Density matrix variational theory: Strength of Weinhold-Wilson inequalities

Maho Nakata, Masahiro Ehara and Hiroshi Nakatsuji*
Department of Synthetic Chemistry and Biological Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606-8501, Japan

Abstract. We examine the strength of the Weinhold-Wilson (WW) inequalities for calculating the second-order density matrix(2-RDM) by the density matrix variational theory (DMVT) using the P, Q and G conditions as subsidiary conditions. We calculated the 2-RDM of various molecular electronic states and found that some violations of WW inequalities occur especially for the systems for which the DMVT(PQG) calculations were less accurate. We then developed the DMVT method including further the WW inequalities as the restrictive conditions, DMVT(PQG+WW), and applied it to CH_4, C_2, $CH_2(^1A_1)$ and H_2O. The WW inequalities certainly improved the results, but the improvement was not so remarkable.

1. Introduction

As far as our world involves only up-to-two body elementary operators, this world should be described solely by the second-order reduced density matrix (2-RDM). Professor Löwdin not only did a lot of great works in this and related field(1; 2), but also encouraged many young researchers. HN is one of such researchers and would like to thank Professor Per-Olov Löwdin for his great contributions in the field of quantum molecular science and his encouragement warmly given to him.

Recently, special attentions have been paid to the direct determination of the reduced density matrix (RDM), which is called as density matrix theory(DMT). This approach adopts the 2-RDM as the basic variable of quantum mechanics and there are two formalisms in the DMT. 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). Recent development of the DET(4; 5; 6) has been remarkable and they have been summarized in the review article (7). The other is based on the Ritz variational principle expressed in terms of the 2-RDM and is referred to as the density matrix variational theory (DMVT). The quality of the calculated 2-RDM in the DMVT is dependent on how well we can restrict our variable 2-RDM to be N-representable(8).

* hiroshi@sbchem.kyoto-u.ac.jp

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The DMVT method was first introduced by Garrod and Percus. They proposed the variational method using P, Q and G conditions and some trivial N-representability conditions(9), and applied it to the ground state of Be(10). Erdahl proposed to use convex programming for the DMVT and applied it to He_2(11). The applications in these early studies were limited to very small systems. Recently, Erdahl and Jin(12) developed the DMVT using 3-RDM as variable and applied it to the model system of one-dimensional periodic lattice of electron pairs. Mazziotti and Erdahl(13) examined the positive semidefinite condition of 3- and 4-RDMs for solving the DMVT combined with the DET and calculated Lipkin model, namely, a boson model of two-energy-level system.

In this series of our DMVT studies(14; 15), we could efficiently implement the DMVT using the semidefinite programming algorithm (SDPA)(16), and successfully calculate the 2-RDMs of the ground states of many different spin-space symmetries for *many atoms and molecules.* We also applied this method to the potential energy surfaces of molecules and reproduced the full-CI curves in good approximation up to the dissociation limit(15); the G condition was found to be very important for describing the dissociation limit.

Another promising approach was initiated by one of the authors(17). Since the exact Ψ is an eigen function of the Hamiltonian that has so simple structure composed of only one- and two-body operators, the Ψ itself should also have a simple structure reflecting this simplicity of the Hamiltonian. Some explicit expressions of the structure of the exact wave function were given and the theories for the ground and excited states was formulated. Applications were given to a simple model system and to atoms and molecules.

For improving the DMVT(PQG) method developed previously(14; 15), we may use some additional N-representability conditions. Some inequalities for the 2-RDM were proposed by Weinhold and Wilson(18), Davidson(19) and McRae and Davidson(20). Since all of these inequalities can be written as linear conditions, it is easy to include these conditions in our formalism. In our previous work(15), we actually examined these inequalities for the resultant 2-RDM of the DMVT(PQG) calculations and found that two linear inequalities were violated in some cases.

In this paper, we examine the Weinhold-Wilson (WW) inequalities for calculating the 2-RDM by the DMVT(PQG) method. Examinations have been done for all the systems that were calculated in the previous studies(14; 15). Then, we propose an efficient formalism for including these conditions as the subsidiary conditions.

