# Investigating Multireference Character and Correlation in Quantum Chemistry

J. P. Coe* and M. J. Paterson*

Institute of Chemical Sciences, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, United Kingdom

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 approach[1] 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 combinations 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 the 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 noninteracting hydrogen molecules and the effect of basis size on the multireference character of a stretched hydrogen molecule.
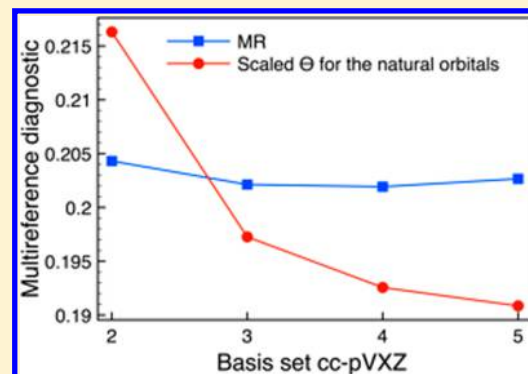
1. INTRODUCTION

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 wave function 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 correlation can become increasingly blurred as the wave function 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 wave function 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 noninteracting 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 cluster[2] have the vector of coefficients $\vec{t}_1$. These are used to give the T_1 coupled cluster diagnostic,[3]

$$T_1 = \frac{\sqrt{\vec{t}_1 \cdot \vec{t}_1}}{\sqrt{N_{corr}}} \tag{1}$$

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

$$|\Psi\rangle_{cc} = e^{\hat{T}_1+\hat{T}_2+\cdots}|\Phi\rangle_{ref} \tag{2}$$

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

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 CCSD[7] calculation. The D_1 diagnostic[8] is also based on $\vec{t}_1$: $D_1 = \|\mathbf{T}\|_2 = [\lambda_{\max}(\mathbf{T}^{\mathrm{T}}\mathbf{T})]^{-1}$. 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 wave function containing no determinants with single substitutions, i.e., given the Brueckner determinant $|B\rangle$, then

$$\langle\Psi|B_i^a\rangle = 0 \tag{3}$$

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

$$\| \Psi - \Phi\|^2 = 2 - 2\Re\langle\Psi|\Phi\rangle \tag{4}$$

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 theorem,[14] then $e^{\hat{T}_1}|\Phi\rangle$ is another single determinant that is not orthogonal to Φ, hence

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

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

$$\langle\Psi|\Phi_i^a\rangle = 0 \tag{6}$$

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 from the approximate distance minimized determinant, one may well expect that the wave function is multireference. With one dominant determinant in the FCI expansion, then they would be expected to be similar; however one could envisage a wave function without important singly substituted determinants but with a large number of important determinants with higher substitutions. Such a wave function 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 wave function: $T_{1,FCI}$.

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

$$T_2 = \frac{\sqrt{\vec{t}_2 \cdot \vec{t}_2}}{\sqrt{N_{corr}}} \tag{7}$$

We use the doubles amplitudes from a CCSD calculation in Molpro.[15] We note that a D_2 diagnostic has also been created,[16] which is similar to D_1 but uses the maximum eigenvalue ($\lambda_{\max}$) of the matrices defined by $[(\mathbf{T}^o)^{\mathrm{T}}\mathbf{T}^o]_{ij} = \sum_{kab} t_{ik}^{ab}t_{jk}^{ab}$ and $[(\mathbf{T}^v)^{\mathrm{T}}\mathbf{T}^v]_{ab} = \sum_{cij} t_{ij}^{ac}t_{ij}^{bc}$ when $\hat{T}_2$ is written in the form $\hat{T}_2 = {}^1/_2\sum_{ijab} t_{ij}^{ab}\hat{E}_{ai}\hat{E}_{bj}$.

