

Semidefinite programs in electronic structure calculation

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Abstract

It has been a long-time dream in electronic structure theory in physical chemistry/chemical physics to compute ground state energies of atomic and molecular systems by employing a variational approach in which the two-body reduced density matrix (RDM) is the unknown variable. Realization of the RDM approach has benefited greatly from recent developments in semidefinite programming (SDP). We present the actual state of this new application of SDP as well as the formulations of these SDPs, which can be arbitrarily large. Numerical experiments using different SDP codes and formulations are given in order to seek for the best choices. The RDM method has several advantages including robustness and provision of high accuracy compared to traditional electronic structure methods, although its computational time and memory consumption are still extremely large.

1 Introduction

Electronic structure theory is the source of some of the largest and most challenging problems in computational science. As the quantum mechanical basis for the computation of properties of molecules and solids it is also of immense practical importance.

Traditional formulations of the electronic structure problem give rise to large linear or nonlinear Hermitian eigenvalue problems, but using the reduced density matrix (RDM) method [3, 6], one is required instead to solve a very large semidefinite programming (SDP) problem. Until recently the RDM method could not compete either in accuracy or in speed with well-established electronic structure methods, but this is changing. Especially Nakata *et al.* [13, 11] showed that a well-established SDP code could be used to solve an SDP having the RDMs as variables with the basic conditions (the “ P ”, “ Q ”, and “ G ” conditions, as will be clarified later) for a wide variety of interesting (although still small) molecules. Later, Zhao *et al.* [20] showed that with the inclusion of additional conditions (“ $T1$ ” and “ $T2$ ”), the accuracy that is obtained for small molecular systems compares favorably with the best widely used electronic structure methods. Very recently, Mazziotti [9, 10] announced results for larger molecular systems using the P , Q and G conditions.

For applied work, the main present challenge for the RDM approach is to develop the efficiency of the solution of the resulting large SDP problems to the stage where one has a method that is genuinely competitive in both accuracy and speed with traditional electronic structure methods. One of the keys to successfully and drastically reduce the

size of the SDP is to formulate it as a dual SDP problem. The dual formulation has many fewer dual variables (primal constraints) than the original primal formulation and can therefore be solved more efficiently. The SDP problems must be solved to high accuracy – typically 7 digits for the optimal value – and this is an extremely important consideration in the choice of solution methods and codes.

In the next section, we present the electronic structure problem and the RDM theory. In Section 2.1, we show the general form of the RDM reformulation, and we explain the concept of N -representability conditions. In Section 2.2, we exhibit the principal N -representability conditions: P , Q , G , $T1$ and $T2$, respectively.

In Section 3, we present the precise formulation of the RDM equations in dual SDP form using inequality and equality constraints. This is an improvement over the previous result [20] where equality constraints were split into a slightly relaxed pair of inequalities. We also consider the computational advantages of the dual SDP formulation compared to the primal one in terms of both number of floating point operations and memory usage.

The main motivation for the current study is to resolve the problem of the necessity of splitting the equality constraints into a slightly relaxed pair of inequalities. As it was pointed out in [5], this relaxation can worsen the real optimal value by at least 0.0005 (Hartree) for the molecule CH_3 with ${}^2A''_2$ state. In Section 4, we make a complete study of different SDP codes: CSDP 5.0 [1], SDPT3 3.1 [17], SeDuMi 1.05 [14] and 1.1, and SDPA 6.20 [19] and 6.20+. The latter version has a slight modification in the step-size control. We also utilize four different formulations. Section 4.1: the original SDP (11-12), Section 4.2: the formulation which treats the free variable \mathbf{x} in (11) as a difference of two non-negative variables, Section 4.3: the conversion proposed in [7] which eliminates the free variable \mathbf{x} from (11), and Section 4.4: the conversion which considers a greedy heuristic method to explore sparsity in the data [7].

Finally, we were able to conclude that SeDuMi 1.05 and 1.1 are the best codes for this class of problems. The best formulations are the ones proposed in Section 4.1 and Section 4.2. Also, since the SDPA 6.20+ can solve now these SDP problems with high accuracy, we can modify the SDPARA [18] accordingly and solve larger problems in a parallel environment using the formulation of Section 4.2.

2 The electronic structure problem and reduced density matrices

2.1 Basic formalism

The electronic structure problem is to determine the ground state energy of a many-electron system (atom or molecule) in a given external potential [15]. For an N -electron system this ground state energy is the smallest eigenvalue of a Hermitian operator (the Schrödinger operator or Hamiltonian) that acts on a space of N -electron *wavefunctions*, which are complex-valued square-integrable functions of N single-electron coordinates simultaneously that are totally antisymmetric under the interchange of any pair of electrons. (*Antisymmetry* will be specified later, but it does differ from the concept of an antisymmetric matrix).

In our work we follow the usual approach of discretizing the many-electron space of wavefunctions by way of a discretization of the single-electron space of wavefunctions, and

for purpose of exposition, we assume that single-electron basis functions ψ_i ($i = 1, 2, \dots, r$) are orthonormal. Under such discretization, we obtain a discrete Hamiltonian (matrix) \mathbf{H} which corresponds to the Schrödinger operator. The discretized ground state problem then asks for the minimum eigenvalue E_0 for $\mathbf{H}\mathbf{c} = E_0\mathbf{c}$, where \mathbf{c} is the discretized wavefunction (vector). The antisymmetry requirement on the wavefunction is also carried over \mathbf{c} , so it has size $r!/(N!(r-N)!)$.

This discrete formulation of the electronic structure problem as an exponentially large eigenvalue problem is also called *full configuration-interaction* (FCI), and it is intractable except for very small systems. More practical approaches [15] involve truncating the many electron basis in some systematic way. These include the SDCI approach (singly and doubly substituted configuration interaction) or the CCSD approach (coupled cluster expansion using single and double excitations).

An entirely different conceptual approach to the ground state electronic structure problem relies on the concept of the two-body reduced density matrix (2-RDM) of a many-electron system. This approach, first articulated in detail in two papers in the early 1960's [3, 6] was the subject of active theoretical and computational investigations through the 1970's, but because of limited success interest waned. See [5] for a complete list of references.

Now we proceed to detail its main concept. We assume that the space of wavefunctions has been discretized as just discussed. Notice that the minimum eigenvalue E_0 of the discretized electronic structure problem can be equivalently computed from the SDP problem

$$\begin{cases} \min & \langle \mathbf{H}, \mathbf{\Gamma}^{\text{full}} \rangle \\ \text{subject to} & \langle \mathbf{\Gamma}^{\text{full}}, \mathbf{I} \rangle = 1, \\ & \mathbf{\Gamma}^{\text{full}} \succeq \mathbf{O}. \end{cases} \quad (1)$$

Here $\langle \cdot, \cdot \rangle$ denotes the inner product in the space of real symmetric matrices $\langle \mathbf{A}, \mathbf{B} \rangle = \sum_{ij} A_{ij}B_{ij}$, and $\mathbf{A} \succeq \mathbf{B}$ means that $\mathbf{A} - \mathbf{B}$ is a positive semidefinite symmetric matrix. $\mathbf{\Gamma}^{\text{full}}$ is the *full density matrix*: a real symmetric matrix of the form $\mathbf{\Gamma}^{\text{full}}(i_1, \dots, i_N; i'_1, \dots, i'_N)$ where the indices i_1, i_2, \dots, i_N take distinct values from 1 to r (the discretization basis size), and like the wavefunction is *antisymmetric* under interchange of any pair of indices, *i.e.*, $\mathbf{\Gamma}^{\text{full}}(i_1, \dots, i_a, \dots, i_b, \dots, i_N; i'_1, \dots, i'_N) = -\mathbf{\Gamma}^{\text{full}}(i_1, \dots, i_b, \dots, i_a, \dots, i_N; i'_1, \dots, i'_N)$; and similarly for the primed indices i'_1, i'_2, \dots, i'_N . $\mathbf{\Gamma}^{\text{full}}$ is an exponentially large object in r and N (number of electrons) that is not suitable as ingredient of an effective computational method. However, a reduction of the problem (1) to a more tractable convex optimization problem is possible.

