden voor elke golffunctie. We beperken de condities nu tot een bepaalde klasse van golffuncties. Voor elk atoom zijn er een aantal orbitalen: dit zijn een soort van energie niveau's waarop een elektron kan geplaatst worden. We beperken ons nu tot het geval waarop alle orbitalen ofwel bezet zijn door twee elektronen ofwel leeg zijn. M.a.w. elk elektron is gepaard met een ander elektron, er mogen geen elektronen zijn die geen partner hebben. Deze restrictie zorgt ervoor dat de twee- en drie-index condities sterk vereenvoudigd worden.

Het vinden van de optimale dichtheidsmatrix en bijhorende energie kan nu worden geschreven als een gekend optimalisatie probleem: een semi-definiet programmeer probleem. Om dit soort problemen op te lossen bestaan er verschillende methoden. In essentie hebben we de keuze tussen twee soorten algoritmes: robuust maar traag, of snel maar onstabiel. Bij de eerste kunnen we de optimalisatie gewoon starten en wachten op het antwoord, bij de tweede moeten we meestal eerst een aantal parameters afstellen voor het antwoord kan gezocht worden.

De beperking tot golffuncties die enkel gepaarde elektronen hebben heeft een belangrijk onderdeel. De energie is nu afhankelijk van de vorm van de orbitalen. Naast de optimale dichtheidsmatrix moeten we ook de optimale vorm van de orbitalen zoeken. Dit is een bijzonder lastig probleem: je moet het diepste dal vinden in een ruig energie-gebergte zonder dat er een kaart beschikbaar is. De enige computationele methoden die dit kunnen zijn bijzonder traag. We gebruiken daarom een benaderende methode. We kiezen een startpunt en gaan van daaruit op zoek naar het laagste punt door steeds te dalen. Als we het startpunt goed kiezen,

dan kunnen we het diepste punt vinden. Als we een optimale vorm van de orbitalen hebben gevonden moeten we ook nog de huidige oplossingen omzetten naar deze nieuwe vorm. In het algemeen is dit ook een dure zaak om te berekenen. Wij lossen dit op door enkel op een bepaalde manier naar beneden te gaan: ruw gezegd zou je het kunnen vergelijken met de beperking dat je enkel in een van de vier hoofdrichtingen van een kompas mag dalen. Op zich is dit geen beperking, je zult misschien niet altijd de kortste weg kunnen volgen, maar je zult wel altijd op je eindbestemming raken. Door deze beperking is het omzetten van een oplossing naar de nieuwe orbitalen veel eenvoudiger en computationeel sneller geworden.

Om te testen hoe goed deze methode werkt, passen we ze toe op een aantal testsystemen. Voor een waterstofmolecule vinden we de exacte oplossing, maar als we twee helium atomen uit elkaar trekken gaat er iets grondig mis. We hebben bij dit systeem gebruik gemaakt van de symmetrie: als je bijvoorbeeld de twee helium atomen van plaats verwisselt, verandert er niks aan het systeem. Deze symmetrie blijkt echter de vorm van de orbitalen te sterk te beperken. Als we de symmetrie loslaten en elke vorm van de orbitalen toestaan, dan vinden we de energie die we verwacht hadden. Het volgende systeem dat we onderzoeken is de vervorming van een rechthoek met op elke hoek een waterstof atoom. Hieruit blijkt nogmaals hoe belangrijk het is dat we de orbitalen niet beperken tot een bepaalde symmetrie en dat de keuze van het startpunt cruciaal is. Vervolgens testen we het uit elkaar trekken van een aantal molecules. Bij N_2 vinden we goede resultaten maar bij CN^- en NO^+ botsen we op een gekend probleem van de techniek. Het aantal elektronen moet mooi verdeeld worden over de atomen, maar onze benadering heeft hier een fout: één elektron zal worden verspreid over beide atomen. Dit lijdt tot een fysisch incorrecte situatie maar door de extra vrijheid is de energie wel lager. Er bestaat een oplossingsmethode voor dit probleem maar ze is complex en traag. De specifieke oplossing suggereert echter dat er misschien een andere snellere methode zou kunnen bestaan om dit op te lossen. Tot slot proberen we nog een CO molecule, en daar zijn de resultaten opnieuw goed.

We hebben in dit werk aangetoond dat door de golffunctie te beperken tot een bepaalde klasse, de voorwaarden voor N -representeerbaarheid veel simpeler worden, en dat de optimalisatie een stuk sneller kan worden uitgerekend. Het nadeel dat de vorm van de orbitalen ook moet worden geoptimaliseerd is aangepakt. De eerst resultaten zijn beloftevol. In de toekomst kunnen we beter optimalisatie technieken voor de orbitalen proberen en de drie-index condities implementeren. Deze zouden de accuraatheid van de methode aanzienlijk moeten verbeteren en de gevonden dichtheidsmatrix zal ook dichter bij de echte liggen.

Abstract

*Nothing is as simple as it seems at first.
Or as hopeless as it seems in the middle.
Or as finished as it seems in the end.*

The world at the level of the atom is described by the branch of science called quantum mechanics. The world of quantum mechanics is very different from our own macroscopic world. It is governed by probabilities and there is a duality between particles and waves. Its foundations were built in the first half of the twentieth century by a large group of physicists. The crown jewel is given by the Schrödinger equation which describes a system of indistinguishable particles, that interact with each other. However, an equation alone is not enough: the solution is what interests us. This is a problem, because only for the smallest system is the analytical solution known. For other systems we must resort to numerical techniques. And even then we are plagued by an exponential scaling of the Hilbert space.

In the second half of the twentieth century, a wide array of approximations were developed. This dissertation concerns itself with one of the oldest approximations: the variational optimization of the second-order reduced density matrix (v2DM). Its main attractive point at the time was the reduction of the exponential scaling of the wave function to a quadratically scaling matrix. Unfortunately, the computational burden was simply shifted to the so-called N -representability problem: does there exist a wave function that is compatible with the given reduced density matrix? The necessary and sufficient conditions for N -representability are known but not in a practically usable form. To make matters worse, we now know that the problem belongs to the class of the hardest problems we know. A general solution is extremely unlikely to exist. Despite this, we can generate approximate solutions to the N -representability problem by using a set of necessary conditions. This leads to the classical $\mathcal{P}$, $\mathcal{Q}$ and $\mathcal{G}$ conditions. It also gives rise to another unique feature of this method: we always find a strict lower bound on the energy.

A major advance came when it was realized that the variational optimization of the second-order reduced density matrix can be expressed as a semidefinite programming problem. One could now use the vast machinery of the convex optimization world. And for a brief period, the technique flourished. Unfortunately, despite major advances the technique is still not on par with the competition: there exist faster and more accurate methods.

This dissertation tries another approach: we assume that the wave function has a Slater determinant expansion where all orbitals are doubly occupied or empty. Every electron has a pairing partner. This assumption drastically reduces the scaling of the two-index and three-index conditions. The downside is that the energy explicitly depends on the used orbitals and thus an orbital optimizer is needed. The hope is that by using this approximation, we can capture the lion's share of the static correlation and that any missing dynamic correlation can be added through perturbation theory.

We combine a boundary point method to optimize the second-order density matrix with an orbital optimizer based on Jacobi rotations. Finding the optimal orbitals is a very hard problem: it means finding the lowest point in an uncharted energy landscape. All methods that can solve this problem in general have one thing in common: they are slow. We follow the standard approximation: a local minimizer combined with a good guess of the starting point. At each iteration, we look for the optimal pair of orbitals to rotate and the optimal angle. The advantage of this method is that we avoid the expensive transformation of the one- and two-body integrals as the Jacobi rotation only mixes two orbitals at a time. As every unitary transformation can be decomposed into a series of Jacobi rotations, our approach forms no restriction in finding the optimal orbitals.

We test our method on several benchmark systems. For the hydrogen molecule, we can reproduce the exact values as expected. For a helium dimer, the dissociation limit is wrong. The spatial symmetry of the orbitals restricts the orbital optimizer. If we allow it to break the spatial symmetry, the correct dissociation limit is recovered. As a prototype for strong correlation, we test a linear H_8 chain. The choice of the starting point turns out to be crucial: only the symmetry broken, localized orbitals can find the lowest energy curve.

Next we study the dissociation of several diatomic molecules. The results for N_2 are good but the CN^- and NO^+ molecule suffer from a known issue with v2DM. The energy as a function of the number of electrons should be piecewise linear: on two dissociated atoms we should find an integer charge. Unfortunately, in v2DM this curve is convex which causes the algorithm to favour fractional charges. By distributing a single electron over both atoms the energy can be artificially lowered. There is a solution to this problem in the form of subsystem constraints but it is expensive to use. However, using the orbitals produced by an exact solver in the v2DM algorithm without orbital optimization does give us the correct energy. This suggest that an alternative solution within the orbital optimizer can be found.

We can conclude that the restriction of the N -representability conditions to a doubly-occupied wave function has promise. The lower scaling makes the method competitive with other methods, while the orbital optimization can be handled efficiently. The issue of the fractional charges still requires a fast solution. There are several interesting paths to investigate in the future: several alternative orbital optimizer schemes are worth pursuing, along with improved guesses of the starting points. The conditions on the third-order reduced density matrix still need testing. A good approximation of the energy does not necessary mean that we also have a good approximation of the second-order reduced density matrix itself. The three-index condition should help in this case.

List of Abbreviations and Glossary

1DM

first-order reduced Density Matrix. 6, 14, 15, 17–20, 23, 34, 40, 41, 46, 53, 101, 112, 197

2DM

second-order reduced Density Matrix. 6–9, 11, 14, 15, 18–20, 23, 25, 26, 28, 31–35, 38–42, 45, 46, 53, 60, 65, 74, 77, 78, 80, 81, 86, 88, 91, 99, 103, 104, 111–114, 203, 207

3DM

third-order reduced Density Matrix. 23, 25, 40, 45, 47, 51, 53, 112, 114, 203

AP1roG

Antisymmetric Product of one-reference-orbital Geminals. 75, 77, 89, 94, 113

APG

Antisymmetric Product of Geminals. 74

BPP

Bounded-Error Probabilistic Polynomial Time. 13, 14

BQP

Bounded-Error Quantum Polynomial Time. 14

CASSCF

Complete Active Space Self-Consistent Field. 83

CC

Coupled Cluster. 53, 100

cc-pVDZ

Correlation Consistent Polarized Valence Double Zeta. 38, 89, 91, 92, 95, 99, 101, 103, 106, 107, 208

CCD

Coupled Cluster with Double excitations. 75

CCSD(T)

Coupled Cluster with Singles, Doubles and Triples in Perturbation. 8, 77, 99, 100

CI

Configuration Interaction. 5, 9, 53, 73, 76, 90, 112, 113

CID

Configuration Interaction with Double excitations. 75

CIDQ

Configuration Interaction with Double and Quadruple excitations. 75

CISD

Configuration Interaction with Single and Double excitations. 74, 75

DFT

Density Functional Theory. 14, 53, 99, 101, 104, 112

DMRG

Density Matrix Renormalization Group. 90, 95, 100, 103, 106, 107

DOCI

Doubly Occupied Configuration Interaction. 39–41, 43, 45, 46, 51, 69, 70, 73–77, 80, 81, 89, 91, 92, 95–97, 99–101, 103, 104, 106–108, 112, 113, 207, 208

ER

Edmiston-Ruedenberg localized orbitals. 92, 95, 98, 113

FLOPS

Floating-Point Operations per Second. 80

FullCI

Full Configuration Interaction. 5, 39, 53, 73, 75–77, 86, 87, 90, 91, 94, 100, 104, 108, 113, 114

FullDOCI

Full Doubly Occupied Configuration Interaction. 76, 77, 90, 92, 95, 99–101, 103–108, 113, 114, 207, 208

geminal

A two-particle state. 74, 75, 103

GHF

General Hartree-Fock. 91

GVB

General Valence Bond. 75

HF

Hartree-Fock. 5, 6, 18, 39, 73, 75, 76, 78, 86, 89, 91, 94, 95, 97, 98

KKT

Karush–Kuhn–Tucker conditions. 68

MA

Merlin-Arthur. 13, 14

MCSCF

Multi-Configurational Self-Consistent Field. 5, 73, 76, 80, 83

MO

Molecular Orbital theory. 75, 89

MPI

Message Passing Interface. 89

MPS

Matrix Product State. 90

NP

Nondeterministic Polynomial Time. 11–14, 28

P

Deterministic Polynomial Time. 12–15

QMA

Quantum Merlin Arthur. 11, 14, 112

RHF

Restricted Hartree-Fock. 76, 86, 89, 91, 94, 108, 113

SA

Simulated Annealing. 76, 89

SDP

Semidefinite Programming. 18, 21, 55–58, 60–63, 67, 68, 70, 71, 77, 111, 112

seniority

The number of unpaired particles in the wave function. 40, 41, 43–47, 49, 51, 53, 74, 75, 112

v2DM

Variational Optimization of the second-order reduced Density Matrix. 6–9, 14, 15, 31, 34, 36, 55, 59, 60, 66, 67, 70, 71, 73, 77–80, 86, 89, 92, 99–101, 104, 106–108, 111–114

v2DM-DOCI

Variational Optimization of the second-order reduced Density Matrix in the DOCI space. 77–80, 88–92, 94, 95, 98–101, 103–108, 113, 114, 207

VB

Valence Bond. 75

VBSCF

Valence Bond Self-Consistent Field. 76

Part I

Variational determination of the two-particle density matrix: the case of doubly-occupied space

Chapter 1

Introduction

We must be clear that when it comes to atoms, language can be used only as in poetry. The poet, too, is not nearly so concerned with describing facts as with creating images and establishing mental connections.

Niels Bohr

Richard Feynman, one of the great physicists of the twentieth century, once asked his students:

If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words?

It is an interesting question and a wide range of answers is possible but Feynman's own idea is what is of interest here:

I believe it is the atomic hypothesis that all things are made of atoms - little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. In that one sentence, you will see, there is an enormous amount of information about the world, if just a little imagination and thinking are applied.

The idea that matter is built out of atoms is of a profound importance. The world of the atom is a strange world, many things that are counterintuitive are possible on the small scale of an atom. It took a long time for science to develop a good understanding of it. The branch of physics that deals with the dynamics of particles on atomic length scales is called quantum mechanics. Its foundations were laid in the beginning of the previous century. One of the many counter-intuitive features of quantum mechanics is that particles are described by a wave equation, the so-called Schrödinger equation. Unfortunately this equation can only be solved exactly for systems which are either very small or have special symmetry properties. For other interesting cases one needs to introduce approximations and use numerical techniques.

In this work we will describe and develop one such technique, the variational determination of the two-particle reduced density matrix, and apply it to a number of non-trivial systems. We will use the second quantization formalism as it is the natural language to explain this technique. A short introduction to the formalism can be found in Chapter B on page 193.

1.1 Variational second-order density matrix optimization

An N -particle quantum system with pairwise interactions is governed by a Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}, \quad (1.1)$$

where $\hat{T}$ are the one-body operators and $\hat{V}$ the two-body operators. We want to find the ground state energy and wave function,

$$\hat{H}\Psi(\mathbf{x}) = E_0\Psi(\mathbf{x}), \quad (1.2)$$

where $\mathbf{x}$ is a vector in the space $\mathbb{C}^{3N} \times \{\uparrow, \downarrow\}^{3N}$. There are few restrictions on the wave function Ψ : it needs to belong to the class L^2 of square-integrable functions, it must be antisymmetric under the exchange of (indistinguishable) particles due to the Pauli exclusion principle and it has to be normalized. In ab-initio quantum chemistry methods, the Hilbert space is usually restricted to a space spanned by a finite, non-complete set of basis functions. This has the advantage that eq. (1.2) is reduced to a discrete Hermitian eigenvalue problem. The construction of these basis sets is a science of its own: most commonly used are linear combinations of Gaussian functions because they allow for efficient computation of the one- and two-electron integrals. From now on, we will work in an M -dimensional space built by single-particle orbitals. We will refer to these single-particle states with Greek letters: $\alpha, \beta, \gamma, \dots$. A single-particle state is always the product of a spatial orbital and a spin state. To refer to the spatial orbital we will use Roman letters: a, b, c , etc.

In the second quantization formalism (see Chapter B), the Hamiltonian (1.1) can be written as

$$\hat{H} = \sum_{\alpha\beta} T_{\alpha\beta} \hat{a}_{\alpha}^{\dagger} \hat{a}_{\beta} + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} V_{\alpha\beta;\gamma\delta} \hat{a}_{\alpha}^{\dagger} \hat{a}_{\beta}^{\dagger} \hat{a}_{\delta} \hat{a}_{\gamma}, \quad (1.3)$$

where $T_{\alpha\beta} = \langle \alpha | \hat{T} | \beta \rangle$ and $V_{\alpha\beta;\gamma\delta} = \langle \alpha\beta | \hat{V} | \gamma\delta \rangle$ are the one- and two-electron integrals. In this work, we only consider Hamiltonians which are field-free (e.g. no magnetic field), non-relativistic and real. The wave function is always over the field $\mathbb{R}$. These are the default assumptions in quantum chemistry. For atoms and molecules, this means that $\hat{T}$ is the sum of the electronic kinetic energy and the nuclei-electron attraction, whereas $\hat{V}$ represents the interelectronic Coulomb repulsion. We always work within the Born-Oppenheimer approximation [1]: we assume that the wave function can be split in its electronic and nuclear degrees of freedom and we neglect the latter. The associated Schrödinger equation in its matrix form is

$$\hat{H} |\psi\rangle = E_0 |\psi\rangle. \quad (1.4)$$

The most simple solution is the mean-field approximation, also known as Hartree-Fock (HF), in which $|\psi\rangle$ is given by a single Slater determinant:

$$|\psi\rangle = \hat{a}_{\alpha_1}^\dagger \hat{a}_{\alpha_2}^\dagger \dots \hat{a}_{\alpha_N}^\dagger | \rangle . \quad (1.5)$$

A Slater determinant is nothing more than the antisymmetric linear combination of a set of orthogonal single-particle states. There are $\frac{M!}{N!(M-N)!}$ possible Slater determinants if the dimension of the single-particle basis is M and N the number of particles. They form a complete basis in which we can expand the wave function

$$|\psi\rangle = \sum_{\alpha_1 \alpha_2 \alpha_3 \dots \alpha_N} c_{\alpha_1 \alpha_2 \alpha_3 \dots \alpha_N} \hat{a}_{\alpha_1}^\dagger \hat{a}_{\alpha_2}^\dagger \hat{a}_{\alpha_3}^\dagger \dots \hat{a}_{\alpha_N}^\dagger | \rangle . \quad (1.6)$$

In the Configuration Interaction (CI) method [2], the wave function is written as a linear combination of a set of Slater determinants. The coefficients are then optimized to find the lowest energy in eq. (1.4). The difficulty in this method lies in picking a suitable set of Slater determinants. The best possible solution within the basis set limit is found when all possible Slater determinant are used. This is called Full Configuration Interaction (FullCI) and coincides with the exact diagonalization of the Hamiltonian matrix. Unfortunately, this is unfeasible for all but the smallest systems.

In practice, the expansion (1.6) is truncated at some point. The usual approach is to use the Hartree-Fock solution as a reference point and then add Slater determinants which are excitations of the reference Slater determinant: one or more occupied orbital are replaced with a unoccupied (virtual) orbital. In this way, a hierarchy is found: Slater determinants can be cataloged according to the number of excitations needed starting from the reference point. The number of excitations used is denoted by a letter: S for single excitations, D for double excitations, T for triple excitations, etc. These methods are called single-reference as they use one reference Slater determinant. This is not always a good approximation: for example during bond-breaking, multiple independent Slater determinants in the wave function (1.6) will become important. The solution here is to use multi-reference methods like Multi-Configurational Self-Consistent Field (MCSCF) [1, 2]. In MCSCF, both the coefficients for the Slater determinants as well as the single-particle orbitals in the Slater determinants are optimized.

The contributions to the energy are usually split up into two parts: dynamic correlation and non-dynamic (static) correlation. There is no unambiguous distinction between both but as a rule of thumb: the FullCI wave function will have a (small) number of dominant Slater determinants. These are responsible for the static correlation. The dynamic correlation is given by the Slater determinants which are excitations of the dominant set.

A more natural way to describe the state of an N -particle quantum system is through the so-called N th-order density matrix [3]. In reality most systems are entangled with their environment and they are described by an ensemble of wave functions. This is elegantly expressed with the N th-order density matrix D

$$D(\mathbf{x}; \mathbf{x}') = \sum_i w_i \Psi_i(\mathbf{x}) \Psi_i(\mathbf{x}'), \quad (1.7)$$

where $w_i \geq 0$ and $\sum_i w_i = 1$. The N th-order density matrix is positive semidefinite and normalized to 1. A special case is a “pure state density”, where the system is characterized by a single wave function,

$$D(\mathbf{x}; \mathbf{x}') = \Psi(\mathbf{x})\Psi(\mathbf{x}'). \quad (1.8)$$

It is characterized by the fact that D should be idempotent: $D^2 = D$. The first-order reduced Density Matrix (1DM) is found by integrating out all degrees of freedom except those belonging to a single particle:

$$\rho(x_1; x'_1) = N \int D(x_1, x_2, \dots, x_N; x'_1, x_2, \dots, x_N) dx_2 \dots dx_N. \quad (1.9)$$

Dirac showed that Hartree-Fock solution can be expressed solely using the 1DM [4]. In other words, the 1DM contains the same information as a single Slater determinant. The p th-order reduced density matrix is defined in a similar way: all degrees of freedom but p are integrated out. From now on, we will only use the second quantization. In this formalism, the 1DM $\rho_{\alpha\beta}$ and the second-order reduced Density Matrix (2DM) $\Gamma_{\alpha\beta;\gamma\delta}$ are given by

$$\rho_{\alpha\beta} = \sum_i w_i \langle \psi_i | \hat{a}_\alpha^\dagger \hat{a}_\beta | \psi_i \rangle, \quad (1.10)$$

$$\Gamma_{\alpha\beta;\gamma\delta} = \sum_i w_i \langle \psi_i | \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\delta \hat{a}_\gamma | \psi_i \rangle, \quad (1.11)$$

for an ensemble of wave functions ($w_i \geq 0$ and $\sum_i w_i = 1$). The pure state case is found when all except one $w_i = 0$. The 1DM and 2DM are not independent, for we can extract the 1DM out of the 2DM as:

$$\rho_{\alpha\beta} = \frac{1}{N-1} \sum_\lambda \Gamma_{\alpha\lambda;\beta\lambda}. \quad (1.12)$$

A key observation is that the ground state energy of the Hamiltonian (1.3) can be expressed as a linear function of the 2DM

$$E_0 = \text{Tr}(K\Gamma) = \frac{1}{4} \sum_{\alpha\beta\gamma\delta} K_{\alpha\beta;\gamma\delta} \Gamma_{\alpha\beta;\gamma\delta} = \sum_{\alpha<\beta} \sum_{\gamma<\delta} K_{\alpha\beta;\gamma\delta} \Gamma_{\alpha\beta;\gamma\delta}, \quad (1.13)$$

where

$$K_{\alpha\beta;\gamma\delta} = \frac{1}{N-1} (T_{\alpha\gamma}\delta_{\beta\delta} - T_{\beta\gamma}\delta_{\alpha\delta} - T_{\alpha\delta}\delta_{\beta\gamma} + T_{\beta\delta}\delta_{\alpha\gamma}) + V_{\alpha\beta;\gamma\delta}, \quad (1.14)$$

is the reduced Hamiltonian. Not only the ground state energy but the expectation value of any one- or two-particle operator can be calculating using the 2DM. Husimi [5] was the first to realize this in 1940. The full wave function contains all the information about the system but is a much more complicated object. The 2DM is a much more compact object which for most practical purposes is sufficient. It comes close to the “ultimate reduction” for an interacting many body problem. This compactness is the main attractive feature of the 2DM: the dimension of the 2DM scales quadratically with the single-particle dimension and is independent of the number of particles. It led to the idea of quantum mechanics without wave functions: the linear function (1.13) is used to variationally optimize the 2DM, henceforth called Variational

Optimization of the second-order reduced Density Matrix (v2DM). However, when Coleman in 1951 performed the first variational optimization of the 2DM on Lithium, he was astonished to find an energy that was 20% below the ground state energy [6]. He realized that he varied over a too large class of trial 2DM's. Independently, Mayer [7] and Löwdin [8] published similar results in 1955. Tredgold [9] pointed out that the variational calculations done by Mayer lead to unphysical results and concluded that additional constraints would be needed. In 1963 Coleman called this the N -representability problem [10]: what are the necessary and sufficient conditions on a 2DM to be derivable from an ensemble of wave functions, *i.e.* eq. (1.11) must hold for all trial 2DM's. Coleman derived the necessary and sufficient conditions for N -representability on the 1DM in his paper, and gave several necessary conditions on the 2DM. In 1963 a major step forward was made by Garrod and Percus [11] who derived the $\mathcal{Q}$ and $\mathcal{G}$ conditions. The computational results using these conditions on the Beryllium atom were promising: the obtained results were quite accurate [12, 13]. However, Beryllium turned out to be a special case: due to its simple electronic structure, the $\mathcal{Q}$ and $\mathcal{G}$ conditions performed extremely well. In other systems, the same conditions unfortunately did not perform as well [14, 15]. This led to a 25-year-long period of darkness. While in the 1960's there was still hope that the N -representability problem could be solved, it became clear that it is a very fundamental problem without a clear path forward.

In the 1990's, a renaissance arrived. Through another method, known as the contracted Schrödinger equation [16, 17], several groups were able to approximate the 2DM directly, without need for an underlying wave functions [18, 19]. This renewed interest in the direct variational calculation of the 2DM. In 2001, Nakata *et al.* [20] realized that the variational optimization problem could be written as a semidefinite program [21], which is a class of well-known convex optimization problems [22]. They used an off-the-shelf semidefinite solver [23] to calculate the energies of several atoms and molecules with good accuracy. Mazziotti [24] also jumped on the wagon and the train seemed unstoppable. In 2004, Zhao *et al.* [25] implemented three-index conditions $\mathcal{T}_1$ and $\mathcal{T}_2$ which led to milliHartree accuracy for some systems [26, 27], and Mazziotti [28, 29] introduced a much faster optimization method that extended the method to larger systems. In recent years, the variational optimization of the 2DM has gained a lot of appeal due to it being complementary to other variational methods: it provides a lower bound on the energy instead, of an upper bound that is found by variational methods that focus on the wave function. Also, in stark contrast with most wave function based methods, the v2DM method does not depend on a reference state. The energy function is exact, only the amount N -representability conditions limit the accuracy (and speed) of the method.

To make further progress in the v2DM method, two clear directions exist: (1) the search for new N -representability conditions which are computationally feasible (cheap); and (2) improving the semidefinite program algorithms to exploit the specific structure of v2DM. On the first path, Verstichel *et al.* [30] introduced subsystems constraints to fix the problem of fractional charges [31]. Shenvi and Izmaylov [32] introduced active-space constraints. Stricter bounds on the two-index conditions were derived [33, 34]. Spin symmetry and point-group symmetry of molecules were exploited [35]. A stronger three-index condition was derived [36]. System-specific constraints were introduced [37, 38]. Even excitation energies were calculated [39] using the variationally optimized 2DM. Additional constraints for non-singlet

states were discussed [40]. Linear inequalities for the 2DM were found [41–43]. This list is far from conclusive and only aims to give a glance of the activity on the N -representability front. Several books and review papers are written about v2DM and they provide an excellent overview of the road so far [6, 44–48].

On the semidefinite programming front, several algorithms were tried and customized to v2DM [28, 49–51]. The boundary point method [52] is currently the fastest, but it is not always stable. In the convex optimization literature, v2DM is known under the category ‘very large scale’: the most common semidefinite programming problems are much smaller. There exist general purpose solvers [23] but they are not efficient enough for our problem size.

Currently, the popularity of v2DM has again stagnated. The method is still not competitive with other popular methods like Coupled Cluster with Singles, Doubles and Triples in Perturbation (CCSD(T)), the so-called golden standard [53] in quantum chemistry. Although at present, much larger systems than in the past can be treated, the fundamental problem remains the N -representability. While the three-index conditions lead to considerably improved accuracy, they are computationally very expensive and thus unfeasible for larger systems. The quest for cheap yet accurate conditions continues.

1.2 Conventions

Greek letters ($\alpha, \beta, \dots$) are used to denote a single-particle state. The spatial part of an orbital will be referred to by Roman letters ($a, b, \dots$). Almost all summations will run over the single-particle states unless explicitly marked otherwise. To lighten the notation, the bounds of the sum over single-particle states will not be shown. The trace of a four-index tensor object is defined as

$$\text{Tr}(A) = \sum_{\alpha < \beta} \sum_{\gamma < \delta} A_{\alpha\beta;\gamma\delta} = \frac{1}{4} \sum_{\alpha\beta\gamma\delta} A_{\alpha\beta;\gamma\delta} \quad (1.15)$$

Chapter 2

The N -representability problem

For a given wave function, the second-order reduced Density Matrix (2DM) can be calculated using its definition (1.11). However, when given a random symmetric matrix, is it possible to find a corresponding (ensemble of) wave function which has the given matrix as the 2DM? This is the essence of the N -representability problem. In the early days of Variational Optimization of the second-order reduced Density Matrix (v2DM), there was still hope that this problem could effectively be solved. Coulson [54] stated its importance at a conference about “Molecular Structure Calculations” in Boulder, Colorado in 1959:

There is an instinctive feeling that matters such as electron correlation should show up in the two-particle reduced density matrix. ... but we still do not know the conditions that must be satisfied by the 2DM. Until these conditions have been elucidated, it is going to be very difficult to make much progress along these lines...

In this chapter we will show that the hope of finding a solution for the N -representability problem is idle. A formal theorem about the necessary and sufficient conditions will be presented which we will use to find some practically usable necessary conditions. We also look at what we effectively can impose from the symmetry of the wave function in the 2DM. In the second part of this chapter, we rederive the conditions for a specific kind of Configuration Interaction (CI) wave function which simplifies these conditions greatly.

There are two kinds of N -representability: pure and ensemble, depending on whether the 2DM is derivable from a pure wave function or an ensemble of wave functions. We will only be concerned with ensemble N -representability in what follows. The set of ensemble N -representable 2DM's is a closed convex set (see Chapter C on page 195). This is interesting because a convex set is completely determined by its extreme points due to the Krein-Milman theorem [55]. It can be shown that the extreme points for ensemble N -representability are the pure states [6, 10]. The convexity will turn out to be paramount importance. For a long time, it was believed that the 2DM for the non-degenerate ground state of a Hamiltonian (with at most two-particle interaction) corresponds to a unique wave function or ensemble of wave functions [6] but recently counterexamples were found [56].

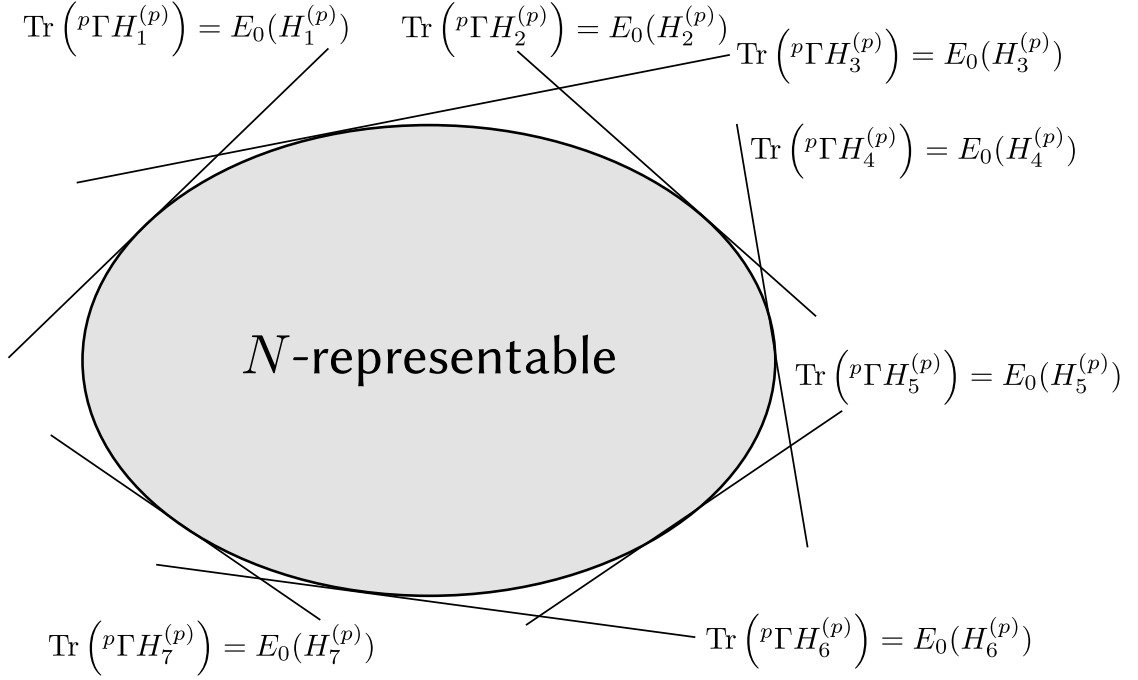


Figure 2.1: Graphical depiction of the necessary and sufficient conditions for N -representability. Every Hamiltonian $H^{(p)}$ can be represented by a hyperplane that bounds the convex set of N -representable ${}^p\Gamma$.

2.1 General N -representability theorem

The following theorem states the necessary and sufficient conditions for N -representability of a p th-order reduced density matrix.

Theorem 1. A p th-order reduced density matrix ${}^p\Gamma$, is N -representability if and only if

$$\forall H^{(p)} : \quad \text{Tr} \left({}^p\Gamma H^{(p)} \right) \geq E_0(H^{(p)}) , \quad (2.1)$$

where $E_0(H^{(p)})$ is the ground state energy of the Hamiltonian $H^{(p)}$.

A graphical depiction of this theorem can be found in Figure 2.1. The boundary of the convex set of N -representable p th-order reduced density matrices is formed by an infinite number of tangent hyperplanes, where each hyperplane represents a p -particle Hamiltonian and its ground state energy. Proving the necessary statement is easy: in case that the p th-order reduced density matrix is N -representable, this theorem simply states that the expectation value of the reduced density matrix with a Hamiltonian cannot be lower than the ground state energy of that Hamiltonian. To prove the sufficient statement, we first make a detour to the separating hyperplane theorem [22]:

Theorem 2. *Let A and B be two disjunct non-empty convex sets than there exists a hyperplane that separates both sets: there exists an a and b such that $\forall x \in A, \langle a, x \rangle \geq b$ and $\forall x \in B, \langle a, x \rangle \leq b$.*

Let us now assume that ${}^p\tilde{\Gamma}$ is not N -representable. The separating hyperplane theorem implies that there exists a Hamiltonian $H^{(p)}$ for which

$$\text{Tr} \left({}^p\tilde{\Gamma} H^{(p)} \right) \leq k, \quad (2.2)$$

while for all N -representable reduced density matrices ${}^p\Gamma$,

$$\text{Tr} \left({}^p\Gamma H^{(p)} \right) \geq k. \quad (2.3)$$

Now we have

$$\text{Tr} \left({}^p\tilde{\Gamma} H^{(p)} \right) \leq k \leq E_0(H^{(p)}) \leq \text{Tr} \left({}^p\Gamma H^{(p)} \right), \quad (2.4)$$

because $E_0(H^{(p)})$ is the lowest possible value obtainable by the last trace due to the variational principle. We can conclude that if a reduced density matrix is not N -representable, there will be a Hamiltonian for which the reduced density matrix will give a ground state energy which is too low.

This theorem also shows that the 2DM corresponding to the ground state wave function of a Hamiltonian will be on the border of the N -representable convex set [6]. One can even say that every point on the border corresponds to the ground state of some Hamiltonian. Note that this in general is not invertible: a 2DM on the border can correspond to the ground state of multiple Hamiltonians.

A noteworthy fact is the unitary invariance of this theorem. The ground state energy of the p -Hamiltonian $H^{(p)}$ is not dependent on the choice of single-particle basis. Any unitary transformation of the single-particle basis will lead to the same ground state. This also means that the N -representability conditions must be unitary invariant.

This theorem is not directly usable as a test for N -representability as it requires the ground state energy of every possible Hamiltonian beforehand. It can however be used as a necessary condition as we will show in Section 2.3.

2.2 N -representability is QMA-complete

Although we now have some insight into the problem, we are still no closer to a real solution. And unfortunately, in the general case, we never will: in 2007, it was proven by Liu, Christandl, and Verstraete [57] that the N -representability problem is QMA-complete. This is the quantum generalization of NP-complete. To explain what this means, we will make a short detour into computational complexity theory. First, we will define some commonly used terms:

- **Polynomial Time:** an algorithm runs in polynomial time if there is an upper bound on the runtime, expressed as a polynomial in the problem size.

- **Deterministic Turing machine:** a theoretical machine [58, 59] devised by Turing in 1937 for computations. Every non-quantum computer today is a deterministic Turing machine. It consists of an infinitely long tape divided into cells, with in each cell a symbol. These symbols belong to a finite alphabet. There is also a head which can read the symbol in the current cell and move the tape to the next or previous cell. The machine has a state register which holds its state and a finite table of instructions that, given the current state and the current symbol, tells what to do next. It can take three consecutive actions: replace the symbol in the current cell with another, move the head to the next or previous cell, and change the state register to a new state.
- **Non-deterministic Turing machine:** in a deterministic Turing machine, the action table holds exactly one action for every possible symbol and state. In a non-deterministic Turing machine, multiple actions are possible and it follows them all in parallel. One could think of it as a Turing machine that can clone itself. A non-deterministic Turing machine and a deterministic Turing machine are equivalent in what they can calculate, they differ in the time it takes them to do it. It should be noted that a quantum computer is not a non-deterministic Turing machine.
- **Decision problem:** a question to which the answer is yes or no. The question can have several inputs. For example: given x , is x a prime number?
- **Promise problem:** a decision problem along with a promise about the inputs. For example: given a natural number x , is x a prime number?

With that knowledge, we can define the classic complexity classes:

- **Deterministic Polynomial Time (P):** a decision problem that can be solved in polynomial time on a deterministic Turing machine. For example: given a natural number x , is x a prime number [60]? Or what is the greatest common divisor for two numbers x and y . These are problems which can be solved efficiently.
- **Nondeterministic Polynomial Time (NP):** a decision problem that can be solved in polynomial time on a non-deterministic Turing machine. However, the proof of the answer can be verified in polynomial time on a deterministic Turing machine. This means that if we are given a specific instance of a problem and a witness (or certificate) that the answer is yes, we can verify that efficiently. For example: integer/prime factorization. Finding the factorization is difficult, but verifying a given factorization is easy.
- **NP-hard:** a problem is NP-hard, when any problem in NP can be reduced to it in polynomial time. These problems are at least as hard as the hardest problems in NP. Furthermore, if a polynomial time algorithm is found for any NP-hard problem, all NP-hard problems are solved. Notice that not all NP-hard problems are in NP: a NP-hard problem does not have to be a decision problem. For example, the traveling salesmen problem: given a set of places and the distances between them, find the shortest route to visit all the places exactly once.

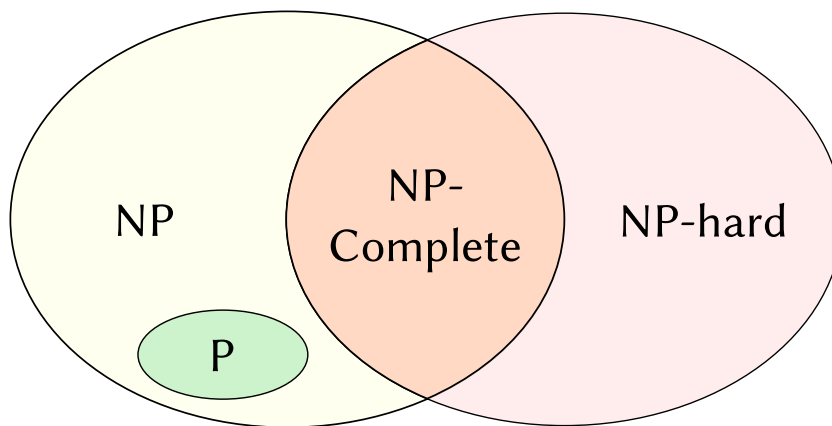


Figure 2.2: The relation between the different complexity classes. The question whether $P=NP$ is one of the unsolved millennium problems and the associated prize is one million dollars [61].

- NP-complete: a problem is NP-complete when it is in NP and in NP-hard. For example, the decision version of the traveling salesmen: when given a total distance L , is there a path with a shorter total distance? As this is a subset of NP, the solution can be verified in polynomial time.
- Bounded-Error Probabilistic Polynomial Time (BPP): runs in polynomial time on probabilistic Turing machine. This is a deterministic Turing machine together with a random number generator: it is allowed to make random decisions but the probability of giving the wrong answer is at most $1/3$ (bounded error). The certainty of a solution can be improved by doing multiple computations. For example, some Monte-Carlo algorithms fall under this class. The class P is clearly a subset of BPP but its relation to NP is not yet known.
- Merlin-Arthur (MA): a class of decision problems that can only be computed non-deterministically. The Merlin-Arthur protocol is a kind of game: in this system, Merlin has access to unlimited computational power and sends a certificate (or proof) of the problem to Arthur. Using a BPP, Arthur then needs to verify the certificate so that if the answer is yes, he must conclude so with a probability of at least $2/3$. If the answer is no, Arthur must accept all certificates with a probability of at most $1/3$.

The relation between the different classes is shown in Figure 2.2. All of these classes have a quantum version, in which probabilities enter the game. But first we must introduce a quantum computer: quantum computers maximally exploit the non-classical features of a quantum (many-body) system. In analogy with classical information theory, information can be encoded in the quantum states of a quantum system, like the two spin projections of a spin $1/2$ particle, also referred to as a *qu*-bit. A qubit can be in a superposition of both 0 and 1. However in sharp contrast with classical bits, two qubits can become entangled, leading

to remarkable quantum algorithms that are impossible on a classical level, such as prime-factorization with a polynomial scaling (in the input size) [62], or $O(\sqrt{N})$ searching in an unsorted database [63].

- Bounded-Error Quantum Polynomial Time (BQP): A quantum version of BPP. It uses a qubit instead of a random number generator. The above mentioned prime-factorization is part of BQP.
- Quantum Merlin Arthur (QMA): the quantum generalization of NP. It is the same as MA but now Arthur has a BQP to help him verify the certificate. The certificate can now take the form of a quantum state. For example, for a given Hamiltonian, is the ground state energy less than $\tilde{E}$? The certificate in this case would be the ground state wave function. Just like the class NP, it is hard to find a solution, but once found, it is easily verified for its correctness.

QMA-hard and QMA-complete have the same relative meaning as in the classical case.

We now return to the original problem of N -representability which was proven to be QMA-complete [57, 64]. Liu, Christandl, and Verstraete [57] proved this first by showing the QMA-hardness of the problem. They did this by reducing the N -representability problem to the 2-local-spin Hamiltonian which was already proven to be QMA-complete [65, 66] (the 2-local refers to a Hamiltonian with spins pairwise interacting). Secondly, they proved that it is part of the QMA class by building a setup in which Arthur can verify the N -representability with the requested accuracy and soundness. The proof for Arthur in this case would be the N th-order density matrix D . It is easy to verify that the original Γ is reducible from this density.

In this regard, the variational optimization of the second-order density matrix is similar to Density Functional Theory (DFT) [67–69]. Both are exact in principle but depend on an unknown: N -representability for v2DM and the universal functional for DFT. The universal functional has also been shown to be QMA-complete [70].

Note that computational complexity theory deals with worst-case scenarios. It might be that in specific cases, the N -representability problem can be solved due to, for example, symmetry. In the case of $N = 2$ and $N = 3$ [71], the necessary and sufficient conditions for N -representability of the 2DM are known. The ensemble N -representability of the first-order reduced Density Matrix (1DM) is an entirely different matter: it belongs to the complexity class P.

2.2.1 Formal definition

The problem of N -representability is special case of a general set of problems known as quantum marginal problems [72–74]. The classical marginal problem [75] is defined as follows: given a set of random variables $X_1, X_2, \dots, X_n$ and their joint probability distribution, $p(X_1, X_2, \dots, X_n)$, we can calculate a k marginal distribution. This is done by integrating over a subset of $n - k$

random variables. For example, one of the $\binom{n}{k}$ marginal distributions is

$$g_n^k(X_1, X_2, \dots, X_k) = \int p(X_{k+1}, X_{k+2}, \dots, X_n) dX_{k+1} \dots dX_n. \quad (2.5)$$

The classical marginal problem is the question, when given the set of all k marginal distributions $g_n^k(\dots)$, does there exist a joint distribution $p(X_1, X_2, \dots, X_n)$ that is compatible with it in the sense of eq. (2.5)? The quantum version of the marginal problem for identical particles is found when the probability distribution is replaced by the N th-order density D . The marginal distribution is then the k th-order reduced density matrix

$${}^k\Gamma_{\alpha_1\alpha_2\dots\alpha_k;\beta_1\beta_2\dots\beta_k} = \sum_{\alpha_{k+1}\dots\alpha_N} \sum_{\beta_{k+1}\dots\beta_N} {}^N D_{\alpha_1\alpha_2\dots\alpha_N;\beta_1\beta_2\dots\beta_N} \quad (2.6)$$

Due to the fact that we work with identical particles and that any permutation of them should result in the same density up to a sign, all $\binom{N}{k}$ marginal distributions are the same. The question in the quantum version is then: what are the necessary and sufficient conditions for eq. (2.6) to hold. We can now also see that the necessary and sufficient conditions for N -representability of the ${}^k\Gamma$ in case of $N = k$ are trivial as the ${}^k\Gamma$ is then the N th-order density D matrix. The conditions on the N th-order density matrix D are much simpler: it should be positive semidefinite, $D \succeq 0$, and the trace should be one, $\text{Tr}(D) = 1$.

2.3 Approximately N -representability conditions

In Section 2.1 on page 10 we showed the necessary and sufficient conditions for N -representability. These required the knowledge of the ground state energy of every possible Hamiltonian and are thus not usable as a sufficient condition. We can, however, use it as a necessary condition: if we restrict (2.1) to Hamiltonians of which we know the ground state energy or a lower bound on it, we can approximate the convex set of N -representable 2DM's. In Figure 2.3 on the next page we give a graphical interpretation of this idea. The approximate set of N -representable 2DM will be larger than the true set: there will be 2DM's which fulfil all the necessary conditions but are still not derivable from an ensemble of wave functions. As a consequence the variational optimization of the 2DM will give a lower bound on the energy. This is one of the highly attractive features of v2DM.

2.3.1 The first-order reduced density matrix

The N -representability conditions for the 1DM are in the computational complexity class P as we will show. The 1DM is defined as

$$\rho_{\alpha\beta} = {}^1\Gamma = \sum_i w_i \langle \psi_i | \hat{a}_\alpha^\dagger \hat{a}_\beta | \psi_i \rangle, \quad (2.7)$$

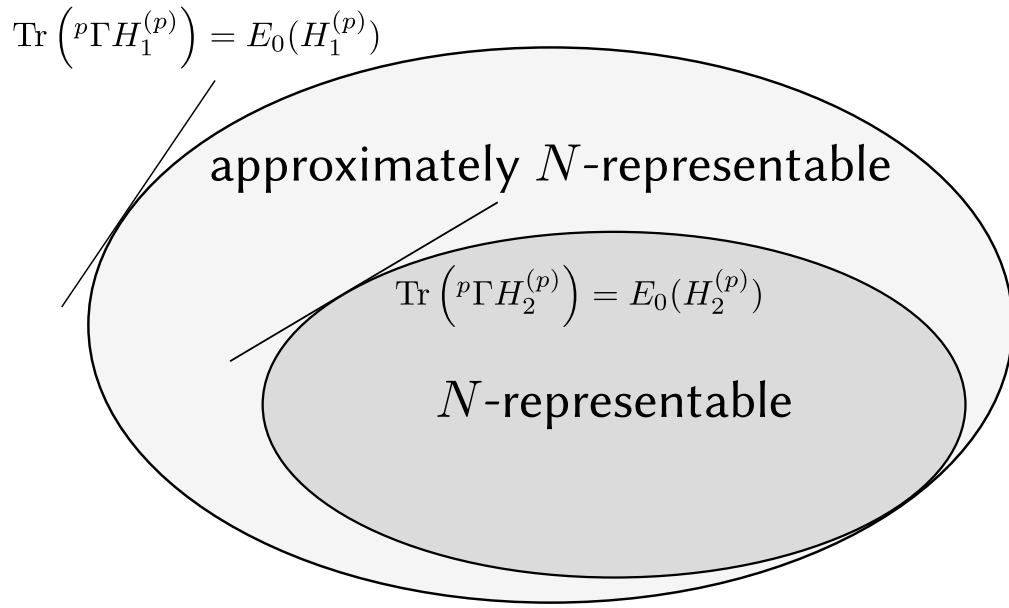


Figure 2.3: Graphical depiction of the necessary conditions for N -representability. $H_1^{(p)}$ belongs to the class of Hamiltonians of which we know a bound on ground state energy while $H_2^{(p)}$ does not. The true convex set of N -representable ${}^p\Gamma$ is smaller than the approximate convex set delimited by the Hamiltonians of the class of $H_1^{(p)}$.

with $\sum_i w_i = 1$ and $w_i \geq 0$. From now on, we will use ρ to denote the 1DM. Several properties can be easily derived from the definition (2.7)

$$\rho_{\alpha\beta} = \rho_{\beta\alpha}, \quad (2.8a)$$

$$\text{Tr}(\rho) = \sum_{\alpha} \rho_{\alpha\alpha} = N, \quad (2.8b)$$

$$\rho \succeq 0. \quad (2.8c)$$

The last equation means that the 1DM must be positive semidefinite (see Chapter C on page 195). This can be understood by thinking of eq. (2.7) as an overlap. If we transform to the single-particle basis which diagonalizes the 1DM, the eigenvalues will be the norm of the states and thus have to be larger or equal to zero. The eigenvalues of the 1DM are called the natural occupation numbers [8] and the corresponding eigenvectors are the natural orbitals or simply the naturals.

A class of Hamiltonians for which we know a lower bound on the ground state energy is giving by

$$\hat{H} = \hat{B}^\dagger \hat{B}, \quad (2.9)$$

as they are positive semidefinite

$$z^\dagger \hat{H} z = z^\dagger \hat{B}^\dagger \hat{B} z = \|Bz\|^2 \geq 0. \quad (2.10)$$

The operator $\hat{B}$ is a p -particle operator. For the 1DM there are two subclasses,

- $\hat{B}^\dagger = \sum_{\alpha} p_{\alpha} \hat{a}_{\alpha}^\dagger$ leads to

$$\sum_{\alpha\beta} p_{\alpha} \langle \psi | \hat{a}_{\alpha}^\dagger \hat{a}_{\beta} | \psi \rangle p_{\beta} \geq 0. \quad (2.11)$$

This is equivalent with the already stated condition that the 1DM has to be positive semidefinite.

- $\hat{B}^\dagger = \sum_{\alpha} q_{\alpha} \hat{a}_{\alpha}$ leads to

$$\sum_{\alpha\beta} q_{\alpha} \langle \psi | \hat{a}_{\alpha} \hat{a}_{\beta}^\dagger | \psi \rangle q_{\beta} \geq 0. \quad (2.12)$$

This can be written as a function of the 1DM using the fundamental anticommutator relations (B.5) to find

$$q = 1 - \rho \succeq 0 \quad (2.13)$$

This condition means that the occupation number of an orbital cannot be greater than one or that the probability of finding a hole has to be positive.

Both conditions together enforce that the eigenvalues of the 1DM have to lay in the interval $[0, 1]$:

$$0 \preceq \rho \preceq 1 \quad (2.14)$$

This is of course nothing but the Pauli Exclusion principle. The bounds are strict: in the Hartree-Fock solution (a single Slater determinant) the orbitals will have an occupation of either zero or one. This makes us wonder if condition (2.14) is also sufficient for N -representability of the 1DM.

We already showed that the N -representability conditions should be unitary invariant for transformations of the single-particle basis. The eigenvalues of the 1DM form a complete set of unitary invariants for transformations of the single-particle basis. As a consequence, the N -representability of the 1DM should be expressible solely as a function of its eigenvalues (and the number of particles N). Furthermore, it can be proven that the extreme elements of the convex set of 1DM's are N -representable by a single Slater determinant [10]. Any element in the convex set can be written as a convex combination of the extreme elements. This means that the condition (2.14) is not only necessary but also sufficient for N -representability!

Instead of optimizing the 2DM, we can also optimize the 1DM. To calculate the energy however, we need the 2DM. It is possible to write the 2DM in the cumulant expansion [18, 45, 76–78]

$${}^2\Gamma = \rho \wedge \rho + \Delta, \quad (2.15)$$

$${}^2\Gamma_{\alpha\beta;\gamma\delta} = \rho_{\alpha\gamma}\rho_{\beta\delta} - \rho_{\alpha\delta}\rho_{\beta\gamma} + \Delta_{\alpha\beta;\gamma\delta}. \quad (2.16)$$

The wedge denotes the Grassmann product (see Chapter C on page 195). The 2DM can be split up into a part expressible in terms of the 1DM and the cumulant Δ , which cannot be expressed as a function of the 1DM. We can approximate the 2DM by setting the cumulant part equal to zero. This boils down to taking an uncorrelated 2DM. The cumulant part holds the two-particle correlations. In fact, the necessary and sufficient conditions for the cumulant to be zero is that the 1DM is idempotent: $\rho^2 = \rho$ [77]. This means that optimizing the 1DM with the cumulant of the 2DM equal to zero is equivalent to Hartree-Fock. The optimization problem for the 1DM is

$$\begin{aligned} E = \min_{\rho} \text{Tr} \left(H^{(1)} \rho \right) + \text{Tr} (\rho V \rho) \quad \text{while} \quad (2.17) \\ \text{Tr} (\rho) = N \\ \rho \succeq 0 \\ 1 - \rho \succeq 0 \end{aligned}$$

The variation is done over all real, symmetric $N \times N$ matrices. The two-particle interaction is represented by V . The energy functional is unfortunately no longer linear in the 1DM, which complicates the optimization. Veeraraghavan and Mazziotti [79, 80] have used this approach to find a global minimum for the Hartree-Fock energy. They rewrote the optimization problem to a Semidefinite Programming form and deduced an upper and lower bound on the Hartree-Fock energy.

2.3.2 The second-order reduced density matrix

The second-order reduced Density Matrix (2DM) is defined by

$$\Gamma_{\alpha\beta;\gamma\delta} = {}^2\Gamma_{\alpha\beta;\gamma\delta} = \sum_i w_i \langle \psi_i | \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\delta \hat{a}_\gamma | \psi_i \rangle. \quad (2.18)$$

Again $\sum_i w_i = 1$ and $w_i \geq 0$. From now on, we will use Γ to denote the 2DM. As with the 1DM, several properties can be derived directly from the definition (2.18)

$$\Gamma_{\alpha\beta;\gamma\delta} = -\Gamma_{\beta\alpha;\gamma\delta} = -\Gamma_{\alpha\beta;\delta\gamma} = \Gamma_{\beta\alpha;\delta\gamma}, \quad (2.19a)$$

$$\Gamma_{\alpha\beta;\gamma\delta} = \Gamma_{\gamma\delta;\alpha\beta}, \quad (2.19b)$$

$$\text{Tr}(\Gamma) = \sum_{\alpha < \beta} \Gamma_{\alpha\beta;\alpha\beta} = \frac{N(N-1)}{2}, \quad (2.19c)$$

$$\Gamma \succeq 0. \quad (2.19d)$$

The last condition can be interpreted in the same way as condition (2.8c) on the 1DM: as the positivity of an overlap matrix in the two-particle space.

As already stated, the N -representability conditions for the 2DM form a much harder problem. While the necessary and sufficient conditions for N -representability on the 1DM can be enforced solely using the spectrum of the 1DM, this cannot be the case for the 2DM. In general, a unitary transformation of the single-particle basis cannot diagonalize the 2DM and thus the spectrum of the 2DM does not form a complete set of unitary invariants. This is one of the reasons why the N -representability problem for the 2DM is so much harder than for the 1DM. Coleman [10] derived upper bounds on the eigenvalues of the 2DM

$$0 \leq \lambda \leq \begin{cases} N-1 & \text{when } N \text{ is odd} \\ N & \text{when } N \text{ is even} \end{cases} \quad (2.20)$$

For the 2DM we can again use the positivity of Hamiltonians of the class (2.9). To lighten the notation, we will not shown the ensemble summation in the conditions. This leads to the following conditions

- $\hat{B}^\dagger = \sum_{\alpha\beta} p_{\alpha\beta} \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger$ gives

$$\sum_{\alpha\beta\gamma\delta} p_{\alpha\beta} \langle \psi | \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\delta \hat{a}_\gamma | \psi \rangle p_{\gamma\delta} \geq 0, \quad (2.21)$$

which is equivalent with condition (2.19d). This condition has several names in the literature: P, D and J condition. We will use the latter. The 1DM can be extracted from the 2DM

$$\rho_{\alpha\beta} = \frac{1}{N-1} \sum_{\lambda} \Gamma_{\alpha\lambda;\beta\lambda}. \quad (2.22)$$

If we enforce this condition, the 1DM is also positive semidefinite

$$\sum_{\alpha\beta} z_\alpha \rho_{\alpha\beta} z_\beta = \frac{1}{N-1} \sum_{\alpha\beta} \sum_{\delta\gamma} z_\alpha \delta_{\gamma\delta} \Gamma_{\alpha\gamma;\beta\delta} z_\beta \geq 0, \quad (2.23)$$

as this is a special case of the general condition (2.21).

- $\hat{B}^\dagger = \sum_{\alpha\beta} q_{\alpha\beta} \hat{a}_\alpha \hat{a}_\beta$ gives

$$\sum_{\alpha\beta\gamma\delta} q_{\alpha\beta} \langle \psi | \hat{a}_\alpha \hat{a}_\beta \hat{a}_\delta^\dagger \hat{a}_\gamma^\dagger | \psi \rangle q_{\gamma\delta} \geq 0, \quad (2.24)$$

which is the $\mathcal{Q}$ condition of Garrod and Percus [11]. We define the $\mathcal{Q}$ matrix as

$$\mathcal{Q}_{\alpha\beta;\gamma\delta} = \langle \psi | \hat{a}_\alpha \hat{a}_\beta \hat{a}_\delta^\dagger \hat{a}_\gamma^\dagger | \psi \rangle. \quad (2.25)$$

Condition (2.24) expresses the positive semidefiniteness of the $\mathcal{Q}$ matrix. The probability of finding a two-hole pair has to be greater than zero. The $\mathcal{Q}$ matrix has the same symmetry in the indices as the 2DM, e.g. (2.19a) and (2.19b). It can be written as a function of the 2DM using the fundamental anticommutator relations eq. (B.5) on page 193

$$\begin{aligned} \mathcal{Q}_{\alpha\beta;\gamma\delta}(\Gamma) &= \delta_{\alpha\gamma} \delta_{\beta\delta} - \delta_{\alpha\delta} \delta_{\beta\gamma} + \Gamma_{\alpha\beta;\gamma\delta} \\ &\quad - \delta_{\alpha\gamma} \rho_{\beta\delta} + \delta_{\beta\gamma} \rho_{\alpha\delta} + \delta_{\alpha\delta} \rho_{\beta\gamma} - \delta_{\beta\delta} \rho_{\alpha\gamma}, \end{aligned} \quad (2.26a)$$

$$\mathcal{Q}(\Gamma) = {}^2\mathbb{1} + \Gamma - {}^1\mathbb{1} \wedge \rho. \quad (2.26b)$$

With $\mathbb{1}$ we denote the identity matrix, the superscript denotes the space. This condition enforces the positive semidefiniteness of the q matrix (2.13) in the same way as eq. (2.23). The $\mathcal{J}$ and $\mathcal{Q}$ condition are enough to enforce the N -representability of the 1DM as the trace is also fixed by condition (2.19c). However, the set over which the variation is done when using the $\mathcal{J}$ and $\mathcal{Q}$ condition is still larger than the true N -representable set of the 2DM and as such the energy be lower than the true ground state energy.

- $\hat{B}^\dagger = \sum_{\alpha\beta} g_{\alpha\beta} \hat{a}_\alpha^\dagger \hat{a}_\beta$ gives

$$\sum_{\alpha\beta\gamma\delta} g_{\alpha\beta} \langle \psi | \hat{a}_\alpha^\dagger \hat{a}_\beta \hat{a}_\delta^\dagger \hat{a}_\gamma | \psi \rangle g_{\gamma\delta} \geq 0, \quad (2.27)$$

which leads to the $\mathcal{G}$ condition [11]

$$\mathcal{G}_{\alpha\beta;\gamma\delta} = \langle \psi | \hat{a}_\alpha^\dagger \hat{a}_\beta \hat{a}_\delta^\dagger \hat{a}_\gamma | \psi \rangle. \quad (2.28)$$

This condition enforces the positive semidefiniteness of the $\mathcal{G}$ matrix which expressed the probability of finding a particle-hole pair must be larger than zero. We can again express the $\mathcal{G}$ condition as a function of the 2DM using the anticommutator relations (B.5)

$$\mathcal{G}_{\alpha\beta;\gamma\delta} = \delta_{\beta\delta} \rho_{\alpha\gamma} - \Gamma_{\alpha\delta;\gamma\beta}. \quad (2.29)$$

A major difference with the $\mathcal{J}$ and $\mathcal{Q}$ condition is that the symmetry within a pair state is gone: $\mathcal{G}_{\alpha\beta;\gamma\delta} \neq \mathcal{G}_{\beta\alpha;\gamma\delta}$. The $\mathcal{G}$ matrix is only symmetric under exchange of the pair: $\mathcal{G}_{\alpha\beta;\gamma\delta} = \mathcal{G}_{\gamma\delta;\alpha\beta}$.

• $\hat{B}^\dagger = \sum_{\alpha\beta} \tilde{g}_{\alpha\beta} \hat{a}_\alpha \hat{a}_\beta^\dagger$ gives

$$\sum_{\alpha\beta\gamma\delta} \tilde{g}_{\alpha\beta} \langle \psi | \hat{a}_\alpha \hat{a}_\beta^\dagger \hat{a}_\gamma \hat{a}_\delta^\dagger | \psi \rangle \tilde{g}_{\gamma\delta} \geq 0, \quad (2.30)$$

We will show that this condition is not independent of the $\mathcal{G}$ condition and therefore it is not used. It expresses the probability of finding a hole-particle pair.

It is possible to use a more general form of the $\hat{B}^\dagger$ operator in the Hamiltonian (2.9). For the so-called $\mathcal{G}'$ condition, we use

$$\hat{B}^\dagger = \sum_{\alpha\beta} g'_{\alpha\beta} \hat{a}_\alpha^\dagger \hat{a}_\beta + C, \quad (2.31)$$

where C is a constant operator. This leads to the following condition

$$\begin{aligned} \langle \psi | \hat{B}^\dagger \hat{B} | \psi \rangle &= \sum_{\alpha\beta\gamma\delta} g'_{\alpha\beta} \mathcal{G}_{\alpha\beta;\gamma\delta} g'_{\gamma\delta} + C \sum_{\alpha\beta} g'_{\alpha\beta} \rho_{\alpha\beta} \\ &\quad + C \sum_{\gamma\delta} g'_{\gamma\delta} \rho_{\gamma\delta} + C^2 \geq 0. \end{aligned} \quad (2.32)$$

It is clear that we find the $\mathcal{G}$ condition (2.27) when we choose $C = 0$. We can rewrite the $\hat{B}^\dagger$ operator

$$\begin{aligned} \hat{B}^\dagger &= \sum_{\alpha\beta} g'_{\alpha\beta} \hat{a}_\alpha^\dagger \hat{a}_\beta + C \\ &= \sum_{\alpha\beta} -g'_{\alpha\beta} \hat{a}_\beta \hat{a}_\alpha^\dagger + \sum_{\alpha\beta} \delta_{\alpha\beta} g'_{\alpha\beta} + C. \end{aligned}$$

If we choose $C = \sum_{\alpha} -g'_{\alpha\alpha}$, we find the condition (2.30). The most strict choice of C is

$$C = - \sum_{\alpha\beta} g'_{\alpha\beta} \rho_{\alpha\beta}, \quad (2.33)$$

which can be understood if we rewrite eq. (2.32) to

$$\sum_{\alpha\beta\gamma\delta} g'_{\alpha\beta} \mathcal{G}_{\alpha\beta;\gamma\delta} g'_{\gamma\delta} + \left(C + \sum_{\alpha\beta} g'_{\alpha\beta} \rho_{\alpha\beta} \right)^2 - \sum_{\alpha\beta\gamma\delta} g'_{\alpha\beta} g'_{\gamma\delta} \rho_{\alpha\beta} \rho_{\gamma\delta} \geq 0.$$

The choice (2.33) will give the lowest upper bound. The major disadvantage is that the condition is not linear in Γ anymore due to the last term. This complicates the Semidefinite Programming problem considerably and is therefore avoided. It turns out that the $\mathcal{G}$ condition will give the same results as using condition (2.31): the nullspace (the eigenspace corresponding to a zero eigenvalue) of both conditions are the same. To understand this, let us look at the condition that the $\mathcal{G}$ matrix has a zero eigenvalue

$$\sum_{\gamma\delta} \mathcal{G}_{\alpha\beta;\gamma\delta} v_{\gamma\delta} = \sum_{\gamma} \rho_{\alpha\gamma} v_{\gamma\beta} - \sum_{\gamma\delta} \Gamma_{\alpha\delta;\gamma\beta} v_{\gamma\delta} = 0. \quad (2.34)$$

If we trace this, we find

$$\begin{aligned} \sum_{\alpha} \sum_{\gamma\delta} \mathcal{G}_{\alpha\alpha;\gamma\delta} v_{\gamma\delta} &= \sum_{\alpha\gamma} \rho_{\alpha\gamma} v_{\gamma\alpha} + (N-1) \sum_{\gamma\delta} \rho_{\delta\gamma} v_{\gamma\delta} \\ &= N \sum_{\alpha\beta} \rho_{\alpha\beta} v_{\beta\alpha} = 0. \end{aligned} \quad (2.35)$$

The $\mathcal{G}'$ condition with the optimal choice for C' (eq. (2.33)) is

$$\mathcal{G}'_{\alpha\beta;\gamma\delta}(\Gamma) = \mathcal{G}_{\alpha\beta;\gamma\delta}(\Gamma) - \rho_{\alpha\beta} \rho_{\gamma\delta}. \quad (2.36)$$

We again look at the condition for a zero eigenvalue

$$\sum_{\gamma\delta} \mathcal{G}'_{\alpha\beta;\gamma\delta} v_{\gamma\delta} = \sum_{\gamma\delta} \mathcal{G}_{\alpha\beta;\gamma\delta} v_{\gamma\delta} - \rho_{\alpha\beta} \sum_{\gamma\delta} \rho_{\gamma\delta} v_{\gamma\delta} = 0. \quad (2.37)$$

This shows that if $\mathcal{G}$ has a zero eigenvalue, then $\mathcal{G}'$ also has a zero eigenvalue with the same eigenvector. The converse is also true. If v is an eigenvector of $\mathcal{G}'$ with zero eigenvalue, then the following vector is an eigenvector of $\mathcal{G}$ with zero eigenvalue

$$v'_{\alpha\beta} = v_{\alpha\beta} - \sum_{\gamma\delta} \rho_{\gamma\delta} v_{\gamma\delta} \frac{\delta_{\alpha\beta}}{N}, \quad (2.38)$$

which can be seen from

$$\begin{aligned} \sum_{\gamma\delta} \mathcal{G}_{\alpha\beta;\gamma\delta} v'_{\gamma\delta} &= \sum_{\gamma\delta} \mathcal{G}'_{\alpha\beta;\gamma\delta} v'_{\gamma\delta} + \sum_{\gamma\delta} \rho_{\alpha\beta} \rho_{\gamma\delta} v'_{\gamma\delta} \\ &= \sum_{\gamma\delta} \rho_{\alpha\beta} \rho_{\gamma\delta} v_{\gamma\delta} - \sum_{\gamma\delta} \text{Tr}(\rho v) \frac{\delta_{\gamma\delta}}{N} \rho_{\alpha\beta} \rho_{\gamma\delta} \\ &= \rho_{\alpha\beta} \text{Tr}(\rho v) - \text{Tr}(\rho v) \rho_{\alpha\beta} \sum_{\gamma} \frac{\rho_{\gamma\gamma}}{N} = 0. \end{aligned}$$

We have used the fact that v' is also an eigenvector of $\mathcal{G}'$

$$\sum_{\gamma\delta} \mathcal{G}'_{\alpha\beta;\gamma\delta} v'_{\gamma\delta} = \sum_{\gamma\delta} \mathcal{G}'_{\alpha\beta;\gamma\delta} v_{\gamma\delta} - \text{Tr}(\rho v) \frac{1}{N} \sum_{\gamma} \mathcal{G}'_{\alpha\beta;\gamma\gamma} = 0,$$

because

$$\begin{aligned} \sum_{\gamma} \mathcal{G}'_{\alpha\beta;\gamma\gamma} &= \sum_{\gamma} \delta_{\beta\gamma} \rho_{\alpha\gamma} - \sum_{\gamma} \Gamma_{\alpha\gamma;\gamma\beta} - \sum_{\gamma} \rho_{\alpha\beta} \rho_{\gamma\gamma} \\ &= \rho_{\alpha\beta} + (N-1) \rho_{\alpha\beta} - N \rho_{\alpha\beta} = 0. \end{aligned}$$

We have shown that the nullspaces of $\mathcal{G}$ and $\mathcal{G}'$ coincide. This means that the boundary of the region where $\mathcal{G}$ and $\mathcal{G}'$ are positive semidefinite is the same and both conditions will produce identical results. As $\mathcal{G}'$ is non-linear in Γ , we always use $\mathcal{G}$.

The combination of the $\mathcal{I}$, $\mathcal{Q}$ and $\mathcal{G}$ conditions are called two-index conditions. For some systems, these conditions produce good results [81]. However, we have seen that a good approximation to the energy does not necessarily mean that we have a good approximation to the 2DM itself. This can be seen if we try to calculate other operators, like the spin expectation value or the correlation functions. To fix this, we can use higher order density matrices.

2.3.3 The third-order reduced density matrix

The third-order reduced Density Matrix (3DM) is defined as

$${}^3\Gamma_{\alpha\beta\gamma;\delta\varepsilon\zeta} = \sum_i w_i \langle \psi_i | \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma^\dagger \hat{a}_\delta \hat{a}_\varepsilon \hat{a}_\zeta | \psi_i \rangle, \quad (2.39)$$

again with $\sum_i w_i = 1$ and $w_i \geq 0$. Several properties can be directly deduced from the definition

$${}^3\Gamma_{\alpha\beta\gamma;\delta\varepsilon\zeta} = \text{sgn}(\sigma)\text{sgn}(\tau) {}^3\Gamma_{\sigma(\alpha)\sigma(\beta)\sigma(\gamma);\tau(\delta)\tau(\varepsilon)\tau(\zeta)} \quad \forall \sigma, \tau \in S_3, \quad (2.40a)$$

$${}^3\Gamma_{\alpha\beta\gamma;\delta\varepsilon\zeta} = {}^3\Gamma_{\delta\varepsilon\zeta;\alpha\beta\gamma}, \quad (2.40b)$$

$$\text{Tr}({}^3\Gamma) = \sum_{\alpha<\beta<\gamma} {}^3\Gamma_{\alpha\beta\gamma;\alpha\beta\gamma} = \frac{N(N-1)(N-2)}{6}, \quad (2.40c)$$

$${}^3\Gamma \succeq 0. \quad (2.40d)$$

Property (2.40a) holds for all elements of the permutation group of 3 elements, S_3 . The 2DM can be calculated from the 3DM

$$\Gamma_{\alpha\beta;\gamma\delta} = \frac{1}{N-2} \sum_{\lambda} {}^3\Gamma_{\alpha\beta\lambda;\gamma\delta\lambda}. \quad (2.41)$$

If the 3DM fulfils condition (2.40d) then the 2DM is also be positive semidefinite. In the same way as for the 1DM and 2DM, we can enforce the positive semidefiniteness of the Hamiltonian class (2.9) where $\hat{B}^\dagger$ has three particle operators.

- $\hat{B}^\dagger = \sum_{\alpha\beta\gamma} p_{\alpha\beta\gamma} \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma^\dagger$ leads to

$$\sum_{\alpha\beta\gamma} \sum_{\delta\varepsilon\zeta} p_{\alpha\beta\gamma} \langle \psi | \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma^\dagger \hat{a}_\delta \hat{a}_\varepsilon \hat{a}_\zeta | \psi \rangle p_{\delta\varepsilon\zeta} \geq 0, \quad (2.42)$$

which is equivalent with condition (2.40d). The probability of finding a three-particle triplet must be larger than zero. This is the ${}^3\mathcal{I}$ condition.

- $\hat{B}^\dagger = \sum_{\alpha\beta\gamma} q_{\alpha\beta\gamma}^1 \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma^\dagger$ leads to

$$\sum_{\alpha\beta\gamma} \sum_{\delta\varepsilon\zeta} q_{\alpha\beta\gamma}^1 \langle \psi | \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma^\dagger \hat{a}_\delta \hat{a}_\varepsilon \hat{a}_\zeta | \psi \rangle q_{\delta\varepsilon\zeta}^1 \geq 0. \quad (2.43)$$

We define the ${}^3\mathcal{E}$ matrix as

$${}^3\mathcal{E}_{\alpha\beta\gamma;\delta\epsilon\zeta} = \langle \psi | \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma \hat{a}_\zeta^\dagger \hat{a}_\delta \hat{a}_\epsilon | \psi \rangle, \quad {}^3\mathcal{E} \succeq 0. \quad (2.44)$$

Rewriting this as a function of the 3DM, we find

$${}^3\mathcal{E}({}^3\Gamma)_{\alpha\beta\gamma;\delta\epsilon\zeta} = \delta_{\gamma\zeta} \Gamma_{\alpha\beta;\delta\epsilon} - {}^3\Gamma_{\alpha\beta\zeta;\delta\epsilon\gamma}. \quad (2.45)$$

- $\hat{B}^\dagger = \sum_{\alpha\beta\gamma} q_{\alpha\beta\gamma}^2 \hat{a}_\alpha^\dagger \hat{a}_\beta \hat{a}_\gamma$ leads to

$$\sum_{\alpha\beta\gamma} \sum_{\delta\epsilon\zeta} q_{\alpha\beta\gamma}^2 \langle \psi | \hat{a}_\alpha^\dagger \hat{a}_\beta \hat{a}_\gamma \hat{a}_\zeta^\dagger \hat{a}_\delta \hat{a}_\epsilon | \psi \rangle q_{\delta\epsilon\zeta}^2 \geq 0. \quad (2.46)$$

We define ${}^3\mathcal{F}$ matrix as

$${}^3\mathcal{F}_{\alpha\beta\gamma;\delta\epsilon\zeta} = \langle \psi | \hat{a}_\alpha^\dagger \hat{a}_\beta \hat{a}_\gamma \hat{a}_\zeta^\dagger \hat{a}_\delta \hat{a}_\epsilon | \psi \rangle, \quad {}^3\mathcal{F} \succeq 0. \quad (2.47)$$

Rewriting this as a function of the 3DM, we find

$$\begin{aligned} {}^3\mathcal{F}({}^3\Gamma)_{\alpha\beta\gamma;\delta\epsilon\zeta} = & {}^3\Gamma_{\alpha\zeta\epsilon;\delta\gamma\beta} + \delta_{\gamma\zeta} \mathcal{G}_{\alpha\beta;\delta\epsilon} - \delta_{\beta\zeta} \mathcal{G}_{\alpha\gamma;\delta\epsilon} \\ & + \delta_{\epsilon\gamma} \Gamma_{\alpha\zeta;\delta\beta} - \delta_{\beta\epsilon} \Gamma_{\alpha\zeta;\delta\gamma} \end{aligned} \quad (2.48)$$

This condition implies the $\mathcal{G}$ condition for the two-index constraint

$$\mathcal{G}_{\alpha\beta;\gamma\delta} = \frac{1}{N+1} \sum_{\lambda} {}^3\mathcal{F}_{\alpha\beta\lambda;\gamma\delta\lambda}. \quad (2.49)$$

- $\hat{B}^\dagger = \sum_{\alpha\beta\gamma} q_{\alpha\beta\gamma}^3 \hat{a}_\alpha \hat{a}_\beta \hat{a}_\gamma$ leads to

$$\sum_{\alpha\beta\gamma} \sum_{\delta\epsilon\zeta} q_{\alpha\beta\gamma}^3 \langle \psi | \hat{a}_\alpha \hat{a}_\beta \hat{a}_\gamma \hat{a}_\zeta^\dagger \hat{a}_\delta^\dagger \hat{a}_\epsilon^\dagger | \psi \rangle q_{\delta\epsilon\zeta}^3 \geq 0. \quad (2.50)$$

We define the ${}^3\mathcal{Q}$ matrix as

$${}^3\mathcal{Q} \succeq 0, \quad {}^3\mathcal{Q}_{\alpha\beta\gamma;\delta\epsilon\zeta} = \langle \psi | \hat{a}_\alpha \hat{a}_\beta \hat{a}_\gamma \hat{a}_\zeta^\dagger \hat{a}_\delta^\dagger \hat{a}_\epsilon^\dagger | \psi \rangle. \quad (2.51)$$

Rewriting this as a function of the 3DM, we find

$$\begin{aligned} {}^3\mathcal{Q}({}^3\Gamma)_{\alpha\beta\gamma;\delta\epsilon\zeta} = & -{}^3\Gamma_{\alpha\beta\gamma;\delta\epsilon\zeta} + \\ & \delta_{\gamma\zeta} \delta_{\beta\epsilon} \delta_{\alpha\delta} - \delta_{\gamma\epsilon} \delta_{\alpha\delta} \delta_{\beta\zeta} + \delta_{\alpha\zeta} \delta_{\gamma\epsilon} \delta_{\beta\delta} - \delta_{\gamma\zeta} \delta_{\alpha\epsilon} \delta_{\beta\delta} + \delta_{\beta\zeta} \delta_{\alpha\epsilon} \delta_{\gamma\delta} - \delta_{\alpha\zeta} \delta_{\beta\epsilon} \delta_{\gamma\delta} \\ & - (\delta_{\gamma\zeta} \delta_{\beta\epsilon} - \delta_{\beta\zeta} \delta_{\gamma\epsilon}) \rho_{\alpha\delta} + (\delta_{\gamma\zeta} \delta_{\alpha\epsilon} - \delta_{\alpha\zeta} \delta_{\gamma\epsilon}) \rho_{\beta\delta} - (\delta_{\beta\zeta} \delta_{\alpha\epsilon} - \delta_{\alpha\zeta} \delta_{\beta\epsilon}) \rho_{\gamma\delta} \\ & + (\delta_{\gamma\zeta} \delta_{\beta\delta} - \delta_{\beta\zeta} \delta_{\gamma\delta}) \rho_{\alpha\epsilon} - (\delta_{\gamma\zeta} \delta_{\alpha\delta} - \delta_{\alpha\zeta} \delta_{\gamma\delta}) \rho_{\epsilon\beta} + (\delta_{\beta\zeta} \delta_{\alpha\delta} - \delta_{\alpha\zeta} \delta_{\beta\delta}) \rho_{\gamma\epsilon} \\ & - (\delta_{\beta\delta} \delta_{\gamma\epsilon} - \delta_{\beta\epsilon} \delta_{\gamma\delta}) \rho_{\alpha\zeta} + (\delta_{\gamma\epsilon} \delta_{\alpha\delta} - \delta_{\alpha\epsilon} \delta_{\gamma\delta}) \rho_{\beta\zeta} - (\delta_{\beta\epsilon} \delta_{\alpha\delta} - \delta_{\alpha\epsilon} \delta_{\beta\delta}) \rho_{\gamma\zeta} \\ & + \delta_{\gamma\zeta} \Gamma_{\alpha\beta;\delta\epsilon} - \delta_{\beta\zeta} \Gamma_{\alpha\gamma;\delta\epsilon} + \delta_{\alpha\zeta} \Gamma_{\beta\gamma;\delta\epsilon} - \delta_{\gamma\epsilon} \Gamma_{\alpha\beta;\delta\zeta} + \delta_{\beta\epsilon} \Gamma_{\alpha\gamma;\delta\zeta} - \delta_{\alpha\epsilon} \Gamma_{\beta\gamma;\delta\zeta} \\ & + \delta_{\gamma\delta} \Gamma_{\alpha\beta;\epsilon\zeta} - \delta_{\beta\delta} \Gamma_{\alpha\gamma;\epsilon\zeta} + \delta_{\alpha\delta} \Gamma_{\beta\gamma;\epsilon\zeta}, \end{aligned} \quad (2.52a)$$

$${}^3\mathcal{Q}({}^3\Gamma) = {}^3\mathbb{1} - {}^2\mathbb{1} \wedge \rho + \Gamma \wedge {}^1\mathbb{1} - {}^3\Gamma. \quad (2.52b)$$

This condition implies the $\mathcal{Q}$ condition for the two-index constraints

$$\mathcal{Q}_{\alpha\beta;\gamma\delta} = \frac{1}{2} \sum_{\lambda} {}^3\mathcal{Q}_{\alpha\beta\lambda;\gamma\delta\lambda}. \quad (2.53)$$

All other permutations of the operator for the ${}^3\mathcal{E}$ and ${}^3\mathcal{F}$ condition are not independent of these conditions. For example: $\hat{B}^\dagger = \sum_{\alpha\beta\gamma} \tilde{f}_{\alpha\beta\gamma} \hat{a}_\alpha \hat{a}_\beta^\dagger \hat{a}_\gamma = \sum_{\alpha\beta\gamma} \tilde{f}_{\alpha\beta\gamma} \hat{a}_\beta^\dagger \hat{a}_\alpha \hat{a}_\gamma + \sum_{\alpha\gamma} \delta_{\alpha\beta} \tilde{f}_{\alpha\alpha\gamma} \hat{a}_\gamma$. This will not generate any additional constraints.

The direct optimization of the 3DM with the conditions ${}^3\mathcal{J}$, ${}^3\mathcal{E}$, ${}^3\mathcal{F}$ and ${}^3\mathcal{Q}$ yields better results than the optimization of the 2DM as all the two-index conditions are included as well [6, 82, 83]. However, due to the computational cost, this is not often done. The middle way is to keep optimizing the 2DM but enforce some three-index constraints which can be written as a function of the 2DM. If we take the anticommutator of a three-index operator, we effectively lower the rank by one and we have something that can be expressed as a function of the 2DM. We enforce the Hamiltonian class

$$\hat{H} = \hat{B}^\dagger \hat{B} + \hat{B} \hat{B}^\dagger. \quad (2.54)$$

We can find three independent conditions from this class. They were first derived by Erdahl [84] and used by Zhao *et al.*, Hammond and Mazziotti [25, 26] in practical calculations.

