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RELATIVE COORDINATE REPRESENTATION FOR LONG-RANGE INTERACTIONS

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Long-range interactions between two molecules are studied using relative (R-) coordinates. In the R-coordinates, not only the potential energy operator but also the kinetic energy operator is separated into intra- and intermolecular parts. This enables us to partition the hypervirial and virial theorems into intra- and intermolecular theorems. The intermolecular theorems reduce the required accuracy of wavefunctions in perturbation calculations at least by one order. The Born–Oppenheimer approximation of the partitioned virial theorem is also discussed.

1. Introduction

In a previous study [1] we have shown that the use of relative (R-) coordinates simplifies the Hellmann–Feynman force theory of long-range interactions in comparison with the use of laboratory fixed (L-) coordinates. The study [1] suggested us that the other theorems, such as the hypervirial and virial theorems, may also be simplified in the R-coordinate representation of long-range interactions – which we investigate in this report.

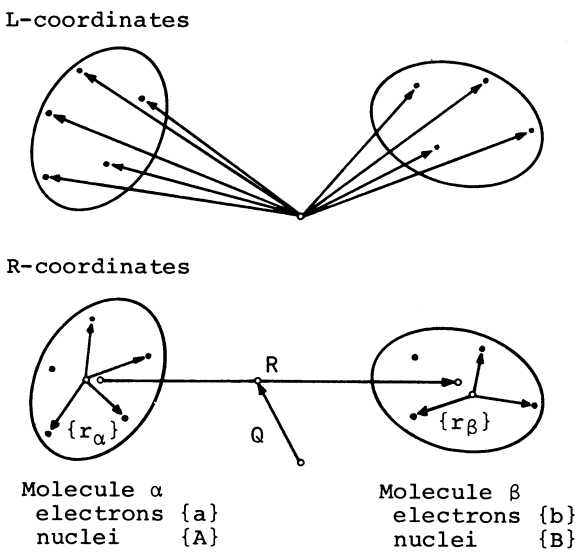

Fig. 1. Definition of the L- and R-coordinates. Molecule α consists of electrons $\{a\}$ and nuclei $\{A\}$. The positions $\{r_\alpha\}$ mean both of $\{r_a\}$ and $\{r_A\}$. Similarly, molecule β consists of $\{b\}$ and $\{B\}$, and $\{r_\beta\}$ mean $\{r_b\}$ and $\{r_B\}$.

The R-coordinates are defined and compared with the L-coordinates in fig. 1. In the L-coordinates, the position of a particle (i.e., electron or nucleus) is measured from the laboratory fixed origin, but in the R-coordinates, it is measured from the relative origin defined as the center of mass of the nuclei of a molecule to which the particle belongs. Such definition is unambiguous when the electron exchange between molecules is negligible, i.e., only for long-range interactions. We write the center of mass of the total system as Q, the intermolecular vector between the centers of mass of the molecules as R†, and the individual particle positions as $\{\boldsymbol{r}\}$. Two nuclear positions from each molecule are omitted from the independent variables ††.

† Note that the starting and end points of the vector R differ from the two relative origins of $\{\boldsymbol{r}\}$. This choice has the merit to exclude the coupling between the electronic and nuclear momenta in the kinetic energy operator $\tilde{T}(\boldsymbol{r})$ (see section 2). Then the intramolecular kinetic energy operator $\tilde{T}(\boldsymbol{r})$ is also expressible as the sum of the electronic and nuclear kinetic energy operators, $\tilde{T}_e(r_e) + \tilde{T}_n(r_n)$, where $\{r_e\}$ and $\{r_n\}$ denote electronic and nuclear coordinates, respectively. This makes that the virial theorem holds separately for electrons and nuclei, leading to the electronic virial theorem (13a) under the Born–Oppenheimer approximation (see sections 3 and 4).

†† The omitted nuclear positions are given by the linear combinations of the independent nuclear positions.

In this paper, we study the R-coordinate representation of long-range interactions between two molecules α and β in a more general manner. In the R-coordinates, not only the potential energy operator but also the kinetic energy operator is separated into intra- and intermolecular parts. Then, we can partition the hypervirial and virial theorems into intra- and intermolecular theorems. The intermolecular theorems reduce the required accuracy of wavefunctions by one order and this is useful in perturbation calculations. We also discuss the Born–Oppenheimer approximation of the partitioned virial theorem. Finally, the R-coordinate representation is compared with the ordinary L- coordinate representation.

