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FULL LENGTH PAPER

# Large-scale semidefinite programs in electronic structure calculation

**Mituhiro Fukuda · Bastiaan J. Braams · Maho Nakata · Michael L. Overton · Jerome K. Percus · Makoto Yamashita · Zhengji Zhao**

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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 formulation of these SDPs, which can be arbitrarily large.

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In memory of Jos Sturm who made many contributions to the theory and practice of semidefinite programming, including the widely used SeDuMi software package, and whose tragic early death is a great loss to our community.
The work of Mituhiro Fukuda was primarily conducted at the Courant Institute of Mathematical Sciences, New York University.

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M. Fukuda (✉)
Department of Mathematical and Computing Sciences, Tokyo Institute of Technology,
2-12-1-W8-29 Oh-okayama, Meguro-ku, Tokyo 152-8552, Japan
e-mail: mituhiro@is.titech.ac.jp

B. J. Braams
Department of Mathematics and Computer Science, Emory University,
Atlanta, GA 30322, USA
e-mail: braams@mathcs.emory.edu

M. Nakata
Department of Applied Chemistry, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
e-mail: chat95@mac.com

M. L. Overton
Department of Computer Science, Courant Institute of Mathematical Sciences,
New York University, New York, NY 10012, USA
e-mail: overton@cs.nyu.edu

Numerical results using parallel computation on high performance computers are given. 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.

**Keywords** Large-scale optimization · Computational chemistry · Semidefinite programming relaxation · Reduced density Matrix · $N$-representability · Parallel computation

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## 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 [5,18], 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. [41,42] 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. [61] showed that with the inclusion of additional conditions ("$T1$" and "$T2$"), the accuracy that is obtained for small molecular systems compares favorably with

J. K. Percus
Courant Institute of Mathematical Sciences and Department of Physics,
New York University, New York, NY 10012, USA
e-mail: percus@cims.nyu.edu

M. Yamashita
Department of Information Systems Creation, Kanagawa University,
3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama-shi, Kanagawa 221-8686, Japan
e-mail: makoto.yamashita@is.kanagawa-u.ac.jp

Z. Zhao
High Performance Computing Research Department,
Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Mail Stop 50F1650,
Berkeley, CA 94720, USA
e-mail: zzhao@lbl.gov

the best widely used electronic structure methods. Very recently, Mazziotti [35,36] 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 seven 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 Sect. 2.1, we show the general form of the RDM reformulation, and we explain the concept of $N$-representability conditions. In Sect. 2.2, we exhibit the principal $N$-representability conditions: $P$, $Q$, $G$, $T1$ and $T2$, respectively, which are semidefinite generalizations of the valid inequalities for the Correlation Polytope in a higher dimensional space, and in Sect. 2.3, we give a chronological overview of numerical computation since 1970s for the RDM equations which are SDPs.

In Sect. 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 [61] 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.

Section 4 gives our main results. Section 4.1 discusses the sizes and the sparsity of this class of SDPs. Section 4.2 gives the ground state energies and the dipole moments of small atomic–molecular systems solving small- and medium-scale SDPs by SeDuMi, which can handle inequality and equality constraints in the dual SDP problem. The numerical results confirm that the RDM approach employing the $P$, $Q$, $G$, $T1$ and $T2$ conditions provides accurate, robust and most of the time better values for the ground state energy and the dipole moment than the traditional electronic structure methods. Section 4.3 gives the same results for large-scale SDPs using the parallel SDPARA-SMP code, which has a better memory storage scheme than SDPARA [57]. Only inequality constraints are considered in the dual SDP formulation here. We also discuss essential techniques to solve large-scale problems in a high performance parallel environment. Possibly, we solved the largest SDP reported with 20,709 dual variables (primal constraints) and largest block matrices with size $3{,}211 \times 3{,}211$ with such density and accuracy. This size was not exceeded because of lack of available hours at the computational provider. Finally, Sect. 4.4 briefly reports our particular experience in using alternative formulations and methods for this problem.

## 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 [50]. 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 $\psi_i$ ($i = 1, 2, \ldots, r$) are orthonormal. Under such discretization, we obtain a discrete Hamiltonian (matrix) $\boldsymbol{H}$ which corresponds to the Schrödinger operator. The discretized ground state problem then asks for the minimum eigenvalue $E_0$ for $\boldsymbol{Hc} = E_0\boldsymbol{c}$, where $\boldsymbol{c}$ is the discretized wavefunction (vector). The antisymmetry requirement on the wavefunction is also carried over $\boldsymbol{c}$, 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 [50] 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 1960s [5,18] (but note as well the earlier refs. [25,29, 30]), was the subject of active theoretical [8,38,13] and computational [27,28, 19,39,47,17] investigations through the 1970s, but because of limited success interest waned.

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

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

Here $\langle \cdot, \cdot \rangle$ denotes the inner product in the space of real symmetric matrices $\langle \boldsymbol{A}, \boldsymbol{B} \rangle = \sum_{ij} A_{ij} B_{ij}$, and $\boldsymbol{A} \succeq \boldsymbol{B}$ means that $\boldsymbol{A} - \boldsymbol{B}$ is a positive semidefinite symmetric matrix. $\mathbf{\Gamma}^{\text{full}}$ is the full density matrix: a real symmetric matrix of the form $\mathbf{\Gamma}^{\text{full}}(i_1,\ldots,i_N;i'_1,\ldots,i'_N)$ where the indices $i_1,i_2,\ldots,i_N$ 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.*, $\mathbf{\Gamma}^{\text{full}}(i_1,\ldots,i_a,\ldots,i_b,\ldots,i_N;$ $i'_1,\ldots,i'_N) = -\mathbf{\Gamma}^{\text{full}}(i_1,\ldots,i_b,\ldots,i_a,\ldots,i_N;i'_1,\ldots,i'_N)$; and similarly for the primed indices $i'_1,i'_2,\ldots,i'_N$. $\mathbf{\Gamma}^{\text{full}}$ 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:

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

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) $\boldsymbol{H}$ 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) $\boldsymbol{H}_1$ and $\boldsymbol{H}_2$ – the one-body and two-body parts of the Hamiltonian (matrix) $\boldsymbol{H}$ – such that on the space of density matrices $\langle\boldsymbol{H},\mathbf{\Gamma}^{\text{full}}\rangle = \langle\boldsymbol{H}_1,\mathbf{\Gamma}_1\rangle + \langle\boldsymbol{H}_2,\mathbf{\Gamma}_2\rangle$.

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

$$\left\{\begin{array}{ll}\min & \langle\boldsymbol{H}_1,\mathbf{\Gamma}_1\rangle+\langle\boldsymbol{H}_2,\mathbf{\Gamma}_2\rangle\\ \text{subject to} & \langle\mathbf{\Gamma}_1,\boldsymbol{I}\rangle=N,\ \langle\mathbf{\Gamma}_2,\boldsymbol{I}\rangle=N(N-1),\ \text{and}\\ & \qquad\qquad\text{“}N\text{-representability”}.\end{array}\right.\tag{3}$$

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 $\mathbf{\Gamma}_2$:

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

$\mathbf{\Gamma}_1$ 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 [5] are:

$$\boldsymbol{I} \succeq \mathbf{\Gamma}_1 \succeq \boldsymbol{O}. \tag{5}$$

For the 2-RDM, a complete family of constructive necessary and sufficient conditions is not known yet. On a smaller subspace of matrices (the "diagonal" 2-RDM's), the $N$-representability problem is well understood: this diagonal $N$-representability problem is equivalent to characterization of the Correlation Polytope, also known as the Boolean Quadric Polytope and equivalent via a linear bijection to the Cut Polytope [9, p. 54]. Optimization over the Boolean Quadric Polytope is $\mathcal{NP}$-hard (it is the same as the unconstrained 0-1 quadratic programming problem), and as is pointed out in [9, p. 397], it follows from a result of Karp and Papadimitriou [26] that a polynomially concise description of all the facets of this polytope is not available unless $\mathcal{NP}$ = co-$\mathcal{NP}$. For earlier investigations into the diagonal $N$-representability problem, we note [8,38, 13]. As the original problem (1) is exponentially large, this complexity barrier 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 [18], but they are also found in [5]) and the $G$ condition [18]. In our previous work [61] we added to this a $T1$ and a $T2$ condition, which as we pointed out are implied by a much earlier paper of Erdahl [13]. All these conditions are of semidefinite form: $\boldsymbol{P} \succeq \boldsymbol{O}$, $\boldsymbol{Q} \succeq \boldsymbol{O}$, $\boldsymbol{G} \succeq \boldsymbol{O}$, $\boldsymbol{T1} \succeq \boldsymbol{O}$, and $\boldsymbol{T2} \succeq \boldsymbol{O}$, where the matrices $\boldsymbol{P}$, $\boldsymbol{Q}$, $\boldsymbol{G}$, $\boldsymbol{T1}$ and $\boldsymbol{T2}$ are defined by linear combinations of the entries of the basic matrices $\boldsymbol{\Gamma}_1$ and $\boldsymbol{\Gamma}_2$. Specifically (all indices range over $1, \ldots, r$ and $\delta$ is the Kronecker delta):

$$\boldsymbol{P} \equiv \boldsymbol{\Gamma}_2, \tag{6}$$

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

The matrices $\boldsymbol{P}$ and $\boldsymbol{Q}$ are of the same size as $\boldsymbol{\Gamma}_2$ and have the same antisymmetry property, so they belong to $\mathbb{S}^{r(r-1)/2}$. Also,

