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Elimination of Translational and Rotational Motions in Nuclear Orbital Plus Molecular Orbital Theory: Contribution of the First-Order Rovibration Coupling

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Abstract: The translation- and rotation-free nuclear orbital plus molecular orbital (TRF−NOMO) theory was developed to determine nonadiabatic nuclear and electronic wave functions. This study implemented a computational program for the TRF−NOMO method including first-order rotational terms, which corresponds to rovibronic coupling. Numerical assessments of first-order TRF−NOMO Hartree−Fock as well as second-order Møller−Plesset perturbation methods were carried out for several small molecules. The first-order contributions give small corrections in energy. Thus, we confirm that the approximate zeroth-order treatment is sufficient for eliminating the rotational contamination.

1. Introduction

Born−Oppenheimer (BO) approximation,[1] which divides nuclear and electronic motions, is a fundamental concept of modern molecular theory. Although BO treatment is suitable for accurately describing various chemical and physical phenomena, it cannot take into account coupling between the nuclear and electronic motions, that is, the non-BO effect.

Adamowicz and co-workers[2−5] proposed the non-BO theory by utilizing the explicit correlated Gaussian (ECG) basis functions, which involve the internal coordinates among nuclei and electrons. The ECG approach has been shown to achieve considerably high accuracy, that is, spectroscopic accuracy. The problem with this approach is that the complexity of the explicit formula increases with an increase of the number (N) of identical particles, which requires different programming codes for different N values. Furthermore, the computational cost increases very rapidly (N factorial).

On the other hand, we have developed the nuclear orbital plus molecular orbital (NOMO) theory,[6−12] which determines nuclear and electronic wave functions simultaneously without BO approximation. In NOMO theory, total wave function is constructed by nuclear orbitals (NOs), one-nucleus wave functions, and molecular orbitals (MOs), one-electron ones. We have proposed that it is convenient to adopt Gaussian basis functions with the center on each atomic position in the appropriate molecular configuration, such as equilibrium and optimized ones.[6−12] The use of Gaussian basis functions has been accepted by other groups[13−28] probably because it is consistent with conventional MO theory within BO approximation. While Gaussian basis functions can describe a vibrational state accurately, translational and rotational states are not adequately reproduced because their motions are limited in some local regions represented by the functions. Thus, we have presented translation-free (TF)− and translation- and rotation-free (TRF)−NOMO theories and clarified the importance of eliminating translational and rotational contaminations in obtaining accurate results in NOMO and similar approaches.[7,10−12]

Sutcliffe has pointed out that it is possible to rigorously construct a TF−NOMO Hamiltonian, but it is impossible to rigorously construct a TRF−NOMO Hamiltonian for general systems.[29] This distinction arises because translations are separable from rotations and vibrations, but rotations and vibrations are coupled for general systems. The essential problems Sutcliffe points out undoubtedly exist, and the TRF treatment for nonrigid rotator systems cannot rigorously succeed in general cases, nor can it do so in the NOMO theory. We have focused on the locality of the Gaussian functions, of which the orbital centers can approximately define the rigid-body rotator. It is possible to define center-of-mass (COM), angular, and internal coordinates uniquely for the rigid-body rotator, while it is impossible for the general case where rotational and vibrational motions couple. Thus, the

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rotational operator has been expanded in a Taylor series with respect to the displacement $\Delta \mathbf{x}$ based on the rigid-body rotator. As a result, the nuclear wave function represented by Gaussian basis functions can be separated into zeroth-order rigid-body rotation and higher-order coupling. TRF−NOMO theory adopts this unique definition of the COM, angular, and internal coordinates for the zeroth-order rotator.[10]

In a previous study, however, we implemented a programming code for the TRF−NOMO method corresponding only to the zeroth-order terms of the rotational Hamiltonian and numerically tested their contributions. Therefore, the assessment of the higher-order contribution is of great importance for investigating the reliability of the zeroth-order treatment and, furthermore, the validity of the TRF−NOMO formalism itself, on the basis of the Taylor expansion of the rotational operator.

The purpose of the present study is to implement the computational program for the TRF−NOMO method involving the first-order rotational terms, which are much more complicated than the zeroth-order terms, and the numerical assessment of their contribution. The organization of this paper is as follows. First, section 2 describes the theoretical aspects of the first-order TRF−NOMO method. Section 3 indicates the implementation of this method. In section 4, we present the numerical assessments of the present treatment. Concluding remarks are summarized in section 5. Furthermore, the second-order Møller−Plesset (MP2) treatment for the first-order TRF−NOMO method is described in the Appendix.

