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Projected Unrestricted Hartree−Fock Calculations within the Intermediate Neglect of Differential Overlap Model

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We develop a stable scheme for full spin projection of an unrestricted Hartree−Fock wave function using ideas originally discussed by Löwdin and Harriman. We examine three test cases within the intermediate neglect of differential overlap/spectroscopic method (INDO/S); a model of ferredoxin, Fe−S enzyme models for nitratases, and Ni_6 clusters. The projected INDO/S UHF method has a remarkable ability to predict spin multiplicities correctly and with far greater ease than corresponding restricted open-shell Hartree−Fock calculations followed by configuration interaction (ROHF/CI).

Introduction

Quantum chemical calculations on open-shell systems, especially when there are many open shells, present particular problems. There are, in general, two ways to proceed. The first is to use the restricted open-shell Hartree−Fock model,[1−8] which creates eigenstates of the spin-squared operator, $\hat{S}^2$, with eigenvalues $S(S+1)$, e.g.,

$$\hat{S}^2\,{}^{2S+1}\Psi_{S_z} = S(S+1)\,{}^{2S+1}\Psi_{S_z} \tag{1}$$

where $2S+1$ is the multiplicity. Since $\hat{S}^2$ commutes with the Hamiltonian typically assumed in the Hartree−Fock procedure, this is a comfortable constraint and leads to *spectroscopic* states, singlets, doublets, etc.

A second way to proceed is to use the unrestricted Hartree−Fock method (UHF).[1,9,10] In such a case, different orbitals are obtained for different spins (DODS),[10] but the wave function is no longer an "eigenfunction of spin" or, more correctly, spin squared. In general,

$$\hat{S}^2\,{}^{2S_z+1}\Psi^{\text{uhf}}_{s_z} \neq S_z(S_z+1)\,{}^{2S_z+1}\Psi^{\text{uhf}}_{s_z} \tag{2}$$

The subscript s_z designates that both the ROHF and UHF wave functions are eigenfunctions of $\hat{S}_z$ by construction, with eigenvalue S_z equal to the sum of the spin molecular orbital s_z values; i.e., $^1/_2$ for α-spin and $^1/_2$ for β-spin.

The UHF energy is generally lower than that obtained from the ROHF model, a consequence of the greater variational freedom to choose two sets of orbitals, i.e., $\{\varphi_i^\alpha\}$ and $\{\varphi_i^\beta\}$, rather than requiring the spin-pairing of electrons in closed-shell orbitals. This difference can become rather dramatic when there are many open shells. A particularly interesting example is met with the Cr_2 dimer. In this case, the UHF antiferromagnetically coupled energy (six up-spin electrons localized on one Cr atom, one in the 4s and one in each of the five 3d orbitals, and six down-spin electrons on the other Cr atom) is some 4000 kJ/mol lower in energy than the ROHF covalent bonded structure.[11−13]

Despite the energy advantage that the UHF procedure has over the ROHF method, the properties calculated with the UHF wave function are often not good. Again, a dramatic example is the case of Cr_2 with a long bond length of about 3.25 Å obtained at a much lower energy than the ROHF minimum energy structure at about 1.64 Å, which is about the right bond length. There are now many examples of failures of the UHF model to predict properties.

We would like here to re-examine the UHF method within the intermediate neglect of differential overlap (INDO) model parametrized for spectroscopy, (INDO/S). The UHF procedure is very efficient compared to the equivalent cases treated by the ROHF method, again, especially in those cases where there are many open shells. The INDO/S model is a very effective one for calculating the electronic structure of very large systems, but this efficiency can be partially lost if an ROHF calculation must be followed by an extensive open-shell configuration interaction (CI) calculation to sort out the various spin states, their relative energies, and their properties.

UHF calculations can be followed by Møller−Plesset type perturbation theory, and this is now a reasonably efficient procedure,[1] but this treatment does little to improve the spin contamination when there are many open shells. Various projection and annihilation schemes have been introduced to correct some of the major problems. Some have been more successful than others, but none are capable of definitively improving the results.

Below we examine the fully projected UHF method (PUHF). This procedure seems to lead to *outstanding* relative energies of the various possible spin states when used within the INDO/S method. The PUHF technique has, in general, been somewhat neglected based on the findings that this procedure often did not give spin densities in accord with that inferred from ESR studies and the fact that most procedures used in this scheme were unstable. This instability was initially also a problem for us but has been eliminated in the procedure we describe, that is, by adopting the paired orbitals of Löwdin and the formalism originally suggested by Harriman.

Other open-shell techniques have also been described in the literature. One, the SUHF procedure of Handy and co-workers,[14] uses a Lagrange constraint, i.e., $\lambda(\hat{S}^2 - S(S+1))$, in the two UHF Fock operators to transform the UHF solution to the ROHF solution with increasing λ. Although this allows one to use

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perturbation theory of the UHF type to refine the energy with less spin contamination, it offers no advantage at the HF level and yields a solution bounded in energy between that of the UHF result and the corresponding ROHF result.

Another interesting technique is the half projected Hartree−Fock, HPHF, method.[15,16] By construction, this method eliminates half of the spin contaminants through the construction of a two-determinant wave function. This construct is only defined for an even number of electrons. There are often multiple solutions to the resultant equations, and the method suffers from convergence problems. Although some of these convergence problems have been addressed by Bone and Pulay[17] by restricting the wave function to two determinants of the form (for singlets and triplets)

$$\Psi = \frac{1}{\sqrt{2}}(|\varphi_1^\alpha \alpha(1)\varphi_1^\beta \beta(2)\ldots| \pm |\varphi_1^\beta \alpha(1)\varphi_1^\alpha \beta(2)\ldots|) \quad (3)$$

the HPHF energy lies above the corresponding UHF energy and considerably above the PUHF energy. These orbitals are, however, convenient for a subsequent CI treatment as shown by Bone and Pulay. Nevertheless, we suspect that they are no more convenient than are the natural orbitals obtained from the UHF wave function, although we have not yet examined this.

