

The Reduced Density Matrix Method for Electronic Structure Calculations and the Role of Three-Index Representability Conditions

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Abstract

The variational approach for electronic structure based on the two-body reduced density matrix is studied, incorporating two representability conditions beyond the previously used P , Q and G conditions. The additional conditions (called $T1$ and $T2$ here) are implicit in work of R. M. Erdahl [Int. J. Quantum Chem. **13**, 697–718 (1978)] and extend the well-known three-index diagonal conditions also known as the Weinhold-Wilson inequalities. The resulting optimization problem is a semidefinite program, a convex optimization problem for which computational methods have greatly advanced during the past decade. Formulating the reduced density matrix computation using the standard dual formulation of semidefinite programming, as opposed to the primal one, results in substantial computational savings and makes it possible to study larger systems than was done previously. Calculations of the ground state energy and the dipole moment are reported for 47 different systems, in each case using an STO-6G basis set and comparing with Hartree-Fock, SDCI, BD(T), CCSD(T) and full CI calculations. It is found that the use of the $T1$ and $T2$ conditions gives a significant improvement over just the P , Q and G conditions, and provides in all cases that we have studied more accurate results than the other mentioned approximations.

1 Introduction

The ground state properties of a fermion system in a given external potential serve as input for the analysis of a boundless variety of physical situations, and reliable solution of the associated N -body Schrödinger equation has remained a focus of activity for many decades. It was noticed by J. E. Mayer back in 1955 [1] that for non-relativistic electrons, which interact via pair forces alone, the system energy depends only upon the two-body reduced density matrix (2-RDM), possessing merely four-particle degrees of freedom. In fact, only two combinations – the pair density and one-body reduced density matrix (1-RDM) – each possessing just two-particle degrees of freedom, are required. This suggested to Mayer that the ground state energy – and density matrix information – could be economically computed by simply carrying out a Rayleigh-Ritz minimization with respect to the pair density and 1-RDM; subject, of course, to a few obvious conditions they must satisfy. But carrying out the process correctly gave horrible results, and a number of researchers found that the reason was that an enormous number of necessary restrictions – mainly inequalities – were being ignored. Progress with this very promising approach – referred to as the RDM method – could therefore only be made by systematizing the listing of these restrictions, determining large classes in explicit form, and then including them in the minimization process. We would like here to report significant success in this endeavor, the result of drawing together advances that have been made in computational as well as analytic techniques over the half-century time span.

Although the 1-RDM and pair density are sufficient to carry out the program outlined above, the advantage that they have of requiring only a small amount of information carries with it the disadvantage that numerous structural relationships which serve as signatures of fermion systems are not available for control purposes. Therefore, almost all of this work has been carried out in the context of the 2-RDM (from which the 1-RDM can be derived). The problem then is to assure in so far as possible that these objects come from *some* N -fermion system. This concept, referred to as N -representability, was first stated clearly by A. J. Coleman [2] and

the most important representability conditions (the P , Q and G conditions) were formulated by Coleman [2] and by C. Garrod and J. K. Percus [3]. References to earlier work involving reduced density matrices (RDM's) may be found in those papers and also in a survey article by Coleman [4]. Subsequent important analytical work on the representability problem was done by W. B. McRae and E. R. Davidson [5], who studied the diagonal problem, and by R. M. Erdahl [6, 7], and J. K. Percus [8]. Because the known explicit conditions are necessary but not sufficient for representability the RDM method involves variation over an enlarged domain, and yields a lower bound for the energy of the system in the model space.

The first empirical studies of the RDM method in atomic and molecular physics were done in the 1970's on atomic Beryllium ($N = 4$) by C. Garrod and M. A. Fusco [9]. These authors imposed the P , Q and G conditions. The numerical methods that were employed include a penalty function approach and also a cutting plane algorithm [10]. This work pointed to the possible high accuracy of the RDM method, but also showed practical computational difficulties in solving the variational problem.

The RDM method using the P , Q and G conditions has the mathematical form of a semidefinite program (SDP): maximize a linear function on the intersection of a linear affine space and the convex cone of block-diagonal positive semidefinite matrices. The field of semidefinite programming has seen tremendous interest in recent years with the advent of interior-point methods [11, 12, 13], and this has rekindled interest in the RDM method for electronic structure as well. Some preliminary investigation along this line were made by M. Nayakkankuppam [14]. Recently H. Nakatsuji *et al.* reinvigorated the RDM method in a study in which they used the P , Q and G conditions for a number of small atoms and molecules [15] and showed that the results were significantly more accurate than those obtained by the Hartree-Fock approximation. In follow-on work Nakatsuji *et al.* also considered the three-index diagonal conditions [5] (also known as the Weinhold-Wilson inequalities [16]), testing to see if they were violated in the solutions found using only the P , Q and G conditions [17].

The present work continues this line of research that is based on the 1960's ideas of Coleman

and of Garrod and Percus. We use semidefinite programming to solve the variational problem for the 2-RDM subject to certain representability conditions to obtain a lower bound (in the model space) for the ground state energy of the system. However, in addition to the P , Q and G conditions we impose a pair of positive semidefinite conditions that has a three-index form; we call them the $T1$ and $T2$ conditions. These conditions extend the three-index diagonal conditions to non-diagonal form. The $T1$ and $T2$ conditions are implicit in the work of Erdahl [6], but they are not spelled out in that paper and have received little notice. We find that including the $T1$ and $T2$ conditions results in a spectacular increase in the accuracy of the results, and gives in the cases studied an accuracy better than that of other more familiar approximate methods: singly and doubly substituted configuration interaction (SDCI), Brueckner doubles (with triples) (BD(T)) and coupled cluster singles and doubles with perturbational treatment of triples (CCSD(T)).

A second advance in the present work is related to the formulation of the SDP. We use a general purpose semidefinite programming code, SDPARA by M. Yamashita *et al.* [18], which is a parallel code based on the SDPA code of K. Fujisawa *et al.* [19]. In order to use a code such as SDPARA we must formulate our optimization problem using either the standard primal or the standard dual formulation of SDP (see Section 3 for definitions of these). The computational cost of solving the SDP scales at least as m^3 , where m is the number of linear equality constraints in the primal form or, equivalently, the number of dual variables in the dual form. One of the obstacles to the use of the RDM method is that m increases rapidly with the basis size r . However, we find that formulating the RDM optimization problem using the dual form of SDP results in a much smaller m than formulating the same problem in the primal form used in previous work [15, 17]. If we use only the P , Q and G conditions then m scales as r^4 in both cases, but with a smaller constant in the dual formulation; when we add the $T1$ and $T2$ conditions, then m scales as r^6 using the primal formulation but continues to scale as r^4 using the dual formulation.

Without attempting any quantitative comparison we wish to note here some approaches that

involve RDM's in different ways than the variational approach following Coleman and Garrod and Percus. One line of work extends density function theory by taking as unknown the 1-RDM. For the 1-RDM the representability conditions are completely known [2], but of course the energy function must be approximated; see for example [20, 21, 22, 23]. Another line of work, going back to H. Nakatsuji and K. Yasuda [24, 25] and to C. Valdemoro and F. Colmenero [26, 27], is based on the contracted Schrödinger equation (density equation) and employs approximate closure relations for the p -RDM ($p = 3, 4, 5$) in terms of the 1-RDM and 2-RDM. For this approach see also recent work by D. Mazziotti, *e.g.*, [28, 29].

