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Investigating multireference character and correlation in quantum chemistry

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Abstract

We review a range of multireference diagnostics for quantum chemistry and discuss them in terms of choices of the molecular orbitals. We show how an approach¹ of P.-O. Löwdin can also be viewed as quantifying the electron correlation via the spatial entanglement relative to a single determinant. We consider three example systems from quantum chemistry that exhibit three different combination of multireference character and correlation: not strongly multireference and not strongly correlated, strongly multireference but not strongly correlated, and strongly multireference together with strong correlation. We find that a multireference measure (MR) does not change substantially with cutoff used for a Monte Carlo configuration interaction calculation and investigate the effect of using natural orbitals. We see that a coupled-cluster singles and doubles diagnostic and a density-functional theory diagnostic give a correct general prediction of the multireference character for these systems. We also look at the issue of multireference character for a collection of non-interacting hydrogen molecules and the effect of basis size on the multireference character of a stretched hydrogen molecule.

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1 Introduction

The concept of multireference character is important in quantum chemistry to suggest when methods built around a single determinant would be expected to be successful. Static correlation tends to be associated with a few important determinants in the exact wavefunction for a given basis while dynamic correlation is considered to be represented by the many remaining determinants with small coefficients. For a system described well by one determinant the dynamic correlation is then that neglected by using the mean-field approach of Hartree-Fock. In this picture, once the static correlation, if any, is accounted for then the small amount of dynamic correlation should be well approximated by using, for example, perturbative methods. However the loosely defined distinction between static and dynamic can become increasingly blurred as the wavefunction becomes strongly multireference with very many important determinants.

Ideally one would not want to employ a multireference method, and its associated computational cost, unless necessary. Therefore methods based on a single reference or approximations in density-functional theory are used to estimate the multireference character and perhaps announce their own domain of applicability. It is then of interest to quantify the multireference character when using methods that can cope with multireference systems and compare this both with that estimated by single reference methods and with full configuration interaction (FCI). One can then ask whether strong multireference character is connected with the choice of molecular orbitals and representation of the wavefunction or if it is an intrinsic aspect, in this basis, of the system which could therefore be viewed as strongly correlated in this basis. Finally there is the problem of whether the multireference or strongly correlated nature persists as the basis set is enlarged.

We first review a range of multireference measures and show how they can, in some instances, be linked to certain types of molecular orbitals. We then illustrate and test these approaches with three archetypal systems: not strongly multireference nor strongly correlated, strongly multireference but not strongly correlated, then strongly multireference

and strongly correlated. We also consider an excited state. We look at the issue of size-intensivity in these measures for a non-interacting collection of hydrogen molecules and additionally investigate the effect of basis size on the multireference character of a hydrogen molecule with an elongated bond.

2 Methods

2.1 T_1

The single excitations that then produce higher excitations through the exponential ansatz of coupled cluster² have the vector of coefficients \vec{t}_1 . These are used to give the T_1 coupled cluster diagnostic,³

$$T_1 = \frac{\sqrt{\vec{t}_1 \cdot \vec{t}_1}}{\sqrt{N_{corr}}}. \quad (1)$$

Here N_{corr} is the number of correlated electrons and intermediate normalization is employed, i.e.,

$$|\Psi\rangle_{cc} = e^{\hat{T}_1 + \hat{T}_2 + \dots} |\Phi\rangle_{ref} \quad (2)$$

where $|\Psi\rangle_{cc}$ is the coupled-cluster wavefunction and $|\Phi\rangle_{ref}$ is the reference wavefunction. Spin-averaging is used so that $\|\vec{t}_1\|^2 = \frac{\|\vec{t}_{1,\alpha}\|^2 + \|\vec{t}_{1,\beta}\|^2}{2}$.

The \vec{t}_1 term results in molecular orbital relaxation in coupled cluster^{4,5} hence its magnitude suggests the appropriateness of the molecular orbitals (usually those of Hartree-Fock) used for the single reference determinant. In Ref. 6 it was suggested that the value should be less than 0.02 for a reliable CCSD⁷ calculation. The D_1 diagnostic⁸ is also based on \vec{t}_1 : $D_1 = \|\mathbf{T}\|_2 = \sqrt{\lambda_{max}(\mathbf{T}^T \mathbf{T})}$. Here \mathbf{T} is the matrix of t_1 coefficients with the location in the matrix signifying the orbital substitution.

The Brueckner orbitals^{9,10} were created when investigating if an effective single-particle Hamiltonian could improve upon that of the Hartree-Fock approach. These orbitals result in the FCI wavefunction containing no determinants with single substitutions, i.e., given the

Brueckner determinant $|B\rangle$ then

$$\langle \Psi | B_i^a \rangle = 0. \quad (3)$$

The Brueckner determinant is also the single determinant Φ that is a stationary point of the distance $\|\Psi - \Phi\|$ where Ψ is the FCI wavefunction.¹¹⁻¹³ We can see this is the case by considering wavefunctions normalized to one where we have that the distance can be written as

$$\|\Psi - \Phi\|^2 = 2 - 2\Re \langle \Psi | \Phi \rangle. \quad (4)$$

We then require that the overlap $\langle \Psi | \Phi \rangle$ is a maximum. For this to be a stationary point then an infinitesimal change in Φ will not change the overlap. By the Thouless theorem¹⁴ then $e^{\hat{T}_1} |\Phi\rangle$ is another single determinant that is not orthogonal to Φ hence

$$\langle \Psi | \Phi + \delta\Phi \rangle = \langle \Psi | e^{\hat{T}_1} |\Phi\rangle = \langle \Psi | 1 + \hat{T}_1 + O(\hat{T}_1^2) |\Phi\rangle. \quad (5)$$

As we may choose an infinitesimal value for any of the t_1 values then for this to be a stationary point we have

$$\langle \Psi | \Phi_i^a \rangle = 0. \quad (6)$$

We note that criteria for the stationary point to be a local maximum were derived in Ref. 12.