It is also possible to annihilate the next "higher" spin component of the UHF wave function, e.g., remove only the triplet component from an open-shell singlet, and renormalize the resultant wave function. This is a quick and efficient method but is reliable only in the cases where there is little spin contamination and only in the case of maximum multiplicity for a given open-shell situation. We review this method in the next section.

Unrestricted Hartree−Fock (UHF)

The unrestricted Hartree−Fock (UHF) wave function[1,9] can be written as

$$^{(N_\alpha\text{-}N_\beta)+1}\Psi^{\mathrm{uhf}} = |\varphi_1^\beta \beta(1)\varphi_2^\beta \beta(2)\ldots\varphi_q^\beta \beta(N_\beta)\varphi_1^\alpha \alpha(N_\beta + 1)\varphi_2^\alpha \alpha(N_\beta + 2)\ldots\varphi_p^\alpha \alpha(N_\alpha + N_\beta)| \quad (4)$$

where N_α is the number of α-spin electrons and N_β the number of β-spin electrons, the total number of electrons $n = N_\alpha + N_\beta$, $\langle \hat{S}_z \rangle = {}^1/_2(N_\alpha - N_\beta)$, and we assume that $N_\alpha \geq N_\beta$. The $|\cdots|$ denotes a Slater determinant.

As is apparent from eq 4, UHF theory defines two different sets of spatial orbitals, one for the α-spin electrons, $\{\varphi_i^\alpha\}$, and one for the β-spin electrons, $\{\varphi_i^\beta\}$, i.e., different orbitals for different spins.[10] The α-spin orbitals are orthonormal as are the β-spin orbitals, but they are not *biorthogonal*, i.e.,

$$\langle \varphi_i^\alpha | \varphi_j^\alpha \rangle = \delta_{ij}, \quad \langle \varphi_i^\beta | \varphi_j^\beta \rangle = \delta_{ij}$$

but

$$\langle \varphi_i^\alpha | \varphi_j^\beta \rangle \neq \langle \varphi_i^\beta | \varphi_j^\alpha \rangle \neq \delta_{ij} \quad (5)$$

in general. Invoking the variational principle for this wave function yields two Fock equations, one for the α-spin orbitals and the second for those of β-spin,[1,18] vis.,

$$f^\alpha(i)\varphi_j^\alpha(i) = \epsilon_j^\alpha\ \varphi_j^\alpha(i) \quad (6)$$

$$f^\beta(i)\varphi_j^\beta(i) = \epsilon_j^\beta\ \varphi_j^\beta(i) \quad (7)$$

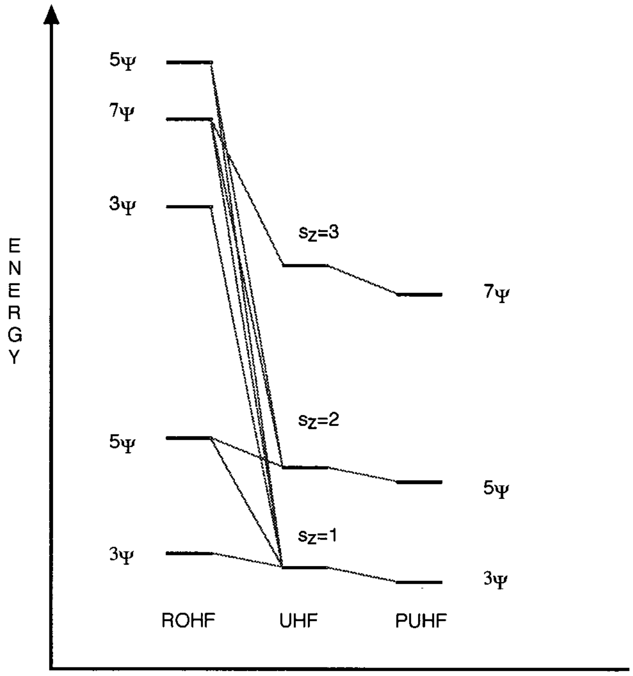


Figure 1. Energy of the UHF wave function compared to ROHF and projected UHF for the case of a ground-state triplet. Note that the UHF function contains information about many ROHF states with *S*(ROHF) ≥ S_z.

These Fock operators differ from the closed-shell case by different exchange operators; that is, only electrons of like-spin can exchange.

$$\langle \mu | \hat{f}^{\,\alpha} | \nu \rangle = h_{\mu\nu} + \sum_{\sigma,\lambda} [P_{\sigma\lambda}^{\mathrm{T}} \langle \mu\sigma | \nu\lambda \rangle - P_{\sigma\lambda}^{\alpha} \langle \mu\nu | \sigma\lambda \rangle] \quad (8)$$

where

$$P_{\sigma\lambda}^{\alpha} = \sum_{\alpha} n_a^\alpha\, C_{\lambda a}^{\alpha *}\, C_{\sigma a}^{\alpha} \quad (9)$$

with similar expressions for $\mathbf{P}^\beta$. In eq 9, n^α (and n^β in the analogous equation for $\mathbf{P}^\beta$) equals 0 or 1. The total density is defined as

$$\mathbf{P}^{\mathrm{T}} = \mathbf{P}^\alpha + \mathbf{P}^\beta \quad (10)$$

and the spin density is similarly defined as

$$\rho = \mathbf{P}^\alpha - \mathbf{P}^\beta \quad (11)$$

Inevitably, the UHF method leads to lower energies than does either of the RHF or ROHF methods (see Figure 1.) and annihilating the components of higher multiplicities generally yields even lower energies. The UHF method is variational and it is a Fock type method, but for the reasons given above it does contain some of the correlation energy, *by definition.*

