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Comparison of the Quadratic Configuration Interaction and Coupled Cluster Approaches to Electron Correlation Including the Effect of Triple Excitations

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Abstract

The recently proposed quadratic configuration interaction (QCI) method is compared with the more rigorous coupled cluster (CC) approach for a variety of chemical systems. Some of these systems are well represented by a single-determinant reference function and others are not. We consider the infinite-order singles and doubles correlation energy, the perturbational triples correlation energy, and a recently devised diagnostic for estimating the importance of multireference effects. We have also calculated the spectroscopic constants of CuH, the equilibrium structure of cis-(NO)₂ and the binding energies of Be₃, Be₄, Mg₃ and Mg₄ using both approaches. The diagnostic for estimating multireference character clearly demonstrates that the QCI method becomes less satisfactory than the CC approach as non-dynamical correlation becomes more important, in agreement with a perturbational analysis of the two methods and the numerical estimates of the triple excitation energies they yield. The results for CuH show that the differences between the two methods become more apparent as the chemical system under investigation becomes more multireference in nature and the QCI results consequently become less reliable. Nonetheless, when the system of interest is dominated by a single reference determinant both QCI and CC give very similar results.

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Introduction

There has been considerable controversy surrounding the quadratic configuration interaction (QCI) electron correlation method suggested by Pople, Head-Gordon and Raghavachari¹ (PHR) in 1987. PHR derived their method from the singles and doubles configuration interaction (CISD) equations by adding the minimum number of terms which ensure exact size-consistency at the singles and doubles level (denoted QCISD). The resulting equations have the following form:

$$\langle \Psi_0 | H - E | (1 + T_1 + T_2) \Psi_0 \rangle = 0 \quad (1)$$

$$\langle \Psi_i^a | H - E | (1 + T_1 + T_2 + T_1 T_2) \Psi_0 \rangle = 0 \quad (2)$$

$$\langle \Psi_{ij}^{ab} | H - E | (1 + T_1 + T_2 + (1/2)T_2^2) \Psi_0 \rangle = 0 \quad (3)$$

Here Ψ_0 is the Hartree-Fock determinant, and T_1 and T_2 are cluster operators generating singly- and doubly-excited configurations Ψ_i^a and Ψ_{ij}^{ab} multiplied by cluster amplitudes t_i^a and t_{ij}^{ab} . Perhaps the least appealing aspect of the QCISD method is the fact that because the singles and doubles equations (2) and (3) are modified in different ways, there is no formally defined wave function associated with QCISD. This has little consequence in practice, however, as molecular properties may be determined efficiently as analytical energy derivatives.

Several papers²⁻⁵ have appeared recently pointing out that QCI theory can be obtained from coupled-cluster theory (CC) by omission of terms from the coupled-cluster singles and doubles (CCSD) equations

$$\langle \Psi_0 | H - E | (1 + T_1 + T_2 + (1/2)T_1^2) \Psi_0 \rangle = 0 \quad (4)$$

$$\langle \Psi_i^a | H - E | (1 + T_1 + T_2 + (1/2)T_1^2 + T_1 T_2 + (1/3!)T_1^3) \Psi_0 \rangle = 0 \quad (5)$$

$$\begin{aligned} \langle \Psi_{ij}^{ab} | H - E | (1 + T_1 + T_2 + (1/2)T_1^2 + T_1 T_2 + (1/3!)T_1^3 \\ + (1/2)T_2^2 + (1/2)T_1^2 T_2 + (1/4!)T_1^4) \Psi_0 \rangle = 0 \end{aligned} \quad (6)$$

As Bartlett has discussed⁵, the use of an exponential cluster ansatz for the wave function guarantees size-extensivity (correct scaling), and this property is then unaffected by the omission of specific contributions like those by which QCISD and CCSD differ. In fact, QCI limited to double excitations is identical to CC theory limited to doubles

(referred to as CPMET⁶ or CCD), as was pointed out by PHR and as is easily seen by comparing (1) and (3) with (4) and (6) after omitting terms in T_1 . Furthermore, it has been shown² that all computational expressions of order n^6 (where n is the number of orbitals) that appear in CCSD theory also appear with the same coefficients in QCISD, so that the ultimate computational cost of efficient implementations of the two methods will be virtually identical. This is what is observed when an efficient, vectorized CCSD code⁷ is modified to perform QCISD calculations. Which method is used would then seem to be largely a matter of taste unless the terms in CCSD which are omitted in QCISD cause the CCSD procedure to give superior (or inferior) results.

