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Self-Consistent-Field Wavefunctions Using a Symmetry-Restricted Annihilation of Single-Excitations Procedure

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Abstract

The form of Brillouin's theorem appropriate for Restricted Hartree-Fock calculations is used to determine rigorous Self-Consistent-Field wavefunctions for the $^3A_1$, ^3E, $^3A_2$, $^1A_2$ and ^1E states of the ... $2e^3 3e$ manifold of CH_3CO^+, a manifold for which traditional Fock operator techniques are unsuitable. The results of an approximate method previously reported are compared with these exact results are found to be in quite good agreement.

I. Introduction

In a previous work[1] it was shown that the low-lying electronic states of the acetyl cation (CH_3CO^+) could be expected to arise from the following orbital occupancies (o.o.) (assuming the geometry of the ion to be C_{3v}).

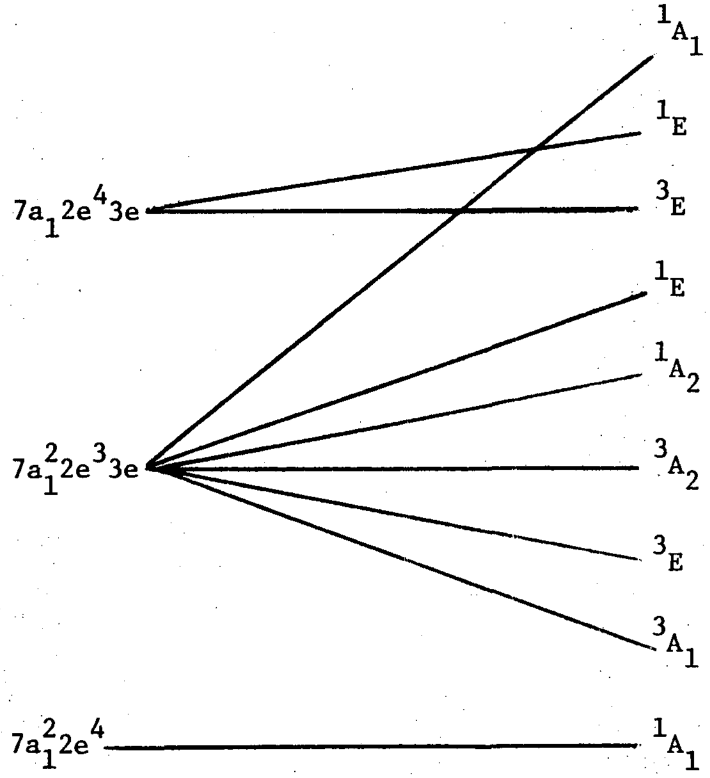
$$1a_1^2\ 2a_1^2\ 3a_1^2\ 4a_1^2\ 5a_1^2\ 6a_1^2\ 7a_1^2\ 1e^4\ 2e^4 \qquad \text{(I.1a)}$$

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 4a_1^2\ 5a_1^2\ 6a_1^2\ 7a_1^2\ 1e^4\ 2e^3\ 3e \qquad \text{(I.1b)}$$

and

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 4a_1^2\ 5a_1^2\ 6a_1^2\ 7a_1\ 1e^4\ 2e^4\ 3e \quad . \qquad \text{(I.1c)}$$

The ordering of the electronic states resulting from these o.o. is as depicted below[1]



While the wavefunctions used in reference 1 were of sufficient accuracy for the approximate description of the electronic spectrum of CH_3CO^+ required in that work, they suffer from a glaring inconsistency. (It will ultimately be shown--as conjectured in reference 1--that this inconsistency has only a small effect on the final results). Although it is possible to obtain rigorous[2] self-consistent-field (SCF) wavefunctions for the electronic states arising from o.o. 1a and 1c using standard Fock operator techniques[3,4] only the ^3E state arising from o.o. 1b was amenable to such a procedure. The remaining five states arising from this o.o. were treated within the fixed orbital (FIXORB) approximation.[1,5] The failure of Fock operator formalisms to treat these states has its roots in o.o. 1b. This o.o. is seen to contain two partially filled multiply degenerate shells which must be coupled together when the required symmetrized trial wavefunctions ψ_T^s are constructed. (See, for example, equation 2 of Appendix I). The energy functionals

