THE SPIN-SYMMETRIZED HARTREE–FOCK METHOD

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It is possible to obtain a spin-polarized solution in the unrestricted Hartree–Fock method with $\rho_\alpha \neq \rho_\beta$ in the singlet state only with strong electron correlation, where ρ_α and ρ_β are the densities of electrons with opposite spins. A new spin-polarized singlet and triplet model is considered that is invariant under time reversal. It is shown that a quasisinglet solution exists for such a model for any value of the electron–electron interaction. This means that the method can be used without constraints in a readily implemented correlation model, in which one uses only an operation of pseudoreversal of $\rho_\alpha \cdot \rho_\beta$.

The concept of differing orbitals for electrons with opposite spins is one of the simplest models for electron correlation. This is known as the unrestricted Hartree–Fock method (UHF) in the theory of molecules, which is usually employed for radicals, triplets, and so on [1-3]. However, the UHF method should be identified with the spin-polarized Hartree–Fock method SPHF for singlet states, since the orbital splitting leads to spin densities that are of course absent in the spin-correct description of a singlet molecule. Only fairly strong electron correlation can force the electrons with spinup (α-shell) that differ from those with spindown (β shell). This is spin polarization of the single level in SPHF, whose physical significance has not yet been completely elucidated.

Such spin-polarized solutions are not realized when there is relatively weak electron interaction, namely the so-called triplet shell stability [2, 4]. If it were not for the latter feature, SPHF would be a simple standard scheme for incorporating electron correlation in molecules of any complexity. For example, it has been shown [5, 6] that SPHF is effective for describing nontrivial physical effects in conjugated polymers. It has been found [7, 8] that similar results are obtained on calculating perturbation effects from the variational and self-consistent schemes, with the latter carried out for SPHF in accordance with [9]. This similarity does not occur in the restricted Hartree–Fock method, although it indicates similarity to the exact solution. Studies have also been made on using SPHF in reaction theory [10]. Therefore, we require an extension to the model that should provide a spin-polarized solution that is continuous for any values of the electron interaction.

It might seem that the necessary formulation has long existed and is known as the spin-extended Hartree–Fock method (EHF). Also, recently there has been a suggestion of a more general approach to spin polarization in the form of the method of one-particle spin pairing amplitudes (OPSPA) [11]. All the same, exact spin projection in EHF introduces substantial complexities into the practical calculations, in spite of the essential improvements in [12-14] and the use of the OPSPA algorithm of [11]. Here we consider a substantially simpler approach, which does not deviate from the initial idea of SPHF, but which guarantees the existence of a spin-polarized solution for the singlet for any conditions, similar to EHF and OPSPA.

Equivalence Restoration for the α and β Shells in the Singlet State

In the SPHF model, one makes an assumption having a physical content that the motions of the electrons with α and β spins are not equivalent. However, it is overlooked here that the electron behavior must be equalized in the final formulation, and this should lead for example to equality of the α and β components of the electron density for spin $s = 0$. In more accurate terms, this is expressed as the requirement that the singlet state is invariant under the operation of time reversal. On the other hand, the $|\Psi_{SPHF}\rangle$ wavefunction does not have that invariance.

The Wigner operator [15] reverses the time for real wavefunctions containing spin:

$$K_T = (-1)^{N/2}\sigma_y(1)\ldots\sigma_y(N),$$

(1)

where the Pauli matrix is $\sigma_y = i(|\beta\rangle\langle\alpha| - |\alpha\rangle\langle\beta|)$ and $|\alpha\rangle$, $|\beta\rangle$ are the standard one-electron spin functions. In a singlet molecule, N is oblige to be even, which together with the equation $\sigma_y^2 = 1$ leads to hermitian and involution behavior $K_T^2 = I$. This enables us to construct a projection operator $1/2(I + K_T)$ providing the necessary invariance.