2. Theory and calculation

2.1. Definitions and basic algorithm

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

$$\gamma_j^i = \langle \Psi | a_i^\dagger a_j | \Psi \rangle \tag{1}$$

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

where $a^\dagger$ and a are creation and annihilation operators, respectively. Practical complete N-representability condition is not known for the 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,

$$P_{j_1 j_2}^{i_1 i_2} = \langle \Psi | a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1} | \Psi \rangle \tag{3}$$

$$Q_{j_1 j_2}^{i_1 i_2} = \langle \Psi | a_{i_1} a_{i_2} a_{j_2}^\dagger a_{j_1}^\dagger | \Psi \rangle \tag{4}$$

$$G_{j_1 j_2}^{i_1 i_2} = \langle \Psi | a_{i_1}^\dagger a_{i_2} a_{j_2}^\dagger a_{j_1} | \Psi \rangle \tag{5}$$

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,

$$E_{\min} = \underset{\Gamma \in \mathcal{P}^{(2)}}{\mathrm{Min}} \ \mathrm{Tr} H \Gamma, \tag{6}$$

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. In the previous papers (14; 15), we performed two types of calculations using the approximate N-representability conditions: the DMVT(PQ) adopts the trivial representability conditions plus P and Q conditions as the approximate conditions, and the DMVT(PQG) further includes G condition. In this work, we also include the Weinhold-Wilson inequalities, and we call the method as the DMVT(PQG+WW) method.

2.2. Weinhold-Wilson inequalities

The Weinhold-Wilson inequalities which are independent from P, Q, G, and 7 trivial conditions are:

Condition IV:

$$1 - \gamma_i^i - \gamma_j^j + 2\Gamma_{ij}^{ij} \geq 0 \tag{7}$$

Condition V:

$$\gamma_i^i - 2\Gamma_{ij}^{ij} \geq 0 \tag{8}$$

Condition VI:

$$\gamma_i^i - 2\Gamma_{ij}^{ij} - 2\Gamma_{ik}^{ik} + 2\Gamma_{jk}^{jk} \geq 0 \tag{9}$$

Condition VII:

$$1 - \gamma_i^i - \gamma_j^j - \gamma_k^k + 2\Gamma_{ij}^{ij} + 2\Gamma_{ik}^{ik} + 2\Gamma_{jk}^{jk} \geq 0 \tag{10}$$

Condition VIII: Positive semidefiniteness of the Ω matrix

$$\Omega = \begin{pmatrix} \gamma_1^1 & 2\Gamma_{12}^{12} & 2\Gamma_{13}^{13} & \cdots & 2\Gamma_{1t}^{1t} & \gamma_1^1 \\ 2\Gamma_{12}^{12} & \gamma_2^2 & 2\Gamma_{23}^{23} & \cdots & 2\Gamma_{2t}^{2t} & \gamma_2^2 \\ 2\Gamma_{13}^{13} & 2\Gamma_{23}^{23} & \gamma_3^3 & \cdots & 2\Gamma_{3t}^{3t} & \gamma_3^3 \\ \vdots & \vdots & \vdots & & \vdots & \vdots \\ 2\Gamma_{1t}^{1t} & 2\Gamma_{2t}^{2t} & 2\Gamma_{3t}^{3t} & \cdots & \gamma_t^t & \gamma_t^t \\ \gamma_1^1 & \gamma_2^2 & \gamma_3^3 & \cdots & \gamma_t^t & 1 \end{pmatrix}. \tag{11}$$

Note that different definition is employed for Γ by factor 2. In this study, we examined the 2-RDM by the DMVT(PQG) method with respect to these five inequalities, and we found that two types of conditions VI and VII were violated for some systems. Therefore, we develop the DMVT method including these conditions.

2.3. DMVT METHOD INCLUDING WEINHOLD-WILSON INEQUALITIES

Since all the Weinhold-Wilson inequalities are linear conditions, it is possible to include all of these inequalities in the SDP formalism simultaneously. However, the number of conditions becomes large since it scales as N^3, and therefore we enforce the inequalities only for those molecules for which the WW inequalities were violated in the preceding DMVT(PQG) calculation. Then, the algorithm of the DMVT (PQG+WW) is as follows:

1. Standard DMVT(PQG) is executed.
2. Weinhold-Wilson inequalities of type IV$\sim$ VIII are examined.
3. DMVT(PQG+WW) is performed with additional WW conditions if some of the WW inequalities are violated.

The procedure of 2 and 3 is repeated until all the inequalities are satisfied. Note that the inequality holds after it is included in the condition. Actually, this iteration is necessary only for one or two times. As noted in section 2.2., the conditions VI and VII were violated for the resultant 2-RDM calculated by the DMVT(PQG), and therefore we developed the method of including only these two WW conditions. In the DMVT method using SDPA, the conditions should be reduced to the standard form and we introduce two types of constraint matrices $\boldsymbol{C}^{\mathrm{VI}}_{ijk}$ and $\boldsymbol{C}^{\mathrm{VII}}_{ijk}$. In the following, we employ the same notations as those in the previous paper(14). In the DMVT(PQG+WW) calculations, we extend the variable matrix $\boldsymbol{Y}$ given by Eq. (3.25) of Ref.(14) as $\boldsymbol{Y}'$,

$$\boldsymbol{Y}' = \begin{pmatrix} \boldsymbol{P} & \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{Q} & \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{G} & \boldsymbol{0} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{W}^{\mathrm{VI}} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{W}^{\mathrm{VII}} \end{pmatrix} = \begin{pmatrix} \boldsymbol{Y} & \boldsymbol{0} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{W}^{\mathrm{VI}} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{W}^{\mathrm{VII}} \end{pmatrix} \tag{12}$$

where $\boldsymbol{W}^{\mathrm{VI}}$, and $\boldsymbol{W}^{\mathrm{VII}}$ are the diagonal matrices and their diagonal elements are given in the right hand sides of Eqs.(9) and (10), respectively.