• $\hat{B}^\dagger = \sum_{\alpha\beta\gamma} t_{\alpha\beta\gamma}^1 \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma^\dagger$ leads to

$$\sum_{\alpha\beta\gamma} \sum_{\delta\epsilon\zeta} t_{\alpha\beta\gamma}^1 \langle \psi | \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma^\dagger \hat{a}_\zeta \hat{a}_\epsilon \hat{a}_\delta + \hat{a}_\zeta \hat{a}_\epsilon \hat{a}_\delta \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma^\dagger | \psi \rangle t_{\delta\epsilon\zeta}^1 \geq 0. \quad (2.55)$$

This is the $\mathcal{T}_1$ condition and we define the $\mathcal{T}_1$ matrix as

$$(\mathcal{T}_1)_{\alpha\beta\gamma;\delta\epsilon\zeta} = \langle \psi | \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma^\dagger \hat{a}_\zeta \hat{a}_\epsilon \hat{a}_\delta + \hat{a}_\zeta \hat{a}_\epsilon \hat{a}_\delta \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma^\dagger | \psi \rangle. \quad (2.56)$$

Notice that $\mathcal{T}_1 = {}^3\mathcal{J} + {}^3\mathcal{Q}$. It can be written as a function of the 2DM using the anticommutator relations (B.5) resulting in

$$\begin{aligned} (\mathcal{T}_1(\Gamma))_{\alpha\beta\gamma;\delta\epsilon\zeta} = & \delta_{\gamma\zeta} \delta_{\beta\epsilon} \delta_{\alpha\delta} - \delta_{\gamma\epsilon} \delta_{\alpha\delta} \delta_{\beta\zeta} + \delta_{\alpha\zeta} \delta_{\gamma\epsilon} \delta_{\beta\delta} - \delta_{\gamma\zeta} \delta_{\alpha\epsilon} \delta_{\beta\delta} + \delta_{\beta\zeta} \delta_{\alpha\epsilon} \delta_{\gamma\delta} - \delta_{\alpha\zeta} \delta_{\beta\epsilon} \delta_{\gamma\delta} \\ & - (\delta_{\gamma\zeta} \delta_{\beta\epsilon} - \delta_{\beta\zeta} \delta_{\gamma\epsilon}) \rho_{\alpha\delta} + (\delta_{\gamma\zeta} \delta_{\alpha\epsilon} - \delta_{\alpha\zeta} \delta_{\gamma\epsilon}) \rho_{\beta\delta} - (\delta_{\beta\zeta} \delta_{\alpha\epsilon} - \delta_{\alpha\zeta} \delta_{\beta\epsilon}) \rho_{\gamma\delta} \\ & + (\delta_{\gamma\zeta} \delta_{\beta\delta} - \delta_{\beta\zeta} \delta_{\gamma\delta}) \rho_{\alpha\epsilon} - (\delta_{\gamma\zeta} \delta_{\alpha\delta} - \delta_{\alpha\zeta} \delta_{\gamma\delta}) \rho_{\epsilon\beta} + (\delta_{\beta\zeta} \delta_{\alpha\delta} - \delta_{\alpha\zeta} \delta_{\beta\delta}) \rho_{\gamma\epsilon} \\ & - (\delta_{\beta\delta} \delta_{\gamma\epsilon} - \delta_{\beta\epsilon} \delta_{\gamma\delta}) \rho_{\alpha\zeta} + (\delta_{\gamma\epsilon} \delta_{\alpha\delta} - \delta_{\alpha\epsilon} \delta_{\gamma\delta}) \rho_{\beta\zeta} - (\delta_{\beta\epsilon} \delta_{\alpha\delta} - \delta_{\alpha\epsilon} \delta_{\beta\delta}) \rho_{\gamma\zeta} \\ & + \delta_{\gamma\zeta} \Gamma_{\alpha\beta;\delta\epsilon} - \delta_{\beta\zeta} \Gamma_{\alpha\gamma;\delta\epsilon} + \delta_{\alpha\zeta} \Gamma_{\beta\gamma;\delta\epsilon} - \delta_{\gamma\epsilon} \Gamma_{\alpha\beta;\delta\zeta} + \delta_{\beta\epsilon} \Gamma_{\alpha\gamma;\delta\zeta} - \delta_{\alpha\epsilon} \Gamma_{\beta\gamma;\delta\zeta} \\ & + \delta_{\gamma\delta} \Gamma_{\alpha\beta;\epsilon\zeta} - \delta_{\beta\delta} \Gamma_{\alpha\gamma;\epsilon\zeta} + \delta_{\alpha\delta} \Gamma_{\beta\gamma;\epsilon\zeta}, \end{aligned} \quad (2.57a)$$

$$\mathcal{T}_1(\Gamma) = {}^3\mathbb{1} - {}^2\mathbb{1} \wedge \rho + \Gamma \wedge {}^1\mathbb{1}. \quad (2.57b)$$

The $\mathbb{1}$ again denotes the identity matrix in the appropriate space.

- $\hat{B}^\dagger = \sum_{\alpha\beta\gamma} t_{\alpha\beta\gamma}^2 \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma$ leads to

$$\sum_{\alpha\beta\gamma} \sum_{\delta\epsilon\zeta} t_{\alpha\beta\gamma}^2 \langle \psi | \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma \hat{a}_\zeta^\dagger \hat{a}_\epsilon \hat{a}_\delta + \hat{a}_\zeta^\dagger \hat{a}_\epsilon \hat{a}_\delta \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma | \psi \rangle t_{\delta\epsilon\zeta}^2 \geq 0. \quad (2.58)$$

This is the $\mathcal{T}_2$ condition and we define the $\mathcal{T}_2$ matrix as

$$(\mathcal{T}_2)_{\alpha\beta\gamma;\delta\epsilon\zeta} = \langle \psi | \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma \hat{a}_\zeta^\dagger \hat{a}_\epsilon \hat{a}_\delta + \hat{a}_\zeta^\dagger \hat{a}_\epsilon \hat{a}_\delta \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma | \psi \rangle. \quad (2.59)$$

Notice that $\mathcal{T}_2 = {}^3\mathcal{E} + {}^3\mathcal{F}$. As a function of the 2DM this becomes

$$\begin{aligned} (\mathcal{T}_2(\Gamma))_{\alpha\beta\gamma;\delta\epsilon\zeta} &= (\delta_{\alpha\delta}\delta_{\beta\epsilon} - \delta_{\alpha\epsilon}\delta_{\beta\delta})\rho_{\gamma\zeta} - \delta_{\alpha\delta}\Gamma_{\gamma\epsilon;\zeta\beta} + \delta_{\gamma\zeta}\Gamma_{\alpha\beta;\delta\epsilon} \\ &\quad + \delta_{\beta\delta}\Gamma_{\gamma\epsilon\zeta\alpha} + \delta_{\alpha\epsilon}\Gamma_{\gamma\delta;\zeta\beta} - \delta_{\beta\epsilon}\Gamma_{\gamma\delta\zeta\alpha} \end{aligned} \quad (2.60)$$

- $\hat{B}^\dagger = \sum_{\alpha\beta\gamma} t_{\alpha\beta\gamma}^3 \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma^\dagger$ leads to

$$\sum_{\alpha\beta\gamma} \sum_{\delta\epsilon\zeta} t_{\alpha\beta\gamma}^3 \langle \psi | \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma^\dagger \hat{a}_\zeta \hat{a}_\epsilon^\dagger \hat{a}_\delta + \hat{a}_\zeta \hat{a}_\epsilon^\dagger \hat{a}_\delta \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma^\dagger | \psi \rangle t_{\delta\epsilon\zeta}^3 \geq 0. \quad (2.61)$$

This is the $\mathcal{T}_3$ condition and we define the $\mathcal{T}_3$ matrix as

$$(\mathcal{T}_3)_{\alpha\beta\gamma;\delta\epsilon\zeta} = \langle \psi | \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma^\dagger \hat{a}_\zeta \hat{a}_\epsilon^\dagger \hat{a}_\delta + \hat{a}_\zeta \hat{a}_\epsilon^\dagger \hat{a}_\delta \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma^\dagger | \psi \rangle. \quad (2.62)$$

As a function of the 2DM this becomes

$$\begin{aligned} (\mathcal{T}_3(\Gamma))_{\alpha\beta\gamma;\delta\epsilon\zeta} &= \delta_{\alpha\delta}\delta_{\beta\gamma}\delta_{\epsilon\zeta} - \delta_{\alpha\delta}\Gamma_{\epsilon\gamma;\beta\zeta} - \delta_{\alpha\zeta}\Gamma_{\epsilon\zeta;\delta\beta} - \delta_{\gamma\delta}\Gamma_{\alpha\epsilon;\beta\zeta} \\ &\quad + \delta_{\beta\epsilon}\Gamma_{\alpha\gamma;\delta\zeta} - \delta_{\gamma\zeta}\Gamma_{\alpha\epsilon;\delta\beta} - \delta_{\alpha\delta}\delta_{\epsilon\zeta}\rho_{\beta\gamma} + \delta_{\alpha\zeta}\delta_{\gamma\beta}\rho_{\epsilon\delta} \\ &\quad + \delta_{\gamma\delta}\delta_{\epsilon\zeta}\rho_{\alpha\beta} + (\delta_{\alpha\delta}\delta_{\gamma\zeta} - \delta_{\alpha\zeta}\delta_{\gamma\delta})\rho_{\beta\epsilon}. \end{aligned} \quad (2.63)$$

Like the $\mathcal{G}'$ condition, it is also possible to derive a $\mathcal{T}'_2$ condition. This condition will turn out be more useful than $\mathcal{G}'$. The $\mathcal{T}'_2$ condition is generated by

$$\hat{H} = \hat{B}_1^\dagger \hat{B}_1 + \hat{B}_2^\dagger \hat{B}_2, \quad (2.64)$$

where

$$\hat{B}_1^\dagger = \sum_{\alpha\beta\gamma} t_{\alpha\beta\gamma}^2 \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma + \sum_{\lambda} \hat{a}_\lambda^\dagger, \quad (2.65a)$$

$$\hat{B}_2^\dagger = \sum_{\alpha\beta\gamma} t_{\alpha\beta\gamma}^2 \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma. \quad (2.65b)$$

As the sum of positive semidefinite operators (2.64) must be positive semidefinite too. The condition consists of the $\mathcal{T}_2$ condition plus additional terms

$$\begin{aligned} &\sum_{\alpha\beta\gamma} \sum_{\delta\epsilon\zeta} t_{\alpha\beta\gamma}^2 (\mathcal{T}_2)_{\alpha\beta\gamma;\delta\epsilon\zeta} t_{\delta\epsilon\zeta}^2 + \sum_{\alpha\beta\gamma\lambda} t_{\alpha\beta\gamma}^2 \langle \psi | \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma \hat{a}_\lambda | \psi \rangle \tilde{t}_\lambda^2 \\ &\quad + \sum_{\mu\delta\epsilon\zeta} \tilde{t}_\mu^2 \langle \psi | \hat{a}_\delta^\dagger \hat{a}_\epsilon^\dagger \hat{a}_\zeta \hat{a}_\mu | \psi \rangle t_{\delta\epsilon\zeta}^2 + \sum_{\lambda\mu} \tilde{t}_\lambda^2 \rho_{\lambda\mu} \tilde{t}_\mu^2 \geq 0. \end{aligned} \quad (2.66)$$

We can write this as a matrix condition

$$\mathcal{T}'_2 = \begin{bmatrix} (\mathcal{T}_2)_{\alpha\beta\gamma;\delta\varepsilon\zeta} & \omega_{\alpha\beta\gamma;\lambda} \\ \omega_{\mu;\delta\varepsilon\zeta} & \rho_{\mu\lambda} \end{bmatrix} \succeq 0, \quad (2.67)$$

with

$$\omega_{\alpha\beta\gamma;\lambda} = \Gamma_{\alpha\beta;\lambda\gamma}. \quad (2.68)$$

The condition (2.67) includes the $\mathcal{T}_2$ condition as a diagonal block of a positive semidefinite matrix must also be positive semidefinite (see Chapter C on page 195). It also encompasses the $\mathcal{T}_3$ condition

$$\begin{aligned} \hat{B}^\dagger &= \sum_{\alpha\beta\gamma} t_{\alpha\beta\gamma}^3 \hat{a}_\alpha^\dagger \hat{a}_\beta \hat{a}_\gamma^\dagger \\ &= - \sum_{\alpha\beta\gamma} t_{\alpha\beta\gamma}^3 \hat{a}_\alpha^\dagger \hat{a}_\gamma^\dagger \hat{a}_\beta + \sum_{\alpha\beta} t_{\alpha\beta\beta}^3 \hat{a}_\alpha^\dagger \end{aligned} \quad (2.69)$$

This is equivalent with condition (2.65a)

$$t_{\alpha\beta\gamma}^2 = -t_{\alpha\beta\gamma}^3, \quad (2.70a)$$

$$\tilde{t}_\lambda^2 = \sum_{\alpha} t_{\lambda\alpha\alpha}^3. \quad (2.70b)$$

In practice, the $\mathcal{T}'_2$ condition is used as it encompasses both the $\mathcal{T}_2$ and the $\mathcal{T}_3$ condition for a negligible additional cost. It has been found that the $\mathcal{T}'_2$ condition produces slightly better results than the combination of $\mathcal{T}_1$ and $\mathcal{T}_2$ [46, 82].

2.3.4 Other Constraints

Until now, we used a class of positive semidefinite Hamiltonians to approximate N -representability. In principle, any knowledge about the ground state of the system can be enforced and can possibly improve the energy or the reduced density matrix. For example, if the ground state should be a singlet ($\hat{S} = 0$), the expectation value of the spin operator can be enforced

$$\text{Tr}(S\Gamma) = 0. \quad (2.71)$$

For spin expectation value, we can even do better as will be explained in Section 2.4.1. In general, we are of course interested in constraints that give the largest improvement of the energy. However, only part of all conceivable constraints will actually improve the energy.

I. Sharp conditions

Another straightforward improvement would be to have stricter bounds on the $\mathcal{J}$, $\mathcal{Q}$ and $\mathcal{G}$ conditions. The $\mathcal{J}$ condition reflects that the probability for a given pair to be occupied cannot be negative. If the used basis set is large enough and the filling is below half, it seems fair to

assume that the lowest eigenvalue of the $\mathcal{J}$ will be zero. However, this does not mean that there is no room for improvement: we can look for the worst possible violation of this and impose it. On the other side, we can also derive the maximal eigenvalue of the $\mathcal{J}$ condition: the condition belongs to a class of exactly solvable Hamiltonian known as the Richardson-Gaudin pairing Hamiltonians [85–87]. It is thus possible to efficiently calculate the largest eigenvalue [33]. In practical procedure, we look for the worst possible violation of the upper bound so that the condition is as tight as possible. For the $\mathcal{Q}$ condition, a similar approach is possible for an upper bound. In contrast with the $\mathcal{J}$ condition, the lower bound can also be improved: the $\mathcal{Q}$ condition expresses that the probability for a given pair to be unoccupied cannot be negative. It seems probable that the lowest eigenvalue will be greater than zero. The $\mathcal{G}$ condition is somewhat different: there is no known way to find stricter upper or lower bounds in the general case, but if we assume that the matrix $g_{\alpha\beta}$ in eq. (2.27) on page 20 is Hermitian ($\hat{B}^\dagger = \hat{B}$), we can [34]. The eigenstates of the $\hat{B}$ operator are now Slater determinants and the eigenvalues simply are the sum of the orbital energies of the occupied orbitals. As we assumed Hermiticity, the eigenvalues of the $\mathcal{G}$ condition are the squares of the eigenvalues of $\hat{B}$. Determining an upper bound is now easy: it is either the sum of the N lowest orbital energies or the N highest. The lower bound is an entirely different story: different eigenvalues can cancel each other. It is basically an integer programming problem. It can be shown to be related to the p -dispersion problems [34, 88], which is NP-hard [89].

These stricter versions of the two-index conditions are known as the sharp condition. For a complete derivation of these sharp constraints, I refer to reference 90. Unfortunately, in practice these conditions do not improve the result for most systems [90], and therefore they are seldom used.

II. Subsystem constraints

Another set of N -representability conditions worth mentioning are the so-called subsystem constraints [30]. The idea is to apply constraints to the 2DM restricted to a subspace of the single-particle Hilbert space. The concept of fractional N -representability is needed for this: using an ensemble of wave functions with a different number of particles, it is possible to give an equivalent definition of fractional N -representability [90]. The full N -representability conditions do not automatically fulfill the same set of conditions for a subsystem. These conditions are needed in the dissociation of diatomic molecules [30, 31, 91].

2.4 Symmetry considerations

Symmetry plays a fundamental role in physics, especially in quantum mechanics [92, 93]. The knowledge of the symmetry of the system allows us to understand a great deal without even knowing the ground state wave function. For example, the existence of the dipole momentum of a molecule can be predicted on symmetry basis alone. There are selection rules for which transitions of energy levels are allowed in a molecule, which are solely based on the symmetry

of the molecule. It also simplifies the possible solutions of the Schrödinger equation as every eigenvalue can be labeled on symmetry grounds. In real life, symmetry is often associated with beauty and harmony. In quantum mechanics, symmetry is also a source of beauty but in the mathematical sense. A symmetry in quantum mechanics means that the system is invariant under an operator. Mathematically this means that the operator must commute with the Hamiltonian of the system: if $\hat{A}$ is the symmetry operator then

$$\hat{H}\hat{A}|\psi\rangle = \hat{A}\hat{H}|\psi\rangle = E\hat{A}|\psi\rangle, \quad (2.72)$$

from which

$$[\hat{H}, \hat{A}] = 0. \quad (2.73)$$

The basic concept in symmetry is the group: this is a set of operations that leave a system invariant, together with following properties. If G is a symmetry group, together with an operation to combine two elements then

- $\forall a \in G$ and $\forall b \in G$ then $ab \in G$.
- There is a unique element $e \in G$ such that $\forall a \in G, ae = ea = a$.
- $\forall a \in G$, there exists an element $b \in G$ such that $ab = ba = e$.
- $\forall a, b, c \in G: a(bc) = (ab)c$.

There are 2 major categories, discrete symmetries and continuous symmetries. A discrete symmetry has a finite number of operations. An example is the group C_s which contains two operations: the identity operator and a reflection around a plane. A continuous symmetry depends on some continuous parameter. For example, a sphere has a continuous symmetry: the group $O(3)$ of all rotations in $\mathbb{R}^3$ around an axis.

The elements of a group are abstract operations, to use them on a system we need a representation of the elements. This is where representation theory comes in [92, 94, 95]. In representation theory, the elements of a group are represented by linear transformations on a vector space. The dimension of the vector space (or representation space) is called the dimension of the representation. The following relation must hold for a representation, where $\phi : G \rightarrow V$ is the image from the group to the vector space: $\forall a, b \in G : \phi(ab) = \phi(a)\phi(b)$. An important concept are the irreducible representations, as these are the building blocks for all other representations. A representation is irreducible if the representation space has no subspaces which are also closed under the group operations. If such a subspace would exist, it is called a subrepresentation. If the only subrepresentation of a representation is the trivial subrepresentation (only the identity), the representation is irreducible. Every other (reducible) representation can be expressed as a direct sum of these. Linear transformations on vector spaces can be represented by matrices. A matrix is non-reducible if there does not exist a similarity transformation that reduces all the matrices in the representation to a block diagonal form. Every group has a trivial representation in which every element is represented by the identity matrix. For a complete introduction into group theory and representation theory, I

refer to references 92, 94–96. In what follows, we will only be concerned with representations of finite groups. We will first look at exploiting the spin symmetry of the system and then the point group symmetry.

2.4.1 Spin symmetry

Spin is a strange, fundamental concept in quantum mechanics. It is the intrinsic angular momentum of a particle [1, 97]. Originally, it was thought be the effect of the particle spinning around its axis, hence the name [98]. Now we understand that spin is a fundamental property of a particle. Wolfgang Pauli is the father of the concept and worked out the mathematical description. Spin also allows us to split all particles into two disjunct groups: fermions and bosons. The latter have an integer spin and are symmetric under particle exchange while the former have a half-integer spin and are antisymmetric under particle exchange (the Pauli exclusion principle). In this work, we are only concerned with fermions and more specifically, electrons with spin $1/2$. In all that follows, we will assume that we are dealing with electrons. We wish to exploit the invariance of the Hamiltonian under rotations in the spin space. The symmetry group for spin $1/2$ fermions is $SU(2)$: the group of all unitary 2×2 matrices with $\det = 1$. The spin operator is given by

$$\hat{S} = \frac{\hbar}{2} \hat{\sigma}, \quad (2.74)$$

with the three Cartesian components

$$S_x = \frac{\hbar}{2} \sigma_x, \quad S_y = \frac{\hbar}{2} \sigma_y, \quad S_z = \frac{\hbar}{2} \sigma_z, \quad (2.75)$$

where σ is given by the three Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (2.76)$$

As angular momentum operators, they have to obey the structure relations of the Lie-algebra of $SU(2)$ [92, 99].

$$[S_x, S_y] = i\hbar S_z, \quad [S_y, S_z] = i\hbar S_x, \quad [S_z, S_x] = i\hbar S_y. \quad (2.77)$$

The Hamiltonian is invariant under spin rotations

$$[\hat{H}, \hat{S}^2] = 0, \quad [\hat{H}, \hat{S}_z] = 0, \quad (2.78)$$

with

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2. \quad (2.79)$$

Furthermore, $[\hat{S}^2, \hat{S}_z] = 0$ so that the eigenvalues and eigenvectors of the Hamiltonian can be labeled with the eigenvalues of $\hat{S}^2$ and $\hat{S}_z$. This means that

$$\hat{S}^2 |\Psi\rangle = S(S+1) |\Psi\rangle, \quad (2.80)$$

$$\hat{S}_z |\Psi\rangle = S_z |\Psi\rangle = M |\Psi\rangle, \quad (2.81)$$

and we can write

$$\hat{H} |\Psi_{SM}\rangle = E_{SM} |\Psi_{SM}\rangle. \quad (2.82)$$

It is also useful to define the ladder operators which can increase or lower M : $\hat{S}_{\pm} = \hat{S}_x \pm i\hat{S}_y$. Their effect is

$$\hat{S}_{\pm} |\Psi_{SM}\rangle = \hbar \sqrt{S(S+1) - M(M \pm 1)} |\Psi_{SM \pm 1}\rangle. \quad (2.83)$$

We now want to exploit this symmetry in v2DM calculations. The idea is to use spin symmetry to reduce the size of the 2DM. In this part, we will explicitly denote the spin in a single-particle state

$$|\alpha\rangle \rightarrow |a\sigma_a\rangle. \quad (2.84)$$

Roman letters will be used to denote the spatial part of the single-particle state, and σ will be used for the associated spin state. We want to couple electrons together. For this we need the Clebsch-Gordan coefficients: these coefficients allow us to reduce a coupled representation into the irreducible (uncoupled) representations. We want to find a state that fulfills all the previously mentioned properties of the spin operator. Let us take a look at the case of coupling of two electrons

$$|ab; SM_S\rangle = \sum_{\sigma_a \sigma_b} \langle \frac{1}{2} \sigma_a \frac{1}{2} \sigma_b | SM_S \rangle |a\sigma_a b\sigma_b\rangle. \quad (2.85)$$

The factor $\langle \frac{1}{2} \sigma_a \frac{1}{2} \sigma_b | SM_S \rangle$ is a Clebsch-Gordan coefficient for $SU(2)$. They can be found in Chapter D on page 199 together with some properties. Two spin- $1/2$ particles can be coupled together to a singlet ($S = 0$) or a triplet ($S = 1$). If we write out eq. (2.85), we find

$$|ab; 00\rangle = \frac{1}{\sqrt{2}} (|a \uparrow b \downarrow\rangle - |a \downarrow b \uparrow\rangle), \quad (2.86a)$$

$$|ab; 1 -1\rangle = |a \downarrow b \downarrow\rangle, \quad (2.86b)$$

$$|ab; 10\rangle = \frac{1}{\sqrt{2}} (|a \uparrow b \downarrow\rangle + |a \downarrow b \uparrow\rangle), \quad (2.86c)$$

$$|ab; 11\rangle = |a \uparrow b \uparrow\rangle. \quad (2.86d)$$

Note that state (2.86a) is symmetric under exchange of $a \Leftrightarrow b$ while eqs. (2.86b) to (2.86d) are antisymmetric. The norm of (2.85) is not unity

$$\langle ab; SM_S | cd; S' M'_S \rangle = \delta_{SS'} \delta_{M_S M'_S} \left(\delta_{ac} \delta_{bd} + (-1)^S \delta_{ad} \delta_{bc} \right). \quad (2.87)$$

With this knowledge, we can now define the spin-coupled version of the $\hat{B}^\dagger$ operator for the $\mathcal{J}$ condition

$$\begin{aligned} \hat{B}_{ab}^{\dagger SM_S} &= \frac{1}{\sqrt{1 + \delta_{ab}}} \left[\hat{a}_a^\dagger \otimes \hat{a}_b^\dagger \right]_M^S \\ &= \frac{1}{\sqrt{1 + \delta_{ab}}} \sum_{\sigma_a \sigma_b} \langle \frac{1}{2} \sigma_a \frac{1}{2} \sigma_b | SM_S \rangle \hat{a}_{a\sigma_a}^\dagger \hat{a}_{b\sigma_b}^\dagger. \end{aligned} \quad (2.88)$$

Using this definition, the 2DM becomes

$${}_{\mathcal{S}\mathcal{M}}\Gamma_{ab;cd}^{SM_S;S'M'_S} = \sum_i w_i \langle \psi_{\mathcal{S}\mathcal{M},i} | \hat{B}_{ab}^{\dagger SM_S} \hat{B}_{cd}^{S'M'_S} | \psi_{\mathcal{S}\mathcal{M},i} \rangle, \quad (2.89)$$

where the sum runs over an ensemble of wave functions with spin $\mathcal{S}$ and spin projection $\mathcal{M}$. We now couple both $\hat{B}$ operators together to total spin S_T

$$\begin{aligned} {}_{\mathcal{S}\mathcal{M}}\Gamma_{ab;cd}^{SM_S;S'M'_S} &= (-1)^{S'-M'_S} \sum_i w_i \sum_{S_T M_T} \langle SM_S S'-M'_S | S_T M_T \rangle \\ &\quad \langle \psi_{\mathcal{S}\mathcal{M},i} | \left[\hat{B}_{ab}^{\dagger SM_S} \otimes \hat{B}_{cd}^{S'M'_S} \right]_{M_T}^{S_T} | \psi_{\mathcal{S}\mathcal{M},i} \rangle. \end{aligned} \quad (2.90)$$

The prefactor appears because the $\hat{B}$ operators need to be spherical tensor operators (see Chapter D). As the ket and bra wave functions have the same spin projection $\mathcal{M}$, we can deduce that $M_T = 0$. Let us now assume that the ensemble consists of singlet wave functions ($\mathcal{S} = \mathcal{M} = 0$). It follows that $S_T = 0$ because of spin conservation and thus $S = S'$. The Clebsch-Gordan coefficient in eq. (2.90) reduces to

$$\langle SM_S S-M_S | 00 \rangle = \frac{(-1)^{S-M_S}}{\sqrt{2S+1}}. \quad (2.91)$$

The spin coupled 2DM for the singlet ensemble is

$$\begin{aligned} {}_{00}\Gamma_{ab;cd}^{SM_S;S'M'_S} &= \frac{\delta_{SS'} \delta_{M_S M'_S}}{2S+1} \\ &\quad \sum_i w_i \langle \psi_{00,i} | \left[\hat{B}_{ab}^{\dagger SM_S} \otimes \hat{B}_{cd}^{SM_S} \right]_0^0 | \psi_{00,i} \rangle. \end{aligned} \quad (2.92)$$

Note that this is independent of M_S . The 2DM is split up into a $S = 0$ block and a three-fold degenerate $S = 1$ block. For a singlet state, our notation can be abbreviated to $\Gamma_{ab;cd}^S$.

For higher spin states a similar reduction is possible provided we use a spin-averaged ensemble for the wave function

$$\begin{aligned} {}_{\mathcal{S}}\Gamma_{ab;cd}^{SM_S;S'M'_S} &= (-1)^{S'-M'_S} \sum_i w_i \sum_{S_T} \langle SM_S S'-M'_S | S_T 0 \rangle \\ &\quad \frac{1}{2\mathcal{S}+1} \sum_{\mathcal{M}} \langle \psi_{\mathcal{S}\mathcal{M},i} | \left[\hat{B}_{ab}^{\dagger SM_S} \otimes \hat{B}_{cd}^{S'M'_S} \right]_0^{S_T} | \psi_{\mathcal{S}\mathcal{M},i} \rangle. \end{aligned} \quad (2.93)$$

All members of the spin multiplet have an equal weight in the ensemble. This forms no restriction because of the spin symmetry: the ground state will be degenerate in the multiplet. If we now apply the Wigner-Eckart theorem (see Chapter D on page 199) to the operator in

eq. (2.93), we find

$$\begin{aligned} \langle \psi_{SM,i} | \left[\hat{B}_{ab}^{\dagger SM_S} \otimes \hat{B}_{cd}^{S'M_S} \right]_0^{S_T} | \psi_{SM,i} \rangle &= (-1)^{S-M} \begin{pmatrix} S & S & S_T \\ \mathcal{M} & -\mathcal{M} & 0 \end{pmatrix} \\ &\langle \psi_{S,i} | \left[\hat{B}_{ab}^{\dagger SM_S} \otimes \hat{B}_{cd}^{S'M_S} \right]_0^{S_T} | \psi_{S,i} \rangle. \end{aligned} \quad (2.94)$$

If we replace the prefactor by following Wigner 3-j symbol (related to Clebsch-Gordan coefficients, see Chapter D)

$$\begin{pmatrix} S & S & 0 \\ \mathcal{M} & -\mathcal{M} & 0 \end{pmatrix} = \frac{(-1)^{S-M}}{2S+1}, \quad (2.95)$$

then we can use the orthogonality relation for Clebsch-Gordan coefficients

$$\sum_{\mathcal{M}} \begin{pmatrix} S & S & 0 \\ \mathcal{M} & -\mathcal{M} & 0 \end{pmatrix} \begin{pmatrix} S & S & S_T \\ \mathcal{M} & -\mathcal{M} & 0 \end{pmatrix} = \delta_{S_T 0} \quad (2.96)$$

to find

$${}_S \Gamma_{ab;cd}^{SM_S;S'M_S} = \delta_{SS'} \frac{1}{2S+1} \frac{1}{2S+1} \sum_i w_i \langle \psi_{S,i} | \left[\hat{B}_{ab}^{\dagger SM_S} \otimes \hat{B}_{cd}^{S'M_S} \right]_0^0 | \psi_{S,i} \rangle. \quad (2.97)$$

Again, we find an expression that is independent of the spin projection. The reduction of the 2DM is the same as for the singlet ensemble: a $S = 0$ block and a three-fold degenerate $S = 1$ block. The same abbreviated notation can be used. The symmetry in the spatial orbital indices is as follows

$$\Gamma_{ab;cd}^S = (-1)^S \Gamma_{ba;cd}^S = (-1)^S \Gamma_{ab;dc}^S = \Gamma_{ba;dc}^S. \quad (2.98)$$

The minus factor is due to the (anti)symmetry in the index, like in eqs. (2.86a) to (2.86d). The $S = 0$ block has dimension $\frac{M}{4} (\frac{M}{2} + 1)$ while the $S = 1$ block has a dimension of $\frac{M}{4} (\frac{M}{2} - 1)$. If we sum these and keep the three-fold degeneracy in mind, we find the full dimension of the uncoupled 2DM, as expected. To summarize, the couple and uncoupled formulas for the 2DM are

$$\Gamma_{a\sigma_a b\sigma_b; c\sigma_c d\sigma_d} = \sqrt{(1 + \delta_{ab})(1 + \delta_{cd})} \sum_{SM} \langle \frac{1}{2}\sigma_a \frac{1}{2}\sigma_b | SM \rangle \quad (2.99a)$$

$$\begin{aligned} &\langle \frac{1}{2}\sigma_c \frac{1}{2}\sigma_d | SM \rangle \Gamma_{ab;cd}^S \\ \Gamma_{ab;cd}^S &= \frac{1}{\sqrt{(1 + \delta_{ab})(1 + \delta_{cd})}} \sum_{\sigma_a \sigma_b} \sum_{\sigma_c \sigma_d} \langle \frac{1}{2}\sigma_a \frac{1}{2}\sigma_b | SM \rangle \\ &\langle \frac{1}{2}\sigma_c \frac{1}{2}\sigma_d | SM \rangle \Gamma_{a\sigma_a b\sigma_b; c\sigma_c d\sigma_d} \end{aligned} \quad (2.99b)$$

The reduction of the 2DM can be seen as

$$\Gamma = \begin{pmatrix} & & & \\ & & & \\ & & & \\ & & & \end{pmatrix} \rightarrow \begin{pmatrix} \Gamma^0 & & & \\ & \Gamma^1 & & \\ & & \Gamma^1 & \\ & & & \Gamma^1 \end{pmatrix}. \quad (2.100)$$

In the same way, all conditions can be spin-adapted. The 1DM splits into two degenerate blocks. The $\mathcal{Q}$ reduction is identical to the 2DM and the $\mathcal{G}$ condition has a similar reduction but without the symmetry in the spatial orbital indices. The three-index conditions are more complicated as an intermediary coupling has to take place and there are several possible paths to couple to the total spin. For a complete description of the spin-adapted conditions, we refer to reference 90.

The reduction of the 2DM using spin symmetry can be seen as an N -representability condition which is necessary but not sufficient. The problem of guaranteeing that the wave function has the desired spin is called the S -representability problem [35, 40, 100–103]. It was introduced by Pérez-Romero, Tel, and Valdemoro [100] as: “we say that an $^p\Gamma$ is S -representable when there is an N -electron wave function corresponding to a pure spin quantum number S from which this $^p\Gamma$ can be derived.” The symmetry reduction due to spin will not alter the energy of the v2DM optimization because both the Hamiltonian and the N -representability conditions already have the correct spin symmetry. This can also be understood from the block structure of the reduced Hamiltonian: any off-block-diagonal element will only increase the energy. It does reduce the optimizing time as it reduces the number of matrix elements. To enforce the spin of the ensemble of wave functions, the most straightforward way is to enforce the expectation value of the $\hat{S}^2$ operator. In the singlet case, we can do even better. Let us take a look at the $\hat{S}_z$ operator.

$$\hat{S}_z = \sum_{a\sigma_a} \sigma_a \hat{a}_{a\sigma_a}^\dagger \hat{a}_{a\sigma_a} = \sum_a \frac{1}{2} \left(\hat{a}_{a\uparrow}^\dagger \hat{a}_{a\uparrow} - \hat{a}_{a\downarrow}^\dagger \hat{a}_{a\downarrow} \right). \quad (2.101)$$

To calculate the $\hat{S}_z$ operator using the 2DM, we must transform it to the two-particle basis

$$\hat{S}_z = \sum_{a\sigma_a} \sigma_a \hat{a}_{a\sigma_a}^\dagger \hat{a}_{a\sigma_a} = \frac{1}{N-1} \sum_{a\sigma_a b\sigma_b} \sigma_a \hat{a}_{a\sigma_a}^\dagger \hat{a}_{b\sigma_b}^\dagger \hat{a}_{b\sigma_b} \hat{a}_{a\sigma_a}, \quad (2.102)$$

the expectation value is

$$S_z = \frac{1}{N-1} \sum_{(a\sigma_a) < (b\sigma_b)} (\sigma_a + \sigma_b) \Gamma_{a\sigma_a b\sigma_b; a\sigma_a b\sigma_b}. \quad (2.103)$$

We want to use the spin-coupled version of eq. (2.101). For a particle-hole operator a slight complication arises which is fully explained in Chapter D

$$\begin{aligned} \hat{S}_z &= \sum_{\sigma_a} (-1)^{\frac{1}{2}-\sigma_a} \sigma_a \sum_a \hat{a}_{a\sigma_a}^\dagger \tilde{a}_{a-\sigma_a} \\ &= \sum_{\sigma_a} (-1)^{\frac{1}{2}-\sigma_a} \sigma_a \sum_S \left\langle \frac{1}{2} \sigma_a \frac{1}{2} - \sigma_a \middle| S 0 \right\rangle \sum_a \left[\hat{a}_{a\sigma_a}^\dagger \otimes \tilde{a}_{a-\sigma_a} \right]_0^S. \end{aligned} \quad (2.104)$$

The prefactor can again be written as a Clebsch-Gordan coefficient

$$\langle j m j - m | 1 0 \rangle = \frac{\sqrt{3}(-1)^{j-m} m}{\sqrt{2j+1} \sqrt{j(j+1)}}. \quad (2.105)$$

If we use this in eq. (2.104), we get

$$\begin{aligned}\hat{S}_z &= \frac{1}{\sqrt{2}} \sum_{\sigma_a} \sum_S \left\langle \frac{1}{2} \sigma_a \frac{1}{2} - \sigma_a | 10 \right\rangle \left\langle \frac{1}{2} \sigma_a \frac{1}{2} - \sigma_a | S0 \right\rangle \sum_a \left[\hat{a}_{a\sigma_a}^\dagger \otimes \tilde{\hat{a}}_{a-\sigma_a} \right]_0^S \\ &= \frac{1}{\sqrt{2}} \sum_a \left[\hat{a}_a^\dagger \otimes \tilde{\hat{a}}_a \right]_0^1,\end{aligned}\quad (2.106)$$

where we used the orthogonality properties of Clebsch-Gordan coefficients. If we want the singlet state, the expectation value of $\hat{S}_z$ should be zero. As this operator acts in the particle-hole space, this would mean that the $\mathcal{G}$ matrix has a zero eigenvalue with eigenvector $\frac{1}{\sqrt{2}} \delta_{S1} \delta_{ab}$:

$$\sum_c \mathcal{G}_{ab;cc}^1(\Gamma) = \langle \psi | \left[\hat{a}_a^\dagger \otimes \hat{a}_b \right]^1 \hat{S}_z | \psi \rangle = 0. \quad (2.107)$$

The beauty of the spin symmetry is that by imposing $\hat{S}_z = 0$, we also impose $\hat{S}_x = \hat{S}_y = 0$ due to the three-fold degenerate $S = 1$ block. The total spin will then also be zero as $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$. This is a stronger condition than only enforcing $\hat{S}^2 = 0$. If we write eq. (2.107) in function of the 2DM directly, we find

$$\begin{aligned}\forall a < b \quad \sum_S (2S+1) \left(\frac{1}{2} \frac{1}{N-1} - (-1)^S \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ \frac{1}{2} & \frac{1}{2} & S \end{Bmatrix} \right) \\ \sum_b \sqrt{(1+\delta_{ab})(1+\delta_{cd})} \Gamma_{ab;cb}^S = 0.\end{aligned}\quad (2.108)$$

This gives us $\frac{M}{4} \left(\frac{M}{2} - 1 \right)$ linear constraints. The $\mathcal{G}$ condition has a zero eigenvalue and this has to be dealt with accordingly (using a pseudo-inverse for example).

For higher spin states we can only enforce the spin expectation value of $\hat{S}^2$ as a linear constraint $\text{Tr}(S^2 \Gamma) = S(S+1)$. The uncoupled operator can be written as

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \frac{1}{2} \left(\hat{S}_+ \hat{S}_- + \hat{S}_- \hat{S}_+ \right) + \hat{S}_z^2, \quad (2.109)$$

where

$$\hat{S}_+ = \sum_a \hat{a}_{a\uparrow}^\dagger \hat{a}_{a\downarrow}, \quad (2.110a)$$

$$\hat{S}_- = \sum_a \hat{a}_{a\downarrow}^\dagger \hat{a}_{a\uparrow}. \quad (2.110b)$$

Using eqs. (2.110a) and (2.110b) in eq. (2.109), we find

$$\begin{aligned}\hat{S}^2 &= \sum_{(a\sigma_a) < (b\sigma_b)} \left(\frac{1}{N-1} (1 + \sigma_a^2 + \sigma_b^2) + 2\sigma_a \sigma_b \right) \hat{a}_{a\sigma_a}^\dagger \hat{a}_{b\sigma_b}^\dagger \hat{a}_{b\sigma_b} \hat{a}_{a\sigma_a} \\ &\quad + \sum_{ab} \hat{a}_{a\uparrow}^\dagger \hat{a}_{b\downarrow}^\dagger \hat{a}_{b\uparrow} \hat{a}_{a\downarrow}.\end{aligned}\quad (2.111)$$

This gives us one linear constraint. It is fair to assume that this condition is less stringent than in the singlet case. A possible solution is to use an ensemble of the maximal spin projection wave functions ($S_z = S$) [35]. On this ensemble, the same game as for the singlet can be played but with the $\hat{S}_+$ operator. Forcing a zero expectation value will again lead to a zero eigenvalue in the $\mathcal{G}$ matrix. The downside of this is that the symmetry reduction is smaller and computationally more demanding. For the singlet case, the maximal spin-projection ensemble and the spin-weighted ensemble are equivalent.

Angular momentum symmetry is mathematically exactly the same as spin symmetry. If a system has total angular momentum symmetry, meaning it is rotation invariant or there is a rotation axis (all linear molecules), this can also be exploited in v2DM. The approach is very similar to the spin case. For a complete derivation, we refer the reader to reference 90.

2.4.2 Spatial point group symmetry

Most small to medium sized molecules have a discrete geometric symmetry. For example, a homonuclear diatomic molecule such as N_2 , will have a mirror plane orthogonal on the connecting axis. We call this point group symmetry. The given example is C_s symmetry. The group consists of two operators: the identity operation and the mirror operation. The name comes from the fact that these symmetry groups leave at least one point invariant in all operations. We will introduce the most often encountered classes of point groups

- C_n : the group of all rotations that leaves an n -fold axis invariant (meaning rotations of $\frac{360^\circ}{n}$). By convention the z-axis is chosen as rotation axis.
- C_s : reflection around a plane.
- C_i : inversion symmetry.
- C_{nv} : C_n with the addition of n mirror planes containing the axis of rotation.
- C_{nh} : C_n with reflection around the plane perpendicular to the rotation axis. $C_{1h} = C_s$.
- D_n : C_n with n two-fold rotation axis perpendicular on to the n -fold axis.
- D_{nh} : C_{nh} with n reflection planes containing the n -fold rotation axis and one of the two-fold axis.

For example, the C_2H_4 molecule shown in Figure 2.4 has D_{2h} symmetry. The main two-fold

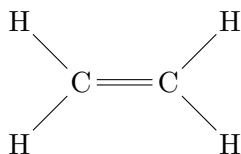


Figure 2.4: The ethylene molecule has D_{2h} symmetry.

	E	C_2
A	1	1
B	1	-1

(a) Character table of C_2

	A	B
A	A	B
B	B	A

(b) Multiplication table of C_2

Table 2.1: C_2 overview: it has 2 classes of operations. The identity operation and rotations over 180° . The two irreducible representations are A and B .

rotation axis is the connecting axis between the two carbon atoms (the z -axis). The two two-fold rotation axes are the x - and y -axis. The three reflection planes are xy , xz and yz .

In quantum chemistry, we will most often use abelian point groups ($\forall a, b \in G : ab = ba$). Abelian symmetry groups have one-dimensional irreducible representations and this simplifies the mathematics involved considerably as we work with scalars instead of matrices. This also means that we will usually use a subgroup of the real symmetry group of the molecule. For example, H_2 molecule has $D_{\infty h}$ symmetry but we will use D_{2h} because the latter is Abelian. The Abelian groups that can be used are C_1 , C_i , C_2 , C_s , C_{2v} , D_2 , C_{2h} and D_{2h} . The group C_1 is a special case. It is equivalent with no symmetry. Its only operation is the identity operation and thus every molecule has at least C_1 symmetry. In the rest of the text, C_1 and symmetry breaking will be used interchangeably. There is a standard nomenclature for the irreducible representations of point groups. I will give a short overview of what is useful for this work. The irreducible representation are classified according to their action on scalars, vector, etc. If under their action, the sign of the quantity does not change, we call it symmetric and the irreducible representation is denoted with an A . If the sign does change, it is called antisymmetric and the irreducible representation is denoted with a B . As an example, we show the character table and the multiplication table of C_2 group in Table 2.1. The character table contains the trace of the matrices of the irreducible representations. It is split up into conjugacy classes as the trace is invariant under a similarity transformation. These tables are extremely useful for decomposing a representation in its irreducible parts. The first irreducible representation A is called the trivial representation because all the representation matrices (scalars in this case) are one. Every group has this irreducible representation.

The basis functions in which the atomic orbitals are represented are usually not orthogonal. It is possible to transform these basis function to symmetry-adapted basis functions [104–107]: linear combinations are made such that the resulting orbitals all transform according to an irreducible representation of the symmetry group. In other words, every orbital can be labeled according to an irreducible representation. This allows for a serious reduction of the computational cost of calculating the one- and two-electron integrals. Symmetry restricts the number of non-zero integrals: two orbitals can only interact when they belong to the same irreducible representation. This means that in order for a matrix element to be non-zero, the representations of the operators in the matrix element have to couple to the trivial irreducible representation. For the one-particle operator: $\langle \psi | \hat{a}_{a\sigma_a}^\dagger \hat{a}_{b\sigma_b} | \psi \rangle$ can only be non-zero when $I_a \otimes I_b = I_1$, where I_a denotes the irreducible representation of orbital a and I_1 is the trivial representation. This is equivalent with $I_a = I_b$. For two-particle operators, the same

condition holds: $\langle \psi | \hat{a}_{a\sigma_a}^\dagger \hat{a}_{b\sigma_b}^\dagger \hat{a}_{d\sigma_d} \hat{a}_{c\sigma_c} | \psi \rangle \neq 0$ when $I_a \otimes I_b \otimes I_c \otimes I_d = I_1$. This is equivalent with $I_a \otimes I_b = I_c \otimes I_d$. This means that a two-particle operator $\hat{B}_{a\sigma_a b\sigma_b}^\dagger$ can be labeled by the irreducible representation $I_a \otimes I_b$: the operator $\hat{B}^\dagger$ can be written as

$$\hat{B}_{a\sigma_a b\sigma_b}^\dagger = \delta_{I_a \otimes I_b, I} \hat{a}_{a\sigma_a}^\dagger \hat{a}_{b\sigma_b}^\dagger. \quad (2.112)$$

The 2DM thus is

$$\Gamma_{a\sigma_a b\sigma_b; c\sigma_c d\sigma_d} = \delta_{I_1 I_2} \langle \psi | \hat{B}_{a\sigma_a b\sigma_b}^{\dagger I_1} \hat{B}_{c\sigma_c d\sigma_d}^{I_2} | \psi \rangle. \quad (2.113)$$

The 2DM falls apart in blocks per irreducible representation: ${}^I \Gamma_{a\sigma_a b\sigma_b; c\sigma_c d\sigma_d}$. Notice that this is independent of the wave function. Combining point group symmetry with spin symmetry is straightforward as both are unrelated: we simply have to attach a label for the irreducible representation to the operator (2.88):

$$\begin{aligned} \hat{B}_{ab}^{\dagger SM_S; I} &= \frac{1}{\sqrt{1 + \delta_{ab}}} \delta_{I_a \otimes I_b, I} \left[\hat{a}_a^\dagger \otimes \hat{a}_b^\dagger \right]_M^S \\ &= \frac{1}{\sqrt{1 + \delta_{ab}}} \delta_{I_a \otimes I_b, I} \sum_{\sigma_a \sigma_b} \langle \frac{1}{2} \sigma_a \frac{1}{2} \sigma_b | SM_S \rangle \hat{a}_{a\sigma_a}^\dagger \hat{a}_{b\sigma_b}^\dagger. \end{aligned} \quad (2.114)$$

The entire analysis of Section 2.4.1 on page 30 can now be repeated with the additional label for the irreducible representation and the constraint that both $\hat{B}$ operators should have the same label. Each spin block will split up into blocks per irreducible representation. The transformation formulas are

$$\begin{aligned} \Gamma_{a\sigma_a b\sigma_b; c\sigma_c d\sigma_d} &= \sqrt{(1 + \delta_{ab})(1 + \delta_{cd})} \delta_{I_a \otimes I_b; I_c \otimes I_d} \\ &\quad \sum_{SM} \langle \frac{1}{2} \sigma_a \frac{1}{2} \sigma_b | SM \rangle \langle \frac{1}{2} \sigma_c \frac{1}{2} \sigma_d | SM \rangle \Gamma_{ab; cd}^{S; I_a \otimes I_b}, \end{aligned} \quad (2.115a)$$

$$\begin{aligned} \Gamma_{ab; cd}^{S; I} &= \frac{1}{\sqrt{(1 + \delta_{ab})(1 + \delta_{cd})}} \delta_{I_a \otimes I_b; I} \delta_{I_c \otimes I_d; I} \sum_{\sigma_a \sigma_b} \sum_{\sigma_c \sigma_d} \\ &\quad \langle \frac{1}{2} \sigma_a \frac{1}{2} \sigma_b | SM \rangle \langle \frac{1}{2} \sigma_c \frac{1}{2} \sigma_d | SM \rangle \Gamma_{a\sigma_a b\sigma_b; c\sigma_c d\sigma_d}, \end{aligned} \quad (2.115b)$$

where $\Gamma^{S; I}$ denotes the block with spin S and irreducible representation I . The symmetry in the spatial orbital indices is unchanged (see eq. (2.98)). The exact reduction that the point group symmetry gives depends on the specific group. The higher the symmetry, the greater the reduction. As an example we take a look at H_2 in the Correlation Consistent Polarized Valence Double Zeta (cc-pVDZ) basis set [108]. The full symmetry group of H_2 is $D_{\infty h}$ but we use the largest Abelian subgroup which is D_{2h} . In this case, there are 5 orbitals per hydrogen atom: $1s2s2p^3$. The number of pairs per irreducible representation can be found in Table 2.2. The full dimension of the 2DM is $\frac{20(20-1)}{2} = 190$. Utilizing spin symmetry reduces this to a 55×55 and 45×45 block. This is already a 7-fold reduction of the number of matrix elements. If we add the D_{2h} symmetry to the picture, we get another 5-fold reduction: Instead of $190 \times 190 = 36100$ matrix elements, we have only 942 elements, a 38-fold total reduction!

Irrep.	$S = 0$	$S = 1$
A_g	16	6
B_{1g}	2	2
B_{2g}	6	6
B_{3g}	6	6
A_u	2	2
B_{1u}	11	11
B_{2u}	6	6
B_{3u}	6	6
	55	45

Table 2.2: The reduction due to spin and point group symmetry (D_{2h}) for the H_2 molecule.

2.5 The doubly-occupied Hilbert space

In previous sections, we only made general assumptions about the (ensemble of) wave functions from which the 2DM is derivable. All wave functions should be normalized and antisymmetric. For symmetry, we made assumptions on the quantum numbers of the wave function: it should be a singlet wave function, or the wave function should transform according to a certain irreducible representation. But we could make other or additional assumptions. If we take a look at the Full Configuration Interaction (FullCI) expansion of the wave function, we see that a Slater determinant is the basic building block

$$|\Psi\rangle = \sum_{\mathbf{k}} \sum_{\mathbf{s}} c_{\mathbf{k};\mathbf{s}} \hat{a}_{k_1 s_1}^\dagger \hat{a}_{k_2 s_2}^\dagger \dots \hat{a}_{k_N s_N}^\dagger |\rangle, \quad (2.116)$$

where the summation runs over all possible orbitals ($\mathbf{k}$) and spin configurations ($\mathbf{s}$). Every vector $\mathbf{k} = (k_1, k_2, \dots, k_N)$ with $k_i \in \{1, \dots, L\}$ contains the N orbitals that are occupied and the vector $\mathbf{s} = (s_1, s_2, \dots, s_N)$ with $s_i \in \{\uparrow, \downarrow\}$ contains the spin states for each orbital. Both are not independent as the Pauli exclusion principle must be obeyed. Classic wave function techniques will start from a reference Slater determinant, usually the results of a Hartree-Fock (HF) calculation, and add excitations on top of that [2]. In the limit where all excitations are added, the best possible result within the used basis set is found. However, the number of possible Slater determinants scales exponentially as $\binom{2L}{N}$ and we know that usually a smaller subset will be dominant: many of the $c_{\mathbf{k}}$ coefficients will be negligible. We will make the choice to only keep the Slater determinants where all orbitals are doubly occupied

$$|\Psi\rangle = \sum_{\mathbf{k}} c_{\mathbf{k}} \hat{a}_{k_1 \uparrow}^\dagger \hat{a}_{k_1 \downarrow}^\dagger \dots \hat{a}_{k_{\frac{N}{2}} \uparrow}^\dagger \hat{a}_{k_{\frac{N}{2}} \downarrow}^\dagger |\rangle. \quad (2.117)$$

We refer to this class of wave functions as Doubly Occupied Configuration Interaction (DOCI). For the motivation of this choice, we refer to Section 4.3 on page 89. Notice that the number of Slater determinants in the DOCI expansion still scales exponentially as $\binom{L}{\frac{N}{2}}$. We examine the

consequence of restricting the ensemble of wave function to DOCI wave functions on the N -representability constraints derived so far. This was originally done by Weinhold and Wilson [109, 110]¹ but to the best of my knowledge, they were never used in a practical calculations. They make a reference to a third paper but it never appeared. However, not all conditions on the 3DM were derived by them. We shall present all of them. Notice that the wave function (2.117) is a singlet state by definition: the expectation value of the operators $\hat{S}_z$, $\hat{S}_+$ and $\hat{S}_-$ are all zero. We denote the pair partner by a bar symbol: $a \uparrow = a$ and $a \downarrow = \bar{a}$ (or vice versa). In this context, the concept of seniority [111] is also very useful: the seniority number is the number of unpaired particles. DOCI is a seniority-zero wave function.

2.5.1 The first-order reduced density matrix

The 1DM derivable from a DOCI ensemble is much simpler

$$\rho_{a\sigma_a b\sigma_b} = \delta_{\sigma_a \sigma_b} \delta_{ab} \sum_i w_i \langle \psi_i | \hat{a}_{a\sigma_a}^\dagger \hat{a}_{a\sigma_a} | \psi_i \rangle = \rho_a = \rho_{\bar{a}}, \quad (2.118)$$

where $w_i \geq 0$ and $\sum_i w_i = 1$. Due to spin symmetry (see Section 2.4.1 on page 30), we known that the 1DM is diagonal in the spin indices, but in the case of DOCI, the 1DM must be diagonal in the spatial orbital index too: we can only break the same pair states in the ket and bra. It even becomes degenerate in the spin. This can be understood because of the number operators: in the DOCI case, $\hat{n}_a = \hat{n}_{\bar{a}}$. The number of particles in a spin-up and spin-down state is equal. The 1DM is reduced from a $2L \times 2L$ matrix to a vector of length L . The properties of the 1DM now are

$$\rho_a \geq 0, \quad (2.119a)$$

$$\sum_a \rho_a = \frac{N}{2}. \quad (2.119b)$$

The necessary and sufficient conditions for N -representability dictate that each element ρ_a should be in the interval $[0, 1]$. Notice that in the DOCI case, the used orbitals are automatically the natural orbitals and the elements of vector ρ_a are the natural occupation numbers. However, DOCI is orbital dependent: the orbital need to be optimized to find the lowest energy. This will be further explained in Section 4.3.

2.5.2 The second-order reduced density matrix

The 2DM is a bit more complex. It is important to realize that all operators need to couple to seniority zero if evaluated between two DOCI wave functions. An operator cannot change the number of broken pairs. This makes the 1DM diagonal as seen above. The $\hat{B}^\dagger$ operator can do two things: created or annihilate a doubly-occupied state (seniority zero), or break

1. E. Bright Wilson, Jr. is the father of Kenneth G. Wilson, who won the Nobel Prize for his work on the renormalisation group.

two doubly-occupied states (seniority two). As seniority must be conserved, the 2DM is block diagonal in the seniority number. Let us first look at the seniority-zero block. We define the $L \times L$ pair matrix as

$$\Pi_{ab} = \Gamma_{a\bar{a};b\bar{b}} = \langle \psi | \hat{a}_a^\dagger \hat{a}_{\bar{a}}^\dagger \hat{a}_b \hat{a}_{\bar{b}} | \psi \rangle, \quad (2.120)$$

where we have left out the ensemble summation to lighten the notation. From the positivity of the Hamiltonian $\hat{B}^\dagger \hat{B}$ with

$$\hat{B}^\dagger = \sum_a p_a \hat{a}_a^\dagger \hat{a}_{\bar{a}}^\dagger, \quad (2.121)$$

it follows that the pair matrix (2.120) must be positive semidefinite

$$\Pi \succeq 0. \quad (2.122)$$

This simply implies that the overlap of the wave function with one pair removed must be positive. The seniority-two block is part of the diagonal of the 2DM: as we break two pairs, the left and right operator must be equal. For $a < b$

$$D_{ab} = \Gamma_{ab;ab} = \langle \psi | \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_b \hat{a}_a | \psi \rangle, \quad (2.123a)$$

$$= \Gamma_{a\bar{b};a\bar{b}} = \langle \psi | \hat{a}_a^\dagger \hat{a}_{\bar{b}}^\dagger \hat{a}_{\bar{b}} \hat{a}_a | \psi \rangle, \quad (2.123b)$$

$$= \Gamma_{\bar{a}b;\bar{a}b} = \langle \psi | \hat{a}_{\bar{a}}^\dagger \hat{a}_b^\dagger \hat{a}_b \hat{a}_{\bar{a}} | \psi \rangle, \quad (2.123c)$$

$$= \Gamma_{\bar{a}\bar{b};\bar{a}\bar{b}} = \langle \psi | \hat{a}_{\bar{a}}^\dagger \hat{a}_{\bar{b}}^\dagger \hat{a}_{\bar{b}} \hat{a}_{\bar{a}} | \psi \rangle. \quad (2.123d)$$

Notice that eqs. (2.123a) and (2.123d) imply $D_{aa} = 0$ while eqs. (2.123b) and (2.123c) do not. As eq. (2.123b) in the case of $a = b$ is equal to Π_{aa} , we will pick $D_{aa} = 0$ from now on. The equality between eqs. (2.123a) to (2.123d) can be understood from

$$\hat{a}_a^\dagger \hat{a}_a = \hat{n}_a = \hat{n}_{\bar{a}} = \hat{a}_{\bar{a}}^\dagger \hat{a}_{\bar{a}} = \hat{a}_a^\dagger \hat{a}_{\bar{a}}^\dagger \hat{a}_{\bar{a}} \hat{a}_a, \quad (2.124)$$

for DOCI wave functions and the fundamental anticommutator relations eq. (B.5) on page 193. The diagonal D_{ab} is fourfold degenerate, corresponding to $S_z = -1, 0, 1$. A positive semidefinite matrix must have positive elements on its diagonal (see Chapter C on page 195) and thus the N -representability conditions on eq. (2.123) are

$$D_{ab} \geq 0. \quad (2.125)$$

This gives us a set of $\frac{L(L-1)}{2}$ linear inequalities to impose. The general 2DM is now reduced to a $L \times L$ matrix inequality and a set of linear inequalities.

There are now three ways of obtaining the 1DM out of the 2DM: via the general relation eq. (2.22) on page 19

$$\rho_a = \frac{1}{N-1} \sum_b (\Gamma_{ab;ab} + \Gamma_{a\bar{b};a\bar{b}}) = \frac{1}{N-1} \left(\Pi_{aa} + 2 \sum_b D_{ab} \right), \quad (2.126)$$

via the seniority-two diagonal D

$$\begin{aligned}\rho_a &= \frac{1}{\frac{N}{2}-1} \sum_b D_{ab} = \frac{2}{N-2} \sum_b D_{ab} \\ &= \frac{2}{N-2} \sum_b \langle \psi | \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_b \hat{a}_a | \psi \rangle,\end{aligned}\tag{2.127}$$

and via the pairing matrix Π

$$\rho_a = \Pi_{aa} = \langle \psi | \hat{a}_a^\dagger \hat{a}_{\bar{a}}^\dagger \hat{a}_{\bar{a}} \hat{a}_a | \psi \rangle.\tag{2.128}$$

These are not independent of each other. To have a consistent 2DM, the equivalence of eq. (2.127) and eq. (2.128) will have to be enforced. The trace of the 2DM remains unaltered but we can now split it over Π and D

$$\text{Tr}(\Pi) = \sum_a \Pi_{aa} = \frac{N}{2},\tag{2.129}$$

$$\text{Tr}(D) = \sum_{a<b} D_{ab} = \frac{1}{2} \sum_{ab} D_{ab} = \frac{N}{8} (N-2),\tag{2.130}$$

$$\text{Tr}(\Gamma) = \text{Tr}(\Pi) + 4\text{Tr}(D) = \frac{N(N-1)}{2},$$

where we keep the fourfold degeneracy of D in mind.

I. The $\mathcal{Q}$ condition

The $\mathcal{Q}$ matrix has the same structure as the 2DM itself. The seniority-zero block is derived from the positivity of

$$\sum_{ab} q_a \langle \psi | \hat{a}_a \hat{a}_{\bar{a}} \hat{a}_b^\dagger \hat{a}_{\bar{b}}^\dagger | \psi \rangle q_b \geq 0.\tag{2.131}$$

We define the $L \times L$ matrix $\mathcal{Q}^\Pi$ as

$$\mathcal{Q}_{ab}^\Pi = \langle \psi | \hat{a}_a \hat{a}_{\bar{a}} \hat{a}_{\bar{b}}^\dagger \hat{a}_b^\dagger | \psi \rangle.\tag{2.132}$$

Equation (2.129) means that $\mathcal{Q}^\Pi$ should be positive semidefinite: $\mathcal{Q}^\Pi \succeq 0$. The $\mathcal{Q}^\Pi$ can again be expressed as a function of the Π and D matrices

$$\mathcal{Q}_{ab}^\Pi(\Pi, D) = \delta_{ab}(1 - \rho_a - \rho_b) + \Pi_{ab}.\tag{2.133}$$

The seniority two part is on the diagonal of the $\mathcal{Q}$ matrix and given by

$$a < b : \quad \langle \psi | \hat{a}_a \hat{a}_b \hat{a}_b^\dagger \hat{a}_a^\dagger | \psi \rangle = 1 - \rho_a - \rho_b + D_{ab} \geq 0.\tag{2.134}$$

Just like for the 2DM, this forms a set of $\frac{L(L-1)}{2}$ linear inequalities.

II. The $\mathcal{G}$ condition

The $\mathcal{G}$ condition is somewhat more elaborate as more combinations are non-zero. We work systematically according to seniority and spin. The full operator $\hat{B}^\dagger$ for the $\mathcal{G}$ condition is

$$\hat{B}^\dagger = \sum_{\alpha\beta} g_{\alpha\beta} \hat{a}_\alpha^\dagger \hat{a}_\beta \quad (2.135)$$

$$= \sum_{ab} \left(g_{ab}^1 \hat{a}_a^\dagger \hat{a}_b + g_{ab}^2 \hat{a}_a^\dagger \hat{a}_{\bar{b}} + g_{ab}^3 \hat{a}_{\bar{a}}^\dagger \hat{a}_b + g_{ab}^4 \hat{a}_{\bar{a}}^\dagger \hat{a}_{\bar{b}} \right). \quad (2.136)$$

Spin projections $S_z = \pm 1$ are equivalent, so we only consider the $S_z = +1$ case: the g^2 and g^3 terms will generate equivalent constraints. We always assume $a \neq b$, since for a DOCI wave function $\hat{a}_a^\dagger \hat{a}_{\bar{a}} = 0$. The particle-hole operators generating this constraint are of the form

$$\hat{B}^\dagger = \sum_{ab} g_{ab}^2 \hat{a}_a^\dagger \hat{a}_{\bar{b}}, \quad (2.137)$$

which leads to the following seniority-2 positivity condition:

$$\begin{aligned} \sum_{abcd} g_{ab}^2 \langle \psi | \hat{a}_a^\dagger \hat{a}_{\bar{b}} \hat{a}_d^\dagger \hat{a}_{\bar{c}} | \psi \rangle g_{cd}^2 &= \\ \sum_{abcd} g_{ab}^2 [\delta_{bd} \delta_{ac} (\rho_a - D_{ab}) - \delta_{ad} \delta_{bc} \Pi_{ab}] g_{cd}^2 &= \\ \sum_{ab} g_{ab}^2 [(\rho_a - D_{ab}) g_{ab}^2 - \Pi_{ab} g_{ba}^2] &\geq 0 \end{aligned} \quad (2.138)$$

This condition is almost diagonal, as g_{ab}^2 is only connected with itself and g_{ba}^2 . If we order the summation

$$\sum_{a < b} g_{ab}^2 (\rho_a - D_{ab}) g_{ab}^2 - g_{ab}^2 \Pi_{ab} g_{ba}^2 + g_{ba}^2 (\rho_b - D_{ab}) g_{ba}^2 - g_{ba}^2 \Pi_{ab} g_{ab}^2 \geq 0, \quad (2.139)$$

we can see that this is equivalent with the positive semidefiniteness of the following set of 2×2 matrices

$$\forall a < b \quad \begin{bmatrix} \rho_a - D_{ab} & -\Pi_{ab} \\ -\Pi_{ab} & \rho_b - D_{ab} \end{bmatrix} \succeq 0. \quad (2.140)$$

For the $S_z = 0$ and seniority-two case, the particle-hole operators are of the form

$$\hat{B}_1^\dagger = \sum_{ab} g_{ab}^1 \hat{a}_a^\dagger \hat{a}_b, \quad (2.141a)$$

$$\hat{B}_4^\dagger = \sum_{ab} g_{ab}^4 \hat{a}_{\bar{a}}^\dagger \hat{a}_{\bar{b}}, \quad (2.141b)$$

with $a \neq b$. These terms are coupled to each other. The diagonal terms, $\hat{B}_1^\dagger \hat{B}_1$ and $\hat{B}_4^\dagger \hat{B}_4$, are

$$\langle \psi | \hat{a}_a^\dagger \hat{a}_b \hat{a}_d^\dagger \hat{a}_{\bar{c}} | \psi \rangle = \delta_{ac} \delta_{bd} (\rho_a - D_{ab}) = \langle \psi | \hat{a}_{\bar{a}}^\dagger \hat{a}_{\bar{b}} \hat{a}_{\bar{d}}^\dagger \hat{a}_{\bar{c}} | \psi \rangle. \quad (2.142)$$

The off-diagonal terms, $\hat{B}_1^\dagger \hat{B}_4$ and $\hat{B}_4^\dagger \hat{B}_1$, are

$$\langle \psi | \hat{a}_a^\dagger \hat{a}_b \hat{a}_d^\dagger \hat{a}_{\bar{c}} | \psi \rangle = \delta_{ad} \delta_{bc} \Pi_{ab} = \langle \psi | \hat{a}_a^\dagger \hat{a}_{\bar{b}} \hat{a}_d^\dagger \hat{a}_c | \psi \rangle , \quad (2.143)$$

which in the same way leads to the set of 2×2 constraint matrices

$$\forall a < b \quad \begin{bmatrix} \rho_a - D_{ab} & \Pi_{ab} \\ \Pi_{ab} & \rho_b - D_{ab} \end{bmatrix} \succeq 0 . \quad (2.144)$$

These only differ with (2.140) in the sign of the off-diagonal elements but the characteristic polynomial of both is the same and thus the conditions are equivalent.

The $S_z = 0$ and seniority-zero part is built by two particle-hole operators

$$\hat{B}_1^\dagger = \sum_a g_a \hat{a}_a^\dagger \hat{a}_a, \quad (2.145a)$$

$$\hat{B}_2^\dagger = \sum_b g_b \hat{a}_b^\dagger \hat{a}_{\bar{b}}. \quad (2.145b)$$

This leads to a $2L \times 2L$ matrix with diagonal elements, $\hat{B}_1^\dagger \hat{B}_1$ and $\hat{B}_2^\dagger \hat{B}_2$,

$$\langle \psi | \hat{a}_a^\dagger \hat{a}_a \hat{a}_b^\dagger \hat{a}_b | \psi \rangle = \delta_{ab} \rho_a + D_{ab} = \langle \psi | \hat{a}_{\bar{a}}^\dagger \hat{a}_{\bar{a}} \hat{a}_{\bar{b}}^\dagger \hat{a}_{\bar{b}} | \psi \rangle , \quad (2.146)$$

and off-diagonal elements, $\hat{B}_1^\dagger \hat{B}_2$ and $\hat{B}_2^\dagger \hat{B}_1$,

$$\begin{aligned} \langle \psi | \hat{a}_a^\dagger \hat{a}_a \hat{a}_{\bar{b}}^\dagger \hat{a}_{\bar{b}} | \psi \rangle &= D_{ab} + \delta_{ab} \Pi_{ab} \\ &= \delta_{ab} \rho_a + D_{ab} \\ &= \langle \psi | \hat{a}_{\bar{a}}^\dagger \hat{a}_{\bar{a}} \hat{a}_{\bar{b}}^\dagger \hat{a}_{\bar{b}} | \psi \rangle . \end{aligned} \quad (2.147)$$

Both blocks are identical. This means we have a positivity condition on a block matrix of the form

$$\begin{bmatrix} A & A \\ A & A \end{bmatrix} . \quad (2.148)$$

Using the following block matrix property of determinants (see Chapter C on page 195)

$$\begin{vmatrix} A & B \\ B & A \end{vmatrix} = |A - B| |A + B| , \quad (2.149)$$

we can see that we only have to impose the positivity of one block to obey the constraint. This leads to the matrix condition $\mathcal{G}^\Pi \succeq 0$ of a $L \times L$ matrix:

$$\mathcal{G}_{ab}^\Pi(\Pi, D) = \delta_{ab} \rho_a + D_{ab} . \quad (2.150)$$

Unlike the $\mathcal{J}$ and $\mathcal{Q}$ conditions, the original $\mathcal{G}$ matrix is never used. We have derived a simpler set of conditions which are equivalent.

Compared to the full $\mathcal{P}$, $\mathcal{Q}$ and $\mathcal{G}$ conditions, these constraints have a much lower scaling. The matrix dimensions are reduced from L^2 to L .

A DOCI wave function is a singlet state by definition. In Section 2.4.1 on page 30 we derived a set of necessary conditions for the singlet state on the 2DM. In the case of DOCI derived 2DM, this condition is automatically fulfilled. The $\hat{S}_z$ operator is

$$\hat{S}_z = \frac{1}{2} \sum_a \left(\hat{a}_a^\dagger \hat{a}_a - \hat{a}_{\bar{a}}^\dagger \hat{a}_{\bar{a}} \right). \quad (2.151)$$

We reevaluated the condition eq. (2.107) on page 35,

$$\begin{aligned} \langle \psi | \hat{a}_c^\dagger \hat{a}_d \hat{S}_z | \psi \rangle &= \\ &= \frac{1}{2} \delta_{cd} \sum_a^L \left(\langle \psi | \hat{a}_c^\dagger \hat{a}_d \hat{a}_a^\dagger \hat{a}_a | \psi \rangle - \langle \psi | \hat{a}_c^\dagger \hat{a}_d \hat{a}_{\bar{a}}^\dagger \hat{a}_{\bar{a}} | \psi \rangle \right) \\ &= \frac{1}{2} \sum_a^L \left(\langle \psi | \hat{a}_a^\dagger \hat{a}_a | \psi \rangle - \langle \psi | \hat{a}_c^\dagger \hat{a}_a^\dagger \hat{a}_c \hat{a}_a | \psi \rangle - \langle \psi | \hat{a}_c^\dagger \hat{a}_{\bar{a}}^\dagger \hat{a}_c \hat{a}_{\bar{a}} | \psi \rangle \right) \\ &= \frac{1}{2} \sum_a^L (\rho_a + (1 - \delta_{ac}) D_{ac} - \Pi_{ac} \delta_{ac} - (1 - \delta_{ac}) D_{ca}) \\ &= 0. \end{aligned}$$

This shows no additional constraints are needed to ensure the singlet state.

2.5.3 The third-order reduced density matrix

The 3DM falls apart in blocks labeled by S_z and the seniority number: we have seniority one and three, combined with $S_z = \pm \frac{1}{2}, \pm \frac{3}{2}$.

The seniority-three part, which breaks up three pairs, must be diagonal so that the three pairs can recombine. The diagonal elements of a positive semidefinite matrix must be positive leading to

$$D_{abc}^3 = \langle \psi | \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_c \hat{a}_b \hat{a}_a | \psi \rangle \geq 0. \quad (2.152)$$

It is clear that D_{abc}^3 will be zero when any two indices are equal. Furthermore, the different permutations of spin-up and spin-down will lead to the same constraint: D_{abc}^3 is fourfold degenerate for the different values of S_z . There is also permutation symmetry in the indices

$$\forall \sigma \in S_3 : \quad D_{abc}^3 = D_{\sigma(a)\sigma(b)\sigma(c)}^3, \quad (2.153)$$

where S_3 is the symmetric group of three elements. This condition gives us a set of $\frac{L(L-1)(L-2)}{6}$ linear constraints. If we sum over the different indices, we find

$$\sum_c D_{abc}^3 = \left(\frac{N}{2} - 2\right) D_{ab}, \quad (2.154a)$$

$$\sum_{bc} D_{abc}^3 = \left(\frac{N}{2} - 1\right) \left(\frac{N}{2} - 2\right) \rho_a, \quad (2.154b)$$

$$\sum_{abc} D_{abc}^3 = \frac{N}{2} \left(\frac{N}{2} - 1\right) \left(\frac{N}{2} - 2\right). \quad (2.154c)$$

The condition (2.152) implies the condition (2.125) on the 2DM.

The seniority-one part means removing an entire pair and breaking another resulting in

$$\begin{aligned} \Pi_{ac}^b = \Pi_{ca}^b &= \langle \psi | \hat{a}_a^\dagger \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_b \hat{a}_c \hat{a}_c | \psi \rangle = \Pi_{ac}^{\bar{b}} = \Pi_{ca}^{\bar{b}} \\ &= \langle \psi | \hat{a}_b^\dagger \hat{a}_a^\dagger \hat{a}_a^\dagger \hat{a}_c \hat{a}_c \hat{a}_b | \psi \rangle \end{aligned} \quad (2.155)$$

This set of L symmetric matrices is twofold degenerate in the upper index. It belongs to $S_z = \pm \frac{1}{2}$. Furthermore, $\Pi_{ab}^a = \Pi_{ab}^b = 0$. The operator

$$\hat{B}^\dagger = \sum_{ab} t_{ab} \hat{a}_a^\dagger \hat{a}_a^\dagger \hat{a}_b^\dagger \quad (2.156)$$

leads to the condition

$$\forall b : \quad \Pi^b \succeq 0. \quad (2.157)$$

We have a set of L positive semidefinite constraints on $(L-1) \times (L-1)$ matrices. Similar as the 2DM, there are some consistency conditions that need to be fulfilled. We have,

$$\Pi_{aa}^b = D_{ab} = D_{ba}, \quad (2.158)$$

which means following 'lifting' and consistency conditions have be enforced

$$\Pi_{aa}^b = \Pi_{bb}^a, \quad (2.159)$$

$$\sum_c D_{abc}^3 = \left(\frac{N}{2} - 2\right) \Pi_{aa}^b, \quad (2.160)$$

where we used eq. (2.154a). Furthermore, the following sums are known

$$\sum_b \Pi_{ac}^b = \left(\frac{N}{2} - 1\right) \Pi_{ac}, \quad (2.161)$$

$$\sum_{ab} \Pi_{aa}^b = \frac{N}{2} \left(\frac{N}{2} - 1\right). \quad (2.162)$$

Every part of the 1DM and 2DM can be calculated by summing over indices. These conditions imply the necessary N -representability conditions for DOCI on the 1DM and 2DM.

I. The ${}^3Q$ condition

The ${}^3Q$ condition has the same structure as the 3DM. The seniority-three condition leads to

$$\langle \psi | \hat{a}_a \hat{a}_b \hat{a}_c \hat{a}_b^\dagger \hat{a}_a^\dagger | \psi \rangle = 1 - \rho_a - \rho_b - \rho_c + D_{ab} + D_{bc} + D_{ac} - D_{abc}^3 \geq 0. \quad (2.163)$$

This gives us a set of $\frac{L(L-1)(L-2)}{6}$ linear constraints. The equivalent of the $\mathcal{T}_1$ condition is found by the sum of the ${}^3J$ and ${}^3Q$ matrix which generates

$$1 - \rho_a - \rho_b - \rho_c + D_{ab} + D_{bc} + D_{ac} \geq 0. \quad (2.164)$$

This is a constraint on the diagonal of the $\mathcal{T}_1$ matrix.

The seniority-one condition produces a set of L matrices of dimension $(L-1) \times (L-1)$. The generating operator is

$$\hat{B}^\dagger = \sum_{ab} q_{ab} \hat{a}_a \hat{a}_{\bar{a}} \hat{a}_b, \quad (2.165)$$

which leads to

$$Q_{ac}^b = \langle \psi | \hat{a}_a \hat{a}_{\bar{a}} \hat{a}_b \hat{a}_b^\dagger \hat{a}_c^\dagger | \psi \rangle \quad (2.166)$$

$$= \delta_{ac} (1 - 2\rho_a - \rho_b + 2D_{ab}) + \Pi_{ac} - \Pi_{ac}^b, \quad (2.167)$$

and this set of matrices has to positive semidefinite

$$\forall b : Q^b \succeq 0. \quad (2.168)$$

We can again find an equivalent $\mathcal{T}_1$ condition by adding Π^b to (2.167)

$$(\mathcal{T}_1)_{ac}^b = \delta_{ac} (1 - 2\rho_a - \rho_b + 2D_{ab}) + \Pi_{ac}, \quad (2.169)$$

$$\forall b : (\mathcal{T}_1)^b \succeq 0.$$

II. The ${}^3\mathcal{E}$ condition

The ${}^3\mathcal{E}$ is more involved. We are looking for a set of conditions that are equivalent with the full ${}^3\mathcal{E}$ as shown derived in Section 2.3.3. The condition will split in blocks labeled by S_z and seniority number. Within such a block, not all states will be coupled to each other. This is what we are looking for.

The generating operator for the ${}^3\mathcal{E}$ is

$$\hat{B}^\dagger = \sum_{\alpha\beta\gamma} q_{\alpha\beta\gamma}^1 \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\gamma, \quad (2.170)$$

which again leads to a seniority one and three combined with $S_z = \pm\frac{1}{2}, \pm\frac{3}{2}$. Just like the $\mathcal{G}$ condition, much more combination are possible, as different terms will be connected.

We begin with the seniority-three sector. This means that we have to break three *different* pairs. For $S_z = \pm \frac{3}{2}$ the generator is $\hat{B}^\dagger = \sum_{abc} q_{abc}^1 \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_{\bar{c}}^\dagger$ ($a \neq b \neq c$) which leads to

$$\langle \psi | \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_{\bar{c}}^\dagger \hat{a}_{\bar{f}}^\dagger \hat{a}_e \hat{a}_d | \psi \rangle = \delta_{cf} \delta_{ad} \delta_{be} (D_{ab} - D_{abc}^3) - \delta_{af} \delta_{be} \delta_{cd} \Pi_{ac}^b - \delta_{bf} \delta_{ce} \delta_{ad} \Pi_{bc}^a. \quad (2.171)$$

This connects three states with the same spatial orbitals, $ab\bar{c}$, $bc\bar{a}$ and $ca\bar{b}$. For $bc\bar{a}$ we find

$$\langle \psi | \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_{\bar{a}}^\dagger \hat{a}_{\bar{d}}^\dagger \hat{a}_f \hat{a}_e | \psi \rangle = \delta_{cf} \delta_{ad} \delta_{be} (D_{bc} - D_{bac}^3) - \delta_{af} \delta_{be} \delta_{cd} \Pi_{ac}^b - \delta_{bd} \delta_{cf} \delta_{ae} \Pi_{ab}^c, \quad (2.172)$$

while for $ca\bar{b}$

$$\langle \psi | \hat{a}_c^\dagger \hat{a}_a^\dagger \hat{a}_{\bar{b}}^\dagger \hat{a}_{\bar{e}}^\dagger \hat{a}_d \hat{a}_f | \psi \rangle = \delta_{cf} \delta_{ad} \delta_{be} (D_{ac} - D_{abc}^3) - \delta_{ad} \delta_{ce} \delta_{bf} \Pi_{bc}^a - \delta_{bd} \delta_{cf} \delta_{ae} \Pi_{ab}^c. \quad (2.173)$$

Combining this will eventually give us a 3×3 matrix condition

$$\begin{array}{ccc} & ab\bar{c} & bc\bar{a} & ca\bar{b} \\ \begin{array}{l} ab\bar{c} \\ bc\bar{a} \\ ca\bar{b} \end{array} & \begin{bmatrix} D_{ab} - D_{abc}^3 & -\Pi_{ac}^b & -\Pi_{bc}^a \\ -\Pi_{ac}^b & D_{bc} - D_{bac}^3 & -\Pi_{ab}^c \\ -\Pi_{bc}^a & -\Pi_{ab}^c & D_{ac} - D_{abc}^3 \end{bmatrix} & \succeq 0, \end{array} \quad (2.174)$$

for $a < b$ and $a \neq b \neq c$. The row and column set of indices are the indices for the left and right. There are $\frac{L(L-1)(L-2)}{2}$ such matrix conditions. We continue with the $S_z = \pm \frac{1}{2}$ sector. There are two generating operators

$$\hat{B}_1^\dagger = \sum_{abc} q_{abc}^1 \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c, \quad (2.175a)$$

$$\hat{B}_2^\dagger = \sum_{abc} q_{abc}^1 \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_{\bar{c}}, \quad (2.175b)$$

with $a \neq b \neq c$. The direct term $\hat{B}_1^\dagger \hat{B}_1$ gives us

$$\langle \psi | \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_{\bar{f}}^\dagger \hat{a}_e \hat{a}_d | \psi \rangle = \delta_{ad} \delta_{be} \delta_{cf} (D_{ab} - D_{abc}^3), \quad (2.176)$$

while the other direct term $\hat{B}_2^\dagger \hat{B}_2$ leads to

$$\langle \psi | \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_{\bar{c}}^\dagger \hat{a}_{\bar{f}}^\dagger \hat{a}_e \hat{a}_d | \psi \rangle = \delta_{ad} \delta_{be} \delta_{cf} (D_{ab} - D_{abc}^3) - \delta_{af} \delta_{be} \delta_{cd} \Pi_{ac}^b. \quad (2.177)$$

For the mixed term we obtain

$$\langle \psi | \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_{\bar{f}}^\dagger \hat{a}_e \hat{a}_d | \psi \rangle = \delta_{ad} \delta_{bf} \delta_{ce} \Pi_{bc}^a - \delta_{bd} \delta_{af} \delta_{ce} \Pi_{ac}^b \quad (2.178)$$

$$= (\delta_{ad} \delta_{bf} - \delta_{bd} \delta_{af}) \delta_{ce} \Pi_{fe}^d \quad (2.179)$$

The second term in eq. (2.178) comes from $a \leftrightarrow b$. Again we see that this couples three terms for a , b and c .

$$\begin{array}{ccc} & abc & cba & cab \\ abc & D_{ab} - D_{abc}^3 & -\Pi_{ac}^b & -\Pi_{bc}^a \\ cba & -\Pi_{ac}^b & D_{bc} - D_{abc}^3 & \Pi_{ab}^c \\ cab & -\Pi_{bc}^a & \Pi_{ab}^c & D_{ac} - D_{abc}^3 \end{array} \succeq 0, \quad (2.180)$$

This condition is equivalent with (2.174): by multiplying the first row and column with -1 we find matrix (2.174) with the sign of the off-diagonal elements flipped. As shown in Chapter C, these gives us matrices with the same spectrum.

