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Debbie Fu-tai Tuan[+], Saul T. Epstein, and Joseph O. Hirschfelder
University of Wisconsin Theoretical Chemistry Institute
Madison, Wisconsin

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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[+] Present address: Department of Chemistry, Kent State University, Kent, Ohio 44240.

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]

$$\mathcal{H} = H + \mu W \tag{1}$$

with normalized eigenfunctions Ψ and with eigenvalues

$$\mathcal{E} = E + \mu E^{(1)} + \mu^2 E^{(2)} + \ldots \tag{2}$$

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 $H_0 \psi = \epsilon \psi$. 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,

$$< W > = < W >_0 + \lambda < W >_1 + \ldots \quad (3)$$

$$< Q > = < Q >_0 + \lambda < Q >_1 + \ldots \quad (4)$$

In this paper we wish to discuss $< W >_1$ and $< Q >_1$ 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. $< W >_0$ is then the familiar Hartree-Fock Approximation to $< W >$ and, as will be shown below, $< Q >_0$ is the uncoupled Hartree-Fock approximation[3,4] to $< Q >$.

As is well known,[5] and as we will rederive below, $< W >_1 \equiv 0$ for this situation. It is our purpose to show that $< Q >_1$ can be calculated using only quantities already available from the calculation of $< Q >_0$.

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 approximation[3] to $< Q >$. Hence the statement that $< Q >_0 + \lambda < Q >_1$ is accurate through first-order, and the statement that coupled Hartree-Fock is accurate through first-order[3] have a somehow different content. We plan to return to this point elsewhere. It is our hope, of course, that $< Q >_0 + \lambda < Q >_1$ 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 $u^o_1, u^o_2, \ldots, u^o_N$. If $\mathcal{A}$ is the antisymmeterizer,

$$\psi = \mathcal{A}\, u_1^{o}(1) \cdots\cdots u_n^{(o)}(N) \tag{5}$$

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

$$\tilde{E} = \langle \psi | H | \psi \rangle \tag{6}$$

If the Hamiltonian is

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

then

$$H_0 = \sum_{i=1}^{N} \left[h(i) + S(i) \right] + C \quad , \tag{8}$$

where

$$S(i) = \sum_{k=1}^{N} \left[\begin{array}{l} \int u_k^{o*}(q) \frac{1}{r_{iq}} u_k^{o}(q)\, d\tau_q \\ - u_k^{o}(i) \int u_k^{o*}(q) \frac{1}{r_{iq}}\, d\tau_q\, P_{iq} \end{array} \right] \tag{9}$$

and P_{iq} commutes the coordinates of electron i into those of electron q

The orbitals satisfy the characteristic equation

$$\left[h(1) + S(1) \right] u^{\circ}_{k}(1) = e^{\circ}_{k}\, u^{\circ}_{k}(1) \tag{10}$$

The constant C may be written in the form

$$C = -\frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left\{ (i^{\circ} j^{\circ} | i^{\circ} j^{\circ}) - (i^{\circ} j^{\circ} | j^{\circ} i^{\circ}) \right\} \tag{11}$$

where we use the notation

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

The Hartree-Fock wave function than satisfies the Schrödinger equation $H_o \psi = \epsilon \psi$ where

$$\epsilon = \sum_{k} e_k^{\circ} + C = \widetilde{E} \tag{13}$$

The errors in the Hartree-Fock approximation correspond to

$$\lambda V = \sum_{i<j} r_{ij}^{-1} - \sum_{i=1}^{N} S(i) - C \tag{14}$$

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

$$E = \epsilon + \lambda \epsilon^{(1)} + \lambda^2 \epsilon^{(2)} + - - - - \tag{15}$$

$\epsilon^{(1)} = 0$ and the difference between E and ϵ 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 theorem[6]).

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

$$\langle \psi / H / \chi_k \rangle = \epsilon \langle \psi / \chi_k \rangle \tag{16}$$

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

$$\begin{aligned} \lambda \langle \psi / V / \chi_k \rangle &= \langle \psi / H - H_0 / \chi_k \rangle \\ &= \epsilon \langle \psi / \chi_k \rangle - \epsilon \langle \psi / \chi_k \rangle \\ &= 0 \end{aligned} \tag{17}$$

III. EVALUATION OF FIRST-ORDER CORRECTIONS

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

$$\Phi = \mathcal{A}\, u_1(1) \cdots u_n(N) \tag{18}$$

where the spin-orbitals u_k satisfy the characteristic equation

$$\left[h(1) + S(1) + \mu w(1) \right] u_k(1) = e_k u_k(1) \tag{19}$$

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

in powers of μ gives

$$u_k(1) = u_k^{0}(1) + \mu\, u_k^{(1)}(1) + \mu^2 u_k^{(2)}(1) + \text{-----} \tag{20}$$

In a similar fashion, Φ can be expanded in powers of μ,

$$\Phi = \psi + \mu\, \psi^{(0,1)} + \mu^2 \psi^{(0,2)} + \text{-----} \tag{21}$$

Here

$$\psi^{(0,1)} = \sum_{i=1}^{N} a\, u_1^{0}(1) \cdots u_i^{(1)}(i) \text{----} u_N^{0}(N) \tag{22}$$

and

$$\psi^{(0.2)} = \sum_{i=1}^{N} a\, u_1^{(0)}(1) \text{----} u_i^{(2)}(i) + \text{---} u_N^{(0)}(N)$$

$$+ \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} a\, u_1^{(0)}(1) \text{----} u_i^{(1)}(i) \cdots u_j^{(1)}(j) \cdots u_N^{(0)}(N) \tag{23}$$

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

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

If we also expand $\mathcal{E}$ as a double power series and use double perturbation theory[1], we can then identify:

$$\langle W\rangle_0 = \langle\psi/W/\psi\rangle \tag{25}$$

and

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

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],

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

and

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

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

$$\langle\bar{\Phi}/V/\bar{\Phi}\rangle = \mu A_1 + \mu^2 A_2 + \ldots\ldots \tag{29}$$

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

$$\langle \bar{\Phi} | V | \bar{\Phi} \rangle = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \begin{bmatrix} (ij|ij) - (ij|ji) \\ -2(ij^0|ij^0) + 2(ij^0|j^0i) \\ + (i^0j^0|i^0j^0) - (i^0j^0|j^0i^0) \end{bmatrix} \quad (30)$$

Expanding the u_k in powers of μ, and collecting terms, gives $A_1 = \langle W \rangle_1 = 0$. Furthermore,

$$A_2 = \langle Q \rangle_1 = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} [(i^1j^1|i^0j^0) - (i^1j^1|j^0i^0) + 2(i^1j^0|i^0j^1)$$

$$+ (i^0j^0|i^1j^1) - (i^0j^0|j^1i^1) - 2(i^1j^0|j^1i^0)] \quad (31)$$

The interesting and important feature of these formulae is that <u>they do not involve the $u_k^{(2)}$</u>. All one needs are $u_k^{(0)}$ and $u_k^{(1)}$ which are already available from the calculation of $\langle Q \rangle_0$. 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 $\langle W \rangle_1 = 0$. 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 $\langle Q \rangle_1$ 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.[7] 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 $\theta_{\pm}$ 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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