

VIRIAL THEOREM FOR A MOLECULE

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The usual virial theorem, relating kinetic and potential energy, is extended to a molecule by the use of the true wave function. The virial theorem is also obtained for a molecule from a trial wave function which is scaled separately for electronic and nuclear coordinates. A transformation to the body fixed system is made to separate the center of mass motion exactly. The virial theorems are then obtained for the electronic and nuclear motions, using exact as well as trial electronic and nuclear wave functions.

If only a single scaling parameter is used for the electronic and the nuclear coordinates, an extraneous term is obtained in the virial theorem for the electronic motion. This extra term is not present if the electronic and nuclear coordinates are scaled differently. Further, the relationship between the virial theorems for the electronic and nuclear motion to the virial theorem for the whole molecule is shown.

In the nonstationary state the virial theorem relates the time average of the quantum mechanical average of the kinetic energy to the radius vector dotted into the force.

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I. INTRODUCTION

The virial theorem, which was originally proved for classical systems by Clausius,¹ relates the time averages of the kinetic energy to the virial of force, i.e., the radius vector dotted into the force. For a homogeneous potential, like the Coulomb potential, the virial is proportional to the time average of the potential energy. With the development of quantum mechanics, Born, Heisenberg, and Jordan² derived the quantum mechanical virial theorem only for the exact solutions in stationary states for homogeneous potentials. An attempt to derive the virial theorem from the variational principle was first made by Fock,³ using a scaled wave function.⁴ The case of a molecule in which the nuclei are fixed was considered by Slater.⁵ Löwdin⁶ used a single scaling parameter and minimized the energy with respect to it to obtain the virial theorem. Thus Löwdin showed the importance of the connection between scaling, the variational principle, and the virial theorem. For a system of electrons, Brown⁷ used different scaling parameters for each electronic coordinate in a trial wave function, antisymmetrized, and varied the energy to obtain the virial theorem.

In this thesis the virial theorem is further extended to a whole molecule by scaling each electronic and nuclear coordinate in the wave function separately. Since the energy is minimized with respect to the scaling parameters, the use of different scaling parameters will give a better energy value.

In order to obtain the virial theorem for a molecule, Fröman's treatment⁸ of the Born-Oppenheimer approximation (BOA) to the body fixed system is made. Fröman⁸ introduced a transformation to the body fixed system in order to separate the center of mass motion first, and then made the BOA to separate the electronic and nuclear equations. Fröman's method of making the BOA is better than the usual approach, because the center of mass motion for the whole system is first separated out exactly. On the other hand, in the usual BOA the center of mass and nuclear motion is separated after the electronic motion.

By using a true wave function in the case of fixed nuclei in a molecule, Slater⁵ obtained an extraneous term in the virial theorem for the electronic motion. Also, if the same scaling parameter is used for the electronic and the nuclear coordinates, the same extra term appears in the virial theorem for the electronic motion.^{6,9,10} However, it is

shown in this thesis that no such extra term is present if the electronic virial theorem in the BOA is derived by scaling each electronic and nuclear coordinate separately.

Finally, the relationship between the virial theorem in BOA and the virial theorem for the whole molecule is shown.

Another new result obtained here is the derivation of the quantum mechanical virial theorem for a nonstationary state. Previously² it was derived only for the stationary state. The virial theorem for nonstationary state is the quantum mechanical analog of the classical virial theorem, and it relates the time average of the expectation values of the quantum mechanical quantities. In the stationary state of the system no time average is needed and the virial theorem is shown to follow directly.

In the next section the virial theorem for a classical system is reviewed. The quantum mechanical virial theorem for a nonstationary state is obtained in Section III.

In Section IV the simple scaling idea is developed first and Löwdin's derivation of the virial theorem is given. The last part of this section deals with generalized scaling and the virial theorem for the whole molecule.

In Section V the transformation to the body-fixed system is made. The center of mass motion is first separated out. Then the nuclear and electronic equations are separated in the BOA.

In Section VI the virial theorem for the electronic and nuclear motions in BOA is obtained, using the exact electronic and nuclear functions. The relationship to the virial theorem for the whole molecule is shown. In Section VII the electronic and nuclear virial theorems in BOA are derived by generalized scaling of the electronic and nuclear trial functions.

The conclusions are given in Section VIII. The details of the calculations are in the Appendices.

II. VIRIAL THEOREM IN CLASSICAL MECHANICS

The virial theorem of Clausius was derived for classical systems.¹ It states that the time average of the kinetic energy of a system of particles is equal to the virial of Clausius for the internal and external forces acting on the particles. For a system of $N+n$ particles, N of which are identical and n of which are different, the derivation of the virial theorem follows from the fundamental equations of motion. This system is the classical analog of a molecule with N electrons and n different nuclei. Newton's second law gives

$$\dot{\underline{p}} = \underline{F} \tag{2.1}$$

where $\underline{p} = \{ \underline{p}_\alpha, \underline{p}_i \}$ is the set of momenta, $\alpha = 1, \dots, N$; $i = 1, \dots, n$.

The position vectors of the $(N+n)$ particles are $\underline{r} = \{ \underline{r}_\alpha \}$, $\underline{R} = \{ \underline{R}_i \}$ where α runs from 1 to N and i from 1 to n .

The forces are $\underline{F} = \{ \underline{F}_\alpha, \underline{F}_i \}$, and include the forces of constraint and internal forces.

Consider the equation of motion for the quantity

$$G = \sum_{\alpha=1}^N \underline{p}_\alpha \cdot \underline{r}_\alpha \tag{2.2}$$

The derivative of G with respect to the time is

$$\frac{dG}{dt} = \sum_{\alpha=1}^N \dot{\tilde{r}}_{\alpha} \cdot \tilde{p}_{\alpha} + \sum_{\alpha=1}^N \tilde{p}_{\alpha} \cdot \dot{\tilde{r}}_{\alpha} \quad (2.3)$$

It is shown in the Appendix in Equation (A.1) that the first term on the right side of Equation (2.3) reduces to twice the "electronic" kinetic energy,

$$\sum_{\alpha=1}^N \dot{\tilde{r}}_{\alpha} \cdot \tilde{p}_{\alpha} = 2 T_e \quad (2.4)$$

Using the equation of motion (2.1), the last term of Equation (2.3) becomes

$$\sum_{\alpha=1}^N \tilde{p}_{\alpha} \cdot \dot{\tilde{r}}_{\alpha} = \sum_{\alpha=1}^N F_{\alpha} \cdot \tilde{r}_{\alpha} \quad (2.5)$$

Thus Equation (2.3) reduces to

$$\frac{dG}{dt} = 2 T_e + \sum_{\alpha=1}^N F_{\alpha} \cdot \tilde{r}_{\alpha} \quad (2.6)$$

The time average on the left side of the Equation (2.6)

is

$$\lim_{\theta \rightarrow \infty} \frac{1}{\theta} \int_0^{\theta} dt \frac{dG}{dt} = \lim_{\theta \rightarrow \infty} \frac{G(\theta) - G(0)}{\theta} \equiv \overline{\frac{dG}{dt}} \quad (2.7)$$

which vanishes if the function G is periodic with period θ , or if G is bounded. Therefore, Equation (2.6) can be

averaged over all the time to give

$$\overline{T_e} = -\frac{1}{2} \overline{\sum_{\alpha=1}^N \underline{F}_{\alpha} \cdot \underline{r}_{\alpha}}, \quad (2.8)$$

which is the virial theorem in classical mechanics for a system of "electrons." The quantity on the right side of Equation (2.8) is called the virial of Clausius.

A similar expression for a system of n "nuclei" is

$$\overline{T_n} = -\frac{1}{2} \overline{\sum_{i=1}^n \underline{F}_i \cdot \underline{R}_i}, \quad (2.9)$$

where the "nuclear" kinetic energy is

$$T_n = \sum_{i=1}^n \dot{\underline{R}}_i \cdot \underline{P}_i. \quad (2.10)$$

The virial theorem for the whole system is

$$\overline{T} = -\frac{1}{2} \overline{\sum_{\alpha=1}^N \underline{F}_{\alpha} \cdot \underline{r}_{\alpha}} - \frac{1}{2} \overline{\sum_{i=1}^n \underline{F}_i \cdot \underline{R}_i}, \quad (2.11)$$

where the total kinetic energy of the system is

$$T = T_e + T_n. \quad (2.12)$$

Further, if the forces \underline{F}_{α} and \underline{F}_i are derived from a potential V , then

$$\underline{F}_{\alpha} = -\frac{\partial V}{\partial \underline{r}_{\alpha}}, \quad \underline{F}_i = -\frac{\partial V}{\partial \underline{R}_i}, \quad (2.13)$$

and the virial theorem becomes

$$\overline{T} = -\frac{1}{2} \overline{\sum_{\alpha=1}^N \underline{r}_{\alpha} \cdot \frac{\partial V}{\partial \underline{r}_{\alpha}}} - \frac{1}{2} \overline{\sum_{i=1}^n \underline{R}_i \cdot \frac{\partial V}{\partial \underline{R}_i}}. \quad (2.14)$$

For a Coulomb potential this gives a simple relation between

the time averages of the kinetic and potential energy [see Equation (A.10) in the Appendix].

$$\overline{T} = -\frac{1}{2} \overline{V} . \quad (2.15)$$

The Coulomb potential V is

$$V = V_{ee} + V_{ne} + V_{nn} , \quad (2.16)$$

where

$$V_{ee} = \frac{1}{2} \sum_{\alpha \neq \beta=1}^N \frac{e^2}{|\underline{r}_\alpha - \underline{r}_\beta|} \quad (2.17)$$

is the electronic potential energy,

$$V_{ne} = -\frac{1}{2} \sum_{\alpha=1}^N \sum_{i=1}^n \frac{Z_i e^2}{|\underline{r}_\alpha - \underline{R}_i|} \quad (2.18)$$

is the nuclear-electronic potential energy, and

$$V_{nn} = \frac{1}{2} \sum_{i \neq j=1}^n \frac{Z_i Z_j e^2}{|\underline{R}_i - \underline{R}_j|} \quad (2.19)$$

is the nuclear potential energy.

In going over to quantum mechanics, all the quantities will be replaced by the corresponding operators, and the time average of the quantum mechanical average will be taken.

III. VIRIAL THEOREM IN QUANTUM MECHANICS FOR THE EXACT WAVE FUNCTION

The virial theorem in quantum mechanics was first obtained for the exact wave function in a stationary state.² It relates the expectation value of the kinetic energy to that of the radius vector dotted with the gradient of the potential.

For a system of N electrons $\underline{r}_1 \dots \underline{r}_N$ of equal mass m and n nuclei $\underline{R}_1 \dots \underline{R}_n$ having masses m_i , the time-dependent Schrödinger equation is

$$H \Phi = i \hbar \frac{\partial \Phi}{\partial t}, \quad (3.1)$$

where \hbar is Planck's constant divided by 2π and Φ is the exact wave function. The Hamiltonian is the sum of the kinetic and potential energy operators

$$H = T + V. \quad (3.2)$$

The kinetic energy operator is the sum of electronic and nuclear kinetic energies

$$T = T_e + T_n. \quad (3.3)$$

The electronic kinetic energy is

$$T_e = \sum_{\alpha=1}^N \frac{p_{\alpha}^2}{2m} = \sum_{\alpha=1}^N -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \underline{r}_{\alpha}^2}, \quad (3.4)$$

where

$$\hat{p}_\alpha = \frac{\hbar}{i} \frac{\partial}{\partial \underline{r}_\alpha} \quad (3.5)$$

is the momentum operator. The nuclear kinetic energy is

$$T_n = \sum_{i=1}^N \frac{\hat{p}_i^2}{2m_i} = \sum_{i=1}^n -\frac{\hbar^2}{2m_i} \frac{\partial^2}{\partial R_i^2}, \quad (3.6)$$

where the momentum operator for the i th nucleus is

$$\hat{p}_i = \frac{\hbar}{i} \frac{\partial}{\partial R_i}. \quad (3.7)$$

The potential for a system of charged particles dealt with here was defined previously in Equation (2.16).

For a derivation of the virial theorem consider the expectation value of the operator $\underline{r}_\alpha \cdot \hat{p}_\alpha$ and $\underline{R}_i \cdot \hat{P}_i$. The time derivatives of $\langle \underline{r}_\alpha \cdot \hat{p}_\alpha \rangle$ and $\langle \underline{R}_i \cdot \hat{P}_i \rangle$ are given in Equations (B.3) and (B.4) of the Appendix to be

$$\frac{d}{dt} \langle \underline{r}_\alpha \cdot \hat{p}_\alpha \rangle = (i\hbar)^{-1} \langle [\underline{r}_\alpha \cdot \hat{p}_\alpha, H] \rangle, \quad (3.8)$$

and

$$\frac{d}{dt} \langle \underline{R}_i \cdot \hat{P}_i \rangle = (i\hbar)^{-1} \langle [\underline{R}_i \cdot \hat{P}_i, H] \rangle, \quad (3.9)$$

where the angular brackets denote the quantum mechanical average with respect to the function Φ and the commutator bracket $[A, H]$ is defined by

$$[A, H] = AH - HA. \quad (3.10)$$

Applying the commutation relation

$$[x, p_x] = i\hbar \quad (3.11)$$

to $[x_\alpha, p_\alpha]$ Equation (B.16) in the Appendix gives

$$\frac{d\langle G \rangle}{dt} = \frac{d}{dt} \sum_{\alpha=1}^N \langle \tilde{r}_\alpha \cdot \tilde{p}_\alpha \rangle = 2 \sum_{\alpha=1}^N \langle \frac{\tilde{p}_\alpha^2}{2m} \rangle - \sum_{\alpha=1}^N \langle \tilde{r}_\alpha \cdot \frac{\partial V}{\partial \tilde{r}_\alpha} \rangle, \quad (3.12)$$

where G is given by the Equation (2.2).

If the time average of this equation is taken with the restriction that the expectation value of G is bounded for all times, the quantum mechanical virial theorem is obtained for the general nonstationary state. From Equation (B.21) in the Appendix

$$\langle T \rangle = \frac{1}{2} \sum_{\alpha=1}^N \langle \tilde{r}_\alpha \cdot \frac{\partial V}{\partial \tilde{r}_\alpha} \rangle + \frac{1}{2} \sum_{i=1}^N \langle \tilde{R}_i \cdot \frac{\partial V}{\partial \tilde{R}_i} \rangle, \quad (3.12)$$

which is the virial theorem for the whole molecule.

For a stationary state no time average is needed and the virial theorem, as obtained in Equation (B.22) in the Appendix, is

$$\langle T \rangle = \frac{1}{2} \sum_{\alpha=1}^N \langle \tilde{r}_\alpha \cdot \frac{\partial V}{\partial \tilde{r}_\alpha} \rangle + \frac{1}{2} \sum_{i=1}^n \langle \tilde{R}_i \cdot \frac{\partial V}{\partial \tilde{R}_i} \rangle. \quad (3.13)$$

In the next section the virial theorem for the energy calculated from a trial wave function is derived.

For a Coulomb potential, from Appendix A, the virial theorem becomes

$$\langle T \rangle = -\frac{1}{2} \langle V \rangle. \quad (3.14)$$

IV. VIRIAL THEOREM FROM A TRIAL WAVE FUNCTION

In the last section the virial theorem from an exact wave function for both the stationary and the nonstationary states was obtained. The stationary-state Schrödinger equation is

$$H \Phi = E_0 \Phi \quad (4.1)$$

where E_0 is the true ground state energy of the system. The Hamiltonian is given by the Equation (2.14).

Many times the exact wave function of a system is not known. Then the energy can be calculated from a trial function. If $\Psi(r_1, \dots, r_N, R_1, \dots, R_n)$ is a trial function, the expectation value of the Hamiltonian is defined by

$$E_c \equiv \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} . \quad (4.2)$$

To get a better energy value, Hylleraas⁴ introduced a scaled function and varied the scaling parameter. A trial function is said to be scaled if all of its coordinates from a fixed origin are stretched or compressed. The wave function can be scaled using a single scaling parameter or different

scaling parameters. The virial theorem will be first derived from the simple scaling and then from the generalized scaling of a trial function.

A. Simple Scaling

1. For The Whole Molecule

A simple derivation of the virial theorem was first obtained by using the simple scaling concept.^{3,4,6} If all the coordinates are multiplied by a factor η , then the scaled function is

$$\Psi_{\eta} = \eta^{\frac{3}{2}(N+n)} \Psi(\eta R_1, \dots, \eta R_n, \eta R_{n+1}, \dots, \eta R_N). \quad (4.3)$$

For the scaled function (4.3) the expectation value of the Hamiltonian for a Coulomb potential is given by

$$E[\eta] = \frac{\langle \Psi_{\eta} | H | \Psi_{\eta} \rangle}{\langle \Psi_{\eta} | \Psi_{\eta} \rangle} = \eta^2 \langle T \rangle + \eta \langle V \rangle. \quad (4.4)$$

If the energy is minimized with respect to η , then

$$0 = \frac{d}{d\eta} E[\eta] = \frac{\partial}{\partial \eta} [2\eta \langle T \rangle + \langle V \rangle] \quad (4.5)$$

where the expectation values are with respect to the wave function of Equation (4.3) with $\eta = 1$. It is shown in Equation (C.7) of the Appendix that the Equation (4.5) yields the relation

$$\langle T \rangle_{\eta} = \frac{1}{2} \sum_{\alpha=1}^N \left\langle \tilde{r}_{\alpha} \cdot \frac{\partial V}{\partial \tilde{r}_{\alpha}} \right\rangle_{\eta} + \frac{1}{2} \sum_{i=1}^n \left\langle \tilde{R}_i \cdot \frac{\partial V}{\partial \tilde{R}_i} \right\rangle_{\eta}, \quad (4.6)$$

which is the virial theorem. The angular brackets $\langle \rangle_{\eta}$ in Equation (4.6) denote the expectation values with respect to the scaled function. For the Coulomb potential given in the Equation (2.16), the Equation (4.6) becomes [see Equation (C.11) in the Appendix],

$$\langle T \rangle_{\eta} = -\frac{1}{2} \langle V \rangle_{\eta}, \quad (4.7)$$

which is the virial theorem first obtained by Löwdin.⁶

The parameter η is obtained from the Equation (4.5), and is

$$\eta = -\frac{1}{2} \frac{\langle V \rangle}{\langle T \rangle} \quad \text{at minimum.} \quad (4.8)$$

Eliminating η from Equation (4.5), the minimum value of the energy is given by

$$E_{\min.} = -\frac{1}{4} \frac{\langle V \rangle^2}{\langle T \rangle}. \quad (4.9)$$

The energy $E[\eta]$ given in Equation (4.4) can be expressed as

$$E[\eta] = E_{\min.} + \langle T \rangle \left[\eta + \frac{\langle V \rangle}{2\langle T \rangle} \right]^2. \quad (4.10)$$

The curve of E against η is a parabola, and for η given by Equation (4.8), a minimum energy is obtained. The virial theorem is then automatically satisfied.

On the other hand, if our trial function is not a good approximation to the exact wave function, then the energy thus obtained will be very much off from the true value. The scaling will, of course, improve the energy value. But the energy will have to be minimized with respect to other parameters of the function. Thus variation with respect to η will not give a good value of the energy, but the virial theorem will still hold.

Therefore, the virial theorem derived from a simple scaled function is a necessary but not a sufficient condition for the minimum energy.

2. Simple Scaling For The Case of Fixed Nuclei

In the case of fixed nuclei the nuclear coordinates $R_n = \{R_i\}, i=1, n$, are to be held fixed by some external forces, and so the nuclear kinetic energy is zero

$$T_n \Phi = 0 \quad (4.11)$$

and the nuclear potential energy V_{nn} is constant. Therefore, the Schrödinger equation of the previous section reduces to

$$H_e \Phi_e = E_{0e} \Phi_e \quad (4.12)$$

The electronic function $\Phi_e(\underline{r}, \underline{R})$ is a function of both the electronic and the nuclear coordinates, but the nuclear coordinates are fixed parameters. Therefore, the electronic energy $E_{oe}(\underline{R})$ depends on the nuclear coordinates, and

$$E_{oe} = E_o - V_{nn}. \quad (4.13)$$

The Hamiltonian is

$$H_e = T_e + V_e. \quad (4.14)$$

The electronic kinetic energy T_e is given by Equation (3.4) and the potential energy V_e is

$$\tilde{V}_e = V_{ee} + V_{ne}, \quad (4.15)$$

where V_{ee} and V_{ne} are given by the Equations (2.17) and (2.18).

For a wave function scaled in both the electronic and nuclear coordinates

$$\tilde{\Psi}_\eta = \eta^{\frac{3N}{2}} \Psi_e(\eta \underline{r}_1, \dots, \eta \underline{r}_N, \eta \underline{R}_1, \dots, \eta \underline{R}_n), \quad (4.16)$$

the expectation value of the Hamiltonian is

$$E_e[\eta] = \frac{\langle \tilde{\Psi}_\eta | H_e | \tilde{\Psi}_\eta \rangle}{\langle \tilde{\Psi}_\eta | \tilde{\Psi}_\eta \rangle} \gg E_{oe}. \quad (4.17)$$

Minimization of the energy with respect to η leads to the relation obtained¹⁰ from the Equation (C.19) in the Appendix:

$$2 \langle T_e \rangle_\eta + \langle V_e \rangle_\eta + \sum_{i=1}^n \left(R_{ni} \cdot \frac{\partial E_e}{\partial R_{ni}} \right) = 0. \quad (4.18)$$

Löwdin's^{6,9} form of the relation is obtained for the diatomic molecule with internuclear distance

$$\underline{R} = \underline{R}_1 - \underline{R}_2 \quad (4.19)$$

$$\frac{\partial E_e}{\partial \underline{R}_1} = - \frac{\partial E_e}{\partial \underline{R}_2} = \frac{\partial E_e}{\partial \underline{R}} \quad (4.20)$$

Equation (4.18) then reduces to

$$2 \langle T_e \rangle_\eta + \langle V_e \rangle_\eta + \underline{R} \cdot \frac{\partial E_e}{\partial \underline{R}} = \alpha \quad (4.21)$$

The extraneous term $\underline{R} \cdot \frac{\partial E_e}{\partial \underline{R}}$ in the Equations (4.18) and (4.21) appears because all the electronic and nuclear coordinates are scaled in the same way, using a single scaling parameter. According to Slater⁵, this extra term is because of the force $-\frac{\partial E_e}{\partial \underline{R}}$ which holds the nuclei fixed. If all the coordinates are scaled differently, no such extra term appears in the virial theorem for the electronic motion.¹¹

B. Generalized Scaling For The Whole Molecule

In the derivation of the virial theorem the energy is minimized with respect to the scaling parameter. Since the Rayleigh-Ritz principle gives an upper bound to the energy, a better value of the energy is obtained if all the coordinates of the trial function are scaled differently. Using

this generalized scaling idea, Brown⁷ gave the proof of the virial theorem for a system of electrons. It will now be extended to the whole molecule. For the sake of simplicity, the nuclei are assumed to be distinguishable. Then the scaled function is obtained by properly antisymmetrizing the trial function for the electrons. The case of nuclei as identical particles, either bosons or fermions or a combination of both, is considered in the Appendix E. Using a set of scaling parameters $\eta = \{\eta_\alpha\}$ for the electronic coordinates and $\xi = \{\xi_i\}$ for the nuclear coordinates, the scaled function can be written as

$$\Psi_{\eta, \xi} = \eta_1^{\frac{3}{2}} \cdots \eta_N^{\frac{3}{2}} \xi_1^{\frac{3}{2}} \cdots \xi_n^{\frac{3}{2}} A \Psi(\eta_1 r_1, \dots, \eta_N r_N, \xi_1 R_1, \dots, \xi_n R_n). \quad (4.22)$$

The antisymmetrizing operator is

$$A = \frac{1}{N!} \sum_{(P \dots N)} (-1)^P \hat{P}, \quad (4.23)$$

where the permutation \hat{P} interchanges the r 's only and not the $\eta_\alpha r_\alpha$'s.

The expectation value of the Hamiltonian with respect to the scaled function is

$$E[\eta, \xi] \equiv \frac{\langle \Psi_{\eta, \xi} | H | \Psi_{\eta, \xi} \rangle}{\langle \Psi_{\eta, \xi} | \Psi_{\eta, \xi} \rangle} \gg E_0. \quad (4.24)$$

Variation of $E[\eta, \xi]$ with respect to all the parameters η and ξ gives a set of $N+n$ equations

$$\frac{\partial}{\partial \eta_\alpha} E[\eta, \xi] = 0, \quad \alpha = 1, \dots, N, \quad (4.25)$$

and

$$\frac{\partial}{\partial \xi_i} E[\eta, \xi] = 0, \quad i = 1, \dots, n, \quad (4.26)$$

which determine η and ξ .

If the Equations (4.25) and (4.26) are combined, it follows

$$\sum_{\alpha=1}^N \eta_\alpha \frac{\partial E}{\partial \eta_\alpha} + \sum_{i=1}^n \xi_i \frac{\partial E}{\partial \xi_i} = 0. \quad (4.27)$$

In Appendix D it is shown that this condition implies

$$\langle T \rangle_{\eta, \xi} = \frac{1}{2} \left\langle \sum_{\alpha=1}^N \frac{p_\alpha}{m} \cdot \frac{\partial V}{\partial \underline{r}_\alpha} + \sum_{i=1}^n \frac{R_i}{m_i} \cdot \frac{\partial V}{\partial \underline{R}_i} \right\rangle_{\eta, \xi}, \quad (4.28)$$

which is the virial theorem for the whole molecule. If V is the Coulomb potential of Equation (2.16), Equation (4.28) reduces to the form of the virial theorem

$$\langle T \rangle_{\eta, \xi} = -\frac{1}{2} \langle V \rangle_{\eta, \xi}, \quad (4.29)$$

giving a relation between the expectation values of kinetic and potential energies. The η and ξ used in Equations (4.28) and (4.29) are solutions to Equation (4.27).

If the N dimensional vector $\underline{\eta} = \{ \eta_\alpha \}$ is orthogonal to the N-dimensional gradient $\frac{\partial E}{\partial \underline{\eta}} = \left\{ \frac{\partial E}{\partial \eta_\alpha} \right\}$ and the n-dimensional vector $\underline{\xi} = \{ \xi_i \}$ is orthogonal to the n-dimensional gradient $\frac{\partial E}{\partial \underline{\xi}} = \left\{ \frac{\partial E}{\partial \xi_i} \right\}$, then the same equation as in Equation (4.27) is obtained:

$$\underline{\eta} \cdot \frac{\partial E}{\partial \underline{\eta}} + \underline{\xi} \cdot \frac{\partial E}{\partial \underline{\xi}} = 0, \quad (4.30)$$

which leads to the virial theorem. Thus the virial theorem is obtained at all the points where $\underline{\eta}$ is orthogonal to $\frac{\partial E}{\partial \underline{\eta}}$ and $\underline{\xi}$ to $\frac{\partial E}{\partial \underline{\xi}}$ as well as the minimum of the energy. Therefore, the validity of virial theorem is a necessary but not a sufficient condition for the minimum energy.

V. BORN-OPPENHEIMER APPROXIMATION

In this section the Born-Oppenheimer approximation (BOA)¹² is discussed in order to separate the electronic and the nuclear equations.

To make the BOA, start off with the total wave Equation (4.1) in the space fixed system $\underline{r} = \{ r_{\alpha} \}$, $\underline{R} = \{ R_i \}$.

$$H \Phi_0 = E_0 \Phi_0, \quad (5.1)$$

and express the total wave function Φ_0 as a product of the electronic and nuclear-translational functions,

$$\Phi_0 = \Phi_{0e}(\underline{r}, \underline{R}) \Phi_{0n}(\underline{R}). \quad (5.2)$$

In the BOA the nuclear coordinates in the electronic function are assumed to be slowly varying in comparison to the electronic coordinates, and can be regarded as fixed parameters. Therefore, the electronic equations can be separated from the nuclear equations.