2. Theory

In this section, we summarize TRF−NOMO/Hartree−Fock (HF) theory,[10] which determines electronic and nuclear wave functions simultaneously while eliminating translational and rotational motions. The total Hamiltonian adopted in the original NOMO theory contaminates translational and rotational motions. Thus, the Hamiltonian is called the translation- and rotation-contaminated (TRC) Hamiltonian:

$$\hat{H}_{\text{TRC}} = \hat{T}^{\text{e}} + \hat{T}^{\text{n}} + \hat{V}^{\text{ee}} + \hat{V}^{\text{en}} + \hat{V}^{\text{nn}} \tag{1}$$

where

$$\hat{T}^{\text{e}} = -\sum_{p} \frac{1}{2}\nabla(\mathbf{x}_p)^2 \equiv \sum_{p} \hat{t}^{\text{e}}(\mathbf{x}_p) \tag{2}$$

$$\hat{T}^{\text{n}} = -\sum_{P} \frac{1}{2m_P}\nabla(\mathbf{x}_P)^2 \equiv \sum_{P} \hat{t}^{\text{n}}(\mathbf{x}_P) \tag{3}$$

$$\hat{V}^{\text{ee}} = \sum_{p<q} \frac{1}{r_{pq}} \tag{4}$$

$$\hat{V}^{\text{en}} = -\sum_{p,P} \frac{Z_P}{r_{pP}} \tag{5}$$

$$\hat{V}^{\text{nn}} = \sum_{P<Q} \frac{Z_P Z_Q}{r_{PQ}} \tag{6}$$

Here, $\hat{T}^{\text{e}}$ and $\hat{T}^{\text{n}}$ are electronic and nuclear kinetic operators, respectively. Two-particle operators consist of e−e ($\hat{V}^{\text{ee}}$), e−n ($\hat{V}^{\text{en}}$), and n−n ($\hat{V}^{\text{nn}}$) interactions. While the summation of p

and q in eqs 2, 4, and 5 runs over electrons, that of P and Q in eqs 3, 5, and 6 runs over nuclei.

We proposed a scheme to eliminate the contribution of translational motion from the TRC Hamiltonian.[7] By subtracting the translational Hamiltonian $\hat{T}_{\text{T}}$ from $\hat{H}_{\text{TRC}}$, the TF Hamiltonian is given by

$$\hat{H}_{\text{TF}} = \hat{H}_{\text{TRC}} - \hat{T}_{\text{T}} \tag{7}$$

where

$$\hat{T}_{\text{T}} = -\frac{1}{2M}\sum_{\mu}\nabla(\mathbf{x}_{\mu})^2 - \frac{1}{M}\sum_{\mu<\nu}\nabla(\mathbf{x}_{\mu})\,\nabla(\mathbf{x}_{\nu}) \tag{8}$$

Here, M is the total mass of all particles. The summation runs over all particles.

We have further proposed a scheme to eliminate the effect of translational and rotational motions from the NOMO calculation.[10] The TRF Hamiltonian is given by subtracting the rotational Hamiltonian $\hat{T}_{\text{R}}$ from $\hat{H}_{\text{TF}}$ as follows:

$$\hat{H}_{\text{TRF}} = \hat{H}_{\text{TF}} - \hat{T}_{\text{R}} = \hat{H}_{\text{TRC}} - \hat{T}_{\text{T}} - \hat{T}_{\text{R}} \tag{9}$$

where

$$\hat{T}_{\text{R}} = \sum_{\alpha}^{x,y,z} \frac{1}{2\hat{I}_{\alpha}}\left(\sum_{\mu}\hat{L}_{\alpha,\mu}^2 + 2\sum_{\mu<\nu}\hat{L}_{\alpha,\mu}\hat{L}_{\alpha,\nu}\right) \tag{10}$$

Here, I_{α} is the principle moment of inertia, which is not a constant but a function (or an operator) due to coupling with the vibration.

NOMO theory adopts Gaussian basis functions, which are localized around the centers. Then, the position of the μth particle $\mathbf{x}_{\mu} = (x_{\mu}, y_{\mu}, z_{\mu})$ is described by the center $\mathbf{x}_{\mu}^0 = (x_{\mu}^0, y_{\mu}^0, z_{\mu}^0)$ and the displacement $\Delta\mathbf{x}_{\mu}$ as follows:

$$\mathbf{x}_{\mu} = \mathbf{x}_{\mu}^0 + \Delta\mathbf{x}_{\mu} \tag{11}$$

Because of the locality of the Gaussian function, it is possible to define a quasi-COM coordinate $\mathbf{x}_{\text{G}}^0$ by

$$\mathbf{x}_{\text{G}}^0 = \frac{\sum\limits_{\mu} m_{\mu}\mathbf{x}_{\mu}^0}{\sum\limits_{\mu} m_{\mu}} \tag{12}$$

The coordinate $\mathbf{x}_{\mu}^0$ is translated to a new coordinate $\tilde{\mathbf{x}}_{\mu}^0$, whose origin agrees with the COM $\mathbf{x}_{\text{G}}^0$:

$$\tilde{\mathbf{x}}_{\mu}^0 = \mathbf{x}_{\mu}^0 - \mathbf{x}_{\text{G}}^0 \tag{13}$$

