Density matrix variational theory: Application to the potential energy surfaces and strongly correlated systems

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The density matrix variational theory (DMVT) algorithm developed previously [J. Chem. Phys. **114**, 8282 (2001)] was utilized for calculations of the potential energy surfaces of molecules, H_4, H_2O, NH_3, BH_3, CO, N_2, C_2, and Be_2. The DMVT(PQG), using the P, Q, and G conditions as subsidiary condition, reproduced the full-CI curves very accurately even up to the dissociation limit. The method described well the quasidegenerate states and the strongly correlated systems. On the other hand, the DMVT(PQ) was not satisfactory especially in the dissociation limit and its potential curves were always repulsive. The size consistency of the method was discussed and the G condition was found to be essential for the correct behavior of the potential curve. Further, we also examined the Weinhold–Wilson inequalities for the resultant 2-RDM of DMVT(PQG) calculations. Two linear inequalities were violated when the results were less accurate, suggesting that this inequality may provide a useful N-representability condition for the DMVT. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1453961]

I. INTRODUCTION

The second-order reduced density matrix (2-RDM) completely describes the N-body fermion system since any observable properties of the system can be calculated from the 2-RDM.[1,2] This fact has motivated us to use 2-RDM as a basic variable of quantum mechanics instead of the wave function Ψ. If we can determine 2-RDM 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). There are two categories in the DMT with respect to the determination of the RDM. One is based on the density equation,[3] which is equivalent to the Schrödinger equation in the necessary and sufficient sense. This approach is called density equation theory (DET). Recently, DET is extensively studied and developed.[4–6] They have been summarized in a recent review paper.[7] The other is based on the Ritz variational principle expressed in terms of 2-RDM. This latter approach is called density matrix variational theory (DMVT). The key in this approach is how well we can restrict our variable 2-RDM to be N-representable.[8]

Garrod and Percus[9] first formulated the DMVT. Kijewski applied the DMVT to C^{2+} and found that the G condition was a rather strong condition.[10] Garrod et al.[11,12] also implemented their method and calculated the ground state of Be atom very accurately. Erdahl proposed to use the convex program for solving the DMVT and performed accurate calculation for the He_2 molecule.[13] Afterwards, the interest for solving 2-RDM using the DMVT has almost disappeared for about 20 years. The reasons were probably that there was no rigorous mathematical and computational algorithm for the DMVT calculation, and the computer facilities were not so powerful at that time, so that their methods were applicable only to extremely small systems from the limitation in the number of variational parameters.

Mazziotti[6] applied variational principle to Lipkin model employing positive semidefiniteness of the 4-RDM and the density equation. Erdahl and Jin[14] considered a merit of using higher (than 2) order RDM in the DMVT for the existence of more effective N-representability condition for the model system of one-dimensional periodic lattice of electron pairs. They extended the work of Garrod and Percus for higher order RDMs, and gave some insights for using higher order RDM as a basic variable.

In our previous study,[15] we could efficiently implement the DMVT using the semidefinite programming algorithm (SDPA)[16–19] and succeeded to calculate the 2-RDM of the ground state of different symmetry for many atoms and molecules. We transformed the DMVT to the standard type problem of SDP. We showed that the positive semidefiniteness conditions of the P, Q,[8] and G[9] matrices were very strong for atoms and molecules, though they are only necessary conditions of the N-representability.

In the recent work of Mazziotti and Erdahl,[20] positive semidefinite condition of 3- and 4-RDMs were examined for solving the DMVT coupled with DET. They demonstrated its performance for a boson model of two-energy-level system with $N=10–75$. Valdemoro et al. also considered the functional reconstruction with respect to the ensemble representability conditions.[21]

Another promising approach was initiated by one of the authors.[22–25] Since the exact Ψ is an eigenfunction of the Hamiltonian that has simple structure composed of only one- and two-body operators, the Ψ itself should also have a simple structure reflecting the simple structure of the Hamiltonian. Some explicit expressions of the structure of the ex-

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act wave function were given and the theories for the ground and excited states was formulated and applied to a simple model system.

In this paper, we extensively apply our DMVT to calculations of the potential energy surfaces of molecules. Previously, we applied our DET to calculations of the potential energy curves of small molecules.[26] Though the results were encouraging around the equilibrium and elongated geometry, the calculation failed to converge at large internuclear distances. Here, special attentions are paid to the performance of DMVT for describing the electronic state of strongly correlated systems and the multiconfigurational systems. We also discuss the size-consistency property of the method in connection with the N-representability condition. We will also examine the Weinhold–Wilson inequalities[27–29] for the obtained 2-RDM and consider their possibilities as another N-representability conditions in our method.

II. THEORY

A. Definitions and basic algorithm

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

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

$$\Gamma_{j_1 j_2}^{i_1 i_2} = \tfrac{1}{2} \langle \Psi | a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1} | \Psi \rangle, \tag{2.2}$$

where $a^\dagger$ and a are creation and annihilation operators, respectively. Practical complete N-representability condition is not known for 2-RDM: we know only some necessary conditions. In the present DMVT, we use P, Q, and G conditions. The P, Q, and G matrices are defined by

$$P_{j_1 j_2}^{i_1 i_2} = \langle \Psi | a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1} | \Psi \rangle, \tag{2.3}$$

$$Q_{j_1 j_2}^{i_1 i_2} = \langle \Psi | a_{i_1} a_{i_2} a_{j_2}^\dagger a_{j_1}^\dagger | \Psi \rangle, \tag{2.4}$$

$$G_{j_1 j_2}^{i_1 i_2} = \langle \Psi | a_{i_1}^\dagger a_{i_2} a_{j_2}^\dagger a_{j_1} | \Psi \rangle, \tag{2.5}$$

respectively. We enforce all of these matrices to be positive semidefinite. We also use seven trivial conditions of 2-RDM, which are antisymmetric condition, hermiticity, trace condition, number of electrons, number of spins, and expectation values of S_z and S^2.

In the DMVT, we take 2-RDM as a variational variable, and minimize the energy within N-representability conditions, namely,

$$E_{\min} = \operatorname*{Min}_{\Gamma \in \mathcal{P}^{(2)}} \operatorname{Tr} H\Gamma, \tag{2.6}$$

where H is the Hamiltonian of the system, $\mathcal{P}^{(2)}$ is a set of 2-RDM that satisfy approximate or nearly complete N-representability condition. We did two types of calculations using the approximate N-representability conditions: one is with the trivial representability condition plus P and Q condition, denoted as DMVT(PQ), and the other is with the trivial condition plus P, Q, and G conditions, denoted as DMVT(PQG).

