Making 2-electron response reduced density matrices N-representable

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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. Furthermore, the 2-RDMs obtained from response theory are not necessarily N-representable. We present a new algorithm for making these non-N-representable 2-RDMs approximately N-representable.

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: $\Gamma_{pqrs} = \langle\Psi|\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_s\hat{a}_r|\Psi\rangle$
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,

$$\Gamma^{response}_{ijkl} = \frac{\partial E}{\partial V_{ijkl}}$$

In general, this response 2-RDM is not N-representable[3]. That is, it does not correspond to an actual physical N-electron system.
A few necessary (but not sufficient) N-representability conditions:

- Symmetry properties: $\Gamma_{pqrs} = \Gamma_{rspq}$

$$\Gamma_{pqrs} = -\Gamma_{qprs} = -\Gamma_{pqsr} = \Gamma_{qpsr}$$

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

$$P \succeq 0 \quad \text{with} \quad P_{pqrs} = \langle\Psi|\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_s\hat{a}_r|\Psi\rangle = \Gamma_{pqrs}$$
$$Q \succeq 0 \quad \text{with} \quad Q_{pqrs} = \langle\Psi|\hat{a}_p\hat{a}_q\hat{a}_s^\dagger\hat{a}_r^\dagger|\Psi\rangle$$
$$G \succeq 0 \quad \text{with} \quad G_{pqrs} = \langle\Psi|\hat{a}_p^\dagger\hat{a}_q\hat{a}_s^\dagger\hat{a}_r|\Psi\rangle$$

Optimization algorithm

Our strategy is to find the 2-RDM that has the largest overlap with the 2-RDM we obtain from response theory, under the constraints that the 2-RDM is symmetric, its trace is normalized and the 2-RDM, Q and G matrices are positive semi-definite.

$$\begin{aligned} \underset{\Gamma}{\text{maximize}} \quad & \mathrm{Tr}\left[\,\Gamma^{response}\cdot\Gamma\,\right] \\ \text{subject to} \quad & \Gamma = \Gamma^\dagger \\ & \mathrm{Tr}(\Gamma) = N(N-1) \\ & \Gamma, Q(\Gamma), G(\Gamma) \succeq 0 \end{aligned}$$

Find the closest, positive semidefinite, symmetric 2-RDM with the correct trace by[5]:
(1) Symmetrizing the 2-RDM.
(2) Setting negative eigenvalues to zero.
(3) Shifting all eigenvalues by a constant to fulfill the trace condition.
(4) Repeating steps (2) and (3) until convergence.
A similar procedure can then be used for the Q and G matrices.
The proposed algorithm can be found in Figure 1: the sequence of correcting the 2-RDM, the Q and the G matrix is continued until convergence is reached i.e. we have found the 2-RDM with the largest overlap to the response 2-RDM, but which is N-representable in the sense that it fulfills the P, Q and G condition. Convergence is measured by the error on the traces and the magnitude of the largest negative eigenvalue.