2. Hamiltonian in the relative coordinates

We consider a long-range interaction between two molecules α and β *without* using the Born–Oppenheimer approximation. In the L-coordinates, the hamiltonian of the system is given by

$$H = H^{(0)} + H^{(1)}\,,\quad H^{(0)} = T + V^{(0)}\,,\quad H^{(1)} = V^{(1)}\,, \tag{1}$$

where T is kinetic energy operator, $V^{(0)}$ the Coulomb potential for the isolated molecules, and $V^{(1)}$ the coulombic interactions between all the charges in molecule α and those in molecule β.

We now express the hamiltonian (1) in the R-coordinate representation. The potential energy operator V is written as

$$\tilde{V} = \tilde{V}^{(0)}(\boldsymbol{r}) + \tilde{V}^{(1)}(\boldsymbol{r}, R)\,, \tag{2}$$

where tilde means the R-coordinate representation of operators. The potential $\tilde{V}^{(0)}$ depends only on $\{\boldsymbol{r}\}$, but $\tilde{V}^{(1)}$ depends on both $\{\boldsymbol{r}\}$ and R. Using the chain rule for derivatives [2], the kinetic energy operator is expressed as

$$\tilde{T} = \tilde{T}(Q) + \tilde{T}(R) + \tilde{T}(\boldsymbol{r})\,. \tag{3}$$

The operator $\tilde{T}(Q)$ represents the translational energy of the total system $-\frac{1}{2}(M_\alpha + M_\beta)^{-1}\partial^2/\partial Q^2$, $\tilde{T}(R)$ the *intermolecular* kinetic energy $-\frac{1}{2}\mu^{-1}\partial^2/\partial R^2$ with $\mu^{-1} = M_\alpha^{-1} + M_\beta^{-1}$, and $\tilde{T}(\boldsymbol{r})$ the *intramolecular* kinetic energy $\tilde{T}_\alpha(\boldsymbol{r}_\alpha) + \tilde{T}_\beta(\boldsymbol{r}_\beta)$ with

$$\tilde{T}_\alpha(\boldsymbol{r}_\alpha) = -\tfrac{1}{2}\left\{\left(\sum_a \partial^2/\partial \boldsymbol{r}_a^2 - M_\alpha^{-1}\sum_{aa'}\partial^2/\partial \boldsymbol{r}_a \partial \boldsymbol{r}_{a'}\right)\right.$$
$$\left. + \left(\sum_A{}' m_A^{-1}\partial^2/\partial \boldsymbol{r}_A^2 - M_\alpha^{-1}\sum_{AA'}{}'\,\partial^2/\partial \boldsymbol{r}_A \partial \boldsymbol{r}_{A'}\right)\right\}\,,$$

where m_A is the mass of the nucleus A, M_α the total mass of the molecule α, and Σ' means the sum over the independent coordinates. We then obtain the R-coordinate representation of the hamiltonian as

$$\tilde{H} = \tilde{H}^{(0)} + \tilde{H}^{(1)}\,,$$
$$\tilde{H}^{(0)} = \tilde{T}(R) + \tilde{T}(\boldsymbol{r}) + \tilde{V}^{(0)}(\boldsymbol{r})\,, \tag{4}$$
$$\tilde{H}^{(1)} = \tilde{V}^{(1)}(\boldsymbol{r}, R)\,,$$

where we have omitted the unnecessary translational kinetic energy operator $\tilde{T}(Q)$. As shown in (4), the R-coordinates clearly distinguish intra- and intermolecular origins of the kinetic and potential energy operators. Especially, the separation of the kinetic energy operator into the intra- and intermolecular parts is important for the discussion of the hypervirial and virial theorems in the subsequent section.

