Spin contamination in single-determinant wavefunctions

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Spin contamination in single-determinant wavefunctions is examined by performing unrestricted Hartree–Fock (UHF) calculations which constrain the $\langle \hat{S}^2 \rangle$ value using a Lagrange multiplier λ. We call this method spin-constrained unrestricted Hartree–Fock (SUHF). It is shown that as $\lambda \to \infty$, restricted open-shell Hartree–Fock (ROHF) solutions are obtained. Small values of λ can significantly reduce the $\langle \hat{S}^2 \rangle$ error, whilst changing the energy only slightly. Calculations are performed with SUHF and its Møller–Plesset counterpart SUMP2. SUMPn calculations with large values of λ appear to be a way to carry out ROHF Møller–Plesset studies. Applications are presented for CN, NH_2 and BH and are compared with UHF and annihilated UHF (AUHF) results.

1. Introduction

The unrestricted Hartree–Fock (UHF) method [1] is arguably the simplest with which to study both closed and open-shell systems. The UHF wavefunction also lends itself readily to a Møller–Plesset (MP) perturbation treatment [2] and is thus a good basis for estimating the correlation energy. However, the UHF wavefunction is not in general a configuration state function (CSF) since it is not an eigenfunction of $\hat{S}^2$. Consequently its use for the study of real spectroscopic states is open to criticism. The effect of spin contamination on the convergence of the unrestricted Møller–Plesset (UMP) series has been investigated using full configuration interaction (FCI) calculations [3,4]. Handy, Knowles and Somasundram [5] report that the greater the spin contamination in the underlying UHF wavefunction the slower the UMPn series is to converge. This can lead to artifacts in potential energy curves of spin contaminated systems. For these reasons much effort has been put into developing methods to project out the spin contamination and this has led to wavefunctions including projected UHF (PUHF) [6], extended Hartree–Fock (EHF) [7,8], annihilated UHF (AUHF) [9,10] and half projected Hartree–Fock (HPHF) [11,12]. These are all based upon the spin projection operator of Löwdin [13]

$$\hat{O}_m = \prod_{l \neq m} \frac{\hat{S}^2 - l(l+1)}{m(m+1) - l(l+1)}. \qquad (1)$$

This operator will project out the spin eigenfunction of multiplicity $2m+1$. However, application of $\hat{O}_m$ leads to a many-determinant expansion where the resulting expressions are difficult to evaluate. Amos and Hall [6] were the first to use these ideas and they suggested that for a wavefunction with major spin component of quantum number S, the components with spin quantum numbers higher than $S+1$ may often be negligible due to their much higher energy. Thus $\tilde{\Psi} = \hat{A}_s \Psi$, where $\hat{A}_s = \hat{S}^2 - (S+1)(S+2)$ annihilates the first spin contaminant, is a good approximation to a spin eigenfunction. The annihilator $\hat{A}_s$ is not idempotent, a consequence of the fact that it affects states other than the one annihilated, and thus the energy should be evaluated through

$$E = \frac{\langle \hat{A}_s \Psi_e | \hat{H}_e | \hat{A}_s \Psi_e \rangle}{\langle \hat{A}_s \Psi_e | \hat{A}_s \Psi_e \rangle}. \qquad (2)$$

In the PUHF method the annihilator is applied after a conventional UHF calculation and therefore the resulting wavefunction is not stationary with respect to its variational parameters. In contrast the EHF wavefunction is stationary, but the significant extra

computational effort makes this method unattractive [14]. The AUHF method is based closely around the UHF method, the effect of the annihilator being incorporated in the density matrices making the method an ad hoc way of removing spin contamination and interpretation of the AUHF function difficult. This method is discussed in more detail below. The HPHF method is only defined for even electron systems and, as will be shown elsewhere [15], has limited applicability.

Spin contamination can be removed entirely at the SCF level using the restricted Hartree–Fock (RHF) and restricted open-shell (ROHF) wavefunctions [16]. However, the ROHF method does not lend itself very readily to a perturbational treatment. Since spin projection schemes essentially lead to a many-determinant description it is also difficult to set up a good perturbation theory based on them [17,18]. Thus when the UHF wavefunction indicates a serious breakdown of the RHF approximation (or when the spin contamination is high) the only approach is to use CI with a multiconfiguration root function where dynamic correlation is automatically introduced [19].

Although all the above is widely understood it is not so well appreciated why, upon going from the RHF/ROHF description to the UHF description of a system the resulting improvement in energy can only occur with the introduction of spin contamination. In this note we highlight this and emphasise that for a single determinant, with non-complex molecular orbitals, an exact spin expectation will imply a RHF/ROHF [#1] description. Further we analyse the natural orbital (NO) occupation numbers [20] of the UHF wavefunction and suggest that the closeness of these to the integers 2, 1 or 0 is the best indication of the deviation of the wavefunction from RHF/ROHF. In section 3 we derive UHF equations where the spin is constrained to have a specific value. Although these equations have no solution when $\hat{S}^2$ assumes the exact value for an open shell system (see text), we can find solutions where $\hat{S}^2$ is close to this value. We recommend this as a practical solution to the problem of spin contamination in UHF wavefunctions. In section 4 we apply Møller–Plesset the-

ory to this new approach, and in section 5 we present applications to NH_2, CN and BH.

