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Open-Shell Systems investigated with Monte Carlo configuration interaction

J. P. Coe*, M. J. Paterson†

July 26, 2016

Abstract

We investigate the open-shell systems of the methyl radical, the allyl radical and molecular oxygen using Monte Carlo configuration interaction. We look at whether modifying Monte Carlo configuration interaction to use the increased flexibility of unrestricted Hartree-Fock orbitals offers any benefits in the description of these systems by the resulting compact wavefunctions. The expectation of the total spin squared when using Slater determinants is calculated to investigate if pure spin states can be evolved by Monte Carlo configuration interaction and how this might be accelerated. We consider the multireference character of these open-shell systems. To this end we demonstrate how a previously introduced way [J. P. Coe and M. J. Paterson, *J. Chem. Theory Comput.* **11**, 4189 (2015)] of viewing a multireference indicator of P.-O. Löwdin [P.-O. Löwdin, *Phys. Rev.* **97**, 1474 (1955)] in terms of the spatial entanglement can be generalized to open-shell systems. In addition we look at whether a measure of multireference character is affected by the use of configuration state functions compared with Slater determinants.

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INTRODUCTION

Molecules can be considered open-shell if they have at least one singly occupied orbital in their qualitatively correct wavefunction. This may present problems for approaches that otherwise work well for closed-shell systems as the wavefunction may not be amenable to being described by a single determinant. Another challenge is spin contamination in that the exact wavefunction must be a pure spin state, e.g. a doublet. However this may not be the case for an approximate wavefunction which may be spin contaminated to such a degree that it could then be argued to not qualitatively describe the system. It has been found that the convergence of Møller-Plesset perturbation theory is slower when using spin-contaminated unrestricted Hartree-Fock wavefunctions.^{3,4} Approaches that use the powerful coupled-cluster formalism for open-shell systems have previously been developed.^{5,6} Unrestricted complete active space self-consistent field (UCASSCF) wavefunctions have also been defined and their spin contamination investigated.⁷

Challenging systems for electronic structure methods may have substantial contributions from what is termed static correlation. This is associated with the occurrence of a few important configurations in the full configuration interaction (FCI) wavefunction and would be expected to require multireference methods to be used to accurately model the system. Dynamic correlation, by contrast, is the remaining correlation when there is a clear small set of dominant configurations and is associated with many small coefficients in the FCI wavefunction. One aspect of this work is that we would like to know whether open-shell systems are more likely to have a wavefunction that would be deemed significantly multireference and so be inherently more difficult to model using approaches based around relatively small corrections to a single determinant.

Towards this aim we bring Monte Carlo configuration interaction (MCCI)^{8,9} to bear on such problems. By stochastically building up a configuration interaction wavefunction then MCCI, in principle, can account for sufficient static and dynamic correlation depending on the threshold used for the retention of configurations (c_{\min}). The calculation does not depend on a restriction of the configuration space using chemical intuition. MCCI has previously been applied to single point energies,¹⁰ dissociation energies,^{11,12} and electronic

excitations.^{13,14} Ground-state potential curves were investigated in Ref. 15 using MCCI. In many circumstances it was found that for small systems much of the accuracy of the FCI result could be captured using a very small fraction of the FCI space. MCCI has been extended to multipole moments,¹⁶ higher-order dipole properties up to the second hyperpolarizability,¹⁷ X-ray emissions¹⁸ and positronic molecules¹⁹ where, again, results could get close to that of FCI for small molecules, but used much fewer configurations. MCCI can use configuration state functions (CSFs) to guarantee that the wavefunction is always a pure spin state. However we mainly use Slater determinants in this work as we are partly interested in if we can stochastically find the pure spin ground-state using MCCI. In addition, the manipulation of Slater determinants is much more straightforward and multiple spin states can be accessed for a given number of α and β electrons.

Through separately optimizing the α and β orbitals that comprise a single determinant wavefunction, unrestricted Hartree-Fock (UHF) offers greater flexibility than restricting the orbitals to be the same for both spins. Therefore the energy can be lower than that using the restricted Hartree-Fock wavefunction, however this can come at the expense of the wavefunction being excessively spin contaminated. For the same underlying basis set the full configuration interaction energy, when no orbitals are frozen, will be the same whether one uses restricted or unrestricted Hartree-Fock molecular orbitals. For the reduced wavefunctions of Monte Carlo configuration interaction this is not necessarily the case. We may then ask whether the increased flexibility in the molecular orbitals can offer any benefits in accuracy or compactness of the wavefunction.

We investigate calculating the total spin squared when using Slater determinants with MCCI for both restricted and unrestricted Hartree-Fock wavefunctions. We ascertain to what extent, and how rapidly, can MCCI reduce the spin contamination due to the use of Slater determinants and whether multiple spin states can be found from a single calculation when using Slater determinants. This approach may then offer the possibility of finding, for example, a singlet and triplet state in tandem despite beginning with a spin contaminated reference.

To look into multireference character in this work we first need a measure appropriate for open-shell systems. We demonstrate how the multireference indicator of P.-O. Löwdin²

when used for a spin-averaged density matrix can be generalized to open-shell systems. We extend a previous result¹ to show that for open-shell systems it is also equivalent to the scaled linear entropy relative to a single determinant and so can be viewed as a measure of electron correlation. We also consider how the values of another multireference indicator (MR) may be fairly compared between wavefunctions using Slater determinants and those using configuration state functions particularly in the case of open-shell systems.

Three open-shell systems are considered for these purposes. We first look at the CH₃ doublet at an equilibrium and then stretched geometry where we compare results with full configuration interaction. We next consider the allyl radical where results for the barrier to rotation between the planar and perpendicular forms are compared with full configuration interaction and experiment. We finally consider molecular oxygen and, in particular, the triplet-singlet gap of this system where we look at a way to accelerate convergence to pure spin states.

METHODOLOGY

MCCI

The MCCI procedure usually begins with a configuration formed from the occupied restricted Hartree-Fock molecular orbitals and is briefly summarized below.

- The current configuration space is augmented using new configurations formed by random symmetry-preserving single and double substitutions in the current space.
- The Hamiltonian matrix is created using the Slater-Condon rules for Slater determinants or the Slater-Condon-Harris rules for configuration state functions, the overlap matrix is calculated in the latter case and then the eigenvalues and eigenvectors of interest are computed.
- Any new configurations with absolute coefficient less than c_{\min} in the resulting wavefunction are removed.
- Every ten iterations all configurations are considered as candidates for deletion.

- The procedure is repeated for 60 iterations and then until the energy has converged as detailed in Ref. 13.

We compute the molecular orbitals and required integrals $\langle \phi_i | \hat{H} | \phi_j \rangle$ from a Hartree-Fock calculation of the desired spin and symmetry using MOLPRO.²⁰ Where this spin and symmetry is not amenable to a Hartree-Fock calculation in MOLPRO²⁰ we mention in the results the molecular orbitals used and choose a reference state using these to set the spin and symmetry for the MCCI calculation.

Unrestricted Hartree-Fock

We adapt the MCCI program to use unrestricted Hartree-Fock (UHF) molecular orbitals. Allowing the α and β spatial orbitals to differ may offer improvements in calculations that do not use the full configuration space such as MCCI. The normalized UHF orbitals are generated with MOLPRO²⁰. The resulting α spatial orbitals are orthogonal within themselves and so are the β spatial orbitals. However an α spatial orbital is not necessarily orthogonal to a β spatial orbital. We modify the RHF Slater-Condon rules in MCCI to use the appropriate MO integrals depending on whether the MOs are α or β :

1. For the one-electron terms the non-zero integrals have either both orbitals with α spin or both with β spin therefore this determines the correct integral to load.
2. The two-electron terms are slightly more complicated in that in addition to checking if all spins are β or all spins are α , there is a third situation where the two spins are α and β from the first determinant and from the second determinant. The appropriate molecular orbital integrals are then used in each case.

Spin states

A Hamiltonian that does not contain spin terms will commute with spin operators and so an exact wavefunction will also be an eigenfunction of \hat{S}^2 and a commuting spin operator usually taken to be \hat{S}_z .

