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ABSTRACT

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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 theory[1] 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 $\Psi = \Psi_0 + \Psi_0^{(1)} + \ldots$. Here $\Psi_0^{(1)}$ is the first order function which is orthogonal to Ψ_0 and satisfies the differential equation

$$(H_0 - \epsilon_0)\Psi_0^{(1)} + (V - \langle \Psi_0 | V | \Psi_0 \rangle)\Psi_0 = 0 . \qquad (1)$$

The expectation value can then be expressed as the sum of the contributions from the various orders of perturbation, $\langle W \rangle = W_0 + W_1 + \ldots$ 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,

$$W_1 = \langle \Psi_0^{(1)} | W | \Psi_0 \rangle + \langle \Psi_0 | W | \Psi_0^{(1)} \rangle . \qquad (2)$$

If W is a one-electron operator, it is usually much easier to use the <u>Dalgarno Interchange Theorem</u>[1] and express W_1 in the mathematically equivalent form

$$W_1 = \langle \chi_0^{(1)} | V | \Psi_0 \rangle + \langle \Psi_0 | V | \chi_0^{(1)} \rangle \qquad (3)$$

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

were the perturbation potential,

$$(H_0 - \epsilon_0)\chi_0^{(1)} + (W - \langle \Psi_0 | W | \Psi_0 \rangle)\Psi_0 = 0 \ . \tag{4}$$

Dalgarno and Lewis[2] suggested that $\chi_0^{(1)}$ be written as the product $F\,\Psi_0$ where F is a function which satisfies the equation

$$\sum_i \nabla_i \cdot (\Psi_0^* \Psi_0 \nabla_i F) = \Psi_0^*(W - W_0)\Psi_0 + \Psi_0(W^* - W_0)\Psi_0^* \ . \tag{5}$$

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 Stewart[3] 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 functions[5] 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, Robinson[6] has shown that the requirement that $W_1 = 0$ is equivalent to satisfying the hypervirial relation

$$\langle \Psi_0 | [H, L] | \Psi_0 \rangle = 0 \quad , \tag{6}$$

where L is an anti-Hermitian operator satisfying the condition

$$\chi_0^{(1)} = F \Psi_0 = L \Psi_0 \quad . \tag{7}$$

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

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

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) becomes[5]

$$\langle \Psi_0 | \sum_K f_K \frac{\partial V}{\partial q_K} | \Psi_0 \rangle = 0 \quad . \tag{9}$$

For a one-dimensional problem, by virtue of Eq. (7), the function f is simply related[5] to the Dalgarno function F,

$$f = \frac{2}{q \Psi_0^* \Psi_0} \int_c^q q \Psi_0^* F \Psi_0 \, dq \quad . \tag{10}$$

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

As Epstein and Hirschfelder[7] 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

$$\Psi_0 \rightarrow \phi(\lambda) = \Psi_0 + \lambda L \Psi_0 = \Psi_0 + \lambda F \Psi_0 \, . \tag{11}$$

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

$$E(\lambda) = \langle \phi(\lambda) | H | \phi(\lambda) \rangle / \langle \phi(\lambda) | \phi(\lambda) \rangle \tag{12}$$

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 $\Psi_0 = N r^{1/2} e^{-\alpha r}$, $F = (\frac{5}{\alpha^2} - r^2)/2\alpha$, and for $\Psi_0 = N r e^{-\alpha r}$, $F = (15/2\alpha^2 - r^2)/2\alpha$. 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

$$F\Psi_0 = -\frac{W - W_0}{\epsilon_1 - \epsilon_0}\Psi_0 + \sum_j{}' \left(\frac{\epsilon_j - \epsilon_1}{\epsilon_j - \epsilon_0}\right) \frac{\langle \Psi_j | W | \Psi_0 \rangle \Psi_j}{(\epsilon_1 - \epsilon_0)} . \quad (13)$$

Here the Ψ_j and the ϵ_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 summation[9],

$$F \approx -(W - W_0)/(\epsilon_1 - \epsilon_0) . \quad (14)$$

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

$$\phi'(\lambda') = (1 + \lambda' W)\Psi_0 \quad . \tag{15}$$

This is the basis for the well known Hylleraas[10] or Hasse[11] 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,

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

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

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

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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