For implementing the minimization problem with these linear and semidefiniteness conditions, we casted this prob-
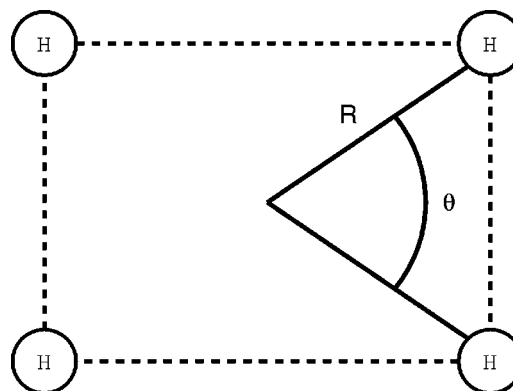

FIG. 1. Coordinates for H_4.

lem into the SDP,[16–18] and we employ SDPA[19] as a standard SDP solver. Details were described in Ref. 15.

B. Additional linear inequalities for the density matrices

Weinhold and Wilson,[27] Davidson,[28] and McRae and Davidson[29] derived some other N-representability conditions that were expressed as linear inequalities using only the diagonal elements of 2-RDM. Among them, the conditions independent from those already used in our present method are as follows.

Condition VI:

$$\gamma_i^i - 2\Gamma_{ij}^{ij} - 2\Gamma_{ik}^{ik} + 2\Gamma_{jk}^{jk} \geq 0. \tag{2.7}$$

Condition VII:

$$1 - \gamma_i^i - \gamma_j^j - \gamma_k^k + 2\Gamma_{ij}^{ij} + 2\Gamma_{ik}^{ik} + 2\Gamma_{jk}^{jk} \geq 0. \tag{2.8}$$

Condition VIII: Positive semidefiniteness of the Ω matrix

$$\Omega = \begin{pmatrix} \gamma_1^1 & 2\Gamma_{12}^{12} & 2\Gamma_{13}^{13} & \cdots & 2\Gamma_{1t}^{1t} & \gamma_1^1 \\ 2\Gamma_{12}^{12} & \gamma_2^2 & 2\Gamma_{23}^{23} & \cdots & 2\Gamma_{2t}^{2t} & \gamma_2^2 \\ 2\Gamma_{12}^{12} & 2\Gamma_{13}^{13} & \gamma_3^3 & \cdots & 2\Gamma_{3t}^{3t} & \gamma_3^3 \\ \vdots & \vdots & \vdots & & \vdots & \vdots \\ 2\Gamma_{1t}^{1t} & 2\Gamma_{2t}^{2t} & 2\Gamma_{3t}^{3t} & \cdots & \gamma_t^t & \gamma_t^t \\ \gamma_1^1 & \gamma_2^2 & \gamma_3^3 & \cdots & \gamma_t^t & 1 \end{pmatrix}. \tag{2.9}$$

These are the representability conditions that may be *stronger* than and/or may reinforce the P, Q, and G conditions. Since these conditions are given as *linear* inequalities, it is easy to include them into the present DMVT formalism within the SDP formalism, since SDP is an extension of the linear programming. In this study, we examine the resultant 2-RDM against these three inequalities, the condition VI, VII, and VIII, and discuss the possibility of using these conditions as the additional constraints in our DMVT formalism.

C. Size-consistency

The positive semidefiniteness of the G matrix includes a necessary condition for size consistency. In the original nonlinear form, the position representation of the G matrix is given by

$$
\begin{aligned}
G(12|1'2') &= \langle ((\psi^\dagger(2)\psi(1) - \langle \psi^\dagger(2)\psi(1)\rangle)^\dagger (\psi^\dagger(2')\psi(1') - \langle \psi^\dagger(2')\psi(1')\rangle)\rangle \\
&= \langle ((\psi^\dagger(1)\psi(2) - \langle \psi^\dagger(2)\psi(1)\rangle^*)(\psi^\dagger(2')\psi(1') - \langle \psi^\dagger(2')\psi(1')\rangle)\rangle \\
&= \langle \psi^\dagger(1)\psi(2)\psi^\dagger(2')\psi(1')\rangle - \langle \psi^\dagger(2)\psi(1)\rangle^* \langle \psi^\dagger(2')\psi(1')\rangle \\
&\quad - \langle \psi^\dagger(1)\psi(2)\rangle \langle \psi^\dagger(2')\psi(1')\rangle + \langle \psi^\dagger(2)\psi(1)\rangle^* \langle \psi^\dagger(2')\psi(1')\rangle \\
&= \langle \psi^\dagger(1)\psi(2)\psi^\dagger(2')\psi(1')\rangle - \langle \psi^\dagger(1)\psi(2)\rangle \langle \psi^\dagger(2')\psi(1')\rangle,
\end{aligned}
\tag{2.10}
$$

where $\psi(i)$ is a field operator defined by using one-particle complete basis set $\{\psi_j\}$,

$$
\psi(i) = \sum_j \psi_j(i)a_j.
\tag{2.11}
$$

A static density–density autocorrelation function $F(1|1')^{30}$ corresponds to the G matrix as

$$
\begin{aligned}
F(1|1') &= \langle n(1)n(1')\rangle - \langle n(1)\rangle\langle n(1')\rangle \\
&= \langle \psi^\dagger(1)\psi(1)\psi^\dagger(1')\psi(1')\rangle \\
&\quad - \langle \psi^\dagger(1)\psi(1)\rangle\langle \psi^\dagger(1')\psi(1')\rangle \\
&= G(11|1'1'),
\end{aligned}
\tag{2.12}
$$

where $n(i)$ is the density operator defined by

$$
n(i) = \psi^\dagger(i)\psi(i).
\tag{2.13}
$$

Using the positive semidefiniteness of $G(12|1'2')$,

$$
\int x(12)G(12|1'2')x(1'2')^* \, d\tau_1 \, d\tau_2 \, d\tau_{1'} \, d\tau_{2'} \geqslant 0,
\tag{2.14}
$$