In atomic units we have

$$\hat{S}_z \Psi = M_S \Psi \quad (1)$$

where $M_S = (N_\alpha - N_\beta) / 2$. Here N_α is the number of electrons of spin α . The total squared magnitude of the spin operator gives

$$\hat{S}^2 \Psi = S(S + 1) \Psi. \quad (2)$$

Here S is the spin quantum number. A configuration interaction wavefunction using Slater determinants (SDs) will be an eigenfunction of \hat{S}_z but not necessarily \hat{S}^2 without reaching the FCI limit. This may mean that the wavefunction does not have the desired spin quantum number and may not be a pure spin state. Configuration state functions (CSFs) are constructed from linear combinations of Slater determinants so that they are eigenfunctions of both \hat{S}_z and \hat{S}^2 . Through the use of CSFs in MCCI the calculation of a state of required spin quantum number can be achieved for $M_S = S$. Furthermore, fewer CSFs are required than SDs,²¹ however the construction of matrix elements is more involved,²² the CSFs are not orthonormal and steps must be taken to ensure they are linearly independent, e.g., MCCI uses a genealogical scheme.⁸ Slater determinants have the advantage of being less complicated and that the lowest spin state can, in principle, be found for a given M_S or multiple spin states can be calculated from one set of MCCI configurations.

We first briefly discuss the calculation of the total squared magnitude of the spin $\langle \Psi | \hat{S}^2 | \Psi \rangle$ for a configuration interaction wavefunction when using Slater determinants and orthonormal molecular orbitals. For a single electron, the operator for the square of the total spin $\hat{s}^2 = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2$ may be written as

$$\hat{s}^2 = \hat{s}_- \hat{s}_+ + \hat{s}_z + \hat{s}_z^2 \quad (3)$$

where $\hat{s}_\pm = \hat{s}_x \pm i\hat{s}_y$ and $[\hat{s}_+, \hat{s}_-] = 2\hat{s}_z$.

For N electrons we sum over the one-particle operators, e.g. , $\hat{S}_- = \sum_{i=1}^N \hat{s}_-(i)$. Here $\hat{s}_-(i)$ acts on particle i to flip an α spin to a β spin or annihilate a β spin. While $\hat{s}_+(i)$ flips β spins and annihilates α spins. We can write

$$\hat{S}^2 = \hat{S}_Z + \hat{S}_Z^2 + \sum_i \hat{s}_-(i) \hat{s}_+(i) + \sum_{i \neq j} \hat{s}_-(i) \hat{s}_+(j). \quad (4)$$

The second summation swaps an α and a β spin while the other terms either annihilate or leave a determinant unchanged. We see that a matrix element will only be non-zero if determinants K and L have zero differences or have two differences that can be removed by an exchange of an α and β spin.

For K and L with no differences, i.e., $K = e_p L$ where e_p is the sign from initially placing the determinants in maximum coincidence, we find that the first summation annihilates α spins but leaves β spins unchanged giving a contribution of N_β , while the second summation can only give the same determinant, with a sign change, for doubly occupied orbitals. This results in

$$\langle L | \hat{S}^2 | K \rangle = e_p \left(M_S(M_S + 1) + N_\beta - \sum_{i,j} \delta_{ij} \right), \quad (5)$$

where i ranges over all occupied α orbitals, j over all occupied β orbitals and δ_{ij} is the Kronecker delta.

If there are two differences related by a spin exchange then

$$\langle L | \hat{S}^2 | K \rangle = e_p e_s. \quad (6)$$

Here e_s is the sign due to placing the spin exchanged determinant K in maximum coincidence with L .

UHF

The lack of orthogonality between α and β orbitals when using unrestricted Hartree-Fock means that the overlap between orbitals needs to be considered to implement a more general approach for the expectation of the total squared magnitude of the spin.

We define the overlap matrix between spatial orbitals of different spin as

$$A_{ij} = \langle \phi_i^\alpha | \phi_j^\beta \rangle. \quad (7)$$

For no differences between the determinants in maximum coincidence we have

$$\langle L | \hat{S}^2 | K \rangle = e_p \left(M_S(M_S + 1) + N_\beta - \sum_{i,j} (A_{ij})^2 \right) \quad (8)$$

where i ranges over all occupied α orbitals and j over all occupied β orbitals.

If there is one difference from α orbitals i and j then the spin of j can be swapped with that of any occupied β orbital followed by a sign change on swapping the spin orbitals back to give a possible non-zero contribution. This results in

$$\langle L | \hat{S}^2 | K \rangle = -e_p \sum_k A_{ik} A_{jk}$$

where k ranges over all occupied β orbitals.

Similarly for one difference in the β orbitals i and j we have

$$\langle L | \hat{S}^2 | K \rangle = -e_p \sum_k A_{ki} A_{kj}$$

where k ranges over all occupied α orbitals.

Finally for two differences from $\phi_i^\alpha, \phi_{i'}^\beta$ in the first determinant, and $\phi_j^\alpha, \phi_{j'}^\beta$ in the second determinant we have

$$\langle L | \hat{S}^2 | K \rangle = e_p e_s A_{ij'} A_{j'i'}$$

where, again, e_s is the sign from swapping spin orbitals so that the spin-exchanged determinant K is in maximum coincidence with L .

Multireference Character

As discussed in the introduction it is of interest to ascertain whether a problem in quantum chemistry would be deemed multireference for a give set of orbitals, i.e., is there more than one important configuration in the wavefunction or can the system be satisfactorily modelled using an approach built around small corrections to a single determinant.

In Ref. 23 the following way of quantifying the multireference character for a give basis and set of molecular orbitals was introduced:

$$MR = \sum_i |c_i|^2 - |c_i|^4, \quad (9)$$

where the c_i are the coefficients of the configurations in the wavefunction. We use a normalization such that $\sum |c_i|^2 = 1$. The calculation is therefore approximate when using

non-orthonormal CSFs. Here $MR = 0$ signifies that there is only one configuration while MR approaches one as the number of important configurations increases. When using Hartree-Fock molecular orbitals and CSFs, previous work¹⁷ found a value of 0.30 for hydrogen fluoride in an aug-cc-pVDZ basis for an MCCI wavefunction. This is a system for which methods based on a single reference would be expected to work well. In contrast for the strongly multireference chromium dimer it was found²³ that the MR of the MCCI wavefunction varied from 0.8 to approaching 1 as the bond length was stretched when using a cc-pVTZ basis.

If we wish to compare MR values between a calculation performed with Slater determinants and one done with non-orthonormal CSFs then the approximate nature of MR in the latter case presents a difficulty. One approach would be to convert the CSFs to Slater determinants. Another approach, that we investigate, is to transform the CSFs to be orthonormal using $\mathbf{S}^{-1/2}$ so that their new overlap matrix \mathbf{S}' is the identity matrix. Here the value of the overlap matrix between configurations CSF_i and CSF_j is defined as $S_{ij} = \langle \text{CSF}_i | \text{CSF}_j \rangle$. The coefficients of the CSFs in the wavefunction will then transform as $\mathbf{c}' = \sqrt{\mathbf{S}}\mathbf{c}$ so that the wavefunction is invariant with respect to the transformation of the CSFs. We diagonalize \mathbf{S} and use $\sqrt{\mathbf{S}} = \mathbf{O}\sqrt{\mathbf{D}}\mathbf{O}^T$. Here D is a diagonal matrix formed using the eigenvalues of S and O is an orthogonal matrix formed using the corresponding eigenvectors as the columns. We note that more efficient approaches to compute the square root of a matrix have been developed, see, e.g., Ref. 24. An approximate transformation of the CSFs to an orthonormal set was put forward in Ref. 13 where off-diagonal elements of the overlap matrix are assumed to be negligible resulting in $c'_i \approx \sqrt{S_{ii}}c_i$ which are then normalized. We look at how these three types of CSFs influence the MR value when comparing with the Slater determinant results. We label approximately orthonormal CSFs as CSFs(A) and orthonormal CSFs as CSFs(O).