$$E^s = \frac{\langle\psi_T^s|H|\psi_T^s\rangle}{\langle\psi_T^s|\psi_T^s\rangle} \tag{I.2}$$

corresponding to these symmetrized ψ_T^s can be expressed in the form

$$E^s = \varepsilon_s + \Sigma(ie_\alpha je_\beta||ke_\gamma \ell e_\delta) \tag{I.3}$$

Here ε_s has the form

$$\varepsilon_s = \Sigma h_i + \Sigma(2a_{ij}\, J_{ij} - b_{ij}\, K_{ij}) \qquad \text{(I.4)}$$

where the one electron (h_i), coulomb (J_{ij}) and exchange (K_{ij}) integrals are as defined by Roothaan.[3a] For

$$(ie_\alpha\, je_\beta || ke_\gamma\, \ell e_\delta) = \int d\vec{r}_1\, d\vec{r}_2\, \frac{ie_\alpha(1)\, je_\beta(1)\, ke_\gamma(2)\, \ell e_\delta(2)}{r_{12}} \qquad \text{(I.5)}$$

no pair (i,α) is repeated in a given integral so that in general this term cannot be expressed as a linear combination of coulomb and exchange integrals. For the problem at hand three distinct $(ie_\alpha\, je_\beta || ke_\gamma\, \ell e_\delta)$ arise

$$\text{(i)} \quad (2e_x 2e_y || 3e_x 3e_y) \qquad \text{(I.6a)}$$

$$\text{(ii)} \quad (2e_x 3e_x || 2e_y 3e_y) \qquad \text{(I.6b)}$$

$$\text{(iii)} \quad (2e_x 3e_y || 3e_x 2e_y) \qquad \text{(I.6c)}$$

Only for the degenerate (to zeroth order in nuclear displacements) ^3E state could a $\psi_T^s = \frac{(\psi_T^{\,{}^3E_x} + \psi_T^{\,{}^3E_y})}{2}$ be found which resulted in an energy functional of the form

$$E^s = \varepsilon_s \qquad \text{(I.7)}$$

Since all standard Fock operator procedures[3,4] presuppose an energy functional of the form of equation 7, they are incapable of determining SCF wavefunctions for these states.

A similar situation obtains when one considers the excited electronic states of CO arising from the o.o.

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^3 2\pi \qquad (I.8)$$

The corresponding 'additional integrals' (equation 5) involved in this problem are exactly those given in expression 6 if the identification $me_\alpha \rightarrow (m-1)\pi_\alpha$ is made. Thus at first glance it would appear that the states resulting from this o.o. should be equally untractable. However Rose and McKoy[6] were able to show that as a consequence of the continuous azimuthal symmetry of the $C_{\infty v}$ point group, the troublesome additional integrals could be expressed as linear combinations of coulomb and exchange integrals. Thus for linear systems the states arising from o.o. such as (8) have become tractable via a standard Fock operator procedure. Unfortunately this extension of Goddard's procedure by Rose and McKoy is applicable only to these linear systems.

In this work we present a method which is of sufficient generality to be able to treat the states arising from an o.o. such as 1b. This procedure, which does not involve in the explicit construction of a Fock operator, uses a generalized form Brillouin's theorem[7] and for this reason (see Section II) is referred as the Symmetry Restricted Annihilation of Single-Excitations (SRAS) procedure. This procedure is discussed in Section II. In Section III its application to the states in question is investigated, the results of the computations presented and compared with the fixed orbital procedure of reference 1. In Section IV some concluding remarks are presented together with a summary of the work presented herein.

