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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<sup>1</sup> 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  $\Psi$  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  $H_0 \psi_0 = \epsilon_0 \psi_0$ . The difference  $H - H_0 = V$  is the perturbation and  $\Psi$  can be expanded in the series  $\Psi = \psi_0 + \psi_0^{(1)} + \dots$ . Here  $\psi_0^{(1)}$  is the first order function which is orthogonal to  $\psi_0$  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 Theorem<sup>1</sup> 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,

$$(H_0 - E_0)\chi_0^{(1)} + (W - \langle \psi_0 | W | \psi_0 \rangle) \psi_0 = 0. \quad (4)$$

Dalgarno and Lewis<sup>2</sup> 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 Stewart<sup>3</sup> 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.<sup>4,5</sup> For the ground state of two electron atoms using hydrogenic approximate wave functions<sup>5</sup> 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<sup>6</sup> 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,<sup>7</sup>

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

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) becomes<sup>5</sup>

$$\langle \psi_0 | \sum_k f_k \frac{\partial V}{\partial q_k} | \psi_0 \rangle = 0 . \quad (9)$$

For a one-dimensional problem, by virtue of Eq. (7), the function  $f$  is simply related<sup>5</sup> to the Dalgarno function  $F$ ,

$$f = \frac{2}{q \psi_0^* \psi_0} \int_c^q q \psi_0^* F \psi_0 dq . \quad (10)$$

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

As Epstein and Hirschfelder<sup>7</sup> 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

$$\psi_0 \rightarrow \phi(\lambda) = \psi_0 + \lambda L \psi_0 = \psi_0 + \lambda F \psi_0 . \quad (11)$$

Thus, if  $\psi_0$  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  $\psi_0$  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

$$\langle \psi_0 | F_0 (V - V_{00}) + (V - V_{00}) F_0 | \psi_0 \rangle \text{ where } V_{00} = \langle \psi_0 | V | \psi_0 \rangle.$$

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  $\alpha$  and  $\langle r \rangle_0$ .

A rougher approximation to  $F$  might be obtained in the following manner. As Lennard-Jones observed<sup>8,1</sup>, 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  $\psi_j$  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 summation<sup>9</sup>,

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

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 Hylleraas<sup>10</sup> or Hasse<sup>11</sup> approximation which leads to good values for the polarizability of molecules.<sup>12</sup> Thus,  $\langle W \rangle$  might be approximated by  $\langle \Phi' | W | \Phi' \rangle$  where the value of  $\lambda'$  is adjusted so as to minimize the expectation value of  $H$ .



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

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

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

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  $r_1^2$ .

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