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A PARTIALLY SPIN-RESTRICTED HARTREE-FOCK FUNCTION BASED ON THE ASYMPTOTIC PROJECTION METHOD

A singe Slater determinant consisting of restricted and unrestricted, in spins, parts is proposed to construct a reference configuration for singlet excited states having the same symmetry as the ground one. A partially restricted Hartree-Fock approach is developed to derive amended equations determining the spatial molecular orbitals for singlet excited states. They present the natural base to describe the electron correlation in excited states using the well-established spin-annihilated perturbation theories. The efficiency of the proposed method is demonstrated by calculations of electronic singlet excitation energies for the Be atom and LiH molecule.

Keywords: partially spin-restricted wave function, orthogonality constraints, excited states, perturbation theory.

1. Introduction

A single Slater determinant (Sladet) forms the basis of many modern quantum methods for studying the electronic structure of atoms and molecules (e.g. [1]). Present – day approaches deal with two extreme schemes of designing a Sladet. A restricted Hartree-Fock (RHF) function with the doubly occupied spatial molecular orbitals (MOs) is usually applied to closed-shell systems. However, in several cases a RHF Sladet cannot even approximately describe the states of a molecular system such as those from regions of the potential energy surface which are far from equilibrium geometry or the singlet excited states (ESs). While, the unrestricted HF (UHF) Sladet, in which the electrons of opposite spins are assigned to spatially different orbitals, is capable correctly describing such situations. A UHF function, however, is not a spin eigenfunction and contains contamination by higher spin states. In systems where contamination is not small, the perturbation theory (PT) for incorporating the correlation effects may lead to weakly converging series (e.g. [2] and references therein). The approaches based on the Lowdin spin projection operator [3] are usually employed to remedy the spin contamination problem. This requires evaluation of expectation values of the Lowdin operator and presents severe computational difficulties.

In this paper we introduce a so-called partially restricted HF (PRHF) function, which consists of restricted and unrestricted parts:

$$\Phi^{(0)} = (N!)^{-1/2} \det | \varphi_1^\alpha \alpha \varphi_1^\beta \beta ... \varphi_q^\alpha \alpha \varphi_q^\beta \varphi_{q+1}^\alpha \alpha \varphi_{q+1}^\beta ... \varphi_{q+p}^\alpha \alpha \varphi_{q+p}^\beta | \qquad (1)$$

There are q orbitals with closed shell character, i.e. the α MOs φ_i^α, $i= 1,2,..., q$, are taken to be spatially identical to the β MOs $\varphi_i^\alpha = \varphi_i^\beta$, $i= 1,2,..., q$. These orbitals form the so-called "core"- subspace. The other p orbitals have different spatial parts for different spins, i.e. $\varphi_i^\alpha \neq \varphi_i^\beta$, $i= q+1, q+2,..., q+p$, and form the unrestricted part (so-called unpaired electrons). In addition $N=q+p$ is the number of electrons.

One the one hand, such a Sladet as well as the UHF function as compared to the RHF function has the freedom of being symmetry broken and can be used as a reference configuration for the calculations of singlet excited states. On the other hand, this model has advantage compared to the fully UHF one due to a simple way to design spin

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eigenstates. For example, such a function with two electrons in the unrestricted part ($p=1$) is just a mixture of singlet and triplet components. The application of a single Amos annihilator [4] to this function provides the pure spin state, whereas for the UHF function this procedure can produce a wave function which, in general, is still far from an eigenfunction of S^2