The remaining sections of the paper are organized as follows. In Section 2 we review the RDM method and the P , Q and G conditions, and we derive the $T1$ and $T2$ conditions. In Section 3 we review semidefinite programming with attention to the primal and dual formulations. In Section 4 we describe our SDP implementation of the RDM method and we review the computational cost, comparing the primal and dual formulations. In Section 5 we present the results of the calculations and demonstrate the efficiency of the $T1$ and $T2$ conditions. We conclude with some remarks on planned future work.

2 The RDM Method

2.1 Reduced Density Matrices

As is customary we consider the N -fermion problem on a discrete orthonormal basis of single particle wavefunctions. Let Ψ be the ground state wavefunction for an N -fermion system (normalized as $\langle\Psi|\Psi\rangle=1$). Then the 1-RDM and 2-RDM (denoted as γ and Γ , respectively) may be defined as

$$\gamma(i, i') = \langle\Psi|a_{i'}^+a_i|\Psi\rangle, \quad (1)$$

$$\Gamma(i, j; i', j') = \langle\Psi|a_{i'}^+a_{j'}^+a_ja_i|\Psi\rangle, \quad (2)$$

where a_i and a_i^+ are the annihilation and creation operators on the single particle state i for the chosen basis set. $\Gamma(i, j; i', j')$ is antisymmetric under interchange of i and j and also under interchange of i' and j' , and γ and Γ are hermitian. These are immediate consequences of the definitions of γ and Γ .

If the Hamiltonian of N -fermion system involves one-body and two-body interactions only, *i.e.*,

$$H = \sum_{i,i'} h_1(i, i')a_i^+a_{i'} + \frac{1}{2} \sum_{i,j;i',j'} h_2(i, j; i', j')a_i^+a_j^+a_{j'}a_{i'},$$

then the ground state energy E can be expressed exactly in terms of the 1-RDM and 2-RDM:

$$E = \text{Tr}(h_1\gamma) + \frac{1}{2} \text{Tr}(h_2\Gamma), \quad (3)$$

where Tr denotes trace, $\text{Tr}(h_1\gamma) = \sum_{i,i'} h_1(i, i')\gamma(i', i)$, $\text{Tr}(h_2\Gamma) = \sum_{i,j;i',j'} h_2(i, j; i', j')\Gamma(i', j'; i, j)$.

The RDM method uses as trial function the pair (γ, Γ) in the space of functions satisfying the stated antisymmetry and hermiticity conditions, and seeks to minimize the right hand side of (3). Additional linear equality and convex inequality conditions are imposed on (γ, Γ) that are necessary to ensure that the trial pair lies in the convex hull of density matrices that are actually derivable from N -fermion wavefunctions; these are called N -representability conditions.

2.2 Well-known N -representability Conditions

For an N -fermion system it is immediate from the definitions that the 1-RDM and 2-RDM satisfy the linear equalities

$$\sum_k \Gamma(i, k; i', k) = (N - 1)\gamma(i, i') \quad \text{for all } i, i' \quad (4)$$

and trace conditions

$$\sum_i \gamma(i, i) = N, \quad (5)$$

and (not independent of the previous conditions)

$$\sum_{i,j} \Gamma(i, j; i, j) = N(N - 1). \quad (6)$$

Further representability conditions on (γ, Γ) are in the form of convex inequalities that do not explicitly involve the particle number N .

For the 1-RDM γ alone, a complete set of representability conditions was given by Coleman [2]:

$$\gamma \succeq 0, \quad I - \gamma \succeq 0, \quad (7)$$

where I denotes the identity matrix, and $\gamma \succeq 0$ denotes that the matrix γ is positive semidefinite. That is, all its eigenvalues are nonnegative.

For the pair (γ, Γ) Coleman also gave what became known as the P and the Q conditions; these two and the related G condition, which was given by Garrod and Percus [3], are the starting point for all implementations of the RDM method.

The P condition states that $\Gamma \succeq 0$, which is immediate from the definition of Γ . Here Γ is interpreted as a hermitian operator on the space of antisymmetric two-body wavefunctions. That an operator Γ on the space of antisymmetric two-body wave functions is positive semidefinite ($\succeq 0$) means that for any antisymmetric function $g(i, j)$,

$$\sum_{i,j;i',j'} g^*(i, j)\Gamma(i, j; i', j')g(i', j') \geq 0. \quad (8)$$

The Q condition follows from the positive semidefinite property of the operator A^+A where $A = \sum_{i,j} g(i,j)a_i^+a_j^+$, and g is an arbitrary antisymmetric function of the two indices. Obviously, $\langle \Psi | A^+A | \Psi \rangle \geq 0$, *i.e.*,

$$\sum_{i,j;i',j'} g^*(i,j) \langle \Psi | a_j a_i a_{i'}^+ a_{j'}^+ | \Psi \rangle g(i',j') \geq 0. \quad (9)$$

This implies that $Q \succeq 0$ (see (8)), where the hermitian matrix Q is defined by

$$Q(i,j;i',j') = \langle \Psi | a_j a_i a_{i'}^+ a_{j'}^+ | \Psi \rangle. \quad (10)$$

It can be expressed in terms of the 1-RDM and 2-RDM by using the fermion commutator relation $a_i a_{i'}^+ = \delta(i,i') - a_{i'}^+ a_i$,

$$\begin{aligned} Q(i,j;i',j') &= \Gamma(i,j;i',j') - \delta(i,i')\gamma(j,j') - \delta(j,j')\gamma(i,i') \\ &\quad + \delta(i,j')\gamma(j,i') + \delta(j,i')\gamma(i,j') + \delta(i,i')\delta(j,j') - \delta(i,j')\delta(j,i'). \end{aligned} \quad (11)$$

The G condition follows from the positive semidefinite property of the operator A^+A where $A = \sum_{i,j} g(i,j)a_i^+a_j$, and g is any function of the two indices. Again, $\langle \Psi | A^+A | \Psi \rangle \geq 0$ implies that $G \succeq 0$, where the hermitian matrix G is defined by

$$G(i,j;i',j') = \langle \Psi | a_j^+ a_i a_{i'}^+ a_{j'} | \Psi \rangle. \quad (12)$$

It depends linearly on the 1-RDM and 2-RDM as

$$G(i,j;i',j') = \Gamma(i,j';j,i') + \delta(i,i')\gamma(j',j). \quad (13)$$

For G there is no antisymmetry under the interchange of (i,j) or (i',j') . As already done by Rosina and Garrod [10] and other authors we write the G condition in the form of a positive semidefinite inequality, with the matrix G depending linearly on γ and Γ . In the original work of Garrod and Percus [3] the matrix G depended quadratically on γ . However, for a system with fixed particle number the two formulations are fully equivalent.

2.3 Erdahl's T -conditions

In the present work we include two additional representability conditions, which we call the $T1$ and $T2$ conditions. The conditions follow from the discussion in Section 8 of R. M. Erdahl's

1978 survey paper on representability [6], but they appear to have been little noticed and as far as we know they have not been employed in other explorations of the RDM method.

