Variational calculations of fermion second-order reduced density matrices by semidefinite programming algorithm

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The ground-state fermion second-order reduced density matrix (2-RDM) is determined variationally using itself as a basic variable. As necessary conditions of the N-representability, we used the positive semidefiniteness conditions, P, Q, and G conditions that are described in terms of the 2-RDM. The variational calculations are performed by using recently developed semidefinite programming algorithm (SDPA). The calculated energies of various closed- and open-shell atoms and molecules are excellent, overshooting only slightly the full-CI energies. There was no case where convergence was not achieved. The calculated properties also reproduce well the full-CI results. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1360199]

I. INTRODUCTION

The ground state of N-body fermion system is completely described by the second-order reduced density matrix (2-RDM) $\Gamma^{(2)}$ because any observable properties of the system can be calculated from the 2-RDM.[1,2] This fact led us to desire to use 2-RDM as a basic variable of quantum mechanics instead of the wave function Ψ; if we can determine $\Gamma^{(2)}$ without using Ψ, we have a closed form of quantum mechanics where the basic variable is 2-RDM. We refer to such formalism of quantum mechanics as density matrix theory (DMT).[3]

In the nonrelativistic case, the determinative equation for Ψ is the Schrödinger equation (SE). Therefore, to establish DMT, we have to formulate the equation for the RDM that is equivalent to the SE in the necessary and sufficient sense.[3] As such an equation, one of the author derived density equation (DE) (Refs. 4 and 5) that has recently been used successfully to calculate the 2-RDMs of atoms and molecules directly without any use of the wave function.[6–9] This approach is called density equation theory (DET) and a review on the DET in chemical physics has recently been summarized together with some later developments.[3]

Another equation that is equivalent to the SE but includes 2-RDM alone as a variable is the variational equation of the form,

$$E_g \leqslant E[\Gamma^{(2)}], \tag{1.1}$$

where E_g is the exact ground-state energy. This method called density matrix variational theory (DMVT) is a straightforward consequence of the Ritz variational principle combined with the fact that the Hamiltonian involves only one- and two-body operators. The problem here is how well we can restrict our variable $\Gamma^{(2)}$ to be N-representable.[10] The N-representability condition that is enforced by the Pauli principle is not completely known for $\Gamma^{(2)}$ and this is an obstacle of the DMT in general.

The P, Q, (Ref. 10) and G (Ref. 11) conditions are the well-known necessary conditions of the N-representability. They are the semidefiniteness conditions of the matrices derived from $\Gamma^{(2)}$. Though these three conditions are not complete, they seem to be quite strong to characterize the N-representability of the ground-state 2-RDM. First calculations along this line were performed in a beautiful way by Garrod *et al.*[12,13] for the ground state of Be, and Mihailović *et al.*[14] for the nuclear ground state of ^{15}O, ^{16}O, ^{17}O, ^{18}O, ^{20}Ne, ^{24}Mg, and ^{28}Si. At that time their method was very heuristic and could hardly be applied to general systems. We found that this method can be elegantly realized using the semidefinite programming algorithm (SDPA),[15] recently developed in the field of mathematical programming. We calculated the ground-state energies of atoms and molecules using these three necessary conditions and employing SDPA as our problem solver.

II. THEORICAL OUTLINE

First and second order reduced density matrices (1-, 2-RDMs), γ and Γ, respectively, are defined by

$$\gamma_j^i = \langle \Psi | a_i^\dagger a_j | \Psi \rangle, \tag{2.1}$$

and

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$$\Gamma^{i_1 i_2}_{j_1 j_2} = \tfrac{1}{2}\langle\Psi|a^\dagger_{i_1}a^\dagger_{i_2}a_{j_2}a_{j_1}|\Psi\rangle, \tag{2.2}$$

where $a^\dagger$ and a denote creation and annihilation operators, respectively. Note we have simplified $\Gamma^{(2)}$ as Γ. Throughout this paper, we assume the elements of 1-RDM and 2-RDM to be real. Complete N-representability condition is known for γ,[10] but for Γ, we know only necessary conditions (the known complete condition is not practical). Some trivial conditions for 2-RDM are:

(1) Antisymmetric condition,

$$\Gamma^{i_1 i_2}_{j_1 j_2} = -\Gamma^{i_2 i_1}_{j_1 j_2} = -\Gamma^{i_1 i_2}_{j_2 j_1}; \tag{2.3}$$

(2) Hermiticity,

$$\Gamma^{i_1 i_2}_{j_1 j_2} = \Gamma^{j_1 j_2}_{i_1 i_2}; \tag{2.4}$$

(3) Trace condition,

$$\sum_k \Gamma^{ik}_{jk} = \frac{2}{N-1}\gamma^i_j; \tag{2.5}$$

(4) Number of electrons,

$$N = \sum_k \gamma^k_k; \tag{2.6}$$

(5) Eigenstate of the number of α (or β) electrons,

$$\mathrm{Tr}\, N_\alpha \Gamma = N_\alpha \quad\text{and}\quad \mathrm{Tr}\, N^2_\alpha \Gamma = N^2_\alpha; \tag{2.7}$$

where the operators of N_α and N^2_α are written as

$$N_\alpha = \sum_i a^\dagger_{i\alpha}a_{i\alpha}, \quad N^2_\alpha = \sum_{ij} a^\dagger_{i\alpha}a_{i\alpha}a^\dagger_{j\alpha}a_{j\alpha}; \tag{2.8}$$

(6) Spin symmetry,

$$\Gamma^{i_1\sigma_1 i_2\sigma_2}_{j_1\sigma'_1 j_2\sigma'_2} = 0; \tag{2.9}$$

when $\sigma_1 \neq \sigma'_1$ or $\sigma_2 \neq \sigma'_2$ and $\sigma_1 \neq \sigma'_2$ or $\sigma_2 \neq \sigma'_1$, where σ denotes spin variable.

(7) Expectation value of S^2,

$$\mathrm{Tr}\, S^2 \Gamma = S(S+1), \tag{2.10}$$

where the spin-squared operator S^2 is given by

$$S^2 = S_z + S^2_z + S_- S_+$$
$$= \frac{1}{2}\sum_i (a^\dagger_{i\alpha}a_{i\alpha} - a^\dagger_{i\beta}a_{i\beta}) + \frac{1}{4}\left(\sum_i a^\dagger_{i\alpha}a_{i\alpha} - a^\dagger_{i\beta}a_{i\beta}\right)^2$$
$$+ \sum_{ij} a^\dagger_{i\beta}a_{i\alpha}a^\dagger_{j\alpha}a_{j\beta}; \tag{2.11}$$

(8) Positive semidefiniteness of P matrix, which is just 2-RDM,

$$\sum x_{i_1 i_2}\Gamma^{i_1 i_2}_{j_1 j_2}x_{j_1 j_2} \geqslant 0, \tag{2.12}$$

where $x_{i_1 i_2}$ is an arbitrary geminal.

Note that except for the condition 8, all of these conditions are linear to 2-RDM.

The Q and G matrices are defined by

$$Q^{i_1 i_2}_{j_1 j_2} = \langle\Psi|a_{i_1}a_{i_2}a^\dagger_{j_2}a^\dagger_{j_1}|\Psi\rangle \tag{2.13}$$

and

$$G^{i_1 i_2}_{j_1 j_2} = \langle\Psi|a^\dagger_{i_1}a_{i_2}a^\dagger_{j_2}a_{j_1}|\Psi\rangle. \tag{2.14}$$

These matrices are semidefinite[11] and linear to Γ as

$$Q^{i_1 i_2}_{j_1 j_2} = (\delta^{i_1}_{j_1}\delta^{i_2}_{j_2} - \delta^{i_1}_{j_2}\delta^{i_2}_{j_1}) - (\delta^{i_1}_{j_1}\gamma^{i_2}_{j_2} + \delta^{i_2}_{j_2}\gamma^{i_1}_{j_1})$$
$$+ (\delta^{i_1}_{j_2}\gamma^{i_2}_{j_1} + \delta^{i_2}_{j_1}\gamma^{i_1}_{j_2}) - 2\Gamma^{i_1 i_2}_{j_1 j_2} \tag{2.15}$$

and

$$G^{i_1 i_2}_{j_1 j_2} = \delta^{i_2}_{j_2}\gamma^{i_1}_{j_1} - 2\Gamma^{i_1 j_2}_{j_1 i_2}. \tag{2.16}$$

We note that originally the G matrix was written in an equivalent nonlinear form.[16]

The Hamiltonian of the system can be written as

$$H^{i_1 i_2}_{j_1 j_2} = w^{i_1 i_2}_{j_1 j_2} + \frac{1}{N-1}(v^{i_1}_{j_1}\delta^{i_2}_{j_2} + v^{i_1}_{j_2}\delta^{i_2}_{j_1}), \tag{2.17}$$

where v and w are 1- and 2-body operators, respectively. Then, the basic equation of DMVT given by Eq. (1.1) is written as the variational minimization of the energy within our constraints,

$$E_{\min} = \min_{\Gamma \in {}^{(2)}\mathcal{P}} \mathrm{Tr}\, H\Gamma, \tag{2.18}$$

where ${}^{(2)}\mathcal{P}$ is the set of 2-RDMs which satisfies the above necessary N-representability conditions, namely,

$${}^{(2)}\mathcal{P} = \{\Gamma\,|\,P, Q, G \text{ matrices are non-negative and the}$$

$$\text{conditions } 1\text{--}7 \text{ are satisfied}\}. \tag{2.19}$$

Either of the P, Q, and G conditions forms compact convex set with trace topology,[17] and a finite combination of compact convex sets is also compact convex set, therefore this method should find a minimum in energy. This method can be applied to the ground state of any space and spin symmetry.