Because $\tilde{\mathbf{x}}_{\mu}^0$ is a constant, the atoms located on $\{\mathbf{x}_{\mu}^0\}$ compose a rigid-body rotator, of which the tensor of inertia is defined by

$$\mathbf{I}^0 = \begin{bmatrix} \sum\limits_{\mu} m_{\mu}(\tilde{y}_{\mu}^{02} + \tilde{z}_{\mu}^{02}) & -\sum\limits_{\mu} m_{\mu}\tilde{x}_{\mu}^0\tilde{y}_{\mu}^0 & -\sum\limits_{\mu} m_{\mu}\tilde{z}_{\mu}^0\tilde{x}_{\mu}^0 \\ -\sum\limits_{\mu} m_{\mu}\tilde{x}_{\mu}^0\tilde{y}_{\mu}^0 & \sum\limits_{\mu} m_{\mu}(\tilde{z}_{\mu}^{02} + \tilde{x}_{\mu}^{02}) & -\sum\limits_{\mu} m_{\mu}\tilde{y}_{\mu}^0\tilde{z}_{\mu}^0 \\ -\sum\limits_{\mu} m_{\mu}\tilde{z}_{\mu}^0\tilde{x}_{\mu}^0 & -\sum\limits_{\mu} m_{\mu}\tilde{y}_{\mu}^0\tilde{z}_{\mu}^0 & \sum\limits_{\mu} m_{\mu}(\tilde{x}_{\mu}^{02} + \tilde{y}_{\mu}^{02}) \end{bmatrix} \tag{14}$$

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By diagonalizing the tensor, the principal moments of inertia and the transformed coordinates are determined as follows:

$$\,^{t}\mathbf{U}\mathbf{I}^0\mathbf{U} = \begin{bmatrix} I_x^0 & 0 & 0 \\ 0 & I_y^0 & 0 \\ 0 & 0 & I_z^0 \end{bmatrix} \tag{15}$$

$$\mathbf{r}_\mu^0 = \mathbf{U}\tilde{\mathbf{x}}_\mu^0 \tag{16}$$

where $\mathbf{U}$ is a unitary transform matrix with three dimensions. The general coordinate $\mathbf{r}_\mu$ of the μth particle, which cannot be treated as a rigid-body rotator, is rewritten by $\mathbf{r}_\mu^0 = (r_{x_\mu}^0, r_{y_\mu}^0, r_{z_\mu}^0)$ and the displacement $\Delta\mathbf{r}_\mu = (\Delta r_{x_\mu}, \Delta r_{y_\mu}, \Delta r_{z_\mu})$:

$$\mathbf{r}_\mu = \mathbf{r}_\mu^0 + \Delta\mathbf{r}_\mu \tag{17}$$

As a result, the rotational term can be uniquely defined using the coordinates $\{\mathbf{r}_\mu\}$.

Furthermore, the rotational operator is expanded in a Taylor series with respect to $\Delta\mathbf{r}_\mu$ as follows:

$$\hat{T}_R = \hat{T}_{R_0} + \hat{T}_{R_1} + O(\Delta\mathbf{r}^2) \tag{18}$$

$$\hat{T}_{R_0} = \sum_\alpha^{x,y,z}\left(\sum_\mu \frac{1}{2I_\alpha^0}\hat{L}_{\alpha,\mu}^{0\,2} + \sum_{\mu<\nu}\frac{1}{I_\alpha^0}\hat{L}_{\alpha,\mu}^0\hat{L}_{\alpha,\nu}^0\right) \tag{19}$$

$$\hat{T}_{R_1} = \sum_\mu\sum_\alpha^{x,y,z}\frac{1}{2I_\alpha^0}\left(\hat{L}_{\alpha,\mu}^{0\,2} + \hat{L}_{\alpha,\mu}^0\Delta\hat{L}_{\alpha,\mu} + \Delta\hat{L}_{\alpha,\mu}\hat{L}_{\alpha,\mu}^0 - \right.$$
$$\left. \frac{2}{I_\alpha^0}\Delta\hat{I}_{\alpha,\mu}\hat{L}_{\alpha,\mu}^{0\,2}\right) + \sum_{\mu<\nu}\sum_\alpha^{x,y,z}\frac{1}{I_\alpha^0}\left\{\hat{L}_{\alpha,\mu}^0\Delta\hat{L}_{\alpha,\nu} + \Delta\hat{L}_{\alpha,\mu}\hat{L}_{\alpha,\nu}^0 - \right.$$
$$\frac{1}{I_\alpha^0}(\Delta\hat{I}_{\alpha,\mu}\hat{L}_{\alpha,\nu}^{0\,2} + \Delta\hat{I}_{\alpha,\nu}\hat{L}_{\alpha,\mu}^{0\,2} + 2\Delta\hat{I}_{\alpha,\mu}\hat{L}_{\alpha,\mu}^0\hat{L}_{\alpha,\nu}^0 +$$
$$\left.2\Delta\hat{I}_{\alpha,\nu}\hat{L}_{\alpha,\mu}^0\hat{L}_{\alpha,\nu}^0)\right\} - \sum_{\mu\neq\nu,\mu\neq\lambda,\nu<\lambda}\sum_\alpha^{x,y,z}\frac{2}{I_\alpha^{0\,2}}\Delta\hat{I}_{\alpha,\mu}\hat{L}_{\alpha,\nu}^0\hat{L}_{\alpha,\lambda}^0 \tag{20}$$

where x components of I_α^0, $\Delta\hat{I}_{\alpha,\mu}$, $\hat{L}_{\alpha,\mu}^0$, and $\Delta\hat{L}_{\alpha,\mu}$ are

$$I_x^0 = \sum_\mu m_\mu(r_{y_\mu}^{0\,2} + r_{z_\mu}^{0\,2}) \tag{21}$$

$$\Delta\hat{I}_{x,\mu} = m_\mu(r_{y_\mu}^0\Delta r_{y_\mu} + r_{z_\mu}^0\Delta r_{z_\mu}) \tag{22}$$

$$\hat{L}_{x,\mu}^0 = -i\left(r_{y_\mu}^0\frac{\partial}{\partial r_{z_\mu}} - r_{z_\mu}^0\frac{\partial}{\partial r_{y_\mu}}\right) \tag{23}$$

$$\Delta\hat{L}_{x,\mu} = -i\left(\Delta r_{y_\mu}\frac{\partial}{\partial r_{z_\mu}} - \Delta r_{z_\mu}\frac{\partial}{\partial r_{y_\mu}}\right) \tag{24}$$