Since $\tilde{H}^{(0)}$ is separable for $\{\boldsymbol{r}\}$ and R, the Schrödinger equation for the unperturbed state, $(\tilde{H}^{(0)} - E^{(0)})|0\rangle = 0$, can be transformed as $|0\rangle = \exp(\pm\, \mathrm{i}PR)\phi^{(0)}(\boldsymbol{r})$ and $E^{(0)} = |P|^2/2\mu + \epsilon^{(0)}$, where $\phi^{(0)}(\boldsymbol{r})$ and $\epsilon^{(0)}$ are the solutions of the Schrödinger equation for the isolated molecules, $(\tilde{T}(\boldsymbol{r}) + \tilde{V}^{(0)} - \epsilon^{(0)})|\phi^{(0)}(\boldsymbol{r})\rangle = 0$. The unperturbed wavefunction represents the molecules moving freely with the intramolecular state $\phi^{(0)}(\boldsymbol{r})$. Since the quantities of $\tilde{H}^{(0)}$ and $\tilde{H}^{(1)}$ are unchanged by the transformation from the L- to the R-coordinates, the perturbation wavefunctions and energies are identical, in each order, with those of the L-coordinate representation.

3. The hypervirial and virial theorems

In the R-coordinates, the partitioning of the hamiltonian allows us to split the hypervirial and virial theorems into intramolecular and intermolecular parts. This is essentially due to the partitioning of the kinetic energy operator.

The hypervirial theorem [3] is

$$\langle[\tilde{H}, \tilde{W}]\rangle \equiv \langle\Psi|[\tilde{H}, \tilde{W}]|\Psi\rangle = 0\,, \tag{5}$$

where $\tilde{W} = \tilde{W}(\boldsymbol{r}, -\mathrm{i}\partial/\partial\boldsymbol{r}, R, -\mathrm{i}\partial/\partial R)$ is the hypervirial operator in the R-coordinates and $|\Psi\rangle$ the eigenfunction

of $\tilde{H}$. When we define intra- and intermolecular hypervirial operators as

$$\tilde{W}^{\text{intra}} \equiv \tilde{W}(\boldsymbol{r}, -\mathrm{i}\partial/\partial\boldsymbol{r}) ,$$
$$\tilde{W}^{\text{inter}} \equiv \tilde{W}(\boldsymbol{R}, -\mathrm{i}\partial/\partial\boldsymbol{R}) , \tag{6}$$

the hypervirial theorem can be splitted into two forms.

$$\langle[(\tilde{T}(\boldsymbol{r}) + \tilde{V}^{(0)} + \tilde{V}^{(1)}), \tilde{W}^{\text{intra}}]\rangle = 0 , \tag{7a}$$

$$\langle[(\tilde{T}(\boldsymbol{R}) + \tilde{V}^{(1)}), \tilde{W}^{\text{inter}}]\rangle = 0 . \tag{7b}$$

These equations may be called *intramolecular* and *intermolecular hypervirial theorems,* respectively.

The partitioned virtial theorems are derived from the partitioned hypervirtial theorems. Choosing $\tilde{W}^{\text{intra}} = \Sigma'_{aAbB}\, \boldsymbol{r}(-\mathrm{i}\partial/\partial\boldsymbol{r})$ in (7a), we get *intramolecular virtial theorem*

$$\langle 2\tilde{T}(\boldsymbol{r}) + \tilde{V}^{(0)}\rangle = -\langle\tilde{\mathcal{V}}^{(1)}\rangle , \tag{8a}$$

where

$$\tilde{\mathcal{V}}^{(1)} = -\sum_{aAbB}{}' \boldsymbol{r}\,\partial V^{(1)}/\partial\boldsymbol{r} = \partial(\boldsymbol{R}V^{(1)})/\partial\boldsymbol{R} .$$

The intramolecular virial theorem is the sum of the electronic and nuclear virial theorems

$$\langle 2\tilde{T}_{\mathrm{e}}(\boldsymbol{r}_{\mathrm{e}}) - \sum_{ab} \boldsymbol{r}_{\mathrm{e}}\,\partial(\tilde{V}^{(0)} + \tilde{V}^{(1)})/\partial\boldsymbol{r}_{\mathrm{e}}\rangle = 0 ,$$

$$\langle 2\tilde{T}_{\mathrm{n}}(\boldsymbol{r}_{\mathrm{n}}) - \sum_{AB}{}' \boldsymbol{r}_{\mathrm{n}}\,\partial(\tilde{V}^{(0)} + \tilde{V}^{(1)})/\partial\boldsymbol{r}_{\mathrm{n}}\rangle = 0 .$$

