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On the Use of UHF Orbitals in Ionization Energy Calculations

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The UHF Hamiltonian and simple Löwdin-like annihilators are formulated in the second quantization formalism. The so formulated Hamiltonian was employed in many-body Rayleigh–Schrödinger perturbation theory to evaluate the corrections to the UHF orbital energies.

Key words: UHF orbital functions for ionization energies

1. Introduction

Many methods based on the orbital model (Hartree–Fock theory) exist in quantum chemistry which include the spin correlation effects in systems with open electronic shells. The most important among them are: the unrestricted Hartree–Fock theory (UHF) [1], the unrestricted method with projection [2] (or annihilation [3, 4]), and the extended Hartree–Fock method [5, 6]. The wave function in the unrestricted Hartree–Fock theory represents one Slater determinant, and the electrons with different spins occupy different space orbitals. The direct use of unrestricted methods is disadvantageous as the unrestricted wave function is not an eigenfunction of S^2 (it contains the contaminations of higher multiplicity states). The projected (or annihilated) Hartree–Fock method yields the spin-projected (or annihilated) wave function from an UHF wave function after energy minimization. However, such a wave function does not obey the variation condition. In the extended Hartree–Fock theory the wave function minimalizes the energy after spin projection of a single Slater determinant.

In contrast to the restricted SCF methods for open shells (Roothaan or method by Longuet–Higgins and Pople), the orbital energies in the unrestricted SCF method have, as in closed-shell systems, a simple physical interpretation; i.e. they represent the ionization energies for removing one electron from a definite level of the studied

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radical neglecting correlation and relaxation effects. In other words the well known Koopmans theorem [7] can be used in unrestricted SCF methods keeping in mind the above mentioned difficulties with spin contamination.

In ionization energy calculations (or, accurately speaking, in the calculation of corrections to the orbital energies) one can employ the current procedures based on many-body perturbation theory [8–15]. These methods have been frequently used in calculations of many closed-shell systems.

In the present paper our attention is focused first on the formulation of the UHF Hamiltonian and simple Löwdin-like annihilators within the second quantization formalism, and then in the second step, we give the many-body theory of ionization energies using the unrestricted wave function with annihilation.

The UHF SCF wave function (but unprojected) has also been used by Purvis and Öhrn [16]. They obtained, solving the Dyson equation with a second-order self energy and using the Grand Canonical averaging procedure, a theoretical photoelectron spectrum of the oxygen molecule.

2. Second Quantization Formulation of UHF Hamiltonian and Spin-Annihilation Operator

Let us define a set of creation $X_{i\sigma}^{+}$ and annihilation $X_{i\sigma}$ operators on a space of one-electron wave function for spin σ. The UHF ground state wave function can be then written

$$|\phi_0\rangle = \prod_{\substack{i\in\langle 1,N\alpha\rangle \\ j\in\langle 1,N\beta\rangle}} X_{i\alpha}^{+} X_{j\beta}^{+} |0\rangle \tag{1}$$

where $|0\rangle$ is the vacuum state vector, N_α, and N_β are the numbers of α- and β-spin electrons, respectively.

The total Hamiltonian in the second quantization has the following form

$$H = \sum_{\substack{i,i \\ \sigma}} \langle i\sigma|h|j\sigma\rangle X_{i\sigma}^{+} X_{j\sigma} + \frac{1}{2} \sum_{\substack{i,j,k,l \\ \sigma,\sigma'}} \langle i\sigma j\sigma'|g|k\sigma l\sigma'\rangle X_{i\sigma}^{+} X_{j\sigma'}^{+} X_{l\sigma'} X_{k\sigma} \tag{2}$$

where h is the one-electron, and g the two-electron operator.

It is easy to show that, after simple algebraic manipulations with creation and annihilation operators, the normal form of Hamiltonian (2) is

$$H = \langle\phi_0|H|\phi_0\rangle + \sum_{i,\sigma} \mathscr{E}_{i\sigma} N[X_{i\sigma}^{+} X_{i\sigma}]$$

$$+ \frac{1}{2} \sum_{\substack{ijkl \\ \sigma'\sigma}} \langle i\sigma j\sigma'|g|k\sigma l\sigma'\rangle N[X_{i\sigma}^{+} X_{j\sigma'}^{+} X_{l\sigma'} X_{k\sigma}] \tag{3}$$

where $\mathscr{E}_{i\sigma}$ is the UHF orbital energy for spin σ, and $N[\cdots]$ means the normal product defined with respect to $|\phi_0\rangle$.

We see that the Hamiltonian (3) in the UHF method has formally the same normal form as its counterpart in the Hartree–Fock theory of closed-shell systems [17], in contrast to the Hamiltonian in the restricted Hartree–Fock theory of open-shell systems, where an additional one-electron interaction term arises [18].