In the traditional BOA the electronic motion is first separated and then the translational and nuclear motions are separated. Therefore, in this case only the center of mass of the nuclei is considered and not the center of mass

of the whole system. However, in a more correct approach, the center of mass motion of the whole system should be exactly separated before making the BOA.⁸ This is done by a transformation to the body fixed coordinates relative to the center of mass.⁸ In the next part of this section the transformation to the body fixed coordinates is made to separate out the center of mass motion. Then the electronic and the nuclear motions are separated in the BOA. The virial theorem can then be derived for the electronic and nuclear equations.

A. Transformation to Body Fixed Coordinates

1. Transformation

In order to separate the center of mass motion, Fröman⁸ first introduced the body fixed coordinates relative to the center of mass for the electrons

$$r_{m\alpha}^{\circ} = r_{m\alpha} - \frac{1}{M_0} \sum_{k=1}^n m_k R_{m_k} \quad , \quad (5.3)$$

and for the nuclei

$$R_{m_l}^{\circ} = R_{m_l} - \frac{1}{M_0} \sum_{k=1}^n m_k R_{m_k} \quad , \quad l \neq p \quad (5.4)$$

where

$$M_0 = \sum_{k=1}^n m_k \quad (5.5)$$

is the total mass of the nuclei. The p^{th} nucleus, which is quite arbitrarily chosen, is given by

$$\vec{R}_p^0 = -\frac{1}{m_p} \sum_{\substack{k=1 \\ k \neq p}}^n m_k \vec{R}_k^0 \quad (5.6)$$

Thus, the p^{th} nucleus is given in terms of the remaining $(n-1)$ nuclei. Thus the number of degrees of freedom of the system is reduced by three. However, these three degrees of freedom reappear as the center of mass coordinates given by

$$\vec{c} = \frac{1}{M} \left[\sum_{k=1}^n m_k \vec{R}_k + m \sum_{\alpha=1}^N \vec{r}_{\alpha} \right] \quad (5.7)$$

The total mass of the system is

$$M = M_0 + Nm. \quad (5.8)$$

There are three degrees of freedom for the center of mass motion and $3N+3(n-1)$ degrees of freedom for the particles (omitting the p^{th} nucleus) referred to the center of mass. Thus the total $3(N+n)$ degrees of freedom are obtained.

2. Transformation of The Hamiltonian

When the transformation of Equations (5.3) to (5.7) to the body fixed coordinates is made on the Hamiltonian of Equation (5.1), it is shown in the Appendix F that Equation (5.1) becomes

$$\begin{aligned}
H(\underline{c}, \underline{r}_1^0, \dots, \underline{r}_N^0, \underline{R}_1^0, \dots, \underline{R}_{p-1}^0, \underline{R}_{p+1}^0, \dots, \underline{R}_n^0) \\
= T_T + T_e^0 + T_n^0 + V_{ee}^0 + V_{ne}^0 + V_{nn}^0,
\end{aligned} \quad (5.9)$$

which is independent of the p^{th} nucleus because p^{th} nucleus is expressed in terms of other nuclei and the center of mass coordinate is introduced. The translational kinetic energy of center of mass is

$$T_T = \frac{-\hbar^2}{2M} \frac{\partial^2}{\partial \underline{c}^2}. \quad (5.10)$$

The electronic kinetic energy is

$$T_e^0 = -\frac{\hbar^2}{2\mu} \sum_{\alpha=1}^N \frac{\partial^2}{\partial \underline{r}_{\alpha}^0{}^2} - \frac{\hbar^2}{2M_0} \sum_{\alpha \neq \beta=1}^N \frac{\partial}{\partial \underline{r}_{\alpha}^0} \cdot \frac{\partial}{\partial \underline{r}_{\beta}^0}, \quad (5.11)$$

where

$$\mu = \left(\frac{1}{m} + \frac{1}{M_0} \right)^{-1} \quad (5.12)$$

is the reduced mass of the electron. The nuclear kinetic energy is

$$T_n^0 = \frac{\hbar^2}{2} \sum_{\substack{k=1 \\ k \neq p}}^n \frac{1}{\mu_k} \frac{\partial^2}{\partial \underline{R}_k^0{}^2} + \frac{\hbar^2}{2M_0} \sum_{\substack{k \neq d=1 \\ k, d \neq p}}^n \frac{\partial}{\partial \underline{R}_k^0} \cdot \frac{\partial}{\partial \underline{R}_d^0}, \quad (5.13)$$

where the reduced mass of the k^{th} nucleus is

$$\mu_k = \left(\frac{1}{m_k} - \frac{1}{M_0} \right)^{-1}. \quad (5.14)$$

It is shown in the Appendix F that the interelectronic potential energy of the system does not change under this transformation, but others change their form. Expressed in terms of the coordinates referred to the center of mass, the interelectronic potential energy is

$$V_{ee}^{\circ} = \frac{1}{2} \sum_{\alpha \neq \beta=1}^N \frac{e^2}{|\underline{r}_{\alpha}^{\circ} - \underline{r}_{\beta}^{\circ}|} \quad (5.15)$$

The nuclear-electronic potential is

$$V_{ne}^{\circ} = -\frac{1}{2} \sum_{\alpha=1}^N \sum_{\substack{k=1 \\ k \neq \alpha}}^n \frac{Z_{\alpha} e^2}{|\underline{r}_{\alpha}^{\circ} - \underline{R}_k^{\circ}|} - \frac{1}{2} \sum_{\alpha=1}^N \frac{Z_{\alpha} e^2}{\left| \underline{r}_{\alpha}^{\circ} - \frac{1}{m_p} \sum_{\substack{i=1 \\ i \neq \alpha}}^n m_i \underline{R}_i^{\circ} \right|} \quad (5.16)$$

and the internuclear potential is

$$V_{nn}^{\circ} = \frac{1}{2} \sum_{\substack{k, l=1 \\ k, l \neq \alpha}}^n \frac{Z_k Z_l e^2}{|\underline{R}_k^{\circ} - \underline{R}_l^{\circ}|} + \frac{1}{2} \sum_{\substack{l=1 \\ l \neq \alpha}}^n \frac{Z_l Z_p e^2}{\left| -\frac{1}{m_p} \sum_{\substack{i=1 \\ i \neq \alpha}}^n m_i \underline{R}_i^{\circ} - \underline{R}_l^{\circ} \right|} \quad (5.17)$$

From Equations (5.11) and (5.13) it follows that the

Hamiltonian of Equation (5.9) contains the terms of the

type $\frac{\partial}{\partial \underline{r}_{\alpha}^{\circ}} \cdot \frac{\partial}{\partial \underline{r}_{\beta}^{\circ}}$, ($\alpha \neq \beta$) and $\frac{\partial}{\partial \underline{R}_k^{\circ}} \cdot \frac{\partial}{\partial \underline{R}_l^{\circ}}$ ($k \neq l$). Also, the electronic and nuclear masses are replaced by their reduced masses.

The fact that there is no coupling term $\frac{\partial}{\partial \underline{R}_k^{\circ}} \cdot \frac{\partial}{\partial \underline{r}_{\alpha}^{\circ}}$ in the Hamiltonian simplifies the separation of the electronic and nuclear motions.

B. Separation of The Center of Mass Motion

The wave function Φ_0 in the new coordinate system depends on the center of mass coordinate, all the electronic coordinates, and all but the p^{th} nuclear coordinates. For separating the center of mass motion Φ_0 is taken as a product of translational and the nuclear-electronic wave functions

$$\Phi_0 = \Phi_{oT}(\underline{c}) \Phi_{oen}(\underline{r}_1^o, \dots, \underline{r}_N^o, \underline{R}_1^o, \dots, \underline{R}_{p-1}^o, \underline{R}_{p+1}^o, \dots, \underline{R}_n^o). \quad (5.18)$$

When this equation is substituted into Equation (5.1) and divided by $\Phi_{oT} \Phi_{oen}$, Equation (5.1) is separated into the center of mass equation

$$-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial \underline{c}^2} \Phi_{oT}(\underline{c}) = E_{CM} \Phi_{oT}(\underline{c}), \quad (5.19)$$

and the equation for the electronic and nuclear motion relative to center of mass

$$\begin{aligned} [T_e^o(\underline{r}^o) + T_n^o(\underline{R}^o) + V_{ee}^o + V_{ne}^o + V_{nn}^o] \Phi_{oen} \\ = (E_0 - E_{CM}) \Phi_{oen}, \end{aligned} \quad (5.20)$$

where E_{CM} is a separation constant which is the kinetic energy of the center of mass, and \underline{r}^o and \underline{R}^o collectively denote all electronic and nuclear coordinates, respectively.

Equation (5.19) is the translational wave equation and its solution is a plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$, where the momentum \mathbf{p} is related to the wave number \mathbf{k} by

$$\mathbf{p} = \hbar \mathbf{k} . \quad (5.21)$$

The energy required for the center of mass motion is

$$E_{CM} = \frac{\hbar^2 k^2}{2M} . \quad (5.22)$$

Thus, if the center of mass energy $E_{CM} \neq 0$, the molecule is in an excited state. In the ground state of the molecule

$$E_{CM} = 0 \quad (5.23)$$

and the center of mass is at rest. Therefore, if the center of mass is assumed to be at rest, then without loss of any generality the separation constant can be set equal to zero.

C. Separation of Electronic and Nuclear Motion

To make the BOA on the wave equation for the motion of the electrons and nuclei relative to the center of mass we assume that the relative wave function Φ_{oen} can be written as

$$\Phi_{oen} = \Phi_{oe}(\mathbf{r}^o, \mathbf{R}^o) \Phi_{on}(\mathbf{R}^o) \quad (5.24)$$

where $\Phi_{oe}(\underline{r}^{\circ}, \underline{R}^{\circ})$ is the electronic wave function which depends on both the electronic and the nuclear coordinates, and $\Phi_{on}(\underline{R}^{\circ})$ is the nuclear function.

Equation (5.20) then becomes

$$(\mathcal{T}_e^{\circ}(\underline{r}^{\circ}) + \mathcal{T}_n^{\circ}(\underline{R}^{\circ}) + V_{ee}^{\circ} + V_{ne}^{\circ} + V_{nn}^{\circ}) \Phi_{oe} \Phi_{on} = E_0 \Phi_{oe} \Phi_{on} \quad (5.25)$$

In the BOA, assume that the nuclear coordinates in the electronic wave function are slowly varying in comparison to the electronic coordinates, and can be regarded as fixed parameters. Therefore, the derivative of electronic function

Φ_{oe} with respect to the nuclear coordinates can be neglected (compared to that of the nuclear function Φ_{on}). It is shown in Appendix G that this approximation leads to the electronic equation

$$(\mathcal{T}_e^{\circ}(\underline{r}^{\circ}) + V_{ee}^{\circ} + V_{ne}^{\circ}) \Phi_{oe} = E_{oe}[\underline{R}^{\circ}] \Phi_{oe} \quad (5.26)$$

where the separation constant $E_{oe}[\underline{R}^{\circ}]$ is the electronic energy and depends on the nuclear coordinates as parameters only. Therefore, $E_{oe}[\underline{R}^{\circ}]$ appears as a potential energy in the nuclear wave equation given by [See Appendix G]

$$[\mathcal{T}_n^{\circ}(\underline{R}^{\circ}) + V_{nn}^{\circ} + E_{oe}] \Phi_{on} = E_0 \Phi_{on} \quad (5.27)$$

where E_0 is the total energy of the system.

Thus the electronic and nuclear motions are separated in the BOA. The derivation of the virial theorem for these equations is given in the next section.

VI. VIRIAL THEOREM IN BORN-OPPENHEIMER
APPROXIMATION FROM AN EXACT
WAVE FUNCTION

After the separation of the electronic and the nuclear equations, we are in a position to derive the virial theorem in the BOA. First the virial theorem from an exact wave function is obtained and then in the next section the trial function is considered.

A. Electronic Equation

In the previous section we obtained the electronic wave equation in the Equation (5.26) given by

$$H_e^0 \Phi_{oe} = E_{oe} \Phi_{oe} \quad , \quad (6.1)$$

where $H_e^0 = T_e^0 + V_e^0$, (6.2)

and T_e^0 is given by the Equation (5.12). V_e is given by

$$V_e^0 = V_{ee}^0 + V_{ne}^0 .$$

V_{ee}^0 and V_{ne}^0 are defined in Equations (5.15) and (5.16).

It is shown in the Equation (H.14) of the Appendix that

$$\langle T_e^0 \rangle = \frac{1}{2} \sum_{\alpha=1}^N \left\langle \vec{r}_\alpha^0 \cdot \frac{\partial V_e^0}{\partial \vec{r}_\alpha^0} \right\rangle , \quad (6.3)$$

which is the virial theorem for an exact wave function of the electronic equation.

For the Coulomb potential given by the Equation (5.15), the Equation (6.3) reduces to

$$\langle T_e^0 \rangle = -\frac{1}{2} \langle V_{ee}^0 \rangle + \sum_{\alpha=1}^N \frac{1}{2} \left\langle \vec{r}_\alpha^0 \cdot \frac{\partial V_{ne}^0}{\partial \vec{r}_\alpha^0} \right\rangle. \quad (6.4)$$

Equation (6.4) cannot be further simplified.

The virial theorem for the nuclear equation is derived in the next part of this section.

B. Nuclear Equation

The nuclear equation as obtained in Equation (5.27) is given by

$$H_n^0 \Phi_{0n} = E_0 \Phi_{0n}, \quad (6.5)$$

$$\text{where } H_n^0 = T_n^0 + V_n^0, \quad (6.6)$$

$$\text{and } V_n^0 = V_{nn}^0 + E_{oe}. \quad (6.7)$$

From the Equation (H21) in the Appendix the virial theorem for the nuclear equation is

$$\langle T_n^0 \rangle = \frac{1}{2} \sum_{\substack{i=1 \\ i \neq p}}^n \left\langle \vec{R}_i^0 \cdot \frac{\partial V_n^0}{\partial \vec{R}_i^0} \right\rangle. \quad (6.8)$$

Equation (6.8) can be reduced to

$$\langle T_n^0 \rangle = -\frac{1}{2} \langle V_{nn}^0 \rangle + \frac{1}{2} \sum_{\substack{i=1 \\ i \neq p}}^n \left\langle \vec{R}_i^0 \cdot \frac{\partial E_{oe}}{\partial \vec{R}_i^0} \right\rangle. \quad (6.9)$$

Further reduction of Equation (6.9) cannot be made. The

Equation (6.9) does not include the p^{th} nucleus, because in the body fixed coordinates the p^{th} nucleus is expressed in terms of the other $(n-1)$ nuclei and the center of mass coordinate is included. However, in the ground state of the molecule, the kinetic energy of the center of mass is zero:

$$\langle T_T \rangle = 0. \quad (6.10)$$

In the next section the virial theorem from a trial wave function for electronic and nuclear equations will be derived.

C. Relation Between The Virial Theorem In The BOA and The Exact Virial Theorem For The Whole Molecule

In separating the electronic and nuclear equations from the total wave equation, the center of mass motion Equation (5.19) is first separated out. This reduces the number of degrees of freedom of the system by three. In order to have all the $(N+n)$ degrees of freedom, the wave function for the center of mass should also be considered. The total wave function is the product of the wave functions for the center of mass, electronic and nuclear coordinates, and is given by

$$\Phi_0 = \Phi_{cT} \Phi_{oe} \Phi_{on}. \quad (6.11)$$

Now the virial theorem in BOA can be expressed for a total wave function Φ_0 . First, the virial theorem for the nuclear equation is expressed in terms of Φ_0 .

1. Virial Theorem for Nuclear Equation in Terms of Total Wave Function

The virial theorem for the nuclear equation is given by the Equation (6.9). For the expectation value $\langle T_n^0 \rangle$ the following expression

$$\begin{aligned} & \left\{ \int d^3 \underline{c} d^{3N} \underline{r}^0 \Phi_{oT}^* \Phi_{oe}^* \langle T_n^0 \rangle \Phi_{oT} \Phi_{oe} \right\} \left\{ \int d^3 \underline{c} d^{3N} \underline{r}^0 \Phi_{oT}^* \Phi_{oe}^* \Phi_{oT} \Phi_{oe} \right\}^{-1} \\ &= \left\{ \int d^3 \underline{c} d^{3N} \underline{r}^0 \Phi_{oT}^* \Phi_{oe}^* \int d^{3(n-1)} \underline{R}^0 \Phi_{on}^* T_n^0 \Phi_{on} \Phi_{oT} \Phi_{oe} \right\} \\ & \left\{ \int d^3 \underline{c} d^{3N} \underline{r}^0 d^{3(n-1)} \underline{R}^0 \Phi_{oT}^* \Phi_{oe}^* \Phi_{on}^* \Phi_{oT} \Phi_{oe} \Phi_{on} \right\}^{-1}, \quad (6.12) \end{aligned}$$

is obtained. Going back to the assumption made in the BOA, according to which the nuclear coordinates appearing in the electronic wave function are slowly varying functions compared to other electronic coordinates and the nuclear functions, it is shown in Appendix I that the Equation (6.12) can be approximated to

$$\begin{aligned} & \left\{ \int d^3 \underline{c} d^{3N} \underline{r}^0 \Phi_{oT}^* \Phi_{oe}^* \langle T_n^0 \rangle \Phi_{oT} \Phi_{oe} \right\} \left\{ \int d^3 \underline{c} d^{3N} \underline{r}^0 \Phi_{oT}^* \Phi_{oe}^* \Phi_{oT} \Phi_{oe} \right\}^{-1} \\ & \cong \left\{ \int d^3 \underline{c} d^{3N} \underline{r}^0 d^{3(n-1)} \underline{R}^0 \Phi_{oT}^* \Phi_{oe}^* \Phi_{on}^* T_n^0 \Phi_{on} \Phi_{oT} \Phi_{oe} \right\} \left\{ \int d^3 \underline{c} d^{3N} \underline{r}^0 \Phi_{oT}^* \Phi_{oe}^* \Phi_{on}^* \Phi_{oT} \Phi_{oe} \Phi_{on} \right\}^{-1} \\ & = \langle T_n^0 \rangle_0, \quad (6.13) \end{aligned}$$

where $\langle \rangle_0$ is the expectation value with respect to the total wave function. Now consider the right-hand side of the Equation (6.9). Proceeding the same way, it follows from the Equation (I. 3) in the Appendix that

$$\begin{aligned} & \int \int d^3\zeta d^{3N}r^0 \Phi_{0T}^* \Phi_{0e}^* \left(-\frac{1}{2} \langle V_{nn}^0 \rangle\right) \Phi_{0T} \Phi_{0e} \} \int \int d^3\zeta d^{3N}r^0 \Phi_{0T}^* \Phi_{0e}^* \Phi_{0T} \Phi_{0e} \}^{-1} \\ & = -\frac{1}{2} \langle V_{nn}^0 \rangle. \end{aligned} \quad (6.14)$$

Finally, the energy E_{0e} is given by

$$E_{0e} = \int \int d^{3N}r^0 \Phi_{0e}^* (T_e^0 + V_{ee}^0 + V_{ne}^0) \Phi_{0e} \} \int \int d^{3N}r^0 \Phi_{0e}^* \Phi_{0e} \}^{-1} \quad (6.15)$$

Under the assumption made in the BOA, the nuclear coordinates in Φ_{0e} are very slowly varying. Therefore, the gradient of

Equation (6.9) with respect to R_{ni}^0 is

$$\frac{\partial E_{0e}}{\partial R_{ni}^0} = \int \int d^{3N}r^0 \Phi_{0e}^* \frac{\partial V_{ne}^0}{\partial R_{ni}^0} \Phi_{0e} \} \int \int d^{3N}r^0 \Phi_{0e}^* \Phi_{0e} \}^{-1}. \quad (6.16)$$

Substituting for $\frac{\partial E_{0e}}{\partial R_{ni}^0}$ from Equation (6.16) into the expectation value $\langle \sum_{i \neq p}^n R_{ni}^0 \cdot \frac{\partial E_{0e}}{\partial R_{ni}^0} \rangle$, the following is obtained in the Equation (I.5) of the Appendix

$$\begin{aligned} & \int \int d^3\zeta d^{3N}r \Phi_{0T}^* \Phi_{0e}^* \left\langle \sum_{i \neq p}^n R_{ni}^0 \cdot \frac{\partial E_{0e}}{\partial R_{ni}^0} \right\rangle \Phi_{0T} \Phi_{0e} \} \int \int d^3\zeta \Phi_{0T}^* \Phi_{0e}^* \Phi_{0T} \Phi_{0e} \}^{-1} \\ & = \sum_{i \neq p}^n \left\langle R_{ni}^0 \cdot \frac{\partial V_{ne}^0}{\partial R_{ni}^0} \right\rangle. \end{aligned} \quad (6.17)$$

Collecting together the Equations (6.13), (6.14), and (6.17), the virial theorem Equation (6.9) reduces to

$$\langle T_n^0 \rangle_0 = -\frac{1}{2} \langle V_{nn}^0 \rangle_0 + \frac{1}{2} \sum_{\substack{i=1 \\ i \neq p}}^n \left\langle R_{ni}^0 \cdot \frac{\partial V_{ne}^0}{\partial R_{ni}^0} \right\rangle_0, \quad (6.18)$$

which is the expression for the virial theorem for the nuclear coordinates in terms of the total wave function.

2. Virial Theorem For Electronic
Equation In Terms of The Total
Wave Function

The virial theorem in the electronic equation is given by the Equation (5.23). The expectation value of the electronic kinetic energy can be written from the Appendix I as

$$\left\{ \int d^3\zeta d^{3(n-1)} \underline{R}^{\circ} \Phi_{OT}^* \Phi_{On}^* \langle T_e^{\circ} \rangle \Phi_{OT} \Phi_{On} \right\} \left\{ \int d^3\zeta d^{3(n-1)} \underline{R}^{\circ} \Phi_{OT}^* \Phi_{On}^* \Phi_{OT} \Phi_{On} \right\}^{-1} = \langle T_e^{\circ} \rangle_0, \quad (6.19)$$

where the expectation value is in terms of the total wave function. In the same way the electronic potential energy is expressed as

$$\left\{ \int d^3\zeta d^{3(n-1)} \underline{R}^{\circ} \Phi_{OT}^* \Phi_{On}^* \langle -\frac{1}{2} V_{ee}^{\circ} \rangle \Phi_{OT} \Phi_{On} \right\} \left\{ \int d^3\zeta d^{3(n-1)} \underline{R}^{\circ} \Phi_{OT}^* \Phi_{On}^* \Phi_{OT} \Phi_{On} \right\}^{-1} = -\frac{1}{2} \langle V_{ee}^{\circ} \rangle_0. \quad (6.20)$$

Finally, in the Appendix I it is shown that the last term of Equation (6.4) can be expressed as

$$\left\{ \int d^3\zeta d^{3(n-1)} \underline{R}^{\circ} \Phi_{OT}^* \Phi_{On}^* \langle \sum_{\alpha=1}^N \frac{1}{2} \underline{r}_{\alpha}^{\circ} \cdot \frac{\partial V_{ne}^{\circ}}{\partial \underline{r}_{\alpha}^{\circ}} \rangle \Phi_{OT} \Phi_{On} \right\} \left\{ \int d^3\zeta d^{3(n-1)} \underline{R}^{\circ} \Phi_{OT}^* \Phi_{On}^* \Phi_{OT} \Phi_{On} \right\}^{-1} = \frac{1}{2} \sum_{\alpha=1}^N \langle \underline{r}_{\alpha}^{\circ} \cdot \frac{\partial V_{ne}^{\circ}}{\partial \underline{r}_{\alpha}^{\circ}} \rangle_0. \quad (6.21)$$

Thus Equation (6.4) reduces to

$$\langle T_e^{\circ} \rangle_0 = -\frac{1}{2} \langle V_{ee}^{\circ} \rangle_0 + \frac{1}{2} \sum_{\alpha=1}^N \langle \underline{r}_{\alpha}^{\circ} \cdot \frac{\partial V_{ne}^{\circ}}{\partial \underline{r}_{\alpha}^{\circ}} \rangle_0, \quad (6.22)$$

which is the virial theorem for the electronic system in terms of the total wave function.

It is shown in the Equation (5.23) that for the ground state of the system the center of mass energy

$$E_{cm} = 0, \quad (6.23)$$

which gives

$$\langle T_T \rangle = 0. \quad (6.24)$$

Thus the total kinetic energy of the system is

$$\begin{aligned} \langle T \rangle_0 &= \langle T_T \rangle_0 + \langle T_e^0 \rangle_0 + \langle T_n^0 \rangle_0 \\ &= \langle T_e^0 \rangle_0 + \langle T_n^0 \rangle_0. \end{aligned} \quad (6.25)$$

Adding the Equations (6.18) and (6.22), the Equation (6.25) yields

$$\begin{aligned} \langle T \rangle_0 &= -\frac{1}{2} \langle V_{ee}^0 \rangle_0 + \frac{1}{2} \sum_{\alpha=1}^N \langle \tilde{V}_\alpha^0 \cdot \frac{\partial V_{ne}^0}{\partial \tilde{V}_\alpha^0} \rangle_0 - \frac{1}{2} \langle V_{nn}^0 \rangle_0 \\ &\quad + \frac{1}{2} \sum_{\substack{i=1 \\ i \neq p}}^n \langle \tilde{R}_i^0 \cdot \frac{\partial V_{ne}^0}{\partial \tilde{R}_i^0} \rangle_0. \end{aligned} \quad (6.26)$$

From the Equation (I.19) in the Appendix,

$$\sum_{\alpha=1}^N \tilde{V}_\alpha^0 \cdot \frac{\partial V_{ne}^0}{\partial \tilde{V}_\alpha^0} + \sum_{\substack{i=1 \\ i \neq p}}^n \tilde{R}_i^0 \cdot \frac{\partial V_{ne}^0}{\partial \tilde{R}_i^0} = -V_{ne}^0. \quad (6.27)$$

Substituting from Equation (6.27), the Equation (6.26) reduces to

$$\langle T \rangle_0 = -\frac{1}{2} \langle V \rangle_0, \quad (6.28)$$

which is the virial theorem for the whole molecule.

As seen from Equation (6.26), the virial theorem for the whole molecule in the body fixed system does not include the p^{th} nucleus. If transformed back to the space-fixed coordinate system, the virial theorem for the whole molecule in Equation (3.14) is obtained.

Thus the virial theorem for the electronic and nuclear equation can be combined to get the virial theorem for the whole molecule. The equalities in this case are approximate and are restricted to the assumption made in BOA.

VII. VIRIAL THEOREM IN BORN-OPPENHEIMER
APPROXIMATION FROM A TRIAL
FUNCTION

The virial theorems are derived from generalized scaled functions for the electronic and the nuclear motions. It is shown in the next part of this section that no extraneous term $\bar{R} \cdot \frac{\partial E_e}{\partial \bar{R}}$, which is obtained using the same scaling parameter for the electronic and the nuclear coordinates,^{6,9,10} appears in the virial theorem for the electronic motion.

A. Virial Theorem for Electronic Equation

The electronic wave equation as obtained in the Equation (5.26) is

$$H_e \Phi_{oe}(\bar{r}^o, \bar{R}^o) = E_{oe} \Phi_{oe}(\bar{r}^o, \bar{R}^o), \quad (7.1)$$

where E_{oe} is the electronic energy and

$$H_e^o = T_e^o + V_e^o. \quad (7.2)$$

Here T_e^o is given by the Equation (5.12) and

$$V_e^o = V_{ee}^o + V_{ne}^o, \quad (7.3)$$

where V_{ee}^o and V_{ne}^o are given in the Equations (5.15) and (5.16). The expectation value of the Hamiltonian with

respect to a trial function $\Psi_e(\underline{r}^0, \underline{R}^0)$ is

$$E_e[\underline{R}^0] \equiv \frac{\langle \Psi_e | H_e^0 | \Psi_e \rangle}{\langle \Psi_e | \Psi_e \rangle} \gg E_{oe} . \quad (7.4)$$

Scaling the electronic and nuclear coordinates, a scaled trial function is obtained. Since the electrons are identical particles, the total function should be antisymmetrized for the electronic coordinates. The antisymmetrized scaled wave function is

$$\Psi_{e\eta, \underline{z}} = \eta_1^{\frac{3}{2}} \dots \eta_N^{\frac{3}{2}} \mathcal{A} \Psi_e(\eta_1 \underline{r}_1^0 \dots \eta_N \underline{r}_N^0, \underline{z}_1 \underline{R}_1^0 \dots \underline{z}_{p+1} \underline{R}_{p+1}^0 \dots \underline{z}_n \underline{R}_n^0), \quad (7.5)$$

where \mathcal{A} is the antisymmetrizer given in the Equation (4.23).

