Making 2-electron response reduced density matrices N-representable

GHENT UNIVERSITY

Caitlin Lanssens[a], Paul W. Ayers[b], Dimitri Van Neck[a], Stijn De Baerdemacker[a], Klaas Gunst[a] and Patrick Bultinck[c]

[a] Center for Molecular Modeling, Ghent University, Tehcnologiepark 903, 9052 Zwijnaarde, Belgium.
[b] Department of Chemistry & Chemical Biology, McMaster University, 1280 Main Street West, L8S 4M1 Hamilton, Ontario, Canada.
[c] Department of Inorganic and Physical Chemistry, Krijgslaan 281 (S3), 9000 Ghent, Belgium.

Introduction

In methods that are solved using the projected Schrödinger equation, such as geminal-based approaches[1] or coupled-cluster[2], direct computation of the 2-electron reduced density matrix (2-RDM) is impractical and one falls back to a 2-RDM based on response theory. However, the 2-RDMs obtained from response theory are not necessarily N-representable. That is, the response 2-RDM does not correspond to an actual physical N-electron system. We present a new algorithm for making these non-N-representable 2-RDMs approximately N-representable, i.e. it has the right symmetry and normalization and it fulfills the P-, Q- and G-conditions. Next to an algorithm which can be applied to any 2-RDM, we have also developed a 2-RDM optimization procedure specifically for seniority-zero 2-RDMs.

N-representability problem

The 2-RDM is a more compact object than the wave function, however, it still contains most of the relevant information about a system.
The 2-RDM is defined as the expectation value of the 2-electron reduced density operator:

$$\Gamma_{\alpha\beta\gamma\delta} = \langle\Psi|\hat{a}^\dagger_\alpha\hat{a}^\dagger_\beta\hat{a}_\delta\hat{a}_\gamma|\Psi\rangle$$

For non-variational methods, direct computation of the 2-RDM as the expectation value can become computationally very expensive. Therefore, it may be better to compute the response 2-RDM, $\Gamma_{\alpha\beta\gamma\delta} = \dfrac{\partial E}{\partial V_{\alpha\beta\gamma\delta}}$

In general, this response 2-RDM is not N-representable[3].
A few necessary (but not sufficient) N-representability conditions:

- Symmetry properties: $\Gamma_{\alpha\beta\gamma\delta} = \Gamma_{\gamma\delta\alpha\beta}$

  $$\Gamma_{\alpha\beta\gamma\delta} = -\Gamma_{\beta\alpha\gamma\delta} = -\Gamma_{\alpha\beta\delta\gamma} = \Gamma_{\beta\alpha\delta\gamma}$$
- Trace condition: $\mathrm{Tr}(\Gamma) = \sum_{\alpha\beta}\Gamma_{\alpha\beta\alpha\beta} = N(N-1)$
- 2-positivity conditions[4]: necessary conditions which impose positive semidefiniteness on the P, Q and G matrices i.e. their eigenvalues are non-negative.

  $$P \succeq 0 \quad \text{with} \quad P_{\alpha\beta\gamma\delta} = \langle\Psi|\hat{a}^\dagger_\alpha\hat{a}^\dagger_\beta\hat{a}_\delta\hat{a}_\gamma|\Psi\rangle = \Gamma_{\alpha\beta\gamma\delta}$$
  $$Q \succeq 0 \quad \text{with} \quad Q_{\alpha\beta\gamma\delta} = \langle\Psi|\hat{a}_\alpha\hat{a}_\beta\hat{a}^\dagger_\delta\hat{a}^\dagger_\gamma|\Psi\rangle$$
  $$G \succeq 0 \quad \text{with} \quad G_{\alpha\beta\gamma\delta} = \langle\Psi|\hat{a}^\dagger_\alpha\hat{a}_\beta\hat{a}^\dagger_\delta\hat{a}_\gamma|\Psi\rangle$$

In seniority-zero space[5], the spatial orbitals are either empty or doubly occupied. The structure of the 2-RDM greatly simplifies and non-zero elements are arranged in two matrices, the pair 2-RDM, Π, and the exchange 2-RDM, D. Both are symmetric and their normalization:

$$\mathrm{Tr}(\Pi) = \sum_a \Pi_{aa} = \frac{N}{2}$$

$$\mathrm{Tr}(D) = \sum_{ab} D_{ab} = \frac{N}{2}\left(\frac{N}{2} - 1\right)$$

The P-, Q- and G-conditions can be reformulated[6]:

$$\Pi \succeq 0, \quad \forall a,b: \quad D_{ab} \geq 0$$
$$Q^\Pi \succeq 0, \quad \forall a,b: \quad Q^D_{ab} \geq 0$$
$$G^\Pi \succeq 0, \quad \forall a<b: \quad G^{(2x2)} = \begin{bmatrix} \Pi_{aa} - D_{ab} & \Pi_{ab} \\ \Pi_{ab} & \Pi_{bb} - D_{ab} \end{bmatrix} \succeq 0$$