Projection

The UHF wave function *breaks* spin symmetry; that is, the UHF wave function is not an eigenfunction of the $\hat{S}^2$ operator, but it can be expanded in terms of spin eigenfunctions that span the same space, vis.,

$$^{2S_z+1}\Psi_{s_z}^{\mathrm{uhf}} = \sum_{S=S_z}^{S_z+N_\beta} \omega_s \sum_{k=0}^{N_\beta} C_k(S,S_z,n)\ {}^{2s+1}\psi_{s_z}^{k} \quad (12)$$

The

$${}^{2S+1}\psi^k_{s_z} = N|\theta_1\theta_2 \ldots \theta_{N_\alpha}\bar{\theta}_1\bar{\theta}_2 \ldots \bar{\theta}_{N_\beta}|[\alpha^{N_\alpha-k}\beta^k|\alpha^k\beta^{N_\beta-k}] \tag{13}$$

where

$$N = \left[(N_\alpha + N_\beta)!\binom{N_\alpha}{k}\binom{N_\beta}{k}\right]^{-1/2} \tag{14}$$

The function $[\alpha^{N_\alpha-k}\beta^k|$ is the sum of all the N_α-factor spin function products involving the $N_\alpha - k$ α-spin functions and k β-spin functions; e.g., if $N_\alpha = 3$ and $k = 1$, then $[\alpha^2\beta^1| = \alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha$. The $|\alpha^k\beta^{N_\beta-k}]$ are similarly defined. This leads to $[\alpha^{N_\alpha-k}\beta^k|\alpha^k\beta^{N_\beta-k}]$ being a sum of $\binom{N_\alpha}{k}\binom{N_\beta}{k}$ terms each of N_α α-spin functions and N_β β-spin functions. The $C_k(S,S_z,n)$ and ω_s were first determined by Sasaki and Ohno.[19] The expressions for evaluating $E({}^{2(S_z+k)+1}\psi_{s_z})$ were derived by Harriman,[20−22] and we have adopted his notation in the above discourse. The squares of the ω_s are known as the weights of the components and for a normalized wave function will sum to unity. Then, from the definition of the ω_s it is easily shown that

$$\langle \hat{S}^2\rangle_{\text{uhf}} = \sum_{k=0}^{N_\beta}\omega^2_{s_z+k}(S_z + k)(S_z + k + 1) \geq S_z(S_z + 1) \tag{15}$$

and

$$E\left({}^{2S_z+1}\Psi^{\text{uhf}}_{s_z}\right) = \sum_{k=0}^{N_\beta}\omega^2_{s_z+k}E({}^{2(S_z+k)+1}\psi_{s_z}) \leq E\left({}^{2S_z+1}\Psi^{\text{rhf}}_{s_z}\right) \tag{16}$$

The functions ${}^{2(S_z+k)+1}\psi_{s_z}$ are akin to CI functions, eq 13, thus the UHF energy contains some of the correlation energy; i.e., the difference between the many-body solution for the nonrelativistic fixed nuclei Hamiltonian and the RHF, or ROHF, method defines the *basis set* correlation energy. For a complete basis, this difference defines the correlation energy.

The Löwdin annihilator[23−28] for removing the t-th spin component is given below.

$$\hat{A}^s_t = \frac{\hat{S}^2 - t(t + 1)}{s(s + 1) - t(t + 1)} \tag{17}$$

If we assume t is the leading spin contaminant, usually the $S = S_z + 1$ component, then

$$\hat{A}^s_t\,{}^{2S_z+1}\Psi^{\text{uhf}}_{s_z} = (1)^{2S_z+1}\Psi_{s_z}C_{S_z} + (0)^{2S_z+3}\Psi_{s_z}C_{S_z+1} + (-{}^1/_2(S_z + 2))^{2S_z+5}\Psi_{s_z}C_{S_z+2} + \ldots \tag{18}$$

A more complete, although more complex, approach *projects* the desired spin state from the UHF wave function.[20−22,29−31]

To obtain an eigenfunction of $\hat{S}^2$, the Löwdin projector $\hat{O}_s$ is applied to eq 12, to remove all but the s spin component, where

$$\hat{O}_s = \prod_{t\neq s}\hat{A}^s_t \tag{19}$$

and

$$\hat{O}^2_s = \hat{O}_s$$

$$\hat{S}^2\hat{O}_s = S(S + 1)\hat{O}_s$$

The operator $\hat{O}_s$ projects out the $(2S + 1)$ spin component and the resulting pure spin state wave function can be written as a linear combination of configuration state functions, vis.,

$$\hat{O}_s\,{}^{2S_z+1}\Psi^{\text{uhf}}_{s_z} = \sum_{k=0}^{N_\beta}C_k(S,S_z,n)\,{}^{2S+1}\psi^k_{s_z} \tag{20}$$

when the $\{{}^{2S+1}\psi^k_{s_z}\}$ are expressed on the basis of the corresponding orbitals of Amos and Hall.[26]

Harriman, through a great deal of tedious algebra, derived closed formulas for the projected energy expressions,[20] which we have no desire to repeat here. Further, he proved that upon projection the natural orbitals of the 1-matrix do not rotate and so chose to express his energy formulas in this basis. As noted above in the basis of the corresponding orbitals (also known as the paired orbitals of Löwdin), the unrestricted wave function can be expressed as a linear combination of restricted determinants, obviously a far more transparent basis in which to understand the result of applying the projector. The corresponding orbitals can be generated in several different ways; we have found that generating them via the pairing theorem of Löwdin[30,31] and constructing the natural orbitals of the 1-matrix from them yields a set of natural orbitals that both properly reflects the spatial symmetry of the system and possesses the proper phasing, a problem first noted by Phillips and Schug.[32] Our use of any other method to obtain the natural orbitals of the 1-matrix inevitably leads to problems, especially for systems of high spatial symmetry, thus rendering whatever utility there was in the alternate method useless. In the Appendix, we demonstrate Löwdin's pairing theorem by using it to generate the paired (or corresponding) orbitals.