For the seniority-one sector, only $S_z = \pm \frac{1}{2}$ is possible as only one pair is broken. The generating operators are

$$\hat{B}_1^\dagger = \sum_{ab} q_{ab} \hat{a}_a^\dagger \hat{a}_a^\dagger \hat{a}_b, \quad (2.181a)$$

$$\hat{B}_2^\dagger = \sum_{ab} q_{ab} \hat{a}_b^\dagger \hat{a}_a^\dagger \hat{a}_{\bar{a}}, \quad (2.181b)$$

$$\hat{B}_3^\dagger = \sum_{ab} q_{ab} \hat{a}_b^\dagger \hat{a}_a^\dagger \hat{a}_a, \quad (2.181c)$$

with $a \neq b$. We begin with the diagonal terms:

- $B_1^\dagger B_1$ leads to

$$\langle \psi | \hat{a}_a^\dagger \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_b^\dagger \hat{a}_c | \psi \rangle = \delta_{bd} (\Pi_{ac} - \Pi_{ac}^b). \quad (2.182)$$

This gives a set of L matrices of size $(L-1) \times (L-1)$. It can be extended by realizing that the missing element (when $a = b$ in eq. (2.181a)) is part of a primed condition with $\hat{B}^\dagger = \sum_c q_c \hat{a}_c^\dagger$

$$\langle \psi | \hat{a}_a^\dagger \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_b^\dagger \hat{a}_c | \psi \rangle = \delta_{bc} \Pi_{ab}, \quad (2.183)$$

$$\langle \psi | \hat{a}_b^\dagger \hat{a}_c | \psi \rangle = \delta_{bc} \rho_b. \quad (2.184)$$

If we included this element, we find for every b the $L \times L$ matrix

$$\begin{bmatrix} \Pi_{ac} - \Pi_{ac}^b & \Pi_{ab} \\ \Pi_{cb} & \rho_b \end{bmatrix} \succeq 0, \quad (2.185)$$

where the index a runs over the columns and c over the rows.

- $B_2^\dagger B_2$ gives us

$$\langle \psi | \hat{a}_b^\dagger \hat{a}_a^\dagger \hat{a}_{\bar{a}}^\dagger \hat{a}_{\bar{a}}^\dagger \hat{a}_d^\dagger \hat{a}_d^\dagger \hat{a}_c | \psi \rangle = \delta_{bc} (\delta_{ad} D_{ab} + D_{abd}^3). \quad (2.186)$$

- $B_3^\dagger B_3$ produces

$$\langle \psi | \hat{a}_b^\dagger \hat{a}_a^\dagger \hat{a}_a^\dagger \hat{a}_d^\dagger \hat{a}_d^\dagger \hat{a}_c | \psi \rangle = \delta_{bc} (\delta_{ad} D_{ab} + D_{abd}^3). \quad (2.187)$$

The mixed terms:

- $B_1^\dagger B_2$ leads to

$$\langle \psi | \hat{a}_a^\dagger \hat{a}_a^\dagger \hat{a}_b \hat{a}_d^\dagger \hat{a}_d \hat{a}_c | \psi \rangle = \delta_{bc} \Pi_{ab}^d \quad (2.188)$$

- $B_1^\dagger B_3$ gives us

$$\langle \psi | \hat{a}_a^\dagger \hat{a}_a^\dagger \hat{a}_b \hat{a}_d^\dagger \hat{a}_d \hat{a}_c | \psi \rangle = \delta_{bc} \Pi_{ab}^d. \quad (2.189)$$

- $B_2^\dagger B_3$ produces

$$\begin{aligned} \langle \psi | \hat{a}_b^\dagger \hat{a}_a^\dagger \hat{a}_a \hat{a}_d^\dagger \hat{a}_d \hat{a}_c | \psi \rangle &= \delta_{bc} \delta_{ad} \Pi_{aa}^b + \delta_{bc} D_{abd}^3 \\ &= \delta_{bc} (\delta_{ad} D_{ab} + D_{abd}^3) \end{aligned} \quad (2.190)$$

- the overlap of the primed condition results in

$$\langle \psi | \hat{a}_b^\dagger \hat{a}_a^\dagger \hat{a}_a \hat{a}_c | \psi \rangle = \delta_{bc} D_{ab}. \quad (2.191)$$

As the $B_2^\dagger B_2$, $B_3^\dagger B_3$ and $B_2^\dagger B_3$ all produces the same element, we can reduce this $2L \times 2L$ matrix to a $L \times L$ matrix in the same way as with the $\mathcal{G}$ condition. This conditions reduces to a set of L matrices

$$[\delta_{ad} D_{ab} + D_{abd}^3] \succeq 0. \quad (2.192)$$

Combining all these results in a set of L matrices with dimensions $(2L - 1) \times (2L - 1)$. We could write it down as

$$\begin{bmatrix} \hat{a}_a^\dagger \hat{a}_a^\dagger \hat{a}_b \hat{a}_b^\dagger \hat{a}_c \hat{a}_c & \hat{a}_a^\dagger \hat{a}_a^\dagger \hat{a}_b \hat{a}_c^\dagger \hat{a}_c \hat{a}_b & \hat{a}_a^\dagger \hat{a}_a^\dagger \hat{a}_b \hat{a}_b \\ \hat{a}_b^\dagger \hat{a}_a^\dagger \hat{a}_a \hat{a}_b^\dagger \hat{a}_c \hat{a}_c & \hat{a}_b^\dagger \hat{a}_a^\dagger \hat{a}_a \hat{a}_c^\dagger \hat{a}_c \hat{a}_b & \hat{a}_b^\dagger \hat{a}_a^\dagger \hat{a}_a \hat{a}_b \\ \hat{a}_b^\dagger \hat{a}_b^\dagger \hat{a}_c \hat{a}_c & \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_c \hat{a}_b & \hat{a}_b^\dagger \hat{a}_b \end{bmatrix} \succeq 0, \quad (2.193)$$

but using the results from above leads to

$$\forall b \neq a, \neq c, \quad \begin{bmatrix} \Pi_{ac} - \Pi_{ac}^b & \Pi_{ab}^c & \Pi_{ab} \\ \Pi_{cb}^a & \delta_{ac} D_{ab} + D_{abc}^3 & D_{ab} \\ \Pi_{bc} & D_{bc} & \rho_b \end{bmatrix} \succeq 0. \quad (2.194)$$

This might not look as a symmetric matrix because it has to be expanded: the index a is column index and c the row index.

III. The ${}^3\mathcal{F}$ condition

The generating operator for the ${}^3\mathcal{F}$ is

$$\hat{B}^\dagger = \sum_{\alpha\beta\gamma} q_{\alpha\beta\gamma}^1 \hat{a}_\alpha^\dagger \hat{a}_\beta \hat{a}_\gamma. \quad (2.195)$$

We expect that this condition will be similar to the ${}^3\mathcal{E}$ condition. Again we have seniority one and three combined with $S_z = \pm\frac{1}{2}, \pm\frac{3}{2}$. We start with seniority-three and $S_z = \pm\frac{3}{2}$. The generator is $\hat{B}^\dagger = \sum_{abc} q_{abc}^1 \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger$ with $a \neq b \neq c$ which leads to

$$\begin{aligned} \langle \psi | \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_d^\dagger \hat{a}_e^\dagger \hat{a}_f^\dagger | \psi \rangle &= \delta_{ad} \delta_{be} \delta_{cf} (\rho_a - D_{ab} - D_{ac} + D_{abc}^3) \\ &+ \delta_{af} \delta_{be} \delta_{cd} (\Pi_{ac}^b - \Pi_{ac}) + \delta_{ae} \delta_{cf} \delta_{bd} (\Pi_{ab}^c - \Pi_{ab}) \end{aligned} \quad (2.196)$$

when we choose an ordering in the indices $a \neq b < c$ (meaning some terms drop out). In the same fashion as for the ${}^3\mathcal{E}$ condition, this couples three terms (abc , cba and bac) leading to a set of 3×3 matrix conditions

$$\begin{bmatrix} \rho_a - D_{ab} - D_{ac} + D_{abc}^3 & \Pi_{ac}^b - \Pi_{ac} & \Pi_{ab}^c - \Pi_{ab} \\ \Pi_{ac}^b - \Pi_{ac} & \rho_c - D_{bc} - D_{ac} + D_{abc}^3 & \Pi_{bc}^a - \Pi_{bc} \\ \Pi_{ab}^c - \Pi_{ab} & \Pi_{bc}^a - \Pi_{bc} & \rho_b - D_{ab} - D_{bc} + D_{abc}^3 \end{bmatrix} \succeq 0, \quad (2.197)$$

for $a \neq b \neq c$ and $b < c$. We can combine the seniority-three, $S_z = +\frac{3}{2}$ matrix of the ${}^3\mathcal{F}$ condition with its $S_z = -\frac{3}{2}$ counterpart of the ${}^3\mathcal{E}$ condition to find a DOCI version of the $\mathcal{T}_2$ condition. If we permute the rows and columns of the matrix (2.174) to the order $bc\bar{a}$, $ab\bar{c}$ and $ca\bar{b}$ and add it to (2.197), the resulting matrix has no elements of the 3DM:

$$\begin{bmatrix} \rho_a - D_{ab} - D_{ac} + D_{bc} & -\Pi_{ac} & -\Pi_{ab} \\ -\Pi_{ac} & \rho_c - D_{bc} - D_{ac} + D_{ab} & -\Pi_{bc} \\ -\Pi_{ab} & -\Pi_{bc} & \rho_b - D_{ab} - D_{bc} + D_{ab} \end{bmatrix} \succeq 0. \quad (2.198)$$

We continue with the $S_z = \pm\frac{1}{2}$ sector. The generating operator is

$$\hat{B}^\dagger = \sum_{ab} q_{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_{\bar{c}}, \quad (2.199a)$$

with $a \neq b \neq c$ which leads to

$$\begin{aligned} \langle \psi | \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_d^\dagger \hat{a}_e^\dagger \hat{a}_f^\dagger | \psi \rangle &= \delta_{ad} \delta_{be} \delta_{cf} (\rho_a - D_{ab} - D_{ac} + D_{abc}^3) \\ &+ \delta_{af} \delta_{be} \delta_{cd} (\Pi_{ac}^b - \Pi_{ac}) + \delta_{ae} \delta_{cf} \delta_{bd} (\Pi_{ab}^c - \Pi_{ab}) \end{aligned} \quad (2.200)$$

This will generate an equivalent constraint as the $S_z = \pm\frac{3}{2}$ case.

For the seniority-one, again only $S_z = \pm\frac{1}{2}$ is possible. The same structure as for the ${}^3\mathcal{E}$ is expected. The generating operators are

$$\hat{B}_1^\dagger = \sum_{ab} q_{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_{\bar{b}}, \quad (2.201a)$$

$$\hat{B}_2^\dagger = \sum_{ab} q_{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_{\bar{a}}, \quad (2.201b)$$

with $a \neq b$. The primed operator is $B^\dagger = \sum_a q_a \hat{a}_{\bar{a}}$.

- $B_1^\dagger B_1$ leads to

$$\langle \psi | \hat{a}_a^\dagger \hat{a}_a \hat{a}_b \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_c | \psi \rangle = \delta_{bd} \delta_{ac} (\rho_c - D_{ab}) + \delta_{bd} D_{ac} - \delta_{bd} D_{abc}^3. \quad (2.202)$$

Combined with the prime term this gives

$$\langle \psi | \hat{a}_a^\dagger \hat{a}_a \hat{a}_b \hat{a}_b^\dagger | \psi \rangle = \delta_{bd} \rho_a - \delta_{bd} D_{ab}. \quad (2.203)$$

- $B_2^\dagger B_2$ produces

$$\langle \psi | \hat{a}_b^\dagger \hat{a}_b \hat{a}_a \hat{a}_a^\dagger \hat{a}_c^\dagger \hat{a}_c | \psi \rangle = \delta_{bd} \delta_{ac} (\rho_b - 2D_{bc}) + \delta_{bd} \Pi_{ac}^b. \quad (2.204)$$

The combination with the primed term leads to

$$\langle \psi | \hat{a}_b^\dagger \hat{a}_b \hat{a}_a \hat{a}_a^\dagger | \psi \rangle = -\delta_{bd} \Pi_{ab}. \quad (2.205)$$

The mixed term between B_1 and B_2 is

$$\langle \psi | \hat{a}_a^\dagger \hat{a}_a \hat{a}_b \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_c | \psi \rangle = \delta_{bd} \delta_{ac} \Pi_{ab} - \delta_{bd} \Pi_{bc}^a. \quad (2.206)$$

Combining this all gives us a set of L positivity conditions on matrices of dimensions $2L - 1$

$$\begin{bmatrix} \delta_{ac} (\rho_c - D_{ab}) + D_{ac} - D_{abc}^3 & \delta_{ac} \Pi_{ab} - \Pi_{bc}^a & \rho_a - D_{ab} \\ \delta_{ac} \Pi_{cb} - \Pi_{ab}^c & \delta_{ac} (\rho_b - 2D_{bc}) + \Pi_{ac}^b & -\Pi_{ab} \\ \rho_c - D_{bc} & -\Pi_{bc} & 1 - \rho_b \end{bmatrix} \succeq 0, \quad (2.207)$$

for $\forall b, a \neq b$ and $c \neq b$. Using its counterpart in the ${}^3\mathcal{E}$ condition, again a $\mathcal{T}_2$ condition can be derived

$$\begin{bmatrix} \delta_{ac} \rho_c + D_{ac} & \delta_{ac} \Pi_{ab} & \rho_a \\ \delta_{ac} \Pi_{bc} & \delta_{ac} (\rho_b - 2D_{bc}) - \Pi_{ac} & 0 \\ \rho_c & 0 & 1 \end{bmatrix} \succeq 0, \quad (2.208)$$

where the first row and column of (2.194) are interchanged before adding it to (2.207).

2.6 Conclusion

In this chapter, we have introduced the N -representability problem and a set of necessary but in general not sufficient conditions for it. We gave the general conditions on the 1DM, 2DM and 3DM. The conditions were also rederived in the specific case that the ensemble of wave functions consist only of seniority-zero wave functions. This led to a considerable reduction of the dimensions of the conditions. We further showed that symmetry can also lead help to reduce the computational complexity of the conditions.

In classical wave function based methods such as Configuration Interaction or Coupled Cluster, there is a systematic way to improve the result: by including higher orders of excitations, they will eventually reach the Full Configuration Interaction (FullCI) limit. In stark contrast, there is no such hierarchy in the necessary N -representability conditions. The three-index condition will improve the results over the two-index condition but beyond that, there are no known conditions that can be expressed as a function of the 2DM. One could use a higher reduced density matrix: the $p+1$ index conditions will include all positivity conditions on the p index conditions. However, this is not computationally feasible and the 2DM already contains all the information for two-particle operators. Claims have been made about a hierarchical solution to the N -representability problem [112, 113] but it remains unclear if this solution is complete. Furthermore, the condition that could be derived in the framework have never been put to the test. In this regard, the similarity with DFT can again be pointed out: there is also no systematic way of improving a functional.

It also been shown that the two- and three-index conditions are expressible as Grassmann integrals [114] but so far, this has not led to new insights.

The N -representability problem has been proven to belong to the hardest kind of problems we know and so far we are “stuck” on the two- and three-index conditions.

To summarize, the optimization problem of the reduced density matrix can now be formulated as

$$\begin{aligned} E_0 &= \min_{\Gamma} \text{Tr}(K\Gamma) \\ \text{while } \text{Tr}(\Gamma) &= \frac{N(N-1)}{2} \\ \bigoplus_i \mathcal{L}_i(\Gamma) &\succeq 0. \end{aligned} \tag{2.209}$$

The minimization goes over all symmetry matrices, while the direct sum in the constraints goes over the enforced N -representability conditions. The $\oplus$ notation means the direct sum of block matrices. For example, for the two-index conditions, this would mean: $\mathcal{L}_i \in \{\mathcal{I}, \mathcal{Q}, \mathcal{G}\}$. The optimization problem for the 3DM is identical in form but the trace has to be adjusted. In the next chapter we will discuss how to solve this optimization problem.

Chapter 3

Semidefinite Programming

Science is knowledge which we understand so well that we can teach it to a computer; and if we don't fully understand something, it is an art to deal with it.

Donald E. Knuth

The world of convex optimization is a rich and interesting world. Due to the convexity, it has many nice features: the nicest one is probably the guarantee that there are no local extrema. In this chapter, we will introduce Semidefinite Programming (SDP), a subclass within convex optimization. Do not let the word programming deceive you, SDP is a convex optimization problem. Even linear programming problems can be expressed as a SDP problem. More importantly, an SDP problem can be solved efficiently, both in theory and practice. After introducing the problem and several of its properties, we discuss several methods to solve it. These methods are then adapted to maximally exploit the specific problem structure of v2DM. There are general purpose codes available to solve the standard form of an SDP problem [23, 115–119], but they are in general too slow for us. SDP problems are encountered in a wide range of fields: control theory [120], combinatorial optimization [121] and statistics [122], to name just a few.

3.1 Primal-dual formalism

Before we continue, let us first repeat the definition of convexity. A set S in a linear space is convex if and only if for every $x_1, x_2 \in S$ holds that $\alpha x_1 + \beta x_2 \in S$ with $\alpha, \beta \geq 0$ and $\alpha + \beta = 1$. This means that the line segment connecting any two points in the set must also be part of the set. A function $f : \mathbb{R}^n \rightarrow \mathbb{R}$ is convex if the domain of f is a convex set and for any two points x and y in the domain of f must hold

$$f(\alpha x + \beta y) \leq \alpha f(x) + \beta f(y), \quad (3.1)$$

with $\alpha, \beta \geq 0$ and $\alpha + \beta = 1$. One can prove that a function is convex if on a convex set its Hessian is positive semidefinite. Furthermore, we will use S^n to denote the set of $n \times n$

symmetric matrices and S_+^n to mark the subset of positive semidefinite matrices. The set S_+^n has the mathematical structure of a cone: for every $A \in S_+^n$ we have that $\lambda A \in S_+^n$, when $\lambda > 0$ ¹.

The standard SDP problem is defined as minimizing a linear function in $x \in \mathbb{R}^n$ subjected to a matrix inequality

$$\begin{aligned} & \min c^T x \\ & \text{while } F(x) \succeq 0, \end{aligned} \quad (3.2)$$

where

$$F(x) = F_0 + \sum_{i=1}^n x_i F_i. \quad (3.3)$$

An SDP problem is defined by a vector $c \in \mathbb{R}^n$ and $n + 1$ symmetric matrices $F_0, F_i \in S^m$. Both the objective ($c^T x$) and constraint ($F(x)$) are convex

$$\alpha \geq 0, \quad F(\alpha x + (1 - \alpha)y) = \alpha F(x) + (1 - \alpha)F(y) \succeq 0. \quad (3.4)$$

To demonstrate what the solution of this problem is, we can examine an example for $x \in \mathbb{R}^2$ in Figure 3.1 on the next page, the value of m is not relevant at the moment. The region where the matrix inequality is satisfied is called the feasible region. The solution of the SDP problem is found by moving as far as possible in the direction $-c$ within the feasible region. The solution or optimal point x_{opt} will always be found on the boundary of the feasible region. This means that $F(x)$ will have at least one zero eigenvalue. Due to the convexity of the feasible region, it is clearly impossible to have a local minimum: in that case it would be impossible to draw a line between the local minimum and global minimum that stays within the feasible region. Note that in the case $m = 1$ one has a linear program.

We will now introduce the dual problem. The problem (3.2) is called the primal problem. The Lagrangian of the primal problem (3.2) is

$$L(x, Z) = c^T x + \text{Tr} \left(\left(F_0 + \sum_{i=1}^n x_i F_i \right) Z \right), \quad (3.5)$$

where $Z \in S^n$ is called the dual variable (or Lagrange multiplier [123, 124]). It has to be negative semidefinite $Z \preceq 0$ because it is the Lagrange multiplier of an inequality: if $F(x)$ is positive and Z negative, the second term in (3.5) will be negative and thus decrease the Lagrangian. If $F(x)$ would be negative, it would increase the Lagrangian. As we prefer to work with positive semidefinite matrices, we will replace Z by $-Z$.

$$L(x, Z) = c^T x - \text{Tr} \left(\left(F_0 + \sum_{i=1}^n x_i F_i \right) Z \right) \quad (3.6)$$

$$\begin{aligned} &= x_1 (c_1 - \text{Tr}(F_1 Z)) + x_2 (c_2 - \text{Tr}(F_2 Z)) + \dots \\ & \quad x_n (c_n - \text{Tr}(F_n Z)) - \text{Tr}(F_0 Z) \end{aligned} \quad (3.7)$$

1. For completeness we should note that the cone of positive semidefinite matrices is self-dual [22]. This will only be used indirectly in this chapter and can be mostly ignored.

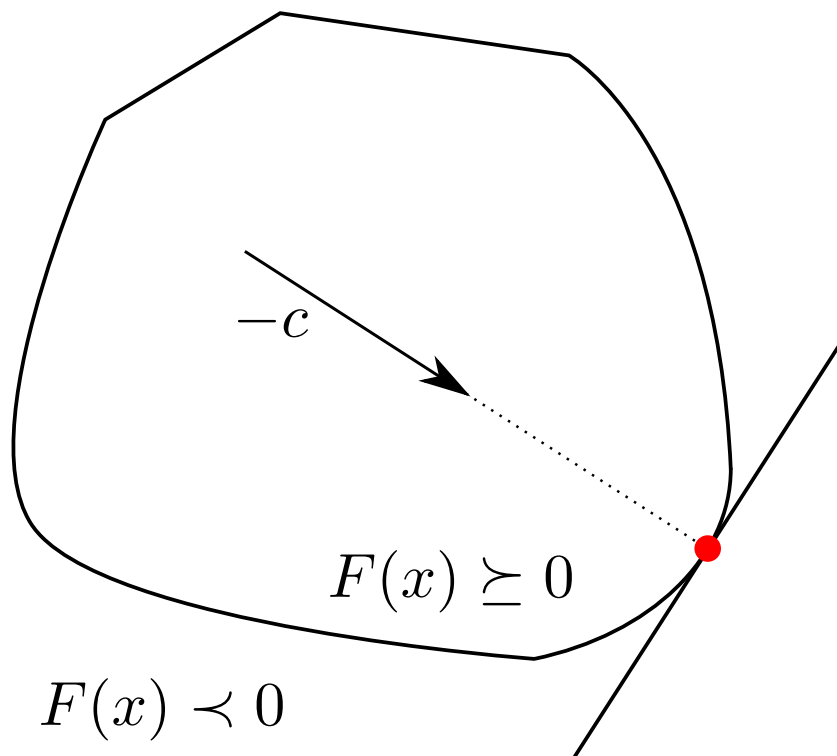


Figure 3.1: A graphical depiction of a SDP problem in two variables. The red dot marks the optimal point. It is found by following the direction $-c$ until the boundary of the feasible region is hit.

We can now define the dual function as

$$g(Z) = \inf_x L(x, Z) = \begin{cases} -\text{Tr}(F_0 Z) & c_i - \text{Tr}(F_i Z) = 0, \quad i = 1 \dots n \\ -\infty & \text{otherwise.} \end{cases} \quad (3.8)$$

We minimize over the primal variables to find a problem in the dual variables. The associated dual problem is

$$\begin{aligned} & \max \quad -\text{Tr}(F_0 Z) \\ \text{while} \quad & Z \succeq 0 \\ & \text{Tr}(F_i Z) = c_i, \quad i = 1 \dots n. \end{aligned} \quad (3.9)$$

This is again an SDP problem and can be rewritten to the standard form in (3.2) [21]. Furthermore, we call Z dual feasible if $Z \succeq 0$ and $\text{Tr}(F_i Z) = c_i$ ($i = 1 \dots n$), and x primal feasible if $F(x) \succeq 0$. Feasible means that the constraints of the problem are fulfilled.

Now, what is the point of all this? The dual problem is very powerful as it provides a lower bound on the primal problem and vice versa. If we assume that x is primal feasible and Z is dual feasible then

$$c^T x + \text{Tr}(F_0 Z) = \sum_{i=1}^n \text{Tr}(Z F_i) x_i + \text{Tr}(F_0 Z) = \text{Tr}(Z F(x)) \geq 0. \quad (3.10)$$

The last inequality follows from the positive semidefiniteness of $F(x)$ and Z (see Chapter C). We now have

$$-\text{Tr}(F_0 Z) \leq c^T x, \quad (3.11)$$

for any feasible value of Z and x , including the optimal points of both. This is called weak duality [22]. The difference between both sides of eq. (3.11) is called the duality gap (or primal-dual gap)

$$\eta = c^T x + \text{Tr}(F_0 Z) = \text{Tr}(Z F(x)) \geq 0. \quad (3.12)$$

The duality gap is zero if we use the optimal points of both the primal and dual problem; in that case we have strong duality. For SDP problems this is the case when the Slater condition is fulfilled [21, 22]: there must be strictly feasible points for either the primal or dual problem. This means that there must be an x for which $F(x) \succ 0$ or a Z for which $Z \succ 0$ and $\text{Tr}(F_i Z) = c_i$ ($i = 1 \dots n$). If the Slater condition holds, we have at the optimal points

$$c^T x = -\text{Tr}(F_0 Z), \quad (3.13)$$

from which it follows that $\text{Tr}(F(x)Z) = 0$ and thus

$$F(x)Z = 0, \quad (3.14)$$

as $F(x) \succeq 0$ and $Z \succeq 0$ (see Chapter C). This is called the complementary slackness condition and can be interpreted as saying that the space spanned by the columns of Z and $F(x)$ must be orthogonal. The duality gap gives us a powerful convergence measure. If we use an iterative

algorithm to solve both the primal and dual problem, we have at iteration k the current optimal value x^k and Z^k and we know that

$$c^T x^k - x_{\text{opt}} \leq \eta^k = c^T x^k + \text{Tr} \left(F_0 Z^k \right). \quad (3.15)$$

If we use, as the stopping criterion $\epsilon > 0$ on the duality gap, then

$$c^T x^k - x_{\text{opt}} \leq c^T x^k + \text{Tr} \left(F_0 Z^k \right) \leq \epsilon. \quad (3.16)$$

In other words, we know (it is guaranteed) that the current optimal value x^k is ϵ suboptimal. This is much more powerful than just converging to a certain tolerance.

3.1.1 Problem definition

The perceptive reader has probably already recognized the similarity between the dual problem (3.9) and v2DM optimization problem (2.209) from Chapter 2. For the two-index optimization, the obvious choice seems to be

$$Z = \Gamma \oplus \mathcal{Q}(\Gamma) \oplus \mathcal{G}(\Gamma), \quad (3.17a)$$

$$F_0 = K \oplus 0 \oplus 0, \quad (3.17b)$$

$$F_1 = \mathbb{1} \oplus 0 \oplus 0, \quad (3.17c)$$

$$c_1 = \frac{N(N-1)}{2}. \quad (3.17d)$$

However, this is not sufficient: Z contains all free variables and the $\mathcal{Q}$ and $\mathcal{G}$ conditions are of course not independent. We need to use the equality constraints to enforce the form of (3.17a). We will write Z as $\oplus_i \mathcal{L}_i$ to have an expression independent of the exact N -representability constraints used and we introduce $\{e_i\}$ as an orthonormal basis in the space of the Z matrix. Let us focus on constraint $\mathcal{L}$. We need to enforce that

$$\text{Tr} \left(Z^{\mathcal{L}} e_i^{\mathcal{L}} \right) = \text{Tr} \left(\mathcal{L}(\Gamma) e_i^{\mathcal{L}} \right), \quad (3.18)$$

where the superscript $\mathcal{L}$ denotes the part of Z corresponding to the constraint $\mathcal{L}$. Before we continue, we must introduce an extremely helpful tool: the Hermitian adjoint map. It is defined as

$$\text{Tr} \left(\mathcal{L}_i(\Gamma) A \right) = \text{Tr} \left(\mathcal{L}_i^{\dagger}(A) \Gamma \right), \quad (3.19)$$

where A is a symmetric matrix in the same space as the constraint $\mathcal{L}_i$ and the Hermitian adjoint is $\mathcal{L}_i^{\dagger}$. Using its definition (3.19), it is possible to derive the adjoint map of all N -representability conditions introduced in Chapter 2. In Chapter F on page 203 we give a list of expressions for the Hermitian adjoint images used in this work. We also require that every N -representability constraint map is homogeneous² as this makes the mathematics involved a lot easier. Using the Hermitian adjoint, we can rewrite eq. (3.18) to

$$\text{Tr} \left(Z^{\mathcal{L}} e_i^{\mathcal{L}} \right) = \text{Tr} \left(\Gamma \mathcal{L}_i^{\dagger}(e_i^{\mathcal{L}}) \right). \quad (3.20)$$

2. A function is homogeneous with degree k when it is scale invariant: $f(\alpha x) = \alpha^k f(x)$.

We can now express this as an equality constraint for the dual problem:

$$\text{Tr} \left(Z F_i^{\mathcal{L}} \right) = 0, \quad (3.21)$$

where $F_i^{\mathcal{L}}$ is a block matrix with two non-zero blocks

$$\left(F_i^{\mathcal{L}} \right)_{\Gamma} = -\mathcal{L}^{\dagger}(e_i^{\mathcal{L}}), \quad (3.22a)$$

$$\left(F_i^{\mathcal{L}} \right)_{\mathcal{L}} = e_i^{\mathcal{L}}. \quad (3.22b)$$

In this way, we enforce the $\mathcal{Q}$, $\mathcal{G}$, ... conditions. The number of F_i matrices will be equal to the number of independent variables in the conditions (plus the trace condition). Using this formalism, Nakata *et al.* [20] implemented the v2DM optimizing problem as an SDP problem and used the SDPA [116] program to solve it. We will use a slightly different formalism.

The core object we want to optimize is the 2DM. There are matrix inequalities and one equality constraint that need to be enforced. We can eliminate the trace condition by choosing a feasible starting point and restrict the optimizing to the space orthogonal to this condition. In this case, we should restrict the optimizing to the traceless space. Let the set $\{f^i\}$ be a complete, orthogonal basis of traceless, symmetric matrices in the two-particle space. Following properties will hold

$$\text{Tr} (f^i) = 0, \quad (3.23a)$$

$$\text{Tr} (f^i f^j) = \delta_{ij}, \quad (3.23b)$$

$$f_{\alpha\beta;\gamma\delta}^i = -f_{\beta\alpha;\gamma\delta}^i = -f_{\alpha\beta;\delta\gamma}^i = f_{\beta\alpha;\delta\gamma}^i = f_{\delta\gamma;\beta\alpha}^i. \quad (3.23c)$$

We can write the 2DM in this basis as

$$\Gamma = \frac{2\text{Tr}(\Gamma)}{M(M-1)} \mathbb{1} + \sum_i \underbrace{\text{Tr}(\Gamma f^i)}_{\gamma_i} f^i, \quad (3.24)$$

where M is used to denote the dimension of the single-particle space (including spin). The energy function can be rewritten as

$$E = \text{Tr}(K\Gamma) = \frac{2\text{Tr}(\Gamma) \text{Tr}(K)}{M(M-1)} + \sum_i \gamma_i h^i, \quad (3.25)$$

where

$$\gamma_i = \text{Tr}(\Gamma f^i), \quad (3.26a)$$

$$h^i = \text{Tr}(K f^i), \quad (3.26b)$$

are the expansion coefficients of the 2DM and reduced Hamiltonian in the traceless basis. We can now restrict the optimization to the set $\{\gamma_i\}$ without having to worry about the trace condition. Using this, our objective function is now

$$\min_{\gamma} \sum_i h^i \gamma_i. \quad (3.27)$$

The matrix constraints can be written as

$$\mathcal{L}(\Gamma) = \frac{2\text{Tr}(\Gamma)}{M(M-1)}\mathcal{L}(\mathbb{1}) + \sum_i \gamma_i \mathcal{L}(f^i), \quad (3.28)$$

which can be simplified by defining

$$u^0 = \frac{N(N-1)}{M(M-1)} \bigoplus_j \mathcal{L}_j(\mathbb{1}), \quad (3.29)$$

$$u^i = \bigoplus_j \mathcal{L}_j(f^i), \quad (3.30)$$

to

$$\mathcal{L}(\Gamma) = u^0 + \sum_i \gamma_i u^i \succeq 0. \quad (3.31)$$

This clearly has the form of the primal problem (3.2). From now on, we will use $X(\Gamma) = \mathcal{L}(\Gamma)$ to specify the constraint matrix in the primal problem. Our optimization is now

$$\begin{aligned} & \min_{\gamma} h^T \gamma \\ \text{while } & X(\gamma) = u^0 + \sum_i \gamma_i u^i \succeq 0. \end{aligned} \quad (3.32)$$

This is a much more compact and elegant expression than the previously derived dual variant of the problem. The dual problem of (3.32) is given by

$$\begin{aligned} & \max \quad -\text{Tr}(Z u_0) \\ \text{while } & Z \succeq 0 \\ & \text{Tr}(Z u_i) = h^i, \forall i \end{aligned} \quad (3.33)$$

Now the optimization problem is clearly defined, we will continue with techniques to solve it³.

3.2 Potential Reduction method

The so-called interior point methods [125] are the standard workhorse of Semidefinite Programming. They try to remain in the feasible region as they approach the optimal point. The convergence properties of these methods have been thoroughly examined and they tend to be very stable. To remain within the feasible region, a barrier function is used

$$\phi(\gamma) = \begin{cases} -\ln \det X(\gamma) & X(\gamma) \succ 0 \\ +\infty & \text{otherwise} \end{cases} \quad (3.34)$$

3. We should note that compared to reference 90, we have switched the primal and dual problem. Everything is equivalent, but the notation is different.

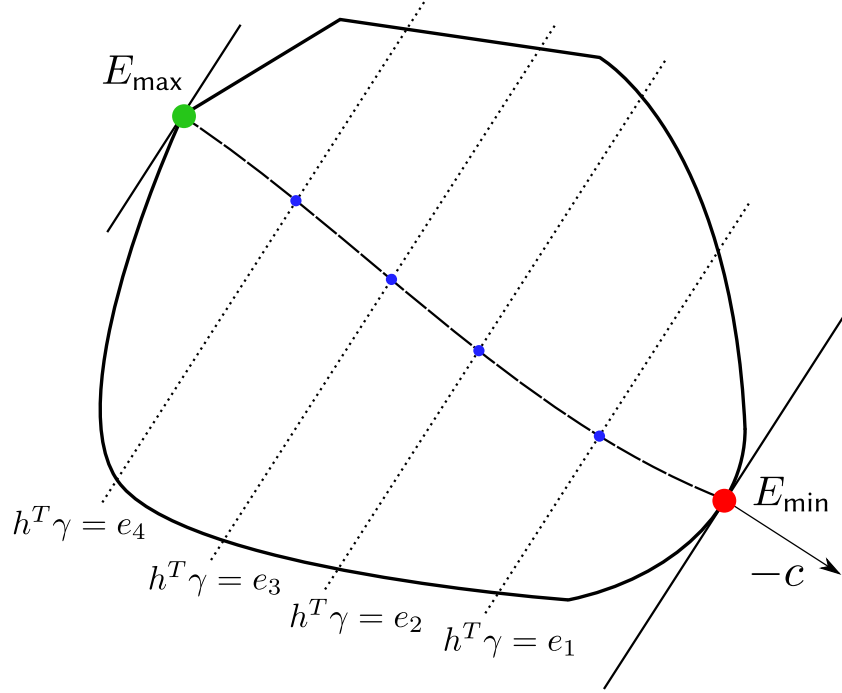


Figure 3.2: Illustration of the central path. Both the minimal value and the maximal value lie on the central path. It is formed by all analytic centers (marked with blue dots).

This barrier function is analytic, strictly convex and self-concordant⁴ [126]. It is $+\infty$ when there is a zero eigenvalue in $X(\gamma)$ and thus forces us to remain inside the feasible region. The point that minimizes the barrier function $\phi(\gamma)$ is called the analytic center of the constraint $X(\gamma) \succ 0$. Using this we can define the central path: the central path is formed by the solution of the following optimization problem

$$\begin{aligned} & \min_{\gamma} \phi(\gamma) \\ \text{while } & h^T \gamma = e \\ & X(\gamma) \succ 0, \end{aligned} \tag{3.35}$$

where $E_{\min} \leq e \leq E_{\max}$. If we solve this problem for all allowed values of e we find the central path. A solution of (3.35) is called the analytic center of the primal feasible set. It is clear that all those analytic centers lie on the central path, including the optimal point of our original SDP problem. An interior point method will try to follow the central path to find the solution. By doing this, it avoids the edge of the feasible region as long as possible, as the problem becomes singular near it. In Figure 3.2 we show the central path of the previous graphical example of an SDP problem. Furthermore, there is a connection between the points on the

4. This is a property that is key in proving the convergence of these methods but unimportant for what we do. A function $f(x)$ is self-concordant when $|f'''(x)| \leq 2f''(x)^{\frac{3}{2}}$.

central path of the primal and dual problem. If we write down the Lagrangian of the problem (3.35), we find

$$L = -\ln \det X(\gamma) + \lambda(h^T \gamma - e). \quad (3.36)$$

The optimality condition for this Lagrangian is

$$\text{Tr}(X(\gamma)^{-1}u^i) = \lambda h^i, \quad i = 1, \dots, n. \quad (3.37)$$

The derivative of the barrier function can found in Chapter C. It is interesting to see that the matrix $X(\gamma)^{-1}/\lambda$ is dual feasible when $\lambda > 0$. The associated duality gap is

$$\eta = \text{Tr}(X(\gamma)Z) = \text{Tr}\left(X(\gamma)\frac{X(\gamma)^{-1}}{\lambda}\right) = \frac{m}{\lambda}, \quad (3.38)$$

where m is the dimension of the $X(\gamma)$ matrix. We see that the Lagrange multiplier is directly related to the duality gap. It can even be shown that $X(\gamma)^{-1}/\lambda$ is an analytic center of the dual problem [21]. In other words, if we have a point on the central path of the primal problem, we can derive its partner point on the central path of the dual problem. It is even so that the optimal points $X(\gamma)$ and Z will be each other's inverse, up to a factor.

We will now focus on potential reduction techniques to solve the primal problem. The idea is simple: we add the barrier function (3.34) to the objective function, but scaled with a parameter t . During the calculation, we will iteratively solve the unconstrained problem. After every iteration we will decrease the barrier, until at convergence the barrier is non-existing and we find the optimal point on the boundary of the feasible region. Our unconstrained objective function is

$$\phi(\gamma) = h^T \gamma - t \ln \det X(\gamma). \quad (3.39)$$

By optimizing the γ_i coefficients, we automatically enforce the trace condition and the barrier function will make sure that the N -representability conditions are positive semidefinite. As a function of t , eq. (3.39) lies on the central path. For $t \rightarrow \infty$, we should find the analytic center of $X(\gamma) \succ 0$ and for $t \rightarrow 0$ we should find the optimal point of the SDP problem. We now look for the minimum of $\phi(\gamma)$ for a fixed value of t . The standard way to minimize an unconstrained objective function is to use the Newton-Raphson method [127]. Under the right conditions (good starting point, well behaving derivatives), it has quadratic convergence. First, we need a second-order Taylor expansion of eq. (3.39)

$$\phi(\gamma_0 + \Delta\gamma) \approx \phi(\gamma_0) + \sum_i \Delta\gamma_i \frac{\partial \phi(\gamma)}{\partial \gamma_i} + \sum_{ij} \frac{1}{2} \Delta\gamma_i \frac{\partial^2 \phi(\gamma)}{\partial \gamma_i \partial \gamma_j} \Delta\gamma_j. \quad (3.40)$$

We search for a step $\Delta\gamma$ that minimize eq. (3.40). By taking the derivative we find

$$\sum_j \frac{\partial^2 \phi(\gamma)}{\partial \gamma_i \partial \gamma_j} \Delta\gamma_j = -\frac{\partial \phi(\gamma)}{\partial \gamma_i}, \quad (3.41a)$$

$$\sum_j \mathcal{H}^{ij} \Delta\gamma_j = -\nabla \phi^i, \quad (3.41b)$$

where the second equation introduces the symbols for the gradient and Hessian of eq. (3.40). If we solve this linear system of equations, we know the optimal update step $\Delta\gamma$. All that is left is finding an expression for the gradient and the Hessian.

The gradient of eq. (3.40) is

$$\nabla\phi^i = \frac{\partial\phi(\gamma)}{\partial\gamma_i} = h^i - t \operatorname{Tr} (X(\gamma)^{-1} u^i). \quad (3.42)$$

By using the adjoint images (see Chapter F) and the structure of $X(\gamma)$ we can simplify this to

$$\nabla\phi^i = h^i - t \sum_j \operatorname{Tr} (\mathcal{L}_j(\Gamma)^{-1} \mathcal{L}_j(f^i)) \quad (3.43)$$

$$= \operatorname{Tr} \left(\left[K - t \sum_j \mathcal{L}_j^\dagger (\mathcal{L}_j(\Gamma)^{-1}) \right] f^i \right), \quad (3.44)$$

where we used the definition of the traceless basis (eq. (3.26)). We used $\mathcal{L}_j(\Gamma)$ where we actually should use $\mathcal{L}_j(\gamma)$, but the former simplifies the notation. The gradient can be written as the projection of a matrix on the traceless two-particle space

$$\nabla\phi = \hat{P}_{\operatorname{Tr}} \left(K - t \sum_j \mathcal{L}_j^\dagger (\mathcal{L}_j(\Gamma)^{-1}) \right), \quad (3.45)$$

with the traceless projection operator

$$\hat{P}_{\operatorname{Tr}}(A) = A - \frac{\operatorname{Tr}(A)}{\dim A} \mathbb{1}. \quad (3.46)$$

The nice thing about this approach is that we never need the traceless basis explicitly! We can simply construct the matrix in eq. (3.45) and do the projection.

The Hessian is a bit more complicated. By taking the derivative of eq. (3.42) we find

$$\mathcal{H}^{ij} = \frac{\partial^2\phi(\gamma)}{\partial\gamma_i\partial\gamma_j} = t \operatorname{Tr} (X(\gamma)^{-1} u^i X(\gamma)^{-1} u^j) \quad (3.47)$$

$$= t \sum_k \operatorname{Tr} (\mathcal{L}_k(\Gamma)^{-1} \mathcal{L}_k(f^i) \mathcal{L}_k(\Gamma)^{-1} \mathcal{L}_k(f^j)). \quad (3.48)$$

We decompose our update step $\Delta\gamma$ in the traceless basis

$$\Delta\gamma = \sum_i \delta\gamma_i f^i, \quad (3.49)$$

and examine the action of the Hessian on this

$$\begin{aligned} \sum_j \mathcal{H}^{ij} \delta\gamma_j &= t \sum_k \operatorname{Tr} \left(\mathcal{L}_k(\Gamma)^{-1} \left[\sum_j \mathcal{L}_k(f^j) \delta\gamma_j \right] \mathcal{L}_k(\Gamma)^{-1} \mathcal{L}_k(f^i) \right) \\ &= t \sum_k \operatorname{Tr} \left(\mathcal{L}_k^\dagger (\mathcal{L}_k(\Gamma)^{-1} \mathcal{L}_k(\Delta\gamma) \mathcal{L}_k(\Gamma)^{-1}) f^i \right). \end{aligned} \quad (3.50)$$

We see that the action of the Hessian on a traceless matrix can be expressed as

$$\mathcal{H}\Delta\gamma = t \hat{P}_{\text{Tr}} \left(\sum_k \mathcal{L}_k^\dagger (\mathcal{L}_k(\Gamma)^{-1} \mathcal{L}_k(\Delta\gamma) \mathcal{L}_k(\Gamma)^{-1}) \right). \quad (3.51)$$

Again, no explicit reference to the traceless basis is used. Notice that eq. (3.51) actually gives us an efficient matrix-vector product to solve eq. (3.41b). The dimension of the 2DM scales as M^2 (with M the size of the single-particle basis) and the dimension of the traceless basis $\{\gamma_i\}$ scales as M^4 , leading to an M^8 scaling for the matrix-vector product of the Hessian. However, eq. (3.51) only scales as M^6 : we work directly without the matrix in the two-particle space with using the traceless basis explicitly. Now that we have an efficient matrix-vector product, we can use a Krylov subspace method to solve the linear system in eq. (3.41b). The idea is that the inverse of a matrix can be expressed as a linear combination of powers of the matrix⁵. The Hessian is positive semidefinite, which leads us to the Conjugate gradient method [127, 128]: this is an iterative method to solve a linear system using only matrix-vector operations. This means that we never have to explicitly construct the Hessian, we only use its action on a vector.

Although the problem is now solved and we can calculate the update step $\Delta\gamma$ for eq. (3.40), we can speed up the convergence process by optimizing the step size. This means calculating α such that $\tilde{\phi}(\alpha) = \phi(\gamma_0 + \alpha\Delta\gamma)$ is minimal. The optimality condition is

$$\frac{d\tilde{\phi}(\alpha)}{d\alpha} = \frac{\partial\phi(\gamma_0 + \alpha\Delta\gamma)}{\partial\alpha} = 0. \quad (3.52)$$

If we use eq. (3.39), we find

$$\frac{d\tilde{\phi}(\alpha)}{d\alpha} = \text{Tr}(K) - t \sum_j \text{Tr}(\mathcal{L}_j(\gamma_0 + \alpha\Delta\gamma)^{-1} \mathcal{L}_j(\Delta\gamma)). \quad (3.53)$$

Every evaluation of this would require calculating the inverse of a matrix. Luckily, this can be avoided. First, we must calculate the eigenvalues of following generalized eigenvalue problem

$$\mathcal{L}(\Delta\gamma)w = \lambda^\mathcal{L} \mathcal{L}(\Gamma)w, \quad (3.54)$$

which can be transformed to an ordinary symmetric eigenvalue problem as

$$\left(\mathcal{L}(\Gamma)^{-\frac{1}{2}} \mathcal{L}(\Delta\gamma) \mathcal{L}(\Gamma)^{-\frac{1}{2}} \right) v = \lambda^\mathcal{L} v, \quad v = \mathcal{L}^{\frac{1}{2}} w. \quad (3.55)$$

It can be shown that eq. (3.53) can be expressed as [90]

$$\frac{d\tilde{\phi}(\alpha)}{d\alpha} = \text{Tr}(K) - t \sum_j \left(\sum_i \frac{\lambda_i^{\mathcal{L}_j}}{1 + \alpha \lambda_i^{\mathcal{L}_j}} \right). \quad (3.56)$$

The summation over i runs over all eigenvalues of eq. (3.54), while j runs over all enforced matrix constraints. This way is much cheaper to calculate the optimal value of α as the

5. This is a direct consequence of the Cayley–Hamilton theorem.

eigenvalues only have to be calculated once and then a simple bisection method [127] can be used to find the roots of eq. (3.56).

To estimate the duality gap, we need an (approximate) solution to the dual problem. If we have found the solution to eq. (3.40), the gradient will be zero

$$0 = h^i - t \operatorname{Tr} (X(\gamma)^{-1} u^i). \quad (3.57)$$

We see that $Z = tX(\gamma)^{-1}$ is dual feasible and using eqs. (3.37) and (3.38) we can estimate the duality gap to be

$$\eta = \operatorname{Tr} (X(\gamma)Z) = mt, \quad (3.58)$$

with m the dimension of $X(\gamma)$ or Z . We use this as our convergence criterion. To conclude

Algorithm 1 The potential reduction algorithm to solve the primal problem tailored for v2DM.

Set $\varepsilon > 0$, $\varepsilon_{\text{NR}} > 0$ and $\beta \in [0, 1]$

$\Gamma = \frac{N(N-1)}{M(M-1)} \mathbb{1}$; $t = 1$

while $nt > \varepsilon$ **do**

▷ The barrier reduction loop

while $\delta > \varepsilon_{\text{NR}}$ **do**

▷ The Newton-Raphson loop

$\nabla\phi = \hat{P}_{\text{Tr}} \left(K - t \sum_j \mathcal{L}_j^\dagger (\mathcal{L}_j(\Gamma)^{-1}) \right)$

 Solve $\mathcal{H}\Delta\gamma = -\nabla\phi$

▷ Solved with Conjugate Gradient

 Solve $\frac{d\tilde{\phi}(\alpha)}{d\alpha} = 0$

$\Gamma \leftarrow \Gamma + \alpha\Delta\gamma$

$\delta \leftarrow \alpha \|\Delta\gamma\|$

end while

$t \leftarrow \beta t$

end while

the expose about the potential reduction method, we give an overview of the algorithm in pseudocode in Algorithm 1.

3.3 Boundary Point method

One of the problems with the barrier function method is that the problem gets harder to solve as the barrier is reduced. When we approach the boundary of the feasible region, the condition number of the Hessian will become worse. As we use an iterative technique to solve the linear system of equations, the number of iterations will sharply increase towards the boundary. For this reason it is not even interesting to start from a better guess: a good guess will be close to the boundary and we want to avoid that as long as possible by walking on the central path. One possible solution to this is to use an Augmented Lagrangian method [123], which adds an additional term to the unconstrained optimization that should help to improve the convergence. This led to the so-called Boundary Point method [129–131] in which the complementary slackness condition (3.14) is always fulfilled. This method jumps between the

cone of positive semidefinite matrices and the space of the other constraints until convergence: at this point the solution is primal and dual feasible. It was first used by Mazzioni [51] in the context of v2DM.

The augmented Lagrangian for the primal SDP problem (3.32) is

$$L = h^T \gamma + \text{Tr} \left(Z \left(X - u^0 - \sum_i \gamma_i u^i \right) \right) + \frac{\sigma}{2} \left\| X - u^0 - \sum_i \gamma_i u^i \right\|^2. \quad (3.59)$$

This has a slightly different form than eq. (3.5) as we include the primal matrix X explicitly, not as a function of γ . Remember that the Lagrangian multiplier Z is the primary variable of the dual problem. Compared to the regular Lagrangian, we added an additional term that adds a quadratic penalty for infeasibility, where $\sigma > 0$ determines the strength of the penalty. In contrast with penalty or barrier functions, σ should not go to ∞ (or 0) to reach the optimal point. Before we continue, let us review the optimality conditions for the primal and dual problem. A solution γ , X and Z is optimal (assuming the Slater condition holds) when

$$X \succeq 0, \quad (3.60a)$$

$$X = u^0 + \sum_i \gamma_i u^i, \quad (3.60b)$$

$$Z \succeq 0, \quad (3.60c)$$

$$\text{Tr}(Z u_i) = h^i, \quad (3.60d)$$

$$XZ = 0. \quad (3.60e)$$

The first four conditions demand the feasibility of the solution and the last condition ensures that the duality gap is zero.

By introducing a new matrix

$$W(\gamma) = u^0 + \sum_i \gamma_i u^i - \frac{1}{\sigma} Z, \quad (3.61)$$

we can rewrite the eq. (3.59) to

$$L = h^T \gamma + \frac{1}{2\sigma} \|Z\|^2 + \frac{\sigma}{2} \|X - W(\gamma)\|^2. \quad (3.62)$$

We now define

$$f(\gamma, X) = h^T \gamma + \frac{\sigma}{2} \|X - W(\gamma)\|^2. \quad (3.63)$$

The method then consists of first minimizing $f(\gamma, X)$ under the constraint $X \succeq 0$, while keeping Z constant. After this, we use the solutions γ and X obtained in the previous step to update Z as

$$Z = \sigma(X - u^0 - \sum_i \gamma_i u^i). \quad (3.64)$$

We first focus on the so-called inner problem

$$\begin{aligned} \min_{\gamma, X} \quad & h^T \gamma + \frac{\sigma}{2} \|X - W(\gamma)\|^2 \\ \text{while} \quad & X \succeq 0. \end{aligned} \quad (3.65)$$

This is a quadratic SDP problem. Its Lagrangian is

$$L = h^T \gamma + \frac{\sigma}{2} \|X - W(\gamma)\|^2 - \text{Tr}(VX), \quad (3.66)$$

where $V \succ 0$ is the Lagrangian multiplier for the constraint $X \succeq 0$. The necessary set of conditions for optimality, the so-called Karush–Kuhn–Tucker (KKT) conditions [22, 132, 133] for (3.65) are

$$\frac{\partial L}{\partial \gamma_i} = h_i - \sigma \text{Tr}((X - W(\gamma)) u^i) = 0, \quad (3.67a)$$

$$\frac{\partial L}{\partial X} = \sigma (X - W(\gamma)) - V = 0, \quad (3.67b)$$

$$V \succ 0, \quad (3.67c)$$

$$X \succeq 0, \quad (3.67d)$$

$$VX = 0. \quad (3.67e)$$

Due to the Slater condition, this set of conditions is also sufficient [22]. We will now try to solve these directly. The gradient conditions eqs. (3.67a) and (3.67b) can be rewritten to

$$\sum_j \gamma_j \text{Tr}(u^i u^j) = \text{Tr} \left(\left(X - u^0 + \frac{1}{\sigma} Z \right) u^i \right) - \frac{h^i}{\sigma}, \quad (3.68)$$

$$V = \sigma (X - W(\gamma)). \quad (3.69)$$

Now, if we keep γ fixed, the optimization problem (3.65) is reduced to the projection of the matrix X on the cone of positive semidefinite matrices

$$\min_{X \succeq 0} \|X - W(\gamma)\|. \quad (3.70)$$

The solution is straightforward: we have to split up $W(\gamma)$ into a positive and negative part. This can be done through a spectral decomposition

$$\begin{aligned} W(\gamma) &= \sum_i \lambda_i U_i U_i^T \\ &= \sum_i \lambda_i^+ U_i U_i^T + \sum_i \lambda_i^- U_i U_i^T \\ &= W^+(\gamma) + W^-(\gamma), \end{aligned} \quad (3.71)$$

where λ_i^+ and λ_i^- denote the positive and negative eigenvalues respectively and U is the associated eigenvector. For a fixed value of γ , the optimal value of $X = W^+(\gamma)$. The optimal value of V follows from eq. (3.69)

$$V = -\sigma W^-(\gamma) \succeq 0. \quad (3.72)$$

The complimentary slackness condition $VX = 0$ is fulfilled as the eigenspaces are orthogonal. For a fixed value of X (and V), the optimal γ can be found by solving the linear system in eq. (3.68). This can be done very efficiently by using the overlap formalism from Verstichel [90]. The set $u^\alpha = \{u^0, u^i\}$ is non-orthogonal and has an overlap S

$$S_{\alpha\beta} = \text{Tr}(u^\alpha u^\beta) = \sum_k \text{Tr}(\mathcal{L}_k(f^\alpha) \mathcal{L}_k(f^\beta)). \quad (3.73)$$

Using the Hermitian adjoint images, this can be expressed as

$$S_{\alpha\beta} = \sum_k \text{Tr}(\mathcal{L}_k^\dagger(\mathcal{L}_k(f^\alpha)) f^\beta). \quad (3.74)$$

In other words, the overlap can be considered as a linear map from two-particle to two-particle space,

$$S(\Gamma) = \sum_k \mathcal{L}_k^\dagger(\mathcal{L}_k(\Gamma)). \quad (3.75)$$

It can be shown that the overlap map can be expressed as a generalized $\mathcal{Q}$ map for all two- and three-index N -representability conditions [90]⁶. In the DOCI case, this does not hold. The inverse of the map (3.75) can again be expressed as a generalized $\mathcal{Q}$ matrix. Compared to the time spent calculating the eigenvalues and eigenvectors of $W(\gamma)$, solving the linear system in eq. (3.68) is negligible.

We see that the inner problem (3.65) can be solved by alternating between solving for X (with γ constant) through eq. (3.70) and solving for γ (with X constant) through eq. (3.68). When the linear system in eq. (3.68) is satisfied after projection on the cone of positive semidefinite matrices, we have reached convergence for the inner problem. The convergence criteria can be rewritten as

$$h_i - \sigma \text{Tr}((X - W(\gamma)) u^i) = h_i - \text{Tr}(V u^i) \leq \varepsilon_{\text{inner}}. \quad (3.76)$$

If we compare this to eq. (3.60d), we see that V is dual feasible. By setting $Z = V$, all conditions in eq. (3.60) are fulfilled. In other words, we can consider the inner loop to be a projection on the dual feasibility. The outer loop in which we update Z , can be interpreted as projecting on the primal feasibility. As convergence criteria, we use the primal infeasibility,

$$\left\| X - u^0 - \sum_i \gamma_i u^i \right\| \leq \varepsilon_{\text{outer}}. \quad (3.77)$$

During the whole optimization we have $XZ = 0$ meaning that the duality gap is always zero. This interpretation also explains the name “Boundary Point method”: during the entire optimization, we keep the duality gap zero and alternately project on the primal and dual feasibility conditions until at convergence both primal and dual feasible are fulfilled. In

6. The complete expressions for the overlap can be found in reference 90

Algorithm 2 The boundary point algorithm to solve the primal and dual problem tailored for v2DM.

```

Set  $\varepsilon_{\text{inner}} > 0$ ,  $\varepsilon_{\text{outer}} > 0$  and  $\sigma > 0$ 
 $X = 0$ ,  $Z = 0$ ,  $k = 0$ 
while  $\delta_{\text{outer}} > \varepsilon_{\text{outer}}$  do ▷ The outer loop
  while  $\delta_{\text{inner}} > \varepsilon_{\text{inner}}$  do ▷ The inner loop
    Solve for  $\gamma^k$ :  $\sum_j \gamma_j^k \text{Tr}(u^i u^j) = \text{Tr}((X^k - u^0 + \frac{1}{\sigma} Z^k) u^i) - \frac{h^i}{\sigma}$ 
     $W(\gamma) = u^0 + \sum_i \gamma_i u^i - \frac{1}{\sigma} Z^k$ 
     $X^k = W^+$ ,  $V^k = -\sigma W^-$ 
     $\delta_{\text{inner}} = \sum_i |h_i - \text{Tr}(V^k u^i)|$  ▷ Dual infeasibility
  end while
   $Z^{k+1} \leftarrow V^k$ 
   $k \leftarrow k + 1$ 
   $\delta_{\text{outer}} = \|X^k - u^0 - \sum_i \gamma_i u^i\|$  ▷ Primal infeasibility
end while

```

Algorithm 2 we show the boundary point algorithm that we have implemented. The bottleneck in the algorithm is the computation of the eigenvalues and eigenvectors of $W(\gamma)$. This scales as the third power of the matrix dimension, giving us an algorithm that scales as M^6 , with M the dimension of the single-particle space. The linear system can be solved very efficiently for the classic two-index and three-index conditions. In the DOCI case, we do not have a closed form for the inverse but a Conjugate gradient algorithm can be used. The number of iterations required to solve the linear system is small and the bottleneck remains the computation of W^+ and W^- .

Compared to other methods to solve SDP problems, the boundary point method is faster but less stable. While the potential reduction method can almost be used as a black box, this is certainly not the case for the boundary point method. By tweaking the parameters, a speedup factor of $5 - 10\times$ can be achieved compared to classic primal-dual methods. In our experience, the following practical considerations have to be taken in account when using the algorithm. It turns out that it is best to limit the number of iterations of the inner loop. We limit it to 1-5 iterations. The penalty parameter σ in the augmented Lagrangian has to be chosen carefully. The algorithm works best when the primal and dual infeasibility are comparable. If the primal infeasibility is greater than the dual feasibility, then we multiply σ with a factor $\tau > 1$. If the primal infeasibility is smaller than the dual feasibility, we divide σ by τ . When starting the algorithm, there is a great variation in σ until the primal and dual problem are in equilibrium and then we have a monotonic convergence rate to primal and dual feasibility. In reference 51, an additional parameter is introduced in the calculation of $W(\gamma)$

$$W(\gamma) = u^0 + \sum_i \gamma_i u^i - \frac{\tau_m}{\sigma} Z. \quad (3.78)$$

We have named this factor τ_m the Mazziotti factor. Setting it to a value in the range $[1, 1.6]$ can speedup the algorithm but also influences the stability of the algorithm. It alters the sensitivity of the $\{\gamma_i\}$ on the dual infeasibility of Z .

3.4 Conclusion

In this chapter, we have introduced a class of convex optimization problems called Semidefinite Programming. The primal and dual formalism of these problems was explored. Our v2DM problem was translated to a primal and dual SDP. We investigate an interior-point method to solve the problem by adding a barrier function to the objective function. This led to the potential reduction algorithm tailored to v2DM. This algorithm is robust, stable and has a scaling of M^6 for the two-index conditions and M^9 for the three-index conditions. Unfortunately, this method becomes slower and slower as we approach the solution. At every iteration, a linear system of the Hessian has to be solved. We have implemented this efficiently using a Conjugate gradient algorithm which avoids building the Hessian: we only need a matrix-vector product. Near the boundary of the feasible set, the condition number of the Hessian gets worse and the number of iterations needed to solve the linear system increases sharply. In practice we see that the first steps are very quick and most of the calculating time is spent near the boundary. This algorithm can be used as a black box and it has only one parameter that might need tweaking: the factor by which the barrier is decreased after every iteration.

An alternative to avoid the downsides of the potential reduction algorithm is the augmented Lagrangian approach. In this method, an additional term is added to the Lagrangian to stabilize the convergence. It leads to the boundary point method which has the same theoretical scaling of M^6 (two-index) or M^9 (three-index) as the potential reduction method, but is nonetheless much faster in reality. This speedup comes at a cost: the boundary point method is much less stable. The parameters of the algorithm need careful tweaking to ensure convergence. The boundary point method was specifically designed for systems with a large number of variables and is at its best in these systems.

As it is the fastest method we have, it will be our preferred method for the rest of this work.

Chapter 4

Results

In the previous chapters, we have introduced the concept of the Variational Optimization of the second-order reduced Density Matrix. In Chapter 2, a necessary set of N -representability conditions were derived and in Chapter 3 we have shown the computational methods that can be used to do the actual optimization. It is time to use this knowledge. First we look into DOCI and explain the motivation for the DOCI N -representability conditions derived in Section 2.5. Next, we explore orbital optimization with the goal to combine it with v2DM restricted to DOCI. We then try our method on several benchmark systems to assess its merits.

4.1 Introduction

Before we begin the story of the marriage between DOCI and v2DM, let us take a step back and consider the origins of DOCI. First we will introduce some classic concepts of wavefunction-based methods [2].

In Configuration Interaction (CI) methods, the wave function is expanded in a (complete) basis of Slater determinants. The classical approach is to pick a reference Slater determinant and add excitations on top. This reference is usually obtained by a Hartree-Fock (HF) calculation. This works well when one Slater determinant is dominant in the expansion of all possible Slater determinants (FullCI), and we speak of a single-reference method. However, this is far from always the case: in a bond-breaking process, multiple Slater determinants become equally important. These are called multi-reference effects and to correctly describe this situation, one can use a method like Multi-Configurational Self-Consistent Field (MCSCF). In this method, both the orbitals in the Slater determinants and the coefficients of the Slater determinants are optimized.

Another important distinction to introduce is static and dynamic correlation. The static correlation is the contribution due to the different dominant Slater determinants and you need a method such as MCSCF to correctly describe it. Dynamic correlation on the other hand is well described by a single reference Slater determinant and the excitations of this reference. A

method like Configuration Interaction with Single and Double excitations (CISD) is very well suited to capture this part of the energy. The difference between these two is not always well defined and both concepts are often used rather loosely in the literature.

After this short introduction, we can introduce a new partitioning of the Slater determinants based on the seniority number. As introduced in Section 2.5, the seniority number is the number of unpaired electrons in a Slater determinant. Notice that it is not a proper quantum number: the seniority operator does not commute with the electronic structure Hamiltonian [111]. It finds its origin in nuclear and condensed matter physics where it is a good quantum number for the pairing Hamiltonian [134]. The seniority operator is defined as

$$\hat{\Omega} = \sum_{a\sigma} \hat{a}_{a\sigma}^\dagger \hat{a}_{a\sigma} - 2 \sum_a \hat{a}_{a\uparrow}^\dagger \hat{a}_{a\downarrow}^\dagger \hat{a}_{a\downarrow} \hat{a}_{a\uparrow}, \quad (4.1)$$

which can be calculated with the 2DM as

$$\begin{aligned} \langle \hat{\Omega} \rangle &= \langle \psi | \hat{\Omega} | \psi \rangle \\ &= \sum_{a\sigma} \rho_{a\sigma;a\sigma} - 2 \sum_a \Gamma_{a\uparrow a\downarrow; a\uparrow a\downarrow} \\ &= N - 2 \sum_a \Gamma_{a\uparrow a\downarrow; a\uparrow a\downarrow}. \end{aligned} \quad (4.2)$$

We are interested in Doubly Occupied Configuration Interaction (DOCI) wave functions or, equivalently, seniority-zero wave functions. The building blocks of DOCI are electron pair states or geminals. The idea of working with electron pairs is very old. It predates the concept of orbitals [135] and is somewhat deviating from the orbital picture [136, 137]. It has links to the concept of a Lewis structure [135], which is still being taught in most high-school chemistry classes. One can build a class of wave functions based on this: the so-called Anti-symmetric Product of Geminals (APG) [138, 139]

$$|\psi_{\text{APG}}\rangle = \prod_{p=1}^P \left(\sum_{k=1}^L c_{p;k} \hat{a}_{p;k}^\dagger \hat{a}_{p;\bar{k}}^\dagger \right) | \rangle, \quad (4.3)$$

where $P = N/2$ is the number of pairs. The geminals are not necessarily orthogonal to each other. In this concept the pairs of electrons can be regarded as weakly correlated to each other, since the wave function has a mean-field product structure in the geminals. Notice that the pairing scheme is not fixed with APG: each geminal has its own pairing scheme. However, the APG wave function is computationally intractable [138, 140]. An often used approach to circumvent this problem is to enforce an orthogonality restriction to the geminals (separated pair restriction). The pairing scheme is usually also enforced to be the same for all geminals. Although in principle any pairing scheme can be exploited, the obvious choice is the most used one: we pair electrons of different spin together in the same spatial orbital. For the rest of this work, we use this pairing scheme. As shown in Section 2.5, this leads to a serious simplification in the structure of the 2DM. For a random pairing scheme, this is not the case. Within the spin-pairing scheme DOCI is the most general type of wave function, built from

Slater determinants in which every orbital is either unoccupied or doubly occupied. It was first mentioned in Weinhold and Wilson [141]. The wave function has the form

$$|\psi_{\text{DOCI}}\rangle = \sum_{\substack{m_i=\{0,1\} \\ \sum m_i=P}} c_{m_1 m_2 \dots m_L} \left(\hat{a}_1^\dagger \hat{a}_1^\dagger\right)^{m_1} \left(\hat{a}_2^\dagger \hat{a}_2^\dagger\right)^{m_2} \dots \left(\hat{a}_L^\dagger \hat{a}_L^\dagger\right)^{m_L} | \rangle \quad (4.4)$$

DOCI is FullCI-like but uses only the doubly occupied Slater determinants. It is computationally cheaper than FullCI but still has a factorial scaling: $\binom{L}{N/2}$ vs $\binom{L}{N/2}^2$ for FullCI with $S_z = 0$. This makes it computationally unfeasible for all but the smallest systems. The geminal idea can also be linked to Valence Bond (VB) theory [142, 143]: in VB, one has to pair orbitals together manually in so-called VB structures, which are similar to Lewis structures. The theory had/has a large traction in the chemical community due to its more intuitive character. Unlike Molecular Orbital theory (MO), the orbitals are localized, making it easier to use chemical intuition in building the wave function. It was very popular in the early days of quantum mechanics but eventually MO became dominant. Due to the use of non-orthogonal orbitals, the computational cost was unfavorable compared to MO. Furthermore, it is much easier to use MO as a black box: a HF calculation is used as starting point and excitations are added on top of this, to improve the result. It turns out that General Valence Bond (GVB) with Perfect Pairing (PP) [144] is a special case of DOCI [145]. In this theory, the valence bond orbitals are expanded in the atomic orbital basis set and they are optimized in a self-consistent way. The perfect pairing refers to the coupling of the two electrons in the pair to a singlet state: only the VB structure with the largest coefficient is used.

DOCI is the most general closed-shell wave function available. Although it received quite some attention in the early days of quantum chemistry, it remained dormant for a very long time due to its scaling. In 2011, Bytautas *et al.* [146] re-examined DOCI as part of a seniority hierarchy-based approximation to the wave function. They found that DOCI or the seniority-zero sector is capable of capturing the lion's share of the static correlation. When adding higher seniority sectors, the result quickly converges to the FullCI result. It was realized that DOCI is the lowest rung on a ladder of the seniority hierarchy which eventually leads to FullCI: by adding Slater determinants with two, four, ... unpaired electrons, we will eventually use all Slater determinants in the Hilbert space. Given the large number of Slater determinants in the DOCI wave function, it cannot really come as a surprise that it is quite good for describing static correlation. Dynamic correlation is better described in *e.g.* CISD. However, using pair excitations on the DOCI wave function, one can recover most of the dynamic correlation [147]. In essence, a single pair excitation is a subclass of Configuration Interaction with Double excitations (CID), a double pair excitation is subclass of Configuration Interaction with Double and Quadruple excitations (CIDQ), etc.

The renewed interest in DOCI led to the construction of mean-field scaling approximations of DOCI wave function, the so-called Antisymmetric Product of one-reference-orbital Geminals (AP1roG) [145, 148, 149] or equivalently Coupled Cluster with Double excitations (CCD) [150,

151]. The wave function has the form

$$|\psi_{\text{AP1roG}}\rangle = \exp\left(\sum_{i=1}^P \sum_{a=P+1}^L t_i^a \hat{a}_a^\dagger \hat{a}_a^\dagger \hat{a}_i \hat{a}_i\right) |\phi\rangle, \quad (4.5)$$

where $|\phi\rangle$ is the reference state, usually a Restricted Hartree-Fock (RHF) state. The coefficients t_i^a needs to be optimized for a given single-particle basis. This approximation can generate results which are virtually indistinguishable from Full Doubly Occupied Configuration Interaction (FullDOCI) [145]. FullDOCI refers to the equivalent of FullCI but restricted to the space of all doubly occupied Slater determinants.

A major downside of DOCI is its orbital dependence. Any truncated CI wave function will be dependent on the orbitals: as part of the Hilbert space is missing, the shape of the orbitals needs to be optimized to find the (ground state) energy. In DOCI for example, only the diagonal one-particle matrix elements $\langle\alpha|\hat{T}|\alpha\rangle$ are used. This greatly complicates matters: one needs an algorithm to find the optimal shape, and the matrix elements for the one- and two-particle integrals need to be transformed to the optimal basis. In MCSCF and Valence Bond Self-Consistent Field (VBSCF), a similar issue arises. The 'full' problem is very challenging to solve: it means finding the global minimum in an uncharted energy landscape. We know that the DOCI landscape is riddled with local minima [152]. The methods that exist and can potentially find the global minima, such as Simulated Annealing (SA) [127, 153, 154], are slow. The situation is grave but not hopeless: given a suitable starting point, a local minimization can bring us to the desired minimum. This is the approach used by most MCSCF and VBSCF methods. In most cases, the HF orbitals are a good choice to start the minimization. The disadvantage is of course that one can never be sure that the lowest energy has been found, but in practice this approach seems to work. However, it comes at a steep computational cost: a gradient and a Hessian matrix have to be calculated, followed by a unitary transformation of the four-index tensor with the two-electron integrals. The latter operation scales as $O(L^5)$. A general unitary transformation U of a single element is

$$V_{abcd} = \sum_{\tilde{a}\tilde{a}} \sum_{\tilde{b}\tilde{b}} \sum_{\tilde{c}\tilde{c}} \sum_{\tilde{d}\tilde{d}} U_{a\tilde{a}} U_{b\tilde{b}} U_{c\tilde{c}} U_{d\tilde{d}} V_{\tilde{a}\tilde{b}\tilde{c}\tilde{d}}. \quad (4.6)$$

This scales as $O(L^4)$. Combined with the loop over all elements, this would give a total scaling of $O(L^8)$. Luckily, this can be reduced to $O(L^5)$ by rewriting eq. (4.6) as

$$\begin{aligned} V_{\tilde{a}\tilde{b}\tilde{c}\tilde{d}} &= \sum_{a\tilde{a}} U_{a\tilde{a}} V_{\tilde{a}\tilde{b}\tilde{c}\tilde{d}}, \\ V_{\tilde{a}\tilde{b}\tilde{c}\tilde{d}} &= \sum_{b\tilde{b}} U_{b\tilde{b}} V_{\tilde{a}\tilde{b}\tilde{c}\tilde{d}}, \\ V_{\tilde{a}\tilde{b}\tilde{c}\tilde{d}} &= \sum_{c\tilde{c}} U_{c\tilde{c}} V_{\tilde{a}\tilde{b}\tilde{c}\tilde{d}}, \\ V_{\tilde{a}\tilde{b}\tilde{c}\tilde{d}} &= \sum_{d\tilde{d}} U_{d\tilde{d}} V_{\tilde{a}\tilde{b}\tilde{c}\tilde{d}}. \end{aligned}$$

We transform index per index and thus have a scaling of $O(L)$ instead of $O(L^4)$. However, this is still computationally more expensive than an energy evaluation in AP1roG (which has L^3 mean-field scaling). In Section 4.2 on page 80, our solution to this problem is discussed.

We can now go back to the marriage of DOCI and v2DM. A general v2DM calculation, using one of the SDP methods from Chapter 3 with two-index conditions, scales as $O(L^6)$. However, the results found by these are not always accurate enough: in many cases, the three-index conditions are needed to capture the correct physics in the system. If we use the three-index commutator conditions, this increases to $O(L^9)$. If we compare this to the so-called 'golden standard' Coupled Cluster with Singles, Doubles and Triples in Perturbation (CCSD(T)) [53], which scales as $O(L^7)$ [155], we must conclude that v2DM is not competitive in terms of accuracy and time. The benefit we have is that v2DM finds a lower bound on the energy while other variational methods will find an upper bound. If we make the assumption that the ensemble of wave functions from which our 2DM should be derivable only consists of DOCI wave functions, we can use the DOCI N -representability conditions shown in Section 2.5. These have the advantage that the matrix dimensions of the two-index conditions are reduced from L^2 to L . We additionally have a set of linear inequalities and 2×2 matrix conditions but those are cheap to enforce. This changes the scaling of v2DM from $O(L^6)$ to $O(L^3)$. In other words, it suddenly puts us in an entirely different ballpark. Of course, the wave function based approximations of DOCI such as AP1roG also have mean-field scaling. The combination of v2DM and the DOCI N -representability constraints will be called Variational Optimization of the second-order reduced Density Matrix in the DOCI space (v2DM-DOCI)¹ [156] from now on. We will show that v2DM-DOCI is a better approximation to FullDOCI than v2DM is to FullCI. Unfortunately, we lose the advantage of the lower bound on the energy: with the same set of orbitals, v2DM-DOCI still produces a lower bound on the FullDOCI energy, but as we have to optimize the orbitals separately, this is meaningless. One thing that remains is that v2DM-DOCI is exact for a two-particle system: DOCI produces the exact energy for a system with only one pair when the orbitals are optimized [146]. This can be seen as follows: the exact wave function for two particles in the singlet ($S = 0$) state is

$$|\psi\rangle = \sum_{ab} c_{ab} \hat{a}_{a\uparrow}^\dagger \hat{a}_{b\downarrow}^\dagger | \rangle. \quad (4.7)$$

In the singlet case, the wave function is antisymmetric when swapping the spin indices and symmetric when swapping the orbital indices (see eq. (2.86a) on page 31): this means that c is a symmetric (real) matrix. When we diagonalize c and transform to the basis of the eigenvectors, the wave function becomes

$$|\psi\rangle = \sum_k \sqrt{\lambda_k^c} \hat{a}_{k\uparrow}^\dagger \hat{a}_{k\downarrow}^\dagger | \rangle. \quad (4.8)$$

From the physical point of view, this can be interpreted as first performing rotations between the occupied and virtual orbitals until all single excitations disappear and one finds the Brueckner determinant [157, 158]. Next, one can rotate the virtual orbitals among each other until

1. An alternative name is vOODo-2DM: variational, Orbital Optimized, Doubly occupied second order Density Matrix.

all double excitations no longer contribute to the wave function. Notice that in this case, the D part of the 2DM will be identically zero and the eigenvalues λ_k^c are the natural occupation numbers, doubly degenerate and summing to one (two when the degeneracy is accounted for). The transformation in eq. (4.8) is equivalent with transforming to the basis spanned by the natural orbitals.

The reduced Hamiltonian (see Equation (1.14) on page 6) for v2DM-DOCI is

$$K_{ab}^{\Pi} = \frac{2}{N-1} T_{aa} \delta_{ab} + V_{aabb}, \quad (4.9a)$$

$$K_{ab}^D = \frac{1}{N-1} (T_{aa} + T_{bb}) + V_{abab} - \frac{1}{2} V_{abba}, \quad (4.9b)$$

where $T_{ab} = \langle a | \hat{T} | b \rangle$ and $V_{abcd} = \langle ab | \hat{V} | cd \rangle$. Notice the round brackets (see eq. (B.10)). The energy function becomes

$$E_{\text{DOCI}} = \sum_{ab} (K_{ab}^{\Pi} \Pi_{ab} + 2K_{ab}^D D_{ab}). \quad (4.10)$$

We have implemented v2DM-DOCI using both a Potential Reduction Method and a Boundary Point method (see Chapter 3). As already said, the latter is much faster. In contrary to general v2DM, the Potential Reduction method is often difficult to converge. It is often necessary to tweak the speed at which the barrier drops and the point where convergence is reached seems to vary greatly. Therefore we have mostly focused on the Boundary Point method. Note that there are some default settings from general v2DM which have to be changed in v2DM-DOCI, for instance the Mazziotti factor is always set to one. We always used primal and dual convergence criteria 10^{-7} and primal-dual criteria of 10^{-3} . The Boundary Point method is fast but not very stable: we added a convergence monitor that checks if the primal convergence keeps going down. If too many steps do not decrease the primal convergence value (typically 2000-3000 steps), the algorithm will halt. This has consequences in the orbital optimizer on which we will expand later.

We have done a scaling test using a linear chain of hydrogen atoms in the STO-3G basis [159]. We used a minimal basis set as this gives us a system which we can let grow linearly: for every additional hydrogen atom, one additional orbital is used. The interatomic distance was kept fixed at 2 Bohr while we increased the chain length. At this distance, the individual hydrogen atoms are still within the interacting region [160]. No orbital optimizations are performed, we directly use the HF orbitals. As reference, we calculated the same chain with general v2DM and the Boundary Point method using spin symmetry and the singlet constraints (see eq. (2.108)). The convergence criteria were the same for both programs. Both were run on a single core of Intel® Xeon® E5-2680 v3 CPU. In Figure 4.1 on the next page we show the calculation time for all chain lengths on a log-log scale. The timings were checked to be reproducible. Notice that for a chain of 34 hydrogen atoms, the difference in runtime between v2DM-DOCI and v2DM is three orders of magnitude. For the v2DM curve (red) all calculated data points are marked, while for the v2DM-DOCI curve (blue) only every third data point is marked. To find the leading power in scaling, we performed a linear fit on the log-log data. The code scales

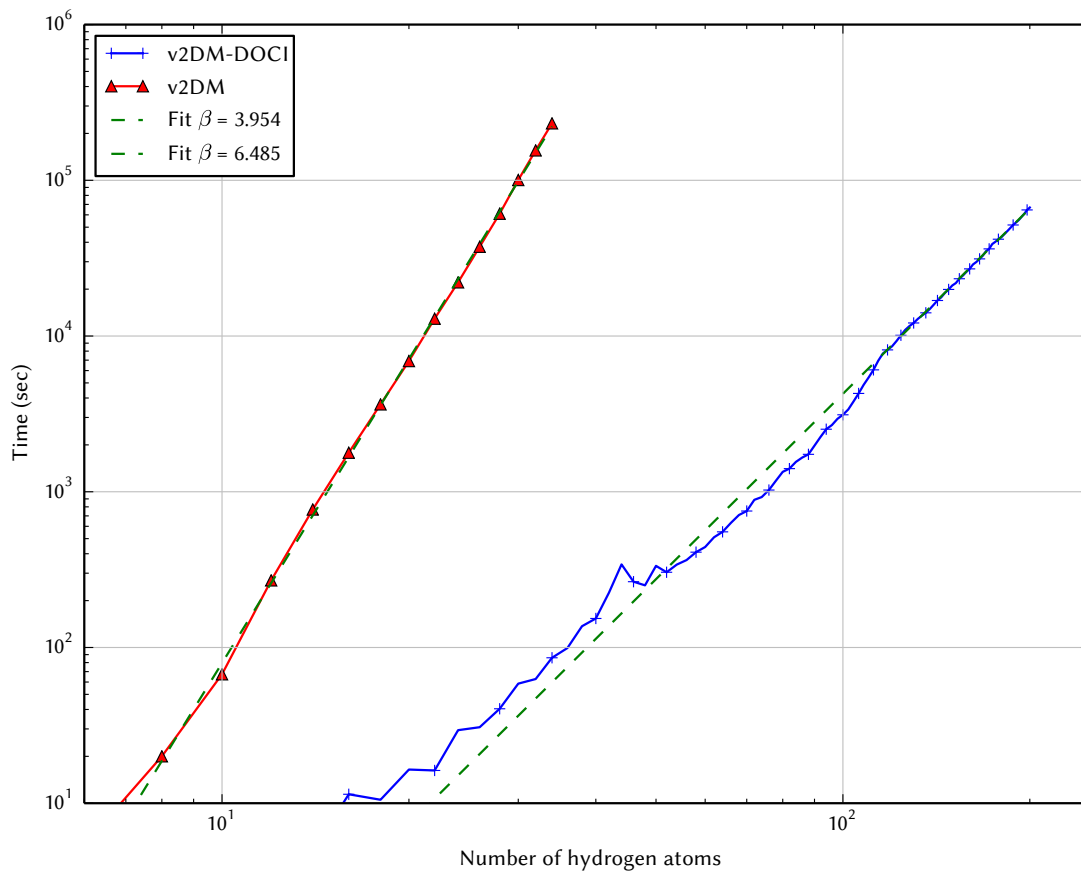


Figure 4.1: The scaling of v2DM vs v2DM-DOCI on a log-log scale. The test system is a linear hydrogen chain in the STO-3G basis. We fitted a linear curve $\beta x + \alpha$ to the data.

	α	β
v2DM	$2.602 \cdot 10^{-5}$	6.485
v2DM-DOCI	$5.268 \cdot 10^{-5}$	3.954

Table 4.1: The resulting coefficients of the linear fit in Figure 4.1

as $f(x) = \alpha x^\beta + \dots$, where we neglect all terms expect for the highest power. On a log-log scale, this becomes

$$\log f(x) = \beta \log x + \log \alpha, \quad (4.11)$$

or a simple linear curve. We used a least squares fit [127] which means minimizing

$$e = \sum_i |\beta \log x_i + \log \alpha - t_i|^2 \quad (4.12)$$

with respect to α and β (the sum goes over the data points). For the v2DM, we used a threshold of 600 seconds resulting in 11 data points for the fit. The v2DM-DOCI fit used a threshold of 10^4 seconds, giving us 35 data points for the fit. Both choices are motivated by Figure 4.1: it is visually clear that both curves only reach a constant scaling when the problem size is sufficiently large. It is interesting to see that v2DM-DOCI needs a much larger chain to have a constant scaling. In Table 4.1, the results of the fit can be found: v2DM-DOCI is two orders faster than v2DM while the leading coefficient changes little. The results deviate from our prediction of $O(L^3)$ for v2DM-DOCI and $O(L^6)$ for v2DM. This can be explained by the internal loop of the Boundary Point method. The actual scaling is iterative $O(L^3)$: for one loop, the number of Floating-Point Operations per Second (FLOPS) scales as $O(L^3)$ but its main loop adds an additional power to this. It is interesting to notice that the additional cost is higher for v2DM-DOCI than for v2DM. Despite its simpler structure, the DOCI N -representability constraints are more difficult to converge than their general counterpart. This agrees with our experience with the code: the Boundary Point method in v2DM-DOCI seems to be more unstable than in general v2DM.

