Theoretical Investigations of the Structures and Binding Energies of Be_n and Mg_n (n=3-5) Clusters

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Abstract

We have determined the equilibrium geometries and binding energies of Be and Mg trimers, tetramers and pentamers using single and double excitation coupled cluster (CCSD) and complete active space self-consistent-field (CASSCF) multireference configuration interaction (MRCI) wave functions in conjunction with extended atomic basis sets. Our best estimates of the cluster binding energies are 24, 83 and 110 kcal/mole for Be_3, Be_4 and Be_5; and 9, 31 and 41 kcal/mole for Mg_3, Mg_4 and Mg_5, respectively. A comparison of the MRCI and CCSD results shows that even the best single-reference approach (limited to single and double excitations) is not capable of quantitative accuracy in determining the binding energies of Be and Mg clusters.

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I. Introduction

Theoretical studies of clusters of metal atoms were originally undertaken as a technique for modelling bulk material, an approach termed cluster abstraction. More recently, however, small metal clusters have become of interest in their own right, with emphasis on the properties of the clusters themselves. This work has been motivated in large part by sophisticated molecular beam experiments in which small clusters of atoms are generated and studied. Small metal clusters are a fruitful area for collaboration between experimentalists and *ab initio* quantum chemists because the size of the clusters is often small enough to allow accurate calculations, and because the experimental and theoretical investigations often yield complementary information.

While accurate calculations on closed-shell polyatomic molecules are possible for systems of 10–15 atoms, it is seldom possible to perform calculations of similar accuracy on metal clusters of this size. Clusters of transition metals generally have a very complicated electronic structure, because of the many low-lying electronic states that can be generated from coupling open d-shell orbitals, and the strong near-degeneracy and correlation effects within the d-shells. Clusters of Al atoms[1] are simpler to treat because there are no d electrons, but problems still arise because of the coupling of open shells. The Be and Mg atoms have closed-shell ground states, and previous work[2-6] has established that small Be clusters also have closed-shell ground states. These systems might therefore appear more amenable to theoretical investigation. However, both Be and Mg have very strong $s - p$ near-degeneracy effects in their atomic ground states, and this may seriously complicate the description of Be and Mg clusters.

SCF calculations on Be and Mg clusters have demonstrated the importance of $s - p$ hybridization in forming effective metal-metal bonds. The energy penalty associated with hybridization is similar in Be and Mg, but, as the analysis by Bauschlicher and co-workers[3] shows, Mg–Mg bonds are much weaker than Be–Be bonds and the binding energy (and degree of hybridization) of a Be cluster is generally considerably larger than that of a Mg cluster of the same size. The influence of electron correlation, both dynamical and non-dynamical (near-degeneracy), on Be cluster binding has been studied by several authors,[2-6] and we shall review their

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findings here.

The smallest Be "cluster" is Be_2, which has proved to be one of the most difficult first-row diatomics to describe theoretically.[7-12] Very sophisticated treatments incorporating both non-dynamical and dynamical correlation effects are required for an adequate description, and several methods that perform well for closed-shell systems fail to give even a qualitatively correct result for the binding energy. Of course, the binding energy in Be_2 is small (2.3 kcal/mole[13]), and the failure of some treatments in this case is not necessarily grounds for pessimism for larger clusters. Be_3 and Be_4 have both been studied previously with a variety of theoretical methods. Multireference configuration interaction (MRCI) calculations have been performed for Be_3 by Harrison and Handy,[4] and these probably provide the best estimate to date of the binding energy. This was computed to be 19 kcal/mol, but by extrapolating for the effects of higher excitations and basis set extensions Harrison and Handy suggested that the true binding energy would be 24±2 kcal/mol. Perturbation theoretic studies by Whiteside and co-workers[2] showed that the Møller-Plesset expansion converges slowly for Be_3, and these authors preferred the binding energy computed using a coupled cluster treatment with double excitations (CCD), but their CCD value of 6 kcal/mole seems much too small. This is presumably due to a failure of the single-reference configuration model, in view of Harrison and Handy's results.

