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Title	Variational calculation of second-order reduced density matrices by strong N-representability conditions and an accurate semidefinite programming solver
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Citation	The Journal of Chemical Physics, Vol. 128, No. 16,
Pub. date	2008, 4
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Variational calculation of second-order reduced density matrices by strong *N*-representability conditions and an accurate semidefinite programming solver

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(Received 10 January 2008; accepted 26 March 2008; published online 29 April 2008)

The reduced density matrix (RDM) method, which is a variational calculation based on the second-order reduced density matrix, is applied to the ground state energies and the dipole moments for 57 different states of atoms, molecules, and to the ground state energies and the elements of 2-RDM for the Hubbard model. We explore the well-known *N*-representability conditions (*P*, *Q*, and *G*) together with the more recent and much stronger *T*1 and *T*2′ conditions. *T*2′ condition was recently rederived and it implies *T*2 condition. Using these *N*-representability conditions, we can usually calculate correlation energies in percentage ranging from 100% to 101%, whose accuracy is similar to CCSD(T) and even better for high spin states or anion systems where CCSD(T) fails. Highly accurate calculations are carried out by handling equality constraints and/or developing multiple precision arithmetic in the semidefinite programming (SDP) solver. Results show that handling equality constraints correctly improves the accuracy from 0.1 to 0.6 mhartree. Additionally, improvements by replacing *T*2 condition with *T*2′ condition are typically of 0.1–0.5 mhartree. The newly developed multiple precision arithmetic version of SDP solver calculates extraordinary accurate energies for the one dimensional Hubbard model and Be atom. It gives at least 16 significant digits for energies, where double precision calculations gives only two to eight digits. It also provides physically meaningful results for the Hubbard model in the high correlation limit. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2911696]

I. INTRODUCTION

We are interested in many-particle fermionic systems with one-particle and two-particle interactions only. For such systems, knowledge of the second-order reduced density matrix (2-RDM) is sufficient to describe all physical quantities. Besides, the number of variables in the 2-RDM is always four regardless of the number of particles involved, whereas for the wavefunction, this number scales linearly. This is the motivation to use the 2-RDM as a basic variable and determine it directly instead of using the wavefunction.

Husimi gave the first definition of the reduced density matrix of general order.[1] Interest in RDMs increased rapidly after Löwdin[2] and Mayer[3] took up his idea without the knowledge of his work. However, Mayer,[3] Ayers[4] Coulson,[5] and Tredgold[6] obtained energies far below from their exact values, and it was evident that some very strong conditions should be applied to the 2-RDM.

Such conditions were first clearly stated as *N*-representability condition by Coleman in his seminal survey paper.[7] The *N*-representability condition is formulated as follows: For a given 2-RDM, there exist some wavefunctions (or ensemble) which are antisymmetric with respect to the change of particles. This is the major target of studies along this line, and is known to be very difficult.[8–10] Thus, how we find a good approximation for the *N*-representability conditions and how we calculate the ground state energy with these *N*-representability are the essentials of this study. On the other hand, in the wavefunction context, the corresponding condition is trivial: The wavefunction must be antisymmetric with respect to the change of two particles.

Well-known necessary *N*-representability conditions are

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P, Q formulated by Coleman,[7] and G formulated by Garrod *et al.*[11] These conditions are of positive semidefinite forms. The first application to Be atom was done by Garrod *et al.* with P, Q, and G conditions as N-representability conditions.[12,13] They studied these conditions via a kind of convex optimization problem which is now called semidefinite programming (SDP), and obtained very good energies compared to full configuration interaction (CI) ones. Even though these results were very promising, it seems they lost their motivation because (i) P, Q, and G conditions are not sufficient for nucleon systems where two body interactions are very strong,[14] (ii) there was no established SDP solver at that time, and (iii) lack of computer resources. Through the next 20 years after the work of Garrod *et al.*, there was certainly theoretical interest in the RDM method, as seen, for example, in Ref. 15. However, there were very little computational works which applied the RDM method to atomic and molecular electronic structure problem: Especially Valdemoro,[16] and Nakatsuji *et al.*[17] in the context of the density equation or the contracted Schödinger equation.[18] See also Mazziotti's summary of their works.[19] Then, there were two breakthroughs in this method. One is by Nakata and co-workers,[20,21] who formulated the RDM method, the variational calculation of the 2-RDM using P, Q, and G as the N-representability conditions and other trivial ones, as a primal standard form of the SDP and solved it with a well-established solver called SDPA.[22] They applied to a variety of small atoms and molecules. These results were far better than Hartree–Fock[20] and even described dissociation limits of diatomic molecules where the traditional quantum chemical methods such as MP2 and CCSD(T) fail.[21] However, the incorporation of only P, Q, and G conditions caught too much correlation energies and these results were still inferior to the chemical accuracy, 1 kcal/mol (about 0.0016 hartree). Little earlier, Erdahl and Jin also applied the RDM method to a quantum lattice problem but emphasis was on the higher order representability conditions.[23,24]

The other breakthrough was reported by Zhao *et al.*[25] They firstly implemented $T1$ and $T2$ conditions stated implicitly in Erdahl's paper[26] and applied them to small atoms and molecules. These results were exciting as they were comparable to the CCSD(T) method. The deviations of the total energy were usually below than 0.1 kcal/mol (about 0.000 16 hartree), thus the RDM method with these N-representability conditions accomplished the spectroscopic accuracy. Also, they reformulated the RDM method as a dual standard form of SDP and reduced the computational cost considerably. Unfortunately, the dual standard form could not directly handle equality constraints in SDPA. They split one equality constraint, for example, constraining the number of electrons, into two inequalities with a small gap and introduced additional numerical errors.

In the present work, we explore two major topics via applying the RDM method to various systems: (1) Incorporating stronger N-representability condition and (2) developing better and accurate SDP solvers. For (1), we use $T2'$ condition which is formulated, implemented, and applied by Braams *et al.*[28] to NH_3, H_3O^+, CF, and O_2^+ which gave the worst four deviations from the fullCI in Ref. 25, and Mazziotti applied it to BH, BeH_2, H_2O, NH_3, CH_4, CO, and to the potential curve of the nitrogen molecule (he calls this condition $\bar{T}2$).[29] In the present article, we explore $T2'$ condition on 57 different atomic and molecular systems including some excited states such as high-spin states. Actually, $T2'$ implies $T2$ condition, thus $T2'$ is really stronger than $T2$, but improvements are not so drastic according to our results. The ground state energies are amended from 0.1 to 0.5 mhartree for about 20 systems. For (2), we solve these systems with an SDP solver which handles equality constraints exactly. Preliminary experiments were carried out in Ref. 30, and computation with equality constraints improves the total energy about 0.1–0.6 mhartree here.

We also analyze the results for calculating the dipole moments. As we see from Refs. 10 and 25, we can obtain better dipole moments when more N-representability conditions are considered. We discuss the effects of degeneracy as well. In some cases, we observe that we need more N-representability conditions.

Furthermore, we develop a general SDP solver with multiple precision arithmetic to obtain ultra high accurate solutions. Even though we have employed the primal-dual interior-point method for solving SDPs, typical accuracy of the computed energy has only seven to eight significant digits for quantum chemical problems. Hammond and Mazziotti[31] calculated three to four significant digits for the Hubbard model. This lack of accuracy becomes a problem if the size of systems becomes larger and/or the ground state becomes quasidegenerated. Here, we apply the newly developed SDP solver to the one dimensional (1D) Hubbard model and Be atom, and obtain extremely accurate energies with at least 16 digits.

For recent progress, Mazziotti[32] implemented a special case of Burer and Monteiro's low-factorization method,[33] in which they reformulated the SDP as a nonlinear and nonconvex optimization problem and applied a combination of the augmented Lagrangian method with the quasi-Newton method. Cancès *et al.*[34] reformulated the same problem in the dual space and solved several larger atoms and molecules. Mazziotti applied positive semidefiniteness of third-order RDMs to small molecules.[29] Also, Kollmar[35] parametrized 2-RDM in terms of CI-like coefficients size extensively, and obtained similar accuracy to CCSD for a variety of small molecules. Kuzelnigg employed 1-RDM and two-particle cumulant as basic variables and employed coupled electron pair approximation to avoid to directly treat N-representability condition.[36] Mazziotti obtained 2-RDM via anti-Hermitian contracted Schrödinger equation.[37] In their methods,[35–37] they avoid to use computationally expensive SDP. Finally, we note the recent work by Shenvi and Whaley on expectation value constraints,[38] which appears more valuable for bosonic than for fermionic systems, and by Juhász *et al.* on linear relaxations of the (semidefinite) $T2$ conditions.[39]

We formulate the problem into a SDP and obtain high accuracy in the RDM method.

This paper is organized as follows. Section II gives a brief summary of the RDM method and N-representability conditions including $T2'$ condition. In Sec. III, we show the

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main numerical results: Details of calculations, the total energy by various N-representability conditions, and the dipole moments for 57 systems. Section IV discusses some other results in detail: Handling equality constraints in the SDP formulations; analysis of error bounds on operators; effects of degeneracy of the Hamiltonian, which becomes crucial for obtaining expectation values, with some cases where the energies were not correctly degenerated; results of the ultrahigh accurate SDP solver on the 1D Hubbard model; and calculation time for the largest systems and for the Hubbard model using the ultrahigh accurate solver. Finally, Sec. V is for conclusion.