2. UHF and RHF/ROHF theory

For a single-determinant wavefunction

$$\Psi = \hat{A}(\psi_1^\alpha(1)...\psi_p^\alpha(p)\phi_1^\beta(p+1)...\phi_q^\beta(n)) \qquad (3)$$

such as the RHF, ROHF and UHF functions, the spin expectation expression in the molecular orbital (MO) basis is given by

$$\langle \hat{S}^2 \rangle = S_z^2 + S_z + q - \sum_{ij}^{pq} S_{ij}^2, \qquad (4)$$

where

$$S_{ij} = \langle \psi_i | \phi_j \rangle . \qquad (5)$$

Without loss of generality we define $p \geq q$, with $p+q=n$. One sees immediately that for RHF/ROHF, where the overlap matrix (5) has only diagonal elements, the last two terms in (4) cancel giving the exact value as expected. However, for the more general UHF wavefunction spin contamination is present and the following inequality holds:

$$\langle \hat{S}^2 \rangle \geq S_z(S_z+1) . \qquad (6)$$

The equality occurs when the UHF MO overlap matrix is equal to that for a RHF/ROHF wavefunction. This relationship between spin contamination and MO overlap will now be investigated further. Eq. (4) can be recast in terms of the natural orbital occupation numbers, σ_i:

$$\langle \hat{S}^2 \rangle = \tfrac{1}{4}(p+q)(p+q+4) - pq - \tfrac{1}{2}\sum_i^n \sigma_i^2, \qquad (7)$$

where for a wavefunction of the form (3), $\{\sigma_i\}$ are the eigenvalues of those orbitals which diagonalise the first-order reduced density matrix $\rho(1, 2)$ [6],

$$\rho(1, 2) = \sum_i^p \psi_i(1)\psi_i(2) + \sum_j^q \phi_j(1)\phi_j(2) . \qquad (8)$$

Such orbitals are called the natural orbitals (NOs). For the RHF/ROHF wavefunctions the canonical MOs are the natural orbitals and thus the NO occupation numbers are either 2, 1 or 0. Thus for an exact spin eigenfunction it follows that

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[#1] In this paper we use ROHF to indicate high-spin open shell SCF.

$$\sum_i \sigma_i^2 = 4q + (p-q) . \tag{9}$$

In their paper Amos and Hall [6] showed that by suitable unitary transformations of the alpha $\{\psi^\alpha\}$ and beta $\{\phi^\beta\}$ sets the UHF wavefunction could equally be written as a determinant of so-called corresponding orbitals, $\{\chi^\alpha\}$ and $\{\eta^\beta\}$. These orbitals have the property that their spatial overlap is diagonal

$$T_{ij} = \int \chi_i \eta_j \, d\tau, \quad T_{ij} = \delta_{ij} T_i . \tag{10}$$

Further they showed that the corresponding orbitals are closely related to the natural orbitals since the NO occupation numbers are given by

$$\sigma_i = 1 \pm T_i, \quad i = 1, ..., 2q ;$$
$$\sigma_i = 1, \quad i = 2q+1, ..., 2q+p . \tag{11}$$

It is easily shown that, for a single-determinant wavefunction, no natural orbital occupation numbers other than the RHF/ROHF values can simultaneously satisfy (9) whilst conserving the total number of electrons. This implies that for a single-determinant wavefunction to be an exact spin eigenfunction the diagonal **T** matrix elements in (10) must be 1. Therefore the corresponding orbital molecular orbital overlap matrix must be that of a RHF/ROHF wavefunction and thus the UHF wavefunction must be simply related to the RHF/ROHF functions by suitable unitary transformations.

For closed shell systems the RHF MO vectors are solutions of the UHF equations and thus, for these systems, pure spin eigenfunctions are possible in the UHF formalism. However, at certain geometries a symmetry broken, spin contaminated solution becomes variationally preferred and the RHF solution is now a saddle point [21].

