

On the SCF Calculation of Excited States: Singlet States in the Two-Electron Problem

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The problem of determining SCF wave functions for excited electronic states is examined for singlet states of two-electron systems using a Lowdin natural orbital transformation of the full CI wave function. This analysis facilitates the comparison of various SCF methods with one another. The distribution of the full CI states among the natural orbital MCSCF states is obtained for the *S* states of helium using a modest Gaussian basis set. For SCF methods that are not equivalent to the full CI wave functions, it is shown that the Hartree-Fock plus all single excitation wave functions are equivalent to that of Hartree-Fock plus one single excitation. It is further shown that these wave functions are equivalent to the perfect pair or TCSCF wave functions in which the CI expansion coefficients are restricted to have opposite signs. The case of the natural orbital MCSCF wave function for two orbitals is examined in greater detail. It is shown that the first excited state must always be found on the lower natural orbital MCSCF CI root, thus precluding the use of the Hylleras-Undeim-MacDonald (HUM) theorem in locating this state. It is finally demonstrated that the solution obtained by applying the HUM theorem (minimizing the upper MCSCF CI root with respect to orbital mixing parameters) is an artifact of the MCSCF method and does not correspond to any of the full CI states.

I. INTRODUCTION

Self-consistent field (SCF) wave functions are attractive because they are compact, easily interpretable, and computationally expedient for evaluating molecular properties. They are also widely used as reference functions for large scale configuration interaction (CI) calculations. Yet despite their dominance of computational quantum chemistry for the last 35 years there are some aspects of these wave functions that remain elusive. The problem of simply counting the non-redundant variational degrees of freedom in some multiconfiguration SCF (MCSCF) wave functions is not always easy nor is the problem of selecting a set of configurations that evenhandedly describe the Born-Oppenheimer electronic state over any given range of molecular geometries.

When applied to excited electronic states, SCF wave functions offer the same advantages as noted above but the problems in determining them are more severe. In particular, attempts to calculate SCF wave functions of excited states which are of the same symmetry as the ground state frequently lead to a variational collapse to the ground state,

or, if open-shell character is imposed on the wave function, to a poor representation of the ground state.

These problems are well known and documented.¹⁻⁴ Moreover, variationally stable methods have been developed for single configuration SCF wave functions which can be legitimately applied to excited states of the same symmetry as the ground state.^{2,5} In particular, Davidson and Stenkamp² have shown that such wave functions give a rigorous upper bound on the excited state energy of interest, and they have devised stable algorithms for computing these wave functions. Most recently, Fitzgerald and Schaefer⁶ have shown that the Davidson and Stenkamp wave function for singlet states (in which the open-shell orbitals are allowed to be nonorthogonal) is equivalent to a two configuration MCSCF wave function with all orbitals orthogonal, just as is the case in the perfect pair GVB wave function.^{6,7} Fitzgerald and Schaefer further demonstrate the utility of this wave function for examining the potential energy surfaces of excited states.

The problem of computing excited states using more general MCSCF wave functions has been addressed by Yeager et al.,⁸ who use

a Newton-Raphson method to converge to a stationary state with the proper number of negative eigenvalues of the Hessian or second derivative matrix. They note that difficulties with root flipping can occur. During optimization the eigenvalue of the CI matrix being followed may fall below another, resulting in a failure to satisfy the Hylleraas-Undheim-MacDonald (HUM) upper bound theorem.⁹

The purpose of the present article is to examine the simplest nontrivial case of an MCSCF wave function, the natural orbital two electron singlet. Although it is mainly of academic interest, the simplicity of the two-electron wave function allows a clear illustration of the nature of the types of problems that can occur when attempting to compute excited state SCF wave functions.

In the following section the case of singlet states with two electrons and N orbitals is examined using familiar matrix operations. This is followed by a more detailed examination of the $N = 2$ case in which the relation between the configuration interaction degree of freedom and the orbital mixing is expressed using simple trigonometric formulae.

