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VIRIAL THEOREM IN ADIABATIC REPRESENTATION

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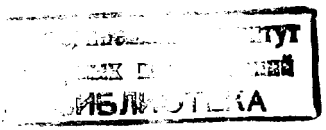

We shall consider an isolated three-particle Coulomb system, two nuclei with the coordinate vectors $\vec{R}_1$ and $\vec{R}_2$ and an electron with vector $\vec{R}_3$. Let further Z_1, Z_2 and e be the charges and M_1, M_2, M_3 the masses of the particles. The center of mass motion is separated in coordinates

$$\vec{R} = \frac{M_1\vec{R}_1 + M_2\vec{R}_2 + M_3\vec{R}_3}{M_1 + M_2 + M_3} \qquad \vec{R} = \vec{R}_2 - \vec{R}_1$$

$$\vec{r} = \vec{R}_3 - \frac{M_1\vec{R}_1 + M_2\vec{R}_2}{M_1 + M_2} \qquad (1)$$

then the internal motion of the system can be described by an internal Hamiltonian

$$H_1 = -\frac{1}{2M}\Delta_{\vec{R}} + \frac{Z_1Z_2}{R} + H_0, \qquad (2)$$

$$H_0 = -\frac{1}{2}\Delta_{\vec{r}} - \frac{Z_1}{r_1} - \frac{Z_2}{r_2}. \qquad (3)$$

Here we introduced the system of units $\hbar = m = e = 1$ and the notation

$$\frac{1}{M} = \frac{1}{M_1} + \frac{1}{M_2} \qquad \frac{1}{m} = \frac{1}{M_3} + \frac{1}{M_1 + M_2}$$

$$\vec{r}_1 = \vec{R}_1 - \vec{R}_3. \qquad \vec{r}_2 = \vec{R}_2 - \vec{R}_3.$$

Then if Ψ_I is a bound-state solution of the equation

$$H_I \Psi_I(\vec{R},\vec{r}) = E \Psi_I(\vec{R},\vec{r}) \tag{4}$$

we have /1/

$$< \Psi_I | [(\vec{R}\nabla_{\vec{R}} + \vec{r}\nabla_{\vec{r}}), H_I] | \Psi_I > = 0 \tag{5}$$

which yields the virial theorem of the general type

$$2 < T_I > + < V_I > = 0 . \tag{6}$$

The adiabatic approach to the problem (4) arises from the expansion

$$\Psi_I(\vec{R},\vec{r}) = \sum_k \Psi_k(\vec{R})\,\phi_k(\vec{r};R), \tag{7}$$

where adiabatic set $\phi_k(\vec{r};R)$ is received from the solution of the Shrödinger equation

$$H\ \phi_k(\vec{r};R) = E_k(R)\,\phi_k(\vec{r};R). \tag{8}$$

If the prolate spheroidal coordinates $\xi = (r_1+r_2)/R$, $\eta = (r_1-r_2)/R$ and ϕ are used to solve the equation (8), then similarly to (5)*

$$< \phi_k | [(\vec{R}\nabla_{\vec{R}} + \vec{r}\nabla_{\vec{r}}),\ H_0] | \phi_k > = < \phi_k | \frac{\partial H_0}{\partial R} | \phi_k > R . \tag{9}$$

It is straightforward to derive from (9) the virial theorem in the form of Slater /2/

$$2 < k | T_0 | k > + < k | V_0 | k > + R \frac{dE_k}{dR} = 0 . \tag{10}$$

In what follows we construct the second virial theorem based on the adiabatic expansion (7). The Schrödinger equation

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* This follows from $\vec{R}\nabla_{\vec{R}} + \vec{r}\nabla_{\vec{r}} = R(\frac{\partial}{\partial R})_{\xi\eta}$, which can be extracted, for example, from a paper /3/.

(4) can be integrated over $\vec{r}$ if the $\phi_k(\vec{r};R)$ are known, becoming /4/.

$$(-\frac{1}{2M}\Delta_{\vec{R}} + E_n(R) + \frac{Z_1 Z_2}{R} - E)\,\psi_n(\vec{R})$$

$$= -\frac{1}{2M}\sum_m [2\vec{Q}_{nm}(\vec{R})\nabla_{\vec{R}} + K_{nm}(\vec{R})]\,\psi_m(\vec{R}) \tag{11}$$

where

$$\vec{Q}_{nm}(\vec{R}) = < n | -\nabla_{\vec{R}} | m >$$
$$K_{nm}(\vec{R}) = < n | -\nabla_{\vec{R}}^2 | m > . \tag{12}$$

The system (11) is usual generalization of the Born-Oppenheimer approximation in the quantum theory of molecule. In this approach the right-hand side of eq. (11) is considered being a correction to the potential energy $W_n(R) = E_n(R) + Z_1 Z_2/R$. But it happened to be fruitful to do just the opposite, namely, to form a generalized momentum in the heavy-particle problem (11)

$$\underline{\vec{P}} = i\underline{\vec{Q}} - i\nabla_{\vec{R}}. \tag{13}$$

Then the coupled equations (11) can be written in a simple matrix from /5/

$$[\frac{1}{2M}\underline{\vec{P}}^2 + \underline{W}(R)]\,\underline{\psi}(\vec{R}) = E\,\underline{\psi}(\vec{R}). \tag{14}$$

The virial theorem for the nuclear motion is derived in a usual manner from the expectation value of the commutator

$$< \underline{\psi}(\vec{R}) | [\vec{R}\,\underline{\vec{P}}, \underline{H}] | \underline{\psi}(\vec{R}) > = 0 , \tag{15}$$

where $\underline{H}$ is the matrix Hamiltonian from (14). It states

$$< \underline{\psi} | 2\,\frac{\underline{\vec{P}}^2}{2M} + \vec{R}(\nabla_{\vec{R}}\underline{W}) - \vec{R}[\underline{W}, \underline{\vec{Q}}] | \underline{\psi} > = 0 . \tag{16}$$

So three different virial theorems can be obtained for the same problem (diatomic molecule). The first is independent

of the representation used, the second is of Slater's form and the third is believed to be a new one. We hope that this "molecular" virial theorem can be employed in mesomolecular calculations.

We shall finish this note by introducing one more relation of the virial theorem type. To this end we make use of the fact that the two-center problem (8) has an additional constant of motion Ω which can be represented in the spheroidal coordinates in the form /6/

$$\Omega = \Omega^{kin} + \Omega^{pot}, \tag{17}$$

where

$$\Omega^{pot} = R\left(Z_1 \frac{\xi\eta + 1}{\xi + \eta} - Z_2 \frac{\xi\eta - 1}{\xi - \eta}\right) \tag{18}$$

and Ω^{kin} is independent of R.

Then from

$$\langle k \left| \frac{\partial \Omega}{\partial R} \right| k \rangle = \frac{\partial \Omega_k}{\partial R} \tag{19}$$

we receive

$$R \frac{\partial \Omega_k}{\partial R} = \langle k \left| \Omega^{pot} \right| k \rangle . \tag{20}$$

The off-diagonal cases of (20) and (8) can also be considered but they appear to be dependent on each other.

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