The most elaborate of the earlier theoretical treatments of Be_4 are single-reference calculations: a single and double excitation CI (CISD) treatment, including Davidson's correction for higher excitations, suggested a binding energy of 66 kcal/mole.[4] Rohlfing and Binkley[5] performed more extensive many-body perturbation theory (MBPT) studies than those in the earlier work of Whiteside et al., and observed erratic behavior at successively higher orders of treatment: their most elaborate MBPT treatment (full fourth-order) gave a binding energy of 85 kcal/mol, while their CCD binding energy was only 59 kcal/mol. Harrison and Handy[4] performed single-reference coupled electron-pair approximation (CEPA) calculations, obtaining a value of 65 kcal/mol, and estimating the true value to be 75±5 kcal/mol. Unlike Be_2 and Be_3, Be_4 is actually bound by a substantial amount at the SCF level and is thus the smallest Be cluster for which the binding is not due entirely to cor-

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relation effects. This is attributable to the major role $s - p$ hybridization plays in the bonding.[3] The larger binding energies and increasing role of $s - p$ hybridization on going from Be_2 to Be_3 and Be_4 suggests that a single-reference correlation treatment might become more appropriate as the cluster size increases, and we shall investigate this question in some detail in the present study.

Considerably fewer investigations have examined the dynamical correlation effects in Mg clusters larger than the dimer. Pacchioni and Koutechy studied the trimer through pentamer using a multireference CI approach, but computational restrictions required the use of an unpolarized basis set and as a result the binding energies were severe underestimates.[14] This basis set limitation has been partially addressed in subsequent calculations on Mg_4, which produced estimates of the binding energy between 7.8 and 11.9 kcal/mol. [3,15,16] However, in light of a more recent study on the dimer[17] it is probable that this is still a substantial underestimate of the true binding energy in Mg_4.

A difficulty with predicting an accurate bond length for Be_2 is the small variation in energy with changes in geometry — the potential energy curve is very flat. In such cases substantial errors in geometry predictions can occur from small errors in the predicted energetics. Consideration must also be given to the fact that if only valence correlation is included, some wave functions, e.g. coupled-pair functional (CPF) or CCSD, will give the same result as a full CI at the separated atom limit for any number of Be atoms. In other words, within a given one-particle basis, there is no error in the correlation treatment at the dissociation limit so that any error in describing electron correlation in the cluster will immediately give rise to errors in the predicted structures. This effect will be exacerbated by the flatness of the potential surface. On the other hand, a method such as finite-order Møller-Plesset perturbation theory or CISD, which fails to reproduce the full CI results at infinity as well as at equilibrium, may happen to give good results through a fortitious cancellation of errors. In Mg clusters this phenomenon is even more apparent, because the binding energies are very small and the surfaces even flatter. Combined with the decrease in importance of $s - p$ hybridization in Mg relative to Be, this suggests that very elaborate correlated wave functions may be required to obtain reliable predictions of bond lengths and binding energies for small Mg

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clusters, a hypothesis partly confirmed by recent calculations[17] on Mg_2.

In the present work, we shall explore the structure and bonding of several small Be and Mg clusters in some detail, investigating the performance of different theoretical methods and how this is affected by near-degeneracy effects. Our largest calculations employ very large one-particle basis sets and elaborate correlation treatments, enabling us to estimate the binding energies of the clusters to within an uncertainty of a few kcal/mole or better. In the next section we describe the various computational methods used, and then in section III we discuss the computed results. The discussion is divided into three parts: a detailed comparison of different computational methods in predicting the structures and binding energies of Be_3, Be_4, and Be_5, a similar comparison for Mg clusters of the same size, and the use of the most reliable results in estimating the true binding energies of the clusters. Our conclusions are presented in section IV.

II. Computational methods

For comparison with previous *ab initio* investigations we begin our studies with one-particle basis sets that have been used previously. For Be a $7s$ segmented contraction of van Duijneveldt's $12s$ primitive basis[18] is supplemented with the three contracted p functions given by Dykstra *et al.* [19] . The smallest basis used is then obtained by adding two sets of d-type Gaussian functions[8] (orbital exponents $\alpha_d = 0.30, 0.10$) which gives a basis designated $7s3p2d$. The second basis augments the first by adding a single f function[20] ($\alpha_f = 0.26$). For Mg the $6s5p$ contraction of the $12s9p$ primitive set of McLean and Chandler[21] is supplemented with two sets of d functions with orbital exponents of $\alpha_d = 0.30$ and 0.10. For these Be and Mg basis sets all Cartesian components of the d and f type functions were included.