In practice, problems arising from spatial symmetry, near degeneracies in the 1-matrix, and machine numerical precision have caused sufficient problems in the past to discourage the general use of this method. Machine precision problems must be trapped and dealt with as they arise. Problems arising due to spatial degeneracies and near degeneracies in the 1-matrix were successfully met by using the pairing theorem.

Computational Algorithm

(1) Converge UHF equations to 1 part in 10^{12} with respect to the energy. (This is important for both reasons of numerical stability and to ensure a minimum of spin contamination.)

(2) Form the corresponding orbitals via the algorithm described in the Appendix.

(3) Construct the natural orbitals of the 1-matrix from the corresponding orbitals.[23] (This ensures their being properly phased[36] and resolves the problems commonly encountered when treating molecular systems of high spatial symmetry.)

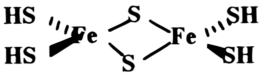
(4) Use the equations given in ref 23 or 36 to compute the weights and energies for each spin state of interest. (Equation 16 can be used as a check of internal consistency when the weights and energies of all spin states are computed.)

Some Examples

The projected UHF model delineated above has been programmed within the quantum chemical models that are present in the ZINDO program system.[33] The examples taken below were obtained using the INDO/S model Hamiltonian.[34−38]

Model Ferridoxins. We examine the case of the 2-Fe model ferrodoxin[39] shown in the structure above Table 1. The $S_z = 5$ UHF calculation (corresponding to all 10 α-spin electrons singly occupying the 10 d-orbitals, or *ferromagnetically* (FM) coupled) is nearly pure undectet $(2S + 1 = 11)$, as can be seen in Table

TABLE 1: Spin Components ("Weights") for 2-Fe Model Ferredoxin Obtained from UHF Calculations in Italics[a]



	S_z					
$2S+1$	5	4	3	2	1	0
1 *w*						*0.18*
E						**0.00**
3 *w*					*0.49*	*0.37*
E					26.1	0.25
5 *w*				*0.81*	*0.36*	*0.29*
E				22.5	27.6	0.76
7 *w*			*0.88*	*0.18*	*0.13*	*0.13*
E			13.5	22.9	30.5	1.60
9 *w*		*0.93*	*0.11*	*0.01*	*0.02*	*0.03*
E		5.76	27.7	25.2	36.1	2.86
11 *w*	*0.9993*	*0.07*	*0.00*	*0.00*	*0.00*	*0.00*
E	3.54	24.6	45.6	33.2	79.6	4.84
13 *w*	*0.0007*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*
E	56.7	82.1	105.0	97.7	126.2	64.8
$\langle S^2\rangle$	*30.008*	*20.66*	*12.95*	*7.26*	*5.11*	*4.72*
$S_z(S_z+1)$	*30*	*20*	*12*	*6*	*2*	*0*
E(UHF)	3.57	6.48	15.3	22.8	27.2	0.63

$\langle S^2\rangle$AF = 5
AF = 0.160 (singlet) + 0.357 (triplet) + 0.298(quintet)

[a] The second line presents relative energies in 1000 cm^{-1} (1000 cm^{-1} = 2.86 kcal/mol).

TABLE 2: Relative Energies of the Fe−S Model Proteins for Nitrile Hydratase (NHase) R−CN + H$_2$O → R−CO−NH$_2$ in kJ/mol (from ref 35)

DABMUO, $C_{16}H_{14}ClFeN_2S_2$ (S(exp) = 3/2) chloro[*N,N′*-ethylenebis(thiosalicylideneiminato)] Fe(III)	
$S = 1/2$	67.2
$S = 3/2$	0.0
$S = 5/2$	37.3
PAVDUL, $C_{39}H_{54}N_3S_3Fe$ (S(exp) = 1/2) (1,4,7-tris(4-tert-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane)Fe(III)	
$S = 1/2$	0.0
$S = 3/2$	50.1
$S = 5/2$	72.7
ZAZNUJ, $FeS_3N_3C_{25}H_{24}$ (S(exp) = 5/2) [Fe{III}(N(CH2-*o*-C6H4S)3)(1-Me-imid)]	
$S = 1/2$	110.8
$S = 3/2$	22.6
$S = 5/2$	0.0
ZEKRIG(+), $C_{16}H_{33}N_5S_2ClFe$ (S(exp) = 1/2) bis(6-amino-2,3-dimethyl-4-azahex-3-ene-2-thiolato)Fe(III) chloride	
$S = 1/2$	0.0
$S = 3/2$	59.1
$S = 5/2$	96.6

1. The pure undectet comprises 0.9993 of the wave function, and the $\langle\hat{S}^2_{\text{uhf}}\rangle$ expectation value is 30.008. If the UHF wave function were a pure undectet, this value would be identically 30. The lowest energy multiplet for this system that we calculate using the INDO/S model is, however, the singlet case. This is obtained from projecting out the $S_z = 0$ antiferromagnetic (AF) case, with all α-spin electrons localized to one Fe(III) ion and all β-spin electrons localized to the other. (Note that the "singlet", i.e., $S_z = 0$, UHF wave function is mostly a $S = 1$, $S_z = 0$ triplet.) The AF case cannot be considered a pure spin state, nor does it even approximate one. The expectation value $\langle\hat{S}^2\rangle$ of a pure AF coupling would be 5, which is close to the 4.72 value actually calculated for the UHF wave function. At the bottom of Table 1, the exact projection of the AF wave function, vis.,

$$^1\Psi^{\text{AF}}_{S_z=0} = |\phi_1^{\alpha}\alpha(1)\phi_2^{\alpha}\alpha(2)\phi_3^{\alpha}\alpha(3)\phi_4^{\alpha}\alpha(4)\phi_5^{\alpha}\alpha(5) \times \phi_6^{\beta}\beta(6)\phi_7^{\beta}\beta(7)\phi_8^{\beta}\beta(8)\phi_9^{\beta}\beta(9)\phi_{10}^{\beta}\beta(10)| \quad (21)$$