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

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

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

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. $\boldsymbol{T1}$ is fully antisymmetric in both its index triples, so it belongs to $\mathbb{S}^{r(r-1)(r-2)/6}$. Finally,

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

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

Observe that if we restrict the constraints to the diagonal entries of the $P$, $Q$, $G$, $T1$, and $T2$ conditions, i.e., replacing the primed indices with the unprimed ones (after applying the alternator operator in $T1$ and $T2$), we precisely obtain the "triangular inequalities" for the Correlation Polytope [9, p. 57].

## 2.3 Previous numerical computations using the RDM method

Following the clear statement of the RDM approach and of the most important $N$-representability conditions [5,18], the first significant computational results came in the 1970s. Kijewski [27,28] applied the RDM method to doubly ionized carbon ($N = 4$), $C^{++}$, using a discretization basis of 10 spin orbitals ($r = 10$). Garrod and co-authors were the first ones to actually solve the SDP imposing the $P$, $Q$ and $G$ conditions, by which they obtained very accurate results for atomic beryllium ($N = 4$ and $r = 10$) [19,47,17]. Mihailović and Rosina also considered the RDM method for nuclear physics [39], but reported rather poor accuracy.

This early work belongs firmly to semidefinite programming, although that name was not yet in use. The analytical work [18] is focused on semidefinite conditions, and the subsequent computational methods would be recognized by anyone working in semidefinite programming today. Rosina and Garrod [47] described two main algorithms to solve the SDP. One successively added cutting planes into the linear programming relaxation of the problem, and the other minimized the objective function incorporating a barrier function for the cone of positive semidefinite matrices!

Because of the high computational cost and the lack of progress on the $N$-representability problem interest in the computational aspects of the RDM approach fell off during the 1980s, but it has been rekindled in recent years. Nakata et al. [41] showed in 2001 using an SDP package that the RDM method with the $P$, $Q$ and $G$ conditions provides ground state energies that compare very favorably to Hartree-Fock results for a wide variety of small molecules ($r$ up to 16). In subsequent work [42], they demonstrated that the method maintains its accuracy when molecular dissociation is modeled – a test that is failed by many of the traditional methods of electronic structure calculation. In a previous paper [61] several of us using SDPARA [57] confirmed and extended the results of [41–43] for the accuracy of the RDM method with $P$, $Q$ and $G$ conditions relative to the Hartree-Fock approximation. We further showed that by adding two additional $N$-representability conditions, which we called $T1$ and $T2$, one obtains for small molecular systems ($r$ up to 20) an accuracy that compares favorably not just with Hartree-Fock but with the best standard methods of quantum chemistry. Although the cost of the RDM method is still very high compared to traditional methods, Mazziotti [35,36] recently announced results for considerably larger systems ($r$ up to 36) for the RDM approach imposing only the $P$, $Q$ and $G$ conditions.

In the present paper we discuss in detail only our chosen approach of optimizing the 2-RDM subject to semidefinite $N$-representability conditions ($P$, $Q$, $G$, $T1$, $T2$), without invoking 3-body or higher RDMs. We note here, however, a related approach being actively pursued that employs 2-body and higher reduced density matrices. In this other approach, under the name of Density Equation (DE) or Contracted Schrödinger Equation (CSE) [4,44,54,7,31,58, 59], the primary unknown is the 1-RDM or 2-RDM and the equations involve an approximate reconstructed 3-RDM or 4-RDM. An excellent survey can be found in the edited volume [3] that includes contributions by Coleman [6], Erdahl [15], Nakatsuji [45], Valdemoro [55] and Mazziotti [32]. Applications of the DE/CSE approach to quantum chemistry include [59,12]. In its original form the DE/CSE method does not impose the basic positivity conditions on the 2-RDM, but Erdahl and Jin [14,15] and Mazziotti [37,33] set up and solve equations closely related to the DE/CSE ones in which positivity conditions are imposed on the 2-RDM and on higher-order reconstructed density matrices [34]. These problems may lead to SDPs with nonlinear equations.

## 3 The SDP formulation of the RDM method

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

The primal SDP is defined as

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

and its dual

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

where $(\boldsymbol{X}, \boldsymbol{x})$ are the primal variables and $(\boldsymbol{S}, \boldsymbol{y})$ 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 in [56,51,40].

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 $\boldsymbol{\Gamma}_1$ and its corresponding Hamiltonian $\boldsymbol{H}_1$ is a two index matrix (see (3)), but the 2-RDM variational variable $\boldsymbol{\Gamma}_2$, the corresponding Hamiltonian $\boldsymbol{H}_2$, as well as $\boldsymbol{Q}$ and $\boldsymbol{G}$ are four index matrices, and moreover, $\boldsymbol{T1}$ and $\boldsymbol{T2}$ 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 $\boldsymbol{\Gamma}_2$, $\boldsymbol{H}_2$ and $\boldsymbol{Q}$, a symmetric matrix of order

$r(r-1)(r-2)/6 \times r(r-1)(r-2)/6$ for $\boldsymbol{T1}$, and a symmetric matrix of order $r^2(r-1)/2 \times r^2(r-1)/2$ for $\boldsymbol{T2}$. 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 $\widetilde{\Gamma}_2(j-i+(2r-i)(i-1)/2, j'-i'+(2r-i')(i'-1)/2)$. 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 $\boldsymbol{\Gamma}_2$ and of the $N$-representability conditions $Q$, $T1$ and $T2$, and also due to the spin symmetry [61, (22)-(27)], all these matrices reduce to block-diagonal matrices of size specified in Table 1.

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

$$\mathrm{svec}(\boldsymbol{U}) = (U_{11}, \sqrt{2}U_{12}, U_{22}, \sqrt{2}U_{13}, \sqrt{2}U_{23}, U_{33}, \ldots, \sqrt{2}U_{1n}, \ldots, U_{nn})^T, \boldsymbol{U} \in \mathcal{S}^n.$$

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

$$\boldsymbol{y} = (\mathrm{svec}(\boldsymbol{\Gamma}_1)^T, \mathrm{svec}(\boldsymbol{\Gamma}_2)^T)^T \in \mathbb{R}^m \text{ and}$$
$$\boldsymbol{b} = (\mathrm{svec}(\boldsymbol{H}_1)^T, \mathrm{svec}(\boldsymbol{H}_2)^T)^T \in \mathbb{R}^m.$$

It is now relatively straightforward to express the $N$-representability conditions (5)–(10) as the dual slack matrix variable $\boldsymbol{S}$ by defining it to have the following diagonal blocks: $\boldsymbol{\Gamma}_1, \boldsymbol{I}-\boldsymbol{\Gamma}_1, \boldsymbol{\Gamma}_2, \boldsymbol{Q}, \boldsymbol{G}, \boldsymbol{T1}, \boldsymbol{T2}$ taking into account the spin symmetry [61, (22)–(27)] and making suitable definitions for the matrices $\boldsymbol{C}, \boldsymbol{A}_p$ ($p = 1, 2, \ldots, m$). The equalities in (3) and (4), and the ones involving the number of electrons with $\alpha$ spin and given total spin $S$ [61, (19)–(21)] will define the vectors $\boldsymbol{c}, \boldsymbol{a}_p$ ($p = 1, 2, \ldots, m$).

The required number of floating point operations when solving these problems for instance using the parallel code SDPARA [57] are as follows. The computational flops per iteration when using SDPARA (Sect. 4.3) can be estimated as $\mathcal{O}(m^2f^2/q + m^3/q + mn_{\max}^2 + n_{\max}^3)$, where $n_{\max}$ is the size of the largest block matrix, $f$ is the maximum number of nonzero elements in each data matrix $\boldsymbol{A}_p$ ($p = 1, 2, \ldots, m$), and $q$ is the number of used processors. 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 $\mathcal{O}(r^{12}/q)$, 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 [41,33,42,43,35,36] as detailed in [61]. 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 $\mathcal{O}(r^{18}/q)$, while the total memory usage becomes $\mathcal{O}(m^2) = \mathcal{O}(r^{12})$.