There has been dissension about this last point. In response to comments asserting that the CCSD approach was more securely founded than QCISD³, Pople and coworkers⁴ expressed the opinion that as long as both approaches are exact for the two-electron problem, and are size-consistent, there is no reason to favor one approach over the other. More recently, however, Raghavachari *et al.*⁸ have performed a perturbational analysis of the QCI and CC methods, following the earlier perturbational analysis of CC methods by Kucharski and Bartlett⁹ and found that CCSD is more complete than QCISD at fifth-order in Møller-Plesset perturbation theory (MP5). MP5 is the lowest order in which QCISD and CCSD differ, although neither method is fully correct to fourth order in perturbation theory (MP4) as the contribution of connected triple excitations is not included. Hence there is at least agreement that from the point of view of a perturbation theory analysis CCSD (or CC theory in general) is the more complete method.²⁻⁹

One important aspect of a reliable single-reference correlation treatment is that it should be possible to determine when multireference effects become large enough to compromise the results. We have recently introduced for this purpose a diagnostic denoted \mathcal{T}_1 , defined by¹⁰

$$\mathcal{T}_1 = ||\mathbf{t}_1||/N^{1/2} \quad (7)$$

where \mathbf{t}_1 is the vector of single excitation amplitudes determined by solving (4) through (6) and N is the number of electrons correlated in the CCSD treatment. Our previous investigation¹⁰ showed that a \mathcal{T}_1 value of 0.02 or greater indicates a degree of multireference character large enough to cast serious doubt on the reliability of single reference correlation treatments. We also observed this diagnostic to be a

more reliable measure of multireference character than either the reference function weight or individual excited configuration weights in a singles and doubles CI (CISD) treatment. In the present work we shall investigate the QCISD analog of \mathcal{T}_1 , denoted \mathcal{Q}_1 and obtained from the formula (7) and the amplitudes from eqs. (1) through (3).

In addition to the QCISD method, PHR also introduced a size-consistent, perturbational approach designed to incorporate the major effects of connected triple excitations and to correctly account for disconnected triple excitations. This method is similar to the +T approach suggested by Bartlett and co-workers^{11,12} for CCSD except that an additional term arising from MP5 is also included. The MP5 term involves the interaction of singles and disconnected triples and its inclusion is argued to be a more consistent treatment of triple excitations. We discuss several approaches for including the effect of triple excitations in the next section: these approaches can be applied in either CCSD or QCISD calculations.⁸

The central theme of the present study is a numerical investigation and comparison of the QCISD and CCSD methods and the various ways of including the effects of triple excitations. PHR presented some comparisons of QCISD with CCSD and full CI (FCI) benchmarks, but the latter are available for a rather limited range of bonding situations and only total energies were compared. We have investigated a large number of molecules (and atoms) which vary from being strongly dominated by the Hartree-Fock reference configuration to exhibiting a large degree of multireference behavior. Our study includes the binding energies of Be and Mg trimers and tetramers, computed with the QCI and CC methods and compared with accurate multireference CI (MRCI) values. In addition, we have determined the equilibrium bond length and harmonic frequency of CuH and the equilibrium structure of *cis*-(NO)₂ at various levels of theory.

The next section contains a brief summary of the theoretical methods used together with a more detailed discussion of the various corrections for triple excitations. The results, including discussion, are presented in the third section and our conclusions in the final section.

Computational methods

Most of the chemical systems considered in this study have been investigated

previously and full references to the basis sets and geometries are given in Tables 1 and 2. The reader is referred to the earlier work for a detailed description of basis sets and geometries. We include here only a brief description of these data. Table 1 gives the size of the primitive and contracted basis, our designation and the reference from which the orbital exponents and contraction coefficients may be obtained. In forming the designation for each basis two rules have been followed. First, a generally contracted atomic natural orbital (ANO) basis set¹³ is denoted by square brackets, e.g., [4321], containing the number of contracted *s*, *p*, *d* and *f* functions, respectively. Second, a basis set constructed using a segmented contraction scheme is designated as 7s3p2d1f, for example. In most cases where a segmented contraction is used, the contraction has been performed over the core atomic orbitals, allowing maximum flexibility in the valence region. For those cases where the polarization function orbital exponents are not given in the appropriate earlier reference the exponents are listed in Table 1. Where more than one level of polarization function has been included (e.g., 7s3p2d Be) the exponents for each level are separated by a semicolon.

Only the valence electrons were correlated in the CC and QCI procedures. For segmented contracted basis sets virtual molecular orbitals that are core counterparts were deleted from the correlation procedure. The molecular orbitals were taken from a closed-shell Hartree-Fock calculation. The diagnostic \mathcal{T}_1 ¹⁰ and the QCISD analog Q_1 were defined in the Introduction.