III. CALCULATION METHOD

The minimization problem with some linear constraints can be achieved by using semidefinite programming algorithm (SDPA) (Ref. 15) as a problem solver. The SDPA has recently been developed in the field of mathematical programming. In this section, we explain how to apply SDPA to our problem of solving $\Gamma^{(2)}$ in the constrained variational method given by Eq. (2.19). The dimensions of the matrices are $n \times n$, if they are not explicitly defined.

A. Simplified problem

First, we introduce a simplified problem which contains all the essentials, that is

Problem (a): Minimize the total energy of the 2-RDM Γ subject to the fixed number of electrons and the positive semidefiniteness of Γ.

The positive semidefiniteness of Γ is the P condition. Note that this problem gives the exact solution for $N=2$. Problem (a) is written as,

$$\text{Problem (a'):} \begin{cases} \text{Minimize } \text{Tr} H\Gamma \\ \text{subject to } \text{Tr} N\Gamma = N \\ \text{and } \Gamma \text{ is positive semidefinite.} \end{cases} \quad (3.1)$$

Formal expression of the problem[15] is,

$$\text{Problem (a''):} \begin{cases} \text{Minimize } \mathbf{F}_0 \cdot \mathbf{Y} \\ \text{subject to } \mathbf{F}_1 \cdot \mathbf{Y} = c_1 \\ \text{and } \mathbf{Y} \text{ is positive semidefinite,} \end{cases} \quad (3.2)$$

where $\mathbf{F}_0$ and $\mathbf{F}_1$ are constant $n \times n$ symmetric matrices, and $\mathbf{Y}$ is $n \times n$ symmetric variable matrix, c_1 is real constant, and $\cdot$ is an operator such that

$$\mathbf{F} \cdot \mathbf{Y} = \sum_{i,j} (\mathbf{F})_{ij} (\mathbf{Y})_{ij}. \quad (3.3)$$

One can easily confirm that problem (a') and problem (a'') are the same when we take $\mathbf{Y}$ as Γ, $\mathbf{F}_0$ as the Hamiltonian, and $\mathbf{F}_1$ as the number of operator. A generalization of the problem (a'') is called semidefinite programming (SDP).

B. Semidefinite programming algorithm (SDPA)

The SDPA (Ref. 15) solves the following form of semidefinite programming and its dual:

$$\text{SDP} \begin{cases} \text{primal: } \text{minimize } \sum_{i=1}^{m} c_i x_i \\ \qquad \text{subject to } \mathbf{X} = \sum_{i=1}^{m} \mathbf{F}_i x_i - \mathbf{F}_0, \quad \mathbf{X} \geqslant \mathbf{0} \\ \text{dual: } \text{maximize } \mathbf{F}_0 \cdot \mathbf{Y} \\ \qquad \text{subject to } \mathbf{F}_i \cdot \mathbf{Y} = c_i (1 \leqslant i \leqslant m), \quad \mathbf{Y} \geqslant \mathbf{0}, \end{cases} \quad (3.4)$$

where $\mathbf{X}$ and $\mathbf{Y}$ are $n \times n$ real symmetric matrices, $\mathbf{F}_i (1 \leqslant i \leqslant m)$ symmetric constraint matrices, c_i and x_i real constant and variable numbers, respectively, $\mathbf{U} \cdot \mathbf{V}$ denotes inner product of the matrices, $\mathbf{U} \cdot \mathbf{V} = \sum_{i,j} \mathbf{U}_{i,j} \mathbf{V}_{i,j}$, and $\mathbf{X} \geqslant \mathbf{0}$ means $\mathbf{X}$ to be positive semidefinite. We assume all the constraint matrices are linearly independent.

Semidefinite programming is usually solved by primal-dual interior-point method.[18,19] This method is based on the primal-dual theorem of SDP, which shows an existence of the optimal solution and gives a necessary and sufficient condition for the optimal solution (minimum in primal problem, and maximum in dual problem): if there exists $(\mathbf{X}, \mathbf{Y}, \mathbf{x})$ such that they satisfy all the constraints and $\mathbf{X} \geqslant \mathbf{0}$ and $\mathbf{Y} \geqslant \mathbf{0}$, then

(1) SDP has an optimal solution;

(2) Necessary and sufficient condition for the optimal solution $(\mathbf{X}^*, \mathbf{Y}^*, \mathbf{x}^*)$ is

$$\mathbf{X}^* \cdot \mathbf{Y}^* = \mathbf{F}_0 \cdot \mathbf{Y}^* - \sum_{i=1}^{m} c_i x_i^* = 0. \quad (3.5)$$

C. Set up of DMVT in SDPA

Our object is to solve the DMVT problem (2.19). It is equivalent to solve the *dual* of problem (3.4), taking $\mathbf{Y}$ as 2-RDM, $\mathbf{F}_0$ as the Hamiltonian, $\mathbf{F}_1$ as the constraint for the

number of electrons, $\mathbf{F}_2$ as the constraint for spin squared operator, etc. Maximization is altered to minimization by just changing the sign of $\mathbf{F}_0$. Problem (2.19) is written as

Minimize $\text{Tr} H\Gamma$

subjected to $\text{Tr} N\Gamma = N$

$$\begin{aligned} &\text{Tr} S^2 \Gamma = S(S+1) \\ &\text{Tr} N_\alpha \Gamma = N_\alpha \\ &\text{Tr} N_\alpha^2 \Gamma = N_\alpha^2 \end{aligned} \quad (3.6)$$

and $\Gamma^{(2)} \geqslant 0$, $\mathbf{Q} \geqslant 0$ and $\mathbf{G} \geqslant 0$.

Note that some of the matrices appeared below have four indices, however, we can reduce them to two indices by mapping indices (i,j) to the composite index k. Imposing linear constraints for N or S^2, etc., is straightforward. Constraining the expectation value of the two body operator A to be c_a ($\text{Tr} A\Gamma = c_a$) is done as follows:

(1) Explicit expression of A is give by

$$A = \sum_{i_1 i_2 j_1 j_2} a_{j_1 j_2}^{i_1 i_2} a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1}, \quad (3.7)$$

where $a_{j_1 j_2}^{i_1 i_2}$ is constant.

(2) Set up the constraint matrix $\mathbf{F}_A$ such that

$$(\mathbf{F}_A)_{j_1 j_2}^{i_1 i_2} = a_{j_1 j_2}^{i_1 i_2}. \quad (3.8)$$

(3) Then, the constraint is given by the equality,

$$\mathbf{F}_A \cdot \Gamma = \sum_{i_1 i_2 j_1 j_2} a_{j_1 j_2}^{i_1 i_2} Y_{j_1 j_2}^{i_1 i_2} = \text{Tr} A\Gamma = c_a. \quad (3.9)$$

For example, we set up the constraint matrix for the number of particles N. Explicit expression of N is,

$$N = \sum_i a_i^\dagger a_i = \frac{N-1}{2} \sum_{ij} a_i^\dagger a_j^\dagger a_j a_i. \quad (3.10)$$

Then, the constraint matrix $\mathbf{F}_N$ for the number of particle is represented by

$$(\mathbf{F}_N)_{kl}^{ij} = \frac{N-1}{2} \delta_{ik} \delta_{jl}, \quad (3.11)$$

and we confirm the following relation:

$$\begin{aligned} \mathbf{F}_N \cdot \mathbf{Y} &= \sum_{ijkl} (\mathbf{F}_N)_{kl}^{ij} \Gamma_{kl}^{ij} \\ &= \sum_{ijkl} \frac{N-1}{2} \delta_{ik} \delta_{jl} \Gamma_{kl}^{ij} \\ &= \frac{N-1}{2} \sum_{ij} \Gamma_{ij}^{ij} \\ &= \frac{N-1}{2} \sum_i \frac{2}{N-1} \gamma_i^i = \sum_i \gamma_i^i = N. \end{aligned} \quad (3.12)$$

Now we consider how to enforce the 2-RDM to satisfy the P, Q, and G conditions, simultaneously. We first explain the case where only P and Q conditions are enforced simultaneously.