To obtain the $T1$ condition we observe that for an arbitrary totally antisymmetric function $g(i, j, k)$ the operators A^+A and AA^+ are both positive semidefinite, where $A = \sum_{i,j,k} g(i, j, k) a_i a_j a_k$. One can express this in terms of the RDM's just as in the derivation of the Q or the G conditions. Separately $\langle \Psi | A^+ A | \Psi \rangle$ and $\langle \Psi | A A^+ | \Psi \rangle$ each involves the 3-RDM (defined as $\langle \Psi | a_{i'}^+ a_j^+ a_k^+ a_i a_j a_k | \Psi \rangle$), but with opposite sign, so that in the sum $\langle \Psi | A^+ A + A A^+ | \Psi \rangle$ only the 1-RDM and 2-RDM are present. Of course this sum is nonnegative as well. The result is that $T1 \succeq 0$, where the hermitian matrix $T1$ is defined by

$$T1(i, j, k; i', j', k') = \left\langle \Psi | a_k^+ a_j^+ a_i^+ a_{i'} a_{j'} a_{k'} + a_{i'} a_{j'} a_{k'} a_k^+ a_j^+ a_i^+ | \Psi \right\rangle. \quad (14)$$

It is related to the 1-RDM and 2-RDM by

$$T1(i, j, k; i', j', k') = \mathcal{A}[i, j, k] \mathcal{A}[i', j', k'] \left(\frac{1}{6} \delta(i, i') \delta(j, j') \delta(k, k') - \frac{1}{2} \delta(i, i') \delta(j, j') \gamma(k, k') + \frac{1}{4} \delta(i, i') \Gamma(j, k; j', k') \right). \quad (15)$$

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.

The $T2$ condition follows in a similar way from the positive semidefinite property of the operator $A^+A + AA^+$ when $A = \sum_{i,j,k} g(i, j, k) a_i^+ a_j a_k$. In this case, $g(i, j, k)$ should be assumed antisymmetric with respect to (j, k) only. The result is that $T2 \succeq 0$, where the hermitian matrix $T2$ is defined by

$$T2(i, j, k; i', j', k') = \left\langle \Psi | a_k^+ a_j^+ a_i a_{i'}^+ a_{j'} a_{k'} + a_{i'}^+ a_{j'} a_{k'} a_k^+ a_j^+ a_i | \Psi \right\rangle. \quad (16)$$

It is related to the 1-RDM and 2-RDM by

$$T2(i, j, k; i', j', k') = \mathcal{A}[j, k] \mathcal{A}[j', k'] \left(\frac{1}{2} \delta(j, j') \delta(k, k') \gamma(i, i') + \frac{1}{4} \delta(i, i') \Gamma(j', k'; j, k) - \delta(j, j') \Gamma(i, k'; i', k) \right). \quad (17)$$

2.4 Detailed Summary of N -representability Conditions

In this work, we implemented the RDM method for an N -electron system. In this context, Ψ is the ground state wavefunction of an N -electron system, the index i denotes the spin orbitals (single particle basis). Let r denote the basis size, then $i = 1, 2, \dots, r$. The index i may be refined by a pair of indices n_i (spatial orbitals) and σ_i (spin states) when the need for explicitly separating the spatial and spin parts occurs. σ_i can take the values α (spin up (\uparrow)) and β (spin down (\downarrow)). The number of spatial orbitals is the half of the basis size r , therefore, n_i may take any of the values $1, 2, \dots, r/2$.

With this notation, we now summarize the N -representability conditions included in our calculation.

1. Hermiticity of the matrices $\gamma, \Gamma, Q, G, T1$ and $T2$.
2. Antisymmetric conditions

$$\Gamma(i, j; i', j') = -\Gamma(j, i; i', j') = -\Gamma(i, j; j', i') . \quad (18)$$

Also, the auxiliary matrices Q and $T1$ are antisymmetric with respect to all pair and triple indices, respectively, and the matrix $T2$ is antisymmetric with respect to the last 2 indices of each triple (refer to (16)).

3. Positive semidefinite ($\succeq 0$) constraints on matrices $\gamma, I - \gamma, \Gamma, Q, G, T1$ and $T2$.

For the linear relations of matrices $Q, G, T1$ and $T2$ to γ and Γ , refer to (11), (13), (15) and (17), respectively.

4. Linear equality constraints involving the electron number N , (4) to (6).
5. Linear equality constraints involving α electron number N_α

$$\sum_{n_i} \gamma(n_i\alpha, n_i\alpha) = N_\alpha , \quad (19)$$

$$\sum_{n_i, n_j} \Gamma(n_i\alpha, n_j\alpha; n_i\alpha, n_j\alpha) = N_\alpha(N_\alpha - 1) . \quad (20)$$

6. A linear equality constraint involving total spin S

$$\begin{aligned} & \sum_{n_i, n_j} (\Gamma(n_i\alpha, n_j\alpha; n_i\alpha, n_j\alpha) + \Gamma(n_i\beta, n_j\beta; n_i\beta, n_j\beta)) \\ & - 2 \sum_{n_i, n_j} \Gamma(n_i\alpha, n_j\beta; n_i\alpha, n_j\beta) - 4 \sum_{n_i, n_j} \Gamma(n_i\alpha, n_j\beta; n_j\alpha, n_i\beta) + 3N = 4S(S+1). \end{aligned} \quad (21)$$

7. Spin symmetries of matrices γ , Γ and Q , G , $T1$ and $T2$

$$\gamma(n_i\sigma_i, n_{i'}\sigma_{i'}) = 0 \quad \text{when } \sigma_i \neq \sigma_{i'}, \quad (22)$$

$$\Gamma(n_i\sigma_i, n_j\sigma_j; n_{i'}\sigma_{i'}, n_{j'}\sigma_{j'}) = 0 \quad \text{when } \sigma_i + \sigma_j \neq \sigma_{i'} + \sigma_{j'}, \quad (23)$$

$$Q(n_i\sigma_i, n_j\sigma_j; n_{i'}\sigma_{i'}, n_{j'}\sigma_{j'}) = 0 \quad \text{when } \sigma_i + \sigma_j \neq \sigma_{i'} + \sigma_{j'}, \quad (24)$$

$$G(n_i\sigma_i, n_j\sigma_j; n_{i'}\sigma_{i'}, n_{j'}\sigma_{j'}) = 0 \quad \text{when } \sigma_i + \sigma_{j'} \neq \sigma_j + \sigma_{i'}, \quad (25)$$

$$T1(n_i\sigma_i, n_j\sigma_j, n_k\sigma_k; n_{i'}\sigma_{i'}, n_{j'}\sigma_{j'}, n_{k'}\sigma_{k'}) = 0 \quad \text{when } \sigma_i + \sigma_j + \sigma_k \neq \sigma_{i'} + \sigma_{j'} + \sigma_{k'}, \quad (26)$$

$$T2(n_i\sigma_i, n_j\sigma_j, n_k\sigma_k; n_{i'}\sigma_{i'}, n_{j'}\sigma_{j'}, n_{k'}\sigma_{k'}) = 0 \quad \text{when } \sigma_i + \sigma_{j'} + \sigma_{k'} \neq \sigma_j + \sigma_k + \sigma_{i'}. \quad (27)$$

Here constraints (19) to (20) and (21) may be derived from the fact that Ψ is the eigenstate of \hat{N}_α (number operator for α electrons) and \hat{S}^2 (spin-squared) [15], respectively. Constraints (22) through (27) immediately follows from definitions of matrices (refer to (1), (2), (10), (12), (14) and (16)), combining with the fact that Ψ is the eigenstate of \hat{N}_α .

We make a few more remarks. First, although in general the Hamiltonian and the RDM's are complex hermitian, for the N -electron system (no magnetic field and no relativistic terms), the Hamiltonian and the RDM's are real under the chosen basis, as are Q , G , $T1$ and $T2$.

