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Abstract

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A METHOD FOR DETERMINING OPTIMAL WAVE FUNCTIONS FOR THE APPROXIMATE CALCULATION OF MATRIX ELEMENTS

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Quantum-mechanical calculations of the probabilities of electronic transitions, dipole moments, and other quantities characterizing atoms and molecules are, as a rule, based on variational wave functions found from the condition that the energy be extremal. Meanwhile, the matrix elements $D_{AB} = \int \psi_A^* D \psi_B \, d\tau$ of an arbitrary operator D, different from the Hamiltonian, do not, generally speaking, possess extremal properties with respect to variation of the wave functions ψ_A and ψ_B, and consequently even small distortions of the wave functions can lead to significant changes in the value of D_{AB}. In particular, any expansion of the class of variational wave functions only improves the mean values of the energy, while the transition probability calculated in this way may either approach or move away from its exact value. It follows from this that, in calculating the matrix element D_{AB}, the choice of the form of the variational wave function cannot be determined solely by the requirement that the energy be extremal. Below we investigate the conditions that approximate wave functions must satisfy in order that the value of the matrix element D_{AB} of interest to us not depend on some—sufficiently large—expansion of the class of variational wave functions of the states A and B.

Let φ_A and φ_B be approximate wave functions of the stationary states A and B of the system under study. Consider variational functions ψ_A and ψ_B of the form

$$\psi_A = \frac{1}{N_A} \left\{ \varphi_A + \sum_{k=1}^{K} a_k (H - E_A)^k \varphi_A \right\}, \tag{1}$$

$$\psi_A = \frac{1}{N_B} \left\{ \varphi_B + \sum_{k=1}^{K} b_k (H - E_B)^k \varphi_B \right\}, \tag{2}$$

where a_k, b_k are constant coefficients or unknown functions of the coordinates, varying slowly in certain regions of space. Here H is the Hamiltonian of the system; $(H-E)^k = (H-E)(H-E)^{k-1}$; E_A and E_B are the exact or approximate values of the energies in the states A and B, respectively; N_A and N_B are normalization factors; the functions φ_A and φ_B are assumed to be normalized. If φ_A and φ_B are exact solutions of the Schrödinger equation, then ψ_A and ψ_B are identically equal to φ_A and φ_B; the additional terms proportional to $(H-E_A)\varphi_A$, $(H-E_B)\varphi_B$ differ from zero in those regions of space where the approximate functions φ_A and φ_B do not satisfy the Schrödinger equation.

The question of whether, under the indicated restrictions on the character of the functions a_k (b_k), it is possible to represent the exact solution of the Schrödinger equation in the form (1) (respectively (2)) is determined by the choice of the approximate wave function φ_A (respectively φ_B). We shall show that if the function φ

is expandable in some finite (arbitrarily large) number of eigenfunctions of the Schrödinger equation Ψ_n, corresponding to states with different energy values E_n, then any of these functions Ψ_n can be represented in the form of the series (1) with constant coefficients a_k. Indeed, since $\varphi = \sum_{n=0}^{M} c_n \Psi_n$, with $c_n \neq 0$, then, according to (1), we have:

$$\psi = \frac{1}{N}\left\{\varphi + \sum_{k=1}^{K} a_k (H-E)\varphi\right\} = \varphi + \sum_{k=0}^{K} \alpha_k (H-E)^k \varphi = \sum_{n=0}^{K} \gamma_n \Psi_n, \qquad (3)$$

where

$$\gamma_n = c_n \left\{1 + \sum_{k=0}^{K} \alpha_k (E_n - E)^k\right\}.$$

It is necessary to show that the constant coefficients α_k can be chosen in such a way that $\gamma_n = \delta_{n0}$. We write these conditions in the following form ($K = M$):

$$\sum_{k=0}^{M} \alpha_k (E_n - E)^k = \frac{1}{c_0}\delta_{n0} - 1 \quad (n = 0, 1, 2, \dots, M). \qquad (4)$$

The characteristic determinant of the system of linear nonhomogeneous algebraic equations (4), $\det\{(E_n - E)^k\}$, is a Vandermonde determinant and, therefore, is nonzero if all E_n are distinct and none of the E_n coincides with E. In this case the system of equations (4) is solvable with respect to the coefficients α_k. If $E = E_0$, then the conditions $\gamma_n = \delta_{n0}$ can be represented as follows:

$$c_0(1+\alpha_0) = \frac{1}{c_0} - 1; \qquad (5)$$

$$\sum_{k=1}^{M} \alpha_k (E_n - E)^k = -1 - \alpha_0 \quad (n = 1, 2, \dots, M). \tag{6}$$

The system of equations (6) is solvable with respect to α_k $(k = 1, 2, \dots, M)$, since its determinant is nonzero; α_0 is found from equation (5). The special case $\alpha_0 = -1$ does not occur, since, according to (5), $\alpha_0 = -1$ would mean that $c_0 = 1$.

Thus, under the stated restrictions on φ and E_n, it is possible to choose the constant coefficients a_k so that the exact solution of the Schrödinger equation is represented through the approximate function φ in the form of the series (1).

In the usual method of solution, in order to refine the value of the matrix element D_{AB}, it is necessary first to find a_k, b_k from the requirement of an extremum of the energy, and $\langle A|D|B\rangle$, generally speaking, depends strongly on a_k, b_k. Instead, we shall determine the conditions that the approximate functions φ_A and φ_B must satisfy so that the desired value of the matrix element does not depend on a_k, b_k.