In contrast, for open shell systems no ROHF-like solution (i.e. with the spatial part of the α and β orbitals the same over the closed shell) exists to the UHF equations. To see this, we write the UHF equations in terms of the total density ($\mathbf{D}^t = \mathbf{D}^\alpha + \mathbf{D}^\beta$) and spin density ($\mathbf{D}^s = \mathbf{D}^\alpha - \mathbf{D}^\beta$) matrices as follows,

$$\langle \chi_v | \hat{F}(\mathbf{D}^t) - \tfrac{1}{2}\hat{K}(\mathbf{D}^s) | \chi_i \rangle = 0 ,$$
$$i = 1, 2, ..., p, \quad v = p+1, ..., \text{nb} ; \tag{12a}$$

$$\langle \eta_v | \hat{F}(\mathbf{D}^t) + \tfrac{1}{2}\hat{K}(\mathbf{D}^s) | \eta_i \rangle = 0 ,$$
$$i = 1, 2, ..., q, \quad v = q+1, ..., \text{nb} , \tag{12b}$$

where

$$\hat{F}(\mathbf{D}^t) = \hat{h} + \hat{J}(\mathbf{D}^t) - \tfrac{1}{2}\hat{K}(\mathbf{D}^t) , \tag{13}$$

with $\hat{h}$ denoting the one-electron Hamiltonian, $\hat{J}$ and $\hat{K}$ the Coulomb and exchange operators respectively and nb the number of basis functions. For a ROHF-like solution the corresponding orbitals, χ_i and η_i, must be the same and therefore (12b) can be written as

$$\langle \eta_v | \hat{F}(\mathbf{D}^t) + \tfrac{1}{2}\hat{K}(\mathbf{D}^s) | \chi_i \rangle = 0 , \tag{14a}$$

where

$$\eta_v = \chi_j, \quad j = p - q + 1, ..., p ;$$
$$\eta_v = \chi_v, \quad v = p+1, ..., \text{nb} . \tag{14b}$$

It is apparent then that eqs. (12a) and (14) cannot be satisfied simultaneously unless $\mathbf{D}^s$ is identically zero, which then corresponds to RHF. The ROHF MOs cannot therefore be solutions to the UHF defining equations. Since we have shown that a spin exact, single-determinant wavefunction must be related to a ROHF function, if follows that no spin exact function is stationary on the UHF surface for open shell systems. Consequently we are interested in UHF wavefunctions which have spin expectation values close to the exact value.

3. The SUHF and AUHF methods

In the atomic orbital (AO) basis (3) becomes

$$\langle \hat{S}^2 \rangle = S_z^2 + S_z + q - \text{Tr}(\mathbf{S}\mathbf{D}^\beta \mathbf{S}\mathbf{D}^\alpha) , \tag{15}$$

where **S** is the AO overlap matrix. By constraining

$$\text{Tr}(\mathbf{S}\mathbf{D}^\beta \mathbf{S}\mathbf{D}^\alpha) = k , \tag{16}$$

where k is a particular constant chosen so that $\langle \hat{S}^2 \rangle$ is close to the exact value, we obtain modified UHF equations

$$(\mathbf{F}^\alpha - 2\lambda \mathbf{S}\mathbf{D}^\beta \mathbf{S})\mathbf{c}^\alpha = \mathbf{S}\mathbf{c}^\alpha \epsilon^\alpha , \tag{17a}$$

$$(\mathbf{F}^\beta - 2\lambda \mathbf{S}\mathbf{D}^\alpha \mathbf{S})\mathbf{c}^\beta = \mathbf{S}\mathbf{c}^\beta \epsilon^\beta , \tag{17b}$$

where

$$\mathbf{F}^{\alpha} = \mathbf{F}(\mathbf{D}^{t}) - \tfrac{1}{2}\mathbf{K}(\mathbf{D}^{s}) \,, \tag{18a}$$

$$\mathbf{F}^{\beta} = \mathbf{F}(\mathbf{D}^{t}) + \tfrac{1}{2}\mathbf{K}(\mathbf{D}^{s}) \tag{18b}$$

and λ is the Lagrange multiplier associated with the spin constraint (16). In our procedure (termed spin-constrained UHF or SUHF) we solve (17) for a particular λ and when converged calculate the energy (the expectation value of $\hat{H}_{e}$) and the spin expectation value. This is then repeated for different λ. The equations (17) are very similar to the conventional UHF equations. Further the minimal extra computation required for their construction involve matrices typically present in these type of calculations making this scheme very easy to implement in existing UHF codes. To accelerate the iterative convergence of SUHF a form of Pulay's direct inversion of iterative subspace (DIIS) [22,23] is used. In our implementation the total error vector, characterising the proximity of the current iteration to convergence, is just the sum of an alpha ($\mathbf{e}^{\alpha}$) and beta ($\mathbf{e}^{\beta}$) error vector, where for example

$$\mathbf{e}^{\alpha} = \mathbf{G}^{\alpha}\mathbf{D}^{\alpha}\mathbf{S} - \mathbf{S}\mathbf{D}^{\alpha}\mathbf{G}^{\alpha} \tag{19}$$

and $\mathbf{G}^{\alpha}$ is the SUHF matrix,

$$\mathbf{G}^{\alpha} = \mathbf{F}^{\alpha} - 2\lambda\mathbf{S}\mathbf{D}^{\beta}\mathbf{S} \,. \tag{20}$$

We have compared SUHF to the UHF, AUHF and ROHF methods. Calculations were performed for the CN radical with the DZP basis set of Huzinaga–Dunning [24] and are presented in section 5.