Second, the objects Γ , Q , G , $T1$ and $T2$ are presented initially as four-index and six-index objects; however, after mapping two indices i, j and three indices i, j, k to a composite index, they are $r^2 \times r^2$ and $r^3 \times r^3$ matrices correspondingly. Due to the antisymmetric properties, all except G can be represented by ‘‘compacted’’ matrices with reduced dimensions by dropping those dependent entries in the matrices (the matrix G is still $r^2 \times r^2$). The ‘‘compacted’’ matrices (denoted by adding a $\tilde{}$ to the corresponding symbol) can be formed by those entries with indices $i < j$, $i' < j'$ in Γ , Q ; $i < j < k$, $i' < j' < k'$ in $T1$; $j < k$, $j' < k'$ in $T2$, respectively (refer to (2), (10), (14), (16)). So, $\tilde{\Gamma}, \tilde{Q} \in \mathcal{S}^{r^2}$, $\tilde{T1} \in \mathcal{S}^{r^3}$ and $\tilde{T2} \in \mathcal{S}^{(r \times r^2)}$, where \mathcal{S}^n denotes the

space of $n \times n$ real symmetric matrices, $r2 = C_r^2$, and $r3 = C_r^3$ (C_r^n is the binomial coefficient).

Thus, the formulas appearing in this section must be changed if they are expressed in terms of “compacted” matrices. For example, the ground state energy E (see (3)) can be expressed as

$$E = \text{Tr}(h_1\gamma) + \text{Tr}(\check{h}_2\tilde{\Gamma}), \quad (28)$$

where $\check{h}_2(i, j; i', j') = h_2(i, j; i', j') - h_2(i, j; j', i')$, and $i < j, i' < j'$.

Third, the matrices $\gamma, \tilde{\Gamma}, \tilde{Q}, G, \tilde{T}1$ and $\tilde{T}2$ are all further partitioned to block diagonal matrices according to the spin symmetry ((22) through (27)); here an appropriate ordering of spin orbitals is involved. Specifically, γ has block sizes $r/2, r/2$; $\tilde{\Gamma}, \tilde{Q}$ have block sizes $C_{r/2}^2, C_{r/2}^2, r^2/4$; G has block sizes $r^2/2, r^2/4, r^2/4$; $\tilde{T}1$ has block sizes $C_{r/2}^3, C_T, C_T, C_{r/2}^3$; and $\tilde{T}2$ has block sizes $C_T + r^3/8, C_T + r^3/8, C_T, C_T$, where $C_T = C_{r/2}^2 \times r/2$.

3 Semidefinite Programming

Semidefinite programs (SDP's) are a class of convex optimization problems that has been intensively studied during the past decade. For good surveys on semidefinite programming and for background on results reviewed here we refer to [11, 12, 13].

An SDP can be summarized as maximization of a linear function on the intersection of a linear affine space and the convex cone of block-diagonal positive semidefinite matrices. Let R^m denote m -dimensional real linear space and let \mathcal{B} denote the space of block-diagonal real symmetric matrices with prescribed block sizes. A data vector $b \in R^m$, and the data matrices $C \in \mathcal{B}$ and $A_p \in \mathcal{B}$ (for $p = 1, 2, \dots, m$) together define an SDP, which is expressed in *primal formulation* as

$$\left\{ \begin{array}{ll} \max_{X \in \mathcal{B}} & \text{Tr}(CX) \\ \text{subject to} & \text{Tr}(A_p X) = b_p, \text{ (for } p = 1, 2, \dots, m) \\ & X \succeq 0, \end{array} \right. \quad (29)$$

where $X \succeq 0$ means that the block-diagonal matrix $X \in \mathcal{B}$ is positive semidefinite (equivalently, each of its blocks is positive semidefinite). Analogously, we write $X \succ 0$ to mean that X is positive definite. The *dual formulation* of the same SDP (29) is

$$\left\{ \begin{array}{ll} \min_{y \in R^m, Z \in \mathcal{B}} & b^t y \\ \text{subject to} & Z \succeq 0, \text{ where } Z = \sum_{p=1}^m A_p y_p - C. \end{array} \right. \quad (30)$$

Here the variables are the vector $y \in R^m$ and the block-diagonal matrix $Z \in \mathcal{B}$, and t denotes transpose. We say that X is a primal feasible point (strictly feasible point) if it satisfies the constraints in (29) (and $X \succ 0$). Likewise, we say that (y, Z) is a dual feasible point (strictly feasible point) if it satisfies the constraints in (30) (and $Z \succ 0$).

Then if (X, y, Z) is a primal-dual feasible point, we have

$$b^t y - \text{Tr}(CX) = b^t y - \text{Tr} \left(\left(\sum_{p=1}^m A_p y_p - Z \right) X \right) = \text{Tr}(XZ) \geq 0, \quad (31)$$

which means that the optimal value of the primal linear function is no larger than the dual one. Furthermore, it is known from duality theory that if both the primal formulation (29) and the

dual formulation (30) have strictly feasible points, then both have optimal solutions and their optimal values coincide with each other, so that the duality gap (the left hand side of (31)) is zero. In the special case that all block sizes of matrices in \mathcal{B} are one, all block-diagonal matrices reduce to diagonal ones and consequently the SDP reduces to a standard linear program.

Several methods to solve SDP's have been developed in the last decade, but among them, the most established and efficient methods are the iterative methods called *primal-dual interior-point methods*. Briefly, these methods are based on the key notion of *primal-dual central path*, which is defined as the set of triples (X_μ, y_μ, Z_μ) satisfying $X_\mu Z_\mu = \mu I$ for some $\mu > 0$ in addition to the constraints of (29) and (30). It is known that, under the strictly feasible point assumption already mentioned, the triple (X_μ, y_μ, Z_μ) always exists and is unique for all real $\mu > 0$, that $X_\mu \succ 0$ and $Z_\mu \succ 0$, that the path is a smooth function of μ , and that as $\mu \searrow 0$, the triple converges to an optimal primal-dual solution of the SDP. (Note that the equation $X_\mu Z_\mu = \mu I$ converges to the condition $XZ = 0$ as $\mu \searrow 0$, which is equivalent to the zero duality gap condition $\text{Tr}(XZ) = 0$). In a primal-dual interior-point method, a technique based on Newton's method is used to numerically trace the central path. At each iteration, it is necessary to solve a linear system of equations with an $m \times m$ dense symmetric positive definite coefficient to obtain a *search direction* that indicates the direction of the next point in the iteration. The step taken along the search direction is chosen to ensure that the next primal and dual iterates X and Z are strictly positive definite. Obtaining a primal-dual feasible starting point for the process is nontrivial, so feasibility of the primal and dual equality constraints is generally obtained only in the limit, but the X and Z iterates are strictly positive definite throughout the iteration (hence the name "interior-point"), converging to the boundary of the semidefinite cone as the optimal primal-dual solution is approached. The iteration is terminated when the duality gap $\text{Tr}(XZ)$ and primal and dual infeasibility are all reduced to sufficiently small quantities, certifying the approximate optimality of the final iterates.

4 SDP Implementation of the RDM Method

In order to use existing semidefinite programming software to solve our problem, we must convert it into one of the standard SDP formulations. However, it is not immediately obvious how best to convert an RDM variational problem to the primal formulation (29) or the dual formulation (30). The primal formulation appears more direct and was used in the previous work [15, 17], but as will be discussed here, use of the dual formulation brings important computational advantages.