The formulation (12) proposed here is novel in the sense that it now includes equality constraints that were previously absent in [61]. The implications of these two different formulations are discussed in Sect. 4.3.

## 4 Numerical results for the RDM method

### 4.1 Sizes and sparsity of SDPs

Table 1 shows the typical size of the SDP relaxation problem (12) as a function of the discretization basis size $r$, itemizing the sizes of block matrices for each of the $N$-representability conditions.

Observe that the number of equality constraints in the primal SDP (11) grows as $m \approx 3r^4/64$, while the size of the largest block matrices corresponding to the $T2$ condition grows as approximately $3r^3/16$, and they do not depend on the number of electrons $N$ of the system.

As one can observe from the $N$-representability conditions given in Sect. 2.2 and the actual formulation (12) as an SDP, all data matrices for our problem have integral values, except the diagonal matrices $\boldsymbol{Diag}(\boldsymbol{c})$, $\boldsymbol{Diag}(\boldsymbol{a}_p)$ $(p = 1, 2, \ldots, m)$ which have rational values, and the objective function vector $\boldsymbol{b}$ which has real values. Also, if we have two different systems with a common discretization basis size $r$, only the diagonal matrices and the objective function vector differ, and the entries corresponding to the semidefinite conditions of $\boldsymbol{\Gamma}_1$ and the ($P$, $Q$, $G$, $T1$, $T2$) conditions will be exactly the same. This fact can eventually be explored to re-solve a new system with the same discretization basis size $r$ once we have the results from a previous one.

Each of the data matrices $(\boldsymbol{C}, \boldsymbol{Diag}(\boldsymbol{c}))$, $(\boldsymbol{A}_p, \boldsymbol{Diag}(\boldsymbol{a}_p))$ $(p = 1, 2, \ldots, m)$ are very sparse in our problem. A more interesting sparsity characterization of the problem can be observed by analyzing the density rate of the dual slack matrix variable $\boldsymbol{S} = \sum_{p=1}^{m} \boldsymbol{A}_p y_p - \boldsymbol{C}$, which has 21 block matrices as itemized in Table 1, for a random nonzero vector $\boldsymbol{y} \in \mathbb{R}^m$. From the definition and the dual SDP

**Table 1** Size of the SDP relaxation problem as a function of the discretization basis size $r$

| | |
|---|---|
| Number of constraints $m$ in primal SDP (11) | $\frac{r}{4}\left(\frac{3r^3}{16} - \frac{r^2}{4} + \frac{9r}{4} + 1\right)$ |
| $N$-representability conditions | Size of block matrices |
| Dimension of the free variable $\boldsymbol{x}$ | $\frac{r}{2}\left(\frac{r}{2}+1\right)+5$ |
| $\boldsymbol{\Gamma}_1 \succeq \boldsymbol{O}$ | $\frac{r}{2}, \frac{r}{2}$ |
| $\boldsymbol{I} - \boldsymbol{\Gamma}_1 \succeq \boldsymbol{O}$ | $\frac{r}{2}, \frac{r}{2}$ |
| $\boldsymbol{P} \equiv \boldsymbol{\Gamma}_2 \succeq \boldsymbol{O}$ | $\frac{r^2}{4}, \frac{r}{4}\left(\frac{r}{2}-1\right), \frac{r}{4}\left(\frac{r}{2}-1\right)$ |
| $\boldsymbol{Q} \succeq \boldsymbol{O}$ | $\frac{r^2}{4}, \frac{r}{4}\left(\frac{r}{2}-1\right), \frac{r}{4}\left(\frac{r}{2}-1\right)$ |
| $\boldsymbol{G} \succeq \boldsymbol{O}$ | $\frac{r^2}{2}, \frac{r^2}{4}, \frac{r^2}{4}$ |
| $\boldsymbol{T1} \succeq \boldsymbol{O}$ | $\frac{r^2}{8}\left(\frac{r}{2}-1\right), \frac{r^2}{8}\left(\frac{r}{2}-1\right), \frac{r}{12}\left(\frac{r}{2}-1\right)\left(\frac{r}{2}-2\right)$, $\frac{r}{12}\left(\frac{r}{2}-1\right)\left(\frac{r}{2}-2\right)$ |
| $\boldsymbol{T2} \succeq \boldsymbol{O}$ | $\frac{r^2}{8}\left(\frac{3r}{2}-1\right), \frac{r^2}{8}\left(\frac{3r}{2}-1\right), \frac{r^2}{8}\left(\frac{r}{2}-1\right), \frac{r^2}{8}\left(\frac{r}{2}-1\right)$ |

formulation (12) we used, one can see that the block matrices corresponding to the 1-RDM $\mathbf{\Gamma}_1$ characterization, the $P$ condition, and the $Q$ condition are fully dense. In addition, the two smallest block matrices of the $G$ condition are fully dense, too. Figure 1 (left) depicts the density of the other block matrices as a function of the discretization basis size $r$. More specifically, this figure shows the density of the largest block matrix of the $G$ condition, and the block matrices corresponding to the $T1$ and $T2$ conditions (see Table 1). The density rate of the two largest block matrices of the $T1$ condition coincides with the rate of the two smallest block matrices of the $T2$ condition here.

A very positive aspect of the density rates is that for all the block matrices corresponding to the $T1$ and $T2$ conditions, the density decreases as $r$ increases. In particular, the crucial block matrix corresponding to the two largest block matrices of the $T2$ condition are the sparsest ones due to the product of Kronecker deltas (10), although they are still rather dense: 19.3% for $r = 26$.

Figure 1 (right) shows the sparsity structure corresponding to the two largest block matrices of the $T2$ condition from $\boldsymbol{S}$ for $r = 12$. These block matrices are still very dense (37.7%) and apparently do not have an obvious sparsity structure which could be exploited.

### 4.2 Numerical results for small- and medium-scale problems

We utilized SeDuMi 1.05 [49] for small- and medium-scale SDPs on a Pentium Xeon 2.4 GHz with 6GB of memory, and a level two cache of size 512 KB. SDPT3 3.1 [53] is the only other software package that can solve SDPs with inequality and equality constraints in the dual SDP (12), but our experiments showed that SeDuMi provides much more accurate solutions.

Table 2 shows the actual sizes, the typical time and memory usage of the SDPs we picked for each discretization basis size $r$ up to 18. We only listed the sizes of the largest block matrices among the 21 block matrices and one diagonal

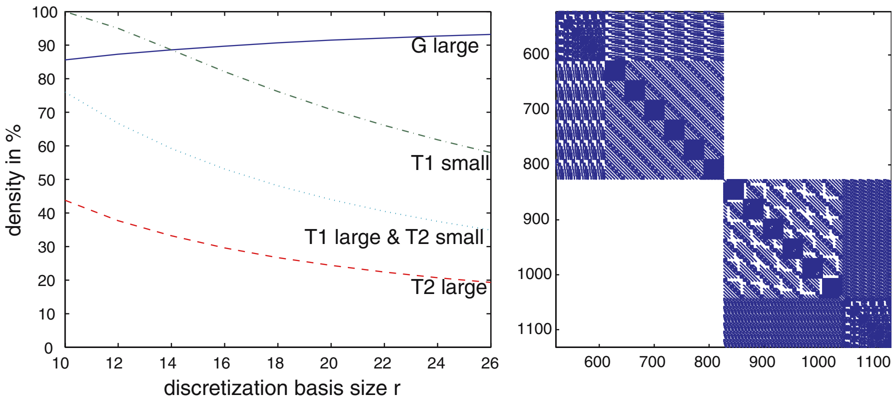


**Fig. 1** Density rates of the sparse block matrices as a function of the discretization basis size $r$ (*left*), and sparsity structure for the two largest block matrices of the $T2$ condition for $r = 12$ (right)