Given a full density matrix $\mathbf{\Gamma}^{\text{full}}$, the corresponding p -body RDM $\mathbf{\Gamma}_p$ is a function of two pairs of p -electron variables defined as a (scaled) partial trace over the remaining $N-p$ variables:

$$\mathbf{\Gamma}_p(i_1, \dots, i_p; i'_1, \dots, i'_p) = \frac{N!}{(N-p)!} \sum_{i_{p+1}, \dots, i_N=1}^r \mathbf{\Gamma}^{\text{full}}(i_1, \dots, i_p, i_{p+1}, \dots, i_N; i'_1, \dots, i'_p, i_{p+1}, \dots, i_N). \quad (2)$$

The p -body RDM $\mathbf{\Gamma}_p$ is also real symmetric and inherits the antisymmetry conditions from the $\mathbf{\Gamma}^{\text{full}}$.

The key property for RDM theory is described in the language of physics and chemistry by saying that the Hamiltonian (matrix) \mathbf{H} involves – for the case of nonrelativistic

electronic structure – one-body and two-body interaction terms only. The mathematical description is that the energy depends only on the one-body and two-body RDMs. Thus we have discrete operators (matrices) \mathbf{H}_1 and \mathbf{H}_2 – the one-body and two-body parts of the Hamiltonian (matrix) \mathbf{H} – such that on the space of density matrices $\langle \mathbf{H}, \mathbf{\Gamma}^{\text{full}} \rangle = \langle \mathbf{H}_1, \mathbf{\Gamma}_1 \rangle + \langle \mathbf{H}_2, \mathbf{\Gamma}_2 \rangle$.

It is easily seen that $\langle \mathbf{\Gamma}_p, \mathbf{I} \rangle = N!/(N-p)!$ and also that the mapping $\mathbf{\Gamma}^{\text{full}} \rightarrow \mathbf{\Gamma}_p$ preserves the positive semidefiniteness property. Now a formulation of the discretized electronic structure problem (1) is obtained as an equivalent convex optimization problem

$$\begin{cases} \min & \langle \mathbf{H}_1, \mathbf{\Gamma}_1 \rangle + \langle \mathbf{H}_2, \mathbf{\Gamma}_2 \rangle \\ \text{subject to} & \langle \mathbf{\Gamma}_1, \mathbf{I} \rangle = N; \langle \mathbf{\Gamma}_2, \mathbf{I} \rangle = N(N-1), \text{ and} \\ & \text{“}N\text{-representability”}. \end{cases} \quad (3)$$

Here, “ N -representability” means: there exists a positive semidefinite matrix $\mathbf{\Gamma}^{\text{full}}$ such that (2) is valid for the variables $\mathbf{\Gamma}_1$ and $\mathbf{\Gamma}_2$ in (3). We also know that all of these N -representability conditions describe a convex set for the matrices $\mathbf{\Gamma}_1$ and $\mathbf{\Gamma}_2$.

The success of this approach might seem to rely now on being able to specify concrete necessary and sufficient conditions for the N -representability that do not require the reconstruction of the large matrix $\mathbf{\Gamma}^{\text{full}}$, but this is understood to be intractable as explained in the next section. Instead the conditions that are known are necessary but not sufficient, and so they serve to define an approximation – a lower-bound approximation – to the original exponentially large problem (1). The conditions that have turned out to be most effective so far are all of semidefinite kind, and therefore, we seek to solve an SDP relaxation of the discretized electronic structure problem (1).

2.2 Specific N -representability conditions

The linear space of $\mathbf{\Gamma}_1$ is the space of real symmetric $r \times r$ matrices, \mathbb{S}^r , where r is the discretization basis size. As defined in (2), $\mathbf{\Gamma}_2$ depends on two pairs of indices, $\mathbf{\Gamma}_2(i, j; i', j')$. Due to the antisymmetry, $\mathbf{\Gamma}_2(i, j; i', j') = -\mathbf{\Gamma}_2(j, i; i', j') = -\mathbf{\Gamma}_2(i, j; j', i') = \mathbf{\Gamma}_2(j, i; j', i')$ and so $\mathbf{\Gamma}_2 \in \mathbb{S}^{r(r-1)/2}$. Observe that the sizes of the variables in (3) now depend only on r and not anymore on N (number of electrons) as in (1).

It is also clear from (2) that $\mathbf{\Gamma}_1$ is itself a scaled partial trace of $\mathbf{\Gamma}_2$:

$$\mathbf{\Gamma}_1(i, i') = \frac{1}{N-1} \sum_{j=1}^r \mathbf{\Gamma}_2(i, j; i', j). \quad (4)$$

$\mathbf{\Gamma}_1$ could therefore be eliminated entirely from the problem. However, both the objective function and the N -representability conditions are more conveniently formulated if $\mathbf{\Gamma}_1$ is retained and if the trace condition (4) is used as a set of linear constraints on the pair $(\mathbf{\Gamma}_1, \mathbf{\Gamma}_2)$. We follow this approach.

The trace conditions on $\mathbf{\Gamma}_1$ and $\mathbf{\Gamma}_2$ were specified in (3). The remaining conditions are in the form of convex inequalities. Moreover, all conditions that we have used are of linear semidefinite form.

For the 1-RDM the remaining necessary and sufficient N -representability conditions [3] are:

$$\mathbf{I} \succeq \mathbf{\Gamma}_1 \succeq \mathbf{O}. \quad (5)$$

For the 2-RDM, a complete family of constructive necessary and sufficient conditions is not known yet. As the original problem (1) is exponentially large, this difficult should not deter us – the RDM method is to be viewed as an approximation method and one works with necessary conditions for N -representability that are known not to be sufficient, and therefore, we are considering an SDP relaxation of the original problem (1).

The basic well known convex inequalities for the 2-RDM are the P and the Q conditions (so named in [6], but they are also found in [3]) and the G condition [6]. In our previous work [20] we added to this a $T1$ and a $T2$ condition, which as we pointed out are implied by a much earlier paper of Erdahl [4]. All these conditions are of semidefinite form: $\mathbf{P} \succeq \mathbf{O}$, $\mathbf{Q} \succeq \mathbf{O}$, $\mathbf{G} \succeq \mathbf{O}$, $\mathbf{T1} \succeq \mathbf{O}$, and $\mathbf{T2} \succeq \mathbf{O}$, where the matrices \mathbf{P} , \mathbf{Q} , \mathbf{G} , $\mathbf{T1}$ and $\mathbf{T2}$ are defined by linear combinations of the entries of the basic matrices Γ_1 and Γ_2 . Specifically (all indices range over $1, \dots, r$ and δ is the Kronecker delta):

$$\mathbf{P} \equiv \Gamma_2, \quad (6)$$

$$\begin{aligned} Q(i, j; i', j') \equiv & \Gamma_2(i, j; i', j') - \delta(i, i')\Gamma_1(j, j') - \delta(j, j')\Gamma_1(i, i') + \delta(i, j')\Gamma_1(j, i') \\ & + \delta(j, i')\Gamma_1(i, j') + \delta(i, i')\delta(j, j') - \delta(i, j')\delta(j, i'). \end{aligned} \quad (7)$$

The matrices \mathbf{P} and \mathbf{Q} are of the same size as Γ_2 and have the same antisymmetry property, so they belong to $\mathbb{S}^{r(r-1)/2}$. Also,

$$G(i, j; i', j') = \Gamma_2(i, j'; j, i') + \delta(i, i')\Gamma_1(j', j). \quad (8)$$

