N-representability conditions on the two- and three-particle density matrix constrained to wave functions of the DOCI class

D. Van Neck

Ghent University

Credits

Journal of Chemical Theory and Computation

Search Citation

Search text

J. Chem. Theory Co

Browse the Journal | Articles ASAP | Current Issue | Submission & Review | Open Access

Article **Prev**

Variational Optimization of the Second-Order Density Matrix Corresponding to a Seniority-Zero Configuration Interaction Wave Function

Ward Poelmans [*†], Mario Van Raemdonck [‡], Brecht Verstichel [†], Stijn De Baerdemacker [†‡], Alicia Torre [§], Luis Lain [§], Gustavo E. Massaccesi [∥], Diego R. Alcoba [⊥], Patrick Bultinck [‡], and Dimitri Van Neck [†]

[†] Center for Molecular Modeling, Ghent University, Technologiepark 903, 9052 Zwijnaarde, Belgium

[‡] Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 (S3), 9000 Gent, Belgium

[§] Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apdo. 644, E-48080 Bilbao, Spain

[∥] Departamento de Ciencias Exactas, Ciclo Básico Común, Universidad de Buenos Aires, Ciudad Universitaria, 1428 Buenos Aires, Argentina

[⊥] Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires and Instituto de Física de Buenos Aires, Consejo Nacional de Investigaciones Científicas y Técnicas, Ciudad Universitaria, 1428 Buenos Aires, Argentina

Overview

- Direct variational determination of the 2DM using N-representability conditions. A.k.a. quantum marginal problem, so...
- Seniority zero or DOCI (doubly-occupied configuration interaction) subspace of N-electron Hilbert space
- N-representability conditions for the 2DM to be derivable from DOCI wave function
- Orbital optimization
- Results
- N-representability conditions for the 3DM to be derivable from DOCI wave function
- No results
- Conclusions

Basic idea

- Usual N-representability conditions (P, Q, G, T1, T2...) are necessary conditions for the 2DM to be derivable from an N-fermion wave function (ensemble).
- Disadvantage: semidefinite solvers scale as M^6 for elementary matrix operations (diagonalisation, inversion, etc.) which are part of iterative loops. For three-index conditions even as M^9.
- Idea is to define a certain subspace of many-electron Hilbert space, which is relevant for quantum chemistry: so-called seniority-zero or Doubly Occupied space.
- For this class, the associated 2DM and 3DM becomes very simple, and the corresponding semidefinite optimization scales a lot faster.
- Disadvantage: extra iterative loop appears: orbital optimization.

Introducing the 2DM

- When interactions are pairwise:

$$V(1,2,3) = V(1,2) + V(2,3) + V(1,3)$$

Hamiltonian has the form (in second quantization):

$$\hat{H} = \sum_{\alpha\beta} t_{\alpha\beta} a^\dagger_\alpha a_\beta + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} V_{\alpha\beta;\gamma\delta} a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma \ .$$

- Energy can be expressed as a function of 2DM:

$$\langle \Psi^N | \hat{H} | \Psi^N \rangle = E(\Gamma) = \sum_{\alpha\beta} t_{\alpha\beta} \rho_{\alpha\beta} + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} V_{\alpha\beta;\gamma\delta} \Gamma_{\alpha\beta;\gamma\delta} \ .$$

with

$$\rho_{\alpha\gamma} = \frac{1}{N-1} \sum_{\beta} \Gamma_{\alpha\beta;\gamma\beta} = \langle \Psi^N | a^\dagger_\alpha a_\gamma | \Psi^N \rangle \ ,$$

$$\Gamma_{\alpha\beta;\gamma\delta} = \langle \Psi^N | a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma | \Psi^N \rangle \ .$$

v2DM: variational determination of 2DM

- Use the 2DM as the central object in a variational scheme to determine the ground-state energy.
- All two-particle ground-state properties can be calculated using the 2DM.
- The dimension of the 2DM only scales quadratically with system size!
- When implemented naively terrible results are obtained because of the N-representability problem!