Another way of viewing the T_1 diagnostic with Hartree-Fock molecular orbitals is then as a measure of how close the Hartree-Fock determinant is to the Brueckner determinant when approximated with CCSD. If the energy minimized determinant is very different to the approximate distance minimized determinant one may well expect that the wavefunction is multireference. With one dominant determinant in the FCI expansion then they would be expected to be similar however one could envisage a wavefunction without important singly substituted determinants but with a large number of important determinants with higher

substitutions. Such a wavefunction would have the same Hartree-Fock orbitals as the exact Brueckner orbitals yet be strongly multireference. We also consider a similar idea by looking at the coefficients for single excitations in the FCI wavefunction: $T_{1,FCI}$.

To seek further information on multireference character when using CCSD we also consider the doubles amplitudes and calculate

$$T_2 = \frac{\sqrt{\vec{t}_2 \cdot \vec{t}_2}}{\sqrt{N_{corr}}}. \quad (7)$$

We use the doubles amplitudes from a CCSD calculation in Molpro.¹⁵ We note that a D_2 diagnostic has also been created¹⁶ which is similar to D_1 but uses the maximum eigenvalue (λ_{max}) of the matrices defined by $[(\mathbf{T}^o)^\top \mathbf{T}^o]_{ij} = \sum_{kab} t_{ik}^{ab} t_{jk}^{ab}$ and $[(\mathbf{T}^v)^\top \mathbf{T}^v]_{ab} = \sum_{cij} t_{ij}^{ac} t_{ij}^{bc}$ when \hat{T}_2 is written in the form $\hat{T}_2 = \frac{1}{2} \sum_{ijab} t_{ij}^{ab} \hat{E}_{ai} \hat{E}_{bj}$.

2.2 A_λ

The B_1 diagnostic¹⁷ was introduced to quantify the multireference character in a bond when using density-functional theory (DFT).^{18,19} Later the A_λ DFT diagnostic for multireference character was proposed²⁰

$$A_\lambda = \frac{1}{\lambda} \left(1 - \frac{TAE[X_\lambda C]}{TAE[XC]} \right) \quad (8)$$

where TAE is the molecular total atomization energy and $X_\lambda C$ is a functional with $\lambda\%$ Hartree-Fock exchange. Both approaches use the idea of comparing DFT results from functionals with and without Hartree-Fock contributions as it is expected that Hartree-Fock exchange will be less accurate for multireference systems.

We use $A_{25\%}$ with the PBE²¹ functional, and this functional with 25% HF exchange known as PBE0.²² These functionals were employed for the comparison of $A_{25\%}$ with other diagnostics in Ref. 20.

2.3 MR

In Ref. 23 a way of quantifying the multireference character for a given basis and set of molecular orbitals when using Monte Carlo configuration interaction (MCCI)^{24,25} was introduced:

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

We use a normalization such that $\sum |c_i|^2 = 1$. This is approximate when using non-orthogonal configuration state functions however in this work we use Slater determinants. Here $MR = 0$ signifies that there is only a single configuration while MR approaches unity as the number of important configurations increases. Previous work²⁶ found a value of 0.30 for hydrogen fluoride in an aug-cc-pVDZ basis with the canonical Hartree-Fock molecular orbitals 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 chromium dimer, which is considered a multireference problem, 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.

This approach is not invariant to the choice of orbitals, but rather gives the multireference character for a given set of molecular orbitals. The quantity MR may be changed by a transformation of the orbitals however for a given set of molecular orbitals (usually the canonical Hartree-Fock orbitals) it reveals whether the MCCI wavefunction is multireference and so should suggest if single reference approaches using the same molecular orbitals would be expected to succeed. By taking this view point there may be systems that are strongly multireference for the Hartree-Fock molecular orbitals but not for another set. This is not a contradiction, but demonstrates an approach based on a correction to the Hartree-Fock wavefunction to include dynamic correlation would not describe the system well, but in a different orbital set there may not be such a very large number of important configurations. To create an orbital invariant measure of multireference character, but one that remains

dependent upon the basis, we use the natural orbitals to give MR_{nat} . As the natural orbitals result in the most compact FCI wavefunction for a given basis then we would expect them to give the lowest value for MR. However as the natural orbitals are not constructed to minimize MR it is possible that another choice of orbitals could produce a lower value, but we would not expect this value to be substantially lower.

2.4 Natural orbitals

When the first-order reduced density matrix (γ) is written in terms of the molecular orbitals the natural orbitals are the eigenfunctions.¹ For M orbitals and N electrons, the construction of γ means it has the properties¹ that it is Hermitian with diagonal entries $0 \leq n_i \leq 1$ and $Tr(\gamma) = N$ hence the eigenvalues λ_i also sum to N .