The AUHF method is described in refs. [9,10]. We understand that the method originated in Schleyer's group at Erlangen; for example the AUHF algorithm is included in the semi-empirical VAMP code [25].

The AUHF algorithm proceeds exactly as with the UHF algorithm, except that the $\mathbf{F}^{\alpha}$ and $\mathbf{F}^{\beta}$ matrices are formed using spin projected density matrices $\bar{\mathbf{D}}^{\alpha}$ and $\bar{\mathbf{D}}^{\beta}$ instead of the matrices $\mathbf{D}^{\alpha}$ and $\mathbf{D}^{\beta}$. $\bar{\mathbf{D}}^{\alpha}$ and $\bar{\mathbf{D}}^{\beta}$ are constructed from $\mathbf{D}^{\alpha}$ and $\mathbf{D}^{\beta}$ by removing the first spin contaminant using $\hat{A}_{s}$, their specific form is given in the paper by Amos and Snyder [26]. The spin expectation value is calculated using the orbitals obtained after the diagonalisation of these $\mathbf{F}^{\alpha}$ and $\mathbf{F}^{\beta}$ matrices. The density matrices $\mathbf{D}^{\alpha}$, $\mathbf{D}^{\beta}$ formed from the orbitals are not equal to the projected matrices $\bar{\mathbf{D}}^{\alpha}$, $\bar{\mathbf{D}}^{\beta}$ even at convergence. Instead convergence is attained when $\mathbf{D}^{\alpha}$, $\mathbf{D}^{\beta}$ (or $\bar{\mathbf{D}}^{\alpha}$, $\bar{\mathbf{D}}^{\beta}$) do not change upon

iteration. The AUHF energy is not stationary with respect to the variational parameters. In our implementation we ensure that the energy is an upper bound by evaluating the expectation value of $\hat{H}_{e}$ for the converged orbitals. In Baker's implementation [9] the energy is evaluated with the projected density matrices, which do not correspond to single-determinant wavefunctions, and this energy is not the correct reference for the perturbation series based on the unprojected molecular orbitals. Baker's many calculations [9] show that the converged value for $\langle \hat{S}^{2} \rangle$ is a great improvement over the UHF value.

4. Møller–Plesset theory for the UHF, SUHF and AUHF methods

Møller–Plesset theory depends upon a suitable identification for $\hat{H}_{0}$ as $\sum f_{i}$. Any form of UHF theory is applicable to this method of introducing the effects of electron correlation. For UHF, SUHF and AUHF theory the appropriate definitions for f are:

UHF: $\quad f \equiv F^{\alpha}(\mathbf{D}), F^{\beta}(\mathbf{D})$,

SUHF: $\quad f \equiv G^{\alpha}, G^{\beta}$,

AUHF: $\quad f \equiv F^{\alpha}(\bar{\mathbf{D}}), F^{\beta}(\bar{\mathbf{D}})$. $\tag{21}$

Following the usual theory, the second-order energy may then be written as

$$E_{2} = -\sum_{ia} \frac{\langle \Psi_{i}^{a} | \hat{H}_{1} | \Psi_{0} \rangle^{2}}{\epsilon_{a} - \epsilon_{i}}$$
$$- \frac{1}{4}\sum_{ijab} \frac{\langle \Psi_{ij}^{ab} | \hat{H}_{1} | \Psi_{0} \rangle^{2}}{\epsilon_{a} + \epsilon_{b} - \epsilon_{i} - \epsilon_{j}} \,. \tag{22}$$

We may replace $\hat{H}_{1}$ by $\hat{H}_{e}$ to obtain

$$\langle \Psi_{i}^{a} | \hat{H}_{e} | \Psi_{0} \rangle = (\phi_{a} | F | \phi_{i}) \,,$$
$$\langle \Psi_{ij}^{ab} | \hat{H}_{e} | \Psi_{0} \rangle = (ai|bj) - (aj|bi) \,. \tag{23}$$

In this spin orbital notation (22) therefore becomes

$$E_{2} = -\sum_{ia} \frac{F_{ai}^{2}}{\epsilon_{a} - \epsilon_{i}}$$
$$- \frac{1}{4}\sum_{ijab} \frac{[(ai|bj) - (aj|bi)]^{2}}{\epsilon_{a} + \epsilon_{b} - \epsilon_{i} - \epsilon_{j}} \,. \tag{24}$$

Note that only in UHF theory is $F_{ai} = 0$. In SUHF and AUHF theories, the single replacement contri-

bution to the second-order energy must be included. Baker appears to ignore this aspect in his discussion of the applications of AUHF theory to the calculation of the Møller–Plesset series [10]. The addition of the extra single-replacement terms to the series is at trivial extra cost, in SUHF $F^\alpha_{ai} = 2\lambda (SD^\beta S)_{ai}$, $F^\beta_{ai} = 2\lambda (SD^\alpha S)_{ai}$.