II. TWO ELECTRONS AND N ORBITALS

The space part of the two electron full CI wave function can be written as

$$\Psi(1, 2) = \text{Tr}[C\Phi^{\circ+}(1)\Phi^{\circ}(2)] \quad (1)$$

where the square matrix C contains the CI coefficients and the row vector Φ° contains the N orthonormal orbitals. The matrix C is symmetric for singlet states and antisymmetric for triplet states. Only the singlet states will be considered here. Letting the orbitals orthogonally mix with one another allows us to replace Φ° by ΦU^+ , where U is a real orthogonal matrix. Replacing Φ by this in eq. (1) results in

$$\begin{aligned} \Psi(1, 2) &= \text{Tr}[CU\Phi^+(1)\Phi(2)U^+] \\ &= \text{Tr}[U^+CU\Phi^+(1)\Phi(2)] \end{aligned} \quad (2)$$

where the second form is obtained by noting that the trace of the product is invariant under cyclic permutation of the matrices. This form shows the relation between the orbital mixing and CI degrees of freedom: orthogonal mixing of the orbitals is equivalent to an orthogonal transformation of C . The natural orbital MCSCF wave function is obtained by

requiring that the C matrix be diagonal. This is equivalent to using the natural orbital transformation of Lowdin and Shull for two-electron singlet wave functions.¹⁰

The form of C for the natural orbital MCSCF wave function together with those of a number of other SCF wave functions is shown in Figure 1. We have already noted the equivalence between forms a and b in the Figure 1. Relationships among some of the remaining forms can be obtained by subjecting the corresponding C matrices to orthogonal transformations. Note, for example that forms d, e, f, g, and h are all of rank two (i.e., the C 's for these forms all have two nonzero eigenvalues). All of these forms have the same number of nonredundant variational degrees of freedom except the open-shell Hartree-Fock form which has one less than the others because of the requirement that C be symmetric. Although forms e, f, g, and h of Figure 1 all have the same number of nonredundant degrees of freedom, they are not equivalent. E is equivalent to f and h is equivalent to g as is readily seen by subjecting e and h to orthogonal transformations which, respectively, diagonalize and tri-diagonalize them. However, the diagonalization of g gives the form f, but with the restriction that the eigenvalues have opposite signs. Thus SCF wave functions of the form f, in which the two diagonal elements have the same sign, cannot be represented by those of the forms g or h.

This last point is of no consequence when one is only interested in the ground-state

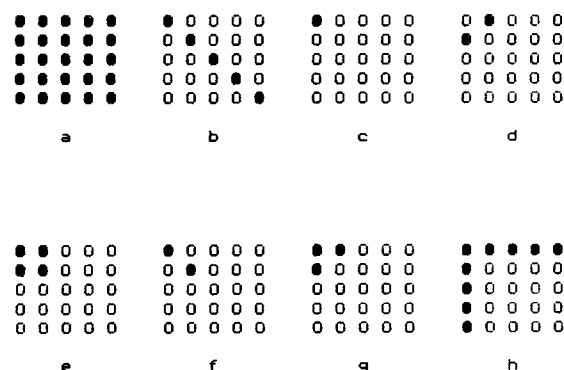


Figure 1. Structure of the symmetric C matrix for singlet SCF wave functions in the two-electron problem. (a) Full CI; (b) natural orbital MCSCF; (c) closed-shell Hartree-Fock; (d) open-shell Hartree-Fock; (e) two-electron two active orbital complete active space MCSCF; (f) TCSCF; (g) Hartree-Fock plus one single excitation; (h) Hartree-Fock plus all single excitations.

wave function. This is because the energy computed with the TCSCF wave function, form f, will always be lower when the coefficients are chosen to be of opposite sign due to the fact that the off diagonal element of the CI Hamiltonian matrix reduces in this case to an exchange integral, which must always be positive.

For excited states, on the other hand, the situation is less clear. The $N(N + 1)/2$ full CI states can be mapped onto the equivalent natural orbital MCSCF wave function. Which of the N MCSCF CI states contain which full CI states? This question must be answered in order to know where to look for any particular excited state in a natural orbital MCSCF calculation. In order to shed light on this question in the N orbital case, we have performed a model calculation of the singlet S states of Helium using Lowdin orthogonalized¹¹ primitive s -type Gaussians.¹² Table I shows the resulting distribution of the states. We note that in all cases the ground state and the first excited ($1s2s$) state are to be found on the lowest CI root in the natural orbital MCSCF wave function, whereas the second, third, and fourth excited states are always found on the second CI root. We also note that the highest full CI state is always on the highest MCSCF CI root and that in all of the cases reported it is the only full CI state to be found on this root. We do not know whether or not the results obtained in this very simple calculation will be generally obtained or not. However, in the case of the natural orbital MCSCF wave function, it seems that the "root flipped" excited states will be the rule.