(in which the first five MO's are essentially Fe d-orbitals localized to the first iron atom and are represented by α-spin orbitals, and the next five MO's are β-spin orbitals localized essentially to the second iron atom) is compared against the undectet, the nine nonets, etc. A comparison of these coefficients with those actually calculated indicates a slight bias in the UHF function to lower multiplicities than that expected in the ideal AF case, consistent with the fact that the calculated $\langle\hat{S}^2\rangle$ value is less than 5. This is likely due to some covalency in the d-orbitals, and these more delocalized orbitals have a greater tendency to electron pair. In general, the UHF energy is most reliable for those states of highest multiplicity for a given number of electrons in a set number of open-shell orbitals. Accordingly, the calculated $\langle\hat{S}^2\rangle$ value deviates more from the $S_z(S_z + 1)$ value the smaller S_z becomes.

As shown in Table 1, the prediction is that the ground state of this model ferridoxin is *diamagnetic*, or singlet. While in general the UHF energy for the highest multiplicity is a good estimate (the projection only lowers the energy by 30 cm^{-1} in this case) this does not necessarily imply that the wave function is *good*, though the $\langle\hat{S}^2\rangle$ value does suggest that this is so in this particular case. There are two additional observations to be gleaned from this table. The first is that the tridectet is of much higher energy, as it requires the uncoupling of spins on the sulfur ligands. Second, only the AF (minimum multiplicity) and FM (maximum multiplicity) seem consistent in their prediction. This is because all other multiplicities involve the loss of one-center exchange, and this raises the energy considerably. The prediction that the FM case projected from the singlet is higher in energy than the AF case by 4840 cm^{-1} is consistent with the FM calculation which produces a value of 3540 cm^{-1}. Finally, note that, despite the considerable spin contamination in the AF case, the spin projection only lowers the projected singlet by 630 cm^{-1}. This is due to the fact that the higher multiplicities that mix into this wave function are the weakly coupled ones; that is, those that result from the coupling of two isolated $S = {}^5/_2$ Fe(III) systems.

FeS Proteins, Nitrile Hydratases. In Table 2, we examine the magnetic predictions of several model nitrile hydratases, the latter of which catalyze the reaction

$$\text{R}-\text{CN} + \text{H}_2\text{O} \rightarrow \text{R}-\text{CO}-\text{NH}_2$$

These are rather complex molecules, as implied by the formulas given in the table. We note that in each case the predicted spin multiplicity agrees with that observed. In the case of ZAZNUJ, this is high spin (${}^5/_2$), and in the case of PAVDUL (Figure 2), this is low spin (${}^1/_2$). The values in this table are from three INDO/S−PUHF calculations, one for each of the three S_z values, ${}^1/_2$, ${}^3/_2$, and ${}^5/_2$. For the two cases presented here, the unprojected UHF result properly predicts the observed spin state (this is not generally the case), indicating that the essential physics is inherent in the INDO/S model. This is not the case for ab initio UHF wave functions and is the major reason for their poor description of spin systems such as these. The projection is usually necessary to predict the observed $\langle\hat{S}^2\rangle$ values.[40] (The chemistry of these complexes is discussed in detail in ref 40, and many more examples are reported.)

Single Sided Annihilation. Single sided annihilation is an attractive alternative to fully projected unrestricted Hartree−

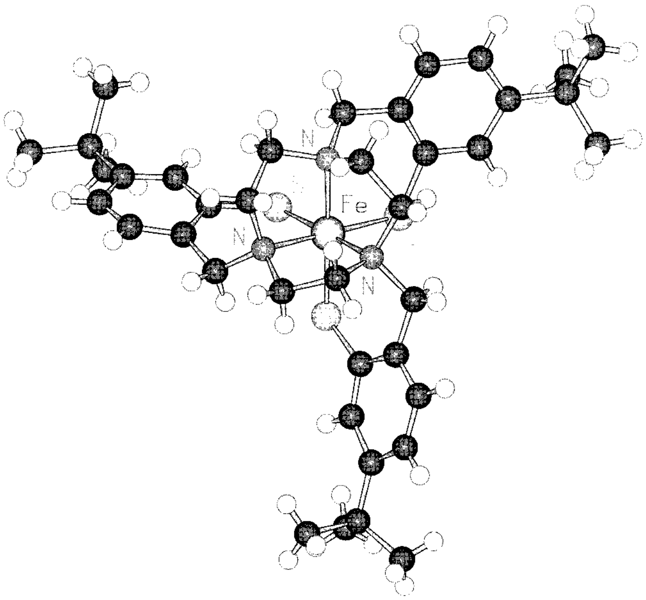


Figure 2. Structure of “PAVDUL”, 1,4,7-tris(4-*tert*-butyl-2-mercaptobenzl)-1,4,7-triacyclononane Fe(III).

TABLE 3: Examination of the UHF Wave Function for PAVDUL; See Table 2 and Figure 2[a]

S	weight	energy (au)
0.5	0.53041104	−344.975524
1.5	0.34766091	−344.905468
2.5	0.10235863	−344.819873
3.5	0.01749960	−344.723620
4.5	0.00192041	−344.617574
5.5	0.00014193	−344.500787
6.5	0.00000722	−344.370987
7.5	0.00000025	−344.224453

unprojected $\langle \hat{S}^2 \rangle = 2.925766$
$E(\text{UHF}) = -344.930067$

Results for Half-Projection

expectation value of the total spin operator, $S(S+1)$	0.750000
$\langle \hat{S}^2 \rangle$ of the UHF wave function	2.925766
expectation value of the annihilated wave function	8.525535
estimated weight of the annihilated $S = {}^3/_2$ component	0.402225
estimated weight of the $S = {}^5/_2$ component	0.057898
energy of the UHF wave function	−344.930067
energy of the one sided annihilated wave function	−345.647713

[a] The reference calculation has $S_Z^{\text{UHF}} = {}^1/_2$.