It has been shown in previous studies on these systems that reasonably large one-particle basis sets for Be and Mg are necessary in order to accurately evaluate the binding energies and geometries (*i.e.*, through f type functions). Therefore, we have investigated the use of atomic natural orbital (ANO) basis sets[22] in order to minimize the resulting $n-$particle expansion length. For Be the van Duijneveldt[18] $12s$ primitive set is augmented with a $7p4d$ primitive basis where the exponents are of the form $\alpha = 2.5^n\alpha_0$; $n = 0,$k with $\alpha_0 = 0.02$ and 0.06 for the p and d functions, respectively. This basis was then contracted to $4s$, $2p$ and $1d$ using CISD ANOs ob-

tained from a density matrix averaged over the $1s^2 2s^2(^1S)$ and $1s^2 2s 2p(^1P)$ atomic states of Be. This takes account of the $2s - 2p$ near-degeneracy effect and produces orbitals with a suitable radial extent for use in molecular calculations. The second ANO basis for Be was constructed by adding $3f$ primitive Gaussian functions and using five, three, two and one ANOs for the s, p, d and f spaces, respectively. The f primitive functions were constructed in a fashion similar to the p and d functions, with $\alpha_0 = 0.12$. These two ANO basis sets will be designated [421] and [5321], respectively. Note that for the ANO basis sets only the pure spherical harmonic components of the d and f functions are included.

Two ANO basis sets were constructed for Mg in a similar fashion. The primitive set is derived from the $(20s\ 12p)$ set of Partridge,[23] augmented with the three p functions optimized for the ^3P state of Mg. To this primitive set, $8d$ ($\alpha_0 = 0.0237$) and $6f$ ($\alpha_0 = 0.0284$) polarization functions were added as described in detail by Partridge $et\ al.$ [17] The smallest ANO basis set was formed from $5s$, $3p$ and $1d$ ANOs, while the larger basis was the $7s$, $6p$, $3d$ and $1f$ contraction recently used[17] for Mg_2. This basis consists of $5s$, $4p$, $2d$ and $1f$ ANOs with the outermost s, p and d primitive functions uncontracted. A diffuse s and p function is added to this basis to allow flexibility for an accurate representation of the Mg atom polarizabilities. These two sets are designated [531] and [7631], respectively. The ANO contraction coefficients were the same as those used in Ref. 17, and were obtained from an average of density matrices for the ^1S and ^3P states of Mg. Again, the s and p contaminants of the Cartesian d and f functions were eliminated in the Mg ANO basis sets. The Be and Mg ANO basis sets are available from the authors upon request.

In all calculations reported here only the valence electrons have been correlated. Furthermore, when using the segmented contractions one virtual orbital was deleted from the correlation procedure for every core orbital frozen. For the Mg clusters a brief investigation into the importance of correlating the 2s and 2p electrons was carried out. This was performed at the CCSD/$6s5p2d$ level of theory which for the pentamer in C_{2v} symmetry resulted in a CCSD wave function of 1 341 112 independent t_1 and t_2 amplitudes. However, when attempting to describe core-valence correlation, the basis set requirements are substantially more

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stringent[17]. Additionally, the basis set superposition error (BSSE), which is negligible ($<$ 0.1 kcal/mole per atom) when only the valence electrons are correlated, becomes much larger. Thus basis sets much larger than those employed here must be used in order to investigate quantitatively the importance of correlating the Mg $2s$ and $2p$ electrons, not only to describe correctly the core-valence correlation,[17] but also to minimize the BSSE correction to the binding energy. These aspects of describing the binding in Mg_2 are discussed in detail in Ref. 17.

Both the CPF and CCSD wave functions are based upon SCF molecular orbitals while the MRCI wave functions are constructed from complete active space SCF (CASSCF) molecular orbitals. The valence s and p-like molecular orbitals of Be and Mg were allowed to be active in the CASSCF procedure. For Be_4 the CASSCF wave functions consisted of 217 336 configurations in C_{2v} symmetry. In some of the MRCI calculations (denoted MRCI(CAS)) the full CASSCF configuration space was used as reference functions, while in other calculations reference selection from the CASSCF space was performed. The reference lists included an occupation if the absolute value of the coefficient of any one of its component spin couplings in the CASSCF wave functions exceeded a specific threshold. This selection was performed near equilibrium and at infinite separation and the reference lists were combined. The selection thresholds used were 0.01, 0.025 and 0.05. An MRCI wave function that utilizes a 0.01 selection threshold is designated MRCI(0.01), etc.

For the MRCI wave functions the importance of higher order excitations may be estimated by using the multireference analogue of the Davidson correction. Since for all the systems studied here the effect of this correction on the binding energies was found to be small, the values have not been reported.