2.2. A_λ. The B_1 diagnostic[17] 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 proposed[20]

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

where TAE is the molecular total atomization energy and $X_\lambda C$ is a functional with λ% 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 PBE[21] 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 the Monte Carlo configuration interaction (MCCI)[24,25] was introduced:

$$MR = \sum_i |c_i|^2 - |c_i|^4 \tag{9}$$

We use a normalization such that $\sum|c_i|^2 = 1$. This is approximate when using nonorthogonal 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 work[26] 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 wave function. 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 found[23] that the MR of the MCCI wave function 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 wave function is multireference and so should suggest if single reference approaches using the same molecular orbitals would be expected to succeed. By taking this viewpoint 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 that an approach based on a correction to the Hartree−Fock wave function 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 wave function 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 properties[1] 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

$$Tr(\gamma - \gamma_0)^2 = Tr(\gamma^2 + \gamma_0^2 - \gamma\gamma_0 - \gamma_0\gamma) \tag{10}$$

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

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 $\sum_i^N n_i$. 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

$$\sum_{i=1}^{k} n_i \leq \sum_{i=1}^{k} \lambda_i \tag{12}$$

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 wave function. 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 natural orbitals will have the least number of orbitals occurring in the wave function.

We calculate the spin-averaged natural orbitals using the approach of ref 29. with Slater determinants. To create the FCI wave function we set $c_{min} = 0$ in MCCI.[24,25]

2.5. Θ_{nat}. Another approach[1] to quantify an orbital invariant multireference character is to use γ in

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

This was put forward[1] by Löwdin in 1955 to express how far the wave function 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 an 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

$$X = 1 - \sum \lambda_i^2 - \mu\left(\sum \lambda_i - N_\alpha\right) \tag{14}$$

so

$$\frac{\partial X}{\partial \lambda_i} = -2\lambda_i - \mu = 0 \tag{15}$$

Hence

$$-2\sum \lambda_i = M\mu \tag{16}$$

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

$$\Theta_{nat}^{max} = 1 - \frac{N_\alpha}{M} \tag{17}$$

Hence, we consider the quantity

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

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 wave function 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 wave function, written as Ψ_0, as we want to construct an indicator of multireference nature that is zero in this case:

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

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

$$\chi_{max} = \frac{1}{N_\alpha} - \frac{1}{M} \tag{20}$$

So a scaled value with a maximum of 1 is then

$$\tilde{\chi} = \frac{N_\alpha M}{M - N_\alpha}\chi \tag{21}$$

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

$$\Theta_{nat} = 1 - N_\alpha \sum_{i=1}^{M} \mu_i^2 \tag{22}$$

We may then write χ in terms of Θ as $\chi = \Theta/N_\alpha$, but then

$$\tilde{\chi} = \tilde{\Theta}_{nat} \tag{23}$$

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 calculated[29] 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 wave function 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 and 35. These methods were then used for classifying the importance of molecular orbitals involved in bond cleavage[36] 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 entanglement[37] 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,

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

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:

$$I = \sum_i^M s(1)_i \tag{25}$$

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 realizable maximum due to the constraint of particle number. We therefore also calculate

$$\tilde{I} = \frac{I}{M \ln 4} \tag{26}$$

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

3. RESULTS

3.1. Equilibrium Carbon Monoxide. We first consider carbon monoxide at its equilibrium geometry[39] of 2.1316 Bohr and use the 3-21G basis. We freeze four orbitals to give a reasonable FCI space of 33 168 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 Molpro[15] and DFT energies with Gaussian.[40] We calculate the approximate correlation energy using $E_{corr} = E_{approx} - E_{HF}$.