II. Symmetry Restricted Annihilation of Single-Excitations

In this section the basic ideas behind the SRAS procedure are outlined. A more detailed discussion of these ideas can be found in reference 5.

In the SRAS method one seeks the best (see below) single configuration wavefunction[8] that can be constructed from a set of two electron functions $\{f_i\}$ constrained to satisfy the following conditions:

(i) the f_i are an orthonormal set, i.e., $\langle f_i | f_j \rangle = \delta_{ij}$ and

(ii) they can be partitioned into shells (see equation I.1), each shell carrying a complete irreducible representation of the group (G) of spatial symmetries of the Hamiltonian.

The wavefunctions possessing these properties are usually referred to as Restricted Hartree Fock (RHF) wavefunctions.[3]

The determination of the set of 'equivalence restricted' functions required to construct these wavefunctions is accomplished with the aid of the variational principal. If one assumes that the spectrum of H ($\sigma(H)$) is a point spectrum[9] [at least for all $\rho < \chi$, $\rho \epsilon \sigma(H)$, $\chi \epsilon R$] the variational principal[10] asserts that if the eigenvalues of H are ordered as follows:

$$E_1 < E_2 < E_3 \dots < \chi$$

then

$$E_i \leq \frac{\langle\psi_T|H|\psi_T\rangle}{\langle\psi_T|\psi_T\rangle} \qquad \text{(II.1a)}$$

for all (∀) ψ_T satisfying

$$\langle\psi_T|\psi_j\rangle = 0 \qquad \forall \;\; j \leq i \qquad \text{(II.1b)}$$

where

$$H\psi_j = E_j\psi_j \quad . \qquad \text{(II.1c)}$$

Therefore if the desired E_i is known to be the lowest eigenvalue of a given (space-spin) symmetry, equations 1a,b reduce to

$$E_i \leq \frac{\langle\psi_T^s|H|\psi_T^s\rangle}{\langle\psi_T|\psi_T\rangle} \equiv E^s(\psi_T^s) \qquad \text{(II.2)}$$

where the superscript s implies that ψ_T is appropriately symmetrized so that equation 1.b is automatically satisfied. Thus according to equation 2 the 'best' set $\{f_i\}$ will be that which minimizes the functional $E^s(\psi_T^s)$. In analogy with the theory of a function of several variables (in fact it is not difficult to make the analogy mathematically precise; see for example reference 5) a stationary point of $E^s(\psi_T^s)$ (which one hopes will be the desired minimum) occurs where

$$\delta\, E(\psi_T^s) = 0 \quad . \qquad \text{(II.3)}$$

If $E^s(\psi_T^s)$ is interpreted as a functional of the set $\{f_i\}$ rather than ψ_T^S, equation 3 becomes

$$\delta_i \; E^S(\{f_i\}) = 0 \qquad \forall i \tag{II.4}$$

where δ_i implies that the i^th^ function is varied while the remaining functions are held fixed. (In the theory of functions of several variables the equivalence of equations 3 and 4 is merely the statement that for $F(\underset{\sim}{\chi})\colon \; R^N \rightarrow R$, $dF = 0 \leftrightarrow \frac{\partial F}{\partial \chi_i} = 0 \; \forall i$).

The equations defining the optimum set $\{f_i\}$ can be deduced from equation 4 with care being taken to require the variations to satisfy the restrictions outlined at the beginning of this section. Recall that if ψ_T were a single Slater determinant (of spin orbitals) the i^th^ component of equation 4 would lead to[11]

$$<\psi_{SE^i_j}|H|\psi_T> = 0 \quad \forall j \tag{II.5}$$

where $\psi_{SE^i_j}$ is the Slater determinant obtained by replacing the i^th^ spin orbital in ψ_T by the j^th^ virtual or unoccupied spin orbital. However it is not hard to see that these 'primitive' first order variations (i.e., spin orbital replacements) do not satisfy the equivalence restrictions described above.[5] The required equivalence restricted variations can be obtained as a linear combination of these primitive variations. It can be shown[5,12] that the required equivalence restricted variations in the i^th^ orbital lead to a system of equations similar to (5) where the $\psi_{SE^i_j}$ are constructed as follows:

(i) Let $i\Gamma_\ell^\alpha$ be an element of the i^{th} shell which carries the irreducible representation Γ^α of G. Further let $j\Gamma_\ell^\alpha$ be an inequivalent occupied or virtual orbital in shell j of the same symmetry. (Two shells are said to be equivalent iff the energy functional - equation 2 - is invariant under a unitary transformation between the functions in these shells).