The CPF and MRCI wave functions were determined with the MOLECULE-SWEDEN system of programs[24] while the CCSD wave functions were evaluated with VCCSD, a vectorized CCSD program[25] . All calculations were performed on the NASA Ames CRAY X-MP/48 or the NAS facility CRAY Y-MP/832.

III. Results and Discussion

Beryllium Clusters

Previous studies of small Be clusters[2-6] have established that they adopt

high symmetry singlet ground states. We therefore limit our study (for both the Be and Mg clusters) to high symmetry geometries. Specifically, the geometries of the trimer, tetramer and pentamer are an equilateral triangle, a tetrahedron and a trigonal bipyramid, respectively. The trimer and tetramer then have only one independent geometrical parameter (a bond length) while the pentamer has two independent bond lengths. When reporting the equilibrium structure of the pentamer, the first bond length given is the distance between equatorial atoms and the second is the distance between an equatorial atom and an apical atom.

Total energies, equilibrium structures and binding energies (D_e) for Be_3 are presented in Table 1. Throughout this study all D_e values have been evaluated by computing the dissociated atom limit directly, as opposed to using thermodynamic cycles involving molecular dissociation products. If the treatment is not size consistent the dissociated atom energy has been evaluated as a supermolecule calculation. The bond lengths in parentheses in Table 1 have not been optimized. Examining the [421] results first, it is evident that essentially all of the binding in Be_3 is due to dynamical electron correlation. This conclusion is supported by the fact that the SCF and CASSCF binding energies are similar even though the CASSCF total energy is significantly below the SCF value.

The excellent agreement between the various MRCI results indicates that the use of selection thresholds of 0.01 or 0.025 does not degrade the MRCI description of the electronic structure. Comparison of the binding energies obtained from the single-reference methods with the MRCI values indicates that single-reference based methods are not capable of recovering the differential dynamical electron correlation energy. The CCSD and CPF methods are exact for the dissociated atoms and are only approximate for the interacting atoms. Therefore, it is not surprising that the D_e is underestimated, though the absolute error is perhaps larger than might have been expected. Despite the rather poor performance of the single-reference methods in determining the binding energy, the CCSD and CPF equilibrium structures are in reasonably good agreement with the MRCI(CAS) value.

It was not possible to use the MRCI(CAS) procedure in conjunction with the [5321] basis set, because the resulting MRCI expansions are too lengthy. We therefore used a smaller reference configuration space, determined by using a se-

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lection threshold such as 0.025. It is important to ascertain whether the resulting MRCI expansion adequately treats the $s-p$ near-degeneracy effects (non-dynamical electron correlation) and this is accomplished by determining D_e using the valence configurations; that is, using the lowest eigenvalue of the Hamiltonian matrix defined by the intersection of the MRCI(0.025) configuration space and the CASSCF configuration space. Given that the Valence(0.025) binding energy is 0.5 kcal/mole and the full CASSCF value is 0.2 kcal/mole it is evident that the use of the 0.025 threshold gives an adequate approximation to the full CASSCF configuration space.

In comparison to the [421] basis set, the [5321] basis set CPF and CCSD binding energies are significantly larger and the difference between the two methods somewhat less. The fraction of the MRCI binding energy recovered using these methods is also increased relative to the smaller basis set, although the absolute error is approximately the same; e.g., for CCSD the error in D_e is 9.9 and 11.1 kcal/mole with the [421] and [5321] basis sets, respectively. Examination of the various equilibrium structures and binding energies obtained with the [5321] basis indicates that the inadequacies of the single-reference-based electron correlation methods are reduced relative to the inadequacies exhibited when the [421] basis set was used. For example, the variation in the Be_3 equilibrium bond length with n-particle treatment is 0.10 Å with the [421] basis set but only 0.04 Å with the [5321] basis set. The smaller variation may indicate a coupling between the one- and n-particle basis sets for Be_3; this results in a cancellation of errors in which deficiencies in the n-particle treatment are partially compensated for by using larger one-particle basis sets. Alternatively, the smaller variation may be a consequence of the significantly larger binding energy which Be_3 has with the [5321] basis set than with the [421] basis set leading to a much deeper well in the potential energy surface.