Figure 1 shows how the correlation energy approaches the FCI value on lowering the cutoff. Even though we have used
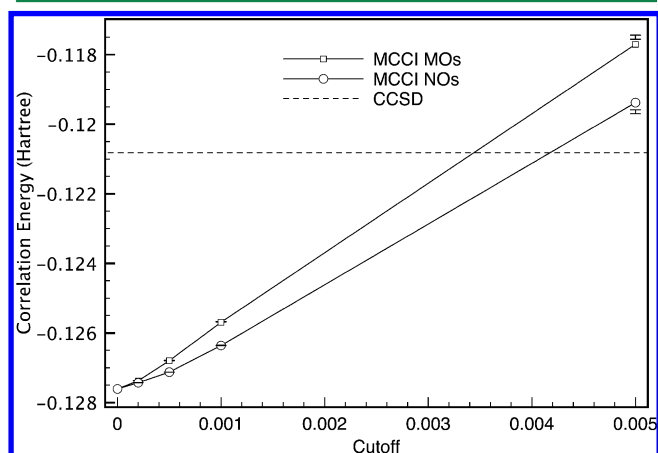

Figure 1. Correlation energy (Hartree) against c_{min} using Slater determinants for CO with a bond length of 2.1316 Bohr with the 3-21G basis and four frozen orbitals. Standard errors around the mean from 10 runs are also plotted.

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 10 runs is a little different to the correlation energy from a single calculation.

In Figure 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
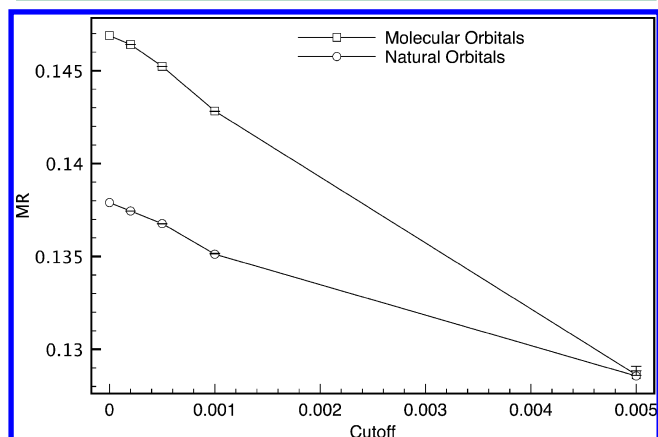

Figure 2. MR against c_{min} using Slater determinants for CO with a bond length of 2.1316 Bohr with the 3-21G basis and four frozen orbitals. Standard errors around the mean from 10 runs are also plotted.

Table 1. Multireference Indicators for Carbon Monoxide with a Bond Length of 2.1316 Bohr with the 3-21G Basis and Four Frozen Orbitals[a]

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

[a]Results use the FCI wavefunction with Slater determinants except for T_1 and $A_{25\%}$ which use CCSD and DFT, respectively.

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 10 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 correlation 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 cutoffs (Figure 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 character;[20] hence this measure also suggests a small amount of multireference character. We find that $I = 1.26$ and $I_{nat} = 1.18$.

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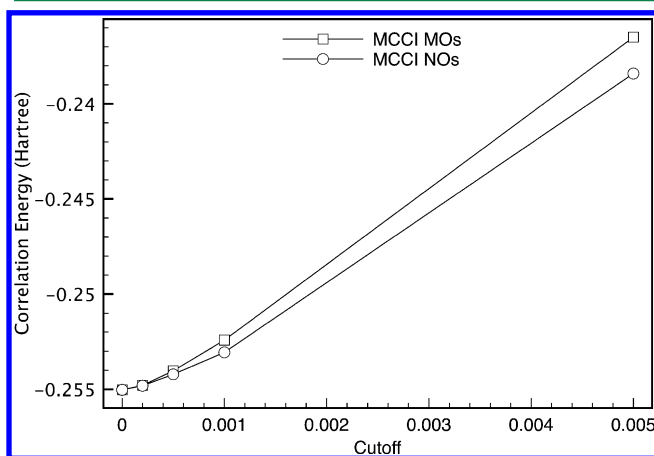
Figure 3. Correlation energy (Hartree) against c_{min} using Slater determinants for CO with a bond length of 4 Bohr with the 3-21G basis and four frozen orbitals.