4.2 Orbital Optimization

We now turn our attention to the orbital optimization of the DOCI orbitals. Like most MCSCF methods, we will use an iterative two-step algorithm: first we optimize the 2DM for a given set of orbitals and secondly we optimize the orbitals using the optimal 2DM. We look for the unitary transformation ($UU^\dagger = U^\dagger U = \mathbb{1}$) of the orbitals that gives us the lowest energy. Notice that as we have restricted ourself to real orbitals, the transformations are actually orthogonal ($UU^T = U^T U = \mathbb{1}$). We want to calculate the energy under a unitary transformation. In general v2DM this would give

$$E' = \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \sum_{\alpha'\beta'\gamma'\delta'} K_{\alpha\beta;\gamma\delta} U_{\alpha\alpha'} U_{\beta\beta'} U_{\gamma\gamma'} U_{\delta\delta'} \Gamma_{\alpha'\beta';\gamma'\delta'}. \quad (4.13)$$

One can both transform the 2DM or the reduced Hamiltonian K . However, this does not hold for DOCI, since a unitary transformation will moves us out of the DOCI space: the one- and two-electron integrals need to be transformed directly. If one transforms the 2DM as in eq. (4.13), then it can only use the current DOCI space, while we want to rotate new information from outside into the DOCI space. The transformation of the one- and two-electron integrals is

$$T'_{ab} = \sum_{a'b'} U_{aa'} U_{bb'} T_{a'b'}, \quad (4.14a)$$

$$V'_{abcd} = \sum_{a'b'c'd'} U_{aa'} U_{bb'} U_{cc'} U_{dd'} V_{a'b'c'd'}. \quad (4.14b)$$

If we substitute this in the reduced Hamiltonian (4.9), we find

$$K_{ab}^{\Pi} = \frac{2}{N-1} \delta_{ab} \sum_{a'b'} U_{aa'} U_{ab'} T_{a'b'} + \sum_{a'b'c'd'} U_{aa'} U_{ab'} U_{bc'} U_{bd'} V_{a'b'c'd'}, \quad (4.15a)$$

$$K_{ab}^D = \frac{1}{N-1} \sum_{a'b'} (U_{aa'} U_{ab'} + U_{ba'} U_{bb'}) T_{a'b'} + \sum_{a'b'c'd'} U_{aa'} U_{bb'} \left(U_{ac'} U_{bd'} - \frac{1}{2} U_{bc'} U_{ad'} \right) V_{a'b'c'd'}. \quad (4.15b)$$

The energy function (4.10) now is

$$E' = \frac{2}{N-1} \sum_{ab} \sum_{a'b'} (\delta_{ab} U_{aa'} U_{ab'} \Pi_{aa} + (U_{aa'} U_{ab'} + U_{ba'} U_{bb'}) D_{ab}) T_{a'b'} + \sum_{ab} \sum_{a'b'c'd'} U_{aa'} U_{ab'} U_{bc'} U_{bd'} V_{a'b'c'd'} \Pi_{ab} + \sum_{ab} \sum_{a'b'c'd'} U_{aa'} U_{bb'} (2U_{ac'} U_{bd'} - U_{bc'} U_{ad'}) V_{a'b'c'd'} D_{ab}. \quad (4.16)$$

An $n \times n$ unitary matrix can be parameterised by a antisymmetric $n \times n$ matrix X as [161]

$$U = \exp X = \mathbb{1} + X + \frac{1}{2} X^2 + \frac{1}{6} X^3 + \dots = \sum_{n=0}^{\infty} \frac{1}{n!} X^n \quad (4.17)$$

with $X^T = -X$.

This parameterization is used since otherwise we would need a Lagrange multiplier [123, 124] to ensure the unitarity of U in a minimization. The most often used approach is to use the second-order approximation of U and substitute it in the energy function (4.16). We then

rewrite the energy as

$$E(\mathbf{x}) = E(\mathbf{0}) + \sum_{ab} x_{ab} \frac{\partial E}{\partial x_{ab}} + \frac{1}{2} \sum_{abcd} x_{ab} \frac{\partial^2 E}{\partial x_{ab} \partial x_{cd}} x_{cd} \quad (4.18a)$$

$$= E(\mathbf{0}) + \mathbf{g}^T \mathbf{x} + \frac{1}{2} \mathbf{x}^T H \mathbf{x}, \quad (4.18b)$$

where $\mathbf{x} = (X_{12}, X_{13}, \dots)$ is the vector with the non-redundant elements of the antisymmetric matrix X , while $\mathbf{g}$ and H are the gradient and Hessian of the orbital optimization. The straightforward way is to use a Newton-Raphson method [127] to find the local minimum starting from an educated guess. Often the Hessian is approximated in some way to speed up the minimization [162]. In the end we still need to transform the one- and two-electron integrals using the found unitary matrix, which scales as $O(L^5)$. We will try to avoid this.

One of the simplest unitary transformations are Jacobi rotations [163]: it is a rotation in the two-dimensional subspace of two orbitals. It is also referred to as a Givens rotation². The Jacobi rotation of orbitals k and l over an angle θ is given by

$$\left(Q^{kl}(\theta)\right)_{ij} = \delta_{ij} + (\delta_{ik}\delta_{jk} + \delta_{il}\delta_{jl})(\cos \theta - 1) + (\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}) \sin \theta, \quad (4.19)$$

or in matrix form

$$Q^{kl}(\theta) = \begin{matrix} & & k & & l & & \\ \begin{matrix} k \\ l \end{matrix} & \begin{pmatrix} 1 & & & & \\ & \ddots & & & \\ & & \cos \theta & \cdots & \sin \theta \\ & & \vdots & \ddots & \vdots \\ & & -\sin \theta & \cdots & \cos \theta \\ & & & & \ddots & \\ & & & & & 1 \end{pmatrix} \end{matrix}. \quad (4.20)$$

Originally, it was used in the Jacobi Eigenvalue algorithm [127, 164]: a sequence of Jacobi rotations were used to zero out all off-diagonal elements of a matrix. Although it is considered not to be competitive with the QR algorithm [164], it has the advantage of being inherently parallelizable. To understand this, let us look at what happens when we perform a Jacobi rotation on a symmetric matrix T

$$T' = Q^{kl}(\theta)T \quad (4.21)$$

$$T'_{ab} = \sum_c \left(Q^{kl}(\theta)\right)_{ac} T_{cb} \quad (4.22)$$

$$= T_{ab} + \delta_{ak} (T_{kb} (\cos \theta - 1) + T_{lb} \sin \theta) + \delta_{al} (T_{lb} (\cos \theta - 1) - T_{kb} \sin \theta). \quad (4.23)$$

2. The correct name would be a Givens rotation but in the Quantum Chemistry literature, the name Jacobi rotation is used consistently.

We can see that only row/column k and l are changed. This is also the reason why we are interested in Jacobi rotations: if T is the matrix with the one-particle integrals, only 2 row/columns need to be updated at each step. For the two-particle matrix elements V_{abcd} the situation is slightly more complicated, but it boils down to the same: only if at least one of the 4 indices is equal to k or l does an update have to occur. If point group symmetry is used, the simplification is even bigger. We always assume that the orbitals k and l belong to the same irreducible representation. Another advantage is that no Taylor expansion is needed: we use the exact unitary transformation instead of a second-order approximation. The antisymmetric parameterization X of U also has a distinct form for a Jacobi rotation: all elements are zero except $X_{kl} = \theta$. With this form, eq. (4.17) will generate the series expansion of a $\cos$ and $\sin$. Furthermore, using a sequence of only Jacobi rotations forms no limitation: any orthogonal transformation can be uniquely decomposed as a series of Jacobi rotations [165]. This leads to a generalization of the Euler angles [166, 167]. There exist MCSCF and Complete Active Space Self-Consistent Field (CASSCF) algorithms that use Jacobi rotations for the orbital optimization step [168, 169].

If we substitute the unitary transformation (4.19) in the energy function (4.16) we find a lengthy expression, which can be simplified as

$$E(\theta) = \tilde{A} \cos^4 \theta + \tilde{B} \sin^4 \theta + \tilde{C} \cos^2 \theta + \tilde{D} \sin^2 \theta + 2\tilde{E} \cos \theta \sin \theta + 2\tilde{F} \cos^2 \theta \sin^2 \theta + 4\tilde{G} \sin \theta \cos^3 \theta + 4\tilde{H} \sin^3 \theta \cos \theta + \tilde{I}, \quad (4.24)$$

where

$$\tilde{A} = V_{kkkk} \Gamma_{k\bar{k};k\bar{k}} + V_{llll} \Gamma_{l\bar{l};l\bar{l}} + 2V_{kkll} \Gamma_{k\bar{k};l\bar{l}} + 2(2V_{klkl} - V_{kkll}) \Gamma_{kl;kl} \quad (4.25a)$$

$$\tilde{B} = V_{kkkk} \Gamma_{l\bar{l};l\bar{l}} + V_{llll} \Gamma_{k\bar{k};k\bar{k}} + 2V_{kkll} \Gamma_{k\bar{k};l\bar{l}} + 2(2V_{klkl} - V_{kkll}) \Gamma_{kl;kl} \quad (4.25b)$$

$$\begin{aligned} \tilde{C} = & \sum_{a \notin \{k,l\}} \left\{ 2V_{kkaa} \Gamma_{k\bar{k};a\bar{a}} + 2V_{llaa} \Gamma_{l\bar{l};a\bar{a}} + 2 \left(2V_{kaka} - V_{kaak} + \frac{2}{N-1} T_{kk} \right) \Gamma_{ka;ka} \right. \\ & \left. + 2 \left(2V_{lala} - V_{laal} + \frac{2}{N-1} T_{ll} \right) \Gamma_{la;la} \right\} + \frac{2}{N-1} (T_{kk} \Gamma_{k\bar{k};k\bar{k}} + T_{ll} \Gamma_{l\bar{l};l\bar{l}}) \end{aligned} \quad (4.25c)$$

$$\begin{aligned} \tilde{D} = \sum_{\substack{a \\ a \notin \{k,l\}}} \left\{ 2V_{kkaa} \Gamma_{\bar{l}\bar{l};a\bar{a}} + 2V_{llaa} \Gamma_{k\bar{k};a\bar{a}} + 2 \left(2V_{kaka} - V_{kaak} + \frac{2}{N-1} T_{kk} \right) \Gamma_{la;la} + \right. \\ \left. 2 \left(2V_{lala} - V_{laal} + \frac{2}{N-1} T_{ll} \right) \Gamma_{ka;ka} \right\} + \frac{2}{N-1} (T_{ll} \Gamma_{k\bar{k};k\bar{k}} + T_{kk} \Gamma_{\bar{l}\bar{l};\bar{l}\bar{l}}) \end{aligned} \quad (5.25d)$$

$$\begin{aligned} \tilde{E} = \sum_{\substack{a \\ a \notin \{k,l\}}} \left\{ 2V_{klaa} (\Gamma_{\bar{l}\bar{l};a\bar{a}} - \Gamma_{k\bar{k};a\bar{a}}) + 2 \left(2V_{kala} - V_{kaal} + \frac{2}{N-1} T_{kl} \right) \right. \\ \left. (\Gamma_{la;la} - \Gamma_{ka;ka}) \right\} + \frac{2}{N-1} T_{kl} (\Gamma_{\bar{l}\bar{l};\bar{l}\bar{l}} - \Gamma_{k\bar{k};k\bar{k}}) \end{aligned} \quad (5.25e)$$

$$\begin{aligned} \tilde{F} = (2V_{kkll} + V_{klkl}) (\Gamma_{k\bar{k};k\bar{k}} + \Gamma_{\bar{l}\bar{l};\bar{l}\bar{l}}) + (V_{kkkk} + V_{llll} - 2(V_{kkll} + V_{klkl})) \Gamma_{k\bar{k};\bar{l}\bar{l}} + \\ (V_{kkkk} + V_{llll} - 6V_{kkll} + 2V_{klkl}) \Gamma_{kl;kl} \end{aligned} \quad (5.25f)$$

$$\tilde{G} = V_{kl\bar{l}\bar{l}} \Gamma_{\bar{l}\bar{l};\bar{l}\bar{l}} - V_{klkk} \Gamma_{k\bar{k};k\bar{k}} + (V_{klkk} - V_{kl\bar{l}\bar{l}}) (\Gamma_{k\bar{k};\bar{l}\bar{l}} + \Gamma_{kl;kl}) \quad (5.25g)$$

$$\tilde{H} = V_{klkk} \Gamma_{\bar{l}\bar{l};\bar{l}\bar{l}} - V_{kl\bar{l}\bar{l}} \Gamma_{k\bar{k};k\bar{k}} - (V_{klkk} - V_{kl\bar{l}\bar{l}}) (\Gamma_{k\bar{k};\bar{l}\bar{l}} + \Gamma_{kl;kl}) \quad (5.25h)$$

$$\tilde{I} = \sum_{\substack{ab \\ a,b \notin \{k,l\}}} \left\{ V_{aabb} \Gamma_{a\bar{a};b\bar{b}} + \left(2V_{abab} - V_{abba} + \frac{2}{N-1} (T_{aa} + T_{bb}) \right) \Gamma_{ab;ab} \right\} \quad (5.25i)$$

The energy expression (4.24) can be simplified even more using trigonometric identities to

$$E(\theta) = A \cos 4\theta + B \cos 2\theta + C \sin 4\theta + D \sin 2\theta + F, \quad (4.26)$$

where the constants are

$$A = \frac{\tilde{A} + \tilde{B}}{8} - \frac{\tilde{F}}{4}, \quad (4.27a)$$

$$B = \frac{\tilde{G} - \tilde{H}}{2}, \quad (4.27b)$$

$$C = \frac{\tilde{A} - \tilde{B} + \tilde{C}}{2} - \frac{\tilde{D}}{2}, \quad (4.27c)$$

$$D = \tilde{E} + \tilde{G} + \tilde{H}, \quad (4.27d)$$

$$F = \frac{3}{8} (\tilde{A} + \tilde{B}) + \frac{\tilde{C} + \tilde{D}}{2} + \frac{\tilde{F}}{4} + \tilde{I}. \quad (4.27e)$$

We now want to know the minima of this one-dimensional function. A direct analytical result seems not feasible, so we resort to numerical techniques: we use the Newton-Raphson method [127], for which we require the gradient and Hessian:

$$\frac{dE(\theta)}{d\theta} = -4A \sin 4\theta - 2B \sin 2\theta + 4C \cos 4\theta + 2D \cos 2\theta, \quad (4.28a)$$

$$\frac{d^2E(\theta)}{d\theta^2} = -16A \cos 4\theta - 4B \cos 2\theta - 16C \sin 4\theta - 4D \sin 2\theta. \quad (4.28b)$$

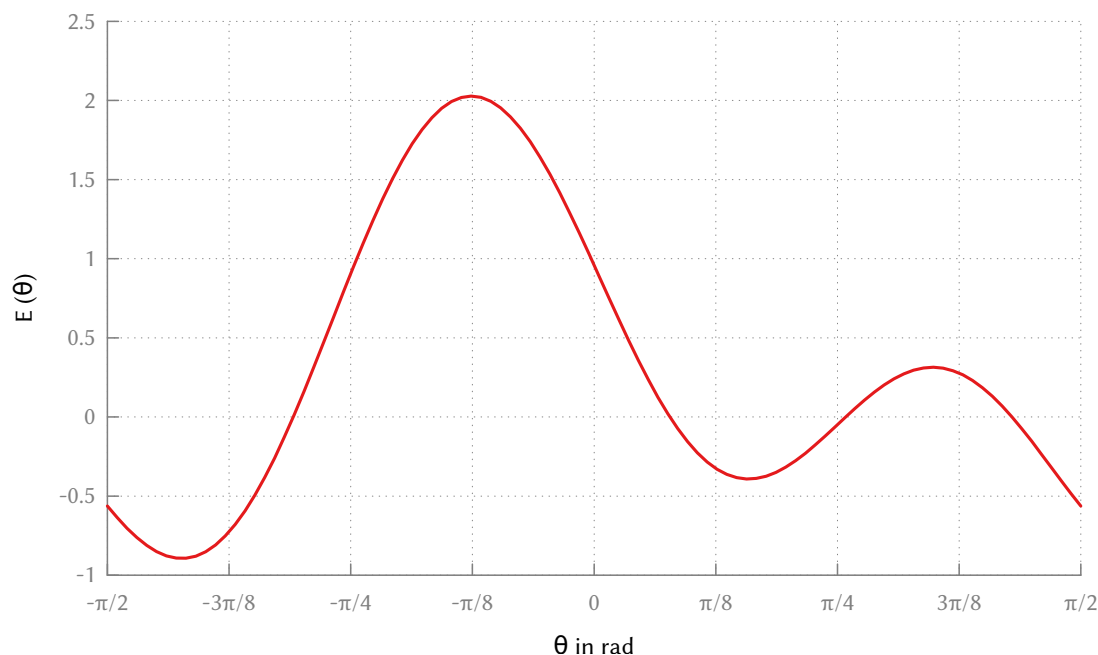


Figure 4.2: Equation (4.26) for the case $A \approx -0.115$, $B \approx -0.839$, $C \approx 0.761$, $D \approx -0.477$ and $F \approx 0.313$.

It is interesting to note here that it is cheaper to compute the gradient or Hessian than it is to evaluating the energy (4.26). This is a direct consequence of the Jacobi rotations: the constant term in eq. (4.26), *e.g.* the I term in eq. (5.25i), has a double summation over all orbitals except k and l , while all other terms have at most a summation over one index. Thus calculating the energy scales as $O(L^2)$ while calculating the gradient and Hessian only scale as $O(L)$. The actual Newton-Raphson will be very fast as it only requires the evaluation of four sine and cosine values. We always start from $\theta = 0$ to find a minimum. Using the Hessian (4.28b) we can make sure that we have a minimum. It is clear that eq. (4.26) is periodic with a period of π , so we limit our search to the interval $[-\frac{\pi}{2}, \frac{\pi}{2}]$. Note that in case of $\theta = \frac{\pi}{2}$, we simply switch two orbitals. It is possible that eq. (4.26) has multiple minima and that we will not find the lowest one when starting from $\theta = 0$. Such a situation can be seen in Figure 4.2. We looked for a pattern in the coefficients to discover this kind of situation, but found none. The easiest way is simply to perform two minimizations starting from two different starting points. This approach works well as each minimization is very fast. In case of a positive Hessian (or maximum), we also simply restart from $\theta = \frac{\pi}{4}$.

We still need to know which pair of orbitals to consider. Looping over all possible pairs of orbitals within an irreducible representation will scale as $O(L^2)$. Combining this with the Newton-Raphson minimization, we have a $O(L^3)$ algorithm to find the optimal set of orbitals. As already said, the update of the one- and two-electron integrals scales as $O(L)$. Explicit formulas to directly calculate the reduced Hamiltonian can be found in Chapter E on page 201.

Doubly occupied orbitals					
$1A_1$	-7.339428	$2A_1$	-0.573370	$3A_1$	-0.246546
Virtual orbitals					
$1B_1$	0.269938	$1B_2$	0.269938	$4A_1$	0.701123

Table 4.2: The restricted Hartree-Fock solution for BH in STO-3G. The orbital energies are in Hartree. We use C_{2v} symmetry, the orbitals are labelled according to irreducible representations A_1 , B_1 or B_2 .

Note that the minimal energy found by eq. (4.26) is not necessarily the actual minimum: the N -representability conditions are unitarily invariant but the v2DM minimum is not. Let us take a look at an example: the BH molecule in the STO-3G [159] basis with an interatomic distance of 2.33 Bohr. This molecule has C_{2v} symmetry with four orbitals transforming according to irreducible representation A_1 , one according to B_1 and one according to B_2 . The result of eq. (4.26) with and without a v2DM optimization can be seen in Figure 4.3 on the next page. As we hoped, around $\theta = 0$, both curves coincide. Most orbital pairs have a minimum very close to $\theta = 0$ except one: the rotation between orbitals $2A_1$ and $3A_1$. But even there, the minimum predicted by the Jacobi rotations is very close to the optimized one: the difference is 0.039 rad. A single Jacobi rotation already brings us very close to the FullCI energy of -24.810 Hartree. This can be understood from the HF solution of BH: the orbital energies (in Hartree) of the RHF solution are given in Table 4.2. The $1A_1$ orbital is the $1s$ orbital on the Bohr atom while the $2A_1$ and $3A_1$ are a mixture of the $1s$ orbital on the hydrogen atom and the $2s$ and $2p_z$ orbital on the Bohr atom. The largest energy gain can be achieved by mixing these orbitals.

It turns out that the picture painted in Figure 4.3 is correct for most molecules: most orbital pairs will have a minimum very close to $\theta = 0$, while a select group will lower the energy. We present our algorithm to find the optimal Jacobi rotation in pseudocode in Algorithm 3.

Algorithm 3 The algorithm used to find the optimal Jacobi rotation in pseudocode. The inputs are the 2DM, and the one- and two-electron integrals. It returns the optimal orbital pair and angle.

```

procedure FINDOPTIMALROTATION( $\Gamma, T, V$ )
  for  $i \leftarrow 1, n_{\text{irrep}}$  do                                ▷ Loop over all irreducible representations
    for all  $(a, b) \in \text{irrep}_i$  do                            ▷ Loop over all orbital pairs in  $\text{irrep}_i$ 
       $(E_{ab}, \theta_{ab}) = \text{FINDMINIMUM}(\Gamma, T, V, a, b)$       ▷ Minimum of (4.26)
    end for
  end for
   $(k, l, \theta) = \text{min}(E, \theta)$                                 ▷ Find the lowest energy over all pairs
  return  $(k, l, \theta_{kl})$                                     ▷ Return the pair of orbitals and the angle
end procedure

```

One of the downsides of using Jacobi rotations versus a procedure with the full gradient and Hessian, is that it can only update two orbitals at a time, whereas a gradient-based method

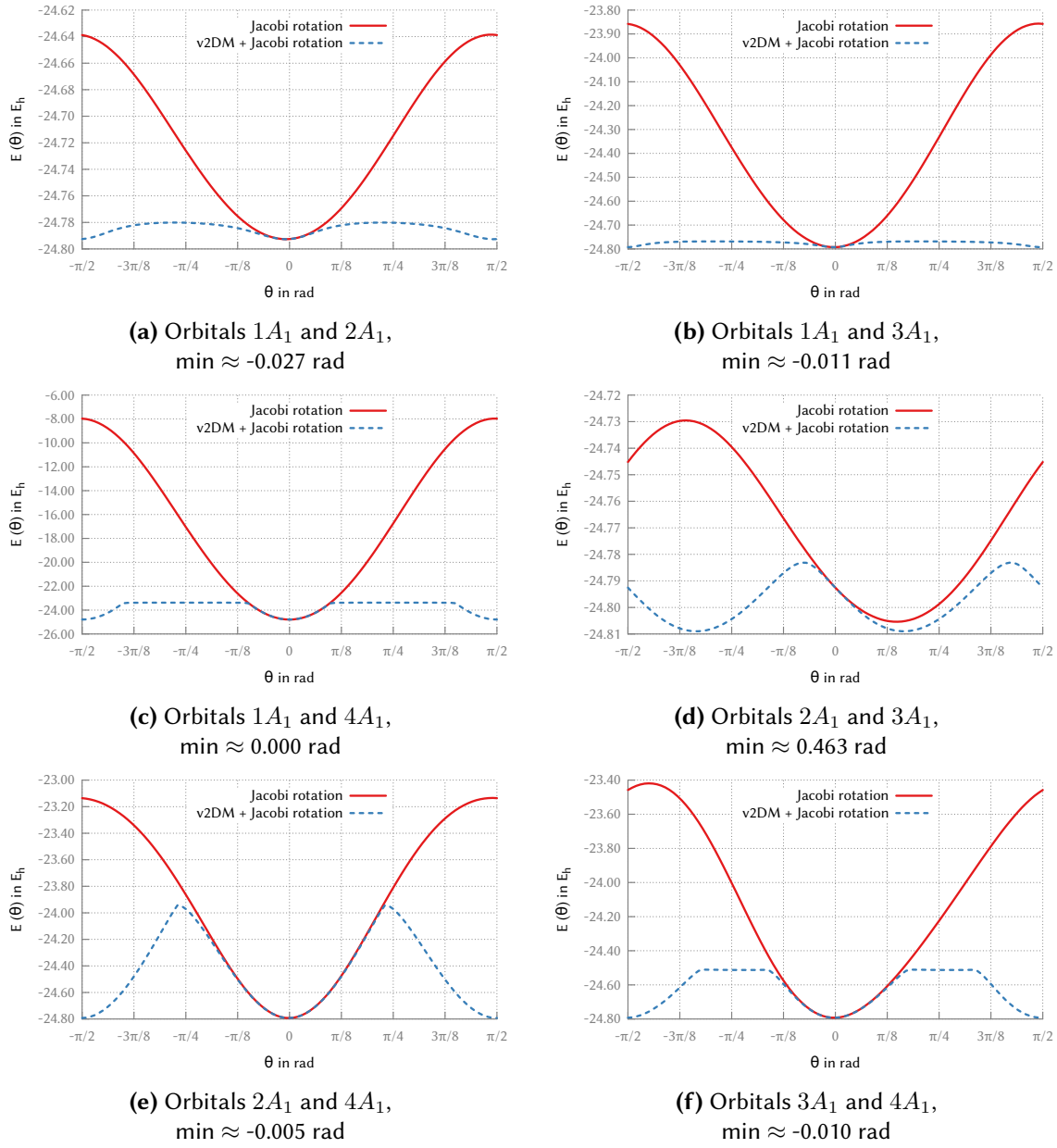


Figure 4.3: The red curve has been calculated using eq. (4.26), while the dashed blue curve uses the same transformed reduced Hamiltonian but an optimized 2DM. The min refers to the minimum of the red curve. The FullCI energy is $-24.810 E_h$.

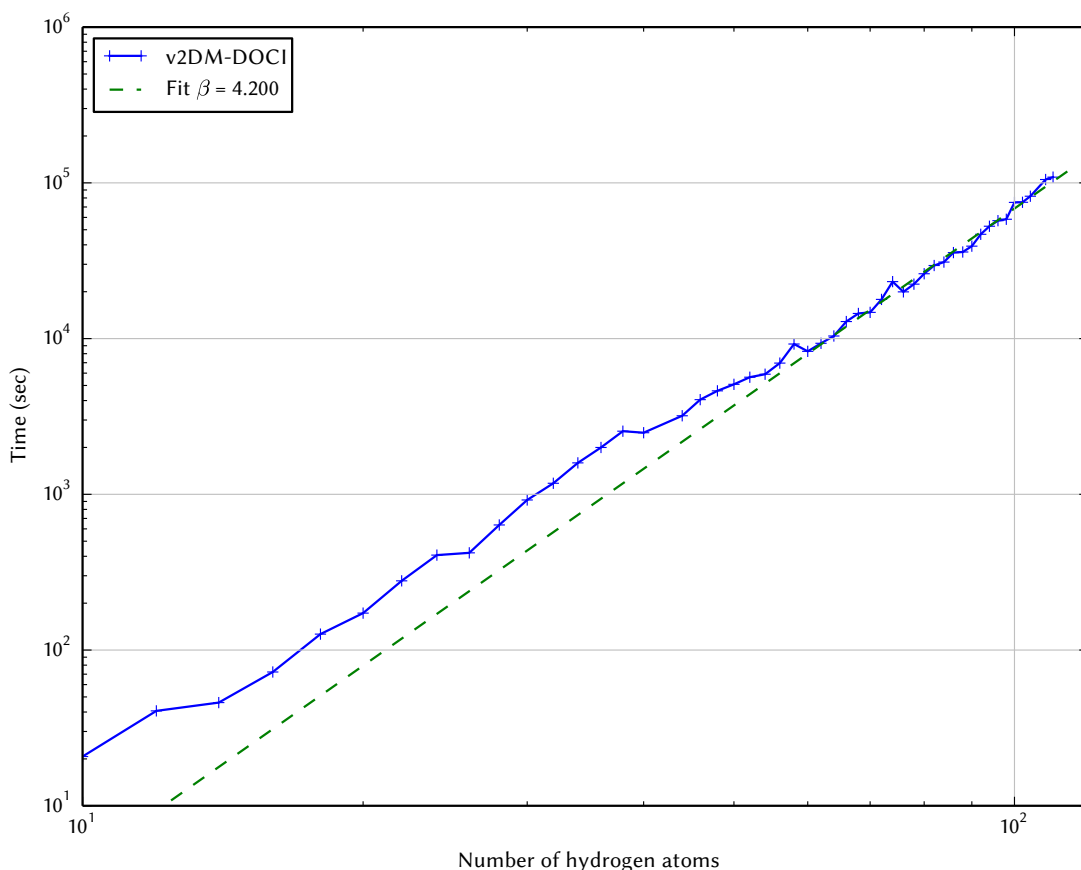


Figure 4.4: The scaling of v2DM-DOCI with orbital optimization on a log-log scale. The test system is a linear hydrogen chain in the STO-3G basis. We fitted a linear curve $\beta x + \alpha$ to the data.

can update all orbitals at the same time. We can partially circumvent this: we found that the first sequence of Jacobi rotations decreases the energy clearly, and is then followed by a long sequence of Jacobi rotations over small angles. For small angles, the 2DM does not change much and we can skip the actual optimization. This leads to a hybrid algorithm: first we combine the Jacobi rotations with the optimization of the 2DM until the energy change in consecutive steps is small enough, then we perform a sequence of Jacobi rotations with an occasional optimization of the 2DM. After the energy decrease is small enough, we restart the original Jacobi rotation with 2DM optimization until convergence has been reached. This procedure can give a considerable speed boost. Let us now revisit our previous test system to fit the scaling. We will use the same linear hydrogen chain as in Figure 4.1 on page 79 but now include orbital optimization. For the linear fit, a threshold of 10^4 seconds was used, resulting in $27.256 \cdot 10^{-5} x^{4.200}$. If we compare this to the values in Table 4.1, we see that the orbital optimization costs us an additional 0.25 in the leading power. This is still clearly faster than

v2DM and AP1roG. It is difficult to draw general conclusions from this because a hydrogen chain in STO-3G [159] is such a special case: only the $1s$ orbital is present.

As reference, we have also implemented a Simulated Annealing (SA) algorithm [127, 153, 154] for the orbital optimization. As already stated, SA is a slow method, but it is able to find the global minimum. It is not often used in the context of electronic structure calculations [170–173] but it has been successfully applied to protein folding [174, 175]. It is a kind of Monte Carlo algorithm but the idea is inspired by annealing in metallurgy. The material is slowly cooled and, once in a while, slightly reheated to minimize the number of defects in the material. In SA, there is an artificial temperature which determinates the probability of accepting a new solution with a higher energy than the previous solution. In a nutshell, the SA algorithm can start at any random point (but a guess close to the actual solution is of course better), it will then make a random move on the DOCI surface and calculate the energy with the new set of orbitals. If the new energy is lower, the algorithm will accept the solution and the cycle restarts. If the new energy is higher, the algorithm will accept it with a probability depending on the temperature: the higher the temperature, the higher the probability it will be accepted. During the cycles, the temperature is slowly decreased until higher energy solutions have a negligible probability of acceptance. We use Jacobi rotations for the random perturbation on the orbitals: a pair of orbitals and the rotation angle are chosen at random at each cycle. As acceptance probability function, we will use a Boltzmann function: $\exp \frac{E_{\text{old}} - E_{\text{new}}}{T}$. There are many parameters that need customizing in a SA algorithm: the acceptance probability function, the temperature change function and the random perturbation generator. Our algorithm is heavily inspired by that of Van Raemdonck *et al.* [147]. Unfortunately, this algorithm is slow: depending on the starting point, many cycles are needed before convergence is reached. As it is a Monte Carlo algorithm, several runs are needed to ensure that we have actually found the correct global minimum. Our algorithm starts several “walkers” in parallel which communicate with each other through the Message Passing Interface (MPI) [176, 177]. They all start again from the lowest energy walker after a certain number of steps. We will only use this algorithm when there is doubt that the Jacobi rotation-based local minimizer finds the correct minimum.

4.3 DOCI tailored v2DM

Before we embark on our tour through the v2DM-DOCI results, let us first sketch the boundary conditions. From now on, we will always use the cc-pVDZ basis [108] unless explicitly specified otherwise. All HF calculations were done with PSI4 [178], an open-source ab initio electronic structure program. The symmetry-adapted molecular one- and two-particle integrals also were extracted from PSI4. As v2DM always needs an orthogonal basis, we work in the symmetry-adapted basis where we applied a Löwdin orthogonalization [179]. This transformation has the interesting property that the orthogonalized orbitals are, in a least-squares sense, the closest to the original orbitals [180, 181]. When we use the RHF orbitals, we use the transformation from the orthogonalized symmetry-adapted basis to the MO orbitals. By doing this, we can use the optimal set of orbitals from one configuration to the next.

We use atomic units [182], namely Bohr for distances and Hartree for energies. The symmetries to which we refer always mean the largest Abelian subgroup of the full point group symmetry. When we refer to FullDOCI, we mean a CI solver which is restricted to all Doubly-occupied Slater determinants within the basis. The code is GPLv3-licensed [183] and available online [184]. We use the same starting point and orbital optimization algorithm in FullDOCI and v2DM-DOCI. All calculations were done on an Intel® Xeon® E5-2680 v3 CPU with 64 GB of RAM. The v2DM-DOCI code is single threaded while the FullDOCI code is parallelized: the sparse Hamiltonian is constructed explicitly and the lowest eigenvalue and eigenvector are found by an implicit restarted Arnoldi algorithm [185, 186]. It is only because of this parallelization that we can find the FullDOCI results in a reasonable time. More details about the working of both codes can be found in Chapter G on page 207. In Algorithm 4 we show a schematic overview of the entire program.

Algorithm 4 Schematic overview of the complete v2DM-DOCI algorithm

```

converged  $\leftarrow$  0
while converged < 25 do                                 $\triangleright$  Do 25 steps within convergence criteria
     $E_{\text{new}}, \Gamma = \text{v2DM}(T, V)$                  $\triangleright$  Do a v2DM-DOCI optimization with electron integrals  $T$ 
    and  $V$ 
     $(k, l, \theta) = \text{FINDOPTIMALROTATION}(\Gamma, T, V)$          $\triangleright$  Find the optimal rotation
     $T, V = \text{TRANSFORMINTEGRALS}(k, l, \theta, T, V)$              $\triangleright$  Rotate the integrals
    if  $|E_{\text{new}} - E_{\text{old}}| < 10^{-6}$  then                 $\triangleright$  Check convergence
        converged  $\leftarrow$  converged + 1
    end if
     $E_{\text{old}} \leftarrow E_{\text{new}}$ 
end while

```

When the size of the problem allowed it, we used the FullCI solver from PSI4 to generate the reference results. For larger problems, we used CheMPS2 [187–190], an open-source spin-adapted implementation of Density Matrix Renormalization Group (DMRG) [191–194] for ab initio quantum chemistry. It uses a Matrix Product State (MPS) [195] as ansatz for the wave function which is then iteratively optimized during a number of sweeps. The size or bond dimension of the matrices in the MPS determine the accuracy and speed. We have always started with a bond dimension of 500 and increased this in steps to 2500. CheMPS2 also fully exploits spin symmetry and point group symmetry. For all practical purposes in this work, we can consider the energy found by CheMPS2 to be FullCI accurate.

4.3.1 Few electron systems

We first investigate a couple of special cases as reference: H_2 , He and He_2 . The first two have only two electrons, and thus we should find the FullCI value using only the $\mathcal{J}$ condition. The latter dissociates in two two-electron systems, and we should thus recover the correct dissociation energy. In Figure 4.5 on the next page the result for H_2 can be seen. As expected, the v2DM-DOCI curve and the FullCI curve coincide. For the neutral atom Helium, we find

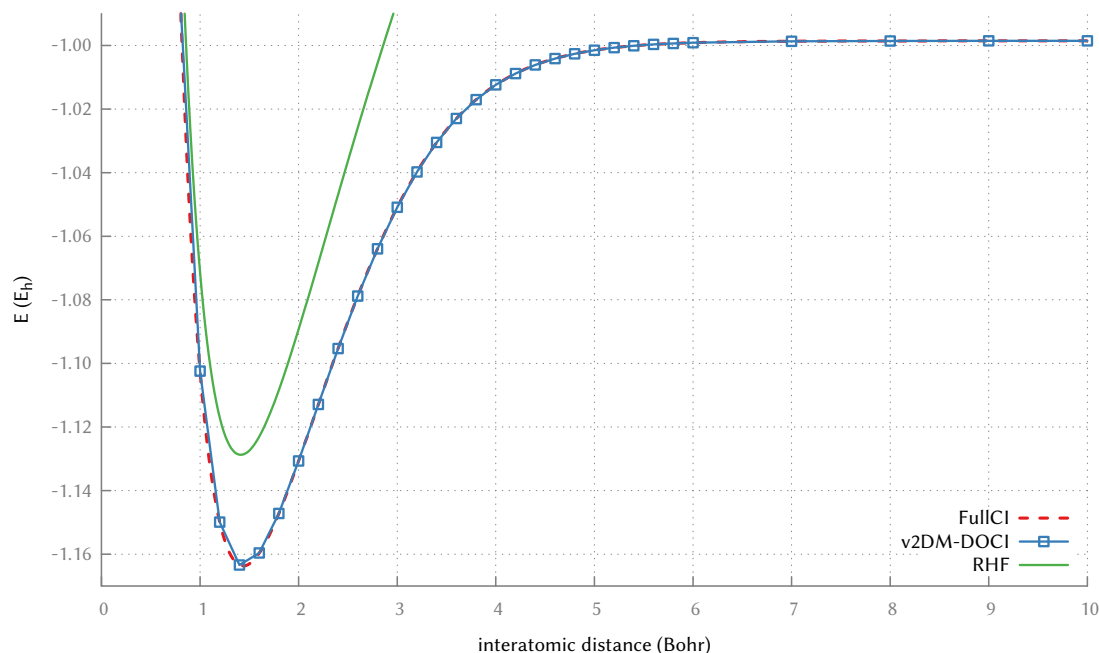


Figure 4.5: The dissociation of H_2 in the cc-pVDZ basis.

a ground state energy of -2.8875948297 Hartree with v2DM-DOCI while FullCI gives us -2.8875948311 Hartree. The difference between both is 1.400 nanoHartree. In both cases we started from the RHF solution. The number of orbital optimization steps was small (< 10). A more interesting case is the Helium dimer in Figure 4.6 on the following page. This system has D_{2h} symmetry and if we calculate v2DM-DOCI using this symmetry, the dissociation limit produces too high an energy. It is only when we break the symmetry (and use C_1 symmetry) that we recover the correct dissociation energy. We tried random starting points for the D_{2h} calculation but never found an energy lower than the one depicted in Figure 4.6. If we look at the occupation numbers, we see exactly what we expect: two orbitals which are doubly occupied. This example shows the importance of symmetry breaking for DOCI. Symmetry breaking has a long history in physics [196–198]. The exact ground state wave function (or 2DM) of a Hamiltonian needs to exhibit the symmetry of the system but this does not hold for the approximated wave function. On the contrary, if we use the classic variational principle, every additional constraint on the wave function will only increase the energy. This was called the symmetry dilemma by Lödwin [199]. The most strict approximation in HF theory is symmetry-adapted RHF: all symmetries are conserved. Each symmetry that is broken leads to a flavour of HF [200, 201], with the most general one being complex General Hartree-Fock (GHF) [202]. In GHF, none of the symmetries of the system are used in the variation, leading to a potentially much lower energy. Afterwards, a projection is done to restore some symmetries such as particle number. However, it turns out that it is difficult to recover a good quantum number once it is lost. In HF theory, this can be solved by a self-consistent variation after projection approach [203]. In the present case of DOCI, we will only break the spatial point-

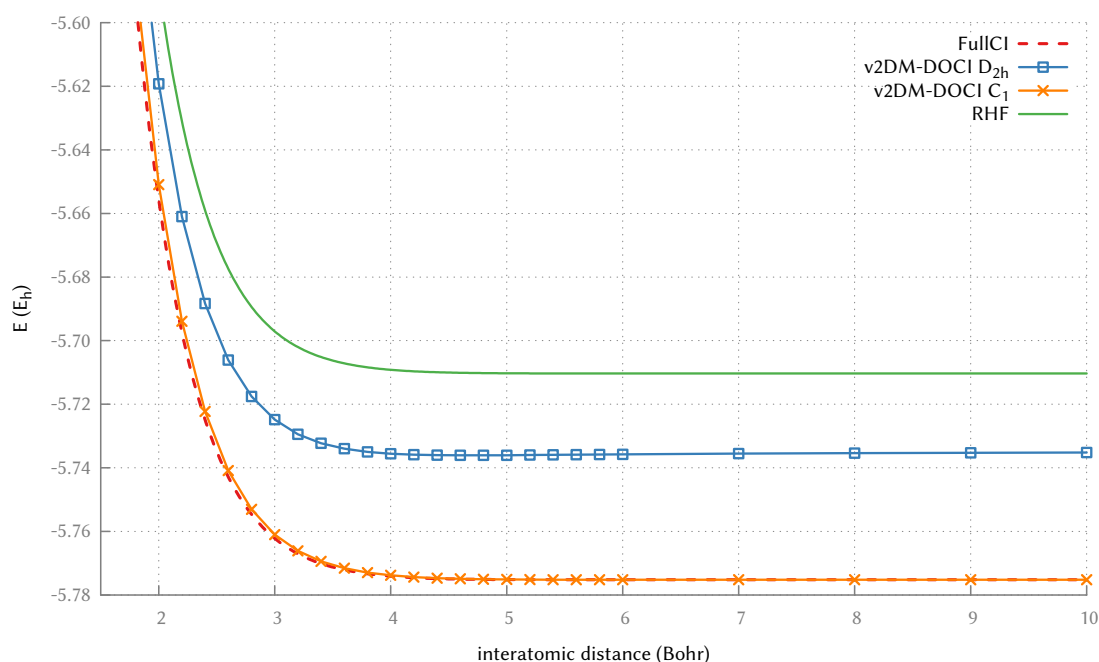


Figure 4.6: The dissociation of He_2 in the cc-pVDZ basis. Both the symmetry-adapted (D_{2h}) and symmetry-broken (C_1) results are shown.

group symmetry. It is important to note that this is not related to v2DM. If we use FullDOCI exactly the same issues arises. It is the DOCI space itself that requires the symmetry breaking.

In Figure 4.7 on the next page we have visualized the natural orbitals using Jmol [204, 205]: an isosurface of the natural orbital is plotted. We show the isosurface $f(x, y, z) = 0.05$ in red and $f(x, y, z) = -0.05$ in blue, where $f(x, y, z)$ is a linear combination of the atom-centered, Gaussian-type orbitals. The atoms are shown at 15% of the van der Waals radius [206]. The effect of symmetry breaking is clear: in the D_{2h} case, both occupied orbitals are a linear combination of the $1s$ and $2s$ of both He atoms, while for C_1 only the s orbital of a single He atom is used for each natural orbital. The DOCI wave function needs this additional degree of freedom to find the correct ground-state energy.

The next molecular system which we examine is a planar configuration of four hydrogen atoms. We will deform a rectangle of 4×1 to 1×4 Bohr. The coordinates of the four hydrogen atoms are $(0, 0)$, $(d, 0)$, $(0, 5 - d)$ and $(d, 5 - d)$ where d is varied in steps from 1 to 4 Bohr. The configuration is depicted in Figure 4.8 on the facing page. Similar systems have already been studied extensively [207–212]. The reason for the interest in this system is the degeneracy in the square configuration: two Slater determinants become equivalent in this case and we have a strongly correlated system. This system has D_{2h} symmetry as the full point group symmetry (instead of as an Abelian subgroup). For the symmetry-broken v2DM-DOCI calculations, we used the Edmiston-Ruedenberg (ER) localized orbitals [213]. These are found by maximizing

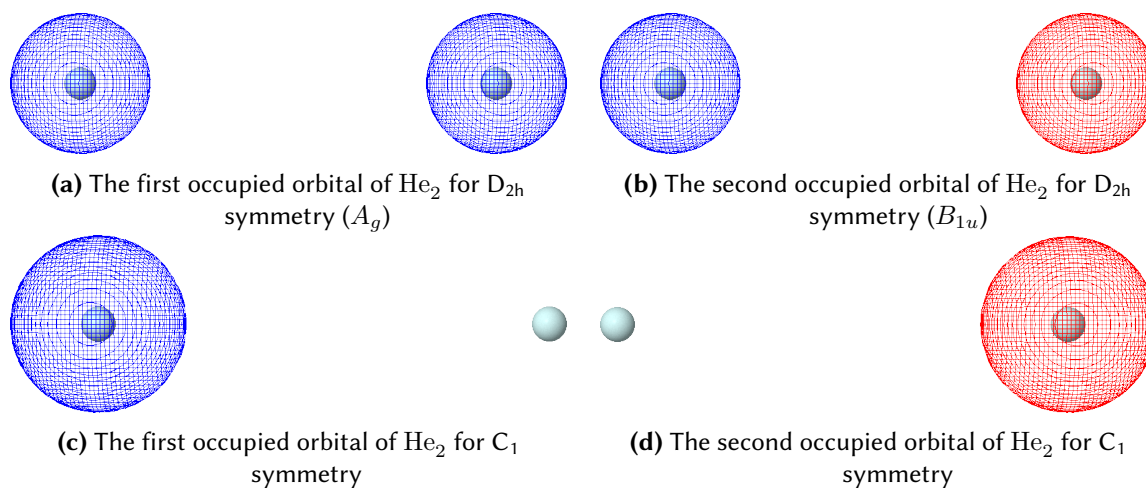


Figure 4.7: The occupied natural orbitals of He_2 at an interatomic distance of 10 Bohr, for both D_{2h} and C_1 symmetry. The colors indicate the relative sign.

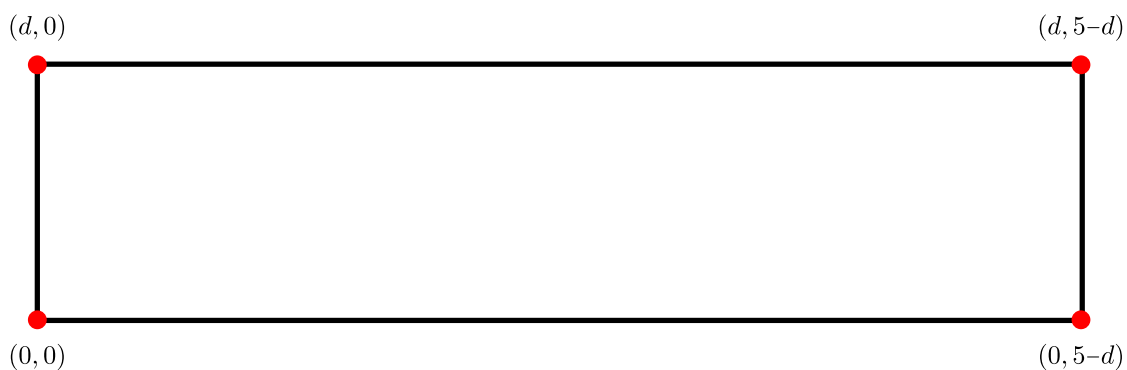


Figure 4.8: The deformation of a planar H_4 system. The parameter d is varied from 1 . . . 4 Bohr.

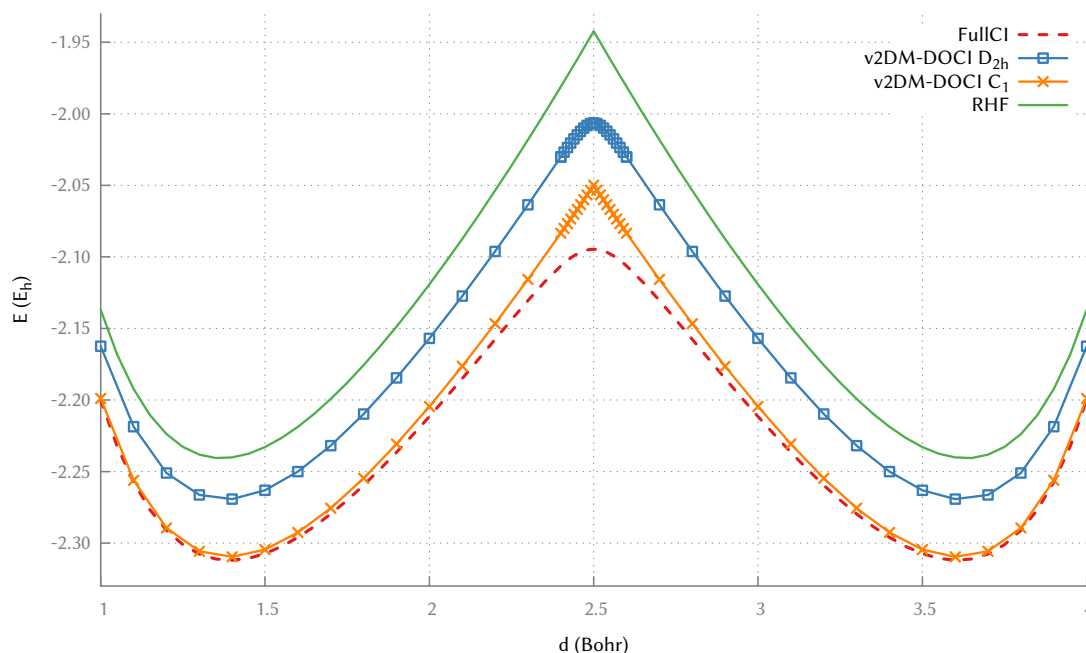


Figure 4.9: The energy of the deformation of a planar H_4 system.

the self-interaction: the unitary transformation which causes the terms V_{iiii} of two-electron integrals to be maximal. We need the symmetry-broken orbitals to find the lowest energy which is very close to the FullCI energy. Both minima are found when two hydrogen atoms are at their equilibrium distance of 1.437 Bohr: in that case, we have two almost uncoupled H_2 molecules which are 3.563 Bohr apart. When $d = 2.5$ Bohr, we have a perfect square and the system is degenerate. The RHF energy has a cusp indicating that a single Slater determinant cannot adequately describe the system. This is also the point where the largest deviation from FullCI is found for v2DM-DOCI. The C_1 curve has a cusp while the D_{2h} curve is smoother. We usually start from the HF orbital around equilibrium and use the optimal orbitals from one calculation as start point for the next calculation. This fails around the peak: the transition is very steep and it is not possible to have a smooth transition using a set of orbitals from one side to the other. Just like the RHF curve, there is a cusp in the energy at the square configuration. These results seem to indicate that the seniority-two sector plays an important role. If we also add the seniority-four sector, we find the FullCI result.

Another interesting system is the symmetric stretch of an equidistant H_8 chain. It is simple yet challenging, because of the strong correlation effects in the transition from metallic hydrogen to dissociated hydrogen. It is often used as a benchmark system for methods (e.g. AP1roG [145]) and it is one of the systems studied by Bytautas *et al.* [146]. Practically every method which claims to have a good description of strong correlation has been tested on this system or a variant of it [214–218]. In Figure 4.10 on the next page the results can be found. This system has D_{2h} symmetry, which in this context is equivalent with parity symmetry with

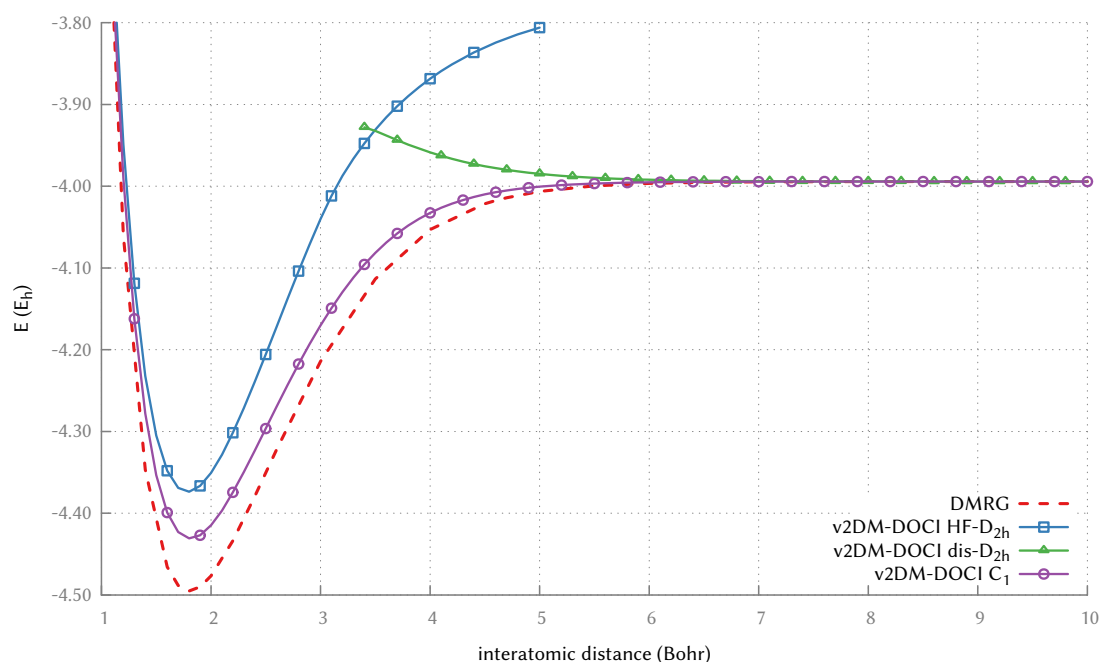


Figure 4.10: The symmetric stretch of a linear H_8 chain in the cc-pVDZ basis. Not all calculated points are marked on the curves.

respect to the middle of the chain. In the limit of dissociated hydrogen, the v2DM-DOCI results coincide with the DMRG results. However, in the transition from metallic hydrogen to dissociated hydrogen, something interesting happens: the symmetry-adapted optimization does not produce a smooth curve between both regimes. The blue curve is the result when starting from the HF orbitals at the equilibrium distance, and then using the optimal set of orbitals as a starting point for the next distance. On the other hand, the green curve was found by a random search at an interatomic distance of 10 Bohr. The symmetry prevents the smooth transition between the orbitals. The energy when starting from the HF orbitals even gives a much higher energy when going to the non-interacting region. Furthermore, the symmetry-adapted orbitals do not find the lowest energy at the equilibrium distance. We tried a random search at this point but no lower energy was found. The picture changes when we use the symmetry-broken orbitals. As a starting point we used the ER localized orbitals. v2DM-DOCI now gives a physically correct picture of the system. Similar results were found by Bytautas *et al.* [146]. They investigated whether the result might be due to an avoided-crossing or a two-state crossing between the ground state and an excited state, but found nothing. In Figure 4.11 on the following page, we have plotted the first excited DOCI state using the optimal set of orbitals found by v2DM-DOCI. This has been calculated using the FullDOCI program. It is clear that the ground state and the first excited state are separated, and no crossings are present.

To better understand what is happening, we have plotted the occupation numbers for both

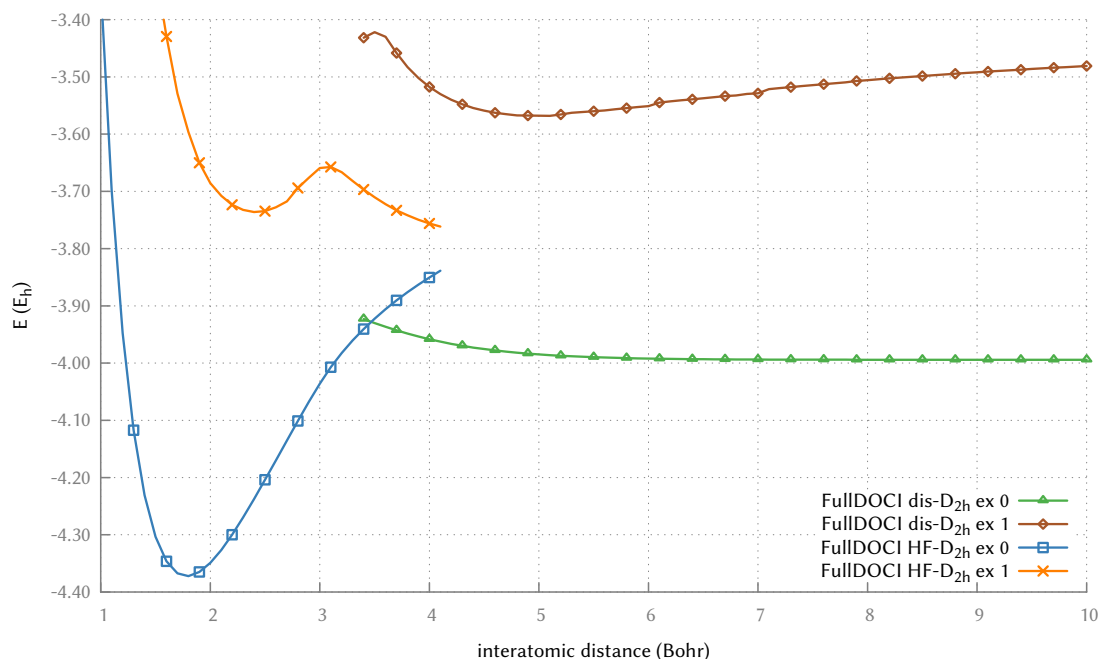
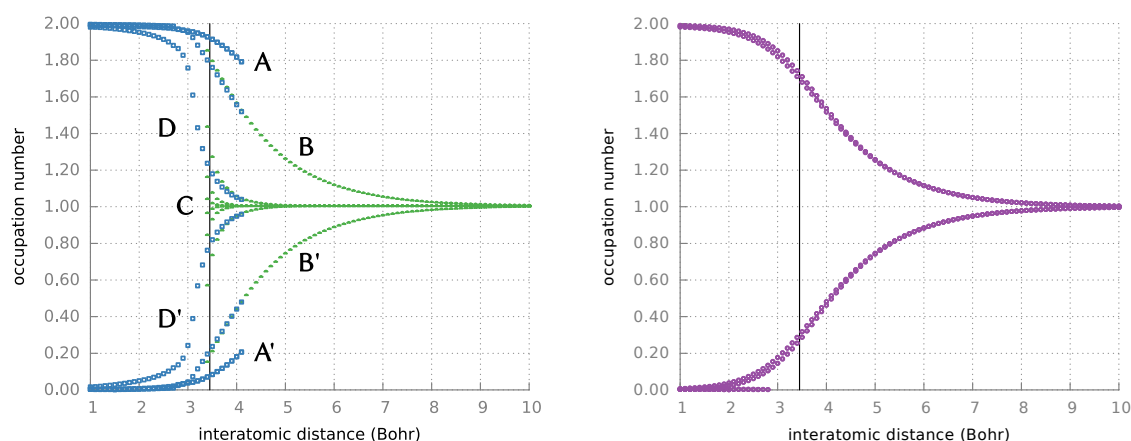


Figure 4.11: The DOCI ground state and the first excited DOCI state of the linear H_8 chain.

symmetries in Figure 4.12 on the next page. The colors of the curves match those in Figure 4.10. In Figure 4.12b on the facing page for the C_1 symmetry, we find the picture we expect: doubly-occupied orbitals which split into single-occupied hydrogen in the dissociation limit. However, in the D_{2h} case (Figure 4.12a), there is an unphysical branch of single-occupied orbitals. There are also orphan branches: they have no connection from the dissociated regime to the metallic regime (and vice versa). Let us examine the situation where all three curves are active: in Figure 4.13 on page 98 we have plotted the occupied natural orbitals of the H_8 chain with an interatomic distance of 4 Bohr for the different curves. In the case of symmetry-broken orbitals we see a familiar picture: the highest-occupied orbitals are the bonding combination of the $1s$ orbitals of two adjacent hydrogen atoms. As we are already near the dissociation, the antibonding orbitals also have a non-negligible occupation. This is in essence what can also be seen in fig. 4.12b: as the interatomic distance increases, the occupation of the bonding orbital decreases and the occupation of the antibonding orbital is increases, until they are degenerate. In the symmetry-adapted calculation, it is not possible to form these combinations due to the mirror plane in the middle. The only possibility to form direct bonding and antibonding orbitals is for the two hydrogen atoms in the center. Indeed, these combinations are present in both fig. 4.13a and fig. 4.13b and the occupations match those in fig. 4.13c. These orbitals are responsible for the curve marked with B and B' in Figure 4.12a: it is possible to have a smooth transition for these from one regime to the other. If we look at the highest occupied orbitals in fig. 4.13a, we see that these correspond to two bonding hydrogen atoms on each side of the chain. The corresponding lower branch in fig. 4.12a (marked with A'), has the antibonding combination on the same hydrogens. In the dissociated solution Figure 4.13b, the orbitals



(a) The natural occupation numbers of the H_8 chain in D_{2h} symmetry. The different curves are labeled to easily identify them in the text. (b) The natural occupation numbers of the H_8 chain in C_1 symmetry.

Figure 4.12: The natural occupied numbers of the H_8 chain. The black line indicates the crossing of the two D_{2h} curves in Figure 4.10. Only points with an occupation $> 10^{-3}$ are shown. The colors match those in Figure 4.10.

are localized and a bonding/antibonding combination does not happen due to symmetry. It consists of all combinations of two localized hydrogen orbitals that are allowed due to the mirror symmetry. The combination of outermost hydrogen atoms leads to the unphysical branch (marked with C) in fig. 4.12a, with no corresponding branch in the other regime. The connecting branch between the two regimes which starts from occupation 1 (marked with D and D') is caused by the set of orbitals present in both fig. 4.13a and fig. 4.13b: the bonding and antibonding combination of atoms three and six. This all shows how the D_{2h} symmetry prevents the orbitals from reaching the lowest energy state shown in fig. 4.13c. We can now also better understand the energy curves in fig. 4.10. With a larger interatomic distance, the localized orbitals are the most accurate description of the chain and therefore, they have the lowest energy. However, as the interatomic distance decreases, the orbitals want to delocalize, and the symmetry constraints make this hard to do. In fact, we know that this delocalized description must lie in a different valley in the DOCI landscape, as the orbital optimizer cannot reach it. From the other side, the HF orbitals are delocalized and provide a better starting point for small interatomic distances. In the same way as before, if we increase the interatomic distance, the symmetry prevents the orbitals from delocalizing and therefore the energy keeps on rising. This system is not stable: a Peierls transition [219] will break the symmetry and there will be two alternative distances between the atoms. The system will break down into four separate H_2 molecules.

This example shows the Achilles heel of our orbital optimizer: it cannot jump to a different valley in the DOCI landscape. Given a suitable starting point it will duly find the minimum in the corresponding valley, but one never be sure.

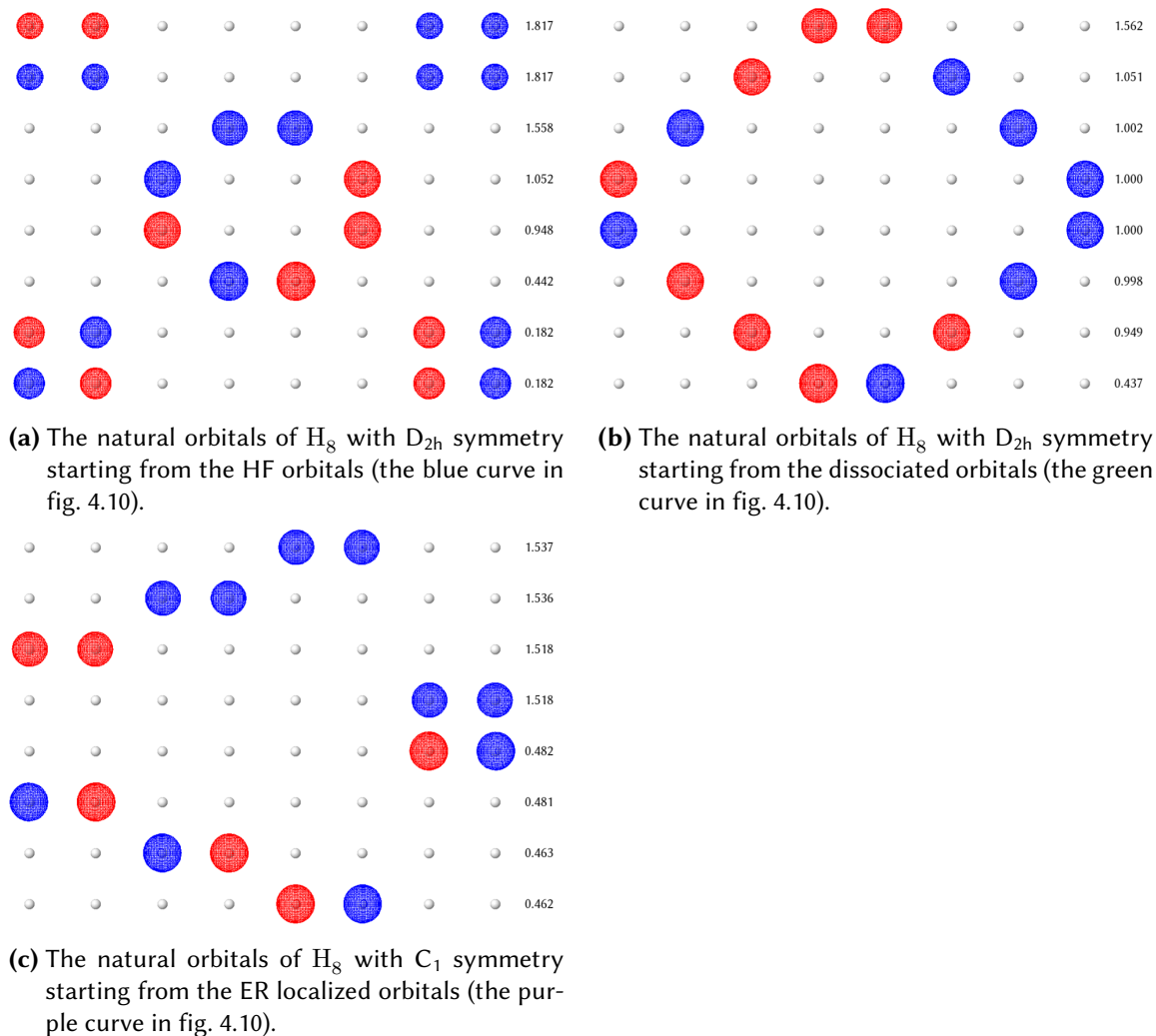


Figure 4.13: The occupied natural orbitals of the H_8 chain at an interatomic distance of 4 Bohr for the different v2DM-DOCI calculations. The occupation numbers are shown on the right of the orbitals. All symmetry-adapted orbitals transform according to either A_g or B_{1u} , depending on whether the orbital changes sign under a mirror operation.

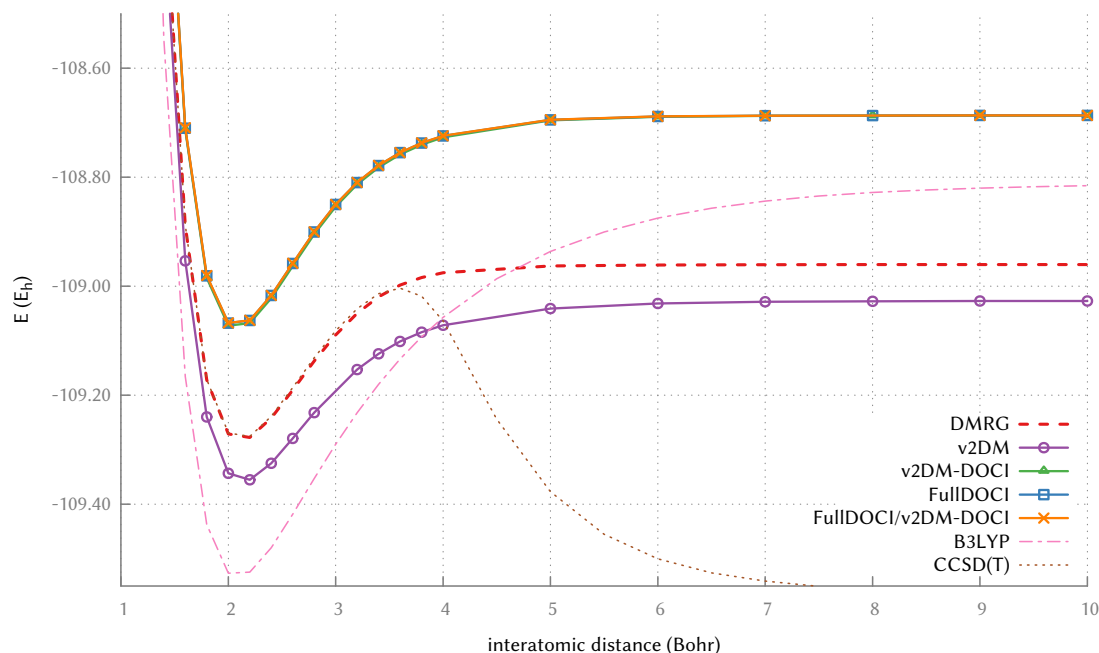


Figure 4.14: The dissociation of N_2 in the cc-pVDZ basis. The DOCI curves shown are for the C_1 symmetry. Note that three curves (v2DM-DOCI, FullDOCI, FullDOCI/v2DM-DOCI) coincide visually.

4.3.2 Molecular systems

Another interesting application is the dissociation of a diatomic molecule in which static correlation is of paramount importance at dissociation. First we must introduce some additional nomenclature for the results: v2DM-DOCI refers to v2DM with the DOCI constraints on the 2DM and with the Jacobi orbital optimization. FullDOCI uses the same orbital optimization algorithm. v2DM-DOCI/FullDOCI is a single-shot v2DM-DOCI calculation using the optimal set of orbitals from a FullDOCI calculation. FullDOCI/v2DM-DOCI is exactly the opposite: a single-shot FullDOCI calculation using the optimal set of orbitals from v2DM-DOCI.

The first system we study is the dissociation of N_2 . This is a challenging system due to the breaking of a triple bond and is often used as a test case [146, 212, 220–222]. In the cc-pVDZ basis, N_2 has 28 orbitals. The results can be seen in Figure 4.14. In order to appreciate the performance of v2DM-DOCI, results of other methods such as CCSD(T)[53] and DFT with B3LYP functional[223, 224] are also presented. All DOCI curves give a qualitatively correct description of the dissociation process. In Table 4.3 on the next page we show the exact values of some selected data points. Unlike the previous examples, symmetry breaking does not significantly alter the energy: the symmetry-broken energy is always lower than the symmetry-adapted value but the difference is in the ≤ 10 milliHartree region. More interesting to see is that the energy difference between v2DM-DOCI and FullDOCI is very

d	Sym.	DMRG	$\Delta v2DM$	$\Delta v2DM-DOCI$	$\Delta FullDOCI$
2.2	D _{2h}	-109.278	-77.375	222.578	224.455
2.2	C ₁	-109.278	-77.375	209.891	214.787
4.0	D _{2h}	-108.975	-96.213	257.013	258.842
4.0	C ₁	-108.975	-96.213	248.396	250.991
10.0	D _{2h}	-108.960	-66.384	282.966	283.108
10.0	C ₁	-108.960	-66.384	273.371	273.464

Table 4.3: Some points on the N_2 curve from Figure 4.14. The interatomic distance (d) is in Bohr. The DMRG energy is in Hartree. For v2DM, v2DM-DOCI and FullDOCI, the deviation from DMRG is given in milliHartree.

d	Sym.	DMRG	$\Delta v2DM$	$\Delta v2DM-DOCI$	$\Delta FullDOCI$
2.2	C _{2v}	-92.596	-70.208	186.967	192.202
2.2	C ₁	-92.596	-70.208	186.967	192.192
4.0	C _{2v}	-92.324	-101.281	219.639	228.307
4.0	C ₁	-92.324	-101.281	219.639	228.300
10.0	C _{2v}	-92.246	-116.686	218.333	253.131
10.0	C ₁	-92.246	-116.686	218.333	253.130
20.0	C _{2v}	-92.246	-127.996	209.275	253.135
20.0	C ₁	-92.246	-127.996	209.275	253.133

Table 4.4: Some points on the CN^- curve from Figure 4.15. The interatomic distance (d) is in Bohr. The DMRG energy is in Hartree. For v2DM, v2DM-DOCI and FullDOCI, the deviation from DMRG is given in milliHartree.

small. It seems that v2DM-DOCI is a better approximation to FullDOCI than v2DM is to FullCI: the difference is 2-3 milliHartree while v2DM usually deviates from FullCI in the dozens of milliHartree. The CCSD(T) curve fails completely in the dissociation limit. This is a known failure and it can be fixed within Coupled Cluster (CC) theory [212]. Note that N_2 dissociates into two N atoms with an odd number of electrons. This forms no problem for DOCI as the orbital optimization can handle this[152]. The difference between the DOCI curves and the DMRG reference is due to dynamical correlations and can be added in a subsequent stage, as shown in reference 225.

Another interesting case is cyanide, CN^- . This heteronuclear molecule also has a triple bond and dissociates in C^- and N. The effect of breaking the C_{2v} symmetry is again minimal (see results in Table 4.4), so in Figure 4.15 we restrict ourselves to the C_1 curve. For this heteronuclear molecule, the dissociation limit for v2DM and v2DM-DOCI is incorrect. This is a known failure for v2DM-based techniques [31]: the energy of the isolated atoms as a function of fractional charge is a convex curve in v2DM whereas it should be a piecewise linear curve [226, 227]. We have plotted the energy as a function of the charge in Figure 4.16 on page 102 for the NO^+

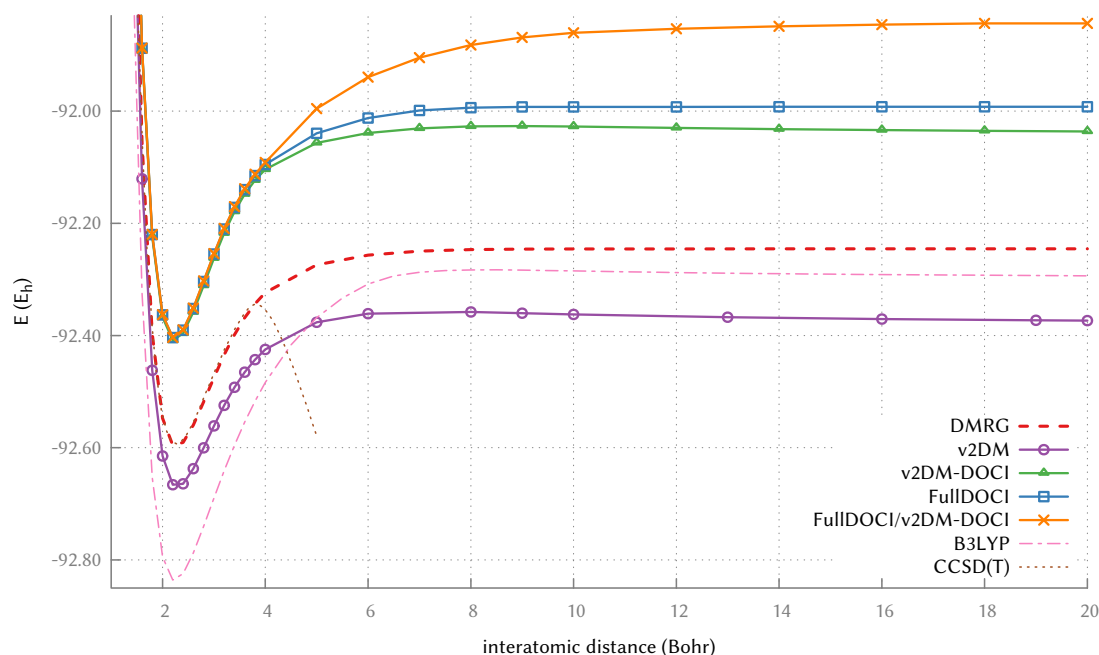


Figure 4.15: The dissociation of CN^- in the cc-pVDZ basis. The DOCI curves shown are for the C_1 symmetry.

molecule: the problem of the convexity can be clearly seen. It will lead to a too low energy. It is the same problem from which DFT suffers [228] and is more commonly referred to as the delocalization error. In DFT the approximate functionals also favour a fractional distribution of the electrons. It can explain the underestimation of the band-gap in DFT calculations [228]. For the same reason, v2DM will favour fractional charges on dissociated atoms and thus give a physically incorrect picture. This can be seen clearly on the FullDOCI/v2DM-DOCI curve: if we use the optimal basis of v2DM-DOCI calculation, the FullDOCI energy is much higher than the true FullDOCI energy, as the FullDOCI solution is far from optimal with the artificial non-integer atomic charges from v2DM-DOCI. The problem can be confirmed through a population analysis. We will perform a Mulliken population analysis [229] at an interatomic distance of 20 Bohr. In this case, the overlap between orbitals centered on the carbon and the oxygen will be negligible. The diagonal elements of 1DM can then be distributed as belonging to either the carbon or oxygen atom. The sum will be the total particle number. When we do this, we find that the net charges are $\text{C}^{-0.43}\text{N}^{-0.57}$ for the v2DM-DOCI calculation. At the same distance, DFT with B3LYP produces $\text{C}^{-0.42}\text{N}^{-0.58}$ while v2DM finds $\text{C}^{-0.60}\text{N}^{-0.40}$. The physical correct dissociation would be $\text{C}^{-1.0}\text{N}^{0.0}$.

Using so-called subsystem constraints [30, 91] (see Section 2.3.4 on page 27), one can force the E vs N curve to be piecewise linear. However, this would require a v2DM(-DOCI) optimization at each nearby integer value of N . This makes it a costly solution with the additional downside that although it fixes the energy in the dissociation limit, the transition to this limit remains

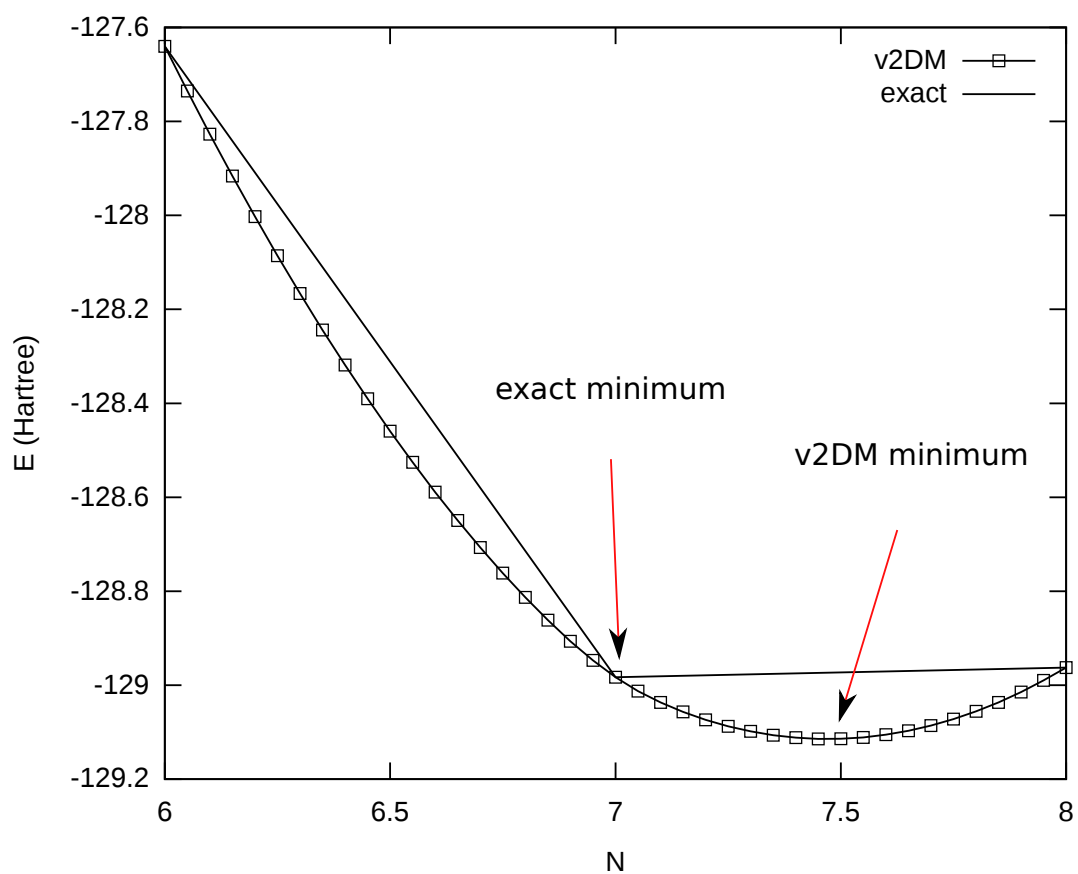


Figure 4.16: The energy as a function of number of electrons on the oxygen atom for the NO^+ molecule. Reproduced from Reference 90 with permission of B. Verstichel.

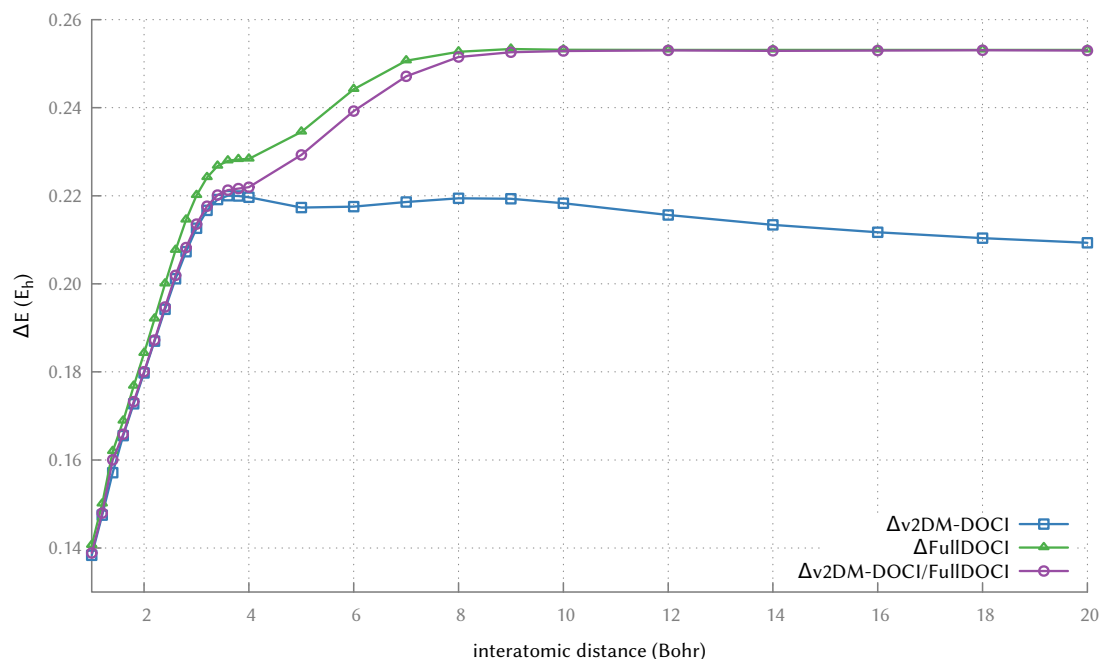


Figure 4.17: The dissociation of CN^- in the cc-pVDZ basis: comparing the v2DM-DOCI/FullDOCI results with v2DM-DOCI and FullDOCI. The deviation from DMRG is plotted.

unphysical: at the point when the subsystem constraints become active the energy curve is 'pulled' towards the correct limit (examples can be found in reference 90). However, there might be another solution. In Figure 4.17, we have used the FullDOCI optimal orbitals for the v2DM-DOCI calculation. In this case, v2DM-DOCI gives the correct DOCI dissociation limit. This suggests that it might be possible to find specific DOCI constraints to solve the problem of fractional charges in v2DM-DOCI.

