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APPROXIMATION OF EXPECTATION VALUES*

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ABSTRACT

The general problem of calculating expectation values for properties other than energy by the use of perturbation theory is considered.

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It is well known that perturbation theory¹ can be used in the quantum mechanical determination of an expectation value $\langle W \rangle = \langle \Psi | W | \Psi \rangle$ of an operator W . Here Ψ is an eigenfunction of the Hamiltonian H . Usually we do not know Ψ . Instead we are given an approximate wave function ψ_0 which satisfies the Schrödinger equation $H_0 \psi_0 = \epsilon_0 \psi_0$. The difference $H - H_0 = V$ is the perturbation and Ψ can be expanded in the series $\Psi = \psi_0 + \psi_0^{(1)} + \dots$. Here $\psi_0^{(1)}$ is the first order function which is orthogonal to ψ_0 and satisfies the differential equation

$$(H_0 - \epsilon_0) \psi_0^{(1)} + (V - \langle \psi_0 | V | \psi_0 \rangle) \psi_0 = 0. \quad (1)$$

The expectation value can then be expressed as the sum of the contributions from the various orders of perturbation, $\langle W \rangle = W_0 + W_1 + \dots$. Here $W_0 = \langle \psi_0 | W | \psi_0 \rangle$ and W_1 represents the first correction for the badness of the approximate wave function,

$$W_1 = \langle \psi_0^{(1)} | W | \psi_0 \rangle + \langle \psi_0 | W | \psi_0^{(1)} \rangle. \quad (2)$$

If W is a one-electron operator, it is usually much easier to use the Dalgarno Interchange Theorem¹ and express W_1 in the mathematically equivalent form

$$W_1 = \langle \chi_0^{(1)} | V | \psi_0 \rangle + \langle \psi_0 | V | \chi_0^{(1)} \rangle \quad (3)$$

where $\chi_0^{(1)}$ would be the first order function if W rather than V

were the perturbation potential,

$$(H_0 - \epsilon_0)\chi_0^{(1)} + (W - \langle \psi_0 | W | \psi_0 \rangle)\psi_0 = 0. \quad (4)$$

Dalgarno and Lewis² suggested that $\chi_0^{(1)}$ be written as the product $F\psi_0$ where F is a function which satisfies the equation

$$\sum_i \nabla_i \cdot (\psi_0^* \psi_0 \nabla_i F) = \psi_0^* (W - W_0) \psi_0 + \psi_0 (W^* - W_0) \psi_0^*. \quad (5)$$

Here the summation is over the electrons. For one-electron W 's, Eq. (5) is frequently separable and F can either be determined exactly or else it can be satisfactorily approximated.

Largely on the basis of intuitive arguments, Dalgarno and Stewart³ suggested that W_0 should be a good approximation to $\langle W \rangle$ provided that a parameter embedded in ψ_0 is adjusted so as to make $W_1 = 0$. A sizeable number of expectation values have been estimated in this manner and found to be surprisingly accurate.^{4,5} For the ground state of two electron atoms using hydrogenic approximate wave functions⁵ and positive definite one-electron operators W , the value of $W_0 + W_1$ is a lower bound to $\langle W \rangle$ and the maximum value of $W_0 + W_1$ is obtained by setting $W_1 = 0$. However, this behaviour is not general as can be seen from the following examples:

Calculate $\langle r \rangle$ for the ground state of the hydrogen atom.

First, using the approximate wave function $\psi_0 = N r^{\frac{1}{2}} \exp(-\alpha r)$, we obtain $\langle r \rangle_0 = 2/\alpha$ and $\langle r \rangle_1 = (9/8 \alpha^2) [\alpha - (32/27)]$. Setting $\alpha = 32/27$ to make $\langle r \rangle_1 = 0$ makes $\langle r \rangle_0 = 54/32$ which is

larger than the correct value $\langle r \rangle = 48/32$. Furthermore, the maximum value of $\langle r \rangle_0 + \langle r \rangle_1$ occurs for $\alpha = 64/75$ and not $\alpha = 32/27$. Similarly, using $\Psi_0 = N r \exp(-\alpha r)$ we obtain $\langle r \rangle_1 = 0$ for $\alpha = 5/4$, in which case $\langle r \rangle_0 = 2$. Furthermore, for the ground state of the helium atom, the orbital $\Psi_0 = N r \exp(-\alpha r)$ leads to $\langle r_1 \rangle_1 = 0$ for $\alpha = 1.9775$ and correspondingly $\langle r_1 \rangle_0 = 1.2642$, which is to be compared with the exact value 0.9293.

