The Electronic Ground State Energy Problem: a New Reduced Density Matrix Approach

Eric CANCES, Mathieu LEWIN, Gabriel STOLTZ

CERMICS, École Nationale des Ponts et Chaussées & CEA/DAM, Bruyères-le-Châtel

http://cermics.enpc.fr/∼stoltz/

The electronic problem in terms of second-order reduced density matrices

Notations

- finite-dimensional space $\mathfrak{h} := \mathrm{span}(\chi_i,\ i = 1, ..., r)$ of the one-body space $L^2(\mathbb{R}^3 \times \{|\uparrow\rangle, |\downarrow\rangle\}, \mathbb{C})$
- electronic Hamiltonian H_N acting on $\bigwedge_{n=1}^N \mathfrak{h}$ (antisymmetric N-body wavefunctions $\Psi(x_1, ..., x_N)$):

$$H_N = \sum_{i=1}^N h_{x_i} + \sum_{1 \le i < j \le N} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} \quad \text{with} \quad h = -\Delta/2 + V$$

- $\mathcal{S}(X)$ is the space of self-adjoint matrices acting on a vector space X, and $\mathcal{P}(X) \subset \mathcal{S}(X)$ the cone of positive semi-definite matrices. Simplified notation $\mathcal{P}_N := \mathcal{P}\left(\bigwedge_1^N \mathfrak{h}\right)$ and $\mathcal{S}_N := \mathcal{S}\left(\bigwedge_1^N \mathfrak{h}\right)$;

The ground-state energy then reads

$$E = \inf_{\substack{\Psi \in \bigwedge_{n=1}^N \mathfrak{h},\\ \|\Psi\|=1}} \langle \Psi, H_N \Psi \rangle = \inf_{\substack{\Upsilon \in \mathcal{P}_N,\\ \mathrm{tr}(\Upsilon)=1}} \mathrm{tr}(H_N \Upsilon). \tag{1}$$

Ground state-energy in terms of the 2-RDM

The 2-RDM Γ associated with an N-body density matrix $\Upsilon \in \mathcal{P}_N$ is defined by means of Kummer's contraction operator [10, 2] L_N^2 as $\Gamma = L_N^2(\Upsilon)$.

The *cone* $\mathcal{C}_N$ *of N-representable two-body density matrices* is by definition the image by L_N^2 of the cone $\mathcal{P}_N$ of N-body density matrices: $\mathcal{C}_N = L_N^2(\mathcal{P}_N) \subset \mathcal{S}_2$, with $\mathrm{tr}(\Gamma) = N(N-1)$.

$$\boxed{E = \inf_{\substack{\Gamma \in \mathcal{C}_N,\\ \mathrm{tr}(\Gamma)=N(N-1)}} \mathrm{tr}(K_N \Gamma)} \quad \text{where} \quad K_N = \frac{h_{x_1} + h_{x_2}}{2(N-1)} + \frac{1}{2|\mathbf{x}_1 - \mathbf{x}_2|}. \tag{2}$$

Impressive numerical results have been obtained recently by two different algorithms for semidefinite programming: primal-dual interior point methods [15, 11, 14, 16, 8], or an augmented Lagrangian formulation using matrix factorization of the 2-RDM [12, 13].

Dual Formulation of the RDM Minimization Problem

Reduction to a one-dimensional optimization problem

The polar cone $\mathcal{C}^*$ of a cone $\mathcal{C}$ in any Hermitian space is defined as $\mathcal{C}^* = \{x \mid \forall y \in \mathcal{C}, \langle x, y \rangle \ge 0\}$ (where $\langle \cdot, \cdot \rangle$ is the scalar product). Formulating (2) in terms of $(\mathcal{C}_N)^*$ instead of $\mathcal{C}_N$:

$$\boxed{E = N(N-1) \sup\{\mu \mid K_N - \mu \in (\mathcal{C}_N)^*\}.} \tag{3}$$

Easily derived from (2) using the Lagrangian inf/sup formulation $E = \inf_{\Gamma \in \mathcal{S}_2} \sup_{B \in (\mathcal{C}_N)^*,\ \mu \in \mathbb{R}} \mathcal{L}(\Gamma, B, \mu)$ with

$$\mathcal{L}(\Gamma, B, \mu) = \mathrm{tr}(K_N \Gamma) - \mathrm{tr}(B\Gamma) - \mu\{\mathrm{tr}(\Gamma) - N(N-1)\},$$

. Optimization problem in dimension 1 over $\mu \in \mathbb{R}$ which is the variable dual to the constraint $\mathrm{tr}(\Gamma) = N(N-1)$.

Identification of the dual cone :N-representability problem

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Necessary conditions for N-representability are selected, of the form $\mathcal{L}_\ell(\Gamma) \ge 0$ where $\mathcal{L}_\ell : \mathcal{S}_2 \to \mathcal{S}(X_\ell)$ is a linear map and X_ℓ is some vector space.