II. THEORY

A. The RDM method

We are interested in the ground state energy and properties of an N-particle fermionic system up to two-particle interactions. In this case, the Hamiltonian of the system can be written in the second quantized form like

$$H = \sum_{ij} v_j^i a_i^\dagger a_j + \frac{1}{2} \sum_{i_1 i_2 j_1 j_2} w_{j_1 j_2}^{i_1 i_2} a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1},$$

where v and w are the one- and two-particle operators and a and $a^\dagger$ are the annihilation and creation operators, respectively. Then the total energy of some N-particle state $|\Psi\rangle$ is given by $\langle\Psi|H|\Psi\rangle$. Furthermore, the total energy E can be expressed by

$$\begin{aligned} E &= \sum_{ij} v_j^i \langle\Psi|a_i^\dagger a_j|\Psi\rangle + \frac{1}{2} \sum_{i_1 i_2 j_1 j_2} w_{j_1 j_2}^{i_1 i_2} \langle\Psi|a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1}|\Psi\rangle \\ &= \sum_{ij} v_j^i \gamma_j^i + \sum_{i_1 i_2 j_1 j_2} w_{j_1 j_2}^{i_1 i_2} \Gamma_{j_1 j_2}^{i_1 i_2}, \end{aligned}$$

where the one-particle reduced density matrix (1-RDM) γ and the two-particle reduced density matrix (2-RDM) Γ are defined by

$$\gamma_j^i = \langle\Psi|a_i^\dagger a_j|\Psi\rangle,$$

and

$$\Gamma_{j_1 j_2}^{i_1 i_2} = \tfrac{1}{2}\langle\Psi|a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1}|\Psi\rangle,$$

respectively. Then, the ground state energy E_g can be obtained by minimizing the Hamiltonian in respect of the N-particle state:

$$E_g = \min_{\Psi} \langle\Psi|H|\Psi\rangle = \min_{\Gamma,\gamma} \left\{ \sum_{ij} v_j^i \gamma_j^i + \sum_{i_1 i_2 j_1 j_2} w_{j_1 j_2}^{i_1 i_2} \Gamma_{j_1 j_2}^{i_1 i_2} \right\}.$$

For a many-particle fermionic system, the wavefunction Ψ must be antisymmetric with respect to the change of particles:

$$\begin{aligned} &\Psi(1,2,3,\ldots,i,\ldots,j,\ldots,N) \\ &\quad = -\Psi(1,2,3,\ldots,j,\ldots,i,\ldots,N). \end{aligned}$$

For 1- and 2-RDMs, this antisymmetric condition becomes part of the N-representability conditions, and this can be understood as follows. For a given 1- or 2-RDM, there exist some wavefunctions (pure representability) or some von Neumann density matrices (ensemble representability) corresponding to it. The pure representability is very difficult and little is known about it. Therefore, we usually deal with the ensemble representability and hereafter N-representability will indicate the ensemble N-representability condition if not explicitly stated. In general, one does not deal even conceptually with the ensemble of antisymmetric Ψ but rather with the elementary properties of the annihilation and creation operators which are the objects that we actually use.

For the 1-RDM, the N-representability conditions are quite trivial; the 1-RDM is N-representable if it satisfies the conditions stated above and its eigenvalues lie between 0 and 1.[7] However, for the 2-RDM, the decision problem "is this RDM N-representable" is quantum Merlin–Arthur complete,[8] and hence, NP-hard, i.e., any polynomially bounded algorithm for solving it would imply a polynomially bounded algorithm for solving any NP problem. Furthermore, there does not exist a polynomial-time concise way of describing all the conditions for the diagonal subproblem unless NP=co-NP.[9,10] Thus, finding an effective or good approximation is a pragmatic approach and essential.

Some trivial conditions for the RDMs are as follows:

(1) the 1-RDM and the 2-RDM are Hermitian,

$$\gamma_j^i = \gamma_i^{j*}, \quad \Gamma_{j_1 j_2}^{i_1 i_2} = \Gamma_{i_1 i_2}^{j_1 j_2 *},$$

(2) the 2-RDM is antisymmetric,

$$\Gamma_{j_1 j_2}^{i_1 i_2} = -\Gamma_{j_1 j_2}^{i_2 i_1} = -\Gamma_{j_2 j_1}^{i_1 i_2} = \Gamma_{j_2 j_1}^{i_2 i_1},$$

(3) trace conditions are valid,

$$\sum_i \gamma_i^i = N, \quad \sum_{ij} \Gamma_{ij}^{ij} = \frac{N(N-1)}{2},$$

and

(4) there is a partial trace condition between the 1- and the 2-RDMs

$$\frac{N-1}{2} \gamma_j^i = \sum_k \Gamma_{jk}^{ik}.$$

For the 2-RDM, some well-known necessary conditions are P, Q,[7] and G (Ref. 11) defined by the positive semidefiniteness of the corresponding matrices,

$$P_{j_1 j_2}^{i_1 i_2} = \langle\Psi|a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1}|\Psi\rangle = 2\Gamma_{j_1 j_2}^{i_1 i_2},$$

$$\begin{aligned} Q_{j_1 j_2}^{i_1 i_2} &= \langle\Psi|a_{i_1} a_{i_2} a_{j_2}^\dagger a_{j_1}^\dagger|\Psi\rangle \\ &= (\delta_{j_1}^{i_1}\delta_{j_2}^{i_2} - \delta_{j_2}^{i_1}\delta_{j_1}^{i_2}) - (\delta_{j_1}^{i_1}\gamma_{j_2}^{i_2} + \delta_{j_2}^{i_2}\gamma_{j_1}^{i_1}) \\ &\quad + (\delta_{j_2}^{i_1}\gamma_{j_1}^{i_2} + \delta_{j_1}^{i_2}\gamma_{j_2}^{i_1}) + 2\Gamma_{j_1 j_2}^{i_1 i_2}, \end{aligned}$$

$$G_{j_1 j_2}^{i_1 i_2} = \langle\Psi|a_{i_1}^\dagger a_{i_2} a_{j_2}^\dagger a_{j_1}|\Psi\rangle = \delta_{j_2}^{i_2}\gamma_{j_1}^{i_1} - 2\Gamma_{j_1 i_2}^{i_1 j_2},$$

where δ is the Kronecker's delta. These conditions are surprisingly good N-representability conditions for atoms and molecules,[10,12,13,20,21,25,28–32,34,40] but not sufficient for nucleon systems.[14]

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Recently, Zhao *et al.*[25] implemented additional N-representability conditions which were implicitly stated in Erdahl's paper.[26] They are referred as $T1$ and $T2$ conditions and specify that the matrices $T1$ and $T2$ defined by the positive semidefiniteness of the following matrices:

$$(T1)^{i_1i_2i_3}_{j_1j_2j_3} = \langle\Psi|a^\dagger_{i_1}a^\dagger_{i_2}a^\dagger_{i_3}a_{j_3}a_{j_2}a_{j_1} + a_{i_1}a_{i_2}a_{i_3}a^\dagger_{j_3}a^\dagger_{j_2}a^\dagger_{j_1}|\Psi\rangle$$
$$= \mathcal{A}[i_1,i_2,i_3]\mathcal{A}[j_1,j_2,j_3]\left(\tfrac{1}{6}\delta^{i_1}_{j_1}\delta^{i_2}_{j_2}\delta^{i_3}_{j_3} - \tfrac{1}{2}\delta^{i_1}_{j_1}\delta^{i_2}_{j_2}\gamma^{j_3}_{j_3} + \tfrac{1}{2}\delta^{i_1}_{j_1}\Gamma^{i_2i_3}_{j_2j_3}\right),$$

$$(T2)^{i_1i_2i_3}_{j_1j_2j_3} = \langle\Psi|a^\dagger_{i_1}a^\dagger_{i_2}a_{i_3}a^\dagger_{j_3}a_{j_2}a_{j_1} + a^\dagger_{i_1}a_{i_2}a_{i_3}a^\dagger_{j_3}a^\dagger_{j_2}a_{j_1}|\Psi\rangle,$$
$$= \mathcal{A}[i_2,i_3]\mathcal{A}[j_2,j_3]\left(\tfrac{1}{2}\delta^{i_2}_{j_2}\delta^{i_3}_{j_3}\gamma^{i_1}_{j_1} + \tfrac{1}{2}\delta^{i_1}_{j_1}\Gamma^{j_2j_3}_{i_2i_3} - 2\delta^{i_2}_{j_2}\Gamma^{i_1j_3}_{j_1i_3}\right),$$

where $\mathcal{A}$ is antisymmetrizer acting on an arbitrary function $f(i,j,k)$,

$$\mathcal{A}[i,j,k]f(i,j,k) = f(i,j,k) - f(i,k,j) - f(j,i,k) + f(j,k,i) + (k,i,j) - f(k,j,i).$$

These conditions are proved to be very good restriction for quantum chemical systems.[10,25,40] However, it is known that these conditions are not sufficient even for some one-particle Hamiltonians.[41]

B. $T2'$ condition

Recently, Braams *et al.* formulated another new representability condition from Erdahl's paper,[26] which they call $T2'$ condition and applied it to NH_3, H_3O^+, CF, and O_2^+.[28] These molecules had the largest deviations of the ground state energies by P, Q, G, $T1$, and $T2$ conditions from the fullCI in Ref. 25. Mazziotti exactly derived the same condition, which he calls $\bar{T}2$ condition,[29] and applied it to BH, BeH_2, H_2O, NH_3, CH_4, CO, and to the potential curve of the nitrogen molecule.

$T2'$ condition is obtained by slightly strengthening $T2$ condition. Recall that $T2$ condition is derived by the semidefiniteness of the form

$$A^\dagger A + AA^\dagger,$$

where A is defined as

$$A = \sum_{i_1i_2i_3} g_{i_1i_2i_3}a^\dagger_{i_1}a^\dagger_{i_2}a_{i_3},$$

and $g_{i_1i_2i_3}$ are real parameters. The sum $A^\dagger A + AA^\dagger$ cancels the 3-RDM out, and thus, it does involve only the 1- and 2-RDMs. Next, consider a slight modification on this type of operator. Let us take B as

$$B = \sum_k h_k a_k,$$

where h_k are real parameters, and consider a combination of these two operators

$$(A+B)^\dagger(A+B) + AA^\dagger,$$

which must be also positive semidefinite, and involves only 1 and 2-RDMs. $T2'$ matrix is defined as

$$T2' = \begin{pmatrix} T_2 & X \\ X^\dagger & \gamma \end{pmatrix}.$$

This matrix has $T2$-matrix and the 1-RDM γ at the diagonal, and X is defined as

$$X^k_{i_1i_2i_3} = \Gamma^{i_1k}_{i_2i_3}.$$

More specifically, we can summarize the four blocks in $T2'$ matrix as follows.

$$(T2')^{i_1i_2i_3}_{j_1j_2j_3} = (T2)^{i_1i_2i_3}_{j_1j_2j_3},$$

$$(T2')^k_{j_1j_2j_3} = X^k_{j_1j_2j_3} = \Gamma^{j_1k}_{j_2j_3},$$

$$(T2')^{i_1i_2i_3}_l = (X^\dagger)^{i_1i_2i_3}_l = \Gamma^{i_2i_3}_{i_1l},$$

and

$$(T2')^k_l = \gamma^k_l.$$

For theoretical and historical details, the reader should refer to Refs. 28 and 29.