The expectation value of the Hamiltonian with respect to the scaled function $\Psi_{e\eta, \underline{z}}$ is¹³

$$E_e[\eta, \underline{z}, \underline{R}^0] = \frac{\int d^{3N} \underline{r}^0 \Psi_{e\eta, \underline{z}}^* H_e^0 \Psi_{e\eta, \underline{z}}}{\int d^{3N} \underline{r}^0 \Psi_{e\eta, \underline{z}}^* \Psi_{e\eta, \underline{z}}} , \quad (7.6)$$

where $\underline{z} = \{ \underline{z}_i \}$, $i \neq p$,

and $\underline{z}, \underline{R}^0 = \{ \underline{z}_1 \underline{R}_1^0 \dots, \underline{z}_{p+1} \underline{R}_{p+1}^0, \underline{z}_{p+1} \underline{R}_{p+1}^0, \dots, \underline{z}_n \underline{R}_n^0 \}$.

The energy $E_e[\eta, \underline{z}, \underline{R}^0]$ is a function of the scaling factors and \underline{z}'_s . Since the nuclear coordinates are fixed parameters, the scaling factors \underline{z}'_s can be considered along with

other parameters of the wave function and can be varied to get a better value of the energy. In order to obtain the virial theorem for the electronic energy, the energy in Equation (7.6) should be minimized only with respect to the scaling factors η_1, \dots, η_N :

$$\frac{\partial E_e[\eta, \mathbb{R}^0]}{\partial \eta_\alpha} = 0, \quad \alpha = 1, \dots, N. \quad (7.7)$$

As is shown in Appendix J,

$$0 = \sum_{\alpha=1}^N \eta_\alpha \frac{\partial E_e}{\partial \eta_\alpha} = 2 \langle T_e^0 \rangle_\eta - \sum_{\alpha=1}^N \left\langle \underline{r}_\alpha^0 \cdot \frac{\partial V_e^0}{\partial \underline{r}_\alpha^0} \right\rangle_\eta, \quad (7.8)$$

which gives the virial theorem

$$\langle T_e^0 \rangle_\eta = \frac{1}{2} \sum_{\alpha=1}^N \left\langle \underline{r}_\alpha^0 \cdot \frac{\partial V_e^0}{\partial \underline{r}_\alpha^0} \right\rangle_\eta. \quad (7.9)$$

Writing the explicit form in Equation (7.9) for the potential energy V_e^0 , Equation (7.9) can further be reduced to

$$\langle T_e^0 \rangle_\eta = -\frac{1}{2} \langle V_{ee}^0 \rangle_\eta + \frac{1}{2} \sum_{\alpha=1}^N \left\langle \underline{r}_\alpha^0 \cdot \frac{\partial V_{ne}^0}{\partial \underline{r}_\alpha^0} \right\rangle_\eta. \quad (7.10)$$

The last term of Equation (7.10) cannot be further simplified.

The virial theorem is also obtained if $\underline{\eta}$ is orthogonal to $\frac{\partial E_e}{\partial \underline{\eta}}$; so the virial theorem does not necessarily imply

minimum energy. However, if the energy is minimum the virial theorem is satisfied.

B. Virial Theorem For Nuclear Part

Separation of the electronic equation in the Born-Oppenheimer approximation yields the nuclear equation given in Equation (5.27):

$$H_n^\circ \Phi_{on}(\underline{R}^\circ) = E_0 \Phi_{on}(\underline{R}^\circ), \quad (7.11)$$

where E_0 is the total true ground state energy and

$$H_n^\circ = T_n^\circ + V_{nn}^\circ + E_{oe}. \quad (7.12)$$

The nuclear kinetic energy operator T_n° is given by the Equation (5.13), and the internuclear potential energy by Equation (5.17). For the sake of simplicity, assume the nuclei to be distinguishable particles. The case of identical particles, either bosons or fermions or both, is considered in Appendix E but does not change any conclusions reached here. Then the scaled wave function is

$$\Psi_{n\zeta} = \zeta_1^{\frac{3}{2}} \cdots \zeta_{p-1}^{\frac{3}{2}} \zeta_{p+1}^{\frac{3}{2}} \cdots \zeta_n^{\frac{3}{2}} \Psi_n(\zeta_1 \underline{R}_1^\circ \cdots \zeta_{p-1} \underline{R}_{p-1}^\circ \zeta_{p+1} \underline{R}_{p+1}^\circ \cdots \zeta_n \underline{R}_n^\circ). \quad (7.13)$$

The expectation value of the Hamiltonian with respect to the scaled function depends on the scaling parameters, and is defined as ¹³

$$E[\xi] \equiv \frac{\int d^{3(n-1)} R^o \Psi_{n\xi}^* H_n \Psi_{n\xi}}{\int d^{3(n-1)} R^o \Psi_{n\xi}^* \Psi_{n\xi}} \gg E_0 \quad (7.14)$$

If the energy is minimized with respect to the parameters ξ_i 's, then from Appendix J,

$$0 = \sum_{\substack{i=1 \\ i \neq p}}^n \xi_i \frac{\partial E}{\partial \xi_i} \\ = 2 \langle T_n^o \rangle_{\xi} - \sum_{\substack{i=1 \\ i \neq p}}^n \langle R_i^o \cdot \frac{\partial V_{nn}^o}{\partial R_i^o} \rangle_{\xi} - \sum_{\substack{i=1 \\ i \neq p}}^n \langle R_i^o \cdot \frac{\partial E_e}{\partial R_i^o} \rangle_{\xi} \quad (7.15)$$

Equation (7.15) reduces to

$$\langle T_n^o \rangle_{\xi} = -\frac{1}{2} \langle V_{nn}^o \rangle_{\xi} + \frac{1}{2} \sum_{\substack{i=1 \\ i \neq p}}^n \langle R_i^o \cdot \frac{\partial E_e}{\partial R_i^o} \rangle_{\xi}, \quad (7.16)$$

which is the virial theorem for the nuclear equation.

The energy $E_e[R_e^e]$ is not a homogeneous function and is not known except that it is obtained as a solution to the electronic Equation (5.26). So $\frac{\partial E_e}{\partial R_i^o}$ cannot be further simplified. Since the p^{th} nucleus is expressed in terms of other nuclei, the Equation (7.16) is the virial theorem for a system of (n-1) nuclei.

If the (n-1) -dimensional vector

$$\xi_{\bar{n}} = \hat{\alpha} \xi_i \xi, \quad i=1, \dots, p-1, p+1, \dots, n, \quad (7.19)$$

is orthogonal to the (n-1) -dimensional gradient

$$\frac{\partial E_e}{\partial \xi_i} = \left\{ \frac{\partial E_e}{\partial \xi_1}, \dots, \frac{\partial E_e}{\partial \xi_{p-1}}, \frac{\partial E_e}{\partial \xi_{p+1}}, \dots, \frac{\partial E_e}{\partial \xi_n} \right\}, \quad (7.20)$$

the same equation as Equation (7.16), which gives the virial theorem, is obtained. Therefore, the virial theorem is satisfied at all the points where ξ is orthogonal to $\frac{\partial E_e}{\partial \xi}$. This proves that the virial theorem is a necessary but not a sufficient condition for the minimum energy.

As shown in the previous section, the relationship between the virial theorem in the BOA and the one for the whole molecule can be obtained by formally scaling the center of mass wave function.

In BOA the electronic energy is first minimized by the Rayleigh-Ritz principle and then used as a potential in the nuclear equation. Finally, the total energy of the system is minimized with respect to the scaling parameters for the nuclear coordinates. Thus the Rayleigh-Ritz principle can give an energy lower than the true energy of the system. Therefore, in general the total energy of the system cannot be obtained by combining the energies for the center of mass, electronic and the nuclear equations, but may be approximated by the sum of these energies.

VIII. CONCLUSIONS

In this thesis the virial theorem is derived, by use of a trial function with a different scaling parameter for each coordinate. This is an extension of the previous result obtained by Brown⁷ for systems of electrons only. Also, the virial theorem is obtained here for a general potential, and then as an example the Coulomb potential is considered.

A transformation to the body fixed coordinate system is made to separate exactly the center of mass motion from the total wave equation. Then in the BOA the electronic and the nuclear equations are separated. The virial theorem is then derived here for the first time in the BOA, using both the exact and the generalized scaled functions in the body fixed system.

Previously in the case of fixed nuclei a single scaling parameter was used for all the coordinates to derive the virial theorem, and so an extra term was obtained.^{6,9,10} According to Slater,⁵ this term was due to the force which keeps the nuclei fixed. On the other hand, it is shown in Section VII that the virial theorem can be exactly obtained if a generalized scaled function is used for the electronic

motion. Combining the virial theorems for the electronic and the nuclear equations together with the center of mass motion, the virial theorem for the whole molecule is obtained. Of course, the equality signs in this case are only approximate. In general, the expectation value of the center of mass, electronic, and the nuclear energies together does not yield the total energy, since there is a coupling between the nuclear and the electronic motions which is neglected in the BOA.

A derivation of the virial theorem for the nonstationary state of an exact wave function is given here for the first time. Obviously, for the stationary state of a function no time average is needed, and the virial theorem follows.

Besides the classical and quantum mechanical cases, the virial theorem has been extended to statistical mechanics.¹⁴ The virial theorem can be used as a check when the energy is minimized. Other related applications are in the references. An application to the H_2^+ molecule will be made in the near future.

APPENDIX A

THE VIRIAL THEOREM FOR CLASSICAL SYSTEMS

For a system of electrons, the electronic kinetic energy T_e can be written as

$$2T_e = \sum_{\alpha=1}^N m \cdot \dot{\vec{r}}_{\alpha}^2 = \sum_{\alpha=1}^N \dot{\vec{r}}_{\alpha} \cdot \vec{p}_{\alpha} \quad (\text{A.1})$$

and so it can be used in Equation (2.3). A similar expression for the nuclear system is

$$2T_n = \sum_{i=1}^n m_i \dot{\vec{R}}_i^2 = \sum_{i=1}^n \dot{\vec{R}}_i \cdot \vec{P}_i \quad (\text{A.2})$$

where T_n is the nuclear kinetic energy.

The total kinetic energy of the system is

$$T = T_e + T_n \quad (\text{A.3})$$

Therefore, from Equations (A.1) and (A.2) the total kinetic energy can be expressed as

$$2T = \sum_{\alpha=1}^N \dot{\vec{r}}_{\alpha} \cdot \vec{p}_{\alpha} + \sum_{i=1}^n \dot{\vec{R}}_i \cdot \vec{P}_i \quad (\text{A.4})$$

For the interelectronic Coulomb potential of Equation (2.17), the gradient

$$\begin{aligned} \frac{\partial V_{ee}}{\partial \underline{r}_\alpha} &= \frac{1}{2} \sum_{\alpha \neq \beta=1}^N \frac{e^2 (\underline{r}_\alpha - \underline{r}_\beta)}{|\underline{r}_\alpha - \underline{r}_\beta|^3} \\ &+ \frac{1}{2} \sum_{\alpha \neq \beta=1}^N \frac{e^2 (\underline{r}_\beta - \underline{r}_\alpha)}{|\underline{r}_\beta - \underline{r}_\alpha|^3} . \end{aligned}$$

Equation (A.5) leads to the following result, (A.5)

$$\sum_{\alpha=1}^N \underline{r}_\alpha \cdot \frac{\partial V_{ee}}{\partial \underline{r}_\alpha} = -\frac{1}{2} \sum_{\alpha \neq \beta=1}^N \frac{e^2}{|\underline{r}_\alpha - \underline{r}_\beta|} = -V_{ee} \quad (\text{A.6})$$

A similar calculation for the nuclear-electronic potential

gives

$$\sum_{\alpha=1}^N \underline{r}_\alpha \cdot \frac{\partial V_{ne}}{\partial \underline{r}_\alpha} + \sum_{i=1}^n \underline{R}_i \cdot \frac{\partial V_{ne}}{\partial \underline{R}_i} = -V_{ne}, \quad (\text{A.7})$$

and for the internuclear potential energy gives,

$$\sum_{i=1}^n \underline{R}_i \cdot \frac{\partial V_{nn}}{\partial \underline{R}_i} = -V_{nn} \quad (\text{A.8})$$

Adding Equations (A.5), (A.7) and (A.8) one obtains

$$\sum_{\alpha=1}^N \underline{r}_\alpha \cdot \frac{\partial V}{\partial \underline{r}_\alpha} + \sum_{i=1}^n \underline{R}_i \cdot \frac{\partial V}{\partial \underline{R}_i} = -V \quad (\text{A.9})$$

The virial theorem (2.14) then reduces to

$$\bar{T} = -\frac{1}{2} \bar{V} .$$

(A.10)

APPENDIX B

VIRIAL THEOREM FROM AN EXACT WAVE FUNCTION

IN QUANTUM MECHANICS

The operator $\underline{r}_\alpha \cdot \underline{p}_\alpha$ has implicit but no explicit time dependence. Taking the time derivative of the expectation

$$\begin{aligned} \frac{d}{dt} \langle \underline{r}_\alpha \cdot \underline{p}_\alpha \rangle &= \frac{d}{dt} \left[\int d^3 \underline{r}_\alpha \Phi^* (\underline{r}_\alpha \cdot \underline{p}_\alpha) \Phi \right] \\ &= \int d^3 \underline{r}_\alpha \left[\frac{\partial \Phi^*}{\partial t} \underline{r}_\alpha \cdot \underline{p}_\alpha \Phi + \Phi^* \underline{r}_\alpha \cdot \underline{p}_\alpha \frac{\partial \Phi}{\partial t} \right] \end{aligned} \quad (\text{B.1})$$

The Schrödinger Equation (3.1) gives

$$\frac{d}{dt} \langle \underline{r}_\alpha \cdot \underline{p}_\alpha \rangle = (i\hbar)^{-1} \int d^3 \underline{r}_\alpha \Phi^* [\underline{r}_\alpha \cdot \underline{p}_\alpha, H] \Phi \quad (\text{B.2})$$

Therefore, it follows that

$$\frac{d}{dt} \langle \underline{r}_\alpha \cdot \underline{p}_\alpha \rangle = (i\hbar)^{-1} \langle [\underline{r}_\alpha \cdot \underline{p}_\alpha, H] \rangle \quad (\text{B.3})$$

and for the nuclear system a similar result is obtained

$$\frac{d}{dt} \langle \underline{R}_i \cdot \underline{P}_i \rangle = (i\hbar)^{-1} \langle [\underline{R}_i \cdot \underline{P}_i, H] \rangle \quad (\text{B.4})$$

Each component of the commutator $[\underline{r}_\alpha \cdot \underline{p}_\alpha, H]$ is simplified to obtain the expectation value.

Consider first the x component of

$$[X_\alpha p_{\alpha x}, H] = [X_\alpha p_{\alpha x}, T + V] \Phi \quad (\text{B.5})$$

$$= [X_\alpha p_{\alpha x}, \frac{p_{\alpha x}^2}{2m}] \Phi + [X_\alpha p_{\alpha x}, V] \Phi$$

$$= (X_\alpha p_{\alpha x} \frac{p_{\alpha x}^2}{2m} - \frac{p_{\alpha x}^2}{2m} X_\alpha p_{\alpha x}) + (X p_x V - V X p_x) \Phi$$

$$= (X_\alpha p_{\alpha x}^2 - p_{\alpha x}^2 X_\alpha) (\frac{p_{\alpha x}}{2m}) \Phi + X_\alpha (p_{\alpha x} V - V p_{\alpha x}) \Phi$$

$$= (p_{\alpha x} X_\alpha p_{\alpha x} - p_{\alpha x}^2 X_\alpha - p_{\alpha x} X_\alpha p_{\alpha x} + X_\alpha p_{\alpha x}^2) (\frac{p_{\alpha x}}{2m}) \Phi$$

$$+ X_\alpha (p_{\alpha x} V - V p_{\alpha x}) \Phi \quad (\text{B.6})$$

so

$$[X_\alpha p_{\alpha x}, H] \Phi = [p_{\alpha x} X_\alpha, p_{\alpha x}] \frac{p_{\alpha x}}{2m} \Phi$$

$$+ [X_\alpha, p_{\alpha x}] \frac{p_{\alpha x}^2}{2m} \Phi$$

$$+ X_\alpha [p_{\alpha x}, V] \Phi \quad (\text{B.7})$$

Making use of the commutation relation

$$[x_{\alpha}, p_{\alpha x}] = i\hbar, \quad (\text{B.8})$$

Equation (B.8) yields

$$[x_{\alpha} p_{\alpha x}, H] \Phi = 2i\hbar \frac{p_{\alpha x}^2}{2m} \Phi + x_{\alpha} [p_{\alpha x}, V] \Phi, \quad (\text{B.9})$$

Similar expressions for the Y and Z components

give

$$[\vec{r}_{\alpha} \cdot \vec{p}_{\alpha}, H] \Phi = 2i\hbar \frac{p_{\alpha}^2}{2m} \Phi + \vec{r}_{\alpha} \cdot [\vec{p}_{\alpha}, V] \Phi. \quad (\text{B.10})$$

Therefore, for a single particle the expectation value of Equation (B.10) is

$$\begin{aligned} \langle [\vec{r}_{\alpha} \cdot \vec{p}_{\alpha}, H] \rangle &= 2i\hbar \langle \frac{p_{\alpha}^2}{2m} \rangle + \int d^3\vec{r}_{\alpha} \Phi^* \vec{r}_{\alpha} \cdot [\vec{p}_{\alpha}, V] \Phi \\ &= 2i\hbar \langle \frac{p_{\alpha}^2}{2m} \rangle + i\hbar \int d^3\vec{r}_{\alpha} \Phi^* \left(-\vec{r}_{\alpha} \cdot \frac{\partial V}{\partial \vec{r}_{\alpha}} \right) \Phi, \end{aligned} \quad (\text{B.11})$$

or

$$\langle [\vec{r}_{\alpha} \cdot \vec{p}_{\alpha}, H] \rangle = 2i\hbar \langle \frac{p_{\alpha}^2}{2m} \rangle - i\hbar \langle \vec{r}_{\alpha} \cdot \frac{\partial V}{\partial \vec{r}_{\alpha}} \rangle. \quad (\text{B.12})$$

A similar relation for the nuclear system

$$\langle [\vec{R}_i \cdot \vec{P}_i, H] \rangle = 2i\hbar \langle \frac{P_i^2}{2m_i} \rangle - i\hbar \langle \vec{R}_i \cdot \frac{\partial V}{\partial \vec{R}_i} \rangle \quad (\text{B.13})$$

is obtained. Therefore Equation (3.8) becomes

$$\frac{d}{dt} \langle \vec{r}_\alpha \cdot \vec{p}_\alpha \rangle = 2 \langle \frac{p_\alpha^2}{2m} \rangle - \langle \vec{r}_\alpha \cdot \frac{\partial V}{\partial \vec{r}_\alpha} \rangle . \quad (\text{B.14})$$

$$\text{If } G \equiv \sum_{\alpha=1}^N (\vec{r}_\alpha \cdot \vec{p}_\alpha) , \quad (\text{B.15})$$

then one obtains

$$\frac{d}{dt} \langle G \rangle = \frac{d}{dt} \sum_{\alpha=1}^N \langle \vec{r}_\alpha \cdot \vec{p}_\alpha \rangle = \sum_{\alpha=1}^N \langle \frac{p_\alpha^2}{2m} \rangle - \sum_{\alpha=1}^N \langle \vec{r}_\alpha \cdot \frac{\partial V}{\partial \vec{r}_\alpha} \rangle . \quad (\text{B.16})$$

So from Equation (2.7) the time average of Equation (B.16)

is zero

$$\overline{\frac{d}{dt} \langle G \rangle} = 0 , \quad (\text{B.17})$$

and thus one gets,

$$\overline{\sum_{\alpha=1}^N \langle \frac{p_\alpha^2}{2m} \rangle} = \frac{1}{2} \overline{\sum_{\alpha=1}^N \langle \vec{r}_\alpha \cdot \frac{\partial V}{\partial \vec{r}_\alpha} \rangle} . \quad (\text{B.18})$$

For the electronic system, Equation (B.8) reduces to the

virial theorem

$$\overline{\langle T_e \rangle} = \frac{1}{2} \overline{\sum_{\alpha=1}^N \langle \vec{r}_\alpha \cdot \frac{\partial V}{\partial \vec{r}_\alpha} \rangle} . \quad (\text{B.19})$$

Similarly the virial theorem for nuclear system is obtained

$$\overline{\langle T_n \rangle} = \frac{1}{2} \overline{\sum_{i=1}^n \langle \vec{R}_i \cdot \frac{\partial V}{\partial \vec{R}_i} \rangle} \quad (\text{B.20})$$

Therefore for the whole system

$$\overline{\langle T \rangle} = \frac{1}{2} \sum_{\alpha=1}^N \overline{\left\langle \vec{r}_{\alpha} \cdot \frac{\partial V}{\partial \vec{r}_{\alpha}} \right\rangle} + \frac{1}{2} \sum_{i=1}^n \overline{\left\langle \vec{R}_i \cdot \frac{\partial V}{\partial \vec{R}_i} \right\rangle} . \quad (\text{B.21})$$

For a stationary state, $\frac{\partial \Phi}{\partial t} = 0$, therefore

$$\frac{d}{dt} \langle \vec{r}_{\alpha} \cdot \vec{p}_{\alpha} \rangle = 0 , \quad (\text{B.22})$$

and the virial theorem directly follows

$$\langle T \rangle = \frac{1}{2} \sum_{\alpha=1}^N \left\langle \vec{r}_{\alpha} \cdot \frac{\partial V}{\partial \vec{r}_{\alpha}} \right\rangle + \frac{1}{2} \sum_{i=1}^n \left\langle \vec{R}_i \cdot \frac{\partial V}{\partial \vec{R}_i} \right\rangle . \quad (\text{B.23})$$

$$\underline{r}'_{\alpha} = \eta \underline{r}_{\alpha} \quad , \quad \alpha = 1, \dots, N$$

and

$$\underline{R}'_i = \eta \underline{R}_i \quad , \quad i = 1, \dots, n$$

to get the proper dummy index of integration, the Equation (C.1) becomes

$$\begin{aligned}
 E[\eta] &= \left\{ \int d^{3N} \underline{r}' \, d^{3n} \underline{R}' \, \Psi^*(\underline{r}', \underline{R}') \right. \\
 &\quad \left[\eta^2 \left(\sum_{\alpha=1}^N -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \underline{r}'_{\alpha}{}^2} + \sum_{i=1}^n -\frac{\hbar^2}{2m_i} \frac{\partial^2}{\partial \underline{R}'_i{}^2} \right) \right. \\
 &\quad \left. \left. + V\left(\frac{\underline{r}'}{\eta}, \frac{\underline{R}'}{\eta}\right) \right] \Psi(\underline{r}', \underline{R}') \right\} \\
 &\quad \left\{ \int d^{3N} \underline{r}' \, d^{3n} \underline{R}' \, \Psi^*(\underline{r}', \underline{R}') \Psi(\underline{r}', \underline{R}') \right\}^{-1} .
 \end{aligned}
 \tag{C.4}$$

$E[\eta]$ is minimized with respect to η to obtain

$$\begin{aligned}
 0 &\equiv \frac{\partial}{\partial \eta} E[\eta] \\
 &= 2\eta \langle T \rangle + \sum_{\alpha=1}^N \left\langle -\frac{\underline{r}'_{\alpha}}{\eta^2} \cdot \frac{\partial V}{\partial \left(\frac{\underline{r}'_{\alpha}}{\eta}\right)} \right\rangle + \sum_{i=1}^n \left\langle -\frac{\underline{R}'_i}{\eta^2} \cdot \frac{\partial V}{\partial \left(\frac{\underline{R}'_i}{\eta}\right)} \right\rangle .
 \end{aligned}
 \tag{C.5}$$

Expressing in terms of the expectation value with respect to Ψ_{η} ,

$$0 = 2 \langle T \rangle_{\eta} - \left\langle \sum_{\alpha=1}^N \left(\vec{r}_{\alpha} \cdot \frac{\partial V}{\partial \vec{r}_{\alpha}} \right) \right\rangle_{\eta} - \left\langle \sum_{i=1}^n \left(\vec{R}_i \cdot \frac{\partial V}{\partial \vec{R}_i} \right) \right\rangle_{\eta} , \quad (\text{C.6})$$

which gives the virial theorem

$$\langle T \rangle_{\eta} = \frac{1}{2} \sum_{\alpha=1}^N \left\langle \vec{r}_{\alpha} \cdot \frac{\partial V}{\partial \vec{r}_{\alpha}} \right\rangle_{\eta} + \frac{1}{2} \sum_{i=1}^n \left\langle \vec{R}_i \cdot \frac{\partial V}{\partial \vec{R}_i} \right\rangle_{\eta} . \quad (\text{C.7})$$

For the Coulomb potential given by the Equations (2.17), (2.18), and (2.19),

$$\sum_{\alpha=1}^N \vec{r}_{\alpha} \cdot \frac{\partial V}{\partial \vec{r}_{\alpha}} = \sum_{\alpha=1}^N \vec{r}_{\alpha} \cdot \frac{\partial V_{ee}}{\partial \vec{r}_{\alpha}} + \sum_{\alpha=1}^N \vec{r}_{\alpha} \cdot \frac{\partial V_{ne}}{\partial \vec{r}_{\alpha}} , \quad (\text{C.8})$$

and for the nuclear system

$$\sum_{i=1}^n \vec{R}_i \cdot \frac{\partial V}{\partial \vec{R}_i} = \sum_{i=1}^n \vec{R}_i \cdot \frac{\partial V_{nn}}{\partial \vec{R}_i} + \sum_{i=1}^n \vec{R}_i \cdot \frac{\partial V_{ne}}{\partial \vec{R}_i} . \quad (\text{C.9})$$

From Appendix A the Equations (C.8) and (C.9) become

$$\sum_{\alpha=1}^N \vec{r}_{\alpha} \cdot \frac{\partial V}{\partial \vec{r}_{\alpha}} + \sum_{i=1}^n \vec{R}_i \cdot \frac{\partial V}{\partial \vec{R}_i} = -V , \quad (\text{C.10})$$

which gives

$$\langle T \rangle_{\eta} = -\frac{1}{2} \langle V \rangle_{\eta} . \quad (\text{C.11})$$

2. Virial Theorem In Simple Scaling For Fixed Nuclei

The nuclei are fixed so from Equation (4.17) the expectation value of the electronic energy is

$$E_e[\eta, \underline{R}] = \frac{\int d^{3N} \underline{r} \eta^3 \Psi_e^*(\eta \underline{r}, \eta \underline{R}) H_e \Psi_e(\eta \underline{r}, \eta \underline{R})}{\int d^{3N} \underline{r} \eta^3 \Psi_e^*(\eta \underline{r}, \eta \underline{R}) \Psi_e(\eta \underline{r}, \eta \underline{R})} \quad (\text{C.12})$$

Making the transformation

$$\underline{r}' = \eta \underline{r} \quad , \quad (\text{C.13})$$

where the electronic coordinates are

$$\underline{r}' = \{ r'_\alpha \} \quad , \quad \alpha = 1, \dots, 3N \quad , \quad (\text{C.14})$$

Equation (C.11) reduces to

$$E_e[\eta, \underline{R}] = \frac{\int d^{3N} \underline{r}' \Psi_e^*(\underline{r}', \eta \underline{R}) \left[\eta^2 T_e + V_e\left(\frac{\underline{r}'}{\eta}, \underline{R}\right) \right] \Psi_e(\underline{r}', \eta \underline{R})}{\int d^{3N} \underline{r}' \Psi_e^*(\underline{r}', \eta \underline{R}) \Psi_e(\underline{r}', \eta \underline{R})} \quad (\text{C.15})$$

Minimizing E_e with respect to η one obtains,

$$0 = \frac{\partial}{\partial \eta} E_e[\eta, \underline{R}] \quad . \quad (\text{C.16})$$

From Equation (C.15) it follows

$$\begin{aligned}
 0 &= \frac{\partial}{\partial \eta} \left\{ \int d^{3N} \underline{r}' \Psi_e^*(\underline{r}', \eta \underline{R}) [\eta^2 T_e + V_e(\frac{\underline{r}'}{\eta}, \underline{R})] \cdot \right. \\
 &\quad \left. \Psi_e(\underline{r}', \eta \underline{R}) \right\} \cdot \\
 &\quad \left\{ \int d^{3N} \underline{r}' \Psi_e^*(\underline{r}', \eta \underline{R}) \Psi_e(\underline{r}', \eta \underline{R}) \right\}^{-1} \\
 &= \left\{ \int d^{3N} \underline{r}' \Psi_e^*(\underline{r}', \eta \underline{R}') [2\eta T_e + \sum_{\alpha=1}^N -\frac{\underline{r}'_{\alpha}}{\eta^2} \cdot \frac{\partial V_e}{\partial(\frac{\underline{r}'_{\alpha}}{\eta})}] \cdot \right. \\
 &\quad \left. \Psi_e(\underline{r}', \eta \underline{R}) \right\} \\
 &\quad \left\{ \int d^{3N} \underline{r}' \Psi_e^*(\underline{r}', \eta \underline{R}') \Psi_e(\underline{r}', \eta \underline{R}) \right\}^{-1} \\
 &+ \sum_{i=1}^n \frac{\partial}{\partial(\eta R_{i'})} \left\{ \left[\int d^{3N} \underline{r}' \Psi_e^*(\underline{r}', \eta \underline{R}) H_e \Psi_e(\underline{r}', \eta \underline{R}) \right] \right. \\
 &\quad \left. \left[\int d^{3N} \underline{r}' \Psi_e^*(\underline{r}', \eta \underline{R}) \Psi_e(\underline{r}', \eta \underline{R}) \right]^{-1} \right\} \frac{\partial(\eta R_{i'})}{\partial \eta} \\
 &= 2\eta \langle T_e \rangle + \sum_{\alpha=1}^N \left\langle -\underline{r}'_{\alpha} \cdot \frac{\partial V_e}{\partial \underline{r}'_{\alpha}} \right\rangle + \sum_{i=1}^n R_{i'} \cdot \frac{\partial E_e}{\partial R_{i'}} \quad (\text{C.17})
 \end{aligned}$$

For Coulomb potential V_e , from Appendix A it follows that

$$\sum_{\alpha=1}^N \underline{r}'_{\alpha} \cdot \frac{\partial V_e}{\partial \underline{r}'_{\alpha}} = -V_e \quad (\text{C.18})$$

Equation (C.16) now reduces to

$$0 = 2\eta \langle T_e \rangle + \langle V_e \rangle + \frac{1}{\eta} \sum_{i=1}^n \tilde{R}_i \cdot \frac{\partial E_e}{\partial \tilde{R}_i} \quad (\text{C.19})$$

Expectation values in Equation (C.18) can now be expressed in terms of the scaled function Ψ_η to get

$$0 = \langle T_e \rangle_\eta + \langle V_e \rangle_\eta + \sum_{i=1}^n \tilde{R}_i \cdot \frac{\partial E_e}{\partial \tilde{R}_i} \quad (\text{C.20})$$

where

$$\langle T \rangle_\eta = \eta^2 \langle T \rangle \quad (\text{C.21})$$

and

$$\langle V \rangle_\eta = \eta \langle V \rangle \quad (\text{C.22})$$

are the expectation values with respect to the scaled function Ψ_η in terms of the expectation values with respect to the unscaled function .