Perturbation theory applied to the ROHF function is problematic because there is no unique way to choose $\hat{H}_0$. This is because there are three Brillouin-type conditions to be obeyed. SUHF theory offers an alternative approach, but there is a difficulty to overcome in that as $\lambda \to \infty$ (i.e. the ROHF wavefunction) both the first q α eigenvalues and the first p β eigenvalues are shifted by approximately -2λ. To counter this effect at SUMP2 we employ a level shift, adding 2λ to these eigenvalues after SUHF convergence. The idea of the level shift means in effect that the SUHF equations we solve are

$$(F^\alpha - 2\lambda SP^\beta S)c^\alpha = Sc^\alpha \epsilon^\alpha , \tag{25a}$$

$$(F^\beta - 2\lambda SP^\alpha S)c^\beta = Sc^\beta \epsilon^\beta , \tag{25b}$$

where

$$P^\alpha_{\gamma\delta} = \sum_{j=1}^{p} (c^\alpha_{\gamma j}c^\alpha_{\delta j} - c^\beta_{\gamma j}c^\beta_{\delta j}) , \tag{26a}$$

$$P^\beta_{\gamma\delta} = \sum_{j=1}^{q} (c^\beta_{\gamma j}c^\beta_{\delta j} - c^\alpha_{\gamma j}c^\alpha_{\delta j}) . \tag{26b}$$

This has no effect on the SUHF energies or wavefunctions, but only changes the eigenvalues and results in making SUHF MP2 theory correct for closed shell, RHF wavefunctions. In section 5 we report some calculations for the second-order energies.

5. Results and discussion

Table 1 tabulates the results for CN, all calculations were performed at the UHF optimised bond length. As expected the UHF method gives the best variational energy. The AUHF and ROHF methods give energies relative to the UHF value of 7.69 and

Table 1
Energy (hartree), spin expectation and natural orbital occupations of CN for different SCF methods with a DZP basis at a bond length of 1.1674 Å

Method	Energy	$\langle S^2 \rangle$	Natural orbital occupations
ROHF	−92.20089	0.75	2, 2, 2, 2, 2, 2, 1
UHF	−92.21782	1.14701	2.0000, 2.0000, 1.9995, 1.9985, 1.8963, 1.8963
			1.0000, 0.1037, 0.1037, 0.0015, 0.0005
AUHF	−92.20556	0.75777	2.0000, 2.0000, 1.9999, 1.9992, 1.9985, 1.9985
			1.0000, 0.0015, 0.0015, 0.0008, 0.0005
SUHF(0.010)	−92.21609	0.96323	–
SUHF(0.020)	−92.21306	0.85785	–
SUHF(0.030)	−92.21074	0.81017	–
SUHF(0.050)	−92.20817	0.77621	–
SUHF(0.100)	−92.20579	0.75860	–
SUHF(0.106)	−92.20564	0.75786	2.0000, 2.0000, 2.0000, 1.9993, 1.9984, 19984
			1.0000, 0.0016, 0.0016, 0.0007, 0.0001
SUHF(1.000)	−92.20220	0.75029	–
SUHF(5.000)	−92.20124	0.75002	–
SUHF(10.00)	−92.20108	0.75000	–
SUHF(20.00)	−92.20098	0.75000	–
SUHF(50.00)	−92.20093	0.75000	2.0000, 2.0000, 2.0000, 2.0000, 2.0000, 2.0000,
			1.0000

10.62 kcal/mol, respectively. A number of SUHF calculations are presented, the value of λ indicated in brackets. As $\lambda \to \infty$ the SUHF energies asymptotically approach the ROHF value. This is in agreement with our previous discussion where we showed that the ROHF solution does not lie on the UHF surface. Negative values of the Lagrangian gave spin values and energies higher than that of the UHF method and were thus ignored. The last column in table 1 gives the natural orbital occupation numbers. This column shows that the better the spin expectation value the closer these numbers are to the integer ROHF values. For comparison we have included the SUHF result ($\lambda = 0.106$) giving the same spin expectation as the AUHF method. The natural orbital occupation numbers and the variational energies indicate the similarity of these two wavefunctions.

By adjusting the value of the Lagrange multiplier λ, it is possible to obtain an SUHF wavefunction with any value for $\langle \hat{S}^2 \rangle$ between the ROHF and UHF values. From our calculations we see that as λ increases, $\langle \hat{S}^2 \rangle$ initially decreases in value more rapidly than the energy increases and thus, for example, the $\langle \hat{S}^2 \rangle$ error can be halved with little change in energy. A value of $\lambda = 0.01$ for CN reduces $\langle \hat{S}^2 \rangle$ from 1.147 to 0.963, raising the energy by only 0.0018 hartree. Lengsfield and Schug [27] altered NO occupations of a projected UHF wavefunction to obtain a lower energy. For SUHF the spin constraint forces changes in the NO occupations but, because we deal with single-determinant wavefunctions, the energy rises.