In accordance with [15] it can be shown that $K_T|\Psi^{(s,0)}\rangle = (-1)^s|\Psi^{(s,0)}\rangle$, where $\Psi^{(s,0)}$ is a wavefunction with spin s and zero spin projection. By virtue of this, $1/2(I + K_T)$ not only restores the invariance in time reflection but also produces selective spin projection, leaving the opponents with even spin in the approximate singlet function Ψ with the property $(S_z|\Psi\rangle = 0$, but $S^2|\Psi\rangle \neq 0)$, i.e., the singlet, quintet, and so on ones. As a result, we arrive at a more correct model for the singlet shell:

$$|\Psi^{s=0}_{\text{SSHF}}\rangle = \frac{1}{2}(I + K_T)|\Psi_{\text{SPHF}}\rangle,$$

(2)

which will be called the spin-symmetrized Hartree—Fock model (SHF). For the triplet state with zero spin projection we have

$$|\Psi^{s=1}_{\text{SSHF}'}\rangle = \frac{1}{2}(I - K_T)|\Psi_{\text{SPHF}}\rangle,$$

(3)

since $1/2(I - K_T)$ retains the triplet, heptet, and so on components in the similar function. Here the vector $|\Psi_{\text{SPHF}}\rangle$ in (3) is different from that in (2) and is chosen from the condition for minimum energy in the given triplet. An analogous phenomenon, namely exact spin projection by an approximate singlet function on a triplet one, is known from EHF theory [13, 16]. We note that the orbital formulation of spin symmetrization for a singlet level was proposed some while ago [17] in the form of a semiprojected method. Spin symmetrization is also desirable in the OPSPA method without projection [11].

We now show that the states of (2) and (3) defined above always exist, i.e., (2) does not reduce to the ordinary determinant Ψ_0 with paired filled MO $\Psi_0 = [\overset{+}{\varphi_1}\overset{-}{\varphi_1}\ldots\overset{+}{\varphi_i}\overset{-}{\varphi_i}\ldots\overset{+}{\varphi_n}\overset{-}{\varphi_n}]$, and (3) does not reduce to zero (we have used the abbreviation $\overset{+}{\varphi} = \varphi|\alpha\rangle$, $\overset{-}{\varphi} = \varphi|\beta\rangle$). For this purpose, in Ψ_0 we break up the i-singlet pair $\overset{+}{\varphi_i}\overset{-}{\varphi_i} \to \overset{+\alpha}{\varphi_i}\overset{-\beta}{\varphi_i}$, where the new spin-polarized MO $\varphi_i^\alpha \neq \varphi_i^\beta$ are taken in the form

$$|\varphi_i^\alpha\rangle = \frac{1}{\sqrt{1 + x^2}}(|\varphi_i\rangle + x|\varphi_p\rangle), \quad |\varphi_i^\beta\rangle = \frac{1}{\sqrt{1 + x^2}}(|\varphi_i\rangle - x|\varphi_p\rangle),$$

(4)

with $|\varphi_p\rangle$ an orbital vacant for Ψ_0 and x the MO splitting parameter. Then Ψ_0 becomes the superposition

$$|\Psi_{\text{SPHF}}\rangle = \frac{1}{1 + x^2}\{|\Psi_0\rangle + \sqrt{2}\,x|\Psi^{s=1}_{i\to p}\rangle - x^2|\Psi_{ii\to pp}\rangle\},$$

(5)

where $|\Psi^{s=1}_{i\to p}\rangle = \frac{1}{\sqrt{2}}[\ldots\overset{+}{\varphi_p}\overset{-}{\varphi_i} - \overset{+}{\varphi_i}\overset{-}{\varphi_p}\ldots]$ is a singly excited triplet configuration and $|\Psi_{ii\to pp}\rangle$ is a doubly excited singlet one. From (5) we construct the singlet SSHF of (2). Because of the antisymmetry $K_T|\Psi^{s=1}_{i\to p}\rangle = -|\Psi^{s=1}_{i\to p}\rangle$, the normalized vector of (2) amounts to $|\Psi^{s=0}_{\text{SSHF}}\rangle = \frac{1}{\sqrt{1 + x^4}}(|\Psi_0\rangle - x^2|\Psi_{ii\to pp}\rangle)$, which is certainly more favorable as regards the energy $E(\Psi)$ than Ψ_0 alone. In fact, for real quantities

$$E(\Psi^{s=0}_{\text{SSHF}}) = E(\Psi_0) + \frac{x^4\lambda_{ii\to pp} - x^2 K_{ip}}{1 + x^4},$$

