Physics

1965

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Abstract

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Physics

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On the Energy of the Ground State of a Molecule in the Adiabatic Approximation

(Presented by Academician V. A. Fock on 27 VII 1964)

The paper proves the inequality $E_A \leq E$, which relates the exact eigenvalue of the molecular Hamiltonian E and its adiabatic approximation E_A. The variational principle gives, as is known, for E the approximate value $E_V \geq E$. Thus, for E we have both an upper and a lower bound.

The Hamiltonian operator determining the internal state of a molecule may be represented in the form

$$H = T_r + T_R + V(\mathbf{r}, \mathbf{R}), \tag{1}$$

where

$$T_r = -{}^1/_2 \sum_i \Delta_{r_i}$$

is the kinetic-energy operator of the electrons;

$$T_R = -{}^1/_2 \sum_j \frac{1}{m_j} \Delta_{R_j}$$

is the kinetic-energy operator of the nuclei;

$$V(\mathbf{r}, \mathbf{R}) = \sum_{i<j} \frac{1}{|r_i - r_j|} - \sum_{i,j} \frac{Z_j}{|R_j - r_i|} + \sum_{i<j} \frac{Z_{iZ}j}{|R_i - R_j|}$$

is the operator of the potential energy of interaction of all particles. Here m_j denotes the masses of the nuclei, and Z_j their charges.

In the adiabatic approximation, the solution of the Schrödinger equation

$$\{T_R + T_r + V(\mathbf{r}, \mathbf{R})\}\Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R})$$

is reduced, as is known, to the successive solution of two equations:

$$\{T_r + V(\mathbf{r},\mathbf{R})\}\Phi_A(\mathbf{r},\mathbf{R}) = \mathcal{E}(\mathbf{R})\Phi_A(\mathbf{r},\mathbf{R}),$$

$$\{T_R + \mathcal{E}(\mathbf{R})\}\varphi_A(\mathbf{R}) = E_A\varphi_A(\mathbf{R}),$$

and the quantity E_A is taken as the approximate value of the energy, while the product $\Phi_A(\mathbf{r},\mathbf{R})\varphi_A(\mathbf{R})$ is taken as the approximate corresponding function.

The normalization of Φ_A and φ_A corresponds to the normalization of Ψ. If Ψ is normalized to unity,

$$\iint |\Psi(\mathbf{r},\mathbf{R})|^2\, d\mathbf{r}\, d\mathbf{R} = 1,$$

then one may set

$$\int |\Phi_A(\mathbf{r};\mathbf{R})|^2\, d\mathbf{r} = 1, \qquad \int |\varphi_A(\mathbf{R})|^2\, d\mathbf{R} = 1.$$

Let E be the least eigenvalue, and let Ψ be the corresponding eigenfunction of the operator (1), normalized to unity. In this case Φ_A and φ_A also correspond to the least eigenvalues $\mathcal{E}(\mathbf{R})$ and E_A. The functions Ψ, Φ_A, and φ_A may obviously be considered real.

We shall prove that

$$E_A \leqslant E. \tag{2}$$

First note that the function $\Psi(\mathbf{r},\mathbf{R})$ can be represented (uniquely up to sign) in the form of the product

$$\Psi(\mathbf{r},\mathbf{R}) = \Phi(\mathbf{r},\mathbf{R})\varphi(\mathbf{R}),$$

in which

$$\int \Phi^2(\mathbf{r},\mathbf{R})\, d\mathbf{r} = 1, \qquad \int \varphi^2(\mathbf{R})\, d\mathbf{R} = 1. \tag{3}$$

For this it is sufficient (and necessary) to put

$$\varphi^2(\mathbf{R}) = \int \Psi^2(\mathbf{r},\mathbf{R})\, d\mathbf{r}, \qquad \Phi(\mathbf{r},\mathbf{R}) = \frac{\Psi(\mathbf{r},\mathbf{R})}{\varphi(\mathbf{R})}.$$

Differentiating (3) with respect to R_j, we obtain

$$\int \Phi(\mathbf{r},\mathbf{R})\frac{\partial\Phi(\mathbf{r},\mathbf{R})}{\partial R_j}\,d\mathbf{r}=0, \tag{4}$$

$$-\int \Phi(\mathbf{r},\mathbf{R})\frac{\partial^2\Phi(\mathbf{r},\mathbf{R})}{\partial R_j^2}\,d\mathbf{r}\,d\mathbf{R}=\int\left[\frac{\partial\Phi(\mathbf{r},\mathbf{R})}{\partial R_j}\right]^2 d\mathbf{r}. \tag{5}$$

Let us now express E through $\Psi(\mathbf{r},\mathbf{R})=\Phi(\mathbf{r},\mathbf{R})\varphi(\mathbf{R})$:

$$\begin{aligned}
E &= \iint \Psi(\mathbf{r},\mathbf{R})\{T_r+T_R+V(\mathbf{r},\mathbf{R})\}\Psi(\mathbf{r},\mathbf{R})\,d\mathbf{r}\,d\mathbf{R}\\
&= \iint \Phi(\mathbf{r},\mathbf{R})\varphi(\mathbf{R})\{T_r+V(\mathbf{r},\mathbf{R})\}\Phi(\mathbf{r},\mathbf{R})\varphi(\mathbf{R})\,d\mathbf{r}\,d\mathbf{R}\\
&\quad+\iint \Phi^2(\mathbf{r},\mathbf{R})\varphi(\mathbf{R})T_R\varphi(\mathbf{R})\,d\mathbf{r}\,d\mathbf{R}+\iint \varphi^2(\mathbf{R})\Phi(\mathbf{r},\mathbf{R})T_R\Phi(\mathbf{r},\mathbf{R})\,d\mathbf{r}\,d\mathbf{R}\\
&\quad-\iint \Phi(\mathbf{r},\mathbf{R})\varphi(\mathbf{R})\sum_j\frac{1}{m_j}\frac{\partial\varphi(\mathbf{R})}{\partial R_j}\frac{\partial\Phi(\mathbf{r},\mathbf{R})}{\partial R_j}\,d\mathbf{r}\,d\mathbf{R}.
\end{aligned}$$