**Table 2** Sizes, required time and memory to solve the SDPs (imposing the ($P$,$Q$,$G$,$T1$,$T2$) conditions) as a function of the discretization basis size $r$ for small- and medium-scale problems using SeDuMi

| Basis size $r$ | Conditions | Number of constraints $m$ | Sizes of the largest block matrices | Time | Memory (GB) |
|---|---|---|---|---|---|
| | $P, Q, G$ | 465 | $50 \times 1, 25 \times 4, 10 \times 4, 5 \times 4$ | 11 s | 0.0 |
| 10 | $P, Q, G, T1$ | 465 | $50 \times 3, 25 \times 4, 10 \times 6, 5 \times 4$ | 10 s | 0.0 |
| | $P, Q, G, T1, T2$ | 465 | $175 \times 2, 50 \times 5, 25 \times 4, 10 \times 6$ | 86 s | 0.1 |
| | $P, Q, G$ | 948 | $72 \times 1, 36 \times 4, 15 \times 4, 6 \times 4$ | 2.3 min | 0.1 |
| 12 | $P, Q, G, T1$ | 948 | $90 \times 2, 72 \times 1, 36 \times 4, 20 \times 2$ | 2.8 min | 0.1 |
| | $P, Q, G, T1, T2$ | 948 | $306 \times 2, 90 \times 4, 72 \times 1, 36 \times 4$ | 17 min | 0.1 |
| | $P, Q, G$ | 1,743 | $98 \times 1, 49 \times 4, 21 \times 4, 7 \times 4$ | 13 min | 0.1 |
| 14 | $P, Q, G, T1$ | 1,743 | $147 \times 2, 98 \times 1, 49 \times 4, 35 \times 2$ | 14 min | 0.1 |
| | $P, Q, G, T1, T2$ | 1,743 | $490 \times 2, 147 \times 4, 98 \times 1, 49 \times 4$ | 1.4 h | 0.2 |
| | $P, Q, G$ | 2,964 | $128 \times 1, 64 \times 4, 28 \times 4, 8 \times 4$ | 41 min | 0.3 |
| 16 | $P, Q, G, T1$ | 2,964 | $224 \times 2, 128 \times 1, 64 \times 4, 56 \times 2$ | 1.4 h | 0.3 |
| | $P, Q, G, T1, T2$ | 2,964 | $736 \times 2, 224 \times 4, 128 \times 1, 64 \times 4$ | 6.4 h | 0.4 |
| | $P, Q, G$ | 4,743 | $162 \times 1, 81 \times 4, 36 \times 4, 9 \times 4$ | 1.9 h | 0.6 |
| 18 | $P, Q, G, T1$ | 4,743 | $324 \times 2, 162 \times 1, 84 \times 2, 81 \times 4$ | 2.7 h | 0.7 |
| | $P, Q, G, T1, T2$ | 4,743 | $1{,}053 \times 2, 324 \times 4, 162 \times 1, 84 \times 2$ | 12 h | 1.0 |

matrix. Here, $306 \times 2$ for instance means that there are two block matrices of sizes $306 \times 306$ each.

Table 3 shows our main result, the ground state energies calculated by the RDM method, imposing the ($P$, $Q$, $G$), ($P$, $Q$, $G$, $T1$), ($P$, $Q$, $G$, $T2$), and ($P$, $Q$, $G$, $T1$, $T2$) conditions (columns 7–10) to verify numerically the effectiveness of each $N$-representability condition. For all the tables that follow, "$r$" 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 ($\alpha$ spin electron) number, and "$2S+1$" is the spin multiplicity. For non-atomic systems, it is also necessary to add the repulsion energies to the optimal values of SDPs to obtain the ground state energies. These results are compared with the mainstream electronic structure methods: coupled cluster singles and doubles with perturbational treatment of triples (CCSD(T)) (from Gaussian 98 [16] – column 11), singly and doubly substituted configuration interaction (SDCI) (from Gamess [48] – column 12), and Hartree-Fock (HF) (from Gamess – column 13). The standard for these comparisons is the Full Configuration Interaction method (FCI) (from Gamess – column 14) which essentially consists in computing the minimum eigenvalue of a symmetric matrix with size $\mathcal{O}(r!/N!(r-N)!)$. All of the energies are given as a difference between them and the FCI values. Since the RDM method is an SDP relaxation of the FCI (1), it always gives a lower bound for the energy. On the other hand, SDCI and HF give upper bounds, and CCSD(T) an approximation for the FCI value. Also, in all the tables that follow, the actual discretization basis is from [10,11,23,22],[1] and the experimen-

[1] Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 02/25/04, as developed and distributed by the Molecular Science Computing

**Table 3** The ground state energies (in difference from that of FCI) calculated by the RDM method adding the ($P$, $Q$, $G$), ($P$, $Q$, $G$, $T1$), ($P$, $Q$, $G$, $T2$), and ($P$, $Q$, $G$, $T1$, $T2$) conditions (columns 7–10), and those obtained by CCSD(T), SDCI, and HF (columns 11–13) from Gamess and Gaussian 98. The last column shows the FCI results. The energy and the energy differences are in Hartree ($= 4.3598 \times 10^{-18}$ J). SDPs solved by SeDuMi

| $r$ | System | Basis | State | $N(N_\alpha)$ | $2S+1$ | $\Delta E_{PQG}$ | $\Delta E_{PQGT1}$ | $\Delta E_{PQGT2}$ | $\Delta E_{PQGT1T2}$ | $\Delta E_{\mathrm{CCSD(T)}}$ | $\Delta E_{\mathrm{SDCI}}$ | $\Delta E_{\mathrm{HF}}$ | $E_{\mathrm{FCI}}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 | Li | STO-6G | $^2S$ | 3(2) | 2 | −0.0000 | −0.0000 | −0.0000 | −0.0000 | +0.0000 | −0.0000 | +0.0003 | −7.4002 |
| 10 | Be | STO-6G | $^1S$ | 4(2) | 1 | −0.0000 | −0.0000 | −0.0000 | −0.0000 | +0.0000 | +0.0000 | +0.0527 | −14.5561 |
| 12 | $H_3$ | Double-$\zeta$ | $^2E'$[a] | 3(2) | 2 | −0.0007 | −0.0005 | −0.0000 | −0.0000 | F/C | +0.0001[b] | +0.0314 | −1.4861 |
| 12 | $BeH^+$ | STO-6G | $^1\Sigma^+$ | 4(2) | 1 | −0.0000 | −0.0000 | −0.0000 | −0.0000 | +0.0000 | +0.0000 | +0.0204 | −14.8433 |
| 14 | $NH_2^-$ | STO-6G | $^1A_1$ | 10(5) | 1 | −0.0020 | −0.0013 | −0.0000 | −0.0000 | +0.0000 | +0.0007 | +0.0454 | −55.1607 |
| 14 | $FH_2^+$ | STO-6G | $^1A_1$ | 10(5) | 1 | −0.0011 | −0.0005 | −0.0000 | −0.0000 | +0.0001 | +0.0006 | +0.0416 | −99.8294 |
| 16 | $CH_3^+$ | STO-6G | $^1E'$ | 8(4) | 1 | −0.0135 | −0.0038 | −0.0002 | −0.0002 | +0.0002 | +0.0016 | +0.0596 | −39.2147 |
| 16 | $CH_3$ | STO-6G | $^2A_2''$ | 9(5) | 2 | −0.0105 | −0.0018 | −0.0001 | −0.0001 | F/C | +0.0016 | +0.0631 | −39.5178 |
| 16 | $NH_3^+$ | STO-6G | $^2A_2''$ | 9(5) | 2 | −0.0098 | −0.0018 | −0.0002 | −0.0002 | F/C | +0.0015 | +0.0618 | −55.7924 |
| 18 | Be | Split-valence | $^1S$ | 4(2) | 1 | −0.0001 | −0.0000 | −0.0000 | −0.0000 | +0.0000 | +0.0000 | +0.0447 | −14.6156 |
| 18 | $CH_4$ | STO-6G | $^1A_1$ | 10(5) | 1 | −0.0195 | −0.0041 | −0.0002 | −0.0002 | +0.0001 | +0.0027 | +0.0802 | −40.1906 |
| 18 | $NH_4^+$ | STO-6G | $^1A_1$ | 10(5) | 1 | −0.0170 | −0.0041 | −0.0002 | −0.0002 | +0.0001 | +0.0028 | +0.0829 | −56.4832 |
| 18 | Na | STO-6G | $^2S$ | 11(6) | 2 | −0.0010 | −0.0004 | −0.0000 | −0.0000 | −0.0001 | +0.0014 | +0.0430 | −161.0770 |

*F/C* fail to converge

[a] At the $^2A_1'$ equilibrium geometry

[b] From Gaussian 98 since Gamess did not converge

tal geometries for these systems are from [20,21,24]. In all calculations using Gaussian 98 and Gamess, we unfroze the core orbitals which are frozen by default. The entry "F/C" means fail to converge.