APPENDIX D

VIRIAL THEOREM BY GENERALIZED SCALING

From Equation (4.27) the expectation value of the energy is

$$\begin{aligned}
 E[\eta, \xi] = & \int d^{3N} \underline{r} d^{3n} \underline{R} \eta_1^3 \dots \eta_N^3 \xi_1^3 \dots \xi_n^3 \Psi^*(\eta, \xi) \\
 & \left[\sum_{\alpha=1}^N -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r_\alpha^2} + \sum_{i=1}^n -\frac{\hbar^2}{2m_i} \frac{\partial^2}{\partial R_i^2} + V \right] \\
 & \cdot \mathcal{A} \Psi(\eta, \xi) \int \\
 & \int d^{3N} \underline{r} d^{3n} \underline{R} \eta_1^3 \dots \eta_N^3 \xi_1^3 \dots \xi_n^3 \\
 & \Psi^*(\eta, \xi) \mathcal{A} \Psi(\eta, \xi) \}^{-1}, \quad (D.1)
 \end{aligned}$$

where \mathcal{A} is antisymmetrizer and is defined in Equation (4.23).

Making the transformation

$$\underline{r}'_\alpha = \eta_\alpha \underline{r}_\alpha, \quad \alpha = 1, \dots, N, \quad (D.2)$$

and

$$\underline{R}'_i = \xi_i \underline{R}_i, \quad i = 1, \dots, n, \quad (D.3)$$

Equation (D.1) reduces to

$$E[\eta, \xi] = \left\{ \int d^{3N} \underline{r}' d^{3n} \underline{R}' \Psi^*(\underline{r}', \underline{R}') \right. \\ \left[\sum_{\alpha=1}^N -\frac{\hbar^2}{2m} \eta_{\alpha}^2 \frac{\partial^2}{\partial \underline{r}'_{\alpha}{}^2} - \sum_{i=1}^n \frac{\hbar^2}{2m_i} \xi_i^2 \frac{\partial^2}{\partial \underline{R}'_i{}^2} \right. \\ \left. \left. + V\left(\frac{\underline{r}'_1}{\eta_1}, \dots, \frac{\underline{r}'_N}{\eta_N}, \frac{\underline{R}'_1}{\xi_1}, \dots, \frac{\underline{R}'_n}{\xi_n}\right) \right] \right.$$

$$\left. \alpha \Psi(\eta_1, \underline{r}'_1, \dots, \eta_N, \underline{r}'_N, \xi_1, \underline{R}'_1, \dots, \xi_n, \underline{R}'_n) \right\}$$

$$\left\{ \int d^{3N} \underline{r}' d^{3n} \underline{R}' \Psi^*(\underline{r}', \underline{R}') \right.$$

$$\left. \alpha \Psi(\eta_1, \underline{r}'_1, \dots, \eta_N, \underline{r}'_N, \xi_1, \underline{R}'_1, \dots, \xi_n, \underline{R}'_n) \right\}^{-1} \quad (\text{D.4})$$

The Equation (4.27) is given by

$$0 = \sum_{\alpha=1}^N \eta_{\alpha} \frac{\partial E}{\partial \eta_{\alpha}} + \sum_{i=1}^n \xi_i \frac{\partial E}{\partial \xi_i}, \quad (\text{D.5})$$

which reduces to

$$\begin{aligned}
0 = & \left\{ \int d^{3N} \underline{r}' d^{3n} \underline{R}' \Psi^*(\underline{r}', \underline{R}') \right. \\
& \left[2 \sum_{\alpha=1}^N -\frac{\hbar^2}{2m} \eta_{\alpha}^2 \frac{\partial^2}{\partial \underline{r}'_{\alpha}{}^2} + 2 \sum_{i=1}^n -\frac{\hbar^2}{2m_i} \xi_i^2 \frac{\partial^2}{\partial \underline{R}'_i{}^2} \right. \\
& \left. + \sum_{\alpha=1}^N -\frac{\underline{r}'_{\alpha}}{\eta_{\alpha}} \cdot \frac{\partial V}{\partial \left(\frac{\underline{r}'_{\alpha}}{\eta_{\alpha}} \right)} + \sum_{i=1}^n -\frac{\underline{R}'_i}{\xi_i} \cdot \frac{\partial V}{\partial \left(\frac{\underline{R}'_i}{\xi_i} \right)} \right] \\
& \left. a \Psi(\eta_1 \underline{r}_1, \dots, \eta_N \underline{r}_N, \xi_1 \underline{R}_1, \dots, \xi_n \underline{R}_n) \right\} \\
& \left\{ \int d^{3N} \underline{r}' d^{3n} \underline{R}' \Psi^*(\underline{r}', \underline{R}') \right. \\
& \left. \left. a \Psi(\eta_1 \underline{r}_1, \dots, \eta_N \underline{r}_N, \xi_1 \underline{R}_1, \dots, \xi_n \underline{R}_n) \right\}^{-1} \\
& + \left\{ \int d^{3N} \underline{r}' d^{3n} \underline{R}' \Psi^*(\underline{r}', \underline{R}') [T+V] \right. \\
& \left. \left[\sum_{\alpha=1}^N \eta_{\alpha} \frac{\partial}{\partial \eta_{\alpha}} + \sum_{i=1}^n \xi_i \frac{\partial}{\partial \xi_i} \right] a \Psi(\eta_1 \underline{r}_1, \dots, \xi_n \underline{R}_n) \right\} \\
& \left\{ \int d^{3N} \underline{r}' d^{3n} \underline{R}' \Psi^*(\underline{r}', \underline{R}') a \Psi(\eta_1 \underline{r}_1, \dots, \xi_n \underline{R}_n) \right\}^{-1} \\
& + \left\{ \int d^{3N} \underline{r}' d^{3n} \underline{R}' \Psi^*(\underline{r}', \underline{R}') [T+V] a \Psi \right\} \\
& \left\{ \sum_{\alpha=1}^N \eta_{\alpha} \frac{\partial}{\partial \eta_{\alpha}} + \sum_{i=1}^n \xi_i \frac{\partial}{\partial \xi_i} \right\} \left\{ \int d^{3N} \underline{r}' d^{3n} \underline{R}' \Psi^* a \Psi \right\}^{-1}.
\end{aligned}$$

In order to simplify Equation (D.6), it is divided into three terms denoted by I, II, and III. The first term is given by

$$\begin{aligned}
 I &= \left\{ \int d^{3N} \underline{r}' d^{3n} \underline{R}' \Psi^*(\underline{r}', \underline{R}') \right. \\
 &\quad \left[2 \sum_{\alpha=1}^N -\frac{\hbar^2}{2m} \eta_{\alpha}^2 \frac{\partial^2}{\partial \underline{r}'_{\alpha}{}^2} + 2 \sum_{i=1}^n -\frac{\hbar^2}{2m_i} \zeta_i^2 \frac{\partial^2}{\partial \underline{R}'_i{}^2} \right. \\
 &\quad \left. + \sum_{\alpha=1}^N -\frac{\underline{r}'_{\alpha}}{\eta_{\alpha}} \cdot \frac{\partial V}{\partial \left(\frac{\underline{r}'_{\alpha}}{\eta_{\alpha}} \right)} + \sum_{i=1}^n -\frac{\underline{R}'_i}{\zeta_i} \cdot \frac{\partial V}{\partial \left(\frac{\underline{R}'_i}{\zeta_i} \right)} \right] \\
 &\quad \left. \mathcal{A} \Psi(\eta_{1i} \underline{r}_i, \dots, \eta_{Ni} \underline{r}_i, \zeta_i \underline{R}_i, \dots, \zeta_n \underline{R}_n) \right\} \\
 &\quad \left\{ \int d^{3N} \underline{r}' d^{3n} \underline{R}' \Psi^*(\underline{r}', \underline{R}') \mathcal{A} \Psi \right\}^{-1} \\
 &= \left\{ \int d^{3N} \underline{r} d^{3n} \underline{R} \Psi_{\eta, \zeta}^*(\underline{r}, \underline{R}) \right. \\
 &\quad \left[2 \sum_{\alpha=1}^N -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \underline{r}_{\alpha}{}^2} + \sum_{i=1}^n -\frac{\hbar^2}{2m_i} \frac{\partial^2}{\partial \underline{R}_i{}^2} \right. \\
 &\quad \left. + \sum_{\alpha=1}^N -\frac{\underline{r}_{\alpha}}{\eta_{\alpha}} \cdot \frac{\partial V}{\partial \underline{r}_{\alpha}} + \sum_{i=1}^n -\frac{\underline{R}_i}{\zeta_i} \cdot \frac{\partial V}{\partial \underline{R}_i} \right] \Psi_{\eta, \zeta} \left. \right\} \\
 &\quad \left\{ \int d^{3N} \underline{r} d^{3n} \underline{R} \Psi_{\eta, \zeta}^* \Psi_{\eta, \zeta} \right\}^{-1}
 \end{aligned}$$

(D.7)

$$\begin{aligned}
I &= 2 \left\langle \sum_{\alpha=1}^N -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \underline{r}_\alpha^2} \right\rangle_{\eta, \xi} + \left\langle \sum_{i=1}^n -\frac{\hbar^2}{2m_i} \frac{\partial^2}{\partial \underline{R}_i^2} \right\rangle_{\eta, \xi} \\
&+ \left\langle \sum_{\alpha=1}^N -\frac{\hbar^2}{m} \cdot \frac{\partial V}{\partial \underline{r}_\alpha} \right\rangle_{\eta, \xi} + \left\langle \sum_{i=1}^n -R_i \cdot \frac{\partial V}{\partial \underline{R}_i} \right\rangle_{\eta, \xi} \\
&= 2 \langle T_e \rangle_{\eta, \xi} + 2 \langle T_n \rangle_{\eta, \xi} \\
&+ \left\langle \sum_{\alpha=1}^N -\frac{\hbar^2}{m} \cdot \frac{\partial V}{\partial \underline{r}_\alpha} \right\rangle_{\eta, \xi} + \left\langle \sum_{i=1}^n -R_i \cdot \frac{\partial V}{\partial \underline{R}_i} \right\rangle_{\eta, \xi}.
\end{aligned}
\tag{D.8}$$

The second term is

$$\begin{aligned}
II &= \left\{ \int d^{3N} \underline{r}' d^{3n} \underline{R}' \Psi^*(\underline{r}', \underline{R}') [T+V] \right. \\
&\left. \left[\sum_{\alpha=1}^N \eta_\alpha \frac{\partial}{\partial \eta_\alpha} + \sum_{i=1}^n \xi_i \frac{\partial}{\partial \xi_i} \right] \mathcal{A} \Psi(\eta_1 \underline{r}_1, \dots, \xi_n \underline{R}_n) \right\} \\
&\left\{ \int d^{3N} \underline{r}' d^{3n} \underline{R}' \Psi^*(\underline{r}', \underline{R}') \cdot \right. \\
&\left. \mathcal{A} \Psi(\eta_1 \underline{r}_1, \dots, \xi_n \underline{R}_n) \right\}^{-1}
\end{aligned}
\tag{D.9}$$

Now for the sake of simplicity assume that all the nuclei are distinguishable. The operator \mathcal{A} operates only on the electronic coordinates \underline{r} , and is defined as

$$\mathcal{A} = \frac{1}{N!} \sum_{\substack{P \\ (1 \dots N)}} (-1)^N \hat{P}
\tag{D.10}$$

where the permutation P is

$$P = \begin{pmatrix} 1 & 2 & \dots & N \\ \alpha_1 & \alpha_2 & \dots & \alpha_N \end{pmatrix} \quad (\text{D.11})$$

applying \hat{P} , Ψ becomes

$$\hat{P}\Psi(\eta_1 \underline{r}_1, \dots, \eta_N \underline{r}_N, R') = \Psi(\eta_1 \underline{r}_{\alpha_1}, \eta_2 \underline{r}_{\alpha_2}, \dots, \eta_N \underline{r}_{\alpha_N}, R'). \quad (\text{D.12})$$

But the primed coordinate is defined as

$$\underline{r}'_{\alpha} = \eta_{\alpha} \underline{r}_{\alpha},$$

and so the permutation operator \hat{P} gives

$$\hat{P}\Psi(\eta_1 \underline{r}_1, \dots, \eta_N \underline{r}_N, R') = \Psi\left(\frac{\eta_1 \underline{r}'_{\alpha_1}}{\eta_{\alpha_1}}, \dots, \frac{\eta_N \underline{r}'_{\alpha_N}}{\eta_{\alpha_N}}, R'\right). \quad (\text{D.13})$$

The \underline{r}'_{α} are now variables of integration, and hence not differentiated. Now apply $\eta_{\beta} \frac{\partial}{\partial \eta_{\beta}}$,

$$\begin{aligned} & \eta_{\beta} \frac{\partial}{\partial \eta_{\beta}} \hat{P}\Psi(\eta_1 \underline{r}_1, \dots, \eta_N \underline{r}_N, R') \\ &= \eta_{\beta} \frac{\partial}{\partial \eta_{\beta}} \Psi\left(\frac{\eta_1 \underline{r}'_{\alpha_1}}{\eta_{\alpha_1}}, \dots, \frac{\eta_{\beta} \underline{r}'_{\alpha_{\beta}}}{\eta_{\alpha_{\beta}}}, \dots, \frac{\eta_N \underline{r}'_{\alpha_N}}{\eta_{\alpha_N}}, R'\right). \end{aligned} \quad (\text{D.14})$$

$$\begin{aligned}
& \eta_\beta \frac{\partial}{\partial \eta_\beta} \hat{P} \Psi(\eta_1 r_1, \dots, \eta_N r_N, R') \\
&= \eta_\beta \frac{r'_{\alpha_\beta}}{\eta_{\alpha_\beta}} \cdot \frac{\partial}{\partial \left(\frac{\eta_\beta r'_{\alpha_\beta}}{\eta_{\alpha_\beta}} \right)} \Psi \left(\frac{\eta_1}{\eta_{\alpha_1}} r'_{\alpha_1}, \dots, \frac{\eta_N}{\eta_{\alpha_N}} r'_{\alpha_N}, R' \right) \\
&+ \eta_\beta \left(\frac{\eta_d r'_{\alpha_d}}{-\eta_{\alpha_d}^2} \right) \cdot \frac{\partial}{\partial \left(\frac{\eta_N r'_{\alpha_d}}{\eta_{\alpha_d}} \right)} \Psi \left(\frac{\eta_1}{\eta_{\alpha_1}} r'_{\alpha_1}, \dots, \frac{\eta_N}{\eta_{\alpha_N}} r'_{\alpha_N}, R' \right) \\
&= r'_{\alpha_\beta} \cdot \frac{\partial}{\partial r'_{\alpha_\beta}} \hat{P} \Psi - r'_{\alpha_\beta} \cdot \frac{\partial}{\partial r'_{\alpha_\beta}} \hat{P} \Psi, \tag{D.15}
\end{aligned}$$

where α_d is assumed to be β . Taking summation over β gives

$$\begin{aligned}
& \sum_{\beta=1}^N \eta_\beta \frac{\partial}{\partial \eta_\beta} \hat{P} \Psi(\eta_1 r_1, \dots, \eta_N r_N, R') \\
&= \left\{ \sum_{\beta=1}^N r'_{\alpha_\beta} \cdot \frac{\partial}{\partial r'_{\alpha_\beta}} - \sum_{\beta=1}^N r'_{\alpha_\beta} \cdot \frac{\partial}{\partial r'_{\alpha_\beta}} \right\} \hat{P} \Psi \\
&= \left\{ \sum_{\beta=1}^N r'_{\alpha_\beta} \cdot \frac{\partial}{\partial r'_{\alpha_\beta}} - \sum_{\beta=1}^N r'_{\alpha_\beta} \cdot \frac{\partial}{\partial r'_{\alpha_\beta}} \right\} \hat{P} \Psi \\
&= 0 \tag{D.16}
\end{aligned}$$

Since the nuclei are assumed to be distinguishable, the transformation of Equation (D.3) makes \underline{z}_i dummy variables of integration and so

$$\sum_{i=1}^n \underline{z}_i \frac{\partial}{\partial \underline{z}_i} \hat{p} \Psi = 0 \quad (\text{D.17})$$

So from the Equation (D.9)

$$\text{II} = 0 \quad (\text{D.18})$$

The third term of the Equation (D.6) is

$$\begin{aligned} \text{III} &= \left\{ \int d^{3N} \underline{r}' d^{3n} \underline{R}' \Psi^*(\underline{r}', \underline{R}') [\text{T} + \text{V}] \alpha \Psi \right\} \\ &\quad \left\{ \int d^{3N} \underline{r}' d^{3n} \underline{R}' \Psi^*(\underline{r}', \underline{R}') \alpha \Psi(\eta_1 \underline{r}_1, \dots, \eta_N \underline{r}_N, \underline{R}') \right\}^2 \\ &\quad \left\{ \int d^{3N} \underline{r}' d^{3n} \underline{R}' \Psi^*(\underline{r}', \underline{R}') \right. \\ &\quad \left. \left[\sum_{\alpha=1}^N \eta_{\alpha} \frac{\partial}{\partial \eta_{\alpha}} + \sum_{i=1}^n \underline{z}_i \frac{\partial}{\partial \underline{z}_i} \right] \alpha \Psi(\eta_1 \underline{r}_1, \dots, \eta_N \underline{r}_N, \underline{R}') \right\} \end{aligned} \quad (\text{D.19})$$

Using Equations (D.16) and (D.17), Equation (D.19) reduces

$$\text{to} \quad \text{III} = 0 \quad (\text{D.20})$$

Now collecting together the Equations (D.8), (D.18), and (D.20), the Equation (D.6) becomes

$$0 = 2 \langle T_e \rangle_{\eta, \xi} + 2 \langle T_n \rangle_{\eta, \xi} - \sum_{\alpha=1}^N \left\langle \vec{r}_\alpha \cdot \frac{\partial V}{\partial \vec{r}_\alpha} \right\rangle_{\eta, \xi} - \sum_{i=1}^n \left\langle \vec{R}_i \cdot \frac{\partial V}{\partial \vec{R}_i} \right\rangle_{\eta, \xi} \quad (D.21)$$

which leads to the virial theorem

$$\langle T \rangle_{\eta, \xi} = \frac{1}{2} \left\langle \sum_{\alpha=1}^N \vec{r}_\alpha \cdot \frac{\partial V}{\partial \vec{r}_\alpha} \right\rangle_{\eta, \xi} + \frac{1}{2} \left\langle \sum_{i=1}^n \vec{R}_i \cdot \frac{\partial V}{\partial \vec{R}_i} \right\rangle_{\eta, \xi} \quad (D.22)$$

where

$$T = T_e + T_n \quad (D.23)$$

APPENDIX E

THE NUCLEI AS IDENTICAL PARTICLES

For the derivation of the virial theorem when the nuclei are identical the following three possibilities are considered.

1. When All The Nuclei Are Bosons

The generalized scaled function is obtained by anti-symmetrizing the fermions and symmetrizing the bosons in the trial function. The scaled function is therefore given by

$$\Psi_{\eta, \zeta} = \eta_1^{\frac{3}{2}} \dots \eta_N^{\frac{3}{2}} \zeta_1^{\frac{3}{2}} \dots \zeta_n^{\frac{3}{2}} \mathcal{A} \Psi(\eta_1, \eta_2, \dots, \eta_N, \zeta_1, \zeta_2, \dots, \zeta_n, R_1, R_2, \dots, R_n, R_N),$$

(E.1)

where \mathcal{A} operates on the electronic coordinates and the operator

$$\mathcal{A} = \frac{1}{n!} \sum_{\substack{P_i \\ (1 \dots n)}} (+1)^{P_i} \hat{P}_i, \quad (E.2)$$

operates only on the nuclear coordinates. The permutation

P_i is

$$P_i = \begin{pmatrix} 1 & 2 & \dots & n \\ i_1 & i_2 & \dots & i_n \end{pmatrix} \quad (E.3)$$

The operators \hat{A} and \hat{A} should be applied before making the transformation to set the dummy index of integration.

Consider

$$\begin{aligned}
 & \hat{P}_1 \Psi(\eta_1 \underline{r}_1, \dots, \eta_N \underline{r}_N, \xi_1 \underline{R}_1, \dots, \xi_n \underline{R}_n) \\
 &= \Psi(\eta_1 \underline{r}_1, \dots, \eta_N \underline{r}_N, \xi_1 \underline{R}_{i_1}, \dots, \xi_n \underline{R}_{i_n}) \\
 &= \Psi(\eta_1 \underline{r}_1, \dots, \eta_N \underline{r}_N, \frac{\xi_1}{\xi_{i_1}} \underline{R}'_{i_1}, \dots, \frac{\xi_n}{\xi_{i_n}} \underline{R}'_{i_n}) \quad (\text{E.4})
 \end{aligned}$$

$\sum_k \frac{\partial}{\partial \xi_k}$ operates only on the nuclear coordinates and so first applying it

$$\begin{aligned}
 \sum_k \frac{\partial}{\partial \xi_k} \hat{P}_1 \Psi &= \sum_k \frac{\partial}{\partial \xi_k} \Psi(\eta_1 \underline{r}_1, \dots, \eta_N \underline{r}_N, \frac{\xi_1}{\xi_{i_1}} \underline{R}'_{i_1}, \dots, \frac{\xi_n}{\xi_{i_n}} \underline{R}'_{i_n}) \\
 &= \sum_k \frac{\underline{R}'_{i_k}}{\xi_{i_k}} \cdot \frac{\partial}{\partial \left(\frac{\xi_k}{\xi_{i_k}} \underline{R}'_{i_k} \right)} \Psi(\eta_1 \underline{r}_1, \dots, \eta_N \underline{r}_N, \frac{\xi_1}{\xi_{i_1}} \underline{R}'_{i_1}, \dots, \frac{\xi_n}{\xi_{i_n}} \underline{R}'_{i_n}) \\
 &+ \sum_k \frac{\xi_j \underline{R}'_{ij}}{(-\xi_j^2)} \cdot \frac{\partial}{\partial \left(\frac{\xi_j}{\xi_{ij}} \underline{R}'_{ij} \right)} \Psi(\eta_1 \underline{r}_1, \dots, \eta_N \underline{r}_N, \frac{\xi_1}{\xi_{i_1}} \underline{R}'_{i_1}, \dots, \frac{\xi_n}{\xi_{i_n}} \underline{R}'_{i_n}) \\
 &= \underline{R}'_{i_k} \cdot \frac{\partial}{\partial \underline{R}'_{i_k}} \hat{P}_1 \Psi - \underline{R}'_{i_k} \cdot \frac{\partial}{\partial \underline{R}'_{i_k}} \hat{P}_1 \Psi \quad (\text{E.5})
 \end{aligned}$$

where $i_j = k$.

A sum over k gives

$$\sum_{k=1}^n z_k \frac{\partial}{\partial z_k} \hat{P}_1 \Psi = 0 \quad . \quad (\text{E.6})$$

The permutation \hat{P} can now be applied to the electrons to obtain

$$\hat{P} \hat{P}_1 \Psi = \Psi \left(\frac{\eta_1}{\eta_\alpha} r'_{\alpha 1}, \dots, \frac{\eta_N}{\eta_\alpha} r'_{\alpha N}, \frac{z_1}{z_{i_1}} R'_{i_1}, \dots, \frac{z_n}{z_{i_n}} R'_{i_n} \right) \cdot \quad (\text{E.7})$$

$\eta_\alpha \frac{\partial}{\partial \eta_\alpha}$ operates only on the electronic coordinates and, as derived in the Appendix D, it follows that

$$\sum_{\alpha=1}^N \eta_\alpha \frac{\partial}{\partial \eta_\alpha} P P_1 \Psi = 0 \quad . \quad (\text{E.8})$$

when the Equations (E.6) and (E.8) are combined and substituted into Equation (D.9) and (D.19), then the second and third terms of Equation (D.4) reduce to

$$\text{II} = 0 \quad (\text{E.9})$$

and

$$\text{III} = 0 \quad (\text{E.10}).$$

Thus as shown in the Appendix D the virial theorem follows.