where again natural orbitals improve the accuracy of the MCCI wave function. Now the CCSD correlation energy is significantly higher with a value of −0.066 Hartree; 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 Figure 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
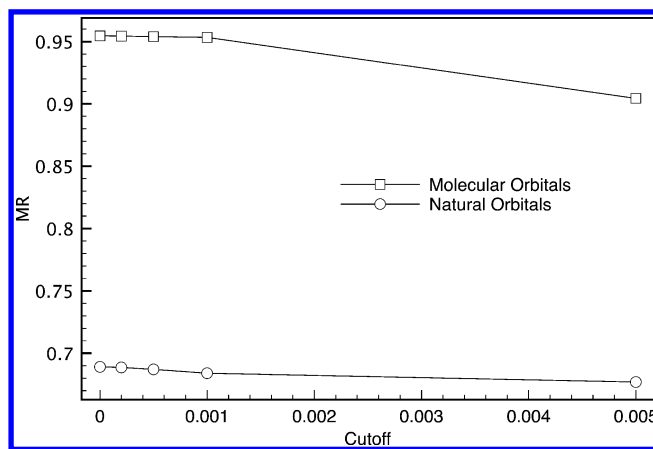
Figure 4. MR against c_{min} using Slater determinants for CO with a bond length of 4 Bohr with the 3-21G basis and four frozen orbitals.

Table 2. Multireference Indicators for Carbon Monoxide with a Bond Length of 4 Bohr with the 3-21G Basis and Four Frozen Orbitals[a]

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

[a]Results use the FCI wavefunction with Slater determinants except for T_1 and $A_{25\%}$, which use CCSD and DFT, respectively.

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 wave function may be written as a single determinant.

3.2.1. Excited State. We also consider the first excited state of singlet carbon monoxide at 2.1316 Bohr using state-averaged MCCI[41] with $c_{min} = 0$. In Table 3, we see that the MR results

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[a]

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

[a]Results use the FCI wavefunction with Slater determinants.

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 wave function that $T_{1,FCI}$ is excessively large due to intermediate normalization, and we therefore do not include it in the table.

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 wave function required 31 752 Slater determinants in this case.

In Figure 5, we see that the natural orbitals do not offer an improvement in the energy accuracy for the largest cutoff
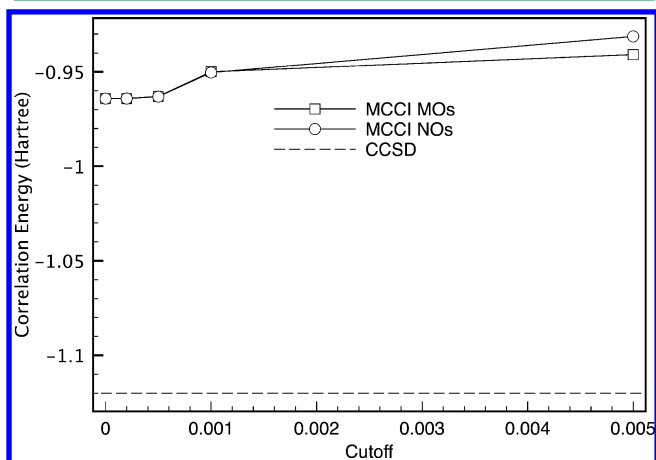

Figure 5. Correlation energy (Hartree) against c_{min} using Slater determinants for a linear chain of hydrogens with bond lengths of 4.2 Bohr and the STO-6G basis.

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 Figure 6 that, similar to the other examples, the MR value does not change substantially with decreasing the
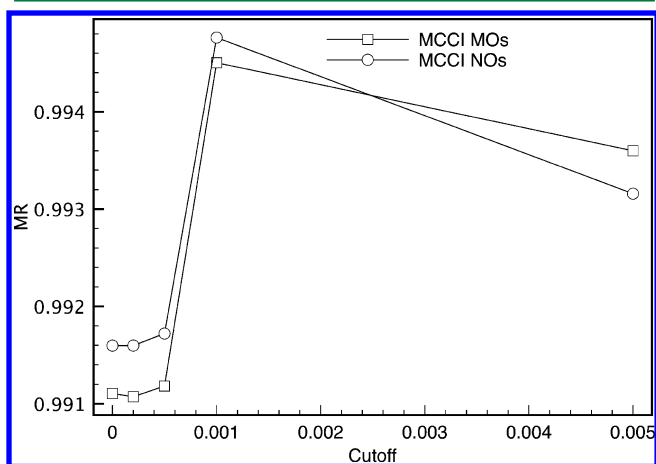