N-representability

- When is a reduced density matrix derivable from a *physical* wave-function ensemble:

$$\Gamma_{\alpha\beta;\gamma\delta} = \sum_i w_i \langle \Psi_i^N | a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma | \Psi_i^N \rangle \qquad \text{with} \qquad \sum_i w_i = 1$$

- Some trivial necessary constraints can be immediately deduced from the definition:

$$\mathrm{Tr}\,\Gamma = \frac{N(N-1)}{2} \;;\; \Gamma_{\alpha\beta;\gamma\delta} = \Gamma_{\gamma\delta;\alpha\beta} \;;\; \Gamma_{\alpha\beta;\gamma\delta} = -\Gamma_{\beta\alpha;\gamma\delta} \;;\; \Gamma \succeq 0 \,.$$

- Many more, non-trivial constraints, are needed. General problem is unsolvable: QMA complete.
- Scaling for PQG is nominally M^6 but with a huge prefactor. Not competitive with e.g. Coupled Cluster methods.

Seniority-zero or DOCI wave functions

- After choosing an orthonormal basis in sp space and a pairing scheme, one can introduce the following notation:

$$a = 1, 2, .., M\,;\ \bar{a} = -1, -2, .., -M$$

where a and $\bar{a}$ usually denote a spatial orbital with spin-up or spin-down.

- DOCI space for $N = 2P$ fermions consists of all "fully-paired" wave functions

$$|\Psi\rangle = \sum_{a_1,..,a_P=1}^{M} X_{a_1,..,a_P} a^\dagger_{a_1} a^\dagger_{\bar{a}_1} .. a^\dagger_{a_P} a^\dagger_{\bar{a}_P},$$

i.e. wave functions in the subspace spanned by Slater determinants in which each spatial orbital is doubly occupied.

Seniority-zero or DOCI wave functions

- Slater determinants can be classified according to the number of unpaired orbitals they contain, the seniority number. DOCI space is spanned by all seniority-zero Slater determinants.
- DOCI space is orbital-dependent, i.e. unitary mixing among spatial orbitals will yield another DOCI space.
- Why DOCI? Chemical relevance. Contains bulk of static correlations (as opposed to dynamical correlations, see talk by Marcel).
- FullDOCI = diagonalization in DOCI space. Still scales factorially, however.
- Need for approximate methods that can approximate FullDOCI at polynomial cost. E.g. v2DM-DOCI.

2DM in DOCI space

- Rule: if one breaks a pair in a DOCI ket, one must restore it to get a nonzero overlap with a DOCI bra.
- The 1DM is automatically diagonal,

$$\langle\Psi|a^\dagger_a a_b|\Psi\rangle = \langle\Psi|a^\dagger_{\bar{a}} a_{\bar{b}}|\Psi\rangle = \delta_{a,b}\rho_a$$

$$\langle\Psi|a^\dagger_a a_{\bar{b}}|\Psi\rangle = \langle\Psi|a^\dagger_{\bar{a}} a_b|\Psi\rangle = 0.$$

- Nonzero elements for 2DM:
  (1) the pairing matrix where a pair is created/annhilated:

$$\langle\Psi|a^\dagger_a a^\dagger_{\bar{a}} a_{\bar{b}} a_b|\Psi\rangle = \Pi_{a,b}, \;\; \forall a, b = 1, .., M$$

  (2) the diagonal elements, two pairs are broken and then restored:

$$\langle\Psi|a^\dagger_a a^\dagger_b a_b a_a|\Psi\rangle = \langle\Psi|a^\dagger_a a^\dagger_{\bar{b}} a_{\bar{b}} a_a|\Psi\rangle = ... = D_{a,b}, \;\; \forall a \neq b = 1, .., M$$