We define the constraint matrix $\boldsymbol{C}^{\mathrm{VI}}_{ijk}$ by

$$(\boldsymbol{C}^{\mathrm{VI}}_{ijk})_{p_1,p_2,q_1,q_2} = \begin{cases} -\frac{2}{N-1}\delta^i_{p_1}\delta^i_{q_1}\delta^{p_2}_{q_2} + 2\delta^i_{p_1}\delta^j_{p_2}\delta^i_{q_1}\delta^j_{q_2} + 2\delta^i_{p_1}\delta^k_{p_2}\delta^i_{q_1}\delta^k_{q_2} \\ \qquad\qquad - 2\delta^j_{p_1}\delta^k_{p_2}\delta^j_{q_1}\delta^k_{q_2}, \\ \qquad \text{for } 1 \le p_1, p_2, q_1, q_2 \le 3n, \\ 1 \qquad \text{for } 3n{+}1 \le p_1, p_2, q_1, q_2 \le 3n{+}n^{\mathrm{VI}}, \\ 0 \qquad \text{otherwise} \end{cases} \tag{13}$$

and C^{VII}_{ijk} by

$$(\boldsymbol{C}^{\mathrm{VII}}_{ijk})_{p_1,p_2,q_1,q_2} = \begin{cases} \frac{2}{N-1}\left(\delta^i_{p_1}\delta^i_{q_1}\delta^{p_2}_{q_2} + \delta^j_{p_1}\delta^j_{q_1}\delta^{p_2}_{q_2} + \delta^k_{p_1}\delta^k_{q_1}\delta^{p_2}_{q_2}\right) \\ \qquad\qquad - 2\delta^i_{p_1}\delta^j_{p_2}\delta^i_{q_1}\delta^j_{q_2} + 2\delta^j_{p_1}\delta^k_{p_2}\delta^j_{q_1}\delta^k_{q_2}, \\ \qquad \text{for } 1 \le p_1, p_2, q_1, q_2 \le 3n, \\ 1 \qquad \text{for } 3n{+}n^{\mathrm{VI}}{+}1 \le p_1, p_2, q_1, q_2 \le 3n{+}n^{\mathrm{VI}}{+}n^{\mathrm{VII}}, \\ 0 \qquad \text{otherwise}, \end{cases} \tag{14}$$

where n^{VI} and n^{VII} are the numbers of the Weinhold-Wilson inequality conditions, which were not satisfied in the previous iteration. The constants for constraints $\boldsymbol{C}^{\mathrm{VI}}$ and $\boldsymbol{C}^{\mathrm{VII}}$ are all 0 and 1, respectively.

Then, these constraints work as

$$\boldsymbol{C}^{\mathrm{VI}}_{ijk} \bullet \boldsymbol{Y}' = \sum_{p_1 p_2 q_1 q_2} (-\frac{2}{N-1}\delta^i_{p_1}\delta^i_{q_1}\delta^{p_2}_{q_2} + 2\delta^i_{p_1}\delta^j_{p_2}\delta^i_{q_1}\delta^j_{q_2}$$

$$
\begin{aligned}
&+2\delta^i_{p_1}\delta^k_{p_2}\delta^i_{q_1}\delta^k_{q_2} - 2\delta^j_{p_1}\delta^k_{p_2}\delta^j_{q_1}\delta^k_{q_2})Y^{p_1p_2}_{q_1q_2} + (\boldsymbol{W}^{\mathrm{VI}})_{ijk} \\
&= -\sum_{p_2}\frac{2}{N-1}\Gamma^{ip_2}_{ip_2} + 2\Gamma^{ij}_{ij} + 2\Gamma^{ik}_{ik} - 2\Gamma^{kj}_{kj} + (\boldsymbol{W}^{\mathrm{VI}})_{ijk} \\
&= -\gamma^i_i + 2\Gamma^{ij}_{ij} + 2\Gamma^{ik}_{ik} - 2\Gamma^{kj}_{kj} + (\boldsymbol{W}^{\mathrm{VI}})_{ijk} \\
&= 0 \qquad (15)
\end{aligned}
$$