Similarly, choosing $\tilde{W}^{\text{inter}} = \boldsymbol{R}(-\mathrm{i}\partial/\partial\boldsymbol{R})$ in (7b), we get the *intermolecular virial theorem:*

$$\langle 2\tilde{T}(\boldsymbol{R}) + \tilde{V}^{(1)}\rangle = \langle\tilde{\mathcal{V}}^{(1)}\rangle , \tag{8b}$$

or

$$\langle 2\tilde{T}(\boldsymbol{R}) - \boldsymbol{R}\partial\tilde{V}^{(1)}/\partial\boldsymbol{R}\rangle = 0 .$$

The sum of (8a) and (8b) gives the total virial theorem $\langle 2\tilde{T} + \tilde{V}\rangle = 0$ which is identical with the ordinary virial theorem [4] in the L-coordinate representation.

In the hypervirial theorems, the intramolecular theorem (7a) contains both of the potentials $\tilde{V}^{(0)}$ and $\tilde{V}^{(1)}$, but the intermolecular theorem (7b) contains only $\tilde{V}^{(1)}$. This means that in the perturbative calculations of the intermolecular properties which are expressible as $[\tilde{T}(\boldsymbol{R}), \tilde{W}^{\text{inter}}]$ for any $\tilde{W}^{\text{inter}}$, the nth-order perturbed wavefunction suffices to determine the $(n+1)$th-order correction. For the corresponding intramolecular properties, we need nth-order wavefunction for the nth-order correction. Thus, in the intermolecular virial theorem (8b), we can reduce the accurac of the wavefunction required for calculating $\langle\tilde{T}(\boldsymbol{R})\rangle$ by one order. For first-order, the intermolecular virial $\langle\boldsymbol{R}\partial\tilde{V}^{(1)}/\partial\boldsymbol{R}\rangle^{(0)}$ vanishes identically * and the intramolecular virial theorem describes the total virial theorem since $\langle\tilde{T}(\boldsymbol{R})\rangle^{(1)} = |P|^2\,\{\langle 0|1\rangle + \langle 1|0\rangle\}/2\mu = 0$.

Using these virial theorems, we can express the expectation values of the *unperturbed* operators $\tilde{T}(\boldsymbol{R})$, $\tilde{T}(\boldsymbol{r})$, and $\tilde{V}^{(0)}$ by the expectation value of only the *perturbed* operator $\tilde{V}^{(1)}$. When the energy of the system is partitioned into direct and induced terms

$$E = E_{\text{di}} + E_{\text{ind}} , \quad E_{\text{di}} = \langle\tilde{H}^{(1)}\rangle , \quad E_{\text{ind}} = \langle\tilde{H}^{(0)}\rangle , \tag{9}$$

the nth-order energies satisfy [5]

$$E_{\text{di}}^{(n)} = nE^{(n)} , \quad E_{\text{ind}}^{(n)} = (1-n)E^{(n)} . \tag{10}$$

Combining these equations with the virial theorems (8), we obtain

$$\langle\tilde{T}(\boldsymbol{R})\rangle^{(n)} = \tfrac{1}{2}\langle\boldsymbol{R}\partial\tilde{V}^{(1)}/\partial\boldsymbol{R}\rangle^{(n-1)} ,$$

$$\langle\tilde{T}(\boldsymbol{r})\rangle^{(n)} = -\langle(1/n)\tilde{V}^{(1)} + \tfrac{1}{2}\boldsymbol{R}\partial\tilde{V}^{(1)}/\partial\boldsymbol{R}\rangle^{(n-1)} , \tag{11}$$

$$\langle\tilde{V}^{(0)}\rangle^{(n)} = (2/n-1)\langle\tilde{V}^{(1)}\rangle^{(n-1)} .$$

Since only the perturbed operator $\tilde{V}^{(1)}$ appears on the rhs, the required accuracy of the wavefunction is reduced by one order in perturbation calculations. When the multipolar expansion is used for the operator $\tilde{V}^{(1)}$, wavefunctions to order n determine the expectation values $\langle\tilde{T}(\boldsymbol{R})\rangle$, $\langle\tilde{T}(\boldsymbol{r})\rangle$, $\langle\tilde{V}^{(0)}\rangle$ *up* to order $2n+1$. This is a merit of the R-coordinate representation.

