

The Configuration Interaction Method, and the Triplet-Singlet Splitting in CH₂

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A configuration-interaction (CI) method in which the interaction matrix is never constructed has been investigated, following the original suggestion of Roos. Two methods have been used (1) for singlet states, which can be represented by a one determinant configuration of doubly occupied orbitals, CI with all singly and doubly excited configurations, (2) for states for which the restricted self-consistent field approximation is a single determinant, CI with all singly and doubly excited determinants. In case (2), the wavefunction may not be exactly an eigenfunction of S^2 .

The methods were investigated using a double-zeta plus polarisation basis for CH₂. Both methods must give the same result for the lowest singlet ground state. Keeping the bond length fixed at 2.10 and 2.04 bohr respectively the bond angle for the singlet and triplet were found to be 100.8° and 132.0°, with energies -39.0312 a.u. and -39.0563 a.u. respectively. These are the lowest variational energies obtained for these systems; the singlet-triplet splitting is thus predicted to be 15.4 kcal/mol.

Key words: CH₂, triplet-singlet splitting in \sim – CI method, special large scale

1. Introduction

The purpose of this work is firstly to examine the original work of Roos [1], and demonstrate that a large scale configuration-interaction (CI) calculation is as easy to perform as the self-consistent field (SCF) method. Secondly it is to apply the methods to CH₂, for which there remains uncertainty in the singlet-triplet energy splitting.

2. Large-Scale Configuration-Interaction Calculations: Using Configurations Which Are Eigenfunctions of S^2 and S_z

It is now apparent that to obtain 50% of the correlation energy (defined as the restricted Hartree-Fock energy minus the exact eigenvalue of Schrödinger's non-relativistic equation), at the equilibrium geometry of a molecule, large scale CI calculations must be undertaken. To perform such calculations, it is necessary to have a method to find the lowest eigenvalue of a large matrix. One of the methods most commonly used is due to Nesbet [2]. The Nesbet method can be summarised as follows:

Let

$$\Psi = \sum_{i=0}^N c_i \Phi_i, \quad (1)$$

where $\Phi_0, \Phi_1 \dots \Phi_N$ denote the configurations, with Φ_0 representing usually the dominant configuration. Let $\mathbf{c} = (c_0, c_1, c_2 \dots c_N)$ be an approximate eigenvector, at any particular stage of the calculation, corresponding to lowest energy. E and S are defined by

$$E = \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad S = \langle \Psi | \Psi \rangle \quad (2)$$

To improve a particular coefficient c_I to $c_I + \Delta c_I$, the formula deducible from the secular equations is

$$\Delta c_I = \sigma_I / (E - H_{II}) \quad (3)$$

where

$$\sigma_I = \sum_{r=0}^N H_{Ir} c_r - E c_I \quad (4)$$

and

$$H_{rs} = \langle \Phi_r | \mathcal{H} | \Phi_s \rangle \quad (5)$$

The corresponding lowering in the variational energy upper bound is

$$\Delta E = \sigma_I \Delta c_I / (S + \Delta S) \quad (6)$$

where

$$\Delta S = 2c_I \Delta c_I + (\Delta c_I)^2 \quad (7)$$

The important quantity required is therefore σ_I , which is determined directly from the I th row of the secular matrix. One approach is therefore to store the secular matrix on magnetic tapes; read the matrix one row at a time, updating the corresponding coefficient c_I , the normalisation integral S and the energy E . The method is quickly convergent if there is one dominant determinant.

Roos [1b] made the point that to calculate and store the symbolic matrix elements for a $10,000 \times 10,000$ matrix on magnetic tapes would need ten magnetic tapes even if only 10% of the elements were non-zero. He therefore proposed an alternative method, using perturbation theory. The key step in the procedure is the simultaneous updating of all the elements of the eigenvector using the relation

$$(E_I - E_0)c_I^{(n)} = \sum_{k=1}^{n-2} E^{(n-k)} c_I^{(k)} - \sigma_I^{(n-1)}, \quad (8)$$

where $E_I = \langle \Phi_I | \mathcal{F} | \Phi_I \rangle$, and \mathcal{F} is an appropriate Fock operator. $E^{(\lambda)}$ is the λ th perturbation correction to the correlation energy, with the corresponding eigenvector correction $c^{(\lambda)}$. $\sigma_I^{(n-1)}$ is given by Eq. (4), calculated using the $(n-1)$ th order eigenvector correction.