2. All Nuclei Are Fermions

The electrons and the nuclei should be properly antisymmetrized to obtain the scaled function

$$\Psi_{\eta, \xi} = \eta_1^{\frac{3}{2}} \dots \eta_N^{\frac{3}{2}} \xi_1^{\frac{3}{2}} \dots \xi_n^{\frac{3}{2}} \mathcal{A} \mathcal{A}_1 \Psi(\eta_1 \underline{r}_1, \dots, \xi_n \underline{R}_n), \quad (\text{E.11})$$

where \mathcal{A}_1 antisymmetrizes only the nuclei and is given by

$$\mathcal{A}_1 = \left(\frac{1}{n!} \right) \sum_{\substack{P_1 \\ (1 \dots n)}} (-1)^{P_1} \hat{P}_1. \quad (\text{E.12})$$

Applying first P_1 and then $\xi_k \frac{\partial}{\partial \xi_k}$, a similar calculation as in the part A of this section yields,

$$\sum_{k=1}^n \xi_k \frac{\partial}{\partial \xi_k} \hat{P}_1 \Psi = 0. \quad (\text{E.13})$$

The proof of virial theorem follows as before.

3. Nuclei Are Combination of Both Bosons and Fermions

If n_1 nuclei are bosons and $n-n_1$ are fermions then the trial function should be antisymmetrized over all the fermions and symmetrized for all the bosons. The scaled function is therefore,

$$\Psi_{\eta, \zeta} = \eta_1^{\alpha_1} \dots \eta_N^{\alpha_N} \zeta_1^{\beta_1} \dots \zeta_n^{\beta_n} \mathcal{A} \mathcal{A}_1 \Psi(\eta_1 r_1 \dots \eta_N r_N, \zeta_1 R_1 \dots \zeta_n R_n) \quad (\text{E.14})$$

The operator \mathcal{A} antisymmetrizes the electrons only and \mathcal{A}_1 operates on the nuclei and is given by

$$\mathcal{A}_1 = \frac{1}{(n-n_1)!} \sum_{P_2}^{(n_1+1 \dots n)} (-1)^{P_2} \hat{P}_2 \quad (\text{E.15})$$

where

$$P_2 = \begin{pmatrix} n_1+1 & \dots & n \\ i_{n_1+1} & \dots & i_n \end{pmatrix} \quad (\text{E.16})$$

The symmetrizer operates on Bosons and is

$$\mathcal{A} = \frac{1}{n!} \sum_{P_1}^{(1 \dots n_1)} (+1)^{P_1} \hat{P}_1 \quad (\text{E.17})$$

where

$$P_1 = \begin{pmatrix} 1 & \dots & n_1 \\ i_1 & \dots & i_{n_1} \end{pmatrix} \quad (\text{E.18})$$

The permutation \hat{P}_1 is first applied to Ψ to get

$$\hat{P}_1 \Psi = \Psi(\eta_1 r_1 \dots \eta_N r_N, \zeta_{i_1}^{\beta_{i_1}} R_{i_1} \dots \zeta_{n_1}^{\beta_{n_1}} R_{n_1}, \zeta_{n_1+1}^{\beta_{n_1+1}} R_{n_1+1} \dots \zeta_n^{\beta_n} R_n) \quad (\text{E.19})$$

For $k = 1, 2, \dots, n_1$, $\zeta_k \frac{\partial}{\partial \zeta_k}$ operates only on the bosons and so it can be applied to and

$$\sum_{k=1}^n \bar{z}_k \frac{\partial}{\partial z_k} \hat{P}_1 \Psi = 0 \quad (\text{E.20})$$

is obtained.

The operator \hat{P}_2 interchanges the nuclei which are fermions giving

$$\hat{P}_2 \hat{P}_1 \Psi = \Psi \left(\eta_1 r_1 \dots \eta_N r_N, \frac{\bar{z}_1}{z_1} R_{i_1}, \dots, \frac{\bar{z}_{i_1}}{z_{i_1}} R_{i_1}, \dots, \frac{\bar{z}_n}{z_n} R_{i_n} \right). \quad (\text{E.21})$$

For $k = n_1 + 1, \dots, n$ it can be shown that

$$\sum_{k=n_1+1}^n \bar{z}_k \frac{\partial}{\partial z_k} \hat{P}_2 \hat{P}_1 \Psi = 0. \quad (\text{E.22})$$

Finally P can be applied to get

$$\sum_{\alpha=1}^N \eta_\alpha \frac{\partial}{\partial \eta_\alpha} \hat{P} \hat{P}_2 \hat{P}_1 \Psi = 0. \quad (\text{E.23})$$

Collecting together Equation (E.20), (E.22), and (E.23)

and again the Equation (D.9) and (D.19) give

$$\underline{\text{II}} = 0, \quad (\text{E.24})$$

and

$$\underline{\text{III}} = 0. \quad (\text{E.25})$$

The case of an arbitrary number of different bosons and fermions can be treated in like manner, and the virial theorem follows.

APPENDIX F

TRANSFORMATION OF THE HAMILTONIAN TO THE BODY FIXED REFERENCE SYSTEM

The Hamiltonian in the space fixed system given in Equation (4.1) is

$$H = \sum_{\alpha=1}^N -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \underline{r}_{\alpha}^2} + \sum_{i=1}^n -\frac{\hbar^2}{2m_i} \frac{\partial^2}{\partial \underline{R}_i^2} + V, \quad (\text{F.1})$$

where the potential V is given in the Equation (2.16) .

A transformation of the electronic and nuclear kinetic energies is first made. Then it is shown that the potential energy is transformed.

1. Transformation of The Electronic Kinetic Energy⁸

In order to make the transformation, consider a function f in the body fixed reference

$$f = f(\underline{r}_1^{\circ}, \dots, \underline{r}_N^{\circ}, \underline{R}_1^{\circ}, \dots, \underline{R}_{P-1}^{\circ}, \underline{R}_{P+1}^{\circ}, \dots, \underline{R}_n^{\circ}, \underline{c}), \quad (\text{F.2})$$

where the body fixed coordinates are given by Equations (5.3),

(5.4), (5.6), and (5.7). Taking the derivative of f with respect to \underline{r}_α , one obtains for the gradient

$$\begin{aligned} \frac{\partial f}{\partial \underline{r}_\alpha} &= \sum_{\beta=1}^N \frac{\partial f}{\partial \underline{r}_\beta^0} \cdot \frac{\partial \underline{r}_\beta^0}{\partial \underline{r}_\alpha} + \sum_{\substack{l=1 \\ l \neq P}}^n \frac{\partial f}{\partial \underline{R}_l^0} \cdot \frac{\partial \underline{R}_l^0}{\partial \underline{r}_\alpha} \\ &+ \frac{\partial f}{\partial \underline{c}} \cdot \frac{\partial \underline{c}}{\partial \underline{r}_\alpha} \\ &= \frac{\partial f}{\partial \underline{r}_\alpha^0} + \frac{m}{M} \frac{\partial f}{\partial \underline{c}}, \end{aligned} \tag{F.3}$$

and for the Laplacian

$$\begin{aligned} \frac{\partial^2 f}{\partial \underline{r}_\alpha^2} &= \sum_{\beta=1}^N \frac{\partial}{\partial \underline{r}_\beta^0} \cdot \frac{\partial f}{\partial \underline{r}_\alpha^0} \delta_{\alpha\beta} + \frac{m}{M} \sum_{\beta=1}^N \frac{\partial}{\partial \underline{r}_\beta^0} \cdot \frac{\partial f}{\partial \underline{c}} \delta_{\alpha\beta} \\ &+ \frac{\partial}{\partial \underline{r}_\alpha^0} \cdot \frac{\partial f}{\partial \underline{c}} \left(\frac{\partial \underline{c}}{\partial \underline{r}_\alpha} \right) + \frac{m^2}{M^2} \frac{\partial^2 f}{\partial \underline{c}^2} \\ &= \frac{\partial^2 f}{\partial \underline{r}_\alpha^0{}^2} + \frac{2m}{M} \frac{\partial}{\partial \underline{r}_\alpha^0} \cdot \frac{\partial f}{\partial \underline{c}} + \frac{m^2}{M^2} \frac{\partial^2 f}{\partial \underline{c}^2}. \end{aligned} \tag{F.4}$$

Summing over all α gives

$$\sum_{\alpha=1}^N \frac{1}{m} \frac{\partial^2 f}{\partial \underline{r}_{\alpha}^2} = \frac{1}{m} \sum_{\alpha=1}^N \frac{\partial^2 f}{\partial \underline{r}_{\alpha}^{\circ 2}} + \frac{2}{M} \sum_{\alpha=1}^N \frac{\partial}{\partial \underline{r}_{\alpha}^{\circ}} \cdot \frac{\partial f}{\partial \underline{c}} + \frac{mN}{M^2} \frac{\partial^2 f}{\partial \underline{c}^2} \quad (\text{F.5})$$

Thus the electronic kinetic energy transforms to

$$T_e = -\frac{\hbar^2}{2m} \sum_{\alpha=1}^N \frac{\partial^2}{\partial \underline{r}_{\alpha}^2} = -\frac{\hbar^2}{2m} \left[\frac{1}{m} \sum_{\alpha=1}^N \frac{\partial^2}{\partial \underline{r}_{\alpha}^{\circ 2}} + \frac{2}{M} \sum_{\alpha=1}^N \frac{\partial}{\partial \underline{r}_{\alpha}^{\circ}} \cdot \frac{\partial}{\partial \underline{c}} + \frac{mN}{M^2} \frac{\partial^2}{\partial \underline{c}^2} \right] \quad (\text{F.6})$$

2. Transformation of Nuclear Kinetic Energy

For $k \neq p$ the derivative of F with respect to

$\underline{R}_{\underline{k}}$ is

$$\frac{\partial f}{\partial \underline{R}_{\underline{k}}} = \sum_{\alpha=1}^N \frac{\partial f}{\partial \underline{r}_{\alpha}^{\circ}} \cdot \frac{\partial \underline{r}_{\alpha}^{\circ}}{\partial \underline{R}_{\underline{k}}} + \sum_{\substack{\lambda=1 \\ \lambda \neq k, p}}^n \frac{\partial f}{\partial \underline{R}_{\underline{\lambda}}} \cdot \frac{\partial \underline{R}_{\underline{\lambda}}}{\partial \underline{R}_{\underline{k}}} + \frac{\partial f}{\partial \underline{R}_{\underline{k}}^{\circ}} \cdot \frac{\partial \underline{R}_{\underline{k}}^{\circ}}{\partial \underline{R}_{\underline{k}}} + \frac{\partial f}{\partial \underline{c}} \cdot \frac{\partial \underline{c}}{\partial \underline{R}_{\underline{k}}}, \quad (\text{F.7})$$

which reduces to

$$\begin{aligned} \frac{\partial f}{\partial R_k} &= -\frac{m_k}{M_0} \sum_{\alpha=1}^N \frac{\partial f}{\partial r_{\alpha}^0} - \frac{m_k}{M_0} \sum_{\substack{l=1 \\ l \neq p, k}}^n \frac{\partial f}{\partial R_l^0} \\ &+ \left(1 - \frac{m_k}{M_0}\right) \frac{\partial f}{\partial R_k^0} + \frac{m_k}{M} \frac{\partial f}{\partial \underline{c}}. \quad (\text{F.8}) \end{aligned}$$

The Laplacian is therefore

$$\begin{aligned} \frac{\partial^2 f}{\partial R_k^2} &= \frac{m_k^2}{M_0^2} \sum_{\alpha, \beta=1}^N \frac{\partial}{\partial r_{\alpha}^0} \cdot \frac{\partial f}{\partial r_{\beta}^0} + \frac{2m_k^2}{M_0^2} \sum_{\beta=1}^N \sum_{\substack{l=1 \\ l \neq p, k}}^n \frac{\partial}{\partial r_{\beta}^0} \cdot \frac{\partial f}{\partial R_l^0} \\ &+ 2\left(-\frac{m_k}{M_0}\right)\left(1 - \frac{m_k}{M_0}\right) \sum_{\beta=1}^N \frac{\partial}{\partial r_{\beta}^0} \cdot \frac{\partial f}{\partial R_k^0} - \frac{2m_k^2}{MM_0} \sum_{\beta=1}^N \frac{\partial}{\partial r_{\beta}^0} \cdot \frac{\partial f}{\partial \underline{c}} \\ &+ \frac{m_k^2}{M_0^2} \sum_{\substack{m=1 \\ m \neq p \\ m \neq k}}^n \sum_{\substack{l=1 \\ l \neq p \\ l \neq k}}^n \frac{\partial}{\partial R_m^0} \cdot \frac{\partial f}{\partial R_l^0} + \left(1 - \frac{m_k}{M_0}\right)^2 \frac{\partial^2 f}{\partial R_k^2} \\ &+ 2\left(-\frac{m_k}{M_0}\right)\left(1 - \frac{m_k}{M_0}\right) \sum_{\substack{l=1 \\ l \neq p, k}}^n \frac{\partial}{\partial R_k^0} \cdot \frac{\partial f}{\partial R_l^0} \\ &+ 2\left(-\frac{m_k}{MM_0}\right)^2 \sum_{\substack{l=1 \\ l \neq p, k}}^n \frac{\partial}{\partial \underline{c}} \cdot \frac{\partial f}{\partial R_l^0} + 2\left(1 - \frac{m_k}{M_0}\right) \frac{m_k}{M} \frac{\partial}{\partial R_k^0} \cdot \frac{\partial f}{\partial \underline{c}} \\ &+ \frac{m_k^2}{M^2} \frac{\partial^2 f}{\partial \underline{c}^2}. \end{aligned}$$

(F.9)

Taking summation over all k , $k \neq p$,

$$\begin{aligned}
& \sum_{\substack{k=1 \\ k \neq p}}^n \frac{1}{m_k} \frac{\partial^2 f}{\partial \underline{R}_k^2} \\
&= \sum_{\substack{k=1 \\ k \neq p}}^n \frac{m_k}{M_0^2} \sum_{\alpha, \beta=1}^N \frac{\partial}{\partial \underline{r}_\alpha^0} \cdot \frac{\partial f}{\partial \underline{r}_\beta^0} + \sum_{\substack{k=1 \\ k \neq p}}^n \frac{m_k}{M_0^2} \sum_{\beta=1}^N \sum_{\substack{l=1 \\ l \neq p, k}}^n \frac{\partial}{\partial \underline{r}_\beta^0} \cdot \frac{\partial f}{\partial \underline{R}_l^0} \\
&\quad - \sum_{\substack{k=1 \\ k \neq p}}^n \frac{2 m_k}{M M_0} \sum_{\beta=1}^N \frac{\partial}{\partial \underline{r}_\beta^0} \cdot \frac{\partial f}{\partial \underline{c}} - \frac{2}{M_0} \sum_{\substack{k=1 \\ k \neq p}}^n \left(1 - \frac{m_k}{M_0}\right) \sum_{\beta=1}^N \frac{\partial}{\partial \underline{r}_\beta^0} \cdot \frac{\partial f}{\partial \underline{R}_k^0} \\
&\quad + \sum_{\substack{k=1 \\ k \neq p}}^n \frac{m_k}{M_0^2} \sum_{\substack{m \neq l=1 \\ m, l \neq p \\ m, l \neq k}}^n \frac{\partial}{\partial \underline{R}_l^0} \cdot \frac{\partial f}{\partial \underline{R}_m^0} + \sum_{k=1}^n \frac{m_k}{M_0^2} \sum_{\substack{l=1 \\ l \neq p, k}}^n \frac{\partial^2 f}{\partial \underline{R}_l^0{}^2} \\
&\quad - \frac{2}{M_0} \sum_{\substack{k=1 \\ k \neq p}}^n \left(1 - \frac{m_k}{M_0}\right) \sum_{\substack{l=1 \\ l \neq p, k}}^n \frac{\partial}{\partial \underline{R}_l^0} \cdot \frac{\partial f}{\partial \underline{R}_k^0} + \sum_{\substack{k=1 \\ k \neq p}}^n \frac{1}{m_k} \left(1 - \frac{m_k}{M_0}\right)^2 \frac{\partial^2 f}{\partial \underline{R}_k^0{}^2} \\
&\quad - \sum_{\substack{k=1 \\ k \neq p}}^n \frac{2 m_k}{M M_0} \sum_{\substack{l=1 \\ l \neq p, k}}^n \frac{\partial}{\partial \underline{c}} \cdot \frac{\partial f}{\partial \underline{R}_l^0} + \frac{2}{M} \sum_{\substack{k=1 \\ k \neq p}}^n \left(1 - \frac{m_k}{M_0}\right) \frac{\partial}{\partial \underline{R}_k^0} \cdot \frac{\partial f}{\partial \underline{c}} \\
&\quad + \sum_{\substack{k=1 \\ k \neq p}}^n \frac{m_k}{M^2} \frac{\partial^2 f}{\partial \underline{c}^2} .
\end{aligned}$$

(F.10)

To simplify Equation (F.10) consider each term separately.

The first term can be written as

$$\begin{aligned} & \sum_{k=1}^n \frac{m_k}{M_0^2} \sum_{\alpha, \beta=1}^N \frac{\partial}{\partial \tilde{r}_{\alpha}^{\circ}} \cdot \frac{\partial f}{\partial \tilde{r}_{\beta}^{\circ}} \\ &= \left(\frac{1}{M_0} - \frac{m_p}{M_0^2} \right) \left[\sum_{\alpha=1}^N \frac{\partial^2 f}{\partial \tilde{r}_{\alpha}^{\circ 2}} + \sum_{\alpha \neq \beta=1}^N \frac{\partial}{\partial \tilde{r}_{\alpha}^{\circ}} \cdot \frac{\partial f}{\partial \tilde{r}_{\beta}^{\circ}} \right]. \end{aligned} \quad (\text{F.11})$$

The second and the fourth terms combine to give

$$\begin{aligned} & \sum_{\substack{k=1 \\ k \neq p}}^n 2 \frac{m_k}{M_0^2} \sum_{\beta=1}^N \sum_{\substack{l=1 \\ l \neq p}}^n \frac{\partial}{\partial \tilde{r}_{\beta}^{\circ}} \cdot \frac{\partial f}{\partial \tilde{r}_l^{\circ}} - \frac{2}{M_0} \sum_{\substack{k=1 \\ k \neq p}}^n \left(1 - \frac{m_k}{M_0} \right) \sum_{\beta=1}^N \frac{\partial}{\partial \tilde{r}_{\beta}^{\circ}} \cdot \frac{\partial f}{\partial \tilde{r}_k^{\circ}} \\ &= - \frac{2m_p}{M_0^2} \sum_{\substack{l=1 \\ l \neq p}}^n \sum_{\beta=1}^N \frac{\partial}{\partial \tilde{r}_l^{\circ}} \cdot \frac{\partial f}{\partial \tilde{r}_{\beta}^{\circ}}. \end{aligned} \quad (\text{F.12})$$

The third term reduces to

$$\begin{aligned} & - \sum_{\substack{k=1 \\ k \neq p}}^n 2 \frac{m_k}{M M_0} \sum_{\beta=1}^N \frac{\partial}{\partial \tilde{r}_{\beta}^{\circ}} \cdot \frac{\partial f}{\partial \tilde{c}} \\ &= - \left(\frac{2}{M} - \frac{2m_p}{M M_0} \right) \sum_{\beta=1}^N \frac{\partial}{\partial \tilde{r}_{\beta}^{\circ}} \cdot \frac{\partial f}{\partial \tilde{c}}, \end{aligned} \quad (\text{F.13})$$

and

$$\begin{aligned}
 & \sum_{\substack{k=1 \\ k \neq p}}^n \frac{m_k}{M_0^2} \sum_{\substack{m \neq l=1 \\ m, l \neq p \\ m, l \neq k}}^n \frac{\partial}{\partial R_l^0} \cdot \frac{\partial}{\partial R_m^0} - \frac{2}{M_0} \sum_{\substack{k=1 \\ k \neq p}}^n \left(1 - \frac{m_k}{M_0}\right) \sum_{\substack{l=1 \\ l \neq p, k}}^n \frac{\partial}{\partial R_l^0} \cdot \frac{\partial f}{\partial R_k^0} \\
 &= \left(-\frac{1}{M_0} - \frac{m_p}{M_0^2}\right) \sum_{l, k \neq p}^n \frac{\partial}{\partial R_l^0} \cdot \frac{\partial f}{\partial R_k^0} \quad (\text{F.14})
 \end{aligned}$$

The following terms reduce to give

$$\begin{aligned}
 & \sum_{k=1}^n \frac{m_k}{M_0^2} \sum_{\substack{l=1 \\ l \neq p, k}}^n \frac{\partial^2 f}{\partial R_l^0{}^2} + \sum_{\substack{k=1 \\ k \neq p}}^n \frac{1}{m_k} \left(1 - \frac{m_k}{M_0}\right)^2 \frac{\partial^2 f}{\partial R_k^0{}^2} \\
 &= \sum_{\substack{l=1 \\ l \neq p}}^n \left(\frac{1}{m_l} - \frac{1}{M_0} - \frac{m_p}{M_0^2}\right) \frac{\partial^2 f}{\partial R_l^0{}^2} \quad (\text{F.15})
 \end{aligned}$$

and

$$\begin{aligned}
 & - \sum_{\substack{k=1 \\ k \neq p}}^n 2 \frac{m_k}{M M_0} \sum_{\substack{l=1 \\ l \neq p, k}}^n \frac{\partial}{\partial c} \cdot \frac{\partial f}{\partial R_l^0} + \frac{2}{M} \sum_{\substack{k=1 \\ k \neq p}}^n \left(1 - \frac{m_k}{M_0}\right) \frac{\partial}{\partial R_k^0} \cdot \frac{\partial f}{\partial c} \\
 &= 2 \frac{m_p}{M M_0} \sum_{\substack{l=1 \\ l \neq p}}^n \frac{\partial}{\partial R_l^0} \cdot \frac{\partial f}{\partial c} \quad (\text{F.16})
 \end{aligned}$$

Finally the last term is

$$\sum_{\substack{k=1 \\ k \neq p}}^n \frac{m_k}{M^2} \frac{\partial^2 f}{\partial \underline{C}^2} = \left(\frac{M_0}{M^2} - \frac{m_p}{M^2} \right) \frac{\partial^2 f}{\partial \underline{C}^2}. \quad (\text{F.17})$$

Now differentiating f with respect to \underline{R}_p gives

$$\begin{aligned} \frac{\partial f}{\partial \underline{R}_p} &= \sum_{\alpha=1}^N \frac{\partial f}{\partial \underline{r}_\alpha^0} \cdot \frac{\partial \underline{r}_\alpha^0}{\partial \underline{R}_p} + \sum_{\substack{l=1 \\ l \neq p}}^n \frac{\partial f}{\partial \underline{R}_l^0} \cdot \frac{\partial \underline{R}_l^0}{\partial \underline{R}_p} + \frac{\partial f}{\partial \underline{C}} \cdot \frac{\partial \underline{C}}{\partial \underline{R}_p} \\ &= -\frac{m_p}{M_0} \sum_{\alpha=1}^N \frac{\partial f}{\partial \underline{r}_\alpha^0} - \frac{m_p}{M_0} \sum_{\substack{l=1 \\ l \neq p}}^n \frac{\partial f}{\partial \underline{R}_l^0} + \frac{m_p}{M} \frac{\partial f}{\partial \underline{C}}, \end{aligned} \quad (\text{F.18})$$

and so

$$\begin{aligned} \frac{1}{m_p} \frac{\partial^2 f}{\partial \underline{R}_p^2} &= \frac{m_p}{M_0^2} \sum_{\alpha=1}^N \frac{\partial^2 f}{\partial \underline{r}_\alpha^0{}^2} + \frac{m_p}{M_0^2} \sum_{\alpha \neq \beta=1}^N \frac{\partial}{\partial \underline{r}_\alpha^0} \cdot \frac{\partial f}{\partial \underline{r}_\beta^0} \\ &\quad + \frac{m_p}{M_0^2} \sum_{\substack{l=1 \\ l \neq p}}^n \frac{\partial^2 f}{\partial \underline{R}_l^0{}^2} + \frac{m_p}{M_0^2} \sum_{m \neq l=1}^n \frac{\partial}{\partial \underline{R}_m^0} \cdot \frac{\partial f}{\partial \underline{R}_l^0} \\ &\quad + \frac{m_p}{M^2} \frac{\partial^2 f}{\partial \underline{C}^2} + \frac{2 m_p}{M_0^2} \sum_{\alpha=1}^N \sum_{\substack{l=1 \\ l \neq p}}^n \frac{\partial}{\partial \underline{r}_\alpha^0} \cdot \frac{\partial f}{\partial \underline{R}_l^0} \\ &\quad - \frac{2 m_p}{M M_0} \sum_{\alpha=1}^N \frac{\partial}{\partial \underline{r}_\alpha^0} \cdot \frac{\partial f}{\partial \underline{C}} - \frac{2 m_p}{M M_0} \sum_{\substack{l=1 \\ l \neq p}}^n \frac{\partial}{\partial \underline{R}_l^0} \cdot \frac{\partial f}{\partial \underline{C}}. \end{aligned} \quad (\text{F.19})$$

Collecting together Equations (F.11), (F.12), (F.13), (F.14), (F.15), (F.16), (F.17), and (F.19), the following expression for the transformation of the nuclear kinetic energy is obtained

$$\begin{aligned}
 T_n &= \sum_{k=1}^n -\frac{\hbar^2}{2m_k} \frac{\partial^2}{\partial \underline{R}_k^2} \\
 &= -\frac{\hbar^2}{2} \left[\frac{1}{M_0} \sum_{\alpha=1}^N \frac{\partial^2}{\partial \underline{r}_\alpha^2} + \frac{1}{M_0} \sum_{\alpha \neq \beta=1}^N \frac{\partial}{\partial \underline{r}_\alpha} \cdot \frac{\partial}{\partial \underline{r}_\beta} \right. \\
 &\quad - \frac{2}{M} \sum_{\beta=1}^N \frac{\partial}{\partial \underline{r}_\beta} \cdot \frac{\partial}{\partial \underline{c}_m} - \frac{1}{M_0} \sum_{\substack{l \neq k=1 \\ l, k \neq p}}^n \frac{\partial}{\partial \underline{R}_l} \cdot \frac{\partial}{\partial \underline{R}_k} \\
 &\quad \left. + \sum_{\substack{k=1 \\ k \neq p}}^n \left(\frac{1}{m_k} - \frac{1}{M_0} \right) \frac{\partial^2}{\partial \underline{R}_k^2} + \frac{M_0}{M^2} \frac{\partial^2}{\partial \underline{c}^2} \right].
 \end{aligned} \tag{F.20}$$

Now adding the nuclear and electronic kinetic energies given by Equations (F.20) and (F.6), the total kinetic energy in the body fixed system is obtained

$$\begin{aligned}
 T &= -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial \underline{c}^2} - \frac{\hbar^2}{2} \left(\frac{1}{m} + \frac{1}{M_0} \right) \sum_{\alpha=1}^N \frac{\partial^2}{\partial \underline{r}_\alpha^2} \\
 &\quad - \frac{\hbar^2}{2} \sum_{\alpha \neq \beta=1}^N \left(\frac{1}{m} + \frac{1}{M_0} \right) \frac{\partial}{\partial \underline{r}_\alpha} \cdot \frac{\partial}{\partial \underline{r}_\beta} \\
 &\quad - \frac{\hbar^2}{2} \sum_{\substack{k=1 \\ k \neq p}}^n \left(\frac{1}{m_k} - \frac{1}{M_0} \right) \frac{\partial^2}{\partial \underline{R}_k^2} + \frac{\hbar^2}{2M_0} \sum_{\substack{l \neq k=1 \\ l, k \neq p}}^n \frac{\partial}{\partial \underline{R}_l} \cdot \frac{\partial}{\partial \underline{R}_k}.
 \end{aligned} \tag{F.21}$$

Thus the total kinetic energy in the body fixed coordinate system can be expressed as

$$T = T_T + T_e^{\circ} + T_n^{\circ}, \quad (\text{F.22})$$

where

$$T_T = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial \underline{C}^2} \quad (\text{F.23})$$

is the kinetic energy for the center of mass motion,

$$T_e^{\circ} = -\frac{\hbar^2}{2} \left(\frac{1}{m} + \frac{1}{M_0} \right) \sum_{\alpha=1}^N \frac{\partial^2}{\partial \underline{r}_{\alpha}^{\circ 2}} - \frac{\hbar^2}{2M_0} \sum_{\alpha \neq \beta=1}^N \frac{\partial}{\partial \underline{r}_{\alpha}^{\circ}} \cdot \frac{\partial}{\partial \underline{r}_{\beta}^{\circ}} \quad (\text{F.24})$$

is the electronic kinetic energy and,

$$T_n^{\circ} = -\frac{\hbar^2}{2} \sum_{k=1}^n \left(\frac{1}{m_k} - \frac{1}{M_0} \right) \frac{\partial^2}{\partial \underline{R}_k^{\circ 2}} - \frac{\hbar^2}{2M_0} \sum_{\substack{k \neq l=1 \\ k, l \neq p}}^n \frac{\partial}{\partial \underline{R}_k^{\circ}} \cdot \frac{\partial}{\partial \underline{R}_l^{\circ}} \quad (\text{F.25})$$

is the nuclear kinetic energy.