Usually convergence can prove quite difficult for highly spin contaminated systems described by the UHF method. Indeed we initially encountered this difficulty with the CN molecule. In comparison however, the SUHF method, by removing most of the spin contamination and thereby describing one electronic surface, shows very stable convergence characteristics. Typically convergence is achieved within 10–12 iterations. We have also tried SUHF for a triplet state (CH_2) and have obtained a similar qualitative picture. However, whilst the SUHF results are encouraging for high-spin open-shell systems, singlet states (i.e. systems for which $p = q$) present difficulties. This is associated with the triplet instability in the wavefunction [28]. For certain geometries it

is not possible to obtain a UHF solution of lower energy than the RHF solution. SUHF is of no help here. In cases where a symmetry broken UHF solution does exist we find that the energy and spin expectation are both sensitive functions of λ. There are two stable regions: the UHF-like solution for small λ and the RHF solution for intermediate and large λ values. Typical results are presented for BH in fig. 1. The transition between the UHF regime and the RHF regime is more rapid than for open-shell systems. We find that for λ slightly above and below a threshold value in this "crossing region" convergence of the SCF equations is impossible. Because of the sharpness of the transition region it is impractical to attempt to find a λ which reduces spin contamination significantly without restoring the RHF solution. Neither is it desirable as RHF solutions may quite easily be obtained from UHF equations with existing code. There is no counterpart to the new idea above that ROHF solutions may be obtained from UHF-like equations. The only simple method which is successful in removing spin contamination from singlet states is the half-projected Hartree–Fock method. Further examples of this will be presented elsewhere [15].

Table 2 (upper half) records the optimised bond lengths, spin expectation values and harmonic frequencies for CN described by UHF, ROHF, AUHF and SUHF. The UHF and ROHF results were obtained by analytical methods using the CADPAC suite of programs [29]. Numerical procedures were
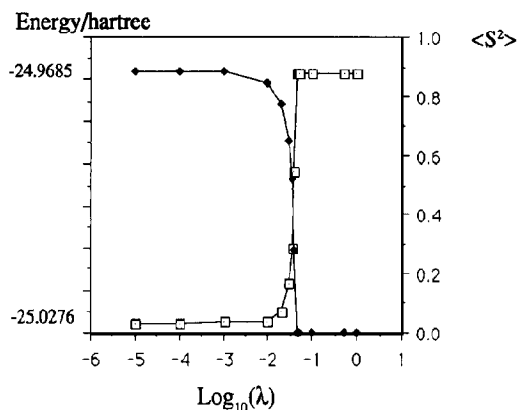

Fig. 1. SUHF energy ($\square$) and $\langle S^2 \rangle$ ($\blacklozenge$) as a function of λ for BH at a bond length of 5.0 bohr with a DZP basis set.

Table 2
Optimised bond length (Å), spin expectation and harmonic frequency (cm^{-1}) of CN [a]

Method [b]	Optimum bond length	$\langle \hat{S}^2 \rangle$	Harmonic frequency
UHF	1.16745	1.14701	1928
SUHF(0.010)	1.16253	0.95163	1990
SUHF(0.020)	1.15288	0.84423	2209
SUHF(0.050)	1.14389	0.77423	2428
SUHF(0.106)	1.14206	0.75762	2436
SUHF(50.00)	1.14087	0.75000	2445
ROHF	1.14086	0.75	2447
AUHF	1.14215	0.75745	2422
UMP2	1.13840	1.04159	2838
SUMP2(0.01)	1.16085	0.94781	2685
SUMP2(0.02)	1.18377	0.87655	2323
SUMP2(0.10)	1.21387	0.75902	1748
SUMP2(1.00)	1.21335	0.75032	1745
SUMP2(10.00)	1.21250	0.75000	1754

[a] Experimental bond length of 1.1718 Å and harmonic frequency of 2069 cm^{-1} from ref. [31].

[b] The upper and lower half give SCF and MP2 methods, respectively.

used for the SUHF and AUHF wavefunctions, a stepsize of 0.01 Å employed to obtain the harmonic frequencies at the respective stationary points. The trend from UHF through SUHF to ROHF is clearly visible from table 2, the frequencies increasing from $\lambda=0$ (UHF, 1928 cm^{-1}) to $\lambda=\infty$ (ROHF, 2447 cm^{-1}).

Table 3 shows the results of SUMP2 calculations on CN, correlating all electrons. We observe that as λ increases the magnitude of the second-order con-

tribution to the energy increases faster than the SUHF energy increases. This results in an overall lowering of the total energy. Indeed large λ values give an SUMP2 energy 0.029 hartree lower than UMP2. It is also apparent from table 3 that the single replacement contributions are small but significant. In table 2 (lower half) harmonic frequencies at the MP2 level are reported. We see a large range of values, but this is not wholly unexpected as CN is an extreme case to study by MP2 methodology. In fact this erratic behaviour has been observed before by Jensen [30] who has reported UMP2, AUMP2 and PMP2 [17] frequencies using a similar basis set. We see that as λ increases the high UMP2 frequency decreases (as required) but that as $\lambda \to \infty$ the frequency drops below the exact value.