4. The Born–Oppenheimer approximation

We define the electronic hamiltonian $\tilde{H}_{\mathrm{e}}$ in the R-coordinates as the sum of the electronic terms in the hamiltonian (4). The electronic Schrödinger equation is $(\tilde{H}_{\mathrm{e}} - E_{\mathrm{e}})|\psi(\boldsymbol{r}_{\mathrm{e}};\boldsymbol{r}_{\mathrm{n}}, \boldsymbol{R})\rangle = 0$. First, we summarize the results for the Hellmann–Feynman theorem in the R-coordinates [1] in order to derive the Born–Oppenheimer approximation of the partitioned virial

* $\langle\theta\rangle^{(n)}$ denotes $\Sigma_{k=1}^{n}\langle k|\theta|n-k\rangle$, where $|n\rangle$ is the nth-order perturbation wavefunction.

Table 1
Comparison of the L- and R-coordinate representations[a)]

Coordinate systems		L-coordinates	R-coordinates: Intramolecular	R-coordinates: Intermolecular
Non-Born–Oppenheimer approximation	Hamiltonian	$H = T + V^{(0)} + V^{(1)}$	$\tilde{H} = \tilde{T}(\boldsymbol{r}) + \tilde{T}(R) + \tilde{V}^{(0)}(\boldsymbol{r}) + \tilde{V}^{(1)}(\boldsymbol{r}, R)$	
	Hypervirial theorem	$\langle [(T + V^{(0)} + V^{(1)}), W] \rangle = 0$	$\langle [(\tilde{T}(\boldsymbol{r}) + \tilde{V}^{(0)} + \tilde{V}^{(1)}), \tilde{W}^{\mathrm{intra}}] \rangle = 0$	$\langle [(\tilde{T}(R) + \tilde{V}^{(1)}), \tilde{W}^{\mathrm{inter}}] \rangle = 0$
	Virial theorem	$\langle 2T + V^{(0)} + V^{(1)} \rangle = 0$	$\left\langle 2\tilde{T}(\boldsymbol{r}) + \tilde{V}^{(0)} - \sum{}' \boldsymbol{r} \frac{\partial \tilde{V}^{(1)}}{\partial \boldsymbol{r}} \right\rangle = 0$	$\left\langle 2\tilde{T}(R) - R \frac{\partial \tilde{V}^{(1)}}{\partial R} \right\rangle = 0$
	Electronic hamiltonian	$H_{\mathrm{e}} = T_{\mathrm{e}} + V^{(0)} + V^{(1)}$	$\tilde{H}_{\mathrm{e}} = \tilde{T}_{\mathrm{e}} + \tilde{V}^{(0)} + \tilde{V}^{(1)}$	
Born–Oppenheimer approximation	Hellmann–Feynman theorem	$\frac{\partial E_{\mathrm{e}}}{\partial \boldsymbol{r}_A} = \left\langle \frac{\partial (V^{(0)} + V^{(1)})}{\partial \boldsymbol{r}_A} \right\rangle_{\mathrm{e}}$	$\frac{\partial E_{\mathrm{e}}}{\partial \boldsymbol{r}_A} = \left\langle \frac{\partial (\tilde{V}^{(0)} + \tilde{V}^{(1)})}{\partial \boldsymbol{r}_A} \right\rangle_{\mathrm{e}}$	$\frac{\partial E_{\mathrm{e}}}{\partial R} = \left\langle \frac{\partial \tilde{V}^{(1)}}{\partial R} \right\rangle_{\mathrm{e}}$
	Virial theorem	$\langle 2T_{\mathrm{e}} + V^{(0)} + V^{(1)} \rangle_{\mathrm{e}} + \sum \boldsymbol{r}_{\mathrm{n}} \frac{\partial E_{\mathrm{e}}}{\partial \boldsymbol{r}_{\mathrm{n}}} = 0$	$\langle 2\tilde{T}_{\mathrm{e}} + \tilde{V}^{(0)} + \tilde{V}^{(1)} \rangle_{\mathrm{e}} + \sum{}' \boldsymbol{r}_{\mathrm{n}} \frac{\partial E_{\mathrm{e}}}{\partial \boldsymbol{r}_{\mathrm{n}}} + R \frac{\partial E_{\mathrm{e}}}{\partial R} = 0$	$2\tilde{T}(R) - R \frac{\partial E_{\mathrm{e}}}{\partial R} = 0$

a) The nuclear virial theorem under the Born–Oppenheimer approximation is omitted.