Fock (eq 17) as it is simpler and much easier to implement, considerably faster in execution time, and is readily available within the INDO model and has been for some time.[28] We examine this method for PAVDUL (Figure 2), one of the model nitrile hydratases of Table 2. In this case, the expectation value $\langle \hat{S}^2 \rangle = 2.926$ for the UHF solution with $S_z = {}^1/_2$, showing a rather large amount of spin contamination for a function with desired $\langle \hat{S}^2 \rangle = 0.75$. Single sided annihilation and renormalization, a procedure which eliminates the quartet component $\langle \hat{S}^2 \rangle = {}^{15}/_4$, yields a value of $\langle \hat{S}^2 \rangle = 8.526$, indicating that the doublet remains a minor component of the wave function that results. The energy obtained, a transition value rather than an expectation value, is 1837 kJ/mol below the PUHF value, and the estimated error from second-order perturbation theory is 0.226919$(E(S) - E(S+2))$, rendering this value meaningless. An analysis of this particular case appears in Table 3. Note the high spin contamination; the UHF wave function is only 53% doublet. Single sided annihilation of the next highest component is a useful procedure only when the wave function shows but little spin contamination, but as seen in Table 4 for PAVDUL even this is not always the case. This is somewhat disappointing, as after the annihilation and renormalization the wave function is 95.8% sextet ($S_z = {}^5/_2$). This is not only disappointing, it is surprising!

TABLE 4: Examination of the UHF Wave Function for PAVDUL; See Table 2 and Figure 2[a]

S	weight	energy (au)
2.5	0.77636908	−344.947771
3.5	0.19065137	−344.870643
4.5	0.02969825	−344.781132
5.5	0.00305902	−344.679032
6.5	0.00021207	−344.562230
7.5	0.00000990	−344.426477
8.5	0.00000031	−344.264844

unprojected $\langle \hat{S}^2 \rangle = 10.651375$
$E(\text{UHF}) = -344.927206$

Results for Half-Projection

expectation value of the total spin operator, $S(S+1)$	8.750000
$\langle \hat{S}^2 \rangle$ of the UHF wave function	10.651375
expectation value of the annihilated wave function	10.708589
estimated weight of the annihilated $S = {}^7/_2$ component	0.193270
estimated weight of the $S = {}^9/_2$ component	0.026896
energy of the UHF wave function	−344.927206
energy of the one sided annihilated wave function	−345.070011

[a] The reference calculation has $S_Z^{\text{UHF}} = {}^5/_2$.

TABLE 5: Relative Valence Energies (eV) Calculated for Ni_6 Structures from PUHF and MRCIS Calculations at the Bulk Geometry (O_h, $R = 2.49$ Å), Symmetry Constrained Optimized Geometry (O_h, $R = 2.36$ Å) and the Jahn-Teller Distorted D_{4h} Structures[a,b]

	multiplicity	O_h, $R = 2.49$ Å	O_h, $R = 2.36$ Å	D_{4h}
	1	$^1A_{2g}$	$^1A_{2g}$	$^1B_{1g}$
PUHF		0.43 (0.158)	0.63 (0.160)	0.27 (0.160)
MRCI		4.63	2.83	3.21
	3	$^3T_{2u}$	$^3T_{2u}$	$^3B_{2u}$
PUHF		0.57 (0.407)	0.33 (0.409)	0.38 (0.408)
MRCI		3.16	1.22	1.71
	5	$^5A_{2g}$	$^5A_{2g}$	$^5B_{1g}$
PUHF		0.27 (0.589)	0.14 (0.596)	0.22 (0.600)
MRCI		2.78	1.09	0.79
	7	$^7A_{2g}$	$^7A_{2g}$	$^7B_{1g}$
PUHF		0.11 (0.736)	0.027 (0.746)	0.027 (0.748)
MRCI		0.95	1.14	1.12
	9	$^9A_{2g}$	$^9A_{2g}$	$^9B_{1g}$
PUHF		0.027 (0.854)	0.0082 (0.863)	0.0054 (0.864)
MRCI		0.30	0.30	0.68
	11	$^{11}E_g$	$^{11}E_g$	$^{11}A_{1g}$
PUHF		0.000 (0.952)*	0.000 (0.963)**	0.000 (0.963)***
MRCI		0.000	0.000[##]	0.000[###]
	13	$^{13}A_{2g}$	$^{13}E_g$	$^{13}B_{1g}$
PUHF		0.38 (0.994)	0.57 (0.996)	0.52 (0.997)
MRCI		0.54	1.17	1.71

[a] The numbers in parentheses are the weights of the given multiplicity from the Sz = S UHF calculation. [b] MRCIS absolute energy values: (#) −244.224 au; (##) −244.295 au; (###) −244.300. PUHF absolute energy values: (*) −244.229 au; (**) −244.372 au; (***) −244.396 au. 1 au = 27.2114 eV.

Ni Clusters. As a final example, we examine the energetics of Ni_6 clusters. Table 5 summarizes our findings for this cluster at three different geometries: O_h symmetry at the observed bulk distance of 2.49 Å, the INDO/1 optimized geometry constrained to O_h symmetry, and the INDO/1 optimized Jahn−Teller distorted geometry of D_{4h} symmetry.[41] The INDO/S−PUHF calculations are as described above; the multireference CI (MRCI) calculations generate single excitations from all symmetry-equivalent configuration state functions for each spin and space assignment and are reasonably time-consuming calculations involving several thousand configurations in each of the irreducible representations in the Abelian subgroup D_{2h}.