and

$$
\begin{aligned}
\boldsymbol{C}^{\mathrm{VII}}_{ijk} \bullet \boldsymbol{Y}' &= \sum_{p_1p_2q_1q_2}(\frac{2}{N-1}\left(\delta^i_{p_1}\delta^i_{q_1}\delta^{p_2}_{q_2} + \delta^j_{p_1}\delta^j_{q_1}\delta^{p_2}_{q_2} + \delta^k_{p_1}\delta^k_{q_1}\delta^{p_2}_{q_2}\right) \\
&\quad - 2\delta^i_{p_1}\delta^j_{p_2}\delta^i_{q_1}\delta^j_{q_2} - 2\delta^i_{p_1}\delta^k_{p_2}\delta^i_{q_1}\delta^k_{q_2} \\
&\quad - 2\delta^j_{p_1}\delta^k_{p_2}\delta^j_{q_1}\delta^k_{q_2})Y^{p_1p_2}_{q_1q_2} + (\boldsymbol{W}^{\mathrm{VII}})_{ijk} \\
&= \gamma^i_i + \gamma^j_j + \gamma^k_k - 2\Gamma^{ij}_{ij} - 2\Gamma^{ik}_{ik} - 2\Gamma^{kj}_{kj} + (\boldsymbol{W}^{\mathrm{VII}})_{ijk} \\
&= 1, \qquad (16)
\end{aligned}
$$

since $(\boldsymbol{W}^{\mathrm{VI}})_{ijk}$ and $(\boldsymbol{W}^{\mathrm{VII}})_{ijk}$ are

$$
\begin{aligned}
(\boldsymbol{W}^{\mathrm{VI}})_{ijk} &= \gamma^i_i - 2\Gamma^{ij}_{ij} - 2\Gamma^{ik}_{ik} + 2\Gamma^{jk}_{jk} \\
(\boldsymbol{W}^{\mathrm{VII}})_{ijk} &= 1 - \gamma^i_i - \gamma^j_j - \gamma^k_k + 2\Gamma^{ij}_{ij} + 2\Gamma^{ik}_{ik} + 2\Gamma^{jk}_{jk}. \qquad (17)
\end{aligned}
$$

We further antisymmetrize the indices $i_1 \leftrightarrow i_2$ and $j_1 \leftrightarrow j_2$, hermitize the indices $(i_1, i_2) \leftrightarrow (j_1, j_2)$ to be suitable for the SDPA formalism, and pack the elements to remove unnecessary variables.

The resultant SDP formalism of the DMVT(PQG+WW) method is now given by,

$$
\begin{cases}
\text{Minimize} & \boldsymbol{H} \bullet \boldsymbol{Y}' \\
\text{subjected to} & \boldsymbol{F}_i \bullet \boldsymbol{Y}' = c_i \\
& \tilde{\boldsymbol{E}}^{i_1i_2}_{j_1j_2} \bullet \boldsymbol{Y}' = \delta^{i_1}_{j_1}\delta^{i_2}_{j_2} - \delta^{i_1}_{j_2}\delta^{i_2}_{j_1} \\
& \tilde{\boldsymbol{J}}^{i_1i_2}_{j_1j_2} \bullet \boldsymbol{Y} = 0, \\
& \boldsymbol{C}^{\mathrm{VI}}_{ijk} \bullet \boldsymbol{Y}' = 0, \\
& \boldsymbol{C}^{\mathrm{VII}}_{ijk} \bullet \boldsymbol{Y}' = 1.
\end{cases} \qquad (18)
$$

where the matrices of $\boldsymbol{F}_i$, $\tilde{\boldsymbol{E}}$, and $\tilde{\boldsymbol{J}}$ are defined in ref.(14).

3. Results

First we examined the Weinhold-Wilson inequalities for the 2-RDM obtained by the DMVT(PQG) calculations. We calculated the various electronic states of molecules, which were studied in the previous

works(14; 15). For N_2, CO, BH_3 and H_2O, the examinations were performed at both the equilibrium geometry and dissociation limit. In table I, we presented the results of the number of the violated conditions whose absolute errors were lager than 1×10^{-5} together with the DMVT(PQG) and full-CI energies. The violation occurred for the conditions VI and VII in some cases, while the conditions IV and V and VIII held for all the electronic states. For all the other atoms and molecules which were calculated in the previous paper and were not included in table I, all of these inequalities were correctly held. As seen in table I, when the DMVT(PQG) calculations are less accurate, the violation of the inequalities becomes large: the number of violations are large for BH_3, $CH_2(^1A_1)$, C_2 and CH_4.