The natural orbitals give the best approximation from a single determinant γ_0 to the FCI first-order reduced density matrix γ in that $Tr(\gamma - \gamma_0)^2$ is minimized.¹¹ This is the Frobenius norm squared of the difference ($\|\gamma - \gamma_0\|_F^2$). We demonstrate this by constructing γ and γ_0 from the same orbitals then

$$Tr(\gamma - \gamma_0)^2 = Tr(\gamma^2 + \gamma_0^2 - \gamma\gamma_0 - \gamma_0\gamma) \quad (10)$$

$$= \sum_{i=1}^M \lambda_i^2 + N - 2 \sum_{i=1}^N n_i \quad (11)$$

where we have used that γ_0 is a diagonal matrix of only ones and zeroes as it is constructed from a single determinant. We note that only the n_i depend upon the choice of orbitals. Let $A = \gamma - \gamma_0$, then A is Hermitian and so has real eigenvalues a_i hence $Tr A^2 = \sum_1^M a_i^2 \geq 0$. Therefore the best approximation is achieved by maximizing $\sum_1^N n_i$. By a theorem of Shur^{27,28} the eigenvalues of a Hermitian matrix majorize the diagonal elements, i.e., if they are ordered by size then

$$\sum_{i=1}^k n_i \leq \sum_{i=1}^k \lambda_i \quad (12)$$

hence by using the natural orbitals with highest occupation to construct a single determinant

$Tr(\gamma - \gamma_0)^2$ is minimized. The majorization of the diagonal elements is another way to see that the natural orbitals will lead to the most compact wavefunction. For the sum of the occupations of the largest N will be as large as possible but the total sum must be N so the sum of the occupations of the remaining orbitals must be as small as possible. Hence the orbitals with the least number occurring in the wavefunction will be natural orbitals.

We calculate the spin-averaged natural orbitals using the approach of Ref. 29 with Slater determinants. To create the FCI wavefunction we set $c_{\min} = 0$ in MCCI.^{24,25}

2.5 Θ_{nat}

Another approach¹ to quantify an orbital invariant multireference character is to use γ in

$$\Theta_{nat} = \frac{1}{N} Tr(\gamma - \gamma^2) = 1 - \frac{1}{N} \sum_{i=1}^M \lambda_i^2. \quad (13)$$

This was put forward¹ by P.-O. Löwdin in 1955 to express how far the wavefunction is from the single determinant of Hartree-Fock in a given basis. This reflects the number and spread of the natural orbitals rather than the configurations. If all of the first N natural orbitals are fully occupied then a single determinant with these orbitals would describe the system and Θ_{nat} is zero. We note that the natural occupation numbers have also been used as a measure of correlation in later work, for example the H_2 molecule was considered in Ref. 30.

For Θ_{nat} we look at equal number of α and β spin electrons and use the spin averaged reduced density matrix so that for M orbitals the M eigenvalues λ_i sum to N_α . Using Lagrange multipliers we have

$$X = 1 - \sum \lambda_i^2 - \mu(\sum \lambda_i - N_\alpha) \quad (14)$$

so

$$\frac{\partial X}{\partial \lambda_i} = -2\lambda_i - \mu = 0. \quad (15)$$

Hence

$$-2 \sum \lambda_i = M\mu. \quad (16)$$

so $\mu = -2N_\alpha/M$ and Θ_{nat} takes its maximum value when all of the eigenvalues of γ are equal to N_α/M resulting in

$$\Theta_{nat}^{max} = 1 - \frac{N_\alpha}{M}. \quad (17)$$

Hence we consider the quantity

$$\tilde{\Theta}_{nat} = \frac{M}{M - N_\alpha} \Theta_{nat} \quad (18)$$

as this ranges from zero to one. We note that the MCCI MR measure is also bounded above for k Slater determinants by $1 - 1/k$ however as k will generally be large compared with the number of orbitals this bound will be close to 1.

The form of Θ_{nat} is similar to that of the linear entropy $L = 1 - Tr(\gamma^2)$ of quantum information. Here γ is the first-order reduced density matrix normalized such that $Tr(\gamma) = 1$ and we now write its eigenvalues as μ_i . This has been used to quantify entanglement in bipartite systems, for example, the spatial entanglement in two-electron systems.^{31,32} By using the first-order reduced density matrix (γ) in terms of the molecular orbitals but normalized so that $Tr(\gamma) = 1$ we may quantify the bipartite entanglement with the rest of the system in a given basis, i.e., how much more do we learn about the wavefunction in this basis if we somehow could measure one electron. If the electrons are completely uncorrelated then this will be zero and will increase as the positions of the electrons become more strongly correlated. This could represent another means of calculating the multireference nature when using natural orbitals and quantifying if the system is strongly correlated. To do this we subtract the quantity for a single determinant wavefunction, written as Ψ_0 , as we want to

construct an indicator of multireference nature that is zero in this case:

$$\chi = L - L(\Psi_0) = - \sum_{i=1}^M \mu_i^2 + \frac{1}{N_\alpha}. \quad (19)$$

As we average over spins we see that $L(\Psi_0)$ is zero for two electrons but not for larger numbers of electrons.

The maximum value is then

$$\chi_{max} = \frac{1}{N_\alpha} - \frac{1}{M}. \quad (20)$$

So a scaled value with a maximum of 1 is then

$$\tilde{\chi} = \frac{N_\alpha M}{M - N_\alpha} \chi \quad (21)$$

When γ is normalized so that $Tr(\gamma) = 1$ then Θ_{nat} can be written in terms of these new eigenvalues as

$$\Theta_{nat} = 1 - N_\alpha \sum_{i=1}^M \mu_i^2. \quad (22)$$

We may then write χ in terms of Θ as $\chi = \frac{\Theta}{N_\alpha}$ but then

$$\tilde{\chi} = \tilde{\Theta}_{nat} \quad (23)$$

so the scaled result of Löwdin is also the scaled linear entropy relative to that of a single determinant.