The MR calculation is not invariant to the choice of orbitals, but instead gives important information about whether the system would be expected to be challenging for approaches built around a single-reference when using easily-available molecular orbitals. This was investigated in Ref. 1 where it was demonstrated that strong multireference nature may not persist when natural orbitals are used. There MR using the natural orbitals was put forward

as one way to quantify intrinsic multireference character or strong correlation in a given basis. P.-O. Löwdin previously proposed² Eq. 10 to quantify the distance of a wavefunction from the Hartree-Fock single determinant:

$$\Theta_{nat} = \frac{1}{N} \text{Tr} (\gamma - \gamma^2), \quad (10)$$

where γ is the first-order reduced density matrix when using a molecular orbital representation. In Ref. 1 it was demonstrated that for equal number of α and β electrons and with spin-averaging then Eq. 10, when scaled to reside between 0 and 1, may be viewed as the scaled spatial entanglement²⁵ relative to the Hartree-Fock wavefunction for the basis used and therefore may be used to suggest whether a wavefunction is strongly correlated. In this context, strongly correlated may be interpreted as a wavefunction that is strongly multireference independent of the single-particle orbitals employed.

We can apply the same approach to situations where the number of α electrons is different to the number of β electrons. As we average over spins in the construction²⁶ of the first-order reduced density matrix, we may calculate the scaled¹ measure of P.-O. Löwdin² by replacing N_α with half the total number of electrons $N/2$.

$$\tilde{\Theta}_{nat} = \frac{M}{M - N/2} \Theta_{nat}. \quad (11)$$

We only use the natural orbital occupations so omit the labels on Θ regarding the orbital type.

When using a spin-averaged reduced density matrix we replace N by $N/2$ in Eq. 10. We then may write Eq. 10 in terms of the eigenvalues λ_i of the spin-averaged first-order reduced density matrix

$$\Theta = 1 - \frac{2}{N} \sum_{i=1}^M \lambda_i^2. \quad (12)$$

These eigenvalues are also the occupations of the natural orbitals.

We note that with spin-averaging Θ is not zero for a single Slater determinant when $N_\alpha \neq N_\beta$. To take this into account we consider the value relative to that of the lowest value for a single Slater determinant when as many orbitals as possible have double occupation, i.e., a restricted open shell Hartree-Fock (ROHF) wavefunction. We therefore define

$$\Theta_{rel} = \Theta - \Theta_{ROHF}. \quad (13)$$

In the case of this ROHF wavefunction we have $|N_\alpha - N_\beta|$ orbitals with single occupation and $(N - |N_\alpha - N_\beta|)/2$ orbitals have double occupation. This results in

$$\begin{aligned}\Theta_{ROHF} &= 1 - \frac{2}{N} \left(\frac{N - |N_\alpha - N_\beta|}{2} + \frac{|N_\alpha - N_\beta|}{4} \right) \\ &= \frac{|N_\alpha - N_\beta|}{2N}.\end{aligned}\quad (14)$$

Using the same argument as Ref. 1 then the maximum value for Θ_{rel} is

$$\Theta_{rel,max} = \frac{2M - N}{2M} - \frac{|N_\alpha - N_\beta|}{2N}.\quad (15)$$

This gives Θ_{rel} scaled to be in the range zero to one as

$$\tilde{\Theta}_{rel} = \frac{2MN}{2MN - N^2 - M|N_\alpha - N_\beta|} \left(\Theta - \frac{|N_\alpha - N_\beta|}{2N} \right).\quad (16)$$

We see that when $N_\alpha = N_\beta$ this becomes the result of Ref. 1. Therefore Eq. 16 is a generalization of $\tilde{\Theta}$ to also encompass situations when $N_\alpha \neq N_\beta$.

We now demonstrate that $\tilde{\Theta}_{rel}$ is equal to the linear entropy relative to that of a single determinant as was done for $\tilde{\Theta}$ in Ref. 1. The linear entropy of quantum information is written as $L = 1 - \gamma^2$ where now the first-order reduced density matrix is normalized so that the trace is equal to one. Therefore the eigenvalues μ_i sum to one rather than $N/2$. The linear entropy, for example, has been used to quantify²⁵ the spatial entanglement of Hooke's atom and may be considered as an approximation to the von Neumann entropy $S = -Tr(\gamma \ln \gamma)$.

When working with a basis set of M functions there are M eigenvalues. For the ROHF wavefunction Ψ_0 we find that

$$\begin{aligned}L(\Psi_0) &= 1 - \left(\frac{2N - 2|N_\alpha - N_\beta|}{N^2} + \frac{|N_\alpha - N_\beta|}{N^2} \right) \\ &= 1 - \frac{2}{N} + \frac{|N_\alpha - N_\beta|}{N^2}.\end{aligned}\quad (17)$$

Then looking at the value of L relative to this ($\chi = L - L(\Psi_0)$) gives

$$\chi = - \sum_{i=1}^M \mu_i^2 + \frac{2}{N} - \frac{|N_\alpha - N_\beta|}{N^2}.\quad (18)$$

χ has its maximum value when all of the eigenvalues are equal to $1/M$ (see Ref. 1) this gives rise to a scaled value of

$$\tilde{\chi} = \frac{N^2 M \chi}{2MN - N^2 - M|N_\alpha - N_\beta|}. \quad (19)$$

If we write Θ in terms of the scaled μ_i eigenvalues we have

$$\Theta = 1 - \frac{N}{2} \sum_{i=1}^M \mu_i^2 \quad (20)$$

so

$$\begin{aligned} \tilde{\Theta}_{rel} &= \frac{2MN}{2MN - N^2 - M|N_\alpha - N_\beta|} \left(1 - \frac{N}{2} \sum_{i=1}^M \mu_i^2 - \frac{|N_\alpha - N_\beta|}{2N} \right) \\ &= \frac{N^2 M \chi}{2MN - N^2 - M|N_\alpha - N_\beta|} \end{aligned} \quad (21)$$

i.e. , $\tilde{\Theta}_{rel} = \tilde{\chi}$ in general. Hence we have extended the demonstration of Ref. 1, which showed that this equality held for $N_\alpha = N_\beta$, to also apply to the general case where $N_\alpha \neq N_\beta$.

RESULTS

Methyl radical

The first open-shell system we consider is the CH_3 doublet. We look at a trigonal planar geometry for CH_3 and investigate the ground-state of B_2 symmetry. We use an optimized bond length found with density-functional theory of 1.083 Å when using the 6-31G basis and the B3LYP functional with the spin-unrestricted Kohn-Sham program in MOLPRO.²⁰

We see in Fig. 1 that the MCCI UHF results are lower in energy than those using RHF orbitals although not substantially so. We note that the $c_{\min} = 0$ result is slightly lower for UHF orbitals as one frozen molecular orbital is used. Fig. 1 also shows that even at larger cutoffs the final MCCI energy varies very little from one run to another.

The UHF wavefunction has $\langle \hat{S}^2 \rangle = 0.762$ and is therefore close to being a pure doublet ($\langle \hat{S}^2 \rangle = 0.75$) but there is some spin contamination. This contamination is substantially

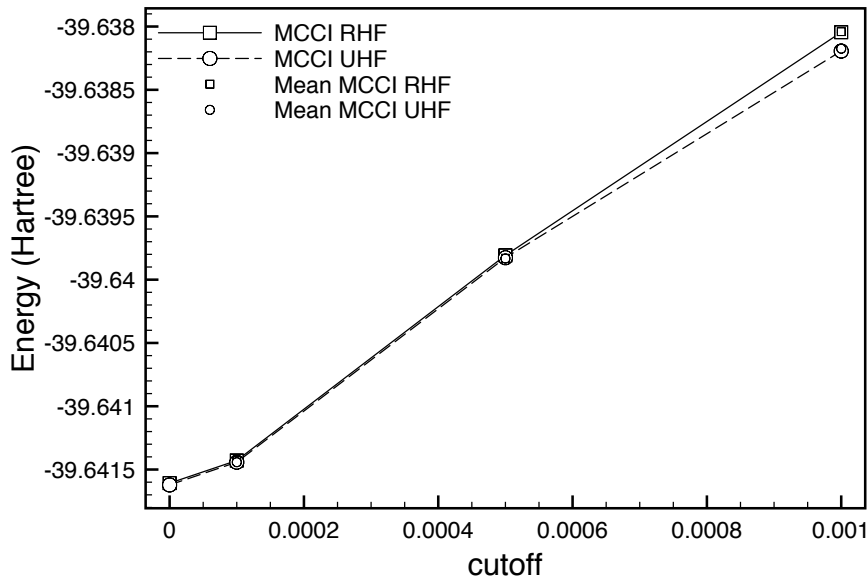


Figure 1: MCCI energy (Hartree) for the 2B_2 state of CH_3 at a trigonal planar geometry with equilibrium bond length plotted against cutoff (c_{\min}) for RHF and UHF orbitals when using the 6-31G basis set with one frozen molecular orbital. Mean values from ten runs are also displayed while the standard error bars are too small to be seen on the scale of the graph.

reduced by the MCCI calculation (Fig. 2). However we see that the MCCI UHF wavefunctions are further from being pure spin states than the MCCI RHF wavefunctions although the difference is slight. We also see in Fig. 2 that there is slightly more variation in the spin expectation than the energy for small cutoffs due to the stochastic nature of MCCI. However the standard errors remain too small to be seen on the scale of the graph.