C. The energy relation

To simplify the notation, we use the corresponding letter as a subscript to indicate which N-representability conditions are imposed. For instance, $PQGT1$ means P, Q, G, and $T1$ conditions. Furthermore, there are obvious inclusion relations between the 2-RDMs satisfying PQG, $PQGT1$, $PQGT1T2$, and $PQGT1T2'$. Hence, the energies obtained by the RDM method with these conditions satisfy

$$E_{PQG} \leqslant E_{PQGT1} \leqslant E_{PQGT1T2} \leqslant E_{PQGT1T2'} \leqslant E_{\mathrm{fullCI}} \leqslant E_{\mathrm{HF}},$$

where E_{PQG} is the ground state energy with PQG, E_{fullCI}, and E_{HF} are the ground state energies computed by the fullCI calculation and Hartree–Fock calculation, respectively. There are no such clear relations for other one- and two-particle properties. See Sec. IV B for details.

D. Formulation as a SDP

We formulate the RDM method as a *dual standard SDP*:

$$\begin{cases} \min\limits_y & b^t y \\ \text{subject to} & \sum\limits_{p=1}^m A_p[y]_p - C \succeq O \\ & y \in \mathbb{R}^m, \end{cases} \tag{2.1}$$

where b and y are real m-dimensional column vectors, and $A_1, A_2, \ldots, A_p$, and C are block-diagonal real symmetric matrices (i.e., multiple symmetric matrices arranged diagonally in a unique large matrix) with prescribed dimensions. The notation b^t denotes the transpose of the vector b, $[y]_p$ is the pth coordinate of the vector y, and $X \succeq O$ means that the matrix X is a positive semidefinite symmetric matrix.

In general lines, the problems arising from the RDM method can be formulate as Eq. (2.1) if we represent all nonrepeating elements of the 1-RDM γ and the 2-RDM Γ

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(after considering the antisymmetric condition on γ and Γ) by the vector $y \in \mathbb{R}^m$. Then, defining an appropriate vector $b \in \mathbb{R}^m$ from the Hamiltonian for the corresponding system, the ground state energy of the system can be computed by minimizing $b^t y$ subject to the N-representability condition on γ and Γ. In this case, P, Q, G, $T1$, and $T2'$ (or $T2$) conditions will correspond to the block-diagonal matrices of $\Sigma_{p=1}^{m} A_p[y]_p - C$. See Refs. 10, 25, 30, and 42 for details.

Equality conditions such as the trace condition on the 1-RDM, $\Sigma_i \gamma_i^i = N$, can only be incorporated in Eq. (2.1) if we split it into two inequalities:

$$\sum_i \gamma_i^i - N \geqslant 0, \quad N - \sum_i \gamma_i^i \geqslant 0. \tag{2.2}$$

Recall that γ is represented by some elements of y in Eq. (2.1). This observation also applies to all equality conditions which are described in Secs. II A and III A.

Previous versions of SDPA (Ref. 22) and SDPARA (Ref. 43) were not able to directly solve problems with Eq. (2.2) and we were forced to introduce a small gap, replacing Eq. (2.2) by

$$\sum_i \gamma_i^i - N \geqslant -\epsilon, \quad N - \sum_i \gamma_i^i \geqslant -\epsilon, \tag{2.3}$$

where we typically set $\epsilon = 10^{-5}$. This enforcement by introducing a small perturbation to the formulation resulted in a lower value for the energy than it actually should be.[10,25]

Recently, we overcame this difficulty[30] by modifying a threshold in a subroutine of SDPA and SDPARA, and now these softwares can solve problems with equalities conditions which are represented by two inequalities of type Eq. (2.2), and finally, formulated as Eq. (2.1). Further discussion of this improvement consequences will be in Sec. IV A.

E. Handling multiple precision arithmetics

Usually, a real number is computed by the IEEE754 standard.[44] The double precision expressed in 52 significant bits represents approximately 16 significant digits. The double precision may probably be the most widely and frequently used precision in computer science, and implemented in the hardware (CPU) with a reliable efficiency. For example, the theoretical peak performance of widely available Pentium 4 2.4 GHz is 4.8 Gflops. It means that it can perform 4.8×10^9 of floating point operations per second. For example, when applying the RDM method to the systems which the ground state energy is quasidegenerated, the double precision is not sufficient. In this case, we need more precision and thus more significant digits. To solve such kind of problems, we developed a multiple precision arithmetic version of SDPA. See Sec. IV D for details. We used the GNU multiprecision arithmetic (GMP) library,[45] which is a library package for handling numbers with very large significant bits.

III. NUMERICAL RESULTS

A. Details of the calculation

We applied the RDM method for 57 atoms and molecules with different space, symmetries, neutral and charged, with different and several basis sets for the calculations. We also calculated the total energy of the 1D Hubbard model,[46] and the total energy and some randomly chosen elements of the 2-RDM of Be atom using the multiple arithmetic version of the SDP solver (see Sec. IV D). We used five different basis sets for the atoms and molecules: (1) Double-ζ (Refs. 47 and 48) for H_3, C($^3P, Sz=0,1$), N(^4S), O(^1D), O($^3P, Sz=0,1$), Ne, LiH, BH, CH, NH($^1\Delta, ^3\Sigma^-$), HF and H_2O, (2) diffuse p-type function with exponent 0.074 added to the double-ζ basis for F^- to describe the anion state better, (3) 6-31G [Ref. 49] basis set for P, (4) split valence[47,48] for Be denoted as SV, and (5) STO-6G (Ref. 50) for others and Be. All the basis sets were taken from the Gaussian basis set order form.[51]

The geometries we used in Tables I and II were the experimental ones from Refs. 52 and 53. The only exception is H_3 molecule, for which we used the meta stable $\tilde{A}$ Rydberg state. In Table III, we also used the experimental ones from Ref. 54. For the SDP calculations, we employed SDPARA (Ref. 43) with a slight modification to treat equality constraints.[30] For ultrahigh precision calculations of the SDPs, we implemented a multiple arithmetic version of SDPA using the GMP library.[45] The GMP enable us to perform calculation with arbitrary precision, and we replaced some double type variables in the source codes of SDPA, LAPACK, and BLAS with variables with arbitrary precision. This version of SDPA is called SDPA-GMP. For the fullCI, SDCI and Hartree–Fock calculations, we used GAMESS (Ref. 55) and for CCSD(T) we used GAUSSIAN98.[56]

For the N-representability conditions on the 1- and 2-RDMs, we imposed seven types of conditions: (1) Hermiticity of the matrices γ, Γ, Q, G, $T1$, $T2$, and $T2'$; (2) antisymmetric conditions; (3) positive semidefinite constraints on matrices γ, $I-\gamma$, Γ, Q, G, $T1$, $T2$, and $T2'$, where I is the identity matrix; (4) linear equality constraints involving the electron number N; (5) linear equality constraints involving the α electron number; (6) a linear equality constraint involving the total spin S; and (7) spin symmetries of matrices γ, Γ, Q, G, $T1$, $T2$, and $T2'$. See Sec. II D (Detailed summary of N-representability conditions) of Ref. 25 for details, except for $T2'$ condition.

Calculation time for some systems are shown in Table VIII.

B. Results with various *N*-representable sets

In Table I, we show the fullCI total energies of the systems and the deviations of the energies from the fullCI using various levels of approximations by the N-representability conditions: PQG, $PQGT1$, $PQGT1T2$, and $PQGT1T2'$, compared to the traditional methods: CCSD(T), SDCI, and Hartree–Fock. In the second row of each system, we present the correlation energy in percentage $\varepsilon_{\mathrm{corr}}$ relative to the Hartree–Fock (0%) and fullCI (100%) results defined as

$$\epsilon_{\mathrm{corr}} = \frac{|E - E_{\mathrm{HF}}|}{E_{\mathrm{HF}} - E_{\mathrm{fullCI}}} \times 100,$$

where E is calculated by the RDM method, CCSD(T) or SDCI; E_{HF} is the Hartree–Fock energy, and E_{fullCI} is the fullCI energy, respectively.

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TABLE I. The ground state energy deviations in hartree from FullCI calculated by the RDM method with various *N*-representability conditions: *PQG*, *PQGT*1, *PQGT*1*T*2, and *PQGT*1*T*2′ (column 7–10), and those obtained by CCSD(T), SDCI, and Hartree–Fock (column (11–13). The last column (column 14) shows the fullCI results. The correlations energies (0% for Hartree–Fock and 100% for fullCI) in percentage are also shown in the second row. N/A means not available. SPDs are solved by SDPARA with a modification.