The best directly computed *ab initio* value of the binding energy of Be_3 is 22.4 kcal/mole obtained from the MRCI(0.025)/[5321] level of theory. Comparing the CCSD $7s3p2d1f$ and [5321] results (the $7s3p2d1f$ r_e is slightly smaller and the D_e is 0.7 kcal/mole larger) it seems clear that the MRCI(0.025)/[5321] D_e is an underestimate. The relevant differences between the segmented and ANO basis sets here are that the outermost s and p functions are contracted in the ANO

set while they are allowed maximum flexiblity for the $7s3p2d1f$ basis set, though the difference in computed results is small. Therefore, while our best results for Be$_3$ yield an r_e of 4.199 a_0 and a D_e of 22.4 kcal/mole, it is likely that the true r_e is slightly shorter and the true D_e is slightly larger.

Theoretical predictions of the equilibrium structure and binding energies of Be$_4$ and Be$_5$ are presented in Table 2. The equilibrium structures of Be$_4$ and Be$_5$ have only been determined at the CCSD level of theory, though based upon the results for Be$_3$ this should be reasonably close to the equilibrium structures of the other correlation methods. Furthermore, the equilibrium bond length obtained for Be$_4$ is similar to the value determined by Bauschlicher et $al.$ at the CISD+Q level of theory.[3] The D_e value for Be$_4$ obtained with the [421] basis set will be discussed first. Consistent with the results for Be$_3$, the SCF and CASSCF binding energies are very close. As expected, Be$_4$ exhibits a large binding energy at the zeroth-order (SCF or CASSCF) level. Since it was not possible to use all of the CASSCF configurations as references, the quality of the 0.025 reference function was judged by comparison of the valence D_e with the CASSCF value. The Valence(0.025) and Valence(0.05) dissociation energies (34.1 and 34.8 kcal/mole) are in very good agreement with the CASSCF D_e (34.9 kcal/mole). The 0.025 and 0.05 selection thresholds thus seem to be a good approximation for Be$_4$.

Comparison of the CCSD and MRCI binding energies (42.9 kcal/mole and 56.0 kcal/mole, respectively) demonstrates that single-reference electron correlation methods also underestimate the binding energy of Be$_4$. Since the SCF and CASSCF binding energies are very similar, it is evident that the major portion of the error in the CCSD D_e is due to an inadequate treatment of dynamical electron correlation.

The SCF and CASSCF binding energies for Be$_4$ (40.0 and 45.0 kcal/mole) are larger with the [5321] basis set. The CCSD [5321] binding energy is comparable to previous results[3] based upon single-reference electron correlation methods. The MRCI(0.05) D_e is substantially larger (77.3 kcal/mole). Again, comparison of the $7s3p2d1f$ and [5321] CCSD predictions indicates that the [5321] MRCI(0.05) D_e is an underestimate of the true binding energy in Be$_4$, suggesting that the true D_e is between 80 and 85 kcal/mole. In their most elaborate (full fourth-order) MBPT treatment, Rohlfing and Binkley obtained 85 kcal/mole for the binding energy, but

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in view of the increase in D_e with basis set observed improvments in the present work it seems likely that the complete basis MBPT(4) binding energy would be a substantial overestimate.

Based upon the previous results for Be_3 and Be_4 it is likely that the $7s3p2d$ CCSD bond lengths in Be_5 are somewhat too long and that the D_e is significantly underestimated. Using the previous results of Be_3 and Be_4 as a guide, our best estimate for the D_e of Be_5 is between 100 and 120 kcal/mole. This is discussed in more detail later.

In reference to the applicability of single-reference-based methods (limited to single and double excitations) to Be clusters, our results show that they appear to be no more appropriate for the trimer and tetramer than for the dimer. To extend these observations to larger clusters is not possible at present, because MRCI calculations are intractable for more than four Be atoms. An alternative probe of the applicability of single-reference treatments is provided by a simple diagnostic based on the CCSD wave function. Lee and Taylor[26] have recently shown that the norm of the vector of single excitation amplitudes from the CCSD wave function (normalized to account for the number of electrons correlated), a quantity denoted T_1 in Ref. 26, allows identification of cases in which a multireference treatment is required. Specifically, if T_1 is greater than 0.02, single-reference results should be viewed with considerable caution, as they may not be even qualitatively correct. For Be_3 in the smaller ANO set T_1 has the value 0.0386, indicating that an MRCI treatment is required; the T_1 values for the tetramer and pentamer are similar. For closed-shell Be_{13}, computed at the optimum geometry of Rohlfing and Binkley[5] using a [42] ANO basis (simply omitting the d ANO from the smaller ANO set) T_1 is found to be 0.0377. The diagnostic thus indicates that the multireference character of Be clusters decreases very slowly with increasing cluster size.