We now investigate a stretched geometry where all bonds are 1.8 \AA . We find that an indicator of multireference character (MR) increases from around 0.1 to 0.44 for $c_{\min} = 0$ when using RHF orbitals and to 0.70 when using UHF orbitals. We see in Fig. 3 that the MCCI RHF energy is slightly lower as the cutoff is increased. than that using UHF orbitals. This is despite the UHF energy being around 0.03 Hartree lower in energy than the RHF energy. This lower energy, however, is at the expense of very substantial spin contamination where the UHF wavefunction now has $\langle \hat{S}^2 \rangle = 1.88$.

The MCCI calculation overcomes this spin contamination as can be seen in Fig. 4 where

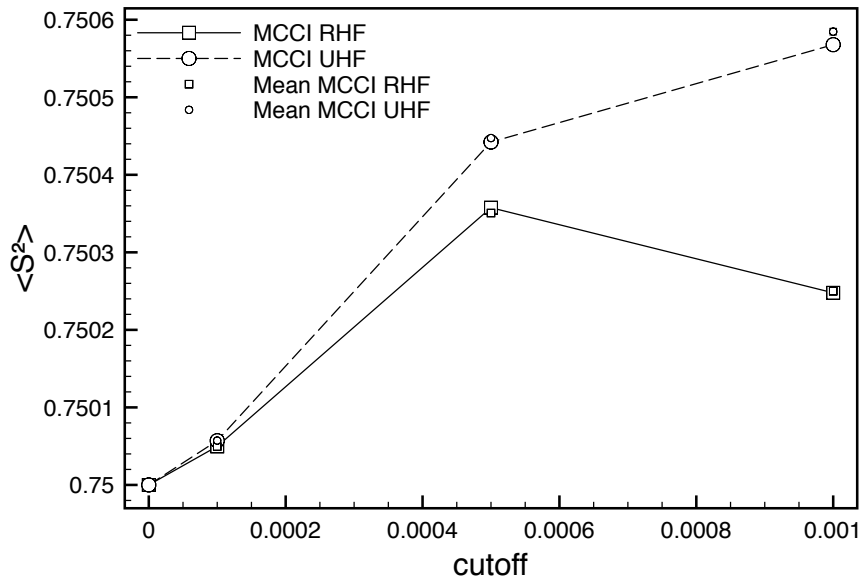


Figure 2: MCCI $\langle \hat{S}^2 \rangle$ for the 2B_2 state of CH_3 at a trigonal planar geometry with equilibrium bond length plotted against cutoff (c_{\min}) for RHF and UHF orbitals when using the 6-31G basis set with one frozen molecular orbital. Mean values from ten runs are also displayed while the standard error bars are too small to be seen on the scale of the graph.

the value of $\langle \hat{S}^2 \rangle$ is depicted as the calculation progresses when $c_{\min} = 10^{-3}$. The UHF value of $\langle \hat{S}^2 \rangle = 1.888$ rapidly reduces to the converged MCCI value of $\langle \hat{S}^2 \rangle = 0.758$ at this cutoff. This required 2048 Slater determinants compared with the FCI space of 88132.

Although the MCCI calculation produces a wavefunction with much less spin contamination than that of the single determinant of UHF there remains more spin contamination than when using RHF orbitals. Fig. 5 shows that for the stretched bond length geometry, in addition to giving a lower energy, RHF orbitals produce noticeably less spin contamination on the scale of the graph.

If we use $\tilde{\Theta}$ for a spin-averaged density matrix then for the equilibrium geometry of this open-shell system we find a value of 0.11 when using FCI. This would appear slightly high given that MR is 0.099 and the values we have seen for MR and $\tilde{\Theta}$ for closed-shell test systems in Ref. 1. When correctly taking into account that the previous approach would be non-zero even for a single-determinant of an open-shell system we calculate a result for $\tilde{\Theta}_{rel}$ more than three times lower at 0.031. We note that employing FCI natural orbitals did

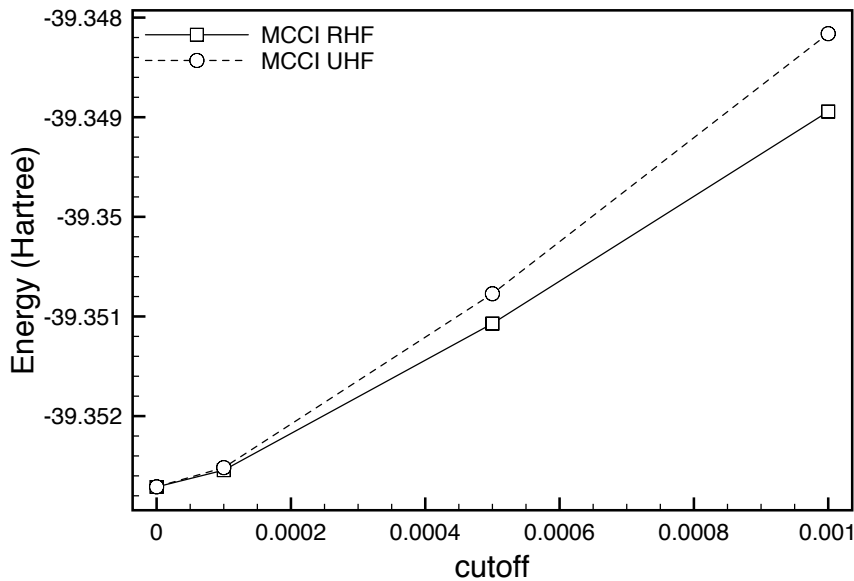


Figure 3: MCCI energy (Hartree) for the 2B_2 state of CH_3 at a trigonal planar geometry with stretched bond length plotted against cutoff (c_{min}) for RHF and UHF orbitals when using the 6-31G basis set with one frozen molecular orbital.

not substantially lower the FCI MR value for the equilibrium system and to two significant figures it remained at 0.099. Furthermore the stretched result changed only slightly from 0.44 to 0.43. Fig. 6 shows that the equilibrium system would not be described as multireference. While with stretched bonds we would categorize it as a multireference problem, but not strongly correlated.