System	State	Basis	r	$N(N_\alpha)$	$2S+1$	ΔE_{PQG}	ΔE_{PQGT1}	$\Delta E_{PQGT1T2}$	$\Delta E_{PQGT1T2'}$	$\Delta E_{\mathrm{CCSD(T)}}$	ΔE_{SDCI}	ΔE_{HF}	E_{FCI}
Li	^2S	STO-6G	10	3(2)	2	−0.0000	−0.0000	−0.0000	−0.0000	+0.000 00	+0.000 00	+0.000 01	−7.400 24
						100.0	100.0	100.0	100.0	99.98	100.00	0	100
Be	^1S	STO-6G	10	4(2)	1	−0.0000	−0.0000	−0.0000	−0.0000	+0.000 00	+0.000 01	+0.052 73	−14.556 09
						100.0	100.0	100.0	100.0	99.99	99.98	0	100
H_3	$^2A_1'$	double-ζ	12	3(2)	2	−0.0008	−0.0005	−0.0000	−0.0000	N/A	+0.000 10	+0.031 42	−1.486 13
						102.4	101.7	100.0	100.0	N/A	99.67	0	100
LiH	$^1\Sigma^+$	STO-6G	12	4(2)	1	−0.0000	−0.0000	−0.0000	−0.0000	+0.000 00	+0.000 01	+0.020 38	−7.972 82
						100.2	100.1	100.0	100.0	99.99	99.94	0	100
BeH^+	$^1\Sigma^+$	STO-6G	12	4(2)	1	−0.0000	−0.0000	−0.0000	−0.0000	+0.000 00	+0.000 02	+0.020 45	−14.843 33
						100.1	100.1	100.0	100.0	99.99	99.92	0	100
BeH	$^2\Sigma^+$	STO-6G	12	5(3)	2	−0.0001	−0.0000	−0.0000	−0.0000	+0.000 55	+0.000 58	+0.022 48	−15.116 27
						100.2	100.1	100.0	100.0	97.58	97.41	0	100
BH^+	$^2\Sigma^+$	STO-6G	12	5(3)	2	−0.0000	−0.0000	−0.0000	−0.0000	+0.000 30	+0.000 73	+0.030 29	−24.801 48
						100.1	100.1	100.0	100.0	98.02	97.58	0	100
NH_2^-	$^1A_1$	STO-6G	14	10(5)	1	−0.0020	−0.0013	−0.0000	−0.0000	+0.000 04	+0.000 66	+0.045 40	−55.160 75
						104.4	102.9	100.0	100.0	99.91	98.54	0	100
FH_2^+	$^1A_1$	STO-6G	14	10(5)	1	−0.0011	−0.0005	−0.0000	−0.0000	+0.000 05	+0.000 61	+0.041 55	−99.829 43
						102.6	101.2	100.0	100.0	99.88	98.53	0	100
CH_3^+	$^1E'$	STO-6G	16	8(4)	1	−0.0135	−0.0038	−0.0002	−0.0002	+0.000 17	+0.001 63	+0.059 58	−39.214 66
						122.6	106.4	100.3	100.3	99.72	97.27	0	100
CH_3	$^2A_2''$	STO-6G	16	9(5)	2	−0.0105	−0.0018	−0.0001	−0.0001	+0.000 41	+0.001 63	+0.063 08	−39.517 76
						116.7	102.8	100.2	100.1	99.35	97.41	0	100
NH_3^+	$^2A_2''$	STO-6G	16	9(5)	2	−0.0098	−0.0018	−0.0002	−0.0001	+0.000 27	+0.001 49	+0.061 85	−55.792 44
						115.8	102.8	100.3	100.2	99.57	97.50	0	100
Be	^1S	Split valence	18	4(2)	1	−0.0001	−0.0000	−0.0000	−0.0000	+0.000 00	+0.000 03	+0.044 66	−14.615 57
						100.1	100.1	100.0	100.0	100.00	99.93	0	100
CH_4	$^1A_1$	STO-6G	18	10(5)	1	−0.0195	−0.0041	−0.0002	−0.0002	+0.000 09	+0.002 73	+0.080 17	−40.190 60
						124.3	105.1	100.2	100.2	99.88	96.59	0	100
NH_4^+	$^1A_1$	STO-6G	18	10(5)	1	−0.0170	−0.0041	−0.0002	−0.0002	+0.000 12	+0.002 83	+0.082 89	−56.483 16
						120.6	105.0	100.3	100.3	99.85	96.59	0	100
Na	^2S	STO-6G	18	11(6)	2	−0.0010	−0.0004	−0.0000	−0.0000	−0.000 14	+0.001 44	+0.043 03	−161.076 97
						102.2	101.0	100.1	100.1	100.33	96.65	0	100
Li_2	$^1\Sigma_g^+$	STO-6G	20	6(3)	1	−0.0004	−0.0003	−0.0000	−0.0000	+0.000 01	+0.000 11	+0.028 76	−14.837 63
						101.3	101.0	100.0	100.0	99.97	99.61	0	100
C	^3P	double-ζ	20	6(4)	3	−0.0039	−0.0031	−0.0004	−0.0001	+0.000 16	+0.001 09	+0.052 02	−37.736 53
						107.5	105.9	100.7	100.1	99.69	97.90	0	100
C	^3P	double-ζ	20	6(3)	3	−0.0173	−0.0135	−0.0022	−0.0020	N/A	N/A	+0.052 02	−37.736 53
						133.4	126.0	104.3	103.9	N/A	N/A	0	100
N	^4S	double-ζ	20	7(5)	4	−0.0024	−0.0009	−0.0001	−0.0000	+0.000 07	+0.000 75	+0.048 17	−54.442 56
						104.9	101.8	100.1	100.0	99.86	98.44	0	100
O	^1D	double-ζ	20	8(4)	1	−0.0187	−0.0137	−0.0013	−0.0012	+0.002 79	+0.014 35	+0.108 78	−74.787 33
						117.2	112.6	101.2	101.1	97.43	86.81	0	100
O	^3P	double-ζ	20	8(5)	3	−0.0120	−0.0063	−0.0006	−0.0002	+0.000 09	+0.001 70	+0.069 05	−74.869 59
						117.4	109.1	100.9	100.4	99.87	97.54	0	100
O	^3P	double-ζ	20	8(4)	3	−0.0234	−0.0189	−0.0020	−0.0016	N/A	N/A	+0.069 05	−74.869 59
						134.0	127.4	102.9	102.3	N/A	N/A	0	100
Ne	^1S	double-ζ	20	10(5)	1	−0.0067	−0.0026	−0.0002	−0.0001	−0.000 05	+0.004 19	+0.116 45	−128.638 81
						105.8	102.3	100.1	100.1	100.04	96.40	0	100
LiF	$^1\Sigma^+$	STO-6G	20	12(6)	1	−0.0016	−0.0013	−0.0002	−0.0002	−0.000 83	+0.011 99	+0.070 67	−106.443 79
						102.3	101.9	100.4	100.3	101.17	83.03	0	100
BeO	$^1\Sigma^+$	STO-6G	20	12(6)	1	−0.0131	−0.0095	−0.0017	−0.0017	+0.002 41	+0.019 01	+0.147 88	−89.199 56
						108.9	106.4	101.2	101.2	98.37	87.14	0	100
BN	$^3\Pi$	STO-6G	20	12(7)	3	−0.0286	−0.0173	−0.0029	−0.0027	+0.023 97	+0.006 08	+0.108 92	−78.823 41
						126.3	115.9	102.7	102.4	77.99	94.42	0	100
C_2	$^1\Sigma_g^+$	STO-6G	20	12(6)	1	−0.0456	−0.0251	−0.0035	−0.0035	+0.002 85	+0.054 17	+0.271 88	−75.434 46
						116.8	109.2	101.3	101.3	98.95	80.08	0	100

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TABLE I. (*Continued.*)

System	State	Basis	r	$N(N_\alpha)$	$2S+1$	ΔE_{PQG}	ΔE_{PQGT1}	$\Delta E_{PQGT1T2}$	$\Delta E_{PQGT1T2'}$	$\Delta E_{\mathrm{CCSD(T)}}$	ΔE_{SDCI}	ΔE_{HF}	E_{FCI}
NaH	$^1\Sigma^+$	STO-6G	20	12(6)	1	−0.0034	−0.0016	−0.0001	−0.0001	−0.000 12	+0.002 75	+0.055 55	−161.737 70
						106.2	103.0	100.1	100.1	100.22	95.06	0	100
BO	$^2\Sigma^+$	STO-6G	20	13(7)	2	−0.0121	−0.0067	−0.0011	−0.0010	+0.002 18	+0.010 98	+0.134 62	−99.257 45
						109.0	105.0	100.8	100.7	98.38	91.84	0	100
CO^+	$^2\Sigma^+$	STO-6G	20	13(7)	2	−0.0179	−0.0092	−0.0015	−0.0014	+0.003 05	+0.014 04	+0.165 66	−112.035 56
						110.8	105.5	100.9	100.9	98.16	91.52	0	100
N_2^+	$^2\Sigma_g^+$	STO-6G	20	13(7)	2	−0.0307	−0.0156	−0.0023	−0.0022	+0.004 54	+0.023 94	+0.212 74	−108.221 30
						114.4	107.3	101.1	101.0	97.86	88.74	0	100
C_2^-	$^2\Sigma_g^+$	STO-6G	20	13(7)	2	−0.0264	−0.0139	−0.0021	−0.0019	+0.003 99	+0.020 42	+0.180 92	−75.313 21
						114.6	107.7	101.2	101.1	97.80	88.72	0	100
CN	$^2\Sigma^+$	STO-6G	20	13(7)	2	−0.0243	−0.0122	−0.0019	−0.0017	N/A	+0.017 72	+0.177 47	−92.070 18
						113.7	106.9	101.1	101.0	N/A	90.02	0	100
BeF	$^2\Sigma^+$	STO-6G	20	13(7)	2	−0.0031	−0.0017	−0.0002	−0.0002	+0.000 04	+0.006 04	+0.061 23	−113.640 65
						105.0	102.8	100.3	100.3	99.93	90.14	0	100
BF	$^1\Sigma^+$	STO-6G	20	14(7)	1	−0.0066	−0.0035	−0.0003	−0.0003	+0.000 41	+0.008 13	+0.084 88	−123.611 98
						107.8	104.1	100.4	100.4	99.51	90.42	0	100
CO	$^1\Sigma^+$	STO-6G	20	14(7)	1	−0.0118	−0.0072	−0.0009	−0.0009	+0.000 86	+0.012 62	+0.139 63	−112.442 97
						108.5	105.1	100.6	100.6	99.38	90.96	0	100
N_2	$^1\Sigma_g^+$	STO-6G	20	14(7)	1	−0.0121	−0.0088	−0.0012	−0.0012	+0.002 24	+0.012 68	+0.158 70	−108.700 52
						107.6	105.5	100.7	100.7	98.59	92.01	0	100
AlH	$^1\Sigma^+$	STO-6G	20	14(7)	1	−0.0023	−0.0008	−0.0000	−0.0000	+0.000 03	+0.001 43	+0.050 11	−241.507 20
						104.5	101.6	100.0	100.0	99.93	97.15	0	100
CF	$^2\Pi_r$	STO-6G	20	15(8)	2	−0.0076	−0.0058	−0.0006	−0.0005	+0.000 66	+0.003 58	+0.076 93	−136.677 34
						109.9	107.5	100.7	100.6	99.14	95.35	0	100
O_2^+	$^2\Pi_g$	STO-6G	20	15(8)	2	−0.0166	−0.0147	−0.0022	−0.0020	+0.003 25	+0.011 27	+0.170 74	−148.793 39
						109.7	108.6	101.3	101.2	98.10	93.40	0	100
HLi_2	$^2A_1$	STO-6G	22	7(4)	2	−0.0010	−0.0006	−0.0001	−0.0000	+0.000 22	+0.000 55	+0.023 50	−15.405 55
						104.3	102.8	100.2	100.1	99.07	97.67	0	100
LiOH	$^1\Sigma^+$	STO-6G	22	12(6)	1	−0.0086	−0.0040	−0.0006	−0.0006	−0.000 51	+0.010 87	+0.094 02	−82.648 42
						109.2	104.2	100.6	100.6	100.54	88.44	0	100
HN_2^+	$^1\Sigma^+$	STO-6G	22	14(7)	1	−0.0253	−0.0113	−0.0015	−0.0014	+0.002 05	+0.014 99	+0.171 80	−108.931 32
						114.7	106.6	100.9	100.8	98.81	91.28	0	100
HNO	$^1A'$	STO-6G	22	16(8)	1	−0.0190	−0.0136	−0.0009	−0.0009	+0.001 23	+0.009 35	+0.149 04	−129.447 91
						112.7	109.1	100.6	100.6	99.18	93.76	0	100
LiH	$^1\Sigma^+$	double-ζ	24	4(2)	1	−0.0003	−0.0002	−0.0000	−0.0000	+0.000 00	+0.000 24	+0.027 59	−8.008 68
						101.2	100.7	100.0	100.0	99.98	99.11	0	100
BH	$^1\Sigma^+$	double-ζ	24	6(3)	1	−0.0065	−0.0047	−0.0001	−0.0001	+0.000 30	+0.003 36	+0.073 98	−25.187 65
						108.8	106.3	100.1	100.1	99.60	95.45	0	100
CH	$^2\Pi_r$	double-ζ	24	7(4)	2	−0.0126	−0.0096	−0.0008	−0.0003	+0.000 31	+0.003 04	+0.078 95	−38.337 35
						115.9	112.2	101.0	100.4	99.60	96.15	0	100
NH	$^1\Delta$	double-ζ	24	8(4)	1	−0.0174	−0.0127	−0.0005	−0.0004	+0.004 57	+0.015 67	+0.114 95	−54.964 40
						115.1	111.1	100.4	100.4	96.20	86.37	0	100
NH	$^3\Sigma^-$	double-ζ	24	8(5)	3	−0.0098	−0.0052	−0.0003	−0.0001	+0.000 21	+0.002 43	+0.085 26	−55.036 14
						111.4	106.1	100.3	100.2	99.75	97.15	0	100
HF	$^1\Sigma^+$	double-ζ	24	10(5)	1	−0.0116	−0.0058	−0.0003	−0.0003	+0.000 32	+0.006 15	+0.138 32	−100.160 29
						108.4	104.2	100.2	100.2	99.77	95.56	0	100
BH_3O	$^1A_1$	STO-6G	26	16(8)	1	−0.0284	−0.0124	−0.0007	−0.0007	+0.000 33	+0.007 83	+0.112 60	−101.065 21
						125.2	111.0	100.6	100.6	99.71	93.04	0	100
CH_3N	$^1A_1$	STO-6G	26	16(8)	1	−0.0385	−0.0164	−0.0010	−0.0010	+0.000 73	+0.011 26	+0.157 41	−93.884 52
						124.5	110.4	100.6	100.6	99.54	92.85	0	100
SiH_4	$^1A_1$	STO-6G	26	18(9)	1	−0.0195	−0.0036	−0.0002	−0.0002	+0.000 18	+0.003 03	+0.073 11	−290.284 90
						126.6	105.0	100.3	100.2	99.75	95.86	0	100
F^-	^1S	DZ+d	26	10(5)	1	−0.0120	−0.0076	−0.0003	−0.0003	+0.000 67	+0.009 56	+0.154 27	−99.597 12
						107.8	104.9	100.2	100.2	99.57	93.80	0	100
P	^4S	6-31G	26	15(9)	4	−0.0008	−0.0003	−0.0001	−0.0000	+0.000 03	+0.000 22	+0.019 08	−340.708 02
						104.2	101.5	100.3	100.1	99.86	98.85	0	100
H_2O	$^1A_1$	double-ζ	28	10(5)	1	−0.0187	−0.0108	−0.0004	−0.0004	+0.000 55	+0.007 60	+0.146 45	−76.155 76
						112.7	107.3	100.3	100.3	99.63	94.81	0	100