In the matrix \mathbf{G} there is no antisymmetry in (i, j) or in (i', j') , so \mathbf{G} belongs to \mathbb{S}^{r^2} . Also,

$$\begin{aligned} T1(i, j, k; i', j', k') = & \mathcal{A}[i, j, k]\mathcal{A}[i', j', k'](\frac{1}{6}\delta(i, i')\delta(j, j')\delta(k, k') \\ & - \frac{1}{2}\delta(i, i')\delta(j, j')\Gamma_1(k, k') + \frac{1}{4}\delta(i, i')\Gamma_2(j, k; j', k')), \end{aligned} \quad (9)$$

where we are using the notation $\mathcal{A}[i, j, k]f(i, j, k)$ to mean an alternator with respect to i, j and k : $f(i, j, k)$ summed over all permutations of the arguments i, j and k , with each term multiplied by the sign of the permutation. $\mathbf{T1}$ is fully antisymmetric in both its index triples, so it belongs to $\mathbb{S}^{r(r-1)(r-2)/6}$. Finally,

$$\begin{aligned} T2(i, j, k; i', j', k') = & \mathcal{A}[j, k]\mathcal{A}[j', k'](\frac{1}{2}\delta(j, j')\delta(k, k')\Gamma_1(i, i') \\ & + \frac{1}{4}\delta(i, i')\Gamma_2(j', k'; j, k) - \delta(j, j')\Gamma_2(i, k'; i', k)). \end{aligned} \quad (10)$$

$T2(i, j, k; i', j', k')$ is antisymmetric in (j, k) and in (j', k') , so it belongs to $\mathbb{S}^{r^2(r-1)/2}$.

3 The SDP formulation of the RDM method

Let \mathbf{C}, \mathbf{A}_p ($p = 1, 2, \dots, m$) be given block-diagonal symmetric matrices with prescribed block sizes, and $\mathbf{c}, \mathbf{a}_p \in \mathbb{R}^s$ ($p = 1, 2, \dots, m$) be given s -dimensional real vectors. We denote by $\mathbf{Diag}(\mathbf{a})$ a diagonal matrix with the elements of \mathbf{a} on its diagonal.

The primal SDP is defined as

$$\begin{cases} \max & \langle \mathbf{C}, \mathbf{X} \rangle + \langle \mathbf{Diag}(\mathbf{c}), \mathbf{Diag}(\mathbf{x}) \rangle \\ \text{subject to} & \langle \mathbf{A}_p, \mathbf{X} \rangle + \langle \mathbf{Diag}(\mathbf{a}_p), \mathbf{Diag}(\mathbf{x}) \rangle = b_p, \quad (p = 1, 2, \dots, m) \\ & \mathbf{X} \succeq \mathbf{O}, \quad \mathbf{x} \in \mathbb{R}^s, \end{cases} \quad (11)$$

and its dual

$$\begin{cases} \min & \mathbf{b}^T \mathbf{y} \\ \text{subject to} & \mathbf{S} = \sum_{p=1}^m \mathbf{A}_p y_p - \mathbf{C} \succeq \mathbf{O}, \\ & \sum_{p=1}^m \mathbf{Diag}(\mathbf{a}_p) y_p = \mathbf{Diag}(\mathbf{c}), \\ & \mathbf{y} \in \mathbb{R}^m, \end{cases} \quad (12)$$

where (\mathbf{X}, \mathbf{x}) are the primal variables and (\mathbf{S}, \mathbf{y}) are the dual variables.

Primal-dual interior-point methods and their variants are the most established and efficient algorithms to solve general SDPs. Details on how these iterative methods work can be found for instance in [16].

In this section, we formulate the RDM method with the $(P, Q, G, T1, T2)$ N -representability conditions as an SDP. Observe that the 1-RDM variational variable Γ_1 and its corresponding Hamiltonian \mathbf{H}_1 is a two index matrix (see (3)), but the 2-RDM variational variable Γ_2 , the corresponding Hamiltonian \mathbf{H}_2 , as well as \mathbf{Q} and \mathbf{G} are four index matrices, and moreover, $\mathbf{T1}$ and $\mathbf{T2}$ are six index matrices. We map each pair i, j or triple i, j, k of indices to a composite index for these matrices, resulting in symmetric matrices of order $r(r-1)/2 \times r(r-1)/2$ for Γ_2 , \mathbf{H}_2 and \mathbf{Q} , a symmetric matrix of order $r(r-1)(r-2)/6 \times r(r-1)(r-2)/6$ for $\mathbf{T1}$, and a symmetric matrix of order $r^2(r-1)/2 \times r^2(r-1)/2$ for $\mathbf{T2}$. For example, the four-index element $\Gamma_2(i, j; i', j')$, with $1 \leq i < j \leq r$, $1 \leq i' < j' \leq r$, can be associated with the two-index element $\bar{\Gamma}_2(j-i+(2r-i)(i-1)/2, j'-i'+(2r-i')(i'-1)/2)$. We assume henceforth that all matrices have their indices mapped to two indices, and we keep the same notation for simplicity. Furthermore, due to the antisymmetry property of Γ_2 and of the N -representability conditions $Q, T1$ and $T2$, and also due to the spin symmetry [20, (22)-(27)], all these matrices reduce to block-diagonal matrices.

Now, let us define a linear transformation $\text{svec} : \mathbb{S}^n \rightarrow \mathbb{R}^{n(n+1)/2}$ as

$$\text{svec}(\mathbf{U}) = (U_{11}, \sqrt{2}U_{12}, U_{22}, \sqrt{2}U_{13}, \sqrt{2}U_{23}, U_{33}, \dots, \sqrt{2}U_{1n}, \dots, U_{nn})^T, \quad \mathbf{U} \in \mathbb{S}^n.$$

To formulate the RDM method with the $(P, Q, G, T1, T2)$ conditions in (3) as the dual SDP (12), define

$$\mathbf{y} = (\text{svec}(\Gamma_1)^T, \text{svec}(\Gamma_2)^T)^T \in \mathbb{R}^m \quad \text{and} \quad \mathbf{b} = (\text{svec}(\mathbf{H}_1)^T, \text{svec}(\mathbf{H}_2)^T)^T \in \mathbb{R}^m.$$

It is now relatively straightforward to express the N -representability conditions (5) through (10) as the dual slack matrix variable \mathbf{S} by defining it to have the following diagonal blocks: $\Gamma_1, \mathbf{I} - \Gamma_1, \Gamma_2, \mathbf{Q}, \mathbf{G}, \mathbf{T1}, \mathbf{T2}$ taking into account the spin symmetry [20, (22)-(27)] and making suitable definitions for the matrices \mathbf{C}, \mathbf{A}_p ($p = 1, 2, \dots, m$). The equalities in (3) and (4), and the ones involving the number of electrons with α spin and given total spin S [20, (19)-(21)] will define the vectors \mathbf{c}, \mathbf{a}_p ($p = 1, 2, \dots, m$).

The required number of floating point operations when solving these problems for instance using the code SDPA [19] are as follows. The computational flops per iteration when using SDPA can be estimated as $\mathcal{O}(m^2 f^2 + m^3 + mn_{\max}^2 + n_{\max}^3)$, where n_{\max} is the size of the largest block matrix and f is the maximum number of nonzero elements in each data matrix \mathbf{A}_p ($p = 1, 2, \dots, m$). In our case, $m = \mathcal{O}(r^4)$, $n_{\max} = \mathcal{O}(r^3)$ and $f = \mathcal{O}(r^2)$, and therefore, the computational flops per iteration is $\mathcal{O}(r^{12})$, while the total memory usage becomes $\mathcal{O}(m^2) = \mathcal{O}(r^8)$.