(ii) Then $\psi_{SE_j^i}$ is given (using a second quantization[13] type notation) by

$$\psi_{SE_j^i} = \sum_{\substack{\ell=1,m(\Gamma^\alpha) \\ \gamma_j \varepsilon\{\alpha,\beta\}}} [(j\ \Gamma_\ell^\alpha\ \gamma_j)^+\ (i\ \Gamma_\ell^\alpha\ \gamma_j)]\psi_T^s \qquad \text{(II.6a)}$$

$$= S(j\ \Gamma^\alpha,\ i\ \gamma^\alpha)\ \psi_T^s \qquad \text{(II.6b)}$$

where $m(\Gamma^\alpha)$ is the dimension of the irreducible representation Γ^α of G, $\{\alpha,\beta\}$ are the usual spinors, and $j\ \Gamma_\ell^\alpha$ is the spatial part of the one electron spin orbital $(j\ \Gamma_\ell^\alpha\ \gamma_j)$ and transforms according to the ℓ^{th} column of Γ^α. (The implementation of equation 6 is discussed in Section III and Appendix I).

The system of coupled equations given by equations 5 and 6 form the basis of the SRAS method and are solved using the iterative natural orbital (INO) procedure of Bender and Davidson.[14] In this procedure, an initial set of orbitals $\{f_i\}$ is used to construct the Hamiltonian matrix corresponding to the set of functions $\{\psi_T,\psi_{SE_j^i}\}$. The lowest eigenvalue of this matrix is found and the approximate natural orbitals (a.n.o.'s) for the corresponding eigenvector are determined. These a.n.o.'s are then taken as the new set of trial orbitals and the procedure is repeated. The procedure terminates, when (or if) equation 5 is satisfied $\forall\ \psi_{SE_j^i}$.

It is perhaps worth noting the following properties of the SRAS equations as given above:

(i) Since $S(j\Gamma^{\alpha}, i\Gamma^{\alpha})$ is, clearly, a totally symmetric operator $\psi_{SE_j^i}$ has the same transformation properties as ψ_T so that equation 5 cannot be satisfied identically.

(ii) If the equation $\langle\psi_{SE_j^i}|H|\psi_T^s\rangle = 0$, (i,j) fixed is interpreted as describing the optimal mixing of the i and j inequivalent shells of symmetry Γ^{α} it can be seen that the above procedure yields exactly 1 equation (see however Section III) to describe this mixing regardless of the dimensionality of Γ^{α}. This is required by equivalence restriction (ii) which renders the mixing of $i\Gamma^{\alpha}_{\ell}$ and $j\Gamma^{\alpha}_{\ell}$ independent of ℓ.

(iii) For equivalent shells $i\Gamma^{\alpha}$ and $j\Gamma^{\alpha}$, the antisymmetry of ψ_T^s implies that $S(j\Gamma^{\alpha}, i\Gamma^{\alpha})\psi_T = 0$. This is necessary since the energy functional is unaffected by a unitary transformation of the $j\Gamma^{\alpha}$ and $i\Gamma^{\alpha}$ shells.

(iv) Equations 5 and 6 can be interpreted as defining the appropriate generalization of Brillouin's theorem for the case of RHF wavefunctions. Once these equations have been solved for the optimal set $\{f_i\}$ and the appropriate ψ^s_{SCF} constructed, equation 5 asserts that this wavefunction (ψ^s_{SCF}) is non-interacting with a certain class of singly excited wavefunctions (i.e., those corresponding to equivalence restricted changes in ψ^s_{SCF}), and thus represents a type of Brillouin's theorem.