In eq 18, the second- and higher-order terms are collected in the last term $O(\Delta\mathbf{r}^2)$. The HF equations for NOs and MOs in the TRF−NOMO formalism with first-order rovibrational coupling are easily derived by applying the variational procedure. The HF equations are similar to the TRC−, TF−, and the zeroth-order TRF−NOMO ones. However, the present first-order TRF−NOMO method involves additional terms, some of which require three-body integrals.

To differentiate between the zeroth- and first-order TRF−NOMO methods, we adopt the abbreviations TR$_0$F and TR$_1$F, respectively.

3. Implementation

We have implemented a computational program[30] for the first-order TRF−NOMO/HF method by modifying the GAMESS program package.[31] For simplicity, we have concentrated here on nuclear contributions of translational and rotational motions, which should be the main parts in those motions. Thus, the translational Hamiltonian is approximated as follows:

$$\hat{T}_T(\mathbf{x}) \approx \hat{T}_T^n(\mathbf{x}) = -\frac{1}{2M^n}\sum_P^{nuc}\nabla(\mathbf{x}_P)^2 - \frac{1}{M^n}\sum_{P<Q}^{nuc}\nabla(\mathbf{x}_P)\,\nabla(\mathbf{x}_Q) \tag{25}$$

where M^n is the total mass of all nuclei. The rotational Hamiltonian is also approximated as follows:

$$\hat{T}_{R_0} \approx \hat{T}_{R_0}^n = \sum_\alpha^{x,y,z}\left(\sum_P^{nuc}\frac{1}{2I_\alpha^{n,0}}\hat{L}_{\alpha P}^{0\,2} + \sum_{P<Q}^{nuc}\frac{1}{I_\alpha^{n,0}}\hat{L}_{\alpha,P}^0\hat{L}_{\alpha,Q}^0\right) \tag{26}$$

$$\hat{T}_{R_1} \approx \hat{T}_{R_1}^n = \sum_P^{nuc}\sum_\alpha^{x,y,z}\frac{1}{2I_\alpha^{n,0}}\left(\hat{L}_{\alpha,P}^0\Delta\hat{L}_{\alpha,P} + \Delta\hat{L}_{\alpha,P}\hat{L}_{\alpha,P}^0 - \right.$$
$$\left.\frac{2}{I_\alpha^{n,0}}\Delta\hat{I}_{\alpha,P}\hat{L}_{\alpha,P}^{0\,2}\right) + \sum_{P<Q}\sum_\alpha^{x,y,z}\frac{1}{I_\alpha^{n,0}}\left\{\hat{L}_{\alpha,P}^0\Delta\hat{L}_{\alpha,Q} + \Delta\hat{L}_{\alpha,P}\hat{L}_{\alpha,Q}^0 - \right.$$
$$\frac{1}{I_\alpha^{n,0}}(\Delta\hat{I}_{\alpha,P}\hat{L}_{\alpha,Q}^{0\,2} + \Delta\hat{I}_{\alpha,P}\hat{L}_{\alpha,Q}^{0\,2} + 2\Delta\hat{I}_{\alpha,P}\hat{L}_{\alpha,P}^0\hat{L}_{\alpha,Q}^0 +$$
$$\left.2\Delta\hat{I}_{\alpha,P}\hat{L}_{\alpha,Q}^0\hat{L}_{\alpha,P}^0)\right\} - \sum_{P\neq Q,P\neq R,Q<R}\sum_\alpha^{x,y,z}\frac{2}{I_\alpha^{n,02}}\Delta\hat{I}_{\alpha,P}\hat{L}_{\alpha,Q}^0\hat{L}_{\alpha,R}^0 \tag{27}$$

where $I_\alpha^{n,0}$ is the principal moment of inertia for the rigid-body rotator, which consists of all nuclei. Because three-body integrals due to first-order rotational operators can be constructed by direct products of one-body integrals, for example, the integral of the three-body term in eq 20 is given by

$$-\sum_{\substack{I\neq J,I\neq K \\ J<K}}\sum_\alpha^{x,y,z}\frac{2}{I_\alpha^{0\,2}}\langle\varphi_I|\Delta\hat{I}_\alpha|\varphi_I\rangle\langle\varphi_J|\hat{L}_\alpha^0|\varphi_J\rangle\langle\varphi_K|\hat{L}_\alpha^0|\varphi_K\rangle \tag{28}$$

Here, I, J, and K represent nuclear occupied orbitals; we first evaluate and save the one-body integrals into memory and then use them reading from the memory. The approximation in eqs 25−27 corresponds to neglecting coupling between electronic motion and translation or rotation. It is noted, however, that the TRF−NOMO method using eqs 25−27 still involves vibronic coupling, that is, a nonadiabatic effect.