In Figure 4.19 on page 105, we have plotted the occupied natural orbitals of both v2DM-DOCI and FullDOCI. Unfortunately, this does not learn us much. While in the FullDOCI case all orbitals have an occupation of either approximately two or one, the valence orbitals of v2DM-DOCI do not. For the core s orbitals, there is no difference. For the p orbitals, an electron is spread out over several orbitals, leading to fractional charges. We also examined the eigenvalues of the 2DM. These present the occupation numbers of the natural geminals. If we look at the eigenvalues of the 2DM from the FullDOCI calculation at an interatomic distance of 20 Bohr, there is a clear structure. The eigenvalues are separated in 4 groups: $[0.995, 1.001]$, $[0.491, 0.508]$, $[0.246, 0.254]$ and $[0, 0.001]$. The number of eigenvalues in each group is 13, 24, 12 and 356. This is not the case in the 2DM from v2DM-DOCI: the eigenvalues are spread over the entire $[0, 1.1]$ range. We have plotted these in Figure 4.18 on the next page, in order to indicate what goes wrong. Figure 4.17 seems to suggest that the problem can be solved without constraints on the 2DM but purely in the orbital optimization: given a suitable set of

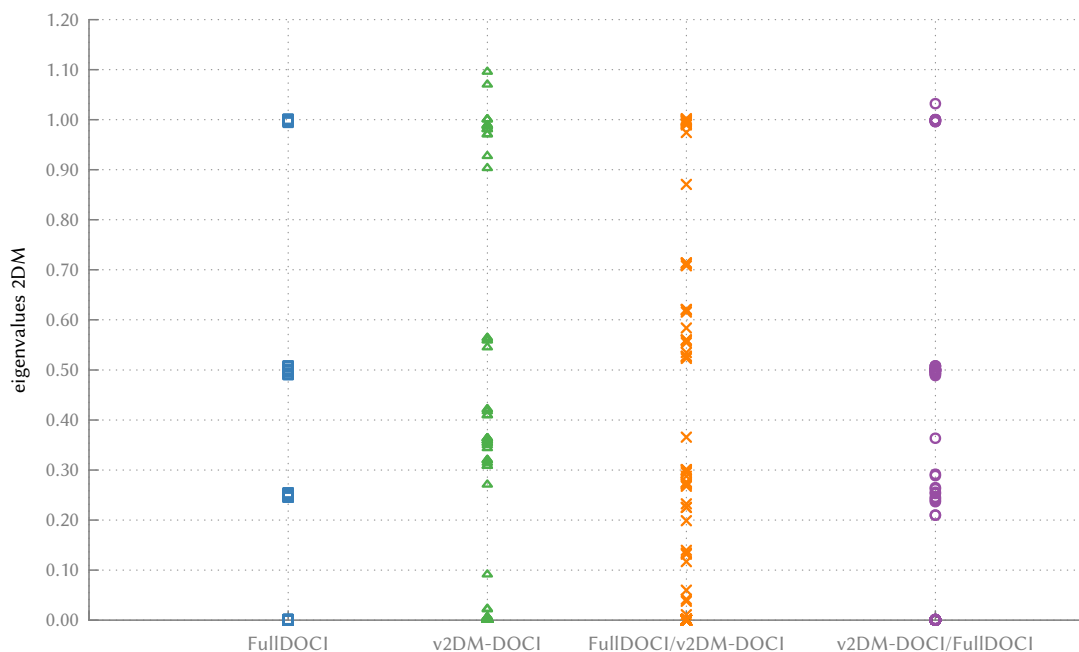
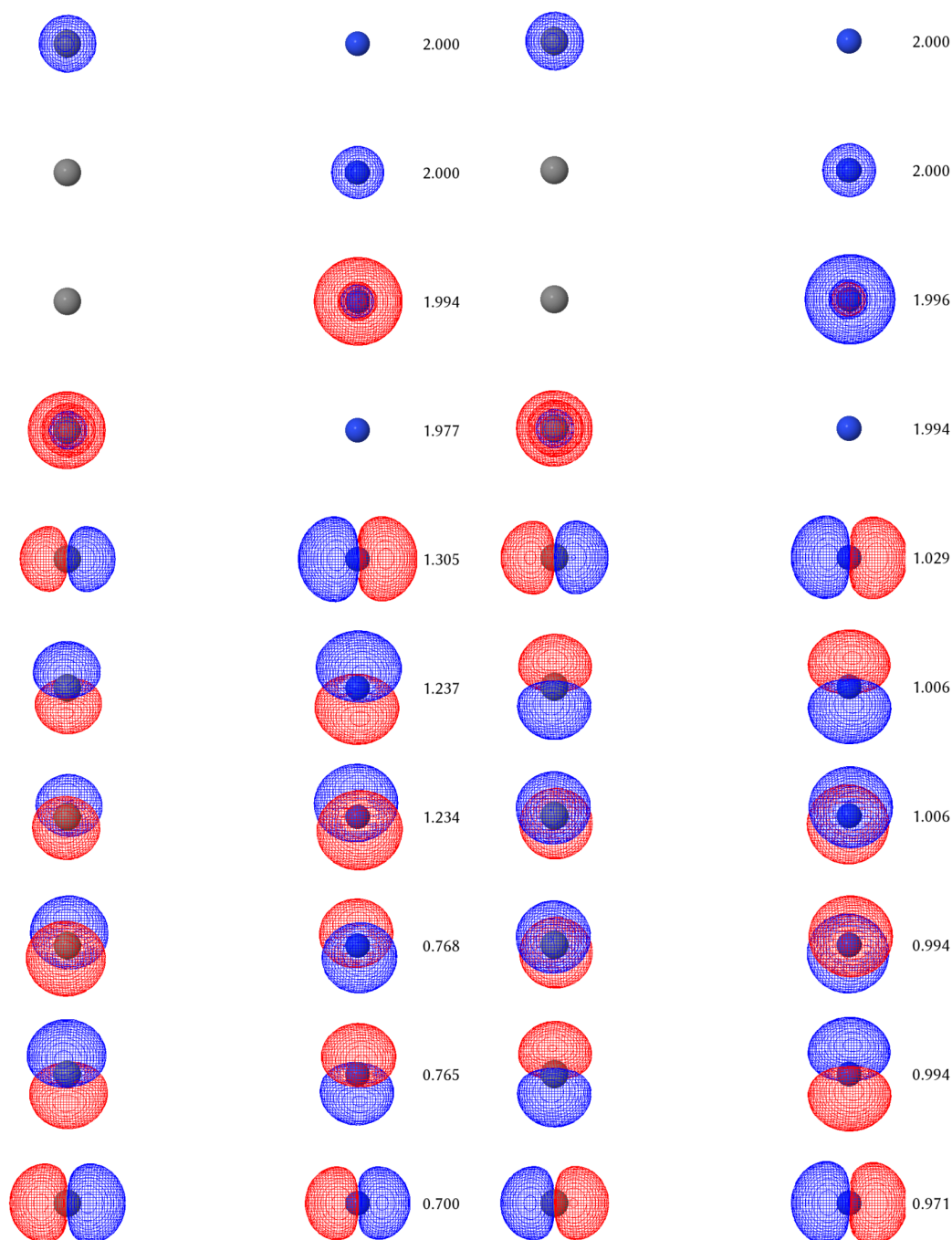


Figure 4.18: The eigenvalues of all the calculated 2DM's for CN^- with an interatomic distance of 20 Bohr.

orbitals, v2DM-DOCI does not necessarily use fractional charges. Although the picture of the eigenvalues of the 2DM in Figure 4.18 may suggest otherwise, there are no fractional charges found in the resulting 2DM for the v2DM-DOCI/FullDOCI optimization. Unfortunately, we have not yet found the necessary constraint on the orbital optimization.

We did a calculation for the NO^+ molecule but the same problem occurs here. In Figure 4.20 on page 106 the energy curves are shown while Table 4.5 on page 106 has the exact value of several selected data points. If we repeat the Mulliken analysis at an interatomic distance of 20 Bohr, we find $\text{N}^{0.45}\text{O}^{0.55}$ for v2DM-DOCI, $\text{N}^{0.67}\text{O}^{0.33}$ for DFT with B3LYP and $\text{N}^{0.47}\text{O}^{0.53}$ for v2DM. The physical correct dissociation would be $\text{N}^{0.0}\text{O}^{1.0}$.

The last system we examined is another member of the isoelectronic series: CO. The results of the calculations can be found in Figure 4.21 on page 107 and Table 4.6 on page 107. Unlike the previous two cases, fractional charges do not seem to be an issue here. A Mulliken population analysis finds $\text{C}^{0.003}\text{O}^{-0.003}$ for the v2DM-DOCI calculation at an interatomic distance of 10 Bohr. However, the ground state of the oxygen atom is a triplet ($S = 1$) state while the carbon atom is a singlet. This means that the total spin of the wave function of the dissociated system should be $S = 1$. The DOCI space is singlet by nature, which means that our resulting solution will have the wrong total spin. Despite this, the results are in agreement with the previous results. We find a energy deviation from FullCI in the range of 200 milliHartree. Although we enforce the singlet constraints (see Section 2.4.1), the v2DM optimization still has the necessary freedom to enter the triplet domain. The singlet constraints are only necessary



(a) The natural orbitals of CN^- calculated by v2DM-DOCI.

(b) The natural orbitals of CN^- calculated by FullDOCI.

Figure 4.19: The occupied natural orbitals of the CN^- with C_1 symmetry at an interatomic distance of 10 Bohr for v2DM-DOCI and FullDOCI. The occupation number is shown on the right of the orbitals.

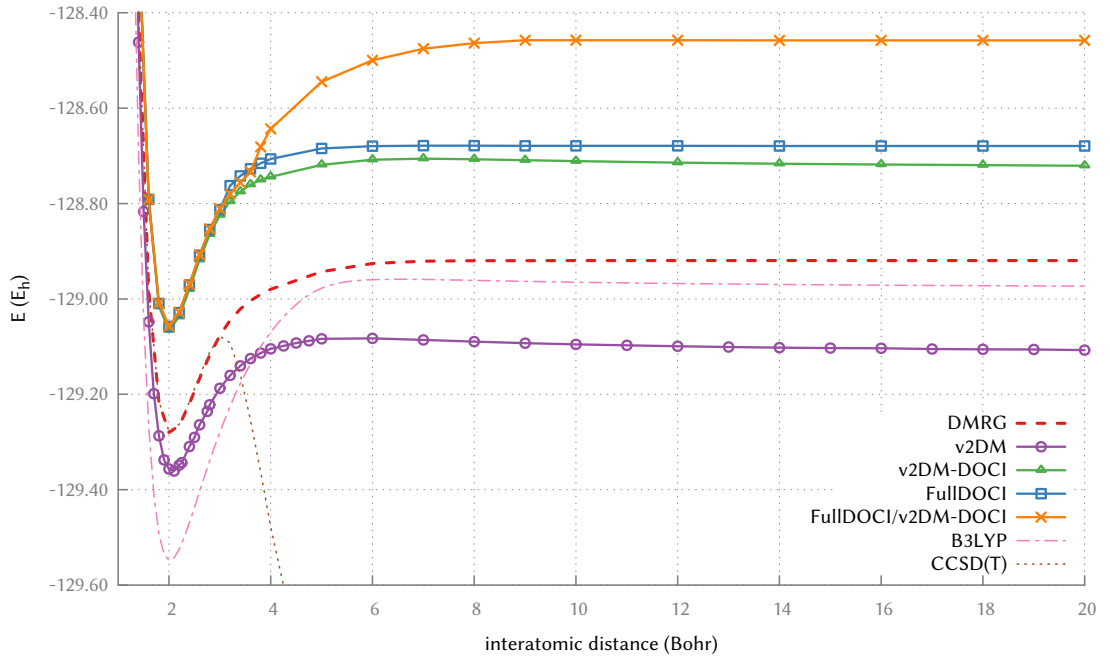


Figure 4.20: The dissociation of NO^+ in the cc-pVDZ basis. The DOCI curves shown are for the C_1 symmetry.

d	Sym.	DMRG	$\Delta v2DM$	$\Delta v2DM\text{-DOCI}$	$\Delta \text{FullDOCI}$
2.2	C_{2v}	-129.266	-82.860	228.039	236.820
2.2	C_1	-129.266	-82.860	228.082	236.934
4.0	C_{2v}	-128.980	-124.913	235.704	424.907
4.0	C_1	-128.980	-124.913	235.708	273.176
10.0	C_{2v}	-128.920	-175.533	208.614	340.015
10.0	C_1	-128.920	-175.533	208.652	240.620
20.0	C_{2v}	-128.920	-187.722	199.268	344.949
20.0	C_1	-128.920	-187.722	198.773	357.722

Table 4.5: Some points on the NO^+ curve from Figure 4.20. The interatomic distance (d) is in Bohr. The DMRG energy is in Hartree. For v2DM, v2DM-DOCI and FullDOCI, the deviation from DMRG is given in milliHartree.

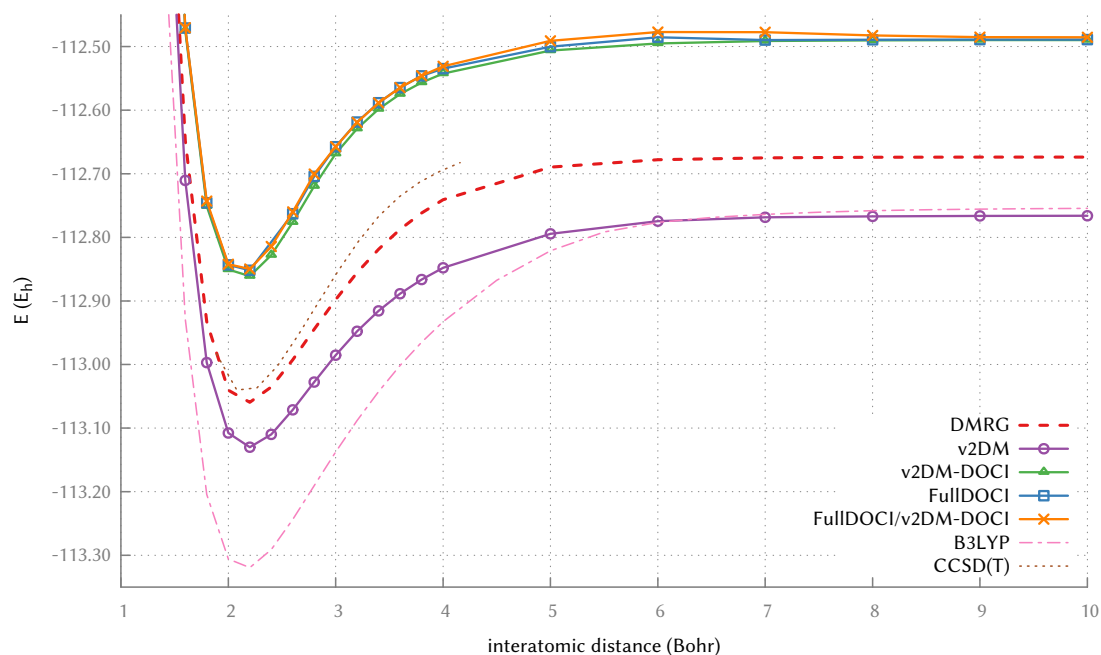


Figure 4.21: The dissociation of CO in the cc-pVDZ basis. The DOCI curves shown are for the C_1 symmetry.

d	Sym.	DMRG	$\Delta v2DM$	$\Delta v2DM-DOCI$	$\Delta FullDOCI$
2.2	C_{2v}	-113.059	-70.607	198.729	207.680
2.2	C_1	-113.059	-70.607	198.416	207.680
4.0	C_{2v}	-112.741	-107.071	201.542	208.968
4.0	C_1	-112.741	-107.071	198.536	206.093
10.0	C_{2v}	-112.673	-92.418	187.388	187.871
10.0	C_1	-112.673	-92.418	183.954	184.604
19.0	C_{2v}	-112.674	-91.970	187.348	188.261
19.0	C_1	-112.674	-91.970	187.262	187.789

Table 4.6: Some points on the CO curve from Figure 4.21. The interatomic distance (d) is in Bohr. The DMRG energy is in Hartree. For v2DM, v2DM-DOCI and FullDOCI, the deviation from DMRG is given in milliHartree.

conditions and not sufficient for the singlet state. But looking at the results, v2DM-DOCI does not use this freedom as FullDOCI produces an energy very close to it.

4.3.3 The Hubbard model

The Fermi-Hubbard model [230] is a model that possesses some of the non-trivial correlations present in a solid. Originally it was formulated as a simple model to study the correlations of d -electrons in transition metals. Since then it has been the subject of intensive research. It is believed that the two-dimensional version holds the key to understanding high temperature superconductivity [231]. It is also an excellent model to study the effects of strong correlation and this is why we will examine the DOCI results of a one-dimensional Hubbard model. The Hamiltonian is given by

$$\hat{H} = -t \sum_{a\sigma_a} \left(\hat{a}_{a\sigma_a}^\dagger \hat{a}_{a-1\sigma_a} + \hat{a}_{a+1\sigma_a}^\dagger \hat{a}_{a\sigma_a} \right) + U \sum_a \hat{n}_{a\uparrow} \hat{n}_{a\downarrow}, \quad (4.29)$$

where the ratio $\frac{U}{t}$ is the only degree of freedom and $\hat{n}_{a\uparrow}$ is the number operator. We assume periodic boundary conditions on the chain.

The Hamiltonian has two competing terms: the first term, called the hopping term favours delocalization of the electrons while the second term, called the on-site repulsion, favours localization. In the site basis the second term is diagonal while in the pseudo-momentum basis the first term is diagonal. It is very interesting how such a simple model can give rise to such complex physics.

The one-dimensional model at half filling (one electron per site) has a known solution given by the Lieb-Wu equations [232–234]. We examine a chain of 22 sites as we increase the on-site interaction strength with a fixed $t = 1$. In Figure 4.22 on the facing page the result is plotted. As the starting point for the orbital optimizer the pseudo-momentum basis was used as this is already a mixture of all sites. At $U = 0$ the exact wave function is given by a single Slater determinant and both v2DM-DOCI and RHF produce the correct energy. At intermediate interaction strength, the deviation from FullCI is the largest. In the limit $U \rightarrow \infty$ the Hubbard model is reduced to a Heisenberg antiferromagnet [235]: every electron is frozen at a site and not a single site will be doubly occupied. Despite this, v2DM-DOCI gives a reasonable approximation to the energy. This result demonstrates the power of orbital optimization.

Notice that over the entire range, the deviation from FullCI for both v2DM and v2DM-DOCI is roughly equal.

We tried a 50 sites Hubbard model but hit a wall with the orbital optimizer. The Hilbert space becomes so large that the number of Jacobi rotations required to find the optimal orbitals becomes unmanageable. In this case, a full Hessian approach would be more beneficial, despite the associated expensive two-body integral transformation.

We end this chapter with the remark that v2DM-DOCI indeed seems like a very good approximation to FullDOCI, when using the same set of orbitals. The major difficulty is finding the optimal set of orbitals: the choice of the starting point is crucial.

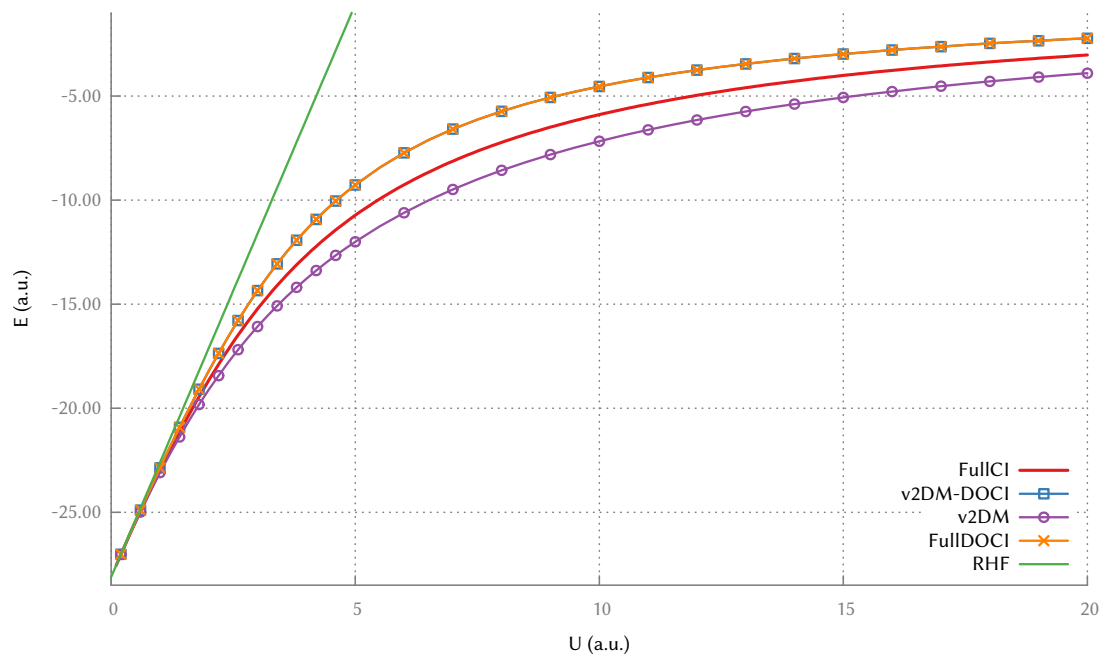


Figure 4.22: The results of a one-dimensional Fermi-Hubbard model with 22 sites. The energy is plotted for increasing interaction strength.

Chapter 5

Conclusions

The true delight is in the finding out rather than in the knowing.

Isaac Asimov

In this work we have introduced the Variational Optimization of the second-order reduced Density Matrix to solve the many-body problem. The second-order reduced Density Matrix (2DM) contains all necessary information to describe such a system, and the expectation value of one- or two-particle operators can be expressed as a linear function of the 2DM. Unlike the more conventional quantum mechanical methods, the wave function is never used. This method itself has a long history and attracted quite some attention in the second half of the previous century. At first glance, it has many interesting properties: the 2DM has a much better scaling than the wave function, and the method is strictly variational. Unlike wavefunction-based methods, it produces a strict lower bound on the energy (instead of an upper bound). Unfortunately, the complexity of the many-body problem has not disappeared, but is shifted to the N -representability problem: what are the necessary and sufficient conditions for a 2DM to be derivable from an ensemble of many-fermion wave functions? In the 1960's, there was still hope that this problem could be solved in some way, but time has learned that it is a very hard problem (see later).

A major breakthrough came when it was realized that the v2DM problem could be formulated as a Semidefinite Programming problem. This opened a whole new toolbox of methods to perform the optimization. It resparked interest, leading to numerous extensions and improvements to the method. However, the difficulty of the N -representability problem reared its ugly head again, and interest in the method is fading. The technique has been called a dead end several times. One of the goals of this work is to show the flexibility of the method: by using a subclass of N -representability conditions, we can increase the performance of the method considerably while still finding a good approximation to the energy. We hope that after reading this work, the reader will agree that there are still interesting paths left to discover. We will first iterate over the contents of the chapters in this work, to end with a general conclusion and outlook.

In Chapter 2 we formally introduced the N -representability problem. A theorem about the necessary and sufficient conditions for N -representability was shown and proven. Unfortunately, this theorem does not give us a practical way to enforce N -representability. We introduced the formal complexity class of the N -representability problem: Quantum Merlin Arthur. This means that in general it is very hard to find a solution to the problem but once a solution has been found, it is easy to verify the correctness of the solution. This scatters all hope of finding a general solution to the N -representability problem. It may be possible to find a solution in specific instances of the problem. This does not necessarily mean that the situation is hopeless, after all Density Functional Theory belongs to the same complexity class and this has not held its practical usage back.

Next we showed how the N -representability theorem can be used to generate a set of necessary conditions. The necessary conditions on the 1DM turn out to be also sufficient. For the 2DM we derive a set of two-index and three-index conditions. Using the same formalism, we derive all three-index conditions with the 3DM as the basic object. These conditions can be simplified by exploiting the symmetry of the system. We show that by utilizing the spin freedom we can reduce the 2DM into a singlet and a (three-fold degenerate) triplet block. The spatial point-group symmetry of a system reduces the 2DM into blocks per irreducible representation. The actual gain is dependent on the specific spatial symmetry.

Until now, the only assumptions we made about the fermionic wave function was that it is normalized and antisymmetric. Now we will restrict ourself to Doubly Occupied Configuration Interaction-type wave functions: in the Configuration Interaction expansion only the Slater determinants where all orbitals are either doubly occupied or empty are used. This is a so-called seniority-zero approximation to the wave function. The structure of all density matrices is greatly simplified by this assumption. The matrix positivity of the 2DM is equivalent with the matrix positivity of an $L \times L$ block (with the L the number of spatial orbitals), combined with a set of linear inequalities. A similar reduction is possible for the 3DM. Finally we formulate the v2DM problem we want to solve using the derived N -representability conditions.

In Chapter 3 we introduce a convex optimization problem called Semidefinite Programming. Its so-called primal and dual formulation are derived, and the relationship between both is shown. We reformulate our v2DM problem as a primal SDP problem. An interior-point method is introduced to solve the problem. By adding a barrier function to the objective function, we cannot leave the feasible region and the problem is reduced to an unconstrained optimization for which we use a Newton-Raphson method. We steadily decrease the barrier until we have found the optimal solution. In every iteration a linear system of equations must be solved. We have implemented this efficiently by using a matrix-vector product of the Hessian without ever constructing the Hessian itself. As we approach the optimal point on the boundary of the feasible region, the condition number of the matrix gets worse and the number of iterations required to solve the linear system increases. This limits the usability of this method for large systems.

As a possible solution, we discuss an augmented Lagrangian technique: the boundary point method. In this method, the duality gap is always zero and we alternately project on the primal and dual feasibility until at convergence we find a point that is both primal and dual feasible.

This method was developed for large systems and it is noticeably faster than other methods, although the principal scaling is the same: L^6 for the two-index conditions and L^9 for the three-index conditions. The disadvantage of the boundary point method is that it is much less stable than the potential reduction method. While the potential reduction method can be used as a black box routine, this is certainly not the case for the boundary point method.

In Chapter 4 we motivate our interest in DOCI wave functions. The idea of using electron pairs as the basic building blocks for wave functions is old. Many types of pairing-based wave functions exist, but if the spin-pairing scheme is used, DOCI is the most general type. It can be considered as the lowest rung on the ladder in the seniority hierarchy. When seniority-two, four, etc. Slater determinants are added, the result quickly converges to FullCI. The hope is that DOCI can capture the bulk of the static correlation. Unfortunately FullDOCI still has a factorial scaling. A mean-field scaling wave function-based approximation to it was developed: AP1roG. We approximate the 2DM as being derivable from a DOCI wave function.

An important aspect of DOCI is its orbital dependence: any truncated CI wave function is orbital dependent. However, finding the optimal set of orbitals is a hard problem: it means finding the global minimum in an uncharted energy landscape. The associated transformation to the new orbitals scales as L^5 and forms the bottleneck in the entire algorithm. Our solution to this is to use Jacobi rotations. As they only mix two orbitals at a time, the integral transformation can be done very efficiently. As any orthogonal transformation can be decomposed in a series of Jacobi rotations, this presents no limitations. The usual approach for orbital optimization is to work with a second order Taylor series for the unitary transformation. Using Jacobi rotations avoids this second-order approximation.

After having derived the necessary transformation formulas and discussed the fine details of the orbital optimizer, we use our new algorithm, v2DM-DOCI, on a few test cases. The DOCI wave function is exact for a two-electron system, as is v2DM: for the H_2 molecule we find the FullCI energy, as expected. However, the dissociation of the He dimer fails. This shows the importance of spatial symmetry breaking. To find the optimal set of orbitals, DOCI needs to break the spatial symmetry of the system. When we perform the calculation using C_1 symmetry, the FullCI energy is recovered by v2DM-DOCI in the limit of full dissociation. A visualization of the natural orbitals shows that by breaking the symmetry, the orbitals on each atom of the dissociated system of two He atoms can optimize separately. The next system we try is the deformation of a H_4 rectangle. At the square configuration, the four hydrogen atoms are degenerate. This leads to a cusp in the RHF energy and the symmetry-broken v2DM-DOCI energy. The symmetry broken solution is found by starting from Edmiston-Ruedenberg localized orbitals.

As a prototype for strong correlation, we test our method on the symmetric dissociation of an H_8 chain. Again the symmetry-adapted v2DM-DOCI energy gives a wrong description of the system. There even seem to be two different regimes. However, looking at the occupation numbers and the shape of the orbitals, the differences can be fully understood. The D_{2h} symmetry of the system forbids the system to go in a state of 4 H_2 atoms.

We continue by testing v2DM-DOCI on the dissociation of N_2 , CN^- , NO^+ and CO. The results for N_2 are good: v2DM-DOCI is consistently a better approximation to FullDOCI than

v2DM to FullCI. However, in case of the CN^- and NO^+ molecule we suffer from a known failure of v2DM *i.e.* fractional charges on the dissociated atoms. As the particle vs energy curve for v2DM is convex instead of piecewise linear, we end up with a fractional electron partitioning over two dissociated atoms. A solution exists in the form of subsystem constraints, but these are expensive to add. The v2DM-DOCI calculation using the optimal set of orbitals from FullDOCI does produce the correct energy. This seems to hint that a solution to this problem can be found in the orbital optimization. The CO molecule does not suffer from this problem, and we see the same picture as in the N_2 case: v2DM-DOCI is a very good approximation to FullDOCI.

We hope that the reader is convinced that there still is a future for v2DM in the form of v2DM-DOCI. It does not suffer from the bad scaling of v2DM and it seems to be a better approximation to FullDOCI than v2DM is to FullCI. However, the story is not yet over. The orbital optimizer still has room for improvement: better starting points still need to be sought. An approximation to the Brueckner determinant might yield a good starting point. It would also be interesting to investigate other methods for finding the optimal orbitals: the basin-hopping method[236] seems interesting. It works by performing a series of local minimizations to approximate the energy landscape. However, it requires a good metric on the landscape to 'jump' to the next valley.

A practical implementation of the 3DM conditions has not yet been realized. It seems reasonable to assume that their effect will be similar to the general case: increase the energy to milliHartree accuracy. Furthermore, we did not verify the correctness of the 2DM itself: a good approximation to the energy does not necessarily produce a good approximation to the 2DM. Using the 3DM conditions will certainly improve this.

As a last step we can use perturbation theory to add the missing dynamic correlation to the energy. This should give us an good approximation to the FullCI energy.

Part II

Papers

Paper 1

Variational Two-Particle Density Matrix Calculation for the Hubbard Model Below Half Filling Using Spin-Adapted Lifting Conditions

Variational Two-Particle Density Matrix Calculation for the Hubbard Model Below Half Filling Using Spin-Adapted Lifting Conditions

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(Received 7 November 2011; published 21 May 2012)

The variational determination of the two-particle density matrix is an interesting, but not yet fully explored technique that allows us to obtain ground-state properties of a quantum many-body system without reference to an N -particle wave function. The one-dimensional fermionic Hubbard model has been studied before with this method, using standard two- and three-index conditions on the density matrix [J. R. Hammond *et al.*, *Phys. Rev. A* **73**, 062505 (2006)], while a more recent study explored so-called subsystem constraints [N. Shenvi *et al.*, *Phys. Rev. Lett.* **105**, 213003 (2010)]. These studies reported good results even with only standard two-index conditions, but have always been limited to the half-filled lattice. In this Letter, we establish the fact that the two-index approach fails for other fillings. In this case, a subset of three-index conditions is absolutely needed to describe the correct physics in the strong-repulsion limit. We show that applying lifting conditions [J. R. Hammond *et al.*, *Phys. Rev. A* **71**, 062503 (2005)] is the most economical way to achieve this, while still avoiding the computationally much heavier three-index conditions. A further extension to spin-adapted lifting conditions leads to increased accuracy in the intermediate repulsion regime. At the same time, we establish the feasibility of such studies to the more complicated phase diagram in two-dimensional Hubbard models.

DOI: 10.1103/PhysRevLett.108.213001

PACS numbers: 31.15.aq, 03.65.Aa

The main problem in many-body quantum mechanics, which comprises nuclear physics, quantum chemistry, and condensed matter physics, is the exponential increase of the dimension of Hilbert space with the number of particles. The challenge has therefore been to develop approximate methods which describe the relevant degrees of freedom in the system without an excessive computational cost, i.e., with a polynomial increase. In one of these methods, the N -particle wave function is replaced by the two-particle density matrix (2DM), and over the last decade, a lot of progress has been made in this field [1–6]. For a Hamiltonian,

$$\hat{H} = \sum_{\alpha\beta} t_{\alpha\beta} a_{\alpha}^{\dagger} a_{\beta} + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} V_{\alpha\beta;\gamma\delta} a_{\alpha}^{\dagger} a_{\beta}^{\dagger} a_{\delta} a_{\gamma}, \quad (1)$$

containing only pairwise interactions, the energy of the system can be expressed as

$$E(\Gamma) = \text{Tr} \Gamma H^{(2)} = \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \Gamma_{\alpha\beta;\gamma\delta} H_{\alpha\beta;\gamma\delta}^{(2)}, \quad (2)$$

in terms of the 2DM:

$$\Gamma_{\alpha\beta;\gamma\delta} = \langle \Psi^N | a_{\alpha}^{\dagger} a_{\beta}^{\dagger} a_{\delta} a_{\gamma} | \Psi^N \rangle, \quad (3)$$

and the reduced two-particle Hamiltonian,

$$H_{\alpha\beta;\gamma\delta}^{(2)} = \frac{1}{N-1} (\delta_{\alpha\gamma} t_{\beta\delta} - \delta_{\alpha\delta} t_{\beta\gamma} - \delta_{\beta\gamma} t_{\alpha\delta} + \delta_{\beta\delta} t_{\alpha\gamma}) + V_{\alpha\beta;\gamma\delta}. \quad (4)$$

Second-quantized notation is used where $a_{\alpha}^{\dagger}$ (a_{α}) creates (annihilates) a fermion in the single-particle state α .

In variational density-matrix optimization (V2DM), originally introduced by Löwdin, Mayer, and Coleman [7–9], one exploits this fact and uses the 2DM as a variable in a variational approach. From the resulting 2DM, all one- and two-body properties of the ground state can be extracted. This should not be implemented naively, however, as there are a number of nontrivial constraints that a 2DM has to fulfill in order to be derivable from an N -particle wave function. This is the N -representability problem [9], which was proven to belong, in general, to the QMA-complete complexity class [10]. In practical approaches, one uses a set of conditions which are necessary but not sufficient, and therefore lead to a lower bound on the ground-state energy. The most commonly used are the two-index conditions, called P (or D), Q , and G [9,11], and the computationally much heavier three-index conditions called T_1 and T_2 [12,13]. They all rely on the fact that for a manifestly positive Hamiltonian $\hat{H} = \sum_i \hat{B}_i^{\dagger} \hat{B}_i$, the expectation value of the energy has to be larger than zero. These conditions can be expressed as linear matrix maps of the 2DM that have to be positive semidefinite. Another type of constraint that has recently been developed is the subsystem or active-space constraints [14–16] in which linear conditions are imposed on only that part of the density matrix that is related to a subspace of the complete single-particle space. This allows one to increase accuracy (in the subspace) without having to use three-index conditions. Such V2DM methods have been used to study a

wide variety of many-body systems: nuclei [17], atoms and molecules [1–6], but also lattice systems [4,14,16,18,19].

The Hubbard Hamiltonian [20] is the simplest schematic Hamiltonian that models the nontrivial correlations in solids as a competition between a delocalizing hopping term and an on-site repulsion term. In one dimension this Hamiltonian reads

$$\hat{H} = -\sum_{a\sigma} (a_{a;\sigma}^\dagger a_{a+1;\sigma} + a_{a+1;\sigma}^\dagger a_{a;\sigma}) + U \sum_a a_{a\uparrow}^\dagger a_{a\uparrow} a_{a\downarrow}^\dagger a_{a\downarrow}, \quad (5)$$

where the sites on a periodic lattice are labeled a , and σ is the (up or down) spin. In previous V2DM studies of the one-dimensional Hubbard model [4,16,19], only the half-filled lattice was studied, and it was found that even the two-index conditions could accurately describe the ground-state energy. In this Letter, we show that the two-index conditions fail to describe the strong correlation limit below half filling, and that the subsystem constraints, as introduced in [15,16], cannot solve this problem. In fact, a particular type of three-index conditions are needed in this limit, and we show that by using the 2.5DM (which is the 3DM diagonal in one spatial index) as the central object, these constraints can be incorporated while keeping the basic matrix manipulations in two-particle space.

In order to demonstrate the problem, Fig. 1 shows the ground-state energy as a function of the on-site repulsion U , for 5 particles in a 6-site lattice. As one can see, the general form of the exact E vs U curve (obtained through diagonalization) is nicely described by the $PQGT$ result (i.e. two- and three-index conditions). On the other hand, the PQG result (only two-index conditions) grossly underestimates the energy when U increases. The large- U limit

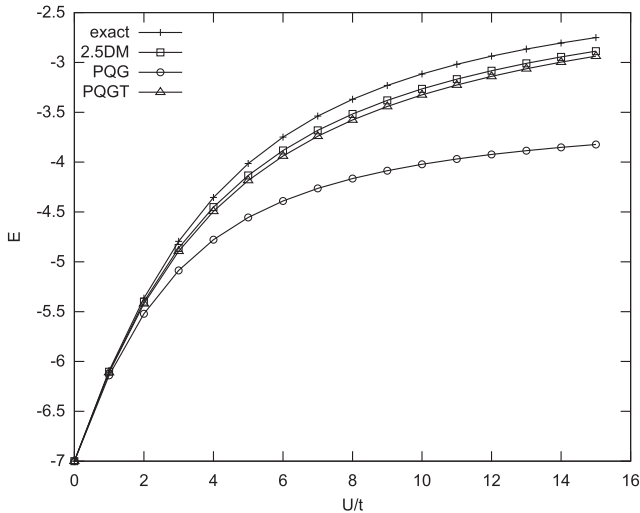


FIG. 1. Ground-state energy as a function of on-site repulsion U for 5 particles on a 6-site lattice. Exact results compared with V2DM results using PQG and $PQGT_1 T_2$, and the V2.5DM results.

is examined in Table I and one notes that PQG fails to get the energy right in this limit, as opposed to the $PQGT$ result. When inspecting the PQG -optimized 2DM in the large- U limit, it was found that the on-site repulsion term vanishes, as it should, since the 2DM elements corresponding to doubly occupied sites are zero:

$$\lim_{U \rightarrow \infty} \Gamma_{a\uparrow a\downarrow; c\uparrow d\downarrow}^{PQG} = 0. \quad (6)$$

So the problem with the two-index conditions lies in its inability to describe the hopping term on a lattice where the sites cannot be doubly occupied. It is readily understood that subsystem constraints cannot solve this issue, because the singly occupied space is a subspace of the full N -particle Hilbert space, and cannot be obtained by a restriction of single-particle space to a subsystem.

The creation and annihilation of particles on a singly occupied lattice can be described by the so-called Gutzwiller operators [21,22]:

$$g_\alpha = a_\alpha (1 - a_{\bar{\alpha}}^\dagger a_{\bar{\alpha}}), \quad (7)$$

$$g_\alpha^\dagger = (1 - a_{\bar{\alpha}}^\dagger a_{\bar{\alpha}}) a_\alpha^\dagger, \quad (8)$$

where α and $\bar{\alpha}$ are single-particle indices on the same site with opposite spin. In analogy with the necessary and sufficient conditions for N representability of the one-particle density matrix [9], one can state that all Hamiltonians expressed as first-order operators of the g_α 's will be correctly optimized if the following ‘‘Gutzwiller’’ matrix positivity conditions are satisfied:

$$\rho^G \geq 0 \quad \text{with} \quad \rho_{\alpha\beta}^G = \langle \Psi^N | g_\alpha^\dagger g_\beta | \Psi^N \rangle, \quad (9)$$

$$q^G \geq 0 \quad \text{with} \quad q_{\alpha\beta}^G = \langle \Psi^N | g_\alpha g_\beta^\dagger | \Psi^N \rangle. \quad (10)$$

These matrices can be expressed as a function of regular fermionic creation and annihilation operators,

$$\rho_{\alpha\beta}^G = \rho_{\alpha\beta} - \Gamma_{\alpha\bar{\beta};\beta\bar{\alpha}} - \Gamma_{\alpha\bar{\alpha};\beta\bar{\beta}} + \langle \Psi^N | a_\alpha^\dagger a_{\bar{\alpha}}^\dagger a_{\bar{\alpha}} a_\beta^\dagger a_{\bar{\beta}} a_\beta | \Psi^N \rangle, \quad (11)$$

$$q_{\alpha\beta}^G = \delta_{\alpha\beta} (1 - \rho_{\alpha\alpha} - \rho_{\beta\beta}) + \Gamma_{\bar{\beta}\bar{\beta};\beta\bar{\alpha}} + \Gamma_{\bar{\alpha}\bar{\alpha};\beta\bar{\beta}} + \langle \Psi^N | a_{\bar{\alpha}}^\dagger a_{\bar{\alpha}} a_\alpha a_\beta^\dagger a_{\bar{\beta}}^\dagger a_{\bar{\beta}} | \Psi^N \rangle, \quad (12)$$

TABLE I. Ground-state energy of a 6-site lattice with 5 particles for $U = 50, 100$, and 1000 , exact results compared with V2DM results using PQG and $PQGT$ results, and V2.5DM results.

U	PQG	$PQGT$	V2.5DM	Exact
50	-3.55	-2.29	-2.28	-2.20
100	-3.49	-2.15	-2.14	-2.08
1000	-3.44	-2.03	-2.01	-2.01

in which ρ is the one-particle density matrix:

$$\rho_{\alpha\beta} = \langle \Psi^N | a_{\alpha}^{\dagger} a_{\beta} | \Psi^N \rangle. \quad (13)$$

It is clear from Eqs. (11) and (12) that the 3DM plays an essential role in describing the strong correlation limit (which is why the two-index conditions fail), but one also sees that the full three-body space is not needed. In fact, the 2.5DM, defined as

$$W^l|_{ab;cd}^{S(S_{ab};S_{cd})} = \frac{1}{2S+1} \sum_{\mathcal{M}} \langle \Psi^{S\mathcal{M}} | B^{\dagger}|_{abl}^{S(S_{ab})} B|_{cdl}^{S(S_{cd})} | \Psi^{S\mathcal{M}} \rangle, \quad (14)$$

is the minimal object from which both the *PQG* conditions and the Gutzwiller conditions can be derived, and for which basic matrix manipulations are still on two-particle space. In Eq. (14), $B^{\dagger}$ creates three particles:

$$B^{\dagger}|_{abl}^{S(S_{ab})} = ([a_a^{\dagger} \otimes a_b^{\dagger}]^{S_{ab}} \otimes a_l^{\dagger})_{S_z}^S, \quad (15)$$

on lattice sites a , b , and l , coupled to total spin S , spin projection S_z , and intermediary spin S_{ab} . Note that the spin-averaged ensemble is used [5] for describing the N -particle state with total spin S . Here one considers an

equal weight ensemble of all spin projections $\mathcal{M}$, and as a result the 2.5DM has no S_z dependence. The 2.5DM is a block-diagonal object, in the sense that it is the 3DM diagonal in one pair of spatial indices. It can be used as the central object in a variational approach, applying constraints that include the *PQG* and Gutzwiller conditions. This is a generalization of an approach used by Mazziotti *et al.* [1,13] in a discussion of partial three-positivity constraints. They used a 3DM diagonal in both spatial *and* spin indices as a variational object in a study of the Lipkin spin model. Letting the spin index be off-diagonal allows us to construct a spin-coupled version of the 2.5DM, which leads to an increase in the speed of the optimization (see, e.g., [5]). Apart from this, the increased flexibility of the 2.5DM is important as it captures more correlation, which leads to a better result for the ground-state energy. We find that going from the spin-uncoupled to the spin-coupled form removes about 20% from the remaining discrepancy with the exact result, in the intermediate U/t region.

The first nontrivial constraint we impose on the 2.5DM is a consistency condition that ensures symmetry between the diagonal third index and the other indices. As an example, one of these relations reads

$$W^l|_{ab;cb}^{S(S_{ab};S_{cd})} = [S_{ab}][S_{cd}] \sum_{S_{al}S_{cl}} [S_{al}][S_{cl}] \left\{ \begin{matrix} S & \frac{1}{2} & S_{al} \\ \frac{1}{2} & \frac{1}{2} & S_{ab} \end{matrix} \right\} \left\{ \begin{matrix} S & \frac{1}{2} & S_{cl} \\ \frac{1}{2} & \frac{1}{2} & S_{cd} \end{matrix} \right\} W^b|_{al;cl}^{S(S_{al};S_{cl})}, \quad (16)$$

with $[S] = \sqrt{2S+1}$. In addition, we add constraints that are analogous to the standard two- and three-index conditions in that they can be expressed as matrix maps of the 2.5DM that have to be positive semidefinite. The first condition is simply that the different blocks of W have to be positive semidefinite:

$$W^l \geq 0. \quad (17)$$

The other five conditions are spin-adapted generalizations of the lifting conditions introduced in [1,13,23], and are of the form,

$$\mathcal{L}(W)^l \geq 0 \quad \text{with} \quad \mathcal{L}(W)^l|_{ab;cd}^{S(S_{ab};S_{cd})} = \frac{1}{2S+1} \sum_{\mathcal{M}} \langle \Psi^{S\mathcal{M}} | B^{\dagger}|_{abl}^{S(S_{ab})} B|_{cdl}^{S(S_{cd})} | \Psi^{S\mathcal{M}} \rangle, \quad (18)$$

in which the $B^{\dagger}$ consist of different combinations of creation and annihilation operators. As an example of such a condition, consider $B^{\dagger}$ defined as

$$B_{abl}^{\dagger S(S_{ab})} = (\tilde{a}_a \otimes [a_b^{\dagger} \otimes a_l^{\dagger}]_{M_{ab}}^{S_{ab}})^S \quad (19)$$

where $\tilde{a}_{am_a} = (-1)^{1/2+m_a} a_{a-m_a}$.

The various $\mathcal{L}$'s arise by considering (aaa) , $(a^{\dagger}a^{\dagger}a)$, $(aaa^{\dagger})$, $(aa^{\dagger}a^{\dagger})$, and $(a^{\dagger}aa)$ combinations, and can all be expressed as a function of W through the use of anti-commutation relations and spin recoupling.

The numerical optimization of the 2.5DM under these positivity constraints is a semidefinite program, and exactly the same methods used for the optimization of the 2DM can be used [4,24,25]. The scaling of the basic matrix

manipulations in this optimization is M^7 , as opposed to the full three-index conditions, which scale as M^9 , with M the size of single-particle Hilbert space. The result of such a V2.5DM calculation is also shown in Fig. 1. It is clear that, as anticipated, the strong interaction limit is described with *PQGT* quality without resorting to the full *PQGT* framework. In fact, the V2.5DM results are slightly better than the *PQGT*. This is because the T_1 and T_2 conditions express the positivity of an anticommutator of three-particle operators, whereas in V2.5DM positivity is imposed on all possible individual products of three-particle operators, be it of a restricted class. Similar results are obtained for a somewhat larger lattice of 10 sites, which is shown in Fig. 2. In this case, direct diagonalization is no longer an option, but we can compare it to quasi-exact

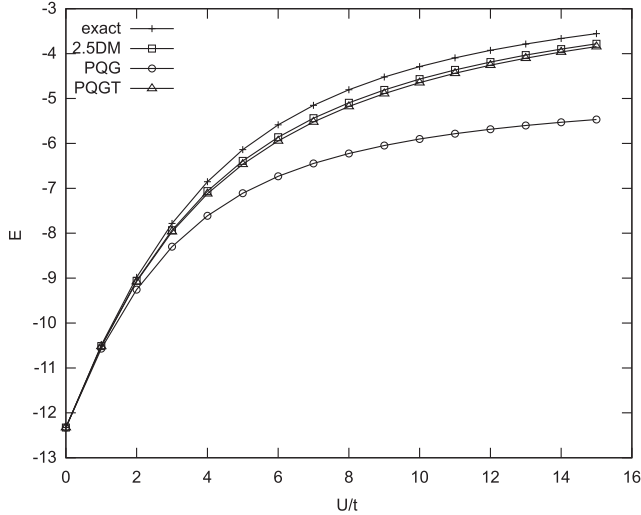


FIG. 2. Ground-state energy as a function of on-site repulsion U for 9 particles on a 10-site lattice. Exact results compared with V2.5DM results using 2.5-index conditions and V2DM results using PQG .

results calculated with a matrix product state optimization [26–28], which is uniquely suited for this kind of one-dimensional lattice problem. Again, the V2DM result using PQG conditions is inaccurate, and one has to incorporate the three-particle correlations captured in the 2.5DM approach. The full-blown $PQGT$ calculation is far more costly than V2.5DM but produces slightly inferior results. Clearly both the $U \rightarrow 0$ and strongly interacting $U \rightarrow \infty$ limit are now exact. The latter statement is demonstrated in Tables I and II and follows from the above discussion about the Gutzwiller conditions.

In summary, we developed the V2.5DM method that takes into account the necessary correlations needed to describe the large- U limit of the Hubbard model, without having to resort to full-blown three-index conditions. It must be stressed that, up to now, we have only included the spin symmetry of the model in our code. If translational symmetry, parity, and pseudospin symmetry are taken into account much larger lattices can be considered. As an example, our fully symmetric PQG version allows lattice sizes up to 100 sites, and the fully symmetric $PQGT$ program up to 20 sites. We expect a fully symmetric version of V2.5DM to be applicable to lattice sizes of

TABLE II. Ground-state energy of a 10-site lattice with 9 particles for $U = 50, 100$, and 1000 , exact results compared with V2DM results using PQG and $PQGT$ results, and V2.5DM results.

U	PQG	$PQGT$	V2.5DM	Exact
50	-4.89	-2.54	-2.53	-2.46
100	-4.77	-2.27	-2.26	-2.22
1000	-4.67	-2.03	-2.03	-2.02

about 50 sites, thereby enabling us to study two-dimensional lattices of a reasonable size.

The diagonality of the third index in the 2.5DM implies that the result will depend on the chosen single-particle basis. For the Hubbard model, it is clear that the site basis is the optimal basis to use for the diagonal third index. It will be interesting to study other systems where it is less clear what the best choice of the single-particle basis would be. An appealing application, e.g., are molecules, where one can hope to get three-index ($T_1 T_2$) precision by applying the V2.5DM method with a carefully chosen basis. In some cases (e.g., dissociation of diatomics) localized molecular orbitals should be preferential, while in other cases one may prefer the basis of natural orbitals, for which it has been shown that the full configuration interaction expansion has the fastest convergence [7]. This is a subject of further study.

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Paper 2

**Extensive v2DM study of the
one-dimensional Hubbard model for
large lattice sizes: Exploiting
translational invariance and parity**



Extensive v2DM study of the one-dimensional Hubbard model for large lattice sizes: Exploiting translational invariance and parity

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ARTICLE INFO

Article history:

Received 6 July 2012

Received in revised form 31 August 2012

Accepted 10 September 2012

Available online 21 September 2012

Keywords:

Variational method

Reduced density matrix

Strongly correlated electrons

ABSTRACT

Using variational density matrix optimization with two- and three-index conditions we study the one-dimensional Hubbard model with periodic boundary conditions at various filling factors. Special attention is directed to the full exploitation of the available symmetries, more specifically the combination of translational invariance and space-inversion parity, which allows for the study of large lattice sizes. We compare the computational scaling of three different semidefinite programming algorithms with increasing lattice size, and find the boundary point method to be the most suited for this type of problem. Several physical properties, such as the two-particle correlation functions, are extracted to check the physical content of the variationally determined density matrix. It is found that the three-index conditions are needed to correctly describe the full phase diagram of the Hubbard model. We also show that even in the case of half filling, where the ground-state energy is close to the exact value, other properties such as the spin-correlation function can be flawed.

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1. Introduction

The reduced density matrix makes its first appearance in the work of Dirac, in which the single-particle density matrix (1DM) is used in the description of Hartree–Fock theory [1]. Husimi [2] was the first to note that, for a system of identical particles interacting only in a pairwise manner, the energy can be expressed exactly as a function of the 2DM. This becomes very clear in second-quantized notation (see e.g. [3,4]), where a system of identical particles interacting pairwise is described by a general Hamiltonian:

$$\hat{H} = \sum_{\alpha\beta} t_{\alpha\beta} a_{\alpha}^{\dagger} a_{\beta} + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} V_{\alpha\beta\gamma\delta} a_{\alpha}^{\dagger} a_{\beta}^{\dagger} a_{\gamma} a_{\delta}. \quad (1)$$

The expectation value for the energy of any ensemble of N -particle wave functions $|\Psi_i^N\rangle$ with positive weights w_i , can then be expressed as a function of the 2DM alone:

$$\sum_i w_i \langle \Psi_i^N | \hat{H} | \Psi_i^N \rangle = \text{Tr} \Gamma H^{(2)} = \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \Gamma_{\alpha\beta\gamma\delta} H_{\alpha\beta\gamma\delta}^{(2)}, \quad (2)$$

in which we have introduced the 2DM:

$$\Gamma_{\alpha\beta\gamma\delta} = \sum_i w_i \langle \Psi_i^N | a_{\alpha}^{\dagger} a_{\beta}^{\dagger} a_{\gamma} a_{\delta} | \Psi_i^N \rangle, \quad \text{with} \quad \sum_i w_i = 1, \quad (3)$$

and the reduced two-particle Hamiltonian,

$$H_{\alpha\beta\gamma\delta}^{(2)} = \frac{1}{N-1} (\delta_{\alpha\gamma} t_{\beta\delta} - \delta_{\alpha\delta} t_{\beta\gamma} - \delta_{\beta\gamma} t_{\alpha\delta} + \delta_{\beta\delta} t_{\alpha\gamma}) + V_{\alpha\beta\gamma\delta}. \quad (4)$$

The idea to use the 2DM as a variable in a variational scheme was first published in literature by Löwdin in his groundbreaking article [5], but even earlier, in 1951, John Coleman tried a practical variational calculation on Lithium. To his surprise, the energy he obtained was far too low, after which he realized the variation was performed over too large a class of 2DM's [6]. Independently and unaware of the work by Löwdin and Coleman, Mayer [7] used the 2DM in a study of the electron gas. In a reply to Mayer's paper, Tredgold [8] pointed out the unphysical nature of the results, and suggested that additional conditions on the density matrix are needed to improve on them.

These results led Coleman, in his seminal review paper [9], to formulate the N -representability problem. This is the problem of finding the necessary and sufficient conditions which a reduced density matrix has to fulfill to be derivable from a statistical ensemble of physical wave functions, i.e. expressible as in Eq. (3). In this paper he also derived the necessary and sufficient conditions for ensemble N -representability of the 1DM, and some bounds on the eigenvalues of the 2DM. A big step forward was the derivation of the $\mathcal{Q}$ and $\mathcal{G}$ matrix non-negativity conditions by Garrod and Percus [10]. These were practical constraints, which allowed for a computational treatment of the problem. The first numerical calculation using these conditions on the Beryllium atom [11,12] was very encouraging, as the results were highly accurate. It turned out, however, that Beryllium, due to its simple electronic structure, is a special case

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where these conditions perform very well. A subsequent study showed that these conditions do not work well at all for nuclei [13,14]. This disappointing result, together with the computational complexity of the problem, caused activity in the field to diminish for the next 25 years. The change came with the development of a new numerical technique, called semidefinite programming, which turned out to be very suited for the determination of the 2DM under matrix non-negativity constraints. Nakata et al. [15] were the first to use a standard semidefinite programming package to calculate the ground-state energies of some atoms and molecules, and obtained quite accurate results. He was quickly followed by the extensive work of Mazziotti [16]. These results reinvigorated interest in the method, and sparked of a lot of developments. New N -representability conditions were introduced, e.g. the three-index $\mathcal{T}$ conditions, set forth by Zhao et al. [17], which led to mHartree accuracy [18–23] for molecules near equilibrium geometries.

In recent years interest in the method has been growing, as the variational determination of the 2DM results in a lower bound, which is highly complementary to the upper bound obtained in variational approaches based on a wave-function ansatz. In addition, the method is essentially non-perturbative in nature, and has a completely different structure quite unrelated to other many-body techniques. A lot of activity has been devoted to the search for new N -representability conditions, which improve the result in a computationally cheap way [24,25]. There have also been efforts to improve the semidefinite programming algorithms by adapting them to the specific problem of density matrix optimization [26–28], allowing the study larger systems.

The one-dimensional Hubbard model [29] is the simplest model possessing non-trivial correlations present in a solid. The Hamiltonian reads:

$$\hat{H} = -t \sum_{i\sigma} (a_{i,\sigma}^\dagger a_{i+1,\sigma} + a_{i+1,\sigma}^\dagger a_{i,\sigma}) + U \sum_i a_{i\uparrow}^\dagger a_{i\uparrow} a_{i\downarrow}^\dagger a_{i\downarrow}. \quad (5)$$

It pertains to a one-dimensional lattice, with sites labeled by $i = 1, \dots, L$. Periodic boundary conditions (PBCs) are assumed.

The complexity of this seemingly simple schematic Hamiltonian lies in the competition between the first term, called the hopping term, which delocalizes the electrons, and the second on-site repulsion term which is diagonal in the site basis. In Fig. 1 a graphic

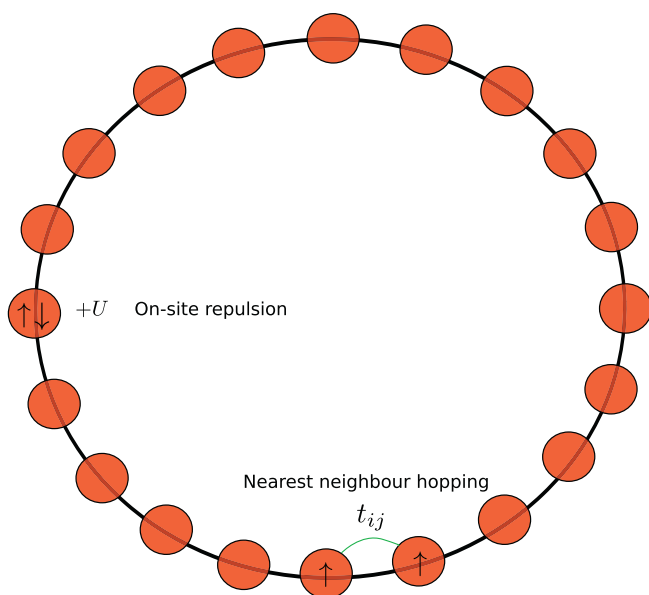


Fig. 1. Illustration of the two terms present in the Hubbard Hamiltonian, electrons can jump to nearest-neighbor sites with amplitude t_{ij} . When two electrons are on the same site, there is an energy penalty of U .

representation of the two terms in the Hubbard Hamiltonian is shown.

In this article the one-dimensional Hubbard is studied using the standard $\mathcal{IQG}$ two-index and $\mathcal{T}_{1,2}$ three-index non-negativity conditions. In the next section we discuss how the huge amount of symmetry which is present in the model can be exploited to get a significant speedup of the programs. More specifically, it is shown how translational invariance and space-inversion parity can be combined. In the subsequent section this symmetry is used to compare the computational scaling of different semidefinite programming algorithms with increasing lattice sites. In the final section we show the v2DM results using two- and three-index constraints for the one-dimensional Hubbard model on a 20- and 50-site lattice with different filling factors. We have not only computed the ground-state energy, but also compared the spin and charge two-particle correlations functions with Quantum Monte Carlo [30] and Bethe ansatz [31] results, to check the validity of the variationally obtained 2DM.

2. Exploiting symmetry in the Hubbard model

As there is no preferred direction in spin space in Eq. (5), spin symmetry can be exploited and all the results from Ref. [32] are taken over. However, far more symmetries are present in the model, which allow for a huge reduction of the matrix dimensions involved.

2.1. Translational invariance

When periodic boundary conditions are assumed (as in Fig. 1) the Hamiltonian is invariant under translations along the lattice. This is an abelian symmetry for which it is easy to block diagonalize the 2DM and its matrix maps, as the correct basis transformation in single-particle space automatically block diagonalizes all matrices on higher-order particle space. Translational invariance is exploited by Fourier transforming the site basis to quasi-momentum space:

$$|k\sigma\rangle = \sqrt{\frac{1}{L}} \sum_j e^{ikj} |j\sigma\rangle, \quad (6)$$

where L is the lattice size, and k takes on the values $\frac{2\pi n}{L}$ for $n = 0, \dots, L-1$. The kinetic or hopping part of the Hamiltonian becomes diagonal in this basis:

$$\hat{H}_{\text{hop}} = -2t \sum_{k\sigma} \cos ka_{k\sigma}^\dagger a_{k\sigma}, \quad (7)$$

from which it follows that in the non-interacting ($U = 0$) ground state, the electrons occupy the states with momenta lower than the Fermi level.

The eigenstates of the Hubbard Hamiltonian have a good total quasi-momentum $\mathcal{K}$. The 2DM for these states, expressed in the quasi-momentum single-particle basis:

$$\Gamma_{k_a k_b; k_c k_d}^S = um_i w_i \frac{1}{[S]^2} \sum_{\mathcal{M}} \langle \Psi_{S, \mathcal{M}, i}^{NK} | B_{k_a k_b}^S B_{k_c k_d}^S | \Psi_{S, \mathcal{M}, i}^{NK} \rangle, \quad (8)$$

where

$$\begin{aligned} B_{k_a k_b}^{iS} &= \frac{1}{\sqrt{1 + \delta_{k_a k_b}}} [a_{k_a}^\dagger \otimes a_{k_b}^\dagger]^S \\ &= \frac{1}{\sqrt{1 + \delta_{k_a k_b}}} \sum_{\sigma_a \sigma_b} \left\langle \frac{1}{2} \sigma_a \frac{1}{2} \sigma_b | SM \right\rangle a_{k_a \sigma_a}^\dagger a_{k_b \sigma_b}^\dagger \end{aligned} \quad (9)$$

is automatically block diagonal, because the only non-zero matrix elements in Eq. (8) are those which conserve momentum: $(k_a + k_b) \% 2\pi = (k_c + k_d) \% 2\pi$.¹ This means we have L blocks Γ^{SK} for every

¹ Here % signifies the modulo operator.

S , with two-particle states that satisfy $K = (k_a + k_b)\%2\pi$, and a block dimension that scales linearly with lattice size L .

The spin-symmetric matrix constraints simplify considerably by including translational invariance, because the 1DM is automatically diagonal in the quasi-momentum basis:

$$\rho_k = \sum_i w_i \frac{1}{[S]^2} \sum_{\mathcal{M}} \langle \Psi_{S\mathcal{M},i}^{NC} | a_{k\sigma}^\dagger a_{k\sigma} | \Psi_{S\mathcal{M},i}^{NC} \rangle. \quad (10)$$

The translationally invariant 1DM can be derived from the 2DM as:

$$\rho_k = \frac{1}{N-1} \sum_S \frac{[S]^2}{2} \sum_{k'} (1 + \delta_{kk'}) \Gamma_{kk';kk'}^{SK}. \quad (11)$$

As an example the translationally invariant form of the $\mathcal{G}$ condition is shown. There is a slight complication because the correct annihilation or hole operator is given by:

$$\tilde{a}_{k\sigma} = (-1)^{\frac{1}{2}+\sigma} a_{\bar{k}-\sigma}, \quad \text{with } \bar{k} = -k\%2\pi. \quad (12)$$

Using this operator the translationally invariant $\mathcal{G}$ map becomes:

$$\mathcal{G}(\Gamma)_{k_a k_b; k_c k_d}^{SK} = \sum_i w_i \frac{1}{[S]^2} \sum_{\mathcal{M}} \langle \Psi_{S\mathcal{M},i}^{KN} | A_{k_a k_b}^{iSK} A_{k_c k_d}^{SK} | \Psi_{S\mathcal{M},i}^{NC} \rangle, \quad (13)$$

where $K = (k_a + k_b)\%2\pi = (k_c + k_d)\%2\pi$ and with the particle-hole operator defined by:

$$A_{k_a k_b}^{iSK} = [a_{k_a}^\dagger \otimes \tilde{a}_{k_b}]^{SK}. \quad (14)$$

The $\mathcal{G}$ map can be expressed as a function of the 2DM:

$$\begin{aligned} \mathcal{G}(\Gamma)_{k_a k_b; k_c k_d}^{SK} &= \delta_{k_b k_d} \delta_{k_a k_c} \rho_{k_a} - \sqrt{(1 + \delta_{k_a \bar{k}_d})(1 + \delta_{k_b \bar{k}_c})} \\ &\times \sum_{S'} \left\{ \begin{matrix} \frac{1}{2} & \frac{1}{2} & S \\ \frac{1}{2} & \frac{1}{2} & S' \end{matrix} \right\} \Gamma_{k_a k_d; k_c \bar{k}_b}^{S'K'}, \end{aligned} \quad (15)$$

from which one can see that the blocks in the $\mathcal{G}$ matrix with $K = (k_a + k_b)\%2\pi = (k_c + k_d)\%2\pi$, correspond to the blocks with $K' = (k_a + k_d)\%2\pi = (k_c + \bar{k}_b)\%2\pi$ in the 2DM, as expected for a particle-hole transformed quantity.

2.2. Parity

The Hubbard model with periodic boundary conditions (PBCs) has more symmetries than spin and translational invariance, one of them being parity. Parity follows from the symmetry under the inversion of space, i.e. $\mathbf{r} \rightarrow -\mathbf{r}$. One can readily appreciate from Fig. 1 that this symmetry is present here, i.e. the Hamiltonian is invariant for the inversion of the site index $i \rightarrow -i\%L$. From the Fourier transform in Eq. (6) it can be seen that the effect of this operator on a momentum state is to transform k into $\bar{k} = -k\%2\pi$. However, this operation does not commute with translation, which means that the eigenstates of the Hamiltonian cannot have good momentum and parity at the same time. From now on we assume that the number of lattice sites L is even.

As a consequence, if the ground state has momentum $|\mathcal{K}\rangle \neq 0$ or π then it is doubly degenerate, forming a doublet with $|\bar{\mathcal{K}}\rangle$. In what follows we will use this degeneracy to exploit both translational invariance and parity to reduce the dimensions of the matrices involved in the program. The following considerations are valid for every $\mathcal{K}$. We start with the simplest case, the 1DM.

Single-particle space is built out of L different momentum states having up or down spin, $|k\sigma\rangle$, for $0 \leq k < 2\pi$ and $\sigma = \pm\frac{1}{2}$. If we transform to a basis with good parity, momentum is no longer a good quantum number:

$$|\bar{k}^\pi\sigma\rangle = {}^\rho N_k (|k\sigma\rangle + \pi |\bar{k}\sigma\rangle), \quad \text{with } 0 \leq \bar{k} \leq \pi. \quad (16)$$

Two states, $k = 0$ and $k = \pi^2$ are mapped on themselves, and only positive parity states can be formed with these momenta. They have norms ${}^\rho N_k = \frac{1}{2}$. For the other states, $0 < k < \pi$, both positive and negative parity combinations can be constructed, with norm ${}^\rho N_k = \frac{1}{\sqrt{2}}$. To take advantage of both symmetries at the same time, we define the 1DM using an ensemble of the $|\mathcal{K}\rangle$ and $|\bar{\mathcal{K}}\rangle$ states:

$$\rho_{\bar{k}^\pi \bar{k}^{\pi'}} = \sum_i w_i \frac{1}{2} \frac{1}{[S]^2} \sum_{\mathcal{M}} \sum_{p \in \pm} \langle \Psi_{S\mathcal{M},i}^{N(p\mathcal{K})} | a_{\bar{k}^\pi \sigma}^\dagger a_{\bar{k}^{\pi'} \sigma} | \Psi_{S\mathcal{M},i}^{N(p\mathcal{K})} \rangle \quad (17)$$

$$= \frac{{}^\rho N_k^2}{2} \sum_{p \in \pm} \left[\delta_{kk'} (\rho_k^{p\mathcal{K}} + \pi \pi' \rho_k^{p\mathcal{K}}) + \delta_{\bar{k}\bar{k}'} (\pi' \rho_k^{p\mathcal{K}} + \pi \rho_k^{p\mathcal{K}}) \right], \quad (18)$$

in which $\rho_k^{p\mathcal{K}}$ is a regular translationally invariant 1DM as defined in Eq. (10). Because of parity symmetry we have,

$$\rho_k^{\mathcal{K}} = \rho_{\bar{k}}^{\bar{\mathcal{K}}}, \quad (19)$$

from which it follows that Eq. (18) is diagonal in π . If we now define:

$$\rho_k = \frac{1}{2} (\rho_k^{\mathcal{K}} + \rho_{\bar{k}}^{\bar{\mathcal{K}}}), \quad (20)$$

the translationally invariant 1DM with good parity reduces to:

$$\rho_{\bar{k}^\pi} = \frac{1}{2} (\rho_k + \rho_{\bar{k}}), \quad (21)$$

which can be seen to be independent of parity. The 1DM is still diagonal in $\bar{k}$, but less elements have to be stored, since for $0 < \bar{k} < \pi$ there is a degeneracy in parity.

In contrast to parity in atomic systems (see e.g. [32]), the parity of a two-particle state for translationally invariant systems is not the product of the parities of the single-particle states building up the two-particle state. Instead, the parity is inherently a two-particle property, and the single-particle states building up the two-particle states have no good parity:

$$|ab; S\bar{K}^\pi\rangle = {}^\Gamma N_{ab}^{\mathcal{K}} (|ab; SK\rangle + \pi |\bar{a}\bar{b}; S\bar{K}\rangle), \quad (22)$$

with

$$0 \leq \bar{K} \leq \pi \quad \text{and} \quad 0 \leq a, b < 2\pi. \quad (23)$$

In general the 2DM is defined using a $p\mathcal{K}$ ensemble:

$$\Gamma_{ab;cd}^{\bar{S}\bar{K}^\pi} = \sum_i w_i \frac{1}{2} \frac{1}{[S]^2} \sum_{\mathcal{M}} \sum_{p \in \pm} \langle \Psi_{S\mathcal{M},i}^{N(p\mathcal{K})} | B_{ab}^{i\bar{S}\bar{K}^\pi} B_{cd} S\bar{K}^\pi | \Psi_{S\mathcal{M},i}^{N(p\mathcal{K})} \rangle, \quad (24)$$

where

$$B_{ab}^{i\bar{S}\bar{K}^\pi} = {}^\Gamma N_{ab}^{\mathcal{K}} \left(B_{ab}^{i\mathcal{K}} + \pi B_{\bar{a}\bar{b}}^{i\bar{\mathcal{K}}} \right), \quad (25)$$

and with $B^{i\mathcal{K}}$ defined as in Eq. (9). Because of this $p\mathcal{K}$ -ensemble definition and the fact that parity symmetry implies that,

$${}^\mathcal{K} \Gamma_{ab;cd}^{SK} = -{}^\mathcal{K} \Gamma_{\bar{a}\bar{b};\bar{c}\bar{d}}^{S\bar{K}}, \quad (26)$$

one sees that the 2DM becomes diagonal in two-particle parity. As was the case for the 1DM, the $\bar{K} = 0$ and π are mapped on themselves, but because the single-particle momenta a, b change, both positive and negative parity combinations can now be formed. Let us take a look at the different possibilities:

$\bar{K} = 0$: for $\bar{K} = 0$ the single-particle indices in Eq. (22) have to satisfy:

$$(a + b)\%2\pi = 0 \quad \text{or} \quad a = \bar{b}. \quad (27)$$

² Note that we use π for both the parity quantum number, $\pi = \pm 1$ as for the transcendent number; in what follows it is always clear from the context what interpretation should be given to π .

This means that $\tilde{K} = 0$ states can be written as:

$$|a\bar{a}; S0^\pi\rangle = {}^rN_{a\bar{a}}^0(|a\bar{a}; S0\rangle + \pi|\bar{a}a; S0\rangle), \quad (28)$$

in which the second term is equal to the first but with exchanged single-particle indices. From previous discussions we know that the symmetry of the two-particle state under the exchange of the single-particle indices depends on the two-particle spin, i.e.

$$|a\bar{a}; S0\rangle = (-1)^S |\bar{a}a; S0\rangle. \quad (29)$$

One can see from Eq. (28) that for $S = 0$ only the positive parity states, and for $S = 1$ only negative parity states remain. The norm is given ${}^rN_{a\bar{a}}^0 = \frac{1}{2}$. In the $\tilde{K} = 0$ case, the definition of the parity-symmetric 2DM as a function of the regular translationally invariant 2DM then reduces to:

$$\Gamma_{ab;cd}^{S0^\pi} = \delta_{\pi(-1)^S} \Gamma_{ab;cd}^{S0}. \quad (30)$$

$0 < \tilde{K} < \pi$: for $0 < \tilde{K} < \pi$ the first and second term in Eq. (22) consist of different single-particle indices $a \neq \bar{b}$, implying that both positive and negative parity combinations can be constructed, with norm ${}^rN_{ab}^K = \frac{1}{\sqrt{2}}$. As shown for the 1DM, the $p\mathcal{K}$ ensemble makes the 2DM diagonal in, and independent of, parity. Hence every block is twofold degenerate. Since $K \neq \bar{K}$ there are only two terms remaining in the definition of the parity-symmetric 2DM:

$$\Gamma_{ab;cd}^{\tilde{S}K^\pi} = \frac{1}{2} \left(\Gamma_{ab;cd}^{SK} + \Gamma_{ab;\bar{c}\bar{d}}^{S\bar{K}} \right). \quad (31)$$

$\tilde{K} = \pi$: Finally, for this block K again equals $\bar{K}$. In this case there is always one state that is mapped on itself, and for which only a positive parity combination can be formed, i.e. $|0\pi; S\pi^+\rangle$, with norm ${}^rN_{0\pi}^\pi = \frac{1}{2}$. For all the other states in this block both positive and negative parity combinations can be formed, with norm ${}^rN_{ab}^\pi = \frac{1}{\sqrt{2}}$. Because of the $p\mathcal{K}$ ensemble, the 2DM falls apart in a positive and negative parity block, and since $K = \bar{K}$, four terms remain in the definition of the 2DM:

$$\Gamma_{ab;cd}^{S\pi^\pi} = {}^rN_{ab}^\pi {}^rN_{cd}^\pi \left(\Gamma_{ab;cd}^{S\pi} + \Gamma_{ab;\bar{c}\bar{d}}^{S\pi} + \pi \left[\Gamma_{ab;\bar{c}\bar{d}}^{S\pi} + \Gamma_{ab;cd}^{S\pi} \right] \right). \quad (32)$$

We observe from Eq. (32) that the original $K = \pi$ block reduces to a positive and negative parity block, for both the $S = 0$ and $S = 1$ part. Also note that there is no degeneracy between the positive and negative parity block!

Similar considerations hold for the matrix constraints, as an example the explicit case of the $\mathcal{G}$ condition is given.

The parity-symmetric form of a particle-hole state is defined as:

$$|ab; S\tilde{K}^\pi\rangle = {}^gN_{ab}^K \left([a_a^\dagger \otimes \tilde{a}_b]^{SK} + [a_a^\dagger \otimes \tilde{a}_{\bar{b}}]^{S\bar{K}} \right) |0\rangle, \quad (33)$$

in which the hole operator $\tilde{a}_{k\sigma}$ is defined as in Eq. (12). Using this parity-symmetric particle-hole operator the $\mathcal{G}$ map is defined in a $p\mathcal{K}$ ensemble, which once again renders the matrix diagonal in particle-hole parity. The particle-hole states can be divided into two classes, on the one hand $\tilde{K} = 0$ or π , and on the other hand those states which are mapped on a different momentum. For simplicity we first consider this last class.

$0 < \tilde{K} < \pi$: in this case one can construct both positive and negative parity combinations, with norm ${}^gN_{ab}^K = \frac{1}{\sqrt{2}}$. The resulting $\mathcal{G}$ matrix contains only two terms, because of momentum conservation, and is independent of particle-hole parity, so every block is twofold degenerate:

$$\mathcal{G}(\Gamma)_{ab;cd}^{\tilde{S}K^\pi} = \frac{1}{2} \left[\mathcal{G}(\Gamma)_{ab;cd}^{SK} + \mathcal{G}(\Gamma)_{ab;\bar{c}\bar{d}}^{S\bar{K}} \right]. \quad (34)$$

This implies the following expression of the $\mathcal{G}$ map as a function of the parity-symmetric 2DM:

$$\mathcal{G}(\Gamma)_{ab;cd}^{\tilde{S}K^\pi} = \delta_{ac}\delta_{bd}\rho_a - \frac{\sqrt{(1+\delta_{ad})(1+\delta_{cb})}}{4{}^rN_{ad}^{K'}{}^rN_{cb}^{K'}} \sum_{S'} [S']^2 \left\{ \begin{matrix} \frac{1}{2} & \frac{1}{2} & S \\ \frac{1}{2} & \frac{1}{2} & S' \end{matrix} \right\} \sum_{\pi'} \Gamma_{ad;cb}^{S'K'\pi'}. \quad (35)$$

$\tilde{K} = 0$ and $\tilde{K} = \pi$: both the $\tilde{K} = 0$ and $\tilde{K} = \pi$ blocks are mapped on themselves. For $\tilde{K} = 0$ the action of the parity operator is again to exchange the single-particle momenta, but in contrast with the two-particle case, there is no symmetry between the particle and the hole index. As a consequence positive and negative parity combinations for both $\tilde{K} = 0$ and $\tilde{K} = \pi$ can be constructed, with norms ${}^gN_{ab}^K = \frac{1}{\sqrt{2}}$. There are a few exceptions however: for $\tilde{K} = 0$, the states with $a = b = 0$ and $a = b = \pi$, and for $\tilde{K} = \pi$ the states with $a = 0, b = \pi$ and $a = \pi, b = 0$, are mapped on themselves and only occur in the positive parity block, with norm ${}^gN_{ab}^K = \frac{1}{2}$. The general form of the parity-symmetric $\mathcal{G}$ map when $K = \bar{K}$, as a function of the regular translationally invariant $\mathcal{G}$ is:

$$\mathcal{G}(\Gamma)_{ab;cd}^{\tilde{S}K^\pi} = {}^gN_{ab}^K {}^gN_{cd}^K \left[\mathcal{G}(\Gamma)_{ab;cd}^{SK} + \mathcal{G}(\Gamma)_{ab;\bar{c}\bar{d}}^{S\bar{K}} + \pi \left(\mathcal{G}(\Gamma)_{ab;\bar{c}\bar{d}}^{SK} + \mathcal{G}(\Gamma)_{ab;cd}^{S\bar{K}} \right) \right]. \quad (36)$$

In this case the expression of $\mathcal{G}$ as a function of the 2DM is a bit more complicated:

$$\begin{aligned} \mathcal{G}(\Gamma)_{ab;cd}^{\tilde{S}K^\pi} &= \delta_{ac}\delta_{bd}\rho_a - {}^gN_{ab}^K {}^gN_{cd}^K \sum_{S'} [S']^2 \left\{ \begin{matrix} \frac{1}{2} & \frac{1}{2} & S \\ \frac{1}{2} & \frac{1}{2} & S' \end{matrix} \right\} \\ &\times \left[\frac{\sqrt{(1+\delta_{ad})(1+\delta_{cb})}}{4{}^rN_{ad}^{K'}{}^rN_{cb}^{K'}} \sum_{\pi'} \Gamma_{ad;cb}^{S'K'\pi'} + \pi \frac{\sqrt{(1+\delta_{ad})(1+\delta_{cb})}}{4{}^rN_{ad}^{K''}{}^rN_{cb}^{K''}} \sum_{\pi'} \Gamma_{ad;cb}^{S'K''\pi'} \right]. \end{aligned} \quad (37)$$

3. Computational performance

In v2DM we want to optimize the energy by varying a matrix, the 2DM, under the constraints that it has the right particle number, and that some linear matrix maps of the 2DM are positive semidefinite, i.e.

$$E_{\text{SDP}}^N(H_v) = \min_{\Gamma} \text{Tr} [\Gamma H_v^{(2)}], \quad (38)$$

$$\text{u.c.t.} \quad \begin{cases} \text{Tr} \Gamma = \frac{N(N-1)}{2}, \\ \mathcal{L}_j(\Gamma) \succeq 0. \end{cases} \quad (39)$$

Here the $\mathcal{L}_j$ are a collection of matrix non-negativity constraints to be applied. It is well known that this problem can be reformulated as a semidefinite program. There is a vast literature on this subject and many different algorithms exist to solve this type of problem. Because of the large amount of symmetry present in the Hubbard model, there is a huge block diagonalization of the 2DM and the matrix constraints. This leads to a significant reduction of the computational cost of a basic matrix computation. This feature has allowed us to go up to large lattice sizes and compare the computational scaling of different algorithms. We have implemented three different semidefinite programming algorithms. Two are so-called interior point methods (a dual-only potential reduction algorithm [32], and a primal-dual interior point algorithm [28]), where the 2DM is optimized from within the N -representable region. In the third one (a boundary point method [27]) the 2DM is not required to be N -representable during the optimization. In this section we compare the computational scaling of these methods for the one-dimensional Hubbard model with $U = 1$ and using $\mathcal{IQG}$ conditions. For details about the implementation of the different algorithms, see the cited references.

All the methods have the same basic computational scaling behavior, being $O(M^6)$ (with M the dimension of single-particle

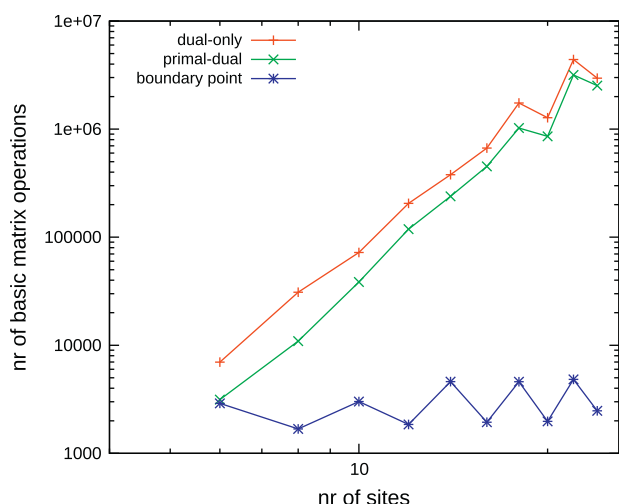


Fig. 2. The number of basic matrix operations needed to converge for different lattice sizes of the one-dimensional Hubbard model, using *IQG* conditions and $U = 1$.