(v) The most important observation, as far as this work is concerned, is that the SRAS method does not involve the explicit construction of a Fock operator. Thus it can be applied to cases for which the usual Fock operator formalisms[3,4] break down.

We now proceed to the application of the SRAS method to the problem at hand. The SRAS equations required for this computation are discussed prior to the presentation of the results. It is hoped that this discussion will serve to clarify the admittedly sketchy development in this section.

III. The ... $2e^3 3e$ Manifold of CH_3CO^+

In this section the results of SRAS calculations on the ... $2e^3 3e$ manifold of CH_3CO^+ will be presented. The purpose of these calculations is threefold:

(i) to demonstrate the viability of the SRAS procedure for a system which cannot be treated by conventional SCF methods.[2,3]

(ii) to test the utility of the fixed orbital approximation previously reported[1]

(iii) to gain an increased understanding of the nature of the manifold splitting by partitioning the splitting energy into contributions due to (a) the recoupling of the Slater determinants (as measured by the fixed orbital approximation) and (b) due to the relaxation of the orbitals (as determined by the SRAS calculations).

To facilitate the achievement of this program it was necessary to carry out the SRAS calculations at the 'fixed orbital geometry', i.e., the C_{3v} 'equilibrium' geometry[1] of the ^3E state of CH_3CO^+ using the standard Dunning[14]-Huzinaga[15] double zeta quality basis of the previous work.[1] The 36 basis function resulting from this choice of basis set can be transformed to a set of symmetry adapted functions, partitioned according to their transformation properties:

20 a_1 functions
8 e_x functions
8 e_y functions

of which, according to orbital occupancy II.b, seven a_1, three e_x and three e_y functions are either fully or partially occupied.

For each of the six states within the manifold in question the SRAS procedure is equivalent to the determination of two unitary matrices.

(i) $\underset{\approx}{U}^{a_1}$ which transforms the initial set of 20 a_1-type functions onto the optimal set and

(ii) $\underset{\approx}{U}^{e}$ which accomplishes the same end for both the 8 e_x and 8 e_y functions.

The fact that only one $\underset{\approx}{U}^{e}$ is allowed for both the e_x and e_y orbitals is, of course, a consequence of the equivalence restriction of Section II.

Now $\underset{\approx}{U}^{a_1}$ is determined in general by 20$\cdot$(20-1)/2 parameters. However the energy functional (equation II.2) is invariant under a unitary transformation among the 13 virtual or unoccupied orbitals and also among the 7 equivalent doubly occupied a_1 orbitals. Therefore only

$$20\cdot(20-1)/2 - 13\cdot 12/2 - 7\cdot 6/2 = 91$$

parameters are required to specify $\underset{\approx}{U}^{a_1}$. Similarly $\underset{\approx}{U}^{e}$ is determined by

$$8\cdot 7/2 - 5\cdot 4/2 - 1\cdot 0/2 = 8$$

parameters so that a total of 109 parameters in all are required to determine the solution of the SCF problem.

To solve this problem within the SRAS formalism a total of 109 $\psi_{SE_i^j}$ (or $S(i\Gamma^{\alpha}, j\Gamma^{\alpha})$) will be required. In the discussion that follows it will be shown that for the ${}^3A_1$, ${}^3E$, ${}^3A_2$, ${}^1A_2$ and ${}^1E$ states the requisite 109 equations are uniquely determined by the prescription of Section II. However for the ${}^1A_1$ state an ambiguity will result as a consequence of the fact that this state is not the lowest state of its overall symmetry.