The present program is capable of performing different kinds of NOMO/HF calculations: TRC−, TF−, TR$_0$F−, and

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Table 1. Even-Tempered Parameters α and β According to eq 37 from the Hydrogen to Fluorine Atom

atom	H	D	T	Li	B	C	N	F
α	2.872	5.741	8.597	19.997	313.790	342.018	399.109	541.491
β	3.162	3.162	3.162	3.162	3.162	3.162	3.162	3.162

Table 2. Total (E_{tot}), Translational (E_{trans}), Zeroth-Order Rotational (E_{rot0}), First-Order Rotational (E_{rot1}), Vibrational (E_{vib}), and Electronic (E_{elec}) Energies (in hartree) Calculated by the TRC−, TF−, TR$_0$F−, and TR$_1$F−NOMO/HF Methods

		TRC	TF	ΔE^{TFa}	TR$_0$F	ΔE^{R_0Fb}	TR$_1$F	ΔE^{R_1Fc}
H$_2$	E_{tot}	−1.052371	−1.074314	−21.943	−1.104088	−29.774	−1.104069	0.019
	E_{trans}	0.018337	(0.027092)		(0.191744)		(0.095525)	
	E_{rot0}	0.011396	0.016916		(0.080830)		(0.081221)	
	E_{rot1}	0.000422	0.000452		−0.000069		(0.000030)	
	E_{vib}	0.006518	0.009723		0.014310		0.014274	
	E_{elec}	−1.089044	−1.101406		−1.118329		−1.118343	
D$_2$	E_{tot}	−1.074233	−1.090522	−16.289	−1.112184	−21.662	−1.112172	0.012
	E_{trans}	0.013614	(0.020054)		(0.068366)		(0.068710)	
	E_{rot0}	0.008534	0.012550		(0.058017)		(0.058320)	
	E_{rot1}	0.000202	0.000208		−0.000042		(0.000018)	
	E_{vib}	0.004877	0.007295		0.010391		0.010372	
	E_{elec}	−1.101460	−1.110576		−1.122533		−1.122544	
T$_2$	E_{tot}	−1.084308	−1.097901	−13.593	−1.115902	−18.001	−1.115893	0.008
	E_{trans}	0.011367	(0.016734)		(0.054419)		(0.054503)	
	E_{rot0}	0.007143	0.010518		(0.046134)		(0.046203)	
	E_{rot1}	0.000139	0.000130		−0.000023		(0.000006)	
	E_{vib}	0.004085	0.006086		0.008308		0.008293	
	E_{elec}	−1.107043	−1.114635		−1.124187		−1.124187	

[a] $\Delta E^{TF} = E_{tot}^{TF} - E_{tot}^{TRC}$ (in mhartree) [b] $\Delta E^{R_0F} = E_{tot}^{TR_0F} - E_{tot}^{TF}$ (in mhartree) [c] $\Delta E^{R_1F} = E_{tot}^{TR_1F} - E_{tot}^{TR_0F}$ (in mhartree)

TR$_1$F−NOMO/HF using the following energy expectations:

$$E_{tot}^{TRC} = \langle \Phi_0 | \hat{H}_{TRC} | \Phi_0 \rangle \quad (29)$$

$$E_{tot}^{TF} = \langle \Phi_0 | \hat{H}_{TRC} - \hat{T}_T^n | \Phi_0 \rangle \quad (30)$$

$$E_{tot}^{TR_0F} = \langle \Phi_0 | \hat{H}_{TRC} - \hat{T}_T^n - \hat{T}_{R_0}^n | \Phi_0 \rangle \quad (31)$$

$$E_{tot}^{TR_1F} = \langle \Phi_0 | \hat{H}_{TRC} - \hat{T}_T^n - \hat{T}_{R_0}^n - \hat{T}_{R_1}^n | \Phi_0 \rangle \quad (32)$$

Furthermore, translational (E_{trans}), zeroth-order rotational (E_{rot0}), first-order rotational (E_{rot1}), and vibrational (E_{vib}) energy components are estimated as follows:

$$E_{trans} = \langle \Phi_0 | \hat{T}_T^n | \Phi_0 \rangle \quad (33)$$

$$E_{rot0} = \langle \Phi_0 | \hat{T}_{R_0}^n | \Phi_0 \rangle \quad (34)$$

$$E_{rot1} = \langle \Phi_0 | \hat{T}_{R_1}^n | \Phi_0 \rangle \quad (35)$$

Because the rest of the nuclear motion corresponds to vibration, the vibrational energy is evaluated by

$$E_{vib} = \langle \Phi_0 | \hat{T}^n - \hat{T}_T^n - \hat{T}_{R_0}^n - \hat{T}_{R_1}^n | \Phi_0 \rangle \quad (36)$$

The electronic energy including nuclear repulsion is given by

$$E_{elec} = \langle \Phi_0 | \hat{T}^e + \hat{V}^{ee} + \hat{V}^{en} + \hat{V}^{nn} | \Phi_0 \rangle \quad (37)$$