We introduce the variable matrix $\mathbf{Y}$ in which P and Q matrices are diagonally arranged,

$$\mathbf{Y} = \begin{pmatrix} \mathbf{P} & \mathbf{0} \\ \mathbf{0} & \mathbf{Q} \end{pmatrix}. \tag{3.13}$$

It is obvious that

$$\mathbf{Y} \geqslant 0 \leftrightarrow \mathbf{P} \geqslant 0 \quad \text{and} \quad \mathbf{Q} \geqslant 0. \tag{3.14}$$

There is a linear relation between Γ and Q matrices,

$$Q_{j_1 j_2}^{i_1 i_2} = (\delta_{j_1}^{i_1} \delta_{j_2}^{i_2} - \delta_{j_2}^{i_1} \delta_{j_1}^{i_2}) - \sum_k \frac{N-1}{2} (\delta_{j_1}^{i_1} \Gamma_{j_2 k}^{i_2 k} + \delta_{j_2}^{i_2} \Gamma_{j_1 k}^{i_1 k})$$

$$+ \sum_k \frac{N-1}{2} (\delta_{j_2}^{i_1} \Gamma_{j_1 k}^{i_2 k} + \delta_{j_1}^{i_2} \Gamma_{j_2 k}^{i_1 k}) - 2\Gamma_{j_1 j_2}^{i_1 i_2}. \tag{3.15}$$

Therefore, we can find a set of linear constraints for *each* element of the Q matrix as

$$\mathbf{E}_{j_1 j_2}^{i_1 i_2} \cdot \mathbf{Y} = c_{j_1 j_2}^{i_1 i_2} = 2\Gamma_{j_1 j_2}^{i_1 i_2} + (\delta_{j_1}^{i_1} \gamma_{j_2}^{i_2} + \delta_{j_2}^{i_2} \gamma_{j_1}^{i_1})$$

$$- (\delta_{j_2}^{i_1} \gamma_{j_1}^{i_2} + \delta_{j_1}^{i_2} \gamma_{j_2}^{i_1}) + Q_{j_1 j_2}^{i_1 i_2}$$

$$= \delta_{j_1}^{i_1} \delta_{j_2}^{i_2} - \delta_{j_2}^{i_1} \delta_{j_1}^{i_2}. \tag{3.16}$$

Using these constraints, the SDP formalism is given by

Minimize $\mathbf{H} \cdot \mathbf{Y}$

subject to $\mathbf{F}_i \cdot \mathbf{Y} = c_i \tag{3.17}$

$$\widetilde{\mathbf{E}}_{j_1 j_2}^{i_1 i_2} \cdot \mathbf{Y} = \delta_{j_1}^{i_1} \delta_{j_2}^{i_2} - \delta_{j_2}^{i_1} \delta_{j_1}^{i_2}.$$

where $\widetilde{\mathbf{E}}_{j_1 j_2}^{i_1 i_2}$ is a symmetric matrix defined by

$$\widetilde{\mathbf{E}}_{j_1 j_2}^{i_1 i_2} = \tfrac{1}{2} (\mathbf{E}_{j_1 j_2}^{i_1 i_2} + \mathbf{E}_{i_1 i_2}^{j_1 j_2}), \tag{3.18}$$

and the explicit expression of the element of the constraint matrix $(\mathbf{E}_{j_1 j_2}^{i_1 i_2})_{l_1 l_2}^{k_1 k_2}$ is given by

$$(\mathbf{E}_{j_1 j_2}^{i_1 i_2})_{l_1 l_2}^{k_1 k_2} = 2 \delta_{k_1}^{i_1} \delta_{k_2}^{i_2} \delta_{l_1}^{j_1} \delta_{l_2}^{j_2} + \delta_{k_1}^{i_1+n} \delta_{k_2}^{i_2+n} \delta_{l_1}^{j_1+n} \delta_{l_2}^{j_2+n}$$

$$+ \frac{N-1}{2} \delta_{j_1}^{i_1} \delta_{k_1}^{i_2} \delta_{l_1}^{j_2} \delta_{l_2}^{k_2} + \frac{N-1}{2} \delta_{j_2}^{i_2} \delta_{k_1}^{i_1} \delta_{l_1}^{j_1} \delta_{l_2}^{k_2}$$

$$- \frac{N-1}{2} \delta_{j_2}^{i_1} \delta_{k_1}^{i_2} \delta_{l_1}^{j_1} \delta_{l_2}^{k_2} - \frac{N-1}{2} \delta_{j_1}^{i_2} \delta_{k_1}^{i_1} \delta_{l_1}^{j_2} \delta_{l_2}^{k_2} \tag{3.19}$$

and the constant $c_{j_1 j_2}^{i_1 i_2}$ in Eq. (3.16) is

$$c_{j_1 j_2}^{i_1 i_2} = \delta_{j_1}^{i_1} \delta_{j_2}^{i_2} - \delta_{j_2}^{i_1} \delta_{j_1}^{i_2}. \tag{3.20}$$

We can confirm Eq. (3.21) holds

$$\mathbf{E}_{j_1 j_2}^{i_1 i_2} \cdot \mathbf{Y} = \sum_{k_1 k_2 l_1 l_2} (\mathbf{E}_{j_1 j_2}^{i_1 i_2})_{l_1 l_2}^{k_1 k_2} (\mathbf{Y})_{l_1 l_2}^{k_1 k_2} = c_{j_1 j_2}^{i_1 i_2} \tag{3.21}$$

as follows. The first two terms of Eq. (3.21) are

$$\sum_{k_1 k_2 l_1 l_2} (2 \delta_{k_1}^{i_1} \delta_{k_2}^{i_2} \delta_{l_1}^{j_1} \delta_{l_2}^{j_2} + \delta_{k_1}^{i_1+n} \delta_{k_2}^{i_2+n} \delta_{l_1}^{j_1+n} \delta_{l_2}^{j_2+n}) (\mathbf{Y})_{l_1 l_2}^{k_1 k_2}$$

$$= 2(\mathbf{Y})_{j_1 j_2}^{i_1 i_2} + (\mathbf{Y})_{j_1+n, j_2+n}^{i_1+n, i_2+n} = 2\Gamma_{j_1 j_2}^{i_1 i_2} + Q_{j_1 j_2}^{i_1 i_2}, \tag{3.22}$$

the second two terms of Eq. (3.21) give,

$$\sum_{k_1 k_2 l_1 l_2} \left(\frac{N-1}{2} \delta_{j_1}^{i_1} \delta_{k_1}^{i_2} \delta_{l_1}^{j_2} \delta_{l_2}^{k_2} + \frac{N-1}{2} \delta_{j_2}^{i_2} \delta_{k_1}^{i_1} \delta_{l_1}^{j_1} \delta_{l_2}^{k_2} \right) (\mathbf{Y})_{l_1 l_2}^{k_1 k_2}$$

$$= \frac{N-1}{2} \sum_k \delta_{j_1}^{i_1} \Gamma_{j_2 k}^{i_2 k} + \frac{N-1}{2} \sum_k \delta_{j_2}^{i_2} \Gamma_{j_1 k}^{i_1 k}$$

$$= \delta_{j_1}^{i_1} \gamma_{j_2}^{i_2} + \delta_{j_2}^{i_2} \gamma_{j_1}^{i_1}, \tag{3.23}$$

and the last term gives

$$\sum_{k_1 k_2 l_1 l_2} \left(-\frac{N-1}{2} \delta_{i_1}^{j_2} \delta_{k_1}^{i_2} \delta_{l_1}^{j_1} \delta_{l_2}^{k_2} - \frac{N-1}{2} \delta_{i_2}^{j_1} \delta_{k_1}^{i_1} \delta_{l_1}^{j_2} \delta_{l_2}^{k_2} \right) (\mathbf{Y})_{l_1 l_2}^{k_1 k_2}$$

$$= -\frac{N-1}{2} \sum_k \delta_{i_1}^{j_2} \Gamma_{j_1 k}^{i_2 k} - \frac{N-1}{2} \sum_k \delta_{i_2}^{j_1} \Gamma_{j_2 k}^{i_1 k}$$

$$= -\delta_{j_2}^{i_1} \gamma_{j_1}^{i_2} - \delta_{j_1}^{i_2} \gamma_{j_2}^{i_1}. \tag{3.24}$$

Combining Eq. (3.22) and Eq. (3.24), we get Eq. (3.16).