(6)

where $\lambda_{ii\to pp}$ is the energy of double excitation and minimization, apart from the trivial case x = 0, with the demonstrated [18] positiveness of the exchange intergrals K_{ip}, which

gives $x^2 = \sqrt{1+C^2} - C$ $(C = \lambda_{ii\to pp}/K_{ip})$ with correlation energy $K_{ip}x^2$. Also, it is evident that energy favors the transition in Ψ_0 from real MO to complex ones[*] followed by isolation of the real part using (2) (K_T is then the complex-conjugate operator). Then $x \to x\sqrt{-1}$, $\Psi^{s=1}_{i\to p} \to \Psi^{s=0}_{i\to p}$, so (6) still applies. The same simple arguments of (4)-(6) illustrates that the EHF solutions are obligatory, which was first shown rigorously in [2] by analyzing the second variation of $E(\Psi_{EHF})$. Finally, from (5) one always isolates the state of (3) in the form of a triplet configuration $\Psi^{s=1}_{i\to p} \neq 0$, while in the complex MO method it is isolated as an excited singlet configuration $\Psi^{s=0}_{i\to p}$. This completes the proof that the solutions exist in the SSHF model.

Calculating Electron Distributions

We now consider the explicit derivation of the SSHF solutions. We follow the operator-reduction method [14] of direct density calculation immediately in matrix (operator) form. As Ψ_{SPHF} is a one-determinant function, N is a particular projector on it $\rho_N = |\Psi_{SPHF}\rangle\langle\Psi_{SPHF}|$. which takes the form [2, 7, 14]

$$\rho_N = A_N \rho(1)...\rho(N), \tag{7}$$

where A_N is an antisymmetrizer and ρ is the Fock–Dirac density matrix. A spin structure for SPHF is

$$\rho = \rho_\alpha |\alpha\rangle\langle\alpha| + \rho_\beta |\beta\rangle\langle\beta|, \tag{8}$$

where $\rho_\alpha = \rho_\alpha^2$, $\rho_\beta = \rho_\beta^2$ are the densities for the α and β shells, and $\rho_\alpha \neq \rho_\beta$. We introduce the symbol $\rho_N(\rho_\alpha; \rho_\beta)$ for the projector of (4) subject to (8). The normalized states of (2) and (3) are denotred by the symbol $|\Psi^\pm\rangle$ with the upper sign for the singlet of (2) and the lower one for the triplet of (3). The projector $\rho_N^\pm = |\Psi^\pm\rangle\langle\Psi^\pm|$ on these states, i.e., the following expression ($\xi \equiv \mathrm{Sp}K_T\rho_N$)

$$\rho_N^\pm = \frac{1}{2(1\pm\xi)}(I \pm K_T)\,\rho_N(\rho_\alpha; \rho_\beta)\,(I \pm K_T) \tag{9}$$

may be put in the more conveninent form

$$\rho_N^\pm = \frac{1}{2(1\pm\xi)}\left\{\rho_N(\rho_\alpha;\rho_\beta) \pm \frac{1}{\xi}[\rho_N(\rho_\alpha\rho_\beta;\rho_\beta\rho_\alpha) + \rho_N(\rho_\beta\rho_\alpha;\rho_\alpha\rho_\beta)] + \rho_N(\rho_\beta;\rho_\alpha)\right\}. \tag{10}$$

We have in mind the identities

$$K_T\rho_N(X;\ Y)K_T = \rho_N(Y;\ X),$$
$$K_T|\Psi\rangle\langle\Psi| = \frac{1}{\langle\Psi|K_T|\Psi\rangle}(K_T|\Psi\rangle\langle\Psi|K_T)|\Psi\rangle\langle\Psi|. \tag{11}$$

It is clear that (10) is completely symmetrical under the substitutions $\rho_\alpha \leftrightarrow \rho_\beta$, so although $\rho_\alpha \neq \rho_\beta$, i.e., the correlation of the α and β shells is explicitly incorporated, the neccesary symmetry is maintained.