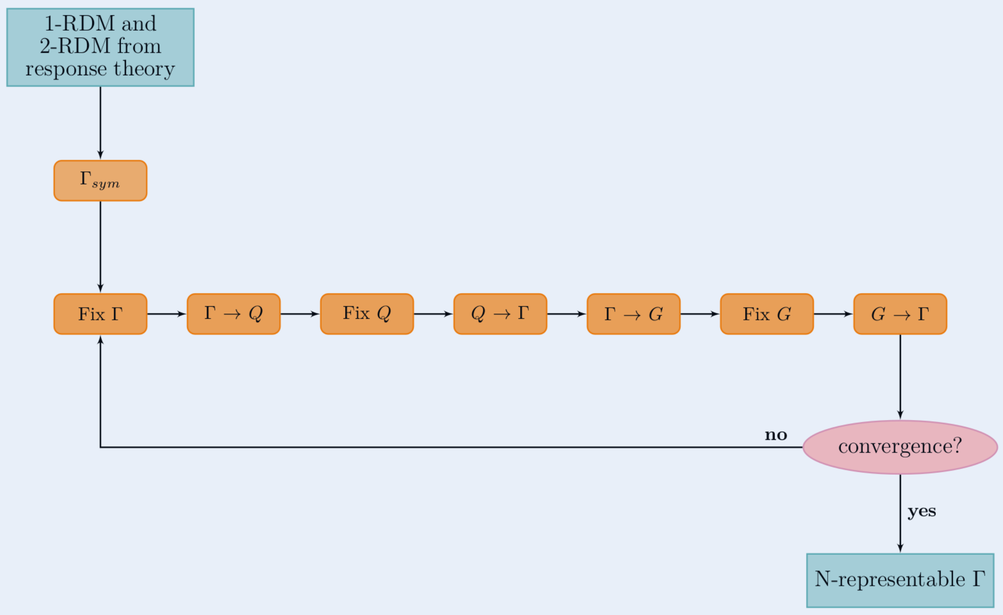

Figure 1. General scheme for the N-representability optimization procedure.

Optimization algorithm

Our strategy is to find the 2-RDM that minimizes the square norm of the difference between the response 2-RDM and the targeted 2-RDM, under the constraints that this 2-RDM is symmetric, its trace is normalized and the 2-RDM, Q and G matrices are positive semi-definite matrices.

$$\begin{aligned} \underset{\Gamma}{\text{minimize}} \quad & \|\Gamma - \Gamma^{response}\|^2 \\ \text{subject to} \quad & \Gamma = \Gamma^T \\ & \mathrm{Tr}(\Gamma) = N(N-1) \\ & \Gamma, Q(\Gamma), G(\Gamma) \succeq 0 \end{aligned}$$

We propose the following iterative procedure to determine the closest, positive semidefinite, symmetric 2-RDM with the correct trace[7]:

(1) Symmetrize the 2-RDM: $\Gamma^{response}_{sym} = \frac{1}{2}\left(\Gamma^{response} + (\Gamma^{response})^T\right)$
(2) Compute the eigenvector decomposition to find the eigenvalues: $\Gamma^{response}_{sym} = UDU^T$
(3)Shift all eigenvalues by a constant σ_0 which is the root of the equation $f(\sigma) = \sum_i \theta(\lambda_i - \sigma)(\lambda_i - \sigma) = \mathrm{Tr}(\Gamma)$
with $\theta(\lambda_i - \sigma)$ the Heaviside step function and set any negative shifted eigenvalues to zero.

$$\lambda^+ = \begin{cases} \lambda - \sigma_0 & \text{if } \lambda > \sigma_0 \\ 0 & \text{if } \lambda \leq \sigma_0 \end{cases}$$

(4) Find an updated 2-RDM from the resulting shifted set of eigenvalues and the original eigenvectors: $\tilde{\Gamma} = U\tilde{D}U^T$

In order for the 2-RDM to also satisfy the Q- and G-condition, a similar procedure can be used for making the Q- and G-matrix positive semidefinite. An overview of the regular N-representability optimization algorithm is given in Fig. 1. We sequentially optimize the 2-RDM, Q-matrix and G-matrix and when convergence is reached we have determined the 2-RDM which is close to the initial response 2-RDM, but which is N-representable in the sense that it fulfills the P-, Q- and G-conditions. The seniority-zero optimization procedure works with the pair and exchange 2-RDM and uses the reformulated P-, Q- and G-conditions. Just as in the regular procedure, these conditions are enforced in a sequential manner.