The RDM method with the ($P$, $Q$, $G$) conditions gives better results than the classic HF. With the ($P$, $Q$, $G$, $T1$) conditions we get improvements, but imposing the ($P$, $Q$, $G$, $T1$, $T2$) conditions, the results are clearly better than the best traditional electronic structure method CCSD(T) (from Gaussian 98). One of the great advantages of the RDM method compared to the traditional electronic structure methods is that it is more numerically robust in the sense that the SDPs can be solved without tuning or sensitive parameter setting required by the traditional electronic structure methods. CCSD(T) solves a nonlinear eigenvalue problem so that there are systems which are hard to solve or do not converge ($H_3$, $CH_3$, $NH_3^+$ in Tables 3 and 6), or due to its non-variational nature, the energy can get lower than the FCI energy (Na, LiOH in Tables 3 and 6). Unfortunately, the RDM method is not competitive in terms of time since heuristic based electronic structure methods provide results in a few seconds.

The RDM method with ($P$, $Q$, $G$, $T1$, $T2$) conditions provides a more reliable approximation of the ground state energy than using only the ($P$, $Q$, $G$) conditions if we pay a price for the computational time and memory as shown in Table 2. However their complexity in terms of floating point operations per iteration (of the interior-point method) and total memory usage are the same: $\mathcal{O}(r^{12})$ and $\mathcal{O}(r^8)$, respectively (see Sect. 3).

It is interesting to comment here that the RDM method, through an SDP relaxation, can always derive an extremely good lower bound for the ground state energy in polynomial time in $r$, while the targeting value from the FCI is only computable in factorial time in $N$ and in a fixed discretization basis $r$. At the same time, though, it is quite impressive that some electronic structure methods like CCSD(T) can often provide comparably good values in a much shorter time.

Observe from Table 3 that we usually require at least seven digits of accuracy for the optimal value of the SDP for systems with less than $-100.0$ Hartrees of energy. This means that, adding to the difficulty of solving large-scale SDPs, we need highly precise optimal values and solutions. This particular requirement apparently excludes the possibility of using methods such as the bundle method, Krylov iterative methods or nonlinear formulations (see refs. in [56,51,52,2]).

The *dipole moment* $\langle\hat{\mu}\rangle$ is defined as the norm of $(\langle\hat{\mu}_x\rangle, \langle\hat{\mu}_y\rangle, \langle\hat{\mu}_z\rangle)$, *i.e.*, $\langle\hat{\mu}\rangle = \sqrt{\langle\hat{\mu}_x\rangle^2 + \langle\hat{\mu}_y\rangle^2 + \langle\hat{\mu}_z\rangle^2}$, where

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Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. http://www.emsl.pnl.gov/forms/basisform.html.

$$\langle \hat{\mu}_x \rangle = \langle \boldsymbol{\mu}_x, \boldsymbol{\Gamma}_1 \rangle, \qquad [\mu_x]_{ij} = \int \psi_i(\boldsymbol{z}) x \psi_j(\boldsymbol{z}) \mathrm{d}\boldsymbol{z}, \quad (i,j = 1,2,\ldots,r)$$

and $\psi_i$ $(i = 1,2,\ldots,r)$ are the basis function for the discretization. $\langle \hat{\mu}_y \rangle$ and $\langle \hat{\mu}_z \rangle$ are also defined in a similar way.

In Table 4, we show (only) the nonzero dipole moments $\langle \hat{\mu} \rangle$ of $H_3$, $BeH^+$, $NH_2^-$, and $FH_2^+$ in Debye. The ground state of $H_3$ is doubly degenerated and the components of its dipole moment are collinear and have opposite directions. The RDM method calculates the ensemble average of these vectors resulting zero for the dipole moment since there is no constraint in the current formulation which identifies such degeneracy. In general, the dipole moments from the RDM method with ($P$, $Q$, $G$) conditions are better than from HF, and worse than from SDCI. But with ($P$, $Q$, $G$, $T1$, $T2$) conditions, they almost reproduce the FCI results.

Finally, the error measures for the approximate optimal solution $(\hat{\boldsymbol{X}}, \hat{\boldsymbol{x}}, \hat{\boldsymbol{S}}, \hat{\boldsymbol{y}})$ of the SDPs are as follows:

(I) duality gap $\equiv \boldsymbol{b}^T \hat{\boldsymbol{y}} - \langle \boldsymbol{C}, \hat{\boldsymbol{X}} \rangle - \langle \boldsymbol{Diag}(\boldsymbol{c}), \boldsymbol{Diag}(\hat{\boldsymbol{x}}) \rangle$,
(II) primal feasibility error $\equiv \max\limits_{p=1,2,\ldots,m} |\langle \boldsymbol{A}_p, \hat{\boldsymbol{X}} \rangle + \langle \boldsymbol{Diag}(\boldsymbol{a}_p), \boldsymbol{Diag}(\hat{\boldsymbol{x}}) \rangle - b_p|$,
(III) dual feasibility error

$$\max \left\{ \max_{i,j=1,2,\ldots,n} \left| \left[ \hat{\boldsymbol{S}} - \sum_{p=1}^{m} \boldsymbol{A}_p \hat{y}_p + \boldsymbol{C} \right]_{ij} \right|, \max_{i=1,2,\ldots,s} \left| \left[ \sum_{p=1}^{m} \boldsymbol{a}_p y_p - \boldsymbol{c} \right]_i \right| \right\},$$

(IV) minimum eigenvalue of $\hat{\boldsymbol{X}}$,
(V) minimum eigenvalue of $\hat{\boldsymbol{S}}$.

The largest errors obtained for the instances solved in this section, not necessarily for the same problem, are (I) $6.86 \times 10^{-7}$, (II) $2.16 \times 10^{-7}$, (III) 0, (IV) $1.93 \times 10^{-9}$, and (V) $3.51 \times 10^{-9}$. Since they are small values, they guarantee that we are very close to the optimal solution (see [56,51,40] for optimality criteria).

Basically, there are two reasons we could not solve larger SDPs by SeDuMi. First, lack of memory caused by the use of MATLAB. Second, the computational time becomes very large for a serial code. Therefore, we solved large-scale SDPs by the parallel code SDPARA [57] using high performance computers in the next subsection.

## 4.3 Numerical results for large-scale problems

SDPARA [57] is a C++ open source parallel code for solving general SDPs under GNU General Public License. It is an implementation of the primal-dual predictor-corrector infeasible interior-point method. The main ways that SDPARA benefits from parallel computation are the following two routines.

**Table 4** The (nonzero) dipole moments in Debye (= $3.356 \times 10^{-30}$ Coulomb meters) calculated by the RDM method adding the ($P$, $Q$, $G$), ($P$, $Q$, $G$, $T1$), ($P$, $Q$, $G$, $T2$), and ($P$, $Q$, $G$, $T1$, $T2$) conditions (columns 7–10), and those obtained by SDCI, HF and FCI (columns 11–13) from Gamess. SDPs solved by SeDuMi

| $r$ | System | Basis | State | $N(N_\alpha)$ | $2S+1$ | $D_{PQG}$ | $D_{PQGT1}$ | $D_{PQGT2}$ | $D_{PQGT1T2}$ | $D_{\mathrm{SDCI}}$ | $D_{\mathrm{HF}}$ | $D_{\mathrm{FCI}}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12 | $H_3$ | Double-$\zeta$ | ${}^2E'$[a] | 3(2) | 2 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.8908[b] | 0.9211[b] | 0.859481 |
| 12 | $BeH^+$ | STO-6G | ${}^1\Sigma_+$ | 4(2) | 1 | 3.730358 | 3.730202 | 3.729455 | 3.729455 | 3.729713 | 3.979810 | 3.729456 |
| 14 | $NH_2^-$ | STO-6G | ${}^1A_1$ | 10(5) | 1 | 1.179561 | 1.173888 | 1.178982 | 1.178952 | 1.186210 | 1.190041 | 1.178952 |
| 14 | $FH_2^+$ | STO-6G | ${}^1A_1$ | 10(5) | 1 | 2.296445 | 2.299526 | 2.303632 | 2.303690 | 2.295315 | 2.465680 | 2.303915 |

[a] At the ${}^2A_1'$ equilibrium geometry

[b] From Gaussian 98 instead, since Gamess calculated a higher energy

In the framework of primal-dual interior-point methods for general SDPs, the most computationally intense routines involve the construction and the solution of a linear equation whose coefficient matrix is known as the Schur complement matrix (SCM). A close look at this matrix [57] reveals that each element can be evaluated on a different processor, independently from the others, if each of them stores the input data matrices $\boldsymbol{A}_p$ $(p = 1, 2, \ldots, m)$ and the variable matrices $\boldsymbol{X}$ and $\boldsymbol{S}$ in their own memory space. This characteristic is well suited for parallel computation. In addition to the evaluation of the SCM, its parallel Cholesky factorization can be done efficiently by a routine provided by ScaLAPACK [1].