3. Transformation of Potential Energy⁸

It is shown that the interelectronic potential energy is invariant but other potential energies change their form because the p^{th} nuclei in the body fixed system is expressed in terms of other nuclei. The potential energy is given by

$$V = V_{ee} + V_{ne} + V_{nn} \quad (\text{F.26})$$

In the space fixed system

$$V_{ee} = \frac{1}{2} \sum_{\alpha \neq \beta=1}^N \frac{e^2}{|\underline{r}_{\alpha} - \underline{r}_{\beta}|} \quad (\text{F.27})$$

Making the transformation to the body fixed system,

$$\underline{r}_{\alpha} - \underline{r}_{\beta} = \underline{r}_{\alpha}^{\circ} + \frac{1}{m_0} \sum_{k=1}^n m_k \underline{R}_k - \underline{r}_{\beta}^{\circ} - \frac{1}{m_0} \sum_{k=1}^n m_k \underline{R}_k, \quad (\text{F.28})$$

or

$$|\underline{r}_{\alpha} - \underline{r}_{\beta}| = |\underline{r}_{\alpha}^{\circ} - \underline{r}_{\beta}^{\circ}| \quad (\text{F.29})$$

The interelectronic potential is therefore

$$V_{ee}^{\circ} = V_{ee} = \frac{1}{2} \sum_{\alpha=1}^N \frac{e^2}{|\underline{r}_{\alpha} - \underline{r}_{\beta}|} = \frac{1}{2} \sum_{\alpha=1}^N \frac{e^2}{|\underline{r}_{\alpha}^{\circ} - \underline{r}_{\beta}^{\circ}|} = V_{ee}^{\circ} \quad (\text{F.30})$$

Thus electronic potential energy does not change form.

The nuclear electronic-potential energy is

$$V_{ne} = -\frac{1}{2} \sum_{\alpha=1}^N \sum_{i=1}^n \frac{z_i e^2}{|\underline{R}_i - \underline{r}_{\alpha}|} \quad (\text{F.31})$$

It can be seen that for

$$\underline{R}_i - \underline{r}_{\alpha} = \underline{R}_i^{\circ} + \frac{1}{m_0} \sum_{k=1}^n m_k \underline{R}_k - \underline{r}_{\alpha}^{\circ} - \frac{1}{m_0} \sum_{k=1}^n m_k \underline{R}_k, \quad (\text{F.32})$$

$$|\underline{R}_i - \underline{r}_\alpha| = |\underline{R}_i^0 - \underline{r}_\alpha^0|, \quad i \neq p \quad (\text{F.33})$$

For $i = p$ we get

$$\begin{aligned} \underline{R}_p^0 - \underline{r}_\alpha^0 &= -\frac{1}{m_p} \sum_{\substack{k=1 \\ k \neq p}}^n m_k \underline{R}_k^0 - \underline{r}_\alpha + \frac{1}{m_0} \sum_{k=1}^n m_k \underline{R}_k \\ &= \underline{R}_p - \underline{r}_\alpha, \end{aligned} \quad (\text{F.34})$$

which gives

$$|\underline{R}_p - \underline{r}_\alpha| = |\underline{R}_p^0 - \underline{r}_\alpha^0|. \quad (\text{F.35})$$

Therefore, for all distances

$$|\underline{r}_\alpha - \underline{R}_i| = |\underline{r}_\alpha^0 - \underline{R}_i^0|, \quad (\text{F.36})$$

so one obtains

$$\begin{aligned} V_{ne} &= -\frac{1}{2} \sum_{\alpha=1}^N \sum_{i=1}^n \frac{z_i e^2}{|\underline{r}_\alpha - \underline{R}_i|} \\ &= -\frac{1}{2} \sum_{\alpha=1}^N \sum_{\substack{i=1 \\ i \neq p}}^n \frac{z_i e^2}{|\underline{r}_\alpha^0 - \underline{R}_i^0|} - \frac{1}{2} \sum_{\alpha=1}^N \frac{z_p e^2}{|\underline{r}_\alpha^0 - \underline{R}_p^0|} \end{aligned}$$

or when expressed in the body fixed frame

$$V_{ne}^0 = -\frac{1}{2} \sum_{\alpha=1}^N \sum_{i=1}^n \frac{z_i e^2}{|\underline{r}_\alpha^0 - \underline{R}_i^0|} - \frac{1}{2} \sum_{\alpha=1}^N \frac{z_p e^2}{\left| \underline{r}_\alpha^0 + \frac{1}{m_p} \sum_{\substack{k=1 \\ k \neq p}}^n m_k \underline{R}_k^0 \right|} \quad (\text{F.37})$$

Thus the nuclear-electronic potential energy has a different form in the body fixed and the space fixed references.

Finally consider the nuclear potential energy

$$V_{kn} = \frac{1}{2} \sum_{i \neq j=1}^n \frac{Z_i Z_j e^2}{|R_i - R_j|} \quad (\text{F.38})$$

For $i, j \neq p$, the displacement between nuclei is

$$\underline{R}_i - \underline{R}_j = \underline{R}_i^0 + \frac{1}{M_0} \sum_{k=1}^n m_k \underline{R}_k^0 - \underline{R}_j^0 - \frac{1}{M_0} \sum_{k=1}^n m_k \underline{R}_k^0 \quad (\text{F.39})$$

and so the distance is

$$|\underline{R}_i - \underline{R}_j| = |\underline{R}_i^0 - \underline{R}_j^0| \quad \text{for } i, j \neq p \quad (\text{F.40})$$

When $i = p$, $j \neq p$ the displacement is

$$\underline{R}_p^0 - \underline{R}_j^0 = -\frac{1}{m_p} \sum_{\substack{k=1 \\ k \neq p}}^n m_k \underline{R}_k^0 - \underline{R}_j^0 + \frac{1}{M_0} \sum_{k=1}^n m_k \underline{R}_k^0, \quad (\text{F.41})$$

and so the distance is

$$|\underline{R}_p^0 - \underline{R}_j^0| = |\underline{R}_p - \underline{R}_j|, \quad j \neq p.$$

(F.42)

The nuclear potential energy now becomes

$$\begin{aligned}
 V_{nn} &= \frac{1}{2} \sum_{\substack{i \neq j=1 \\ i, j \neq p}}^n \frac{Z_i Z_j e^2}{|\underline{R}_i - \underline{R}_j|} \\
 &= \frac{1}{2} \sum_{\substack{i \neq j=1 \\ i, j \neq p}}^n \frac{Z_i Z_j e^2}{|\underline{R}_i^{\circ} - \underline{R}_j^{\circ}|} + \frac{1}{2} \sum_{\substack{j=1 \\ j \neq p}}^n \frac{Z_p Z_j e^2}{|\underline{R}_p^{\circ} - \underline{R}_j^{\circ}|}
 \end{aligned}$$

or when expressed in the body fixed frame

$$V_{nn}^{\circ} = \frac{1}{2} \sum_{\substack{i \neq j=1 \\ i, j \neq p}}^n \frac{Z_i Z_j e^2}{|\underline{R}_i^{\circ} - \underline{R}_j^{\circ}|} + \frac{1}{2} \sum_{\substack{j=1 \\ j \neq p}}^n \frac{Z_p Z_j e^2}{\left| -\frac{1}{m_p} \sum_{\substack{k=1 \\ k \neq p}}^n m_k \underline{R}_k^{\circ} - \underline{R}_j^{\circ} \right|}$$

(F.43)

The total potential energy V thus is the same in the space and body fixed references, but does not have the same form.

The Hamiltonian in the body fixed system thus becomes

$$\begin{aligned}
 H &(\underline{Q}, \underline{r}_1^{\circ}, \dots, \underline{r}_N^{\circ}, \underline{R}_1^{\circ}, \dots, \underline{R}_{p-1}^{\circ}, \underline{R}_{p+1}^{\circ}, \dots, \underline{R}_n^{\circ}) \\
 &= T_T + T_e^{\circ} + T_n^{\circ} + V_{ee}^{\circ} + V_{ne}^{\circ} + V_{nn}^{\circ} .
 \end{aligned}$$

(F.44)

APPENDIX G

SEPARATION OF ELECTRONIC AND NUCLEAR
EQUATIONS IN BOA

From Equation (5.25)

$$[T_e^0(\underline{r}^0) + T_n^0(\underline{R}^0) + V^0] \Phi_{oe} \Phi_{on} = E_0 \Phi_{oe} \Phi_{on} \quad (G.1)$$

Dividing by $\Phi_{oe} \Phi_{on}$, gives

$$\begin{aligned} & \frac{1}{\Phi_{oe} \Phi_{on}} T_e^0(\underline{r}^0) [\Phi_{oe}(\underline{r}^0, \underline{R}^0) \Phi_{on}(\underline{R}^0)] \\ & + \frac{1}{\Phi_{oe} \Phi_{on}} T_n^0(\underline{R}^0) [\Phi_{oe}(\underline{r}^0, \underline{R}^0) \Phi_{on}(\underline{R}^0)] + V^0 = E_0, \end{aligned} \quad (G.2)$$

which reduces to

$$\begin{aligned} & \frac{1}{\Phi_{oe}} T_e^0(\underline{r}^0) \Phi_{oe}(\underline{r}^0, \underline{R}^0) + \frac{1}{\Phi_{oe} \Phi_{on}} T_n^0(\underline{R}^0) [\Phi_{oe}(\underline{r}^0, \underline{R}^0) \Phi_{on}(\underline{R}^0)] \\ & + V^0 = E_0. \end{aligned} \quad (G.3)$$

The nuclear kinetic energy is

$$T_n^0 = -\frac{\hbar^2}{2} \sum_{\substack{k=1 \\ k \neq p}}^n \left(\frac{1}{m_k} - \frac{1}{m_0} \right) \frac{\partial^2}{\partial R_k^0{}^2} - \frac{\hbar^2}{2m_0} \sum_{\substack{k \neq l=1 \\ k, l \neq p}}^n \frac{\partial}{\partial R_k^0} \cdot \frac{\partial}{\partial R_l^0} \quad (G.4)$$

In the BOA the nuclear coordinates in the electronic wave function Φ_{oe} are assumed to be slowly varying as compared to the electronic coordinates, and therefore can be assumed to be fixed. Thus the nuclear kinetic energy does not operate on Φ_{oe} and

$$T_n^\circ(\underline{R}^\circ) \Phi_{oe}(\underline{r}^\circ, \underline{R}^\circ) \Phi_{on}(\underline{R}^\circ) = \Phi_{oe}(\underline{r}^\circ, \underline{R}^\circ) T_n^\circ(\underline{R}^\circ) \Phi_{on}(\underline{R}^\circ), \quad (\text{G.5})$$

Equation (G.3) now reduces to

$$\frac{1}{\Phi_{oe}} T_e^\circ \Phi_{oe} + \frac{1}{\Phi_{on}} T_n^\circ \Phi_{on} + V_{ee}^\circ + V_{ne}^\circ + V_{nn}^\circ = E_o. \quad (\text{G.6})$$

The electronic equation can be separated to give

$$(T_e^\circ + V_{ee}^\circ + V_{ne}^\circ) \Phi_{oe}(\underline{r}^\circ, \underline{R}^\circ) = E_{oe}[\underline{R}^\circ] \Phi_{oe}(\underline{r}^\circ, \underline{R}^\circ), \quad (\text{G.7})$$

where E_{oe} is the electronic energy which is the separation "constant."

The nuclear equation is then obtained from Equations (G.3) and (G.7)

$$(T_n^\circ + V_{nn}^\circ + E_{oe}^\circ) \Phi_{on}(\underline{R}^\circ) = E_o \Phi_{on}(\underline{R}^\circ). \quad (\text{G.8})$$

APPENDIX H

THE VIRIAL THEOREM FOR WAVE FUNCTIONS IN BOA

The virial theorem is derived here from a wave function in the BOA.

1. Virial Theorem For The Electronic Equation

The electronic equation in the body fixed system is

$$H_e^\circ \Phi_{oe}(\underline{r}^\circ, \underline{R}^\circ) = E_{oe} \Phi_{oe}(\underline{r}^\circ, \underline{R}^\circ). \quad (\text{H.1})$$

The time dependence of a stationary state wave function can be expressed as

$$\Phi_{oe}(\underline{r}^\circ, \underline{R}^\circ, t) = e^{-\frac{i}{\hbar} E_{oe} t} \Phi_{oe}(\underline{r}^\circ, \underline{R}^\circ). \quad (\text{H.2})$$

The expectation value of the operator $\sum_{r=1}^N \underline{r}_r^\circ \cdot \underline{p}_r^\circ$ with respect to the wave function $\Phi_{oe}(\underline{r}^\circ, \underline{R}^\circ, t)$ is

$$\begin{aligned} \left\langle \sum_{r=1}^N (\underline{r}_r^\circ \cdot \underline{p}_r^\circ) \right\rangle &= \int d^{3N} \underline{r}^\circ \Phi_{oe}^* (\underline{r}^\circ, \underline{R}^\circ, t) \\ &\quad \left[\sum_{r=1}^N \underline{r}_r^\circ \cdot \underline{p}_r^\circ \right] \Phi_{oe} (\underline{r}^\circ, \underline{R}^\circ, t) \int \\ &\quad \left\{ \int d^{3N} \underline{r}^\circ \Phi_{oe}^* (\underline{r}^\circ, \underline{R}^\circ, t) \Phi_{oe} (\underline{r}^\circ, \underline{R}^\circ, t) \right\}^{-1} \\ &= \int d^{3N} \underline{r}^\circ e^{\frac{i}{\hbar} E_{oe} t} \Phi_{oe}^* (\underline{r}^\circ, \underline{R}^\circ) \sum_{r=1}^N (\underline{r}_r^\circ \cdot \underline{p}_r^\circ) e^{-\frac{i}{\hbar} E_{oe} t} \Phi_{oe} (\underline{r}^\circ, \underline{R}^\circ) \\ &\quad \left\{ \int d^{3N} \underline{r}^\circ \Phi_{oe}^* (\underline{r}^\circ, \underline{R}^\circ, t) \Phi_{oe} (\underline{r}^\circ, \underline{R}^\circ, t) \right\}^{-1} \quad (\text{H.3}) \end{aligned}$$

Differentiating with respect to t , the Equation (H.3) yields

$$\begin{aligned} \frac{\hbar}{i} \frac{d}{dt} \left\langle \sum_{i=1}^N \underline{r}_i^{\circ} \cdot \underline{p}_i \right\rangle &= \left\{ \int d^{3N} \underline{r}^{\circ} \left[E_{oe} \Phi_{oe}^* (\underline{r}^{\circ}, \underline{p}^{\circ}) \left(\sum_{i=1}^N \underline{r}_i^{\circ} \cdot \underline{p}_i^{\circ} \right) \Phi_{oe} \right. \right. \\ &\quad \left. \left. - \Phi_{oe}^* \left(\sum_{i=1}^N \underline{r}_i^{\circ} \cdot \underline{p}_i^{\circ} \right) E_{oe} \Phi_{oe} (\underline{r}^{\circ}, \underline{p}^{\circ}) \right] \right\} \\ &\quad \left\{ \int d^{3N} \underline{r}^{\circ} \left[\Phi_{oe}^* (\underline{r}^{\circ}, \underline{p}^{\circ}) \Phi_{oe} (\underline{r}^{\circ}, \underline{p}^{\circ}) \right] \right\}^{-1} \end{aligned} \quad (\text{H.4})$$

For the stationary state of the function Φ_{oe} the equation of motion (H.1) can be used in the Equation (H.4) to get

$$\begin{aligned} 0 &= \left\{ \int d^{3N} \underline{r}^{\circ} \left[H_e^{\circ} \Phi_{oe}^* \left(\sum_{i=1}^N \underline{p}_i^{\circ} \cdot \underline{p}_i^{\circ} \right) \Phi_{oe} \right. \right. \\ &\quad \left. \left. - \Phi_{oe}^* \left(\sum_{i=1}^N \underline{r}_i^{\circ} \cdot \underline{p}_i^{\circ} \right) H_e^{\circ} \Phi_{oe} \right] \right\} \\ &\quad \left\{ \int d^{3N} \underline{r}^{\circ} \Phi_{oe}^* \Phi_{oe} \right\}^{-1} \\ &= \left\{ \int d^{3N} \underline{r}^{\circ} \Phi_{oe}^* H_e^{\circ} \left(\sum_{i=1}^N \underline{r}_i^{\circ} \cdot \underline{p}_i^{\circ} \right) \Phi_{oe} \right\} \left\{ \int d^{3N} \underline{r}^{\circ} \Phi_{oe}^* \Phi_{oe} \right\}^{-1} \\ &\quad - \left\{ \int d^{3N} \underline{r}^{\circ} \Phi_{oe}^* \left(\sum_{i=1}^N \underline{r}_i^{\circ} \cdot \underline{p}_i^{\circ} \right) H_e^{\circ} \Phi_{oe} \right\} \left\{ \int d^{3N} \underline{r}^{\circ} \Phi_{oe}^* \Phi_{oe} \right\}^{-1} \end{aligned} \quad (\text{H.5})$$

where the hermitian property of the Hamiltonian is used. The Hamiltonian H_e° in the body fixed system is given by

$$H_e^{\circ} = T_e^{\circ} + V_e^{\circ} \quad (\text{H.6})$$

where the kinetic energy is

$$T_e^{\circ} = -\frac{\hbar^2}{2} \left(\frac{1}{m} + \frac{1}{M_0} \right) \sum_{\alpha=1}^N \frac{\partial^2}{\partial \tilde{r}_{\alpha}^{\circ 2}} - \frac{\hbar^2}{2M_0} \sum_{\alpha \neq \beta=1}^N \frac{\partial}{\partial \tilde{r}_{\alpha}^{\circ}} \cdot \frac{\partial}{\partial \tilde{r}_{\beta}^{\circ}}, \quad (\text{H.7})$$

and the potential energy is

$$V_e^{\circ} = V_{ee}^{\circ} + V_{ne}^{\circ}. \quad (\text{H.8})$$

In order to operate H_e° on $\sum_{d=1}^N \tilde{r}_d^{\circ} \cdot \tilde{p}_d^{\circ} \Phi_{oe}$ consider each term in H_e° separately. The first term is

$$\begin{aligned} & \sum_{\alpha=1}^N \frac{\partial^2}{\partial \tilde{r}_{\alpha}^{\circ 2}} \cdot \left[\sum_{d=1}^N (\tilde{r}_d^{\circ} \cdot \tilde{p}_d^{\circ}) \Phi_{oe} \right] \\ &= \frac{\hbar}{i} \sum_{\alpha=1}^N \frac{\partial}{\partial \tilde{r}_{\alpha}^{\circ}} \cdot \left[\frac{\partial}{\partial \tilde{r}_{\alpha}^{\circ}} + \sum_{d=1}^N \tilde{r}_d^{\circ} \cdot \frac{\partial}{\partial \tilde{r}_d^{\circ}} \cdot \frac{\partial}{\partial \tilde{r}_d^{\circ}} \right] \Phi_{oe} \\ &= \left[\frac{2\hbar}{i} \sum_{\alpha=1}^N \frac{\partial^2}{\partial \tilde{r}_{\alpha}^{\circ 2}} + 2 \frac{\hbar}{i} \sum_{\alpha, d=1}^N \tilde{r}_d^{\circ} \cdot \frac{\partial^2}{\partial \tilde{r}_{\alpha}^{\circ 2}} \cdot \frac{\partial}{\partial \tilde{r}_d^{\circ}} \right] \Phi_{oe} \\ &= \frac{2\hbar}{i} \left[\sum_{\alpha=1}^N \frac{\partial^2}{\partial \tilde{r}_{\alpha}^{\circ 2}} + \sum_{\alpha, d=1}^N \tilde{r}_d^{\circ} \cdot \frac{\partial^2}{\partial \tilde{r}_{\alpha}^{\circ 2}} \cdot \frac{\partial}{\partial \tilde{r}_d^{\circ}} \right] \Phi_{oe} \end{aligned} \quad (\text{H.9})$$

Now consider the second term

$$\begin{aligned}
& \sum_{\alpha \neq \beta=1}^N \frac{\partial}{\partial \tilde{r}_{\alpha}^{\circ}} \cdot \frac{\partial}{\partial \tilde{r}_{\beta}^{\circ}} \left[\sum_{d=1}^N \tilde{r}_d^{\circ} \cdot \underline{p}_d^{\circ} \right] \bar{\Phi}_{oe} \\
&= \frac{\hbar}{i} \sum_{\alpha \neq \beta=1}^N \frac{\partial}{\partial \tilde{r}_{\alpha}^{\circ}} \cdot \left[\frac{\partial}{\partial \tilde{r}_{\beta}^{\circ}} + \sum_{d=1}^N \tilde{r}_d^{\circ} \cdot \frac{\partial}{\partial \tilde{r}_{\beta}^{\circ}} \cdot \frac{\partial}{\partial \tilde{r}_d^{\circ}} \right] \bar{\Phi}_{oe} \\
&= 2 \frac{\hbar}{i} \left[\sum_{\alpha \neq \beta=1}^N \frac{\partial}{\partial \tilde{r}_{\alpha}^{\circ}} \cdot \frac{\partial}{\partial \tilde{r}_{\beta}^{\circ}} + \sum_{\alpha \neq \beta=1}^N \sum_{d=1}^N \tilde{r}_d^{\circ} \cdot \frac{\partial}{\partial \tilde{r}_{\alpha}^{\circ}} \cdot \frac{\partial}{\partial \tilde{r}_{\beta}^{\circ}} \cdot \frac{\partial}{\partial \tilde{r}_d^{\circ}} \right] \bar{\Phi}_{oe} \tag{H.10}
\end{aligned}$$

From Equations (H.9) and (H.10), we obtain

$$\begin{aligned}
& \text{He} \left[\sum_{d=1}^N \tilde{r}_d^{\circ} \cdot \underline{p}_d^{\circ} \right] \bar{\Phi}_{oe} \\
&= \frac{\hbar}{i} \left\{ \left(-\frac{2\hbar^2}{2} \right) \left(\frac{1}{m} + \frac{1}{m_0} \right) \left[\sum_{\alpha=1}^N \frac{\partial^2}{\partial \tilde{r}_{\alpha}^{\circ 2}} + \sum_{\alpha, d=1}^N \tilde{r}_d^{\circ} \cdot \frac{\partial^2}{\partial \tilde{r}_{\alpha}^{\circ 2}} \cdot \frac{\partial}{\partial \tilde{r}_d^{\circ}} \right] \right. \\
&\quad - \frac{2\hbar^2}{2m_0} \left[\sum_{\alpha \neq \beta=1}^N \frac{\partial}{\partial \tilde{r}_{\alpha}^{\circ}} \cdot \frac{\partial}{\partial \tilde{r}_{\beta}^{\circ}} + \sum_{\alpha \neq \beta=1}^N \sum_{d=1}^N \tilde{r}_d^{\circ} \cdot \frac{\partial}{\partial \tilde{r}_{\alpha}^{\circ}} \cdot \frac{\partial}{\partial \tilde{r}_{\beta}^{\circ}} \cdot \frac{\partial}{\partial \tilde{r}_d^{\circ}} \right] \\
&\quad \left. + V_e \left[\sum_{d=1}^N \tilde{r}_d^{\circ} \cdot \frac{\partial}{\partial \tilde{r}_d^{\circ}} \right] \right\} \bar{\Phi}_{oe} \tag{H.11}
\end{aligned}$$

Applying $\sum_{d=1}^N \tilde{r}_d^{\circ} \cdot \underline{p}_d^{\circ}$ to He° , the following is obtained

$$\begin{aligned}
& \left[\sum_{d=1}^N \underline{r}_d^{\circ}, \underline{p}_d^{\circ} \right] H_e^{\circ} \Phi_{oe} \\
&= \frac{\hbar}{i} \left\{ \left[-\frac{\hbar^2}{2} \sum_{d=1}^N \sum_{\alpha=1}^N \underline{r}_d^{\circ} \cdot \frac{\partial}{\partial \underline{r}_d^{\circ}} \cdot \frac{\partial^2}{\partial \underline{r}_d^{\circ 2}} \right. \right. \\
&\quad \left. \left. - \frac{\hbar^2}{2m_0} \sum_{\alpha \neq \beta=1}^N \sum_{d=1}^N \underline{r}_d^{\circ} \cdot \frac{\partial}{\partial \underline{r}_d^{\circ}} \cdot \frac{\partial}{\partial \underline{r}_\beta^{\circ}} \cdot \frac{\partial}{\partial \underline{r}_\beta^{\circ}} \right] \right. \\
&\quad \left. + \left[\sum_{d=1}^N V_e^{\circ} \left(\underline{r}_d^{\circ}, \frac{\partial}{\partial \underline{r}_d^{\circ}} \right) + \sum_{d=1}^N \left(\underline{r}_d^{\circ} \cdot \frac{\partial V_e^{\circ}}{\partial \underline{r}_d^{\circ}} \right) \right] \right\} \Phi_{oe} .
\end{aligned} \tag{H.12}$$

Combining Equations (H.11) and (H.12) the Equation (H.5) gives.

$$\begin{aligned}
0 = & \left\{ \int d^{3N} \underline{r}^{\circ} \Phi_{oe}^* \left[-\frac{\hbar^2}{2} \left(\frac{1}{m} + \frac{1}{m_0} \right) \sum_{\alpha=1}^N \sum_{d=1}^N \frac{\partial^2}{\partial \underline{r}_d^{\circ 2}} \right. \right. \\
& \left. \left. - \frac{\hbar^2}{2m_0} \sum_{\alpha \neq \beta=1}^N \sum_{d=1}^N \frac{\partial}{\partial \underline{r}_d^{\circ}} \cdot \frac{\partial}{\partial \underline{r}_\beta^{\circ}} - \sum_{d=1}^N \underline{r}_d^{\circ} \cdot \frac{\partial V_e^{\circ}}{\partial \underline{r}_d^{\circ}} \right] \Phi_{oe} \right\} \\
& \left\{ \int d^{3N} \underline{r}^{\circ} \Phi_{oe}^* \Phi_{oe} \right\}^{-1} ,
\end{aligned} \tag{H.13}$$

which gives the result

$$0 = 2 \langle T_e^{\circ} \rangle - \sum_{d=1}^N \left\langle \underline{r}_d^{\circ} \cdot \frac{\partial V_e^{\circ}}{\partial \underline{r}_d^{\circ}} \right\rangle . \tag{H.14}$$

The virial theorem follows for the electronic equation in BOA. For the interelectronic Coulomb potential

$$V_{ee}^{\circ} = \frac{1}{2} \sum_{\alpha \neq \beta=1}^N \frac{e^2}{|\underline{r}_\alpha^{\circ} - \underline{r}_\beta^{\circ}|} = \frac{1}{2} \sum_{\alpha \neq \beta=1}^N \frac{e^2}{|\underline{r}_\alpha - \underline{r}_\beta|} .$$

(H.15)