4. Numerical Assessment

Numerical assessment on the effect of the first-order rotational terms in the TRF−NOMO treatment was per-

formed for small molecules: H$_2$, D$_2$, T$_2$, Li$_2$, B$_2$, N$_2$, F$_2$, H$_3^+$, BH$_3$, CH$_4$, and C$_2$H$_4$. We have carried out HF calculations for the TRC−, TF−, TR$_0$F−, and TR$_1$F−NOMO methods. Primitive functions, of which exponents correspond to correlation-consistent polarization plus valence triple-ζ (cc-pVTZ) bases of Dunning,[32] were adopted as electronic basis functions (EBFs): (5s2p1d), (11s5p2d1f), and (10s5p2d1f) functions for {H, D, T}, Li, and {B, C, N, F}, respectively. For nuclear basis functions (NBFs), we used (7s7p7d) primitive Gaussian functions. The exponents ζ_n of the NBFs are determined by the even-tempered scheme.[7,33]

$$\zeta_n = \alpha \beta^n \quad (38)$$

Table 1 shows the values of α and β of each atom. Orbital centers of both EBFs and NBFs in H$_2$, D$_2$, and T$_2$ molecules were settled at the experimental geometries,[34] and those of others are the optimized geometry at the conventional MO/HF level.

Table 2 summarizes the results of the TRC−, TF−, TR$_0$F−, and TR$_1$F−NOMO/HF calculations for H$_2$, D$_2$, and T$_2$ molecules. The total energies decrease in the order of the TRC−, TF−, and TR$_0$F−NOMO/HF methods. The energy difference between E_{tot}^{TRC} and E_{tot}^{TF}, which is represented by ΔE^{TF}, corresponds to the energetic improvement achieved by eliminating the contamination of the translational motion. ΔE^{TF} values for H$_2$, D$_2$, and T$_2$ are −21.9, −16.3, and −13.6 mhartree, respectively. The energy difference between E_{tot}^{TF} and $E_{tot}^{TR_0F}$, given by ΔE^{R_0F}, corresponds to the elimination of zeroth-order rotational motion, that is, the rigid-body rotator. ΔE^{R_0F} values for H$_2$, D$_2$, and T$_2$ are −29.8, −21.6, and −18.0 mhartree, respectively. Thus, the elimina-

Table 3. Total Energies (in hartree) of Several Small Molecules Calculated by the TRC−, TF−, TR$_0$F−, and TR$_1$F−NOMO/ HF Methods

	TRC	TF	ΔE^{TF}[a]	TR$_0$F	ΔE^{R_0F}[b]	TR$_1$F	ΔE^{R_1F}[c]
Li$_2$	−14.553448	−14.643200	−89.753	−14.763556	−120.356	−14.763556	0.000
B$_2$	−48.170671	−48.382923	−212.252	−48.671256	−288.333	−48.671258	−0.003
N$_2$	−107.637234	−108.020683	−383.449	−108.541786	−521.104	−108.541786	0.000
F$_2$	−196.803609	−197.361041	−557.432	−198.087631	−726.590	−198.087631	0.000
H$_3^+$	−1.192826	−1.210845	−18.019	−1.239881	−29.036	−1.239819	0.061
BH$_3$	−25.898990	−26.099861	−200.871	−26.123998	−24.138	−26.124007	−0.008
CH$_4$	−39.518843	−39.779765	−260.922	−39.801179	−21.414	−39.801338	−0.159
C$_2$H$_4$	−76.842228	−77.093110	−250.882	−77.260050	−166.940	−77.259630	0.421

[a] $\Delta E^{TF} = E_{tot}^{TF} - E_{tot}^{TRC}$ (in mhartree) [b] $\Delta E^{R_0F} = E_{tot}^{TR_0F} - E_{tot}^{TF}$ (in mhartree) [c] $\Delta E^{R_1F} = E_{tot}^{TR_1F} - E_{tot}^{TR_0F}$ (in mhartree)

tion of these contaminations is of great importance to improving accuracy.

On the other hand, the energy changes from the TR$_0$F treatment to the TR$_1$F one are extremely small. Moreover, they increase slightly. ΔE^{R_1F} values, which are defined by the difference between $E_{tot}^{TR_0F}$ and $E_{tot}^{TR_1F}$, for H$_2$, D$_2$, and T$_2$ are less than 0.1 mhartree. Therefore, it is confirmed that TR$_0$F treatment is a good approximation with chemical accuracy.

In Table 2, the energy components, E_{tot}, E_{trans}, E_{rot0}, E_{rot1}, E_{vib}, and E_{elec} are also given. In TRC treatment, the translational and zeroth-order rotational contaminations, that is, E_{trans}^{TRC} and E_{rot0}^{TRC}, are less than $|\Delta E^{TF}|$ and $|\Delta E^{R_0F}|$, respectively. Similarly, E_{rot0}^{TF} in the TF treatment is less than $|\Delta E^{R_0F}|$. Thus, $E_{tot}^{TRC} - E_{trans}^{TRC}$ and $E_{tot}^{TF} - E_{rot0}^{TF}$ are higher than E_{tot}^{TF} and $E_{tot}^{TR_0F}$. This means that the self-consistent-field (SCF) procedure is important for the adequate removal of the translational and rotational contaminations.