An estimate of the energy lowering due to connected triple excitations was evaluated using the CCSD+T(CCSD)¹¹ (or QCISD+T(QCISD)) and CCSD(T)⁸ (or QCISD(T)¹) approximations. For simplicity we abbreviate CCSD+T(CCSD) to CCSD+T, and likewise QCISD+T. These +T methods involve using the converged t_2 amplitudes from the CCSD (or QCISD) equations in evaluating the connected triples contribution to fourth order in perturbation theory¹⁴, denoted MP4(T). The CCSD(T) and QCISD(T) approaches include an additional term, denoted MP5(ST), arising in fifth order of perturbation theory and involving the interaction of triple excitations with singles^{1,8}. This term is included in the CCSDT-1 method and other more elaborate CC treatments^{11,12}.

The formula for $E_{(T)}$ (the CCSD(T) triples energy) has been given previously in a spin-orbital basis⁸, but not in a spin-adapted form for the closed-shell case. We

therefore present the necessary equations here in order to aid future implementations.

$$E_{(T)} = \frac{1}{3} \sum_{ijk} \sum_{abc} (W_{ijk}^{abc} + V_{ijk}^{abc}) \times \quad (8)$$

$$(4W_{ijk}^{abc} + W_{kij}^{abc} + W_{jki}^{abc} - 4W_{kji}^{abc} - W_{ikj}^{abc} - W_{jik}^{abc}) / D_{ijk}^{abc}$$

where V_{ijk}^{abc} and W_{ijk}^{abc} are given by

$$V_{ijk}^{abc} = (jb|kc)t_i^a + (ia|kc)t_j^b + (ia|jb)t_k^c, \quad (9)$$

$$W_{ijk}^{abc} = P_{ijk}^{abc} \left[\sum_f (ia|bf)t_{kj}^{cf} - \sum_m (ia|jm)t_{mk}^{bc} \right], \quad (10)$$

and the permutation operator P_{ijk}^{abc} is defined by

$$P_{ijk}^{abc}(abc) = (abc) + (bac) + (cba) + (acb) + (cab) + (bca). \quad (11)$$

D_{ijk}^{abc} is the triples energy denominator

$$D_{ijk}^{abc} = f_{ii} + f_{jj} + f_{kk} - f_{aa} - f_{bb} - f_{cc}. \quad (12)$$

The matrix elements f_{ii} etc are diagonal elements of the closed-shell Fock operator, and the t_i^a , t_{ij}^{ab} amplitudes are those defined by Scuseria *et al.*¹⁵. In the above equations indices i , j and k refer to occupied spatial orbitals while a , b and c refer to unoccupied orbitals. E_{+T} — the MP4(T) energy expression — is obtained by omitting V_{ijk}^{abc} from equation (8). The QCISD(T) triples energy is obtained by replacing V_{ijk}^{abc} in equation (8) with $2V_{ijk}^{abc}$ and using the QCISD rather than the CCSD amplitudes in equations (9) and (10). This factor of 2 appears because while part of the disconnected triples contribution to the MP5 energy is included in the CCSD equations, this is not true for the QCISD equations. We note that equation (10) for W_{ijk}^{abc} leads directly to the spin-adapted form of t_{ijk}^{abc} presented by Noga and Bartlett¹⁶ and Scuseria and Schaefer¹⁷ for the CCSDT-1 method.

The CC and QCI energies were determined with VCCSD, a vectorized closed-shell CCSD program.⁷ The integral and SCF calculations and integral transformations were performed with MOLECULE-SWEDEN¹⁸. All calculations were performed on the NASA Ames ACF and NAS Facility CRAY Y-MP/832 computers.

Results and Discussion

A. Total Energies

The geometries and basis sets used for the systems studied here are listed in Table 2. The unique bond length is specified for the Be_3 , Mg_3 , Be_4 and Mg_4 clusters. The trimers form an equilateral triangle and the tetramers adopt a tetrahedral structure. The pentamers, Be_5 and Mg_5 , adopt a trigonal bipyramidal structure and their geometry is specified by two bond lengths. The first refers to the distance between equatorial atoms and the second gives the distance from an apical atom to an equatorial atom. The bond lengths and bond angles for FOOF, $(\text{NO})_2$ and FN NF are the DZP MP2 structures reported in Ref. 19. Total energies for all systems considered are listed in Table 3.

We consider first the CCSD and QCISD correlation energies in Table 3. It is apparent from the results that the terms present in CCSD but missing in the QCISD procedure reduce the magnitude of the correlation energy: in all cases reported here the QCISD correlation energy is larger in magnitude than the CCSD correlation energy. It is noteworthy that the difference between the two methods is smallest for those systems strongly dominated by a single reference configuration (that is, those that have the smallest values of \mathcal{T}_1 or \mathcal{Q}_1). Clearly, the terms in eqs (5) and (6) that are missing in eqs (2) and (3) become more important as the dominance of the single reference configuration is reduced. For example, the CCSD and QCISD correlation energies for Ar are very close, at -0.23426 and $-0.23428 E_h$ respectively, but for O_3 (where the SCF configuration is a much poorer reference) the difference between the QCISD correlation energy of $-0.59237 E_h$ and the CCSD value (-0.58861) is two orders of magnitude larger. This observation is consistent for all of the systems included in Table 3, so that the better the SCF wave function approximates the true wave function, the better the agreement between the QCISD and CCSD correlation energies. Where they disagree, the QCISD value is larger in magnitude than the CCSD result.