The formulation of the RDM method as a dual SDP, as considered here, has a clear advantage over the primal SDP formulation [13, 8, 11, 12, 9, 10] as detailed in [20]. When using the primal SDP formulation with the $(P, Q, G, T1, T2)$ conditions, we have $m = \mathcal{O}(r^6)$, $n_{\max} = \mathcal{O}(r^3)$ and $f = \mathcal{O}(1)$, and then, the computational flops per iterations becomes $\mathcal{O}(r^{18})$, while the total memory usage becomes $\mathcal{O}(m^2) = \mathcal{O}(r^{12})$.

4 Numerical results for the RDM method

We concluded from our previous study [5] that SeDuMi 1.05 [14] was the most suitable software to solve our SDPs. We also did some experiments using SDPT3 3.1 [17] but it could not provide us the necessary accuracy, *i.e.*, an absolute duality gap lesser than 10^{-5} . However, these two codes can only run in a single CPU and do not allow us to solve larger instances of SDPs in a practical time-frame.

The SDPARA [18] or the parallel version of the CSDP [2] could be the solution but these codes have a limitation of not accepting equality constraints $\sum_{p=1}^m \mathbf{Diag}(\mathbf{a}_p) y_p = \mathbf{Diag}(\mathbf{c})$ in the dual SDP (12). Therefore, as a pragmatic alternative, we reformulated the dual SDP (12) replacing the equality constraints by a pair of inequalities [20, 5]:

$$-\epsilon \leq \left[\sum_{p=1}^m \mathbf{a}_p y_p \right]_i - c_i, \quad \left[\sum_{p=1}^m \mathbf{a}_p y_p \right]_i - c_i \leq \epsilon \quad (i = 1, 2, \dots, s) \quad (13)$$

where $\mathbf{c}, \mathbf{a}_p \in \mathbb{R}^s$ ($p = 1, 2, \dots, m$) and ϵ is a suitable small number. This reformulation at least allowed us to solve very large instances of SDPs (with discretization basis r up to 26) using the SDPARA [5]. Though, this “relaxation” of the SDP (11-12) only provides a lower bound for the optimal value we really want to determine.

The current study tries to correct this minor detail, namely, we want to solve the SDPs (11-12) without employing the above relaxation. We use four different reformulations testing four different codes and their variations.

The four different formulations we used are (i) the original SDP (11-12) (Section 4.1); (ii) the formulation which treats the free variable \mathbf{x} in (11) as a difference of two non-negative variables (Section 4.2); (iii) the conversion proposed in [7] which eliminates the free variable \mathbf{x} from (11) (Section 4.3); (iv) the conversion which considers a greedy heuristic method to explore sparsity in the data [7] (Section 4.4).

The four codes we used are as follows: (i) CSDP 5.0 [1] using ATLAS instead of BLAS library. Parameter “axtol” and “atytol” were set to 10^{-7} ; (ii) SDPT3 3.1 [17]. Parameter “OPTIONS.gaptol” was set from 10^{-8} to 10^{-1} . (iii) SeDuMi [14] versions 1.05 and 1.1. Parameter “pars.eps” was set to 10^{-11} ; (iv) the default SDPA 6.20 [19] and its variation which we call SDPA 6.20+. This latter has a minor modification in the step-size control. Parameters “ ϵ^* ” was set to 10^{-11} and “ $\bar{\epsilon}$ ” from 10^{-10} to 10^{-5} .

We ran all these codes on an Opteron 850 (2.4GHz), 8GB of physical memory and 1MB of L2 cache size with SuSE Linux Enterprise Server 9.

Table 1 shows the actual sizes of the SDPs (11-12) for each discretization basis size r up to 16. We only listed the sizes of the largest block matrices among the 21 block matrices and one diagonal matrix. Here, 306x2 for instance means that there are two block matrices of sizes 306×306 each.

Table 1: Sizes of the SDPs (imposing the $(P,Q,G,T1,T2)$ conditions) as a function of the discretization basis size r .

Basis size r	# constraints m	Sizes of the largest block matrices
10	465	175x2,50x5,25x4,10x6
12	948	306x2,90x4,72x1,36x4
14	1743	490x2,147x4,98x1,49x4
16	2964	736x2,224x4,128x1,64x4

Another characteristic of this class of problems is that the primal SDP (11) has a strict feasible solution, but its dual (12) is feasible and does not have a strict feasible solution.

The error measures for the quality of the approximate optimal solution $(\hat{\mathbf{X}}, \hat{\mathbf{x}}, \hat{\mathbf{S}}, \hat{\mathbf{y}})$ we obtained are:

$$(I) \text{ duality gap} \equiv \mathbf{b}^T \hat{\mathbf{y}} - \langle \mathbf{C}, \hat{\mathbf{X}} \rangle - \langle \mathbf{Diag}(\mathbf{c}), \mathbf{Diag}(\hat{\mathbf{x}}) \rangle,$$

$$(II) \text{ primal feasibility error} \equiv \max_{p=1,2,\dots,m} |\langle \mathbf{A}_p, \hat{\mathbf{X}} \rangle + \langle \mathbf{Diag}(\mathbf{a}_p), \mathbf{Diag}(\hat{\mathbf{x}}) \rangle - b_p|,$$

$$(III) \text{ dual feasibility error} \equiv \max \left\{ \max_{i,j=1,2,\dots,n} \left| \left[\hat{\mathbf{S}} - \sum_{p=1}^m \mathbf{A}_p \hat{y}_p + \mathbf{C} \right]_{ij} \right|, \max_{i=1,2,\dots,s} \left| \left[\sum_{p=1}^m \mathbf{a}_p \hat{y}_p - \mathbf{c} \right]_i \right| \right\},$$

$$(IV) \text{ minimum eigenvalue of } \hat{\mathbf{X}},$$

$$(V) \text{ minimum eigenvalue of } \hat{\mathbf{S}},$$

for the SDP (11-12) (Section 4.1), and

$$(I') \text{ duality gap} \equiv \mathbf{b}^T \hat{\mathbf{y}} - \langle \mathbf{C}, \hat{\mathbf{X}} \rangle,$$

$$(II') \text{ primal feasibility error} \equiv \max_{p=1,2,\dots,m} |\langle \mathbf{A}_p, \hat{\mathbf{X}} \rangle - b_p|,$$

$$(III') \text{ dual feasibility error} \equiv \max_{i,j=1,2,\dots,n} \left| \left[\hat{\mathbf{S}} - \sum_{p=1}^m \mathbf{A}_p \hat{y}_p + \mathbf{C} \right]_{ij} \right|,$$

with appropriate dimensions for the other formulations (Sections 4.2, 4.3, and 4.4).

All the values are given by $-\log_{10}(|\cdot|)$ at the following tables except the time. “ r ” is the discretization basis size, “basis” is the spin orbital (one-electron) basis, “state” is the equilibrium state of the system, “ $N(N_\alpha)$ ” is the electron (α spin electron) number, and “ $2S + 1$ ” is the spin multiplicity. See [20, 5] to compare the quality of these results with the mainstream electronic structure methods. The actual description of the SDP problems we solved can be found in [5].

4.1 The original formulation

Table 2 gives the error measures of the approximate optimal solution and the time to solve the corresponding SDP problems (11-12). “tpi” means time per iteration. Only SeDuMi 1.05 [14] and 1.1 and SDPT3 1.1 [17] can solve these problems by default. As we mentioned, we require high accurate optimal values. In fact, we typically need a precision higher than 10^{-5} for the absolute duality gap, *i.e.*, a number greater than 5.0 in the corresponding column. SeDuMi 1.05 and 1.1 satisfy this condition, however SDPT3 3.1 was not able to satisfy it as we already knew.