We separate out the spin variables in (10). For this purpose a transfer to the spinless $\overset{\circ}{\rho}_N(\rho_\alpha; \rho_\beta)$. For N = 2n, this corresponds to the complete projector of (7), which allows of the representation

$$\rho_N(\rho_\alpha;\rho_\beta) = A_N\overset{\circ}{\rho}_N(\rho_\alpha;\rho_\beta)\,\sigma_N A_N \frac{N!}{n!\,n!}, \tag{12}$$

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[*] M. M. Mestechkin directed the author's attetntion to this aspect of the complex MO method.

where $\sigma_N = |\alpha(1)\ldots\alpha(n)\beta(n+1)\ldots\beta(N)\rangle\langle\alpha(1)\ldots\alpha(n)\beta(n+1)\ldots\beta(N)|$.

From (7) and (8) we find that

$$\overset{\circ}{\rho}_N(\rho_\alpha;\ \rho_\beta) = \overset{\circ}{A}_n(1\ldots n)\rho_\alpha(1)\ldots\rho_\alpha(n)\overset{\circ}{A}_n(n+1\ldots N)\rho_\beta(n+1)\ldots\rho_\beta(N), \tag{13}$$

where $\overset{\circ}{A}$ is a purely spinless n-particle antisymmetrizer. In view of (12) and (13), we can draw up an expression for the spinless projector $\overset{\circ}{\rho}{}_N^\pm$ in (4). To do this, all the complete operatios (containing sping) $\rho_N(X;Y)$ in (4) must be replaced by the spinpless ones $\overset{\circ}{\rho}_N(X;Y)$ with the expansion of (13). Further, we incorporate the fact that the following nozero spinless components remain in the calculations on the one-particle and two-particle density matrices with the given spinless operator $\overset{\circ}{\rho}_N$ in (12), namely the one-electron ones

$$\Gamma_\alpha = n \operatorname*{Sp}_{(2\ldots N)} \overset{\circ}{\rho}_N, \quad \Gamma_\beta = n \operatorname*{Sp}_{(2\ldots N)} \overset{\circ}{P}_{1n+1}\overset{\circ}{\rho}_N\overset{\circ}{P}_{1,n+1} \tag{14}$$

and the two-electron ones

$$\Gamma_{\alpha\alpha} = \frac{n(n-1)}{2} \operatorname*{Sp}_{(3\ldots N)} \overset{\circ}{P}_N, \quad \Gamma = n^2 \operatorname*{Sp}_{(3\ldots N)} \overset{\circ}{P}_{2,n+1}\overset{\circ}{\rho}_N\overset{\circ}{P}_{2,n+1},$$

$$\Gamma_{\beta\beta} = \frac{n(n-1)}{2} \operatorname*{Sp}_{(3\ldots N)} \overset{\circ}{P}_{1,n+1}\overset{\circ}{P}_{2,n+1}\overset{\circ}{\rho}_N\overset{\circ}{P}_{1,n+1}\overset{\circ}{P}_{2,n+2}, \tag{15}$$

which have been given in a somewhat different form in [2, 16]; $\overset{\circ}{P}_{ij}$ is spinless transposition . We apply these formulas to $\overset{\circ}{\rho}{}_N^\pm$ to get the one-electron densities

$$\Gamma_\alpha^\pm = \Gamma_\beta^\pm = \frac{1}{2(1\pm\xi^{(n)})}\left[\rho_\alpha + \rho_\beta \pm \left(\pi_1^{(n)} + \pi_2^{(n)+}\right)\right] \tag{16}$$

and the two-electron ones

$$\Gamma_{\alpha\alpha}^\pm = \Gamma_{\beta\beta}^\pm = \frac{1}{2(1+\xi^{(n)})}\left\{\overset{\circ}{A}_2\left(\rho_\alpha|\rho_\alpha + \rho_\beta|\rho_\beta\right) \pm \left(\pi_2^{(n)} + \pi_2^{(n)+}\right)\right\},$$

$$\Gamma_{\alpha\beta}^\pm = \frac{1}{2(1+\xi^{(n)})}\left\{\rho_\alpha|\rho_\beta + \rho_\beta|\rho_\alpha \pm \frac{1}{\xi^{(n)}}\left(\pi_1^{(n)}|\pi_1^{(n)+} + \pi_1^{(n)+}|\pi_1^{(n)}\right)\right\}. \tag{17}$$