A similar trend is found when comparing the MP4 part of the triples energy, MP4(T), obtained with the CCSD and QCISD amplitudes. The energy lowering due to the connected triples is always larger in absolute value when determined with the QCISD doubles amplitudes. Note that the MP4(T) contribution is necessarily negative

(provided that the occupied orbitals are lower in energy than the virtual orbitals). Conversely, the fifth-order contribution MP5(ST) is observed to be positive for all the systems studied here (although there is no formal reason for this to be so), and it is also larger when evaluated with the QCISD amplitudes than with the CCSD amplitudes. There is no doubt that for the MP5 term much of the difference between QCI and CC is due to the factor of two difference in the energy contribution discussed above, but this alone does not explain the larger QCI MP5 term for any of the systems investigated here.

Since the MP4(T) term is negative and the MP5(ST) term is observed to be positive, and given that these are both larger in magnitude when evaluated with the QCISD amplitudes than when determined with the CCSD amplitudes, it is not certain, *a priori*, which method will yield the larger $E_{(T)}$. In fact, in all cases the total energy lowering due to triple excitations is always greater when evaluated with the CCSD amplitudes rather than with the QCISD amplitudes. However, since the QCISD energy is lower than the CCSD energy, the QCISD(T) energy is usually lower than the CCSD(T) value. As a consequence of the cancellation discussed above the energy difference $E_{CCSD(T)} - E_{QCISD(T)}$ is smaller than $E_{CCSD} - E_{QCISD}$.

The \mathcal{T}_1 and \mathcal{Q}_1 diagnostics reported in Table 3 follow the same trend as the singles and doubles correlation energy. Thus the two diagnostics are very similar for those molecules which are well represented by a single determinant reference wave function (i.e., for those cases where \mathcal{T}_1 and \mathcal{Q}_1 are small⁸) but begin to exhibit differences as the multireference nature of the chemical system increases. For example, the \mathcal{T}_1 and \mathcal{Q}_1 diagnostics for Ar are both 0.0025 (\mathcal{Q}_1 is actually slightly larger than \mathcal{T}_1 in the fifth decimal place) but for FOOF \mathcal{T}_1 and \mathcal{Q}_1 are 0.0308 and 0.0345, respectively. It is also important to note that in all cases investigated here $\mathcal{Q}_1 > \mathcal{T}_1$, demonstrating that QCISD results will deteriorate faster than CCSD results as non-dynamical correlation becomes more important. Up to diagnostic values of 0.02 (our suggested threshold for the onset of important non-dynamical correlation effects), or even somewhat larger values for the Be and Mg clusters, the similarity of the \mathcal{Q}_1 and \mathcal{T}_1 results suggest that \mathcal{Q}_1 should provide a useful criterion for the adequacy of a single reference treatment. However, \mathcal{Q}_1 will become somewhat too pessimistic (i.e. will increase too rapidly) as the multireference character increases: the best numerical example of this is given by

CuH, where T_1 and Q_1 have the values 0.0356 and 0.0557, respectively. In the next section we will discuss what effect this has on computed spectroscopic constants.

B. CuH

It has been shown²⁰ that CuH is a difficult system to describe correctly because of the strong mixing of different atomic asymptotes of Cu in the molecule. Since the results for CuH exhibit the largest differences between the QCI and CC approaches, it is of interest to investigate this molecule in more detail. Table 4 lists the equilibrium bond length and harmonic frequency obtained from a parabolic fit in $1/r$ of three points around the minimum. Comparing the SCF results with those from QCI and CC it is evident that electron correlation shortens the CuH bond length and increases the harmonic frequency. On examining the CCSD, CCSD+T and CCSD(T) values a consistent picture is obtained: the CCSD r_e value is shorter than the SCF result, while ω_e is larger; the CCSD+T bond length is even shorter than the CCSD value and the CCSD+T harmonic frequency is correspondingly larger. As expected, the MP5(ST) term somewhat reduces the effect of the triples (consistent with the behavior of the total energy), and the CCSD(T) spectroscopic constants lie between the CCSD and CCSD+T values.