In order to convert an RDM variational problem into the primal formulation, one begins by writing the primal linear function as the negative energy of (28):

$$-E = \max_{\gamma, \tilde{\Gamma}} \left(-\text{Tr}(h_1\gamma) - \text{Tr}(\check{h}_2\tilde{\Gamma}) \right) . \quad (32)$$

Then one casts the positive semidefinite N -representability conditions in the form $X \succeq 0$ by defining the primal block-diagonal matrix $X \in \mathcal{B}$ to have the following diagonal blocks: γ , $I - \gamma$, $\tilde{\Gamma}$, \tilde{Q} , G , $\tilde{T}1$, and $\tilde{T}2$. The linear relations of $I - \gamma$, \tilde{Q} , G , $\tilde{T}1$ and $\tilde{T}2$ to γ and $\tilde{\Gamma}$ (see (11), (13), (15), (17)), and the equality conditions (4) to (6) and (19) to (21) are all incorporated into the linear constraints of (29) by suitable definitions of the matrices $A_p \in \mathcal{B}$ for $p = 1, 2, \dots, m$; these matrices are very sparse. The data matrix $C \in \mathcal{B}$ is defined from (32) accordingly. The difficulty with this approach is that m , the number of primal constraints, is equal to the number of independent elements of the block-diagonal matrices $X \in \mathcal{B}$ (*i.e.*, $I - \gamma$, \tilde{Q} , G , $\tilde{T}1$, $\tilde{T}2$) plus the number of equality conditions (4) to (6) and (19) to (21). This total scales as r^6 due to the T conditions.

A much more efficient approach is obtained by converting an RDM variational problem into the dual formulation (30). Given $U \in \mathcal{S}^n$, let us define $svec : \mathcal{S}^n \rightarrow R^{n(n+1)/2}$ as

$$svec(U) = \left[U_{11}, \sqrt{2}U_{12}, U_{22}, \sqrt{2}U_{13}, \sqrt{2}U_{23}, U_{33}, \dots, \sqrt{2}U_{1n}, \dots, U_{nn} \right]^t .$$

Define $y \in R^m$ and $b \in R^m$ in (30) as $y = [svec(\gamma)^t \ svec(\tilde{\Gamma})^t]^t$ and $b = [svec(h_1)^t \ svec(\check{h}_2)^t]^t$.

Then, the ground state energy (28) can be rewritten as the dual linear function

$$E = \min_y b^t y .$$

It now becomes relatively straightforward to express the N -representability conditions in the dual form $Z \succeq 0$ of (30) by defining the dual variable $Z \in \mathcal{B}$ to have the following diagonal blocks: γ , $I - \gamma$, $\tilde{\Gamma}$, \tilde{Q} , G , $\tilde{T}1$ and $\tilde{T}2$, making suitable definitions of the matrices $C \in \mathcal{B}$ and $A_p \in \mathcal{B}$ for $p = 1, 2, \dots, m$ which are all sparse. With this approach, we have that m , the dimension of y , scales as r^4 .

One difficulty arises: how may we define the equality conditions ((4) to (6) and (19) to (21)) if the dual formulation (30) does not permit equality constraints? This is resolved by replacing each equality by a pair of inequalities, which must be slightly relaxed to obtain a strictly feasible region for the dual formulation (30). Thus, if ϵ is a suitably small number (in our computations $\epsilon = 10^{-5}$), then an equation such as $\text{Tr} \gamma - N = 0$ can be replaced by $\epsilon \geq \text{Tr} \gamma - N$ and $\text{Tr} \gamma - N \geq -\epsilon$. This procedure introduces an extra diagonal block in the block-diagonal data matrices $C \in \mathcal{B}$ and $A_p \in \mathcal{B}$ for $p = 1, 2, \dots, m$. The presence of the additional diagonal blocks does not significantly add to the computational cost.

A key point here is that the dual formulation that we are proposing is *not* the dual of the natural primal formulation used in [15, 17], which has far larger m (order r^6 compared to r^4). There is, of course, a primal interpretation for our dual formulation, but it is the dual interpretation that arises naturally.

For an idea of the difference that the dual formulation makes, the largest SDP problem we solved in Section 5 with basis size $r = 20$ has $m = 7230$, and the largest blocks in the data matrices have size 1450×1450 . The additional diagonal blocks have order only 230. If we were to attempt the primal formulation we would have $m = 2561915$, while the largest blocks in the data matrices remain the same. The time required to solve the SDP problem by standard primal-dual interior-point methods scales at least as m^3 . Using the dual formulation is advantageous even when only the P , Q and G conditions are applied, and the advantage is overwhelming

when the $T1$ and $T2$ conditions are added. The modest size of m leaves open the possibility of incorporating more N -representability conditions in the future.

5 Results and Discussion

Tables 1 and 2 show the ground state energies calculated by the RDM method for 47 molecules, imposing the (P,Q) , (P,Q,G) , $(P,Q,G,T1)$, $(P,Q,G,T2)$ and $(P,Q,G,T1,T2)$ conditions (columns 6–10). These results are compared with results obtained by other more familiar methods with use of the Gaussian 98 code [30]: singly and doubly substituted configuration interaction (SDCI), Brueckner doubles (with triples) (BD(T)) and coupled cluster singles and doubles with perturbational treatment of triples (CCSD(T)). The geometries used are the experimental ones from [31] and the basis set is STO-6G for all systems. (CCSD(T) is arguably the most accurate single method available in Gaussian 98 [32]). Table 1 listed only those molecules for which the full CI result is available (last column), and the energies are given as a difference from that of the full CI. We also compared with MP2 (2nd order Møller-Plesset method) from Gaussian 98, but as the MP2 method almost always gives less accurate results than CCSD(T), BD(T) and SDCI methods, its results are not displayed in the tables.

The RDM method provides a lower bound for the full CI result in the same model space, and it gives exact solutions for the cases $N = 2$ and $N = r - 2$ using only the P and Q conditions [3]. These predictions are confirmed in our calculations (see the “–” signs of columns 6–10 and see the results for molecules OH^- and HF in Table 1 when only the P and Q conditions are imposed). Previous numerical results of Nakata *et al.* [15, 17] suggest that adding the G condition to the P and Q conditions is essential to obtain a solution that is competitive at least with the Hartree-Fock approximation, and our present results confirm that conclusion for a larger set of molecules. In certain cases (LiH , BeH , BH^+ , CH^- , NH , NH^- , OH^+ , OH , OH^- , HF^+ , HF , SiH^- , HS^+) the difference between the result of the RDM method using P , Q and G conditions (simply the RDM (P,Q,G) hereafter) and the full CI result is around 0.1 milli-Hartree (mH) or less as seen in Table 1. In those cases the accuracy also compares favorably with the CCSD(T), BD(T) and SDCI approximations. In the other cases in Table 1 the RDM (P,Q,G) errors are several mH: up to 16.7 mH for O_2^+ . In those cases the RDM (P,Q,G) errors

are still well below the Hartree-Fock error in magnitude, but the other approximations are in turn typically much better than the RDM (P,Q,G) result.

The results of the RDM method are improved by inclusion of the $T1$ condition, and improved spectacularly by adding both the $T1$ and $T2$ conditions (or even $T2$ alone). As mentioned in previous sections, these are the three-index positive semidefinite conditions that extend the Weinhold-Wilson diagonal conditions. We see that the RDM method with P , Q , G , $T1$ and $T2$ conditions gives almost the exact full CI values for the ground state energies, with error around 0.1 mH or less, for most of the cases in Table 1. The exceptions are NH_3 , H_3O^+ , CF and O_2^+ , and even in those cases the error is below 2.8 mH and compares favorably with the error that is associated with the other methods.

One may be tempted to conclude from the tables that the $T2$ condition implies the $T1$ condition, but this is not true as can be seen by considering the diagonal case when the two conditions each generate one of the Weinhold-Wilson inequalities. Indeed, an occasional case like Li_2 and B_2 shows that the $T1$ condition has some strength independent of $T2$.