2DM in DOCI space

- Note that (assuming real wave functions) $\Pi_{a,b} = \Pi_{b,a}$, $D_{a,b} = D_{b,a}$, and $\Pi_{a,a} = \rho_a$. So the $M \times M$ matrices Π and D fully contain all 2DM information: serious reduction compared to general case!
- The following sum rules, linking the D matrix and the 1DM and fixing the normalization, must be imposed as well:

$$\sum_b D_{a,b} = (P-1)\rho_a \ ; \ \sum_a \rho_a = P$$

N-representability in DOCI space: the P condition

- We now look at how the usual N-representability conditions simplify when limited tot the DOCI subspace. Greek indices will denote a general sp state, i.e. $\alpha = a$ or $\bar{a}$.
- The P condition implies the positive-semidefiniteness of $\langle \Psi | B^\dagger B | \Psi \rangle$, where $B^\dagger = \sum_{\alpha > \beta} b_{\alpha,\beta} a^\dagger_\alpha a^\dagger_\beta$ is a general two-fermion state.
- In view of the structure of the DOCI 2DM, we must have

$$D_{a,b} \geq 0, \;\; \forall a > b$$

which is not a matrix equation, but a series of linear inequalities; and

$$[\Pi]_{a,b} \succeq 0$$

which is the positive-semidefiniteness condition for the $M \times M$ pair matrix Π .

N-representability in DOCI space: the Q condition

- Here we have to express the positive-definiteness of $\langle\Psi|B^\dagger B|\Psi\rangle$ with
$$B^\dagger = \sum_{\alpha>\beta} b_{\alpha,\beta} a_\alpha a_\beta$$
- The structure is exactly the same as for P:
$$\langle\Psi|a_a a_b a_b^\dagger a_a^\dagger|\Psi\rangle = D_{a,b} + 1 - \rho_a - \rho_b \geq 0, \ \ \forall a > b$$
which is again a set of linear inequalities, and the $M \times M$ matrix inequality
$$[\Pi_{a,b} + \delta_{a,b}(1 - 2\rho_a)]_{a,b} \succeq 0$$
- Up to now, the scaling is M^2 for the inequalities and M^3 for the matrix manipulations. This should be compared with M^6 in the general case.

N-representability in DOCI space: the G condition

- More complicated!
- We have to express the positive-definiteness of $\langle\Psi|B^\dagger B|\Psi\rangle$ with

$$B^\dagger = \sum_{\alpha\beta} b_{\alpha\beta} a^\dagger_\alpha a_\beta = \sum_{ab} \left(b^1_{ab} a^\dagger_a a_b + b^2_{ab} a^\dagger_a a_{\bar{b}} + b^3_{ab} a^\dagger_{\bar{a}} a_b + b^4_{ab} a^\dagger_{\bar{a}} a_{\bar{b}} \right)$$

- Due to spin considerations, the b^2 ($S_z = 1$) and b^3 ($S_z = -1$) terms act separately, whereas the b^1 and b^4 (both $S_z = 0$) terms are coupled.

N-representability in DOCI space: the G condition

- For the b^2 term we have to express the positive-semidefiniteness of

$$[\langle\Psi|a^\dagger_a a_{\bar{b}} a^\dagger_{\bar{d}} a_c|\Psi\rangle]_{ab;cd} \succeq 0$$

or, after some algebra,

$$[\delta_{a,c}\delta_{b,d}(\rho_a - D_{a,b}) - \delta_{a,d}\delta_{b,c}\Pi_{a,c}]_{ab;cd} \succeq 0.$$

- At first sight this is bad news: it involves a matrix with the dimension of the complete (general) G-matrix. However, the condition is "almost diagonal" (because of the Kronecker delta's). It can be simplified to, for any $a > b$, the positive semi-definiteness of a 2×2 matrix:

$$\begin{pmatrix} \rho_a - D_{a,b} & -\Pi_{a,b} \\ -\Pi_{a,b} & \rho_b - D_{a,b} \end{pmatrix} \succeq 0$$

and the total condition is very cheap (scaling like M^2).