A PRHF function was first applied in [5] for describing a transition from the diradicals to the dicarbens. A modified coupling operator method has been used for the determination the ground state MOs which result from three coupled equations with different Fock operators. Generally, they represent fifth-order equations in LCAO coefficients. The formalism proposed in [5] as well as the open-shell Roothaan method [6] does not lend itself very readily to a well-defined PT. PT calculations based on this formalism are problematic because there is no unique way to choose off-diagonal Lagrange multipliers coupling the closed and open-shell MOs (see, e.g. [7]). In [8, 9] we have proposed alternative open-shell HF method that does not involve off-diagonal Lagrange multipliers from which PT can be performed using the UHF formalism for the *ground state* and, therefore, ambiguity problems do not appear . Unlike [5, 8, 9], in the present work we shall consider *singlet excited state calculations* based on a PRHF reference function. Conceptual simplicity of such a function allows one, on the one hand, to develop the PT , which takes for ESs the same practically computational time as the genuine Moller-Plesset PT for the ground state and, on the other hand, to optimize a finite basis set for each individual state. It is especially important for the excited state calculations performed with restricted basis sets where the effects of basis incompleteness are comparable to the electron correlation effects.

2. Singlet excited states and annihilated perturbation theory based on a PRHF function

(i) We shall consider systems with the number of α electrons equal to the number of β electrons, $n^\alpha = n^\beta = p+q$, $S = S_z = 0$ and $n^\alpha + n^\beta = N$ is the number of electrons. Let $\Phi_0^{(0)}$ be the Sladet describing the ground state and constructed by the RHF method for closed shells. For simplicity, consider only the first singlet excited state. In [5], from the very beginning, the PRHF function (1) with the *identical* "core" α and β orbitals was used to derive the equations for MOs. Unlike [5], for the excited state we start from an UHF Sladet where all the α orbitals, φ_i^α, are permitted to be spatially different from the β orbitals, φ_i^β.

Some restrictions should be imposed on MOs to obtain a PRHF function for the first excited state.

First, the subspaces of the closed-shell 'core' determined by φ_i^α, $i = 1,2,..., q$, and φ_i^β, $i = 1,2,..., q$, must coincide. This requirement may be written as the following orthogonality constraint [8]:

$$\sum_{i=1}^{q} \left\langle \varphi_i^\beta \left| (I - P_c^\alpha) \right| \varphi_i^\beta \right\rangle = 0, \ i=1,2,...,q \tag{2}$$

where $P_c^\alpha = \sum_{i=1}^{q} \left| \varphi_i^\alpha \right\rangle \left\langle \varphi_i^\alpha \right|$ is the orthoprojector on the "core" subspace of MO^α.

Second, the requirement that provides the orthogonality of states:

$$\left\langle \Phi^{(0)} \left| \Phi_0^{(0)} \right\rangle = 0. \tag{3}$$

116

The restriction (3) allows one to avoid collapsing into the ground state. One can show that (3) can be written in terms of spatial orbitals in the form:

$$\sum_{i=1}^{p+q} \left\langle \varphi_i^{\alpha} \left| P_0 \right| \varphi_i^{\alpha} \right\rangle = 0. \text{ with } P_0 = \left| \varphi_{0n}^{\alpha} \right\rangle \left\langle \varphi_{0n}^{\alpha} \right| \tag{4}$$

where φ_{0n}^{α} is the highest in orbital energy occupied MO from the ground state Sladet $\Phi_0^{(0)}$. To obtain the equations for the MOs we require that the total energy

$$E^{UHF} = \left\langle \Phi^{(0)} \left| H \right| \Phi^{(0)} \right\rangle$$

be stationary subject to the orthogonality constraints (2) and (4). These restrictions can be easily introduced into variational process using our asymptotic projection (AP) method developed earlier [10,11]. Then the stationary condition

$$\delta L = \delta[E^{UHF} + \lambda \sum_{i=1}^{q} \left\langle \varphi_i^{\beta} \left| (I - P_c^{\alpha}) \right| \varphi_i^{\beta} \right\rangle + \lambda_1 \sum_{i=1}^{p+q} \left\langle \varphi_i^{\alpha} \left| P_0 \right| \varphi_i^{\alpha} \right\rangle = 0,$$

and AP methodology leads to the amended UHF equations for ES orbitals:

$$P(F^{\alpha} - \lambda P_c^{\beta} + \lambda_1 P_0 - \varepsilon_i^{\alpha}) P \left| \varphi_i^{\alpha} \right\rangle = 0, \lambda_1, \lambda \to \infty,$$

$$P(F^{\beta} - \lambda P_c^{\alpha} - \varepsilon_i^{\beta}) P \left| \varphi_i^{\beta} \right\rangle = 0. \tag{5}$$

