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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 theory\(^1\) can be used in the quantum mechanical determination of an expectation value \( \langle \Psi | W | \Psi \rangle \) of an operator \( W \). Here \( \Psi \) is an eigenfunction of the Hamiltonian \( H \). Usually we do not know \( \Psi \). Instead we are given an approximate wave function \( \Psi_0 \) which satisfies the Schrödinger equation

\[
H_0 \psi_0 = E_0 \psi_0 .
\]

The difference \( H - H_0 = V \) is the perturbation and \( \Psi \) 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 \( \Psi_0 \) and satisfies the differential equation

\[
(H_0 - E_0)\psi_0^{(1)} + (V - \langle \Psi_0 | V | \Psi_0 \rangle)\psi_0 = 0 .
\]  

(1)

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

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,

\[
W_1 = \langle \psi_0^{(1)} | W | \psi_0 \rangle + \langle \psi_0 | W | \psi_0^{(1)} \rangle .
\]  

(2)

If \( W \) is a one-electron operator, it is usually much easier to use the Dalgarno Interchange Theorem\(^1\) and express \( W_1 \) in the mathematically equivalent form

\[
W_1 = \langle \chi_0^{(1)} | V | \psi_0 \rangle + \langle \psi_0 | V | \chi_0^{(1)} \rangle
\]  

(3)

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

\[(H_0 - \epsilon_0)\chi^{(1)} + (W - \langle \Psi_0 | W | \Psi_0 \rangle) \Psi_0 = 0.\]  \hspace{1cm} (4)

Dalgarno and Lewis\(^2\) suggested that \(\chi^{(1)}_0\) be written as the product \(F \Psi_0\) where \(F\) is a function which satisfies the equation

\[\sum_i \nabla_i \cdot (\Psi_i^* \Psi_0 \nabla_i F) = \Psi_0^* (W - W_0) \Psi_0 + \Psi_0 (W^* - W_0) \Psi_0^*.\]  \hspace{1cm} (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 \(\Psi_0\) 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

\[
\langle \Psi_0 | [H, L] | \Psi_0 \rangle = 0 ,
\]

where \( L \) is an anti-Hermitian operator satisfying the condition

\[
\chi_0'' = F \Psi_0 = L \Psi_0 .
\]

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

\[
L = \sum_k \left( \frac{f_k}{g} \right)^{1/2} \frac{\partial}{\partial q_k} \left( q^{1/2} f_k q^{1/2} \right) ,
\]

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\(^5\)
\[ \langle \psi_0 | \sum_k f_k \frac{\partial V}{\partial q_k} | \psi_0 \rangle = 0. \] (9)

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

\[ f = \frac{2}{q \psi_0^* \psi_0} \int_q \psi_0^* F \psi_0 \, dq. \] (10)

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

As Epstein and Hirschfelder showed, the satisfaction of the hypervirial relation Eq. (6) assures that the wave function \( \psi_0 \) is energetically stable with respect to variations of the type

\[ \psi_0 \rightarrow \phi(\lambda) = \psi_0 + \lambda L \psi_0 = \psi_0 + \lambda F \psi_0. \] (11)

Thus, if \( \psi_0 \) satisfies Eq. (6), then the lowest value of

\[ E(\lambda) = \frac{\langle \phi(\lambda) | H | \phi(\lambda) \rangle}{\langle \phi(\lambda) | \phi(\lambda) \rangle} \] (12)

is given by \( \lambda = 0 \). Conversely, if \( \psi_0 \) does not satisfy Eq. (6), then the function \( \phi \) with the energy optimized value of \( \lambda \) will satisfy the hypervirial relation. Hence \( \langle \phi | W | \phi \rangle \) should give the best approximation to \( \langle W \rangle \) when \( \lambda \) is energy optimized.

If it is difficult to determine the function \( F \) corresponding to an approximate wave function \( \psi_0 \), perhaps one might not make
a large error in using a function $F_0$ which would be appropriate for a simpler function $\psi'_0$. 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 $F_0 = \left(\frac{3}{\alpha^2} - \frac{r^2}{2}\right)/2\alpha$ for $W = r$. On the other hand, for the function

$$\psi'_0 = N r^{\frac{1}{2}} e^{-\alpha r},$$

$F = \left(\frac{5}{\alpha^2} - \frac{r^2}{2}\right)/2\alpha$, and for

$$\psi'_0 = N r e^{-\alpha r}$$

$F = \left(\frac{15}{2\alpha^2} - \frac{r^2}{2}\right)/2\alpha$. 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 $\alpha$ and $<r>$. A rougher approximation to $F$ might be obtained in the following manner. As Lennard-Jones observed, a first order perturbed wave function may be expressed in the spectral form

$$F \psi'_0 = -\frac{W - W_0}{\epsilon_i - \epsilon_o} \psi'_0 + \sum_j \left(\frac{\epsilon_j - \epsilon_i}{\epsilon_j - \epsilon_o}\right) \frac{\langle \psi_j | W | \psi'_0 \rangle \psi'_0}{(\epsilon_i - \epsilon_o)}.$$ (13)

Here the $\psi_j$ and the $\epsilon_j$ 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$^9$,

$$F \approx -\frac{(W - W_0)}{(\epsilon_i - \epsilon_o)}.$$ (14)
To this approximation, $\Phi(\lambda)$ might be replaced by

$$\phi'(\lambda') = (1 + \lambda' \mathcal{W}) \psi_0$$

(15)

This is the basis for the well known Hylleraas\textsuperscript{10} or Hasse\textsuperscript{11} approximation which leads to good values for the polarizability of molecules.\textsuperscript{12} Thus, $\langle \mathcal{W} \rangle$ might be approximated by $\langle \phi' | \mathcal{W} | \phi' \rangle$ where the value of $\lambda'$ is adjusted so as to minimize the expectation value of $\mathcal{H}$. 
REFERENCES


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,

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

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

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

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 $r_1^2$. 

11. H. R. Hasse, Proc. Cambridge Phil. Soc. 26, 542 (1930);
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