N-representability in DOCI space: the G condition

- For the coupled $b^1 - b^4$ terms in the G condition we must express the positive semidefiniteness of the matrix

$$\begin{pmatrix} A & B \\ B & A \end{pmatrix} \succeq 0$$

  with

$$A_{ab,cd} = \delta_{a,c}\delta_{b,d}(\rho_a - D_{a,b}) + \delta_{a,b}\delta_{c,d}D_{a,c}$$

  and

$$B_{ab,cd} = \delta_{a,d}\delta_{b,c}\Pi_{a,b} + \delta_{a,b}\delta_{c,d}D_{a,c}$$

- This looks ugly again, but using the fact that the eigenvalue spectrum is the same as that for the combined $A \pm B$ matrices, and because of the Kronecker-delta structure, simple conditions again emerge.

N-representability in DOCI space: the G condition

- Namely, the positive semidefiniteness of the $M \times M$ matrix

$$[\delta_{a,c}\rho_a + D_{a,c}]_{a,c} \succeq 0$$

- In all cases so far considered (P,Q,G), the DOCI N-representability conditions scale at most as M^3!
- These DOCI N-representability conditions were already derived in another way by F. Weinhold and E.B. Wilson, JCP 1967, but have not been implemented so far.
- v2DM-DOCI = variational determination of the 2DM with DOCI structure having the lowest energy, under the constraints of the the DOCI N-representability conditions.

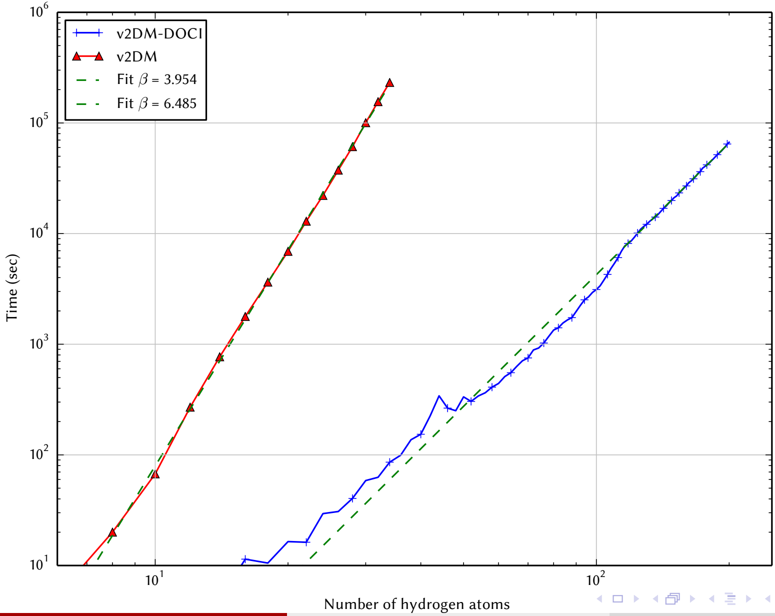
Orbital optimization

- DOCI space is not invariant under a unitary rotation in spatial orbital space: higher-seniority configurations (with respect to the original basis) are generated.
- We alternate energy-minimization in v2DM-DOCI with energy minimization using orbital optimization.
- For the orbital optimization step we rely on a sequence of Jacobi rotations, in which a single pair of orbitals is rotated.
- We loose the strict variational lower bound with respect to FullCI. All we can say is that for the same orbitals, v2DM-DOCI is a strict lower bound to FullDOCI, and that for any set of orbitals FullDOCI has a larger energy than FullCI.