We also consider $\tilde{\Theta}_{MO}$ where the molecular orbital occupation numbers are used rather than those of the natural orbitals. The diagonal elements of the first-order reduced density matrix in the MO basis are straightforwardly calculated²⁹ by weighting the total occurrence of each orbital by the coefficient squared of the configuration and averaging over spins. Such an approach will indicate how far the wavefunction is from a single determinant when using the molecular orbitals. $\tilde{\Theta}_{MO}$ cannot be lower than $\tilde{\Theta}_{nat}$ as it was proved in Ref. 1 that Θ

takes its minimum value when the natural orbitals are used.

2.6 Orbital entanglement

We also look at the total orbital entanglement I . The orbital entanglement was considered for single orbitals and pairs of orbitals in Ref. 33 using the approaches of Refs. 34,35. These methods were then used for classifying the importance of molecular orbitals involved in bond cleavage³⁶ where going beyond single-orbital entanglement provided further information about the nature of correlations in the system. The orbital entanglement is a form of the local or site entanglement³⁷ applied to orbitals and, for example, the site entanglement has been compared with the spatial entanglement in Ref. 38. The single orbital entanglement $s(1)_i$ for orbital i is calculated using the von Neumann entropy,

$$s(1)_i = - \sum_j w_{j,i} \ln w_{j,i}, \quad (24)$$

of which the linear entropy may be viewed as an approximation. Here $w_{j,i}$ is the occupation of type j of orbital i , where j ranges over double occupation, spin up, spin down and empty. The total value I is then found by summing over all orbitals:

$$I = \sum_i^M s(1)_i. \quad (25)$$

We also calculate this in terms of the natural orbitals to give I_{nat} . An upper bound for I is $M \ln 4$ when every type of occupation is equally likely for each orbital although this may not be a realisable maximum due to the constraint of particle number. We therefore also calculate

$$\tilde{I} = \frac{I}{M \ln 4} \quad (26)$$

and similarly \tilde{I}_{nat} .

3 Results

3.1 Equilibrium Carbon Monoxide

We first consider carbon monoxide at its equilibrium geometry³⁹ of 2.1316 Bohr and use the 3-21G basis. We freeze four orbitals to give a reasonable FCI space of 33168 Slater determinants. Initially we investigate the behavior of the correlation energy and MR with reducing the cutoff (c_{\min}) in MCCI^{24,25} with Slater determinants to indicate if, when using reasonable cutoffs, the estimate of multireference character is accurate. We use a convergence criterion of 0.001 Hartree for the energy. For $c_{\min}=0$ we note that the number of configurations had also converged demonstrating that we had reached the FCI result which we also verified with Molpro.¹⁵ We compute CCSD results with Molpro¹⁵ and DFT energies with Gaussian.⁴⁰ We calculate the approximate correlation energy using $E_{corr} = E_{approx} - E_{HF}$.

Fig. 1 shows how the correlation energy approaches the FCI value on lowering the cutoff. Even though we have used the experimental equilibrium geometry for the system we see that the correlation is lower than CCSD when using a cutoff of 0.001 for MCCI. The increased accuracy from using the natural orbitals when the cutoff is reasonably large is apparent and we note that the correlation energy represents 0.11% of the total energy for the FCI result. We see that the variability of the results due to the stochastic nature is negligible on the scale of the graph except for the largest cutoff considered where the mean for ten runs is a little different to the correlation energy from a single calculation.

In Fig. 2 we see that the indicator of multireference character, MR, does not change substantially on lowering the cutoff in that it increases from around 0.13 to 0.15 when using the Hartree-Fock molecular orbitals. The natural orbitals lower the multireference character as would be expected. Similarly to the correlation results we see that only for the largest cutoff is the standard error around the mean for ten runs noticeable on the plot.

Table 1 shows how the system would not be considered multireference when using the Hartree-Fock molecular orbitals due to the low values for MR and $\tilde{\Theta}$ shows that the cor-

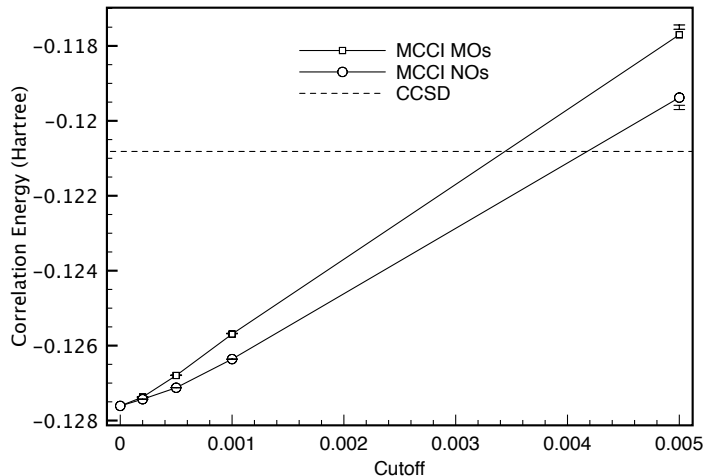


Figure 1: Correlation energy (Hartree) against c_{\min} using Slater determinants for CO with a bond length of 2.1316 Bohr with the 3-21G basis and four frozen orbitals. Standard errors around the mean from ten runs are also plotted.

relation is low. However the CCSD T_1 is a little over 0.02 and this fits in with the CCSD correlation energy being higher than MCCI even at relatively large cut-offs (Fig. 1). We also find that $T_2 = 0.088$. For the $A_{25\%}$ DFT diagnostic values between 0 and 0.1 were suggested to indicate no multireference character²⁰ hence this measure also suggests a small amount of multireference character. We find that $I = 1.26$ and $I_{nat} = 1.18$.