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TABLE II. The dipole moments in Debye calculated by the RDM method with *PQG* (μ_{PQG}), *PQGT*1 (μ_{PQGT1}), *PQGT1T2* ($\mu_{PQGT1T2}$), *PQGT1T2′* ($\mu_{PQGT1T2'}$) conditions (columns 7–10) and those obtained by fullCI (μ_{FCI}), SDCI (μ_{SDCI}), and Hartree–Fock (μ_{HF}) (columns 11–13) for comparison.

System	State	Basis	r	$N(N_\alpha)$	$2S+1$	μ_{PQG}	μ_{PQGT1}	$\mu_{PQGT1T2}$	$\mu_{PQGT1T2'}$	μ_{FCI}	μ_{SDCI}	μ_{HF}
H_3	$^2A_1'$	double-ζ	12	3(2)	2	0.0000	0.0000	0.0000	0.0000[a]	0.859 48	0.860 38	0.921 10
LiH	$^1\Sigma^+$	STO-6G	12	4(2)	1	4.6898	4.6894	4.6890	4.6890	4.689 02	4.689 24	4.915 59
BeH^+	$^1\Sigma^+$	STO-6G	12	4(2)	1	3.7289	3.7289	3.7281	3.7280	3.728 05	3.728 31	3.978 76
BeH	$^2\Sigma^+$	STO-6G	12	5(3)	2	0.5046	0.5042	0.5042	0.5042	0.504 25	0.493 39	0.650 05
BH^+	$^2\Sigma^+$	STO-6G	12	5(3)	2	0.4268	0.4267	0.4267	0.4268	0.426 72	N/A	0.533 25
NH_2^-	$^1A_1$	STO-6G	14	10(5)	1	1.1796	1.1739	1.1789	1.1790	1.178 95	1.186 21	1.190 04
FH_2^+	$^1A_1$	STO-6G	14	10(5)	1	2.2965	2.2995	2.3037	2.3037	2.303 91	2.295 31	2.465 68
LiF	$^1\Sigma^+$	STO-6G	20	12(6)	1	2.0818	2.0931	2.1445	2.1445	2.157 34	2.025 55	3.694 90
BeO	$^1\Sigma^+$	STO-6G	20	12(6)	1	1.8827	2.0478	2.3085	2.3086	2.379 63	2.523 01	4.359 19
BN	$^3\Pi$	STO-6G	20	12(7)	3	1.0195	1.1564	1.3201	1.3211	1.404 70	1.368 15	2.260 35
NaH	$^1\Sigma^+$	STO-6G	20	12(6)	1	6.1247	6.1317	6.1400	6.1401	6.141 30	6.237 78	6.685 81
BO	$^2\Sigma^+$	STO-6G	20	13(7)	2	0.9495	1.0224	1.0771	1.0777	1.098 42	1.001 76	1.997 35
CO^+	$^2\Sigma^+$	STO-6G	20	13(7)	2	1.9801	2.0782	2.1372	2.1378	2.151 91	2.149 12	2.883 64
CN	$^2\Sigma^+$	STO-6G	20	13(7)	2	0.9456	1.0392	1.1388	1.1387	1.152 43	1.322 21	1.869 67
BeF	$^2\Sigma^+$	STO-6G	20	13(7)	2	0.5547	0.5346	0.5054	0.5048	0.498 86	0.597 49	0.391 85
BF	$^1\Sigma^+$	STO-6G	20	14(7)	1	1.3758	1.3405	1.3305	1.3305	1.325 88	1.370 95	1.037 21
CO	$^1\Sigma^+$	STO-6G	20	14(7)	1	0.6098	0.6052	0.5825	0.5825	0.570 43	0.720 11	0.102 12
AlH	$^1\Sigma^+$	STO-6G	20	14(7)	1	1.3492	1.3612	1.3671	1.3671	1.366 97	1.384 37	1.286 65
CF	$^2\Pi_r$	STO-6G	20	15(8)	2	1.1451	1.1389	1.0796	1.0796	1.070 22	1.101 53	0.615 31
HLi_2	$^2A_1$	STO-6G	22	7(4)	2	0.5619	0.5709	0.5759	0.5759	0.575 99	0.582 75	0.529 82
LiOH	$^1\Sigma^+$	STO-6G	22	12(6)	1	0.2144	0.2244	0.3191	0.3191	0.330 52	0.277 22	1.994 49
HN_2^+	$^1\Sigma^+$	STO-6G	22	14(7)	1	3.0863	3.1299	3.1685	3.1685	3.170 07	3.290 41	3.161 95
HNO	$^1A'$	STO-6G	22	16(8)	1	1.2122	1.2118	1.2503	1.2503	1.254 62	1.286 76	1.467 86
LiH	$^1\Sigma^+$	double-ζ	24	4(2)	1	5.5377	5.5417	5.5485	5.5485	5.548 57	5.573 12	5.937 83
BH	$^1\Sigma^+$	double-ζ	24	6(3)	1	1.5585	1.5656	1.5947	1.5948	1.594 51	1.662 81	2.030 62
CH	$^2\Pi_r$	double-ζ	24	7(4)	2	1.6483	1.6412	1.6370	1.6380	1.638 28	1.673 03	1.806 99
NH	$^1\Delta$	double-ζ	24	8(4)	1	1.8854	1.8792	1.8868	1.8869	1.888 22	1.873 16	1.998 42
NH	$^3\Sigma^-$	double-ζ	24	8(5)	3	1.8720	1.8655	1.8866	1.8873	1.887 63	1.892 02	1.924 96
HF	$^1\Sigma^+$	double-ζ	24	10(5)	1	2.2553	2.2605	2.2818	2.2817	2.282 09	2.283 78	2.378 62
BH_3O	$^1A_1$	STO-6G	26	16(8)	1	1.9053	1.8283	1.8414	1.8414	1.839 52	1.812 10	1.552 48
CH_3N	$^1A_1$	STO-6G	26	16(8)	1	1.6252	1.6626	1.7024	1.7023	1.706 17	1.715 63	1.871 75
H_2O	$^1A_1$	double-ζ	28	10(5)	1	2.5462	2.5503	2.5850	2.5850	2.585 82	2.600 57	2.681 89

[a]Result by SDPA-GMP.

We first discuss the results of *PQG* calculations. The correlation energies in percentage are from 100% to 110% for Li, Be (STO-6G), H_3, LiH (STO-6G), BeH^+, BeH, BH^+, NH_2^-, FH_2^+, Be (SV), Na, Li_2, $C(^3P,Sz=1)$, N, Ne, LiF, BeO, NaH, BO, BeF, BF, CO, N_2, AlH, CF, O_2^+, HLi_2, LiOH, LiH (double-ζ), BH, HF, F^-, and P; from 110% to 120% for CH_3, NH_3^+, $O(^1D)$, $O(^3P,Sz=1)$, C_2, CO^+, N_2^+, C_2^-, CN, HN_2^+, HNO, CH, $NH(^1\Delta)$, $NH(^3\Sigma^-)$, and H_2O; and from 120% to 140% for CH_3^+, CH_4, NH_4^+, $C(^3P,Sz=0)$, $O(^3P,Sz=0)$, BN, BH_3O, CH_3N, and SiH_4. The correlation energy errors are especially large for systems having three or four hydrogen atoms and high spins with $Sz=0$ state.