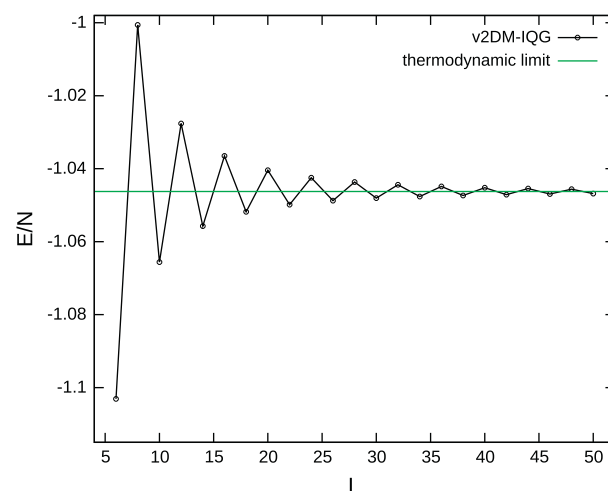


Fig. 4. Ground-state energy per particle as a function of the lattice size L , indicating how fast the finite size results converge to the thermodynamic limit for half filling.

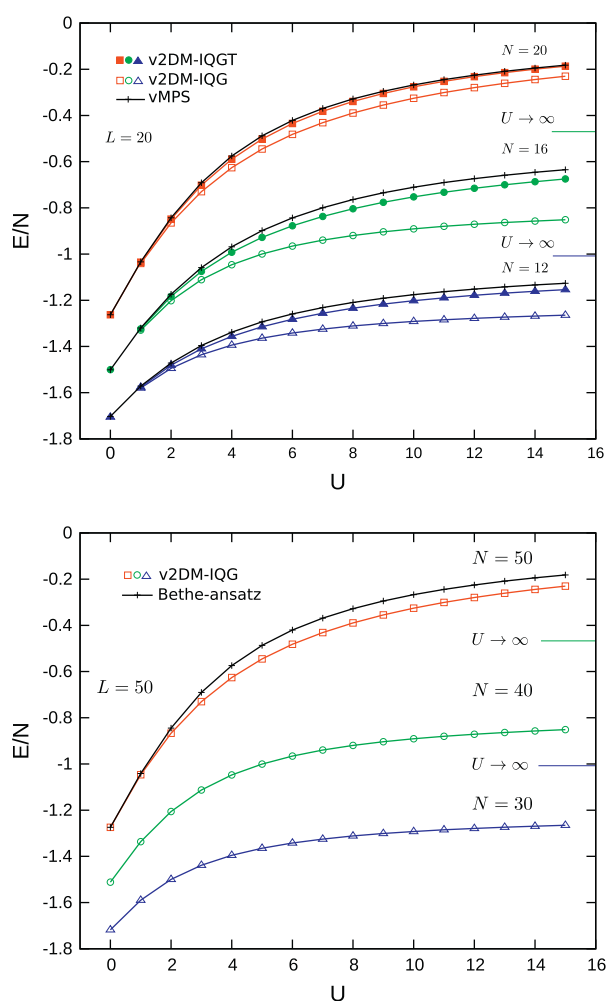


Fig. 3. Ground-state energy per particle as a function of on-site repulsion U of the Hubbard model for a 20-site (top) and 50-site (bottom) lattice at half-, $\frac{4}{10}$ and $\frac{3}{10}$ filling. For the 20-site lattice a comparison is made between v2DM using the *IQG* and *IQGT* conditions, and a quasi-exact result using MPS. For the 50-site lattice only *IQG* conditions are feasible, and these have been compared to the exact (Bethe-ansatz) result for half filling.

Table 1

Energy per site of the v2DM calculations away from half filling at large values of U , compared to the MPS and the Bethe-ansatz results where available.

L	N	U	<i>IQG</i>	<i>IQGT</i>	vMPS	Exact
20	12	50	-1.2259	-1.0804	-1.0488	*
		100	-1.2177	-1.0646	-1.03116	*
		∞	*	*	*	-1.0008
	16	50	-0.7972	-0.5458	-0.5205	*
		100	-0.7860	-0.5179	-0.49513	*
		∞	*	*	*	-0.4639
L	N	U	<i>IQG</i>			Exact
50	30	50		-1.2272		*
		100		-1.2191		*
		∞		*		-1.0008
	40	50		-0.7974		*
		100		-0.7862		*
		∞		*		-0.4671

Hilbert space) required for multiplying, inverting or diagonalizing a matrix. In Fig. 2 the number of these operations needed to converge to the optimum is plotted as a function of lattice size. The interior point methods both have to solve a linear system of size M^4 , so it is not surprising that the scaling, on top of the basic matrix computations, of these methods is M^4 . More surprising is that there seems to be no, or a very limited, scaling for the boundary point method. The number of iterations required remains around 3000, irrespective of the size of the system. It must be stressed that this is a result limited to the one-dimensional Hubbard model, and cannot be extrapolated to other systems, like molecules, where the convergence properties of the boundary point method can be completely different. One reason for the success of the boundary point method applied to the Hubbard model is the amount of symmetry present in the system. The boundary point method is designed for problems with a huge amount of dual variables or primal constraints. For most physical systems the dimensions of the matrices involved are already unfeasibly large before the boundary point method would become advantageous. The Hubbard model, however, contains many symmetries, implying that the matrix dimensions are considerably reduced, and the number of dual variables can get very large before the matrix computations involved become unfeasible. In this case, the domain where the boundary point method is advantageous is actually reached.

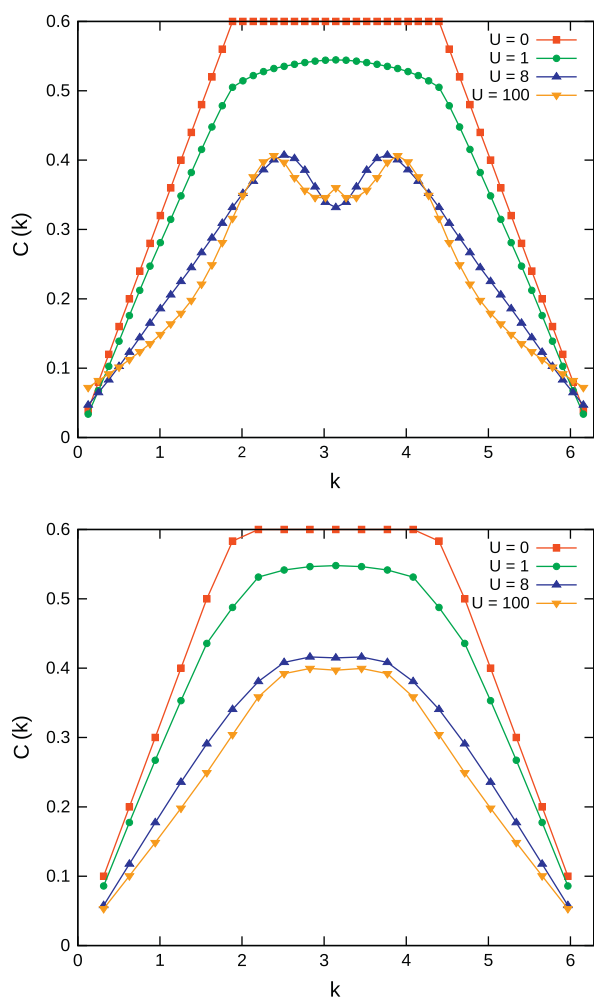


Fig. 5. Two-particle charge correlation function $C(k)$, as a function of momentum, for a $\frac{3}{10}$ filled lattice and various values of on-site repulsion U , using IQG (top) and $IQGT$ (bottom) conditions.

4. Results

In this section we present and discuss the results of v2DM calculations, taking advantage of all the symmetries, on a 50-site lattice with the IQG conditions, and on a 20-site lattice with the $IQGT_1T_2$ ($IQGT$) conditions. The Hubbard model has been studied before using the v2DM method, see e.g. [33,34,19,35], but only the energy was considered, and this for relatively small lattice sizes (up to $L=14$). In this paper we study different filling factors, and extract various properties like the ground-state energy and two-particle correlation functions in order to assess the quality of the variationally obtained 2DM. The v2DM results discussed in this section were all obtained using the primal–dual predictor corrector semidefinite programming algorithm [28]. Although the one-dimensional Hubbard model can be solved exactly using the Bethe ansatz [36–39], it is hard to extract information about the solution for finite systems. For the calculations on a 20-site lattice, we compare the data with the quasi-exact results obtained through a variational Matrix Product State (MPS) algorithm [40–42], written by co-worker Wouters et al. [43]. For the 50-site lattice, however, this is no longer computationally feasible. At half filling a simplification in the Bethe-ansatz equations occurs, which allows to calculate the ground-state energy of finite systems by solving a set of non-linear equations Lieb and Wu [44]. At other fillings no data is available for comparison.

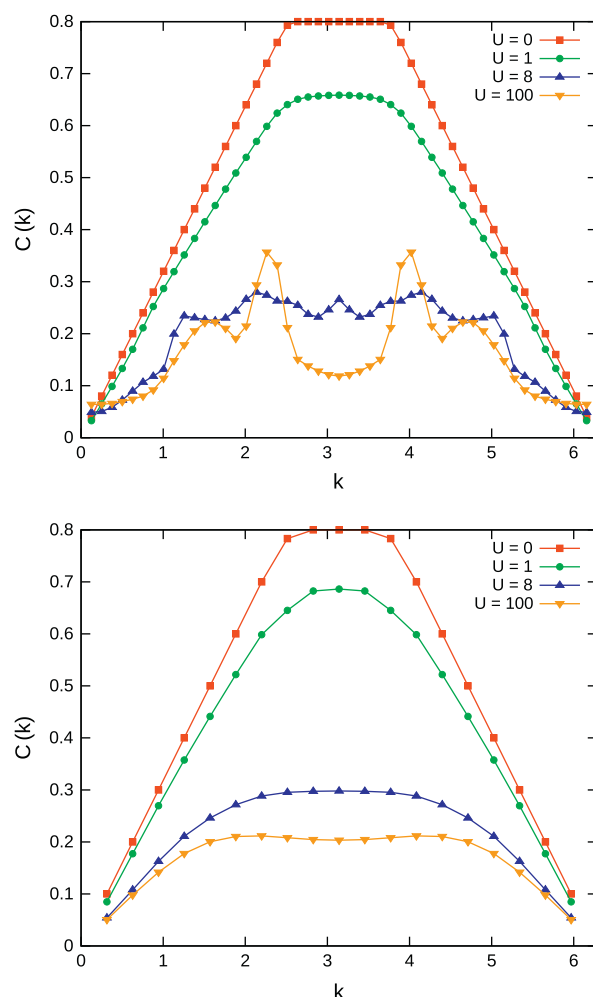


Fig. 6. Two-particle charge correlation function $C(k)$, as a function of momentum, for a $\frac{4}{10}$ filled lattice and various values of on-site repulsion U , using IQG (top) and $IQGT$ (bottom) conditions.

4.1. Ground-state energy

In Fig. 3 the ground-state energy per particle of the one-dimensional Hubbard model is plotted as a function of the on-site repulsion U (the hopping parameter t will always be taken equal to unity). In the top figure the v2DM results for the 20-site lattice are shown for three different fillings, 12 particles ($\frac{3}{10}$), 16 particles ($\frac{4}{10}$) and half filling. These were calculated using both the IQG and the $IQGT$ conditions, and are compared to the quasi-exact variational MPS results. In the bottom figure the v2DM results for the 50-site lattice are shown for the same fillings (i.e. 30 particles ($\frac{3}{10}$), 40 particles ($\frac{4}{10}$) and half filling). For the 50-site lattice it was only possible to perform the calculations using the IQG conditions, and compare to the exact solution obtained by solving the Lieb–Wu equations for the half-filled lattice [44].

One interesting thing to notice is that the IQG energy per particle for the 20-site lattice and the 50-site lattice, at the same filling, are very similar. This is due to the periodic boundary conditions which make the results converge quite rapidly for increasing lattice size L , implying that one can already extract relevant results for the thermodynamic limit by studying relatively small lattices. This fast convergence can be clearly seen in Fig. 4, where we plotted the energy per particle of a Hubbard model with $U=1$ at half filling, as a function of the lattice size L . This result seems to indicate that the method is more or less size extensive

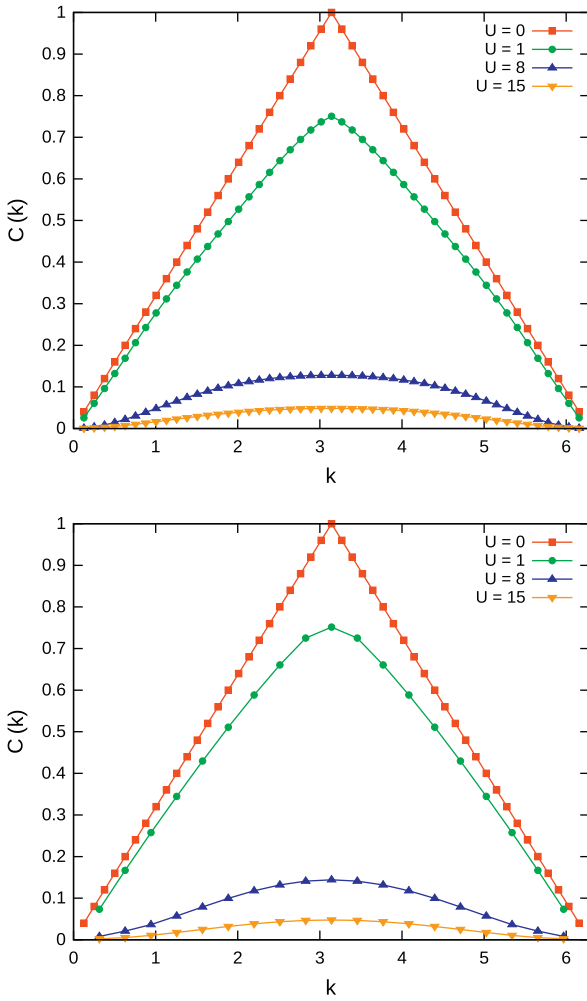


Fig. 7. Two-particle charge correlation function $C(k)$, as a function of momentum, for a half-filled lattice and various values of on-site repulsion U , using IQG (top) and $IQGT$ (bottom) conditions.

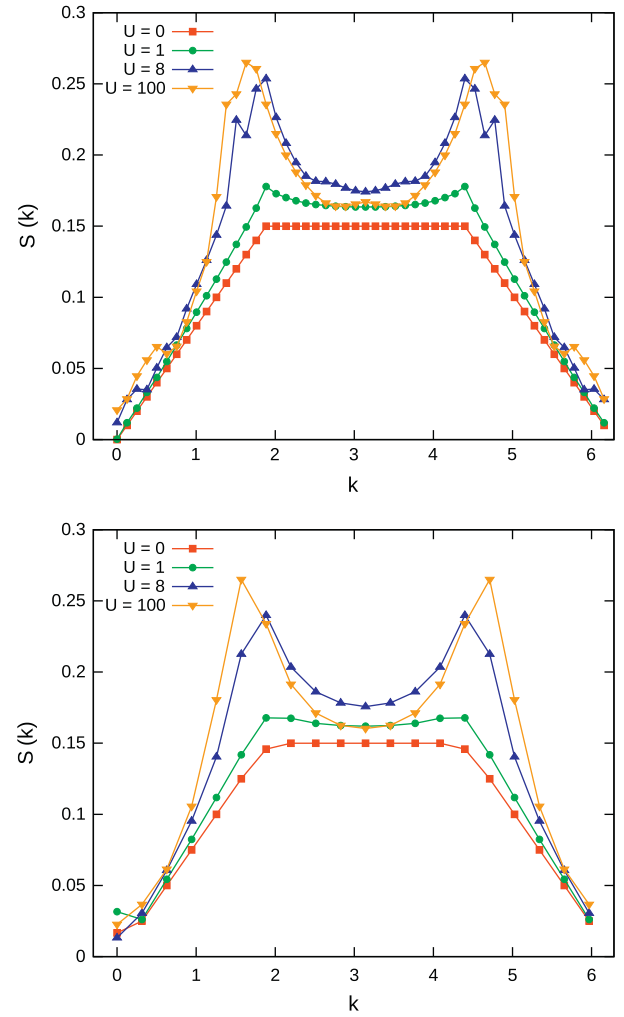


Fig. 8. Two-particle spin correlation function $S(k)$, as a function of momentum, for a $\frac{2}{3}$ -filled lattice and various values of on-site repulsion U , using IQG (top) and $IQGT$ (bottom) conditions.

for the Hubbard model, which is surprising since in general v2DM is not size extensive [45,46].

Another thing to remark in Fig. 3 is that for the 20-site lattice, the difference between IQG and $IQGT$ is rather small for the half-filled lattice, but larger for the other fillings, and that the difference gets larger when U increases. For the 50-site lattice we see that the IQG result agrees nicely with the solution of the Lieb–Wu equations. For the other fillings no reference data are available. There are, however, two limits of the model that are exactly solvable. The first limit is the rather trivial case of no interaction, i.e. $U=0$, for which the solution has already been given in Eq. (7). The Hamiltonian reduces to a single-particle operator, which means this limit is already described correctly by including the $\mathcal{I}$ and $\mathcal{Q}$ conditions alone. The other exactly solvable limit is when $U \rightarrow +\infty$. In this limit the physics of the model decouples into two independent parts, one describing the spin of the system, and the other the movement of the particles (this is called spin-charge separation [31]). This decoupling shows up in the Bethe-ansatz wave function: the charge degrees of freedom are described by a Slater determinant of spinless fermions, whereas the spin degrees of freedom become equivalent to a spin- $\frac{1}{2}$ Heisenberg model. The single-particle energy spectrum changes slightly compared to Eq. (7) because the boundary conditions for spinless fermions are periodic/antiperiodic if N is even/odd [31,47]:

$$\epsilon_k = -2t \cos k \quad \text{where} \quad \begin{cases} k = \frac{2\pi n}{L} & \text{if } N\%2 = 0, \\ k = \frac{(2n+1)\pi}{L} & \text{if } N\%2 = 1. \end{cases} \quad (40)$$

When the lattice is half-filled all the single-particle states are occupied, and the total energy sums up to zero, which is correctly described by the IQG results in Fig. 3. Away from half filling, however, the energy has a finite limit which can be calculated using Eq. (40). From the figure we can see that the IQG conditions do not suffice to correctly describe the large- U limit. Only when the $\mathcal{T}$ conditions are added, the results converge to the right limit. Calculations at very large values of U have been performed that confirm this statement, and these results are shown in Table 1.

4.2. Correlation functions

Two-particle correlation functions are important quantities in the analysis of lattice systems, because they usually display the physics (for instance the appearance of magnetism) present in the system. In this section we show that in our approach, these correlation functions are easily extracted from the 2DM, and compare our results to those in [30,31].

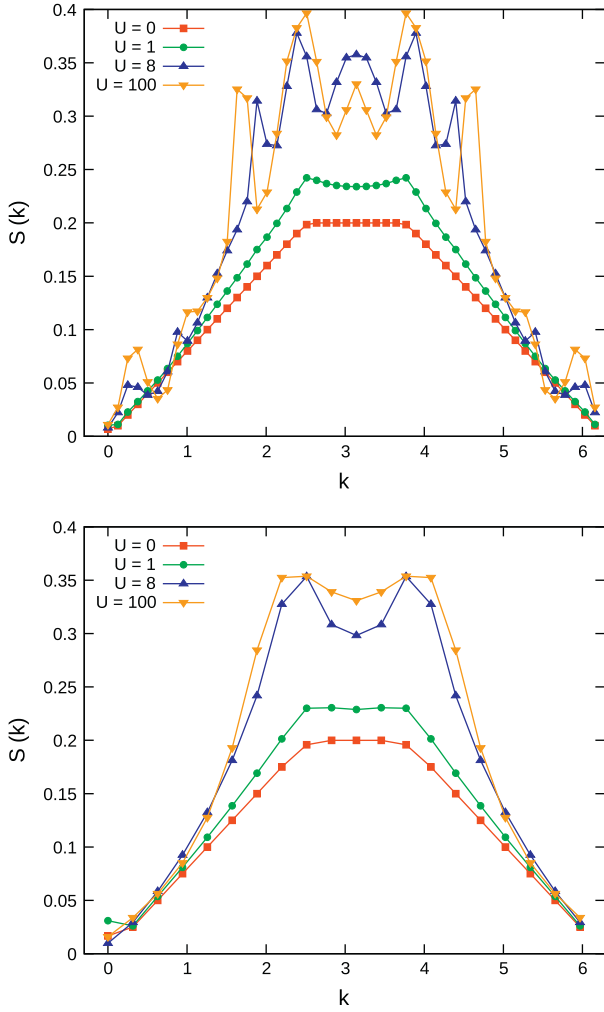


Fig. 9. Two-particle spin correlation function $S(k)$, as a function of momentum, for a $\frac{4}{10}$ filled lattice and various values of on-site repulsion U , using IQG (top) and $IQGT$ (bottom) conditions.

Charge correlation. The two-particle charge correlation function is defined as:

$$C(r) = \langle \hat{n}_j \hat{n}_{j+r} \rangle = \sum_{\sigma\sigma'} \langle a_{j\sigma}^\dagger a_{j\sigma} a_{j+r,\sigma'}^\dagger a_{j+r,\sigma'} \rangle, \quad (41)$$

in which the notation $\langle \cdot \rangle$ denotes the expectation value. The function is independent of the specific choice of the index j because of the periodic boundary conditions. The expression in Eq. (41) can be written in terms of the $\mathcal{G}(\Gamma)$ matrix:

$$C(r) = \sum_{\sigma\sigma'} \mathcal{G}(\Gamma)_{j\sigma j\sigma; (j+r)\sigma' (j+r)\sigma'}, \quad (42)$$

and in fact only the singlet part of the $\mathcal{G}$ matrix appears:

$$C(r) = 2\mathcal{G}(\Gamma)_{jj; (j+r)(j+r)}^0. \quad (43)$$

In translationally invariant systems one usually takes the Fourier transform of the correlation function,

$$C(k) = \sum_r e^{ikr} C(r) = 2 \sum_{k_a k_b k_c k_d} \mathcal{G}(\Gamma)_{k_a k_b; k_c k_d}^{0k}. \quad (44)$$

In Figs. 5–7, $C(k)$ has been plotted for $\frac{3}{10}$, $\frac{4}{10}$ and half filling respectively, using both IQG and $IQGT$ conditions. Comparing the IQG with the $IQGT$ results the same trends can be noticed

as for the energy and the momentum distributions. For half filling (Fig. 7) the IQG and $IQGT$ results are in nice agreement. Moving away from half-filling (Figs. 5 and 6) there is only agreement for small values of U . For larger values of U strange oscillations appear in the IQG results. So in this limit not only the energy, but the entire physical content of the IQG -2DM cannot be trusted. This is once again an indication that the IQG conditions fail to describe the strong-correlation limit away from half-filling. The $IQGT$ results compare well, both in shape and magnitude, with the results from Quantum Monte Carlo [30], and the Bethe-ansatz results in the strong-correlation limit [31].

Spin correlation. The two-particle spin-correlation function defined as:

$$S(r) = \langle S_z^i S_z^{i+r} \rangle = \sum_{\sigma\sigma'} \sigma\sigma' \langle a_{j\sigma}^\dagger a_{j\sigma} a_{j+r,\sigma'}^\dagger a_{j+r,\sigma'} \rangle \quad (45)$$

can be expressed as a function of the $\mathcal{G}$ matrix:

$$S(r) = \sum_{\sigma\sigma'} \sigma\sigma' \mathcal{G}(\Gamma)_{j\sigma j\sigma; (j+r)\sigma' (j+r)\sigma'}. \quad (46)$$

Written in terms of the spin-coupled $\mathcal{G}$ matrix, only the triplet $S=1$ part contributes:

$$S(r) = \frac{1}{2} \mathcal{G}(\Gamma)_{jj; (j+r)(j+r)}^1. \quad (47)$$

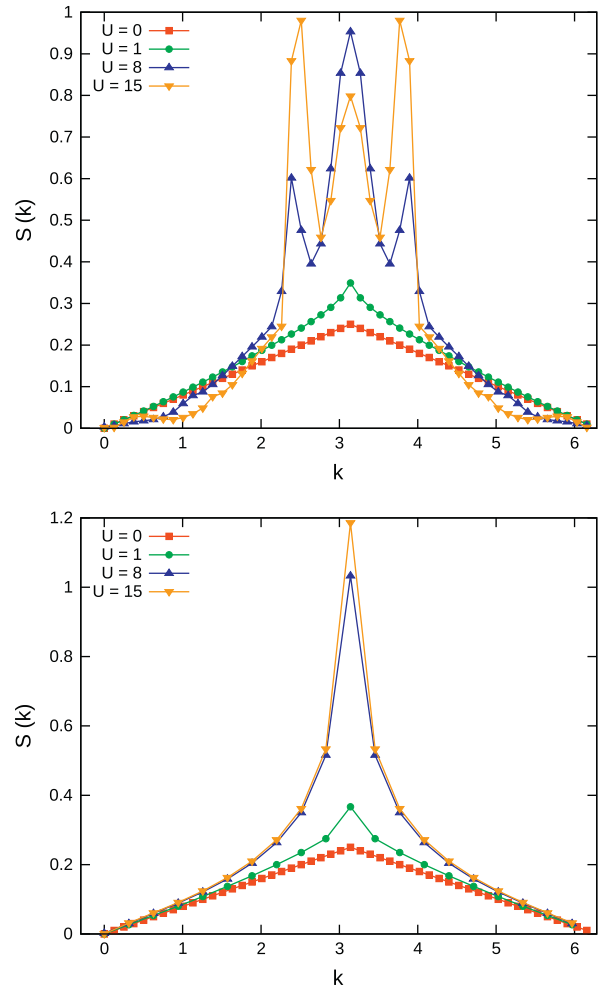


Fig. 10. Two-particle spin correlation function $S(k)$, as a function of momentum, for a half-filled lattice and various values of on-site repulsion U , using IQG (top) and $IQGT$ (bottom) conditions.

Fourier transforming $S(r)$ yields the momentum dependent spin-correlation function:

$$S(k) = \sum_r e^{ikr} S(r) = \frac{1}{2} \sum_{k_a k_b} \sum_{k_c k_d} g_{k_a k_b, k_c k_d}^{1k} \quad (48)$$

We have plotted this object in Figs. 8–10 for $\frac{3}{10}$, $\frac{4}{10}$ and half filling respectively, using both IQG as $IQGT$ conditions. Unsurprisingly, a good agreement is observed between the IQG and $IQGT$ results for small values of U . At larger values of U , away from half filling, results are very poor with the IQG conditions, especially in the $\frac{4}{10}$ -filled case, where the correlation function is wildly oscillating. More surprising, is that the spin-correlation function for the half-filled lattice in the large- U limit is also incorrect in the IQG approximation. In the strong-correlation limit, for half-filling, the spin part of the Hubbard model is identical to the Heisenberg model [31], for which the spin-correlation function has a singularity at two times the Fermi momentum $2k_F = \pi$, which is exactly what we see in the $IQGT$ results. Below half-filling the singularity in the large- U limit splits and shifts to smaller values of k , as observed in the $IQGT$ Figs. 8 and 9. This is in agreement with the results in [31,30]. In conclusion we can say that the 2DM obtained with the $IQGT$ conditions, correctly describes the physics that governs the spin-correlation function, whereas the IQG conditions do not. It is also important to note, that even though the IQG results for the energy are good for the half-filled lattice, the 2DM is flawed, because the spin-correlation function is not correctly described.

5. Conclusion

In this article we have studied the one-dimensional Hubbard model at various fillings using the v2DM method with both two- and three-index constraints. We have shown that it is possible to obtain a huge reduction in the computational cost of a basic matrix computation by exploiting all available symmetries, i.e. spin, translation invariance and space-inversion parity. Using this reduction it was possible to compare the computational scaling of different semidefinite programming algorithms with increasing lattice size. We found that, for this particular type of problem, the boundary point method outperforms interior point methods by several orders of magnitude. To gauge the quality of the variationally obtained 2DM we compared several ground-state properties to reference results. We found that, for half filling, the ground-state energy is well described by the two-index conditions. When moving away from half filling, however, we see that the three-index conditions are needed to obtain decent results. An explanation of why this happens has been the subject of a different article [35]. The need for three-index constraints was even more obvious when we looked at the spin and charge correlation functions. It was also seen that, even though the energy was relatively correct for the half-filled lattice, the 2DM was flawed, because the spin correlation function was incorrect. This study shows that the exploitation of symmetry opens the possibility for a study of the two-dimensional Hubbard model for relevant lattice sizes. To obtain a decent accuracy, however, it will be necessary to include the three-index constraints, which is computationally hard. One way around this was set forward in [35] with the use of lifting conditions [16,18].

Acknowledgements

We gratefully acknowledge financial support from FWO-Flanders and the research council of Ghent University. B.V., H.V.A., W.P., S.W. and D.V.N. are Members of the QCMM alliance Ghent-Brussels.

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Paper 3

Variational optimization of the 2DM: approaching three-index accuracy using extended cluster constraints

Variational optimization of the 2DM: approaching three-index accuracy using extended cluster constraints

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Received 23 August 2013 / Received in final form 30 November 2013

Published online 10 March 2014 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2014

Abstract. The reduced density matrix is variationally optimized for the two-dimensional Hubbard model. Exploiting all symmetries present in the system, we have been able to study 6×6 lattices at various fillings and different values for the on-site repulsion, using the highly accurate but computationally expensive three-index conditions. To reduce the computational cost we study the performance of imposing the three-index constraints on local clusters of 2×2 and 3×3 sites. We subsequently derive new constraints which extend these cluster constraints to incorporate the open-system nature of a cluster on a larger lattice. The feasibility of implementing these new constraints is demonstrated by performing a proof-of-principle calculation on the 6×6 lattice. It is shown that a large portion of the three-index result can be recovered using these extended cluster constraints, at a fraction of the computational cost.

1 Introduction

Although the underlying physical laws and mathematical formalism describing many-electron systems are fully understood, solving the associated quantum many-body problem remains a very challenging task. This is because the dimension of the associated Hilbert space increases exponentially with system size. To obtain results for correlated electron systems one therefore resorts to approximate techniques, which try to capture the relevant parts of the physics in the system. This paper deals with variational density matrix optimization (v2DM), a many-body method which removes the wave function from quantum mechanics by replacing it with the two-body reduced density matrix (2DM), at the benefit of having nicer scaling properties. This appealing idea originates from the 1940's with Husimi [1] and was brought to focus by Coleman in his excellent review paper [2]. In subsequent years a lot of effort was put in the formulation of the problem [3,4] and the first numerical calculations were performed [5,6]. However, some disappointing results [7,8] and the computational complexity of the problem caused activity in the field to drop. It was not until Nakata et al. [9] and Mazziotti [10] introduced a numerical technique called semidefinite programming to v2DM, that interest in the field was renewed. Since then a lot of progress has been made, both by developing better algorithms suited to the physics problem at hand [11–14], as well as by increasing the accuracy of the approximation by deriving new

constraints [15–19]. A large variety of systems has been studied using v2DM, mostly atomic and molecular systems [14,16,20–23], but also nuclear [7,8], and spin and lattice systems [14,19,24–27]. Recently it was observed that this standard approach fails to describe the dissociation limit of certain diatomic molecules [28]. This failure was shown to originate from the lack of size-extensivity of the method [18,29], and several ways to cure this behaviour have been set forth [18,30,31].

This paper focuses on how the standard v2DM approach performs for the 2D Hubbard model, and proposes a computationally much cheaper way in which these results can be approximated. It should be noted that the proposed new conditions are approximations to the standard non-negativity constraints, and as such they do not intend to cure the non-size extensivity of the method.

The Hubbard model is a schematic model [32] developed to describe electron correlation in solids by means of the Hamiltonian:

$$\hat{H} = -t \sum_{\langle ij \rangle} (a_{i\sigma}^\dagger a_{j\sigma} + a_{j\sigma}^\dagger a_{i\sigma}) + U \sum_i n_i^\uparrow n_i^\downarrow,$$

with

$$n_i^\sigma = a_{i\sigma}^\dagger a_{i\sigma}, \quad (1)$$

in which the sum $\langle ij \rangle$ goes over nearest neighbouring sites only, and using second-quantized notation where $a_\alpha^\dagger/a_\alpha$ creates/annihilates a fermion in a single-particle state $\alpha = \{i\sigma\}$ with i the lattice label and σ the spin projection ($\sigma = \pm \frac{1}{2}$), see e.g. [33,34]. The 2D version is of particular

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interest because it is thought to exhibit high-temperature superconductivity [35,36]. This simple model has a rich phase diagram and is therefore challenging to solve. This is due to the competition between the delocalizing first term (see Eq. (1)), which allows for hopping from one site to its neighbours, and the second term, which locally repels electrons that are on the same site. A lot of numerical studies have been carried out for this system, using various methods such as quantum Monte Carlo [37], and the density matrix renormalization group (DMRG) [38]. For an excellent overview of numerical studies performed on the 2D Hubbard model, we refer to the review by Scalapino [36]. In spite of all these numerical studies, surprisingly few reference results exist for the ground-state energy on finite size lattices. An earlier v2DM study focussed on the 4×4 lattice and was limited to the half-filled case [39]. In this paper we present results obtained by v2DM with the accurate three-index ($\mathcal{PQGT}'$) conditions (see Sect. 2) on a 6×6 lattice at various fillings and for different values of the on-site repulsion U . In Section 2 we give a short introduction to the general framework behind v2DM, and show how the symmetry present in the model can be exploited to obtain a substantial computational speed up. Subsequently we present and discuss the exact variational *lower bound* results on the 6×6 lattice obtained using the computationally heavy $\mathcal{PQGT}'$ conditions and the much faster but less accurate two-index ($\mathcal{PQG}$) conditions. We compare these with an exact variational *upper bound* obtained through a DMRG framework developed by one of us [40]. In Section 3 we look for a way to recover three-index precision without losing computational efficiency, by imposing three-index constraints on local clusters. In Section 4 we derive new constraints which extend these local cluster constraints in a way that reflects the open-system nature of a cluster. We demonstrate the feasibility of this approach by performing a proof-of-principle calculation imposing a subset of these constraints. It is shown that the computationally very expensive $\mathcal{PQGT}'$ results can be closely approximated by imposing only a limited subset of the extended cluster constraints, at a fraction of the computational cost.

2 Theoretical framework

2.1 Introduction to v2DM

The Hamiltonian of a system interacting in up to two-body terms is:

$$\hat{H}_{\alpha\beta;\gamma\delta} = \sum_{\alpha\beta} t_{\alpha\beta} a_{\alpha}^{\dagger} a_{\beta} + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} V_{\alpha\beta;\gamma\delta} a_{\alpha}^{\dagger} a_{\beta}^{\dagger} a_{\delta} a_{\gamma}, \quad (2)$$

so the expectation value of the energy corresponding to an arbitrary N -particle state $|\Psi^N\rangle$ can be expressed using but the 2DM of that state:

$$E(\Gamma) = \text{Tr } \Gamma H^{(2)} = \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \Gamma_{\alpha\beta;\gamma\delta} H_{\alpha\beta;\gamma\delta}^{(2)}, \quad (3)$$

with the 2DM defined as:

$$\Gamma_{\alpha\beta;\gamma\delta} = \langle \Psi^N | a_{\alpha}^{\dagger} a_{\beta}^{\dagger} a_{\delta} a_{\gamma} | \Psi^N \rangle, \quad (4)$$

and the reduced two-body Hamiltonian:

$$H^{(2)} = \frac{1}{N-1} [\delta_{\alpha\gamma} t_{\beta\delta} - \delta_{\alpha\delta} t_{\beta\gamma} - \delta_{\beta\gamma} t_{\alpha\delta} + \delta_{\beta\delta} t_{\alpha\gamma}] + V_{\alpha\beta;\gamma\delta}. \quad (5)$$

The key idea underpinning v2DM is to use equation (3) to determine the 2DM variationally. Once the approximate ground-state 2DM is found, we can extract all one- and two-body ground-state properties. This approach eliminates the need to reference the exponentially scaling wave function, and requires only the much more compact 2DM. A complication arises because the variation has to be performed over a limited set of 2DM's, i.e. those that are derivable from an ensemble of N -particle wave functions. This is known as the N -representability problem [2]. Using the variational principle and the fact that the set of N -representable 2DM's is convex, one can derive a formal solution to the N -representability problem. This necessary and sufficient condition states that a 2DM is N -representable if and only if

$$\text{Tr } \Gamma H_{\nu}^{(2)} \geq E_0^N(H_{\nu}^{(2)}), \quad (6)$$

for all 2-particle Hamiltonians $H_{\nu}^{(2)}$, with corresponding ground-state energies $E_0^N(H^{(2)})$. These conditions are obviously not practically implementable, but can be used to derive a set of necessary constraints. Consider the class of positive Hamiltonians:

$$\hat{H} = B^{\dagger} B \quad \text{with} \quad B^{\dagger} = \sum_{\alpha\beta} g_{\alpha\beta} a_{\alpha}^{\dagger} a_{\beta}. \quad (7)$$

Inserting this class of Hamiltonians into equation (6) leads to the inequality:

$$\sum_{\alpha\beta\gamma\delta} g_{\alpha\beta} \langle \Psi^N | a_{\alpha}^{\dagger} a_{\beta} a_{\delta}^{\dagger} a_{\gamma} | \Psi^N \rangle g_{\gamma\delta} \geq 0, \quad (8)$$

from which the matrix-positivity condition [3]

$$\mathcal{G}(\Gamma) \succeq 0 \quad \text{with} \quad \mathcal{G}(\Gamma)_{\alpha\beta;\gamma\delta} = \delta_{\beta\delta} \rho_{\alpha\gamma} - \Gamma_{\alpha\delta;\gamma\beta}, \quad (9)$$

follows. In this fashion one can derive two more necessary conditions [2], one is simply the non-negativity condition on the 2DM itself, another requires the non-negativity of:

$$\mathcal{Q}(\Gamma) \succeq 0 \quad \text{with} \quad \mathcal{Q}(\Gamma)_{\alpha\beta;\gamma\delta} = \langle \Psi^N | a_{\alpha} a_{\beta} a_{\delta}^{\dagger} a_{\gamma}^{\dagger} | \Psi^N \rangle. \quad (10)$$

These three combined form the so-called two-index conditions, often referred to as $\mathcal{PQG}$.

Another class of constraints is derived using the positive Hamiltonian [15,20,41]:

$$\hat{H} = B^{\dagger} B + B B^{\dagger}, \quad (11)$$

in which the $B^\dagger$ is a three-body operator. Two conditions are derived in this way:

$$\mathcal{T}_1(\Gamma) \succeq 0 \quad \text{using} \quad B^\dagger = \sum_{\alpha\beta\gamma} t_{\alpha\beta\gamma}^1 a_\alpha^\dagger a_\beta^\dagger a_\gamma^\dagger, \quad (12)$$

and

$$\mathcal{T}_2'(\Gamma) \succeq 0 \quad \text{using} \quad B^\dagger = \sum_{\alpha\beta\gamma} t_{\alpha\beta\gamma}^2 a_\alpha^\dagger a_\beta^\dagger a_\gamma + \sum_{\mu} s_\mu a_\mu^\dagger. \quad (13)$$

These are matrix-positivity constraints on, respectively, three-particle and two-particle-one-hole space, and are referred to as three-index constraints. Enforcing these conditions usually greatly improves the accuracy of the results, but at a considerable computational cost.

v2DM can now be formulated as the following constrained optimization problem:

$$\min_{\Gamma} \text{Tr} \Gamma H^{(2)}, \quad (14)$$

on the condition that

$$\text{Tr} \Gamma = \frac{N(N-1)}{2}, \quad (15)$$

$$\mathcal{L}(\Gamma) \succeq 0 \quad \forall \mathcal{L} \in \{\mathcal{P}, \mathcal{Q}, \mathcal{G}, \mathcal{T}_1, \mathcal{T}_2\}. \quad (16)$$

Because the set of 2DM's over which the optimization is performed is too large, one obtains a variational lower bound to the energy, complementary to variational wave-function techniques where one finds an upper bound.

This problem is an instance of the class of semidefinite programs (SDP). This is a well studied optimization problem for which many algorithms have been developed. A number of these algorithms have been tailored to the specific case of v2DM, and they can be divided into two classes. On the one hand there are the interior-point methods [9,11] which are very robust, but have a slow computational scaling of about $\mathcal{O}(M^{12})$, regardless of when two- and three-index conditions are imposed, where M is the dimension of single-particle space. On the other hand there are first-order algorithms such as the boundary point method [12,42], which have a better scaling of $\mathcal{O}(M^9)$ when the three-index conditions are included, but these do not have the nice convergence properties of the interior point methods. In this study a boundary point method has been used.

2.2 Symmetry adaptation of the constraints

The 2D Hubbard model on a square lattice with periodic boundary conditions (PBC), i.e. the 2D Hubbard model on a torus, has a lot of symmetry. This symmetry can be used to block diagonalize the constraint matrices $\mathcal{L}$, allowing for a reduction of the computational cost of the SDP. Full exploitation of this symmetry allows us to push our calculations to reasonably sized lattices, up to 20×20 when only two-index conditions are imposed, and up to 6×6 with the three-index conditions included. We will impose three different symmetries: spin symmetry, translational invariance and the point-group symmetry of the lattice.

2.2.1 Spin symmetry

The invariance of the Hubbard Hamiltonian under rotations in spin space can be exploited by introducing the spin-averaged ensemble [43]. The $\mathcal{G}$ condition, when defined in a spin-averaged way as:

$$\mathcal{G}(\Gamma)_{ab;cd}^S = \frac{1}{2S+1} \sum_{\mathcal{M}} \langle \Psi^{S\mathcal{M}} | [a_a^\dagger \otimes \tilde{a}_b]^S \times \left([a_c^\dagger \otimes \tilde{a}_d]^S \right)^\dagger | \Psi^{S\mathcal{M}} \rangle, \quad (17)$$

breaks down into four blocks, one $S = 0$ block and three degenerate $S = 1$ blocks. This does not change the scaling of the algorithm, but elementary matrix computations are performed 32 times faster. Analogous results are obtained for the other constraints.

2.2.2 Translational invariance

Because periodic boundary conditions are assumed, the Hamiltonian is invariant under lattice translations in both the x - and y -direction. It is straightforward to exploit this symmetry: by transforming the single-particle basis to quasi-momentum eigenstates:

$$|k_x k_y; \sigma\rangle = \frac{1}{L} \sum_{x,y=1}^L e^{ik_x x} e^{ik_y y} |xy; \sigma\rangle, \quad (18)$$

in which L is the linear dimension of the lattice. The constraint matrices then decompose into blocks with the same two-particle or particle-hole quasi-momentum (K_x, K_y) , e.g. the $S = 0$ part of the $\mathcal{G}$ matrix falls apart in L^2 blocks of dimension L^2 . This *does* change the scaling of the program. Instead of the $\mathcal{O}(L^{12})$ scaling of a matrix multiplication on the $\mathcal{G}$ matrix without translational invariance, we now have a scaling of $\mathcal{O}(L^8)$.

2.2.3 Point group symmetry

The final symmetry we exploit is the point-group symmetry (C_{4v}) of the lattice. Combined with translational invariance this forms the space group $P4mm$. There are three independent transformations which leave the Hamiltonian invariant:

$$|x, y\rangle \rightarrow |-x, y\rangle \quad \text{reflection symmetry in the } x\text{-direction} \quad (19)$$

$$|x, y\rangle \rightarrow |x, -y\rangle \quad \text{reflection symmetry in the } y\text{-direction} \quad (20)$$

$$|x, y\rangle \rightarrow |y, x\rangle \quad \text{reflection symmetry along the diagonal} \quad (21)$$

These operations do not commute with the translation operator, which means they map different (K_x, K_y) blocks in the constraint matrices onto each other. This can be used to reduce the number of blocks we have to store and

Table 1. Ground-state energy per particle for the 4×4 lattice with different fillings. PQG and $PQGT'$ results are compared with exact diagonalization result from references [44,45], and the previous v2DM reference results from [39].

U	$N = 16$					$N = 14$			$N = 10$		
	Exact	$PQGT'$	$PQGT'$ [39]	PQG	PQG [39]	Exact	$PQGT'$	PQG	Exact	$PQGT'$	PQG
4	-0.8514	-0.8607	-0.8607	-0.9343	-0.9341	-1.1246	-1.1486	-1.2664	-1.9581	-1.9595	-2.0106
8	-0.5329	-0.5476	-0.5476	-0.6604	-0.6603	-0.8478	-0.9124	-1.1162	-1.7510	-1.7597	-1.8806
12	-0.3745	-0.3909	*	-0.5054	*	-0.7180	-0.8024	-1.1050	-1.6455	-1.6626	-1.8284
16	-0.2882	-0.30101	*	-0.4073	*	-0.6475	-0.7409	-1.0136	-1.5843	-1.6085	-1.8014

Table 2. Ground-state energy per particle for 6×6 lattice with different fillings and on-site repulsion, obtained with $PQGT'$ conditions, compared with DMRG results for $N = 36, 34$ and 30 .

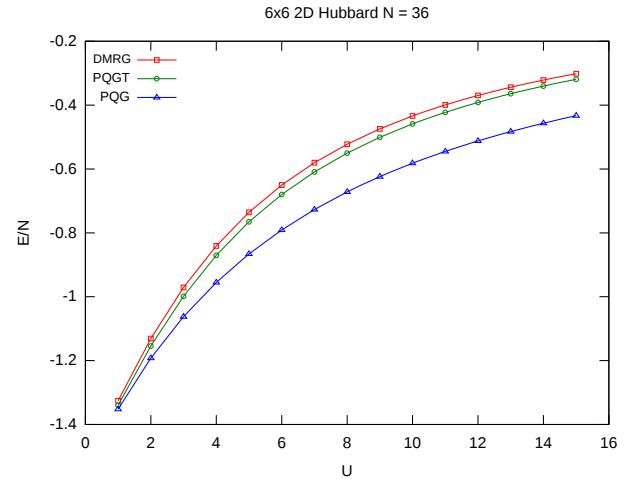
U	$N = 36$		$N = 34$		$N = 30$		$N = 24$	$N = 18$	$N = 12$	$N = 6$
	DMRG	$PQGT'$	DMRG	$PQGT'$	DMRG	$PQGT'$	$PQGT'$	$PQGT'$	$PQGT'$	$PQGT'$
1	-1.3256	-1.3399	-1.4272	-1.4398	-1.6710	-1.6775	-2.0981	-2.5533	-2.9286	-3.3131
2	-1.1310	-1.1543	-1.2396	-1.2646	-1.5036	-1.5194	-1.9720	-2.4606	-2.8716	-3.2976
3	-0.9708	-0.9985	-1.0835	-1.1212	-1.3629	-1.3910	-1.8694	-2.3851	-2.8299	-3.2851
4	-0.8409	-0.8702	-0.9577	-1.0066	-1.2473	-1.2892	-1.7870	-2.3237	-2.7945	-3.2751
5	-0.7356	-0.7654	-0.8555	-0.9145	-1.1540	-1.2094	-1.7212	-2.2738	-2.7602	-3.2664
6	-0.6501	-0.6798	-0.7746	-0.8395	-1.0790	-1.1463	-1.6688	-2.2329	-2.7369	-3.2594
7	-0.5803	-0.6092	-0.7080	-0.7776	-1.0186	-1.0957	-1.6268	-2.1992	-2.7167	-3.2539
8	-0.5226	-0.5504	-0.6538	-0.7261	-0.9697	-1.0546	-1.5926	-2.1711	-2.7000	-3.2498
9	-0.4744	-0.5009	-0.6083	-0.6828	-0.9296	-1.0207	-1.5646	-2.1475	-2.6858	-3.2451
10	-0.4339	-0.4588	-0.5707	-0.6459	-0.8953	-0.9924	-1.5414	-2.1275	-2.6737	-3.2421
11	-0.3994	-0.4228	-0.5388	-0.6144	-0.8671	-0.9686	-1.5217	-2.1104	-2.6632	-3.2382
12	-0.3696	-0.3916	-0.5114	-0.5871	-0.8410	-0.9483	-1.5050	-2.0956	-2.6541	-3.2354
13	-0.3439	-0.3643	-0.4872	-0.5633	-0.8210	-0.9308	-1.4906	-2.0827	-2.6461	-3.2325
14	-0.3214	-0.3405	-0.4671	-0.5424	-0.8036	-0.9157	-1.4780	-2.0715	-2.6390	-3.2305
15	-0.3016	-0.3194	-0.4489	-0.5239	-0.7881	-0.9025	-1.4669	-2.0615	-2.6328	-3.2282

perform calculations on. A problem arises in blocks that are mapped onto themselves by the symmetry operations. For consistency the symmetry then has to be enforced in these blocks by imposing linear constraints on the 2DM during the optimization.

2.3 Reference results

Using the method discussed in Sections 2.1 and 2.2 we have performed ground-state $PQGT'$ calculations for the 6×6 Hubbard model, for different values of on-site repulsion U and at various fillings. For reference, we compare our calculations of the energy per particle number on a 4×4 lattice with exact diagonalization results by Fano et al. [44] and an exact diagonalization program written by one of us [45]. As can be seen in Table 1, the $PQGT'$ results are about 1% below the exact result. As expected, just imposing the PQG constraints does not give satisfactory results. We also compare our v2DM results to those obtained by Anderson et al. in [39], and it is shown that they correspond.

In Table 2 the $PQGT'$ results for the ground-state energy per particle on a 6×6 lattice for different filling factors and on-site repulsion U are given for future reference. They provide rigorous lower bounds on the energy. For the 6×6 lattice with 36, 34 and 30 particles we can compare with a variational upper bound on the energy obtained with a two-site $SU(2) \otimes U(1)$ spin- and particle number-adapted DMRG code developed by one

**Fig. 1.** Ground-state energy per particle as a function of on-site repulsion U for 36 particles on a 6×6 lattice (cf. Tab. 2). DMRG results are compared with v2DM results using $PQGT'$ and PQG conditions.

of us [40], with 7500 reduced renormalized basis states at each boundary. Note that this corresponds to a much larger number of effective renormalized basis states, as in a spin-adapted DMRG code only one basis state per multiplet is retained.

In Figures 1–3 the v2DM results obtained with both the PQG and $PQGT'$ conditions are compared to the

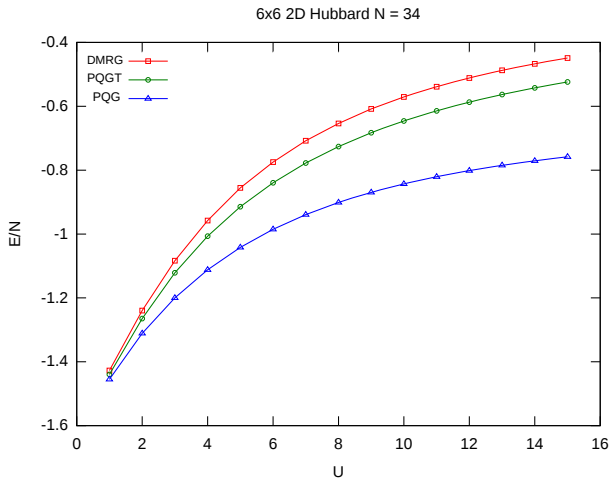


Fig. 2. Ground-state energy per particle as a function of on-site repulsion U for 34 particles on a 6×6 lattice (cf. Tab. 2). DMRG results are compared with v2DM results using $PQGT'$ and PQG conditions.

DMRG results. We notice that for half filling, the $PQGT'$ and DMRG results are very close. PQG results, however, do not follow the same trend and deviate significantly from the other results. This discrepancy becomes even worse when we move away from half filling. There the PQG energies are almost twice the $PQGT'$ results at large values of U . The gap between the upper bound provided by the DMRG results and the lower bound $PQGT'$ results also becomes larger when we dope the lattice. This means that the $PQGT'$ conditions perform worse when the system is more delocalized. The DMRG results also become less accurate when the system is delocalized, but are closer to the exact result. In Appendix an estimate of the error on the DMRG result is made by looking at the relation between the discarded weight and the energy. In the remainder of this paper we look for ways to bridge the gap between the PQG and $PQGT'$ results while avoiding the considerable computational burden that is associated with the three-index constraints.

3 Cluster constraints

As the 2D Hubbard Hamiltonian only connects nearest neighbouring sites, it is reasonable to assume that the local correlations, occurring between adjacent sites, are particularly important. Various many-body methods take advantage of this observation and treat the local degrees of freedom on a higher level than the rest of the system [46–48]. In a related approach we propose to impose the three-index conditions on smaller local clusters of 2×2 or 3×3 sites, while the full system is treated on a PQG level. This means we impose non-negativity only on those blocks of the $\mathcal{T}_1$ and $\mathcal{T}_2'$ matrices for which all single-particle indices are on the local cluster. A problem with imposing these local constraints is that we have to Fourier transform the 2DM back from the quasi-momentum basis to the site basis, which leads to some overhead. However, the matrix

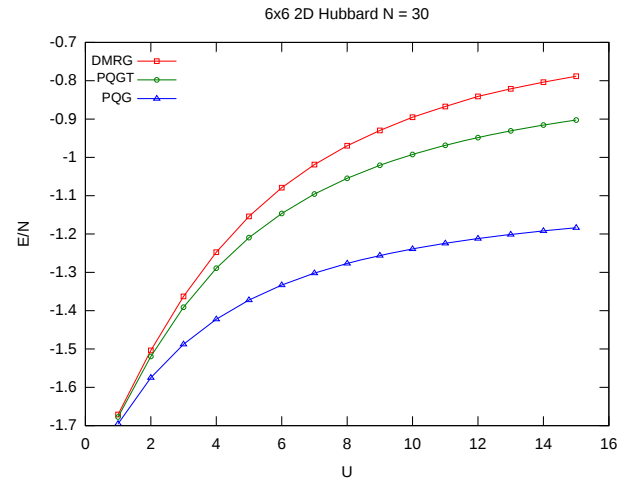


Fig. 3. Ground-state energy per particle as a function of on-site repulsion U for 30 particles on a 6×6 lattice (cf. Tab. 2). DMRG results are compared with v2DM results using $PQGT'$ and PQG conditions.

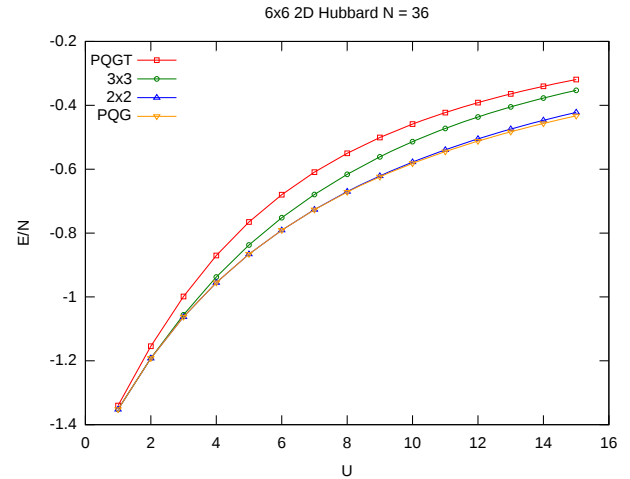


Fig. 4. Ground-state energy per particle as a function of on-site repulsion U for 36 particles on a 6×6 lattice. Results of the three-index constraints imposed on clusters of 2×2 and 3×3 sites compared with the full $PQGT'$ results and PQG results.

computations are the bottleneck of the program, and these become cheaper, since only subcluster matrices are considered. As a result the algorithm runs much faster than the full 6×6 $PQGT'$ calculations. Because translational invariance is still imposed, only one cluster constraint has to be taken into account. In Figures 4–6 it is shown what the improvement upon PQG is when implementing the three-index constraints on clusters of 2×2 and 3×3 sites. The 2×2 clusters seem to be too small, and the constraints only become active for larger values of on-site repulsion U . At half filling the three-index constraints on 3×3 clusters do a decent job, they bridge about half of the gap between PQG and $PQGT'$. For 34 particles the performance is similar, whereas for 30 particles the result gets slightly worse, but the cluster constraints still manage to

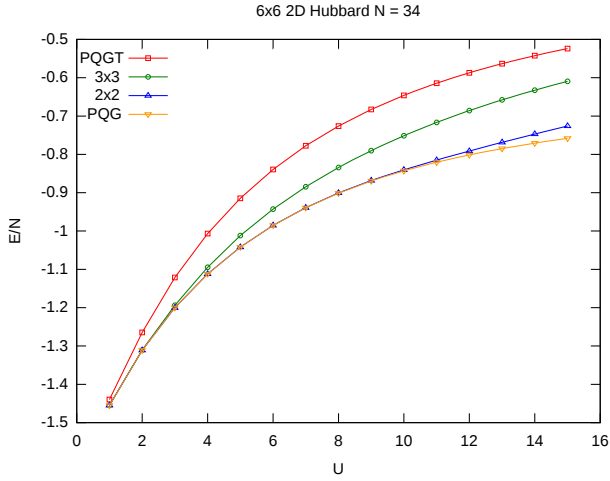


Fig. 5. Ground-state energy per particle as a function of on-site repulsion U for 34 particles on a 6×6 lattice. Results of the three-index constraints imposed on clusters of 2×2 and 3×3 sites compared with the full $PQGT'$ results and PQG results.

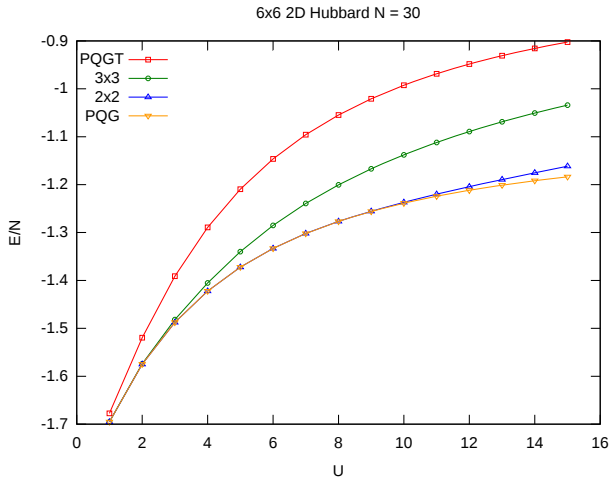


Fig. 6. Ground-state energy per particle as a function of on-site repulsion U for 30 particles on a 6×6 lattice. Results of the three-index constraints imposed on clusters of 2×2 and 3×3 sites compared with the full $PQGT'$ results and PQG results.

recover a substantial part of the correlation. This decrease in accuracy when moving away from half filling is not surprising, because one would not expect local constraints to be as effective in more delocalized systems.

In fact it is a bit naive to impose the three-index constraints on clusters, because one implicitly assumes that the subsystem is a closed system, i.e. that particle number is conserved on the cluster. The full Hamiltonian (1), however, allows for the hopping of particles between the cluster and the rest of the system. We have access to the full system 2DM, which contains all the information about the communication between the cluster and the rest of the system. This observation suggests that there must be a way to extend the three-index cluster constraints to include the open system characteristics of the cluster, using

the full system 2DM. In the next section we derive new constraints which do exactly that, and we demonstrate the feasibility of the approach by implementing them in a proof-of-principle calculation.

4 Extended cluster constraints

4.1 The extended $\mathcal{T}_1$ constraint: $e\mathcal{T}_1$

To simplify the presentation, the constraints are derived in a spin-uncoupled form. The actual implementation of the constraints, however, was performed in a spin-coupled fashion. This changes nothing to the generality of the derived conditions or to the quality of the obtained results. As explained in Section 2 the $\mathcal{T}_1$ condition is derived by demanding the non-negativity of the class of Hamiltonians:

$$\hat{H} = \{B^\dagger, B\}, \quad \text{where} \quad B^\dagger = \sum_{\alpha\beta\gamma} t_{\alpha\beta\gamma}^\dagger a_\alpha^\dagger a_\beta^\dagger a_\gamma^\dagger. \quad (22)$$

When we limit the $\mathcal{T}_1$ condition to a cluster we impose the non-negativity of a subclass of Hamiltonians generated by the three-particle operator:

$$B^\dagger = \sum_{abc} t_{abc}^\dagger a_a^\dagger a_b^\dagger a_c^\dagger, \quad (23)$$

in which Latin indices a are used to denote cluster states, overlined Latin indices $\bar{a}$ to denote the rest of the system and Greek indices α for general states. A better approximation to the full system $B^\dagger$ is obtained if one allows one or two creation operators to be outside the cluster:

$$B^\dagger = \sum_{abc} t_{abc}^\dagger a_a^\dagger a_b^\dagger a_c^\dagger + \sum_{ab\bar{c}} t_{ab\bar{c}}^\dagger a_a^\dagger a_b^\dagger a_{\bar{c}}^\dagger + \sum_{\bar{a}bc} t_{\bar{a}bc}^\dagger a_{\bar{a}}^\dagger a_b^\dagger a_c^\dagger. \quad (24)$$

In this way it is clear that the hopping in and out of the cluster is included. However, we want to construct a condition which only depends on the cluster indices. This can be accomplished by factorizing the terms in equation (24) which contain both cluster and non-cluster indices:

$$t_{ab\bar{c}}^\dagger = x_{ab} p_{\bar{c}}, \quad (25)$$

$$t_{\bar{a}bc}^\dagger = g_{\bar{a}\bar{b}} z_c. \quad (26)$$

The new $B^\dagger$ operator only depends on cluster indices, a one-particle ($p^\dagger = \sum_{\bar{c}} p_{\bar{c}} a_{\bar{c}}^\dagger$) and a two-particle state ($g^\dagger = \sum_{\bar{a}\bar{b}} g_{\bar{a}\bar{b}} a_{\bar{a}}^\dagger a_{\bar{b}}^\dagger$) outside of the cluster:

$$B^\dagger = \sum_{abc} t_{abc}^\dagger a_a^\dagger a_b^\dagger a_c^\dagger + \sum_{ab} x_{ab} a_a^\dagger a_b^\dagger p^\dagger + \sum_c z_c g^\dagger a_c^\dagger. \quad (27)$$

With this $B^\dagger$, a new cluster constraint can be constructed, containing the three-index $\mathcal{T}_1$ and extending it with two- and one-index terms:

$$\left(\begin{array}{ccc} (\mathcal{T}_1)_{abc;dez} & X(p)_{abc;st} & Z(g)_{abc;v} \\ X^\dagger(p)_{mn;dez} & X^{(2)}(p)_{mn;st} & (XZ)(p, g)_{mn;v} \\ Z^\dagger(g)_{u;dez} & (XZ)^\dagger(p, g)_{u;st} & Z^{(2)}(g)_{u;v} \end{array} \right) \geq 0, \quad (28)$$

$$\begin{pmatrix} (\mathcal{T}_2)_{abc;dez} & P_{abc;w} & X(h)_{abc;st} & Y(p)_{abc;pq} & Z(g)_{abc;v} & R(d)_{abc;l} \\ P_{r;dez}^\dagger & P_{r;w}^{(2)} & PX(h)_{r;st} & PY(p)_{r;pq} & PZ(g)_{r;v} & PR^\dagger(d)_{r;l} \\ X^\dagger(h)_{mn;dez} & PX^\dagger(h)_{mn;w} & X^{(2)}(h)_{mn;st} & XY(h,p)_{mn;pq} & XZ(h,g)_{mn;v} & XR(h,d)_{mn;l} \\ Y^\dagger(p)_{xy;dez} & PY^\dagger(p)_{xy;w} & XY^\dagger(h,p)_{xy;st} & Y^{(2)}(p)_{xy;pq} & YZ(p,g)_{xy;v} & YR(p,d)_{xy;l} \\ Z^\dagger(g)_{u;dez} & PZ^\dagger(g)_{u;w} & XZ^\dagger(h,g)_{u;st} & YZ^\dagger(p,g)_{u;pq} & Z^{(2)}(g)_{u;v} & ZR(g,d)_{u;l} \\ R^\dagger(d)_{k;dez} & PR^\dagger(d)_{k;w} & XR^\dagger(h,d)_{k;st} & YR^\dagger(p,d)_{k;pq} & ZR^\dagger(g,d)_{k;v} & R^{(2)}(d)_{k;l} \end{pmatrix} \succeq 0 \quad (37)$$

where the different tensors are defined as:

$$X(p)_{abc;st} = \langle a_a^\dagger a_b^\dagger a_c^\dagger p a_t a_s + p a_t a_s a_a^\dagger a_b^\dagger a_c^\dagger \rangle, \quad (29)$$

$$Z(g)_{abc;v} = \langle a_a^\dagger a_b^\dagger a_c^\dagger a_v g + a_v g a_a^\dagger a_b^\dagger a_c^\dagger \rangle, \quad (30)$$

$$X^{(2)}(p)_{mn;st} = \langle a_m^\dagger a_n^\dagger p^\dagger p a_t a_s + p a_t a_s a_m^\dagger a_n^\dagger p^\dagger \rangle, \quad (31)$$

$$XZ(p,g)_{mn;v} = \langle a_m^\dagger a_n^\dagger p^\dagger a_v g + a_v g a_m^\dagger a_n^\dagger p^\dagger \rangle, \quad (32)$$

$$Z^{(2)}(g)_{u;v} = \langle g^\dagger a_u^\dagger a_v g + a_v g g^\dagger a_u^\dagger \rangle. \quad (33)$$

All these extra terms can be constructed using the full system 2DM and the knowledge of some predefined one- and two-particle states p and g outside the cluster.

4.2 The extended $\mathcal{T}'_2$ constraint: $e\mathcal{T}'_2$

In an analogous way as for the $\mathcal{T}_1$ we can construct extensions which include cluster-system information to the $\mathcal{T}'_2$ condition. The two-particle-one-hole operator which constructs the full system $\mathcal{T}'_2$ (see Eq. (13)) can be approximated on the cluster by:

$$\begin{aligned} B^\dagger = & \sum_{abc} t_{abc}^2 a_a^\dagger a_b^\dagger a_c + \sum_m s_m a_m^\dagger + \sum_{ab} x_{ab} a_a^\dagger a_b^\dagger h \\ & + \sum_{bc} y_{bc} p^\dagger a_b^\dagger a_c + \sum_c z_c g^\dagger a_c + \sum_a r_a a_a^\dagger d^\dagger, \end{aligned} \quad (34)$$

in which the different states outside the cluster are defined as:

$$h = \sum_{\bar{c}} h_{\bar{c}} a_{\bar{c}}, \quad p^\dagger = \sum_{\bar{a}} p_{\bar{a}} a_{\bar{a}}^\dagger, \quad (35)$$

$$g^\dagger = \sum_{\bar{a}\bar{b}} g_{\bar{a}\bar{b}} a_{\bar{a}}^\dagger a_{\bar{b}}^\dagger, \quad d^\dagger = \sum_{\bar{b}\bar{c}} d_{\bar{b}\bar{c}} a_{\bar{b}}^\dagger a_{\bar{c}}^\dagger. \quad (36)$$

As before this leads to a new non-negativity constraint which includes the old $\mathcal{T}'_2$ on the cluster and extends it with four new terms.

(See equation (37) above)

in which the extra tensor terms are defined as:

$$X(h)_{abc;st} = \langle a_a^\dagger a_b^\dagger a_c^\dagger h^\dagger a_t a_s + h^\dagger a_t a_s a_a^\dagger a_b^\dagger a_c^\dagger \rangle,$$

$$Y(p)_{abc;pq} = \langle a_a^\dagger a_b^\dagger a_c^\dagger a_p p + a_p^\dagger a_p p a_a^\dagger a_b^\dagger a_c^\dagger \rangle,$$

$$Z(g)_{abc;v} = \langle a_a^\dagger a_b^\dagger a_c^\dagger a_v g + a_v^\dagger g a_a^\dagger a_b^\dagger a_c^\dagger \rangle,$$

$$R(d)_{abc;l} = \langle a_a^\dagger a_b^\dagger a_c^\dagger d a_l + d a_l a_a^\dagger a_b^\dagger a_c^\dagger \rangle,$$

$$X^{(2)}(h)_{mn;st} = \langle a_m^\dagger a_n^\dagger h h^\dagger a_t a_s + h^\dagger a_t a_s a_m^\dagger a_n^\dagger h \rangle,$$

$$XY(h,p)_{mn;pq} = \langle a_m^\dagger a_n^\dagger h a_p^\dagger a_q p + a_p^\dagger a_q p a_m^\dagger a_n^\dagger h \rangle,$$

$$XZ(h,g)_{mn;v} = \langle a_m^\dagger a_n^\dagger h a_v^\dagger g + a_v^\dagger g a_m^\dagger a_n^\dagger h \rangle,$$

$$XR(h,d)_{mn;l} = \langle a_m^\dagger a_n^\dagger h d a_l + d a_l a_m^\dagger a_n^\dagger h \rangle,$$

$$XP(h)_{mn;w} = \langle a_m^\dagger a_n^\dagger h a_w \rangle,$$

$$Y^{(2)}(p)_{xy;pq} = \langle p^\dagger a_x^\dagger a_y a_q^\dagger a_p p + a_q^\dagger a_p p p^\dagger a_x^\dagger a_y \rangle$$

$$YZ(p,g)_{xy;v} = \langle p^\dagger a_x^\dagger a_y a_v^\dagger g + a_v^\dagger g p^\dagger a_x^\dagger a_y \rangle,$$

$$YR(p,d)_{xy;v} = \langle p^\dagger a_x^\dagger a_y d a_l + d a_l p^\dagger a_x^\dagger a_y \rangle$$

$$YP(p)_{xy;w} = \langle p^\dagger a_x^\dagger a_y a_w \rangle,$$

$$Z^{(2)}(g)_{u;v} = \langle g^\dagger a_u a_v g + a_v g g^\dagger a_u \rangle$$

$$ZR(g,d)_{u;l} = \langle g^\dagger a_u d a_l + d a_l g^\dagger a_u \rangle,$$

$$ZP(g)_{u;w} = \langle g^\dagger a_u a_w \rangle,$$

$$R^{(2)}(d)_{k;l} = \langle a_k^\dagger d^\dagger d a_l + d a_l a_k^\dagger d^\dagger \rangle,$$

$$RP(d)_{k;w} = \langle a_k^\dagger d^\dagger a_w \rangle.$$

which can all be constructed using the full system 2DM and the different states (h, p, g and d) outside the cluster.

4.3 Finding the optimal constraint

In Sections 4.1 and 4.2 we derived new constraints which include and extend the three-index constraints imposed on local clusters on the lattice. These new constraints depend on states defined outside of the cluster, giving rise to additional complications. In this section we explore a method to choose these states, optimizing the class of positive Hamiltonians generated by equations (27) and (34) to make the constraints as strict as possible. In what follows we limit ourselves to the extended constraints with only one index outside of the cluster, i.e. for the $e\mathcal{T}_1$ there is only the dependence on the single-particle state p , whereas the $e\mathcal{T}'_2$ depends on the single-hole state h and the single-particle state p .

The problem we discuss is the following: given a 2DM Γ from some previous calculation, for what state p , outside of the cluster, is the $e\mathcal{T}_1(\Gamma)$ constraint maximally violated. We have chosen to define the most violated constraint as the $e\mathcal{T}_1$ which has the lowest eigenvalue, i.e. we optimize the following cost function:

$$\phi^{e\mathcal{T}_1}(p) = \lambda_0^{e\mathcal{T}_1}(p) + \mu(|p|^2 - C)^2, \quad (38)$$

as a function of the single-particle state p , in which μ scales the quadratic potential that makes sure the p vector is normalized, and $\lambda_0^{e\mathcal{T}_1}(p)$ is the lowest eigenvalue of the $e\mathcal{T}_1$ matrix for the current value of the state p . The gradient of this cost function can be evaluated analytically using the Hellman-Feynman theorem [49]:

$$\frac{\partial \lambda_0^{e\mathcal{T}_1}}{\partial p_{\bar{z}}} = \langle \Psi_0 | \left(\frac{\partial e\mathcal{T}_1(p)}{\partial p_{\bar{z}}} \right) | \Psi_0 \rangle,$$

with

$$e\mathcal{T}_1(\Gamma)|\Psi_0\rangle = \lambda_0^{e\mathcal{T}_1}|\Psi_0\rangle. \quad (39)$$

The cost function can then be optimized using a simple non-linear conjugate gradient algorithm [50]. For the construction of an efficient conjugate gradient algorithm it is essential to have a fast evaluation of the lowest eigenvalue and eigenvector of the constraint with a certain state p . This can be achieved because the largest block, the $\mathcal{T}_1$ on the cluster, remains unchanged during the optimization. If we prediagonalize the large block on the cluster, we need a fast method to solve the following problem:

$$\begin{bmatrix} \lambda_1 & 0 & \dots & 0 & b_{11} & \dots & b_{1m} \\ 0 & \lambda_2 & \dots & 0 & b_{21} & \dots & b_{2m} \\ & & \ddots & & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \lambda_n & b_{n1} & \dots & b_{nm} \\ b_{11} & b_{21} & \dots & b_{n1} & d_{11} & \dots & d_{1m} \\ \vdots & \vdots & \dots & \vdots & \vdots & \dots & \vdots \\ b_{1m} & b_{2m} & \dots & b_{nm} & d_{m1} & \dots & d_{mm} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \\ y_1 \\ \vdots \\ y_m \end{bmatrix} = \epsilon \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \\ y_1 \\ \vdots \\ y_m \end{bmatrix}, \quad (40)$$

in which the b and d coefficients represent the extensions to the cluster constraint, which depend on the variable p , the λ_i 's are the precalculated eigenvalues of the $\mathcal{T}_1$ on the cluster, and ϵ is the lowest eigenvalue of the total matrix. This leads to $n + m$ linear equations:

$$\lambda_i x_i + \sum_{j=1}^m b_{ij} y_j = \epsilon x_i \quad \text{for } i = 1 \dots n, \quad (41)$$

$$\sum_{i=1}^n b_{ij} x_i + \sum_j d_{ij} y_i = \epsilon y_j \quad \text{for } j = 1 \dots m. \quad (42)$$

From the first n equations the x_i 's can be eliminated and expressed as a function of the y 's:

$$x_i = \frac{1}{\epsilon - \lambda_i} \sum_{k=1}^m b_{ik} y_k. \quad (43)$$

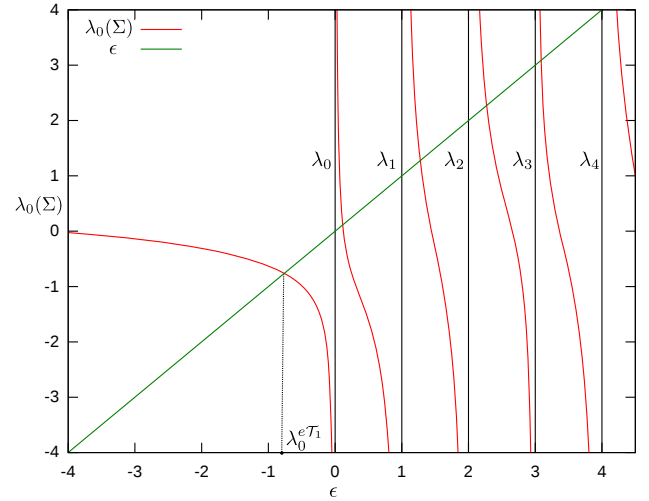


Fig. 7. Illustration of the self-consistent eigenvalue problem (44). The solution is found when the lowest eigenvalue of $\Sigma(\epsilon)$ ($\lambda_0(\Sigma)$) equals ϵ . The black vertical lines are poles in $\Sigma(\epsilon)$ and correspond to the precalculated eigenvalues of the $\mathcal{T}_1$ matrix on the cluster.

When this is substituted into the remaining m equations we get the following self-consistent eigenvalue problem:

$$\sum_{k=1}^m \Sigma(\epsilon)_{jk} y_k = \epsilon y_j, \quad \text{for } j = 1 \dots m,$$

with

$$\Sigma(\epsilon)_{jk} = \sum_{i=1}^n \frac{b_{ij} b_{ik}}{\epsilon - \lambda_i} + d_{kj}. \quad (44)$$

These equations can be solved easily and quickly using the bisection method. As shown in Figure 7, the lowest eigenvalue of the full matrix $\lambda_0^{e\mathcal{T}_1}$ is always below the lowest eigenvalue of the block matrix (the black vertical lines). This means one can easily bracket the lowest eigenvalue $\lambda_0^{e\mathcal{T}_1}$ and improve the approximation to it using the bisection method at the cost of just a couple of diagonalizations of an $m \times m$ matrix.

4.4 Results

The procedure introduced in Section 4.3 has been applied to optimize the p state for $e\mathcal{T}_1$, and the p and h states for the $e\mathcal{T}'_2$ condition. In Figures 8 and 9 we show the percentage of the gap between the results obtained by imposing only $\mathcal{PQG}$ constraints and the full $\mathcal{PQGT}'$ result that has been recovered by the addition of the pure cluster constraints, and the improvement caused by imposing the extended cluster constraints with optimized non-cluster states. For the 2×2 constraints one sees that, whereas the original cluster constraints have little to no effect, the extended constraints are active and improve the result. The extensions on the 3×3 cluster improve the result significantly for lower values of U , where the pure cluster

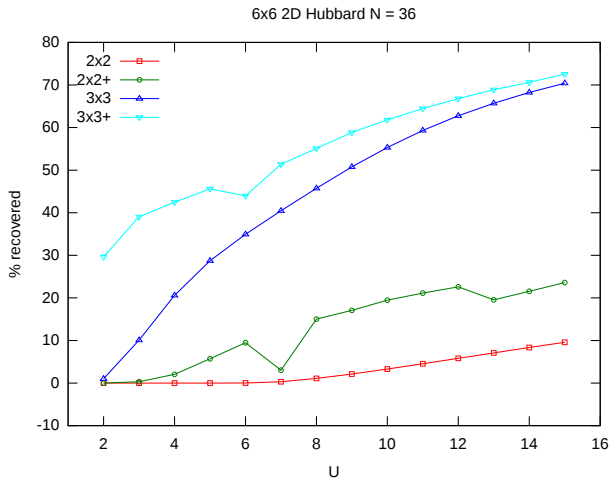


Fig. 8. Percentage of the gap between the PQG and the $PQGT'$ results recovered by the addition of the pure and extended cluster constraints with optimized non-cluster states p and h . For the 6×6 Hubbard model at half filling.

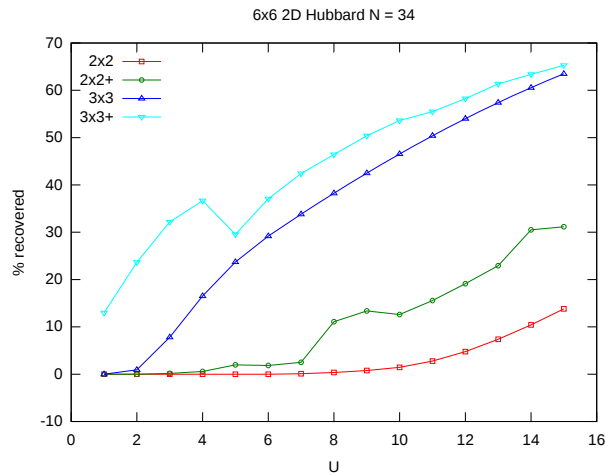


Fig. 9. Percentage of the gap between the PQG and the $PQGT'$ results recovered by the addition of the pure and extended cluster constraints with optimized non-cluster states p and h . For the 6×6 Hubbard model with 34 particles.

constraints perform poorly. At higher values of U they still enhance the result, although the pure cluster constraints already do a good job. We notice that the improvements are discontinuous as a function of U . This is probably a manifestation of the fact that the cost function is not convex, and the conjugate gradient algorithm ends up in different local optima for various U -values.

5 Conclusion and outlook

In this paper the ground-state energy of the 2D Hubbard model has been calculated using the v2DM method. Results have been obtained using the accurate $PQGT'$ conditions for lattices up to 6×6 at different fillings. Hereby a rigorous variational *lower bound* is obtained which can be used as a reference for future calculations in combination

with the *upper bound* obtained by the DMRG algorithm. Imposing the three-index constraints gives results that are of a significant better quality than imposing just the two-index conditions, but at a computational cost which prevents us from scaling to larger lattice sizes. We have therefore imposed the three-index conditions on local clusters of 2×2 and 3×3 sites, in an attempt to capture the relevant local correlation at the three-index level while avoiding the computational cost of the full $PQGT'$ conditions. This worked reasonably well provided the cluster size was large enough. However, imposing these constraints is equivalent to treating the cluster as a closed system, whereas the cluster subsystem should rather be treated as an open system, including communication between the subsystem and the rest of the system. This observation led us to derive new constraints, which take the open-system nature into account, and are dependent on states outside of the cluster. We have shown how to choose these states by performing an eigenvalue optimization, which can be done efficiently using a conjugate gradient algorithm. The results of these proof-of-principle calculations show that adding a limited set of the extended cluster constraints already improve the quality of the results substantially. The increase in accuracy was largest where the pure cluster constraints failed to recover a large part of the difference between PQG and $PQGT'$. The improvements brought about by imposing these extended constraints come at a very small additional computational cost.

In this paper we have set forth the new conditions, and implemented a proof-of-principle example. There are, however, many improvements that can be made. A first point is that the constraint depends on our choice for the cost function. There is no guarantee that the constraint with the lowest eigenvalue will lead to the largest increase in energy when imposed. We have seen that local minima occur, because our cost function is non-linear, so the conjugate gradient algorithm is bound to get stuck there. Using a Monte Carlo optimization of the function, a global optimum of the cost function might be found. In this discussion we have limited ourselves to single states outside of the cluster. It can be expected, however, that multiple orthogonal states will provide better results. If we allowed two states outside the cluster, the $e\mathcal{T}_1$ would be constructed using the operator:

$$B^\dagger = \sum_{abc} t_{abc}^1 a_a^\dagger a_b^\dagger a_c^\dagger + \sum_{ab} x_{ab}^1 a_a^\dagger a_b^\dagger p^\dagger + \sum_{ab} x_{ab}^2 a_a^\dagger a_b^\dagger p_\perp^\dagger, \quad (45)$$

which leads to another quadratic addition in the $\mathcal{T}_1$ matrix. If more and more terms of this sort are added one should converge to the full $PQGT'$ result. Of course, the hope is that convergence is achieved by adding just a few states.

For the proof-of-principle calculations a limited set of the extended constraints have been used, namely those that have one-particle terms outside of the cluster. It is likely that correlations that include two-particle and particle-hole terms outside of the cluster are important, and that adding those would improve the result considerably.

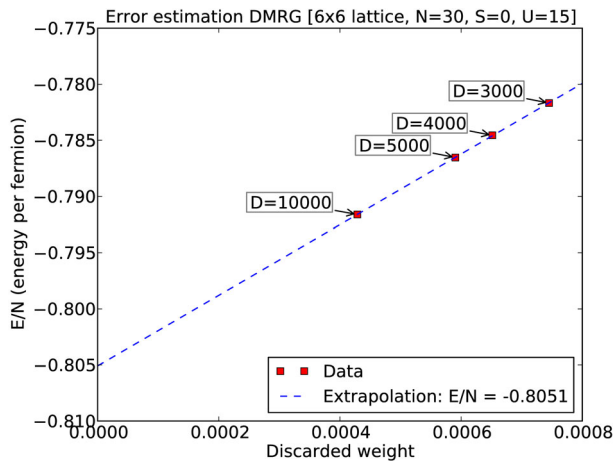


Fig. A.1. Rough estimate of the true ground state energy for the 6×6 lattice, filled with $N = 30$ fermions, in the $S = 0$ singlet state, with the on-site repulsion $U = 15$. The estimate is based on a linear extrapolation between the discarded weight and the obtained variational energy, for several DMRG calculations using different values of reduced renormalized basis states D .

As a final note we mention that these constraints are general and not limited to the 2D Hubbard model. They can be used in molecular calculations as an active space method to include three-index conditions on a limited space to recover a portion of the $PQGT'$ result without the heavy computational burden.