Table 1: Multireference indicators for carbon monoxide with a bond length of 2.1316 Bohr with the 3-21G basis and four frozen orbitals. Results use the FCI wavefunction with Slater determinants except for T_1 and $A_{25\%}$ which use CCSD and DFT respectively.

MR	MR_{nat}	Θ_{nat}	Θ_{MO}	T_1	$T_{1,FCI}$	$A_{25\%}$	I	I_{nat}
0.15	0.14	0.034	0.035	0.026	0.022	0.30	0.050	0.047

3.2 Stretched Carbon Monoxide

We next apply these measures to the previous carbon monoxide system, but with the bond length stretched to 4 Bohr. The correlation energy convergence with the cutoff of MCCI is depicted in Fig. 3 where again natural orbitals improve the accuracy of the MCCI wavefunction. Now the CCSD correlation energy is significantly higher with a value of -0.066 Hartree

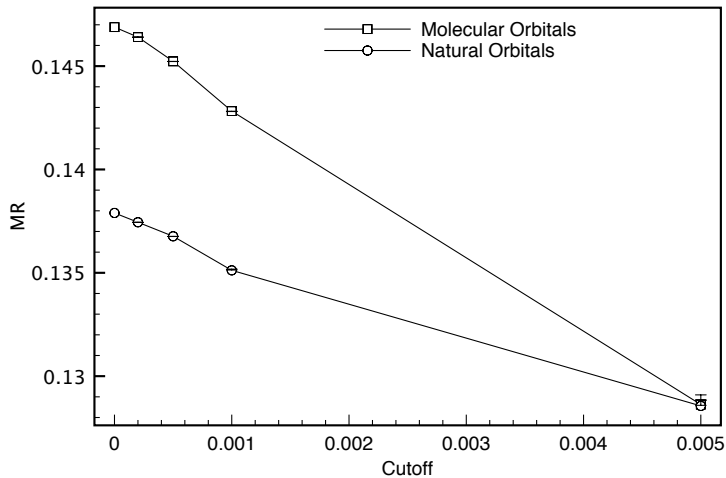


Figure 2: MR against c_{\min} using Slater determinants for CO with a bond length of 2.1316 Bohr with the 3-21G basis and four frozen orbitals. Standard errors around the mean from ten runs are also plotted.

hence we do not include it on the plot. The FCI correlation energy now represents double the fraction of the total energy at 0.23%.

In Fig. 4, we see that MR does not change substantially on lowering the cutoff but there is a marked difference when using the natural orbitals. Hence this system is very strongly multireference when using the Hartree-Fock molecular orbitals but this does not remain at such a high level when using the natural orbitals although there is still significant multireference character.

The CCSD and DFT diagnostic predict that the problem has a strong multireference nature when using the Hartree-Fock molecular orbitals (Table 2) and $T_2 = 0.22$. The lowering when moving from MR to MR_{nat} and that $\tilde{\Theta}_{nat}$ is at only 20% of its maximum value portray the system as strongly multireference but not strongly correlated. I also displays a reduction when using the natural orbitals where we find $I = 7.30$ and $I_{nat} = 5.10$. We would generally expect I and MR to decrease when natural orbitals are used. However natural orbitals do not guarantee the lowest values for these quantities except when the wavefunction may be written as a single determinant.

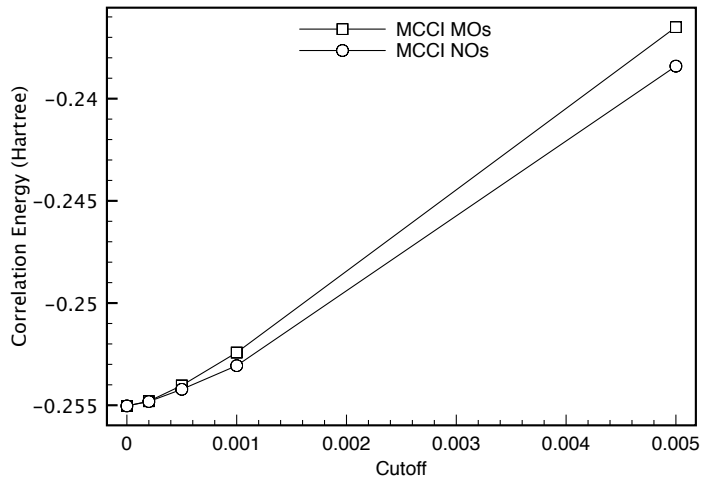


Figure 3: Correlation energy (Hartree) against c_{\min} using Slater determinants for CO with a bond length of 4 Bohr with the 3-21G basis and four frozen orbitals.

Table 2: Multireference indicators for carbon monoxide with a bond length of 4 Bohr with the 3-21G basis and four frozen orbitals. Results use the FCI wavefunction with Slater determinants except for T_1 and $A_{25\%}$ which use CCSD and DFT respectively.