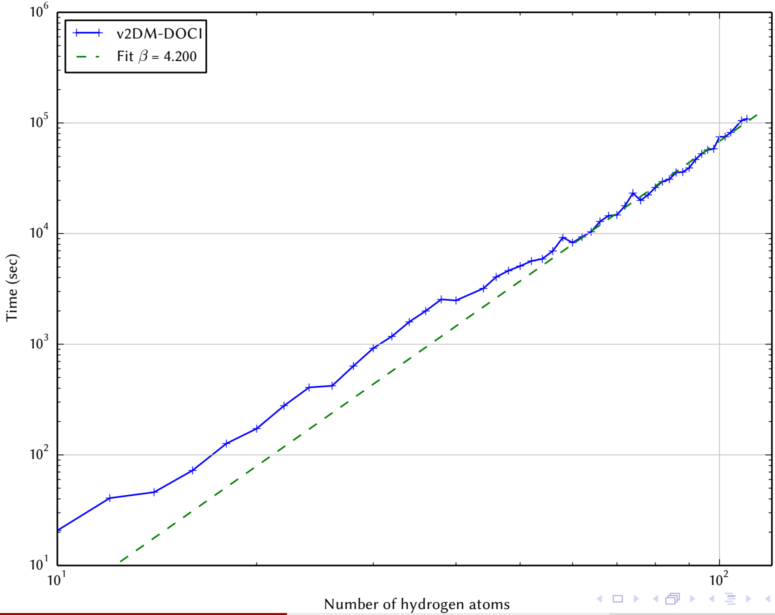
Scaling results

- First we tested scaling properties with respect to the number of orbitals, using a linear equidistant chain of N hydrogen atoms in a minimal STO-3G basis set (i.e. 1 orbital for each H atom). Distance is 2 Bohr (still in interacting regime).
- We fitted a power-law αN^{β} to the CPU time and compared general v2DM with v2DM-DOCI (non orbital optimized).
- For 34 H-atoms, v2DM-DOCI is 1000 times faster than the general v2DM.
- Deviations from the nominal scaling (N^6 and N^3, resp.) are observed.
- Next figure: including orbital optimization: β increases from 3.954 to 4.200 .

Scaling results



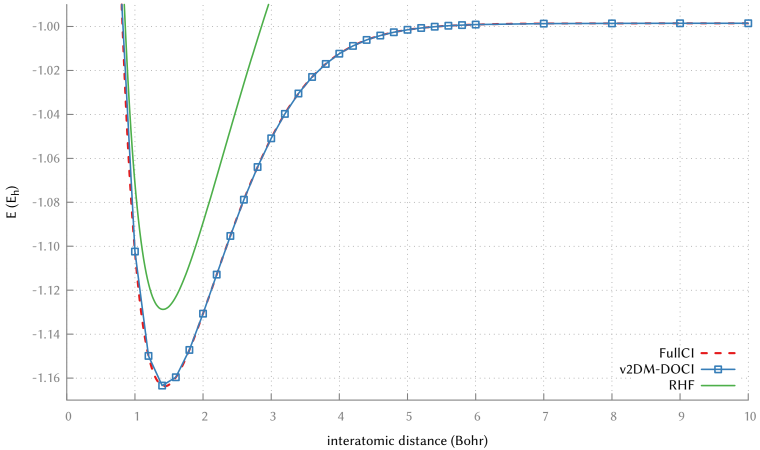
Scaling results



Results for diatomics

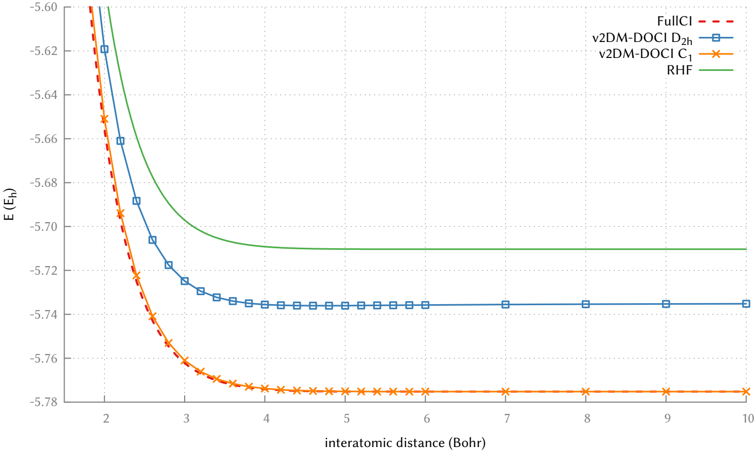
- All calculations in cc-pVDZ basis set.
- For H_2 : check that v2DM-DOCI + OO (like general v2DM) generates exact results. The same holds for any 2-electron system.
- For He_2 (helium dimer): DOCI needs orbitals with broken spatial symmetry.