It is easily seen that there are exactly

$$\begin{array}{rl} 7\cdot 13 = 91 & (a_1 \text{ occupied-to-virtual pairs}) \\ +\ 3\cdot 5 = 15 & (e \text{ occupied-to-virtual pairs}) \\ \underline{+\ 3 \quad = \ 3} & (e \text{ occupied-to-occupied pairs}) \\ 109 & \end{array}$$

pairs of shells from which to construct S operators. For each of the occupied-to-virtual pairs it is possible to construct only one S operator which leads to a non-trivial wavefunction. The construction of this wavefunction for the 2e → me ($m \neq 3$) excitation with ψ_T^s taken as $\psi_T^{^3A_1}$ is illustrated in Appendix I. The (1e, 3e) and (1e, 2e) pairs also yield only one S operator corresponding to a non-trivial wavefunction since the 1e shell is fully occupied. The situation is not quite as simple for the (2e, 3e) pair. For this pair there are two possible S operators:

$$S_1 = S(3e,\ 2e) \qquad \text{(III.1a)}$$

and

$$S_2 = S(2e,\ 3e) \qquad \text{(III.1b)}$$

If ψ_T^s is taken to correspond to the $^3A_2$, ^3E, $^3A_1$, $^1A_2$, or ^1E states, it is not hard to see that

$$S_1\psi_T^s = \psi_{SE_{3e}^{2e}} \neq 0 \qquad \text{(III.2a)}$$

while

$$S_2\psi_T^s = \psi_{SE_{2e}^{3e}} \equiv 0 \qquad \text{(III.2b)}$$

so that for these five states the required 109 $\psi_{SE_j^i}$ are unambiguously determined. However for the ψ_T^s corresponding to the $^1A_1$ state one finds that

$$S_1\psi_T^{^1A_1} = \psi_{SE_{2e}^{3e}} \neq 0 \qquad \text{(III.2c)}$$

and

$$S_2\psi_T^{^1A_1} = \psi_{SE_{2e}^{3e}} \equiv \psi_{gs} \neq 0 \qquad \text{(III.2d)}$$

where ψ_{gs} denotes the unique wavefunction resulting from the ground state orbital occupancy (I.1a). According to Section II then one can require either

$$\langle\psi_{SE_{2e}^{3e}}|H|\psi_T^{^1A_1}\rangle = 0 \qquad \text{(III.3a)}$$

or

$$\langle\psi_{gs}|H|\psi_T^{^1A_1}\rangle = 0 \qquad \text{(III.3b)}$$

but not both without relaxing the equivalence constraints. If equation 3a (3b) is used in the SRAS procedure we shall say that the resulting wavefunction is variational from above (below).

Not only does the connection of the $^1A_1$ wavefunction from the $2e^3 3e$ manifold with the $^1A_1$ ground state wavefunction lead to an ambiguity in the SRAS equations but it also appears to be responsible for the failure of the INO procedure as described in Section II to converge to a solution of these equations (regardless of whether equation 3a or 3b is selected). At present alternative procedures are being considered which should circumvent this difficulty. However for the remainder of this work we will have to content ourselves with a discussion of the five states which are the lowest of their symmetry.

Thus we now turn to a discussion of the SRAS results for the five states in question, as given in Table I. Note that for both the SRAS and FIXORB results the $^3A_2$ and $^1A_2$ states are nearly degenerate. This approximate degeneracy is not accidental. In the limit $C_{nv} \rightarrow C_{\infty v}$ this degeneracy becomes exact (for the single configuration approximation used here).[5,6] Reference to the actual wavefunctions (not presented here) shows that the contributions to the 2e and 3e orbitals from atomic orbitals located on the H_3 cluster is negligible. Since the remaining portion of the molecule possesses $C_{\infty v}$ symmetry the reason for the approximate degeneracy becomes clear. The next point to be made concerns the corrections in the manifold splitting due to orbital relaxation, as defined by equation 4, and given in the final column of Table I.