MR	MR_{nat}	$\tilde{\Theta}_{nat}$	$\tilde{\Theta}_{MO}$	T_1	$T_{1,FCI}$	$A_{25\%}$	\tilde{I}	\tilde{I}_{nat}
0.96	0.69	0.20	0.30	0.096	0.56	4.22	0.29	0.20

3.2.1 Excited State

We also consider the first excited state of singlet carbon monoxide at 2.1316 Bohr using state-averaged MCCI⁴¹ with $c_{\min} = 0$. In Table 3 we see that the MR results are less affected by using natural orbitals in this case and, despite MR_{nat} being higher than for the ground state of the stretched molecule, $\tilde{\Theta}_{nat}$ is lower. Hence the system is still not strongly correlated although MR_{nat} is a little higher than for the ground state stretched geometry. Here $I = 5.08$ and $I_{nat} = 4.85$. The coefficient of the Hartree-Fock reference is so small in the FCI wavefunction that $T_{1,FCI}$ is excessively large due to intermediate normalisation and we therefore do not include it in the table.

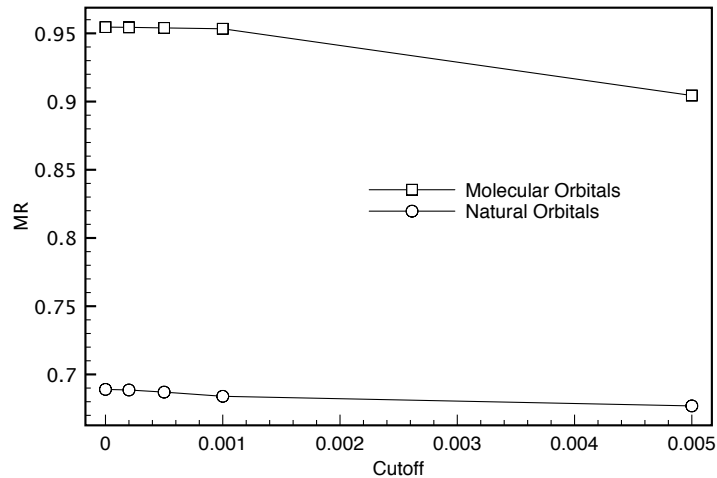


Figure 4: MR against c_{\min} using Slater determinants for CO with a bond length of 4 Bohr with the 3-21G basis and four frozen orbitals.

Table 3: Multireference indicators for the second singlet state of carbon monoxide with a bond length of 2.1316 Bohr with the 3-21G basis and four frozen orbitals. Results use the FCI wavefunction with Slater determinants.

MR	MR_{nat}	$\tilde{\Theta}_{nat}$	$\tilde{\Theta}_{MO}$	\tilde{I}	\tilde{I}_{nat}
0.80	0.78	0.16	0.20	0.20	0.19

3.3 Hydrogen Lattice

We now investigate these measures on a linear chain of 10 hydrogens with lattice spacing of 4.2 Bohr using the STO-6G basis with no frozen orbitals. The FCI wavefunction required 31752 Slater determinants in this case.

In Fig. 5 we see that the natural orbitals do not offer an improvement in the energy accuracy for the largest cutoff considered however the number of determinants reduced very slightly from 250 to 247. We force the CCSD calculation to continue to convergence and find that the CCSD correlation energy is too large, and less accurate than that found with the largest considered cutoff of 5×10^{-3} . The correlation energy of the FCI result represents 20.3% of the total energy.

We see in Fig. 6 that, similar to the other examples, the MR value does not change substantially with decreasing the cutoff in MCCI. However MR is now not monotonically

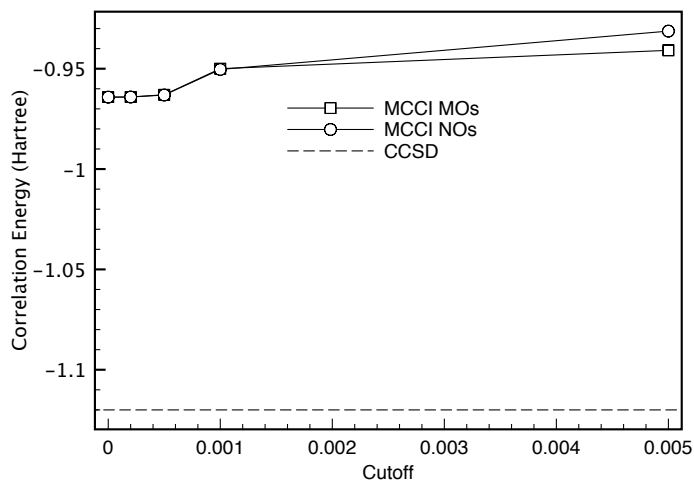


Figure 5: Correlation energy (Hartree) against c_{\min} using Slater determinants for a linear chain of hydrogens with bond lengths of 4.2 Bohr and the STO-6G basis.

increasing as the cutoff is lowered. There is no reason for an approximate wavefunction to have less multireference character than the FCI wavefunction but if the general makeup of the wavefunction does not change then one would expect MR to increase slightly as the number of configurations increases. The natural orbitals do not necessarily lower the MR value for this system although the results are very close to those using the Hartree-Fock molecular orbitals.