The QCI procedure, on the other hand, does not yield a consistent picture of the effects of including electron correlation. Specifically, r_e decreases in the order SCF > QCISD > QCISD+T > QCISD(T) and ω_e increases in the order SCF < QCISD(T) < QCISD < QCISD+T, so there is no one-to-one correspondence between changes in bond length and changes in frequency. In addition, the changes to ω_e are much larger in magnitude than was the case for the CC procedure: the effect of the MP5(ST) term is -149 cm^{-1} using the QCISD amplitudes but only -33 cm^{-1} using CCSD amplitudes. Such large effects at higher orders of perturbation theory suggest that the domain in which the QCI-based expansion can be safely applied is much smaller than for CCSD. It certainly appears that neither QCISD nor the versions that include perturbational triples are capable of treating the non-dynamical correlation effects in CuH adequately.

C. Energy Differences

Table 5 presents a comparison of the CCSD(T), QCISD(T) and MRCI binding energies for the Be_n and Mg_n ($n = 3,4$) clusters and a comparison of the CCSD(T) and

QCISD(T) estimates of the barrier to inversion of CH_3^- . The MRCI results are taken from Ref. 21, where it was also shown that the CCSD procedure was incapable of predicting accurate binding energies for small Be and Mg clusters. Such clusters represent something of a special case since in the dissociation limit, assuming only the valence electrons are correlated, a size-consistent, infinite-order singles and doubles procedure (such as CCSD or QCISD) represents a full CI. As the atoms begin to interact these procedures are, of course, no longer equivalent to a full CI and consequently there is a bias towards the dissociation limit in the description of bond formation. The binding energies of these systems are thus usually underestimated by the more elaborate single-reference correlation treatments, and this is well illustrated in Table 5 by comparing the CCSD and QCISD results with those obtained from MRCI wave functions. On the other hand, the CCSD(T) and QCISD(T) methods reproduce the accurate MRCI values very well, and there is little difference between the CC and QCI approaches for these systems. The CCSD(T) and QCISD(T) binding energies of the trimers are still about 2 kcal/mole too small, but for Mg_4 the CCSD(T) and QCISD(T) binding energies are nearly equal to the MRCI value and for Be_4 they are actually larger than the MRCI value. We may therefore draw two conclusions from these results: for small Be and Mg clusters there is little difference between the CCSD(T) and QCISD(T) energies and, more importantly, these procedures appear to yield very good binding energies for small Be and Mg clusters. We should note here that this conclusion does not apply to the very smallest clusters, the dimers, for which only the MRCI treatment is satisfactory. Bonding in the higher oligomers of Be and Mg is quite unlike that in the dimers, and it is difficult to draw any conclusions about bonding in the former from calculations on the latter. Thus Sosa *et al.*²² have shown that the full triples contribution T_3 from CCSDT strongly affects the results for Be_2 , but the significance of this for the higher oligomers is not clear.

The excellent Be and Mg cluster binding energy predictions from CCSD(T) and QCISD(T) are somewhat unexpected, and merit further consideration. Given the large degree of non-dynamical correlation in Be and Mg clusters, it is not clear why even a very elaborate single-reference correlation treatment should be appropriate. The importance of connected triple excitations for metallic systems has been known for some time²³, though there is no published evidence that a simple perturbation

theory estimate of their energy contribution would be adequate, and in any event it is not clear how relevant considerations based on metallic systems are to these small clusters. While the MP4(T) energy contribution is large, as can be seen from the total energies of the clusters given in Table 3, the MP5(ST) contribution is much smaller (by some two orders of magnitude). It would therefore appear that the disconnected triple excitation contribution is small, suggesting that whether it is partly included (as would be the case for CCSD) or neglected, as in QCISD, makes little difference. This is again rather surprising: in view of the large non-dynamical correlation effects and strong orbital relaxation indicated by the \mathcal{T}_1 and \mathcal{Q}_1 diagnostics, disconnected triples might have been expected to be important in describing these clusters. In fact, the ratio of the MP4(T) and MP5(ST) contributions is larger than for any other system in Table 3 except for the argon atom, and the latter is the system most strongly dominated by the SCF reference configuration of any in the table. What makes this ratio so large is that the MP4(T) energies for the Be and Mg clusters are much larger than for other systems with the same number of electrons correlated. Overall, the results presented here support the rather surprising conclusion that a perturbation theory estimate of the energy lowering due to triple excitations works very well for small Be and Mg clusters. It is possible that this is due to a cancellation between the omission of terms in connected quadruple and higher excitations and the omission of terms in higher orders of perturbation theory involving connected triples, but this is beyond the scope of the present work. Whatever the cause, if the perturbational triples estimate works well for a variety of cluster sizes it will allow the determination of accurate binding energies and structures for larger Be and Mg clusters, for which the MRCI procedure used for the trimers and tetramers becomes impractically expensive.

