

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

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## Abstract

We present here a formulation of the electronic ground-state energy in terms of the second order reduced density matrix, using a duality argument. It is shown that the computation of the ground-state energy reduces to the search of the projection of some two-electron reduced Hamiltonian on the dual cone of  $N$ -representability conditions. Some numerical results validate the approach, both for equilibrium geometries and for the dissociation curve of  $N_2$ .

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## I. INTRODUCTION

As early as in 1951, it was noticed by Coleman that the electronic  $N$ -body ground-state energy could be obtained by minimizing over the set of  $N$ -representable two-body reduced density matrices (2-RDM), and Mayer definitely opened the field in 1955 with his pioneering article [1]. At a conference in 1959, Coulson then proposed to completely eliminate wavefunctions from Quantum Chemistry, since all the electronic ground-state properties of molecular systems can be computed from the 2-RDM [1–3]. Unfortunately, the set of  $N$ -representable 2-RDM is not known explicitly. Some mathematical characterizations were provided [4–6] but they could not be used to derive a numerical method with a complexity of a lower order than the usual  $N$ -body problem. Analytical approaches for model systems (see e.g. [7]) were also proposed in order to precise the accuracy of the  $N$ -representability conditions in specific cases. In practice, only *approximate* RDM minimization problems, in which only a few necessary  $N$ -representability conditions are imposed (see the geometric constraints of [8], or the so-called P,Q,G conditions [9, 10]), can be considered. The first numerical studies relying on this strategy gave encouraging results [11].

Recently a new interest in the Reduced Density Matrix (RDM) approach arose. Impressive numerical results have been obtained by two different strategies issued from semidefinite programming: primal-dual interior point methods [12–15] on the one hand, augmented Lagrangian formulations using matrix factorizations of the 2-RDM [16–18] on the other hand. These results use a small number of known *necessary conditions* of  $N$ -representability. Yet, the so-obtained ground-state energies are as accurate as the ones obtained with coupled-cluster methods, see e.g. [16, 17]. In addition, these energies provide lower bounds of the Full CI energies, whereas the variational post Hartree-Fock methods, such as CI or MCSCF, all provide upper bounds.

Although the current implementations of variational 2-RDM algorithms are limited to the simulation of small molecules in small basis sets, we believe that improvements of the algorithms and increase of computational power will make it possible to simulate larger molecules and to use larger basis sets in a near future. This will allow in particular to assess the convergence of the RDM approach with respect to the size of the basis set, for a given molecular system.

Since the RDM method is a linear minimization problem over a convex set of complicated

structure, it is natural to use the concept of duality to mathematically characterize and numerically compute the minimum. Duality is an underlying issue in all the RDM studies [4–6, 10, 19, 20], but surprisingly, the specific form of the dual formulation of the RDM problem has not yet been used to derive an efficient algorithm. The current methods (see, e.g. [12, 13, 15–17]) all use general duality considerations in their algorithms, but none of them solves directly (and only) the dual RDM problem. The purpose of the present article is to present such an approach. As will be shown below, the associated dual optimization problem boils down to the search of the zero of a one-dimensional convex function.

The paper is organized as follows. After setting the problem in section II, we derive the RDM and the approximate RDM dual problems by standard Lagrangian methods in section III. Then, in section IV, we propose a new algorithm which aims at solving directly the dual problem. Section V eventually presents some numerical results demonstrating that this new method is an interesting and efficient alternative to the existing methods.