where $x(12)$ is an arbitrary two particle function, $F(1|1')$ is shown to be also positive semidefinite by integrating the G matrix with respect to the two particle function $x(12)$ given by $x(12) = x(1)\delta(1-2)$, as

$$
\begin{aligned}
0 &\leqslant \int x(12)G(12|1'2')x(1'2')^* \, d\tau_1 \, d\tau_2 \, d\tau_{1'} \, d\tau_{2'} \\
&= \int x(1)\delta(1-2)G(12|1'2')x(1')^*\delta(1'-2')^* \\
&\quad \times d\tau_1 \, d\tau_2 \, d\tau_{1'} \, d\tau_{2'} \\
&= \int x(1)G(11|1'1')x(1')^* \, d\tau_1 \, d\tau_{1'} \\
&= \int x(1)F(1|1')x(1')^* \, d\tau_1 \, d\tau_{1'},
\end{aligned}
\tag{2.15}
$$

where $x(1)$ is an arbitrary one-particle function. From the positive semidefiniteness of $F(1|1')$, it is shown that $F(1|1')$ is everywhere non-negative.

The size consistency requires more strict condition; when $|1-1'| \to \infty$, $F(1|1')$ should asymptotically go to zero, namely,

$$
\lim_{|1-1'|\to\infty} F(1|1') = 0.
\tag{2.16}
$$

The positive semidefiniteness of the G matrix guarantees only the non-negativity of $F(1|1')$, but does not guarantee this asymptotical condition. Thus, the DMVT(PQG) includes a necessary condition for the size-consistency, while in the DMVT(PQ), even $F(1|1')$ is not necessarily non-negative.

III. RESULTS AND DISCUSSIONS

A. H$_4$ system

First, we applied our DMVT to the potential energy surface of H_4. This system has been frequently used as a benchmark molecule of many methods for the quasidegenerate situation:[31,32] the $a_g b_{2u}$ and $a_g b_{3u}$ configurations become equivalent for a square geometry and therefore, become degenerate. We used the DZ basis set[33,34] for H and defined the potential energy surface with the coordinates (θ, R) depicted in Fig. 1. R gives the size of the molecule and θ defines the asymmetry of the structure. We calculated three different cuts of the potential energy surface that were also tested in Ref. 31.

First, we examined the cut of stretching R with $\theta = 90°$ fixed, namely, the square structure as a function of R. The results are summarized in Table I. The DMVT(PQG) reproduced the full-CI curve quite accurately. For large R, it gave almost identical total energy and the errors were within 1 mhartree for $R > 1.0$ Å, though the total correlation energies

TABLE I. Total energy and correlation energy in (%) for H$_4$ as a function of R with θ fixed at 90 degree.

R(Å)	DMVT(PQ)	DMVT(PQG)	Full-CI	Hartree–Fock
0.6	−2.0405(186)	−1.9553(104)	−1.9511(100)	−1.8474(0)
0.8	−2.1485(168)	−2.0629(101)	−2.0610(100)	−1.9330(0)
1.0	−2.1881(177)	−2.0693(101)	−2.0684(100)	−1.9122(0)
1.2	−2.2210(191)	−2.0480(100)	−2.0474(100)	−1.8568(0)
1.4	−2.2407(194)	−2.0251(100)	−2.0246(100)	−1.7939(0)
1.6	−2.2367(183)	−2.0087(100)	−2.0085(100)	−1.7340(0)
1.8	−2.2226(141)	−1.9993(100)	−1.9992(100)	−1.4551(0)
2.0	−2.2055(141)	−1.9945(100)	−1.9945(100)	−1.4818(0)

TABLE II. Total energy and correlation energy in (%) for H$_4$ as a function of θ with R fixed at the equilibrium value of 0.869 Å.

θ(degrees)	DMVT(PQ)	DMVT(PQG)	Full-CI	Hartree–Fock
90.0	−2.1656(170)	−2.0711(101)	−2.0697(100)	−1.9326(0)
89.9	−2.1656(170)	−2.0711(101)	−2.0697(100)	−1.9335(0)
89.5	−2.1656(172)	−2.0713(101)	−2.0698(100)	−1.9372(0)
89.0	−2.1655(174)	−2.0718(101)	−2.0703(100)	−1.9418(0)
88.0	−2.1654(177)	−2.0738(101)	−2.0721(100)	−1.9509(0)
85.0	−2.1673(180)	−2.0849(102)	−2.0830(100)	−1.9777(0)
80.0	−2.1869(185)	−2.1120(101)	−2.1106(100)	−2.0205(0)
70.0	−2.2337(185)	−2.1727(101)	−2.1721(100)	−2.0992(0)

TABLE III. Total energy and correlation energy in (%) for H_4 as a function of θ with R fixed at 1.738 Å.

θ(degrees)	DMVT(PQ)	DMVT(PQG)	Full-CI	Hartree–Fock
90.0	$-2.2275(174)$	$-2.0016(100)$	$-2.0015(100)$	$-1.6962(0)$
89.9	$-2.2275(174)$	$-2.0015(100)$	$-2.0015(100)$	$-1.6967(0)$
89.5	$-2.2276(175)$	$-2.0017(100)$	$-2.0015(100)$	$-1.6988(0)$
89.0	$-2.2276(175)$	$-2.0019(100)$	$-2.0015(100)$	$-1.7014(0)$
88.0	$-2.2278(177)$	$-2.0023(100)$	$-2.0018(100)$	$-1.7067(0)$
85.0	$-2.2289(181)$	$-2.0041(100)$	$-2.0033(100)$	$-1.7231(0)$
80.0	$-2.2327(188)$	$-2.0087(100)$	$-2.0080(100)$	$-1.7523(0)$
70.0	$-2.2465(207)$	$-2.0258(100)$	$-2.0255(100)$	$-1.8198(0)$

were large, for example, 0.51 a.u. for $R=2.0$ Å. The method was found to give a good description for the quasidegenerate system. On the other hand, the DMVT(PQ) gave 40–90% errors of the correlation energies.

Second, the cut of θ ranging from 70.0° to 90.0° with $R=0.869$ Å, which is near equilibrium distance is examined in Table II. At $\theta=90°$, electronic state becomes quasidegenerate. The DMVT(PQG) gave very smooth potential curve parallel to the full-CI without artificial cusp at $\theta=90°$.[31] The deviations were within 2 mhartree and 2% of the total correlation energy throughout the geometries. For this system, the errors were constant regardless of the quasidegeneracy.