Here F^{α} and F^{β} are standard Fock operators in the UHF method and P is the ortoprojector onto the subspace spanned by the chosen basis set optimized for a given ES that is different from the basis set of the ground one. As long ago as 1958 Shull and Lowdin [12] pointed out *"the desirability of using different basis sets for different states"*. This approach can provide a more compact representation of the accurate excited state wave functions than the traditional use of a common basis set for ground and excited states.

As one can see from Eqs.(5) our formalism deals as does the UHF theory with the cubic equations with respect to the LCAO coefficients whereas a method developed in [5] leads to the fifth-degree equations. Eqs. (5) differ from the canonical UHF equations only by the terms $\langle \varphi_i | P_0 | \varphi_i \rangle$ and $\langle \varphi_i | P_c^{\gamma}) | \varphi_i \rangle$, $\gamma = \alpha, \beta$, which are easily calculated. In accordance with the AP method the constraint vector (e.g. from the term $\lambda_1 P_0$ this vector is φ_{0n}^{α}) tends to the eigenvector of the modified operator $F^{\alpha} + \lambda_1 P_0$ if $\lambda_1 \to \infty$ [10,11]. Then the fulfillment of the condition (4) will follow automatically due to the orthogonality of the eigenvectors, which correspond to different eigenvalues of a self-conjugate operator. In practice, the values $\lambda_1, \sim 10^3$ and $\lambda \sim 10^2$ have provided the accuracy required.

(ii) Eqs. (5) present the natural base to apply the known results of the spin-annihilated PT (e.g. [13]) for calculating the correlation energy of excited states. In particular, the zeroth-order Hamiltonian $H^{(0)}$ for the first excited state can be chosen in the form of the sum of Fock operators for each electron

$$H^{(0)} = \sum_{k}^{n^{\alpha}} F^{\alpha}(k) + \sum_{k}^{n^{\beta}} F^{\beta}(k), \tag{6}$$

$$\text{with } F^{\alpha} = \sum_{i}^{M-1} \left| \varphi_i^{\alpha} \right\rangle \varepsilon_i^{\alpha} \left\langle \varphi_i^{\alpha} \right| \text{ and } F^{\beta} = \sum_{i}^{M} \left| \varphi_i^{\beta} \right\rangle \varepsilon_i^{\beta} \left\langle \varphi_i^{\beta} \right|$$

In our calculations we used the PRHF function with two unpaired in the unrestricted part. The application of a single annihilator [4]

$$A_{s+1} = [S^2 - (s+1)(s+2)]/[\langle S^2 \rangle - (s+1)(s+2)], \ \langle S^2 \rangle = \left\langle \Phi^{(0)} \left| S^2 \right| \Phi^{(0)} \right\rangle$$

to the function (1) leads to the pure singlet spin-state function

$$\Phi_{proj} = A_{s+1}\Phi = (N!)^{-1/2} \frac{1}{\sqrt{2}} [\det | \varphi_1^{\alpha}\alpha\varphi_1^{\beta}\beta...\varphi_q^{\alpha}\alpha\varphi_q^{\beta}\beta\varphi_{q+1}^{\alpha}\alpha\varphi_{q+1}^{\beta}\beta | +$$

$$\det | \varphi_1^{\alpha}\alpha\varphi_1^{\beta}\beta...\varphi_q^{\alpha}\alpha\varphi_q^{\beta}\beta\varphi_{q+1}^{\beta}\alpha\varphi_{q+1}^{\alpha}\beta | .$$

Following the results of Ref. [13] we have for the projected SCF energy:

$$E_{proj}^{SCF} = \left\langle \Phi^{(0)} \left| HA_{s+1} \right| \Phi^{(0)} \right\rangle$$