In many situations it is the lowest excited state that is of interest. We recall that the Fitzgerald and Schaefer reformulation of the Davidson and Stenkamp excited singlet wave function resulted in a TCSCF wave function in which the coefficients had opposite signs. The equivalence between this form (form f of Fig. 1) and forms e, g, and h

suggests that when the lowest excited state is desired, an alternative to the Davidson and Stenkamp approach to computing it would be to optimize the second CI root of one of these alternative MCSCF forms in the many electron case. Whether or not this leads to an improvement over the Davidson and Stenkamp sequential orthogonalization algorithm² remains to be seen.

III. TWO ELECTRONS AND TWO ORBITALS

For the case of $N = 2$ it is convenient to define the three orthonormal two particle singlet basis states as

$$\psi_x^\circ = \frac{1}{\sqrt{2}}[\Phi_a(1)\Phi_b(2) + \Phi_b(1)\Phi_a(2)] \quad (3)$$

$$\psi_y^\circ = \frac{1}{\sqrt{2}}[\Phi_b(1)\Phi_b(2) - \Phi_a(1)\Phi_a(2)] \quad (4)$$

$$\psi_z^\circ = \frac{1}{\sqrt{2}}[\Phi_b(1)\Phi_b(2) + \Phi_a(1)\Phi_a(2)] \quad (5)$$

where Φ_a and Φ_b refer to the two orthonormal one particle basis functions. The normalized full CI wave function can then be written as

$$\Psi_{\text{FCI}}(\theta, \varphi) = \cos\theta\Psi_z^\circ + \sin\theta\Psi_w^\circ(\varphi) \quad (6)$$

where

$$\Psi_w^\circ(\varphi) = \cos\varphi\Psi_x^\circ + \sin\varphi\Psi_y^\circ \quad (7)$$

This wave function, as written in terms of polar coordinates, can thus be represented as a point on the normalization sphere with the angles $0^\circ < \theta < 180^\circ$ and $0^\circ < \varphi < 360^\circ$ referring to the polar and longitudinal angles. In allowing the basis functions to mix, we replace Φ_a and Φ_b by

$$\Phi_a(\alpha) = \cos\alpha\Phi_a^\circ + \sin\alpha\Phi_b^\circ \quad (8)$$

$$\Phi_b(\alpha) = -\sin\alpha\Phi_a^\circ + \cos\alpha\Phi_b^\circ \quad (9)$$

where α is the orbital mixing degree of freedom. The full CI wave function can then be written as a function of the three variational degrees of freedom as

$$\Psi_{\text{FCI}}(\theta, \varphi, \alpha) = \Psi_{\text{FCI}}(\theta, \varphi + 2\alpha) \quad (10)$$

after some trigonometric manipulations. The redundancy between the orbital mixing parameter and one of the configuration mixing parameters is thus clearly displayed. By regarding 2α as the longitudinal angle the various SCF wave functions can also be plotted as lines which are closed paths on the same nor-

Table I. Distribution of the $N(N + 1)/2$ energies of the full CI calculation among the N CI roots of the natural orbital MCSCF for the S states of Helium.

| | |
|---------|---|
| $N = 2$ | 1 1 2 |
| $N = 3$ | 1 1 2 2 2 3 |
| $N = 4$ | 1 1 2 2 2 3 3 3 3 4 |
| $N = 5$ | 1 1 2 2 2 3 3 3 3 4 4 4 4 4 5 |
| $N = 6$ | 1 1 2 2 2 3 2 2 3 4 4 4 4 4 5 5 5 5 5 6 |

malization sphere as the full CI wave function. Thus the closed-shell Hartree Fock wave function is obtained by setting $\theta = 45^\circ$ or 135° and the open-shell Hartree Fock wave function by setting $\theta = 90^\circ$. The natural orbital MCSCF wave function (which is the same as the TCSCF wave function when $N = 2$) has two branches, corresponding to the two roots of the MCSCF CI energies. The remainder of this article will focus on this natural orbital MCSCF wave function.