Magnesium Clusters

Table 3 contains the total energies, equilibrium bond lengths and dissociation energies for Mg_3. The [531] basis set results show that the binding in Mg_3, like Be_3, is due entirely to dynamical electron correlation. Although there appears to be a difference between the CASSCF and SCF binding energies, this effect is due

almost completely to the different geometries at which the dissociation energies were determined. Examination of the various MRCI equilibrium bond lengths and dissociation energies indicates that any type of selection threshold has a much larger effect on both quantities than was found with the Be clusters. However, for our purposes the 0.025 threshold results are accurate enough to determine the quality of the single-reference-based electron correlation methods.

Two important conclusions may be derived from the CPF and CCSD [531] results. First, single-reference-based methods (limited to single and double excitations) are not reliable for the accurate prediction of the binding energy nor the equilibrium structure of Mg_3. Second, unlike the Be clusters, small errors in the binding energy may lead to rather large structural errors due to the flatness of the potential energy curves which in turn results from the smaller degree of $s - p$ hybridization in small Mg clusters. In other words, since the bonding in small Mg clusters is so dominated by dynamical electron correlation, incomplete account of it will result in large geometrical errors.

The [7631] basis set SCF and CASSCF results for Mg_3 demonstrate that dynamical electron correlation is even more important than for the smaller basis sets; at the SCF and CASSCF level the molecule is even more unbound. Consequently the larger MRCI(0.025) binding energy obtained with the [7631] basis is due entirely to an increased importance of dynamical electron correlation.

The CPF [7631] results are a significant improvement over the CPF [531] values (relative to the MRCI results). The CCSD [7631] D_e is an improvement over the [531] result, but is still poor (much less than the MRCI value). However, the CCSD equilibrium bond length is improved considerably with the [7631] basis set. Based on these comparisons it is evident that Mg clusters also exhibit a large coupling between the one- and n-particle basis sets.

Our best computed binding energy for Mg_3 is 6.3 kcal/mole, which is undoubtedly an underestimate of the true D_e. Even though the actual binding in both Be_3 and Mg_3 is due mostly to dynamical electron correlation, the D_e values of these two compounds are very different. The larger D_e value for Be_3 is due to the larger degree of $s - p$ hybridization which occurs for Be_3 but not for Mg_3.

Theoretical predictions of the equilibrium structure and binding energy of

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Mg_4 and Mg_5 are presented in Table 4. As with the equivalent Be clusters, the structural parameters have only been optimized at the CCSD level of theory. In striking contrast to the analogous Be clusters, Mg_4 and even Mg_5 are not bound at the zeroth-order (SCF or CASSCF) level of theory. This observation is consistent with the results for Mg_3 in that $s - p$ hybridization is substantially less for Mg clusters than for similar Be clusters, further decreasing the reliability of single-reference based electron correlation methods for Mg clusters.

Comparison of the CCSD and MRCI results for Mg_3 indicates that the CCSD equilibrium bond lengths for the Mg clusters will be too large, especially with the smaller basis set. However, even at the CCSD level of theory, the equilibrium bond length(s) of the Mg clusters decrease(s) as the cluster size increases. This phenomenon is particularly noticeable when comparing the CCSD/$6s5p2d$ structures of Mg_3 and Mg_4. Given that the clusters are not bound at the SCF level of theory, it would seem that dynamical electron correlation becomes more important as the cluster size increases and that the CCSD method recovers enough of the dynamical electron correlation energy to account, at least partially, for this effect.

Due to the inablity to carry out MRCI calculations for Mg_4 with the large basis set, the best computed value for the binding energy (16.2 kcal/mole) is undoubtedly an underestimate, possibly by as much as 15 kcal/mole. Similarly our calculated binding energy for Mg_5 of 13.1 kcal/mole will also be a significant underestimate. It is nonetheless apparent that the Mg_4 and Mg_5 binding energies are substantially less than the corresponding values for Be_4 and Be_5. This result is consistent with the fact that the bulk binding energy[27] is significantly larger for Be metal than it is for Mg metal.