Constraining P, Q, and G matrices to be positive semidefinite is done in essentially the same way as above. In this case, the variable matrix $\mathbf{Y}$ is defined as

$$\mathbf{Y} = \begin{pmatrix} \mathbf{P} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{Q} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{G} \end{pmatrix}. \tag{3.25}$$

We have a linear relation between Γ and G,

$$G_{j_1 j_2}^{i_1 i_2} = \delta_{j_2}^{i_2} \sum_k \frac{N-1}{2} \Gamma_{j_1 k}^{i_1 k} - 2\Gamma_{j_1 i_2}^{i_1 j_2}, \tag{3.26}$$

which is described by a set of linear constraints $\mathbf{J}_{j_1 j_2}^{i_1 i_2}$ for each element of G matrix as

$$\mathbf{J}_{j_1 j_2}^{i_1 i_2} \cdot \mathbf{Y} = 0 = -\delta_{j_2}^{i_2} \gamma_{j_1}^{i_1} + 2\Gamma_{j_1 i_2}^{i_1 j_2} + G_{j_1 i_2}^{i_1 j_2}, \tag{3.27}$$

and an explicit expression of the constraint matrix $(\mathbf{J}_{j_1 j_2}^{i_1 i_2})_{l_1 l_2}^{k_1 k_2}$ is given by

$$(\mathbf{J}_{j_1 j_2}^{i_1 i_2})_{l_1 l_2}^{k_1 k_2} = 2 \delta_{k_1}^{i_1} \delta_{k_2}^{i_2} \delta_{l_1}^{j_1} \delta_{l_2}^{j_2} + \delta_{k_1}^{i_1+2n} \delta_{k_2}^{i_2+2n} \delta_{l_1}^{j_1+2n} \delta_{l_2}^{j_2+2n}$$

$$- \frac{N-1}{2} \delta_{j_2}^{i_2} \delta_{k_1}^{i_1} \delta_{l_1}^{j_1} \delta_{l_2}^{k_2}, \tag{3.28}$$

which is further symmetrized as

$$\widetilde{\mathbf{J}}_{j_1 j_2}^{i_1 i_2} = \tfrac{1}{2} (\mathbf{J}_{j_1 j_2}^{i_1 i_2} + \mathbf{J}_{i_1 i_2}^{j_1 j_2}). \tag{3.29}$$

Thus, the DMVT using the P, Q, and G conditions is formulated into SDPA as

Minimize $\mathbf{H} \cdot \mathbf{Y}$

subjected to $\mathbf{F}_i \cdot \mathbf{Y} = c_i$

$$\widetilde{\mathbf{E}}_{j_1 j_2}^{i_1 i_2} \cdot \mathbf{Y} = \delta_{j_1}^{i_1} \delta_{j_2}^{i_2} - \delta_{j_2}^{i_1} \delta_{j_1}^{i_2} \tag{3.30}$$

$$\widetilde{\mathbf{J}}_{j_1 j_2}^{i_1 i_2} \cdot \mathbf{Y} = 0.$$

It is convenient to fold our 2-RDM into a compact form,

$$P_{j_1 j_2}^{i_1 i_2} \rightarrow P_j^i \tag{3.31}$$

TABLE I. Total energy and correlation energy in % in parentheses calculated by the DMVT with $P+Q$ and $P+Q+G$ conditions compared with those obatined by the wave function methods, full CI, and Hartree–Fock. The basis set is STO-6G except for notice.

System	State	Active MO[a]	Ele($\alpha+\beta$)[b]	DM($P+Q$)	DM($P+Q+G$)	Full CI	Hartree–Fock
Be[c]	^1S	4	4(2+2)	$-14.5934(176)$	$-14.5827(100)$	$-14.5827(100)$	$-14.5685(0)$
Be	^1S	5	4(2+2)	$-14.5579(103)$	$-14.5561(100)$	$-14.5561(100)$	$-14.5034(0)$
Be[d]	^1S	5	4(2+2)	$-14.6064(200)$	$-14.5895(100)$	$-14.5895(100)$	$-14.5725(0)$
Be[c]	^3S	4	4(3+1)	$-13.3168(120)$	$-13.3146(100)$	$-13.3146(100)$	$-13.3036(0)$
Be[d]	^3S	5	4(3+1)	$-14.3346(177)$	$-14.3241(100)$	$-14.3241(100)$	$-14.3105(0)$
LiH[c]	$^1\Sigma^+$	6	4(2+2)	$-8.0034(139)$	$-7.9924(100)$	$-7.9922(100)$	$-7.9635(0)$
LiH	$^1\Sigma^+$	6	4(2+2)	$-7.9731(104)$	$-7.9724(100)$	$-7.9723(100)$	$-7.9519(0)$
LiH[c]	$^3\Sigma^+$	6	4(3+1)	$-7.8997(167)$	$-7.8939(98)$	$-7.8940(100)$	$-7.8854(0)$
LiH	$^3\Sigma^+$	6	4(3+1)	$-7.8554(191)$	$-7.8552(97)$	$-7.8552(100)$	$-7.8549(0)$
BeH$^+$	$^1\Sigma^+$	6	4(2+2)	$-14.8452(106)$	$-14.8439(100)$	$-14.8438(100)$	$-14.8226(0)$
BH$^+$	$^2\Sigma^+$	6	5(3+2)	$-24.8169(151)$	$-24.8015(100)$	$-24.8015(100)$	$-24.7712(0)$
BH	$^1\Sigma^+$	6	6(3+3)	$-25.1234(211)$	$-25.0630(106)$	$-25.0593(100)$	$-25.0015(0)$
CH$^+$	$^1\Sigma^+$	6	6(3+3)	$-37.9618(227)$	$-37.8896(107)$	$-37.8853(100)$	$-37.8251(0)$
CH$^-$	$^3\Sigma^-$	6	8(5+3)	$-37.9834(148)$	$-37.9714(99)$	$-37.9718(100)$	$-37.9477(0)$
CH	$^2\Pi$	6	7(4+3)	$-38.2472(240)$	$-38.1917(111)$	$-38.1871(100)$	$-38.1443(0)$
NH$^+$	$^2\Pi$	6	7(4+3)	$-54.4510(248)$	$-54.3957(111)$	$-54.3914(100)$	$-54.3510(0)$
NH$^-$	$^2\Pi$	6	9(5+4)	$-54.5292(161)$	$-54.5150(99)$	$-54.5151(100)$	$-54.4920(0)$
NH	$^3\Sigma^-$	6	8(5+3)	$-54.8280(144)$	$-54.8160(100)$	$-54.8161(100)$	$-54.7887(0)$
OH$^+$	$^3\Sigma^-$	6	8(5+3)	$-74.7805(138)$	$-74.7719(100)$	$-74.7720(100)$	$-74.7491(0)$
OH$^-$	$^1\Sigma^+$	6	10(5+5)	$-74.8127(100)$	$-74.8112(95)$	$-74.8127(100)$	$-74.7851(0)$
OH	$^2\Pi$	6	9(5+4)	$-75.1164(158)$	$-75.1013(99)$	$-75.1014(100)$	$-75.0756(0)$
HF$^+$	$^2\Pi$	6	9(5+4)	$-99.1376(153)$	$-99.1278(100)$	$-99.1279(100)$	$-99.1096(0)$
HF	$^1\Sigma^+$	6	10(5+5)	$-99.5258(100)$	$-99.5229(89)$	$-99.5258(100)$	$-99.4998(0)$
BH$_2$	$^2A_1$	7	7(4+3)	$-25.7549(235)$	$-25.7089(115)$	$-25.7031(100)$	$-25.6649(0)$
BH$_2$	$^2B_1$	7	7(4+3)	$-25.7317(233)$	$-25.6837(113)$	$-25.6783(100)$	$-25.6383(0)$
CH$_2$	$^1A_1$	7	8(4+4)	$-38.9301(294)$	$-38.8228(119)$	$-38.8110(100)$	$-38.7497(0)$
CH$_2$	$^3B_1$	7	8(5+3)	$-38.9043(214)$	$-38.8566(107)$	$-38.8534(100)$	$-38.8089(0)$
CH$_2$	$^3\Sigma_u^-$	7	8(5+3)	$-38.8836(187)$	$-38.8358(103)$	$-38.8342(100)$	$-38.7772(0)$
NH$_2$	$^2A_1$	7	9(5+4)	$-55.4134(244)$	$-55.3570(111)$	$-55.3525(100)$	$-55.3101(0)$
NH$_2$	$^2B_1$	7	9(5+4)	$-55.4856(243)$	$-55.4195(108)$	$-55.4157(100)$	$-55.3670(0)$
H$_2$O	$^1A_1$	7	10(5+5)	$-75.7953(232)$	$-75.7310(104)$	$-75.7290(100)$	$-75.6789(0)$
H$_2$O$^+$	$^2A_1$	7	9(5+4)	$-75.4912(262)$	$-75.4218(106)$	$-75.4192(100)$	$-75.3748(0)$
FH$_2^+$	$^1A_1$	7	10(5+5)	$-99.8894(244)$	$-99.8305(103)$	$-99.8294(100)$	$-99.7879(0)$
BH$_3$	$^1A_1$	8	8(4+4)	$-26.4681(258)$	$-26.3932(120)$	$-26.3827(100)$	$-26.3287(0)$
CH$_3$	$^2A_2$	8	9(5+4)	$-39.6375(290)$	$-39.5283(117)$	$-39.5178(100)$	$-39.4547(0)$
NH$_3$	$^1A_1$	8	10(5+5)	$-56.2061(334)$	$-56.0617(115)$	$-56.0516(100)$	$-55.9855(0)$
NH$_3$ (dis)	^1A	8	10(5+5)	$-56.1808(326)$	$-56.0394(115)$	$-56.0293(100)$	$-55.9622(0)$
H$_3$O$^+$	$^1A_1$	8	10(5+5)	$-75.9422(276)$	$-75.8636(103)$	$-75.8621(100)$	$-75.8166(0)$

[a]Number of active MOs.
[b]Number of electrons with the number of α and β electrons in parentheses.
[c]Basis set is double-ζ.
[d]Basis set is triple-ζ.

by renumbering $i=i_1+\{[i_2(i_2-1)]/2\}$ if $i_1>i_2$ and discarding P when $i_1 \leqslant i_2$. This helps to cut down unnecessary variables and to automatically assume that 2-RDM has antisymmetric property. Similarly, the Q matrix and other linear constraints are also folded. Note that the G matrix does not have such a symmetry property, so that we use all the elements.