$$\Delta E^{s}_{\substack{ORB\\REL}} = (E^{3}_{SRAS} - E^{^3E}_{SRAS}) - (E^{s}_{FIXORB} - E^{^3E}_{FIXORB})$$

$$\equiv E^{s}_{SRAS} - E^{s}_{FIXORB} \qquad \text{(III.4)}$$

The method of calculation, of course, requires these numbers to be negative since $E_{SRAS} \leq E_{FIXORB}$. Note, however, that in each case these corrections are small, being < 10% of the contribution due to the recoupling of the Slater determinants for the $^3A_1$, $^3A_2$ and $^1A_2$ states and ∿ 18% for the ^1E state. Thus we can conclude that for the type of manifold splitting considered here orbital relaxation is unimportant and the fixed orbital approximation should be adequate. Finally we observe the essentially exact agreement between the ^3E energy computed by the SRAS procedure and the OCBSE method. (The small differences actually observed are probably the result of an integral truncation scheme used to speed the OCBSE calculation). This result together with the more stringent tests presented in reference 5 demonstrate the correctness of SRAS procedure.

IV. Summary

We have presented here the form of Brillouin's theorem appropriate for Restricted Hartree Fock (RHF) calculations (equations II.5 and II.6). The correctness of this formulation is demonstrated by comparison with existing RHF procedures (see remarks at close of Section III). This formulation of the Hartree Fock approximation has the advantage of being applicable to moderately symmetric open shell systems which often cannot be handled by standard Fock operator procedures. Although not discussed in this work, this formulation is readily extended to a large class of Multi-Configuration-Self-Consistent-Field (MCSCF) problems. The details of this extension are given in reference 5.

The SRAS procedure was used to study the ... $2e^3 3e$ manifold of CH_3CO^+. Comparison of exact SRAS results with the approximate fixed orbital method allowed the manifold splitting energies to be partitioned into an orbital relaxation contribution and a recoupling contribution (Table I, columns 5 and 6). As the orbital relaxation contributions were seen to be small we conclude that the fixed orbital approximation is adequate to describe this type of manifold splitting.

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Appendix I

Here the use of the S operator in constructing the required $\psi_{SE_j^i}$ (as defined in Section II) is illustrated for the case

$$\psi_{SE_{me}^{2e}} = S(me,\ 2e)\ \psi_T^{^3A_1} \quad m > 3 \tag{AI.1}$$

In the following all fully occupied shells are omitted for clarity.

$$\psi_T^{^3A_1} = A(2e_x\alpha\ 2e_y{}^2\ 3e_x\alpha + 2e_x{}^2\ 2e_y\alpha\ 3e_y\alpha) \tag{AI.2}$$

and arises from the o.o.

$$2e^3 3e \quad . \tag{AI.3}$$

The shell excitation in question converts o.o.(3) into the following o.o.

$$(2e^2\ me)3e \tag{AI.4}$$

In accordance with the variational procedure outlined in Section II, (i.e., varying the orbitals one at a time) the $(2e^2,me)$ pair must be ^2E coupled since the parent shell (the $2e^3$ shell) was so coupled. However even with this restriction it is possible to construct 3 linearly independent $^3A_1$ wavefunctions $\{\chi_i\}_{i=1}^3$ corresponding to, for example, the following partial geneologies

$$^3A_2\ (2e^2) \otimes {}^2E\ (me) = {}^2E \tag{AI5.a}$$

$$^{1}A_{1}\ (2e^{2}) \otimes {}^{2}E\ (me) = {}^{2}E \qquad \text{(AI5.b)}$$

$$^{1}E\ (2e^{2}) \otimes {}^{2}E\ (me) = {}^{2}E \qquad \text{(AI5.c)}$$

The 3 particle functions resulting from these geneologies are then coupled to the 3e shell to yield the final $^{3}A_{1}$ wavefunction. The three functions produced in this manner are given in terms of Slater Determinants (S.D.) in Table II. Note that the starred S.D. differ from both of those in equation 2 by more than 1 spin orbital and thus none of the χ_1 can be constructed as a linear combination of primitive (spin orbital) excitations.