Table 2: Error measures of the approximate optimal solution in $-\log_{10}(|\cdot|)$ and the time in seconds to obtain it for the original formulation (11-12).

r	System	Basis	State	$N(N_\alpha)$	$2S+1$	code	duality gap	primal f.	dual f.	$\bar{\mathbf{X}}_{\min}$	$\bar{\mathbf{S}}_{\min}$	time (s)	tpi (s)
10	Li	STO-6G	2S	3(2)	2	SDPT3 3.1	3.9	3.4	10.2	6.7	10.6	12.0	0.5
						SeDuMi 1.05	9.8	11.1	$+\infty$	13.1	12.0	23.7	1.1
						SeDuMi 1.1	10.9	10.9	$+\infty$	14.0	15.0	33.6	1.3
10	Be	STO-6G	1S	4(2)	1	SDPT3 3.1	3.4	3.6	11.1	7.5	11.3	12.0	0.5
						SeDuMi 1.05	9.4	10.6	$+\infty$	12.6	11.5	30.9	1.1
						SeDuMi 1.1	11.8	11.4	$+\infty$	13.0	10.8	32.5	1.1
12	H ₃	double- ζ	${}^2A'_1$	3(2)	2	SDPT3 3.1	3.4	3.5	11.3	7.0	11.6	247.0	9.1
						SeDuMi 1.05	7.6	9.0	$+\infty$	10.7	9.6	296.8	8.0
						SeDuMi 1.1	7.8	9.0	$+\infty$	10.9	9.6	258.0	8.6
12	BeH ⁺	STO-6G	${}^1\Sigma^+$	4(2)	1	SDPT3 3.1	2.9	2.4	10.6	6.4	10.9	102.2	4.3
						SeDuMi 1.05	9.3	10.6	$+\infty$	12.7	11.6	237.2	6.8
						SeDuMi 1.1	8.6	9.2	$+\infty$	12.0	13.6	256.3	8.5
14	NH ₂ ⁺	STO-6G	1A_1	10(5)	1	SDPT3 3.1	-0.6	2.2	5.7	3.6	6.3	745.7	49.7
						SeDuMi 1.05	8.5	10.0	$+\infty$	12.3	11.0	1681.6	40.0
						SeDuMi 1.1	10.1	10.0	$+\infty$	12.5	10.9	1337.5	43.1
14	FH ₂ ⁺	STO-6G	1A_1	10(5)	1	SDPT3 3.1	1.1	3.2	8.1	5.8	8.5	1214.5	50.6
						SeDuMi 1.05	7.9	9.4	$+\infty$	11.7	10.6	1711.6	41.7
						SeDuMi 1.1	7.7	8.5	$+\infty$	11.6	12.8	1915.1	66.0
16	CH ₃ ⁺	STO-6G	${}^1E'$	8(4)	1	SDPT3 3.1	-0.7	1.6	6.0	3.2	6.6	3520.0	220.0
						SeDuMi 1.05	8.4	10.1	$+\infty$	12.3	11.2	8542.4	189.8
						SeDuMi 1.1	8.0	10.2	$+\infty$	12.7	10.8	7736.7	221.0
16	CH ₃	STO-6G	${}^2A'_2$	9(5)	2	SDPT3 3.1	2.3	2.3	11.3	6.5	11.0	6216.7	230.2
						SeDuMi 1.05	5.9	7.5	$+\infty$	9.2	8.5	11098.3	201.8
						SeDuMi 1.1	8.1	7.7	$+\infty$	9.2	8.7	14573.9	280.3
16	NH ₃ ⁺	STO-6G	${}^2A'_2$	9(5)	2	SDPT3 3.1	1.6	1.9	11.2	6.4	11.0	6101.0	226.0
						SeDuMi 1.05	5.7	7.4	$+\infty$	9.1	8.5	10102.0	194.3
						SeDuMi 1.1	5.7	8.3	$+\infty$	10.0	9.2	17523.3	324.5

We also cannot decide for the best version of the SeDuMi from the computational time they took.

4.2 Difference of two non-negative variables

In this formulation, the free variable $\mathbf{x} \in \mathbb{R}^s$ in (11) is replaced by $\mathbf{x}^+ - \mathbf{x}^-$ such that $\mathbf{x}^+, \mathbf{x}^- \geq \mathbf{0}$, and the corresponding dual problem becomes:

$$\left\{ \begin{array}{l} \min \quad \mathbf{b}^T \mathbf{y} \\ \text{subject to} \quad \mathbf{S} = \sum_{p=1}^m \mathbf{A}_p y_p - \mathbf{C} \succeq \mathbf{O}, \\ \mathbf{s}^+ = \sum_{p=1}^m \mathbf{Diag}(\mathbf{a}_p) y_p - \mathbf{Diag}(\mathbf{c}) \geq \mathbf{0}, \\ \mathbf{s}^- = -\sum_{p=1}^m \mathbf{Diag}(\mathbf{a}_p) y_p + \mathbf{Diag}(\mathbf{c}) \geq \mathbf{0}, \\ \mathbf{y} \in \mathbb{R}^m. \end{array} \right.$$

Notice that this formulation can be also obtained replacing the ϵ by zero in (13).

In principle, one might expect that codes based on interior-point methods will face problems since the vectors \mathbf{s}^+ , \mathbf{s}^- need to be close to null near the optimal solution, and because the dual SDP does not have a strictly feasible solution. Surprisingly, all the tested codes converged except SDPT3 3.1 as we can see from Table 3.

SDPT3 3.1 and the SDPA 6.20 could not attain the required accuracy for the absolute duality gap. SeDuMi 1.05 and 1.1 are the winners in terms of accuracy and time. Then SDPA 6.20+ and CSDP 5.0 follow in this order.

4.3 Conversion

Here we use the formulation proposed by Kobayashi-Nakata-Kojima [7] where the equality constraints $\sum_{p=1}^m \mathbf{Diag}(\mathbf{a}_p)y_p = \mathbf{Diag}(\mathbf{c})$ are eliminated from the dual SDP (12). This formulation is favorable for the stability of the numerical computation, but it can worsen the time to solve them for sparse data problems as our case. In the Table 4, we omitted the primal and dual feasibility errors since they were difficult to compute, “time (s)” means the length to solve the converted SDP problem, and “conv. time (s)” the length to convert into and re-convert from the formulation proposed in [7].

In general, we can observe the same tendency as the previous section in terms of the SDP codes except that CSDP 5.0 is faster than the SDPA 6.20+ in some cases. The SDPA 6.20+ could not get the required accuracy for CH_3 and NH_3^+ only. We also notice that SDPT3 3.1 was not able to attain the desired accuracy since it forcibly stops at a certain iteration when the relative duality gap gets lesser than the primal-dual feasibility error (one of the stopping criterion) or it encounters numerical problems. Unfortunately, we could not resolve this problem by just changing the parameters.

Usually, it takes much more time to solve the converted problem than the one which formulates the free variables as a difference of two non-negative vectors presented in the previous section.

4.4 Conversion with a greedy heuristic method

Finally, this formulation also proposed by Kobayashi-Nakata-Kojima [7] employs a greedy heuristic method to enhance the data sparsity of the converted problem. In general, the computational time is better for this formulation than of Section 4.3.

We obtain the same conclusions as the previous sections. The computational time has improve if compared with the formulation which does not use the greedy heuristic method, but is still slower than the one in Section 4.2.