Table 4 shows the results of SUMP2 calculations on $NH_2(^2B_1)$ with a 6-31G basis and frozen core at three different geometries. Also tabulated are UMP4 and FCI results taken from Handy, Knowles and Somasundram [5]. At $1.0r_e$ the spin contamination in the underlying UHF wavefunction is slight ($\langle \hat{S}^2 \rangle = 0.757$) and consequently the UMP2 and SUMP2 results are similar; both giving energies of approximately 0.016 hartree above the FCI value. However, at $1.5r_e$ the UHF determinant has a large spin contamination with $\langle \hat{S}^2 \rangle = 1.661$ but the SUHF functions significantly reduce the spin error, the expectation value dropping as 1.416, 0.756, 0.750 etc., down the table. The Møller–Plesset second-order energies are now quite different and we see that the SUMP2 energies lie between the UMP2 and FCI energies with the UMP2 0.060 hartree above the FCI

Table 3
Energy contributions (hartree) to SUMP2 total energy for the CN molecule with a DZP basis at a bond length of 1.1674 Å

λ	SUHF	Singles contribution	Total second-order energy	Total energy
0.01	−92.21609	−2.057×10^{-4}	−0.26790	−92.48400
0.05	−92.20817	−6.679×10^{-4}	−0.28798	−92.49615
0.10	−92.20579	−8.365×10^{-4}	−0.29286	−92.49865
1.00	−92.20220	−1.820×10^{-3}	−0.29508	−92.49728
5.00	−92.20124	−2.339×10^{-3}	−0.29543	−92.49667
10.00	−92.20108	−2.437×10^{-3}	−0.29549	−92.49657
50.00	−92.20093	−2.525×10^{-3}	−0.29554	−92.49648
100.00	−92.20091	−2.537×10^{-3}	−0.29555	−92.49647
500.00	−92.20090	−2.546×10^{-3}	−0.29556	−92.49646
0.00	−92.21782	0	−0.24963	−92.46745

Table 4
SUMP2 energies for NH_2 (C_{2v}, $r_e = 1.013$ Å, $\theta = 103.2°$, 6-31G basis, frozen core) compared with high order UMP and FCI energies

Method	r_e	$1.5r_e$	$2r_e$
UMP2	−55.617760	−55.467259	−55.413470
UMP4	−55.631188	−55.487348	−55.422186
SUMP2(0.01)	−55.617814	−55.478316	−55.415006
SUMP2(0.10)	−55.617881	−55.491808	−55.366383
SUMP2(1.00)	−55.617578	−55.490296	−55.358014
SUMP2(10.0)	−55.617417	−55.490104	−55.357751
SUMP2(50.0)	−55.617394	−55.490082	−55.357726
FCI	−55.633276	−55.526658	−55.440931

energy and SUMP2 typically only 0.035 hartree higher than FCI. Handy et al. have presented MPn/UMPn calculations for stretched H_2O [5] and these enable us to arrive at some understanding as to the cause for the UMP2/SUMP2 differences. For H_2O with bond lengths 1.5 times their equilibrium value the RHF MPn series shows good, though slightly erratic, convergence whilst the UMPn series, despite having a smaller correlation energy to obtain, is much slower to converge. Consequently at second order the RHF formalism gives an energy only 0.025 hartree higher than the FCI value compared to 0.070 hartree for the UHF based Møller–Plesset series. These numbers compare quite reasonably to those of the UMP2 and SUMP2 calculations on NH_2 and suggest that SUMPn calculations with a moderate λ (hence low spin error) may have comparable convergence characteristics to the Møller–Plesset series based on closed-shell, spin exact determinants. This conclusion is further supported by the results at $2.0r_e$. At this bond length we see that the SUMP2 total energies are above the UMP2 value by approximately 0.050 hartree. This is in qualitative agreement with the MPn/UMPn calculations on H_2O by Handy et al. at a similarly stretched geometry. By comparison to the H_2O calculations we therefore expect that the SUHF Møller–Plesset series for NH_2 will be superior to UMPn from fourth order onwards at this geometry.

6. Conclusion

In this paper we have presented a new method,

called SUHF, for the calculation of single-determinant wavefunctions. The orbitals are different for different spins, and they are constructed using an SCF formalism with the operators $F^\alpha - 2\lambda SD^\beta S$, $F^\beta - 2\lambda SD^\alpha S$; the Lagrange multiplier associated with the constraint that $\langle \hat{S}^2 \rangle = k$. When $\lambda = 0$ the method is UHF, and as λ increases to infinity the method tends to ROHF. Because this method is based on a well-defined zeroth-order Hamiltonian, Møller–Plesset theory may be applied for electron correlation, although single replacement contributions enter at second order because Brillouin's condition is not obeyed.