## II. NOTATION

Let us consider a finite-dimensional space  $\mathfrak{h} := \text{span}(\chi_i, i = 1, \dots, r)$  where  $(\chi_i)_{i \geq 1}$  is a Hilbert basis of the one-body space  $L^2(\mathbb{R}^3 \times \{|\uparrow\rangle, |\downarrow\rangle\}, \mathbb{C})$ . Most of our analysis is also valid in infinite dimension but for the sake of simplicity, we restrict to the finite-dimensional case. The electronic Hamiltonian  $H_N$  acts on the  $N$ -body fermionic space  $\bigwedge_{n=1}^N \mathfrak{h}$  of antisymmetric  $N$ -body wavefunctions  $\Psi(x_1, \dots, x_N)$  and is formally defined as

$$H_N = \sum_{i=1}^N h_{x_i} + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}$$

where  $h = -\Delta/2 + V$  and  $V$  is the external Coulomb potential generated by the nuclei. In the whole paper, we denote by  $x = (\mathbf{x}, \sigma)$  the vector containing both the space variable  $\mathbf{x} \in \mathbb{R}^3$  and the spin variable  $\sigma \in \{|\uparrow\rangle, |\downarrow\rangle\}$ . For any vector space  $X$ , we denote by  $\mathcal{S}(X)$  the space of self-adjoint matrices acting on  $X$ , and by  $\mathcal{P}(X) \subset \mathcal{S}(X)$  the cone of positive semi-definite matrices. We also use the 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

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

The second equality holds true for the infimum of the energy over the set of mixed states coincides with the infimum of the energy over the set of pure states. In mathematical words, the minimum of a linear function over a convex set is attained on an extremal point of the convex set.

The 2-RDM  $\Gamma$  associated with an  $N$ -body density matrix  $\Upsilon \in \mathcal{P}_N$  is defined by means of Kummer's contraction operator  $L_N^2$  as [4, 6]

$$\Gamma_{i_1, i_2}^{j_1, j_2} = L_N^2(\Upsilon)_{i_1, i_2}^{j_1, j_2} = N(N-1) \sum_{k_3, \dots, k_N=1}^r \Upsilon_{i_1 i_2 k_3 \dots k_N}^{j_1 j_2 k_3 \dots k_N}. \quad (2)$$

Then, 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:

$$\mathcal{C}_N = L_N^2(\mathcal{P}_N) \subset \mathcal{S}_2.$$

Of course the 2-RDMs of physical interest are the elements  $\Gamma \in \mathcal{C}_N$  which arise from a normalized  $N$ -body density matrix  $\Upsilon$ , i.e. which additionally satisfy  $\text{tr}(\Gamma) = N(N-1)$ .

Since the Hamiltonian  $H_N$  only contains two-body interactions, the energy of the system can be expressed in terms of the two-body density matrix  $\Gamma$  only (see, e.g. [4, 14]):

$$E = \inf_{\substack{\Gamma \in \mathcal{C}_N, \\ \text{tr}(\Gamma) = N(N-1)}} \text{tr}(K_N \Gamma) \quad (3)$$

where we have introduced

$$K_N = \frac{h_{x_1} + h_{x_2}}{2(N-1)} + \frac{1}{2|\mathbf{x}_1 - \mathbf{x}_2|}.$$

Formula (3) is an obvious consequence of the identity  $H_N = (L_N^2)^* K_N$  where  $(L_N^2)^*$  is the adjoint of  $L_N^2$  sometimes also called a *lifting operator*. Notice that we did not impose any constraint on the spin state in (3), but such constraints can be easily taken into account.

### III. DUAL FORMULATION OF THE RDM MINIMIZATION PROBLEM

We now present the dual formulation of the minimization (3). We recall that the polar cone  $\mathcal{C}^*$  of a cone  $\mathcal{C}$  in any Hermitian space is defined as  $\mathcal{C}^* = \{x \mid \forall y \in \mathcal{C}, \langle x, y \rangle \geq 0\}$ , where  $\langle \cdot, \cdot \rangle$  denotes the considered scalar product. The dual method then consists in formulating (3) in terms of  $(\mathcal{C}_N)^*$  instead of  $\mathcal{C}_N$ :

$$E = N(N-1) \sup\{\mu \mid K_N - \mu \in (\mathcal{C}_N)^*\}. \quad (4)$$

We therefore obtain an optimization problem in dimension 1 over  $\mu \in \mathbb{R}$  which is the variable dual to the constraint  $\text{tr}(\Gamma) = N(N - 1)$ . Of course characterizing the polar cone  $(\mathcal{C}_N)^*$  is as difficult as characterizing  $\mathcal{C}_N$ , this issue is called the *N-representability problem*. Indeed  $\mathcal{C}_N = (\mathcal{C}_N)^{**}$ . Even if the dual formulation (4) does not simplify the theoretical N-representability problem, it turns out to be more convenient for numerical purposes, as will be shown below.