Minimization over approximated cone and its dual

$$\mathcal{C}_{\mathrm{app}} := \{\Gamma \in \mathcal{S}_2 \mid \forall \ell = 1...L,\ \mathcal{L}_\ell(\Gamma) \ge 0\}, \quad (\mathcal{C}_{\mathrm{app}})^* := \left\{ \sum_{\ell=1}^L (\mathcal{L}_\ell)^* B_\ell \mid B_\ell \in \mathcal{S}(X_\ell),\ B_\ell \ge 0 \right\},$$

The associated approximate energy is then a *lower bound* to the true energy

$$\boxed{E_{\mathrm{app}} = \inf_{\substack{\Gamma \in \mathcal{C}_{\mathrm{app}},\\ \mathrm{tr}(\Gamma)=N(N-1)}} \mathrm{tr}(K_N \Gamma) = N(N-1) \sup\{\mu \mid K_N - \mu \in (\mathcal{C}_{\mathrm{app}})^*\}.} \tag{4}$$

We denote by $\mu^*_{\mathrm{app}} = E_{\mathrm{app}}/(N(N-1))$.

Usual necessary N-representability conditions

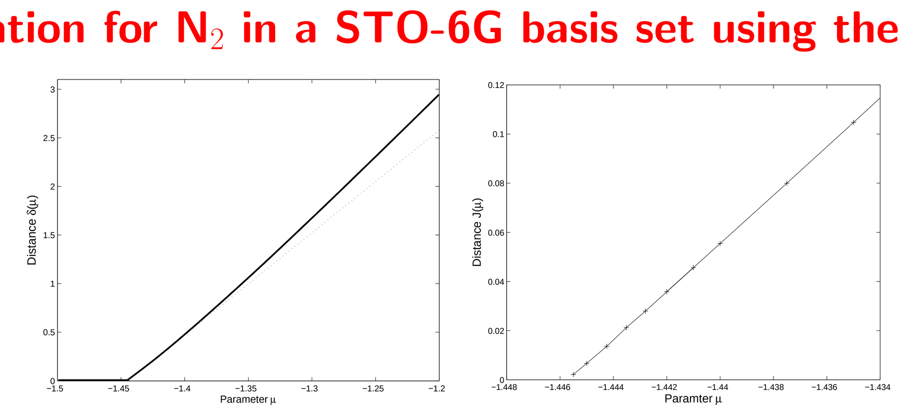
We consider the P, Q, G conditions [9, 2]. Additional necessary conditions can be considered, such as Erdahl's T_1 and T_2 conditions [6, 16, 8]

$$\mathcal{L}_P(\Gamma) = \Gamma, \quad [\mathcal{L}_G(\Gamma)]_{i_1,j_2}^{j_1,i_2} = -\Gamma_{i_1,j_2}^{j_1,i_2} + \delta_{i_1}^{j_1} \gamma_{i_2}^{j_2},$$

$$[\mathcal{L}_Q(\Gamma)]_{i_1,i_2}^{j_1,j_2} = \Gamma_{i_1,i_2}^{j_1,j_2} - \delta_{i_1}^{j_1} \gamma_{i_2}^{j_2} - \delta_{i_2}^{j_2} \gamma_{i_1}^{j_1} + \delta_{i_1}^{j_2} \gamma_{i_2}^{j_1} + \delta_{i_2}^{j_1} \gamma_{i_1}^{j_2} + (\delta_{i_1}^{j_1} \delta_{i_2}^{j_2} - \delta_{i_1}^{j_2} \delta_{i_2}^{j_1}) \frac{\mathrm{tr}(\Gamma)}{N(N-1)},$$

where $\gamma_i^j = \frac{1}{N-1} \sum_{k=1}^r \Gamma_{i,k}^{j,k}$ is the one-body RDM associated with the two-body RDM Γ (notice that $\mathcal{L}_G(\Gamma)$ is not antisymmetric).

Exemple: Minimization for N_2 in a STO-6G basis set using the P,Q,G conditions



Plot of the distance to the cone: $\delta(\mu) = \mathrm{dist}\left(K_N - \mu, (\mathcal{C}_{\mathrm{app}})^*\right)$. Notice that this function is convex on $\mathbb{R}$, increasing on $[\mu^*_{\mathrm{app}}, \infty)$, and $\delta \equiv 0$ on $(-\infty, \mu^*_{\mathrm{app}}]$.

Algorithm for solving the dual problem

We use a Newton-like scheme to minimize the distance to the dual cone $(\mathcal{C}_{\mathrm{app}})^*$, using

$$\forall \mu > \mu^*_{\mathrm{app}}, \quad \delta'(\mu) = -\frac{\mathrm{tr}(K_N - \mu - A_\mu)}{\|K_N - \mu - A_\mu\|} \tag{5}$$

where A_μ denotes the projection of $K_N - \mu$ onto the polar cone $(\mathcal{C}_{\mathrm{app}})^*$.