Table 3 shows the dipole moments in atomic unit (a.u.) calculated by the RDM method for the same molecules using the various representability conditions (columns 6–10), and those obtained by methods SDCI and Hartree-Fock (columns 11–12) from Gaussian 98. The molecules in Table 3 are those of Tables 1 and 2 that have a non-zero dipole moment. The last column shows the values obtained by full CI where we could do the calculation. (Dipole moments are not available from CCSD(T) and BD(T) in Gaussian 98.) Like the results for the ground state energy the results for the dipole moment are very encouraging. For the RDM (P,Q,G) we obtain an error of around 0.0001 a.u. or less (with respect to the full CI result) for LiH , BeH , BH^+ , CH^- , NH , NH^- , OH^+ , OH , OH^- , HF^+ , HF , SiH^- and HS^+ ; this is the same list of molecules for which the RDM (P,Q,G) gave a highly accurate ground state energy.

When the $T1$ and $T2$ conditions are added the dipole moment error falls to around 0.0001 a.u. or less for most of the remaining molecules in the list for which the full CI result is available; the exceptions are CH_2 (error 0.0003 a.u.), H_2O^+ (error 0.0002 a.u.), H_3O^+ (error 0.0002 a.u.),

CF (error 0.0045 a.u.), and NF (error 0.0005 a.u.). Even in those cases, and in general, the RDM ($P, Q, G, T1, T2$) results for the dipole moment compare very favorably to the accuracy obtained using SDCI.

For the dipole moment calculation, the RDM method does not provide a bound (lower or upper) for the full CI result. We also see that once the energy is obtained with high accuracy, the dipole moment calculation also reaches high accuracy. This is another advantage of the RDM method over the other traditional variational methods in which a first order error in the trial wavefunction results in a second order error in the energy, so a poor trial function may produce amazingly good result on the ground state energy, but not on the other ground state properties [3].

We close this section with some remarks about the numerics. To solve the SDP's of the RDM method we used the SDPARA code [18], which is a parallel implementation of the primal-dual interior-point method, derived from the SDPA code [19]. The calculations were performed on an IBM SP RS/6000 (Power3 375MHz processor \times 16 CPUs, and 32 GB of main memory).

SDPARA gives very accurate solutions for our problems. As discussed in Section 3, once we have primal and dual feasible solutions, the quality of the solution can be measured by the duality gap, or difference between the primal and dual objective functions. SDPARA outputs the following error values: the relative duality gap $|b^t y - Tr(CX)| / \max\{1.0, (|b^t y| + |Tr(CX)|)/2\}$, the primal feasibility error $\max\{|Tr(A_p X) - b_p| : p = 1, 2, \dots, m\}$, and the dual feasibility error: $\max\{|\sum_{p=1}^m A_p y_p - C - Z]_{rs}| : r, s = 1, 2, \dots, n\}$. For all numerical experiments we conducted with the SDPARA, the relative duality gap, the primal feasibility error and the dual feasibility error were less than 10^{-7} , 10^{-6} , and 10^{-12} , respectively, which give reliable numerical accuracy for our results.

6 Conclusions

The RDM method has been used to compute the ground state energy and dipole moment of a collection of small molecules and molecular ions, both open- and closed-shells. Analysis of the computational cost shows a large advantage for the dual formulation (as opposed to the primal one) for solving the semidefinite programs that arise. The addition of the three-index representability conditions $T1$ and $T2$ provided a significant improvement of accuracy both on the ground state energy and the dipole moment over that obtained using only the P , Q and G conditions. In the cases studied, the error in the ground state energy (in the model space) was below 0.9 milli-Hartree (except the O_2^+ molecule, 2.8 mH); and the error in the dipole moment was below 0.0005 a.u. (except the CF molecule, 0.0045 a.u.).

As indicated by the two exceptions (the molecules O_2^+ and CF), the $(P, Q, G, T1, T2)$ family of conditions still leaves room for improvement. Some version of the higher-index diagonal conditions [5] (which must hold for any choice of one-electron basis) and of the Hamiltonian-related N -representability conditions (*e.g.*, [8]) may find their roles in the RDM method.

All our calculations were done using a general-purpose semidefinite programming software. Certainly the systems that we were able to handle this way are very small by the standards of *ab initio* quantum chemistry, and a challenge for future work will be to develop optimized computational methods for the present application while preserving the high accuracy that is obtained by use of the SDPARA code.

The familiar determinantal approximations are poor at representing the cusp in the wavefunction where two electron positions coincide. For high accuracy calculations the RDM formulations seems a perfect setting for incorporating cusp conditions. This will require choosing a different basis for the 2-RDM than the one formed by the antisymmetrized products of the 1-RDM basis functions, and it will affect the linear relations between the 1-RDM, 2-RDM, and the matrices that occur in the representability conditions. Ways of incorporating the cusp into the 2-RDM need to be investigated.

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Tables

Table 1: The ground state energies (in difference from that of the full CI) calculated by the RDM method adding (P,Q) , (P,Q,G) , $(P,Q,G,T1)$, $(P,Q,G,T2)$, $(P,Q,G,T1,T2)$ conditions (columns 6–10), and those obtained by methods CCSD(T), BD(T), SDCI and Hartree-Fock (columns 11–14) from Gaussian 98. The last column shows the full CI result. The energy and the energy differences are in Hartree. Here r is the basis size, $N(N_\alpha)$ is the electron (α electron) number, and $2S + 1$ is the multiplicity. The geometries used are the experimental ones from [31]. The basis set is STO-6G for all systems.