Last, the cut of $\theta=70°–90°$ with R elongated to 1.738 Å, namely, $2\times R_e$, is examined in Table III. Surprisingly, the DMVT(PQG) gave almost identical results with the full-CI ones: the deviations were less than 1 mhartree for all the geometries. Though the present calculations did not include polarization functions, the DMVT(PQG) gave very accurate potential energy surface of H_4.

For this system all the Weinhold–Wilson inequalities were satisfied for all the potential energy surfaces examined here. This also supports the high quality of 2-RDM calculated by the DMVT(PQG).

B. Ne and the equilibrium geometry of N_2, CO, C_2, LiF, and CH_4

Next, the DMVT is applied to the ground state of Ne, N_2, CO, C_2, LiF, and CH_4, which were not calculated in the previous study.[15] In Table IV, we summarized the total energy for these systems. In all calculations, we adopted STO-6G minimal basis[35] and experimental geometries[36,37] except for Ne. For Ne, $[3s2p]$ basis set was used. The $1s$ orbitals of the second raw atoms were fixed as cores.

Generally, the results of DMVT(PQG) calculations were satisfactory except for C_2 and CH_4. The DMVT(PQ) calculations overshoot the energy of these molecules, especially for C_2, by 802%. The DMVT(PQG) recovered it up to 117%. The deviation is still not small, however, the convergence to the exact value is encouraging since the ground state of C_2 is known to be quasidegenerate even at the equilibrium geometry. We also obtained remarkable improvement for other systems by requiring the G condition.

The Weinhold–Wilson inequalities VI, VII, and VIII were examined for these systems. For CO, LiF, and Ne, all of the inequalities were satisfied. For CH_4 and C_2, the inequality type VI and VII were violated, and for N_2, the inequality type VI was violated but others were satisfied, though the violations were very small as $-0.000\,297$–$-0.002\,063$ (CH_4, type VI), $-0.000\,127$–$0.001\,803$(CH_4, type VII), $-0.004\,169$–$-0.019\,446$(C_2, type VI), $-0.000\,169$–$-0.030\,852$(C_2, type VII) and $-0.002\,83$–-0.00551 (N_2, type VI), respectively. These violations were parallel to the errors of the DMVT(PQG) calculations: the deviations CH_4(124%), C_2(117%), and N_2(108%) were larger than those of the other systems. This implies that the inequalities VI and VII may be adopted as one of the additional N-representability conditions for the DMVT.

C. Potential curves of H_2O, NH_3, and BH_3

Double dissociation of H_2O and triple dissociation of NH_3 and BH_3 are interesting examples, since four and six electrons are correlated in the bond dissociation processes. We calculated the potential curves for the symmetric stretching mode of these systems at several points within $R=0.5–5.0$ Å, and the results were shown in Figs. 2–4. We used STO-6G basis set and kept $1s$ orbitals of O, N, and B to be frozen. Spectroscopic constants of equilibrium distance (r_e), harmonic frequency (ω_e), and dissociation energy (D_e) were summarized in Table V. The potential energy curve was fit with the 6th extended Rydberg function for some points near the equilibrium geometry and the ω_e was calculated by the Dunhum method.[38] The H–O–H and H–N–H angles were fixed at the experimental values and only the H–O and H–N bonds were symmetrically stretched: ω_e was defined for this coordinate and therefore different from that of the normal mode analysis.

For H_2O and NH_3, DMVT(PQG) simulated the full-CI curves very accurately even up to the dissociation limit and the two curves almost overlapped. H_2O and NH_3 dissociate

TABLE IV. Total energy and correlation energy in (%) Ne, CO, N_2, LiF, C_2, and CH_4 at equilibrium geometry.

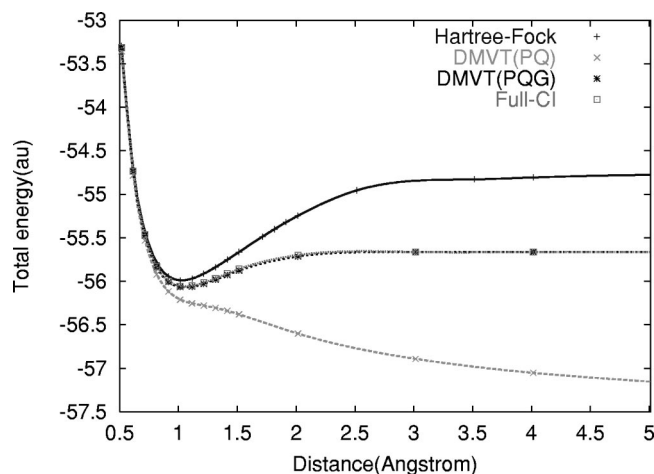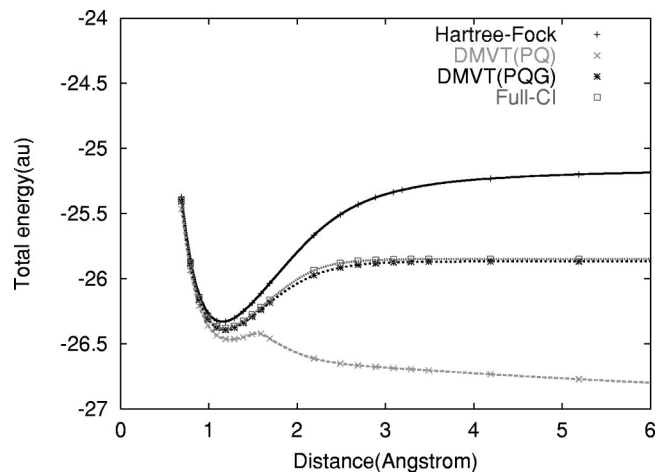| System	State	MO[a]	Act. Ele[b]	DMVT(PQ)	DMVT(PQG)	Full-CI	Hartree–Fock
Ne	^1S	8(9)	8	$-129.2430(705)$	$-128.6292(105)$	$-128.6245(100)$	$-128.5224(0)$
CO	$^1\Sigma$	8(10)	12	$-113.1163(584)$	$-112.4544(108)$	$-112.4426(100)$	$-112.3033(0)$
N_2	$^1\Sigma_g^+$	8(10)	12	$-109.4466(571)$	$-108.7123(108)$	$-108.7002(100)$	$-108.5418(0)$
LiF	$^1\Sigma$	8(10)	10	$-106.7727(568)$	$-106.4448(102)$	$-106.4435(100)$	$-106.3731(0)$
C_2	$^1\Sigma_g^+$	8(10)	10	$-77.3387(802)$	$-75.4793(117)$	$-75.4340(100)$	$-75.1626(0)$
CH_4	$^1A_1$	8(10)	8	$-40.4335(403)$	$-40.2100(124)$	$-40.1905(100)$	$-40.1102(0)$