The computation of the distance $\delta(\mu)$ to the cone, and of the projection A_μ of $K_N - \mu$ is the difficult part of the procedure. We chose to minimize, for a given μ, the objective function

$$J_\mu(B) = \frac{1}{2} \left\| K_N - \mu - \sum_{\ell=1}^L (\mathcal{L}_\ell)^* B_\ell \right\|^2,$$

under the constraints $B_\ell \ge 0$ ($\ell = 1...L$), using a classical limited-memory BFGS algorithm, keeping the last $m = 3$ descent directions. The positivity constraints were parametrized by $B_\ell = (C_\ell)^2$ with C_ℓ symmetric, as suggested by Mazziotti in [12, 13].

Finally, since the convergence is poor below the Hartree-Fock level, we use the quasi-linearity of the distance for small μ to devise an efficient stopping criterion.

Numerical results

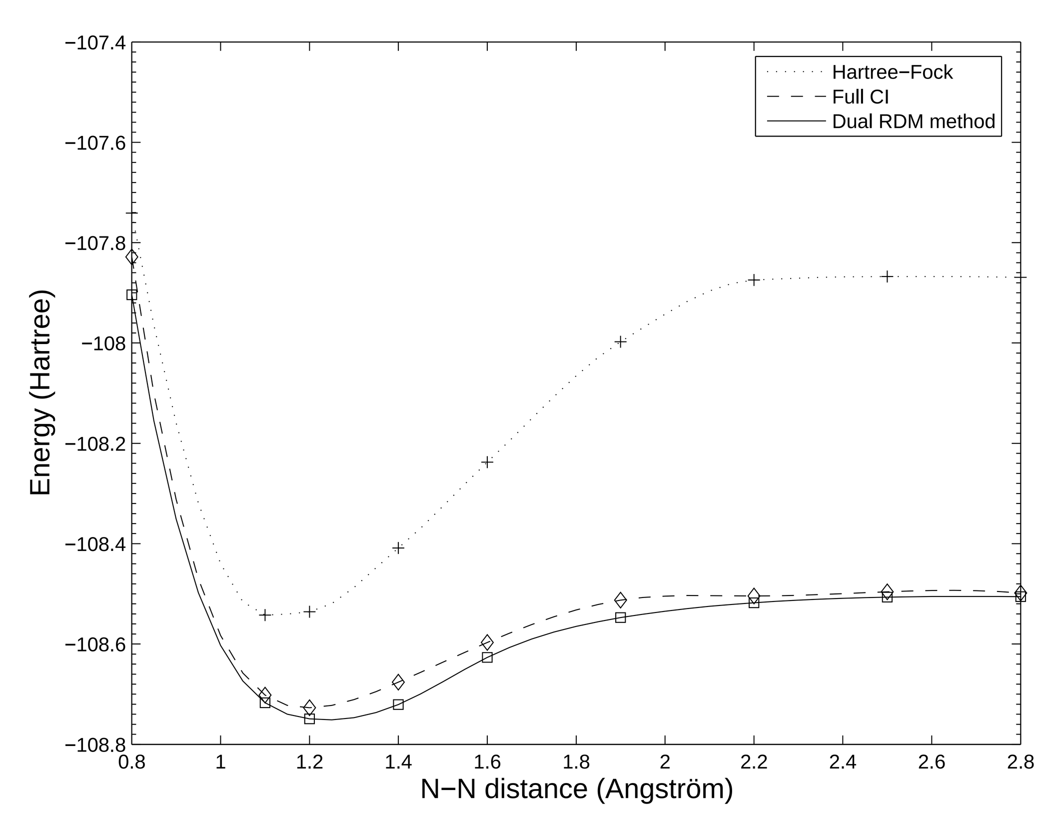
Correlation energies in a STO-6G basis set

System	FCI energy	Correlation energy	Dual RDM energy (% of the correlation energy)
Be	-14.556086	-0.0527274	-14.556123 (100.07)
LiH	-7.972557	-0.0190867	-7.9727078 (100.79)
BH	-25.058806	-0.0569044	-25.061771 (105.21)
Li_2	-14.837571	-0.0286889	-14.839066 (105.21)
BeH_2	-15.759498	-0.0335151	-15.761284 (105.33)
H_2O	-75.735839	-0.0546392	-75.738582 (105.02)
NH_3	-56.0586005	-0.0693410	-56.074805 (123.37)

Correlation energies in a 6-31G basis set

System	FCI energy	Correlation energy	Dual RDM energy (% of correlation energy)
Be	-14.613545	-0.0467812	-14.613653 (100.23)
LiH	-7.995678	-0.0185565	-7.9959693 (101.57)
BH	-25.171730	-0.0630461	-25.176736 (107.94)
Li_2	-14.893607	-0.0277581	-14.895389 (106.42)
BeH_2	-15.798440	-0.0402691	-15.801066 (106.52)
H_2O	-76.120220	-0.1401501	-76.142125 (115.63)
NH_3	-56.291315	-0.1336141	-56.318065 (120.02)

Dissociation curve for N_2 in a STO-6G basis set



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