5 Conclusion and further directions

The RDM method, which provides a lower bound for the ground state energy of a many-electron system subject to a given external potential, can be formulated as an SDP problem through the known $(P, Q, G, T1, T2)$ N -representability conditions. The new formulation presented here as a dual SDP (12) seems the most suitable one for the state-of-art software to solve general SDPs. The numerical experiments carried out since 2001, demonstrate for the first time the quality, the strength, and the actual effectiveness of the N -representability conditions known for more than forty years in electronic structure

Table 3: Error measures of the approximate optimal solution in $-\log_{10}(|\cdot|)$ and the time in seconds to obtain it for the formulation using the difference of two non-negative vectors for the free variable \mathbf{x} .

r	System	Basis	State	$N(N_\alpha)$	$2S+1$	code	duality gap	primal f.	dual f.	$\bar{\mathbf{x}}_{\min}$	$\bar{\mathbf{S}}_{\min}$	time (s)	tpi (s)
10	Li	STO-6G	2S	3(2)	2	CSDP 5.0	7.1	11.1	8.8	10.5	10.2	82.2	3.4
						SDPT3 3.1	2.3	1.6	8.3	4.8	9.0	7.7	0.6
						SeDuMi 1.05	9.8	11.1	$+\infty$	13.1	11.9	23.1	1.1
						SeDuMi 1.1	10.2	10.3	$+\infty$	$+\infty$	14.3	35.0	1.4
						SDPA 6.20	5.7	9.5	6.7	11.2	13.9	60.8	1.6
						SDPA 6.20+	7.7	10.1	8.7	13.3	14.4	59.6	1.6
10	Be	STO-6G	1S	4(2)	1	CSDP 5.0	6.6	9.6	9.8	10.0	10.7	92.5	3.4
						SDPT3 3.1	1.1	1.0	8.5	5.0	9.0	7.7	0.6
						SeDuMi 1.05	9.4	10.6	$+\infty$	12.6	11.3	31.8	1.1
						SeDuMi 1.1	11.9	11.4	$+\infty$	$+\infty$	10.8	32.0	1.1
						SDPA 6.20	4.5	10.1	5.8	13.4	13.4	59.9	1.6
						SDPA 6.20+	7.9	10.3	9.1	15.7	13.2	58.9	1.6
12	H_3	double- ζ	$^2A'_1$	3(2)	2	CSDP 5.0	8.2	7.3	10.6	10.8	13.1	1154.6	22.2
						SDPT3 3.1	0.8	0.5	8.9	4.7	9.6	178.1	9.9
						SeDuMi 1.05	8.0	9.2	$+\infty$	10.9	9.5	319.7	8.4
						SeDuMi 1.1	9.9	9.5	$+\infty$	$+\infty$	9.9	362.9	9.8
						SDPA 6.20	4.6	10.7	6.1	11.7	11.7	355.0	12.2
						SDPA 6.20+	6.7	9.9	8.3	10.4	11.2	378.9	12.6
12	BeH^+	STO-6G	$^1\Sigma^+$	4(2)	1	CSDP 5.0	6.6	9.4	9.8	10.3	11.0	735.0	22.3
						SDPT3 3.1	-0.2	2.2	6.8	3.2	7.3	55.9	5.1
						SeDuMi 1.05	9.2	10.6	$+\infty$	12.7	11.3	260.6	7.4
						SeDuMi 1.1	8.6	9.2	$+\infty$	$+\infty$	13.1	263.1	8.8
						SDPA 6.20	4.7	9.8	6.1	12.7	13.4	411.7	11.8
						SDPA 6.20+	6.7	9.7	8.2	12.7	13.4	469.3	11.7
14	NH_2^-	STO-6G	1A_1	10(5)	1	CSDP 5.0	6.1	8.4	9.7	10.4	11.8	3861.8	110.3
						SDPT3 3.1	0.2	-0.1	8.3	4.0	9.0	676.0	52.0
						SeDuMi 1.05	8.5	10.0	$+\infty$	12.3	10.7	1742.5	41.5
						SeDuMi 1.1	10.1	10.0	$+\infty$	$+\infty$	10.9	1507.9	48.6
						SDPA 6.20	3.4	9.7	5.1	13.1	13.7	2095.3	63.5
						SDPA 6.20+	6.2	8.5	8.1	14.3	14.1	2151.9	63.3
14	FH_2^+	STO-6G	1A_1	10(5)	1	CSDP 5.0	5.9	7.6	9.9	10.2	11.6	3796.8	111.7
						SDPT3 3.1	-0.5	-0.2	9.2	3.7	9.8	903.4	53.1
						SeDuMi 1.05	8.3	9.9	$+\infty$	12.1	10.8	1944.1	45.2
						SeDuMi 1.1	7.7	8.4	$+\infty$	$+\infty$	12.4	1860.6	64.2
						SDPA 6.20	3.8	9.7	5.7	13.8	12.7	2090.7	65.3
						SDPA 6.20+	6.8	7.9	8.6	13.4	14.4	2620.0	72.8
16	CH_3^+	STO-6G	$^1E'$	8(4)	1	CSDP 5.0	6.2	7.2	9.9	10.5	12.5	19096.7	465.8
						SDPT3 3.1	-1.0	-1.0	8.2	4.0	8.8	4732.6	236.6
						SeDuMi 1.05	8.4	10.1	$+\infty$	12.3	10.9	9058.1	201.3
						SeDuMi 1.1	8.0	10.2	$+\infty$	$+\infty$	10.7	7257.4	207.4
						SDPA 6.20	4.0	8.8	6.0	12.2	13.4	10789.0	337.2
						SDPA 6.20+	6.0	7.6	8.4	13.5	13.2	10990.9	333.1
16	CH_3	STO-6G	$^2A''_2$	9(5)	2	CSDP 5.0	5.1	5.6	8.8	9.8	12.4	27945.8	499.0
						SDPT3 3.1	-0.3	0.2	8.1	5.2	8.7	5000.0	238.1
						SeDuMi 1.05	5.9	7.5	$+\infty$	9.2	8.2	10439.9	189.8
						SeDuMi 1.1	5.9	7.8	$+\infty$	$+\infty$	8.8	19081.0	360.0
						SDPA 6.20	3.8	7.9	5.9	11.2	13.3	10785.2	337.0
						SDPA 6.20+	5.2	5.6	8.2	9.6	13.3	10773.0	347.5
16	NH_3^+	STO-6G	$^2A''_2$	9(5)	2	CSDP 5.0	5.5	5.1	9.0	9.6	12.6	26662.3	493.7
						SDPT3 3.1	-0.7	-0.0	8.1	3.6	8.7	5014.3	227.9
						SeDuMi 1.05	5.7	7.4	$+\infty$	9.1	8.2	9641.0	185.4
						SeDuMi 1.1	5.3	7.8	$+\infty$	$+\infty$	9.1	12771.4	271.7
						SDPA 6.20	3.8	7.7	6.1	11.9	13.9	11300.9	342.5
						SDPA 6.20+	5.4	5.9	8.1	9.5	13.7	10609.8	342.3

calculation. In fact, they demonstrate that the RDM method with the $(P, Q, G, T1, T2)$ conditions can give better ground state energies than the current electronic structure methods [20, 5], although it is not competitive in terms of time at least at present. It also

Table 4: Error measures of the approximate optimal solution in $-\log_{10}(|\cdot|)$ and the time in seconds to obtain it for the formulation which eliminates the equality constraint in the dual SDP (12) proposed by Kobayashi-Nakata-Kojima [7].