[a]Number of active MOs, with the number of total MOs in parentheses.
[b]Number of active electrons.
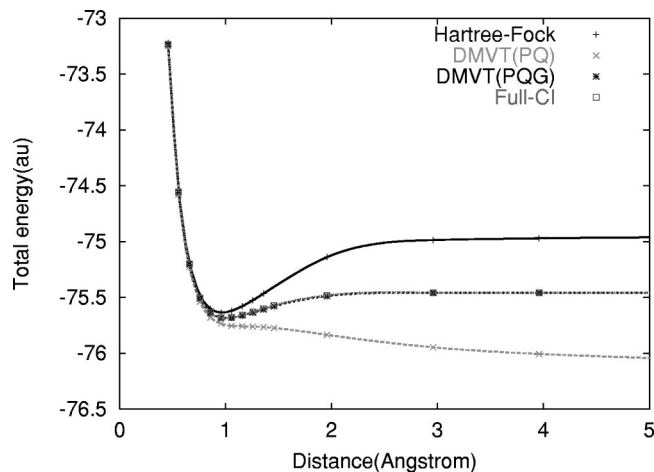
FIG. 2. Potential curve for the double dissociation of H_2O.

FIG. 4. Potential curve for the triple dissociation of BH_3.

into $O(^3P) + H(^1S) + H(^1S)$ and $N(^4S) + H(^1S) + H(^1S) + H(^1S)$, respectively, and at the dissociation limit, the electronic state becomes a multiconfigurational state. DMVT(PQG) accurately described these multiconfigurational states, namely, static electron correlations: the deviations from the full-CI were less than 0.5 mhartree in the dissociation limit. On the other hand, while DMVT(PQ) reproduced the curves in the short bond region, it failed at the large internuclear distances. DMVT(PQ) curve did not bound. For BH_3, even the DMVT(PQG) curve slightly deviates from the full-CI curve for $R_{B-H} > 2.0$ Å. The dissociation limit of BH_3 is heavily quasidegenerate: the electronic state is represented by several configurations including quadruple excitations. DMVT(PQ) curve for BH_3 has a hump at around 1.5 Å, and, the potential curve is repulsive in nature.

Since DMVT(PQG) calculations gave accurate potential curves, their spectroscopic constants were also accurate. For these systems, the deviations from the full-CI were within 0.003 Å and 30 cm^{-1}, for r_e and ω_e, respectively. The dissociation energies (D_e) were estimated slightly larger by 0.06, 0.27, and 0.26 eV, for H_2O, NH_3 and BH_3, respectively. This is because DMVT(PQG) calculations overshoot

the full-CI energy around the equilibrium geometries rather than deviate in the dissociation limit. Since the dissociations of these systems are homolytic and include multiple bonds, the Hartree–Fock description of the dissociation limit was of course very crude.

We examined the Weinhold–Wilson inequalities for BH_3, since the deviation from the full-CI was large for this molecule. Actually, the violations of the conditions VI and VII at the equilibrium distance ranged $-0.000\,019-$ $-0.003\,018$ and $-0.000\,391--0.002\,608$, respectively, and those of the conditions VI and VII were $-0.004\,804-$ $-0.013\,975$, and $-0.001\,448--0.001\,956$ at the dissociation limit ($R = 5$ Å).

D. Potential curves of CO, C_2, N_2, and Be_2

Next, we apply the DMVT to the potential energy curves of CO, C_2, N_2, and Be_2, since their electronic states are

FIG. 3. Potential curve for the triple dissociation of NH_3.

TABLE V. Spectroscopic constants of H_2O, NH_3, BH_3, C_2, N_2, and CO.

| System	Method	r_e(Å)	ω_e(cm^{-1})	D_e(eV)
H_2O	Hartree–Fock	1.824	3952	18.471
	Full-CI	1.895	3253	6.162
	DMVT(PQG)	1.894	3276	6.227
NH_3	Hartree–Fock	1.025	3750	33.008
	Full-CI	1.057	3324	10.686
	DMVT(PQG)	1.057	3291	10.956
BH_3	Hartree–Fock	1.154	3115	31.284
	Full-CI	1.178	2883	14.280
	DMVT(PQG)	1.181	2854	14.537
C_2	Hartree–Fock	1.233	2207	16.876
	Full-CI	1.257	2035	6.790
	DMVT(PQG)	1.299	1679	7.212
N_2	Hartree–Fock	1.129	2715	31.211
	Full-CI	1.210	2061	6.220
	DMVT(PQG)	1.199	1980	6.622
CO	Hartree–Fock	1.146	2461	12.692
	Full-CI	1.193	2063	9.328
	DMVT(PQG)	1.201	1990	9.540
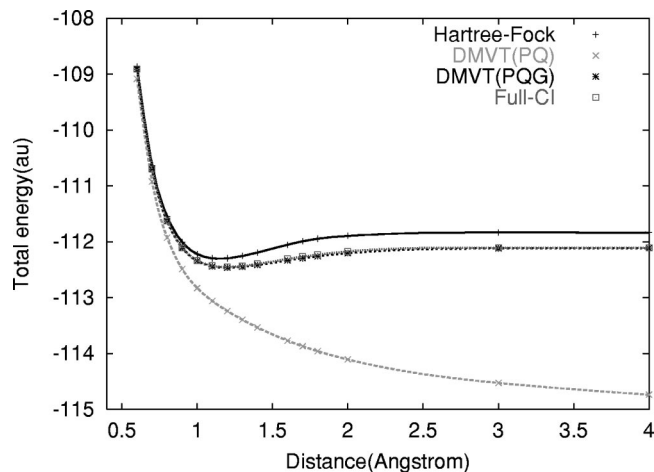
FIG. 5. Potential curve of CO.
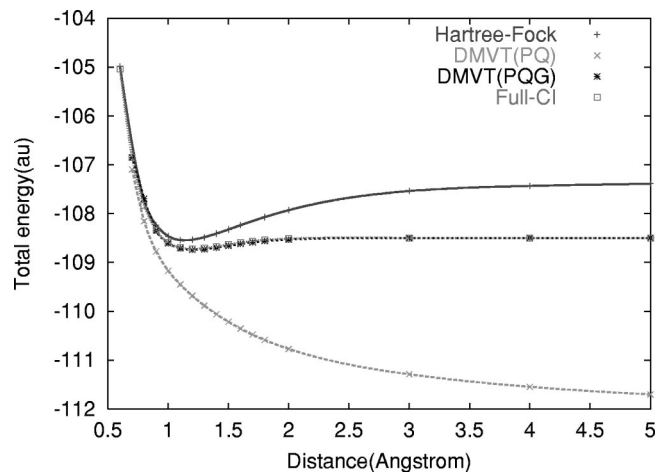
FIG. 7. Potential curve of N_2.