In writing (16) and (17), we have used not only the symbol $X|Y \equiv X(1)Y(2)$ but also the operator invariants constructed in [14]:

$$\pi_1^{(n)} = n \operatorname*{Sp}_{(2\ldots n)} \overset{\circ}{A}_n(1\ldots n)\pi(1)\ldots\pi(n), \quad \pi_2^{(n)} = \frac{n(n-1)}{2} \operatorname*{Sp}_{(2\ldots n)} A_n(1\ldots n)\ \pi(1)\ldots\pi(n) \tag{18}$$

for the one-electron quantity $\pi = \rho_\alpha\rho_\beta$. The number coinciding with ξ in (10) is $\xi^{(n)} = $. $\operatorname{Sp}\pi_1^{(n)}/n$.

Energy and One-Electron Equations

Calculating the energy E amounts to taking two spinless traces:

$$E = \operatorname*{Sp}_{(1)} (\Gamma_\alpha + \Gamma_\beta)\,h + \operatorname*{Sp}_{(1,2)} (\Gamma_{\alpha\alpha} + \Gamma_{\beta\beta} + \Gamma_{\alpha\beta})\,g(12), \tag{19}$$

where h(1) is the one-electron hamiltonian and g(12) is the two-electron interaction. By $E(\rho_\alpha;\rho_\beta)$ we denote the standard SPHF energy, where

$$E(X;Y) = \frac{1}{2}\operatorname{Sp}[(h + f(X;Y))X + (h + f(Y;X))Y], \tag{20}$$

$$f(X;Y) = h + \hat{J}(X+Y) - \check{K}(X),$$

and $\hat{J}$ and $\hat{K}$ are the Roothaan Coulomb and exchange operators. The in SSHF, the energies of the states (2) and (3) derived from (16)-(19) takes the form

$$E^{\pm} = \frac{1}{1 \pm \xi^{(n)}} \left\{ E\left(\rho_\alpha; \rho_\beta\right) \pm \xi^{(n)} E\left(U; U^+\right) \right\}. \tag{21}$$

In (21) we have incorporated the features of the quantitites of (15) when n coincides with the rank π of the matrix (the rank of $\rho_\alpha \rho_\beta$ is not more than n, since ρ_α and ρ_β project on n MO in each shell), namely

$$\xi^{(n)} = \det |\pi|, \quad \pi_1^{(n)} = \xi^{(n)} U, \quad \pi_2^{(n)} = \xi^{(n)} \overset{0}{A}_2 \pi \,|\, \pi,$$

where $U = U^2$ is a nonhermittian operator. This is deived together with $\xi^{(n)}$ by a recurrent method. For this purpose we construct the sequence of matrices [11]

$$\sigma^{(k)} = \xi^{(k-1)} I - \sigma^{(k-1)} \pi, \quad \xi^{(k)} = \mathrm{Sp}\, \pi \sigma^{(k)}/k, \quad \pi = \rho_\alpha \rho_\beta, \tag{22}$$

beginning with $\xi^{(0)} = 1$, $\sigma^{(0)} = 0$. The recursion is carried through to k = n, and then we get $U = \sigma^{(n)} \pi / \xi^{(n)}$ with the property $\pi \pi^{-1} = U$, where $\pi^{-1} = \sigma^{(n)}/\xi^{(n)}$ is a pseudoinverse matrix. In fact, the construction of $\sigma^{(n)}$ corresponds to the Hamilton—Caley method for Moore—Penrose pseudoinversion [20].