E_{vib} is related to the zero-point energy (ZPE). Experimental ZPEs of H$_2$, D$_2$, and T$_2$ are 0.010, 0.007, and 0.006 hartree, respectively. While E_{vib}^{TRC} of H$_2$ is about 0.003 hartree smaller than the experimental value, $E_{vib}^{TR_0F}$ and $E_{vib}^{TR_1F}$ are about 0.004 hartree larger. E_{vib}^{TF} is comparatively close to the experimental value. Similar trends are seen for D$_2$ and T$_2$. However, this does not mean that TF treatment is the most suitable for evaluating ZPEs. The agreement brought about by TF treatment may be due to cancellation between the effect of the rotational elimination and the many-body effect, that is, e−n, n−n, and e−e correlations. A related discussion is mentioned in the Appendix.

Table 3 shows the results of the TRC−, TF−, TR$_0$F−, and TR$_1$F−NOMO/HF calculations for Li$_2$, B$_2$, N$_2$, F$_2$, H$_3^+$, BH$_3$, CH$_4$,[34] and C$_2$H$_4$ molecules. As in the cases of H$_2$, D$_2$, and T$_2$, the total energies decrease considerably in the order of TRC−, TF−, and TR$_0$F−NOMO/HF for all molecules. On the other hand, the energy changes from the TR$_0$F treatment to the TR$_1$F one are considerably smaller. While ΔE^{R_1F} values, corresponding to the first-order rovibration coupling of the diatomic molecules, are on the order of microhartrees, ΔE^{R_1F} values of the polyatomic molecules are from tens to hundreds of microhartrees. The maximum ratio $|\Delta E^{R_1F}/\Delta E^{R_0F}|$ is 0.742% for CH$_4$. This indicates that the contribution of first-order rovibration coupling is significantly smaller than zeroth-order rotational contamination. Furthermore, it shows the validity of the TRF−NOMO formalism, based on the Taylor expansion of the rotational operator.

5. Conclusions

In the present study, we have implemented the computational code for the TR$_1$F−NOMO/HF method. Numerical assessments of the TRC−, TF−, TR$_0$F−, and TR$_1$F−NOMO/HF methods, which were performed for 11 small molecules, have clarified the importance of the elimination of translational and rotational contaminations. The results demonstrated that the zeroth-order rigid-body term for rotational motion makes the main contribution, and the first-order rovibrational coupling term is significantly smaller in energy. In other words, it is true that the rovibrational coupling exists in the TR$_0$F and TR$_1$F Hamiltonian, although the effect is shown to be negligibly small in the present assessment. For rigid molecules, we confirm that the approximate zeroth-order treatment is sufficient for eliminating rotational contamination and that the Taylor expansion with respect to displacement $\Delta \mathbf{x}$ for the rotational operator is reasonable to achieve chemical accuracy (millihartrees) in NOMO calculations. In the case of estimating the nonadiabatic effect, which often requires spectroscopic accuracy (microhartrees), it might be necessary to take into account the first- and higher-order rovibrational coupling. Furthermore, the estimation of the first- and higher-order rovibrational coupling contribution in nonrigid molecules or the excited state is an interesting subject and will be examined in the near future.

Appendix: TRF−NOMO/MP2 Theory

We have formulated TRF−NOMO/HF and MP2 methods in our previous work.[10,12] However, numerical assessments of TRF−NOMO/HF and MP2 methods were limited to zeroth-order rotational terms. The main body in this paper shows the implementation of the TR$_1$F−NOMO/HF calcula-

Table 4. Total (E_{tot}), Translational (E_{trans}), Zeroth-Order Rotational (E_{rot0}), First-Order Rotational (E_{rot1}), Vibrational (E_{vib}), and Electronic (E_{elec}) Energies (in hartree) Calculated by the TRC−, TF−, TR$_0$F−, and TR$_1$F−NOMO/MP2 Methods

		TRC	TF	ΔE^{TFa}	TR$_0$F	ΔE^{R_0Fb}	TR$_1$F	ΔE^{R_1Fc}
H$_2$	E_{tot}	−1.110118	−1.131626	−21.508	−1.143040	−11.414	−1.143494	−0.454
	E_{trans}	0.018500	(0.033951)		(0.194822)		(0.098315)	
	E_{rot0}	0.010485	0.011443		(0.078776)		(0.079352)	
	E_{rot1}	0.000375	0.000416		-0.000092		(0.000602)	
	E_{vib}	0.007315	0.008372		0.013309		0.013353	
	E_{elec}	−1.146791	−1.151858		−1.156258		−1.156847	
D$_2$	E_{tot}	−1.124192	−1.140331	−16.138	−1.149150	−8.820	−1.149418	−0.267
	E_{trans}	0.013718	(0.025071)		(0.070578)		(0.070842)	
	E_{rot0}	0.007927	0.008606		(0.057963)		(0.056900)	
	E_{rot1}	0.000180	0.000190		-0.000054		(0.000357)	
	E_{vib}	0.005402	0.006239		0.009633		0.009659	
	E_{elec}	−1.151419	−1.155366		−1.158729		−1.159076	
T$_2$	E_{tot}	−1.130901	−1.144174	−13.273	−1.152012	−7.838	−1.152189	−0.177
	E_{trans}	0.011457	(0.020742)		(0.056194)		(0.056207)	
	E_{rot0}	0.006646	0.007375		(0.044988)		(0.045094)	
	E_{rot1}	0.000125	0.000119		-0.000031		(0.000225)	
	E_{vib}	0.004508	0.005233		0.007687		0.007698	
	E_{elec}	−1.153635	−1.156900		−1.159668		−1.159887	