very characteristic. In the potential curve of CO, the Hartree–Fock configuration is dominant at around the equilibrium distance, but its weight decreases as the distance increases and finally becomes zero at the dissociation limit. C_2 has unoccupied $p\sigma$ MO, therefore, the ground state is always quasidegenerate even in the equilibrium geometry. N_2 includes triple-bond dissociation, therefore its potential curve is highly quasidegenerate at large internuclear distance. Be_2 has no bonding interaction. Potential curves of these molecules were calculated for $R = 0.5$–5.0 Å. Minimal STO-6G basis set was used and the $1s$ orbitals were kept as frozen. The potential curves were shown in Figs. 5–8 and the spectroscopic constants were given in Table V.

As in other systems, DMVT(PQG) curves almost overlapped with the full-CI curves, while DMVT(PQ) curves were calculated as repulsive. The deviations of DMVT(PQG) from the full-CI increases in the order of N_2, CO, and C_2. Though it is true that the description of the quasidegeneracy of C_2 is difficult, there is another factor in the accuracy. Since we used minimal basis set, the calculations of N_2 and CO were for 16 spin orbitals with 12 electrons, namely, 4 hole spin orbitals, while those of C_2 are for 16 spin orbitals with 10 electrons; 6 hole spin orbitals. We

think this also affected the accuracy of the results. The potential curve of Be_2 was repulsive, since van der Waals interaction was not described by the present basis set. The DMVT(PQ) gave better description than other systems.

The DMVT(PQG) results for the spectroscopic constants of these diatomic molecules were less accurate than those for H_2O and NH_3. The deviations were ~ 0.01 Å and ~ 80 cm^{-1} for r_e and ω_e, respectively, for CO and N_2. For C_2, the errors were as large as 0.04 Å and 350 cm^{-1}. These results reflect the quality of the DMVT around the equilibrium geometry.

We also calculated the Weinhold–Wilson inequalities for C_2 and CO. As expected, large violations occurred for the inequalities VI and VII. For C_2, the violations were calculated as $-0.001\,810$–$-0.027\,667$ and $-0.000\,900$–$-0.011\,494$ for conditions VI and VII, respectively, at $R = 1.5$ Å, and $-0.003\,047$–$-0.002\,500$ only for condition VI at $R = 5.0$ Å: the violations at $R = 1.5$ Å were larger than those at $R = 5.0$ Å. The ground state of C_2 is quasidegenerate even at the equilibrium geometry and this is the reason of the crude spectroscopic constants for C_2 by the DMVT(PQG). For CO, the violations ranged $-0.008\,185$–$-0.008\,434$ for condition VI at the dissociation
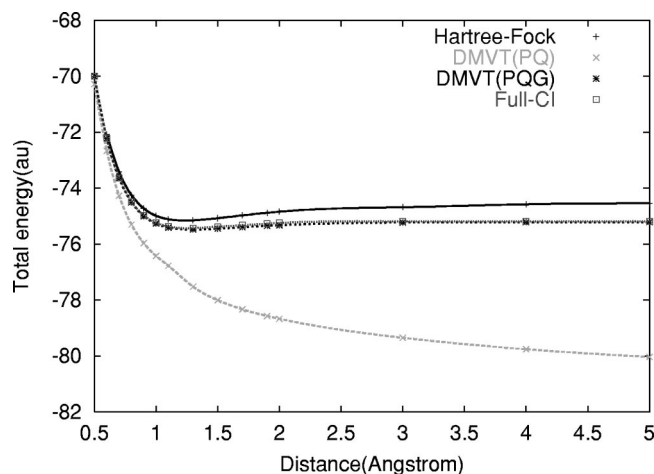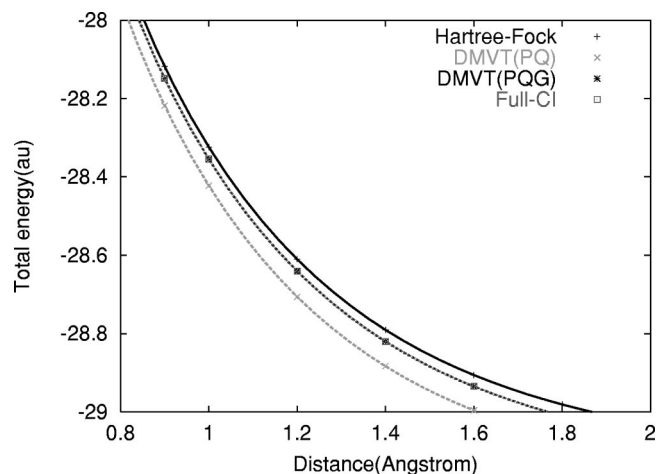
FIG. 6. Potential curve of C_2.

FIG. 8. Potential curve of Be_2.

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TABLE VI. Examination of size consistency for Ne and H_2O, NH_3, BH_3, Be_2, CO, and C_2.