theorem. The Hellmann–Feynman theorem with respect to a nuclear position $\boldsymbol{r}_A$ gives for the force on nucleus A [6]:

$$F_A = -\partial E_{\mathrm{e}}/\partial \boldsymbol{r}_A = \langle -\partial(\tilde{V}^{(0)} + \tilde{V}^{(1)})/\partial \boldsymbol{r}_A \rangle_{\mathrm{e}}$$

$$\equiv \langle \psi | -\partial(\tilde{V}^{(0)} + \tilde{V}^{(1)})/\partial \boldsymbol{r}_A | \psi \rangle . \quad (12a)$$

The Hellmann–Fyenman theorem with respect to the intermolecular vector $\boldsymbol{R}$ gives

$$F_\alpha = -\partial E_{\mathrm{e}}/\partial \boldsymbol{R} = \langle -\partial V^{(1)}/\partial \boldsymbol{R} \rangle_{\mathrm{e}} , \quad (12b)$$

which depends only on $\tilde{V}^{(1)}$. This was called force on whole particles or force on molecule in a previous paper* [1]. It has a merit to reduce the required accuracy of the perturbed wavefunction by one order.

The intra- and intermolecular virial theorems take the following form in the Born–Oppenheimer approximation:

$$\left.\begin{aligned} &\langle 2\tilde{T}_{\mathrm{e}} + \tilde{V}^{(0)} + \tilde{V}^{(1)} \rangle_{\mathrm{e}} + \sum_{AB}{}' \boldsymbol{r}_{\mathrm{n}} \, \partial E_{\mathrm{e}}/\partial \boldsymbol{r}_{\mathrm{n}} \\ &\qquad + R \partial E_{\mathrm{e}}/\partial R = 0 , \\ &2\tilde{T}_{\mathrm{n}} - \sum_{AB}{}' \boldsymbol{r}_{\mathrm{n}} \, \partial E_{\mathrm{e}}/\partial \boldsymbol{r}_{\mathrm{n}} = 0 , \end{aligned}\right\} \quad (13a)$$

$$2\tilde{T}(R) - R \partial E_{\mathrm{e}}/\partial R = 0 , \quad (13b)$$

where we have used the Hellmann–Feynman theorems (12). The intramolecular virial theorem (13a) is identical with the virial theorem in the L-coordinates. The intermolecular theorem (13b) represents the "classical" virial theorem for the molecules moving in the potential field E_{e}.

5. Discussion and summary

In table 1, the R-coordinate representation is summarized and compared with the ordinary L-coordinate representation. The intramolecular theorems in the R-coordinates involve both of the potentials $\tilde{V}^{(0)}$ and $\tilde{V}^{(1)}$, as is also the case for the theorems in the L-coordinates, but the intermolecular theorems involve only the perturbation operator $\tilde{V}^{(1)}$. Then, in perturbation calculations of intermolecular properties, we need wavefunctions to order $n - 1$ in order to determine the nth-order correction. Moreover, if the multipolar expansion is applied for the interaction potential $\tilde{V}^{(1)}$, wavefunctions to order n will determine the properties up to order $2n + 1$. Under the Born–Oppenheimer approximation, the electronic hamiltonian in the R-coordinates $\tilde{H}_{\mathrm{e}}$ is the same as that in the L-coordinates H_{e}, and therefore the intramolecular Hellmann–Feynman and virial theorems are identical with those in the L-coordinate representation.

* Although the present definition of R-coordinates differs slightly from the previous one (ref. [1]), the results for the Hellmann–Feynman theorem are identical.

The results of the R-coordinate representation of long-range interactions are:

(1) In the R-coordinates, the kinetic energy operator is separated into intra- and intermolecular parts. This enables us to partition the hypervirial and virial theorems into intra- and intermolecular theorems.

(2) Use of the partitioned hypervirial and virial theorems reduces the accuracy of the wavefunction required in perturbation calculations at least by one order.

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