The second-order correction to the energy, $E^{(2)}_{proj}$, of the first ES takes the form:

$$E_{proj}^{(2)} = \sum_{i}^{occ} \sum_{a}^{virt} | \left\langle \Phi_{proj}^{(0)} \left| H \right| \Phi_i^a \right\rangle |^2 \ (\varepsilon_i - \varepsilon_a)^{-1} +$$

$$\sum_{i>j}^{occ} \sum_{a>b}^{virt} | \left\langle \Phi_{proj}^{(0)} \left| H \right| \Phi_{ij}^{ab} \right\rangle |^2 \ (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)^{-1} - \qquad (8)$$

$$\left\langle \Phi_{proj}^{(0)} \left| H \right| \Phi_0^{(0)} \right\rangle \left\langle \Phi_0^{(1)} \left| \Phi^{(0)} \right\rangle \right.$$

Then the total energy E_{total} is

$$E_{total} = E_{proj}^{SCF} + E_{proj}^{(2)}$$

The sums run over spin-orbitals, *a, b* are virtual orbitals, while *i, j* are occupied MOs and **H** is the Hamiltonian of a system. In contrast to the canonical PT for the ground state, singly excited configurations enter at $E^{(2)}_{proj.}$ The third term in (8) appears because of the orthogonality constraint (3) imposed on the approximate lower state function and coupling integral $\langle \Phi^{(0)}_{proj}| H | \Phi_0^{(0)} \rangle \neq 0$, in general. Our experience showed that the last term contributes much less than other terms and at this stage of the calculations one may neglect the third term.

3. Applications to electronic singlet excitation energies

In this Section, the performance of the proposed method is demonstrated by calculations of excitation energies from the closed-shell ground state to the singlet ESs for the Be atom and LiH molecule. The corresponding results are given in Tables 1, 2. Our calculations were carried out with basis sets consisting of s-type Gaussians: *18s4p*. In addition, each p - function was represented by a linear combination of two s-functions (so-called lobe representation). The orbital exponents and their positions (for LiH) , were

118

determined by invoking the variational principles: for *s*-functions these parameters were found by minimizing the energy in the single determinant approximation whereas the parameters of p-functions were determined by the best energy lowering in the second-order PT. This makes it possible to minimize the error associated with truncation of one-particle basis sets and, thus, to observe more clearly the errors of the method itself. More information about of such basis sets can be found in [14,15]. We compare our results with those of the precisional *ab initio* calculations obtained with extended basis sets and experimental data [16, 17].

As one can see from Tables 1,2 the proposed method is capable of providing the balanced description of the ground and excited singlet states.

Table 1

Excitation energies (eV) from the ground state $1s^2 2s^2$ to singlet excited states of Be

State ^{1}S	Expt [16]	Our method	CISD [16]	CCSD [16]	FCI [16]
$1s^2 2s3s$	6.779	6.774	7.693	6.772	6.765
$1s^2 2s4s$	8.089	8.093	8.973	8.078	8.076

Table 2

Total energies and vertical excitation energies ΔE (hartrees) of LiH at R=3.015 bohr

Method	X $^1\Sigma^+$	A $^1\Sigma^+$	ΔE
Our method	-8.047770	-7.913637	0.134567
CI [17]	-8.0640	-7.9301	0.1339
Expt [17]	-8.0705	-7.9360	0.1345

4. Conclusions

In this paper we have proposed the partially spin-restricted Hartree-Fock function to describe the singlet excited states of atoms and molecules. One the one hand, such a function as well as the UHF function as compared to the RHF function has the freedom of being symmetry broken and can be used as a reference configuration for the calculations of singlet excited states. On the other hand, this model has advantage compared to the fully UHF one due to a simple way to design spin eigenstates.

The efficiency of the method has been demonstrated by calculations of electronic singlet excitation energies for the Be atom and LiH molecule.

It is also useful to note that when an excited state under consideration is not described within the framework of the single-configuration, the PRHF model can be used to generate a multireference space of configurations (e.g. [18]).

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119

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