r	System	Basis	State	$N(N_\alpha)$	$2S+1$	code	duality gap	\hat{X}_{\min}	\hat{S}_{\min}	time (s)	tpi (s)	conv. time (s)
10	Li	STO-6G	2S	3(2)	2	CSDP 5.0	7.8	11.1	13.0	153.9	5.5	0.9
						SDPT3 3.1	3.8	8.0	13.8	17.7	1.0	-
						SeDuMi 1.05	11.0	14.2	13.0	29.1	1.3	-
						SeDuMi 1.1	10.2	13.8	13.1	29.3	1.3	-
						SDPA 6.20	6.6	12.0	15.1	109.6	3.0	-
						SDPA 6.20+	9.2	15.7	13.7	105.1	2.8	-
10	Be	STO-6G	1S	4(2)	1	CSDP 5.0	7.3	10.7	11.0	162.3	5.6	0.9
						SDPT3 3.1	2.5	7.0	11.1	14.2	1.1	-
						SeDuMi 1.05	10.1	13.8	12.0	34.3	1.4	-
						SeDuMi 1.1	9.9	13.1	11.0	34.3	1.4	-
						SDPA 6.20	5.5	13.9	16.2	95.0	2.9	-
						SDPA 6.20+	7.3	12.0	14.5	100.2	3.0	-
12	H_3	double- ζ	$^2A'_1$	3(2)	2	CSDP 5.0	6.9	10.9	12.9	1986.6	38.2	3.3
						SDPT3 3.1	3.4	6.9	12.3	309.0	19.3	-
						SeDuMi 1.05	8.5	10.4	10.6	616.6	12.3	-
						SeDuMi 1.1	9.6	10.3	9.6	354.4	10.7	-
						SDPA 6.20	5.3	12.2	12.8	1014.1	37.6	-
						SDPA 6.20+	6.4	12.2	12.7	795.6	28.4	-
12	BeH^+	STO-6G	$^1\Sigma^+$	4(2)	1	CSDP 5.0	7.0	10.6	12.7	1216.5	38.0	3.3
						SDPT3 3.1	1.9	6.1	11.4	136.3	9.1	-
						SeDuMi 1.05	9.2	12.7	11.3	309.6	9.1	-
						SeDuMi 1.1	11.9	12.6	10.7	322.9	8.5	-
						SDPA 6.20	4.9	13.5	14.4	1001.7	29.5	-
						SDPA 6.20+	8.8	13.4	16.0	1124.7	30.4	-
14	NH_2^-	STO-6G	1A_1	10(5)	1	CSDP 5.0	6.4	10.6	12.7	8784.1	219.6	10.2
						SDPT3 3.1	1.1	5.7	10.7	1512.4	116.3	-
						SeDuMi 1.05	8.6	12.0	10.3	2530.0	49.6	-
						SeDuMi 1.1	10.6	11.6	9.9	2338.2	44.1	-
						SDPA 6.20	3.9	13.8	13.1	7929.7	264.3	-
						SDPA 6.20+	6.3	12.2	14.0	9236.7	279.9	-
14	FH_2^+	STO-6G	1A_1	10(5)	1	CSDP 5.0	5.9	10.2	12.3	8402.0	283.4	10.4
						SDPT3 3.1	1.5	5.6	10.3	1523.9	117.2	-
						SeDuMi 1.05	8.4	11.8	10.2	2444.3	49.9	-
						SeDuMi 1.1	10.6	11.6	9.9	2625.7	46.1	-
						SDPA 6.20	4.4	14.0	12.7	6766.8	225.6	-
						SDPA 6.20+	6.1	12.4	12.9	8047.0	243.8	-
16	CH_3^+	STO-6G	$^1E'$	8(4)	1	CSDP 5.0	6.8	13.0	12.6	89592.7	1210.7	27.8
						SDPT3 3.1	0.7	4.7	10.4	9176.8	764.7	-
						SeDuMi 1.05	9.6	13.0	11.5	13736.9	236.8	-
						SeDuMi 1.1	10.9	11.7	10.2	11107.7	188.3	-
						SDPA 6.20	4.2	12.6	13.1	97168.7	3470.3	-
						SDPA 6.20+	6.1	12.9	15.1	93548.0	2672.8	-
16	CH_3	STO-6G	$^2A''_2$	9(5)	2	CSDP 5.0	5.5	12.2	12.3	106308.0	1312.4	28.2
						SDPT3 3.1	-1.0	4.0	10.7	12648.5	744.0	-
						SeDuMi 1.05	8.2	10.1	10.0	19458.6	237.3	-
						SeDuMi 1.1	8.8	9.8	9.4	15970.1	204.7	-
						SDPA 6.20	4.1	12.0	14.0	94483.3	3047.8	-
						SDPA 6.20+	4.8	11.8	13.6	91473.3	3154.3	-
16	NH_3^+	STO-6G	$^2A''_2$	9(5)	2	CSDP 5.0	5.4	10.9	12.5	120923.4	1511.5	27.9
						SDPT3 3.1	-0.8	4.7	10.4	11749.6	783.3	-
						SeDuMi 1.05	8.1	10.1	10.1	21323.9	242.3	-
						SeDuMi 1.1	8.7	9.7	9.4	16270.9	206.0	-
						SDPA 6.20	4.1	14.2	12.2	87098.0	2809.7	-
						SDPA 6.20+	4.8	12.0	13.2	104002.2	3356.0	-

has the advantage of robust convergence which is not the case for the traditional electronic structure methods.

The numerical experiments reported here suggests that the formulation (11-12) or

Table 5: Error measures of the approximate optimal solution in $-\log_{10}(|\cdot|)$ and the time in seconds to obtain it for the formulation which eliminates the equality constraint in the dual SDP (12) with the greedy heuristic method proposed by Kobayashi-Nakata-Kojima [7].

r	System	Basis	State $N(N_\alpha)$	$2S+1$	code	duality gap	\bar{X}_{\min}	\bar{S}_{\min}	time (s)	tpi (s)	conv. time (s)	
10	Li	STO-6G	2S	3(2)	2	CSDP 5.0	7.1	11.1	10.8	114.9	5.2	0.6
						SDPT3 3.1	4.0	7.6	13.1	16.8	1.0	-
						SeDuMi 1.05	9.6	12.9	11.9	26.7	1.3	-
						SDPA 6.20	9.3	12.8	12.6	28.5	1.3	-
						SDPA 6.20+	5.6	14.1	15.0	121.2	3.3	-
						SDPA 6.20+	8.9	13.8	14.4	107.4	3.1	-
10	Be	STO-6G	1S	4(2)	1	CSDP 5.0	6.8	10.2	12.0	147.0	5.2	0.6
						SDPT3 3.1	2.6	6.6	10.8	14.5	1.1	-
						SeDuMi 1.05	9.2	12.6	11.5	33.9	1.3	-
						SeDuMi 1.1	9.3	12.8	11.0	33.1	1.3	-
						SDPA 6.20	4.5	11.4	15.2	99.3	2.9	-
						SDPA 6.20+	6.5	13.0	15.6	98.5	3.0	-
12	H_3	double- ζ	${}^2A'_1$	3(2)	2	CSDP 5.0	6.8	10.9	13.3	2063.3	36.8	1.7
						SDPT3 3.1	2.0	5.7	10.6	229.4	17.6	-
						SeDuMi 1.05	8.0	10.3	9.9	537.2	11.2	-
						SeDuMi 1.1	9.5	10.3	9.7	496.2	12.1	-
						SDPA 6.20	4.7	12.0	12.0	936.3	36.0	-
						SDPA 6.20+	7.0	10.7	11.4	1014.0	37.6	-
12	BeH^+	STO-6G	${}^1\Sigma^+$	4(2)	1	CSDP 5.0	8.0	11.3	12.7	1643.4	36.5	1.7
						SDPT3 3.1	2.0	5.7	10.6	229.4	17.6	-
						SeDuMi 1.05	10.0	13.6	12.3	311.9	8.9	-
						SeDuMi 1.1	9.6	13.5	13.7	289.6	9.7	-
						SDPA 6.20	4.9	14.2	13.3	1269.2	38.5	-
						SDPA 6.20+	6.7	14.9	14.4	1254.4	34.8	-
14	NH_2^+	STO-6G	1A_1	10(5)	1	CSDP 5.0	6.5	10.5	12.3	9040.2	200.9	4.7
						SDPT3 3.1	0.9	6.0	10.6	1172.1	90.2	-
						SeDuMi 1.05	8.0	11.7	10.1	2186.7	49.7	-
						SeDuMi 1.1	10.7	11.6	9.7	2187.4	45.6	-
						SDPA 6.20	3.8	15.0	13.7	3826.8	127.6	-
						SDPA 6.20+	7.0	11.5	13.6	4841.0	146.7	-
14	FH_2^+	STO-6G	1A_1	10(5)	1	CSDP 5.0	6.1	10.3	11.8	8197.7	199.9	4.8
						SDPT3 3.1	2.5	5.6	10.2	1355.7	104.3	-
						SeDuMi 1.05	7.7	11.5	10.0	2183.8	50.8	-
						SeDuMi 1.1	7.8	12.1	11.8	1416.3	48.8	-
						SDPA 6.20	3.8	15.0	13.7	3826.8	127.6	-
						SDPA 6.20+	6.2	12.8	14.8	4259.7	118.3	-
16	CH_3^+	STO-6G	${}^1E'$	8(4)	1	CSDP 5.0	6.8	10.7	11.9	44729.2	912.8	9.6
						SDPT3 3.1	0.3	5.5	11.1	6188.3	442.0	-
						SeDuMi 1.05	8.6	12.4	11.0	8586.3	178.9	-
						SeDuMi 1.1	10.7	11.7	10.1	7519.5	203.2	-
						SDPA 6.20	4.2	12.5	13.0	32163.5	1148.7	-
						SDPA 6.20+	6.2	11.2	13.8	41272.8	1289.8	-
16	CH_3	STO-6G	${}^2A''_2$	9(5)	2	CSDP 5.0	5.2	11.3	12.3	94703.7	1018.3	9.7
						SDPT3 3.1	-0.3	4.1	10.5	9329.5	548.8	-
						SeDuMi 1.05	7.6	10.0	10.0	13011.3	200.2	-
						SeDuMi 1.1	6.2	9.4	8.5	13835.6	261.0	-
						SDPA 6.20	4.8	11.9	13.3	31768.3	1058.9	-
						SDPA 6.20+	4.9	11.2	12.8	38351.3	1278.4	-
16	NH_3^+	STO-6G	${}^2A''_2$	9(5)	2	CSDP 5.0	5.0	10.5	12.4	86197.5	1002.3	9.6
						SDPT3 3.1	-0.6	4.0	10.8	12579.9	571.8	-
						SeDuMi 1.05	7.5	10.0	10.1	14274.8	213.1	-
						SeDuMi 1.1	9.1	10.0	9.9	15342.9	251.5	-
						SDPA 6.20	3.6	13.2	13.0	38082.9	1269.4	-
						SDPA 6.20+	4.9	12.9	14.2	39586.7	1237.1	-