The UHF wave function consists of components with various multiplicity and it can be generally written as

$$|\phi_0\rangle = \sum_{r=0}^{N_\beta} C_{s'+r}|\phi_{s'+r}\rangle \tag{4}$$

where $S' = (N_\alpha - N_\beta)/2$ and $s = s' + N_\beta$ are the indices of components with lowest and highest multiplicity, respectively.

Amos *et al.* [3, 4] have shown that the most important components in $|\phi_0\rangle$ are those with $r = 0$ and $r = 1$, and that the coefficients with $r > 1$ are negligibly small. They proposed to use a simple projector-annihilator, so that

$$|\phi_s\rangle = A_s|\phi_0\rangle \tag{5}$$

where

$$A_s = S^2 - (s + 1)(s + 2) \tag{6}$$

is the annihilator and $|\phi_s\rangle$ is the component with multiplicity $(2s + 1)$.

We suppose for the sake of simplicity that the spin annihilator A_s is an idempotent operator. Since this operator commutes with every spin-free operator $\mathcal{O}$, the mean value of an operator is given by

$$\langle\mathcal{O}\rangle = \langle\phi_0|\mathcal{O}A_s|\phi_0\rangle/\langle\phi_0|A_s|\phi_0\rangle. \tag{7}$$

Introducing the modified spin annihilator $\mathscr{A}_s$

$$\mathscr{A}_s = A_s/\langle\phi_0|A_s|\phi_0\rangle \tag{8}$$

the norm of the function (5) in which A_s is replaced by $\mathscr{A}_s$ is

$$\langle\phi_s|\phi_s\rangle = 1. \tag{9}$$

In the following we focus our attention on the second quantization form of the spin annihilator (8). One can show, after simple but tedious algebraic operations with an immediate use of Wick's theorem, that the normal form of this operator is

$$A_s = 1 + \frac{1}{2}\sum_{\substack{ijkl\\ \sigma\sigma'\tau\tau'}} \mathscr{M}_{ijkl}^{\sigma\sigma'\tau\tau'} N[X_{i\sigma}^+ X_{k\tau}^+ X_{l\tau'} X_{j\sigma'}] + \sum_{\substack{ij\\ \sigma}} \mathscr{N}_{ij}^{\sigma} N[X_{i\sigma}^+ X_{j\sigma}] \tag{10}$$

where the matrix elements $\mathscr{M}_{ijkl}^{\sigma\sigma'\tau\tau'}$ and $\mathscr{N}_{ij}^{\sigma}$ are defined by the relations

$$\mathscr{M}_{ijkl}^{\sigma\sigma'\tau\tau'} = \mathscr{S}_{ij}^{\alpha\beta}\mathscr{S}_{kl}^{\beta\alpha}\,\delta_{\sigma\alpha}\,\delta_{\sigma'\beta}\,\delta_{\tau\beta}\,\delta_{\tau'\alpha} + \mathscr{S}_{ij}^{\beta\alpha}\mathscr{S}_{kl}^{\alpha\beta}\,\delta_{\sigma\beta}\,\delta_{\sigma'\alpha}\,\delta_{\tau\alpha}\,\delta_{\tau'\beta}, \tag{11a}$$

$$\mathscr{N}_{ij}^{\sigma} = \sum_{\mu,\nu}[C_{\mu i}^{\alpha}(\tfrac{1}{2}\delta_{\mu\nu} - P_{\mu\nu}^{\beta})C_{\nu j}^{\alpha}\,\delta_{\sigma\alpha} + C_{\mu i}^{\beta}(\tfrac{1}{2}\delta_{\mu\nu} - P_{\mu\nu}^{\alpha})C_{\nu j}^{\beta}\,\delta_{\sigma\beta}]. \tag{11b}$$