The correct $\psi_{SE^{2e}_{me}}$ which results from

$$S(me,2e)\psi_{T}^{^{3}A_{1}} =$$

$$\{(me_x\alpha)^{+}(2e_x\alpha) + (me_x\beta)^{+}(2e_x\beta) + (me_y\alpha)^{+}(2e_y\alpha) + (me_y\beta)^{+}(2e_y\alpha)\}$$

$$A\,(2e_x\alpha 2e_y\alpha 2e_y\beta 3e_x\beta + 2e_x\alpha 2e_x\beta 2e_y\alpha 3e_y\alpha) \qquad \text{(AI.6)}$$

is also given in Table II. Note that $\psi_{SE^{2e}_{me}}$ contains only S.D. which differ by exactly 1 spin orbital from one of the S.D. in equation 2 Finally we also observe that $\psi_{SE^{2e}_{me}}$ can be expressed as the following linear combination of the χ_i

$$\psi_{SE^{2e}_{me}} = -\frac{1}{\sqrt{2}}\chi_1 - \frac{1}{\sqrt{6}}\chi_2 + \frac{1}{\sqrt{3}}\chi_3 \qquad \text{(AI.7)}$$

Table I. The ...$2e^3 3e$ Manifold of CH_3CO

Electron Occupancy	State	Energy[c] (SRAS)	Energy[c] FIX ORB[b]	Splitting[d] (FIX ORB)	Splitting[d] correction due to Relaxation
$2e^3 3e$	$^3A_1$	-151.824115	-151.822613	-0.489	-0.041
	^3E[a]	-151.804624(0) -151.804624(5)	-151.804624	0	0
	$^3A_2$	-151.788011	-151.786636(2)	0.489	-0.037
	$^1A_2$	-151.788010	-151.786635(5)	0.489	-0.037
	^1E	-151.782491	-151.777439	0.739	-0.137

[a] Calculated using SRAS (upper) and OCBSE[4] (lower) methods.

[b] Fixed orbitals correspond to the SCF orbitals for the ^3E state.

[c] Energy in hartrees.

[d] Energy in electron volts.

Table II. $^3A_1$ Wavefunctions Resulting from the Orbital Occupancy ... $(2e^2me)3e$

Slater Determinant (open shell part only)	χ_1	χ_2	χ_3	$\psi_{SE_{3e}^{2e}}$
$2e_x\alpha 2e_y\beta me_y\alpha 3e_x\alpha$	$1/2\sqrt{3}$	0	$-1/\sqrt{8}$	$-1/\sqrt{6}$
$2e_x\alpha 2e_y\alpha me_y\beta 3e_x\alpha$	$-1/\sqrt{3}$	0	0	$1/\sqrt{6}$
*$2e_x\alpha 2e_y\beta me_x\beta 3e_y\alpha$	$-1/2\sqrt{3}$	0	$-1/\sqrt{8}$	0
$2e_x\alpha 2e_y\alpha me_x\beta 3e_y\alpha$	$1/\sqrt{3}$	0	0	$-1/\sqrt{6}$
*$2e_x\beta 2e_y\alpha me_y\alpha 2e_x\alpha$	$1/2\sqrt{3}$	0	$1/\sqrt{8}$	0
$2e_x\beta 2e_y\alpha me_x\alpha 3e_y\alpha$	$-1/2\sqrt{3}$	0	$1/\sqrt{8}$	$1/\sqrt{6}$
*$2e_x\alpha 2e_x\beta me_x\alpha 3e_x\alpha$	0	$-1/2$	$-1/\sqrt{8}$	0
$2e_x\alpha 2e_x\beta me_y\alpha 3e_y\alpha$	0	$-1/2$	$1/\sqrt{8}$	$1/\sqrt{6}$
$2e_y\alpha 2e_y\beta me_x\alpha 3e_x\alpha$	0	$-1/2$	$1/\sqrt{8}$	$1/\sqrt{6}$
*$2e_y\alpha 2e_y\beta me_y\alpha 3e_y\alpha$	0	$-1/2$	$-1/\sqrt{8}$	0

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