We installed SDPARA on two IBM RS/6000 SPs, *seaborg* (16 × 375 MHz Power3+ with level two cache of size 8MB, and a maximum of 64GB of memory per Nighthawk node) at the National Energy Research Scientific Computing Center (NERSC), and *eagle* (4 × 375 MHz Power3-II with level two cache of size 8MB, and 2GB of memory per Winterhawk-II thin node) at Oak Ridge National Laboratory. We also installed SDPARA on an IBM pSeries 690, *cheetah* (32 × 1.3 GHz Power4 with level two cache of size 1.5 MB per chip, level three cache of size 32 MB, and maximum of 128 GB memory per Regatta node) at Oak Ridge National Laboratory. We chose to report the time and the total memory usage for *seaborg* since we performed most of the computation there.

SDPARA was compiled with IBM C++. We also made two modifications to SDPARA 0.90 [57], which limited the size of SDPs that could be solved to $r = 20$ with $m = 7,230$ and $n_{\max} = 1,450$ [61]. First, a check point was introduced, permitting a re-start of SDPARA after a certain number of iterations. This was due to a technical restriction on the running time of twelve hours at these multiple-user facilities. Second, the memory storage was changed. SDPARA 0.90 keeps duplicate copies of three type of matrices: the input data matrices $\boldsymbol{C}, \boldsymbol{A}_p$ $(p = 1, 2, \ldots, m)$, the variable matrices $\boldsymbol{X}$ and $\boldsymbol{S}$, and a considerable number of auxiliary matrices such as $\boldsymbol{X}^{-1}$, $\boldsymbol{S}^{-1}$, various matrix products, and the search direction at each processor. See [57] for details. Storing the input data matrices and the variable matrices at each processor is essential for constructing the SCM elements by parallel processing. The advantage of also storing the auxiliary matrices at each processor is that this reduces communication time, but the disadvantage is the excessive use of local memory. We modified the code to just keep a single copy of the auxiliary matrices at a specific processor. Before evaluating the SCM elements at each iteration of the interior-point method, we transmit copies of only the updated variable matrices from the specific processor to all other processors. We will call this version of the code SDPARA-SMP.

Table 5 shows the great reduction in total memory usage that resulted from this change, where the last column indicates the number of processors used. Here we solved SDPs with discretization basis size $r$ up to 26. Furthermore, a reduction in the running time was also achieved, especially for problems with ($P$, $Q$, $G$) and ($P$, $Q$, $G$, $T1$) conditions, by making a minor improvement in handling zero block matrices. Fortunately, the computational time was not

**Table 5** Sizes, required time, memory, and number of processors to solve the SDP (imposing the ($P$, $Q$, $G$, $T1$, $T2$) conditions) as a function of the discretization basis size $r$ using SDPARA 0.90 and SDPARA-SMP

| | | | | SDPARA 0.90 | | SDPARA-SMP | | |
|---|---|---|---|---|---|---|---|---|
| Basis size $r$ | conditions | Number of constraints $m$ | Sizes of the largest block matrices | Time | Memory (GB) | Time | Memory (GB) | Number of processors |
| | $P, Q, G$ | 465 | $50\times1, 25\times4, 10\times4, 5\times4$ | 5.8 s | 0.2 | 5.3 s | 0.2 | 16 |
| 10 | $P, Q, G, T1$ | 465 | $50\times3, 25\times4, 10\times6, 5\times4$ | 9.7 s | 0.2 | 8.0 s | 0.2 | 16 |
| | $P, Q, G, T1, T2$ | 465 | $175\times2, 50\times5, 25\times4, 10\times6$ | 37 s | 0.5 | 36 s | 0.2 | 16 |
| | $P, Q, G$ | 948 | $72\times1, 36\times4, 15\times4, 6\times4$ | 16 s | 0.3 | 13 s | 0.2 | 16 |
| 12 | $P, Q, G, T1$ | 948 | $90\times2, 72\times1, 36\times4, 20\times2$ | 26 s | 0.3 | 21 s | 0.2 | 16 |
| | $P, Q, G, T1, T2$ | 948 | $306\times2, 90\times4, 72\times1, 36\times4$ | 3.2 min | 1.1 | 3.1 min | 0.4 | 16 |
| | $P, Q, G$ | 1,743 | $98\times1, 49\times4, 21\times4, 7\times4$ | 45 s | 0.4 | 37 s | 0.3 | 16 |
| 14 | $P, Q, G, T1$ | 1,743 | $147\times2, 98\times1, 49\times4, 35\times2$ | 1.7 min | 0.5 | 1.3 min | 0.4 | 16 |
| | $P, Q, G, T1, T2$ | 1,743 | $490\times2, 147\times4, 98\times1, 49\times4$ | 15 min | 2.6 | 15 min | 0.8 | 16 |
| | $P, Q, G$ | 2,964 | $128\times1, 64\times4, 28\times4, 8\times4$ | 2.1 min | 0.6 | 1.7 min | 0.5 | 16 |
| 16 | $P, Q, G, T1$ | 2,964 | $224\times2, 128\times1, 64\times4, 56\times2$ | 4.3 min | 1.0 | 3.6 min | 0.6 | 16 |
| | $P, Q, G, T1, T2$ | 2,964 | $736\times2, 224\times4, 128\times1, 64\times4$ | 55 min | 5.6 | 54 min | 1.5 | 16 |
| | $P, Q, G$ | 4,743 | $162\times1, 81\times4, 36\times4, 9\times4$ | 6.9 min | 1.0 | 5.7 min | 0.9 | 16 |
| 18 | $P, Q, G, T1$ | 4,743 | $324\times2, 162\times1, 84\times2, 81\times4$ | 15 min | 1.9 | 12 min | 1.1 | 16 |
| | $P, Q, G, T1, T2$ | 4,743 | $1{,}053\times2, 324\times4, 162\times1, 84\times2$ | 3.3 h | 11.2 | 3.3 h | 2.9 | 16 |
| | $P, Q, G$ | 7,230 | $200\times1, 100\times4, 45\times4, 10\times4$ | 19 min | 1.8 | 16 min | 1.6 | 16 |
| 20 | $P, Q, G, T1$ | 7,230 | $450\times2, 200\times1, 120\times2, 100\times4$ | 37 min | 3.5 | 34 min | 2.0 | 16 |
| | $P, Q, G, T1, T2$ | 7,230 | $1{,}450\times2, 450\times4, 200\times1, 120\times2$ | 14 h | 27.2 | 13 h | 5.7 | 16 |
| | $P, Q, G$ | 10,593 | $242\times1, 121\times4, 55\times4, 11\times4$ | 1.3 h | 3.3 | 56 min | 2.9 | 16 |
| 22 | $P, Q, G, T1$ | 10,593 | $605\times2, 242\times1, 165\times2, 121\times4$ | 2.3 h | 6.3 | 2.0 h | 3.6 | 16 |
| | $P, Q, G, T1, T2$ | 10,593 | $1{,}936\times2, 605\times4, 242\times1, 165\times2$ | [a] | 48.4 | 2.0 days | 10.2 | 16 |
| | $P, Q, G$ | 15,018 | $288\times1, 144\times4, 66\times4, 12\times4$ | 3.2h | 5.8 | 2.3 h | 5.3 | 16 |
| 24 | $P, Q, G, T1$ | 15,018 | $792\times2, 288\times1, 220\times2, 144\times4$ | 7.5 h | 10.9 | 6.9 h | 6.4 | 16 |
| | $P, Q, G, T1, T2$ | 15,018 | $2{,}520\times2, 792\times4, 288\times1, 220\times2$ | [a] | [a] | 3.3 days | 26.3 | 32 |
| | $P, Q, G$ | 20,709 | $338\times1, 169\times4, 78\times4, 13\times4$ | 8.3 h | 10.2 | 6.2 h | 9.3 | 16 |
| 26 | $P, Q, G, T1$ | 20,709 | $1{,}014\times2, 338\times1, 286\times2, 169\times4$ | 21 h | 18.5 | 21h | 11.2 | 16 |
| | $P, Q, G, T1, T2$ | 20,709 | $3{,}211\times2, 1{,}014\times4, 338\times1, 286\times2$ | [a] | [a] | 5.4days | 73.9 | 64 |

[a] Memory was exceeded or the running time would have been excessive

increased by these modifications, mostly because most of communications were done within the node, which shares a common memory space between several processors, and not between different nodes.