As shown in Appendix A

$$\sum_{\alpha=1}^N \underline{r}_\alpha^{\circ} \cdot \frac{\partial V_{ee}^{\circ}}{\partial \underline{r}_\alpha^{\circ}} = -V_{ee}^{\circ} \quad , \quad (\text{H.16})$$

and the virial theorem for the electronic motion becomes

$$\langle T_e^{\circ} \rangle = -\frac{1}{2} \langle V_{ee}^{\circ} \rangle + \frac{1}{2} \sum_{\alpha=1}^N \sum_{\substack{i=1 \\ i \neq \alpha}}^n \langle \underline{r}_\alpha^{\circ} \cdot \frac{\partial V_{ne}^{\circ}}{\partial \underline{r}_\alpha^{\circ}} \rangle \quad . \quad (\text{H.17})$$

2. Virial Theorem For The Nuclear Equation

Proceeding as in the electronic case one obtains from

the time derivative of $\langle \sum_{\substack{i=1 \\ i \neq p}}^n \underline{R}_i^{\circ} \cdot \underline{P}_i^{\circ} \rangle$,

$$\begin{aligned} 0 &= \left\{ \int d^{3(n-1)} \underline{R}^{\circ} \Phi_{0n}^* H_n^{\circ} \left[\sum_{\substack{i=1 \\ i \neq p}}^n \underline{R}_i^{\circ} \cdot \underline{P}_i^{\circ} \right] \Phi_{0n} \right\} \\ &\quad \left\{ \int d^{3(n-1)} \underline{R}^{\circ} \Phi_{0n}^* \Phi_{0n} \right\}^{-1} \\ &\quad - \left\{ \int d^{3(n-1)} \underline{R}^{\circ} \Phi_{0n}^* \left[\sum_{\substack{i=1 \\ i \neq p}}^n \underline{R}_i^{\circ} \cdot \underline{P}_i^{\circ} \right] H_n^{\circ} \Phi_{0n} \right\} \\ &\quad \left\{ \int d^{3(n-1)} \underline{R}^{\circ} \Phi_{0n}^* \Phi_{0n} \right\}^{-1} \end{aligned} \quad (\text{H.18})$$

where the nuclear hamiltonian is

$$H_n^{\circ} = T_n^{\circ} + V_n^{\circ} \quad (\text{H.19})$$

When in Equation (H.18) H_n° and $\sum_{\substack{i=1 \\ i \neq p}}^n \underline{R}_i^{\circ} \cdot \underline{P}_i^{\circ}$ are operated it follows that

$$0 = \int d^{3(n-1)} \tilde{R}^{\circ} \Phi_{0n}^* \left[2T_n^{\circ} - \sum_{\substack{i=1 \\ i \neq p}}^n \tilde{R}_i^{\circ} \cdot \frac{\partial V_n^{\circ}}{\partial \tilde{R}_i^{\circ}} \right] \Phi_{0n} \} \quad (H.20)$$

$$\left\{ \int d^{3(n-1)} \tilde{R}^{\circ} \Phi_{0n}^* \Phi_{0n} \right\}^{-1}$$

which gives the virial theorem for the nuclear motion

$$\langle T_n^{\circ} \rangle = \frac{1}{2} \sum_{\substack{i=1 \\ i \neq p}}^n \left\langle \tilde{R}_i^{\circ} \cdot \frac{\partial V_n^{\circ}}{\partial \tilde{R}_i^{\circ}} \right\rangle. \quad (H.21)$$

Expressing the potential energy V_n° as

$$V_n^{\circ} = V_{nn}^{\circ} + E_{oe} \quad ; \quad (H.22)$$

Equation (H.21) becomes

$$\langle T_n^{\circ} \rangle = \frac{1}{2} \sum_{\substack{i=1 \\ i \neq p}}^n \left\langle \tilde{R}_i^{\circ} \cdot \frac{\partial V_{nn}^{\circ}}{\partial \tilde{R}_i^{\circ}} \right\rangle + \frac{1}{2} \sum_{\substack{i=1 \\ i \neq p}}^n \left\langle \tilde{R}_i^{\circ} \cdot \frac{\partial E_{oe}}{\partial \tilde{R}_i^{\circ}} \right\rangle. \quad (H.23)$$

Since V_{nn}° is a Coulomb potential given in Equation (5.17)

$$V_{nn}^{\circ} = \frac{1}{2} \sum_{\substack{t=1 \\ t \neq p}}^n \sum_{\substack{l=1 \\ l \neq p}}^n \frac{Z_t Z_l e^2}{|\tilde{R}_t^{\circ} - \tilde{R}_l^{\circ}|} + \sum_{\substack{l=1 \\ l \neq p}}^n \frac{Z_p Z_l e^2}{\left| \tilde{R}_p^{\circ} + \frac{1}{m_p} \sum m_x \tilde{R}_x^{\circ} \right|}, \quad (H.24)$$

its derivative with respect to \tilde{R}_i° for $i \neq p$ is

$$\begin{aligned}
\tilde{R}_i^{\circ} \cdot \frac{\partial V_{nn}^{\circ}}{\partial \tilde{R}_i^{\circ}} &= \frac{1}{2} \sum_{\substack{l=1 \\ l \neq i, p}}^n \frac{-R_i^{\circ} \cdot (R_i^{\circ} - R_l^{\circ}) Z_i Z_l e^2}{|\tilde{R}_i^{\circ} - \tilde{R}_l^{\circ}|^3} \\
&+ \frac{1}{2} \sum_{\substack{t=1 \\ t \neq i, p}}^n \frac{-R_i^{\circ} \cdot (R_i^{\circ} - R_t^{\circ}) Z_t Z_i e^2}{|\tilde{R}_i^{\circ} - \tilde{R}_t^{\circ}|^3} \\
&- \left(\frac{m_i}{m_p} \tilde{R}_i^{\circ} + R_i^{\circ} \right) \cdot \frac{\left[\frac{1}{m_p} \left(\sum_{\substack{k=1 \\ k \neq p}}^n m_k R_k^{\circ} \right) + R_i^{\circ} \right] Z_i Z_p e^2}{\left| R_i^{\circ} + \frac{1}{m_p} \left(\sum_{\substack{k=1 \\ k \neq p}}^n m_k R_k^{\circ} \right) \right|^3} \\
&- \sum_{\substack{l=1 \\ l \neq i, p}}^n \frac{m_l}{m_p} \tilde{R}_i^{\circ} \cdot \frac{\left[R_l^{\circ} + \frac{1}{m_p} \left(\sum_{\substack{k=1 \\ k \neq p}}^n m_k R_k^{\circ} \right) \right] Z_l Z_p e^2}{\left| R_l^{\circ} + \frac{1}{m_p} \left(\sum_{\substack{k=1 \\ k \neq p}}^n m_k R_k^{\circ} \right) \right|^3} .
\end{aligned} \tag{H.25}$$

When summed over all i , $i \neq p$ Equation (H.25) reduces to

$$\begin{aligned}
\sum_{i=1}^n \underline{R}_i^{\circ} \cdot \frac{\partial V_{nn}^{\circ}}{\partial \underline{R}_i^{\circ}} &= \frac{1}{2} \sum_{\substack{l=1 \\ l \neq i, p \\ i \neq p}}^n - \frac{\underline{R}_i^{\circ} \cdot (\underline{R}_i^{\circ} - \underline{R}_l^{\circ}) \underline{Z}_i \underline{Z}_l e^2}{|\underline{R}_i^{\circ} - \underline{R}_l^{\circ}|^3} \\
&+ \frac{1}{2} \sum_{\substack{l=1 \\ l \neq i}}^n \frac{\underline{R}_i^{\circ} \cdot (\underline{R}_l^{\circ} - \underline{R}_i^{\circ}) \underline{Z}_i \underline{Z}_l e^2}{|\underline{R}_l^{\circ} - \underline{R}_i^{\circ}|^3} \\
&+ \sum_{\substack{i=1 \\ i \neq p}}^3 \left[\frac{m_i}{m_p} \underline{R}_i^{\circ} \cdot \left(\frac{1}{m_p} \sum_{\substack{k=1 \\ k \neq p}}^n m_k \underline{R}_k^{\circ} \right) + \frac{m_i}{m_p} \underline{R}_i^{\circ} \cdot \underline{R}_i^{\circ} \right. \\
&\quad \left. + \underline{R}_i^{\circ} \cdot \left(\frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^{\circ} \right) + \underline{R}_i^{\circ} \right] \underline{Z}_i \underline{Z}_p e^2 \\
&\quad \left[|\underline{R}_i^{\circ} + \left(\frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^{\circ} \right)|^{-3} \right] \\
&+ \sum_{\substack{i \neq 1 \\ l \neq p}} \left[\frac{m_i}{m_p} \underline{R}_i^{\circ} \cdot \underline{R}_l^{\circ} + \frac{m_l}{m_p} \underline{R}_l^{\circ} \cdot \left(\frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^{\circ} \right) \right] \underline{Z}_i \underline{Z}_p e^2 \\
&\quad \left| \underline{R}_l^{\circ} + \frac{1}{m_p} \left(\sum_{k \neq p}^n m_k \underline{R}_k^{\circ} \right) \right|^3
\end{aligned}$$

(H.26)

The terms in the Equation (H.26) can be rearranged by writing out the double summations in terms of a single summation to obtain,

$$\begin{aligned}
& \sum_{\substack{i=1 \\ i \neq p}}^n \underline{R}_i^0 \cdot \frac{\partial V_{un}^0}{\partial \underline{R}_i^0} \\
&= \frac{1}{2} \sum_{k \neq l}^n \frac{Z_i Z_l e^2}{|\underline{R}_i^0 - \underline{R}_l^0|} + \sum_{\substack{i=1 \\ i \neq p}}^n \frac{Z_i Z_p e^2 \underline{R}_i^0{}^2}{\left| \underline{R}_i^0 + \frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^0 \right|^3} \\
&+ \frac{1}{2} \sum_{k=1}^n \left\{ Z_i Z_p e^2 \left[\frac{m_i}{m_p} \underline{R}_i^0 \cdot \left(\frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^0 \right) + \frac{m_k}{m_p} \underline{R}_i^0{}^2 \right. \right. \\
&\quad \left. \left. + \underline{R}_i^0 \cdot \left(\frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^0 \right) \right] \right. \\
&\quad \left. \left[\underline{R}_i^0 + \frac{1}{m_p} \left(\sum_{k \neq p}^n m_k \underline{R}_k^0 \right) \right]^{-3} \right\} \\
&+ \sum_{\substack{i \neq k \\ i, l \neq p}} \frac{m_i}{m_p} \underline{R}_i^0 \cdot \sum_{\substack{i \neq k \\ i, l \neq p}} \left[\frac{Z_i Z_p e^2 \underline{R}_i^0{}^2}{\left| \underline{R}_i^0 + \frac{1}{m_p} \left(\sum_{k \neq p}^n m_k \underline{R}_k^0 \right) \right|^3} \right] \\
&+ \frac{\sum_{\substack{i \neq k \\ i, l \neq p}} \left[\left(\sum_{\substack{i=1 \\ i \neq p}}^n \frac{m_i}{m_p} \underline{R}_i^0 \right) \cdot \left(\frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^0 \right) \right] Z_i Z_p e^2}{\left| \underline{R}_i^0 + \frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^0 \right|^3} \\
&= \frac{1}{2} \sum_{k \neq l}^n \frac{Z_k Z_l e^2}{|\underline{R}_i^0 - \underline{R}_l^0|} + \sum_i \frac{Z_i Z_p e^2 \underline{R}_i^0{}^2}{\left| \underline{R}_i^0 + \left(\frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^0 \right) \right|^3} \\
&+ \sum_{k \neq p}^n \left[\frac{\left(\sum_i \frac{m_i}{m_p} \underline{R}_i^0 \right)^2 Z_i Z_p e^2}{\left| \underline{R}_i^0 + \frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^0 \right|^3} + \sum_{i=1}^n \frac{\underline{R}_i^0 \left(\frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^0 \right) Z_i Z_p e^2}{\left| \underline{R}_i^0 + \frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^0 \right|^3} \right. \\
&\left. + \sum \left[\underline{R}_i^0 \left(\frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^0 \right) Z_i Z_p e^2 \right] \left[\left| \underline{R}_i^0 + \frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^0 \right|^3 \right] \right] \\
&\hspace{15em} (H.27)
\end{aligned}$$

When terms in the Equation (H.27) can be combined, Equation (H.27) becomes,

$$\begin{aligned}
 & \sum_{i=1}^n \frac{R_i^{\circ}}{m_i} \cdot \frac{\partial V_{nn}^{\circ}}{\partial R_i^{\circ}} \\
 &= -\frac{1}{2} \sum_{\substack{i \neq l \\ i, l \neq p}}^n \frac{Z_i Z_l e^2}{|R_i^{\circ} - R_l^{\circ}|} - \sum_{\substack{i=1 \\ i \neq p}}^n Z_i Z_p e^2 \left[\frac{R_i^{\circ}}{m_i} + \frac{1}{m_p} \left(\sum_{\substack{k=1 \\ k \neq p}}^n m_k R_k^{\circ} \right) \right]^2 \\
 &= -V_{nn}^{\circ} \\
 & \hspace{20em} \text{(H.28)}
 \end{aligned}$$

Thus for a Coulomb potential the virial theorem for the nuclear equation becomes

$$\langle T_n^{\circ} \rangle = -\frac{1}{2} \langle V_{nn}^{\circ} \rangle + \frac{1}{2} \sum_{\substack{i=1 \\ i \neq p}}^n \left\langle \frac{R_i^{\circ}}{m_i} \cdot \frac{\partial E_{oe}}{\partial R_i^{\circ}} \right\rangle$$

(H.29)

APPENDIX I

RELATION BETWEEN THE VIRIAL THEOREM IN BOA AND

THE WHOLE MOLECULE IN BODY FIXED SYSTEM

The virial theorem in nuclear and electronic equations is expressed in terms of the total wave function.

1. Virial Theorem With Respect To The Total Wave Function For Nuclear Equation

From the expression in Equation (7.24) can be written

$$\frac{\int d^3 \underline{c} d^{3N} \underline{r}^o \Phi_{oT}^* \Phi_{oe}^* \langle T_n^o \rangle \Phi_{oT} \Phi_{oe}}{\int d^3 \underline{c} d^{3N} \underline{r}^o \Phi_{oT}^* \Phi_{oe}^* \Phi_{oT} \Phi_{oe}}$$

$$= \left\{ \int d^3 \underline{c} d^{3N} \underline{r}^o \Phi_{oT}^*(\underline{c}) \Phi_{oe}^*(\underline{r}^o; \underline{R}^o) \right.$$

$$\left. \left[\int d^{3(n-1)} \underline{R}^o \Phi_{on}^* T_n \Phi_{on} \right] \left[\int d^{3(n-1)} \underline{R}^o \Phi_{on}^* \Phi_{on} \right]^{-1} \right.$$

$$\left. \Phi_{oT} \cdot \Phi_{oe} \right\}$$

$$\left\{ \int d^3 \underline{c} d^{3N} \underline{r}^o \Phi_{oT}^* \Phi_{oe}^* \Phi_{oT} \Phi_{oe} \right\}^{-1}$$

(I.1)

Assuming that the nuclear coordinates in the function $\Phi_{oe}(\underline{r}^o, \underline{R}^o)$ are slowly varying, and can be considered as fixed parameter with respect to the variable of integration \underline{R}^o ,

Equation (I.1) becomes

$$\begin{aligned}
 & \left\{ \int d^3 \underline{\xi} d^{3N} \underline{r}^o \Phi_{oT}^* \Phi_{oe}^* \langle T_n^o \rangle \Phi_{oT} \Phi_{oe} \right\} \\
 & \left\{ \int d^3 \underline{\xi} d^{3N} \underline{r}^o \Phi_{oT}^* \Phi_{oe}^* \Phi_{oT} \Phi_{oe} \right\}^{-1} \\
 & = \left\{ \int d^3 \underline{\xi} d^{3N} \underline{r}^o d^{3(n-1)} \underline{R}^o \Phi_{oT}^* \Phi_{oe}^* \Phi_{on}^* T_n^o \Phi_{oT} \Phi_{oe} \Phi_{on} \right\} \\
 & \quad \left\{ \int d^3 \underline{\xi} d^{3N} \underline{r}^o d^{3(n-1)} \underline{R}^o \Phi_{oT}^* \Phi_{oe}^* \Phi_{on}^* \Phi_{oT} \Phi_{oe} \Phi_{on} \right\}^{-1} \\
 & = \langle T_n^o \rangle_o, \tag{I.2}
 \end{aligned}$$

where $\langle \rangle_o$ is the expectation value with respect to the total wave function. Similarly it can be shown that

$$\begin{aligned}
 & \left\{ \int d^3 \underline{\xi} d^{3N} \underline{r}^o \Phi_{oT}^* \Phi_{oe}^* \langle -\frac{1}{2} V_{nn}^o \rangle \Phi_{oT} \Phi_{oe} \right\} \\
 & \left\{ \int d^3 \underline{\xi} d^{3N} \underline{r}^o \Phi_{oT}^* \Phi_{oe}^* \Phi_{oT} \Phi_{oe} \right\}^{-1} \\
 & = \left\{ \int d^3 \underline{\xi} d^{3N} \underline{r}^o d^{3(n-1)} \underline{R}^o \Phi_{oT}^* \Phi_{oe}^* \Phi_{on}^* (-\frac{1}{2}) V_{nn}^o \Phi_{oT} \Phi_{oe} \Phi_{on} \right\} \\
 & \quad \left\{ \int d^3 \underline{\xi} d^{3N} \underline{r}^o d^{3(n-1)} \underline{R}^o \Phi_{oT}^* \Phi_{oe}^* \Phi_{on}^* \Phi_{oT} \Phi_{oe} \Phi_{on} \right\}^{-1} \\
 & = -\frac{1}{2} \langle V_{nn}^o \rangle_o. \tag{I.3}
 \end{aligned}$$

Since the nuclear coordinates in Φ_{oe} are assumed to be fixed parameters, the Equation (I.3) can be written as.

$$\begin{aligned} & \left\langle \sum_{\substack{i=1 \\ i \neq p}}^n \underline{R}_i^{\circ} \cdot \frac{\partial E_{oe}}{\partial \underline{R}_i^{\circ}} \right\rangle \\ &= \left\{ \int d^{3(n-1)} \underline{R}^{\circ} d^{3N} \underline{x}^{\circ} \Phi_{on}^* \Phi_{oe}^* \sum_{\substack{i=1 \\ i \neq p}}^n \underline{R}_i^{\circ} \cdot \frac{\partial V_{ne}^{\circ}}{\partial \underline{R}_i^{\circ}} \Phi_{oe} \Phi_{on} \right\} \\ & \left\{ \int d^{3(n-1)} \underline{R}^{\circ} d^{3N} \underline{x}^{\circ} \Phi_{on}^* \Phi_{oe}^* \Phi_{oe} \Phi_{on} \right\}^{-1}, \end{aligned}$$

(I.4)

and so

$$\begin{aligned} & \left\{ \int d^3 \underline{c} \Phi_{oT}^* \left\langle \sum_{\substack{i=1 \\ i \neq p}}^n \underline{R}_i^{\circ} \cdot \frac{\partial E_{oe}}{\partial \underline{R}_i^{\circ}} \right\rangle \Phi_{oT} \right\} \left\{ \int d^3 \underline{c} \Phi_{oT}^* \Phi_{oT} \right\}^{-1} \\ &= \left\{ \int d^3 \underline{c} d^{3N} \underline{x}^{\circ} d^{3(n-1)} \underline{R}^{\circ} \Phi_{oT}^* \Phi_{oe}^* \Phi_{on}^* \left(\sum_{\substack{i=1 \\ i \neq p}}^n \underline{R}_i^{\circ} \cdot \frac{\partial V_{ne}^{\circ}}{\partial \underline{R}_i^{\circ}} \right) \Phi_{oT} \Phi_{oe} \Phi_{on} \right\} \\ & \left\{ \int d^3 \underline{c} d^{3N} \underline{x}^{\circ} d^{3(n-1)} \underline{R}^{\circ} \Phi_{oT}^* \Phi_{oe}^* \Phi_{on}^* \Phi_{oT} \Phi_{oe} \Phi_{on} \right\}^{-1} \\ &= \sum_{\substack{i=1 \\ i \neq p}}^n \left\langle \underline{R}_i^{\circ} \cdot \frac{\partial V_{ne}^{\circ}}{\partial \underline{R}_i^{\circ}} \right\rangle. \end{aligned} \quad (I.5)$$

From Equation (I.2), (I.3) and (I.5), the nuclear virial theorem in terms of the total wave function is

$$\langle T_n^{\circ} \rangle_0 = -\frac{1}{2} \langle V_{nn}^{\circ} \rangle_0 + \frac{1}{2} \sum_{\substack{i=1 \\ i \neq p}}^n \left\langle \underline{R}_i^{\circ} \cdot \frac{\partial V_{ne}^{\circ}}{\partial \underline{R}_i^{\circ}} \right\rangle_0.$$

(I.6)

2. The Virial Theorem In Terms Of The Total Wave Function For Electronic Equation

The expectation value of the electronic kinetic energy is

$$\langle T_e^0 \rangle = \frac{\int \int d^{3N} \underline{r}^0 \Phi_{oe}^*(\underline{r}^0, \underline{R}^0) T_e^0 \Phi_{oe}(\underline{r}^0, \underline{R}^0)}{\int \int d^{3N} \underline{r}^0 \Phi_{oe}^* \Phi_{oe}}^{-1} \quad (\text{I.7})$$

Equation (I.7) can be expressed by

$$\begin{aligned} & \int \int d^3 \underline{c} d^{3(n-1)} \underline{R}^0 \Phi_{oT}^* \Phi_{on}^* \langle T_e^0 \rangle \Phi_{oT} \Phi_{on} \\ & \int \int d^3 \underline{c} d^{3(n-1)} \underline{R}^0 \Phi_{oT}^* \Phi_{on}^* \Phi_{oT} \Phi_{on} \}^{-1} \\ & = \int \int d^3 \underline{c} d^{3(n-1)} \underline{R}^0 \Phi_{oT}^* \Phi_{on}^* \left[\int d^{3N} \underline{r}^0 \Phi_{oe}^*(\underline{r}^0, \underline{R}^0) T_e^0 \Phi_{oe}(\underline{r}^0, \underline{R}^0) \right] \\ & \quad \Phi_{oT} \Phi_{on} \} \\ & \int \int d^3 \underline{c} d^{3(n-1)} \underline{R}^0 \Phi_{oT}^* \Phi_{on}^* \Phi_{oT}^* \Phi_{oe}^* \Phi_{oT} \Phi_{on} \Phi_{oe} \}^{-1} \\ & = \int \int d^3 \underline{c} d^{3N} \underline{r}^0 d^{3(n-1)} \underline{R}^0 \Phi_{oT}^* \Phi_{oe}^* \Phi_{on}^* T_e \Phi_{oT} \Phi_{oe} \Phi_{on} \} \\ & \int \int d^3 \underline{c} d^{3N} \underline{r}^0 d^{3(n-1)} \underline{R}^0 \Phi_{oT}^* \Phi_{oe}^* \Phi_{oe}^* \Phi_{oT} \Phi_{oe} \Phi_{oe} \}^{-1} \\ & = \langle T_e^0 \rangle_0 \quad (\text{I.8}) \end{aligned}$$

Similarly the expectation value of the $\sum_{\alpha=1}^N \left(\underline{r}_{\alpha}^0 \cdot \frac{\partial V_e^0}{\partial \underline{r}_{\alpha}^0} \right)$ can be expressed as

$$\begin{aligned} & \int \int d^3 \underline{c} d^{3(n-1)} \underline{R}^0 \Phi_{oT}^* \Phi_{on}^* \left\langle \sum_{\alpha=1}^N \underline{r}_{\alpha}^0 \cdot \frac{\partial V_e^0}{\partial \underline{r}_{\alpha}^0} \right\rangle \Phi_{oT} \Phi_{on} \} \\ & \int \int d^3 \underline{c} d^{3(n-1)} \underline{R}^0 \Phi_{oT}^* \Phi_{on}^* \Phi_{oT} \Phi_{on} \}^{-1} \\ & = \sum_{\alpha=1}^N \langle \underline{r}_{\alpha}^0 \cdot \frac{\partial V_e^0}{\partial \underline{r}_{\alpha}^0} \rangle_0 \quad (\text{I.9}) \end{aligned}$$

For a Coulomb potential it is shown in the Appendix A that

$$V_{ee}^{\circ} = \frac{1}{2} \sum_{\alpha \neq \beta=1}^N \frac{e^2}{|\underline{r}_{\alpha}^{\circ} - \underline{r}_{\beta}^{\circ}|} = \frac{1}{2} \sum_{\alpha \neq \beta=1}^N \frac{e^2}{|\underline{r}_{\alpha} - \underline{r}_{\beta}|} = V_{ee} \quad ,$$

and therefore

$$\sum_{\alpha=1}^N \underline{r}_{\alpha}^{\circ} \cdot \frac{\partial V_{ee}^{\circ}}{\partial \underline{r}_{\alpha}^{\circ}} = -V_{ee}^{\circ} \quad .$$

The virial theorem in the electronic coordinate for a Coulomb potential reduces to

$$\langle T_e^{\circ} \rangle_0 = -\frac{1}{2} \langle V_{ee}^{\circ} \rangle_0 + \frac{1}{2} \sum_{\alpha=1}^N \langle \underline{r}_{\alpha}^{\circ} \cdot \frac{\partial V_{ne}^{\circ}}{\partial \underline{r}_{\alpha}^{\circ}} \rangle_0 \quad (I.10)$$

Adding Equations (I.6) and (I.10) the following is obtained

$$\begin{aligned} \langle T_n^{\circ} \rangle_0 + \langle T_e^{\circ} \rangle_0 &= -\frac{1}{2} \langle V_{ee}^{\circ} \rangle_0 - \frac{1}{2} \langle V_{nn}^{\circ} \rangle_0 \\ &+ \frac{1}{2} \sum_{\alpha=1}^N \langle \underline{r}_{\alpha}^{\circ} \cdot \frac{\partial V_{ne}^{\circ}}{\partial \underline{r}_{\alpha}^{\circ}} \rangle_0 \\ &+ \frac{1}{2} \sum_{\substack{i=1 \\ i \neq P}}^n \langle \underline{R}_i^{\circ} \cdot \frac{\partial V_{ne}^{\circ}}{\partial \underline{R}_i^{\circ}} \rangle_0 \quad (I.11) \end{aligned}$$

Since in the ground state the center of mass energy is zero, it follows that

$$\langle \overline{T} \rangle_0 = 0, \quad (\text{I.12})$$

and so

$$\langle T_n^0 \rangle_0 + \langle T_e^0 \rangle_0 = \langle T^0 \rangle_0, \quad (\text{I.13})$$

where T is the total kinetic energy of the system. Equation (I.11) becomes

$$\begin{aligned} \langle T^0 \rangle_0 &= -\frac{1}{2} \langle V_{ee}^0 \rangle_0 - \frac{1}{2} \langle V_{nn}^0 \rangle_0 \\ &\quad + \frac{1}{2} \sum_{\alpha=1}^N \langle \underline{r}_{\alpha}^0 \cdot \frac{\partial V_{ne}^0}{\partial \underline{r}_{\alpha}^0} \rangle_0 + \frac{1}{2} \sum_{\substack{i=1 \\ i \neq p}}^n \langle \underline{R}_i^0 \cdot \frac{\partial V_{ne}^0}{\partial \underline{R}_i^0} \rangle_0 \end{aligned} \quad (\text{I.14})$$

which will be shown to reduce to the virial theorem. The gradient of V_{ne}^0 with respect to the electronic coordinates is

$$\begin{aligned} \frac{\partial V_{ne}^0}{\partial \underline{r}_{\alpha}^0} &= \frac{\partial}{\partial \underline{r}_{\alpha}^0} \left[-\frac{1}{2} \sum_{\beta=1}^N \sum_{i=1}^n \frac{Z_i e^2}{|\underline{r}_{\alpha}^0 - \underline{R}_i^0|} - \frac{1}{2} \sum \frac{Z_p e^2}{|\underline{r}_{\alpha}^0 + \frac{1}{m_p} \sum_{\substack{k=1 \\ k \neq p}}^n m_k \underline{R}_k^0|} \right] \\ &= -\frac{1}{2} \sum_{\substack{i=1 \\ i \neq p}}^n \frac{\underline{r}_{\alpha}^0 \cdot (\underline{r}_{\alpha}^0 - \underline{R}_i^0) Z_i e^2}{|\underline{r}_{\alpha}^0 - \underline{R}_i^0|^3} \\ &\quad - \frac{1}{2} (\underline{r}_{\alpha}^0) \cdot \frac{(\underline{r}_{\alpha}^0 + \frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^0)}{|\underline{r}_{\alpha}^0 + \frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^0|^3} \end{aligned} \quad (\text{I.15})$$