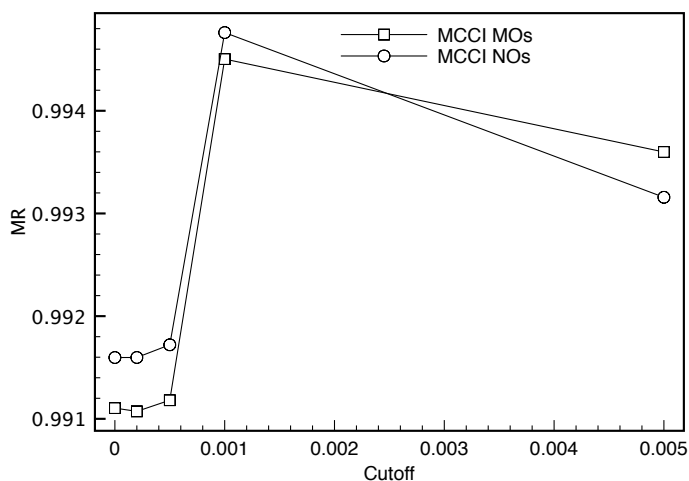


Figure 6: MR against c_{\min} using Slater determinants for a linear chain of hydrogens with bond lengths of 4.2 Bohr and the STO-6G basis.

The system has almost the maximum value for MR independent of the choice of orbitals. That $\tilde{\Theta}_{nat}$ is also close to its maximum value reveals the system as strongly correlated in addition to strongly multireference. This fits in with the large fraction of correlation energy in the total energy. The molecular orbitals are very close to the natural orbitals in this case as $\tilde{\Theta}_{nat} = \tilde{\Theta}_{MO}$ to two decimal places and this suggests why the natural orbitals do not necessarily improve the correlation energy in this case for the stochastic approach of MCCI. I is at the highest value for the systems considered in this work of 12.70 while $I_{nat} = 12.72$. Interestingly $T_{1,FCI}$ is not much larger than 0.02 as the FCI wavefunction does not contain significant determinants with only single substitutions from the Hartree-Fock reference. The CCSD approximation correctly predicts that the problem has multireference character with $T_1 = 0.037$ although this is lower than the result for stretched CO. However we find that $T_2 = 0.56$ is at its highest value of the systems considered. The large value of $A_{25\%}$ also suggests strong multireference character although a negative value was not observed in Ref. 20.

Table 4: Multireference indicators for a linear chain of 10 hydrogens with a bond length of 4.2 Bohr using the STO-6G basis with no frozen orbitals. Results use the FCI wavefunction with Slater determinants except for T_1 and $A_{25\%}$ which use CCSD and DFT respectively.

MR	MR_{nat}	$\tilde{\Theta}_{nat}$	$\tilde{\Theta}_{MO}$	T_1	$T_{1,FCI}$	$A_{25\%}$	\tilde{I}	\tilde{I}_{nat}
0.99	0.99	0.91	0.91	0.037	0.025	-4.38	0.92	0.92

For this system we also consider the effect of orbital localization. When using Molpro¹⁵ to generate Pipek-Mezey localized⁴² orbitals we find $MR = 0.99$, $\tilde{I} = 0.84$ and $\tilde{\Theta} = 0.91$.

3.4 Size Intensity

We use the STO-6G basis and compare results for one H_2 molecule with a bond length of 1.6 Å with four such molecules separated by 10 Å. As these subsystems are essentially non-interacting then the correlation strength should not increase and can be termed size-intensive.⁸ The fraction of the correlation energy in the FCI energy is high (10.3%) due to

the stretched bond length and, as would be expected, does not change when the number of molecules increases.

As there are only two basis functions and two electrons for H_2 , the configuration space is completely described by going up to double excitations from the reference determinant. Hence CISD describes the system exactly in this basis. A collection of non-interacting hydrogen molecules is then described exactly by CCSD as the coupled cluster ansatz means this approach is size extensive. From Table 5 we can infer that the FCI wavefunction contains negligible single excitations ($T_{1,FCI} = 0$) when using the Hartree-Fock molecular orbitals. Because CCSD can produce the FCI wavefunction in this case then T_1 is zero and remains so for four molecules. T_2 is suggestive of multireference character, when compared with the other examples in this work, and decreases slightly from 0.31 to 0.29 on moving to the larger system. The DFT diagnostic suggests that the single molecule has multireference character but the non-interacting collection is no more challenging.

However we see that the MR quantity increases with the number of molecules (Table 5). That the MR quantity is not size intensive reflects that the system has a configuration interaction wavefunction that is indeed more multireference. This is demonstrated by CISD describing a single molecule exactly but when applied to four separated molecules the error is 0.11 Hartree compared with FCI. I also does not display size intensity nor size extensivity as it increases from 0.87 to 4.88 and \tilde{I} also increases. The use of natural orbitals seems not to substantially change the measures, hence in this case the natural orbitals are essentially equivalent to the molecular orbitals. This measure suggests that the collection of non-interacting subsystems is no more correlated than the individual molecule with N electrons. For a collection of K such non-interacting subsystems we would expect to have K copies of the natural orbitals of one molecule with only the location of the orbitals changing and NK electrons. As $\tilde{\Theta}_{nat}$ divides the natural orbital occupation by the number of electrons (Eq. 13) then $\tilde{\Theta}_{nat}$ will be size intensive. We note that the difference in MR with $\tilde{\Theta}_{nat}$ could be made more severe by considering more copies of a less multireference subsystem.

Table 5: Hydrogen molecules with a bond length of 1.6 \AA separated by 10 \AA using the STO-6G basis. Results use the FCI wavefunction with Slater determinants except for T_1 and $A_{25\%}$ which use CCSD and DFT respectively.