We also calculated the artificially correlation enhanced system, introduced in the previous study(15): namely, the Hamiltonian is partitioned into F, Fock operator and the rest, V as:

$$H = F + \lambda V, \tag{19}$$

where λ is a real parameter that controls the strength of the electron correlation. Using this Hamiltonian, the DMVT(PQG) calculations were performed for H_2O and the results for some λ were summarized in table II. The violations have occurred for the condition VI and they were large for $\lambda = 1.5$. Note that no violation has occurred for large λ.

We examined the violations in details for C_2, $CH_2(^1A_1)$ and CH_4 and artificially correlation enhanced system with $\lambda = 1.5$ of H_2O. In tables III$\sim$ VI, we listed the violations with the indices and values, whose absolute value is larger than 1×10^{-5} for C_2, CH_4 and H_2O at the equilibrium geometry. As seen in table III, large violations occurred for both conditions VI and VII for C_2: the largest values were in the order of 1×10^{-2}. The violations mainly occurred for the valence orbitals, which are $p\sigma$, $p\pi$ and $p\pi^*$ orbitals, except for some violations with respect to the 1s orbital for condition VI. The violation of conditions VI and VII was also found for the $^1A_1$ state of CH_2. In this case, the violation occurred for the variable for the valence orbitals and not for the 1s core orbitals. In the case of CH_4, the order of the violations was smaller and the absolute errors were within 2.1×10^{-3} as shown in table V. In this case, the violations were also found for the 1s orbital of C. For H_2O with artificially correlation enhanced Hamiltonian of $\lambda = 1.5$, the violations occur only for the condition VI. The errors are calculated to be very small: the order is 1×10^{-4}. As shown in these examples, the absolute values of the violations are related to the accuracy of the DMVT(PQG), which indicates that these conditions may be effective as the necessary conditions for the DMVT method.

We performed, therefore, the DMVT(PQG+WW) calculations including these two WW conditions. The results were presented in table VII. The largest improvement was obtained for C_2 as expected, but it was not so drastic as 7.2×10^{-4} au in total energy. The deviation from the full-CI value is still large. For other systems, $CH_2(^1A_1)$, CH_4 and H_2O, the effect of these conditions was not so prominent and the improved energies were 1.7×10^{-4}, 9.0×10^{-5} and 1.0×10^{-5} au, respectively. These N-representability conditions actually improved the results, however, did not effectively work at least in the combination with the DMVT(PQG) calculation.

4. Conclusion

We examined the Weinhold-Wilson inequalities for the 2-RDM determined by the DMVT(PQG) method. The violations of the conditions VI and VII were found for some electronic states of several molecules, though they were not so large; the largest error was in the order of 1×10^{-2}. We therefore developed the formalism of the DMVT including these inequalities for the SDPA, which is denoted as DMVT(PQG+WW). These conditions certainly improved the results, however, they were not so drastic; the largest improvement was in the order of mhartree. These conditions were not so effective at least for the DMVT method including P, Q and G conditions.

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Table I. Number of violated Weinhold-Wilson inequalities for the 2-RDM determined by DMVT(PQG), whose absolute errors are larger than 1×10^{-5}.

System	State	Violation	DMVT(PQG)	FullCI
BH_3 [a]	$^1A_1$	VI: 12, VII: 12	-26.3926(120)	-26.3822(100)
BH_3 [b]	$^1A_1$	VI: 14, VII: 6	-25.8678(103)	-25.8482(100)
C_2 [a]	$^1\Sigma$	VI: 16, VII: 32	-75.4793(117)	-75.4340(100)
C_2 [b]	$^1\Sigma$	VII: 4	-75.2187(105)	-75.1855(100)
CO [a]	$^1\Sigma$	No	-112.4544(108)	-112.4426(100)
CO [b]	$^1\Sigma$	VI: 12	-112.1156(102)	-112.1096(100)
N_2 [a]	$^1\Sigma_g^+$	VI: 4	-108.7123(108)	-108.7002(100)
N_2 [b]	$^1\Sigma_g^+$	No	-108.4982(100)	-108.4982(100)
H_2O [a]	$^1A_1$	VI: 6	-75.7310(104)	-75.7290(100)
H_2O [b]	$^1A_1$	No	-75.4589(100)	-75.4589(100)
BH_2	$^2A_1$	VII: 6	-25.7089(115)	-25.7032(100)
CH^+	$^1\Sigma^+$	VI: 8	-37.8896(107)	-37.8853(100)
CH^-	$^3\Sigma^-$	VII: 2	-37.9714(99)	-37.9718(100)
CH	$^2\Pi$	VI: 2	-38.1916(111)	-38.1871(100)
CH_2	$^1A_1$	VI: 14, VII: 17	-38.8228(119)	-38.8110(100)
CH_2	$^3B_1$	VI: 2, VII: 4	-38.8556(107)	-38.8534(100)
CH_2(linear)	$^3\Sigma_u^-$	VI: 10, VII: 8	-38.8358(103)	-38.8342(100)
FH_2^+	$^1A_1$	VI: 8	-99.8305(103)	-99.8294(100)
H_2O^+	$^2A_1$	VI: 5	-75.4218(106)	-75.4192(100)
NH_2	$^2A_1$	VI: 4, VII: 8	-55.3570(111)	-55.3525(100)
NH_2	$^2B_1$	VI: 1, VII: 3	-55.4195(108)	-55.4157(100)
CH_4	$^1A_1$	VI: 30, VII:24	-40.2030(124)	-40.1905(100)