The present method involves very large number of linear constraints and may not be efficient; a merit is that the SDPA program is used without any modification. However, if we make a problem-specific SDP solver, it would be much more efficient than the present one, and such study is now in progress.

The DMVT formulated above has been applied to the ground states of different space and spin symmetries of neutral and charged species of 16 different atoms and molecules. They are Be(^1S), Be(^3S), LiH($^1\Sigma^+$), LiH($^3\Sigma^+$), BeH$^+$

BH$^+$, BH, CH$^+$, CH, CH$^-$, NH$^+$, NH$^-$, NH, OH$^+$, OH$^-$, OH, HF$^+$, HF, BH$_2$($^2A_1$), BH$_2$($^2B_1$), CH$_2$($^1A_1$), CH$_2$($^3B_1$), linear CH$_2$($^3\Sigma_u^-$), NH$_2$($^2A_1$), NH$_2$($^2B_1$), H$_2$O, H$_2$O$^+$, FH$_2^+$, BH$_3$, CH$_3$, NH$_3$, NH$_3$(dis) ("dis" stands for distorted in the sense that one bond length is shortened by 0.9 time, another one is lengthened by 1.1 time) and H$_3$O$^+$.

We used three different basis sets, double and triple-ζ s-type GTOs and STO-6G, for Be, and double-ζ s-type GTOs by Huzinaga[20] and Dunning[21] and STO-6G for LiH. For all the other molecules, we used the STO-6G basis set.[22] The geometries we used are the experimental ones.[23,24]

IV. RESULTS AND DISCUSSION

We show in Table I the total energy of the system calculated by the present method and in parentheses the calculated correlation energy in percentage relative to the

TABLE II. Dipole moments caluclated by the DMVT with $P+Q$ and $P+Q+G$ conditions compared with those obtained by the wave function method. The basis set is STO-6G except for notice.

Molecule	State	DM($P+Q$)	DM($P+Q+G$)	Full CI	Hartree–Fock
LiH[a]	$^1\Sigma^+$	1.6445	1.6164	1.6192	2.0764
LiH	$^1\Sigma^+$	1.7372	1.7523	1.7519	1.9339
LiH[a]	$^3\Sigma^+$	0.6225	0.6258	0.6258	0.6261
LiH	$^3\Sigma^+$	1.5897	1.5906	1.5907	1.5915
BeH$^+$	$^1\Sigma^+$	1.3203	1.3188	1.3196	1.2987
BH$^+$	$^2\Sigma^+$	0.0495	0.0223	0.0223	0.0197
BH	$^1\Sigma^+$	0.2833	0.2935	0.2994	0.3806
CH$^+$	$^1\Sigma^+$	0.6893	0.6764	0.6905	0.7253
CH$^-$	$^3\Sigma^-$	0.1826	0.1925	0.1929	0.1669
CH	$^2\Pi$	0.6016	0.4878	0.5044	0.4406
NH$^+$	$^2\Pi$	0.8937	0.8729	0.8804	0.8789
NH$^-$	$^2\Pi$	0.1359	0.1311	0.1321	0.1431
NH	$^3\Sigma^-$	0.4730	0.4995	0.4996	0.5233
OH$^+$	$^3\Sigma^-$	0.9988	0.9741	0.9742	0.9875
OH$^-$	$^1\Sigma^+$	0.0620	0.0637	0.0620	0.0725
OH	$^2\Pi$	0.4497	0.4738	0.4745	0.5166
HF$^+$	$^2\Pi$	0.9600	0.9993	0.9999	1.0786
HF	$^1\Sigma^+$	0.5420	0.5383	0.5420	0.5228
BH$_2$	$^2A_1$	0.0037	0.0328	0.0344	0.0466
CH$_2$	$^1A_1$	0.2435	0.5057	0.5293	0.6224
CH$_2$	$^3B_1$	0.0838	0.0857	0.0934	0.1006
NH$_2$	$^2A_1$	0.5170	0.5407	0.5509	0.5580
NH$_2$	$^2B_1$	0.6433	0.6816	0.6896	0.7200
H$_2$O	$^1A_1$	0.5993	0.6460	0.6487	0.6927
H$_2$O$^+$	$^2A_1$	0.8718	0.9857	0.9920	1.0724
FH$_2^+$	$^1A_1$	1.0368	1.0429	1.0437	1.0560
NH$_3$	$^1A_1$	0.6903	0.6901	0.6922	0.6935
NH$_3$ (dis)	^1A	0.6660	0.6634	0.6767	0.6937
H$_3$O$^+$	$^1A_1$	1.4162	1.4286	1.4289	1.4320

[a]Basis set is double-ζ.

TABLE III. Virial coefficients caluclated by the DMVT with the $P+Q$ and $P+Q+G$ conditions compared with those obtained by the wave function methods. The basis set is STO-6G except for notice.

System	State	DM($P+Q$)	DM($P+Q+G$)	Full CI	Hartree–Fock
Be[a]	^1S	1.9975	1.9989	1.9989	1.9994
Be	^1S	1.9621	1.9614	1.9614	1.9558
Be[b]	^1S	2.0017	2.0006	2.0006	2.0000
Be[a]	^3S	1.7459	1.7461	1.7461	1.7464
Be[b]	^3S	1.9774	1.9766	1.9766	1.9759
LiH[a]	$^1\Sigma^+$	2.0038	1.9977	1.9977	1.9929
LiH	$^1\Sigma^+$	1.9832	1.9826	1.9826	1.9837
LiH[a]	$^3\Sigma^+$	1.9908	1.9875	1.9875	1.9826
LiH	$^3\Sigma^+$	1.9579	1.9577	1.9577	1.9574
BeH$^+$	$^1\Sigma^+$	2.0036	2.0031	2.0031	2.0041
BH$^+$	$^2\Sigma^+$	1.9918	1.9919	1.9918	1.9931
BH	$^1\Sigma^+$	1.9574	1.9565	1.9566	1.9550
CH$^+$	$^1\Sigma^+$	2.0044	2.0040	2.0039	2.0025
CH$^-$	$^3\Sigma^-$	1.9393	1.9392	1.9393	1.9396
CH	$^2\Pi$	1.9781	1.9778	1.9777	1.9773
NH$^+$	$^2\Pi$	2.0164	2.0156	2.0154	2.0144
NH$^-$	$^2\Pi$	1.9596	1.9597	1.9597	1.9601
NH	$^3\Sigma^-$	1.9941	1.9939	1.9938	1.9939
OH$^+$	$^3\Sigma^-$	2.0199	2.0194	2.0194	2.0183
OH$^-$	$^1\Sigma^+$	1.9672	1.9671	1.9672	1.9678
OH	$^2\Pi$	1.9967	1.9965	1.9965	1.9965
HF$^+$	$^2\Pi$	2.0218	2.0212	2.0212	2.0201
HF	$^1\Sigma^+$	2.0001	2.0001	2.0001	1.9999
BH$_2$	$^2A_1$	1.9722	1.9727	1.9731	1.9738
BH$_2$	$^2B_1$	1.9699	1.9702	1.9705	1.9712
CH$_2$	$^1A_1$	1.9849	1.9840	1.9840	1.9841
CH$_2$	$^3B_1$	1.9889	1.9884	1.9886	1.9886
CH$_2$	$^3\Sigma_u^-$	1.9882	1.9876	1.9878	1.9877
NH$_2$	$^2A_1$	1.9950	1.9943	1.9942	1.9940
NH$_2$	$^2B_1$	1.9956	1.9955	1.9955	1.9956
H$_2$O	$^1A_1$	1.9966	1.9968	1.9968	1.9967
H$_2$O$^+$	$^2A_1$	2.0176	2.0152	2.0151	2.0138
FH$_2^+$	$^1A_1$	2.0183	2.0159	2.0158	2.0143
BH$_3$	$^1A_1$	1.9835	1.9836	1.9843	1.9853
CH$_3$	$^2A_2$	1.9941	1.9939	1.9944	1.9948
NH$_3$	$^1A_1$	1.9981	1.9985	1.9984	1.9985
NH$_3$ (dis)	^1A	1.9973	1.9976	1.9974	1.9976
H$_3$O$^+$	$^1A_1$	1.9972	1.9941	1.9941	1.9934

[a]Basis set is double-ζ.
[b]Basis set is triple-ζ.

Hartree–Fock (0%) and full-CI (100%) results. Two types of SDP relaxation calculations are performed. One uses the P and Q conditions together with the seven conditions given by Eqs. (2.3)–(2.10); it is referred to as DM($P+Q$). The other uses the G condition additionally and it is denoted as DM($P+Q+G$).