Direct variation applied to (21) gives equations of Hartree—Fock type defining the α and β MO φ_i^α and φ_i^β in the SSHF method:

$$F\left(\rho_\alpha; \rho_\beta\right) \left| \varphi_i^\alpha \right\rangle = \varepsilon_i^\alpha \left| \varphi_i^\alpha \right\rangle, \quad F\left(\rho_\beta; \rho_\alpha\right) \left| \varphi_i^\beta \right\rangle = \varepsilon_i^\beta \left| \varphi_i^\beta \right\rangle, \tag{23}$$

$$F\left(\rho_\alpha; \rho_\beta\right) = f\left(\rho_\alpha; \rho_\beta\right) \pm \xi^{(n)} \left[U f\left(U; U^+\right)(I - U) + \left(I - U^+\right) f\left(U^+; U\right) U^+ \pm \frac{\lambda}{\xi^{(n)}} \left(U + U^+\right) \right], \tag{24}$$

with the operators $\rho_\alpha = \Sigma \left(\varphi_i^\alpha \right\rangle \left\langle \varphi_i^\alpha \right|$, $\rho_\beta = \Sigma \left| \varphi_i^\beta \right\rangle \left\langle \varphi_i^\beta \right|$, $\lambda = E^{\pm} - E\left(\rho_\alpha; \rho_\beta\right)$ being the spin-symmetriza-tion energy. The exchange $\rho_\alpha \leftrightarrow \rho_\beta$ denotes also $U \leftrightarrow U^+$. Together, (21)-(24) are the basic relations in the SSHF method.

In general, $\left| \Psi_{SSMF}^{s=n} \right\rangle$ does not give the exact zero value of

$$\langle S^2 \rangle = - N/4 + \underset{(1,2)}{\mathrm{Sp}}\, \overset{0}{P}_{12} \Gamma_{\alpha\beta} = - N/2 + \frac{1}{1 + \xi^{(n)}} \mathrm{Sp} \left[\rho_\alpha \rho_\beta + \xi^{(n)} U U^+ \right]. \tag{25}$$

However, in what follows it is not proposed to use any spin projector O_s on a pure spin state with spin s if we wish to remain within the scope of SSHF. In the converse, we arrive at the corresponding projected model, since O_s and K_T commutate, and spin symmetrization is then superfluous.

It is evident from (4) that we need to introduce asymmetry Δ in numerical calculations based on the starting density matrix ρ_0 in the restricted method:

$$\rho_\alpha = \rho_0 + \Delta, \quad \rho_\beta = \rho_0 - \Delta, \tag{26}$$

whereas Δ we can in fact take any matrix $\neq \rho_0$. In deriving the triplet solutions, it is better to start from Δ in the form of the solution $\widehat{\Pi}(\Delta) = \lambda_{min}\Delta$, where $\widehat{\Pi}$ is a superoperator defining the triplet-excitation spectrum for a superposition of singly excited configura-tions (p. 248 of [2]. This follows from an analysis of E^- with the condition of (26), since the first nontrivial term in the expansion of E^- with respect to Δ has the form $\sim \mathrm{Sp}\widehat{\Pi}$ $(\Delta)\Delta$. We give for completeness the expression for the spin density Q in the SSHF triplet of (3) found from universal spin constraints [19].

$$Q = \Gamma_\alpha - \mathrm{Sp}\, \overset{\circ}{P}_{12}\Gamma_{\alpha\beta} = \frac{1}{2(1 - \xi^{(n)})}\left[\rho_\alpha + \rho_\beta - \rho_\alpha\rho_\beta - \rho_\beta\rho_\alpha + \xi^{(n)}(UU^+ + U^+U - U - U^+)\right]. \tag{27}$$

One-Parameter SSHF Model

We consider the scope for the method on an elementary model corresponding to the one-parameter alternant-orbital method in SPHF and EHF. We take the following form for the spin-polarized solution $\rho_\alpha \neq \rho_\beta$ in the alternant π system in the basis of the AO divided up into two sets (labeled and unlabeled atoms):

$$\rho_\alpha = \rho(z), \quad \rho_\beta = \rho(-z), \quad \rho(z) = \frac{1}{2}\begin{Vmatrix} (1+z)I_* & \sqrt{1-z^2}\, P_{*0} \\ \sqrt{1-z^2}\, P_{*0}^+ & (1-z)I_0 \end{Vmatrix}, \tag{28}$$