We have investigated this new method with calculations on NH_2 and CN. From these results and those of similar, unpublished, calculations on NO we may conclude and suggest the following:

(1) As λ increases, $\langle \hat{S}^2 \rangle$ decreases much more rapidly than the energy increases. Thus it is possible to substantially reduce the $\langle \hat{S}^2 \rangle$ error with an energy that is hardly changed from the UHF value. We find that $\lambda = 0.01$ approximately halves the UHF $\langle \hat{S}^2 \rangle$ error. We suggest either using this value or alternatively, iterating on λ to find the value that precisely halves the $\langle \hat{S}^2 \rangle$ error. Such a method has to be an improvement over the UHF procedure.

(2) Because the SUHF wavefunction is optimised subject to a constraint, the application of gradient theory will be more complicated than for UHF.

(3) Our investigations with the SUMP2 version of Møller–Plesset theory show that it is a reliable alternative to UMP2. We find that the SUMP2 energies lie below the UMP2 energies and, from our limited calculations on NH_2 at three geometries, we suggest that the convergence of the SUMP series will be similar to the convergence of he MP series for closed-shell systems. It is possible to carry out SUMP3 and SUMP4 calculations and we shall investigate further the SUMP Møller–Plesset series.

(4) Calculations with large values of λ approach the ROHF solution. We suggest that SUMP calculations with large λ offer for the first time a practical way forward for perturbation theory based on the ROHF wavefunction and, in a forthcoming publication, we shall investigate analytically this limit.

References

[1] J.A. Pople and R.K. Nesbet, J. Chem. Phys. 22 (1954) 571.

[2] C. Møller and M.S. Plesset, Phys. Rev. 46 (1934) 618.

[3] R.J. Harrison and N.C. Handy, Chem. Phys. Letters 95 (1983) 386.

[4] C.W. Bauschlicher Jr., S.R. Langhoff, P.R. Taylor, N.C. Handy and P.J. Knowles, J. Chem. Phys. 85 (1986) 1469.

[5] N.C. Handy, P.J. Knowles and K. Somasundram, Theoret. Chim. Acta 68 (1985) 87.

[6] A.T. Amos and G.G. Hall, Proc. Roy. Soc. A 263 (1961) 483.

[7] P.O. Löwdin, Phys. Rev. 97 (1955) 1474.

[8] N.C. Handy and J.E. Rice, in: Studies in physical and theoretical chemistry, Vol. 2. Proceedings of an International Workshop on Quantum Chemistry, Girona, Spain, June 1988, ed. R. Carbo, p. 145.

[9] J. Baker, J. Chem. Phys. 91 (1989) 1789.

[10] J. Baker, Chem. Phys. Letters 152 (1988) 227.

[11] Y.G. Smeyers and L. Doreste-Suarez, Intern. J. Quantum Chem. 7 (1973) 687.

[12] P.A. Cox and M.H. Wood, Theoret. Chim. Acta 41 (1976) 269.

[13] P.O. Löwdin, Phys. Rev. 97 (1955) 1509.

[14] I. Mayer, Advan. Quantum Chem. 12 (1980) 189.

[15] R.G.A. Bone and P. Pulay, in preparation.

[16] C.C.J. Roothaan, Rev. Mod. Phys. 32 (1960) 179.

[17] H.B. Schlegel, J. Chem. Phys. 84 (1986) 4530.

[18] P.J. Knowles and N.C. Handy, J. Chem. Phys. 88 (1988) 6991.

[19] H.-J. Werner and P.J. Knowles, J. Chem. Phys. 89 (1988) 5803.

[20] P.O. Löwdin, Phys. Rev. 101 (1956) 1730.

[21] I. Mayer, Intern J. Quantum Chem. 14 (1978) 29.

[22] P. Pulay, Chem. Phys. Letters 73 (1980) 393.

[23] P. Pulay, J. Comput. Chem. 3 (1982) 556.

[24] T.H. Dunning Jr., J. Chem. Phys. 53 (1970) 2823.

[25] VAMP; Erlangen vectorised molecular orbital package.

[26] A.T. Amos and L.C. Snyder, J. Chem. Phys. 41 (1964) 1773.

[27] B.H. Lengsfield III and J.C. Schug, Chem. Phys. Letters 57 (1978) 442.

[28] J. Čížek and J. Paldus, J. Chem. Phys. 47 (1967) 3976.

[29] R.D. Amos and J.E. Rice, CADPAC: The Cambridge analytical derivatives package, issue 4.0, Cambridge, 1987.

[30] F. Jensen, Chem. Phys. Letters 169 (1990) 519.

[31] K. P. Huber and G. Herzberg, Molecular spectra and molecular structure, Vol. 4. Constants of diatomic molecules (Van Nostrand Reinhold, New York, 1979).