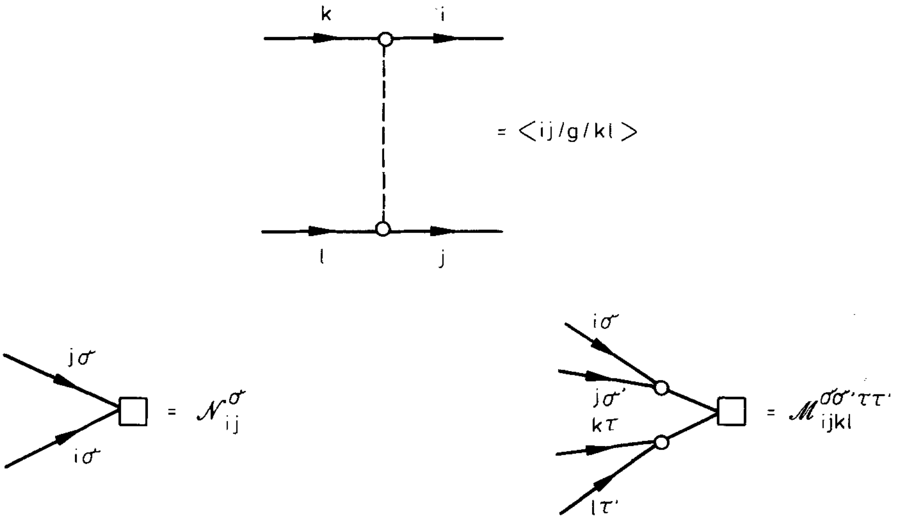

Fig. 1. The diagrammatic interpretation of the perturbation H_1 and matrix elements $\mathcal{M}^{\sigma_1\sigma_2\tau_1\tau_2}_{ijkl}$ and $\mathcal{N}^{\sigma}_{ij}$

In these expressions the δ's are the Kronecker delta symbols, $\mathcal{S}^{\sigma\tau}_{ij}$ represents the overlap integral between spatial parts of spinorbitals $|i\sigma\rangle$ and $|j\tau\rangle$, i.e.

$$\mathcal{S}^{\sigma\tau}_{ij} = \langle i_\sigma | j_\tau \rangle \tag{12}$$

where in a given basis of atomic orbitals $\{|\mu\rangle\}$ the spinorbital $|i\sigma\rangle$ is

$$|i\sigma\rangle = |i_\sigma\rangle|\sigma\rangle = \sum_{\mu} C^{\sigma}_{\mu i}|\mu\rangle|\sigma\rangle. \tag{13}$$

We will now suppose the orthonormality of the atomic orbitals $\{|\mu\rangle\}$. The entity $P^{\sigma}_{\mu\nu}$ in expression (11b) is the element of the density matrix

$$P^{\sigma}_{\mu\nu} = \sum_{i\in\langle 1,N_\sigma\rangle} C^{\sigma}_{\mu i} C^{\tau}_{\mu i}. \tag{14}$$

The mean value of the spin annihilator A_s in state $|\phi_0\rangle$ can be written as

$$\langle A_s\rangle_0 = \langle\phi_0|A_s|\phi_0\rangle = \tfrac{1}{4}(N_\alpha - N_\beta)^2 + \tfrac{1}{2}(N_\alpha + N_\beta) - \operatorname{Tr}(P^{\alpha}P^{\beta}) - (s+1)(s+2). \tag{15}$$

This equation is valid only for an orthonormal set of orbitals $\{|\mu\rangle\}$.

The annihilator $\mathcal{A}_s$ acting on the wave function $|\phi_0\rangle$ generates the mono- and bi-excited states. Its diagrammatic interpretation (namely of its one- and two-electronic parts together with a diagrammatic representation of the perturbation $H_1 = \frac{1}{2}\sum_{ijkl,\sigma,\sigma'}\langle i\sigma j\sigma'|g|k\sigma l\sigma'\rangle N[X^{+}_{i\sigma}X^{+}_{j\sigma'}X_{l\sigma'}X_{k\sigma}]$) is illustrated in Fig. 1.

3. Calculation of Ionization Energies Using the UHF SC Method

As mentioned in the Introduction, some difficulties arise in the application of unrestricted SCF orbitals. Using these orbitals in the calculations of ionization energies in systems with one or more unpaired electrons, it becomes very difficult to define the spin multiplicity of the individual states.

Despite these complications we will subsequently formulate, using the annihilation of the first higher multiplicity state, the perturbation corrections to the orbital energies. We will restrict our considerations to the first-order of perturbation theory, which gives in closed-shell systems generally no contribution to the perturbation corrections.

Let us suppose that the ground electronic state of an open-shell electronic system is described by the wave function (1). The model space Ω_0 corresponding to singly ionized states is then spanned by the following vectors

$$|\phi(i,\sigma)\rangle = X_{i\sigma}|\phi_0\rangle. \tag{16}$$

These vectors are the eigenfunctions of the unperturbed Hamiltonian $H_0 = \sum_{i\sigma} \mathscr{E}_{i\sigma} N[X_{i\sigma}^{+} X_{i\sigma}]$

$$H_0|\phi(i,\sigma)\rangle = -\mathscr{E}_{i\sigma}|\phi(i,\sigma)\rangle. \tag{17}$$

Because of the spin contamination of the state vector $|\phi_0\rangle$ we will use the spin-annihilated state vector $|\phi_s\rangle$. Then the new model space Ω_s spanned by the unperturbed vectors can be introduced

$$|\phi_s(i,\sigma)\rangle = X_{i\sigma}|\phi_s\rangle. \tag{18}$$

In a similar way as in the preceding case, these vectors are also the eigenvectors of the unperturbed Hamiltonian

$$H_0|\phi_s(i,\sigma)\rangle = \mathscr{E}_s^{(0)}(i,\sigma)|\phi_s(i,\sigma)\rangle. \tag{19}$$