We first examine the results of DM($P+Q$) calculations. We see that the results for OH$^-$ and HF are excellent, but this is not a good news but simply due to the too restrictive variational space: 10 electrons are distributed into six orbitals and therefore in this case $P+Q$ condition gives the complete N-representability condition (2 hole system).[25] Similarly, the extent of overshooting is relatively small because the variational space is too restrictive. When the variation is reasonably free, the DM($P+Q$) energy overshoots too much the full-CI energy up to 334% of the full-CI correlation energy for NH$_3$. This result shows that the $P+Q$ condition together with the above seven conditions is still too far from the complete N-representability condition.

When we impose further the G condition, we obtain the results shown under DM($P+Q+G$). They are much improved in comparison with the results of DM($P+Q$). The calculated correlation energy percentages range within 100%–110% for atoms and diatomic molecules, while they range in 110%–120% for triatomic molecules. This means that the G condition is a nice restrictive condition for the

N-representability. We investigated distorted ammonia to examine whether the spatial symmetry affects the N-representability condition, however, this calculation shows that there is no effect by such a small distortion; the accuracies of the two calculations are almost the same.

The SDP variational method should give, in principle, a lower bound for energy, however, compared to the full-CI results, the breakdown where the calculated SDPA energy is *higher* than the full-CI energy occurs for LiH($^3\Sigma$, STO-6G), LiH($^3\Sigma$, double-ζ), CH$^-$, NH$^-$, OH, OH$^-$, and HF, though the violations are within 1 mhartree. It seems that these breakdowns are related to the numerical errors in the SDPA procedure, which we discuss later.

In Table II, we show the (nonzero) dipole moments of the molecules calculated here. The dipole moment obtained at the level of DM($P+Q$) is not so good. In particular, those for CH, NH$^+$, CH$_2$, H$_2$O, and H$_2$O$^+$ are worse than the Hartree–Fock results. At the DM($P+Q+G$) level, how-

TABLE IV. Number of the constraints and the numerical errors of the $DM(P+Q)$ calculations. The basis set is STO-6G except for notice.

System	State	Active[a] MOs	Ele$(\alpha+\beta)$[b] constraints	No. of constraints	Primal feasible error	Dual feasible error	Gap
Be[c]	^1S	4	4(2+2)	183	1.87×10^{-14}	9.24×10^{-11}	1.17×10^{-9}
Be	^1S	5	4(2+2)	440	7.87×10^{-14}	4.35×10^{-11}	8.03×10^{-13}
Be[d]	^1S	5	4(2+2)	440	5.49×10^{-14}	1.41×10^{-10}	1.89×10^{-11}
Be[c]	^3S	4	4(3+1)	183	4.12×10^{-11}	1.17×10^{-7}	3.87×10^{-8}
Be[d]	^3S	5	4(3+1)	440	7.86×10^{-12}	1.12×10^{-7}	9.58×10^{-9}
LiH[c]	$^1\Sigma^+$	6	4(2+2)	911	7.24×10^{-14}	9.24×10^{-9}	3.46×10^{-9}
LiH	$^1\Sigma^+$	6	4(2+2)	911	8.52×10^{-14}	1.08×10^{-9}	4.76×10^{-11}
LiH[c]	$^3\Sigma^+$	6	4(3+1)	911	3.80×10^{-12}	1.75×10^{-6}	3.64×10^{-7}
LiH	$^3\Sigma^+$	6	4(3+1)	911	3.41×10^{-11}	4.57×10^{-8}	1.89×10^{-8}
BeH$^+$	$^1\Sigma^+$	6	4(2+2)	911	1.16×10^{-13}	3.02×10^{-11}	5.73×10^{-13}
BH$^+$	$^2\Sigma^+$	6	5(3+2)	911	6.69×10^{-14}	1.86×10^{-10}	3.26×10^{-12}
BH	$^1\Sigma^+$	6	6(3+3)	911	4.43×10^{-14}	8.29×10^{-10}	2.41×10^{-11}
CH$^+$	$^1\Sigma^+$	6	6(3+3)	911	3.62×10^{-14}	1.30×10^{-9}	9.62×10^{-12}
CH$^-$	$^3\Sigma^-$	6	8(5+3)	911	5.49×10^{-12}	8.97×10^{-8}	6.05×10^{-9}
CH	$^2\Pi$	6	7(4+3)	911	5.91×10^{-14}	2.23×10^{-9}	2.80×10^{-11}
NH$^+$	$^2\Pi$	6	7(4+3)	911	3.15×10^{-14}	9.98×10^{-10}	1.49×10^{-11}
NH$^-$	$^2\Pi$	6	9(5+4)	911	8.57×10^{-12}	7.06×10^{-8}	3.70×10^{-9}
NH	$^3\Sigma^-$	6	8(5+3)	911	9.79×10^{-12}	4.97×10^{-7}	1.85×10^{-8}
OH$^+$	$^3\Sigma^-$	6	8(5+3)	911	6.77×10^{-12}	8.16×10^{-8}	2.49×10^{-9}
OH$^-$	$^1\Sigma^+$	6	10(5+5)	911	7.50×10^{-12}	5.25×10^{-7}	7.32×10^{-8}
OH	$^2\Pi$	6	9(5+4)	911	5.54×10^{-12}	1.35×10^{-7}	3.48×10^{-9}
HF$^+$	$^2\Pi$	6	9(5+4)	911	2.36×10^{-12}	8.42×10^{-8}	2.96×10^{-9}
HF	$^1\Sigma^+$	6	10(5+5)	911	6.82×10^{-12}	1.12×10^{-7}	6.65×10^{-9}
BH$_2$	$^2A_1$	7	7(4+3)	1692	6.43×10^{-14}	4.94×10^{-10}	4.65×10^{-11}
BH$_2$	$^2B_1$	7	7(4+3)	1692	5.66×10^{-14}	8.16×10^{-12}	3.20×10^{-12}
CH$_2$	$^1A_1$	7	8(4+4)	1692	3.25×10^{-14}	3.26×10^{-11}	3.19×10^{-10}
CH$_2$	$^3B_1$	7	8(5+3)	1692	3.98×10^{-14}	5.94×10^{-11}	5.75×10^{-10}
CH$_2$	$^3\Sigma_u^-$	7	8(5+3)	1692	4.12×10^{-14}	6.59×10^{-11}	5.88×10^{-11}
NH$_2$	$^2A_1$	7	9(5+4)	1692	3.63×10^{-14}	1.21×10^{-9}	1.22×10^{-10}
NH$_2$	$^2B_1$	7	9(5+4)	1692	3.99×10^{-14}	2.46×10^{-11}	3.91×10^{-10}
H$_2$O	$^1A_1$	7	10(5+5)	1692	3.33×10^{-14}	2.88×10^{-10}	1.29×10^{-10}
H$_2$O$^+$	$^2A_1$	7	9(5+4)	1692	3.31×10^{-14}	3.02×10^{-11}	2.64×10^{-10}
FH$_2^+$	$^1A_1$	7	10(5+5)	1692	3.46×10^{-14}	3.19×10^{-10}	1.12×10^{-10}
BH$_3$	$^1A_1$	8	8(4+4)	2897	6.57×10^{-14}	7.62×10^{-10}	3.37×10^{-11}
CH$_3$	$^2A_2$	8	9(5+4)	2897	3.87×10^{-14}	1.12×10^{-11}	8.68×10^{-10}
NH$_3$	$^1A_1$	8	10(5+5)	2897	4.07×10^{-14}	5.16×10^{-11}	1.02×10^{-10}
NH$_3$ (dis)	^1A	8	10(5+5)	2897	4.38×10^{-14}	5.87×10^{-10}	1.62×10^{-10}
H$_3$O$^+$	$^1A_1$	8	10(5+5)	2897	4.13×10^{-14}	5.29×10^{-10}	6.77×10^{-11}

[a]Number of active MOs.
[b]Number of electrons with the number of α and β electrons in parentheses.
[c]Basis set is double-ζ.
[d]Basis set is triple-ζ.

ever, the dipole moments are drastically improved and all the results well reproduce the full-CI ones, except for NH$_3$ and NH$_3$(dis) for which even Hartree–Fock calculations give good results and the deviations are very small.

In Table III, we show the virial coefficient $\langle V\rangle/\langle T\rangle$, where $\langle V\rangle$ and $\langle T\rangle$ denote average potential and kinetic energies, respectively, which must be two for completely variational wave function. When we use $DM(P+Q+G)$ approximation, the calculated virial is almost completely identical with the full-CI result.

Next, we discuss the numerical accuracy of the SDP method. In Tables IV and V, we summarize the number of the constraints and the numerical errors of the $DM(P+Q)$ and $DM(P+Q+G)$ calculations. The primal feasible error is defined by

$$\max\left\{\left|\left[\mathbf{X}-\sum_{i=1}^{m}\mathbf{F}_i x_i+\mathbf{F}_0\right]_{pq}\right| \;:\; p,q=1,2,\ldots,n\right\} \quad (4.1)$$

and the dual feasible error is defined by

$$\max\{|\mathbf{F}_i\cdot\mathbf{Y}-c_i| \;:\; i=1,2,\ldots,m\}. \quad (4.2)$$

The gap denotes the difference between the primal and dual functions defined by

$$\left|\sum_{i=1}^{m}c_i x_i-\mathbf{F}_0\cdot\mathbf{Y}\right|. \quad (4.3)$$

These three quantities give criteria of the accuracy of the SDPA. In the SDPA, our object is the minimization of the

TABLE V. Number of the constraints and the numerical errors of the DM($P+Q+G$) calculations. The basis set is STO-6G except for notice.