The barrier to planarity in CH_3^- is found to be 2.3 kcal/mole using both the CCSD(T) and QCISD(T) methods. This value is slightly less than the CCSD estimate (2.4 kcal/mole). Thus triple excitations affect the barrier to planarity very little, and the CC and QCI approaches yield essentially identical results. This is consistent with the value for the \mathcal{T}_1 and \mathcal{Q}_1 values given in Table 3, which suggest that non-dynamical effects are relatively unimportant for describing the inversion process.

D. cis-(NO)₂

Our final comparison concerns the equilibrium structure of cis-(NO)₂, which is

not known reliably, although there has been a recent determination of the vibrationally averaged rotational constants.²⁴ The two gas-phase structural determinations which have been published differ substantially in the N-N distance and the NNO angle.^{25,26} The results of several theoretical studies^{19,27-29} also yield equilibrium structures with large differences. In a recent study¹⁹ a range of single-reference correlation treatments, including perturbation theory and the CCSD method, were used to compute equilibrium structures. The predictions showed a marked variation with the type of correlation treatment, but little variation with respect to the one-particle basis set (provided this was of at least DZP quality). In view of the strong dependence of the predicted geometry on the correlation treatment, it is of interest to investigate how the CCSD and QCISD results (with and without triple excitations) compare. A full comparison of computed and experimentally deduced structures would require anharmonic force field data for vibrational averaging, but here we are concerned only with the relative performance of the QCI and CC approaches.

Comparison of the QCISD and CCSD equilibrium structures of Table 6 shows relatively small differences, with the CCSD N-N distance being slightly longer and the NNO angle slightly smaller. The QCISD(T) and CCSD(T) equilibrium structures are also similar, although the differences between the CC and QCI values for the N-N distance and the NNO angle are somewhat larger when the triples are included. This is probably related to the importance of non-dynamical correlation for cis-(NO)₂. The effect of triple excitations themselves is much larger than any difference between the QCI and CC results. The CCSD(T) N-N distance is much longer than the CCSD value and the CCSD(T) NNO angle is 6.8° smaller than the CCSD result. As with CuH, the correlation effects on the structure from higher than double excitations augment the effects due to single and double excitations: there is no cancellation between the various contributions.

Conclusions

Comparison of the singles and doubles electron correlation energy for several molecules demonstrates that the QCISD correlation energy is larger in magnitude than the CCSD correlation energy. Conversely, the sum of the MP4(T) and MP5(ST) energy, when evaluated with the CCSD t_i^a and t_{ij}^{ab} amplitudes, is generally larger in

magnitude than when evaluated with the corresponding QCISD amplitudes. As a result, it is not obvious how the QCISD(T) and CCSD(T) correlation energies will compare: our observation is that for all systems we have studied, other than CuH, the QCISD(T) total correlation energy is larger in magnitude than the CCSD(T) result. A very significant observation is that the inclusion of triple excitations generally reduces substantially the difference between the CC and QCI treatments: the difference $E_{CCSD(T)} - E_{QCISD(T)}$ is usually smaller than the difference $E_{CCSD} - E_{QCISD}$. The only exception is again CuH, for which the triples energy evaluated using the QCISD amplitudes is only half that given by the CCSD.

The \mathcal{T}_1 and \mathcal{Q}_1 diagnostics demonstrate conclusively that the QCI method is less able to describe non-dynamical electron correlation than the CC method, at least at the level of single and double excitations. Perturbational inclusion of triple excitations assists to some extent, but even here QCI is less stable than CC for extreme cases like CuH. While inclusion of still higher excitations would presumably improve the stability of both CC and QCI methods, this seems to be impractical at present. The diagnostic suggested in Ref. 10 allows an easy identification of troublesome cases, and correlates well with the stability of the QCI method: as the value of the diagnostic \mathcal{T}_1 becomes larger, the the difference between the QCI and CC results becomes greater, and the QCI values become less satisfactory. Conversely, where \mathcal{T}_1 is small the system is well described by a single reference configuration and the differences between the QCI and CC results are small.

Somewhat surprisingly, the CCSD(T) and QCISD(T) methods both give very good binding energies for the Be₃, Be₄, Mg₃ and Mg₄ clusters as determined by comparison with very accurate MRCI results. Our previous study of these systems shows that the correlation effect on binding is entirely due to dynamical correlation, but that since non-dynamical correlation effects on the total energy are large and must be accounted for properly in order to describe the dynamical correlation accurately, reliable binding energies require an accurate treatment of both non-dynamical and dynamical correlation. With large non-dynamical correlation effects it is not surprising that triple excitations are very important in a single-reference-based treatment, but it is surprising that the perturbation theory estimates are so good. It is conceivable that there is a cancellation between the (neglected) infinite-order effects of triples and the effects of

connected quadruple and higher excitations, but at present CCSD(T) appears to offer the best prospect for obtaining reliable structures and binding energies for Be and Mg pentamers and larger clusters.