Best Estimates

Table 5 contains best estimates of the binding energy of all the clusters included in this study. These values were determined by considering the remaining sources of error in the *ab initio* data presented in the previous sections. Considering the trimers first, the best computed binding energies for Be_3 and Mg_3 are 22.4 and 6.3 kcal/mole, respectively. For these systems it is evident that improvements in the one- and n-particle basis sets would be expected to increase the binding energies;

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we estimate $\sim$ 1.5 and 2 kcal/mole for Be_3 and Mg_3 respectively. For Mg_3 we expect that the improved one- and n-particle treatments will result in a shorter bond length which will contribute another $\sim$ 1 kcal/mole to the binding. The effect of core-valence correlation on the Mg cluster binding energies is uncertain, but is not expected to be substantial[17] . Taking these considerations into account we arrive at estimated binding energies, expected to be accurate to within a few kcal/mole, of 24 and 9 kcal/mole for Be_3 and Mg_3, respectively. Our best estimate for Be_3 is in good agreement with that of Harrison and Handy.[4]

For Be_4 the one- and n-particle basis set effects will be somewhat larger than for Be_3. The resulting best estimate of 83 kcal/mole ($\sim$ 3.0 and 2.5 kcal/mole for the one- and n-particle effects, respectively) should again be accurate to within a few kcal/mole. Conversely, the estimation of binding energies of Mg_4 and particularly the pentamers is less definite. In the case of Mg_4, an estimate of $\sim$ 22 kcal/mole may be made for the MRCI binding energy in the [7531] basis by examination of the [531] basis set results. Further, considerations of the effects discussed above, with their concomitant bond length reduction, lead to a best estimate of $\sim$ 31 kcal/mole. Taking into account the one- and n-particle basis set limitations for Be_5 and Mg_5 (and the bond length reduction for the latter), we arrive at best estimates of $\sim$ 110 and $\sim$ 41 kcal/mole for the binding energies of Be_5 and Mg_5, respectively.

Although it is difficult to place error bars on the estimates, the values for Be_3, Be_4 and Mg_3 are most reliable, because the MRCI dissociation energies may be used as a guide. Moreover, as each dissociated atom contains only two electrons in the valence shell, the CCSD dissociation limit corresponds to a full CI. Thus, since even our best treatments describe the separated atoms better than the cluster, the above estimates are likely to be lower bounds to the true D_e.

For both the Be and Mg clusters the tetramer has a significantly larger binding energy per atom than the trimer. Comparing the D_e/bond (where "bond" refers to a pairwise bonding interaction) for the trimer and tetramer it is apparent that the larger binding energy of the tetramers is not due solely to the larger number of bonds per atom, but also to effects attributable to the $s - p$ hybridization. The latter gives rise to two contributions both favoring larger clusters. First, as the size

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of the cluster increases the ratio of the energy required to promote an electron from each atom into a p-orbital to the number of bonds formed continually decreases, and second, the directional nature of the sp hybrid orbitals would tend to favor the tetramer and pentamer.

The pentamers also posses large binding energies per atom, but the binding per bond is less than that of the tetramers. These observations are explained by the fact that the pentamers have a larger number of nearest neighbor interactions per atom than the tetramers, but the geometry about each atom is not as favorable for $s - p$ hybridization.

Comparison of the cluster binding energies with the bulk values demonstrates the large differences that exist between small homogeneous clusters and bulk material. The D_e/atom for all the clusters is substantially below the bulk value. However, it is interesting that for both Be and Mg, the bulk value for the D_e/bond is very similar to that obtained for the tetramers and pentamer. Hence our results show that the D_e/bond converges rapidly to the bulk value for Be and Mg. Finally, thermodynamic arguments would suggest that it will be very difficult to form Be_3 under conditions in which clusters can interact, given the much greater stability of Be_4.

IV. Conclusions

Single-reference-based electron correlation methods, truncated at the single and double excitation level, encounter significant problems in the description of the electronic structure of the Be_n and Mg_n $(n = 3,5)$ clusters. For the Be clusters this inadequacy manifests itself in the form of large underestimates of the binding energies (D_e) of the clusters. However, the CCSD and CPF methods obtain reasonable equilibrium structures for these clusters, indicating that the $s - p$ hybridization is probably the dominant factor in determining the geometries. The $s - p$ hybridization is much weaker in the Mg clusters (consistent with the bulk dissociation energies and an earlier study[3]) and so small errors in the determination of the D_e may lead to rather large errors in the equilibrium geometry. Consequently the single-reference-based methods do not perform very well in the theoretical prediction of equilibrium structures of the Mg clusters because of the importance of

dynamical electron correlation. These methods perform better, at least in a relative sense, for Be_4 and Be_5 because the binding energy for these systems does not arise entirely from dynamical electron correlation.