[a] At equilibrium geometry
[b] At dissociation limit

Table II. Number of violated Weinhold-Wilson inequalities for the 2-RDM of H_2O determined by DMVT(PQG), whose absolute errors are larger than 1×10^{-5}.

λ	Violation	DMVT(PQG)	FullCI
0.5	VI: 8	-56.5158(102)	-56.5155(100)
1.0	VI: 6	-75.7310(104)	-75.7290(100)
1.5	VI: 8	-95.0064(106)	-94.9978(100)
$\lambda > 1.5$	No	-	-

Table III. Violation of Weinhold-Wilson inequalities for C_2

Condition VI

(i,j,k)	violation	(i,j,k)	violation	(i,j,k)	violation	(i,j,k)	violation
$(5,\overline{4},\overline{7})$	-1.95×10^{-2}	$(\overline{5},4,7)$	-1.94×10^{-2}	$(\overline{5},3,6)$	-1.94×10^{-2}	$(5,\overline{3},\overline{6})$	-1.941×10^{-2}
$(6,4,7)$	-9.29×10^{-3}	$(\overline{6},\overline{4},\overline{7})$	-9.29×10^{-3}	$(\overline{7},\overline{3},\overline{6})$	-9.29×10^{-3}	$(7,3,6)$	-9.28×10^{-3}
$(7,\overline{5},\overline{7})$	-8.01×10^{-3}	$(\overline{7},5,7)$	-8.00×10^{-3}	$(\overline{6},5,6)$	-7.99×10^{-3}	$(6,\overline{5},\overline{6})$	-7.98×10^{-3}
$(\overline{7},\overline{3},6)$	-4.19×10^{-3}	$(7,3,\overline{6})$	-4.17×10^{-3}	$(6,4,\overline{7})$	-4.17×10^{-3}	$(\overline{6},\overline{4},7)$	-4.17×10^{-3}

Condition VII

(i,j,k)	violation	(i,j,k)	violation	(i,j,k)	violation	(i,j,k)	violation
$(2,5,\overline{5})$	-3.09×10^{-2}	$(\overline{2},5,\overline{5})$	-3.09×10^{-2}	$(3,4,\overline{6})$	-1.37×10^{-2}	$(\overline{3},\overline{4},6)$	-1.37×10^{-2}
$(3,4,\overline{7})$	-1.36×10^{-2}	$(\overline{3},\overline{4},7)$	-1.36×10^{-2}	$(3,\overline{3},6)$	-9.03×10^{-3}	$(3,\overline{3},\overline{6})$	-9.02×10^{-3}
$(4,\overline{4},7)$	-9.01×10^{-3}	$(4,\overline{4},\overline{7})$	-9.00×10^{-3}	$(\overline{3},\overline{4},\overline{6})$	-6.50×10^{-3}	$(3,4,6)$	-6.49×10^{-3}
$(3,4,7)$	-6.50×10^{-3}	$(\overline{3},\overline{4},\overline{7})$	-6.50×10^{-3}	$(2,\overline{5},\overline{6})$	-6.40×10^{-3}	$(\overline{2},5,6)$	-6.38×10^{-3}
$(\overline{2},5,7)$	-6.45×10^{-3}	$(2,\overline{5},\overline{7})$	-6.43×10^{-3}	$(2,5,7)$	-2.67×10^{-3}	$(\overline{2},\overline{5},\overline{7})$	-2.67×10^{-3}
$(2,5,6)$	-2.67×10^{-3}	$(\overline{2},\overline{5},\overline{6})$	-2.67×10^{-3}	$(2,4,7)$	-1.49×10^{-3}	$(\overline{2},\overline{4},\overline{7})$	-1.49×10^{-3}
$(2,3,6)$	-1.48×10^{-3}	$(\overline{2},\overline{3},\overline{6})$	-1.47×10^{-3}	$(\overline{3},\overline{5},\overline{6})$	-1.26×10^{-3}	$(3,5,6)$	-1.26×10^{-3}
$(\overline{4},\overline{5},\overline{7})$	-1.25×10^{-3}	$(4,5,7)$	-1.24×10^{-3}	$(1,5,8)$	-1.76×10^{-4}	$(\overline{1},\overline{5},\overline{8})$	-1.69×10^{-4}