For the energy $\mathscr{E}_s^{(0)}(i,\sigma)$ we can write the following expression

$$\mathscr{E}_s^{(0)}(i,\sigma) = -\mathscr{E}_{i\sigma}(1 + A_{i\sigma}^s + B_{i\sigma}^s) + C_{i\sigma}^s + D_{i\sigma}^s. \tag{20}$$

The individual coefficients in expression (20) are

$$A_{i\sigma}^s = \langle A_s\rangle_0^{-1} \sum_{\mathrm{I}} \mathscr{N}_{ph}^{\sigma'} \tag{21a}$$

$$B_{i\sigma}^s = \langle A_s\rangle_0^{-1} \sum_{\mathrm{II}} \mathscr{M}_{p_1p_2h_1h_2}^{\sigma_1\sigma_2\tau_1\tau_2} \tag{21b}$$

$$C_{i\sigma}^s = \langle A_s\rangle_0^{-1} \sum_{\mathrm{I}} (\mathscr{E}_{p\sigma'} - \mathscr{E}_{h\sigma'})\mathscr{N}_{ph}^{\sigma'} \tag{21c}$$

$$D_{i\sigma}^s = \langle A_s\rangle_0^{-1} \sum_{\mathrm{II}} (\mathscr{E}_{p_1\sigma_1} + \mathscr{E}_{p_2\sigma_2} - \mathscr{E}_{h_1\tau_1} - \mathscr{E}_{h_2\tau_2})\mathscr{M}_{p_1p_2h_1h_2}^{\sigma_1\sigma_2\tau_1\tau_2} \tag{21d}$$

where the summations $\sum_{\mathrm{I}}$, $\sum_{\mathrm{II}}$ are defined

$$\sum_{\mathrm{I}} = \sum_{\substack{h \neq i \cap \sigma' \neq \sigma \\ h \in \langle 1, \sigma' \rangle}} ; \qquad \sum_{\mathrm{II}} = \sum_{\substack{h_1 \neq i \cap \tau_1 \neq \sigma \\ h_1, h_2 \in \langle 1, N_\tau \rangle}} \sum_{\substack{h_2 \neq i \cap \tau_2 \neq \sigma \\ p_1, p_2 > N\sigma_1, N\sigma_2}} . \tag{22}$$

The eigenenergy $\mathscr{E}_s^{(0)}(i,\sigma)$ represents the zeroth-order orbital energy with annihilation of the first higher multiplicity state.

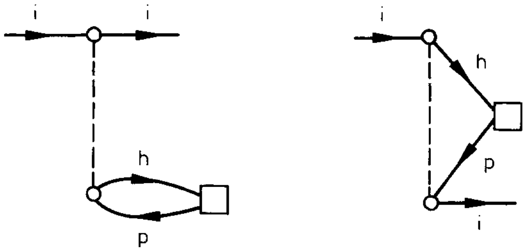

Fig. 2. First order diagrams

Keeping in mind the mathematical properties of the operator $\mathscr{A}_s$ (see part 2) then the first order perturbation correction to the orbital energies is given by

$$\mathscr{E}_s^{(1)}(i,\sigma) = \langle\phi_0(i,\sigma)|H_1|\phi_s(i,\sigma)\rangle. \tag{23}$$

Using the diagrammatic interpretation of individual components of the annihilator $\mathscr{A}_s$ and perturbation H_1 (Fig. 1), the first-order term (23) can be expressed in Goldstone diagrammatic technique by two diagrams (Fig. 2).

The algebraic interpretation of diagrams in Fig. 2 has the following form

$$\mathscr{E}_s^{(1)}(i,\sigma) = \sum_{\substack{h,p\\ \sigma}} (\langle i_\sigma h_{\sigma'}|g|i_\sigma p_{\sigma'}\rangle - \langle i_\sigma h_\sigma|g|p_\sigma i_\sigma\rangle)\mathscr{N}_{ph}^{\sigma'}. \tag{24}$$

Analogously, it is possible to present the higher-order perturbation terms; of course, these diagrams and their algebraic interpretation will have a more complicated form.

4. Concluding Remarks

In the preceding parts we have shown that it is possible to calculate the orbital energies of radical systems within the UHF SCF method, in which the first higher multiplicity state is annihilated. Because of the correlation and relaxation corrections (by perturbation theory), the calculated orbital energies are expected to be good approximations to the ionization energies. The resulting formulae are relatively simple and suitable for direct use on the computer.

In conclusion, we would like to point out our belief that the theoretical formalism developed in this paper could be of use for studying the low-lying ionization energies of any open-shell molecular or atomic system.

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