Table 1 shows that, at the equilibrium geometry, the multireference nature is similar for UHF and RHF orbitals. The MR value for CSFs is much higher than with SDs but would still be classed as well described by a single reference based on values for CSF wavefunctions seen in previous work.¹⁷ When making the CSFs approximately orthonormal the MR value decreases. The MR value lowers further to become the same as the SD value when orthonormal CSFs are used. As would be expected, the MR values for the stretched system would categorize it as a multireference problem and a similar effect is observed on transforming the CSFs to be orthonormal. Interestingly the UHF value for the stretched system is noticeably higher than when using RHF orbitals which we attribute to these UHF orbitals being a poor choice to describe this system as, although the UHF energy is lower than the RHF result, the

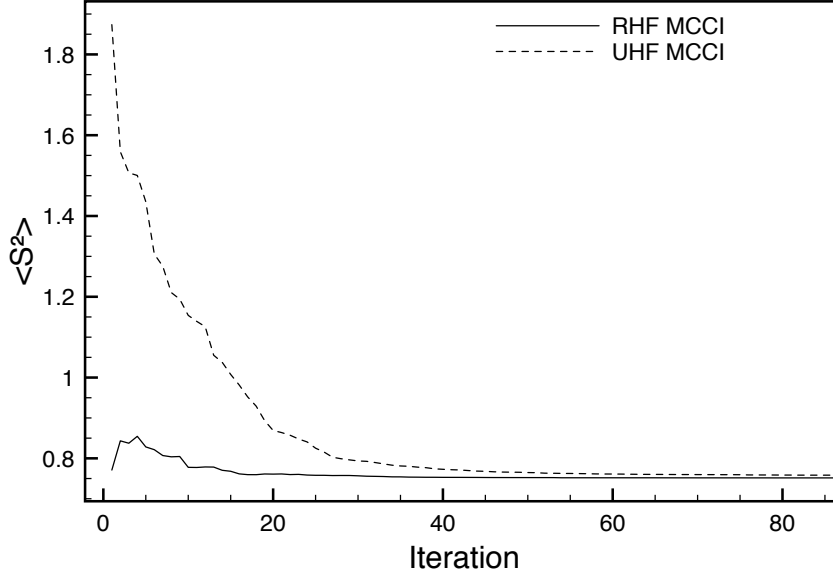


Figure 4: MCCI $\langle \hat{S}^2 \rangle$ for the 2B_2 state of CH_3 at a trigonal planar geometry with stretched bond length plotted against iteration number when using a cutoff of $c_{\min} = 10^{-3}$ for UHF and RHF orbitals when using the 6-31G basis set with one frozen molecular orbital.

spin contamination is very large. In addition the previously mentioned very small change in MR when using natural orbitals compared with RHF orbitals for this system suggests that the RHF orbitals are appropriate to model the stretched system. The tabulated results use a large cut-off of 10^{-3} but we note that the multireference nature was seen to not be strongly affected by the cut-off in Fig. 6.

Table 1: Indicators of multireference character (MR) for the MCCI wavefunction when using a cutoff of 10^{-3} for the 2B_2 state of CH_3 at a trigonal planar geometry with the 6-31G basis and one frozen orbital with equilibrium and stretched bonds. CSFs(A) and CSFs(O) are approximately orthonormal and orthonormal respectively.

	SDs	UHF SDs	CSFs	CSFs(A)	CSFs(O)
MR eq	0.090	0.085	0.31	0.19	0.091
MR stretch	0.43	0.67	0.82	0.68	0.43

We also investigate the effect of basis size on the results. The full configuration space

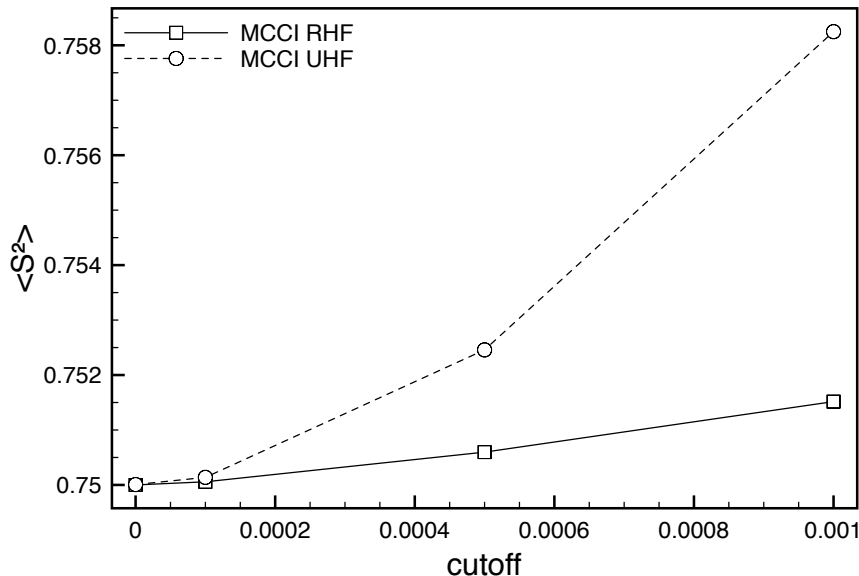


Figure 5: MCCI $\langle \hat{S}^2 \rangle$ for the 2B_2 state of CH_3 at a trigonal planar geometry with stretched bond length plotted against cutoff (c_{\min}) for RHF and UHF orbitals when using the 6-31G basis set with one frozen molecular orbital.

when using the cc-pVDZ basis would comprise around 10^7 determinants while for the cc-pVTZ basis around 10^{10} determinants would be required. The size of the latter configuration space means that a full configuration interaction calculation is beyond our current capabilities in this case. When using RHF orbitals the MCCI calculation with $c_{\min}=5 \times 10^{-4}$ for the stretched geometry needed 7143 determinants when the cc-pVDZ basis was employed and this increased to 10404 when the basis was enlarged to cc-pVTZ. Table 2 shows how changing the basis does not substantially alter the results at the equilibrium bond length. For example, the final MCCI wavefunctions when $c_{\min}=5 \times 10^{-4}$ are essentially pure spin states regardless of basis size. The multireference nature as quantified by MR increases slightly with increasing basis. For a system well-described by methods based on a single reference then this would be expected if the initial basis is reasonably appropriate: with all other things being equal then increasing the basis size should result in an increase in configurations in the MCCI wavefunction until saturation is reached for a given cutoff. The $\tilde{\Theta}_{rel}$ values are relatively stable, but there is a decrease when moving to the largest basis set considered. This could be due to the MCCI wavefunction becoming slightly less accurate at this reasonable cutoff

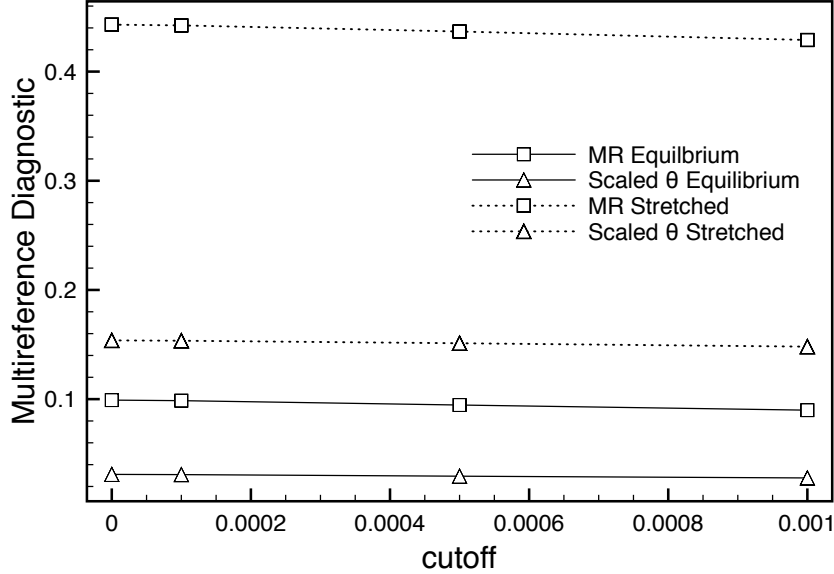


Figure 6: Multireference diagnostics for the MCCI wavefunction for the 2B_2 state of CH_3 at a trigonal planar geometry with equilibrium and stretched bond lengths against cutoff (c_{\min}) for RHF orbitals when using the 6-31G basis set with one frozen molecular orbital.

when faced with such a large configuration space. However the spin contamination remains practically zero so suggests that there is no great loss of accuracy, and the absolute change in $\tilde{\Theta}_{rel}$ is fairly negligible.

Table 2: Effect of basis on the MCCI wavefunction with either RHF or UHF orbitals when using a cutoff of 5×10^{-4} for the 2B_2 state of CH_3 at a trigonal planar geometry with equilibrium bonds and one frozen orbital.