Table IV. Violation of Weinhold-Wilson inequalities for $CH_2(^1A_1)$

Condition VI

(i,j,k)	violation	(i,j,k)	violation	(i,j,k)	violation	(i,j,k)	violation
$(5,\overline{4},\overline{5})$	-1.07×10^{-3}	$(\overline{5},4,5)$	-1.07×10^{-3}	$(7,\overline{4},\overline{6})$	-6.48×10^{-4}	$(\overline{7},4,6)$	-6.46×10^{-4}
$(2,\overline{3},\overline{6})$	-3.56×10^{-4}	$(\overline{2},3,6)$	-3.57×10^{-4}	$(6,\overline{6},\overline{7})$	-2.16×10^{-4}	$(\overline{6},6,7)$	-2.17×10^{-4}
$(\overline{6},\overline{2},7)$	-6.98×10^{-5}	$(6,2,\overline{7})$	-6.90×10^{-5}	$(\overline{2},3,\overline{6})$	-4.02×10^{-5}	$(2,\overline{3},6)$	-3.89×10^{-5}
$(2,3,6)$	-3.66×10^{-5}	$(\overline{2},\overline{3},\overline{6})$	-3.61×10^{-5}				

Condition VII

(i,j,k)	violation	(i,j,k)	violation	(i,j,k)	violation	(i,j,k)	violation
$(\overline{2},5,\overline{7})$	-2.39×10^{-3}	$(2,\overline{5},7)$	-2.39×10^{-3}	$(\overline{2},\overline{5},7)$	-1.60×10^{-3}	$(2,5,\overline{7})$	-1.59×10^{-3}
$(2,5,7)$	-1.54×10^{-3}	$(\overline{2},\overline{5},\overline{7})$	-1.54×10^{-3}	$(3,4,6)$	-1.54×10^{-3}	$(\overline{3},\overline{4},\overline{6})$	-1.54×10^{-3}
$(\overline{2},5,7)$	-1.21×10^{-3}	$(2,\overline{5},\overline{7})$	-1.20×10^{-3}	$(3,4,\overline{6})$	-1.14×10^{-3}	$(\overline{3},\overline{4},6)$	-1.14×10^{-3}
$(2,4,5)$	-4.47×10^{-4}	$(\overline{2},\overline{4},\overline{5})$	-4.47×10^{-4}	$(3,6,7)$	-4.46×10^{-4}	$(\overline{3},\overline{6},\overline{7})$	-4.47×10^{-4}
$(\overline{3},6,7)$	-1.87×10^{-4}	$(3,\overline{6},\overline{7})$	-1.86×10^{-4}				

Table V. Violation of Weinhold-Wilson inequalities for CH_4

Condition VI

(i,j,k)	violation	(i,j,k)	violation	(i,j,k)	violation	(i,j,k)	violation
$(3,\overline{1},5)$	-2.06×10^{-3}	$(\overline{3},1,\overline{5})$	-2.06×10^{-3}	$(4,\overline{1},6)$	-2.06×10^{-3}	$(\overline{4},1,\overline{6})$	-2.06×10^{-3}
$(5,3,\overline{8})$	-1.21×10^{-3}	$(\overline{5},\overline{3},8)$	-1.21×10^{-3}	$(6,4,\overline{8})$	-1.21×10^{-3}	$(\overline{6},\overline{4},8)$	-1.21×10^{-3}
$(4,\overline{1},\overline{6})$	-9.15×10^{-4}	$(\overline{4},1,6)$	-9.15×10^{-4}	$(3,\overline{1},\overline{5})$	-9.15×10^{-4}	$(\overline{3},1,5)$	-9.15×10^{-4}
$(4,1,\overline{6})$	-5.49×10^{-4}	$(\overline{4},\overline{1},6)$	-5.49×10^{-4}	$(3,1,\overline{5})$	-5.49×10^{-4}	$(\overline{3},\overline{1},5)$	-5.49×10^{-4}
$(1,3,\overline{4})$	-4.87×10^{-4}	$(1,\overline{3},4)$	-4.87×10^{-4}	$(\overline{1},\overline{3},4)$	-4.87×10^{-4}	$(\overline{1},3,\overline{4})$	-4.86×10^{-4}
$(1,\overline{2},\overline{3})$	-4.76×10^{-4}	$(\overline{1},2,3)$	-4.75×10^{-4}	$(\overline{1},2,4)$	-4.76×10^{-4}	$(1,\overline{2},\overline{4})$	-4.76×10^{-4}
$(1,\overline{3},\overline{4})$	-4.75×10^{-4}	$(\overline{1},3,4)$	-4.75×10^{-4}	$(\overline{5},3,8)$	-2.97×10^{-4}	$(5,\overline{3},\overline{8})$	-2.97×10^{-4}
$(6,\overline{4},\overline{8})$	-2.97×10^{-4}	$(\overline{6},4,8)$	-2.97×10^{-4}				