A difficulty with this method appears to be that once perturbation theory is used the method may not be convergent. Roos does say that convergence can be obtained using variation-perturbation theory, but 10–15 order perturbation theory is necessary to obtain convergence to six significant figures in the correlation energy.

Another difficulty with this approach appears to be its extension to states other than singlet states – in the following section it will be argued why this may be practically impossible.

Roos' basic idea using perturbation theory for performing large scale CI calculations, when it is not possible to hold all the two-electron molecular integrals in core, appears excellent.

3. The Construction of σ for Configurations Which Are Eigenfunctions of S^2 and S_z

In the simplest case, the dominant configuration is a single determinant of doubly occupied molecular orbitals. This is a case discussed by Roos [1a]. He denoted double replacements by Ψ_{ii}^{aa} , Ψ_{ij}^{aa} , Ψ_{ii}^{ab} , Ψ_{ij}^{ab} , where the latter, for example, denotes the replacement of the occupied orbitals i and j by some excited orbitals a and b . Because there are two independent spin eigenfunctions Ψ_{ij}^{ab} , there are therefore five different types of double replacements. The formulae for σ can be expressed in terms of two-electron and one-electron molecular integrals, for example

$$\sigma_{ij \rightarrow ab} = \sum_{k,l} A_{\mu\nu}(ik|jl)c_{kl \rightarrow ab} + \dots \quad (9)$$

$\sigma_{ij \rightarrow ab}$ is the σ corresponding to Ψ_{ij}^{ab} , $c_{kl \rightarrow ab}$ is the coefficient of Ψ_{kl}^{ab} , and $(ik|jl)$ is a two electron molecular integral. μ, ν take values between one and five, and denote the types of double replacements Ψ_{ij}^{ab} , Ψ_{kl}^{ab} respectively. A is a 5×5 matrix of coupling coefficients. Most of the formulae are given by Roos (Ref. [1a], Eqs. (22–24)). Unfortunately, the matrix A and similar 5×5 matrices A' , B , B' , C , C' are given incorrectly by Roos in his paper, but he will be publishing corrected versions later. It is sufficient to note here that these matrices are not symmetric. We found some difficulty in deriving the correct formulae.

Hence $\sigma_{ij \rightarrow ab}$ can be constructed from the list of two and one-electron molecular integrals. In our calculations it was possible to hold them all in core, and thus the Nesbet eigenvalue method can be followed exactly. We found the calculations to be quickly convergent, the correlation energy converging to 7 places of decimals in three full iterations.

We further found that no loss of accuracy was obtained (to this accuracy), if the two electron molecular integrals and the eigenvector were stored in single precision, the remainder of the program being in double precision. The reason for this is that the Nesbet method for the lowest eigenvalue does not accumulate errors. On our IBM 360/175, this meant that if 300 Kbytes were available at 4 bytes per two-electron molecular integral, approximately $N^4/8$ with $N=26$ (molecular orbitals) could be stored. It will be seen that this is ideal for the AH₂ molecules in which we were interested.

An attempt was then made to extend the method to a triplet state with a dominant configuration of the form $\mathcal{A}(\phi_1^2 \phi_2^2 \dots \phi_n^2 \phi_{n+1}^2 \phi_{n+2}^2)$. The number of different types of singly and doubly excited configurations increased significantly as compared to the singlet state. These are

$$\Psi_{ii}^{aa}, \Psi_{ij}^{aa}, \Psi_{ii}^{ab}, \Psi_{n+1, n+2}^{ab}, \Psi_{i, n+1}^{ab}, \Psi_{i, n+2}^{ab}, \Psi_{ij}^{n+1, a}, \Psi_{ij}^{n+2, a}, \Psi_{ij}^{n+1, n+2}, \Psi_i^a, \Psi_{n+1}^a, \Psi_{n+2}^a, \Psi_i^{n+1}, \Psi_i^{n+2} \quad (10)$$

In (10), $1 \leq i < j \leq n$ and a, b denote excited orbitals. It became apparent that it was extraordinarily difficult to derive the formula for σ because of these many different types of configurations, besides the increase in the number of spin eigenfunctions of each type. It was decided to abandon this particular procedure for triplet states.

4. The Alternative Approach Using Determinants instead of Configurations

In this approach, it is assumed that there is a dominant configuration in the form of a single determinant

$$\mathcal{A}(\varphi_1^2 \varphi_2^2 \cdots \varphi_n^2 \varphi_{n+1}^\alpha \varphi_{n+2}^\alpha \cdots \varphi_{n+m}^\alpha) \quad (11)$$

This is of course an eigenfunction of S^2 and S_z , and can be obtained from a Restricted SCF calculation.

