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A VARIATIONAL PRINCIPLE FOR THE CALCULATION OF A CORRECTION, QUADRATIC WITH RESPECT TO THE MAGNETIC FIELD INTENSITY, TO THE ELECTRON ENERGY IN A MOLECULE

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A variational principle is formulated for the calculation of the diamagnetic correction to the ground-state energy of an electron in a molecule. The method is based on the variation of the gauge-transformation functions of the vector potential.

In a constant magnetic field

$$\mathbf{H} = \operatorname{curl} \mathbf{A} \tag{1}$$

the correction to the i-th nondegenerate electron energy level in a molecule, quadratic with respect to H, is represented in the form

$$E_i^{(2)} = \frac{e^2}{2mc^2} \langle i \,|\, \mathbf{A}^2 \,|\, i \rangle + \frac{e^2 h^2}{m^2 c^2} \sum_{k \neq i} \frac{|\langle k \,|\, \mathbf{A}\nabla + {}^1/_2 \operatorname{div} \mathbf{A} \,|\, i \rangle|^2}{E_i - E_k}. \tag{2}$$

Here E_i and ψ_i are the energy and wave function of the i-th stationary state in the absence of a magnetic field,

$$\langle k \,|\, L \,|\, i \rangle = \int \psi_k L \psi_i d\tau. \tag{3}$$

The functions ψ_k are assumed real. This corresponds to an absence of orbital magnetic moments in unperturbed states. The summation over the index k denotes here and below summation over the discrete and integration over the continuous spectrum of the unperturbed problem.

Unlike the first (so-called "diamagnetic") term of formula (2), the computation of the second ("paramagnetic"*) term causes serious difficulties, since it requires the knowledge of all eigenvalues and eigenfunctions of the unperturbed problem. We shall show that these difficulties can be avoided if we use the gauge invariance of H.

We shall represent the vector potential in the form

$$\mathbf{A} = \mathbf{A}_0 + \nabla f, \tag{4}$$

where $\mathbf{A}_0$ is some fixed vector potential, satisfying the conditions

$$\operatorname{curl} \mathbf{A}_0 = \mathbf{H}, \qquad \operatorname{div} \mathbf{A}_0 = 0. \tag{5}$$

The value of $E_i^{(2)}$ is invariant with respect to the choice of the function f. However at the same time the individual terms in (2) depend substantially on the form of the function f. In particular, the "paramagnetic" term in (2) becomes zero if we assume in (4) that $f = f_i$ where the function f_i satisfies the equation

$$\tfrac{1}{2} \psi_i \nabla^2 f_i + \nabla \psi_i \nabla f_i + \mathbf{A}_0 \nabla \psi_i = 0. \tag{6}$$

The solution of this equation can be found by various approximation methods as well as by expansion in the functions ψ_k. In the latter case we have, for example

$$f_i = \frac{1}{\psi_i} \sum_{k \neq i} \frac{\langle k \,|\, \mathbf{A}_0 \nabla \,|\, i \rangle}{E_k - E_i} \psi_k. \tag{7}$$

The important point now is the existence of a solution of Eq. (6). $E_i^{(2)}$ is now represented in the form

$$E_i^{(2)} = \frac{e^2}{2mc^2} \int \psi_i^2 (\mathbf{A}_0 + \nabla f_i)^2 d\tau. \tag{8}$$

Multiplying (4) by $\psi_i f_i$ and integrating, we obtain

$$\int \psi_i^2 (\mathbf{A}_0 \nabla f_i + \nabla f_i \nabla f_i)\, d\tau = \int [\psi_i^2 (f_i \mathbf{A}_0 + f_i \nabla f_i)]\, dS = 0. \tag{9}$$

Taking (9) into account, expression (8) is transformed into the form

$$E_i^{(2)} = (e^2 / 2mc^2) \int \psi_i^2 (\mathbf{A}_0^2 + \mathbf{A}_0 \nabla f_i)\, d\tau. \tag{10}$$

Since the integral (8) is not negative, the magnetic susceptibility of the electron in a state with zero orbital momentum is of diamagnetic character.* One must, however, take it into account that the proof of the inequality $E_i^{(2)} \geq 0$ is based on

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*We note that this term is unconditionally paramagnetic only for the lowest energy level (for i = 1).

*The inequality $E_1^{(2)} > 0$ for real wave functions was first proved by a different method.[1]

the existence of the volume integrals entering Eqs. (8) and (9). From (7) it can be seen that the integral $\int \psi_i^2 \nabla f_i \nabla f_i d\tau$ may not exist if the functions ψ_i have a nodal surface (or surfaces). Therefore, the statement about the diamagnetic character of the magnetic susceptibility is proved only for the ground state $(i = 1)$. For excited states of the electron $(i > 1)$, $E_i^{(2)}$ may be smaller than zero. This is in agreement with the results of direct calculations of the diamagnetic susceptibility of π electrons in aromatic molecules and (in contradiction to reference 1) indicates that in principle the existence of the so-called van Fleck temperature-independent paramagnetism is possible.

The above considerations allow a formulation of the following variational principle. The correction, quadratic with respect to the constant magnetic field intensity, to the electron energy for the ground state with a real wave function ψ_0, is equal to the minimum of the integral

$$I_0 = (e^2 / 2mc^2) \int \psi_0^2 (\mathbf{A}_0 + \nabla f)^2 d\tau, \qquad (11)$$

which is a functional of the function f [here, as in (4), A_0 is some fixed vector potential satisfying conditions (5)]. Indeed, Euler's equation for the function f is identical with Eq. (6) and, consequently, the minimum of I_0 is equal to $E_i^{(2)}$ [see Eqs. (11) and (8)]. The significance of minimizing I_0 lies in the search of a vector-potential gauge for which the paramagnetic term in (2) vanishes. The variational principle (11) is very convenient for practical calculations. In addition, the form of functional (11) emphasizes the diamagnetic character of the correction $E_i^{(2)}$ and shows that it is fully determined by the density distribution of the electron charge in the ground state.

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[1] Guy, Tillieu, and Baudet, Compt. rend. **246**, 574 (1958).

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