reformulating the same problem by replacing the free variable \mathbf{x} in the primal SDP (11) by a difference of two non-negative vectors are the best formulation. SeDuMi 1.05 and

1.1 were the winners in terms of accuracy and time. Then it is followed by SDPA 6.20+ and CSDP 5.0. It also seems that SDPT3 3.1 faces some internal code limitation which prevents to provide high accurate solutions for this class of problems.

We are satisfied with these results. Now, it is possible to incorporate the same changes on the SDPARA [18] as we did in SDPA 6.20+, and we will be able to solve larger RDM problems with the required accuracy without further relaxations.

Acknowledgement

This work would not have been possible without the support of the National Science Foundation (NSF) via Grant No. ITR-DMS 0113852, which provided essential funding for M.F. and B.J.B, summer support for Z.Z., and short-term visiting support to New York University for M.N. and M.Y. The authors M.F. and M.N. were also supported by fellowships from the Japan Society for the Promotion of Science and Grant-in-Aids for Scientific Research from the Japanese Ministry of Education, Culture, Sports, Science and Technology, B.J.B by Department of Energy (DOE) Grant No. DE-FG02-86ER53223, M.L.O. by NSF Grant No. DMS-0412049, J.K.P. by DOE Grant No. DE-FG02-02ER15292, and Z.Z. by a teaching fellowship at the Department of Physics, New York University.

References

- [1] Borchers, B.: CSDP 5.0 User's guide. September 2005. <http://infohost.nmt.edu/~borchers/csdp.html>
- [2] Borchers, B., Young, J.: Implementation of a primal-dual method for SDP on a parallel architecture. Technical Report, September 2005.
- [3] Coleman, A.J.: Structure of fermion density matrices. *Rev. Mod. Phys.* **35**, 668–687 (1963)
- [4] Erdahl, R.M.: Representability. *Int. J. Quantum Chem.* **13**, 697–718 (1978)
- [5] Fukuda, M., Braams, B.J., Nakata, M., Overton, M.L., Percus, J.K., Yamashita, M., Zhao, Z.: Large-scale semidefinite programs in electronic structure calculation. Research Report B-413, Department of Mathematical and Computing Sciences, Tokyo Institute of Technology, February 2005, revised August 2005.
- [6] Garrod, C., Percus, J.K.: Reduction of the N -particle variational problem. *J. Math. Phys.* **5**, 1756–1776 (1964)
- [7] Kobayashi, K., Nakata, K., Kojima, M.: A conversion of an SDP having free variables into the standard form SDP. Research Report B-416, Department of Mathematical and Computing Sciences, Tokyo Institute of Technology, June 2005, revised September 2005.
- [8] Mazziotti, D.A.: Variational minimization of atomic and molecular ground-state energies via the two-particle reduced density matrix. *Phys. Rev.* **A65**, 062511 (2002)

- [9] Mazziotti, D.A.: Realization of quantum chemistry without wave functions through first-order semidefinite programming. *Phys. Rev. Lett.* **93**, 213001 (2004)
- [10] Mazziotti, D.A.: First-order semidefinite programming for the direct determination of two-electron reduced density matrices with application to many-electron atoms and molecules. *J. Chem. Phys.* **121**, 10957–10966 (2004)
- [11] Nakata, M., Ehara, M., Nakatsuji, H.: Density matrix variational theory: Application to the potential energy surfaces and strongly correlated systems. *J. Chem. Phys.* **116**, 5432–5439 (2002)
- [12] Nakata, M., Ehara, M., Nakatsuji, H.: Density matrix variational theory: Strength of Weinholt-Wilson inequalities. In: *Fundamental World of Quantum Chemistry*, Löwdin, P.-O., Kryachko, E.S., (eds.), Kluwer Academic, Boston, 2003, pp. 543–557
- [13] Nakata, M., Nakatsuji, H., Ehara, M., Fukuda, M., Nakata, K., Fujisawa, K.: Variational calculations of fermion second-order reduced density matrices by semidefinite programming algorithm. *J. Chem. Phys.* **114**, 8282–8292 (2001)
- [14] Sturm, J.F.: Using SeDuMi 1.02, a MATLAB toolbox for optimization over symmetric cones. *Optim. Methods Softw.* **11–12**, 625–653 (1999). <http://sedumi.mcmaster.ca/>
- [15] Szabo, A., Ostlund, N.S.: *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*. Dover Publications, Inc., Mineola, New York, 1996
- [16] Todd, M.J.: Semidefinite optimization. *Acta Numer.* **10**, 515–560 (2001)
- [17] Toh, K.-C., Tütüncü, R.H., Todd, M.J.: On the implementation of SDPT3 (version 3.1) – a Matlab software package for semidefinite-quadratic-linear programming. *IEEE Conference on Computer-Aided Control System Design*, 2004
- [18] Yamashita, M., Fujisawa, K., Kojima, M.: SDPARA : SemiDefiniteProgramming Algorithm paRAllel version. *Parallel Comput.* **29**, 1053–1067 (2003). <http://grid.r.dendai.ac.jp/sdpa/>
- [19] Yamashita, M., Fujisawa, K., Kojima, M.: Implementation and evaluation of SDPA 6.0 (SemiDefinite Programming Algorithm 6.0). *Optimization Methods and Software* **18**, 491–505 (2003). <http://grid.r.dendai.ac.jp/sdpa/>
- [20] Zhao, Z., Braams, B.J., Fukuda, M., Overton, M.L., Percus, J.K.: The reduced density matrix method for electronic structure calculations and the role of three-index representability conditions. *J. Chem. Phys.* **120**, 2095–2104 (2004)