The single and double replacement determinants formed from (11) are easily written down

$$\Psi_i^a, \bar{\Psi}_i^a, \Psi_{ij}^{ab}, \bar{\Psi}_{ij}^{ab}, \Psi_{ij}^{\bar{a}\bar{b}}, \bar{\Psi}_{ij}^{\bar{a}\bar{b}} \quad (12)$$

In this notation a bar denotes a space orbital associated with β spin and no bar denotes association with α spin. Further the notation implies

$$1 \leq \bar{i} \leq n; \quad 1 \leq i \leq n+m; \quad n+1 \leq \bar{a}; \quad n+m+1 \leq a \quad (13)$$

and in Ψ_{ij}^{ab} , $i > j$ and $a > b$, and similarly for $\bar{\Psi}_{ij}^{\bar{a}\bar{b}}$. The set of space orbitals are assumed to be orthonormal. Such a set can be obtained if the Fock operator

$$F = K + V + \sum_{j=1}^n (2J_j - K_j) + \sum_{j=n+1}^{n+m} J_j \quad (14)$$

is used in the Restricted SCF program (this facility is available in the ATMOL series of programs). The set of space orbitals are eigenfunctions of the matrix representation of this Fock operator.

The formula for σ corresponding to the determinants in (12) is easily written down. It takes a similar form to Eq. (9), but the coefficients $A_{\mu\nu}$ no longer have a complicated form, and are simply ± 1 . σ is a linear combination of two (or one) electron integrals multiplied by either $c_{i \rightarrow a}$, $c_{\bar{i} \rightarrow \bar{a}}$, $c_{ij \rightarrow ab}$, $c_{\bar{i}\bar{j} \rightarrow \bar{a}\bar{b}}$, $c_{\bar{i}\bar{j} \rightarrow a\bar{b}}$. We understand that similar formulae will be published by Roos in a forthcoming review, and so they will not be given here.

The eigenfunctions obtained in this method will not necessarily be eigenfunctions of S^2 but when the dominant determinant is a singlet, the eigenfunctions will be eigenfunctions of S^2 and S_z . Hence the energies obtained by this and the previous method must be identical in this case. But, when the dominant determinant is a triplet, for example, the eigenfunction is not an eigenfunction of S^2 . This is simply demonstrated by a CI calculation using the determinants

$$\begin{aligned} \Psi_0 &= \mathcal{A}(1^\alpha 1^\beta 2^\alpha 3^\alpha), \\ \Psi_1 &= \mathcal{A}(1^\alpha 4^\beta 2^\alpha 3^\alpha), \\ \Psi_2 &= \mathcal{A}(4^\alpha 1^\beta 2^\alpha 3^\alpha). \end{aligned} \quad (15)$$

Ψ_1 and Ψ_2 are single replacement determinants of Ψ_0 . Although Ψ_0 and $\Psi_1 + \Psi_2$ are pure triplet, $\Psi_1 - \Psi_2$ is a mixture of triplet and quintet. The eigenfunction of the CI calculation will therefore not be pure triplet. To overcome this difficulty some double replacement determinants must be included. The same problem occurs if all single and double replacement determinants are included – to obtain pure triplet eigenfunctions some triple replacements must be included.

This type of CI calculation may be called “Unrestricted” configuration interaction. It will give an upper bound to the lowest eigenvalue, and therefore if the triplet is the ground state at a particular geometry, the calculations will give an upper bound to the energy of this state. The problem can be put another way by noting that if a CI calculation on a triplet state using spin eigenfunctions is performed, then necessarily some three replacement determinants are implicitly included in the calculation. In calculations in which the determinant (11) has coefficient near unity (for a normalised wavefunction), the three replacement effects are extremely small. This is the case in the present calculations, and so the difference between our results and pure triplet results should be negligible.

Roos has also discussed this alternative approach using determinants [1c], but has concentrated on the case for which the dominant determinant was obtained from an unrestricted Hartree-Fock calculation. We think that the method here is more advantageous (a) for the above reason and (b) because there is only one set of spatial orbitals with which to deal; this has significant computational advantages.

5. Calculations on CH₂

The CI method outlined in section 4 is suitable for calculating upper bounds to the energy of the lowest singlet and triplet states of CH₂.