System	State	Active[a] MOs	Ele$(\alpha+\beta)$[b]	No. of constraints	Primal feasible error	Dual feasible error	Gap
Be[c]	^1S	4	4(2+2)	983	6.55×10^{-11}	1.87×10^{-7}	2.87×10^{-6}
Be	^1S	5	4(2+2)	2365	7.02×10^{-12}	4.93×10^{-7}	1.42×10^{-6}
Be[d]	^1S	5	4(2+2)	2365	7.92×10^{-11}	4.15×10^{-7}	2.48×10^{-6}
Be[c]	^3S	4	4(3+1)	983	1.12×10^{-10}	7.44×10^{-7}	3.08×10^{-6}
Be[d]	^3S	5	4(3+1)	2365	1.41×10^{-11}	1.65×10^{-7}	2.94×10^{-7}
LiH[c]	$^1\Sigma^+$	6	4(2+2)	4871	5.72×10^{-12}	2.33×10^{-5}	4.50×10^{-6}
LiH	$^1\Sigma^+$	6	4(2+2)	4871	5.77×10^{-12}	7.55×10^{-8}	1.69×10^{-6}
LiH[c]	$^3\Sigma^+$	6	4(3+1)	4871	3.53×10^{-11}	6.35×10^{-7}	2.41×10^{-5}
LiH	$^3\Sigma^+$	6	4(3+1)	4871	5.79×10^{-11}	6.56×10^{-7}	2.58×10^{-6}
BeH$^+$	$^1\Sigma^+$	6	4(2+2)	4871	2.42×10^{-11}	1.88×10^{-7}	1.93×10^{-6}
BH$^+$	$^2\Sigma^+$	6	5(3+2)	4871	7.84×10^{-12}	7.50×10^{-8}	7.82×10^{-7}
BH	$^1\Sigma^+$	6	6(3+3)	4871	2.80×10^{-11}	1.43×10^{-5}	1.61×10^{-8}
CH$^+$	$^1\Sigma^+$	6	6(3+3)	4871	3.75×10^{-12}	2.41×10^{-7}	9.68×10^{-7}
CH$^-$	$^3\Sigma^-$	6	8(5+3)	4871	1.43×10^{-11}	3.73×10^{-7}	2.13×10^{-5}
CH	$^2\Pi$	6	7(4+3)	4871	6.06×10^{-12}	8.54×10^{-6}	1.91×10^{-7}
NH$^+$	$^2\Pi$	6	7(4+3)	4871	4.15×10^{-12}	3.64×10^{-6}	4.98×10^{-7}
NH$^-$	$^2\Pi$	6	9(5+4)	4871	6.89×10^{-12}	3.39×10^{-6}	1.37×10^{-5}
NH	$^3\Sigma^-$	6	8(5+3)	4871	8.69×10^{-11}	1.88×10^{-5}	2.90×10^{-6}
OH$^+$	$^3\Sigma^-$	6	8(5+3)	4871	7.98×10^{-12}	4.05×10^{-7}	1.90×10^{-6}
OH$^-$	$^1\Sigma^+$	6	10(5+5)	4871	2.54×10^{-11}	5.65×10^{-6}	2.72×10^{-5}
OH	$^2\Pi$	6	9(5+4)	4871	1.01×10^{-11}	2.78×10^{-6}	6.15×10^{-6}
HF$^+$	$^2\Pi$	6	9(5+4)	4871	1.09×10^{-11}	1.40×10^{-6}	6.07×10^{-6}
HF	$^1\Sigma^+$	6	10(5+5)	4871	1.39×10^{-11}	7.37×10^{-6}	3.99×10^{-5}
BH$_2$	$^2A_1$	7	7(4+3)	8993	2.50×10^{-12}	8.84×10^{-8}	8.00×10^{-7}
BH$_2$	$^2B_1$	7	7(4+3)	8993	9.48×10^{-12}	1.23×10^{-6}	1.59×10^{-6}
CH$_2$	$^1A_1$	7	8(4+4)	8993	4.14×10^{-12}	3.54×10^{-6}	2.69×10^{-7}
CH$_2$	$^3B_1$	7	8(5+3)	8993	1.57×10^{-10}	4.05×10^{-5}	1.28×10^{-7}
CH$_2$	$^3\Sigma_u^-$	7	8(5+3)	8993	4.72×10^{-12}	3.98×10^{-7}	1.58×10^{-6}
NH$_2$	$^2A_1$	7	9(5+4)	8993	7.65×10^{-12}	4.30×10^{-6}	1.30×10^{-6}
NH$_2$	$^2B_1$	7	9(5+4)	8993	2.36×10^{-12}	3.22×10^{-8}	2.16×10^{-6}
H$_2$O	$^1A_1$	7	10(5+5)	8993	1.54×10^{-12}	1.05×10^{-7}	3.63×10^{-7}
H$_2$O$^+$	$^2A_1$	7	9(5+4)	8993	1.12×10^{-11}	6.86×10^{-6}	7.63×10^{-7}
FH$_2^+$	$^1A_1$	7	10(5+5)	8993	3.78×10^{-12}	5.14×10^{-7}	6.07×10^{-7}
BH$_3$	$^1A_1$	8	8(4+4)	15 313	5.02×10^{-11}	5.34×10^{-7}	2.88×10^{-7}
CH$_3$	$^2A_2$	8	9(5+4)	15 313	4.26×10^{-12}	6.16×10^{-7}	9.01×10^{-8}
NH$_3$	$^1A_1$	8	10(5+5)	15 313	1.65×10^{-12}	4.62×10^{-7}	4.39×10^{-7}
NH$_3$ (dis)	^1A	8	10(5+5)	15 313	3.29×10^{-12}	1.42×10^{-6}	4.14×10^{-6}
H$_3$O$^+$	$^1A_1$	8	10(5+5)	15 313	1.59×10^{-12}	2.30×10^{-7}	2.24×10^{-6}

[a]Number of active MOs.
[b]Number of electrons with the number of α and β electrons in parentheses.
[c]Basis set is double-ζ.
[d]Basis set is triple-ζ.

dual form of the problem, so that the dual feasible error is an important quantity, indicating the numerical accuracy of the calculation.

For DM($P+Q$), the dual feasible error is in the range of 10^{-7}–10^{-12}, while for DM($P+Q+G$), it ranges 10^{-5}–10^{-8}. As the number of the constraints increases drastically in the $P+Q+G$ calculations, the numerical accuracy becomes much worse in the DM($P+Q+G$) results. The gap value shows the same tendency. The worst five are HF(3.99×10^{-5}), OH$^-$ (2.72×10^{-5}), LiH(double-ζ, $^3\Sigma$; 2.41×10^{-5}), CH$^-$ (2.31×10^{-5}), and NH$^-$ (1.37×10^{-5}). We notice that they have the DM($P+Q+G$) energies *higher* than the full-CI ones, though these values must be *lower* than the full-CI values. There seems to be some relation between the gap value and the numerical accuracy in the SDPA technique. Another reason is certainly the too small

variational freedom in the calculations of HF and OH$^-$; actually in these cases P and Q conditions are already sufficient; the number of holes is 2, so the 2-hole system with Q condition is just like performing variational calculation for the 2-electron system with the P condition. Therefore enforcing P, Q, and G conditions is essentially the same as enforcing P and Q conditions.

The primal feasible values are very small (10^{-12}–10^{-14}) for DM($P+Q$) calculations and also small (10^{-10}–10^{-12}) for DM($P+Q+G$) calculations. We do not find any relationship between the accuracies of the present calculations and the primal feasible errors. So the accuracy of the present calculation seems to be related only to that of the primal problem.

In Table VI, we show the occupation numbers (eigenval-

TABLE VI. Occupation number calculated by the DMVT with $P+Q$ and $P+Q+G$ conditions compared with those obatined by the wave function methods, full CI, and Hartree–Fock, for Be, H_2O, and CH_2.

