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REMARK ON THE VARIATIONAL CALCULATIONS OF THE POLARIZABILITY

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It is shown that in constructing the trial function for the variational calculation of the polarizability of an electron in an excited state it is necessary to take into account the orthogonality of the perturbed wave functions. The polarizabilities of the excited states of an electron in a hydrogen atom or a one-dimensional infinitely deep potential well calculated with account of the above-mentioned orthogonality condition are in satisfactory agreement with the exact values (approaching them from below).

THE formulas of Kirkwood[1] and similar variational formulas for the polarizability have been derived without taking into account the orthogonality of the perturbed wave functions. These formulas, therefore, give values for the polarizability of excited states of the electron which are far too high. It can be shown that the variational values approach the exact values from below if the trial function is properly chosen.

The variational problem of finding the polarizability $\alpha_i = -2E_i^{(2)}$ for the i-th state of the electron must be formulated in the following way:

$$E_i^{(2)} = J[\psi_i^{(1)}]_{min} = \int \psi_i^{(1)} (H_0 - E_i^{(0)}) \psi_i^{(1)} \, d\tau + 2\int \psi_i^{(1)} z \psi_i^{(0)} d\tau \tag{1}$$

with the condition

$$\int \psi_i^{(1)} \psi_i^{(0)} d\tau = 0, \tag{2}$$

which follows from the normalization of the perturbed function ψ_i, and

$$\int \psi_i^{(1)} \psi_k^{(0)} d\tau = -\int \psi_k^{(1)} \psi_i^{(0)} d\tau = z_{ik} / (E_i^{(0)} - E_k^{(0)}), \tag{3}$$

which follow from the orthogonality of the function ψ_i to the functions ψ_k corresponding to states with energies lying below that of the i-th state. [We assume that the polarizing field is oriented along the z axis. Formulas (1) to (3) are written in terms of real functions, for convenience.]

The Euler equation for the functional (1) with account of the subsidiary conditions (2) and (3) has the form

$$(H_0 - E_i^{(0)}) \psi_i^{(1)} = (\lambda_i - z) \psi_i^{(0)} + \sum_k \lambda_k \psi_k^{(0)}. \tag{4}$$

It is easy to show that $\lambda_i = E_i^{(1)} = z_{ii}$, $\lambda_k = 0$, so that (4) coincides with the known perturbation theoretical equation for $\psi_i^{(1)}$.

If, instead of looking for an exact solution of Eq. (4), one solves the variational problem approximately by substituting a trial function φ_i with variational parameters in (1), one must require that φ_i satisfy conditions (2) and (3) for arbitrary values of these parameters. For φ_i one often uses an expression of the form

$$\varphi_i = [f_i - (f_i)_{ii}] \psi_i^{(0)}, \tag{5}$$

where f_i is a function of the variational parameters, and

$$(f_i)_{ik} = \int \psi_i^{(0)} f_i \psi_k^{(0)} d\tau.$$

However, expression (5) does not in general satisfy the conditions (3). Instead of (5), it is reasonable to use the expression

$$\varphi_i = [f_i - (f_i)_{ii}] \psi_i^{(0)} + \sum_k c_{ik} \psi_k^{(0)}, \tag{6}$$

where

$$c_{ik} = z_{ik} / (E_i^{(0)} - E_k^{(0)}) - (f_i)_{ik}.$$

Expression (6) defines a set of admissible trial functions. Substituting (6) in (1), we find

$$E_i^{(2)} \leqslant J[\varphi_i]_{min} = 2[(z - z_{ii}) + \tfrac{1}{4}(\operatorname{grad} f_i)^2]_{ii} + 2\sum_k c_{ik}[(E_k^{(0)} - E_i^{(0)}) f_i + z]_{ik} + \sum_k c_{ik}^2 (E_k^{(0)} - E_i^{(0)}). \tag{7}$$

Choosing $f_i = a_i z$, where a_i is the variational parameter, we obtain, instead of the Kirkwood formula

$$\alpha_i = 4[z_{ii}^2 - (z_{ii})^2]^2 \tag{8}$$

the new variational formula*

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*Formula (9) can also be obtained by averaging, according to Vinti,[2] the denominators of only those terms in $\alpha_i = 2\sum_k{}' (z_{ik})^2 / (E_k^{(0)} - E_i^{(0)})$ which correspond to transitions to a state which lies above the i-th state energetically.

$$\alpha_i = 4\left[z_{ii}^2 - (z_{ii})^2 - \sum_k (z_{ik})^2\right]^2 \Big/ \left[1 + 2\sum_k (E_i^{(0)} - E_k^{(0)})(z_{ik})^2\right] - 2\sum_k (z_{ik})^2 / (E_i^{(0)} - E_k^{(0)}). \quad (9)$$

In Table I we compare the values of the polarizabilities $\alpha_{n_1 n_2 m}$ of several states of the hydrogen atom calculated with the help of formulas (8) and (9) with the corresponding exact values (see, for example, reference 3). Here $\alpha_{n_1 n_2 m}$ is the polarizability of the state characterized by the parabolic quantum numbers n_1 and n_2 and the magnetic quantum number m.

Table I

	α_{000}	α_{100}	α_{001}	α_{200}	α_{110}	α_{101}	α_{002}
By formula (8)	4	196	144	2916	2916	2450	1296
By formula (9)	4	148	144	1402	1590	1477	1296
Exact value	4.5	168	156	1620	1741	1620	1377

In Table II we make an analogous comparison for several states of an electron moving in an infinitely deep potential well of width $l = 10$ atomic units (α_n is the polarizability of the state characterized by the quantum number n). The exact values of α_n were found by the methods of reference 4. In both tables the polarizabilities are given in atomic units.

Table II

	α_1	α_2	α_3	α_4
By formula (8)	42.7	199,7	241.5	257.0
By formula (9)	42,7	—14.0	—8.5	—5.3
Exact value	43.9	—13,1	—7,8	—4,8

It is clearly evident from Tables I and II that, in contrast to the Kirkwood formula, the new variational formula gives in all cases results which do not exceed the exact values of the polarizability and are, moreover, in satisfactory agreement with the latter.

This formula can be used for the calculation of the polarizability of a many-electron system, regarding the polarizability of the system as the sum of the polarizabilities of the individual electrons. The resulting values of the polarizabilities of atoms and ions are much closer to the values computed by the method of Sternheimer[5] than the usual variational values.

In conclusion we note that the account of the orthogonality of the perturbed wave functions should be important not only in the derivation of the variational formulas for the polarizability, but also in variational calculations of other physical quantities in second order perturbation theory, as, for example, the Van-der-Waals forces.

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[2] J. P. Vinti, Phys. Rev. **41**, 432 (1932).

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[5] R. Sternheimer, Phys. Rev. **96**, 951 (1954).

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