We gratefully acknowledge financial support from FWO-Flanders and the research council of Ghent University. S.W. has a PhD fellowship from the FWO-Flanders. S.D.B and B.V. are post-doctoral fellows of the FWO-Flanders. The authors are Members of the QCMM alliance Ghent-Brussels.

Appendix: Error estimation of the DMRG results

Underlying the DMRG algorithm is the class of matrix product state wavefunctions. The minimal energy encountered during a DMRG sweep is therefore a variational upper bound to the exact ground state energy. This energy can be improved by increasing the number of retained renormalized basis states. To allow for an extrapolation to the true ground state energy, a linear relationship between the so-called discarded weight and the energy has been advocated [51–53]. For several numbers of retained renormalized basis states, the maximal discarded weight and the minimal variational energy obtained from the last (converged) sweep are plotted. A linear fit then allows to obtain a rough estimate for the true ground state energy.

For the 6×6 lattice, filled with $N = 30$ fermions, in the $S = 0$ singlet state, with the on-site repulsion $U = 15$, the v2DM and the DMRG results deviate the most in Table 2. For this case, we have tried to obtain a rough estimate for the exact ground state energy in Figure A.1, with the

method described above. Note that D is the number of *reduced* renormalized basis states which are retained during the sweeps. The true ground state energy estimation for $N = 30$ and $U = 15$ allows to attribute 15% of the corresponding v2DM-DMRG gap to DMRG and 85% to v2DM.

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Paper 4

Variational Optimization of the Second-Order Density Matrix Corresponding to a Seniority-Zero Configuration Interaction Wave Function

Variational Optimization of the Second-Order Density Matrix Corresponding to a Seniority-Zero Configuration Interaction Wave Function

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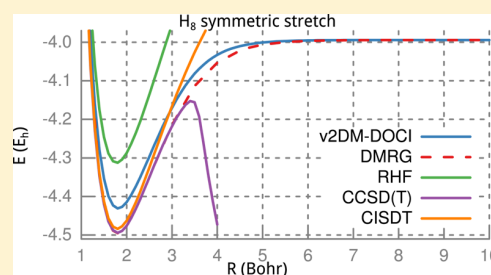
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Supporting Information

ABSTRACT: We perform a direct variational determination of the second-order (two-particle) density matrix corresponding to a many-electron system, under a restricted set of the two-index N -representability $\mathcal{P}$ -, $\mathcal{Q}$ -, and $\mathcal{G}$ -conditions. In addition, we impose a set of necessary constraints that the two-particle density matrix must be derivable from a doubly occupied many-electron wave function, i.e., a singlet wave function for which the Slater determinant decomposition only contains determinants in which spatial orbitals are doubly occupied. We rederive the two-index N -representability conditions first found by Weinhold and Wilson and apply them to various benchmark systems (linear hydrogen chains, He, N₂, and CN⁻). This work is motivated by the fact that a doubly occupied many-electron wave function captures in many cases the bulk of the static correlation. Compared to the general case, the structure of doubly occupied two-particle density matrices causes the associated semidefinite program to have a very favorable scaling as L^3 , where L is the number of spatial orbitals. Since the doubly occupied Hilbert space depends on the choice of the orbitals, variational calculation steps of the two-particle density matrix are interspersed with orbital-optimization steps (based on Jacobi rotations in the space of the spatial orbitals). We also point to the importance of symmetry breaking of the orbitals when performing calculations in a doubly occupied framework.



1. INTRODUCTION

The main problem in many-body quantum mechanics, which comprises nuclear physics, quantum chemistry, and condensed matter physics, is the exponential increase in the dimension of the Hilbert space with the number of particles. Of course, a complete diagonalization in many-electron space, Full Configuration Interaction (FullCI), will provide the exact answer but is prohibitively expensive except for small systems.¹ The challenge has therefore been to develop approximate methods capturing the relevant degrees of freedom in the system without an excessive computational cost, i.e., with a polynomial increase.

Many approximate methods have been developed over the years.^{1,2} A standard approach is to start from a mean-field (Hartree–Fock) solution and improve on this by adding excitations of increasing complexity (Coupled Cluster Theory,^{3,4} Perturbation Theory,⁴ etc.). These single-reference methods only work well when the wave function is dominated by a single Slater determinant. In bond-breaking processes, for example, the Hartree–Fock (HF) approximation is qualitatively wrong and a multi-reference approximation is needed.⁵ In Multiconfiguration

Self-Consistent Field (MCSCF),^{1,6} one expands the wave function as a linear combination of Slater determinants (configurations), and the Configuration Interaction (CI) coefficients and the orbitals building the Slater determinants are optimized together.

In the last decades, new methods for strongly correlated systems were developed. The Density Matrix Renormalization Group (DMRG)^{7–10} can be made as accurate as FullCI while extending the computational limits far beyond what is possible with classical FullCI. Projected symmetry-broken Hartree–Fock^{11–13} is a mean-field scaling method in which all symmetries are broken. While it is difficult to recover symmetries once they are lost, a self-consistent variation-after-projection technique can overcome these issues.¹⁴

Another technique which has received renewed interest is Doubly-Occupied Configuration Interaction (DOCI).^{15–20} In DOCI, all spatial orbitals are doubly occupied by two (spin-up/down) electrons. This is also called a seniority-zero wave function,

Received: April 22, 2015

Published: July 6, 2015

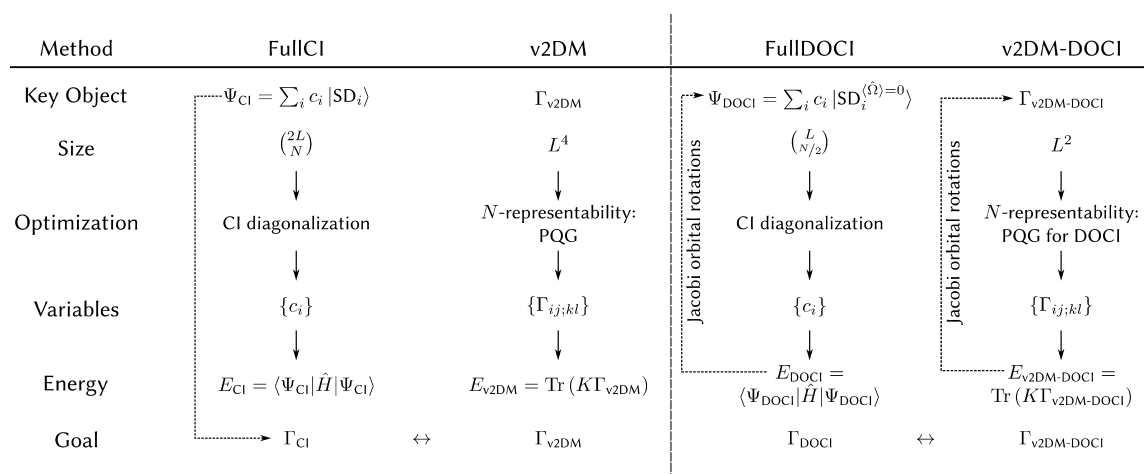


Figure 1. Overview of the methods used in this paper. SD denotes a Slater determinant, Γ is the two-particle density matrix, and K the associated reduced Hamiltonian. $\hat{\Omega}$ is the seniority-number operator.

where the seniority number equals the number of unpaired electrons.^{15,21,22} FullDOCI is an exact diagonalization of the Hamiltonian (like FullCI), but in the Hilbert space restricted to Slater determinants where every spatial orbital is doubly occupied or empty. However, FullDOCI still suffers from factorial scaling. The interest in DOCI is motivated by its ability to describe the static correlation.^{15,23} It was also realized that DOCI is the lowest rung on the ladder in a seniority hierarchy leading to FullCI.^{24,25} If one adds configurations of higher seniority (2, 4, ...) in the wave function expansion, one will eventually reach the FullCI limit.^{15,25} Furthermore, the chemical relevance of this approach is supported by the fact that General Valence Bond with perfect pairing is a special case of DOCI.¹⁹ An efficient and low-scaling approximation to DOCI is available, the so-called AP1roG (antisymmetric product of 1-reference-orbital geminals)^{16,18,19} or pair-Coupled Cluster Doubles^{17,20} (which are equivalent). However, like any truncated CI wave function, DOCI is orbital dependent^{15,23,24} and approximations such as AP1roG need an orbital optimizer. This leads to a deterioration of the scaling.

In the present paper, we focus on an alternative way to approximate the ground state of an N -electron system, where we dispense with the wave function altogether and concentrate on the two-particle density matrix (2DM).^{26,27} The 2DM contains all relevant information, such as all expectation values of two-particle operators, but its dimension only scales as L^4 , with L the dimension of spatial orbital space. Unlike the Density (Matrix) functional theory, the energy can be expressed as an exact yet simple linear function of the 2DM, and a variational optimization can be used to find the ground-state energy (v2DM)²⁸ where the optimization should be constrained to the class of 2DMs^{29,30} that can be derived from an antisymmetric wave function, the so-called N -representable 2DMs. The wave function is not used in this method, and we directly start from a 2DM. The burden is shifted to the characterization of the N -representable class of 2DMs. Since the complete characterization is known to be a QMA complete problem,³¹ one has to use a set of necessary but not (in general) sufficient conditions on the 2DM. The role of the necessary N -representability conditions is to enforce that the resulting 2DM approximates a wave function derivable 2DM as best as possible. Since the minimization of the energy is carried out over a too large a set, one obtains lower bounds to the exact energy.³⁰

The most commonly used conditions are derived from positive semidefinite Hamiltonians and express the fact that their expectation value in any wave function should be positive. Examples are the standard $\mathcal{P}$, $\mathcal{Q}$, and $\mathcal{G}$ two-index conditions^{30,32} and the $\mathcal{T}_1$ and $\mathcal{T}_2$ three-index conditions.³³ Other kinds of conditions exist, such as subsystem constraints³⁴ or active-space constraints.³⁵ The resulting constrained optimization problem is known as a semidefinite program (SDP). This is a well-known class of convex optimization problems^{36–38} for which a large collection of solvers exists.³⁹ We created a SDP solver tailored to v2DM;^{40–48} for the two-index conditions, basic matrix operations exhibit a scaling of $(2L)^6$ and for the three-index conditions, $(2L)^9$. Unfortunately, on the whole, the v2DM approach is not competitive with, for example, CCSD methods.^{49,50}

In this paper, we aim to study the 2DM variational optimization restricted to DOCI space, henceforth called v2DM-DOCI. In Figure 1, we give an overview of all the relevant methods. We impose necessary conditions that the wave function from which the 2DM was derived has the form of a DOCI wave function. This greatly simplifies the structure of the 2DM^{51,52} and leads to much better scaling. We need an orbital optimization scheme, which is far from trivial as the energy landscape contains a large number of local minima, many very close to or even degenerate with the ground-state energy.²⁴ The same problem is also encountered in MCSCF^{53,54} and the Valence Bond Self-Consistent Field⁵⁵ where several solutions are at hand.^{53,56,57} Most wave function-based methods^{16–20} construct the 2DM in order to perform the orbital optimization. In contrast, the v2DM method works directly with the 2DM, although the 2DM is not completely N -representable. If a good starting point in the orbital space is available, a simple local minimizer can generate good results. In this paper, we use an algorithm utilizing Jacobi rotations⁵⁸ to avoid the full simultaneous four-index transformation of the two-electron integrals.

In section 2, we introduce the v2DM framework and apply it to the case of a DOCI wave function, leading to v2DM-DOCI. In section 3, the orbital optimization scheme is presented in detail, and in section 4, results are shown for several illustrative test cases, including situations where a multi-reference description is needed. A summary and discussion is presented in section 5.

2. VARIATIONAL 2DM

We use Greek letters $\alpha, \beta, \dots$ to denote a general spinorbital ($2L$ in total), and Roman letters $a, b, \dots$ to denote the spatial part of the

orbital (L in total). With the bar symbol, the pairing partner of a state is denoted: a and $\bar{a}$ form a pair of the same spatial orbital with opposite spin, e.g., $a = a\uparrow$ and $\bar{a} = a\downarrow$. All summations runs over either the spinorbitals or the orbitals depending on whether Greek or Roman summation indices were used. We use the second-quantization formalism; $\hat{a}_\alpha^\dagger$ ($\hat{a}_\alpha$) denotes a creation (annihilation) operator for a fermion in the single particle state α . It is also assumed that the many-electron wave function is real.

2.1. General v2DM. In second quantization, a Hamiltonian with pairwise interactions can be written as⁵⁹

$$\hat{H} = \sum_{\alpha\beta} \langle \alpha | \hat{T} | \beta \rangle \hat{a}_\alpha^\dagger \hat{a}_\beta + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | \hat{V} | \gamma\delta \rangle \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\delta \hat{a}_\gamma \quad (1)$$

where $\hat{T}$ and $\hat{V}$ are the one- and two-particle operators. It should be noted that the formalism is completely general for Hamiltonians up to two-body interactions; however, all operators discussed in the present paper concern field-free, nonrelativistic, electronic structure Hamiltonians, i.e., $\hat{T}$ is the sum of the electronic kinetic energy and the nuclei-electron attraction, whereas $\hat{V}$ represents the interelectronic Coulomb repulsion. The ground-state energy can be expressed solely in terms of the second-order reduced density matrix (2DM)²⁶ Γ ,

$$E = \text{Tr}(K\Gamma) = \frac{1}{4} \sum_{\alpha\beta\gamma\delta} K_{\alpha\beta;\gamma\delta} \Gamma_{\alpha\beta;\gamma\delta} \quad (2)$$

where

$$\Gamma_{\alpha\beta;\gamma\delta} = \langle \psi | \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\delta \hat{a}_\gamma | \psi \rangle \quad (3)$$

$$K_{\alpha\beta;\gamma\delta} = \frac{1}{N-1} (T_{\alpha\gamma} \delta_{\beta\delta} - T_{\beta\gamma} \delta_{\alpha\delta} - T_{\alpha\delta} \delta_{\beta\gamma} + T_{\beta\delta} \delta_{\alpha\gamma}) + V_{\alpha\beta\gamma\delta} \quad (4)$$

with $|\psi\rangle$ the ground-state wave function for the Hamiltonian (eq 1) with matrix elements $T_{\alpha\beta} = \langle \alpha | \hat{T} | \beta \rangle$ and $V_{\alpha\beta\gamma\delta} = \langle \alpha\beta | \hat{V} | \gamma\delta \rangle$. N is the number of particles, and eqs 3 and 4 define matrix elements of the 2DM and the reduced Hamiltonian $K_{\alpha\beta;\gamma\delta}$ respectively. Some elementary properties are easily derived,

$$\Gamma_{\alpha\beta;\gamma\delta} = -\Gamma_{\beta\alpha;\gamma\delta} = -\Gamma_{\alpha\beta;\delta\gamma} = \Gamma_{\beta\alpha;\delta\gamma} \quad (5)$$

$$\Gamma_{\alpha\beta;\gamma\delta} = \Gamma_{\gamma\delta;\alpha\beta} \quad (6)$$

$$\text{Tr}(\Gamma) = \frac{1}{2} \sum_{\alpha\beta} \Gamma_{\alpha\beta;\alpha\beta} = \frac{N(N-1)}{2} \quad (7)$$

The idea of variational 2DM is to minimize the energy function (eq 2). The 2DM is a much more compact object than the wave function as its matrix dimension scales as L^2 . However, a direct approach produces unrealistic energies.²⁸ The variation has to be limited to the class of N -representable 2DMs;^{29,30} for every 2DM, there must exist a wave function $|\psi\rangle$ such that eq 3 is satisfied. Unfortunately, there exists no straightforward way of establishing whether a 2DM is N -representable. The necessary and sufficient conditions are formally known;^{60,61} a 2DM is N -representable if and only if, for every two-particle Hamiltonian $\hat{H}_\phi$, the following inequality is true:

$$\text{Tr}(K_\phi \Gamma) \geq E_0(\hat{H}_\phi) \quad (8)$$

with K_ϕ the reduced Hamiltonian and $E_0(\hat{H}_\phi)$ the exact ground-state energy of the Hamiltonian $\hat{H}_\phi$. This theorem cannot be used as a sufficient condition for N -representability as that would require

the ground-state energy of every possible two-particle Hamiltonian $\hat{H}_\phi$, but it can be used as a necessary condition; the theorem in eq 8 can be relaxed to Hamiltonians for which a lower bound to its ground-state energy is known. A straightforward choice is

$$\hat{H} = \hat{B}^\dagger \hat{B} \quad (9)$$

a class of manifestly positive semidefinite Hamiltonians. If we restrict $\hat{B}$ to the two-particle space, we find the well-known $\mathcal{P}$, $\mathcal{Q}$, and $\mathcal{G}$ two-index conditions:

1. The $\mathcal{P}$ condition: $\hat{B} = \sum_{\alpha\beta} p_{\alpha\beta} \hat{a}_\alpha \hat{a}_\beta$, for arbitrary $p_{\alpha\beta}$. This trivial condition imposes the positive semidefiniteness of the 2DM itself:

$$\begin{aligned} \mathcal{P}(\Gamma)_{\alpha\beta;\gamma\delta} &= \langle \psi | \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\delta \hat{a}_\gamma | \psi \rangle \\ \mathcal{P}(\Gamma) &= \Gamma \geq 0 \end{aligned} \quad (10)$$

2. The $\mathcal{Q}$ condition:³⁰ $\hat{B} = \sum_{\alpha\beta} q_{\alpha\beta} \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger$, for arbitrary $q_{\alpha\beta}$ leading to

$$\mathcal{Q}(\Gamma) \geq 0 \quad (11)$$

where

$$\begin{aligned} \mathcal{Q}(\Gamma)_{\alpha\beta;\gamma\delta} &= \langle \psi | \hat{a}_\alpha \hat{a}_\beta \hat{a}_\delta^\dagger \hat{a}_\gamma^\dagger | \psi \rangle \\ &= \Gamma_{\alpha\beta;\gamma\delta} + (\delta_{\alpha\gamma} \delta_{\beta\delta} - \delta_{\beta\gamma} \delta_{\alpha\delta}) \frac{2\text{Tr}(\Gamma)}{N(N-1)} \\ &\quad - \delta_{\alpha\gamma} \rho_{\beta\delta} + \delta_{\beta\gamma} \rho_{\alpha\delta} + \delta_{\alpha\delta} \rho_{\beta\gamma} - \delta_{\beta\delta} \rho_{\alpha\gamma} \end{aligned} \quad (12)$$

and the single-particle density matrix (1DM) is defined as

$$\rho_{\alpha\beta} = \langle \psi | \hat{a}_\alpha^\dagger \hat{a}_\beta | \psi \rangle = \frac{1}{N-1} \sum_\lambda \Gamma_{\alpha\lambda;\beta\lambda} \quad (13)$$

3. The $\mathcal{G}$ condition:³² $\hat{B} = \sum_{\alpha\beta} g_{\alpha\beta} \hat{a}_\alpha^\dagger \hat{a}_\beta$, for arbitrary $g_{\alpha\beta}$

$$\mathcal{G}(\Gamma) \geq 0 \quad (14)$$

with

$$\mathcal{G}(\Gamma)_{\alpha\beta;\gamma\delta} = \langle \psi | \hat{a}_\alpha^\dagger \hat{a}_\beta \hat{a}_\delta^\dagger \hat{a}_\gamma | \psi \rangle = \delta_{\beta\delta} \rho_{\alpha\gamma} - \Gamma_{\alpha\delta;\gamma\beta} \quad (15)$$

Furthermore, there are the so-called three-index commutator conditions,^{33,48,62–65} which are computationally much more demanding and are not used in this paper. All these conditions are necessary but not sufficient; the true N -representable space is much more restricted. Because of this, v2DM will always find a lower bound to the FullCI energy.

The variational optimization of the 2DM can now be expressed as

$$\begin{aligned} \min \text{Tr}(K\Gamma) \quad \text{while} \\ \mathcal{P}(\Gamma) \oplus \mathcal{Q}(\Gamma) \oplus \mathcal{G}(\Gamma) \geq 0 \\ \text{Tr}(\Gamma) = \frac{N(N-1)}{2} \end{aligned} \quad (16)$$

This optimization problem can be formulated as a semidefinite program (SDP),^{46,47} a class of well-known convex optimization problems³⁶ for which general purpose solvers exists.^{39,66,67} Earlier we developed SDP solvers customized for v2DM that exploit the specific structure of the problem.^{40,43,44,68} Such solvers are much more efficient than the general purpose solvers. In this paper, we use a boundary point method^{41,69,70} to solve the SDP problem. In this method, the primal-dual gap is zero by definition, and convergence is reached when both

primal and dual feasibility is achieved. The computationally most intensive step in this algorithm is the calculation of the eigenvalues and eigenvectors of the constraint matrices. The computational cost of the program scales as L^6 for floating-point operations and L^4 for memory when using the two-index conditions. A detailed explanation of the solvers can be found in ref 68.

2.2. DOCI Tailored v2DM. We now impose the additional condition that $|\psi\rangle$ in eq 3 is a DOCI wave function. In principle, any pairing scheme can be used, but the natural choice is the singlet pairing scheme, in which each spatial orbital is occupied by two electrons of opposite spin. This is based on the assumption that the most important static correlations in a closed-shell molecule can be captured in this way.¹⁵ In CI terms, the wave function can be expanded in Slater determinants where all spatial orbitals are doubly occupied. This is also called a seniority-zero wave function. Formally, the DOCI wave function can be written as

$$|\psi\rangle = \sum_{a_1 \dots a_{N/2}} c_{a_1 \dots a_{N/2}} \prod_{k=1}^{N/2} \hat{a}_{a_k}^\dagger \hat{a}_{\bar{a}_k}^\dagger |l\rangle \quad (17)$$

where the $a_i = 1 \dots L$ summations are over all spatial orbitals (L), and $|l\rangle$ is defined as the particle vacuum.

A simple approach would be to project the reduced Hamiltonian (eq 4) onto DOCI space and use existing v2DM codes. However, this does not lead to the desired result as internal consistency conditions on the 2DM are needed (see below). Also, any computational advantages due to the DOCI structure are lost as the scaling of the program remains unaltered.

It is much more efficient to adapt the N -representability conditions to the DOCI case as they are drastically simplified. The adapted DOCI conditions were already derived by Weinhold and Wilson,^{51,52} but to the best of our knowledge never exploited in practical calculations.

Since we work in DOCI space, all operators evaluated between two DOCI wave functions need to have seniority-zero, i.e., they cannot change the number of broken pairs. This immediately implies that the 1DM is diagonal and that the chosen set of orbitals is also the set of natural orbitals of $|\psi\rangle$:

$$\begin{aligned} \rho_{ab} &= \langle \psi | \hat{a}_a^\dagger \hat{a}_b | \psi \rangle = \langle \psi | \hat{a}_a^\dagger \hat{a}_{\bar{b}} | \psi \rangle = \delta_{ab} \rho_a, \\ \langle \psi | \hat{a}_a^\dagger \hat{a}_{\bar{b}} | \psi \rangle &= \langle \psi | \hat{a}_a^\dagger \hat{a}_b | \psi \rangle = 0 \end{aligned} \quad (18)$$

Furthermore, it is clear that

$$\rho_a \geq 0 \quad (19)$$

$$\sum_a \rho_a = \frac{N}{2} \quad (20)$$

A similar simplification occurs for the 2DM and the $\mathcal{PQG}$ conditions:

1. The $\mathcal{P}$ condition: The operator $\hat{B}$ in eq 9 acting on a DOCI wave functions can create both a seniority-0 and seniority-2 state. The corresponding $\hat{B}^\dagger$ operator can only connect states of the same seniority, and therefore, block diagonalization will occur. The seniority-0 block is the pair density matrix,

$$\forall a, b: \langle \psi | \hat{a}_a^\dagger \hat{a}_a^\dagger \hat{a}_{\bar{b}} \hat{a}_b | \psi \rangle = \Gamma_{a\bar{a}, b\bar{b}} = \Pi_{ab} \quad (21)$$

From the positivity of the Hamiltonian $\hat{B}^\dagger \hat{B}$ with

$$\hat{B}^\dagger = \sum_a p_a \hat{a}_a^\dagger \hat{a}_a^\dagger \quad (22)$$

it follows that the $L \times L$ pair density matrix has to be positive semidefinite,

$$\Pi \geq 0 \quad (23)$$

The seniority-2 block is a part of the diagonal of the 2DM:

$$\begin{aligned} \forall a \neq b: \langle \psi | \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_{\bar{b}} \hat{a}_a | \psi \rangle &= \langle \psi | \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_{\bar{b}} \hat{a}_a | \psi \rangle = \\ \langle \psi | \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_{\bar{b}} \hat{a}_a | \psi \rangle &= \langle \psi | \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_{\bar{b}} \hat{a}_a | \psi \rangle = \\ \Gamma_{ab, ab} &= D_{ab} \geq 0 \end{aligned} \quad (24)$$

For convenience, we put $D_{aa} = 0$. Equation 24 provides

$\frac{L(L-1)}{2}$ linear inequalities that have to be imposed. There are now two independent ways of obtaining the 1DM out of the 2DM: via the trace relation (eq 13) and via the diagonal part of the pairing matrix:

$$\rho_a = \frac{2}{N-2} \sum_b D_{ab} \quad (25)$$

$$\rho_a = \Pi_{aa} \quad (26)$$

as the operators $\hat{a}_a^\dagger \hat{a}_a = \hat{a}_a^\dagger \hat{a}_a = \hat{a}_a^\dagger \hat{a}_a^\dagger \hat{a}_a \hat{a}_a$ have the same expectation value for a DOCI wave function. These consistency conditions have to be separately enforced. Note that the trace condition eq 7 can be written in two alternative ways:

$$\sum_a \Pi_{aa} = \frac{N}{2} \quad \text{and} \quad \sum_{ab} D_{ab} = \frac{N}{4}(N-2) \quad (27)$$

2. The $\mathcal{Q}$ condition has exactly the same structure as the $\mathcal{P}$ condition. The constraint for the seniority-0 block is derived from

$$\sum_{ab} q_a \langle \psi | \hat{a}_a \hat{a}_a^\dagger \hat{a}_{\bar{b}} \hat{a}_b^\dagger | \psi \rangle q_b \geq 0 \quad (28)$$

which leads to the positivity condition $\mathcal{Q}^\Pi \geq 0$ on a $L \times L$ matrix $\mathcal{Q}^\Pi$, with elements

$$\mathcal{Q}_{ab}^\Pi = \delta_{ab}(1 - \rho_a - \rho_b) + \Pi_{ab} \quad (29)$$

The seniority-2 part gives rise to a set of linear inequalities,

$$\begin{aligned} \forall a \neq b: \\ \langle \psi | \hat{a}_a \hat{a}_b \hat{a}_b^\dagger \hat{a}_a^\dagger | \psi \rangle &= 1 - \rho_a - \rho_b + D_{ab} \geq 0 \end{aligned} \quad (30)$$

3. The $\mathcal{G}$ condition is somewhat more complex as more combinations are non-zero. We work systematically according to seniority and spin.

Spin projections $M_S = \pm 1$ are equivalent, so we only consider the $M_S = +1$ case and always assume $a \neq b$, since in DOCI space $\hat{a}_a^\dagger \hat{a}_a | \psi \rangle = 0$. The particle-hole operators generating this constraint are of the form $\hat{B}^\dagger = \sum_{ab} g_{ab} \hat{a}_a^\dagger \hat{a}_{\bar{b}}$ which lead to the following seniority-2 positivity condition:

$$\begin{aligned} \sum_{abcd} g_{ab} [\delta_{ba} \delta_{ac} (\rho_a - D_{ab}) - \delta_{aa} \delta_{bc} \Pi_{ab}] g_{cd} = \\ \sum_{ab} g_{ab} [(\rho_a - D_{ab}) g_{ab} - \Pi_{ab} g_{ba}] \geq 0 \end{aligned} \quad (31)$$

This condition is almost diagonal, as g_{ab} is only connected with itself and g_{ba} , leading to the following 2×2 positivity condition:

$$\forall a < b \quad \begin{bmatrix} \rho_a - D_{ab} & -\Pi_{ab} \\ -\Pi_{ab} & \rho_b - D_{ab} \end{bmatrix} \geq 0 \quad (32)$$

For the $M_S = 0$ and seniority-2 case, the particle-hole operators are of the form $\hat{B}_1^\dagger = \sum_{ab} g_{ab} \hat{a}_a^\dagger \hat{a}_b$ and $\hat{B}_2^\dagger = \sum_{ab} g_{ab} \hat{a}_a^\dagger \hat{a}_{\bar{b}}$, with $a \neq b$. These terms are coupled to each other. The diagonal terms ($\hat{B}_1^\dagger \hat{B}_1$ and $\hat{B}_2^\dagger \hat{B}_2$) are

$$\langle \psi | \hat{a}_a^\dagger \hat{a}_b \hat{a}_d^\dagger \hat{a}_c | \psi \rangle = \delta_{ac} \delta_{bd} (\rho_a - D_{ab}) \quad (33)$$

The off-diagonal terms ($\hat{B}_1^\dagger \hat{B}_2$ and $\hat{B}_2^\dagger \hat{B}_1$) are

$$\langle \psi | \hat{a}_a^\dagger \hat{a}_b \hat{a}_d^\dagger \hat{a}_{\bar{c}} | \psi \rangle = \delta_{ad} \delta_{bc} \Pi_{ab} \quad (34)$$

which leads to the 2×2 constraint matrix

$$\forall a < b \quad \begin{bmatrix} \rho_a - D_{ab} & \Pi_{ab} \\ \Pi_{ab} & \rho_b - D_{ab} \end{bmatrix} \geq 0 \quad (35)$$

which is equivalent to eq 32.

The $M_S = 0$ and seniority-0 part is built by two particle-hole operators $\hat{B}_1^\dagger = \sum_a g_a \hat{a}_a^\dagger \hat{a}_a$ and $\hat{B}_2^\dagger = \sum_b g_b \hat{a}_b^\dagger \hat{a}_{\bar{b}}$. This leads to a $2L \times 2L$ matrix with diagonal elements ($\hat{B}_1^\dagger \hat{B}_1$ and $\hat{B}_2^\dagger \hat{B}_2$)

$$\langle \psi | \hat{a}_a^\dagger \hat{a}_a \hat{a}_b^\dagger \hat{a}_b | \psi \rangle = \delta_{ab} \rho_a + D_{ab} \quad (36)$$

and off-diagonal elements ($\hat{B}_1^\dagger \hat{B}_2$ and $\hat{B}_2^\dagger \hat{B}_1$)

$$\begin{aligned} \langle \psi | \hat{a}_a^\dagger \hat{a}_a \hat{a}_b^\dagger \hat{a}_{\bar{b}} | \psi \rangle &= D_{ab} + \delta_{ab} \Pi_{ab} \\ &= \delta_{ab} \rho_a + D_{ab} \end{aligned} \quad (37)$$

Both blocks are identical, which means that L eigenvalues will be zero, and we only have to impose the positivity $\mathcal{G}^\Pi \geq 0$ of a $L \times L$ matrix:

$$\mathcal{G}_{ab}^\Pi = \delta_{ab} \rho_a + D_{ab} \quad (38)$$

The $\mathcal{P}$ conditions correspond to eqs 24a and 30 in Weinhold and Wilson,⁵² the $\mathcal{Q}$ conditions to eq 24b and 34, and the $\mathcal{G}$ conditions to eq 24c, 44, and 18.

We now look at the reduced Hamiltonian eq 4, which simplifies to the same structure as the $\mathcal{P}$ condition. The DOCI reduced Hamiltonian is

$$\begin{aligned} K_{ab}^\Pi &= \frac{2}{N-1} T_{aa} \delta_{ab} + V_{aabb}, \\ K_{ab}^D &= \frac{1}{N-1} (T_{aa} + T_{bb}) + V_{abab} - \frac{1}{2} V_{abba} \end{aligned} \quad (39)$$

The energy functional (eq 2) for DOCI becomes

$$E = \sum_{ab} (K_{ab}^\Pi \Pi_{ab} + 2K_{ab}^D D_{ab}) \quad (40)$$

An advantage of v2DM-DOCI is that the resulting 2DM belongs to a singlet state, while the general v2DM needs additional constraints to ensure the singlet:

$$\langle \psi | \hat{a}_\alpha^\dagger \hat{a}_\beta \hat{S}_z | \psi \rangle = 0 \quad (41)$$

with the $\hat{S}_z$ operator defined as,

$$\hat{S}_z = \frac{1}{2} \sum_a (\hat{a}_a^\dagger \hat{a}_a - \hat{a}_{\bar{a}}^\dagger \hat{a}_{\bar{a}}) \quad (42)$$

In full v2DM, this constraint needs to be enforced by a zero eigenvalue in the $\mathcal{G}$ matrix.^{49,68} In v2DM-DOCI however,

$$\begin{aligned} \langle \psi | \hat{a}_c^\dagger \hat{a}_d \hat{S}_z | \psi \rangle &= \\ &= \frac{1}{2} \delta_{cd} \sum_a (\langle \psi | \hat{a}_c^\dagger \hat{a}_d \hat{a}_a^\dagger \hat{a}_a | \psi \rangle - \langle \psi | \hat{a}_c^\dagger \hat{a}_d \hat{a}_{\bar{a}}^\dagger \hat{a}_{\bar{a}} | \psi \rangle) \\ &= \frac{1}{2} \sum_a (\langle \psi | \hat{a}_a^\dagger \hat{a}_a | \psi \rangle - \langle \psi | \hat{a}_c^\dagger \hat{a}_d \hat{a}_c \hat{a}_d | \psi \rangle - \langle \psi | \hat{a}_c^\dagger \hat{a}_{\bar{d}} \hat{a}_{\bar{c}} \hat{a}_{\bar{d}} | \psi \rangle) \\ &= \frac{1}{2} \sum_a (\rho_a + (1 - \delta_{ac}) D_{ac} - \Pi_{ac} \delta_{cd} - (1 - \delta_{ac}) D_{ca}) \\ &= 0 \end{aligned}$$

which means that the singlet condition is automatically fulfilled. It must be noted that eq 41 is a necessary but not sufficient condition for the 2DM to be derivable from a $S = 0$ wave function.

In these DOCI N -representability conditions, the largest matrix dimension encountered is L as compared to $(2L)^2$ in the general case. The remainder of the conditions are linear inequalities and the positive semidefiniteness of 2×2 matrices which are trivial to impose. The scaling of our code has been reduced from L^6 to L^3 for the floating point operations and from L^4 to L^2 for the memory. In Figure 2, the scaling of the v2DM and v2DM-DOCI (with and without orbital optimization) is shown for a growing chain of equidistant hydrogen atoms (interatomic distance = 2 Bohr) in the STO-3G basis. Note that for 30 H atoms, the v2DM-DOCI is already 3 orders of magnitude faster than the general v2DM code. We used a v2DM code that exploits spin symmetry, and the singlet conditions are enforced, so we can make a fair comparison with v2DM-DOCI. The v2DM-DOCI starts to exhibit a smooth scaling with the number of hydrogen atoms when the runtime was at least 10^4 seconds, whereas the general v2DM reaches this point sooner (10^3 seconds). We performed a linear fit on a log-log plot to find the power of the leading term in the scaling (αx^β) resulting in the coefficients found in Table 1. The scaling is 2 orders better, while the prefactor changes little. If we include the orbital optimization introduced in the next section, the scaling deteriorates with 0.25. We cannot draw any general conclusion from this about the scaling of the entire method (including the orbital optimization) as a hydrogen chain in STO-3G is a fairly special case. Note that the actual scaling parameters $\beta = 6.4$ (v2DM) and $\beta = 3.9$ (v2DM-DOCI) deviate from the theoretical scaling parameters $\beta = 6$ (v2DM) and $\beta = 3$ (v2DM-DOCI) involved in the v2DM floating point operations as any v2DM algorithm contains an iterative scheme with a number of loops that slowly increases with L .

3. ORBITAL OPTIMIZATION

The DOCI energy is orbital dependent; therefore, the choice of the orbitals is crucial. Like in many MCSCF methods, we use an iterative two-step algorithm^{1,54,57,71-73} in which we first optimize the 2DM and then the orbitals. Orbital optimization is a hard problem as it requires finding the global minimum in a

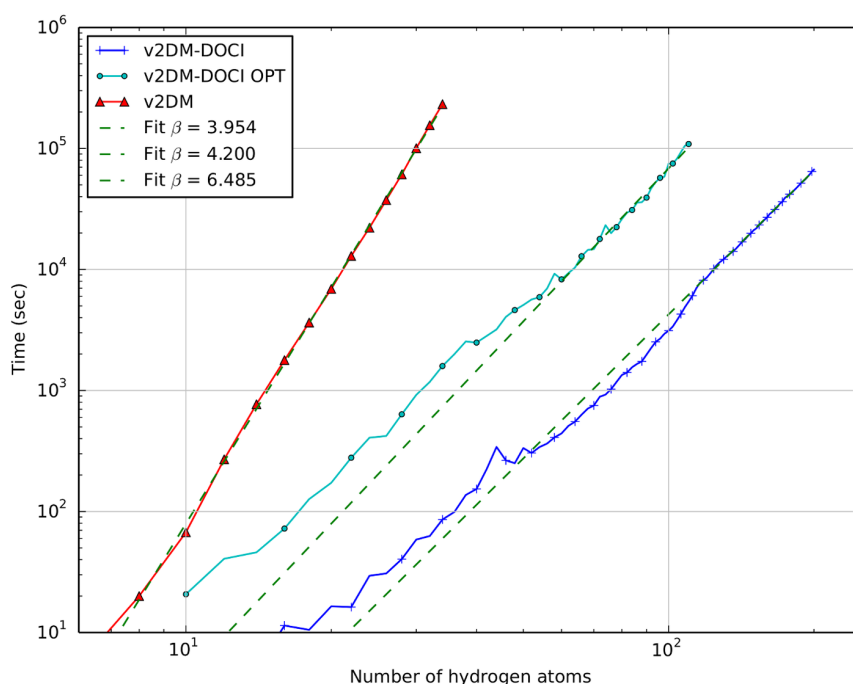


Figure 2. Scaling of v2DM vs v2DM-DOCI (with and without orbital optimization) on a hydrogen chain (interatomic distance = 2 Bohr) in the STO-3G basis on a log–log plot. We fitted a linear curve ($\beta x + \alpha$) to the data.

rough and uncharted landscape.²⁴ There are no known computationally feasible techniques for achieving this in a general way. The most often used approach is to pick a good starting point and use a Newton–Raphson based algorithm to find a local minimum.^{56,57} This involves calculating the computationally expensive Jacobian and Hessian. Furthermore, the four-index transformation of the two-electron integrals is not cheap.

We use a different approach; a Jacobi rotation is performed in every step. A Jacobi rotation^{58,74} is a unitary transformation that rotates in a two-dimensional subspace of the orbital space. While in a Newton–Raphson method all orbitals are updated at every step, in a Jacobi rotation only two orbitals are updated in each step. Jacobi rotations have the advantage of simplicity; only 2 rows and columns need to be updated, which makes the transformation of the two-electron integrals much faster. The Jacobi rotation of orbitals k and l over an angle θ is determined by the rotation matrix

$$Q^{kl} = \begin{pmatrix} & k & l & & \\ & & & & \\ & & & & \\ k & & \cos \theta & \cdots & -\sin \theta \\ & & \vdots & \ddots & \vdots \\ l & & \sin \theta & \cdots & \cos \theta \\ & & & & \\ & & & & \ddots \\ & & & & & 1 \end{pmatrix}, \quad (43)$$

or more formally,

$$Q_{ij}^{kl} = \delta_{ij} + (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})(\cos \theta - 1) + (\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk})\sin \theta \quad (44)$$

Table 1. Resulting Coefficients of the Linear Fit in Figure 2

	α	β
v2DM	2.602×10^{-5}	6.485
v2DM-DOCI	5.268×10^{-5}	3.954
v2DM-DOCI OPT	2.726×10^{-4}	4.200

If we apply a unitary transformation to the matrix elements (eq 39) and insert them in the energy function (eq 40), we find

$$E' = \frac{2}{N-1} \sum_{ab} \sum_{a'b'} [\delta_{ab} Q_{aa'} Q_{ab'} \Pi_{ab} + (Q_{aa'} Q_{ab'} + Q_{ba'} Q_{bb'}) D_{ab}] T_{a'b'} + \sum_{ab} \sum_{a'b'c'd'} Q_{aa'} Q_{ab'} Q_{bc'} Q_{bd'} V_{a'b'c'd'} \Pi_{ab} + \sum_{ab} \sum_{a'b'c'd'} Q_{aa'} Q_{bb'} (2Q_{ac'} Q_{bd'} - Q_{bc'} Q_{ad'}) V_{a'b'c'd'} D_{ab} \quad (45)$$

Substituting eq 44 into eq 39 yields, after some work, the following expression for the energy,

$$E'(\theta)^{kl} = A \cos 4\theta + B \cos 2\theta + C \sin 4\theta + D \sin 2\theta + F \quad (46)$$

for the rotation over of an angle θ between orbitals k and l . The constants A , B , C , D , and F , of which the complete expression is given in the Supporting Information, depend on the elements of the 2DM, T_{ab} and V_{abcd} . As eq 46 has a period of π , we only consider the interval $[-(\pi/2), (\pi/2)]$. The N -representability conditions of section 2 are unitarily invariant, so we are guaranteed that a Jacobi rotation does not affect the N -representability, but the energy is not necessarily minimal. This means that the calculated energy

Algorithm 1 The algorithm used to find the optimal Jacobi rotation in pseudocode

```

procedure FINDOPTIMALROTATION( $\Gamma, T, V$ )
  for  $i \leftarrow 1, n_{\text{irrep}}$  do                                ▷ Loop over all irreducible representations
    for all  $(a, b) \in \text{irrep}_i$  do                        ▷ Loop over all pairs of orbitals belonging to irrep  $i$ 
       $(E_{ab}, \theta_{ab}) = \text{FINDMINIMUM}(\Gamma, T, V, a, b)$     ▷ Minimum of (46)
    end for
  end for
   $(k, l, \theta) = \min (E, \theta)$                                 ▷ Find the lowest energy over all pairs
  return  $(k, l, \theta_{kl})$                                 ▷ Return the pair of orbitals and the angle
end procedure

```

Algorithm 2 Schematic overview of the complete v2DM-DOCI algorithm

```

converged  $\leftarrow 0$ 
while converged < 25 do                                ▷ Do 25 steps within convergence criteria
   $E_{\text{new}}, \Gamma = \text{v2DM}(T, V)$                         ▷ Do a v2DM-DOCI optimization with electron integrals  $T$ 
  and  $V$ 
   $(k, l, \theta) = \text{FINDOPTIMALROTATION}(\Gamma, T, V)$         ▷ Find the optimal rotation
   $T, V = \text{TRANSFORMINTEGRALS}(k, l, \theta, T, V)$           ▷ Rotate the integrals
  if  $|E_{\text{new}} - E_{\text{old}}| < 10^{-6}$  then                  ▷ Check convergence
    converged  $\leftarrow$  converged + 1
  end if
   $E_{\text{old}} \leftarrow E_{\text{new}}$ 
end while

```

(eq 46) will always be greater than or equal to the optimized v2DM minimum.

It is easy and cheap to calculate the gradient and Hessian of this equation. Using a Newton–Raphson algorithm, we can thus easily find the angle for which eq 46 is minimal. The constant term (F) in eq 46 is the only one involving a double sum over the orbitals; it is the original double sum appearing in eq 40 over all orbitals except orbitals k and l . This implies that an evaluation of the energy scales as L^2 , but the energy difference, gradient, and the Hessian only scale computationally as L . If we iterate over all pairs of orbitals (scaling as L^2) and find the optimal angle for minimization, we have an L^3 algorithm to find the new Jacobi rotation optimizing the energy decrease. If symmetry-adapted orbitals are used, only rotations between orbitals in the same irreducible representation are allowed, which simplifies the two-electron integral transformation even more. A schematic overview is given in Algorithm 1. In the previous section, we measured the scaling of the v2DM-DOCI algorithm combined with the Jacobi orbital optimizer and found a scaling of 4.200. The starting point were the molecular orbitals. One should be careful to draw general conclusions from this. It merely shows that, given a suitable starting point, the algorithm has an interesting scaling.

As an example, we consider the BH molecule at equilibrium distance (2.32 Bohr) in the STO-3G basis. Figure 3 contains the energy as a function of the rotation angle between several pairs of orbitals starting from the Hartree–Fock molecular orbitals. The full (red) curve is the energy as calculated with eq 46 keeping the 2DM fixed, whereas the dashed (blue) curve involves a 2DM optimization at each point. We used C_{2v} symmetry for BH (the largest Abelian point group of BH), and we only considered the four orbitals that transformed according to irreducible representation A_1 (the other two orbitals transformed according to B_1 and B_2 , respectively). The orbital energies (in Hartree) of the restricted Hartree–Fock solution are given in Table 2.

The pictures shown for the BH molecule are characteristic for most calculations that we have done. For most pairs of orbitals, the lowest energy is obtained for very small rotation angles except for a few where a larger decrease in energy can be achieved. In

Table 2. Restricted Hartree–Fock Solution for BH^a

doubly occupied orbitals	
1A ₁	−7.339428
2A ₁	−0.573370
3A ₁	−0.246546
virtual orbitals	
1B ₁	0.269938
1B ₂	0.269938
4A ₁	0.701123

^aThe orbital energies are in Hartree. We use C_{2v} symmetry; the orbitals are labelled according to irreducible representations A_1 , B_1 , or B_2 .

Figure 3b, there is a clear new minimum, and the angle found using eq 46 is very close to the v2DM optimized minimum. The 1A₁ orbital is the localized 1s orbital on the Boron atom. The 2A₁ and 3A₁ orbitals are a mixture of the 1s on the hydrogen atom and the 2s and 2p_z on the Boron atom. The largest energy gain can be achieved by mixing these orbitals, and this already brings us very close to the FullCI energy (−24.810 E_h).

4. RESULTS

We have developed a code to perform variational 2DM optimizations using the DOCI constraints derived in section 2.2 in conjunction with orbital optimization according to eq 46. The one- and two-particle integrals are transformed with the optimized Jacobi rotation (see Algorithm 1) and a new v2DM optimization is started. We continue this loop until the ground-state energy is converged to within 10^{-6} E_h during at least 25 steps. For the v2DM calculations, we used a boundary point method with a primal and dual convergence criterion of 10^{-7} (see ref 68). The flow of our program is shown in Algorithm 2.

The code used to generate the data presented can be found online⁷⁵ under the GPLv3 license. All simulations were run single-threaded on a Intel Xeon E5-2680 v3 with 64GB of RAM. We used PSI4⁷⁶ to generate the one- and two-electron integrals in the Gaussian basis set and the Hartree–Fock molecular orbitals. Unless specified otherwise, the Hartree–Fock molecular orbitals are the starting point for the orbital optimization. In all calculations, the cc-pVDZ basis was used. Benchmark results are provided by CheMPS2,^{77–80} an

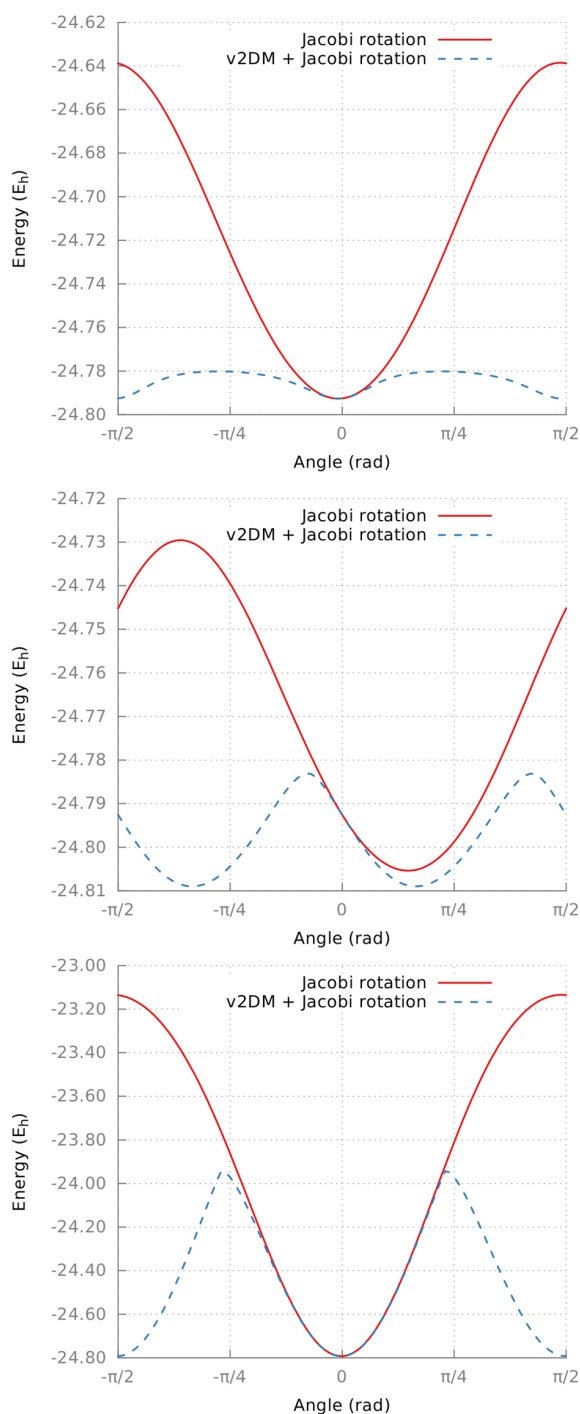


Figure 3. Red curve has been calculated using eq 46, while the blue curve uses the same transformed reduced Hamiltonian but an optimized 2DM-DOCI. These results are for BH in STO-3G. We used an interatomic distance of 2.32 Bohr. The min refers to the minimum of the eq 46 (red curve). The FullCI energy is $-24.810 E_h$.

open-source spin-adapted implementation of the Density Matrix Renormalization Group (DMRG) for ab initio quantum chemistry that generates results with FullCI accuracy. To monitor the convergence in CheMPS2, we increased the bond dimension in steps from 500 to 2500 for all calculations. FullDOCI is the result of a CI solver restricted to the doubly

occupied Slater determinants, combined with the same orbital optimization scheme as v2DM-DOCI (unless specified otherwise).

4.1. Two- and Four-Electron Systems. The DOCI wave function for a two-electron system is exact, provided that the orbitals are optimized.¹⁵ General v2DM using only the $\mathcal{P}$ condition is also exact for a two-electron system.^{30,49} It is easy to prove that v2DM-DOCI combined with orbital optimization also generates exact results for any two-electron system. This is illustrated by the numerical results in Table 3 for H_2 and He. Note that in Table 3 the FullDOCI results were obtained with the optimal orbitals produced by v2DM-DOCI.

In the dissociated He_2 dimer the effect of symmetry breaking is shown in the third and fourth row of Table 3. When we allow the point-group symmetry to break down from D_{2h} to C_1 , the orbital optimization algorithm is no longer restricted to orbitals transforming according to the same irreducible representation. When the symmetry is not broken (D_{2h}), the s orbitals of the two He atoms are coupled, in the sense that only (anti)symmetric combinations are retained. In this case, v2DM-DOCI cannot recover the FullCI energy. When we decouple the orbitals and use C_1 symmetry, the full correlation energy is found. It is important to note the difference with the general v2DM optimization; general v2DM always gives a lower bound to the exact ground-state energy, but in the v2DM-DOCI case, the energy is orbital dependent. The v2DM-DOCI energy can be higher or lower than the FullCI result. We almost always find a higher energy. It is still true, however, that the v2DM-DOCI must be lower than or equal to FullDOCI with the same set of orbitals. In principle, we combine a lower-bound method (v2DM) with an upper-bound method (Jacobi rotations). A cancellation of errors can occur, and that is why we always compare to FullDOCI as it uses an exact energy solver.

4.2. Hydrogen Chain. The symmetric stretching of an equidistant chain of hydrogen atoms is a standard test case for a new method aimed at strong static correlations. It is simple yet challenging because of the strong correlation effects in the transition from metallic hydrogen to dissociated hydrogen. We use a H_8 chain^{15,19} in the cc-pVDZ basis with D_{2h} (symmetry-adapted) or C_1 (symmetry-broken) orbitals. The results shown in Figure 4 indicate the importance of the choice of the starting point in the orbital optimization scheme as this dictates the valley in which the local minimizer is active. The underlying basis for the one- and two-electron integrals is always taken to be the Löwdin orthogonalized Gaussian basis set (symmetry-adapted if specified). For the HF- D_{2h} curve, we first performed a calculation at equilibrium distance starting from the Hartree–Fock molecular orbitals. The resulting orthogonal transformation matrix, describing the transition from the Löwdin orthogonalized Gaussian basis set to the optimal set of orbitals at equilibrium, was used as a starting point in the orbital optimization for all other points on the curve. It is clear from the figure that this procedure does not lead to a satisfactory description of the metallic to the noninteracting region, as the dissociation limit is much higher in energy than the FullCI curve.

For the curve labeled dis- D_{2h} , we performed a calculation at 10 Bohr determining the optimal orbital transformation with a random search and used this orbital transformation as a starting point for all other distances in the curve. This procedure correctly describes the dissociation limit, but the energy rises artificially when we go into the metallic regime. So symmetry-adapted D_{2h} orbitals cannot describe the transition from metallic

Table 3. Ground-State Energy for Some Small Systems in the cc-pVDZ Basis^a

system	Sym	d	HF	FullCI	Δ v2DM-DOCI	Δ FullDOCI
H ₂	D _{2h}	1.438	−1128.629	−1163.673	0.000	0.000
He	D _{2h}		−2855.160	−2887.595	0.000	0.000
He ₂	D _{2h}	10.000	−5710.321	−5775.190	40.013	40.022
He ₂	C ₁	10.000	−5710.321	−5775.190	0.000	0.000

^aEnergies are in milliHartree, interatomic distance (d) in Bohr. The columns labeled v2DM-DOCI and FullDOCI contain the deviation from FullCI. The orbital optimization is done with the specified Abelian symmetry in the column labeled 'Sym'.

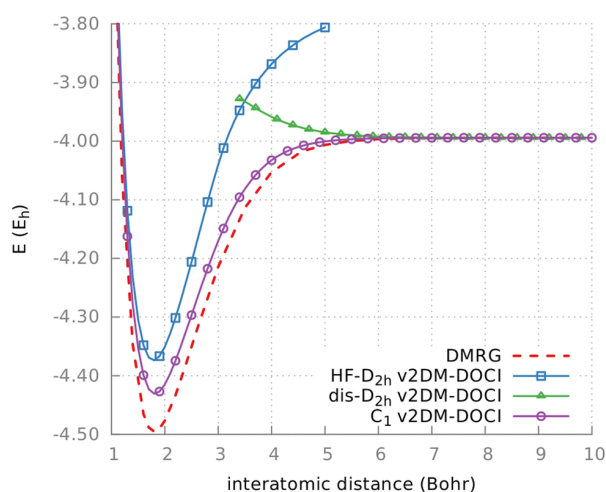


Figure 4. Symmetric stretch of H₈ in the cc-pVDZ basis. Not all calculated points are marked. For the C₁ curve, the largest deviation from DMRG is 45 milliHartree around the minimum at 1.8 Bohr.

to noninteracting localized hydrogen atoms. When starting from several random points, we could not find a lower energy curve for the D_{2h} case. The whole picture changes when we break the symmetry (the curve labeled C₁), and v2DM-DOCI now gives a physically correct description of the transition. This curve was found by starting from the optimal orbital transformation of a v2DM-DOCI calculation at 10 Bohr using localized orbitals as starting point. Similar results were already reported by Bytautas et al.;¹⁵ they verified that the behavior is not a two-state crossing or avoided crossing between the ground state and an excited state.

In Figure 5, we have plotted the natural orbital occupation numbers from the 1DM extracted from v2DM-DOCI for both symmetries. In the C₁ symmetry, there is a smooth transition from doubly occupied hydrogen to singly occupied hydrogen. In the D_{2h} symmetry, the 'localized' orbitals corresponding to the dis-D_{2h} curve in Figure 4 have a branch of singly occupied hydrogen that is not present in the C₁ symmetry. The 'molecular orbitals' corresponding to the HF-D_{2h} curve in Figure 4 also have branches with no counterpart in the localized orbitals. It is clear that only v2DM-DOCI results with symmetry-broken optimized orbitals provide a correct description of the transition.

As far as the details of the orbital optimization scheme are concerned, we found that the procedure can be accelerated by not performing a v2DM-DOCI optimization at each rotation; in practice, we see that the energy decreases considerably in the first steps. In subsequent steps, the convergence goes more slowly as the algorithm can only update two orbitals at a time. In this tail of the minimization, we can safely skip the optimization of the 2DM for a number of updates as all rotation angles are small, only to restart the algorithm with the optimal

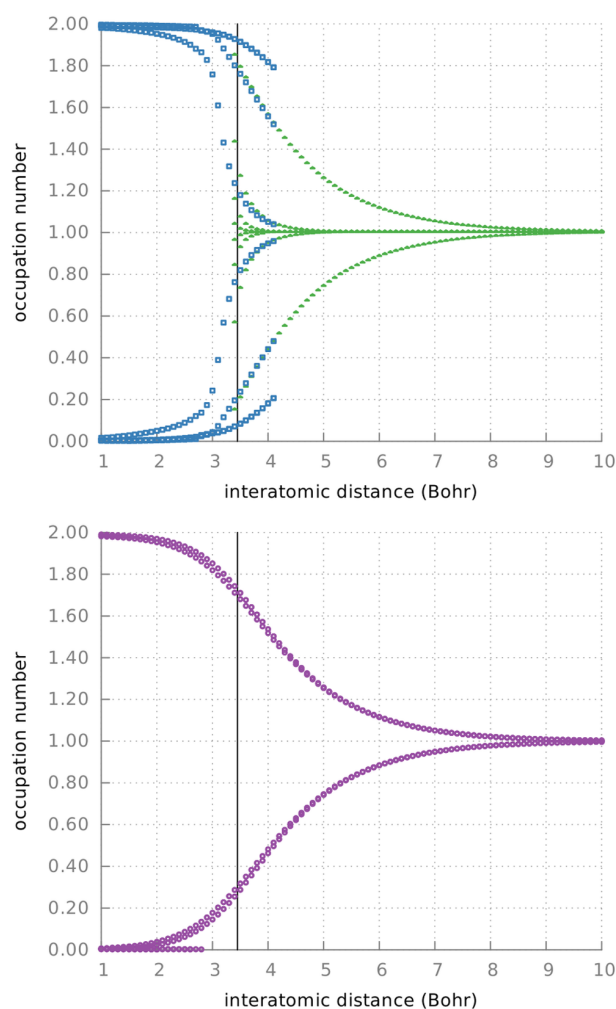


Figure 5. v2DM-DOCI natural orbital occupation numbers for both symmetries of the symmetric stretch of H₈. Only points with an occupation number larger than 10^{−3} are shown. The black line marks the energy crossing of the D_{2h} curves in Figure 4. The colors also match the curves in Figure 4.

solution from the previous step at the very end. This technique partially circumvents the downside of the Jacobi rotations, i.e., that only two orbitals are updated at the same time.

4.3. Molecular Systems. Another interesting test is the dissociation of a diatomic molecule in which static correlation is of paramount importance at dissociation. The cc-pVDZ basis is used for all molecules. The nomenclature used for the results is as follows: v2DM-DOCI refers to v2DM with the DOCI constraints on the 2DM (section 2.2) and with the Jacobi orbital optimization (section 3). FullDOCI uses the same orbital optimization algorithm. v2DM-DOCI/FullDOCI is a

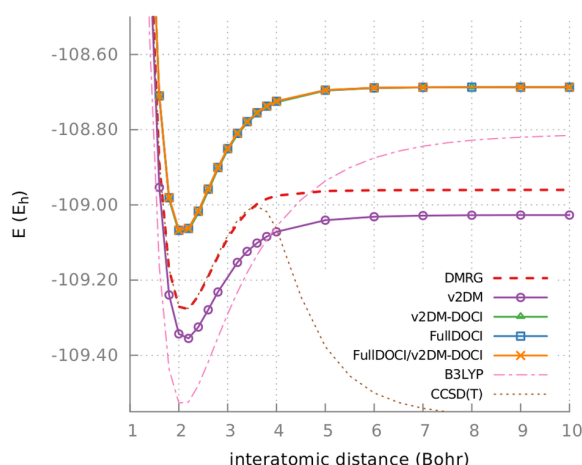


Figure 6. Dissociation of N_2 in the cc-pVDZ basis. The DOCI curves shown are for the C_1 symmetry. Note that three curves (v2DM-DOCI, FullDOCI, FullDOCI/v2DM-DOCI) coincide visually.

Table 4. Some Points on the N_2 Curve from Figure 6^a

d	Sym	DMRG	$\Delta v2DM$	$\Delta v2DM-DOCI$	$\Delta FullDOCI$
2.2	D_{2h}	-109.278	-77.375	222.578	224.455
2.2	C_1	-109.278	-77.375	209.891	214.787
4.0	D_{2h}	-108.975	-96.213	257.013	258.842
4.0	C_1	-108.975	-96.213	248.396	250.991
10.0	D_{2h}	-108.960	-66.384	282.966	283.108
10.0	C_1	-108.960	-66.384	273.371	273.464

^aThe interatomic distance (d) is in Bohr. The DMRG energy is in Hartree. For v2DM, v2DM-DOCI, and FullDOCI, the deviation from DMRG is given in milliHartree.

single-shot v2DM-DOCI calculation using the optimal set of orbitals from a FullDOCI calculation. FullDOCI/v2DM-DOCI is exactly the opposite: a single-shot FullDOCI calculation using the optimal set of orbitals from v2DM-DOCI.

We first present the dissociation of N_2 . This is challenging because of the breaking of a triple bond and is often used as a test case.^{15,81–84} In the cc-pVDZ basis, N_2 has 28 orbitals, and we perform calculations with both D_{2h} and C_1 symmetry. The results are presented in Figure 6 and detailed in Table 4. The results are to be compared to DMRG calculations,^{77–80} which are to be considered as the FullCI reference. In order to appreciate the performance of v2DM-DOCI, results of other methods such as Coupled-Cluster with Singles, Doubles, and perturbative Triples (CCSD(T))⁸⁵ and density functional theory with B3LYP functional^{86,87} are also presented. All DOCI curves give a qualitatively correct description of the dissociation process. In Table 4, one can notice that v2DM-DOCI is a better approximation to FullDOCI than v2DM is to FullCI. The effect of symmetry breaking is very small for N_2 ; the energy gains are in the milliHartree region. Note that N_2 dissociates into two N atoms with an odd number of electrons. This forms no problem for FullDOCI as the orbital optimization can handle this.²⁴ The difference between the DOCI curves and the DMRG reference is due to dynamical correlations and can be added in a subsequent stage, as shown in ref 88.

Another interesting case is cyanide, CN^- . This heteronuclear molecule also has a triple bond and dissociates in C^- and N. The effect of breaking the C_{2v} symmetry is again minimal (see results in Table 5), so in Figure 7, we restrict ourselves to the C_1

Table 5. Some Points on the CN^- Curve from Figure 7^a

d	Sym	DMRG	$\Delta v2DM$	$\Delta v2DM-DOCI$	$\Delta FullDOCI$
2.2	C_{2v}	-92.596	-70.208	186.967	192.202
2.2	C_1	-92.596	-70.208	186.967	192.192
4.0	C_{2v}	-92.324	-101.281	219.639	228.307
4.0	C_1	-92.324	-101.281	219.639	228.300
10.0	C_{2v}	-92.246	-116.686	218.333	253.131
10.0	C_1	-92.246	-116.686	218.333	253.130
20.0	C_{2v}	-92.246	-127.996	209.275	253.135
20.0	C_1	-92.246	-127.996	209.275	253.133

^aThe interatomic distance (d) is in Bohr. The DMRG energy is in Hartree. For v2DM, v2DM-DOCI, and FullDOCI, the deviation from DMRG is given in milliHartree.

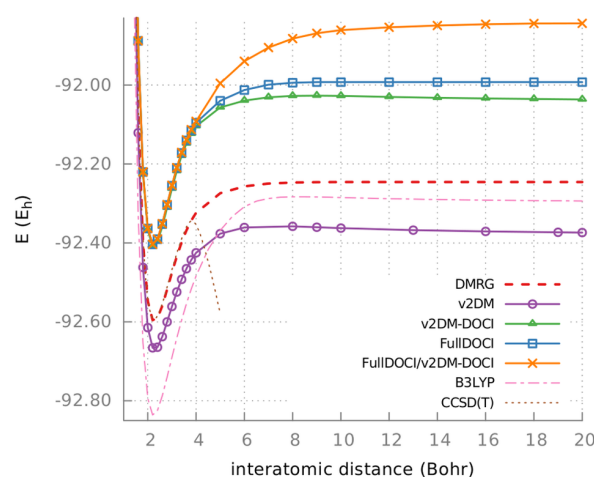


Figure 7. Dissociation of CN^- in the cc-pVDZ basis. The DOCI curves shown are for the C_1 symmetry.

curve. For this heteronuclear molecule, the dissociation limit for v2DM and v2DM-DOCI is incorrect. This is a known failure for v2DM-based techniques;⁸⁹ the energy of the isolated atoms as a function of fractional charge is a convex curve in v2DM, whereas it should be a piecewise linear curve.⁹⁰ Because of this, v2DM will favor fractional charges on dissociated atoms and thus give a physically incorrect picture. This is clearly shown on the FullDOCI/v2DM-DOCI curve; if we use the optimal basis of v2DM-DOCI, the FullDOCI energy is much higher than the true FullDOCI energy as the FullDOCI solution cannot use the artificial noninteger atomic charges. A Mulliken population analysis⁹¹ confirms this; at an interatomic distance of 20 Bohr, the net charges are $C^{-0.48}N^{-0.52}$. Using so-called subsystem constraints,^{34,92} one can force the E vs N curve to be piecewise linear. However, this would require a v2DM(-DOCI) optimization at each nearby integer value of N . In Figure 8, we have used the FullDOCI optimal orbitals for the v2DM-DOCI calculation. In this case, v2DM-DOCI gives the correct DOCI dissociation limit. This suggests that it might be possible to find specific DOCI constraints to solve the problem of fractional charges in v2DM-DOCI.

5. CONCLUSIONS

In this paper, we applied specific necessary N -representability constraints for a second-order density matrix derived from a seniority-zero CI wave function. The standard two-particle conditions $\mathcal{P}$, $\mathcal{Q}$, and $\mathcal{G}$ reduce to a simpler form that allows for

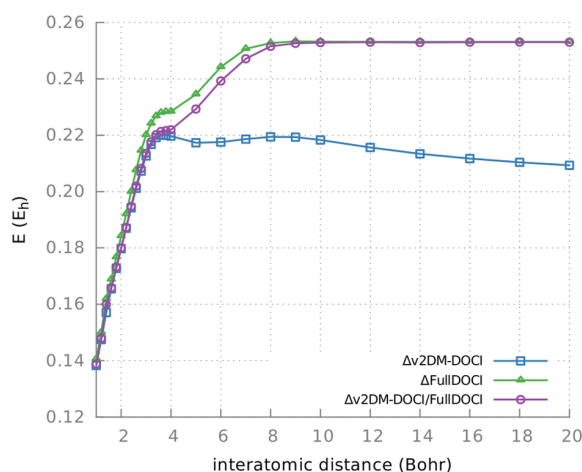


Figure 8. Dissociation of CN^- in the cc-PVDZ basis: comparing the v2DM-DOCI/FullDOCI results with v2DM-DOCI and FullDOCI. The deviation from DMRG is plotted.

a better theoretical scaling: L^3 instead of L^6 . As any truncated CI wave function is orbital dependent, an orbital optimization scheme has been included. We use an orbital optimizer based on elementary Jacobi rotations. Only two orbitals are optimized at each step, implying that the associated two-electron integral transformation is much more efficient. The theoretical scaling of the orbital optimizer is L^3 . In practice, the molecular systems in this manuscript needed less than 50 Jacobi rotations with optimization to convergence. The runtime was on average less than 1 hour. Both of course are very dependent on the used starting point. We have tested our method on several challenging cases. For the H_8 equidistant chain, we find that the symmetry of the system must be broken in order to find the correct DOCI energy curve. The orbital optimizer needs the additional degrees of freedom to find the physically correct set of orbitals. For the dissociation of N_2 , v2DM-DOCI gives good results, and symmetry breaking hardly gives any improvement. It is shown that v2DM-DOCI provides a good approximation to FullDOCI; the v2DM-DOCI and FullDOCI energies are consistently closer to each other than the v2DM and FullCI energies. In the dissociation of CN^- , v2DM, and v2DM-DOCI fail due to fractional charges although FullDOCI still gives a good description. We note that v2DM-DOCI with the FullDOCI optimal basis can reproduce the correct FullDOCI energy. This indicates that there could exist specific DOCI constraints to fix the problem of fractional charges in v2DM-DOCI.

The orbital optimizer works well provided it is given a suitable starting point. Near equilibrium, the Hartree–Fock molecular orbitals are usually a good choice, whereas in the dissociation limit, localized orbitals often give a better starting point. Unfortunately, this does not always hold; for instance, for the H_8 chain, the equilibrium energy could only be found by starting from the localized orbitals. However, if a single optimal point is found in the correct DOCI valley, it can usually be used as a starting point for all other calculations on the same system.

The main results of this paper support the idea that DOCI combined with orbital optimization captures the lion's share of the static correlations. Subsequently, the missing dynamic correlations could be added through perturbation theory.⁸⁸ We find that v2DM-DOCI is a good and fast approximation to FullDOCI.

■ ASSOCIATED CONTENT

● Supporting Information

A complete expression of eq 46, including the constants A , B , C , D , and F can be found. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.5b00378.

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The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

W.P., M.V.R., B.V., S.D.B., P.B., and D.V.N. are members of the QCMM alliance Ghent-Brussels. W.P., S.D.B., and B.V. acknowledge the support from the Research Foundation Flanders (FWO Vlaanderen). P.B. and D.R.A. acknowledge the Research Foundation Flanders (FWO Vlaanderen) and the Ministerio de Ciencia, Tecnología e Innovación Productiva (Argentina) for a collaborative research grant. A.T. and L.L. acknowledge the Universidad del País Vasco (Spain) for the research grants GIU12/09 and UFI11/07. D.R.A. acknowledges the Universidad de Buenos Aires (Argentina) and the Consejo Nacional de Investigaciones Científicas y Técnicas (Argentina) for the research grants UBACYT 20020100100197, PIP 11220090100061, and PIP 11220130100377CO. The computational resources (Stevin Supercomputer Infrastructure) and services used in this work were provided by the VSC (Flemish Supercomputer Center), funded by Ghent University, the Hercules Foundation, and the Flemish Government - department EWI. W.P. thanks Pieter Claeys for the fruitful discussions.

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Paper 5

Polynomial scaling approximations and Dynamic Correlation Corrections to Doubly Occupied Configuration Interaction wave functions

Polynomial scaling approximations and Dynamic Correlation Corrections to Doubly Occupied Configuration Interaction wave functions

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(Dated: 25 August 2015)

A class of polynomial scaling methods that approximate Doubly Occupied Configuration Interaction (DOCI) wave functions and improve the description of dynamic correlation is introduced. The accuracy of the resulting wave functions is analysed by comparing energies and studying the overlap between the newly developed methods and full configuration interaction (FCI) wave functions, showing that a low energy does not necessarily entail a good approximation of the exact wave function. Due to the dependence of DOCI wave functions on the single-particle basis chosen, several orbital optimisation algorithms are introduced. An energy-based algorithm using the simulated annealing (SA) method is used as a benchmark. As a computationally more affordable alternative, a seniority number minimising algorithm is developed and compared to the energy based one revealing that the seniority minimising orbital set performs well. Given a well-chosen orbital basis, it is shown that the newly developed DOCI based wave functions are especially suitable for the computationally efficient description of static correlation and to lesser extent dynamic correlation.

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I. INTRODUCTION

The exact solution of the Schrödinger equation^{1,2} for an N -electron system is given, within any basis set, by the full configuration interaction (FCI) procedure. Unfortunately, the FCI method is usually intractable except for small systems. Typically, the computational cost is reduced by incorporating only a selected set of N -electron Slater determinants in the configuration interaction (CI) wave functions, leading to the so-called truncated CI methods, for example CI with only single and double electron excitations (CISD). These excitations are defined with respect to a given reference, e.g. the restricted Hartree-Fock (RHF) determinant². This kind of methods is typically well suited to account for dynamic correlation as they are closely related to performing perturbation theory around a good reference state. A different way of reducing the FCI space is by projecting the wave function only on the determinants with a specified seniority number, where the seniority number equals the number of singly occupied orbitals in a determinant³. The seniority number operator may be formulated as:

$$\hat{\Omega} = \sum_{i,\sigma} a_{i\sigma}^\dagger a_{i\sigma} - \sum_{i,\sigma_1,\sigma_2} a_{i\sigma_1}^\dagger a_{i\sigma_2}^\dagger a_{i\sigma_2} a_{i\sigma_1}, \quad (1)$$

where $a_{i\sigma}^\dagger$ creates a particle in the i -th orbital of an orthonormal basis with spin σ (α or β type) and $a_{i\sigma}$ is the corresponding annihilation operator. In terms of reduced density matrices, the expectation value of the seniority number operator can be obtained as:

$$\begin{aligned} \langle \hat{\Omega} \rangle &= \langle \Psi | \hat{\Omega} | \Psi \rangle \\ &= \sum_i \gamma_{i,i} - 2 \sum_{ii} \Gamma_{ii,ii} \end{aligned} \quad (2)$$

where $\sum_i \gamma_{i,i}$ is the trace over the first-order spin summed reduced density matrix γ , which equals the number of electrons N , and $\sum_{ii} \Gamma_{ii,ii}$ is the partial trace of the second order spin-summed reduced density matrix (2-RDM) Γ . The Doubly Occupied Configuration Interaction (DOCI) method is an example of this class of seniority number based methods, as it lies in the seniority zero sector of the FCI wave function^{4,5}. For a system with L orbitals, and $K = \frac{N}{2}$ electron pairs, the DOCI wave function is given by

$$|\Psi_{\text{DOCI}}\rangle = \sum_{j=1}^{\binom{L}{K}} c_j \prod_{i=1}^K S_{\mathbf{j}(i)}^\dagger |\theta\rangle \quad (3)$$

where $|\theta\rangle$ is the pair vacuum, and $S_i^\dagger = a_{i\alpha}^\dagger a_{i\beta}^\dagger$ are the pair creation operators in the i -th orbital. Each j value corresponds to a vector $\mathbf{j}$ that refers to the string of doubly occupied orbitals for all K pairs. The complexity of a DOCI wave function is much reduced compared to a FCI wave function and therefore comes with a lower computational cost. The interest in DOCI wave functions for chemical purposes lies in its connections with Geminal-based theories for chemical bonding⁶. From a FCI point of view, DOCI is a singlet wave function that is able to describe any possible pairing structure of the chemical bond. As a matter of fact, recent calculations⁴ have established that DOCI wave functions are perfectly suited to capture the static correlations associated to chemical bonds. Furthermore, DOCI wave functions are size extensive. Unfortunately, several problems remain with the DOCI method. Although the number of determinants expanding the DOCI wave function is strongly reduced compared to that of the FCI wave function, the factorial scaling persists. The first goal of this paper is to examine whether truncated DOCI solutions give comparably good quality results at polynomial scaling computational cost. Reduced-cost DOCI solutions have previously been obtained either by a projected Schrödinger equation approach^{7,8}, or by using exactly solvable models⁹ or a variant of the variational 2-RDM method projected on the seniority zero sector of the Hilbert space¹⁰.

DOCI performs well at accounting for static correlation but fails in describing dynamic correlation⁴ whereas CISD wave functions perform rather well for the latter². A second aim of the paper is therefore to establish how methods based on the union of truncated DOCI and truncated one-electron excitations based CI spaces perform for both types of electron correlation at reduced computational cost. We report several DOCI variants and examine the quality of the corresponding wave functions by computing not only their corresponding energies but also their overlap with more advanced wave functions.

An important feature that is typical for non-FCI wave functions is that their quality depends on the single-particle basis chosen. FCI wave functions always lead to equivalent wave functions irrespective of the (orthonormal) basis chosen, be it e.g. natural orbitals, RHF molecular orbitals or any other orthonormal basis. This is no longer true for approximate wave functions such as DOCI and its variants. Hence the need to find the solution with the lowest energy obtainable through a unitary transformation of the orthonormal orbitals. Another aim of the paper is therefore to develop an orbital optimisation algorithm well suited to escape from local energy minima. A good candidate for this purpose was found to be

simulated annealing (SA)¹¹. Although the SA procedure works very well for small systems, we found that it is not practically usable in those cases where the number of active orbitals or electrons is large ($N > 20$), so we also propose a new orbital basis suitable for DOCI and its variants. Some of us have previously shown that the orbital basis that minimises the seniority number of a FCI wave function can be used to achieve a more compact determinantal expansion, where the determinants with zero seniority number are the dominant contributions to the FCI wave function¹². In practice, this means that this orbital basis can be used as a good approximation to the energy optimised DOCI orbitals. As FCI wave functions are hardly tractable for larger systems, we examine whether a seniority number minimising basis derived from a truncated CI wave function serves equally well.

The different wave functions corresponding to the methods reported in this paper can be elegantly summarised using the Venn diagram in Fig. 1. In all cases, a bar ($\bar{}$) notation means that each excitation involves two paired electrons. $\text{CI}\bar{\text{S}}$ for example, means that only excitations of a single electron pair with respect to a closed-shell reference Slater determinant are considered, whereas $\text{CISD}\bar{\text{D}}$ means that all single and double electron excitations plus all double electron-pair excitations are taken into account. $\text{CI}\bar{\text{S}}$ is therefore a subset of CID, $\text{CISD}\bar{\text{D}}$ is a subset of CISDQ, etc.. In Fig. 1, the green circle stands for the DOCI space which comprises up to $\bar{K}$ electron-pair excitations, and the yellow ellipse underneath for the CISD space. The intersection of the DOCI and the CISD spaces is the $\text{CI}\bar{\text{S}}$ space. Furthermore we can distinguish within the DOCI space the double electron-pair excitations (with respect to the same reference as the CISD determinants). We will also discuss hybrid methods that consider the union of DOCI and truncated CI spaces, such as CISD, which will be denoted as $(\text{CISD} \cup \text{DOCI})$, and is contained in the red boundary, and the polynomial scaling approximate hybrid methods such as $\text{CISD}\bar{\text{D}}$, enclosed by a blue dotted line. All methods from Fig. 1 can be used with any choice of (orthonormal) orbitals. We choose for either molecular orbitals as obtained from a preceding Self Consistent Field (SCF) calculation, (globally) energy optimised orbitals by means of SA, or seniority number minimising orbitals.

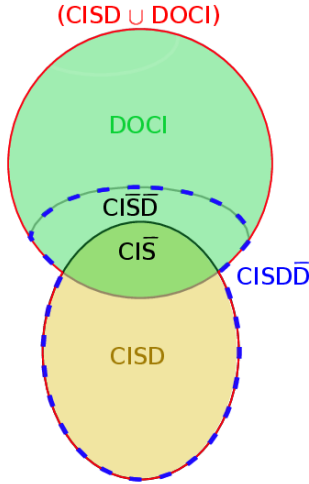


FIG. 1. Overview of the wave functions used for approximations and extensions of the DOCI wave function.

II. ALGORITHMS

A. Computational details and CI solver

In order to assess the accuracy of the methods reported in section I, we consider the symmetric bond stretching of the BeH_2 , H_2O and N_2 molecules, which are standard tests for methods that aim at describing strongly correlated systems. The used atomic basis sets range from minimal STO-3G to split valence cc-pVDZ. The use of minimal basis sets is considered appropriate here given the nature of the methods tested. All one- and two-particle integrals needed are generated by the PSI4 package¹³. For the interface with PSI4 we used the Hamiltonian class of CheMPS2^{14,15}.

For all DOCI, truncated DOCI and hybrid DOCI calculations a general CI solver is used that takes as argument a list of Slater determinants. These Slater determinants, in turn, are built from an orthonormal set of orbitals that may correspond to molecular orbitals or some other orthonormal set. All determinants are encoded as binary strings in terms of

this set and the Hamiltonian is represented in the Slater determinant basis. The variational problem of determining the Slater determinant coefficients is solved using an implicitly restarted Arnoldi algorithm¹⁶ to locate the chosen number of low lying energy states. All potential energy curves reported below describe the ground state.

B. Orbital optimisation algorithms

DOCI and its variants depend on the chosen orthonormal orbital basis used in the Slater determinants entering the CI expansion. Limacher et al.¹⁷ have shown that the basis-dependent DOCI energy surface has many local minima. To cope with those local minimum problems, we now introduce an orbital optimisation algorithm tailored at locating the global energy minimum. For this the simulated annealing algorithm is chosen as an orbital optimiser. Such techniques have been used previously in quantum chemistry¹⁸ albeit to limited extent, often because of their prohibitive computational cost. Here such calculations are nevertheless used whenever feasible because they give good benchmark results.

1. *Energy based orbital optimisation through simulated annealing*

SA is a probabilistic method introduced by Kirkpatrick et al.¹¹ for finding the global minimum of a cost function that may possess several local minima. It does so by emulating the physical process where a solid is gradually cooled and eventually freezes in a minimum energy configuration. This method performs particularly well when there are many local energy minima, as in the case of DOCI wave functions¹⁷. The work flow for the SA procedure pertaining to the orbital optimisation of CI methods is depicted in Fig. 2. In our implementation, we perform a sequence of elementary Jacobi rotations¹⁹ between randomly selected pairs of orbitals over a randomly chosen angle α . These rotations result in a new orthonormal basis that yields a new energy value. The new basis is then, depending on its energy, accepted or rejected with a certain probability depending on a “temperature” T . The rotation angles α are drawn from a normal distribution around zero, and are limited to the interval $[-\alpha_{\max}, \alpha_{\max}]$. Both the temperature T and the maximal angle $\alpha_{\max}$ decrease in the consecutive steps. The starting temperature T is chosen high enough to explore the entire energy surface. Based on our experience, a good choice is $T = 0.5 E_h$. The rate at which

T decreases after each step is chosen as $\delta T = 0.99$. For $\alpha_{\max}$, an initial value $\alpha_{\max} = 1.4$ rad is chosen, and the rate of decrease of the maximum angle is set to $\delta\alpha_{\max} = 0.9999$ as we have found that it is convenient to decrease the maximum angle very slowly so that the flexibility to escape local minima remains. This process is repeated until convergence. For simplicity, we initialise the same T , $\alpha_{\max}$, δT , $\delta\alpha_{\max}$ for all pairs of orbitals.

After the rotation of two orbitals, the energy is calculated (E_{new}) with the chosen level of theory and compared to the energy of the previous orbital configuration (E_{old}). If $E_{\text{new}} < E_{\text{old}}$, the change in the orbitals is always accepted. If $E_{\text{new}} \geq E_{\text{old}}$, a uniform random number $R_{0,1}$ between zero and one is drawn, and if

$$R_{0,1} < \frac{\exp \frac{E_{\text{old}} - E_{\text{new}}}{T}}{\exp \frac{E_{\text{old}} - E_{\text{new}}}{T} + 1} \quad (4)$$

the change is also accepted. This means that the energy may occasionally increase which helps escaping local minima. When T has lowered sufficiently, the chances of such energy increases become negligibly small.