	MR	MR_{nat}	$\tilde{\Theta}_{nat}$	$\tilde{\Theta}_{MO}$	T_1	$T_{1,FCI}$	$A_{25\%}$	\tilde{I}	\tilde{I}_{nat}
H_2	0.27	0.27	0.53	0.53	0.00	0.00	1.59	0.31	0.31
$4H_2$	0.72	0.73	0.53	0.53	0.00	0.00	1.59	0.44	0.47

For the single molecule we attribute that $\tilde{\Theta}_{nat}$ is larger than MR due to the use of only two orbitals in the description of the system and that we scale Θ_{nat} so it lies between zero and one. We see in Fig. 7 that by increasing the basis size $\tilde{\Theta}_{nat}$ decreases below MR. The initial reduction on moving from a minimal basis set is large but then the results do not vary much with basis size for this system.

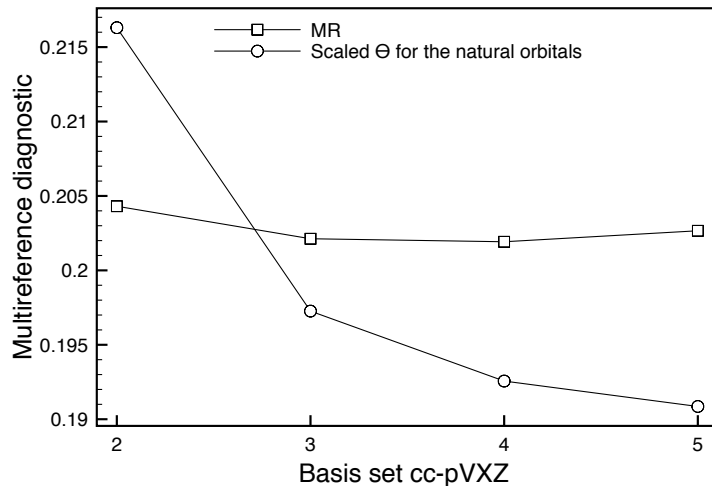


Figure 7: MR and $\tilde{\Theta}_{nat}$ against basis set (cc-pVXZ where $X = 2$ represents cc-pVDZ etc.) calculated using the FCI wavefunction using Slater determinants for a hydrogen molecule with a bond length of 1.6 \AA .

3.5 Summary

We have demonstrated that an approach¹ of P.-O. Löwdin (Θ_{nat}) to quantify the distance of a wavefunction from the Hartree-Fock solution can be viewed as a way of calculating the correlation. In that it is equivalent to using the linear entropy for a calculation of the spatial

entanglement relative to a single determinant when both measures are suitably scaled so they take values between 0 and 1.

We saw that an approach to calculate the multireference character of the wavefunction (MR) was not strongly affected by the cutoff used in Monte Carlo configuration interaction when compared with the full configuration interaction result although this and the error in the correlation energy could be lowered by using natural orbitals.

By applying a range of multireference indicators to three example systems we illustrated that strongly multireference was not necessarily strongly correlated. We saw, with the basis sets employed, that carbon monoxide with an equilibrium geometry was not strongly multireference nor strongly correlated. When using a stretched geometry the system was strongly multireference when using the Hartree-Fock molecular orbitals but this was noticeably less multireference when the natural orbitals were employed and $\tilde{\Theta}_{nat}$ was not large enough to suggest strong correlation. As quantum chemistry calculations usually employ the Hartree-Fock molecular orbitals, and the exact natural orbitals are unavailable without implementing a full configuration interaction, then MR still offers useful information about the challenging nature of the system for approaches based around a single determinant.

For a linear chain of ten hydrogen atoms with a minimal basis we observed that the MR measure was almost at its maximum value regardless of the orbital choice as was $\tilde{\Theta}_{nat}$ demonstrating that this wavefunction is both very strongly multireference and very strongly correlated. We note that although Θ takes its minimum when the natural orbitals are used, this is not guaranteed for MR or the orbital entanglement (I) but we would not expect them to be far from their minimum. We observed that localized orbitals could give a lower value than natural orbitals for I .

It was found that a coupled-cluster singles and doubles diagnostic (T_1) and a density-functional theory diagnostic ($A_{25\%}$) gave a correct general prediction of the multireference character for these systems. By also considering a coupled-cluster singles and doubles T_2 diagnostic we found that these systems could be correctly ordered in terms of their correlation

strength.

We finally looked at a collection of essentially non-interacting hydrogen molecules. Here we saw that the configuration interaction wavefunction became more multireference as the number of molecules increased but the correlation as quantified by $\tilde{\Theta}_{nat}$ did not and the latter measure is size-intensive. In this special case the multireference nature due to the replication of the non-interacting subsystems can be overcome by size extensive methods based on a single reference that can be thought of as exploiting the structure of the wavefunction. The basis size was seen to not dramatically affect the multireference character for a hydrogen molecule with a stretched bond except when using a minimal basis set.

We therefore suggest that *MR* can be used to give the multireference nature of a configuration interaction wavefunction for a given basis and set of molecular orbitals, while $\tilde{\Theta}_{nat}$ can be used to quantify the correlation regardless of the choice of molecular orbitals although still dependent on the basis set.

In this work we saw that the multireference nature of a configuration interaction wavefunction may be affected by, individually or in combination, the choice of orbitals, increasing numbers of non-interacting subsystems and the amount of electron correlation.

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