TABLE III. The ground state energy deviations in hartree from fullCI calculated by the RDM method with *PQGT1T2* conditions. $\Delta E_{PQGT1T2(\epsilon)}$, All equality conditions are treated via splitting to two inequalities with a small gap ($\epsilon=1.0\times10^{-5}$); $\Delta E_{PQGT1T2}$, Equality constraints without artificial gaps; and E_{FCI}, fullCI results. Note that for BH, $\Delta E_{PQGT1T2(\epsilon)}$ was calculated with *PQGT2*. $\Delta E_{PQGT1T2(\epsilon)}$ were taken from Refs. 10 and 25. For the basis sets, we used double-ζ for C, O, BH and HF, and STO-6G for the others.

System	State	N	r	$\Delta E_{PQGT1T2(\epsilon)}$	$\Delta E_{PQGT1T2}$	E_{FCI}
C	^3P	6	20	−0.0009	−0.0004	−37.736 53
O	^1D	8	20	−0.0019	−0.0013	−74.787 33
O_2^+	$^2\Pi_g$	15	20	−0.0028	−0.0022	−148.793 39
HLi_2	$^2A_1$	7	22	−0.0002	−0.0001	−14.405 55
LiOH	$^1\Sigma^+$	12	22	−0.0007	−0.0006	−82.648 42
HN_2^+	$^1\Sigma^+$	14	22	−0.0017	−0.0015	−108.931 32
BH	$^1\Sigma^+$	6	24	−0.0006	−0.0001	−25.187 66
HF	$^1\Sigma^+$	14	24	−0.0003	−0.0003	−100.160 31
CH_3N	$^1A_1$	16	26	−0.0013	−0.0010	−93.884 52

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The calculated correlation energies for *PQGT*1 in percentages were almost all from 100% to 105%; from 105% to 110% for CH_3^+, CH_4, NH_4^+, $C(^3P,Sz=1)$, $O(^3P,Sz=1)$, BeO, C_2, BO, CO^+, N_2^+, C_2^-, CN, CO, N_2, CF, O_2^+, HN_2^+, HNO, BH, $NH(^3\Sigma^-)$, SiH_4, and H_2O; from 110% to 120% for $O(^1D)$, BN, CH, $NH(^1\Delta)$, BH_3O, CH_3N. $C(^3P,Sz=0)$, and $O(^3P,Sz=0)$ have very large correlation energies.

*PQGT*1*T*2 conditions drastically improve the energies, and the correlation energy errors become very small and within excellent agreement with the fullCI calculations. They are between 100% and 101% for all the systems except for only $C(^3P,Sz=0)$, $O(^1D)$, $O(^3P,Sz=0)$, BeO, BN, C_2, N_2^+, C_2^-, CN, O_2^+, and CH. Note that these systems are also difficult to calculate with CCSD(T). The multireference methods are needed for $C(^3P,Sz=0)$ and $O(^3P,Sz=0)$. The molecules BN, CN, and O_2^+ are in the high spin states where the correlations are strong. C_2 is a closed shell system but the correlation is strong too. Both the absolute energy errors of *PQGT*1*T*2 and CCSD(T) are at the same order, −0.0035 and +0.002 85 hartree, respectively. We are not sure why the result of CCSD(T) for BN ($^3\Pi$) is so poor and the convergence is not achieved for CN. We suspect that the STO-6G basis set is not flexible for complicated electronic states like these systems. Particularly, *PQGT*1*T*2 calculation for H_2O with double-ζ basis set is slightly better than CCSD(T).

Replacing *T*2 condition by *T*2′ condition improves the energy slightly, improvements are found for 22 systems of more than 0.1 mhartree. The largest improvement is 0.5 mhartree for CH. Usually, the improvements are 0.1 to 0.2 mhartree and they are observed for high spin states and/or degenerated states [exceptions are $Ne(^1S)$ and $HN_2^+(^1\Sigma^+)$]. The absolute energy difference from the fullCI are worse than CCSD(T) for 12 systems CH_3^+, CH_4, NH_4^+, $O(^3P,Sz=1)$, Ne, C_2, BeF, CO, LiOH, BH_3O, CH_3N, and SiH_4, whose worst was C_2 with 0.65 mhartree out of total 57 systems. The deviations of *T*2′ calculations from the fullCI were very small. As it is apparent from their formulations, the required computational time for *PGQT*1*T*2 and *PQGT*1*T*2′ are almost the same, thus we should use *PQGT*1*T*2′ instead of *PQGT*1*T*2 in general. Note that the RDM method with *PQGT*1*T*2′ conditions calculates better energies for high spin states, anion states, and dissociation limits where SDCI or CCSD(T) fails.[21,40]

C. Dipole moments

In Table II, we show 32 systems with nonzero dipole moments for the atoms and molecules calculated here. Apparently, the dipole moment calculated with *PQG*, μ_{PQG}, is the worst dipole moment among those calculated by *PQGT*1, *PQGT*1*T*2, and *PQGT*1*T*2′. Generally speaking, the dipole moments become more close to the fullCI results as more *N*-representability conditions are included, but the convergence is not guaranteed to be monotone. Such exceptions are $\mu_{PQGT1T2}$ and $\mu_{PQGT1T2'}$ of BH^+, NH_2^-, CN, BH, NH ($^1\Delta$ and $^3\Sigma^-$), HF, and CH_3N, whose violations were very small, less than 0.1 mD. Usually, μ_{PQG} is better than the Hartree–Fock calculation and is comparable to the SDCI calculation. The results of *PQGT*1*T*2 and *PQGT*1*T*2′ reproduce well the fullCI results. We would like to note that a zero dipole moment is calculated for H_3, and this will be discussed in the Sec. IV B.

IV. DISCUSSIONS AND APPLICATIONS

A. Handling equality constraints in the SDP formulation

In Sec. II D, we discussed an improvement in the dual standard SDP formulation which was not possible before due to the limitations of previous versions of SDPA and SDPARA on handling equality constraints.

Table III shows the actual energy improvements when replacing the formulation with a small gap [Eq. (2.3)] by a formulation with no gap [Eq. (2.2)], which corresponds to handling simply an equality constraint. We selected some systems from Table I. The column $\Delta E_{PQGT1T2(\epsilon)}$ indicates the energy deviation obtained by the formulation with a small gap [Eq. (2.3)] and $\Delta E_{PQGT1T2}$ is the energy deviation without [Eq. (2.2)]. Here, ϵ was set to 1.0×10^{-5}. The energy deviations $\Delta E_{PQGT1T2(\epsilon)}$ of O_2^+ was taken from Ref. 25 and others were from Ref. 10. Note that the geometries employed for BH and HF were different here. In Ref. 10, we used the geometries from Ref. 54.

There are differences on the improvements without a notable tendency on a particular system. There is no improvement for HF, while the energy improved by 0.6 mhartree for O and O_2^+, but all of them are typically of submhartree level.

The variational space becomes larger if we replace equalities by pairs of inequalities having a small gap [Eq. (2.3)], and thus the energies become lower in the latter case. For instance, let us infer the properties of the neighborhood of the minimizer 2-RDM for O_2^+. Since there is a difference of 0.0006 hartree between $\Delta E_{PQGT1T2(\epsilon)}$ and $\Delta E_{PQGT1T2}$, O_2^+ seems to be unstable at the minimum. If the ground state energy does not change by the inclusion of inequalities, like for the HF molecule, then the system is very stable against perturbations.

In all other calculations in this article, except Table III, we used the formulation without a small gap [Eq. (2.2)], that is, handling indirectly the equality constraint in the dual standard SDP [Eq. (2.1)].

B. Bounds on operators

For the dipole moment, which is another property up to two-particle interaction, there is no variational relation such as

$$\mu_{PQG} \leqslant \mu_{PQGT1} \leqslant \mu_{PQGT1T2} \leqslant \mu_{PQGT1T2'} \leqslant \mu_{\text{full CI}},$$

in contrast to the ground state energy. Therefore, its accuracy cannot be evaluated strictly as for the ground state energy.

If we want the expectation value of a bounded operator *O*, it is possible to obtain tighter bounds on *O* using both RDM and CI energies for $H+\lambda O$ at two values of λ.[57] However, it is interesting to observe that a much less labor intensive method can also be used to obtain good estimates for bounds on $\langle O\rangle$.

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Consider a bounded necessary N-representable 2-RDM set $\tilde{\mathcal{P}}$, and a complete N-representable 2-RDM set $\mathcal{P}$. Let $\Gamma \in \mathcal{P}$ be the ground state 2-RDM by fullCI and $\tilde{\Gamma} \in \tilde{\mathcal{P}}$ be the computed ground state 2-RDM for some Hamiltonian H. Suppose that Γ and $\tilde{\Gamma}$ differ by a norm ϵ,

$$\|\tilde{\Gamma} - \Gamma\| = \epsilon,$$

where $\|\cdot\|$ is the Frobenius norm. In other words, $\tilde{\Gamma} \in \{\Gamma + N(\epsilon)\}$, where $N(\epsilon)$ is an ϵ-sphere; $N(\epsilon) = \{\bar{\Gamma} \,|\, \|\bar{\Gamma}\| \leqslant \epsilon\}$. Now, we define a bounded operator O as

$$O = \sum_{i_1 i_2 j_1 j_2} O^{i_1 i_2}_{j_1 j_2} a^\dagger_{i_1} a^\dagger_{i_2} a_{j_2} a_{j_1},$$

and calculate its expectation value in relation to Γ. Then, it is also bounded,

$$\inf_{\bar{\Gamma} \in \{\Gamma + N(\epsilon)\}} \mathrm{Tr}\, \bar{\Gamma} O \leqslant \mathrm{Tr}\, \bar{\Gamma} O \leqslant \sup_{\bar{\Gamma} \in \{\Gamma + N(\epsilon)\}} \mathrm{Tr}\, \bar{\Gamma} O. \tag{4.1}$$

From $N(\epsilon) = \epsilon N(1)$, Eq. (4.1) becomes

$$\mathrm{Tr}\{\Gamma O\} + \epsilon \inf \mathrm{Tr}\{N(1) O\} \leqslant \mathrm{Tr}\, \tilde{\Gamma} O \leqslant \mathrm{Tr}\{\Gamma O\} + \epsilon \sup \mathrm{Tr}\{N(1) O\}.$$

Since O is bounded, $\inf \mathrm{Tr}\, N(1) O$ and $\sup \mathrm{Tr}\, N(1) O$ are finite. Therefore, we can find upper and lower bounds for any bounded operator O in terms of ϵ,

$$|\mathrm{Tr}\{\tilde{\Gamma} O\} - \mathrm{Tr}\{\Gamma O\}| \leqslant \epsilon \times \max\{|\inf \mathrm{Tr}\{N(1) O\}|, |\sup \mathrm{Tr}\{N(1) O\}|\}.$$

If we find a better N-representable set that reduces the Frobenius norm ϵ, these bounds become stringent thus we will obtain a better expectation value. Unfortunately, we cannot say, in general, that the dipole moment from $PQGT1T2'$ calculation is always better than PQG because $\epsilon_{PQGT1T2'}$ is not necessarily smaller than ϵ_{PQG} and/or bounds might not be restrictive. Nevertheless, we usually observe that $\epsilon_{PQGT1T2'} < \epsilon_{PQG}$ and the dipole moment $\mu_{PQGT1T2'}$ is usually better than μ_{PQG} as we expected.