H2



E (E_h)
-1.00
-1.02
-1.04
-1.06
-1.08
-1.10
-1.12
-1.14
-1.16
0
1
2
3
4
5
6
7
8
9
10
interatomic distance (Bohr)
FullCI
v2DM-DOCI
RHF

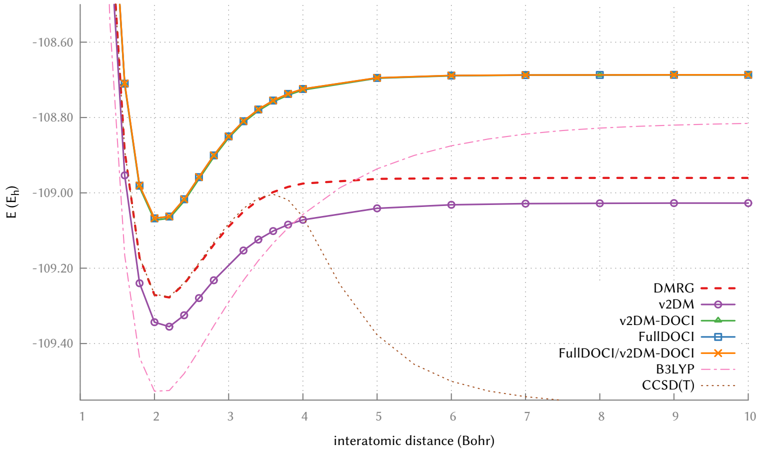
He2


FullCI
v2DM-DOCI D_{2h}
v2DM-DOCI C_1
RHF
E (E_h)
-5.60
-5.62
-5.64
-5.66
-5.68
-5.70
-5.72
-5.74
-5.76
-5.78
2
3
4
5
6
7
8
9
10
interatomic distance (Bohr)

Results for diatomics

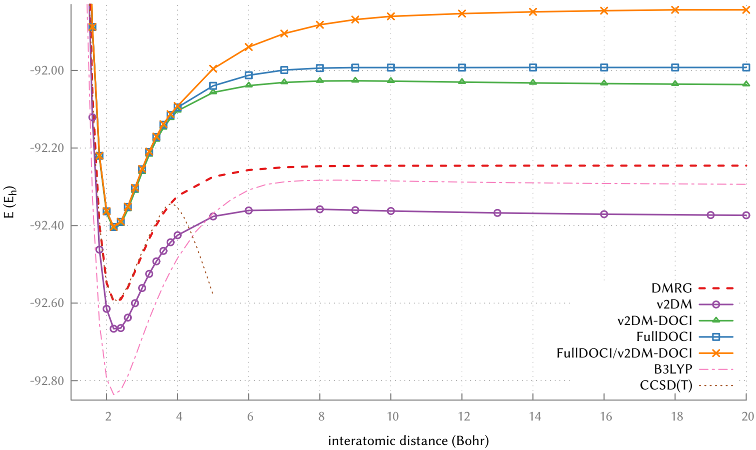
- For N_2 : All DOCI curves have qualitatively correct dissociative behavior. Energy difference between v2DM-DOCI and FullDOCI is very small (a few milliHartree), and much smaller than the difference between general v2DM and FullCI.
- For CN^- : Dissociates into C^- and neutral N. v2DM has a problem with fractional charges, so does v2DM-DOCI. FullDOCI does not. If the optimal FullDOCI orbitals are used in a v2DM-DOCI calculation, the dissociation is also correct.