We recall from the previous section that due to the positive nature of the exchange integral, the two TCSCF coefficients must have opposite signs for the ground state. In the present representation, this implies that the ground-state TCSCF wave function must have θ restricted to lie between 45° and 135° . This must also be true for the entire lower MCSCF CI root curve. Using a similar argument for the highest (or second in the $N = 2$ case) excited state we conclude that this state must lie on the upper root MCSCF CI curve. Since for any value of 2α the two states must be orthogonal, we further conclude that the entire upper root curve is confined to the regions $0^\circ < \theta < 45^\circ$ and $135^\circ < \theta < 180^\circ$. We refer to these as the polar regions.

From the above information alone (i.e., from the fact that exchange integrals are positive) it is possible to deduce that the first excited state must lie on the lower root curve. Stanton has pointed out that in the $N = 2$ case, the full CI stationary states can be represented by three mutually perpendicular vectors originating at the center of the normalization sphere.¹³ If the vector corresponding to the doubly excited state is confined to the polar regions then any vector perpendicular to it must lie in the region $45^\circ < \theta < 135^\circ$. Since the full CI stationary states are also MCSCF CI stationary states (meaning that the energy is stationary with respect to both orbital rotation and configuration mixing degrees of freedom) the first excited state must lie on the lower root curve. Yeager et al. have shown that the Hessian for the first excited state must have exactly one negative eigenvalue.⁸ Thus, the first excited state must be a maximum on the lower root curve. This does not imply, however, that this state can be located by an algorithm which maximizes the energy with respect to the orbital rotation parameter at fixed values of the CI parameter

θ . If the coupling between the two variational parameters is strong (i.e., if the off diagonal element of the Hessian is large) then it is possible that both diagonal elements of the Hessian are positive when evaluated at the first excited state. In such cases the energy will be a minimum with respect to varying the orbital rotation parameter when the CI parameter is held fixed at its value for the first excited state.

It is an interesting and amusing exercise to deduce other properties of the full CI wave functions from geometric arguments. Suppose, for example, that the ground state is accurately described by the closed-shell Hartree Fock wave function. This corresponds to $\theta = 45^\circ$ (with $\theta = 135^\circ$ at the other end of the ground-state vector). Since the doubly excited state vector is perpendicular to this vector and is also confined to the polar region, it too must have $\theta = 45^\circ$. The first or singly excited state vector must be perpendicular to both of these and, therefore, must have $\theta = 90^\circ$ and orbitals that are obtained by a 45° rotation of the closed-shell Hartree Fock orbitals. Thus in the two orbital case we see that whenever the closed-shell Hartree Fock wave function is a good description of the ground state, then the open-shell Hartree Fock wave function will give an accurate representation of the first excited state. Although this corresponds to our intuition, it is due entirely to the positive nature of exchange integrals.

We conclude by asking what would the result be if we were to attempt to locate the first excited state using the TCSCF wave function and the HUM theorem.⁹ We note that in this $N = 2$ case root flipping will not be a problem because of the noncrossing rule. The energy expression for the upper root as a function of the rotated orbitals defined in eqs. (8) and (9) can be written as

$$E_+ = H_{zz}^\circ + (ab/ab) \left[\sqrt{1 + \frac{(E_b - E_a)^2}{(ab/ab)}} - 1 \right] \quad (11)$$

where

$$E_a = h_{aa} + \frac{1}{2}(aa/aa) \quad (12)$$

$$E_b = h_{bb} + \frac{1}{2}(bb/bb) \quad (13)$$

and

$$H_{zz} = \langle \Psi_z | H | \Psi_z \rangle \quad (14)$$

Here h_{aa} and h_{bb} refer to matrix elements of the one electron part of the Hamiltonian over the orbitals defined in eqs. (8) and (9) and where (ab/ab) is the exchange integral over these orbitals. Since it is readily verified that Ψ_z is independent of the orbital rotation parameter, we see that the minimum value of eq. (11) is H_{zz}^0 and occurs when $E_a = E_b$, corresponding to $\theta = 0^\circ$ or $\theta = 180^\circ$. Although this wave function gives an upper bound on the first excited state it is clearly an artifact of the MCSCF calculation and in the absence of symmetry does not correspond to any of the full CI states. When both the ground and first excited state are well represented by open-shell Hartree Fock wave functions, such as in some biradicals,¹⁴ then the highest excited state will be of this zwitterionic form.

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