System, state, basis	DM($P+Q$)	DM($P+Q+G$)	Full CI	Hartree–Fock
Be, ^1S, STO-6G	$0.036\,641\times4, 0.036\,642\times2$	$0.035\,909\times6$	$0.035\,901\times6$	0×6
	$0.890\,243\times2$	$0.892\,275\times2$	$0.892\,298\times2$	1×4
	$0.999\,832\times2$	$0.999\,997\times2$	$0.999\,998\times2$	
Be, ^1S, triple-ζ	$0.000\,202\times2$	$0.000\,064\times2$	$0.000\,055\times2$	0×6
	$0.001\,041\times2$	$0.000\,595\times2$	$0.000\,590\times2$	
	$0.006\,149\times2$	$0.004\,153\times2$	$0.004\,119\times2$	
	$0.993\,649\times2$	$0.995\,837\times2$	$0.995\,879\times2$	1×4
	$0.998\,959\times2$	$0.999\,352\times2$	$0.999\,357\times2$	
Be, ^3S, triple-ζ	$0.000\,004$	$0.000\,000$	$0.000\,000$	0×6
	$0.000\,187$	$0.000\,001$	$0.000\,000$	
	$0.000\,573$	$0.000\,011$	$0.000\,007$	
	$0.000\,645$	$0.000\,013$	$0.000\,009$	
	$0.000\,702$	$0.000\,707$	$0.000\,707$	
	$0.001\,511$	$0.000\,712$	$0.000\,711$	
	$0.998\,534$	$0.999\,280$	$0.999\,284$	1×4
	$0.999\,252$	$0.999\,286$	$0.999\,287$	
	$0.999\,293$	$0.999\,990$	$0.999\,995$	
	$0.999\,299$	$0.999\,998$	$1.000\,000$	
H_2O, $^1A_1$, STO-6G	$0.029\,795\times2$	$0.013\,850\times2$	$0.013\,304\times2$	0×4
	$0.031\,585\times2$	$0.014\,766\times2$	$0.013\,509\times2$	
	$0.970\,205\times2$	$0.986\,433\times2$	$0.986\,732\times2$	1×10
	$0.970\,570\times2$	$0.987\,475\times2$	$0.988\,323\times2$	
	$0.998\,733\times2$	$0.998\,702\times2$	$0.998\,973\times2$	
	$0.999\,114\times2$	$0.998\,776\times2$	$0.999\,161\times2$	
	$0.999\,998\times2$	$0.999\,999\times2$	$0.999\,999\times2$	
CH_2, $^1A_1$, STO-6G	$0.037\,796\times4$	$0.014\,336\times2$	$0.010\,854\times2$	0×6
	$0.314\,251\times2$	$0.016\,294\times2$	$0.012\,979\times2$	
	$0.685\,804\times2$	$0.069\,501\times2$	$0.050\,589\times2$	
	$0.962\,204\times4$	$0.929\,480\times2$	$0.947\,809\times2$	1×8
	$0.999\,945\times2$	$0.984\,098\times2$	$0.987\,470\times2$	
		$0.986\,297\times2$	$0.990\,307\times2$	
		$0.999\,993\times2$	$0.999\,993\times2$	

ues of 1-RDM) for Be(^1S, STO-6G), Be(^1S, triple-ζ), Be(^3S, triple-ζ), H_2O($^1A_1$, STO-6G), and CH_2($^1A_1$, STO-6G). For Be(^1S, STO-6G), the occupation numbers of the $2p$ orbitals should be sixfold degenerate. Although we did not impose such constraints, this degeneracy accurately holds in both DM($P+Q$) and DM($P+Q+G$) calculations. For singlet states, both DM($P+Q$) and DM($P+Q+G$) calculations reproduced the degeneracy of the twofold occupation without constraints. Generally, the occupation numbers of the DM calculations are much more distributed over all the natural orbitals than those of the full CI. Although such a trend is reduced for the DM($P+Q+G$) calculation, it contradicts our expectation; the occupation numbers are ex-

pected to be less distributed in the calculations with less sufficient N-representability conditions. An extreme case was CH_2, this tendency is very amplified and the accidental degeneracy of occupation are found in the DM($P+Q$) calculation.

In Table VII, the root-mean-square (rms) deviation d of the 2-RDM from the full CI,

$$d = \sqrt{\sum_{i_1 i_2 j_1 j_2} \{(\Gamma_{\text{calculated}})_{j_1 j_2}^{i_1 i_2} - (\Gamma_{\text{full CI}})_{j_1 j_2}^{i_1 i_2}\}^2} \qquad (4.4)$$

is presented for the systems examined in Table VI. The deviations of the 2-RDM are quite small in DM($P+Q+G$)

TABLE VII. RMS deviations of the 2-RDMs calculated by DMVT with $P+Q$ and $P+Q+G$ conditions from those by full CI for Be, H_2O, and CH_2.

System, state, basis	DM($P+Q$)	DM($P+Q+G$)	Full CI	Hartree–Fock
Be, ^1S, STO-6G	0.049 208	0.000 162	0	0.526 569
Be, ^1S, triple-ζ	0.049 615	0.003 567	0	0.100 331
Be, ^3S, triple-ζ	0.029 401	0.000 715	0	0.039 123
H_2O, $^1A_1$, STO-6G	0.467 084	0.029 694	0	0.266 154
CH_2, $^1A_1$, STO-6G	1.604 712	0.153 503	0	0.484 788

TABLE VIII. Comparison of largest eigenvalues P, Q, G-matrices and smallest G-matrix calculated by DMVT with $P+Q$ and $P+Q+G$ conditions compared with those obtained by the wave function methods, full CI, and Hartree–Fock for Be, H_2O, and CH_2.

System, state, basis	DM($P+Q$)	DM($P+Q+G$)	Full CI	Hartree–Fock
Be, ^1S, STO-6G				
Largest P	1.005 284	1.000 907	1.000 874	1
Largest Q	2.264 502	2.259 861	2.259 834	2
Largest G	3.675 970	3.682 340	3.682 407	4
Smallest G	−0.007 288	0.000 000	0.000 000	0
Be, ^1S, triple-ζ				
Largest P	1.004 751	1.000 672	1.000 612	1
Largest Q	2.008 541	2.002 209	2.002 072	2
Largest G	3.978 475	3.985 686	3.985 726	4
Smallest G	−0.002 482	0.000 000	0.000 000	0
Be, ^3S, triple-ζ				
Largest P	1.002 019	0.999 991	0.999 995	1
Largest Q	2.005 387	2.000 230	2.000 233	2
Largest G	3.994 883	3.997 833	3.997 849	4
Smallest G	−0.001 439	0.000 000	0.000 000	0
H_2O, $^1A_1$, STO-6G				
Largest P	1.034 378	1.010 041	1.008 652	1
Largest G	9.805 708	9.900 236	9.904 312	10
Smallest G	−0.188 367	0.000 000	0.000 000	0
CH_2, $^1A_1$, STO-6G				
Largest P	1.090 030	1.024 402	1.019 529	1
Largest Q	2.227 026	2.059 546	2.042 417	2
Largest G	6.942 144	7.679 238	7.746 013	8
Smallest G	−0.208 966	0.000 001	0.000 000	0

calculation especially for small systems, where DM($P+Q+G$) give the identical total energy and virial coefficient to full CI. However, DM($P+Q$) calculations gave worse results and even worse than Hartree–Fock for H_2O and CH_2.

In Table VIII, we compare the largest eigenvalues of P, Q, and G-matrices and smallest eigenvalues of G-matrix, for the same systems. Largest eigenvalues of P and Q-matrices become smaller as the calculation quality becomes better, while those of G-matrix become larger. In DM($P+Q$) calculations, smallest eigenvalues of G-matrix are negative. As we expected, smallest eigenvalue of G-matrix becomes smaller when electron correlation gets larger. We did not show the smallest eigenvalues of P and Q-matrices since in any case, they are almost zero (absolute values are smaller than 10^{-6}). The deviation of these values that are large for the CH_2 [largest eigenvalue of G-matrix for DM($P+Q+G$)] calculation is 7.679 238 compared to the full CI's one 7.746 013, while the SDPA errors are small (primal and dual feasibilities are 4.14×10^{-12} and 3.54×10^{-6}, respectively, and gap is 2.69×10^{-7}). Therefore, we conclude that the error originates from the insufficiency of the N-representability conditions rather than that of the SDPA.

The trace of the Q matrix is normalized to $(r-N)\times(r-N+1)$, where r is number of MO (or rank of 1-RDM) and N is the number of the electrons. This condition is satisfied when we impose the constraint for the number of the electrons.

Lastly, we note that we find essentially no problem in

finding the minimum and this should be the case for other systems. This is certainly a merit of the present method.

V. CONCLUSION

The DMVT is developed systematically by using SDPA as a problem solver. This technique is very stable and there were no example where we could not get a convergence. In addition to several trivial conditions, the $P+Q$ condition is insufficient, while the $P+Q+G$ condition gives satisfactory results, the extent of overshooting the full-CI energy being small for the systems presently examined. The dipole moment and the virial coefficient calculated by the DM($P+Q+G$) method are also very close to the full-CI values. This method is applicable to the ground state of any spin- and space symmetry of closed and open-shell systems.

In this DMVT approach, the calculated energy is a lower bound of the exact energy. The errors of the present DM($P+Q+G$) method are permissible in both energy and properties. Though most quantum chemical method available give the ground-state energy higher than the full-CI one, the present method giving lower energy is equally permissible as an approximate quantum chemical method, if it is stable and feasible in cost performance. For the second requirement, the present stage of the theory is an infant stage, but much progress is expected in future.

ACKNOWLEDGMENT

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