Figure 6. MR against c_{min} using Slater determinants for a linear chain of hydrogens with bond lengths of 4.2 Bohr and the STO-6G basis.

cutoff in MCCI. However, MR is now not monotonically increasing as the cutoff is lowered. There is no reason for an approximate wave function to have less multireference character than the FCI wave function, but if the general makeup of the wave function 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.

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 wave function 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 $T_1 = 0.037$ (see Table 4), 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.

For this system, we also consider the effect of orbital localization. When using Molpro[15] to generate Pipek-Mezey localized[42] orbitals, we find MR = 0.99, $\tilde{I} = 0.84$, and $\tilde{\Theta} = 0.91$.

3.4. Size Intensivity. 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 noninteracting, 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 noninteracting 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 wave function contains negligible single excitations ($T_{1,FCI} = 0$) when using the Hartree−Fock molecular orbitals. Because CCSD can produce the FCI wave function 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

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[a]

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

[a]Results use the FCI wavefunction with Slater determinants except for T_1 and $A_{25\%}$ which use CCSD and DFT, respectively.

Table 5. Hydrogen molecules with a bond length of 1.6 Å separated by 10 Å 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

has multireference character, but the noninteracting 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 wave function 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 intensivity 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 noninteracting subsystems is no more correlated than the individual molecule with N electrons. For a collection of K such noninteracting 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.

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 $\tilde{\Theta}_{nat}$ so it lies between zero and one. We see in Figure 7 that by increasing the basis size, $\tilde{\Theta}_{nat}$

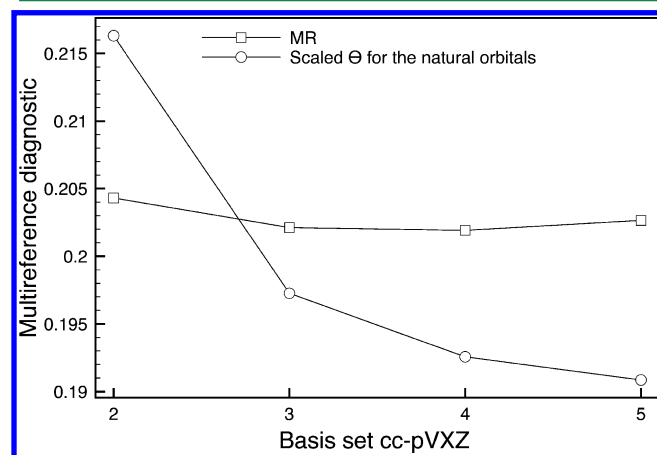**Figure 7.** MR and $\tilde{\Theta}_{nat}$ against basis set (cc-pVXZ where X = 2 represents cc-pVDZ etc.) calculated using the FCI wave function using Slater determinants for a hydrogen molecule with a bond length of 1.6 Å.

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.

3.5. Summary. We have demonstrated that the approach[1] of Löwdin (Θ_{nat}) to quantify the distance of a wave function 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 wave function (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 10 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 wave function 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 noninteracting hydrogen molecules. Here, we saw that the configuration interaction wave function 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 noninteracting subsystems can be overcome by size extensive methods based on a single reference that can be thought of as exploiting the structure of the wave function. 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 wave function 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 wave function may be affected by, individually or in combination, the choice of orbitals, increasing numbers of noninteracting subsystems, and the amount of electron correlation.

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: J.Coe@hw.ac.uk.
*E-mail: M.J.Paterson@hw.ac.uk.
Notes
The authors declare no competing financial interest.

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