Especially, Zhao[58] calculated the Frobenius norm of the difference between 2-RDMs and fullCI 2-RDMs for various molecules with PQ, PQG, $PQGT1$, $PQGT2$ and $PQGT1T2$ respectively, in Tables V–VII. The norms become smaller by one order of magnitude when adding G condition to PQ conditions, and adding $T2$ condition to $PQGT1$ conditions, respectively. For example, for the CH^+ molecule, the Frobenius norm by PQ is 1.100 118, PQG is 0.061 588, $PQGT1$ is 0.033 614, and $PQGT1T2$ is 0.000 314, respectively. The differences of the dipole moment between the FullCI method and the RDM method are 0.2873 (PQ), 0.0238 (PQG), 0.0047 ($PQGT1$), and 0.0003 ($PQGT1T2$).[25] We observe similar tendency for other molecules as well.

C. Degeneracies by symmetry of the Hamiltonian

First, we discuss the spin degeneracy of some atomic systems. In Table I, C ($^3P, Sz=1$) and C ($^3P, Sz=0$) must have the same energy, and O ($^3P, Sz=1$) and O ($^3P, Sz=0$) as well. However, the RDM method with all four level of approximations (PQG, $PQGT1$, $PQGT1T2$, and $PQGT1T2'$) calculates different energies, and always gives worse energies for $Sz=0$ cases. For example, the energy deviation by PQG calculation for C ($^3P, Sz=0$) is −0.0173 hartree, whereas for C ($^3P, Sz=1$) is −0.0039 hartree, and for O ($^3P, Sz=0$) is −0.0234 hartree, whereas for O ($^3P, Sz=1$) is −0.0120 hartree. Of course, these energy deviations should be the same because these two states are degenerated. The absolute deviation differences become smaller as the approximation level is tightened, but even with $PQGT1T2'$, we still observe a difference between $Sz=1$ and $Sz=0$. The S-representability condition is automatically satisfied because we explicitly set constraints on the S^2 and Sz.[59] Thus, this is a very strange behavior and we do not obtain the triplet state with $Sz=0$ energy as a convex combination of a higher spin state and a singlet state; the triplet state is the ground state of carbon and oxygen atoms. Thus we may consider the necessity of a new representability condition.

This fact becomes a problem when we discuss the dissociation limit of a molecule. Consider the ground state C_2 ($^1\Sigma_g^+$) dissociating to two C (^3P) atoms. At the dissociation limit, each carbon has $Sz=0$ because the total spin is zero and the spin is unchanged in the process. The dissociation energy is calculated by the ground state energy for the equilibrium geometry minus twice of the ground state energy of the carbon atom ^3P. However, the RDM method calculates different energies; the energy between ^3P, $Sz=0$ state and ^3P, $Sz=1$ state are different. Thus, this is one reason for $PQGT1T2'$ conditions cannot satisfy the size-consistency property. We need some other N-representability conditions.[21] Hammond *et al.* treated a similar problem.[60]

Next, we discuss the dipole moment of H_3 shown in Table II. This H_3 molecule is repulsive and unstable with respect to H_2+H. Therefore, we consider the geometry as triangular, from the metastable Rydberg state $\tilde{A}$. Then, the ground state is E' which is doubly degenerated. In this case, we can choose two dipole moments which have the same magnitude and perpendicular directions. Currently, the RDM method considers ensemble N-representability conditions, and the SDP solver calculates the ensemble average of these degeneracies resulting a zero dipole moment. This fact does not contradict the discussion on the bounds on the operators in the last section. In this case, ϵ does not approaches to zero, since Γ is obtained by the fullCI method, or equivalently, by the RDM method with the pure representable set and not by the ensemble representable set.

In general, we do not know whether the degeneracy is present in a given Hamiltonian, as some may be hidden. This is the case why we need pure representability conditions. Hence, properties other than the ground state energy must be carefully analyzed. We can work around this problem by adding a small perturbation, say V, to break this degeneracy or symmetry, and taking its limit to zero. However, we may encounter problems. (1) How we find such a V? Even though the degeneracy is from the symmetry of the Hamiltonian, we do not know about the symmetry beforehand in general. In some cases, however, applying a distortion to a molecule or a weak electronic field is usually enough, and H_3 is such a case; (2) if the symmetry breaking operator is of three-or

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TABLE IV. The ground state energy calculated for the one dimensional Hubbard model with the nearest neighbor hopping and periodic boundary condition. Lattice size $L=4$, total spin number $S=0$, and number of electrons $N=4$ (half-filled). Calculations were performed for $U/t=10$, 10.0, 100.0, 1000.0, and 10 000.0, where U is the strength of electron-electron repulsion parameter and t is the hopping parameter, respectively, by SDPA (double) and SDPA-GMP with PQG conditions and fullCI.

U/t	SDPA (double)	SDPA-GMP	FullCI
10 000.0	0	$-1.199\,999\,880\,000\,025\,1\times10^{-3}$	$-1.199\,999\,880\times10^{-3}$
1 000.0	-1.2×10^{-2}	$-1.199\,988\,000\,250\,793\,4\times10^{-2}$	$-1.999\,988\,000\,2\times10^{-2}$
100.0	-1.991×10^{-1}	$-1.198\,802\,501\,371\,799\,3\times10^{-1}$	$-1.198\,802\,489\,46\times10^{-1}$
10.00	−1.1000	−1.099 940 044 122 293 4	−1.099 877 772 750
1.0	−3.3417	−3.341 674 807 025 995 6	−3.340 847 617 248

four-particle ones, it is impossible to deal with it since our current formulation incorporates only 2-RDMs; (3) we may encounter artificial degeneracies since we can usually apply only incomplete (necessary) N-representability conditions.[41]

The 1-RDM with doubly degenerate eigenvalues occurs widely in physics and chemistry when singlet states are calculated and the Hamiltonians are invariant under time reversal (for example, no external magnetic fields are present).[61] Such RDMs are derived by at least one wavefunction.[62]

The $PQGT1T2'$ calculation for H_3 was somehow unstable and we used SDPA-GMP to obtain accurate results. We will discuss SDPA-GMP in the next subsection.

D. Ultrahigh accurate SDP solver and the RDM method

The Hubbard model[46] is known as a very good model of electron correlation, metals and a model of interacting hydrogen molecules. We consider the following Hamiltonian

$$H=-t\sum_{\langle i,j\rangle}^{L}\sum_{\sigma=\uparrow,\downarrow}a_{i,\sigma}^{\dagger}a_{j,\sigma}+U\sum_{j=1}^{L}a_{j,\uparrow}^{\dagger}a_{j,\uparrow}a_{j,\downarrow}^{\dagger}a_{j,\downarrow},$$

where U and t are real parameters, L is the number of sites on the lattice, and $\langle i,j\rangle$ means summing over when ith and jth sites are the nearest neighbor. We are especially interested in high U/t limits, known as strong coupling limit. In this limit, the Hubbard model becomes the t-J model[63] and the electronic state becomes nearly degenerated. Sebold and Percus first applied the RDM method to the Hubbard model,[64] and Hammond *et al.* calculated the ground state energies of the Hubbard model up to $L=14$ with $PQGT2$ conditions.[31] For these cases, the optimal solution of the SDP becomes also degenerated and even the primal-dual interior-point method with double precision cannot solve such problems accurately.

To solve difficult SDPs with $U/t\to\infty$ limit, we implemented SDPA-GMP described in the Sec. II E. In this study, we prepare 200 significant bits, which represents about 60 significant digits for the calculations. Therefore, observe that SDPA-GMP is not suitable for problems like in Ref. 41, where the N-representability conditions P, Q, G, $T1$, and $T2$ are not strong enough.

In Table IV, we present highly accurate results with the original SDPA based on double precision, SDPA (double), and SDPA-GMP for the Hubbard model. We calculated the ground state energies of the Hubbard model with $U/t=1.0, 10.0, 100.0, 1000.0, 10\,000.0$, and periodic boundary condition. The number of sites L equals to four and the number of electrons N equals four (half-filled). We used PQG conditions for L equals to four, and calculated the fullCI for comparison.

For $U/t=1.0$, 10.0 and 100.0, SDPA (double) gives five significant digits, however, for $U/t=1000.0$, it gives only two significant digits. For $U/t=10\,000.0$ case, SDPA (double) gives only one significant digit, while SDPA-GMP gives 17 significant digits and the following error limits: Relative duality gap 8.48×10^{-22}, primal feasible error 5.76×10^{-36}, and dual feasible error 1.91×10^{-28}. See Sec. IV of Ref. 10 for the definitions of the relative duality gap, the primal feasible error and the dual feasible error. These values are sufficiently small, hence these results are trustful. For the same problem, SDPA (double) calculates a relative duality gap 2.11×10^{-3}, a primal feasible error 7.49×10^{-8}, and a dual feasible error 9.01×10^{-5}. Since the relative duality gap is not so small, we can only trust two or three significant digits for the energy in general. Apparently, such accuracy for the energies are not

TABLE V. The ground state energy calculated for the one dimensional Hubbard model with nearest the neighbor hopping and periodic boundary condition. Lattice size $L=6$, the total spin number $S=0$, and number of electrons $N=6$ (half filled). Calculations were performed for $U/t=1.0$, 10.0, 100.0, 1000.0, and 10 000.0, where U is the strength of electron-electron repulsion parameter and t is the hopping parameter, respectively, by SDPA (double) and SDPA-GMP with $PQGT1T2$ conditions and fullCI.

U/t	SDPA (double)	SDPA-GMP	FullCI
10 000.0	0	$-1.724\,995\,119\,574\,952\,5\times10^{-3}$	$-1.721\,110\,121\times10^{-3}$
1 000.0	-1×10^{-2}	$-1.725\,536\,031\,043\,130\,4\times10^{-2}$	$-1.721\,103\,471\,3\times10^{-2}$
100.0	-1.730×10^{-1}	$-1.730\,215\,714\,059\,433\,9\times10^{-1}$	$-1.720\,433\,380\,97\times10^{-1}$
10.0	−1.6954	−1.695 384 327 685 444 7	−1.664 362 733 287
1.0	−6.6012	−6.601 204 221 780 628 6	−6.601 158 293 375

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TABLE VI. The ground state energy in hartree calculated for Be (^1S) atom by SDPA (double), and SDPA-GMP with *PQG* and *PQGT*1*T*2′ conditions, and fullCI. We used the STO-6G basis set. *PQG* conditions gave a slightly lower energy than fullCI, and *PQGT*1*T*2′ actually improved the total energy.