Another limitation in using SDPARA-SMP is that it does not handle equality constraints in the dual SDP (12) as SeDuMi does. Therefore, we introduced a small perturbation into the formulation which is equivalent to a further relaxation of the problem (12) [61]. Equalities like $\langle \boldsymbol{\Gamma}_1, \boldsymbol{I} \rangle = N$ were all replaced by $-\epsilon \leq \langle \boldsymbol{\Gamma}_1, \boldsymbol{I} \rangle - N$, and $\langle \boldsymbol{\Gamma}_1, \boldsymbol{I} \rangle - N \leq \epsilon$, where $\epsilon$ was fixed to $10^{-5}$ for SDP relaxations with ($P$, $Q$, $G$, $T2$) or ($P$, $Q$, $G$, $T1$, $T2$) conditions and $r \geq 16$, and $10^{-7}$ otherwise.

Table 6 gives the ground state energy for all systems we solved using SDPARA-SMP, including the small- and medium-scale ones we solved previously using SeDuMi. The basic conclusions about the quality of the results of the RDM method compared to the traditional electronic structure methods are the same as previously stated. A comparison between this table and Table 3 shows that the small perturbations we included in the formulation can lower the energy in some cases as much as 0.0005 Hartrees ($CH_3$ with ($P$, $Q$, $G$, $T1$, $T2$) conditions), which is still acceptable but not desirable. On the other hand, this means that the actual energies obtained by the SDPs especially imposing the ($P$, $Q$, $G$, $T1$, $T2$) conditions with equality constraints should be slightly higher than shown in Table 6, and they still must give comparably better results than CCSD(T).

In particular, we believe that we solved the largest SDP found in the literature so far ($m = 20,709$, largest block matrix $n_{\max} = 3,211$) with this density and accuracy. Larger problems could not be solved because we had limited access to these high performance computers.

Table 7 shows the nonzero dipole moments for the corresponding molecules. We derive the same conclusions as in Sect. 4.2.

Finally, we give the error measures for the approximate optimal solution $(\hat{\boldsymbol{X}}, \hat{\boldsymbol{S}}, \hat{\boldsymbol{y}})$ for the SDPs. Now that we do not have the equality constraints in the dual SDP (12), the errors (I), (II) and (III) can be restated as follows:

$$
\begin{aligned}
&(\mathrm{I}') \quad \text{duality gap} \equiv \boldsymbol{b}^T \hat{\boldsymbol{y}} - \langle \boldsymbol{C}, \hat{\boldsymbol{X}} \rangle, \\
&(\mathrm{II}') \quad \text{primal feasibility error} \equiv \max_{p=1,2,\ldots,m} |\langle \boldsymbol{A}_p, \hat{\boldsymbol{X}} \rangle - b_p|, \\
&(\mathrm{III}') \quad \text{dual feasibility error} \equiv \max_{i,j=1,2,\ldots,n} \left|\left[\hat{\boldsymbol{S}} - \sum_{p=1}^{m} \boldsymbol{A}_p \hat{y}_p + \boldsymbol{C}\right]_{ij}\right|.
\end{aligned}
$$

The largest errors obtained for the instances solved in this section, not necessary for the same problem, are (I′) $1.73 \times 10^{-5}$, (II′) $1.28 \times 10^{-6}$, (III′) $4.48 \times 10^{-13}$, (IV) $2.27 \times 10^{-10}$, and (V) $3.85 \times 10^{-12}$.

## 4.4 Considerations on alternative methods

The small perturbations we introduced into the formulation, splitting one equality constraint into two inequality constraints, as explained at Sect. 4.3, are not

**Table 6** The ground state energies (in difference from that of the FCI) calculated by the RDM method adding the $(P, Q, G)$, $(P, Q, G, T1)$, $(P, Q, G, T2)$, and $(P, Q, G, T1, T2)$ conditions (columns 7–10), and those obtained by CCSD(T), SDCI, and HF (columns 11–13) from Gamess and Gaussian 98. The last column shows the FCI results. The energy and the energy differences are in Hartree ($= 4.3598 \times 10^{-18}$ J). SDPs solved by SDPARA-SMP

| $r$ | System | Basis | State | $N(N_\alpha)$ | $2S+1$ | $\Delta E_{PQG}$ | $\Delta E_{PQGT1}$ | $\Delta E_{PQGT2}$ | $\Delta E_{PQGT1T2}$ | $\Delta E_{\mathrm{CCSD(T)}}$ | $\Delta E_{\mathrm{SDCI}}$ | $\Delta E_{\mathrm{HF}}$ | $E_{\mathrm{FCI}}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 | Li | STO-6G | $^2S$ | 3(2) | 2 | −0.0000 | −0.0000 | −0.0000 | −0.0000 | +0.0000 | −0.0000 | +0.0003 | −7.4002 |
| 10 | Be | STO-6G | $^1S$ | 4(2) | 1 | −0.0000 | −0.0000 | −0.0000 | −0.0000 | +0.0000 | +0.0000 | +0.0527 | −14.5561 |
| 12 | $H_3$ | Double-$\zeta$ | $^2E'$[a] | 3(2) | 2 | −0.0008 | −0.0006 | −0.0000 | −0.0000 | F/C | +0.0001[b] | +0.0314 | −1.4861 |
| 12 | $BeH^+$ | STO-6G | $^1\Sigma^+$ | 4(2) | 1 | −0.0000 | −0.0000 | −0.0000 | −0.0000 | +0.0000 | +0.0000 | +0.0204 | −14.8433 |
| 14 | $NH_2^-$ | STO-6G | $^1A_1$ | 10(5) | 1 | −0.0020 | −0.0013 | −0.0000 | −0.0000 | +0.0000 | +0.0007 | +0.0454 | −55.1607 |
| 14 | $FH_2^+$ | STO-6G | $^1A_1$ | 10(5) | 1 | −0.0011 | −0.0005 | −0.0000 | −0.0000 | +0.0001 | +0.0006 | +0.0416 | −99.8294 |
| 16 | $CH_3^+$ | STO-6G | $^1E'$ | 8(4) | 1 | −0.0135 | −0.0038 | −0.0003 | −0.0003 | +0.0002 | +0.0016 | +0.0596 | −39.2147 |
| 16 | $CH_3$ | STO-6G | $^2A_2''$ | 9(5) | 2 | −0.0106 | −0.0018 | −0.0006 | −0.0006 | F/C | +0.0016 | +0.0631 | −39.5178 |
| 16 | $NH_3^+$ | STO-6G | $^2A_2''$ | 9(5) | 2 | −0.0098 | −0.0018 | −0.0005 | −0.0005 | F/C | +0.0015 | +0.0618 | −55.7924 |
| 18 | Be | Split-valence | $^1S$ | 4(2) | 1 | −0.0001 | −0.0001 | −0.0001 | −0.0000 | +0.0000 | +0.0000 | +0.0447 | −14.6156 |
| 18 | $CH_4$ | STO-6G | $^1A_1$ | 10(5) | 1 | −0.0195 | −0.0041 | −0.0004 | −0.0004 | +0.0001 | +0.0027 | +0.0802 | −40.1906 |
| 18 | $NH_4^+$ | STO-6G | $^1A_1$ | 10(5) | 1 | −0.0171 | −0.0041 | −0.0004 | −0.0004 | +0.0001 | +0.0028 | +0.0829 | −56.4832 |
| 18 | Na | STO-6G | $^2S$ | 11(6) | 2 | −0.0010 | −0.0005 | −0.0001 | −0.0001 | −0.0001 | +0.0014 | +0.0430 | −161.0770 |
| 20 | C | Double-$\zeta$ | $^3P$ | 6(4) | 3 | −0.0039 | −0.0031 | −0.0010 | −0.0009 | +0.0002 | +0.0011 | +0.0520 | −37.7365 |
| 20 | O | Double-$\zeta$ | $^1D$ | 8(4) | 1 | −0.0187 | −0.0140 | −0.0021 | −0.0019 | +0.0028 | +0.0144 | +0.1088 | −74.7873 |
| 20 | Ne | Double-$\zeta$ | $^1S$ | 10(5) | 1 | −0.0067 | −0.0026 | −0.0010 | −0.0007 | −0.0000 | +0.0042 | +0.1165 | −128.6388 |
| 22 | $HLi_2$ | STO-6G | $^2A_1$ | 7(4) | 2 | −0.0010 | −0.0007 | −0.0002 | −0.0002 | +0.0002 | +0.0005 | +0.0235 | −15.4055 |
| 22 | LiOH | STO-6G | $^1\Sigma^+$ | 12(6) | 1 | −0.0086 | −0.0040 | −0.0007 | −0.0007 | −0.0005 | +0.0109 | +0.0940 | −82.6484 |
| 22 | $HN_2^+$ | STO-6G | $^1\Sigma^+$ | 14(7) | 1 | −0.0253 | −0.0113 | − 0.0017 | −0.0017 | +0.0020 | +0.0150 | +0.1718 | −108.9313 |
| 22 | HNO | STO-6G | $^1A'$ | 16(8) | 1 | −0.0190 | −0.0136 | −0.0010 | −0.0010 | +0.0012 | +0.0093 | +0.1499 | −129.4479 |