System	State	$N(N_\alpha)$	r	$2S + 1$	ΔE_{PQ}	ΔE_{PQG}	ΔE_{PQGT1}	ΔE_{PQGT2}	$\Delta E_{PQGT1T2}$	$\Delta E_{CCSD(T)}$	$\Delta E_{BD(T)}$	ΔE_{SDCI}	ΔE_{HF}	E_{FCI}
LiH	$^1\Sigma^+$	4(2)	12	1	-0.0008	-0.0000	-0.0000	-0.0000	-0.0000	+0.0002	+0.0002	+0.0002	+0.0204	-7.9723
BeH	$^2\Sigma^+$	5(3)	12	2	-0.0106	-0.0000	-0.0000	-0.0000	-0.0000	+0.0006	+0.0005	+0.0008	+0.0222	-15.1163
BH ⁺	$^2\Sigma^+$	5(3)	12	2	-0.0155	-0.0000	-0.0000	-0.0000	-0.0000	+0.0006	+0.0005	+0.0008	+0.0295	-24.8014
BH	$^1\Sigma^+$	6(3)	12	1	-0.0641	-0.0037	-0.0015	-0.0000	-0.0000	+0.0005	+0.0005	+0.0022	+0.0579	-25.0594
CH ⁺	$^1\Sigma^+$	6(3)	12	1	-0.0765	-0.0043	-0.0019	-0.0000	-0.0000	+0.0003	+0.0003	+0.0020	+0.0601	-37.8852
CH	$^2\Pi$	7(4)	12	2	-0.0601	-0.0046	-0.0017	-0.0000	-0.0000	+0.0001	+0.0001	+0.0010	+0.0416	-38.1871
CH ⁻	$^3\Sigma^-$	8(5)	12	3	-0.0113	-0.0000	-0.0000	-0.0000	-0.0000	+0.0001	+0.0001	+0.0001	+0.0185	-37.9672
NH ⁺	$^2\Pi$	7(4)	12	2	-0.0610	-0.0043	-0.0019	-0.0000	-0.0000	+0.0001	+0.0001	+0.0008	+0.0403	-54.3974
NH	$^3\Sigma^-$	8(5)	12	3	-0.0119	-0.0000	-0.0000	-0.0000	-0.0000	+0.0002	+0.0002	+0.0002	+0.0231	-54.8162
NH ⁻	$^2\Pi$	9(5)	12	2	-0.0142	-0.0001	-0.0000	-0.0000	-0.0000	+0.0001	+0.0001	+0.0001	+0.0225	-54.5167
OH ⁺	$^3\Sigma^-$	8(5)	12	3	-0.0086	-0.0000	-0.0000	-0.0000	-0.0000	-0.0001	-0.0001	-0.0001	+0.0190	-74.7719
OH	$^2\Pi$	9(5)	12	2	-0.0150	-0.0001	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	+0.0247	-75.1014
OH ⁻	$^1\Sigma^+$	10(5)	12	1	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	+0.0002	+0.0002	+0.0002	+0.0247	-74.8037
HF ⁺	$^2\Pi$	9(5)	12	2	-0.0097	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	+0.0173	-99.1278
HF	$^1\Sigma^+$	10(5)	12	1	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.0001	-0.0001	-0.0001	+0.0258	-99.5256
BH ₂	2A_1	7(4)	14	2	-0.0517	-0.0057	-0.0015	-0.0001	-0.0001	+0.0005	+0.0005	+0.0011	+0.0377	-25.7031
CH ₂	1A_1	8(4)	14	1	-0.1186	-0.0118	-0.0032	-0.0001	-0.0001	+0.0005	+0.0005	+0.0031	+0.0610	-38.8106
CH ₂	3B_1	8(5)	14	3	-0.0501	-0.0031	-0.0002	-0.0000	-0.0000	+0.0002	+0.0002	+0.0007	+0.0378	-38.8533
NH ₂	2B_1	9(5)	14	2	-0.0699	-0.0038	-0.0013	-0.0000	-0.0000	+0.0001	+0.0001	+0.0008	+0.0462	-55.4157
H ₂ O ⁺	2B_1	9(5)	14	2	-0.0710	-0.0027	-0.0008	-0.0000	-0.0000	+0.0000	+0.0001	+0.0006	+0.0416	-75.4187
H ₂ O	1A_1	10(5)	14	1	-0.0660	-0.0020	-0.0011	-0.0000	-0.0000	+0.0001	+0.0001	+0.0008	+0.0500	-75.7287
NH ₃	1A_1	10(5)	16	1	-0.1442	-0.0109	-0.0024	-0.0003	-0.0003	+0.0003	+0.0003	+0.0018	+0.0628	-56.0142
H ₃ O ⁺	1A_1	10(5)	16	1	-0.1794	-0.0073	-0.0020	-0.0002	-0.0002	+0.0002	+0.0002	+0.0016	+0.0633	-76.1046
CF	$^2\Pi$	15(8)	20	2	-0.3018	-0.0076	-0.0058	-0.0009	-0.0009	+0.0010	+0.0016	+0.0064	+0.0761	-136.6775
O ₂ ⁺	$^2\Pi_g$	15(8)	20	2	-0.6932	-0.0167	-0.0147	-0.0028	-0.0028	+0.0033	+0.0034	+0.0124	+0.1701	-148.7933
O ₂	$^3\Sigma_g^-$	16(9)	20	3	-0.3168	-0.0039	-0.0036	-0.0001	-0.0001	+0.0018	+0.0019	+0.0051	+0.1119	-149.1639
SiH	$^2\Pi$	15(8)	20	2	-0.0488	-0.0031	-0.0009	-0.0001	-0.0001	+0.0024	+0.0024	+0.0030	+0.0366	-288.3775
SiH ⁻	$^3\Sigma^-$	16(9)	20	3	-0.0116	-0.0000	-0.0000	-0.0000	-0.0000	+0.0016	+0.0016	+0.0016	+0.0190	-288.1319
NO ⁻	$^3\Sigma^-$	16(9)	20	3	-0.2410	-0.0027	-0.0023	-0.0001	-0.0001	+0.0009	+0.0015	+0.0036	+0.0828	-128.6657
NF	$^3\Sigma^-$	16(9)	20	3	-0.1859	-0.0015	-0.0012	-0.0000	-0.0000	+0.0013	+0.0019	+0.0028	+0.0603	-153.2449
HS ⁺	$^3\Sigma^-$	16(9)	20	3	-0.0103	-0.0000	-0.0000	-0.0000	-0.0000	+0.0000	+0.0000	+0.0000	+0.0220	-396.4986

Table 2: The ground state energies in Hartree calculated by the RDM method adding (P,Q) , (P,Q,G) , $(P,Q,G,T1)$, $(P,Q,G,T2)$, $(P,Q,G,T1,T2)$ conditions (columns 6–10), and those obtained by methods CCSD(T), BD(T), SDCI and Hartree-Fock (columns 11–14) from Gaussian 98. Here r is the basis size, $N(N_\alpha)$ is the electron (α electron) number, and $2S + 1$ is the multiplicity. The geometries used are the experimental ones from [31]. The basis set is STO-6G for all systems. The values marked with * in column 11 are calculated by the CCSD method (CCSD(T) is not able to solve them under the chosen basis).

System	State	$N(N_\alpha)$	r	$2S + 1$	E_{PQ}	E_{PQG}	E_{PQGT1}	E_{PQGT2}	$E_{PQGT1T2}$	$E_{\text{CCSD(T)}}$	$E_{\text{BD(T)}}$	E_{SDCI}	E_{HF}
Li ₂	$^1\Sigma g^+$	6(3)	20	1	-14.8437	-14.8380	-14.8379	-14.8378	-14.8377	-14.8368	-14.8368	-14.8368	-14.8089
B ₂	$^3\Sigma g^-$	10(6)	20	3	-49.8855	-49.0475	-49.0367	-49.0177	-49.0176	-48.9235	-48.9223	-48.9113	-48.7835
C ₂ ⁺	$^4\Sigma g^-$	11(7)	20	4	-76.0511	-75.0994	-75.0891	-75.0790	-75.0790	-75.0723*	-75.0714	-75.0637	-74.9354
C ₂	$^1\Sigma g^+$	12(6)	20	1	-77.3398	-75.4800	-75.4595	-75.4382	-75.4382	-75.4311	-75.4310	-75.3799	-75.1626
C ₂ ⁻	$^2\Sigma g^+$	13(7)	20	2	-76.4526	-75.3395	-75.3271	-75.3162	-75.3162	-75.3060	-75.3082	-75.2926	-75.1374
LiF	$^1\Sigma^+$	12(6)	20	1	-106.7810	-106.4453	-106.4450	-106.4440	-106.4440	-106.4443	-106.4401	-106.4315	-106.3731
BeO	$^1\Sigma^+$	12(6)	20	1	-90.2936	-89.2128	-89.2091	-89.2015	-89.2015	-89.1967	-89.1938	-89.1802	-89.0517
NaH	$^1\Sigma^+$	12(6)	20	1	-161.9805	-161.7413	-161.7395	-161.7380	-161.7380	-161.6945	-161.6945	-161.6945	-161.6821
BeF	$^2\Sigma^+$	13(7)	20	2	-113.9778	-113.6438	-113.6424	-113.6410	-113.6410	-113.6403	-113.6388	-113.6335	-113.5806
BO	$^2\Sigma^+$	13(7)	20	2	-100.0635	-99.2696	-99.2642	-99.2591	-99.2591	-99.2549	-99.2542	-99.2445	-99.1333
N ₂ ⁺	$^2\Sigma g^+$	13(7)	20	2	-109.5025	-108.2520	-108.2370	-108.2246	-108.2246	-108.2132*	-108.2158	-108.1974	-108.0162
N ₂	$^1\Sigma g^+$	14(7)	20	1	-109.4479	-108.7126	-108.7093	-108.7018	-108.7018	-108.6980	-108.6980	-108.6876	-108.5418
CO ⁺	$^2\Sigma^+$	13(7)	20	2	-113.0459	-112.0536	-112.0448	-112.0379	-112.0379	-112.0321	-112.0320	-112.0184	-111.8890
CO	$^1\Sigma^+$	14(7)	20	1	-113.1175	-112.4547	-112.4501	-112.4439	-112.4439	-112.4418	-112.4407	-112.4300	-112.3033
BF	$^1\Sigma^+$	14(7)	20	1	-123.9645	-123.6187	-123.6156	-123.6125	-123.6125	-123.6112	-123.6110	-123.6035	-123.5271
AlH	$^1\Sigma^+$	14(7)	20	1	-241.5615	-241.5095	-241.5081	-241.5073	-241.5073	-241.5005	-241.5005	-241.4996	-241.4571