where P_{*0} is the matrix for the orders of the bonds between the atoms in the different sets, and $P_{*0}P_{*0}^+ = I_*$, $P_{*0}^+P_{*0} = I_0$. Calculation of the characteristic SSHF quantities gives

$$\rho_\alpha\rho_\beta = (1 - z^2)\, U, \quad U = \frac{1}{2}\begin{Vmatrix} I_* & \sqrt{\frac{1+z}{1-z}}\, P_{*0} \\ \sqrt{\frac{1-z}{1+z}}\, P_{*0}^+ & I_0 \end{Vmatrix}, \quad \xi^{(n)} = (1 - z^2)^n. \tag{29}$$

We use also Hubbard's approximation for the Coulomb intergrals $\gamma_{\mu\nu} = \gamma_0\delta_{\mu\nu}$. Then the SSHF energy of (21) in $B = -\mathrm{Sp}\, h\,[2\rho(0) - I]$ units is

$$E^\pm_{\mathrm{SSHF}} = (-\sqrt{y} + Cy)\frac{1 \pm y^{n-1}}{1 \pm y^n}, \quad y = 1 - z^2, \quad C = N\gamma_0/4B. \tag{30}$$

In the same model of (28), subsequent exact SSHF spin projection lead to the energy in the EHF method obtained by means of the formulas from [14]:

$$E^\pm_{\mathrm{EHF}} = (-\sqrt{y} + Cy)\, r_n/r_{n+1}, \quad r_n \equiv (1 - y^n)/n,$$
$$E^-_{\mathrm{EHF}} = (-\sqrt{y} + Cy)\frac{(n-1)\, r_{n+1}/n - xr_{n-1}}{nr_{n+2}/(n+1) - xr_n}. \tag{31}$$

For N large, all the energies of (30) and (31) tend to come together. However, for N small, the EHF results and those from the simpler SSHF method are fairly similar, as is evident from the table for the π system of benzene, where $B = 8|\beta|$, $C = 3\gamma_0/16|\beta|$. We used the $|\beta| = 2.8$ eV and $\gamma_0 = 4$ eV. With these parameters, the correlation energy λ_{EHF} gives 63% of the exact value calculated in [21]. In turn, the projected value of the energy of (31) with z_{SSHF} gives about 80% of λ_{EHF}. We note also that the SPHF solution of (28) exists only for $C \geqslant 0.5$, , so this example with $C = 0.268$ illustrates the performance of the SSHF model far from the threshold of triplet instability.

TABLE 1. Correlation Energy λ and Triplet Excitation Energy ΔE in One-Parameter Models for the π Shell of Benzene

Singlet			Triplet		
z	$\lambda_{\mathrm{SSHF}}{}^{(z)}$	$\lambda_{\mathrm{EHF}}{}^{(z)}$	z	$\Delta E_{\mathrm{SSHF}}{}^{(z)}$	$\Delta E_{\mathrm{EHF}}{}^{(z)}$
$z^+_{\mathrm{SSHF}} = 0{,}358$	0,206	0,306	$z^-_{\mathrm{SSHF}} = 0{,}548$	5,32	5,47
$z^+_{\mathrm{EHF}} = 0{,}486$	—	0,402	$z^-_{\mathrm{EHF}} = 0{,}579$	—	5,46

Note: $z^\pm_{\mathrm{CCX\Phi}}$ and $z^+_{\mathrm{PX\Phi}}$ are derived from the minimum in $E^\pm_{\mathrm{CCX\Phi}}$ of of (30) and $E^\pm_{\mathrm{PX\Phi}}$ (31) correspondingly with $C = 0.2679$. All the energies $\lambda(z) - E^+(0)$, $\Delta E(z) = E^-(z) - E^+(z)$ are given in eV

CONCLUSIONS

Therefore, in the SSHF model one performs inexplicitly a fairly successful approximate spin projection, which allows a spin-polarazed singlet solution to exist for any correlation energy. The method can be used, as is evident from the example of the benzene molecule, for calculations of EHF type exact in a spin respect if one takes the densities ρ_α and ρ_β readily derived from (23) and (24) as good approximations to their EHF values. However, a more important point is that the subsequent multiconfiguration calculations are realized in the basis of the spin-symmetrized MO of (23). Such calculations enable one to improve the description of the ground state more effectively than spin projection of $|\Psi_{SPHF}\rangle$ alone, and they also provide well-correlated wavefunctions for the exicted states, which is much more difficult to ensure form models of EHF and OPSPA type.