In answer to the question of which method, QCISD or CCSD, should be used, our numerical investigations suggest that where the wave function is dominated by a single reference configuration there is little difference between the results of the two methods, and so there are only formal reasons for preferring CCSD. Commonly, the effects of including triple excitations bring the two sets of results into even better agreement. The \mathcal{T}_1 and \mathcal{Q}_1 diagnostics provide a useful guide to increasing importance of non-dynamical correlation effects (although the former diagnostic seems more reliable than the latter), and to situations where neither CCSD or QCISD are suitable. In cases in which non-dynamical correlation is beginning to influence the results, QCISD seems to be less widely applicable, in terms of showing erratic behavior, than CCSD. This cannot always be corrected by including triple excitations, at least not at the level of perturbational inclusion of triples, so that in such cases the CC-based methods would be preferable.

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Table 1
Basis set designations and definitions used in this study.

Atom	Primitive Basis	Designation	Reference	Polarization Exponents
H	4s	DZP	30,31	0.75
H	6s2p	TZ2P	30,33	1.0,0.33
H	8s6p	[32]	13	-
He	8s2p	6s2p	32	1.0,0.33
Li	9s4p	4s3p	32	-
Be	12s5p2d	7s3p2d	32	0.3,0.1
Be	12s7p4d2f	[5321]	21	-
C	10s6p2d	TZ2P ^a	30,33	1.5,0.35
C	11s7p4d1f	TZ4Pf+diffuse ^b	30,33	2.25,0.75,0.25,0.06;0.8
N	9s5p1d	DZP	30,31	0.80
N	10s6p2d	TZ2P ^a	30,33	1.5,0.35
O	9s5p1d	DZP	30,31	0.85
O	10s6p2d	TZ2P ^a	30,33	1.5,0.35
F	9s5p1d	DZP	30,31	1.0
F	10s6p2d	TZ2P ^a	30,33	1.5,0.35
Ne	10s6p2d	TZ2P ^c	32	4.5,1.3
Mg	12s9p2d	6s5p2d	34	0.3,0.1
Mg	20s15p8d	[531]	21	-
Mg	21s16p8d6f	[7631]	21	-
Ar	17s12p8d6f	[8753]	13	-
Cu	14s11p6d3f	8s6p4d1f	35	-

^a The 5s3p contraction of reference 33 was used.

^b The 5s4p contraction of reference 33 was used.

^c A 5s3p contraction, similar to those given in reference 33, was constructed.

Table 2
Basis sets and molecular geometries^a.

Molecule	Basis Set	Geometry	Reference
CuH	b	2.850	20
Be ₃	7s3p2d	4.273	21
Be ₄	7s3p2d	3.915	21
Be ₅ ^c	7s3p2d	3.831,3.929	21
Mg ₃	6s5p2d	7.522	21
Mg ₄	6s5p2d	6.102	21
Mg ₅ ^c	6s5p2d	5.967,6.667	21
FOOF	DZP	d	19
(NO) ₂	DZP	d	19
cis-FNNF	DZP	d	19
trans-FNNF	DZP	d	19
TS-FNNF ^e	DZP	d	19
O ₃	DZP	2.406,117.1°	36
CH ₃ ⁻	TZ4Pf+diffuse	2.070,110.8°	7
p-CH ₃ ⁻ ^f	TZ4Pf+diffuse	2.044	7
HF	TZ2P	1.734	-
H ₂ O	TZ2P	1.809,104.8°	-
CH ₄	TZ2P	2.052	-
Ne	TZ2P	-	-
Ar	[8753]	-	-

^a Bond lengths are in atomic units, a_0 .

^b The Cu basis from Table 1 and the [32] hydrogen ANO basis set.

^c Trigonal bipyramidal. The first distance corresponds to a side of the triangular base and the second to a side of the pyramid.

^d The MP2/DZP equilibrium structures of Ref. 19.

^e Transition state of cis-trans isomerization.

^f Planar CH₃⁻; D_{3h} symmetry.

Table 3
 Comparison of the \mathcal{T}_1 , \mathcal{Q}_1 diagnostics and the various
 CC and QCI correlation energies^a.