System	Method	E_{mol}[a]	E_{atom}[b]	ΔE
H_2O	DMVT(PQG)	-75.4589	-75.4589	0.0000
	Full-CI	-75.4588	-75.4588	0.0000
NH_3	DMVT(PQG)	-55.6622	-55.6622	0.0000
	Full-CI	-55.6622	-55.6622	0.0000
BH_3	DMVT(PQG)	-25.8680	-25.8482	0.0198
	Full-CI	-25.8482	-25.8482	0.0000
Be_2	DMVT(PQG)	-29.1655	-29.1654	0.0001
	Full-CI	-29.1654	-29.1654	0.0000
CO	DMVT(PQG)	-112.1153	-112.1095	0.0058
	Full-CI	-112.1095	-112.1095	0.0000
C_2	DMVT(PQG)	-75.2187	-75.1854	0.0333
	Full-CI	-75.1854	-75.1854	0.0000
N_2	DMVT(PQG)	-108.4982	-108.4982	0.0000
	Full-CI	-108.4982	-108.4982	0.0000

[a]Energy of molecule at the dissociation limit.
[b]Sum of the energies of the isolated atoms.

limit and $-0.000\,546$ for condition VI at $R=1.3$ Å. There were no errors of conditions VII and VIII for CO.

E. Size consistency

As we discussed in Sec II C, the G condition is very important for the size-consistent property of the method. Here, we examine the size consistency of the results. In Table VI, the total energy of the molecule in the dissociation limit and the sum of the total energies of the isolated atoms are compared for H_2O, NH_3, BH_3, N_2, C_2, CO, and Be_2. For H_2O, NH_3, and N_2, the total energies calculated by DMVT(PQG) agree within numerical accuracy, which shows the size consistency holds for these systems. In these systems, Weinhold–Wilson inequalities were also satisfied and the calculations were quite accurate. As seen from the potential curves, DMVT(PQ) calculations gave miserable results from the standpoint of the size consistency. The G condition is apparently indispensable for the size-consistent property. For other systems, BH_3, C_2, CO, and Be_2, the size consistency of DMVT(PQG) was not satisfactory. This is because the G condition is not a sufficient condition for the size consistency. Note that the Weinhold–Wilson inequalities VI and VII were not satisfied for these systems.

F. Artificially correlation enhanced system

It is interesting to see the performance of the present method for the strongly correlated system. We here introduced the model Hamiltonian in which the electron correlations are controlled by a parameter. The Hamiltonian is partitioned into F, Fock operator and the rest, V:

$$H = F + \lambda V, \tag{3.1}$$

where λ is a real parameter that controls the strength of the electron correlations and $\lambda=1$ corresponds to the original Hamiltonian. We adopted Be and H_2O and changed λ form $0.1-10\,000$ and the results were shown in Tables VII and VIII, respectively.

For Be system, the DMVT(PQG) reproduced the exact correlation energy quite accurately and the deviations were even tempered for the variation of λ within 1%. On the other hand, the DMVT(PQ) gave random errors for the variation of λ. For H_2O, the errors of the DMVT(PQG) became large, but, were within 15% relative to the total electron correlations. The DMVT(PQG) calculations converged even for the heavily correlated systems ($\lambda=10\,000$), though the absolute errors were not small.

We did not see the Weinhold–Wilson violations in the Be system for all λ. The violations for H_2O were not so simple. For $\lambda=1.0$, the violations of the condition VI occurred as $-0.000\,54--0.003\,68$, but no violations occurred for $\lambda=2.0$, which has the largest correlation energy error in percent. For $\lambda=10\,000$, we got large violations as $-0.008\,71--0.001\,036$.

IV. CONCLUSION

The DMVT was applied to the calculations of the potential energy surfaces of the atoms and small molecules, Ne, H_4, H_2O, NH_3, BH_3, CO, N_2, C_2, and Be_2. This is the first study in which the bond dissociation was properly described by the DMVT. In the previous DET study of potential curves,[26] the results were good up to $R \sim 2R_e$, but at large distances, the calculations failed to converge. Generally, the DMVT(PQG) calculation reproduced the full-CI curves very accurately and they sometimes overlapped even in the dissociation limit, though the potential curves for BH_3 and C_2 were less accurate than others. The quasidegenerate states were well described by the DMVT(PQG) calculations. On

TABLE VII. Total energy for the model Hamiltonian, $H=F+\lambda V$ of Be and the correlation energy in (%).

λ	DMVT(PQ)	DMVT(PQG)	Full-CI	Hartree–Fock
0.10	$-10.5324(249)$	$-10.5322(100)$	$-10.5322(100)$	$-10.5321(0)$
0.50	$-12.3365(226)$	$-12.3317(100)$	$-12.3317(100)$	$-12.3278(0)$
1.00	$-14.6064(200)$	$-14.5895(100)$	$-14.5895(100)$	$-14.5725(0)$
2.00	$-19.2097(151)$	$-19.1600(100)$	$-19.1596(100)$	$-19.0619(0)$
3.00	$-24.1197(115)$	$-24.0491(100)$	$-24.0469(100)$	$-23.5513(0)$
4.00	$-29.6662(139)$	$-29.2180(101)$	$-29.2115(100)$	$-28.0407(0)$
5.00	$-37.1084(212)$	$-34.7026(100)$	$-34.6922(100)$	$-32.5301(0)$
10.00	$-76.5823(165)$	$-68.0991(100)$	$-68.0414(100)$	$-54.9771(0)$
10 000.0	$-81\,838.44(102)$	$-81\,294.14(100)$	$-81\,290.74(100)$	$-44\,904.03(0)$

TABLE VIII. Total energy for the model Hamiltonian, $H = F + \lambda V$ of H_2O and the correlation energy in (%).

λ	DMVT(PQ)	DMVT(PQG)	Full-CI	Hartree–Fock
0.10	−41.1669(234)	−41.1664(100)	−41.1664(100)	−41.1661(0)
0.50	−56.5293(233)	−56.5158(102)	−56.5155(100)	−56.5051(0)
1.00	−75.7953(232)	−75.7310(104)	−75.7290(100)	−75.6789(0)
1.50	−95.1938(235)	−95.0064(106)	−94.9978(100)	−94.8526(0)
2.00	−115.0471(222)	−114.5560(115)	−114.4863(100)	−114.0264(0)
3.00	−155.4737(137)	−154.6553(101)	−154.6348(100)	−152.3740(0)
4.00	−196.0891(124)	−195.0768(101)	−195.0347(100)	−190.7215(0)
5.00	−236.8429(120)	−235.6115(101)	−235.5285(100)	−229.0690(0)
10.00	−441.1663(116)	−438.6811(102)	−438.3447(100)	−420.8068(0)
10 000.0	−417 093.18(124)	−411 089.69(102)	−410 645.30(100)	−383 512.82(0)

the other hand, the curves by DMVT(PQ) were always repulsive, which showed the potential importance of the G condition.