It is also possible to construct a doublet wavefunction for a radical $|\Psi_{SSHF}^{s=1/2}\rangle$ from a spin-polarized singlet in the spirit of second quantization methods:

$$|\Psi_{SSHF}^{s=1/2}(1\ldots N-1)\rangle = \sqrt{N}\langle\bar{\varphi}(N)|\Psi_{SSHF}^{s=0}(1\ldots N)\rangle_{(N)}, \tag{32}$$

where $|\bar{\varphi}\rangle = |\varphi\rangle|\beta\rangle$ is an additional viarional orbital. In this way we arrive at spin pairing for the α and β shells in the radical different from that in UHF or EHF. We elucidate this on a simple example for a three-electron system $N-1=3$. We first construct the four-electron SSHF function of the form

$$|\Psi_{SSHF}^{s=0}(1234)\rangle = \left|\overset{+}{\varphi_1}\overset{+}{\varphi_2}\overset{-}{\Psi_1}\overset{-}{\Psi_2} + \overset{+}{\Psi_1}\overset{+}{\Psi_2}\overset{-}{\varphi_1}\overset{-}{\varphi_2}\right\rangle, \tag{33}$$

with spin-orbital antisymmetrization. We take here $\varphi_i = \varphi_2 = \Psi_2$ and find the following apart from coefficients:

$$|\Psi_{SSMF}^{s=1/2}(123)\rangle = \left|\overset{+}{\varphi_1}\overset{+}{\varphi}\overset{-}{\Psi_1} + \overset{+}{\Psi_1}\overset{+}{\varphi}\overset{-}{\varphi_1}\right\rangle, \tag{34}$$

which coincides with the so-called maximal pairing function. This function is [22] preferable to a projected state constructed from the same MO:

$$|\Psi_{EHF}^{s=1/2}\rangle = \hat{O}_{s=1/2}\left|\overset{+}{\varphi_1}\overset{+}{\varphi}\overset{-}{\Psi_1}\right\rangle = \left|2\overset{+}{\varphi_1}\overset{+}{\varphi}\overset{-}{\Psi_1} + \overset{+}{\Psi_1}\overset{+}{\varphi}\overset{-}{\varphi_1} + \overset{+}{\varphi_1}\overset{+}{\Psi_1}\overset{-}{\varphi}\right\rangle.$$

The state of (34) is a pure doublet, but in the general case in (28) we lack only multiplets with spin $s = (2k+1)/2$.

We denote the energy of a function of (32) by E_{N-1}. According to formulas from [14], to calculate this we require the two-electron and three-electron densities, which are obtained from (13) on the basis of the obvious correspondence $\rho_\alpha \to U$, $\rho_\beta \to U^+$ for the term in square brackets in (10). After all the calculations, the result for φ is formulated as a general problem for the eigenvalues of the operator

$$\hat{\Theta} = (\rho_\alpha + \rho_\beta)E(\rho_\alpha;\ \rho_\beta) - \rho_\alpha f(\rho_\alpha;\ \rho_\beta)\rho_\alpha - \rho_\beta f(\rho_\beta;\ \rho_\alpha)\rho_\beta +$$
$$+ \xi^{(n)}[(U + U^+)E(U;\ U^+) - Uf(U;\ U^+)U - U^+f(U^+;\ U)U^+], \tag{35}$$

namely:

$$\hat{\Theta}|\varphi\rangle = E_{N-1}[\rho_\alpha + \rho_\beta + \xi^{(n)}(U + U^+)]|\varphi\rangle. \tag{36}$$

In principle, ρ_α and ρ_β should be found by optimizing E_{N-1}, which incorporates the orbital relaxation on ionization. Then by means of SSHF we can hope also for a reltively simple solution to the problem of spin pairing in radicals.

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