N2



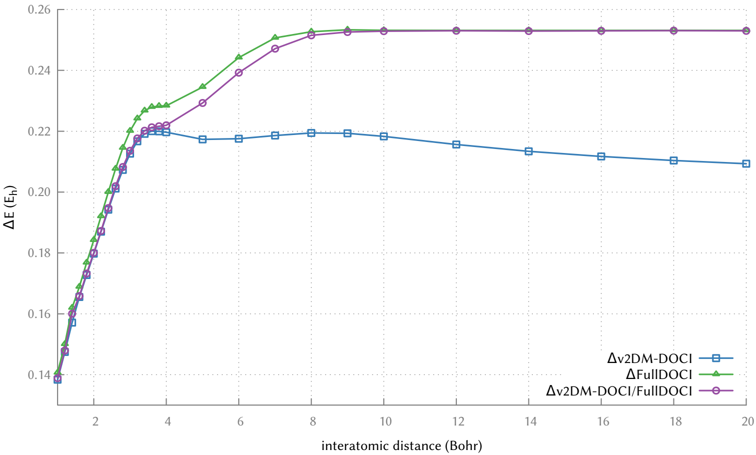
E (E_h)
-108.60
-108.80
-109.00
-109.20
-109.40
1
2
3
4
5
6
7
8
9
10
interatomic distance (Bohr)
DMRG
v2DM
v2DM-DOCI
FullDOCI
FullDOCI/v2DM-DOCI
B3LYP
CCSD(T)

CN-



E (E_h)
-92.00
-92.20
-92.40
-92.60
-92.80
2
4
6
8
10
12
14
16
18
20
interatomic distance (Bohr)
DMRG
v2DM
v2DM-DOCI
FullDOCI
FullDOCI/v2DM-DOCI
B3LYP
CCSD(T)

CN- : difference with FullCI



3DM in DOCI space

- Acting with three annihilation operators on a DOCI wave function $|\Psi\rangle$ one can generate a seniority-3 or seniority-1 wavefunction.
- For seniority-3 (breaking 3 different pairs) the nonzero 3DM elements are purely diagonal,

$$D^3_{a,b,c} = \langle\Psi|a^\dagger_a a^\dagger_b a^\dagger_c a_c a_b a_a|\Psi\rangle, \forall a \neq b \neq c.$$

The $D^3_{a,b,c}$ object is symmetric upon permutation of its indices and $D^3_{abb} = 0$ whenever indices are the same.

3DM in DOCI space

- For seniority-1 (one broken pair) the nonzero elements of the 3DM constitute a "half-diagonal" matrix:

$$\Pi^{b}_{a,c} = \langle \Psi | a^{\dagger}_{a} a^{\dagger}_{\bar{a}} a^{\dagger}_{b} a_{b} a_{\bar{c}} a_{c} | \Psi \rangle, \forall a, b, c \text{ with } a \neq b,\ c \neq b$$

  Obviously, this object is diagonal in the " pair-breaking" index b. For any fixed b, the $M \times M$ matrix $\Pi^{b}_{a,c} = \Pi^{b}_{c,a}$ is symmetric.
- The $D^{3}_{a,b,c}$ and $\Pi^{b}_{a,c}$ are the only nonzero 3DM elements, so storage scales as M^{3}.
- The N-representability conditions for the 3DM have been derived (but not yet implemented). The scaling of matrix manipulations is M^{4}, making applications to reasonable systems within reach.

Conclusions

- N-representability conditions were derived for the 2DM and 3DM to be compatible with wave functions of the DOCI subspace of general N-electron Hilbert space.
- The corresponding variational determination of the 2DM-DOCI was tested on a few small sytems.
- v2DM-DOCI was seen to be a better approximation to FullDOCI than general v2DM is to FullCI.
- Orbital optimization is absolutely necessary.
- In some cases, symmetry breaking of the spatial orbitals is needed.