We examined the size consistency of the present method. The G condition is found to be related to the size consistency of the method and shown to be essential to the behavior of the potential curves of DMVT(PQG), especially in the dissociation limit.

We also examined the Weinhold–Wilson inequalities for the 2-RDM of DMVT(PQG) calculations where the results were less accurate, and found that the inequalities VI and VII were violated. We think these inequalities may be new candidates for the N-representability condition of the DMVT. Since these are linear conditions, it would be easily included in the conditions of the DMVT relaxed with the SDP. Such study is now in progress.

ACKNOWLEDGMENTS

[1] K. Husimi, Proc. Phys. Math. Soc. Jpn. **22**, 264 (1940).
[2] P.-O. Löwdin, Phys. Rev. **99**, 1474 (1955).
[3] H. Nakatsuji, Phys. Rev. A **14**, 41 (1976).
[4] C. Valdemoro, Phys. Rev. A **45**, 4462 (1992); F. Colmenero, C. Pérez del Valle, and C. Valdemoro, *ibid.* **47**, 971 (1993); F. Colmenero and C. Valdemoro, *ibid.* **47**, 979 (1993).
[5] H. Nakatsuji and K. Yasuda, Phys. Rev. Lett. **76**, 1039 (1996); K. Yasuda and H. Nakatsuji, Phys. Rev. A **56**, 2648 (1997).
[6] D. A. Mazziotti, Phys. Rev. A **57**, 4219 (1998); Chem. Phys. Lett. **289**, 419 (1998).
[7] H. Nakatsuji, in *Many-Electron Densities and Reduced Density Matrices*, edited by J. Cioslowski (Kluwer Academic, New York, 2000).
[8] A. J. Coleman, Rev. Mod. Phys. **35**, 668 (1963).
[9] C. Garrod, and J. K. Percus, J. Math. Phys. **5**, 1756 (1964).
[10] L. J. Kijewski and J. K. Percus, Phys. Rev. A **2**, 1659 (1970); L. J. Kijewski, *ibid.* **6**, 1659 (1972); L. J. Kijewski, *ibid.* **9**, 2263 (1974).
[11] C. Garrod, M. V. Mihailović, and M. Rosina, J. Math. Phys. **16**, 868 (1975).
[12] C. Garrod and M. A. Fusco, Int. J. Quantum Chem. **10**, 495 (1976).
[13] R. M. Erdahl, Rep. Math. Phys. **15**, 147 (1979).
[14] R. M. Erdahl, and B. Jin, J. Mol. Struct.: THEOCHEM **527**, 207 (2000); R. M. Erdahl and B. Jin, in *Many-Electron Densities and Reduced Density Matrices*, edited by J. Cioslowski (Kluwer Academic, New York, 2000).
[15] M. Nakata, H. Nakatsuji, M. Ehara, M. Fukuda, K. Nakata, and K. Fujisawa, J. Chem. Phys. **114**, 8282 (2001).
[16] Y. Nesterov and A. S. Nemirovskii, *Interior Point Polynomial Method in Convex Programming: Theory and Applications* (SIAM, Philadelphia, 1993).
[17] L. Vandenberghe and S. Boyd, SIAM Rev. **38**, 4 9 (1996).
[18] M. Kojima, Semidefinite Programming and Interior-Point Methods, http://www.is.titech.ac.jp/~ kojima/wabun.html, 1996 (in Japanese).
[19] K. Fujisawa, M. Kojima, and K. Nakata, SDPA (SemiDefinite Programming Algorithm) User's Manual Version 5.00, August 1999. http://is-mj.archi.kyoto-u.ac.jp/~ fujisawa/software.html
[20] D. A. Mazziotti and R. M. Erdahl, Phys. Rev. A **63**, 042113 (2001).
[21] C. Valdemoro, L. M. Tel, and E. Perez-Romero, Phys. Rev. A **61**, 032507 (2000).
[22] H. Nakatsuji, J. Chem. Phys. **113**, 2949 (2000).
[23] H. Nakatsuji and E. R. Davidson, J. Chem. Phys. **115**, 2000 (2001).
[24] H. Nakatsuji, J. Chem. Phys. **115**, 2465 (2001).
[25] H. Nakatsuji J. Chem. Phys. **116**, 1811 (2002).
[26] M. Ehara, M. Nakata, H. Kou, K. Yasuda, and H. Nakatsuji, Chem. Phys. Lett. **305**, 483 (1999).
[27] F. Weinhold and E. B. Wilson, Jr., J. Chem. Phys. **47**, 2298 (1967).
[28] E. R. Davidson, J. Math. Phys. **10**, 725 (1969).
[29] W. B. McRae and E. R. Davidson, J. Math. Phys. **13**, 1527 (1972).
[30] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, Harcourt Brace, New York, 1990).
[31] T. V. Voorhis and M. Head-Gordon, J. Chem. Phys. **113**, 8873 (2001).
[32] J. Paldus, P. Piecuch, L. Pylypow, and B. Jezirovski, Phys. Rev. A **47**, 2738 (1993).
[33] S. Huzinaga, J. Chem. Phys. **42**, 1293 (1970); T. H. Dunning, Jr., *ibid.* **53**, 2823 (1970); T. H. Dunning, J. and P. J. Hay, *In Method of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum, New York, 1977), Vol. 2.
[34] Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 4/22/01, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352. http://www.emsl.pnl.gov:2080/forms/basisform.html
[35] W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys. **51**, 2657 (1969).
[36] J. H. Callomon, E. Horita, K. Kuchitsu, W. J. Lafferty, A. G. Maki, and C. S. Pote, *Landolt–Börnstein* (Springer-Verlag, Berlin, 1976).
[37] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV, Electronic Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
[38] J. L. Dunhum, Phys. Rev. **41**, 713, 721 (1932); H. M. Hulburt and J. O. Hirschfelder, J. Chem. Phys. **9**, 61 (1941).