All calculations used either 14 atomic Slater-type basis functions or 25 such basis functions. The 14 function basis set was double-zeta using Carbon *1s* functions (exponents 5.23, 7.97), *C2s* (1.17, 1.82), *C2p* (1.26, 2.73) and *H1s* (1.4, 1.9). The 25 function basis set had in addition the polarisation functions *C3d* (exponent 1.5) and *H2p* (2.2). All atomic integrals were calculated using the ATMOL modification of Stevens' [5] package for Slater-type integrals to an accuracy of 1×10^{-7} .

Calculations on the singlet state were performed using the ATMOL restricted SCF program. The integrals were transformed to molecular basis using the 4-index transformation program of the ATMOL package. Molecular two-electron integrals less than 1×10^{-7} were assumed to be zero. They were then truncated to single precision for the CI calculations. Likewise SCF calculations on the triplet state were performed (using the same atomic basis set and exponents) using the ATMOL restricted SCF open shell program, with the Fock operator defined by (14).

It is thought that the atomic basis set is near optimal for both states, although this has not been checked in detail. In the singlet calculations the bond length was held fixed at 2.10 bohr, and in the triplet calculations the bond length was held fixed at 2.04 bohr. These are very close to the optimum values determined

by Bender *et al.* in their CI calculations, of 2.126 and 2.056 bohr respectively. It is thought that any adjustment in bond lengths will not affect the energies by more than 0.5 kcal/mole. The experimental values for the bond lengths are 2.10 bohr and 2.035 bohr respectively.

The 14 basis function calculations gave energies as follows:

	Angle	SCF (hartrees)	CI (hartrees)
Singlet	107°	-38.85753	-38.95198
Triplet	136°	-38.91214	-38.99463

At these non-optimised geometries the triplet-singlet splitting is predicted to be 26.8 kcal/mole.

It has been well established by Bender *et al.* [3] that the inclusion of polarisation functions is important for both the SCF and CI calculations. More searching calculations with the 25 function basis set were performed. The results are presented in Table 1.

For the 1A_1 state, the SCF minimum appears to be at 102.3° and the CI minimum at 100.8°. The basis set used by Bender *et al.* was contracted-gaussian in character, and appears to roughly correspond to double-zeta plus polarisation. In their CI calculations they considered at most double excitations from a two configuration representation of the ground state, but did not include excitations from the inner shell or more than one excitation from the valence shell (which was defined to include the $1b_1$, $4a_1$ and $2b_2$ orbitals). They used 469 configurations to predict a bond angle of 101.0° and an energy of -38.9898 hartrees.

For the 3B_1 state, the SCF minimum appears to be at 128.4° and the CI minimum at 132.0°. Bender *et al.* give a CI energy of -39.0129 with 617 configurations for a bond angle of 134°. It is to be noted that their SCF energy minimum is -38.9327 hartrees, compared to our minimum of approximately -38.9300 hartrees.

Our calculated value for the singlet-triplet splitting is 15.4 kcal/mole, to be compared with Bender *et al.*'s prediction of 14.1 kcal/mole. Thus although the CI methods are slightly different and their basis set is slightly more flexible than ours, the calculations present results which are essentially in agreement. It does not appear necessary to add to the remarks of these authors on both the theoretical

Table 1. Energies in Hartrees for singlet and triplet state of CH₂

Angle (degree)	SCF	Correlation energy	CI	Methylene state (bond length)
105°	-38.88819	—	—	
103°	-38.88838	-0.14334	-39.03172	1A_1 (2.98 bohr)
101°	-38.88835	-0.14350	-39.03185	
99°	-38.88809	-0.14368	-39.03177	
130°	-38.92995	-0.12634	-39.05630	
132°	-38.92978	-0.12658	-39.05636	3B_1 (2.038 bohr)
134°	-38.92947	-0.12683	-39.05630	
136°	-38.92904	-0.12711	-39.05614	

and experimental uncertainties in the value for this splitting, other than to state that they suggest a further reduction in the splitting of approximately 3 kcal/mole could be obtained by a more accurate calculation. The interested reader is therefore referred to this reference and references therein.

6. Conclusion

This paper has examined a particular large scale CI method introduced by Roos. It appears to be a clearly successful method for singlet states for which the dominant configuration is a single determinant, but it seems very difficult to extend it to states of other symmetry. As an alternative we have implemented the method which uses determinants instead of spin eigenfunctions.

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