To first order in $a_k(H - E_A)^k\varphi_A$, $b_k(H - E_B)^k\varphi_B$, the nondiagonal matrix element of the operator D is equal to

$$D_{AB} = \int \psi_A^* D \psi_B \, d\tau = \langle A|D|B\rangle +$$

$$+ \sum_k \{\langle A|(H - E_A)^k a_k^* D|B\rangle + \langle A|D b_k (H - E_B)^k|B\rangle -$$

$$-\langle A|D|B\rangle(\langle A|(H - E_A)^k a_k^*|B\rangle + \langle A|b_k(H - E_B)^k|B\rangle)\}, \tag{7}$$

where

$$\langle A|L|B\rangle = \int \varphi_A^* L \varphi_B \, d\tau, \tag{8}$$

and L is any of the operators $D, H^k, a_k(H - E_A)^{kD}$, etc. The quantity D_{AB} will be stable with respect to the expansion of the class of variational wave functions under consideration if one requires the differences of the integrals to be equal to zero

$$\langle A|(H - E_A)^k a_k^* D|B\rangle - \langle A|D|B\rangle\langle A|(H - E_A)^k a_k^*|B\rangle; \tag{9}$$

$$\langle A|D b_k (H - E_B)^k|B\rangle - \langle A|D|B\rangle\langle A|b_k(H - E_B)^k|B\rangle \tag{10}$$

for $k = 1, 2, \ldots$, independently of a_k, b_k. Assuming that a_k, b_k are constant coefficients or functions of the coordinates that vary slowly in those regions of space where the rest of the integrand is substantially different from zero (and this can occur only where the functions φ_A, φ_B substantially fail to satisfy the Schrödinger equation), a_k and b_k in expressions (9), (10) may be taken out from under the integral sign. Consequently, in order that the quantity D_{AB} in first order in the unknown inaccuracies of the approximate wave functions be independent of these inaccuracies, the approximate functions φ_A and φ_B must satisfy the conditions

$$\langle A|H^{kD}|B\rangle = \overline{E_A^k}\,\langle A|D|B\rangle; \tag{11}$$

$$\langle A|DH^k|B\rangle = \overline{E_B^k}\,\langle A|D|B\rangle, \tag{12}$$

where $\overline{E_A^k} = \langle A|H^k|A\rangle$, $\overline{E_B^k} = \langle B|H^k|B\rangle$.

Analogous, but stronger, conditions can also be obtained in second order in a_k, h_k. It is also obvious that the corresponding conditions for the optimal choice of the approximate wave function in calculating the mean value of an operator D (different from the Hamiltonian) have the form

$$\langle A|DH^k|A\rangle = \overline{E_A^k}\,\langle A|D|A\rangle. \tag{13}$$

Let us note that in the particular case of a transition between the two lowest states of the discrete spectrum, A and B, possessing different symmetry, conditions for the independence of the matrix element D_{AB} from the inaccuracy of the approximate wave function, similar to conditions (11)–(12), can be obtained directly, without relying on the variational method. The corresponding proof is based on expanding the error in the calculation of the matrix element in powers of the ratios of the energies of excited states to the energy of the lowest state of the same symmetry.

Conditions (11)–(12) admit a simple physical interpretation. Let $k = 1$: instead of equations (11), (12), consider their sum and difference:

$$\langle A|[HD]_\pm|B\rangle = (\overline{E_A} \pm \overline{E_B})\,\langle A|D|B\rangle, \tag{14}$$

where $[HD]_\pm = HD \pm DH$. If by φ_A and φ_B we mean the wave functions of states A and B, including the time factor, then formula (14) represents the requirement that the time derivative of the matrix element D_{AB} coincide with the matrix element of the time derivative of the operator D (the operator D is Hermitian and does not explicitly depend on time). For $k > 1$, conditions (11), (12) are equivalent to the requirement of equality of analogous derivatives of higher orders (up to replacing $\overline{E^k}$ by $(\overline{E})^k$).

If the approximate wave functions φ_A and φ_B have been found by some method, then satisfaction of conditions (11)–(12), (14) should be regarded as a criterion of the applicability of φ_A and φ_B for calculating the matrix element D_{AB}. When using crude variational wave functions, there may occur

It may turn out that the ratio of the quantities standing on the right- and left-hand sides of formulas (11)–(14) differs substantially from unity ([1], [2]). In this case it appears more expedient to determine the parameters of the approximate wave functions from equations (11)–(14), and not from the condition of extremality of the energy. It must be emphasized that the function φ_A found in this way determines, strictly speaking, not the state of the system under investigation, but only the magnitude of the matrix element D_{AB}, and changes depending on which of the transitions A—B, A—C, $\cdots$is being considered. A strong change of φ_A upon replacing, in (11)–(13), the function φ_B by φ_C, $\cdots$ indicates only that a very crude representation of the wave functions has been chosen, suitable only for a limited range of problems. This is consistent with the fact that, in the usual determination of wave functions by the variational method, the given function φ_A may lead to the correct value of the matrix element D_{AB}, but prove inapplicable for calculating the matrix element D_{AC} of the transition from state A to a state C different from B.

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Note: Figure translations are in progress. See original paper for figures.

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