Formula (4) can be easily derived from (3). Introducing the Lagrangian

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

it follows

$$E = \inf_{\Gamma \in \mathcal{S}_2} \sup_{B \in (\mathcal{C}_N)^*, \mu \in \mathbb{R}} \mathcal{L}(\Gamma, B, \mu). \quad (5)$$

It then suffices to exchange the inf and the sup in (5) to obtain (4). Indeed, it is a general fact that for any cone  $\mathcal{C}$  in a finite-dimensional space

$$\inf_{x \in \mathcal{C}, \langle b, x \rangle = 1} \langle a, x \rangle = \sup \{ \mu \mid a - b\mu \in \mathcal{C}^* \}. \quad (6)$$

Note that this property has been already used in the RDM setting by Erdahl [20]. We shall use it again below.

Since both  $(\mathcal{C}_N)^*$  and  $\mathcal{C}_N$  are unknown and difficult to characterize, it is necessary to approximate (4) by a variational problem that can be carried out numerically. To this end, some necessary conditions for N-representability are selected. We consider in this paper  $L$  conditions of the following general form

$$\forall \ell = 1 \dots L, \quad \mathcal{L}_\ell(\Gamma) \geq 0 \quad (7)$$

where for any  $\ell$ ,  $\mathcal{L}_\ell : \mathcal{S}_2 \rightarrow \mathcal{S}(X_\ell)$  is a linear map and  $X_\ell$  is some vector space. For instance, the so-called P-condition  $\mathcal{L}_1(\Gamma) = \Gamma \geq 0$  (with  $X_1 = \mathfrak{h} \wedge \mathfrak{h}$ ) originates from the Kummer operator preserving positivity, and will always be considered. Other classical necessary conditions of N-representability will be introduced below. Imposing only the necessary conditions (7) means that  $\mathcal{C}_N$  is replaced by the approximate cone  $\mathcal{C}_{\text{app}} \supset \mathcal{C}_N$  defined as

$$\mathcal{C}_{\text{app}} := \{ \Gamma \in \mathcal{S}_2 \mid \forall \ell = 1 \dots L, \mathcal{L}_\ell(\Gamma) \geq 0 \}.$$

Its polar cone can easily be shown to be

$$(\mathcal{C}_{\text{app}})^* := \left\{ \sum_{\ell=1}^L (\mathcal{L}_\ell)^* B_\ell \mid B_\ell \in \mathcal{S}(X_\ell), B_\ell \geq 0 \right\}, \quad (8)$$

and the associated approximate energy is then, in view of (6),

$$E_{\text{app}} = \inf_{\substack{\Gamma \in \mathcal{C}_{\text{app}}, \\ \text{tr}(\Gamma) = N(N-1)}} \text{tr}(K_N \Gamma) \quad (9)$$

$$= N(N-1) \sup\{\mu \mid K_N - \mu \in (\mathcal{C}_{\text{app}})^*\}. \quad (10)$$

Let us emphasize that, since  $\mathcal{C}_{\text{app}} \supset \mathcal{C}_N$ , the energy  $E_{\text{app}}$  is a *lower bound* to the full CI energy in the chosen basis,  $E_{\text{app}} \leq E$ . We present below an algorithm for solving problem (10). Notice that we obtain only the ground-state energy (and not the ground state density matrix), but, resorting to first order perturbation theory, any observable including at most two-body interaction terms can be obtained by a finite difference of energies.

