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IMPROVEMENT OF UNCOUPLED HARTREE-FOCK EXPECTATION VALUES
FOR PHYSICAL PROPERTIES

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ABSTRACT

It is shown that if one uses the uncoupled Hartree-Fock method as a zero-order approximation for calculating atomic and molecular second-order properties (either static or dynamic), then the first order corrections to this approximation are determined solely by quantities already available from the zero-order calculations. No new equations need be solved.

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I. INTRODUCTION

First-order properties, such as permanent dipole and quadrupole moments, diamagnetic susceptibility, charge density at the nucleus, etc., are the straight expectation values of operators W which are the sum of one electron operators $w(i)$. For a system with Hamiltonian H in a state with energy E , such expectation values can be brought into the framework of perturbation theory by introducing a perturbed Hamiltonian^{1,2}

$$\mathcal{H} = H + \mu W \quad (1)$$

with normalized eigenfunctions ψ and with eigenvalues

$$E_e = E + \mu E^{(1)} + \mu^2 E^{(2)} + \dots \quad (2)$$

Here $E^{(1)} = \langle W \rangle$, the expectation value of W . Second-order properties such as electric polarizabilities, paramagnetic susceptibility, optical rotatory constants, chemical shifts, and nuclear shielding constants are proportional to $E^{(2)} = \langle Q \rangle$ where Q can be regarded as the symbolic operator $Q = - (W - \langle W \rangle) (H - E)^{-1} (W - \langle W \rangle)$.

Since the exact eigenfunctions for many-electron atoms and molecules are not known, the calculation of first- and second-order properties starts with an approximate eigenfunction ψ which satisfies a Schrödinger equation $H_0 \psi = E \psi$. The Hamiltonian H can be written in the form $H = H_0 + \lambda V$ where λV is the correction for the "badness" of the approximate eigenfunction. The first and second-order properties can then be expanded in powers of λ ,

$$\langle W \rangle = \langle W \rangle_0 + \lambda \langle W \rangle_1 + \dots \quad (3)$$

$$\langle Q \rangle = \langle Q \rangle_0 + \lambda \langle Q \rangle_1 + \dots \quad (4)$$

In this paper we wish to discuss $\langle W \rangle$ and $\langle Q \rangle$ when ψ is the Hartree-Fock approximation to the wave function of a ground state atom or molecule containing an even number, $N = 2n$, of electrons. $\langle W \rangle_0$ is then the familiar Hartree-Fock Approximation to $\langle W \rangle$ and, as will be shown below, $\langle Q \rangle_0$ is the uncoupled Hartree-Fock approximation^{3,4} to $\langle Q \rangle$.

As is well known,⁵ and as we will rederive below, $\langle W \rangle_1 = 0$ for this situation. It is our purpose to show that $\langle Q \rangle_1$ can be calculated using only quantities already available from the calculation of $\langle Q \rangle_0$.

Thus values of second-order properties can be made accurate through first-order in λ with out too much extra effort.

It is important to note however that first-order in λV is not the same as first-order in the error of the coupled Hartree-Fock approximation³ to $\langle Q \rangle$. Hence the statement that $\langle Q \rangle_0 + \lambda \langle Q \rangle_1$ is accurate through first-order, and the statement that coupled Hartree-Fock is accurate through first-order³ have a somehow different content. We plan to return to this point elsewhere. It is our hope, of course, that $\langle Q \rangle_0 + \lambda \langle Q \rangle_1$ will have a accuracy comparable to that of the coupled Hartree-Fock approximation, but yet be easier to evaluate.

II. REVIEW OF HARTREE-FOCK THEORY

ψ is a single Slater determinant composed of ortho-normal spin-orbitals $u_1^0, u_2^0, \dots, u_N^0$. If \mathcal{A} is the antisymmetrizer,

$$\psi = \mathcal{A} u_1^0(1) \dots u_N^0(N) \quad (5)$$

The spin-orbitals are determined by minimizing the expectation values of H ,

$$\tilde{E} = \langle \psi | H | \psi \rangle \quad (6)$$

If the Hamiltonian is

$$H = \sum_{i=1}^N h(i) + \sum_{i < j} \frac{1}{r_{ij}} \quad (7)$$

then

$$H_0 = \sum_{i=1}^N [h(i) + J(i)] + C \quad (8)$$

where

$$J(i) = \sum_{k=1}^N \left[\int u_k^{0*}(q) \frac{1}{r_{iq}} u_k^0(q) d\tau_q \right. \\ \left. - u_k^0(i) \int u_k^{0*}(q) \frac{1}{r_{iq}} d\tau_q P_{iq} \right] \quad (9)$$