Recently, Robinson⁶ has shown that the requirement that $W_1 = 0$ is equivalent to satisfying the hypervirial relation

$$\langle \Psi_0 | [H, L] | \Psi_0 \rangle = 0, \quad (6)$$

where L is an anti-Hermitian operator satisfying the condition

$$\chi_0''' = F \Psi_0 = L \Psi_0. \quad (7)$$

There is no uniqueness in the functional form of L . It might be assumed to be a first order differential operator,⁷

$$L = \sum_k \left(\frac{f_k}{g} \right)^{1/2} \frac{\partial}{\partial q_k} \left(g^{1/2} f_k^{1/2} \right), \quad (8)$$

where g is the product of the metric scale factors of the generalized coordinates q_k and the functions f_k may be functions of all of the q_k . With this form of L , the hypervirial relation Eq. (6) becomes⁵

$$\langle \Psi_0 | \sum_k f_k \frac{\partial V}{\partial q_k} | \Psi_0 \rangle = 0 . \quad (9)$$

For a one-dimensional problem, by virtue of Eq. (7), the function f is simply related⁵ to the Dalgarno function F ,

$$f = \frac{2}{\int_c^d \Psi_0^* \Psi_0} \int_c^d q \Psi_0^* F \Psi_0 dq . \quad (10)$$

Thus, it is not difficult to obtain the required hypervirial operator L associated with a property W .

As Epstein and Hirschfelder⁷ showed, the satisfaction of the hypervirial relation Eq. (6) assures that the wave function Ψ_0 is energetically stable with respect to variations of the type

$$\Psi_0 \rightarrow \phi(\lambda) = \Psi_0 + \lambda L \Psi_0 = \Psi_0 + \lambda F \Psi_0 . \quad (11)$$

Thus, if Ψ_0 satisfies Eq. (6), then the lowest value of

$$E(\lambda) = \langle \phi(\lambda) | H | \phi(\lambda) \rangle / \langle \phi(\lambda) | \phi(\lambda) \rangle \quad (12)$$

is given by $\lambda = 0$. Conversely, if Ψ_0 does not satisfy Eq. (6), then the function ϕ with the energy optimized value of λ will satisfy the hypervirial relation. Hence $\langle \phi | W | \phi \rangle$ should give the best approximation to $\langle W \rangle$ when λ is energy optimized.

If it is difficult to determine the function F corresponding to an approximate wave function Ψ_0 , perhaps one might not make

a large error in using a function F_0 which would be appropriate for a simpler function ψ'_0 . That is, approximate W_1 by $\langle \psi_0 | F_0 (V - V_{00}) + (V - V_{00}) F_0 | \psi_0 \rangle$ where $V_{00} = \langle \psi_0 | V | \psi_0 \rangle$.

The function F changes only slightly as one goes from a crude approximate wave function to the exact function. For example,

using the correct ground state function for the hydrogen atom,

$\psi'_0 = Ne^{-\alpha r}$, we find $F_0 = (\frac{3}{\alpha^2} - r^2)/2\alpha$ for $W=r$. On the

other hand, for the function $\psi_0 = Nr^{1/2}e^{-\alpha r}$, $F = (\frac{5}{\alpha^2} - r^2)/2\alpha$,

and for $\psi_0 = Nre^{-\alpha r}$, $F = (15/2\alpha^2 - r^2)/2\alpha$. In the latter

two cases, the value of W_1 is unchanged if F_0 is used instead

of the correct F , that is $\langle \psi_0 | (V - V_{00}) F_0 | \psi_0 \rangle =$

$\langle \psi_0 | (V - V_{00}) F | \psi_0 \rangle$. Thus using F_0 in place of F leads

to the same optimum value for α and $\langle r \rangle_0$.

A rougher approximation to F might be obtained in the following manner. As Lennard-Jones observed^{8,1}, a first order perturbed wave function may be expressed in the spectral form

$$F\psi_0 = -\frac{W - W_0}{E_1 - E_0} \psi_0 + \sum_j' \left(\frac{E_j - E_1}{E_j - E_0} \right) \frac{\langle \psi_j | W | \psi_0 \rangle \psi_j}{(E_1 - E_0)}. \quad (13)$$

Here the ψ_j and the E_j are the complete set of eigenfunctions and eigenvalues of H_0 . The state "1" may be chosen so as to make the summation as small as possible. Neglecting the summation⁹,

$$F \approx -(W - W_0)/(E_1 - E_0). \quad (14)$$

To this approximation, $\Phi(\lambda)$ might be replaced by

$$\Phi'(\lambda') = (1 + \lambda'W)\Psi_0. \quad (15)$$

This is the basis for the well known Hylleraas¹⁰ or Hasse¹¹ approximation which leads to good values for the polarizability of molecules.¹² Thus, $\langle W \rangle$ might be approximated by $\langle \Phi' | W | \Phi' \rangle$ where the value of λ' is adjusted so as to minimize the expectation value of H .

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9. According to Ref. (5), for the ground state of the helium atom with hydrogenic zeroth order wave function, we have exact expressions for F for $W = r_1^n$. Thus, in the proper units,

$$W = r_1^{-1} \quad , \quad F = r_1 - (3/2)$$

$$W = r_1 \quad , \quad F = 3 - r_1^2$$

$$W = r_1^2 \quad , \quad F = \frac{11}{2} - r_1^2 - \frac{r_1^3}{3}$$

In this case, Eq. (15) would be a good approximation if W were equal to r_1 , but not for W equal either to r_1^{-1} or to r_1^2 .

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