Some well-known necessary conditions of the form (7) are the P, Q, G conditions [4, 10]. Additional necessary conditions can be considered, such as Erdahl's  $T_1$  and  $T_2$  conditions [12, 13, 19]. The P, Q and G conditions correspond to the following linear operators in (7):

$$\mathcal{L}_1(\Gamma) = \Gamma,$$

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

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

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  $\Gamma$ . Expressions for the adjoint operators  $(\mathcal{L}_Q)^*$  and  $(\mathcal{L}_G)^*$  were presented in [14] for example. Notice that for any  $\Gamma \in \mathcal{S}_2$ ,  $\mathcal{L}_P(\Gamma)$  and  $\mathcal{L}_Q(\Gamma)$  also are antisymmetric, whereas  $\mathcal{L}_G(\Gamma)$  is not. Therefore,  $X_P = X_Q = \mathfrak{h} \wedge \mathfrak{h}$  and  $X_G = \mathfrak{h} \otimes \mathfrak{h}$  in the above general formalism. Notice also that Erdahl's three-index conditions  $T_1, T_2$  require  $X_{T_i} = \mathfrak{h} \otimes \mathfrak{h} \otimes \mathfrak{h}$ .

Our numerical tests were performed using the P, Q, G conditions but our algorithm for solving (10) is valid for any set of necessary conditions of the form (7).

#### IV. ALGORITHM FOR SOLVING THE DUAL PROBLEM

Let us introduce the distance to the dual cone  $(\mathcal{C}_{\text{app}})^*$

$$\delta(\mu) = \text{dist}(K_N - \mu, (\mathcal{C}_{\text{app}})^*).$$

Denoting  $\mu_{\text{app}}^* = E_{\text{app}}/(N(N-1))$ , the function  $\delta$  satisfies the following properties:

(i)  $\delta \equiv 0$  on  $(-\infty, \mu_{\text{app}}^*]$  and is increasing on  $[\mu_{\text{app}}^*, \infty)$ ;

(ii)  $\delta$  is convex on  $\mathbb{R}$ ;

(iii)  $\delta^2$  is continuously differentiable on  $\mathbb{R}$ , thus  $\delta$  is continuously differentiable on  $\mathbb{R} \setminus \{\mu_{\text{app}}^*\}$  and

$$\forall \mu > \mu_{\text{app}}^*, \quad \delta'(\mu) = -\frac{\text{tr}(K_N - \mu - A_\mu)}{\|K_N - \mu - A_\mu\|} \quad (11)$$

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

Proofs for (ii) – (iii) can be found in [21]. To prove (i), one notices that when  $\mu \leq \mu_{\text{app}}^*$ ,  $K_N - \mu = K_N - \mu^* + (\mu^* - \mu)$  belongs to  $(\mathcal{C}_{\text{app}})^*$  since  $\mu^* - \mu \in \mathcal{P}_2 \subset (\mathcal{C}_{\text{app}})^*$ . To illustrate the above properties, we provide a plot of  $\delta(\mu)$  for  $\text{N}_2$  in a STO-6G basis set, see Figure 1.

In order to compute  $\mu_{\text{app}}^*$ , we use a Newton-like scheme that strongly exploits the above mentioned properties in a natural way: starting from an initial energy above  $\mu_{\text{app}}^*$  (such as the Hartree-Fock energy for instance) and using the convexity of the function  $\delta$ , the Newton algorithm ensures that the energy  $\mu$  decreases at each step of the optimization process and converges to  $\mu_{\text{app}}^*$ . The right derivative of  $\delta$  at  $\mu_{\text{app}}^*$  being always positive, the convergence rate is guaranteed to be at least superlinear.

Of course, the most difficult part of the algorithm is the computation of the distance  $\delta(\mu)$  to the cone, and of the projection  $A_\mu$  of  $K_N - \mu$ . To this end, we chose to minimize, for a given  $\mu$ , 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  $B_\ell \geq 0$  ( $\ell = 1 \dots L$ ), according to the definition (8) of the polar cone  $(\mathcal{C}_{\text{app}})^*$ . The above minimization is performed using a classical limited-memory BFGS algorithm [22], keeping the last  $m = 3$  descent directions. The positivity constraints were parametrized by  $B_\ell = (C_\ell)^2$  with  $C_\ell$  symmetric, as suggested by Mazziotti in [16, 17].