After each step i the temperature and maximum rotation angle are reduced for the next step $i + 1$:

$$T^{(i+1)} = T^{(i)} \delta T \quad (5)$$

$$\alpha_{\max}^{(i+1)} = \alpha_{\max}^{(i)} \delta \alpha_{\max} \quad (6)$$

At the end of each cycle two convergence criteria are checked:

1. Has the maximum number of cycles been reached (here 20000)?
2. Has the maximum number of consecutive non-acceptance steps been reached (here 1000)?

If one of them is fulfilled, the simulated annealing loop is stopped. Otherwise the procedure is repeated.

In order to increase the chances of locating the global minimum, several separate SA calculations are performed and the optimal unitary matrix and energy are selected. After this, an extra SA run is performed with very low T and very small maximum angle, in order to locally optimise the minimum further. Our calculations point out that the SA procedure is very effective, as it consistently produces lower energies than those obtained from methods

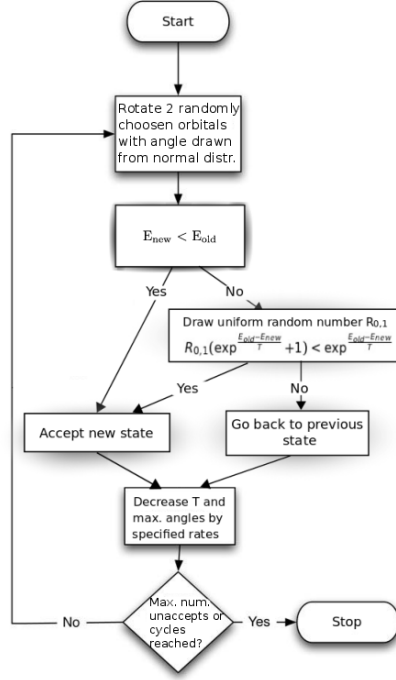


FIG. 2. The work flow of the simulated annealing (SA) orbital optimisation procedure for CI methods as implemented for this paper.

using the orbital gradient and Hessian or the generalised Brillouin theorem^{2,20–22}. The SA results may therefore serve as a benchmark for other optimisation schemes.

In practice, we first perform all DOCI and related calculations using Hartree-Fock molecular orbitals and henceforth results obtained using this basis are labelled with the caption MO. Subsequently, the orbital basis is optimised. A first SA procedure allows only rotations among orbitals that belong to the same irreducible representation. Results using this optimised basis are denoted by OO. In a second procedure, rotations among all orbitals are allowed thereby permitting symmetry breaking. Results with this basis are denoted OO-c1.

2. Seniority based orbital optimisation

For large systems SA is no longer viable. Some of us have previously shown¹² that a promising basis is the one that minimises the seniority number (Eq. (2)) of a FCI wave function. Unfortunately, the computational cost of a FCI calculation severely limits the

applicability of this method. Here we propose to use an orbital basis that minimises the seniority number of a wave function that scales more favorably, e.g., CISD.

Our procedure to minimise the seniority number of a wave function is a very fast converging iterative process based on the algorithm of Subotnik et al.²³, originally introduced for the determination of localised molecular orbitals such as Edmiston-Ruedenberg orbitals²⁴. It follows from Eq. (2) that if the partial trace of the spin summed second order reduced density matrix is maximised, the seniority number of the total wave function is minimised. Our adaptation of the procedure of Subotnik et al.²³ to minimise the seniority number proceeds as follows¹²:

1. Start with a set of orthonormal orbitals, e.g. the RHF molecular orbitals.
2. For $k \geq 0$ (k indicates the number of cycles) determine the 2-RDM for which we want to minimise the seniority number.
3. Construct the matrix $R_{ji}^{(k)} = \Gamma_{ji,ii}^{(k)}$
4. Construct the unitary transformation $U^{(k+1)} = R^{(k)} \left[(R^{(k)})^\dagger R^{(k)} \right]^{-\frac{1}{2}}$.
5. Transform the current orbitals to the new basis with the unitary matrix $U^{(k+1)}$.
6. Set $k = k + 1$, repeat steps 2-6 until $R^{(k)}$ is sufficiently close to a symmetric matrix and the process has converged.

The matrix U in step 4 is guaranteed to be unitary through the polar decomposition of a square complex matrix²⁵. The orbitals produced by minimising the seniority number of a FCI wave function are denoted by the labels Mmin and Mmin-c1, depending respectively on whether only rotations between orbitals of the same irreducible representation are considered or symmetry breaking is allowed. If the seniority number is minimised using a wave function other than FCI, a subscript is added to denote the wave function used (e.g., Mmin_{CISD} when the seniority of a CISD wave function is minimised without symmetry breaking).

III. RESULTS AND DISCUSSION

In the following both the orbital optimisation algorithms and newly described DOCI methods are tested for a set of small molecules with emphasis on their dissociation curves

for the ground state. In the first section III A, the bond breaking curve of BeH_2 through linear symmetric stretching is examined with focus on the effect of different bases on the one hand (subsection III A 1) and the effect of extending DOCI with non-seniority conserving excitations on the other hand (subsection III A 2). As in both cases the OO basis is used, only a minimal basis set is considered. In the second section III B, we report on the performance of truncated DOCI methods (subsection III B 1) and truncated DOCI supplemented with non-seniority conserving excitations (subsection III B 2). Due to the fact that the truncation reduces the computational cost significantly while adding only limited non-seniority conserving excitations, we report results obtained using larger basis sets thereby allowing more insight in dynamic electron correlation effects.

A. Orbital optimisation and dynamic correlation in BeH_2

1. *Basis dependence of DOCI wave functions and energies*

We first describe the impact of the chosen orthonormal orbital basis on the DOCI energy in case of bond breaking in BeH_2 through linear symmetric stretching. This small molecule is computationally tractable for FCI methods and has significant multireference character at bond breaking, making it an ideal test for proof of principle calculations. Table I reports DOCI energies using the STO-3G atomic basis set for orbitals optimised with the SA approach (OO and OO-c1) and for the seniority number minimising ones (Mmin and Mmin-c1 derived from both FCI and CISD), along with the DOCI energy obtained using restricted Hartree-Fock (RHF) based molecular orbitals (MO). Although the STO-3G basis set has its shortcomings due to its size, it still captures the essence of the physics as the shape of the potential energy curve for BeH_2 remains similar for larger basis sets (see below). The lowest energies, obtained using the OO-c1 basis arising from the energy driven global optimisation, can be considered reference values.

Figs. 3(a) and 3(b) show the DOCI potential energy curves in the selected bases with the RHF and FCI curves as references. Fig. 4 depicts DOCI energy differences for the different bases considered.

Table I and Figs. 3 and 4 illustrate several important points. First, the MO basis is found to perform quite well for small interatomic distances compared to the computationally

TABLE I. STO-3G DOCI energy values and differences for the symmetric stretch of BeH₂ using different orthonormal bases. R is the length of the Be-H bonds.

	DOCI Energy/ E_h								
R (Å)	MO	OO	Mmin	Mmin _{CISD}	Mmin _{CISD} - OO	OO-c1	Mmin-c1	Mmin _{CISD} -c1	Mmin _{CISD} -c1 - OO-c1
0.86	-15.295973	-15.296475	-15.296470	-15.296465	0.000010	-15.299640	-15.294537	-15.294546	0.005094
1.02	-15.490483	-15.490920	-15.490914	-15.490907	0.000013	-15.496264	-15.489413	-15.489420	0.006844
1.34	-15.578003	-15.578459	-15.578436	-15.578419	0.000039	-15.590358	-15.590139	-15.590199	0.000159
1.66	-15.510719	-15.511515	-15.511405	-15.511344	0.000170	-15.533722	-15.533153	-15.533328	0.000393
1.98	-15.402028	-15.404541	-15.403776	-15.403513	0.001028	-15.440935	-15.439646	-15.439380	0.001555
2.13	-15.347166	-15.353874	-15.350794	-15.350214	0.003660	-15.395504	-15.391057	-15.391663	0.003841
2.29	-15.297031	-15.328067	-15.306903	-15.305553	0.022514	-15.354530	-15.342597	-15.342969	0.011561
2.45	-15.255160	-15.325976	-15.288084	-15.282966	0.043011	-15.325976	-15.288084	-15.282966	0.043011
2.61	-15.225362	-15.328124	-15.307317	-15.288895	0.039229	-15.328124	-15.307317	-15.288895	0.039229
2.77	-15.210719	-15.330642	-15.325165	-15.307031	0.023611	-15.330642	-15.325165	-15.307031	0.023611
3.09	-15.226272	-15.334189	-15.333775	-15.330958	0.003231	-15.334189	-15.333775	-15.330958	0.003231

much more expensive OO basis. Beyond an internuclear distance of 1.66 Å the energies start to differ dramatically with differences going up to 120 mE_h at 2.77 Å (see Fig. 4(a)). Optimising the orbitals is therefore of utmost importance at longer bond distances although the differences decrease again at still longer distances. (see Fig. 4(a)). Fig. 4(b) shows that the energy obtained from the Mmin basis lies much closer to the OO energy over a larger range of interatomic distances, with differences up to only 38 mE_h near 2.45 Å. Moreover, the difference between energies obtained with the Mmin_{CISD} and the Mmin bases is rather small as can be seen from Table I. Fig. 3(c), which depicts the overlap of the DOCI wave function with the FCI wave function, illustrates the deficiencies of the DOCI wave function in the MO, OO and OO-c1 basis to approximate the FCI wave function around a bond distance of 2.45 Å.

Symmetry breaking has an effect at slightly shorter bond lengths than those where the highest deviations between the Mmin and OO based energies occur (see Fig. 4(c)). As expected for a variational method, symmetry-breaking may lower the energy. Note that the sharp angle in the DOCI(OO-c1) energy curve is not due to states crossing but due to a sudden change in the basis. A similar finding was reported previously by Bytautas et al.⁴ for H₈. In the case of the OO-c1 versus OO basis, symmetry breaking leads to a maximum energy lowering of 42 mE_h at an internuclear distance of 2.13 Å. Such an effect does not necessarily occur for the Mmin and Mmin-c1 bases. Here symmetry breaking may result in higher energies especially at short bond lengths. Although counterintuitive,

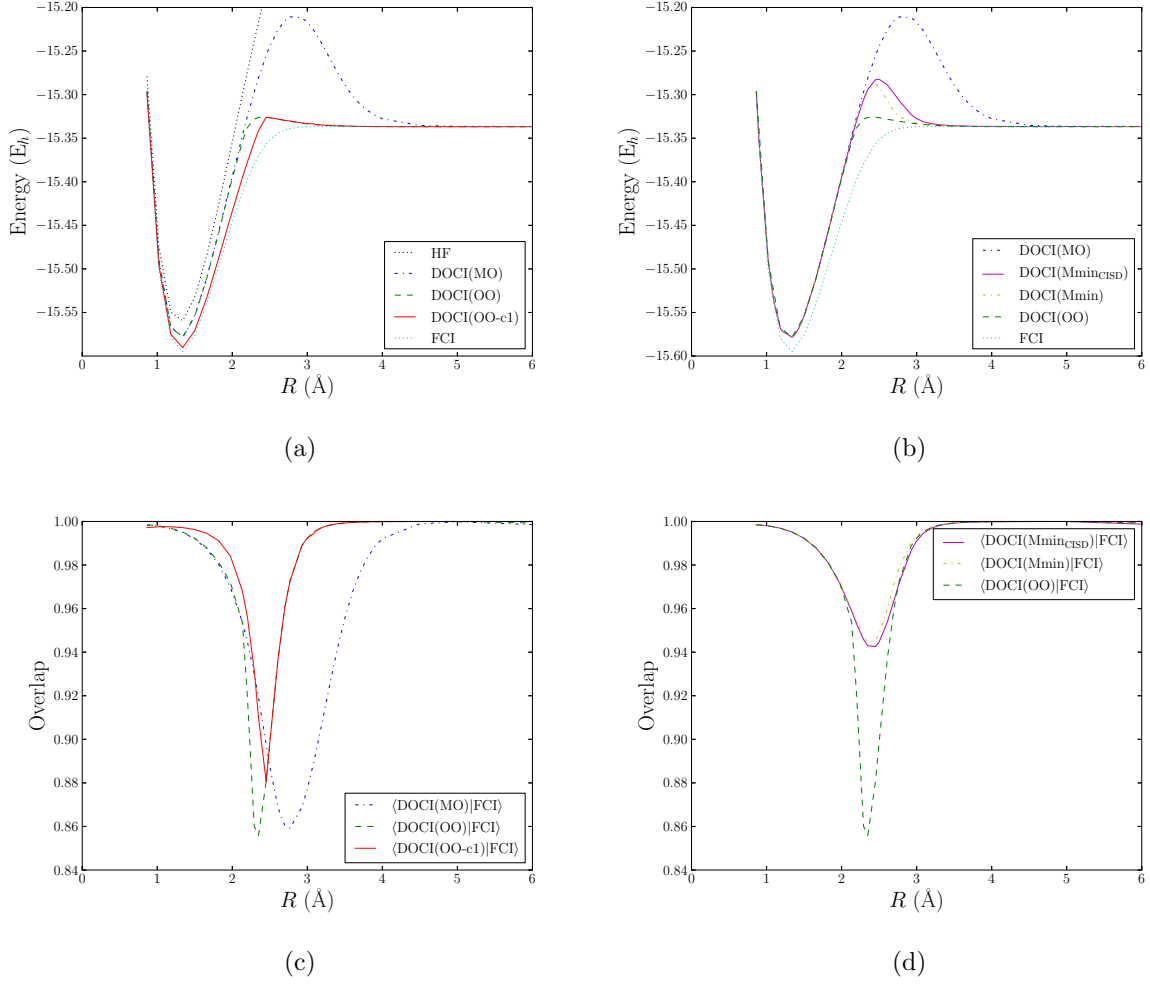


FIG. 3. Symmetric stretch potential energy curves as a function of the Be-H distance (R) in BeH_2 for the (a) RHF, DOCI(MO), DOCI(OO), DOCI(OO-c1), and FCI wave functions, and (b) DOCI(MO), DOCI(Mmin_{CISD}), DOCI(Mmin), DOCI(OO), and FCI wave functions in the STO-3G atomic basis set. (c) overlap between the STO-3G DOCI and FCI wave functions in the MO, OO, and OO-c1 bases. (d) overlap of the STO-3G DOCI and FCI wave functions in the OO, Mmin, and Mmin_{CISD} bases.

this is not in stride with the minimisation condition behind the Mmin procedure, as this procedure searches for a minimum in *seniority number*, rather than in *energy*. By breaking the symmetry, the method can better pair the electrons, irrespective of the energy. Still, the energy increase is marginal with a maximum of 2 mE_h while for the vast majority of the energy curve symmetry breaking still lowers the energy.

As a whole, for most of the interatomic distances, the seniority-number minimising basis

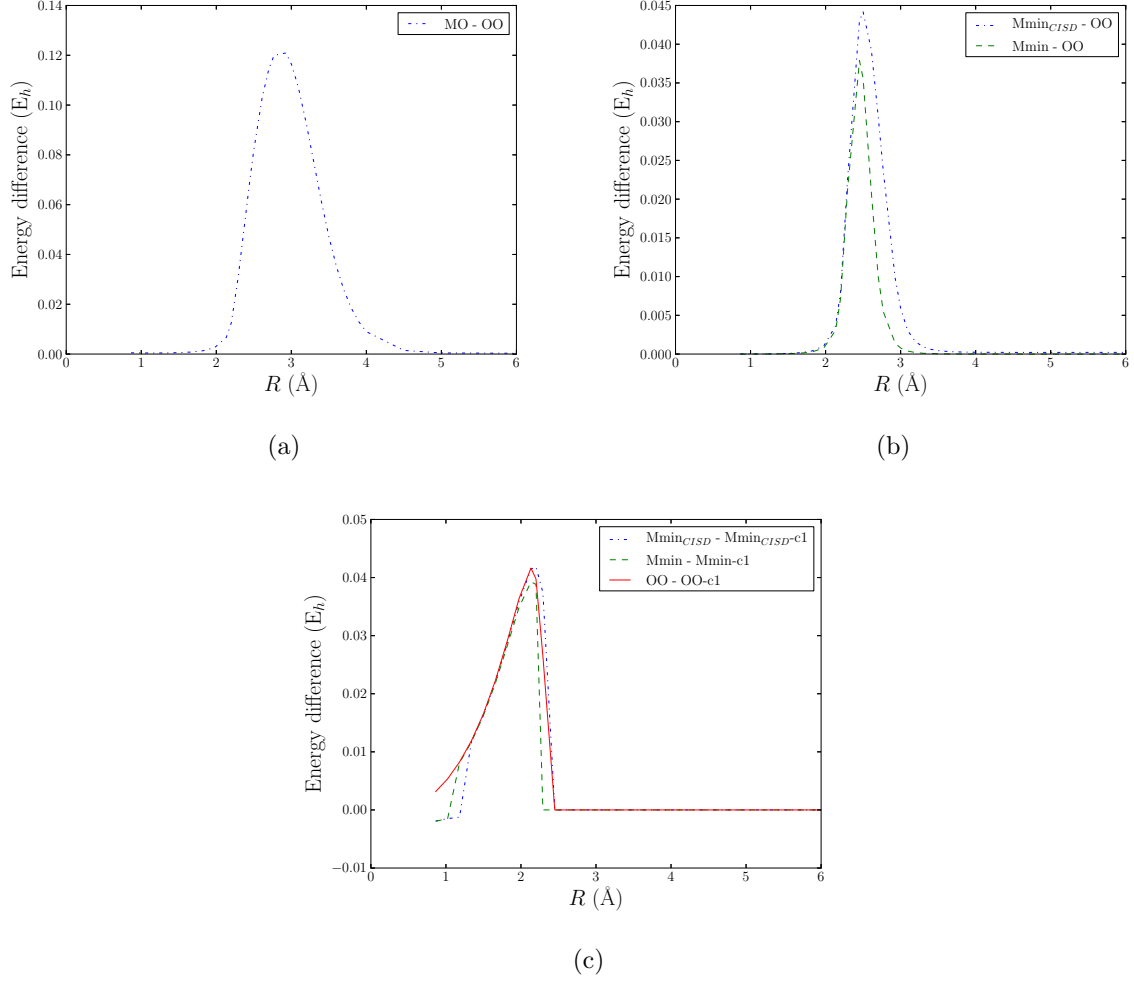


FIG. 4. STO-3G DOCI energy differences between different bases as a function of the Be-H distance (R) in BeH_2 . (a) effect of energy based orbital optimisation, (b) comparison between energies obtained with the energy optimised (OO) and Mmin and Mmin_{CISD} seniority optimised orbitals, and (c) effect of symmetry breaking.

is a good alternative to the energy based optimised orbitals with the computationally cheap Mmin_{CISD} basis also performing rather well.

2. *Dynamic correlation and hybrid DOCI wave functions.*

It is clear from Table I and Figs. 3(a) and 3(b), that one can distinguish between three different regimes during bond breaking. At small bond distances Hartree-Fock theory yields a fairly good wave function. Indeed, near the equilibrium bond length the RHF determinant

is the most important determinant in the FCI expansion. This regime extends well across the valley of the FCI potential minimum. This is consistent with the observation that, in this regime, the FCI natural orbitals have occupations roughly zero or two (see Fig. 5).

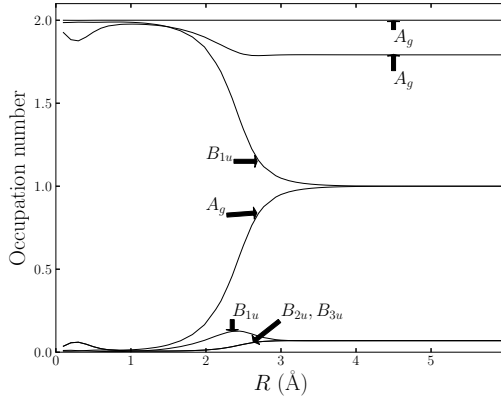


FIG. 5. Occupation numbers of the STO-3G FCI natural orbitals as a function of the Be-H bond length (R) for the symmetric bond stretching of BeH_2 . The symmetry labels used are based on the D_{2h} Abelian point group used in the calculations.

As soon as bond breaking starts, dynamic correlation becomes increasingly important, while farther towards dissociation static correlation gains importance. The interval where in BeH_2 dynamic correlation dominates corresponds approximately to $[1.8 \text{ \AA}, 2.5 \text{ \AA}]$. In this interval the occupation number of the natural orbitals closest to the Fermi level (between the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) levels from Hartree-Fock) start to differ from zero or two, although the complete smearing out of occupation numbers as in the strong correlation limit does not occur.

In the so-called static correlation regime it is no longer possible to find a good single reference approximation to the general wave function, e.g. the RHF energy deviates strongly from the FCI energy (see Fig. 3(a)). This is well reflected in the fact that many more natural orbitals have significant occupation numbers and hence, the distinction between occupied and virtual orbitals vanishes. The strong static correlation regime is characterised by degenerate strongly-occupied molecular orbitals. The particular structure of the DOCI wave function turns out to be very suitable to describe this, since the DOCI wave function is a complete CI expansion in terms of electron pairs⁴.

As can be observed from Fig. 3(a), the peculiar hump in the DOCI(MO) potential

energy curve within the dynamic correlation regime reflects the difficulties of the DOCI wave function to describe dynamic correlation properly in the MO basis. The hump itself is not an artefact of the minimal basis set as DOCI(MO) calculations using the 6-31G and cc-pVDZ basis set also show a similar feature (see below). Using the OO and OO-c1 bases reduces the extent of the problem but does not completely alleviate it. As the importance of dynamic correlation increases, the FCI and DOCI energies differ more. Once static correlation becomes more important than dynamic correlation, the particular structure of the DOCI wave functions causes this difference to decrease. The problems of the DOCI wave function in the dynamic correlation regime can be solved by applying multi-reference perturbation theory^{26,27}, or by adding extra determinants in its expansion²⁸.

To better understand the correspondence between the DOCI wave function in different bases and the FCI wave function, Fig. 3(c) shows the overlap between both wave functions in the MO, OO, and OO-c1 bases in the STO-3G basis set. This figure illustrates the failure of DOCI in the dynamic correlation regime. At shorter bond distances and near equilibrium, DOCI performs well as it basically acts as a correction scheme for the dominant RHF ground-state. At large internuclear separation, in the strong correlation limit, we again find high overlap between DOCI and FCI wave functions. In the dynamic correlation regime the overlap is much lower with a minimum of about $|\langle \text{DOCI}(\text{OO}) | \text{FCI} \rangle|^2 = (0.86)^2 = 0.74$ around 1.7 Å, pointing out that the FCI wave function carries important contributions from configurations outside the DOCI space. Note that orbital optimisation from the MO to the OO basis does reduce the range of bond distances where these problems occur, but does not eliminate the effects of dynamic correlations completely. Also note that the poor overlap persists, however shifted towards shorter R . Remarkably, the overlap between the Mmin or Mmin_{CISD} based DOCI wave function and the FCI wave function is significantly better than the OO based one (see Fig. 3(d)) although the Mmin and Mmin_{CISD} based DOCI wave functions do not yield the lowest energies (see Fig. 3(b)). This is consistent with the previous reports^{29,30} that energy minimisation alone does not guarantee finding the wave function most similar to the FCI one. The OO basis is designed to lower the energy and will do so by focussing on those determinants that assist it maximally whereas the treatment of (incipient) static correlation is less important. The Mmin basis, on the other hand, capitalises maximally on zero seniority determinants typically important to properly treat static correlation. Breaking the symmetry as in the OO-c1 basis does improve the quality of

the wave function in the dynamic correlation regime. Note that Fig. 3(c) shows that even the DOCI(MO) wave function has significantly higher overlap with the FCI wave function than the DOCI(OO) one for $2.1\text{\AA} \leq R \leq 2.5\text{\AA}$. To conclude, one should be cautious when performing energy optimisation, as this process may reduce the overlap with the exact wave function, even if a variational method is used (see Fig. 3(c)).

Although the Mmin and Mmin_{CISD} bases significantly improve the overlap of the DOCI wave function with the FCI wave function in the dynamic correlation regime compared with the OO, and even OO-c1 orbitals, there still remains a small discrepancy at intermediate bond distances (with a minimum of $|\langle \text{DOCI}(\text{Mmin}) | \text{FCI} \rangle|^2 = (0.94)^2 = 0.88$). In an attempt

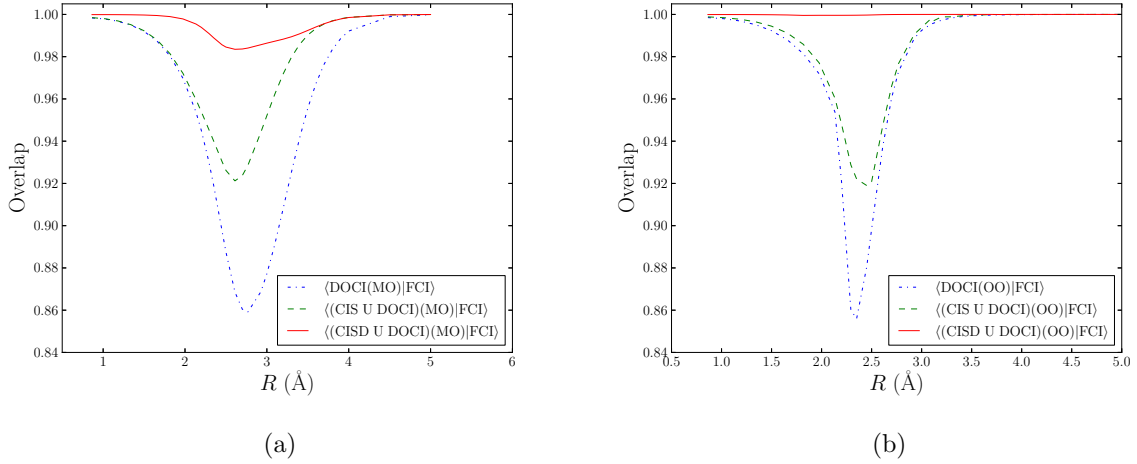


FIG. 6. Overlap of the DOCI, $(\text{CIS} \cup \text{DOCI})$, $(\text{CISD} \cup \text{DOCI})$ wave function with the FCI wave function in the (a) MO and (b) OO bases for the BeH_2 molecule in the STO-3G atomic basis set. R is the distance of the stretched Be-H bonds.

to improve the DOCI wave function, extra determinants from the CIS and CISD spaces are now added to the Slater determinant expansion. This leads to the hybrid $(\text{CIS} \cup \text{DOCI})$ and $(\text{CISD} \cup \text{DOCI})$ wave functions, respectively. Fig. 6 shows the overlap between the DOCI, $(\text{CIS} \cup \text{DOCI})$, and $(\text{CISD} \cup \text{DOCI})$ wave functions and the FCI one, for the MO (Fig. 6(a)) and OO bases (Fig. 6(b)). These figures show that the overlap improves dramatically upon inclusion of broken pair excitations, again consistent with the described importance of dynamic correlation. This agrees with the fact that second order perturbation theory (MP2) improves on the description of dynamic correlation by including doubly excited determinants both inside and outside DOCI space. The advantage of methods that unite DOCI and

truncated CI spaces is that, compared to FCI, the number of determinants remains smaller. For instance, in the case of BeH_2 , the number of determinants required in the STO-3G (CISD $\cup$ DOCI) and FCI methods are 227 and 1225, respectively, while the overlap between the (CISD $\cup$ DOCI) and FCI wave functions remains consistently large over the entire bond-breaking curve (see Fig. 6(b)).

B. New approximate DOCI methods

1. *Truncated DOCI*

DOCI is a powerful method for the description of static correlation, but unfortunately still scales exponentially as it is a complete CI method albeit in electron-pair space. As in standard one-electron excitation based CI, it is therefore of interest to examine whether a truncated DOCI approach is viable. Henceforth, truncated DOCI wave functions will be denoted by $\text{CI}\bar{\text{S}}$, $\text{CI}\bar{\text{S}}\bar{\text{D}}$, etc., for a single reference closed-shell determinant supplemented with either all single electron-*pair* excitations or all single and double electron-*pair* excitations respectively. DOCI then corresponds to $\text{CI}\bar{\text{S}}\bar{\text{D}}\bar{\text{T}}\bar{\text{Q}}\dots\bar{K}$. To analyse how much information of the DOCI wave function remains in the truncated DOCI wave functions, the overlap between both is computed as well as the corresponding energies during the bond breaking of the N_2 molecule and the symmetric stretch of the BeH_2 molecule (see Figs. 7, 8, and 9). The MO basis obtained from a Hartree-Fock calculation with the 6-31G atomic basis set is used for all analyses in this subsection as the MO basis is the commonly used reference for one-electron excitation based CI.

Fig. 7 shows that the truncated DOCI methods yield energies fairly close to the DOCI result although the required level of truncation varies (N_2 requiring up to three electron-pair excitations whereas for the other molecule $\text{CI}\bar{\text{S}}\bar{\text{D}}$ largely suffices). Note that Fig. 7(a) shows a clear hump in the DOCI(MO) energy, reminiscent of what was found in Fig. 3(a) where a minimal basis set was used. The overlap of the truncated DOCI and DOCI wave functions is depicted in Fig. 8. It is clear that at small and intermediate bond distances single electron-pair excitations alone are able to describe the DOCI wave function with high accuracy. However, at larger bond distances single and double electron-pair excitations are needed for BeH_2 , and even single, double and triple electron-pair excitations must be considered for N_2 .

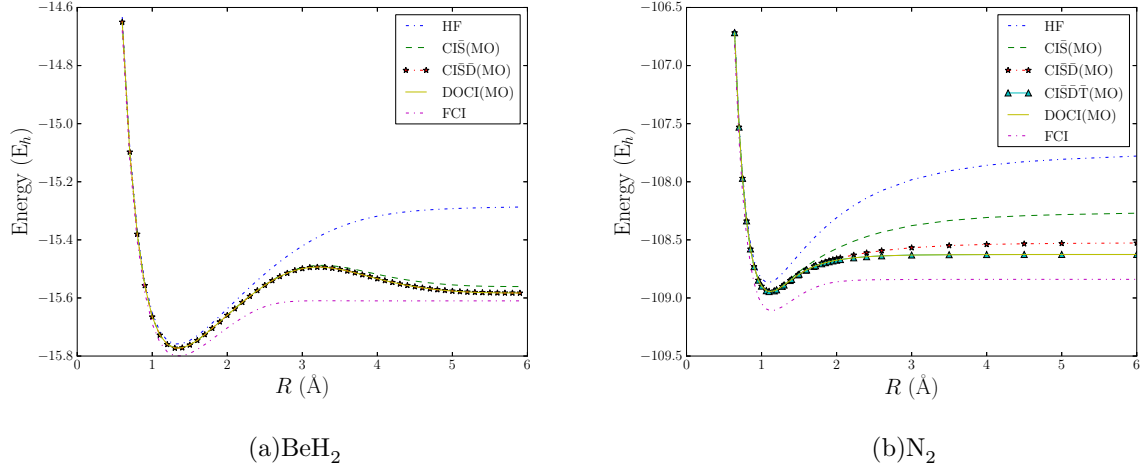


FIG. 7. Potential energy curves for the symmetric stretch of (a) linear BeH₂ and (b) the N₂ molecule, at the RHF, CI $\bar{S}$, CI $\bar{S}\bar{D}$, DOCI and FCI levels of theory with 6-31G based MO orbitals. For N₂ the CI $\bar{S}\bar{D}\bar{T}$ method is also included. R is the length of the stretched bond.

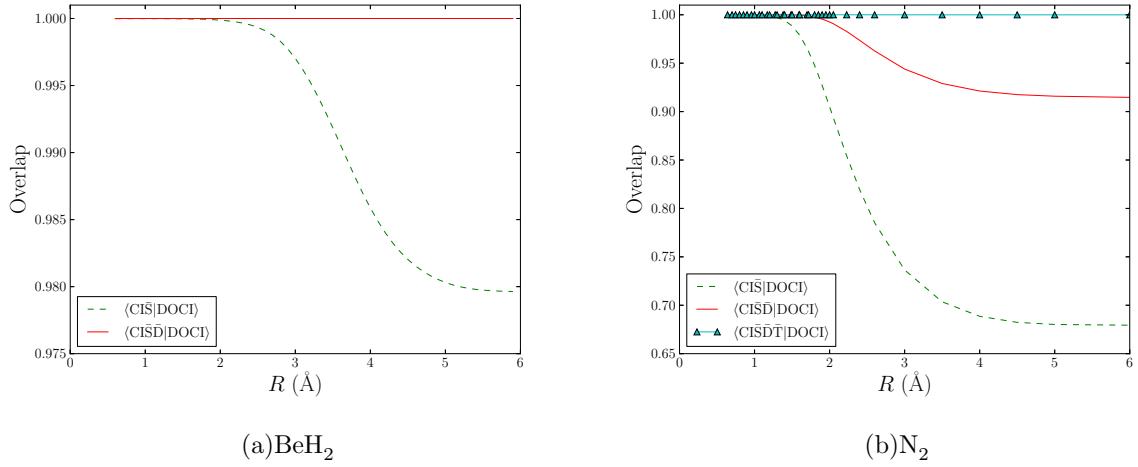


FIG. 8. Overlap of the CI $\bar{S}$ and CI $\bar{S}\bar{D}$ wave function with the DOCI one using 6-31G based MO orbitals for the symmetric stretch of (a) linear BeH₂ and (b) the N₂ molecule. For N₂ the overlap with the CI $\bar{S}\bar{D}\bar{T}$ wave function is also included. R is the length of the stretched bond.

There the overlap with DOCI is almost perfect over the entire range of distances. Finally, Fig. 9 shows the sum of the squares of the coefficients of the RHF determinant (RHF(DET)), and all single ($\bar{S}$ (DET)) and double ($\bar{D}$ (DET)) electron-pair excited determinants of the DOCI wave function for the BeH₂ and N₂ molecules. For N₂, also the sum of the squares of the coefficients of triple electron-pair excited determinants ($\bar{T}$ (DET)) are included. This

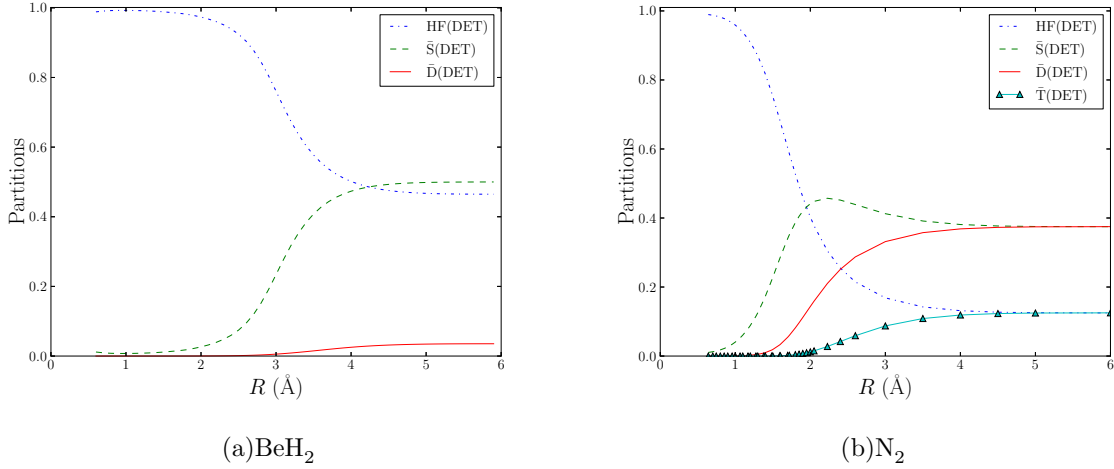


FIG. 9. Sums of squared Slater determinant coefficients of different excitation levels in the DOCI wave function using 6-31G based MO orbitals for the symmetric stretch of (a) linear BeH_2 and (b) the N_2 molecule. R is the length of the stretched bond.

reflects the amount of information of the DOCI wave function that is contained in its parts. The figure confirms the trends expected from the earlier findings: RHF performs well at short bond distances and the contributions of higher excited determinants to the DOCI wave function become larger as the bond distance increases.

2. Approximate hybrid DOCI

On the one hand, hybrid methods based on the addition of disjoint determinant spaces to supplement the DOCI wave function, as described above in section III A 2 and previously by some of us²⁸, still scale less than desirable with system size. On the other hand, fairly good approximations to DOCI are possible by truncating DOCI to lower excitation levels only, as put forward in section III B 1. Combining truncation of DOCI and extending it with electron-pair breaking determinants from standard one-electron excitation based CI, we come naturally to approximate methods that incorporate some lower *one-electron* excitations of a reference along with electron-*pair excited* determinants from DOCI. Examples of such combinations are the CISD $\bar{\bar{D}}$ and CISD $\bar{\bar{D}}\bar{\bar{T}}$ levels of theory, where CISD is augmented with two electron-*pair* excited determinants or two and three electron-*pair* excited determinants respectively. CISD $\bar{\bar{D}}$ is therefore a subset of CISDQ where, among the quadru-

ple excitations, only those determinants are withheld that correspond to excitations of two electron-*pairs*. In this way, it is possible to add many relevant higher excitations in a computationally feasible way. This can be combined with the seniority number minimising basis which is obtained through a fast iterative process and yet improves the description of the electronic structure in the static correlation regime (see Fig. 10). Seniority minimisation using a CISD wave function allows a further gain in speed compared to seniority number minimising directly in the approximate hybrid space as the CISD wave function contains fewer determinants compared to most approximate hybrid methods. The advantage of the present type of approximate hybrid methods is thus that the computational cost scales much more favourably with system size (in this case polynomial scaling, see Table II) providing accurate energies at much smaller cost (e.g., CISD $\bar{D}$ for BeH₂ in the cc-pVDZ basis set contains 5986 Slater determinants compared to the 4096576 Slater determinants included in the FCI wave function).

TABLE II. Number of determinants, N_{det} , for a selection of discussed methods for BeH₂ and N₂ in cc-pVDZ, together with the percentage of the FCI determinants contained.

Methods	BeH ₂		N ₂	
	N_{det}	$\frac{N_{det}}{N_{det}(FCI)} 100$	N_{det}	$\frac{N_{det}}{N_{det}(FCI)} 100$
CIS	64	0.002	148	$1.100 \cdot 10^{-8}$
CIS $\bar{D}$	694	0.017	4558	$3.250 \cdot 10^{-7}$
CIS $\bar{D}\bar{T}$	2024	0.049	51108	$3.645 \cdot 10^{-6}$
DOCI	2024	0.049	1184040	$8.446 \cdot 10^{-5}$
CISD	5356	0.131	30724	$2.192 \cdot 10^{-6}$
CISD $\bar{D}$	5986	0.146	35134	$2.506 \cdot 10^{-6}$
CISD $\bar{D}\bar{T}$	7316	0.179	81684	$5.826 \cdot 10^{-6}$
(CISD $\cup$ DOCI)	7316	0.179	1214616	$8.664 \cdot 10^{-5}$
FCI	4096576	100	1401950721600	100

Fig. 10 shows the symmetric stretching potential energy curve for BeH₂ obtained using the CIS $\bar{D}$ (Mmin_{CISD}), DOCI(Mmin_{CISD}), CISD(MO), CISD $\bar{D}$ (MO), CISD $\bar{D}$ (Mmin_{CISD}) methods for the cc-pVDZ atomic basis set, and the FCI and coupled cluster CCSD(T) methods as references. It shows the improved description of the dissociation limit by adding extra pair excitations to the CISD wave function, and the enhancing effect of the Mmin_{CISD} basis on those pair excitations. Both CISD $\bar{D}$ curves lie fairly close to the FCI one but with still a relevant improvement from using the seniority number minimising basis (Mmin_{CISD}). The remaining errors lie in the mE_h scale. Note that CCSD(T)^{31,32} (in the MO basis) does

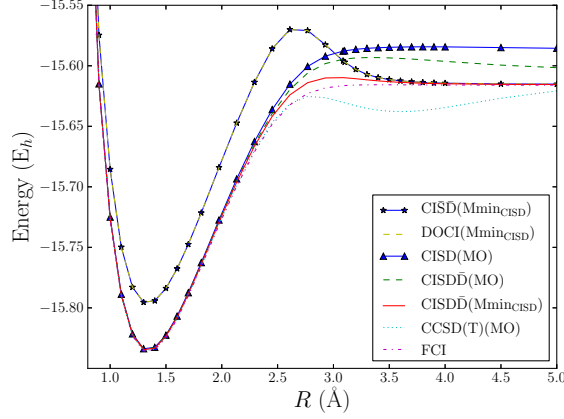


FIG. 10. Potential energy curve for symmetric stretching of BeH_2 using the $\text{CISD}\bar{\bar{D}}$, DOCI and $\text{CISD}\bar{\bar{D}}$ methods in the seniority number minimising basis ($\text{Mmin}_{\text{CISD}}$) and CISD , $\text{CISD}\bar{\bar{D}}$ and CCSD(T) methods in the MO basis with FCI as reference. All calculations were performed with the cc-pVDZ atomic basis set. R denotes the Be-H bond length.

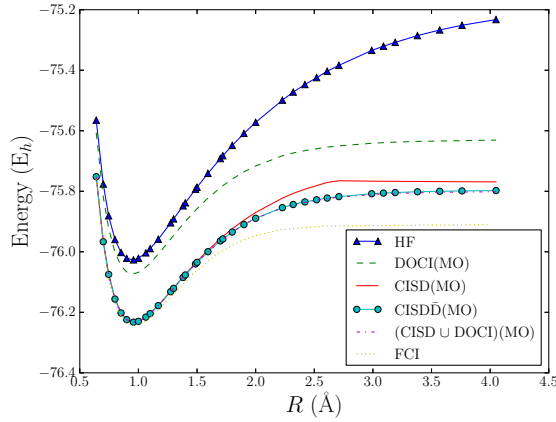


FIG. 11. Potential energy curve for symmetric stretching of the H-O bonds in H_2O using the RHF, DOCI , CISD , $(\text{CISD} \cup \text{DOCI})$, $\text{CISD}\bar{\bar{D}}$, and FCI methods using MO obtained from the cc-pVDZ atomic basis set. R denotes the H-O bond length.

not perform well when static correlation is important. The most significant deviation of the $\text{CISD}\bar{\bar{D}}(\text{Mmin}_{\text{CISD}})$ energy from the FCI one is in the regime where dynamic correlation is dominant. This is most likely a remnant of the fact that the $\text{Mmin}_{\text{CISD}}$ basis does not yield very good energies in this regime. Note also that $\text{CISD}\bar{\bar{D}}(\text{MO})$ still results in a hump somewhat reminiscent of that observed earlier albeit now at larger distances and that it is

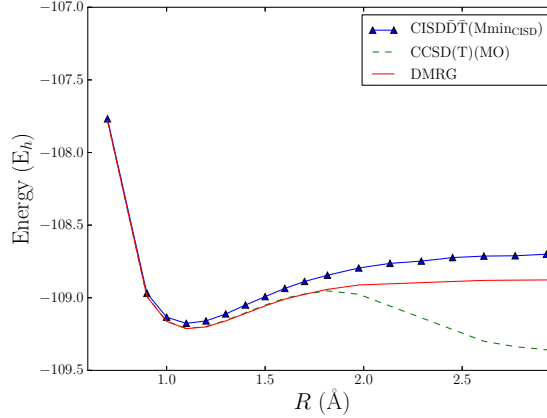


FIG. 12. Potential energy curve for the N_2 dimer for CCSD(T) in the MO basis, CISDD $\bar{T}$ (Mmin_{CISD}, CAS(10,18)) and DMRG^{14,15} using the cc-pVDZ atomic basis set. R is the interatomic distance.

much smaller. This is thanks to the inclusion of the one electron and unpaired two electron excitations that assist in properly accounting for dynamic correlation. The most important observation in Fig. 10 is that the CISDD $\bar{T}$ (Mmin_{CISD}) energies follow closely the CISD(MO) energy curve wherever the latter method lies close to FCI and that it lies very close to the DOCI(Mmin_{CISD}) results towards dissociation. In the area between both regimes, the energy error with respect to FCI is the smallest among all methods tested.

Fig. 11 shows the potential energy curve of the symmetric stretching of the H_2O molecule at several levels of theory for the cc-pVDZ atomic basis set. It shows that the (CISD $\cup$ DOCI) and CISDD $\bar{T}$ potential energy curves are indistinguishable over the entire bond length range, and that both methods improve significantly on CISD in the static correlation regime. In general, for systems with not too many electrons, such as H_2O , the difference in energy between this approximate hybrid (CISDD $\bar{T}$) method and the hybrid method (CISD $\cup$ DOCI) is negligible.

Finally, Fig. 12 shows the potential energy surface for N_2 in the cc-pVDZ basis. The methods compared are CCSD(T) in the MO basis and the CISDD $\bar{T}$ (Mmin_{CISD}, CAS(10,18)). Density matrix renormalisation group (DMRG)^{14,15} energies with FCI accuracy are added as a reference. CCSD(T) performs better at equilibrium and intermediate bond distances, but the approximate hybrid method outperforms CCSD(T) in the dissociation limit. The basic implementation of our routines made us resort to an active space of

10 electrons in 18 orbitals for N_2 in cc-pVDZ. This was probably the reason why CISD $\bar{\bar{T}}$ ($M_{\text{min}_{\text{CISD}}}$) is less accurate at equilibrium (see Fig. 12).

IV. CONCLUSIONS

The orbital dependence of DOCI wave functions and energies has been scrutinised. This is done firstly by comparing the DOCI energies, obtained using different bases, among each other and with reference FCI energies, and secondly by studying wave function overlaps. The straightforward use of molecular orbitals often results in rather poor DOCI energies and wave functions. To ameliorate this, a technique based on simulated annealing (SA) is described to search for the optimal single-particle basis that globally minimises the energy. This approach is found to significantly reduce the energy difference between DOCI and the FCI wave function, especially in the dynamic correlation regime. The SA approach is computationally, however, too costly and it is shown that an orbital optimisation algorithm minimising the seniority of the CISD wave function, is an efficient alternative yielding nearly as good results, especially in the static correlation regime. Moreover, this basis often results in better overlap with the reference wave functions despite a slightly higher energy than that obtained with the SA optimised basis. This shows that better agreement in wave function and energy do not always coincide.

Next, a set of new methods related to DOCI has been introduced. The first type of methods are truncated DOCI methods where the level of pair excitations considered is reduced to e.g., only one pair, two pairs etc., much like in one electron excitation based CIS, CISD, ... The results obtained using this method show that static correlation, as present near bond dissociation, is already captured with a limited level of excitations. Dynamic correlation is not properly accounted for at this level. In order to properly describe dynamic correlation, in the second set of methods these truncated DOCI methods are supplemented with determinants obtained from unpaired electron excitations resulting in methods that combine e.g., one and two pair excitations from the determinants contained in DOCI with all unpaired one and two electron excitations. The resulting methods scale polynomially with system size, making them computationally attractive and affordable for larger systems.

ACKNOWLEDGMENTS

M.V.R., W.P., S.D.B., P.B. and D.V.N. are members of the QCMM alliance Ghent-Brussels. M.V.R., W.P., S.D.B. and P.B. acknowledge the support from the Research Foundation Flanders (FWO Vlaanderen). P.B. and D.R.A. acknowledge the FWO Vlaanderen and the Ministerio de Ciencia, Tecnología e Innovación Productiva (Argentina) for collaborative research grant VS.0001.14N. D.R.A. acknowledges the Universidad de Buenos Aires (Argentina) and the Consejo Nacional de Investigaciones Científicas y Técnicas (Argentina) for research grants Nos. UBACYT 20020100100197, PIP 11220090100061 and PIP 11220130100377CO. A.T. and L.L. acknowledge the Universidad del Pais Vasco (Spain) for research grants Nos. GIU12/09 and UFI11/07. The computational resources (Stevin Supercomputer Infrastructure) and services used in this work were provided by the VSC (Flemish Supercomputer Center), funded by Ghent University, the Hercules Foundation and the Flemish Government - department EWI.

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Appendices

Appendix A

List of publications

- B. Verstichel, H. van Aggelen, W. Poelmans, D. Van Neck, “Variational Two-Particle Density Matrix Calculation for the Hubbard Model Below Half Filling Using Spin-Adapted Lifting Conditions”, *Physical Review Letters* **108**, 213001 (2012)
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- B. Verstichel, W. Poelmans, S. De Baerdemacker, S. Wouters, D. Van Neck, “Variational optimization of the 2DM: approaching three-index accuracy using extended cluster constraints”, *The European Physical Journal B* **87**, 59 (2014)
- S. Wouters, W. Poelmans, P.W. Ayers, D. Van Neck, “CheMPS2: a free open-source spin-adapted implementation of the density matrix renormalization group for ab initio quantum chemistry”, *Computer Physics Communications*, **185**, 1501-1514 (2014)
- M. Van Houteghem, A. Ghysels, T. Verstraelen, W. Poelmans, M. Waroquier, V. Van Speybroeck, “Critical analysis of the accuracy of models predicting or extracting liquid structure information”, *Journal of Physical Chemistry B*, **118**, 2451–2470, (2014)
- S. Wouters, W. Poelmans, S. De Baerdemacker, P.W. Ayers, D. Van Neck, “CheMPS2: Improved DMRG-SCF routine and correlation functions”, *Computer Physics Communications*, **191**, 235-237, (2015)
- W. Poelmans, M. Van Raemdonck, B. Verstichel, S. De Baerdemacker, A. Torre, L. Lain, G. Massaccesi, D. Alcoba, P. Bultinck, D. Van Neck, “Variational optimization of the second order density matrix corresponding to a seniority-zero configuration interaction wave function”, *Journal of Chemical Theory and Computation*, **11**, 4064-4076, (2015)
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- K. Lejaeghere, G. Bihlmayer, T. Björkman, P. Blaha, S. Blügel, V. Blum, D. Caliste, I. E. Castelli, S. J. Clark, A. Dal Corso, S. de Gironcoli, T. Deutsch, J. Kay Dewhurst, I. Di Marco, C. Draxl, M. Dułak, O. Eriksson, J. A. Flores-Livas, K. F. Garrity, L. Genovese, P. Giannozzi, M. Giantomassi, S. Goedecker, X. Gonze, O. Grånäs, E. K. U. Gross, A. Gulans, F. Gygi, D. R. Hamann, P. J. Hasnip, N. A. W. Holzwarth, D. Iușan, D. B. Jochym, F. Jollet, D. Jones, G. Kresse, K. Koepernik, E. Küçükbenli, Y. O. Kvashnin, I. L. M. Locht, S. Lubeck, M. Marsman, N. Marzari, U. Nitzsche, L. Nordström, T. Ozaki, L. Paulatto, C. J. Pickard, W. Poelmans, M. I. J. Probert, K. Refson, M. Richter, G. Rignanese, S. Saha, M. Scheffler, M. Schlipf, K. Schwarz, S. Sharma, F. Tavazza, P. Thunström, A. Tkatchenko, M. Torrent, D. Vanderbilt, M. J. van Setten, V. Van Speybroeck, J. M. Wills, J. R. Yates, G. Zhang, S. Cottenier, “The Kohn-Sham equation of state for elemental solids: a solved problem”, *Science* (2015) (submitted)

Appendix B

Second quantization

The second quantization formalism is used in this work. This appendix will give a very short introduction to the fermionic case. A complete introduction can be found in references 237 and 2. The state on which the operators acts is the antisymmetric N particle state,

$$|\alpha_1 \alpha_2 \dots \alpha_N\rangle = -|\alpha_2 \alpha_1 \dots \alpha_N\rangle. \quad (\text{B.1})$$

The operator $\hat{a}_\alpha^\dagger$ creates a particle in the single-particle state α

$$\hat{a}_\alpha^\dagger |\alpha_1 \alpha_2 \dots \alpha_N\rangle = |\alpha \alpha_1 \alpha_2 \dots \alpha_N\rangle, \quad (\text{B.2})$$

while the annihilation operator, $\hat{a}_\alpha$, does the opposite

$$\hat{a}_\alpha |\alpha \alpha_1 \alpha_2 \dots \alpha_N\rangle = |\alpha_1 \alpha_2 \dots \alpha_N\rangle. \quad (\text{B.3})$$

We will use $|\rangle$ to denote the particle vacuum,

$$\hat{a}_\alpha |\rangle = 0. \quad (\text{B.4})$$

The addition and removal operators obey the fundamental anticommutation relations:

$$\{\hat{a}_\alpha, \hat{a}_\beta^\dagger\} = \hat{a}_\alpha \hat{a}_\beta^\dagger + \hat{a}_\beta^\dagger \hat{a}_\alpha = \delta_{\alpha\beta}, \quad (\text{B.5a})$$

$$\{\hat{a}_\alpha, \hat{a}_\beta\} = \{\hat{a}_\alpha^\dagger, \hat{a}_\beta^\dagger\} = 0. \quad (\text{B.5b})$$

Note that the Pauli exclusion principle nicely follows from this:

$$\hat{a}_\alpha^\dagger \hat{a}_\alpha^\dagger = -\hat{a}_\alpha^\dagger \hat{a}_\alpha^\dagger = 0, \quad (\text{B.6})$$

i.e. every single-particle state can be occupied by at most one fermion. A one-body operator $\hat{T}$ can be written in this formalism as

$$\hat{T} = \sum_{\alpha\beta} \langle \alpha | T | \beta \rangle \hat{a}_\alpha^\dagger \hat{a}_\beta. \quad (\text{B.7})$$

For a two-body operator $\hat{V}$, this becomes

$$\hat{V} = \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | V | \gamma\delta \rangle \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\delta \hat{a}_\gamma. \quad (\text{B.8})$$

Note that the order for γ and δ in the operators and the two-body matrix element is different. An alternative form for eq. (B.8) is

$$\hat{V} = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} (\alpha\beta | V | \gamma\delta) \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\delta \hat{a}_\gamma, \quad (\text{B.9})$$

where

$$\langle \alpha\beta | V | \gamma\delta \rangle = (\alpha\beta | V | \gamma\delta) - (\alpha\beta | V | \delta\gamma), \quad (\text{B.10})$$

and $|\alpha\beta\rangle$ is a direct product state (not antisymmetric). A much used operator is the number operator

$$\hat{n} = \sum_{\alpha} \hat{a}_\alpha^\dagger \hat{a}_\alpha, \quad (\text{B.11})$$

which simply counts the number of particles in a state:

$$\hat{n} |\alpha_1 \alpha_2 \dots \alpha_N\rangle = N |\alpha_1 \alpha_2 \dots \alpha_N\rangle \quad (\text{B.12})$$

Appendix C

Mathematics

All results shown here can be found in references 22, 161, 164.

C.1 Convexity

A set S in a linear space is convex if and only if for every $x_1, x_2 \in S$ holds

$$\alpha x_1 + \beta x_2 \in S, \quad (\text{C.1})$$

with $\alpha, \beta \geq 0$ and $\alpha + \beta = 1$. This means that the line segment connecting any two points in the set must also be part of the set.

A function $f : \mathbb{R}^n \rightarrow \mathbb{R}$ is convex if the domain of f is a convex set and for any two points x and y in the domain of f must hold

$$f(\alpha x + \beta y) \leq \alpha f(x) + \beta f(y), \quad (\text{C.2})$$

with $\alpha, \beta \geq 0$ and $\alpha + \beta = 1$. One can prove that a function is convex if on a convex set its Hessian is positive semidefinite.

C.2 Positive semidefinite matrices

We now restrict ourself to symmetric matrices. A symmetric matrix is always diagonalizable by a orthogonal matrix and has real eigenvalues. We call a symmetric matrix $A \in \mathbb{R}^{n \times n}$ positive semidefinite when

$$\forall z \in \mathbb{R}^n : \quad z^T A z \geq 0. \quad (\text{C.3})$$

When the inequality is strict, the symmetric matrix is positive definite. In exactly the same way a negative (semi)definite matrix can be introduced. When a matrix is neither positive or negative, it is called indefinite. From now on, we will use $\succeq$ to denote that a matrix is positive semidefinite.

In a sense, a positive semidefinite matrix is the equivalent of a positive number. The most important property of a positive semidefinite matrix is that all its eigenvalues are real and non-negative. From this follows, if $A \succeq 0$ then

$$\det A \geq 0, \quad (\text{C.4})$$

$$\text{Tr}(A) \geq 0, \quad (\text{C.5})$$

$$A_{ii} \geq 0, \quad (\text{C.6})$$

$$\exists! S \succeq 0 \quad A = SS. \quad (\text{C.7})$$

Furthermore, when $A \succeq 0$ and $B \succeq 0$ then

$$A \succeq 0, B \succeq 0 \Rightarrow A + B \succeq 0, \quad (\text{C.8})$$

$$[A, B] = 0 \Rightarrow AB \succeq 0, \quad (\text{C.9})$$

$$ABA \succeq 0, BAB \succeq 0, \quad (\text{C.10})$$

$$\text{Tr}(AB) = 0 \Rightarrow AB = 0, \quad (\text{C.11})$$

The set of positive semidefinite matrices has the mathematical structure of a cone: for every $A \succeq 0$ we have that $\lambda A \succeq 0$, when $\lambda > 0$. A cone is a substructure of a vector space. It is convex when any combination $\alpha A + \beta B$ is also an element of the cone for $\alpha > 0$ and $\beta > 0$. Every cone has a dual cone. Let C be the cone and V the underlying vector space of real-symmetric matrices, then the set

$$v \in V : \forall w \in C, \text{Tr}(vw) \geq 0, \quad (\text{C.12})$$

is the dual cone of C . The dual cone is not important for this work as the cone of positive semidefinite matrices is self-dual: the cone and the dual cone are the same.

C.3 Eigenvalues of symmetric matrices

A real symmetric $n \times n$ matrix A will have the same spectrum as a matrix B if they only differ in the sign of the off-diagonal matrix elements:

$$A = \begin{bmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & a_{n2} & \dots & a_{nn} \end{bmatrix} \quad B = \begin{bmatrix} a_{11} & -a_{12} & \dots & -a_{1n} \\ -a_{21} & a_{22} & \dots & -a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ -a_{n1} & -a_{n2} & \dots & a_{nn} \end{bmatrix}$$

We call this the Verstichel-Claeys theorem. It is trivial in the case of a 2×2 matrix. For a 3×3 matrix it can be proven by first diagonalizing the upper 2×2 block:

$$A = \begin{bmatrix} \lambda_1 & 0 & a_{13} \\ 0 & \lambda_2 & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \quad B = \begin{bmatrix} \lambda_1 & 0 & -a_{13} \\ 0 & \lambda_2 & -a_{23} \\ -a_{31} & -a_{32} & a_{33} \end{bmatrix}$$

If we multiple the last row/column of B with -1 , its determinant remains unchanged. As the determinant of A and B are now the same, they will have the same spectrum (as the first two eigenvalues are already equal). In this fashion, the 4×4 case can also be proven. By induction it can be proven for arbitrary n .

C.4 Useful results for determinants

- Let M be a symmetric block matrix of the form

$$M = \begin{bmatrix} A & B \\ B & A \end{bmatrix}, \quad (\text{C.13})$$

then the determinant of M is

$$\det M = \det (A + B) \det (A - B). \quad (\text{C.14})$$

- For any real symmetric matrix function $A(x)$, we can define the function $\phi(x)$ as

$$\phi(x) = -\log \det A(x). \quad (\text{C.15})$$

The derivative is given by

$$\frac{\partial \phi(x)}{\partial x} = -\text{Tr} \left(A(x)^{-1} \frac{\partial A(x)}{\partial x} \right). \quad (\text{C.16})$$

C.5 Wedge product

The wedge product of two antisymmetric maps $a : \mathbb{R}^n \rightarrow \mathbb{R}$ and $b : \mathbb{R}^m \rightarrow \mathbb{R}$ is given by

$$a \wedge b(x_1, \dots, x_n, x_{n+1}, \dots, x_{m+n}) = \sum_{\sigma \in Sh_{k,m}} \text{sgn} \sigma \, a(x_{\sigma(1)}, \dots, x_{\sigma(n)}) \, b(x_{\sigma(n+1)}, \dots, x_{\sigma(n+m)}), \quad (\text{C.17})$$

where the summation runs over all so-called n, m shuffles. This the set of permutations on $n + m$ objects, such that the first n elements and the last m elements are ordered: $\sigma(1) \leq \dots \leq \sigma(n)$ and $\sigma(n+1) \leq \dots \leq \sigma(n+m)$. As an example, let us look at the wedge product of two 1DM's

$$(\rho \wedge \rho)_{\alpha\beta;\gamma\delta} = \rho_{\alpha\gamma}\rho_{\beta\delta} - \rho_{\alpha\delta}\rho_{\beta\gamma}. \quad (\text{C.18})$$

Appendix D

Clebsch-Gordan coefficients

In general Clebsch-Gordan coefficients are the coefficients needed to couple multiple irreducible representations of a group. This appendix is about the Clebsch-Gordan coefficients for the $SU(2)$ group, which are needed to couple the fermion spins. We refer to references 99, 238 and 92 for a full overview.

We want to couple two spins j_1 and j_2 together to good total spin J

$$|j_1 j_2; JM\rangle = \sum_{m_1 m_2} \langle j_1 m_1 j_2 m_2 | JM \rangle |j_1 m_1\rangle |j_2 m_2\rangle, \quad (D.1)$$

where $\langle j_1 m_1 j_2 m_2 | JM \rangle$ is the Clebsch-Gordan coefficient. The inverse transformation is

$$|j_1 m_1\rangle |j_2 m_2\rangle = \sum_{JM} \langle j_1 m_1 j_2 m_2 | JM \rangle |j_1 j_2; JM\rangle. \quad (D.2)$$

There are orthogonality relations

$$\sum_{m_1 m_2} \langle j_1 m_1 j_2 m_2 | JM \rangle \langle j_1 m_1 j_2 m_2 | J' M' \rangle = \delta_{JJ'} \delta_{MM'}, \quad (D.3)$$

$$\sum_{JM} \langle j_1 m_1 j_2 m_2 | JM \rangle \langle j_1 m'_1 j_2 m'_2 | JM \rangle = \delta_{m_1 m'_1} \delta_{m_2 m'_2}. \quad (D.4)$$

An alternative notation are the Wigner 3j-symbols

$$\langle j_1 m_1 j_2 m_2 | j_3 m_3 \rangle = (-1)^{j_1 - j_2 + m_3} \frac{1}{\sqrt{2j_3 + 1}} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{pmatrix}. \quad (D.5)$$

In this case, the orthogonality relations eqs. (D.3) and (D.4) become

$$\sum_{m_1 m_2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j'_3 \\ m_1 & m_2 & m'_3 \end{pmatrix} = \delta_{j_3 j'_3} \delta_{m_3 m'_3} \frac{1}{2j_3 + 1}, \quad (D.6)$$

$$\sum_{j_3 m_3} (2j_3 + 1) \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ m'_1 & m'_2 & m_3 \end{pmatrix} = \delta_{m_1 m'_1} \delta_{m_2 m'_2}. \quad (D.7)$$

The Clebsch-Gordan coefficients have the following symmetry,

$$\langle j_1 m_1 j_2 m_2 | JM \rangle = (-1)^{j_1+j_2-J} \langle j_2 m_2 j_1 m_1 | JM \rangle, \quad (\text{D.8})$$

$$= (-1)^{j_1+j_2-J} \langle j_1 -m_1 j_2 -m_2 | J-M \rangle. \quad (\text{D.9})$$

In the case of $J = 0$, we have

$$\langle j_1 m_1 j_2 m_2 | 00 \rangle = \delta_{j_1 j_2} \delta_{m_1 - m_2} \frac{(-1)^{j_1 - m_1}}{\sqrt{2j_1 + 1}}. \quad (\text{D.10})$$

In the case of $j_1 = j_2 = 1/2$, we have

$$\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} | 11 \rangle = \langle \frac{1}{2} - \frac{1}{2} \frac{1}{2} - \frac{1}{2} | 1-1 \rangle = 1, \quad (\text{D.11})$$

$$\langle \frac{1}{2} - \frac{1}{2} \frac{1}{2} \frac{1}{2} | 10 \rangle = \langle \frac{1}{2} \frac{1}{2} \frac{1}{2} - \frac{1}{2} | 10 \rangle = \sqrt{\frac{1}{2}}, \quad (\text{D.12})$$

$$\langle \frac{1}{2} - \frac{1}{2} \frac{1}{2} \frac{1}{2} | 00 \rangle = -\sqrt{\frac{1}{2}}, \quad (\text{D.13})$$

$$\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} - \frac{1}{2} | 00 \rangle = \sqrt{\frac{1}{2}}. \quad (\text{D.14})$$

In a Hilbert space with an angular momentum operator $\hat{J}$, one can define a spherical tensor operator $\hat{A}_m^j$ as an operator that obeys the following commutator relations

$$[\hat{J}_+, \hat{A}_m^j] = \sqrt{(j \pm m + 1)(j \mp m)} \hat{A}_{m \pm 1}^j, \quad (\text{D.15})$$

$$[\hat{J}_z, \hat{A}_m^j] = m \hat{A}_m^j. \quad (\text{D.16})$$

It is a generalization of the eigenstates $|jm\rangle$ for the $\hat{J}_z$ operator. Spherical tensor operators are important in the context of the Wigner-Eckart theorem. What is important to note, is that the Hermitian adjoint of a spherical tensor operator is not a spherical tensor operator, but needs an additional factor

$$\tilde{A}_m^j = (-1)^{j+m} \left(A_{-m}^j \right)^\dagger. \quad (\text{D.17})$$

The spherical tensor operators used in this work are

$$\hat{a}_{jm}^\dagger, \quad \tilde{\hat{a}}_{jm} = (-1)^{j+m} \hat{a}_{j-m}. \quad (\text{D.18})$$

Appendix E

Formulas for Jacobi rotations

In Section 4.2 on page 80 we have introduced an orbital optimizer based on Jacobi rotations. The energy change under a Jacobi rotation can be calculated using Equation (4.24). In this appendix we give the formula to update the reduced Hamiltonian for a Jacobi rotation. If we rotate between orbitals k and l over an angle θ then the update formulas are for the case $\forall a, b \notin \{k, l\}$

$$K'_{a\bar{a};b\bar{b}} = K_{a\bar{a};b\bar{b}}, \quad K'_{ab;ab} = K_{ab;ab}, \quad (\text{E.1})$$

while for the case $\forall b \notin \{k, l\}$

$$K'_{k\bar{k};b\bar{b}} = \cos^2 \theta V_{k k b b} - 2 \cos \theta \sin \theta V_{k l p p} + \sin^2 \theta V_{l l p p}, \quad (\text{E.2})$$

$$K'_{l\bar{l};b\bar{b}} = \cos^2 \theta V_{l l b b} + 2 \cos \theta \sin \theta V_{k l p p} + \sin^2 \theta V_{k k p p}, \quad (\text{E.3})$$

$$\begin{aligned} K'_{kb;kb} = & \frac{1}{N-1} (T_{bb} + \cos^2 \theta T_{kk} - 2 \sin \theta \cos \theta T_{kl} + \sin^2 \theta T_{ll}) + \\ & \cos^2 \theta \left(V_{k b k b} - \frac{1}{2} V_{k b b k} \right) - 2 \cos \theta \sin \theta \left(V_{k b l b} - \frac{1}{2} V_{k b b l} \right) + \\ & \sin^2 \theta \left(V_{l b l b} - \frac{1}{2} V_{l b b l} \right), \end{aligned} \quad (\text{E.4})$$

$$\begin{aligned} K'_{lb;lb} = & \frac{1}{N-1} (T_{bb} + \cos^2 \theta T_{ll} - 2 \sin \theta \cos \theta T_{kl} + \sin^2 \theta T_{kk}) + \\ & \cos^2 \theta \left(V_{l b l b} - \frac{1}{2} V_{l b b l} \right) + 2 \cos \theta \sin \theta \left(V_{k b l b} - \frac{1}{2} V_{k b b l} \right) + \\ & \sin^2 \theta \left(V_{k b k b} - \frac{1}{2} V_{k b b k} \right). \end{aligned} \quad (\text{E.5})$$

The remaining cases are

$$\begin{aligned} K'_{k\bar{k};k\bar{k}} = & \frac{2}{N-1} (\cos^2 \theta T_{kk} - 2 \sin \theta \cos \theta T_{kl} + \sin^2 \theta T_{ll}) + \\ & \cos^4 \theta V_{k k k k} + \sin^4 \theta V_{l l l l} + \cos^2 \theta \sin^2 \theta (4 V_{k k l l} + 2 V_{k l k l}) - \end{aligned}$$

$$4 \cos \theta \sin^3 \theta V_{klll} - 4 \cos^3 \theta \sin \theta V_{klkk}, \quad (\text{E.6})$$

$$\begin{aligned} K'_{\bar{l};\bar{l}} = & \frac{2}{N-1} (\cos^2 \theta T_{ll} + 2 \sin \theta \cos \theta T_{kl} + \sin^2 \theta T_{kk}) + \cos^4 \theta V_{llll} + \\ & \sin^4 \theta V_{kkkk} + \cos^2 \theta \sin^2 \theta (4V_{kkll} + 2V_{klkl}) + \\ & 4 \cos \theta \sin^3 \theta V_{klkk} + 3 \cos^3 \theta \sin \theta V_{klll}, \end{aligned} \quad (\text{E.7})$$

$$\begin{aligned} K'_{k\bar{k};\bar{l}} = & (\cos^4 \theta + \sin^4 \theta) V_{kkll} + \cos^2 \theta \sin^2 \theta (V_{kkkk} + V_{llll} - 2V_{klkl} + V_{kkll}) + \\ & 2 (\cos^3 \theta \sin \theta - \cos \theta \sin^3 \theta) (V_{klkk} - V_{klll}), \end{aligned} \quad (\text{E.8})$$

$$\begin{aligned} K'_{kl;kl} = & \frac{1}{N-1} (T_{kk} + T_{ll}) + \cos^2 \theta \sin^2 \theta \left(\frac{1}{2} V_{kkkk} + V_{llll} - 3V_{kkll} + V_{klkl} \right) + \\ & (\cos^4 \theta + \sin^4 \theta) \left(V_{klkl} - \frac{1}{2} V_{kkll} \right) + \\ & (\cos^3 \theta \sin \theta - \cos \theta \sin^3 \theta) (V_{klkk} - V_{klll}). \end{aligned} \quad (\text{E.9})$$

Appendix F

Hermitian adjoint images

All N -representability constraints are expressed as an image of the 2DM (or 3DM). We require that these images are homogeneous¹, as it simplifies the mathematical treatment. This means that they must be scale invariant. In our case, they are even linear. We require that for $\alpha \in \mathbb{R}$

$$\mathcal{L}_i(\alpha\Gamma) = \alpha\mathcal{L}_i(\Gamma), \quad (\text{F.1})$$

where $\mathcal{L}_i$ can be any N -representability constraint. As a consequence we have to change the $\mathcal{Q}$ condition: the first term is simply the unity matrix which can be rewritten in homogeneous form using the trace condition

$$\begin{aligned} \mathcal{Q}_{\alpha\beta;\gamma\delta}(\Gamma) = & (\delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma}) \frac{2\text{Tr}(\Gamma)}{N(N-1)} + \Gamma_{\alpha\beta;\gamma\delta} \\ & - \delta_{\alpha\gamma}\rho_{\beta\delta} + \delta_{\beta\gamma}\rho_{\alpha\delta} + \delta_{\alpha\delta}\rho_{\beta\gamma} - \delta_{\beta\delta}\rho_{\alpha\gamma}. \end{aligned} \quad (\text{F.2})$$

Any non-homogeneous image can be adapted in the same way.

Another very important and helpful concept are the Hermitian adjoint images which are defined by

$$\text{Tr}(\mathcal{L}_i(\Gamma)A) = \text{Tr}(\mathcal{L}_i^\dagger(A)\Gamma). \quad (\text{F.3})$$

The adjoint image transforms from the constraint space to the 2DM space. The easiest way to derive them is to use the definition eq. (F.3). For the $\mathcal{J}$ and $\mathcal{Q}$ images, this is simple: they are self-adjoint, meaning that the image is also its adjoint. For the $\mathcal{G}$ condition, we have

$$\begin{aligned} \mathcal{G}^\dagger(A)_{\alpha\beta;\gamma\delta} = & \frac{1}{N-1} [\delta_{\beta\delta}\bar{A}_{\alpha\gamma} - \delta_{\alpha\delta}\bar{A}_{\beta\gamma} - \delta_{\beta\gamma}\bar{A}_{\alpha\delta} + \delta_{\alpha\gamma}\bar{A}_{\beta\delta}] \\ & - A_{\alpha\delta;\gamma\beta} + A_{\beta\delta;\gamma\alpha} + A_{\alpha\gamma;\delta\beta} - A_{\beta\gamma;\delta\alpha}, \end{aligned} \quad (\text{F.4})$$

where

$$\bar{A}_{\alpha\gamma} = \sum_{\lambda} A_{\alpha\lambda;\gamma\lambda}. \quad (\text{F.5})$$

1. A function is homogeneous with degree k when it is scale invariant: $f(\alpha x) = \alpha^k f(x)$.

For the $\mathcal{T}_1$ image, it gets a bit more complicated. The adjoint transform from the three-particle space to the two-particle space. For the Hermitian adjoint image, we find

$$\begin{aligned} \mathcal{T}_1^\dagger(A)_{\alpha\beta;\gamma\delta} = & \frac{2}{N(N-1)} (\delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma}) \text{Tr } A + \bar{A}_{\alpha\beta;\gamma\delta} \\ & - \frac{1}{2(N-1)} \left[\delta_{\beta\delta}\bar{A}_{\alpha\gamma} - \delta_{\alpha\delta}\bar{A}_{\beta\gamma} - \delta_{\beta\gamma}\bar{A}_{\alpha\delta} + \delta_{\alpha\gamma}\bar{A}_{\beta\delta} \right], \end{aligned} \quad (\text{F.6})$$

with

$$\bar{A}_{\alpha\beta;\gamma\delta} = \sum_{\lambda} A_{\alpha\beta\lambda;\gamma\delta\lambda}, \quad (\text{F.7})$$

$$\bar{A}_{\alpha\gamma} = \sum_{\lambda\kappa} A_{\alpha\lambda\kappa;\gamma\lambda\kappa}. \quad (\text{F.8})$$

The Hermitian adjoint for the $\mathcal{T}_2$ image is

$$\begin{aligned} \mathcal{T}_2^\dagger(A)_{\alpha\beta;\gamma\delta} = & \frac{1}{2(N-1)} \left[\delta_{\beta\delta}\tilde{A}_{\alpha\gamma} - \delta_{\alpha\delta}\tilde{A}_{\beta\gamma} - \delta_{\beta\gamma}\tilde{A}_{\alpha\delta} + \delta_{\alpha\gamma}\tilde{A}_{\beta\delta} \right] \\ & + \bar{A}_{\alpha\beta;\gamma\delta} - \left[\tilde{A}_{\delta\alpha;\beta\gamma} - \tilde{A}_{\delta\beta;\alpha\gamma} - \tilde{A}_{\gamma\alpha;\beta\delta} + \tilde{A}_{\gamma\beta;\alpha\delta} \right], \end{aligned} \quad (\text{F.9})$$

where

$$\tilde{A}_{\alpha\gamma} = \sum_{\lambda\kappa} A_{\lambda\kappa\alpha;\lambda\kappa\gamma}, \quad (\text{F.10})$$

$$\bar{A}_{\alpha\beta;\gamma\delta} = \sum_{\lambda} A_{\alpha\beta\lambda;\gamma\delta\lambda}, \quad (\text{F.11})$$

$$\tilde{A}_{\alpha\beta;\gamma\delta} = \sum_{\lambda} A_{\lambda\alpha\beta;\lambda\gamma\delta}. \quad (\text{F.12})$$

The Hermitian adjoint image for the $\mathcal{T}'_2$ condition is a bit more complex. It is found by requiring that

$$\begin{aligned} \text{Tr } (\mathcal{T}'_2(\Gamma)A) &= \text{Tr} \left(\left[\begin{pmatrix} \mathcal{T}_2(\Gamma) & \omega \\ \omega^\dagger & \rho \end{pmatrix} \begin{pmatrix} A_{\mathcal{T}} & A_{\omega} \\ A_{\omega}^\dagger & A_{\rho} \end{pmatrix} \right] \right) \\ &= \text{Tr} \left((\mathcal{T}'_2)^\dagger(A)\Gamma \right). \end{aligned} \quad (\text{F.13})$$

This leads to

$$\begin{aligned} \mathcal{T}'_2{}^\dagger(A)_{\alpha\beta;\gamma\delta} = & \mathcal{T}_2^\dagger(A_{\mathcal{T}}) + (A_{\omega})_{\alpha\beta\delta;\gamma} + (A_{\omega})_{\gamma\delta\beta;\alpha} \\ & - (A_{\omega})_{\alpha\beta\gamma;\delta} - (A_{\omega})_{\gamma\delta\alpha;\beta} \\ & + \frac{1}{N-1} \left(\delta_{\beta\delta} (A_{\rho})_{\gamma\alpha} - \delta_{\alpha\delta} (A_{\rho})_{\gamma\beta} - \delta_{\beta\gamma} (A_{\rho})_{\delta\alpha} + \delta_{\alpha\gamma} (A_{\rho})_{\delta\beta} \right). \end{aligned} \quad (\text{F.14})$$

F.1 Spin symmetry

Since the matrices $\mathcal{L}^\dagger(A)$ are two-particle matrices, the spin-coupled version of the Hermitian adjoint maps is defined as:

$$\mathcal{L}^\dagger(A)_{ab;cd}^S = \frac{1}{\sqrt{(1+\delta_{ab})(1+\delta_{cd})}} \sum_{\sigma_a \sigma_b} \sum_{\sigma_c \sigma_d} \langle \frac{1}{2} \sigma_a \frac{1}{2} \sigma_b | SM \rangle \langle \frac{1}{2} \sigma_c \frac{1}{2} \sigma_d | SM \rangle \mathcal{L}^\dagger(A)_{a\sigma_a b\sigma_b; c\sigma_c d\sigma_d} . \quad (\text{F.15})$$

The $\mathcal{G}^\dagger$ map: the first non-trivial Hermitian adjoint map is the $\mathcal{G}^\dagger$. Its spin-coupled form can be derived by substituting eq. (F.4) in eq. (F.15) and performing the necessary angular momentum algebra. This leads to:

$$\begin{aligned} \mathcal{G}^\dagger(\Gamma)_{ab;cd}^S = & \frac{1}{\sqrt{(1+\delta_{ab})(1+\delta_{cd})}} \left(\frac{1}{N-1} [\delta_{ac} \bar{A}_{bd} + (-1)^S \delta_{ad} \bar{A}_{bc} \right. \\ & \left. + (-1)^S \delta_{bc} \bar{A}_{ad} + \delta_{bd} \bar{A}_{ac}] - \sum_{S'} (2S' + 1) \left\{ \begin{matrix} \frac{1}{2} & \frac{1}{2} & S \\ \frac{1}{2} & \frac{1}{2} & S' \end{matrix} \right\} \right. \\ & \left. \left[A_{ad;cb}^{S'} + (-1)^S A_{bd;ca}^{S'} + (-1)^S A_{ac;db}^{S'} + A_{bc;da}^{S'} \right] \right) , \quad (\text{F.16}) \end{aligned}$$

in which the bar function for spin-coupled particle-hole matrices is defined as:

$$\bar{A}_{ac} = \frac{1}{2} \sum_S (2S + 1) \sum_b A_{ab;cb}^S . \quad (\text{F.17})$$

The spin-coupled Hermitian adjoint maps for the three-index conditions can be derived in a similar but more complicated fashion. We refer to reference 90 for the full expressions.

Appendix G

Computer codes

In this appendix we give some background on the computer codes used in this work. All codes are open source under the GPLv3-license [183] and available online [184, 239]. They are written in C++ using the BLAS and LAPACK libraries for linear algebra operations and the HDF5¹ library for storing data. The one- and two-electron integrals are calculated using PSI4 [178] and stored in a HDF5 file using the HAMILTONIAN class of CheMPS2 [187–190].

G.1 doci_sdp-atom

The program `doci_sdp-atom` [239] implements the v2DM-DOCI method using both the boundary point method and the potential reduction method. It can use a Jacobi-based orbital optimizer or a simulated annealing-based orbital optimizer. The code is single-threaded as it is very difficult to parallelize a boundary point method: you can only parallelize within a single step and every step is already very fast. The boundary point method has a convergence checker: if the algorithm gets stuck, it will stop it. This has consequences for all the following steps: if the 2DM is not properly convergence, the orbital optimizer might not make a good decision about which orbital to rotate next. It can take a while for the program recovers from this.

G.2 DOCI-Exact

The program `DOCI-Exact` [184] implements a FullDOCI algorithm. The DOCI Hamiltonian is build and then diagonalized to find the groundstate energy and state. It can build and store the Hamiltonian as a sparse matrix and then utilize a implicit restarted Arnoldi algorithm [185, 186] to find the groundstate energy using only a sparse matrix-vector product. Every N -particle state is represented by a bit string. Calculating a single element of the Hamiltonian

1. <http://www.hdfgroup.org>

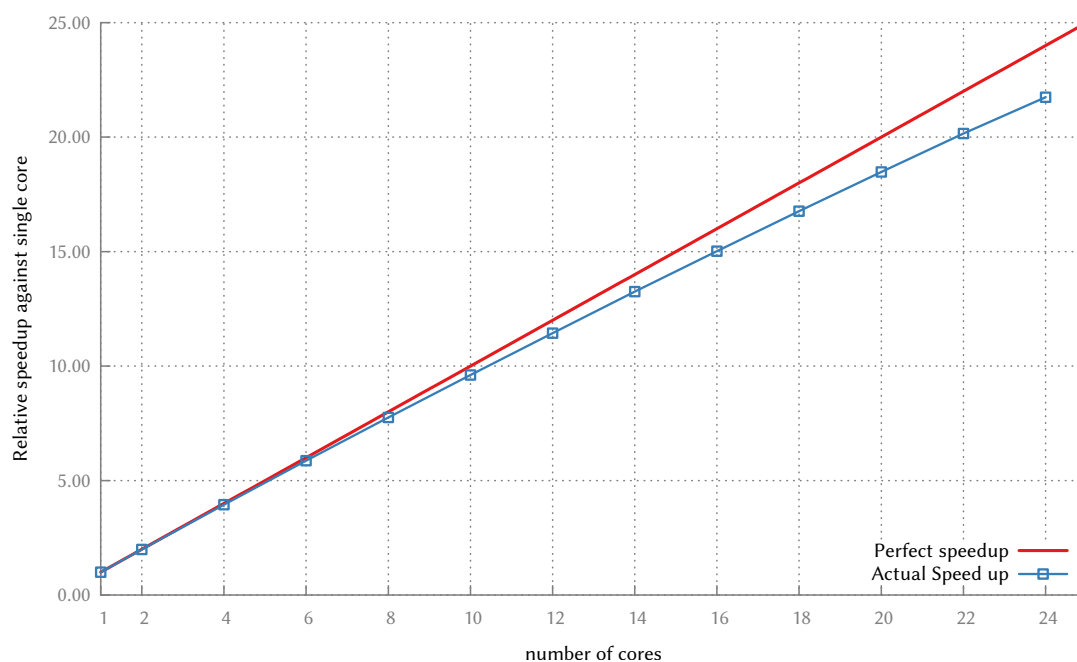


Figure G.1: The speedup of parallelizing the FullDOCI program.

is very quick and as all elements are independent, this is very well suited for parallelization. In Figure G.1 the speed up is shown. It is this parallelization that makes it possible to do DOCI calculations in the cc-pVDZ basis. The same orbital optimization algorithm as for `doci_sdp-atom` program are used.

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