Basis	$\langle \hat{S}^2 \rangle$ (RHF)	$\langle \hat{S}^2 \rangle$ (UHF)	MR (RHF)	MR (UHF)	$\tilde{\Theta}_{rel}$ (RHF)
6-31G	0.750	0.750	0.0946	0.0892	0.0294
6-31G*	0.750	0.751	0.105	0.0998	0.0291
cc-pVDZ	0.750	0.751	0.115	0.111	0.0295
cc-pVTZ	0.751	0.751	0.117	0.114	0.0267

We see in table 3 that varying the basis when considering a stretched bond length does not strongly affect whether the MCCI wavefunction is a pure spin state when using RHF

orbitals although the very small increase in spin contamination is greater than when considering the equilibrium bond length. For UHF orbitals the increase in spin contamination is more noticeable, but still rather small particularly when compared with the strongly spin contaminated UHF single determinant reference. Both MR and $\tilde{\Theta}_{rel}$ decrease when increasing the basis size but the categorization of the system as multireference remains. This accompaniment of an increase in $\langle \hat{S}^2 \rangle$ by a decrease in MR suggests that, for this reasonable cutoff of $c_{min}=5 \times 10^{-4}$, the MCCI wavefunction with UHF orbitals does not describe this multireference system quite as well when the configuration space becomes very large due to increasing the basis size.

Table 3: Effect of basis on the MCCI wavefunction with either RHF or UHF orbitals when using a cutoff of 5×10^{-4} for the 2B_2 state of CH_3 at a trigonal planar geometry with stretched bonds and one frozen orbital.

Basis	$\langle \hat{S}^2 \rangle$ (RHF)	$\langle \hat{S}^2 \rangle$ (UHF)	MR (RHF)	MR (UHF)	$\tilde{\Theta}_{rel}$ (RHF)
6-31G	0.751	0.752	0.437	0.684	0.151
6-31G*	0.751	0.756	0.427	0.680	0.134
cc-pVDZ	0.752	0.766	0.401	0.636	0.114
cc-pVTZ	0.755	0.811	0.369	0.578	0.0938

Allyl radical

The allyl radical (C_3H_4) and its barrier to rotation between twisted and planar forms is a well-known open-shell problem (see for example Ref. 27). Experimentally²⁸ a rotational barrier of 15.7 ± 1.0 kcal/mol has been found.

We initially optimize the geometry of the planar (C_{2v}) and twisted (C_s) forms which are again calculated using the 6-31G basis and UKS with the B3LYP functional in MOLPRO.²⁰

We find that the symmetry of the ground-state C_{2v} wavefunction is A_2 and that of the C_s wavefunction is A' . C_{2v} has substantially more spin contamination than C_s when using UHF ($\langle \hat{S}^2 \rangle = 0.98$ versus $\langle \hat{S}^2 \rangle = 0.82$). The barrier to rotation is 5.99 kcal/mol for RHF and 20.72 kcal/mol for UHF due to the C_{2v} energy being lowered more by UHF at the cost

of spin contamination.

We first freeze 8 orbitals so that the FCI calculation is tractable. The FCI space is around 2×10^7 for C_{2v} while due to the reduction in symmetry C_s has around twice as many configurations. With frozen orbitals then the FCI energy is slightly lower when using UHF compared with RHF (table 4).

Table 4: Allyl radical barrier to rotation from C_{2v} to C_s forms in kcal/mol using the 6-31G basis with 8 frozen orbitals.

Orbitals	FCI	MCCI 5×10^{-4}	MCCI 2×10^{-4}
RHF	11.64	12.09	11.97
UHF	11.31	11.86	11.68

We see in table 4 that the barrier calculated with UHF orbitals is lower however the percentage error when compared with the FCI result using the same orbitals is slightly higher at 3.3% for the lowest cutoff compared with 2.8% for RHF. The MCCI wavefunction has negligible spin contamination (table 5) when using RHF and, although there is a small amount of spin contamination when using UHF orbitals, the MCCI wavefunction has significantly improved upon the UHF reference (0.98 for C_{2v}) even when the cutoff is 5×10^{-4} .

Table 5: $\langle \hat{S}^2 \rangle$ for the MCCI wavefunctions for the allyl radical with the 6-31G basis and 8 frozen orbitals for the C_{2v} and C_s forms.

Orbitals	MCCI 5×10^{-4}	MCCI 2×10^{-4}
RHF C_{2v}	0.750	0.750
UHF C_{2v}	0.773	0.769
RHF C_s	0.750	0.750
UHF C_s	0.765	0.764

We now reduce the number of frozen orbitals to three for a better comparison with experiment. However this means that the FCI calculation is no longer tractable for us due to around 10^{14} determinants in the FCI space. Table 6 shows that the MCCI calculation substantially improves upon the single determinant approximation to give values close to

experimental results²⁸ when only three orbitals are frozen. However we acknowledge that we do not use a very large basis set.

Table 6: Allyl radical barrier to rotation from C_{2v} to C_s forms in kcal/mol using the 6-31G basis with 3 frozen orbitals.

Orbitals	HF	MCCI 5×10^{-4}	MCCI 2×10^{-4}
RHF	5.99	13.93	15.06
UHF	20.72	15.49	14.92

Table 7 displays that, in this case, the spin contamination increases when the size of the configuration space is larger. The MCCI wavefunction still reduces the spin contamination compared with the reference UHF wavefunction and the values of $\langle \hat{S}^2 \rangle$ for the smallest cutoff considered are reasonable.

Table 7: $\langle \hat{S}^2 \rangle$ for the MCCI wavefunctions for the allyl radical with the 6-31G basis and 3 frozen orbitals for the C_{2v} and C_s forms.

Orbitals	HF	MCCI 5×10^{-4}	MCCI 2×10^{-4}
RHF C_{2v}	0.750	0.752	0.752
UHF C_{2v}	0.982	0.805	0.767
RHF C_s	0.750	0.753	0.751
UHF C_s	0.819	0.770	0.760

The allyl MR values for Slater determinants are displayed in table 8 and there is more multireference character than for the previously considered CH_3 system at the equilibrium bond length (table 1). The multireference character is not large enough to suggest that either of the geometries should present a significant challenge for methods built around small corrections to a single reference. We highlight that the MR value did not drastically change on lowering the cutoff or using UHF orbitals. At 5×10^{-4} the value for CSFs was 0.64 for C_{2v} which lowered to 0.46 with approximately orthonormal CSFs and to 0.24 with orthonormal CSFs. The C_s wavefunction lowered from 0.37 to 0.25 for approximately orthonormal CSFs

and then to 0.21 for orthonormal CSFs. This again demonstrates that the MR values are similar between orthonormal CSFs and Slater determinants.

Table 8: Multireference diagnostics for the MCCI wavefunctions with $c_{\min} = 5 \times 10^{-4}$ for the allyl radical with the 6-31G basis and 3 frozen orbitals for the C_{2v} and C_s forms.

Orbitals	MR	$\tilde{\Theta}_{rel}$
C_{2v}	0.229	0.058
C_s	0.207	0.058

Oxygen molecule

The triplet ground-state of molecular oxygen has often been used as an important test case for multireference methods, for example Refs. 29,30. We finally look at the triplet-singlet gap in molecular oxygen at a bond length of 1.21\AA . We use the 6-31G basis with two frozen molecular orbitals. Using FCI we calculate the spin gap as 1.15 eV. This calculation required around eight million SDs when symmetry is taken into account. The triplet wavefunction is of B_{1g} symmetry in D_{2h} while the singlet wavefunction is of A_g symmetry. These symmetries correspond to the first two electronic states of ${}^3\Sigma_g^-$ and ${}^1\Delta_g$ when the full point group ($D_{\infty h}$) is used. These states experimentally have a gap of around 0.97 eV (see, e.g., Ref. 31).

The MCCI result with $c_{\min} = 5 \times 10^{-4}$ and CSFs used around 3000 configurations and gave a spin gap of 1.11 eV. With Slater determinants and $c_{\min} = 5 \times 10^{-4}$ we first use the HF orbitals from the A_g singlet calculation. We find a spin gap of 1.14 eV between the MCCI calculations of B_{1g} and A_{1g} when starting with equal numbers of α and β electrons. The $\langle \hat{S}^2 \rangle$ values are 2.000 and 0.001 respectively demonstrating that essentially pure spin states have been found.