Computing  $\delta(\mu)$  with sufficient accuracy when  $\mu$  is close to  $\mu_{\text{app}}^*$  can be difficult because the minimization of  $J_\mu(B)$  then is ill-conditioned. We therefore consider a “truncated” version of the Newton algorithm where  $\mu$  is updated by a fraction  $0 < a \leq 1$  of the Newton step. We then use the linearity of  $\delta$  for values close to  $\mu_{\text{app}}^*$  to devise a stopping criterion limiting the number of iterations. The algorithm is as follows:

**Algorithm 1** Consider an initial value  $\mu^0$  (for example the Hartree-Fock value  $\mu_{\text{HF}}$ ), and  $0 < a \leq 1$ . Compute the projection  $A_{\mu^0}$  of  $K_N - \mu^0$  on  $(\mathcal{C}_{\text{app}})^*$  and the distance  $d^0 = \delta(\mu^0)$ , and consider  $\mu^1 = \mu^0 - \frac{\delta(\mu^0)}{\delta'(\mu^0)}$ . For  $n \geq 1$ ,

- *Step 1.* Compute the projection  $A_{\mu^n} = \sum_{\ell=1}^L (\mathcal{L}_\ell)^* [(C_\ell^n)^2]$  of  $K_N - \mu^n$  on  $(\mathcal{C}_{\text{app}})^*$ , the associated distance  $d^n = \delta(\mu^n) = \|K_N - \mu^n - A_{\mu^n}\|$  and the derivative  $\delta'(\mu^n)$ ;
- *Step 2.* Compute the interpolation slope  $p^n = \frac{d^{n-1} - d^n}{\mu^{n-1} - \mu^n}$ ;
- *Step 3.* If  $p^n \leq (1 + \epsilon)\delta'(\mu^n)$ , then the linear assumption is satisfied and the final value is extrapolated from the current position as  $\mu^* = \mu^n - \frac{\delta(\mu^n)}{\delta'(\mu^n)}$ ;
- *Step 4.* Otherwise, set  $\mu^{n+1} = \mu^n - a \frac{\delta(\mu^n)}{\delta'(\mu^n)}$  and start again from (1) using as initial guess  $C_\ell^{n+1} = C_\ell^n$  for any  $\ell = 1 \dots L$ .

In practice, the above algorithm converges in a few iterations. The only time consuming step is the projection performed in Step 1. As described above, this projection is done iteratively by minimizing the objective function  $J_\mu$  by a limited-memory BFGS algorithm. The cost of one BFGS iteration scales as  $O(r^6)$ . We did not observe a clear scaling of the number of BFGS iterations with respect to the basis set size. The memory requirements scale as  $O(r^4)$ . Both computational time and memory requirements are comparable to those of [16].

## V. NUMERICAL RESULTS

We have tested the method on several molecules at equilibrium geometries using data from [23], for STO-6G and 6-31G basis sets. The results are reported in Table I and II respectively.

The reference Full CI (FCI) energies have been computed using GAMESS [24]. The correlation energies are recovered with a good accuracy. This is consistent with previous results already obtained with different RDM methods [12, 13, 15–17].

In general, we have observed that the function  $\delta$  is almost linear in quite large a right neighborhood of  $\mu_{\text{app}}^*$  (see Figure 1). One iteration of the Newton algorithm already provides a very correct approximation of the exact RDM energy, even when starting from the Hartree-Fock level. Usually, only 3 or 4 Newton iterations are necessary to achieve convergence.