Table 1. Energy difference w.r.t. DOCI for AP1roG and the fixed 2-RDM, using a 6-31g* basis set. The equilibrium bond lengths are taken from the NIST CCCBDB database for CCSD(T) geometries. All energy differences are given in atomic units. The cost function is defined as $f = \sum\left(\Gamma_{ijkl} - \tilde{\Gamma}_{ijkl}\right)^2$.

molecule	C_2	BN	BeO	LiF	N_2	CO	BF
$R_e(\AA)$	1.2562	1.3369	1.3490	1.5658	1.1191	1.1472	1.2829
				Interatomic distance $R = R_e$			
ΔE_{AP1roG}	3.0×10^{-5}	2.8×10^{-4}	2.0×10^{-5}	-6.3×10^{-6}	-8.4×10^{-5}	-2.9×10^{-5}	-1.7×10^{-5}
$\Delta E_{fix2RDM}$	-1.5×10^{-3}	-5.5×10^{-4}	-4.8×10^{-5}	-2.0×10^{-5}	-3.2×10^{-4}	-1.5×10^{-4}	-5.8×10^{-5}
Cost function	2.9×10^{-3}	1.0×10^{-3}	7.1×10^{-7}	1.6×10^{-8}	3.1×10^{-6}	6.2×10^{-7}	9.9×10^{-8}
				Interatomic distance $R = R_e + 1.00\AA$			
ΔE_{AP1roG}	8.1×10^{-5}	6.8×10^{-5}	-1.6×10^{-4}	2.0×10^{-6}	1.5×10^{-3}	4.9×10^{-3}	1.1×10^{-4}
$\Delta E_{fix2RDM}$	-2.2×10^{-2}	-7.5×10^{-3}	-7.5×10^{-4}	-2.0×10^{-5}	-4.0×10^{-2}	-1.6×10^{-2}	-4.4×10^{-4}
Cost function	2.0×10^{-2}	3.3×10^{-2}	2.8×10^{-6}	4.2×10^{-8}	1.1×10^{-2}	3.8×10^{-3}	1.0×10^{-5}
				Interatomic distance $R = 5.00\AA$			
ΔE_{AP1roG}	-6.2×10^{-4}	1.1×10^{-5}	-3.8×10^{-5}	2.3×10^{-5}	2.6×10^{-4}	1.2×10^{-3}	2.1×10^{-5}
$\Delta E_{fix2RDM}$	-9.3×10^{-2}	-1.4×10^{-1}	-5.7×10^{-3}	-7.2×10^{-5}	-9.1×10^{-1}	-1.3×10^{-1}	-4.8×10^{-4}
Cost function	3.0×10^{-1}	1.9×10^{-1}	2.7×10^{-2}	3.6×10^{-5}	6.2×10^{0}	1.3×10^{-1}	5.6×10^{-4}

Results: linear hydrogen chain

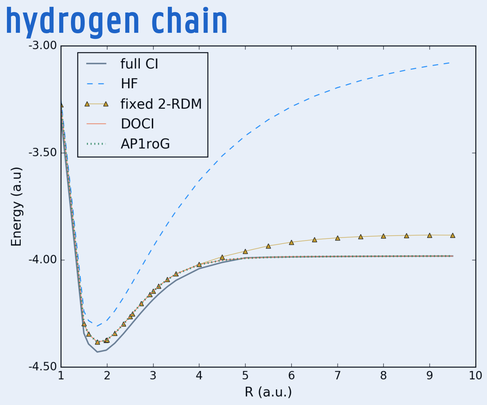

Figure 2. Symmetric dissociation of a linear H_8 chain with interatomic distance R using an ANO-2s basis set. Total energies predicted by full CI, Hartree-Fock, AP1roG[9] (with optimized orbitals), DOCI (with optimized orbitals) and fixed 2-RDM energy.
→ AP1roG and DOCI nearly indistinguishable; deviation from full CI due to lack of dynamical correlation in seniority-zero methods[9].
→ fixed 2-RDM energy difference with DOCI increases with increasing bond length which is a result of constraining the 2-RDM during the optimization procedure.
→ structure of response 2-RDM deviates more and more from N-representability with increasing bond length.

Results: attractive Richardson pairing Hamiltonian

Push the 2-RDM optimization algorithm into a regime where AP1roG is known to fail, i.e. the attractive pairing Hamiltonian[9] $\hat{H} = \sum_p \varepsilon_p \hat{a}^\dagger_p\hat{a}_p + g\sum_{pq}\hat{a}^\dagger_p\hat{a}^\dagger_{\bar{p}}\hat{a}_{\bar{q}}\hat{a}_q$

with g the interaction strength, g < 0 for the attractive region. The set $\{\varepsilon_i\}$ are the single particle energies. Specifically, we investigate the half-filled pairing Hamiltonian with twelve equally spaced levels, the so-called picket-fence model[10].