and P_{iq} commutes the coordinates of electron i into those of electron q . The orbitals satisfy the characteristic equation

$$[h(1) + S(1)] u_k^{\circ}(1) = e_k^{\circ} u_k^{\circ}(1) \quad (10)$$

The constant C may be written in the form

$$C = -\frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \{u_i^{\circ} j^{\circ} | i^{\circ} j^{\circ} \rangle - u_i^{\circ} j^{\circ} | j^{\circ} i^{\circ} \rangle\} \quad (11)$$

where we use the notation

$$(i^{\alpha} j^{\beta} | k^{\gamma} l^{\delta} \rangle = \iint u_i^{\alpha*}(1) u_j^{\beta*}(2) \frac{1}{r_{12}} u_k^{\gamma}(1) u_l^{\delta}(2) d\tau_1 d\tau_2 \quad (12)$$

The Hartree-Fock wave function then satisfies the Schrödinger equation

$$H_0 \psi = E \psi \quad \text{where}$$

$$E = \sum_k e_k^{\circ} + C = \tilde{E} \quad (13)$$

The errors in the Hartree-Fock approximation correspond to

$$\lambda V = \sum_{i,j} v_{ij}^{-1} - \sum_{i=1}^N \delta(i) - C \quad (14)$$

However, since $\langle \psi | V | \psi \rangle = 0$, if one expands E in powers of λ ,

$$E = E + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots \quad (15)$$

$E^{(1)} = 0$ and the difference between \tilde{E} and E is second-order in λ .

An important property of the Hartree-Fock wave function is that it is stable with respect to one electron excitations (Brillouin's theorem⁶).

That is, if a Slater determinant χ_R differs from the Hartree-Fock ψ only in having the one spin-orbital u_k^0 replaced by a spin-orbital v_k , then

$$\langle \psi | H | \chi_R \rangle = \epsilon \langle \psi | \chi_R \rangle \quad (16)$$

For our purposes, it is convenient to restate the Brillouin theorem in the form

$$\begin{aligned} \lambda \langle \psi | V | \chi_R \rangle &= \langle \psi | H - H_0 | \chi_R \rangle \\ &= \epsilon \langle \psi | \chi_R \rangle - \epsilon \langle \psi | \chi_R \rangle \\ &= 0 \end{aligned} \quad (17)$$

III. EVALUATION OF FIRST-ORDER CORRECTIONS

We now consider the Schrödinger equation $(H_0 + \mu W)\Phi = E^* \Phi$ where H_0 is the Hartree-Fock Hamiltonian given by Eq. (8). Since $H_0 + \mu W$ is the sum of one electron operators, Φ can be expressed as the Slater determinant

$$\Phi = a u_1(1) \dots u_n(N) \quad (18)$$

where the spin-orbitals u_k satisfy the characteristic equation

$$[h(1) + S(1) + \mu w(1)] u_k(1) = e_k u_k(1) \quad (19)$$

The $u_k(1)$ and the e_k can then be determined as solutions to a one electron perturbation problem starting with $u_k^0(1)$ and e_k^0 as the zeroth order eigenfunction and eigenvalue respectively. Expanding $u_k(1)$

in powers of μ gives

$$u_k^{(1)} = u_k^{(0)} + \mu u_k^{(1)} + \mu^2 u_k^{(2)} + \dots \quad (20)$$

In a similar fashion, $\bar{\Phi}$ can be expanded in powers of μ ,

$$\bar{\Phi} = \psi + \mu \psi^{(0,1)} + \mu^2 \psi^{(0,2)} + \dots \quad (21)$$

Here

$$\psi^{(0,1)} = \sum_{i=1}^N a u_i^{(0)} \dots u_i^{(1)} \dots u_N^{(0)} \quad (22)$$

and

$$\begin{aligned} \psi^{(0,2)} = & \sum_{i=1}^N a u_i^{(0)} \dots u_i^{(2)} \dots u_N^{(0)} \\ & + \sum_{i=1}^{N-1} \sum_{j=i+1}^N a u_i^{(0)} \dots u_i^{(1)} \dots u_j^{(1)} \dots u_N^{(0)} \end{aligned} \quad (23)$$