Therefore, the only limiting step of the method is the computation of the distance  $\delta(\mu)$  and of the projection  $A_\mu$  of  $K_N - \mu$  on the polar cone. The method is very robust with respect to initial choices of the energy  $\mu^0$  and the matrices  $C_k^0$ . However, we have observed that the computational time needed for finding the projection  $A_\mu$  highly depends on the quality of the initial guess. The choice of genuine initial conditions is not obvious since we are manipulating abstract objects (dual elements of 2-RDM). Some CPU times are reported in Table III for very crude initial conditions  $C_k^0 = \text{Id}$  and  $\mu^0 \simeq 0.9\mu_{\text{HF}}$ .

We would like to underline that our projection algorithm is far from being optimal. There is clearly much room for improvement here. Let us also mention that the curve  $\mu \rightarrow \delta(\mu)$  can be easily sampled using parallel computing (one value of  $\mu$  per processor).

We also present in Figure 2 dissociation curves for  $\text{N}_2$  in a STO-6G basis set. This example was already studied in several works [25–27]. The agreement of our results with the reference Full CI is excellent, and the dissociation energy is therefore recovered with a very good accuracy.

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## Table and Figures captions

- **Figure I.** Left: Distance  $\delta(\mu)$  of  $K_N - \mu$  to the cone  $(\mathcal{C}_{\text{app}})^*$  as a function of  $\mu$  for  $\text{N}_2$  in a STO-6G basis set. The tangent at the estimated value for  $\mu_{\text{app}}^*$  is also displayed (dotted line). Right: Zoom near the FCI reference value. The Hartree-Fock value is  $\mu_{\text{HF}} = -1.4435153$  while the reference FCI value is  $\mu_{\text{CI}} = -1.4453909$ .
- **Table I.** Correlation energies in a STO-6G basis set.
- **Table II.** Correlation energies in a 6-31G basis set.
- **Table III.** CPU time (s) in a STO-6G basis using very crude initial guesses ( $C_l = I$ ).
- **Figure II.** Dissociation curve for  $\text{N}_2$  in a STO-6G basis set.

TABLE I: Cancès et al., Journal of Chemical Physics.

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 <sub>2</sub>	-14.837571	-0.0286889	-14.839066 (105.21)
BeH <sub>2</sub>	-15.759498	-0.0335151	-15.761284 (105.33)
H <sub>2</sub> O	-75.735839	-0.0546392	-75.738582 (105.02)
NH <sub>3</sub>	-56.0586005	-0.0693410	-56.074805 (123.37)