Molecule	\mathcal{T}_1	E_{CCSD}	E_T^b	\mathcal{Q}_1	E_{QCISD}	E_T^b
CuH	0.0356	-0.43617	-0.02153	0.0557	-0.44247	-0.02683
			0.00477			0.01711
Be ₃	0.0360	-0.15322	-0.01390	0.0370	-0.15334	-0.01411
			0.00018			0.00041
Be ₄	0.0318	-0.21197	-0.02488	0.0337	-0.21267	-0.02548
			0.00056			0.00128
Be ₅	0.0290	-0.28023	-0.03796	0.0313	-0.28125	-0.03864
			0.00086			0.00199
Mg ₃	0.0127	-0.10740	-0.00297	0.0128	-0.10742	-0.00297
			0.00002			0.00005
Mg ₄	0.0204	-0.16172	-0.01386	0.0214	-0.16215	-0.01404
			0.00033			0.00072
Mg ₅	0.0226	-0.20338	-0.01797	0.0241	-0.20397	-0.01828
			0.00046			0.00103
FOOF	0.0308	-0.81039	-0.05186	0.0345	-0.81574	-0.05542
			0.00480			0.01194
(NO) ₂	0.0209	-0.71363	-0.03960	0.0225	-0.71855	-0.04114
			0.00409			0.00929
cis-FNNF	0.0182	-0.69366	-0.02780	0.0200	-0.69805	-0.02917
			0.00319			0.00729
trans-FNNF	0.0163	-0.69131	-0.02670	0.0176	-0.69536	-0.02773
			0.00293			0.00655
TS-FNNF	0.0251	-0.70960	-0.03611	0.0311	-0.71652	-0.04056
			0.00505			0.01381

Table 3 continued

Molecule	T_1	E_{CCSD}	E_T^b	Q_1	E_{QCISD}	E_T^b
O ₃	0.0284	-0.58861	-0.03501 0.00311	0.0309	-0.59237	-0.03709 0.00760
CH ₃ ⁻	0.0139	-0.22726	-0.01009 0.00039	0.0144	-0.22777	-0.01018 0.00079
p-CH ₃ ⁻	0.0111	-0.22737	-0.01017 0.00036	0.0113	-0.22786	-0.01023 0.00074
HF	0.0104	-0.23704	-0.00562 0.00046	0.0107	-0.23774	-0.00573 0.00097
H ₂ O	0.0096	-0.24139	-0.00693 0.00031	0.0098	-0.24190	-0.00700 0.00064
CH ₄	0.0073	-0.20143	-0.00567 0.00018	0.0074	-0.20168	-0.00569 0.00035
Ne	0.0065	-0.23922	-0.00349 0.00022	0.0066	-0.23955	-0.00352 0.00046
Ar	0.0025	-0.23426	-0.00803 0.00002	0.0025	-0.23428	-0.00803 0.00005

^a All correlated wave functions are based upon SCF molecular orbitals. Only valence electrons have been included in the correlation procedure. Correlation energies are in atomic units, E_h .

^b The upper value corresponds to the MP4(T) term and the lower value corresponds to the MP5(ST) term. All triples energies were evaluated with the converged singles and doubles amplitudes. See the text for further details.

Table 4The equilibrium bond distance and harmonic frequency of CuH.^a

Method	$r_e(a_0)$	$\omega_e(\text{cm}^{-1})$
SCF	2.952	1687
QCISD	2.830	1830
QCISD+T	2.813	1948
QCISD(T)	2.803	1799
CCSD	2.835	1781
CCSD+T	2.807	1852
CCSD(T)	2.814	1819

^a The basis set described in table 3 was used.

Table 5
 Comparison of QCISD(T) and CCSD(T)
 in determining energy differences.^a

Molecule	Basis Set	Geometry	ΔE_{CC}	ΔE_{QCI}	ΔE_{MRCI}^b
Be ₃	[5321]	4.199 ^c	20.4(11.3)	20.5(11.4)	22.4
Be ₄	[5321]	3.900 ^c	79.4(63.5)	79.8(64.0)	77.3
Mg ₃	[7631]	6.373 ^c	5.7(1.7)	5.8(1.8)	6.3
Mg ₄	[531]	6.102 ^c	15.9(8.1)	16.0(8.3)	16.2
CH ₃ ⁻	TZ4Pf+diffuse	d	2.3(2.4)	2.3(2.4)	-

^a For the Be and Mg clusters ΔE refers to the dissociation energy whereas for CH₃⁻ it is the barrier to planarity. Bond lengths given in atomic units and energy differences in kcal/mole. Values in parentheses are the singles and doubles results.

^b Taken from Ref. 21.

^c Optimized MRCI geometries from Ref. 21.

^d Geometries for the planar and pyramidal CH₃⁻ given in table 2.

Table 6
The equilibrium structure of cis-(NO)₂.^a

Parameter	CISD	QCISD	CCSD	QCISD(T)	CCSD(T)
Energy	-259.111315	-259.173099	-259.168101	-259.208994	-259.208030
T_1 or Q_1	-	0.02281	0.02094	0.02218	0.02111
r_{N-N}	1.742	1.927	1.931	2.319	2.354
r_{N-O}	1.164	1.181	1.177	1.181	1.180
$\angle NNO$	106.4°	102.2°	102.1°	95.8°	95.3°

^a The DZP basis set described in table 1 was used. The CISD results are taken from reference 19. Energies are in Hartrees, E_h , and bond lengths are in Å.