The $\psi^{(0,1)}$, $\psi^{(0,2)}$, ... are terms in the double expansion of $\bar{\Psi}$,

$$\bar{\Psi} = \sum_{n=0} \sum_{m=0} \lambda^n \mu^m \psi^{(n,m)} \quad (24)$$

If we also expand \mathcal{E} as a double power series and use double perturbation theory¹, we can then identify:

$$\langle W \rangle_0 = \langle \psi | W | \psi \rangle \quad (25)$$

and

$$\langle Q \rangle_0 = \langle \psi^{(0,1)} | W | \psi \rangle \quad (26)$$

the formula for $\langle Q \rangle_0$ being exactly that of the uncoupled Hartree-Fock approximation.^{3,4} Furthermore, as a result of the Dalgarno Interchange Theorem^{1,2},

$$\langle W \rangle_1 = \langle \psi^{(0,1)} | V | \psi \rangle + \langle \psi | V | \psi^{(0,1)} \rangle \quad (27)$$

and

$$\langle Q \rangle_1 = \langle \psi^{(0,2)} | V | \psi \rangle + \langle \psi^{(0,1)} | V | \psi^{(0,1)} \rangle + \langle \psi | V | \psi^{(0,2)} \rangle \quad (28)$$

Let us now expand $\langle \bar{\Phi} | V | \bar{\Phi} \rangle$ in powers of μ in the form

$$\langle \bar{\Phi} | V | \bar{\Phi} \rangle = \mu A_1 + \mu^2 A_2 + \dots \quad (29)$$

Then, since V is independent of μ , it follows from

Eqs. (21), (27) and (28) that $\langle W \rangle_1 = A_1$ and $\langle Q \rangle_1 = A_2$.

Making use of Eqs. (9), (11), and (14), together with the notation of Eq. (12), we then find

$$\langle \bar{\Phi} | V | \bar{\Phi} \rangle = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \left[\begin{aligned} & (i_j | i_j) - (i_j | j_i) \\ & - 2(i_j^0 | i_j^0) + 2(i_j^0 | j^0 i) \\ & + (i_j^0 | i_j^0) - (i_j^0 | j^0 i^0) \end{aligned} \right] \quad (30)$$

Expanding the u_k in powers of μ , and collecting terms, gives $A_1 = \langle W \rangle = 0$. Furthermore,

$$A_2 = \langle Q \rangle = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \left[\begin{aligned} & (i_j^1 | i_j^1) - (i_j^1 | j^0 i^0) + 2(i_j^1 | i_j^0) \\ & + (i_j^0 | i_j^1) - (i_j^0 | j^1 i^0) - 2(i_j^0 | j^1 i^0) \end{aligned} \right] \quad (31)$$

The interesting and important feature of these formulae is that they do not involve the $u_k^{(2)}$. All one needs are $u_k^{(0)}$ and $u_k^{(1)}$ which are already available from the calculation of $\langle Q \rangle$. This simplification has come about in the following way:

Since $\psi^{(0,1)}$ is the sum of one electron excitation Slater determinants, it follows from the Brillouin Theorem, Eq. (17), that $\langle \psi^{(0,1)} | V | \psi \rangle = 0$ and hence $\langle W \rangle = 0$. In a similar manner, since $\psi^{(0,2)}$ only involves $u_k^{(2)}$ through one electron excitation Slater determinants, $\langle \psi^{(0,2)} | V | \psi \rangle$ is independent of the second-order spin-orbitals. Thus, Eq. (31) provides us with a very simple expression for $\langle Q \rangle$ which only

requires the knowledge of the unperturbed and first-order spin-orbitals.

Similar results can be shown to hold in the calculation of second-order frequency dependent properties. In the notation of reference 1, Chapter 9, one can prove that if $\psi^{(0)}$ is the Hartree-Fock function then (i) one electron excitation terms in θ_{\pm} do not contribute to L , and (ii), the two electron excitation terms in $\theta_{+} + \theta_{-}$, which is the quantity one needs to compute L , are all expressible in terms of the spin-orbitals of $\psi_{\pm}^{(0)}$ which are available from the zero order calculation.

Details and results of calculations for specific examples will be published as soon as possible.

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REFERENCES

1. J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, "Adv. Quantum Chem. 1, 255 (1964).
2. A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. (London) A247, 245 (1958).
3. A. Dalgarno, Proc. Roy. Soc. (London), A251, 282 (1959).
4. There are different schemes of uncoupled Hartree-Fock approximation, which have been discussed by P. W. Langhoff, M. Karplus and R. P. Hurst. "Approximations to Hartree-Fock Perturbation Theory" (preprint). Our discussion in this paper is limited to Dalgarno's uncoupled Hartree-Fock approximation³ (Approximation "C" of Langhoff, et al) with $S(i)$ defined by Eq. (9).
5. G. G. Hall, Adv. Quan. Chem. 1, 241 (1964) and references given there.
6. L. Brillouin, Act. Sci. et Ind., Nos. 71, 159 (1933-34).
7. However, small corrections to uncoupled Hartree-Fock are probably not of much interest for frequency dependent properties because the frequency dependence of the uncoupled approximation is qualitatively incorrect (see for example reference 4).