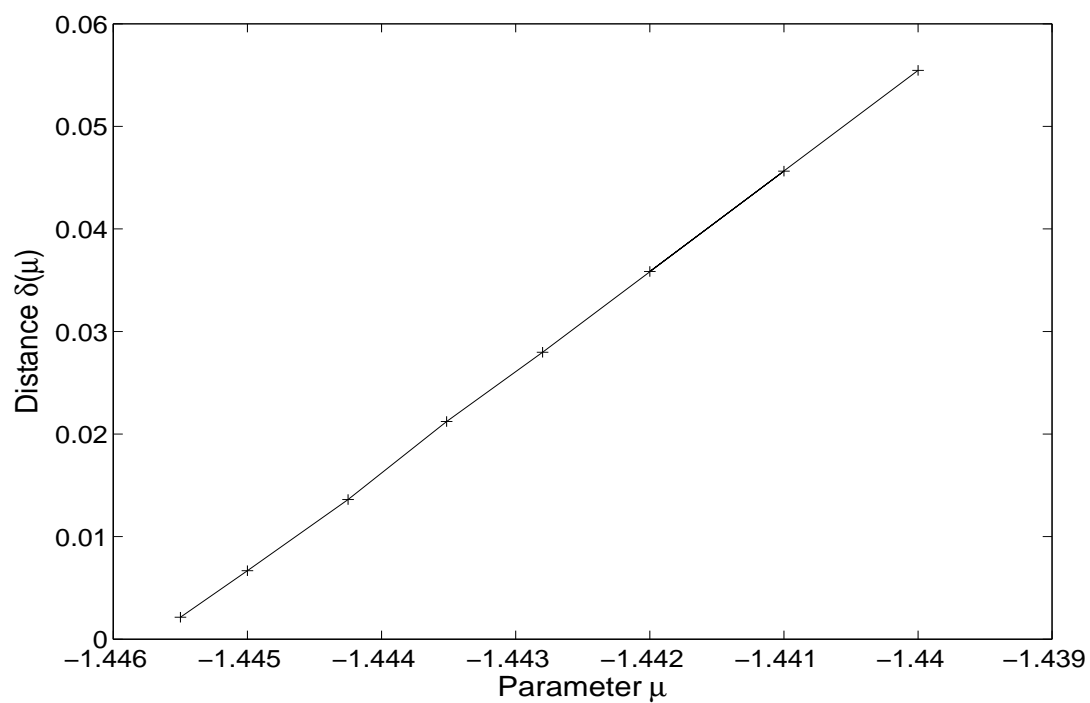
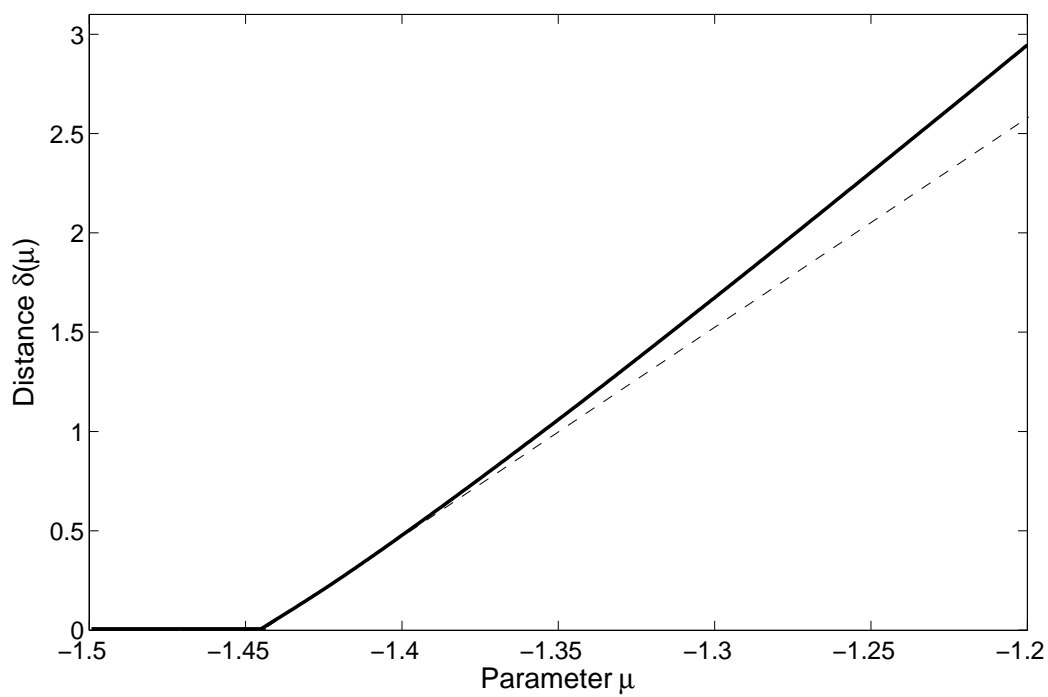


TABLE II: Cancès et al., Journal of Chemical Physics.

System	FCI energy	Correlation energy	Dual RDM energy (% of the 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 <sub>2</sub>	-14.893607	-0.0277581	-14.895389 (106.42)
BeH <sub>2</sub>	-15.798440	-0.0402691	-15.801066 (106.52)
H <sub>2</sub> O	-76.120220	-0.1401501	-76.142125 (115.63)
NH <sub>3</sub>	-56.291315	-0.1336141	-56.318065 (120.02)

TABLE III: Cancès et al., Journal of Chemical Physics.

System	Spatial basis size $r$	CPU time (s)	Newton iterations
Be	5	25.7	2
LiH	6	240.9	3
H <sub>2</sub> O	7	958.8	4
BeH <sub>2</sub>	7	1143.3	3