$^a \Delta E^{TF} = E_{tot}^{TF} - E_{tot}^{TRC}$ (in mhartree) $^b \Delta E^{R_0F} = E_{tot}^{TR_0F} - E_{tot}^{TF}$ (in mhartree) $^c \Delta E^{R_1F} = E_{tot}^{TR_1F} - E_{tot}^{TR_0F}$ (in mhartree)

Table 5. Total Energies (in hartree) of Several Small Molecules Calculated by the TRC−, TF−, TR$_0$F−, and TR$_1$F−NOMO/MP2 Methods

	TRC	TF	ΔE^{TFa}	TR$_0$F	ΔE^{R_0Fb}	TR$_1$F	ΔE^{R_1Fc}
Li$_2$	−14.697667 (−144.220)	−14.794092 (−150.892)	−96.425	−14.872552 (−108.996)	−78.460	−14.872556 (−109.000)	−0.004
B$_2$	−48.585915 (−415.244)	−48.796114 (−413.191)	−210.198	−48.972819 (−301.563)	−176.705	−48.972831 (−301.572)	−0.012
N$_2$	−108.412959 (−775.726)	−108.809830 (−789.147)	−396.870	−109.107783 (−565.997)	−297.953	−109.107798 (−566.012)	−0.015
F$_2$	−197.860037 (−1056.428)	−198.462909 (−1101.868)	−602.872	−198.867987 (−780.356)	−405.077	−198.867997 (−780.366)	−0.010
H$_3^+$	−1.261926 (−69.100)	−1.278850 (−68.004)	−16.923	−1.292210 (−52.329)	−13.360	−1.292606 (−52.787)	−0.396
BH$_3$	−26.174954 (−275.965)	−26.337320 (−237.460)	−162.366	−26.363152 (−239.154)	−25.832	−26.363193 (−239.187)	−0.041
CH$_4$	−39.937333 (−418.490)	−40.147101 (−367.335)	−209.767	−40.168661 (−367.482)	−21.560	−40.168842 (−367.504)	−0.181
C$_2$H$_4$	−77.563113 (−720.885)	−77.806160 (−713.050)	−243.047	−77.919316 (−659.266)	−113.156	−77.918563 (−658.934)	0.753

$^a \Delta E^{TF} = E_{tot}^{TF} - E_{tot}^{TRC}$ (in mhartree) $^b \Delta E^{R_0F} = E_{tot}^{TR_0F} - E_{tot}^{TF}$ (in mhartree) $^c \Delta E^{R_1F} = E_{tot}^{TR_1F} - E_{tot}^{TR_0F}$ (in mhartree)

tion and the numerical assessments. We examine the contribution of the first-order rotational term to the TR$_1$F−NOMO/MP2 calculation.

Table 4 shows the energy components, E_{tot}, E_{trans}, E_{rot0}, E_{rot1}, E_{vib}, and E_{elec}, of H$_2$, D$_2$, and T$_2$ calculated by the TRC−, TF−, TR$_0$F−, and TR$_1$F−NOMO/MP2 methods. The electronic and nuclear basis functions are the same as the NOMO/HF calculations presented in section 3. For the energy components, similar trends to those in Table 2 were seen in Table 4. All ΔE^{R_1F} values in Table 4 are on the order of 0.1 mhartree. In Table 2, E_{vib}^{TF} at the HF level is close to the experimental ZPE rather than E_{vib}^{TRC}, $E_{vib}^{TR_0F}$, and $E_{vib}^{TR_1F}$. However, the inclusion of a many-body effect decreases E_{vib}^{TF}, $E_{vib}^{TR_0F}$, and $E_{vib}^{TR_1F}$. As a result, the discrepancy of E_{vib}^{TF} from the experimental ZPE increases with the MP2 treatment, although those of $E_{vib}^{TR_0F}$ and $E_{vib}^{TR_1F}$ decrease. Therefore, we think that the agreement brought

about by TF treatment at the HF level is due to cancellation between the effect of the rotational elimination and the many-body effect.

Table 5 shows the results of the TRC−, TF−, TR$_0$F−, and TR$_1$F−NOMO/MP2 calculations for several small molecules except for H$_2$, D$_2$, and T$_2$. The electronic and nuclear basis functions are the same as the above calculations. The correlation energies, which involve the e−e, e−n, and n−n contributions, are given in parentheses. The many-body effect becomes more important as the nuclear charges or numbers of nuclei and electrons increase. The correlation energies are approximately comparable to the effect of the elimination of the translational and rotational contaminations. The total energies decrease considerably in the order of TRC−, TF−, and TR$_0$F−NOMO/MP2 for all molecules. On the other hand, the total energy differences between the TR$_0$F and TR$_1$F treatments are significantly smaller, that is, less

than 1 mhartree. This trend is the same as that of the HF treatment. Therefore, approximate zeroth-order treatment is sufficient for eliminating the rotational contamination, and the Taylor expansion with respect to displacement $\Delta\mathbf{x}$ for the rotational operator is reasonable in the MP2-level calculation.

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