The undectet ($2S + 1 = 11$) is predicted to have the lowest energy in all cases, although the PUHF calculations suggest that multiplicities of 7, 9, and 11 are essentially degenerate, i.e., within a kcal/mol (1 hartree = 627.58 kcal/mol), with the exception being the septet at the bulk geometry that lies 2.5 kcal/mol above the PUHF undectet. The MRCI calculations separate the energies of the multiplets by a greater amount. In all cases, the PUHF calculations yield a lower energy than do the far more complex MRCI calculations. At the bulk geometry, this difference in energy is only 3 kcal/mol, but it increases to nearly 6 kcal/mol at the other geometries. In other words, it is quite difficult for the ROHF−CI procedure to produce energies as low as those easily obtained from the PUHF procedure.

Analysis indicates that the PUHF results are more systematic than are those of the MRCI calculations in the sense that a Heisenberg spin Hamiltonian can be fit to the results obtained for each geometry with a standard deviation of 0.002 hartree compared to 0.02 hartree for each MRCI structure. Of curiosity is the observation that these fits suggest that the lowest multiplicity predicted from the PUHF calculations is the septet; the undectet remains the lowest energy from the fits to the MRCI calculations, although the nonet becomes nearly degenerate.

For comparison, DFT calculations on the distorted D_{4h} structure predict that a multiplicity of 7 lies lowest,[42] but density functional theory has recently been shown to favor lower multiplicities.[43] CASSCF/CI calculations at the bulk geometry seem to also suggest that a septet lies lowest in energy.[44]

Conclusions

We have re-examined the projected UHF procedure as an inexpensive tool to obtain pure spin states, following the procedure originally delineated by Harriman and stabilized by use of the pairing theorem of Löwdin. We develop a robust procedure that is very capable of yielding correctly the spin multiplicities of open-shell systems. The energies we obtain are difficult to match using ROHF−CI procedures. Although the wave functions we obtain "seem" to be much improved over that of the UHF model, we still have very little experience with the performance of this model with respect to other observables.

Appendix: The Paired Orbitals of Löwdin

Let us consider the two sets of basis functions

$$\mathbf{a} = \{|a_1\rangle, |a_2\rangle, ..., |a_m\rangle\}$$

$$\mathbf{b} = \{|b_1\rangle, |b_2\rangle, ..., |b_n\rangle\}$$

of order m and n, respectively, with $m \geq n$. Further, we assume the sets to be orthonormal. Then one has the overlap integral matrixes

$$\mathbf{S}_{m\times n} = \mathbf{a}^{\dagger}\mathbf{b}$$

$$\mathbf{S}^{\dagger}_{n\times m} = \mathbf{a}^{\dagger}\mathbf{b}$$

Theorem. There exists two unitary transformations **U** and **V** having the property that if

$$\mathbf{a}' = \mathbf{aU}$$

$$\mathbf{b}' = \mathbf{bU}$$

then the overlap matrices, i.e.,

$$\mathbf{S}' = \mathbf{a}'^{\dagger}\mathbf{b}'$$

$$\mathbf{S}'^{\dagger} = \mathbf{b}'^{\dagger}\mathbf{a}'$$

are going to be diagonal, leading to a natural *pairing* of the basis functions.

Consider the two product matrices $\mathbf{SS}^{\dagger}$ and $\mathbf{S}^{\dagger}\mathbf{S}$, which are Hermitian and of dimension $m \times m$ and $n \times n$, respectively. (If $m > n$, then $\mathbf{SS}^{\dagger}$ has at least $m - n$ eigenvalues equal to zero.) Then there exists a unitary matrix **V** such that

$$\mathbf{V}^{-1}(\mathbf{S}^{\dagger}\mathbf{S})\mathbf{V} = \mathbf{u}$$

where **u** is diagonal, and for the sake of simplicity assumed to be of dimension $n \times n$ (i.e., no vanishing eigenvalues). Also $u_k \geq 0$ since $\mathbf{S}^{\dagger}\mathbf{S}$ is positive definite.

Now let us define

$$\mathbf{U} = \mathbf{SVu}^{-1/2}$$

where

$$\mathbf{U}^{\dagger}\mathbf{U} = \mathbf{u}^{-1/2}\mathbf{V}^{\dagger}\mathbf{S}^{\dagger}\mathbf{SVu}^{-1/2} = \mathbf{u}^{-1/2}\mathbf{uu}^{-1/2} = \mathbf{I}_{n\times n}$$

and

$$\mathbf{U}^{\dagger}\mathbf{SV} = \mathbf{u}^{-1/2}\mathbf{V}^{\dagger}\mathbf{S}^{\dagger}\mathbf{SV} = \mathbf{u}^{-1/2}\mathbf{u} = \mathbf{u}^{1/2}$$

If for convenience we define

$$T_r = u_r^{1/2}$$

then

$$\langle \mathrm{a}'_r|\mathrm{b}'_s\rangle = T_r\delta_{rs}$$

and

$$\langle \mathrm{b}'_r|\mathrm{a}'_s\rangle = T_r\delta_{rs}$$

which is the pairing theorem. (The pairing theorem is a special case of the mirror theorem.[20,25,26])

The value of the overlap T_r ranges between $0 < T_r \leq 1$. If $T_r = 1$, then $\mathbf{a}'_r = \mathbf{b}'_r$ and corresponds to a doubly occupied orbital with no paring properties. Those orbital pairs having $T_r < 1$ are referred to as the corresponding orbitals of Amos and Hall[21] or the paired orbitals of Löwdin. The $m - n$ extra eigencolumns of $\mathbf{SS}^{\dagger}$, associated with the $-n$ *zero* eigenvalues, are of zero length.