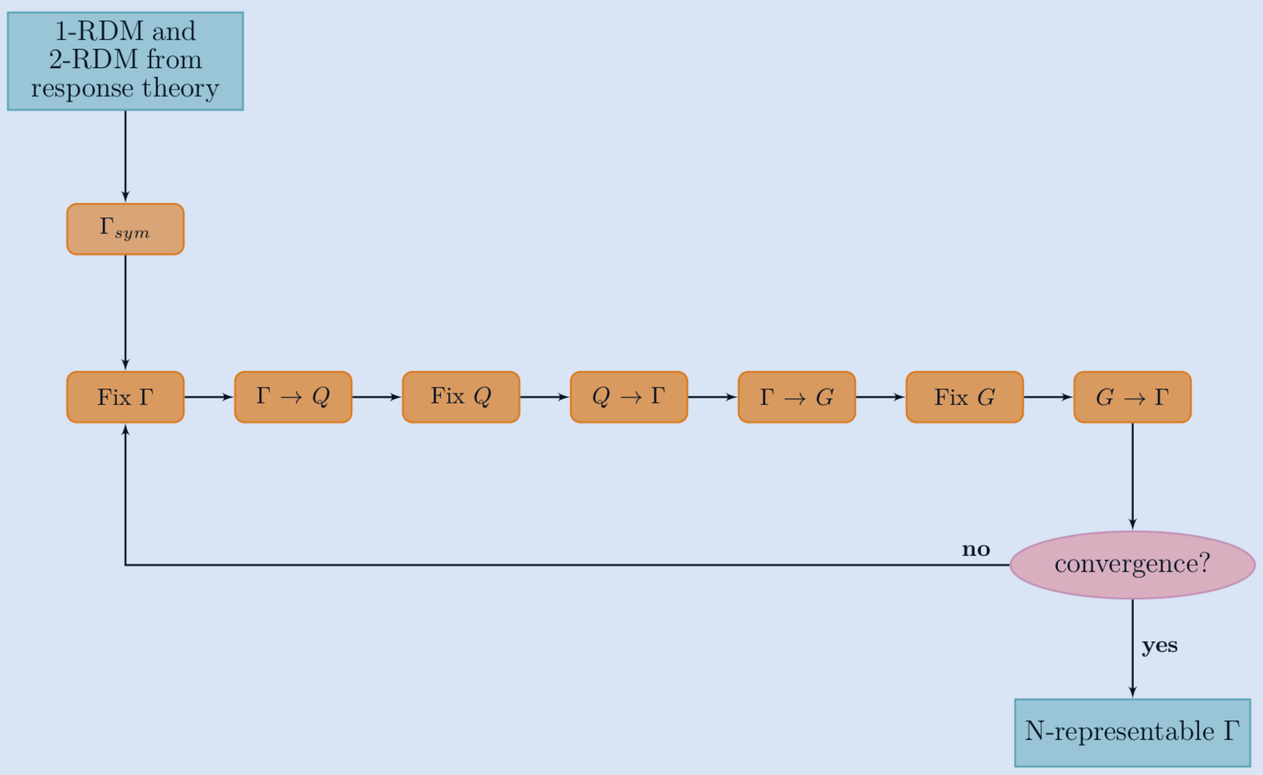

Figure 1. N-representability optimization algorithm.

Molecule	$E_{AP1roG} - E_{FCI}$	$E_{non-opt} - E_{FCI}$	$E_{opt} - E_{FCI}$
C_2	0.182089	0.182209	0.183865
BN	0.228113	0.231880	0.232826
BeO	0.156687	0.156665	0.156677
LiF	0.126681	0.126677	0.126680
CN^+	0.194517	0.194688	0.196147
BeF^+	0.063146	0.063141	0.063144
N_2	0.215751	0.215672	0.215676
CO	0.196208	0.196171	0.196181
BF	0.114844	0.114838	0.114842

Table 1. AP1roG energy, non-regularized 2-RDM and regularized 2-RDM compared to FCI energy for some 12- and 14-electron species at equilibrium (6-31g* basis set). Energies are given in atomic units.

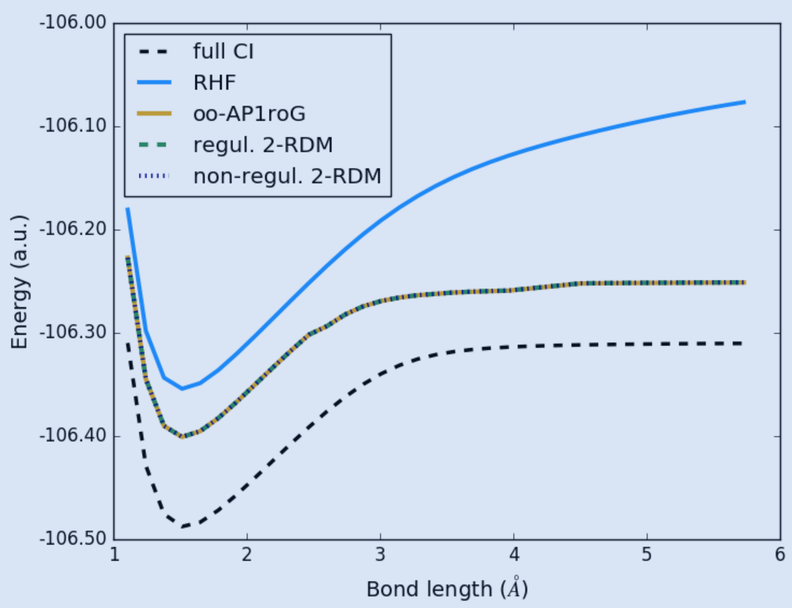

Figure 2. Energy dissociation curves for LiF (3-21g basis set).

Results

- Current algorithm includes the P and Q condition.
- Bond lengths for the single-point calculations are taken from the NIST CCCBDB database[6]. FCI energies are obtained with MOLPRO[7] and the Hartree-Fock and geminals (AP1roG with orbital optimization) calculations are done with HORTON[8].
- Single-point calculations on 12- and 14-electron species (Table 1): $E_{regul.} > E_{non\text{-}regul.}$ and E_{ap1rog} sometimes higher, sometimes lower. Energy differences of the order of milliHartree.
- Dissociation curve for LiF (Figure 2): energy difference between $E_{regul.}$ and $E_{non\text{-}regul.}$ of the order 10^{-6} a.u. and E_{ap1rog} also very close.
  → suggests that the response 2-RDMs resulting from the geminals calculations is very close to being N-representable!

Conclusions and further research

- Until now no convergence problems
- Response 2-RDM from AP1roG seems to be close to N-representability
- More testing is needed to further investigate the performance, stability, conditioning and usability of this algorithm.
- We need to find molecules with 2-RDMs that deviate more from N-representability or that follow from other wave function models e.g. coupled cluster theory.

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