Condition VII

(i,j,k)	violation	(i,j,k)	violation	(i,j,k)	violation	(i,j,k)	violation
$(1,5,\overline{6})$	-1.80×10^{-3}	$(1,\overline{5},6)$	-1.80×10^{-3}	$(\overline{1},5,\overline{6})$	-1.80×10^{-3}	$(\overline{1},\overline{5},6)$	-1.80×10^{-3}
$(1,\overline{5},\overline{6})$	-1.15×10^{-3}	$(\overline{1},5,6)$	-1.15×10^{-3}	$(1,\overline{5},\overline{7})$	-1.15×10^{-3}	$(\overline{1},5,7)$	-1.15×10^{-3}
$(1,\overline{6},\overline{7})$	-1.15×10^{-3}	$(\overline{1},6,7)$	-1.15×10^{-3}	$(3,\overline{4},8)$	-7.38×10^{-4}	$(3,\overline{4},\overline{8})$	-7.38×10^{-4}
$(\overline{3},4,8)$	-7.38×10^{-4}	$(\overline{3},4,\overline{8})$	-7.38×10^{-4}	$(2,4,5)$	-5.50×10^{-4}	$(\overline{2},\overline{4},\overline{5})$	-5.50×10^{-4}
$(2,3,6)$	-5.50×10^{-4}	$(\overline{2},\overline{3},\overline{6})$	-5.50×10^{-4}	$(2,4,\overline{8})$	-1.27×10^{-4}	$(\overline{2},\overline{4},8)$	-1.27×10^{-4}
$(2,3,\overline{8})$	-1.27×10^{-4}	$(\overline{2},\overline{3},8)$	-1.27×10^{-4}	$(3,4,\overline{8})$	-1.27×10^{-4}	$(\overline{3},\overline{4},8)$	-1.27×10^{-4}

Table VI. Violation of condition VI for H_2O with various λ

$\lambda = 0.50$			
(i,j,k)	violation	(i,j,k)	violation
$(5,\overline{4},\overline{5})$	-1.05×10^{-5}	$(\overline{5},4,5)$	-9.78×10^{-6}
$(5,\overline{5},7)$	-6.82×10^{-6}	$(\overline{5},5,\overline{7})$	-6.43×10^{-6}
$(5,2,\overline{5})$	-4.94×10^{-6}	$(\overline{5},\overline{2},5)$	-4.79×10^{-6}
$(5,\overline{5},\overline{6})$	-4.47×10^{-6}	$(\overline{5},5,6)$	-4.12×10^{-6}
$\lambda = 1.00$			
(i,j,k)	violation	(i,j,k)	violation
$(5,\overline{4},\overline{5})$	-7.52×10^{-5}	$(\overline{5},4,5)$	-7.46×10^{-5}
$(\overline{5},\overline{2},5)$	-4.25×10^{-5}	$(5,2,\overline{5})$	-4.15×10^{-5}
$(5,\overline{5},6)$	-3.40×10^{-6}	$(\overline{5},5,\overline{6})$	-2.53×10^{-6}
$\lambda = 1.50$			
(i,j,k)	violation	(i,j,k)	violation
$(\overline{5},\overline{2},5)$	-3.69×10^{-4}	$(5,2,\overline{5})$	-3.68×10^{-4}
$(\overline{5},3,5)$	-3.00×10^{-4}	$(5,\overline{3},\overline{5})$	-2.99×10^{-4}
$(\overline{5},4,5)$	-1.83×10^{-4}	$(5,\overline{4},\overline{5})$	-1.81×10^{-4}
$(5,\overline{5},6)$	-5.63×10^{-5}	$(\overline{5},5,\overline{6})$	-5.44×10^{-5}

Table VII. Total energy by DMVT(PQG), DMVT(PQG+WW), and FullCI.

	DMVT(PQG)	DMVT(PQG+WW)	ΔE^a	FullCI
CH_4, STO-6G, 1s core	-40.20999	-40.20990	9.0×10^{-5}	-40.19049
C_2, STO-6G, 1s core	-75.47932	-75.47860	7.2×10^{-4}	-75.43398
$H_2O(\lambda = 1.50)$, STO-6G	-95.00638	-95.00637	1.0×10^{-5}	-94.99780
$CH_2(^1A_1)$, STO-6G	-38.82261	-38.82278	1.7×10^{-4}	-38.81099

[a] Improvement by including Weinhold-Wilson conditions.