If we use $M_S = 1$ for the B_{1g} state then we find a gap of 1.21 eV and again the wavefunction is a pure triplet. We see in table 9 that the M_S value of the triplet substantially changes its multireference nature. This fits in with the qualitative molecular orbital picture (see, e.g., Ref. 32) where the $M_S = 1$ state can be created from a single determinant with the π_g^x and π_g^y orbitals singly occupied, but two determinants are needed for $M_S = 0$.

The spin-averaged natural orbital occupations are similar for all three states so this alone would not correctly discriminate between their multireference natures. However $\tilde{\Theta}_{rel}$, by taking into account the difference in α and β electrons, gives an order of multireference character in agreement with MR. When approximate natural orbitals are used from the MCCI calculation with $c_{min} = 5 \times 10^{-4}$ we find that the MR value only lowers slightly to 0.597 for 1A_g . This, and the $\tilde{\Theta}_{rel}$ value, suggests that the wavefunction is intrinsically multireference in the 6-31G basis. However the approximate natural orbitals do result in a reduction in the number of determinants in the MCCI wavefunction: 3211 SDs compared with 4172 SDs for the original A_g calculation.

The MCCI 1A_g wavefunction's two most important configurations are approximately equally important and only differ in sign and in that one has a doubly occupied π_g^x orbital while the other has a doubly occupied π_g^y orbital. This also corroborates the molecular orbital picture where the degenerate π_g^x and π_g^y orbitals suggest that two determinants are required. The configuration of the wavefunction means that we would not classify it as open-shell. It is then interesting to point out that the largest multireference character seen in this work is not for a stretched bond open-shell system but the oxygen molecule in its lowest singlet state.

Table 9: Slater determinant MCCI results with $c_{min} = 5 \times 10^{-4}$ and the A_g singlet HF orbitals for O_2 with the 6-31G basis and two frozen orbitals. Energies (E) are in Hartree.

State	M_S	E	MR	$\tilde{\Theta}_{rel}$
1A_g	0	-149.736	0.603	0.161
${}^3B_{1g}$	0	-149.778	0.596	0.158
${}^3B_{1g}$	1	-149.780	0.195	0.034

In table 10 we see again that orthonormal CSFs reduce the MR value but by a smaller amount for the singlet than the triplet. The value from orthonormal orbitals represents a higher percentage of the original value for the singlet state (82%) than the triplet (36%). This might hint that transforming the CSFs to be orthonormal is necessary to compare CSF MR values with SD results for open-shell systems but perhaps not for a qualitative

comparison in closed-shell systems.

Table 10: CSF MCCI results with $c_{\min} = 5 \times 10^{-4}$ and HF orbitals for the state of interest for O_2 with the 6-31G basis and two frozen orbitals.. CSFs(A) are approximately orthonormal and CSFs(O) are orthonormal. Energies (E) are in Hartree.

State	M_S	E	MR	MR CSFs(A)	MR CSFs(O)
1A_g	0	-149.739	0.74	0.63	0.61
$^3B_{1g}$	1	-149.780	0.47	0.36	0.17

We now try using a triplet B_{1g} Hartree-Fock calculation to create the orbitals. For the B_{1g} $M_S = 1$ MCCI calculation we find that the improved description of the ground state increases the gap to 1.21 eV. UHF orbitals had a negligible effect on this MCCI calculation despite the UHF reference being almost 0.5 eV lower in energy than the ROHF reference.

We then use $M_S = 0$ but starting with an open shell configuration (two orbitals singly occupied in the reference) this reference is spin contaminated with $\langle \hat{S}^2 \rangle = 1$. We do not use symmetry thereby allowing us to calculate both states at the same time with the RHF singlet orbitals using state-averaged MCCI.¹⁴ This gives the spin gap as 1.11 eV and required around 4000 SDs. The \hat{S}^2 expectation values were 1.99 and 0.01 showing that the triplet and singlet have been reached. We see in Fig. 7 that the wavefunctions are not pure spin states until the calculation approaches convergence. The multireference nature was similar for the two wavefunctions calculated in this way with MR being 0.59 for the triplet and 0.60 for the singlet. In this case the MCCI 1A_g wavefunction had two dominant configurations with singly occupied orbitals so would be classified as an open-shell singlet.

For the $M_s = 0$ calculation we also investigate if we can improve convergence by creating spin paired determinants, i.e., for each new configuration we also create a configuration with the α and β spin molecular orbitals swapped. This approach gives a spin gap of 1.13 eV with \hat{S}^2 expectation values of 2.001 and 0.002 again requiring around 4000 SDs. Fig. 8 displays how pure spin states are reached sooner using this approach and the overall convergence requires fewer iterations.

Although the spin gap was slightly closer to that of FCI when using spin paired SDs than

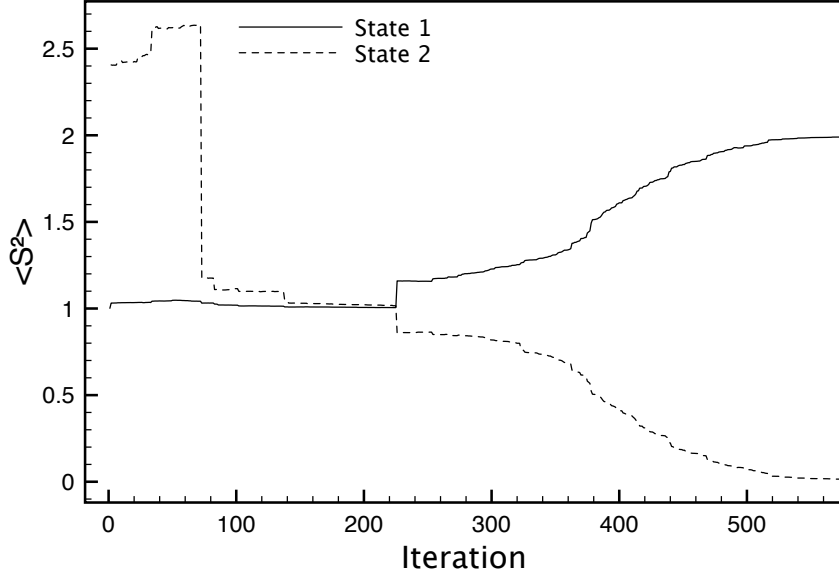


Figure 7: Expectation of \hat{S}^2 against iteration number for the MCCI wavefunctions of the first two states of O_2 when $M_S = 0$ starting from an open shell configuration using SDs, $c_{\min} = 5 \times 10^{-4}$ and the 6-31G basis set with two frozen molecular orbitals.

when using CSFs we note that the individual energies remained higher than the results with CSFs. We find that when considering three states the third state remains spin contaminated with $\langle \hat{S}^2 \rangle = 1$ and it requires four states for this to become a singlet with the fourth state a triplet. However this approach without symmetry finds a second singlet state at around 6.0 eV rather than the A_g singlet lying around 1.7 eV above the ground state as found in FCI or MCCI calculations using symmetry. Using SA-MCCI with symmetry we find that the second A_g singlet state is in agreement with FCI at 1.67 eV and corresponds to the third electronic state ${}^1\Sigma_g^+$ (see, e.g., Ref. 32) that is experimentally³³ found to be 0.65 eV above the lowest singlet state and therefore around 1.63 eV above the ground-state triplet. The second triplet when not using symmetry is at 6.2 eV and this agrees with the FCI result of a B_{1u} triplet at 6.3 eV.