Equation (I.15) gives

$$\sum_{\alpha=1}^N \frac{\partial V_{ne}^0}{\partial \underline{r}_{\alpha}^0} = -\frac{1}{2} \sum_{\alpha=1}^N \sum_{\substack{i=1 \\ i \neq p}}^n \left[\frac{\underline{r}_{\alpha}^0 \cdot (\underline{r}_{\alpha}^0 - \underline{R}_i^0) Z_i e^2}{|\underline{r}_{\alpha}^0 - \underline{R}_i^0|^3} \right] \\ - \frac{1}{2} \sum_{\alpha=1}^N \left[\frac{\underline{r}_{\alpha}^0 \cdot \left(\underline{r}_{\alpha}^0 + \frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^0 \right) Z_p e^2}{\left| \underline{r}_{\alpha}^0 + \frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^0 \right|^3} \right] \quad (I.16)$$

Also the gradient of V_{en}^0 with respect to the nuclear coordinates

$$\text{is } \frac{\partial V_{ne}^0}{\partial \underline{R}_i^0} = \frac{\partial}{\partial \underline{R}_i^0} \left[-\frac{1}{2} \sum_{\alpha=1}^N \sum_{\substack{l=1 \\ l \neq p}}^n \frac{Z_l e^2}{|\underline{r}_{\alpha}^0 - \underline{R}_l^0|} - \frac{1}{2} \sum_{\alpha=1}^N \frac{Z_p e^2}{\left| \underline{r}_{\alpha}^0 + \frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^0 \right|} \right] \\ = -\frac{1}{2} \sum_{\alpha=1}^N \left[\frac{-\underline{R}_i^0 \cdot (\underline{r}_{\alpha}^0 - \underline{R}_i^0) Z_i e^2}{|\underline{r}_{\alpha}^0 - \underline{R}_i^0|^3} \right] \\ - \frac{1}{2} \sum_{\alpha=1}^N \frac{m_i \underline{R}_i^0 \cdot \left(\underline{r}_{\alpha}^0 + \frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^0 \right) Z_p e^2}{\left| \underline{r}_{\alpha}^0 + \frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^0 \right|^3} \quad (I.17)$$

Therefore

$$\sum_{\substack{i=1 \\ i \neq p}}^n \frac{\partial V_{ne}^0}{\partial \underline{R}_i^0} \cdot \underline{R}_i^0 = -\frac{1}{2} \sum_{\alpha=1}^N \sum_{\substack{i=1 \\ i \neq p}}^n \frac{\underline{R}_i^0 \cdot (\underline{R}_i^0 - \underline{r}_{\alpha}^0) Z_i e^2}{|\underline{r}_{\alpha}^0 - \underline{R}_i^0|^3} \\ - \frac{1}{2} \sum_{\alpha=1}^N \frac{\left(\sum_{\substack{i=1 \\ i \neq p}}^n m_i \underline{R}_i^0 \right) \cdot \left[\underline{r}_{\alpha}^0 + \frac{1}{m_p} \left(\sum_{k \neq p}^n m_k \underline{R}_k^0 \right) \right]}{\left| \underline{r}_{\alpha}^0 + \frac{1}{m_p} \sum_{k \neq p}^n m_k \underline{R}_k^0 \right|^3} \quad (I.18)$$

Adding (I.17) and (I.18) to obtain

$$\sum_{\alpha=1}^N r_{\alpha}^{\circ} \cdot \frac{\partial V_{ne}^{\circ}}{\partial r_{\alpha}^{\circ}} + \sum_{i=1}^n R_{\tilde{n}i}^{\circ} \cdot \frac{\partial V_{ne}^{\circ}}{\partial R_{\tilde{n}i}^{\circ}} = -V_{ne}^{\circ} \quad (\text{I.19})$$

Thus Equation (I.14) reduces to the virial theorem

$$\langle T^{\circ} \rangle_0 = -\frac{1}{2} \langle V_{nn}^{\circ} \rangle_0 - \frac{1}{2} \langle V_{ee}^{\circ} \rangle_0 - \frac{1}{2} \langle V_{ne}^{\circ} \rangle_0 \quad (\text{I.20})$$

or

$$\langle T \rangle = -\frac{1}{2} \langle V \rangle \quad (\text{I.21})$$

APPENDIX J

VIRIAL THEOREM IN BOA FROM A TRIAL FUNCTION

1. Virial Theorem for Electronic Equation

The expectation value of the electronic Hamiltonian with respect to a scaled function given in the Equation (7.6) gives

$$\begin{aligned}
 E_e[\eta, \{R^0\}] &= \left\{ \int d^{3N} \underline{r}^0 \eta_1^3 \dots \eta_N^3 \right. \\
 &\quad \Psi_e^* (\eta_1 \underline{r}_1^0 \dots \eta_N \underline{r}_N^0, \xi_1 R_1^0, \dots, \xi_{p-1} R_{p-1}^0, \xi_{p+1} R_{p+1}^0, \dots, \xi_n R_n^0) \\
 &\quad \left. \text{He}^0 \Psi_e (\eta_1 \underline{r}_1^0 \dots \eta_N \underline{r}_N^0, \xi_1 R_1^0, \dots, \xi_{p-1} R_{p-1}^0, \xi_{p+1} R_{p+1}^0, \dots, \xi_n R_n^0) \right\} \\
 &= \left\{ \int d^{3N} \underline{r}^0 \eta_1^3 \dots \eta_N^3 \Psi_e^* \Psi_e \right\}^{-1}
 \end{aligned}$$

(J.1)

Making the transformation

$$\eta_\alpha \underline{r}_\alpha^0 = \underline{r}_\alpha', \quad \alpha = 1 \dots N,$$

one gets

$$E_e[\eta, \mathbb{R}^0]$$

$$= \left\{ \int d^{2N} \underline{x}' \Psi_e^*(\underline{x}', \mathbb{R}^0) \left[-\frac{\hbar^2}{2} \left(\frac{1}{m} + \frac{1}{M_0} \right) \sum_{\alpha=1}^N \eta_\alpha^2 \frac{\partial^2}{\partial x_\alpha'^2} - \frac{\hbar^2}{2M_0} \sum_{\alpha \neq \beta}^N \eta_\alpha \eta_\beta \frac{\partial}{\partial x_\alpha'} \frac{\partial}{\partial x_\beta'} \right] + V_e \left(\frac{x'_1}{\eta_1}, \dots, \frac{x'_N}{\eta_N} \right) \cdot \Psi_e(\eta \underline{x}', \mathbb{R}^0) \right\}$$

$$\left\{ \int d^{3N} \underline{x}' \Psi_e^*(\underline{x}', \mathbb{R}^0) \Delta \Psi_e(\eta \underline{x}', \mathbb{R}^0) \right\}^{-1}$$

(J.2)

The Equation (7.7) now can be expressed as

$$\begin{aligned} 0 &= \sum_{\alpha=1}^N \eta_\alpha \frac{\partial E_e}{\partial \eta_\alpha} \\ &= \left\{ \int d^{3N} \underline{x}' \Psi_e^*(\underline{x}', \mathbb{R}^0) \left[2T_e^0 + \sum_{\alpha=1}^N \eta_\alpha \frac{\partial V_e^0}{\partial \eta_\alpha} \right] \Psi_e(\underline{x}', \mathbb{R}^0) \right\} \\ &\quad \left\{ \int d^{3N} \underline{x}' \Psi_e^* \Delta \Psi_e \right\}^{-1} \\ &+ \left\{ \int d^{3N} \underline{x}' \Psi_e^* H_e^0 \sum_{\alpha=1}^N \eta_\alpha \frac{\partial}{\partial \eta_\alpha} \Delta \Psi_e \right\} \left\{ \int d^{3N} \underline{x}' \Psi_e^* \Delta \Psi_e \right\}^{-1} \\ &+ \left\{ \int d^{3N} \underline{x}' \Psi_e^* H_e^0 \Delta \Psi_e \right\} \left\{ \int d^{3N} \underline{x}' \Psi_e^* \Delta \Psi_e \right\}^{-2} \\ &\quad \left\{ \int d^{3N} \underline{x}' \Psi_e^* \sum_{\alpha=1}^N \eta_\alpha \frac{\partial}{\partial \eta_\alpha} \Delta \Psi_e \right\} \end{aligned}$$

Following the derivation in Appendix D it can be shown that

$$\frac{\partial}{\partial \eta_\alpha} A \Psi_e = 0 \quad . \quad (J.4)$$

Thus Equation (J.3) becomes

$$0 = \left\{ \int d^{3N} \underline{r}' \Psi_e^* \left[2 T_e^0 + \sum_{\alpha=1}^N \eta_\alpha \frac{\partial V_e^0}{\partial \eta_\alpha} \right] A \Psi_e \right\} \\ \left\{ \int d^{3N} \underline{r}' \Psi_e^* A \Psi_e \right\}^{-1} .$$

$$0 = 2 \langle T_e^0 \rangle + \left\{ \int d^{3N} \underline{r}' \Psi_e^* \sum_{\alpha=1}^N \eta_\alpha \frac{\partial V_e^0}{\partial \eta_\alpha} A \Psi_e \right\} \\ \left\{ \int d^{3N} \underline{r}' \Psi_e^* A \Psi_e \right\}^{-1} . \quad (J.5)$$

For $V_e = V_{ee} + V_{ne}$ the derivative is

$$\sum_{\alpha=1}^N \eta_\alpha \frac{\partial V_e}{\partial \eta_\alpha} = \sum_{\alpha=1}^N \eta_\alpha \frac{\partial V_{ee}}{\partial \eta_\alpha} + \sum_{\alpha=1}^N \eta_\alpha \frac{\partial V_{ne}}{\partial \eta_\alpha} . \quad (J.6)$$

For the electronic Coulomb potential given by Equation (5.15)

$$V_{ee} = \frac{1}{2} \sum_{\alpha \neq \beta=1}^N \frac{e^2}{\left| \frac{\underline{r}'_\alpha}{\eta_\alpha} - \frac{\underline{r}'_\beta}{\eta_\beta} \right|} .$$

(J.7)

So the derivative is

$$\frac{\partial V_{ee}^c}{\partial \eta_\alpha} = \frac{1}{2} \frac{\partial}{\partial \eta_\alpha} \sum_{\dagger \neq \beta=1}^N \frac{e^2}{\left| \frac{r_\alpha'}{\eta_\alpha} - \frac{r_\beta'}{\eta_\beta} \right|} \quad (\text{J.8})$$

$$= \frac{1}{2} \sum_{\beta \neq \alpha} \frac{r_\alpha'}{\eta_\alpha^2} \cdot \left(\frac{r_\alpha'}{\eta_\alpha} - \frac{r_\beta'}{\eta_\beta} \right) \frac{e^2}{\left| \frac{r_\alpha'}{\eta_\alpha} - \frac{r_\beta'}{\eta_\beta} \right|^3} \\ + \frac{1}{2} \sum_{\dagger \neq \alpha} \frac{r_\alpha'}{\eta_\alpha^2} \cdot \left(-\frac{r_\dagger}{\eta_\dagger} + \frac{r_\alpha'}{\eta_\alpha} \right) \frac{e^2}{\left| \frac{r_\dagger}{\eta_\dagger} - \frac{r_\alpha'}{\eta_\alpha} \right|^3} \quad (\text{J.9})$$

Interchanging $\alpha \rightarrow \beta$ and $\dagger \rightarrow \alpha$ in the second term, the Equation (J.9) gives

$$\sum_{\alpha=1}^N \eta_\alpha \frac{\partial V_{ee}^c}{\partial \eta_\alpha} = \frac{1}{2} \sum_{\alpha \neq \beta=1}^N \frac{r_\alpha'}{\eta_\alpha} \cdot \left(\frac{r_\alpha'}{\eta_\alpha} - \frac{r_\beta'}{\eta_\beta} \right) \frac{e^2}{\left| \frac{r_\alpha'}{\eta_\alpha} - \frac{r_\beta'}{\eta_\beta} \right|^3} \\ + \frac{1}{2} \sum_{\alpha \neq \beta=1}^N \frac{r_\beta'}{\eta_\beta} \cdot \left(\frac{r_\beta'}{\eta_\beta} - \frac{r_\alpha'}{\eta_\alpha} \right) \frac{e^2}{\left| \frac{r_\beta'}{\eta_\beta} - \frac{r_\alpha'}{\eta_\alpha} \right|^3} \\ = \frac{1}{2} \sum_{\alpha \neq \beta=1}^N \frac{e^2}{\left| \frac{r_\alpha'}{\eta_\alpha} - \frac{r_\beta'}{\eta_\beta} \right|} \\ = V_{ee}^o \quad (\text{J.10})$$

For a general electronic potential the derivative is

$$\sum_{\alpha=1}^N \eta_{\alpha} \frac{\partial V_{ee}^{\circ}}{\partial \eta_{\alpha}} = - \sum_{\alpha=1}^N \frac{r_{\alpha}'}{\eta_{\alpha}} \frac{\partial V_{ee}^{\circ} \left(\frac{r_1'}{\eta_1} \dots \frac{r_N'}{\eta_N} \right)}{\partial \left(\frac{r_{\alpha}'}{\eta_{\alpha}} \right)}, \quad (\text{J.11})$$

and

$$\sum_{\alpha=1}^N \eta_{\alpha} \frac{\partial V_{ne}^{\circ}}{\partial \eta_{\alpha}} = \sum_{\alpha=1}^N \frac{r_{\alpha}'}{\eta_{\alpha}} \cdot \frac{\partial V_{ne}^{\circ} \left(\frac{r_1'}{\eta_1} \dots \frac{r_N'}{\eta_N}, R^{\circ} \right)}{\partial \left(\frac{r_{\alpha}'}{\eta_{\alpha}} \right)}, \quad (\text{J.12})$$

where V_{ne} is the nuclear electronic potential energy.

Substituting in Equation (J.5) from (J.11) and (J.12)

the virial theorem follows

$$\langle T_e^{\circ} \rangle_{\eta} = \frac{1}{2} \sum_{\alpha=1}^N \left\langle \frac{r_{\alpha}^{\circ}}{\eta_{\alpha}^{\circ}} \cdot \frac{\partial V_{ee}^{\circ}}{\partial \eta_{\alpha}^{\circ}} \right\rangle_{\eta} + \frac{1}{2} \sum_{\alpha=1}^N \left\langle \frac{r_{\alpha}^{\circ}}{\eta_{\alpha}^{\circ}} \cdot \frac{\partial V_{ne}^{\circ}}{\partial \eta_{\alpha}^{\circ}} \right\rangle_{\eta}. \quad (\text{J.15})$$

For a Coulomb potential it is

$$\langle T_e^{\circ} \rangle_{\eta} = -\frac{1}{2} \langle V_{ee}^{\circ} \rangle_{\eta} + \frac{1}{2} \sum_{\alpha=1}^N \left\langle \frac{r_{\alpha}^{\circ}}{\eta_{\alpha}^{\circ}} \cdot \frac{\partial V_{ne}^{\circ}}{\partial \eta_{\alpha}^{\circ}} \right\rangle_{\eta} \quad (\text{J.16})$$

2. Virial Theorem For Nuclear Equation

For a scaled function the energy in Equation (7.14) is

$$\begin{aligned}
 E[\xi] = & \int \int d^{3(n-1)} \underline{R}^0 \xi_1^3 \dots \xi_{p-1}^3 \xi_{p+1}^3 \dots \xi_n^3 \\
 & \Psi_n^* (\xi_1 \underline{R}_1^0 \dots \xi_{p-1} \underline{R}_{p-1}^0 \xi_{p+1} \underline{R}_{p+1}^0 \dots \xi_n \underline{R}_n^0) \\
 & H_n^0 Q \Psi_n (\xi_1 \underline{R}_1^0 \dots \xi_{p-1} \underline{R}_{p-1}^0 \xi_{p+1} \underline{R}_{p+1}^0 \dots \xi_n \underline{R}_n^0) \Big\} \\
 & \int \int d^{3(n-1)} \underline{R}^0 \xi_1^3 \dots \xi_{p-1}^3 \xi_{p+1}^3 \dots \xi_n^3 \\
 & \Psi_n^* (\xi_1 \underline{R}_1^0 \dots \xi_{p-1} \underline{R}_{p-1}^0 \xi_{p+1} \underline{R}_{p+1}^0 \dots \xi_n \underline{R}_n^0) \\
 & Q \Psi_n (\xi_1 \underline{R}_1^0 \dots \xi_{p-1} \underline{R}_{p-1}^0 \xi_{p+1} \underline{R}_{p+1}^0 \dots \xi_n \underline{R}_n^0) \Big\}^{-1}
 \end{aligned}
 \tag{J.17}$$

For $\xi_i \underline{R}_i^0 = \underline{R}_i'$, $i = 1 \dots p-1, p+1 \dots n$,

(J.18)

the Equation (J.18) reduces to

$$\begin{aligned}
E[\xi] = & \left\{ \int d^{3(n-1)} \underline{R}' \Psi_n^* (\underline{R}') \right. \\
& \left[-\frac{\hbar^2}{2} \sum_{\substack{k=1 \\ k \neq p}}^n \left(\frac{1}{m_k} - \frac{1}{m_0} \right) \eta_k^2 \frac{\partial^2}{\partial \underline{R}'_k{}^2} \right. \\
& \left. + \frac{\hbar^2}{2} \sum_{\substack{k \neq l=1 \\ k, l \neq p}}^n \eta_k \eta_l \frac{\partial}{\partial \underline{R}'_k} \cdot \frac{\partial}{\partial \underline{R}'_l} + V_n^0 + E_e \right] \\
& \left. \int d^{3(n-1)} \underline{R}' \Psi_n^* \Psi_n \right\}^{-1} \\
& \left\{ \int d^{3(n-1)} \underline{R}' \Psi_n^* \Psi_n \right\}^{-1}
\end{aligned} \tag{J.19}$$

The Equation (J-19) gives on differentiation

$$\begin{aligned}
0 = & \sum_{\substack{i=1 \\ i \neq p}}^n \xi_i \frac{\partial E}{\partial \xi_i} \\
= & \left\{ \int d^{3(n-1)} \underline{R}' \Psi_n^* \left[2 T_n^0 + \sum_{\substack{i=1 \\ i \neq p}}^n \xi_i \frac{\partial V_n^0}{\partial \xi_i} \right] \Psi_n \right\} \\
& \left\{ \int d^{3(n-1)} \underline{R}' \Psi_n^* \Psi_n \right\}^{-1},
\end{aligned} \tag{J.20}$$

where

$$\sum_{\substack{i=1 \\ i \neq p}}^n \xi_i \frac{\partial V_n^0}{\partial \xi_i} = - \sum_{i=1}^n \frac{R_i^0}{\xi_i} \cdot \frac{\partial V_n^0}{\partial \left(\frac{R_i^0}{\xi_i} \right)}, \tag{J.21}$$

and

$$\sum_{\substack{i=1 \\ i \neq p}}^n \xi_i \frac{\partial E_e}{\partial \xi_i} = - \sum_{\substack{i=1 \\ i \neq p}}^n \frac{R_i^1}{\xi_i} \frac{\partial E_e}{\partial \left(\frac{R_i^1}{\xi_i} \right)}. \tag{J.22}$$

Thus the virial theorem

$$\begin{aligned} \langle T_n^0 \rangle_{\mathfrak{Z}} &= \frac{1}{2} \sum_{\substack{i=1 \\ i \neq p}}^n \left\langle R_{\tilde{r}_i^0} \cdot \frac{\partial V_{nn}^0}{\partial R_{\tilde{r}_i^0}} \right\rangle_{\mathfrak{Z}} \\ &+ \frac{1}{2} \sum_{\substack{i=1 \\ i \neq p}}^n \left\langle R_{\tilde{r}_i^0} \cdot \frac{\partial E_e}{\partial R_{\tilde{r}_i^0}} \right\rangle_{\mathfrak{Z}} \end{aligned} \quad (\text{J.23})$$

is obtained.

For a Coulomb potential it is shown in the Equation (H28) of Appendix H that

$$\sum_{\substack{i=1 \\ i \neq p}}^n R_{\tilde{r}_i^0} \cdot \frac{\partial V_{nn}^0}{\partial R_{\tilde{r}_i^0}} = - V_{nn}^0, \quad (\text{J.24})$$

so the Equation (J.24) becomes

$$\begin{aligned} \langle T_n^0 \rangle_{\mathfrak{Z}} &= - \frac{1}{2} \langle V_{nn}^0 \rangle_{\mathfrak{Z}} \\ &+ \frac{1}{2} \sum_{\substack{i=1 \\ i \neq p}}^n \left\langle R_{\tilde{r}_i^0} \cdot \frac{\partial E_e}{\partial R_{\tilde{r}_i^0}} \right\rangle_{\mathfrak{Z}} \end{aligned}$$

(J.25)

REFERENCES AND NOTES

1. H. Goldstein, Classical Mechanics (Addison-Wesley Publishing Co., Reading Mass., 1950), p. 69ff.
2. M. Born, W. Heisenberg, and P. Jordan [Z. Physik 35, 557 (1926)] prove the virial theorem in quantum mechanics for homogeneous potential in their Equation (17). J. C. Slater [J. Chem. Phys. 1, 687 (1933)] proves the quantum mechanical virial theorem for an arbitrary potential in his Appendix. E. Merzbacher, Quantum Mechanics (John Wiley and Sons Inc., New York, 1970), p. 168ff., gives the proof of virial theorem for a single particle system.
3. V. Fock, Z. Physik 54, 347 (1930).
4. E. A. Hylleraas [Z. Physik 54, 347 (1929)] introduced the scaled wave function in his treatment of the helium atom.
5. J. C. Slater [J. Chem. Phys. 1, 687 (1933)]; Quantum Theory of Matter (McGraw-Hill Book Company, New York, 1968) p. 400ff. In his derivation of the virial theorem for the case of fixed nuclei, he includes the external applied forces F_{α} , which act on the nuclei to hold

them at rest. His form of the virial theorem is

$$\langle T_e \rangle + \frac{1}{2} \langle V_e \rangle + \frac{1}{2} \sum_{i=1}^n \langle \vec{R}_i \cdot \frac{\partial E_e}{\partial \vec{R}_i} \rangle = 0,$$

which does not have the external forces. However, he

interprets $-\frac{\partial E_e}{\partial \vec{R}_i}$ as the external force. If the external forces acting on the nuclei are present, the virial theorem for a molecule would be

$$\langle T \rangle = -\frac{1}{2} \langle V \rangle - \frac{1}{2} \sum_{i=1}^n \langle \vec{R}_i \cdot \vec{F}_i \rangle.$$

As shown in the section III for the electrons, the virial theorem is

$$\langle T_e \rangle = \frac{1}{2} \sum_{\alpha=1}^N \langle \vec{r}_\alpha \cdot \frac{\partial V_e}{\partial \vec{r}_\alpha} \rangle,$$

where $V_e = V_{ee} + V_{ne}$. For the nuclei the

virial theorem is

$$\langle T_n \rangle = \frac{1}{2} \sum_{i=1}^n \langle \vec{R}_i \cdot \frac{\partial V_n}{\partial \vec{R}_i} \rangle - \frac{1}{2} \sum_{i=1}^n \langle \vec{R}_i \cdot \vec{F}_i \rangle,$$

where

$$V_n = V_{nn} + V_{ne}.$$

If the nuclei are held fixed by the external forces, then

$$\langle T_n \rangle = 0, \text{ and the two terms on the right side}$$

cancel. Thus there is no external force appearing

in the virial theorem for the electrons when the nuclei are held fixed.

6. P. O. Löwdin, J. Mol. Spect. 3, 46 (1959).
7. R. T. Brown, J. Chem. Phys. 48, 4698 (1968).
8. A. Fröman, J. Chem. Phys. 36, 1490 (1962).

9. In Ref. 6, Löwdin uses a scaled wave function in which both the electronic and nuclear coordinates are scaled by a single parameter η . In the case of fixed nuclei in a diatomic molecule this procedure leads to the relation

$$\langle T_e \rangle + \frac{1}{2} \langle V_e \rangle + \frac{1}{2} \underline{R} \cdot \frac{\partial E_e}{\partial \underline{R}} = 0,$$

where \underline{R} is internuclear distance.

10. E. C. Herrmann [Chem. Phys. Letters 1, 253 (1967)] used a single scaling parameter in a trial function and extended the proof of the virial theorem to an arbitrary potential. In the case of fixed nuclei he also obtained the result

$$\langle T_e \rangle + \frac{1}{2} \langle V_e \rangle + \frac{1}{2} \sum_{i=1}^n \underline{R}_i \cdot \frac{\partial E_e}{\partial \underline{R}_i} = 0.$$

11. See Section IV.
12. J. C. Slater, Quantum Theory of Matter (McGraw-Hill Book Company, New York, 1968), p. 378ff.
13. The transformation of the volume element in the space fixed system to the body fixed system is given by

$$d_{\underline{r}}^{3N} d_{\underline{R}}^{3n} = d_{\underline{r}^0}^{3N} d_{\underline{c}}^3 d_{\underline{R}^0}^{3(n-1)} J \left(\frac{\underline{r}_1^0 \dots \underline{r}_N^0 \underline{c} \underline{R}_1^0 \dots \underline{R}_{P-1}^0 \underline{R}_{P+1}^0 \dots \underline{R}_n^0}{\underline{r}_1 \dots \underline{r}_N \underline{R}_1 \dots \underline{R}_n} \right)$$

where the Jacobian of transformation

$$J \left(\frac{\underline{r}_1^0 \dots \underline{r}_N^0 \underline{c} \underline{R}_1^0 \dots \underline{R}_{P-1}^0 \underline{R}_{P+1}^0 \dots \underline{R}_n^0}{\underline{r}_1 \dots \underline{r}_N \underline{R}_1 \dots \underline{R}_n} \right) = \text{Constant}.$$

Thus the Jacobian of the transformation does not depend on the variables of integration. The expectation value of an operator A in the space fixed coordinate system

is

$$\langle A \rangle = \frac{\int d^{3N} \underline{r} d^{3n} \underline{R} \Phi_0^*(\underline{r}, \underline{R}) A(\underline{r}, \underline{R}) \Phi_0(\underline{r}, \underline{R})}{\int d^{3N} \underline{r} d^{3n} \underline{R} \Phi_0^*(\underline{r}, \underline{R}) \Phi_0(\underline{r}, \underline{R})},$$

and in the body fixed coordinate system is

$$\langle A \rangle = \frac{J \int d^3 \underline{c} d^{3N} \underline{r}^0 d^{3(n-1)} \underline{R}^0 \Phi_0^*(\underline{c}, \underline{r}^0, \underline{R}^0) A(\underline{c}, \underline{r}^0, \underline{R}^0) \Phi_0(\underline{c}, \underline{r}^0, \underline{R}^0)}{J \int d^3 \underline{c} d^{3N} \underline{r}^0 d^{3(n-1)} \underline{R}^0 \Phi_0^*(\underline{c}, \underline{r}^0, \underline{R}^0) \Phi_0(\underline{c}, \underline{r}^0, \underline{R}^0)}.$$

The Jacobian of the transformation cancels out.

14. K. Huang, Statistical Mechanics (John Wiley and Sons, Inc., New York, 1963), p. 150ff.
15. D. H. Kobe and M. A. Ranade, "Hypervirial Theorem in Statistical Mechanics," 1971 (unpublished).