Table 3: Dipole moments in a.u. calculated by the RDM method adding (P,Q) , (P,Q,G) , $(P,Q,G,T1)$, $(P,Q,G,T2)$, $(P,Q,G,T1,T2)$ conditions (columns 6–10), by methods SDCI and Hartree-Fock (columns 11–12) from Gaussian 98, and by full CI (last column). Here r is the basis size, $N(N_\alpha)$ is the electron (α electron) number, and $2S + 1$ is the multiplicity. The geometries used are the experimental ones from [31]. The basis set is STO-6G for all systems. Symbol “—” in the last column means that we do not have a full CI result.

System	State	$N(N_\alpha)$	r	$2S + 1$	D_{PQ}	D_{PQG}	D_{PQGT1}	D_{PQGT2}	$D_{PQGT1T2}$	D_{SDCI}	D_{HF}	D_{FCI}
LiH	$^1\Sigma^+$	4(2)	12	1	1.8346	1.8449	1.8449	1.8448	1.8448	1.8454	1.9339	1.8448
BeH	$^2\Sigma^+$	5(3)	12	2	0.1821	0.1984	0.1984	0.1984	0.1984	0.1999	0.2532	0.1984
BH ⁺	$^2\Sigma^+$	5(3)	12	2	0.1407	0.1680	0.1679	0.1679	0.1679	0.1672	0.2054	0.1679
BH	$^1\Sigma^+$	6(3)	12	1	0.0358	0.2333	0.2425	0.2412	0.2412	0.2471	0.3806	0.2412
CH ⁺	$^1\Sigma^+$	6(3)	12	1	0.1870	0.4296	0.4420	0.4489	0.4489	0.4569	0.5855	0.4490
CH	$^2\Pi$	7(4)	12	2	0.2717	0.3811	0.3839	0.3791	0.3791	0.3824	0.4427	0.3792
CH ⁻	$^3\Sigma^-$	8(5)	12	3	0.3203	0.3294	0.3294	0.3294	0.3294	0.3765	0.3641	0.3294
NH ⁺	$^2\Pi$	7(4)	12	2	0.5271	0.6831	0.6848	0.6874	0.6874	0.6917	0.7813	0.6875
NH	$^3\Sigma^-$	8(5)	12	3	0.4730	0.4996	0.4996	0.4996	0.4996	0.4996	0.5290	0.4996
NH ⁻	$^2\Pi$	9(5)	12	2	0.2242	0.2218	0.2219	0.2219	0.2219	0.2498	0.2441	0.2219
OH ⁺	$^3\Sigma^-$	8(5)	12	3	0.7809	0.8118	0.8118	0.8118	0.8118	0.8117	0.8826	0.8118
OH	$^2\Pi$	9(5)	12	2	0.4497	0.4744	0.4745	0.4745	0.4745	0.4746	0.5173	0.4745
OH ⁻	$^1\Sigma^+$	10(5)	12	1	0.1099	0.1099	0.1099	0.1099	0.1099	0.1222	0.1218	0.1099
HF ⁺	$^2\Pi$	9(5)	12	2	0.8661	0.9059	0.9060	0.9060	0.9060	0.9059	0.9828	0.9060
HF	$^1\Sigma^+$	10(5)	12	1	0.4683	0.4683	0.4683	0.4683	0.4683	0.4683	0.5228	0.4683
BH ₂	2A_1	7(4)	14	2	0.0037	0.0328	0.0347	0.0344	0.0344	0.0351	0.0498	0.0344
CH ₂	1A_1	8(4)	14	1	0.2439	0.5073	0.5264	0.5308	0.5308	0.5483	0.6243	0.5311
CH ₂	3B_1	8(5)	14	3	0.0941	0.0965	0.0936	0.0937	0.0937	0.0939	0.0964	0.0937
NH ₂	2B_1	9(5)	14	2	0.6433	0.6817	0.6856	0.6895	0.6895	0.6908	0.7207	0.6896
H ₂ O ⁺	2B_1	9(5)	14	2	0.7921	0.8916	0.8957	0.8985	0.8985	0.9001	0.9572	0.8987
H ₂ O	1A_1	10(5)	14	1	0.6003	0.6467	0.6461	0.6492	0.6492	0.6509	0.6931	0.6493
NH ₃	1A_1	10(5)	16	1	0.0785	0.0748	0.0791	0.0799	0.0799	0.0803	0.0789	0.0800
H ₃ O ⁺	1A_1	10(5)	16	1	0.6435	0.7106	0.7179	0.7202	0.7201	0.7216	0.7504	0.7203
LiF	$^1\Sigma^+$	12(6)	20	1	4.6284	0.8191	0.8235	0.8433	0.8433	0.9697	1.4537	—
BeO	$^1\Sigma^+$	12(6)	20	1	5.1010	0.7407	0.8056	0.9072	0.9077	1.1655	1.7150	—
NaH	$^1\Sigma^+$	12(6)	20	1	2.0351	2.4098	2.4125	2.4155	2.4155	2.4409	2.6303	—
BeF	$^2\Sigma^+$	13(7)	20	2	2.9972	0.2181	0.2103	0.2001	0.2001	0.1430	0.1428	—
BO	$^2\Sigma^+$	13(7)	20	2	2.0005	0.3737	0.4022	0.4218	0.4218	0.4937	0.6661	—
CO ⁺	$^2\Sigma^+$	13(7)	20	2	1.1007	0.7792	0.8177	0.8393	0.8393	0.9237	1.0091	—
CO	$^1\Sigma^+$	14(7)	20	1	1.1469	0.2399	0.2382	0.2291	0.2292	0.2117	0.0402	—
BF	$^1\Sigma^+$	14(7)	20	1	2.1362	0.5413	0.5274	0.5236	0.5236	0.4906	0.4082	—
AlH	$^1\Sigma^+$	14(7)	20	1	0.4699	0.5311	0.5358	0.5382	0.5381	0.5385	0.5065	—
CF	$^2\Pi$	15(8)	20	2	1.6818	0.4505	0.4480	0.4255	0.4255	0.3929	0.2440	0.4210
SiH	$^2\Pi$	15(8)	20	2	0.1202	0.0795	0.0838	0.0920	0.0920	0.0900	0.0700	0.0919
SiH ⁻	$^3\Sigma^-$	16(9)	20	3	0.1317	0.1244	0.1244	0.1244	0.1244	0.1308	0.1669	0.1244
NO ⁻	$^3\Sigma^-$	16(9)	20	3	0.7477	0.3683	0.3681	0.3592	0.3592	0.3755	0.1723	0.3591
NF	$^3\Sigma^-$	16(9)	20	3	1.1850	0.2502	0.2500	0.2415	0.2415	0.2320	0.0773	0.2410
HS ⁺	$^3\Sigma^-$	16(9)	20	3	0.4708	0.5126	0.5126	0.5127	0.5127	0.5135	0.5834	0.5127