Thanks to (3) and (4),

$$\iint \Phi^2(\mathbf{r},\mathbf{R})\varphi(\mathbf{R})T_R\varphi(\mathbf{R})\,d\mathbf{r}\,d\mathbf{R}=\int \varphi(\mathbf{R})T_R\varphi(\mathbf{R})\,d\mathbf{R},$$

$$\begin{aligned}
\iint \Phi(\mathbf{r},\mathbf{R})\varphi(\mathbf{R})\sum_j\frac{1}{m_j}\frac{\partial\varphi(\mathbf{R})}{\partial R_j}\frac{\partial\Phi(\mathbf{r},\mathbf{R})}{\partial R_j}\,d\mathbf{r}\,d\mathbf{R}&=\sum_j\frac{1}{m_j}\int\varphi(\mathbf{R})\frac{\partial\varphi(\mathbf{R})}{\partial R_j}\left[\int \Phi(\mathbf{r},\mathbf{R})\frac{\partial\Phi(\mathbf{r},\mathbf{R})}{\partial R_j}\,d\mathbf{r}\right]d\mathbf{R}\\
&=0,
\end{aligned}$$

and the expression for E is somewhat simplified:

$$\begin{aligned}
E &= \int \varphi(\mathbf{R})\left\{T_R+\int \Phi(\mathbf{r},\mathbf{R})[T_r+V(\mathbf{r},\mathbf{R})]\Phi(\mathbf{r},\mathbf{R})\,d\mathbf{r}\right\}\varphi(\mathbf{R})\,d\mathbf{R}\\
&\quad+\iint \varphi^2(\mathbf{R})\Phi(\mathbf{r},\mathbf{R})T_R\Phi(\mathbf{r},\mathbf{R})\,d\mathbf{r}\,d\mathbf{R}.
\end{aligned}$$

Using (5), we have

$$\iint \varphi^2(\mathbf{R})\Phi(\mathbf{r},\mathbf{R})T_R\Phi(\mathbf{r},\mathbf{R})\,d\mathbf{r}\,d\mathbf{R}=\iint \varphi^2(\mathbf{R})\sum_j\frac{1}{m_j}\left(\frac{\partial\Phi(\mathbf{r},\mathbf{R})}{\partial R_j}\right)^2 d\mathbf{r}\,d\mathbf{R}\geqslant 0.$$

Consequently,

$$E \geqslant \int \varphi(\mathbf{R}) \left\{ T_R + \int \Phi(\mathbf{r},\mathbf{R})[T_r + V(\mathbf{r},\mathbf{R})]\Phi(\mathbf{r},\mathbf{R})\, d\mathbf{r} \right\} \varphi(\mathbf{R})\, d\mathbf{R}.$$

For any $\mathbf{R}$, according to the definition of $\mathcal{E}(\mathbf{R})$ as the smallest eigenvalue of the operator $T_r + V(\mathbf{r},\mathbf{R})$,

$$\mathcal{E}(\mathbf{R}) \leqslant \int \Phi(\mathbf{r},\mathbf{R})\{T_r + V(\mathbf{r},\mathbf{R})\}\Phi(\mathbf{r},\mathbf{R})\, d\mathbf{r}.$$

Hence

$$E \geqslant \int \varphi(\mathbf{R})\{T_R + \mathcal{E}(\mathbf{R})\}\varphi(\mathbf{R})\, d\mathbf{R}.$$

But E_A is the least eigenvalue of the operator $T_R + \mathcal{E}(\mathbf{R})$ and, consequently,

$$\int \varphi(\mathbf{R})\{T_R + \mathcal{E}(\mathbf{R})\}\varphi(\mathbf{R})\, d\mathbf{R} \geq E_A.$$

Thus, indeed, $E \geq E_A$. On the other hand,

$$E \leq \iint \Phi_A(\mathbf{r},\mathbf{R})\varphi_A(\mathbf{R})\{T_r + T_R + V(\mathbf{r},\mathbf{R})\}\Phi_A(\mathbf{r},\mathbf{R})\varphi_A(\mathbf{R})\, d\mathbf{r}\, d\mathbf{R} =$$

$$= E_A + \iint \varphi_A^2(\mathbf{R})\Phi_A(\mathbf{r},\mathbf{R})T_R\Phi_A(\mathbf{r},\mathbf{R})\, d\mathbf{r}\, d\mathbf{R}.$$

Together with (2) this gives the following estimate for the difference $E - E_A$:

$$0 \leq E - E_A \leq \iint \varphi_A^2(\mathbf{R})\Phi_A(\mathbf{r},\mathbf{R})T_R\Phi_A(\mathbf{r},\mathbf{R})\, d\mathbf{r}\, d\mathbf{R}.$$

Hence, in particular, it follows that as $m = \min_j\{m_j\} \to \infty$ the difference

$$E - E_A \to 0$$

no more slowly than $\dfrac{1}{m}$.

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Received
1 VII 1964