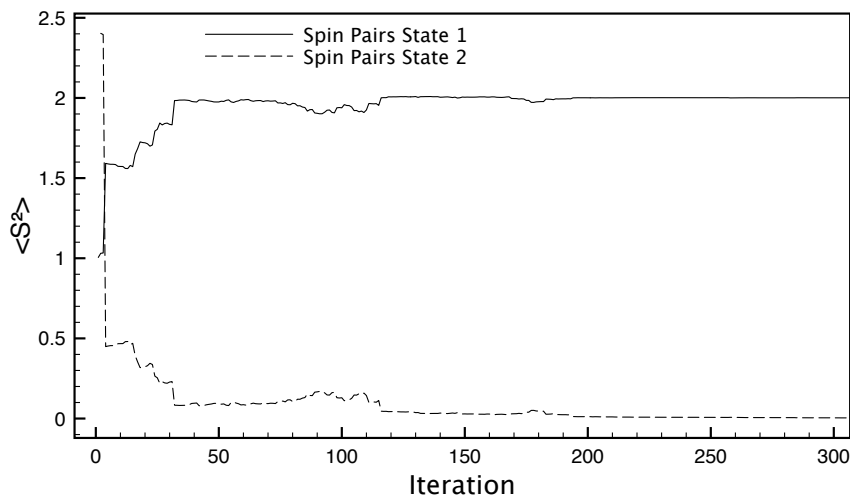


Figure 8: Expectation of \hat{S}^2 against iteration number when using spin paired configurations for the MCCI wavefunctions of the first two states of O_2 when $M_S = 0$ starting from an open shell configurations using SDs, $c_{\min} = 5 \times 10^{-4}$ and the 6-31G basis set with two frozen molecular orbitals.

CONCLUSIONS

In this paper we have considered three open-shell molecules: the methyl radical, the allyl radical and molecular oxygen. We have shown how calculations of $\langle \hat{S}^2 \rangle$ can be achieved with Monte Carlo configuration interaction (MCCI) when using Slater determinants. We then demonstrated that the compact wavefunctions found by MCCI can approach pure spin states, even for open-shell systems when starting from a spin contaminated configuration, despite using only a small fraction of the full configuration interaction space. We adapted MCCI to use unrestricted Hartree-Fock (UHF) orbitals to test the hypothesis that the increased flexibility in the molecular orbitals could offer improvements in the MCCI results. We did not discover any substantial benefit from using UHF orbitals in MCCI for these systems and the calculation could actually become more challenging for MCCI when the spin contamination was large. However both MCCI approaches could give the rotational barrier for the allyl radical in line with experiment despite the restricted Hartree-Fock barrier being too low and the UHF barrier too high. For the methyl radical we found that there remained essentially no spin contamination in the MCCI wavefunction at a reasonable cutoff when enlarging the

basis at the equilibrium bond length. For a stretched bond length and UHF orbitals there was a small amount of spin contamination for the largest basis considered, but this was still a significant improvement over the UHF single determinant.

We also investigated if these open-shell systems are inherently more multireference in character. We generalized previous work¹ on multireference character to show how also for open-shell systems a multireference indicator of P.-O. Löwdin² can be considered as the spatial entanglement relative to a single determinant and therefore can be used for quantifying the electron correlation. This gave rise to $\tilde{\Theta}_{rel}$ which reduces to the previously investigated¹ $\tilde{\Theta}$ in the closed-shell case. We found that the magnitude of the multireference indicator (MR) was larger when configuration state functions were used than for Slater determinants and this difference was much more noticeable for open-shell systems. We looked into transforming the configuration state functions to be orthonormal and found that they now gave similar values for MR to Slater determinants. Hence when comparing MR between wavefunctions composed of Slater determinants and configuration state functions then it seems that the configuration state functions should be transformed to be orthonormal in the case of open-shell systems. We did not find that the open-shell systems were intrinsically multireference in character and in fact the system with the most multireference character of those considered was the lowest singlet state of molecular oxygen which we classified as closed-shell. However a degenerate open-shell singlet for oxygen was also found with a similar multireference character. This appeared more challenging as suggested, by both multireference indicators, than even the methyl radical with a stretched bond length.

We finally showed that state-averaged MCCI¹⁴ could evolve wavefunctions in tandem describing the lowest triplet and singlet state in molecular oxygen when starting from a spin contaminated configuration without the constraints of molecular symmetry. This calculation could then be accelerated in its convergence to pure spin states by modifying MCCI to create new determinants in pairs where the α and β electrons are swapped. To correctly locate the third electronic state we needed to use molecular symmetry however we have demonstrated that for a given number of α and β electrons we can find different pure spin states using the compact Slater determinant wavefunctions of MCCI.

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References

1. J. P. Coe and M. J. Paterson, *J. Chem. Theory Comput.* **11**, 4189 (2015).
2. P.-O. Löwdin, *Phys. Rev.* **97**, 1474 (1955).
3. N. C. Handy, P. J. Knowles, and K. Somasundram, *Theor. Chim. Acta* **68**, 87 (1985).
4. R. H. Nobes, J. A. Pople, L. Radom, N. C. Handy, and P. J. Knowles, *Chem. Phys. Lett.* **138**, 385 (1987).
5. P. J. Knowles, C. Hampel, and H.-J. Werner, *J. Chem. Phys.* **99**, 5219 (1993).
6. P. J. Knowles, C. Hampel, and H.-J. Werner, *J. Chem. Phys.* **112**, 3106 (2000).
7. P. Cassam-Chenaï and G. Chandler, *International journal of quantum chemistry* **46**, 593 (1993).
8. J. C. Greer, *J. Comp. Phys.* **146**, 181 (1998).
9. L. Tong, M. Nolan, T. Cheng, and J. C. Greer, *Comp. Phys. Comm.* **131**, 142 (2000), see <https://github.com/MCCI/mcci>.
10. J. C. Greer, *J. Chem. Phys.* **103**, 1821 (1995).
11. J. C. Greer, *J. Chem. Phys.* **103**, 7996 (1995).
12. T. P. Kelly, A. Perera, R. J. Bartlett, and J. C. Greer, *J. Chem. Phys.* **140**, 084114 (2014).
13. W. Győrffy, R. J. Bartlett, and J. C. Greer, *J. Chem. Phys.* **129**, 064103 (2008).
14. J. P. Coe and M. J. Paterson, *J. Chem. Phys.* **139**, 154103 (2013).
15. J. P. Coe, D. J. Taylor, and M. J. Paterson, *J. Chem. Phys.* **137**, 194111 (2012).
16. J. P. Coe, D. J. Taylor, and M. J. Paterson, *J. Comput. Chem.* **34**, 1083 (2013).
17. J. P. Coe and M. J. Paterson, *J. Chem. Phys.* **141**, 124118 (2014).

18. J. P. Coe and M. J. Paterson, *Theor. Chem. Acc.* **134**, 58 (2015).
19. J. P. Coe and M. J. Paterson, *Chem. Phys. Lett.* **645**, 106 (2016).
20. H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, et al., *Molpro, version 2012.1, a package of ab initio programs* (2012), see <http://www.molpro.net>.
21. J. Paldus, *J. Chem. Phys.* **61**, 5321 (1974).
22. F. E. Harris, *J. Chem. Phys.* **46**, 2769 (1967).
23. J. P. Coe, P. Murphy, and M. J. Paterson, *Chem. Phys. Lett.* **604**, 46 (2014).
24. Å. Björck and S. Hammarling, *Linear Algebra Appl.* **52**, 127 (1983).
25. J. P. Coe, A. Sudbery, and I. D'Amico, *Phys. Rev. B* **77**, 205122 (2008).
26. J. P. Coe and M. J. Paterson, *J. Chem. Phys.* **137**, 204108 (2012).
27. T. Bally and W. T. Borden, in *Reviews in Computational Chemistry*, edited by K. B. Lipkowitz and D. B. Boyd (Wiley-VCH, New York, 1999), vol. 13, p. 1.
28. H. Korth, H. Trill, and R. Sustmann, *J. Am. Chem. Soc.* **103**, 4483 (1981).
29. L. Bytautas and K. Ruedenberg, *J. Chem. Phys.* **132**, 074109 (2010).
30. W. Jiang and A. K. Wilson, *J. Chem. Phys.* **134**, 034101 (2011).
31. D. R. Kearns, *Chemical Reviews* **71**, 395 (1971).
32. M. J. Paterson, O. Christiansen, F. Jensen, and P. R. Ogilby, *Photochemistry and Photobiology* **82**, 1136 (2006).
33. J. F. Noxon, *Canadian Journal of Physics* **39**, 1110 (1961).