System	SDPA (double)	SDPA-GMP	FullCI
Be (*PQG*)	−14.556 089 0	−14.556 089 013 043 374	−14.556 088 567
Be (*PGGT*1*T*2′)	−14.556 088 67	−14.556 088 670 078 075	

acceptable. In Table V, we present the same results when the number of sites L and the number of electrons were six, and we used *PQGT*1*T*2 as the N-representability condition. SDPA-GMP calculates very good energies with many significant digits similarly to Table IV. We recognize, however, that employing SDPA-GMP to solve highly correlated system is a brute force method.

In Table VI, we show the results of the Be atom with STO-6G basis set. The total energy by *PQG* with SDPA (double) is −14.556 089 0 hartree and with SDPA-GMP is −14.556 089 013 043 374 hartree. With *PQGT*1*T*2′ conditions, the total energy improved slightly (0.3 μhartree), but we can computationally confirm that adding *T*2′ really improves the energy and that *PQGT*1*T*2′ are not sufficient conditions for Be, yet. In Table VII, we show ten randomly selected elements of 2-RDM calculated with SDPA (double) and SDPA-GMP using *PQGT*1*T*2′ as N-representability conditions, and of the fullCI for comparison. We used the Hartree–Fock orbital for expanding the 2-RDMs. The results show that even though SDPA (double) and SDPA-GMP very well reproduce the total energy of the fullCI energy up to eight digit figures, they compute quite different elements of 2-RDMs. First, compare SDPA (double) and SDPA-GMP results. Only eight significant digits coincide for $(1,\bar{1},1,\bar{1})$ and three for $(1,\bar{1},4,\bar{4})$, about four or five significant digits for the other elements. Next, we compare the 2-RDM by SDPA-GMP and fullCI. For $(1,\bar{1},1,\bar{1})$, eight significant digits coincide, while only one significant digit for $(2,\bar{3},2,\bar{3})$.

E. Calculation time for the largest systems

In Table VIII, we show the calculation time for the largest systems we solved using SDPARA (Table I), SDPA, and SDPA-GMP (Table V). We used two machines for these calculations: Machine I, a cluster of Itanium 2 (1.3 GHz) with four processors per node, and machine II, an Opteron 250 (2.4 GHz) with two processors per node.

The largest system in this study is H_2O with double-ζ basis set. It took about 24 days for *PQGT*1*T*2′ with eight processors on machine I. The second largest one is SiH_4 with STO-6G basis. It took about 5.1 days for *PQGT*1*T*2′ with sixteen processors on the same machine. The calculation time does not increase considerably when replacing *PQGT*1*T*2 with *PQGT*1*T*2′: 4.9 days against 5.1 days for SiH_4, and 20 days against 24 days for H_2O, respectively.

SDPA-GMP is about 440 and 680 times slower than SDPA (double) calculation for the 1D Hubbard model with $L=6$, $S=0$, $N=6$, and *PQG*, *PQGT*1*T*2 as the N-representability conditions, respectively (Table V). Typically, SDPA-GMP is one hundred to one thousand times slower than SDPA for larger systems.

V. CONCLUSION

The RDM method was explored for 57 atoms and molecules with various states. We solved the SDPs of these systems by the newly developed SDP solver which can handle equality constraints. The results with *PQGT*1*T*2′ were very good for the ground state energies of atoms and molecules calculated by the RDM method. They usually resulted in

TABLE VII. Randomly selected elements of the ground state 2-RDM calculated for Be (^1S) atom with STO-6G basis by SDPA (double) and SDPA-GMP with *PQGT*1*T*2′ conditions, and fullCI. Ten significant digits are shown. The Hartree–Fock orbital is used to expand 2-RDMs. The bar over the number indicates the beta orbital and the other indicates the alpha orbital, respectively. Convergence of each elements seem to be very slow. Although SDPA-GMP calculated extremely accurate energies, the elements of 2-RDM are quite different when compared to fullCI.

Elements	SDPA (double)	SDPA-GMP	FullCI
$(1,\bar{1},1,\bar{1})$	$-4.999\,648\,894\times10^{-1}$	$4.999\,648\,876\times10^{-1}$	$4.999\,648\,930\times10^{-1}$
$(1,\bar{1},3,\bar{3})$	$-4.657\,462\,030\times10^{-4}$	$-4.657\,600\,311\times10^{-4}$	$-4.657\,674\,588\times10^{-4}$
$(1,\bar{1},4,\bar{4})$	$-4.657\,450\,111\times10^{-4}$	$-4.657\,600\,311\times10^{-4}$	$-4.657\,674\,588\times10^{-4}$
$(\bar{1},2,1,\bar{2})$	$-1.688\,098\,791\times10^{-5}$	$-1.688\,168\,309\times10^{-5}$	$-1.688\,331\,957\times10^{-5}$
$(1,\bar{2},1,\bar{2})$	$4.461\,648\,307\times10^{-1}$	$4.461\,645\,659\times10^{-1}$	$4.461\,651\,178\times10^{-1}$
$(2,\bar{3},2,\bar{3})$	$5.991\,918\,677\times10^{-6}$	$5.991\,842\,495\times10^{-6}$	$5.9177\,881\,803\times10^{-6}$
$(3,\bar{3},5,\bar{5})$	$1.795\,065\,732\times10^{-2}$	$1.795\,073\,437\times10^{-2}$	$1.795\,058\,851\,4\times10^{-2}$
$(\bar{1},5,\bar{2},5)$	$-3.189\,697\,637\times10^{-4}$	$-3.189\,896\,861\times10^{-4}$	$-3.190\,132\,639\,0\times10^{-4}$
$(5,\bar{5},2,\bar{2})$	$-8.946\,232\,105\times10^{-2}$	$-8.946\,248\,192\times10^{-2}$	$-8.946\,216\,352\,4\times10^{-2}$
$(5,\bar{5},5,\bar{5})$	$1.795\,076\,203\times10^{-2}$	$1.795\,083\,821\times10^{-2}$	$1.795\,074\,527\,74\times10^{-2}$

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TABLE VIII. Calculation time for the largest systems by SDPARA using *PQG*, *PQGT*1*T*2, and *PQGT*1*T*2′ (Table I). And for the one dimensional Hubbard Model with nearest neighbor hopping and periodic boundary condition with $U/t=10000.0$, $L=6$, $S=0$, $N=6$ using SDPA (double) and SDPA-GMP (Table V): Calculations are performed on Machine I: Itanium 2 (1.3 GHz) four processors per node; Machine II: Opteron 250 (2.4 GHz) two processors per node. The SDPA-GMP does not utilize multi-core.

System, State, Basis	r	Machine	N-rep. conditions	Solver	Time	Processors
SiH_4, $^1A_1$, STO-6G	26	I	*PQG*	SDPARA	2.6 h	16
SiH_4, $^1A_1$, STO-6G	26	I	*PQGT*1*T*2	SDPARA	4.9 days	16
SiH_4, $^1A_1$, STO-6G	26	I	*PQGT*1*T*2′	SDPARA	5.1 days	16
H_2O, $^1A_1$, double-ζ	28	I	*PQG*	SDPARA	2.2 h	8
H_2O, $^1A_1$, double-ζ	28	I	*PQGT*1*T*2	SDPARA	20 days	8
H_2O, $^1A_1$, double-ζ	28	I	*PQGT*1*T*2′	SDPARA	24 days	8
1D Hubbard model	12	II	*PQG*	SDPA (double)	16 s	1
1D Hubbard model	12	II	*PQGT*1*T*2	SDPA (double)	4.2 min	1
1D Hubbard model	12	II	*PQG*	SDPA-GMP	2.0 h	1
1D Hubbard model	12	II	*PQGT*1*T*2	SDPA-GMP	2.0 days	1

correlation energies between 100% and 101% and were almost at the same magnitude as CCSD(T). Also, there were some cases in which the RDM calculated successfully but CCSD(T) failed. Handling directly the equality constraints improved the total energies by several submhartrees, and *T*2′ condition gave another improvement in the same magnitude compared to our previous results. We also implemented the multiple arithmetic version of SDPA, SDPA-GMP, which was used for the one dimensional Hubbard model and Be atom, and obtained extremely accurate energies. In particular, for the Hubbard model with high correlation limit, large $|U/t|$, we obtained at least sixteen significant figures whereas the ordinal method gave only two to four significant figures. We obtained physically meaningful results for large $|U/t|$ with this new solver. However, its computational time was typically one hundred to one thousand times slower than SDPA. The total energy of Be were the same up to eight significant digits with SDPA (double), SDPA-GMP, and fullCI, but the resulting elements of 2-RDM were quite different, and only had few digits in common.

The RDM method was applied for a variety of atoms and molecules and resulted in comparable energies to CCSD(T) for equilibrium geometries. Besides, it can be applicable to bond breaking, formation and high correlation systems which are difficult with the traditional quantum chemistry methods.[21,29] Even though computational cost is somewhat demanding,[10,42] we can conclude that the RDM method with *PQGT*1*T*2′ is very promising. For future directions, we should develop better algorithms which are applicable for larger systems, find better *N*-representability conditions, and apply them to realistic systems.

ACKNOWLEDGMENTS

M.N. was supported by the Japan Science and Technology Agency (JST), and he and M.F. were also partially supported by the fellowships from the Japan Society for the Promotion of Science (JSPS). M.F. was supported by MEXT's program "Promotion of Environmental Improvement for Independence of Young Researchers" under the Special Coordination Funds for Promoting Science and Technology, and in part by the JSPS Global COE program "Computationism as a Foundation for the Sciences." M.N., M.F., and M.Y. were also partially supported by Grant-in-Aids for Scientific Research from the Japanese Ministry of Education, Culture, Sports, Science and Technology. B.J.B. was supported by U.S. Department of Energy under Grant No. DE-FG02-07ER5914 and Office of Naval Research under Grant No. N00014-05-1-0460. J.K.P. was supported by the Department of Energy (DOE) under Grant No. DE-FG02-02ER15292, and Z.Z. by DOE Grant No. DE-AC02-05CH11231. We are grateful to the Grid Technology Research Center (GTRC) in the National Institute of Advanced Industrial Science and Technology (AIST) for providing us the AIST Super Cluster for solving large-scale SDPs.

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