**Table 6** continued

| $r$ | System | Basis | State | $N(N_\alpha)$ | $2S+1$ | $\Delta E_{PQG}$ | $\Delta E_{PQGT1}$ | $\Delta E_{PQGT2}$ | $\Delta E_{PQGT1T2}$ | $\Delta E_{\text{CCSD(T)}}$ | $\Delta E_{\text{SDCI}}$ | $\Delta E_{\text{HF}}$ | $E_{\text{FCI}}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 24 | LiH | Double-$\zeta$ | $^1\Sigma^+$ | 4(2) | 1 | −0.0003 | −0.0002 | −0.0001 | – | +0.0000 | +0.0002 | +0.0276 | −8.0087 |
| 24 | BH | Double-$\zeta$ | $^1\Sigma^+$ | 6(3) | 1 | −0.0065 | −0.0047 | −0.0006 | – | +0.0003 | +0.0034 | +0.0740 | −25.1877 |
| 24 | HF | Double-$\zeta$ | $^1\Sigma^+$ | 10(5) | 1 | −0.0116 | −0.0058 | −0.0003 | −0.0003 | +0.0003 | +0.0134 | +0.1383 | −100.1603 |
| 26 | $CH_3N$ | STO-6G | $^1A_1$ | 16(8) | 1 | −0.0385 | −0.0164 | −0.0013 | −0.0013 | +0.0007 | +0.0113 | +0.1574 | −93.8845 |

*F/C* fail to converge, – not computed

[a] At the $^2A_1'$ equilibrium geometry

[b] From Gaussian 98 since Gamess did not converge

**Table 7** The (nonzero) dipole moments in Debye (= $3.3356 \times 10^{-30}$ Cm) calculated by the RDM method adding the $(P, Q, G)$, $(P, Q, G, T1)$, $(P, Q, G, T2)$, and $(P, Q, G, T1, T2)$ conditions (columns 7–10), and those obtained by SDCI, HF and FCI (columns 11–13) from Gamess. SDPs solved by SDPARA-SMP

| $r$ | System | Basis | State | $N(N_\alpha)$ | $2S+1$ | $D_{PQG}$ | $D_{PQGT1}$ | $D_{PQGT2}$ | $D_{PQGT1T2}$ | $D_{\mathrm{SDCI}}$ | $D_{\mathrm{HF}}$ | $D_{\mathrm{FCI}}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12 | $H_3$ | Double-$\zeta$ | $^2E'$[a] | 3(2) | 2 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.8908[b] | 0.9211[b] | 0.859481 |
| 12 | $BeH^+$ | STO-6G | $^1\Sigma_+$ | 4(2) | 1 | 3.730328 | 3.730157 | 3.729477 | 3.729459 | 3.729713 | 3.979810 | 3.729456 |
| 14 | $NH_2^-$ | STO-6G | $^1A_1$ | 10(5) | 1 | 1.179587 | 1.173864 | 1.178975 | 1.178942 | 1.186210 | 1.190041 | 1.178952 |
| 14 | $FH_2^+$ | STO-6G | $^1A_1$ | 10(5) | 1 | 2.296407 | 2.299562 | 2.303633 | 2.303682 | 2.295315 | 2.465680 | 2.303915 |
| 22 | $HLi_2$ | STO-6G | $^2A_1$ | 7(4) | 2 | 0.561751 | 0.570898 | 0.574802 | 0.574843 | 0.582754 | 0.529818 | 0.575991 |
| 22 | LiOH | STO-6G | $^1\Sigma_+$ | 12(6) | 1 | 0.214317 | 0.224562 | 0.318120 | 0.318062 | 0.277222 | 1.994491 | 0.330520 |
| 22 | $HN_2^+$ | STO-6G | $^1\Sigma_+$ | 14(7) | 1 | 3.086371 | 3.130303 | 3.168295 | 3.168292 | 3.290407 | 3.161953 | 3.170072 |
| 22 | HNO | STO-6G | $^1A'$ | 16(8) | 1 | 1.212286 | 1.211767 | 1.249927 | 1.250139 | 1.286756 | 1.467859 | 1.254617 |
| 24 | LiH | Double-$\zeta$ | $^1\Sigma_+$ | 4(2) | 1 | 5.537220 | 5.541333 | 5.547012 | – | 5.572690 | 5.937220 | 5.548159 |
| 24 | BH | Double-$\zeta$ | $^1\Sigma_+$ | 6(3) | 1 | 1.558380 | 1.565279 | 1.593296 | – | 1.662481 | 2.030271 | 1.594179 |
| 24 | HF | Double-$\zeta$ | $^1\Sigma_+$ | 10(5) | 1 | 2.255452 | 2.260646 | 2.281847 | 2.281844 | 2.283955 | 2.378904 | 2.282259 |
| 26 | $CH_3N$ | STO-6G | $^1A_1$ | 16(8) | 1 | 1.625011 | 1.662642 | 1.701920 | 1.701928 | 1.715631 | 1.871751 | 1.706174 |

– not computed

[a] At the $^2A_1'$ equilibrium geometry

[b] From Gaussian 98 instead, since Gamess calculated a higher energy

desirable. Instead, we tried to eliminate some variables (at $\boldsymbol{y}$ in (12)) using these equalities as equations, producing an equivalent SDP with fewer variables and no equality constraints. Preliminary numerical experiments demonstrated, however, that these linear transformations introduce undesirable numerical properties into the problem and SDPARA was not able to get enough accuracy [60, Sect. 5.3.3]. Therefore, incorporation of equality constraints as a standard option, as done in SeDuMi and SDPT3, certainly is a desirable addition to SDPARA's capability.

Alternative methods such as discussed by [40] may be worth considering, but we have felt up until now that they are not able to deliver the accuracy that we require for this application. This is certainly our experience with the spectral bundle method; early experiments reported in [46] indicated that is very difficult to obtain satisfactory accuracy. We also experimented with the new code SDPLR 1.01 [2] which combines an augmented Lagrangian technique with limited-memory BFGS. However, we even could not solve the smallest problems to the accuracy that we need since the number of internal limited-memory BFGS iterations increases prohibitively as the optimal solution is approached. Surprisingly, Mazziotti [35,36] very recently announced some results for larger systems ($r = 36$, with an estimate $m \approx 390,000$ and $n_{\max} \approx 600$, using only the $(P, Q, G)$ conditions), for which he solved the SDPs by a method similar to that used in SDPLR.

The use of the conjugate gradient method to solve the SCM system or other iterative methods to solve the related indefinite "augmented system" (see [52]) could be a further alternative, but the extreme ill-conditioning of these linear systems makes it very difficult to obtain the accuracy that we need. It is possible that eliminating some of the degeneracies in the system could lead to improved performance of these methods.

## 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, including the ones reported here, 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 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, although it is not competitive in terms of time at least at present. It also has the advantage of robust convergence which is not the case for the traditional electronic structure methods. In addition, our results for the dipole moment confirm that the RDM itself is computed with excellent accuracy compared with traditional wavefunction-based methods.

We also report results for the largest problems in literature using the ($P$, $Q$, $G$, $T1$, $T2$) conditions with discretization basis size $r = 26$ ($m = 20,709$, $n_{\max} = 3,211$), while the previous ones were $r = 20$ ($m = 7,230$, $n_{\max} = 1,450$) [61]. The SDPs which arise from this application can be arbitrarily large, and may require special techniques for their solution. Parallel computation and large memory management are indispensable. In fact, it seems that we will always face a dual hardware limitation in solving large-scale problems: time and memory, both of which depend on the number of available processors and physical memory.

The recent series of numerical results for this application opens up a whole research field which was once very active, and at the same time raises many questions for future investigations.

Some fundamental questions for physicists are the search for new $N$-representability conditions and understanding the role of the known conditions. Chemists might be interested in understanding why the same ($P$, $Q$, $G$, $T1$, $T2$) conditions provide very good approximations for some systems and not for others, and also in studying many desirable properties obtainable by this unique method, like dissociation processes of highly-correlated systems having multiple bonds and high spin states, which are difficult to calculate. And finally, optimizers have the challenge of solving larger SDPs with $m > 20,000$ and $n > 3,000$ with high accuracy. However, it is certain that novel algorithms and exploration of new physical properties of the $N$-representability conditions are necessary in order for the RDM method to become practical.

As a final observation, we recognize that there is a need to provide physicists/chemists easy-to-use black box SDP solvers based on their own terminology.

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