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References and Notes

(1) Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry*; McGraw-Hill: New York, 1997.
(2) Roothaan, C. C. J. *Rev. Mod. Phys.* **1960**, *32*, 179.
(3) Davidson, E. R. *Chem. Phys. Lett.* **1973**, *21*, 565.
(4) Jackels, C. F.; Davidson, E. R. *Intern. J. Quantum. Chem.* **1974**, *8*, 707.
(5) Veillard, A. In *Computational Techniques in Quantum Chemistry*; Diercksen, G. H. F., Sutcliffe, B. T., Veillard, A., Eds.; NATO Adv. Ser. C; D. Reidel: Boston, 1975.
(6) Edwards, W. D.; Zerner, M. C. *Theor. Chim. Acta* **1987**, *72*, 347.

(7) Zerner, M. C. *Intern. J. Quantum Chem.* **1989**, *35*, 567.

(8) Siegbahn, P. E. M. *Adv. Phys. Chem.* **1996**, *93*, 219.

(9) Pople, J. A.; Nesbet, R. J. *Chem. Phys.* **1954**, *22*, 571.

(10) Löwdin, P. O. *Symposium in Molecular Physics at Nikko*; Japan, Mazurin, Tokyo, 1954.

(11) Bauschlicher, C. W., Jr.; Partridge, H. *J. Chem. Phys.* **1990**, *93*, 3333.

(12) Goodgame, M. M.; Goddard, W. A., III *J. Phys. Chem.* **1981**, *85*, 215.

(13) Correa de Mello, P.; Edwards, W. D.; Zerner, M. C. *J. Am. Chem. Soc.* **1982**, *104*, 1440.

(14) Andrews, J. S.; Jayatilaka, D.; Bone, R. G. A.; Amos, R. D.; Handy, N. C. *Chem. Phys. Lett.* **1991**, *183*, 423.

(15) Cox, P. A.; Wood, M. H. *Theor. Chim. Acta* **1976**, *41*, 269.

(16) Smyers, Y. G.; Doreste-Suarez, L. *Intern. J. Quantum Chem.* **1973**, *7*, 687.

(17) Bone, R. G. A.; Pulay, P. *Intern. J. Quantum Chem.* **1992**, *45*, 133.

(18) McWeeny, R. *Methods in Molecular Quantum Mechanics*, 2nd ed.; Academic Press: London, 1989.

(19) Sasaki, F.; Ohno, K. *J. Math Phys.* **1963**, *4*, 1140.

(20) Harriman, J. *J. Chem. Phys.* **1964**, *40*, 2827.

(21) Hardisson, A.; Harriman, J. *J. Chem. Phys.* **1967**, *46*, 3639.

(22) Sando, K.; Harriman, J. *J. Chem. Phys.* **1967**, *47*, 180.

(23) Löwdin, P. O. *Phys. Rev.* **1955**, *97*, 1509.

(24) Löwdin, P. O. *Rev. Mod. Phys.* **1960**, *32***,** 328.

(25) Löwdin, P. O. *Quantum Theory of Atoms, Molecules and the Solid State*; Academic Press: New York, 1966.

(26) Amos, A. T.; Hall, G. G. *Proc. R. Soc. (London)* **1961**, *A263*, 483.

(27) Amos, T.; Snyder, L. C. *J. Chem. Phys.* **1964**, *41*, 1773.

(28) Bacon, A. D.; Zerner, M. C. *Theor. Chim. Acta* **1979**, *53*, 21.

(29) Pauncz, R. *Spin Eigenfunctions*; Plenum Press: New York, 1979.

(30) Löwdin, P. O. *J. Appl. Phys.* **1962**, *33*, 251.

(31) Löwdin, P. O. *Set Theory and Linear Algebra − some mathematical tools to be used in Quantum Theory*; Technical Note 490, Quantum Theory Project, University of Florida: Gainesville, 1976.

(32) Phillips, D.; Schug, J *J. Chem. Phys.* **1974**, *61*, 1031.

(33) Michael Zerner; Ridely, J. E.; Bacon, A.; McKelvey, J.; Edwards, W. D.; Head, J. D.; Culberson, C.; Cory, M. G.; Zheng, X.; Parkinson, W.; Yu, Y.; Cameron, A.; Tamm, T.; Pearl, G.; Broo, A.; Albert, K.; et. al. *ZINDO*; Quantum Theory Project, The University of Florida: Gainesville, FL. Distributed by Biosym. Technologies, 10065 Barnes Canyon Rd., San Diego, CA 92121.

(34) Pople, J. A.; Beveridge, D.; Dobosch, P. *J. Chem. Phys.* **1967**, *47*, 2026.

(35) Ridley, J. E.; Zerner, M. C. *Theor. Chim. Acta* **1973**, *32*, 111.

(36) Zerner, M. C.; Loew, G. H.; Kirschner, R. F.; Müller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1980**, *102*, 589.

(37) Zerner, M. C. In *Reviews of Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH Publishing: New York, 1991; Vol. 2, pp 313−366.

(38) Martin, C.; Zerner, M. C. To be published.

(39) Cory, M. G.; Stavrev, K.; Zerner, M. C. *Intern. J. Quantum Chem.* **1997**, *63*, 781.

(40) Boone, A.; Cory, M. G.; Zerner, M. C.; Richards, N. *J. Am. Chem. Soc.*, submitted.

(41) Cory, M. G.; Estiu, G.; Zerner, M. C. *J. Phys. Chem*., submitted.

(42) Reuse, F. A.; Khanna, S. N. *Chem. Phys. Lett.* **1995**, *234*, 77.

(43) Dupuis, M. Presented at the Sanibel Symposia, St. Augustine, Florida, 1997.

(44) Groppen, O.; Almlöf, J. *Chem. Phys. Lett.* **1992**, *191*, 306.