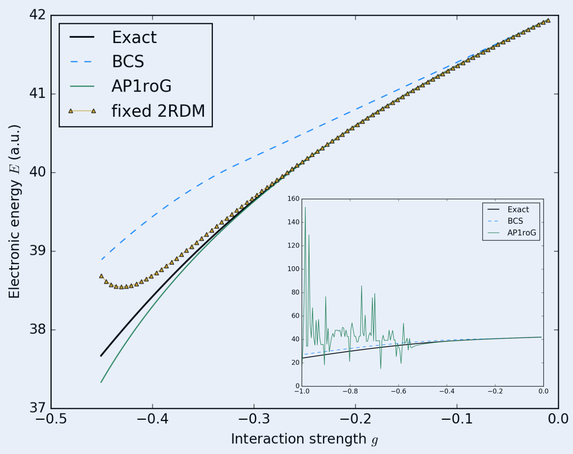

Figure 3. Total energies predicted by the AP1roG and BCS methods, the fixed 2-RDM energy and the exact solution according to Richardson as a function of g.
→ AP1roG breaks down near a critical pairing interaction strength of g_c = 0.35 which is the transition point to a superconducting system, i.e. the HF to BCS transition point.
→ AP1roG goes below the exact solution which is possible since it is not a variational method but solved through the projected Schrödinger equation.
→ N-representability fixing of the 2-RDM results in energies that are above the exact energy

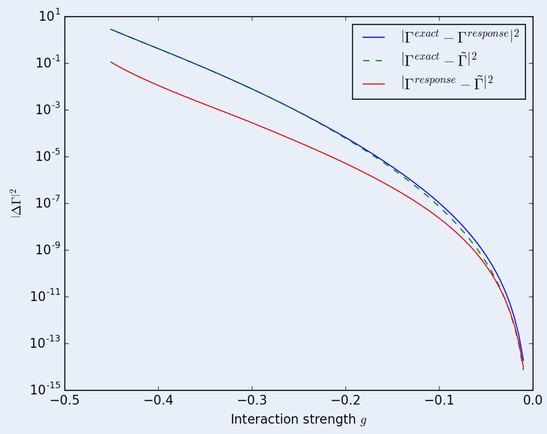

Figure 4. Cost functions of the AP1roG response 2-RDM and the fixed 2-RDM w.r.t. the exact 2-RDM and of the response 2-RDM w.r.t. fixed 2-RDM as a function of the interaction strength g.
→ cost functions increase with increasing interaction strength, i.e. deviations from N-representability increase.
→ cost functions of response 2-RDM and fixed 2-RDM w.r.t. exact 2-RDM nearly overlap indicating that although we bring the 2-RDM closer to N-representability, the distance to the exact 2-RDM does not change much.
→ the optimization procedure brings the 2-RDM closer to the set of N-representable 2-RDMs but it does not necessarily bring the fixed 2-RDMs closer to the exact solution.

1. Johnson, P.A.; Ayers, P.W.; Limacher, P.A.; De Baerdemacker, S.; Van Neck, D.; Bultinck, P. Comput. Theor. Chem. **2013**, 1003, 101-113.
2. Shavitt, I; Bartlett R.J. Many-body methods in chemistry and physics: MBPT and coupled-cluster theory; Cambridge University Press, **2009**.
3. Coleman, A.J. Rev. Mod Phys. **1963**, 35, 668-687.
4. Rice, S.A.; Mazziotti, D.A Reduced-density-matrix-mechanics: with application to many-electron atoms and molecules; John Wiley & Sons, **2007**.
5. Weinhold, F.; Wilson E.B. J. Chem. Phys. **1967**, 46, 2752-2758 / J. Chem. Phys. **1967**, 47, 2298-2311.
6. Poelmans, W.; Van Raemdonck M.; Verstichel, B.; De Baerdemacker, S.; Torre, A.; Lain, L.; Massaccesi, G.E.; Alcoba D.R.; Bultinck, P.; Van Neck, D. J. Chem. Theory Comput. **2015**, 11, 4064-4076.
7. Higham N.J. Linear Algebra and its applications. **1988**, 103, 103-118.
8. Limacher, P.A.; Ayers, P.W.; Johnson, P.A.; De Baerdemacker, S.; Van Neck, D.; Bultinck, P. J. Chem. Theory Comput. **2013**, 9, 1394-1401.
9. Richardson, R. Nucl. Phys Lett. **1963**, 3, 277-279 / Richardson, R.; Sherman, N. Nucl. Phys. **1964**, 52, 221-238.
10. Sambataro, M.; Phys. Rev. C. **2007**, 75, 054314 / De Baerdemacker, S. Phys. Rev. C. **2012**, 86, 044332.

CENTER FOR MOLECULAR MODELING

HERTON

Caitlin.Lanssens@UGent.be
http://CMM.ugent.be