Recently there has been considerable interest in extending single-reference coupled cluster theory to include the effects of linked triple excitations.[28-30] The usefulness of incorporating the effects of higher order excitations in this manner, for systems like those studied here, is not yet clear. Preliminary investigations of the newly proposed CCSD(T) method[30] are encouraging (e.g. the binding energies of Be_3 and Mg_3 are predicted to be 20.4 and 5.7 kcal/mole, respectively using the larger ANO basis sets). Further studies of the CCSD(T) method are currently in progress.

Acknowledgements

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Table 1

Total energies (E_H), equilibrium bond lengths (a_0) and dissociation energies (kcal/mole) for Be_3 obtained at various levels of theory.

Method	Basis Set	E	r_e	D_e
SCF	[421]	-43.713665	(4.472)	-3.2
CCSD	[421]	-43.862029	4.472	4.2
CISD+Q	[421]	-43.876727	(4.472)	8.9
CPF	[421]	-43.869153	4.488	8.6
CASSCF	[421]	-43.846451	(4.372)	-2.3
MRCI(0.025)	[421]	-43.877283	4.373	14.2
MRCI(0.01)	[421]	-43.877967	4.372	14.1
MRCI(CAS)	[421]	-43.878197	4.372	14.1
CCSD	7s3p2d	-43.870187	4.272	9.3
CCSD	7s3p2d1f	-43.874729	4.237	12.0
SCF	[5321]	-43.716571	(4.240)	-1.4
CCSD	[5321]	-43.874323	4.240	11.3
CPF	[5321]	-43.881685	4.202	14.9
CASSCF	[5321]	-43.850516	(4.199)	0.2
Valence(0.025)	[5321]	-43.850257	(4.199)	0.5
MRCI(0.025)	[5321]	-43.891968	4.199	22.4

Table 2

Total energies (E_H), equilibrium bond lengths (a_0)
and dissociation energies (kcal/mole) for Be_4 and Be_5.

Method	Basis Set	E	r_e	D_e
Be_4				
SCF	[421]	-58.344089	(3.900)	32.9
CCSD	[421]	-58.542284	(3.900)	42.9
CASSCF	[421]	-58.522424	(3.900)	34.9
Valence(0.025)	[421]	-58.519311	(3.900)	34.1
MRCI(0.025)	[421]	-58.561751	(3.900)	56.0
Valence(0.05)	[421]	-58.518588	(3.900)	34.8
MRCI(0.05)	[421]	-58.560199	(3.900)	56.1
CCSD	7s3p2d	-58.568397	3.915	59.3
CCSD	7s3p2d1f	-58.577359	3.900	64.7
SCF	[5321]	-58.355535	(3.900)	40.0
CCSD	[5321]	-58.576321	(3.900)	63.5
CASSCF	[5321]	-58.538602	(3.900)	45.0
MRCI(0.05)	[5321]	-58.595343	(3.900)	77.3
CISD+Q[a]	TZ2P	-	(3.92)	64.2
Be_5				
SCF	7s3p2d	-72.943250	(3.831,3.929)	49.3
CCSD	7s3p2d	-73.223478	3.831,3.929	82.3

a. Reference 3.

Table 3

Total energies (E_H), equilibrium bond lengths (a_0) and dissociation energies (kcal/mole) for Mg_3 obtained at various levels of theory.

Method	Basis Set	E	r_e	D_e
SCF	[531]	-598.840906	(8.089)	-1.7
CCSD	[531]	-598.945579	8.089	1.0
CPF	[531]	-598.947417	7.023	2.2
CASSCF	[531]	-598.929542	(6.704)	-5.4
MRCI(0.025)	[531]	-598.949225	6.738	3.7
MRCI(0.01)	[531]	-598.949882	6.714	3.9
MRCI(CAS)	[531]	-598.950150	6.704	3.9
CCSD	6s5p2d	-598.923857	7.522	1.4
SCF	[7631]	-598.836768	(6.926)	-4.4
CCSD	[7631]	-598.948758	6.926	2.1
CPF	[7631]	-598.951893	6.545	4.1
CASSCF	[7631]	-598.927247	(6.373)	-6.9
MRCI(0.025)	[7631]	-598.954974	6.373	6.3

Table 4

Total energies (E_H), equilibrium bond lengths (a_0)
and dissociation energies (kcal/mole) for Mg_4 and Mg_5.

Method	Basis Set	E	r_e	D_e
Mg_4				
CCSD	6s5p2d	-798.578939	6.102	10.5
SCF	[531]	-798.447061	(6.102)	-7.0
CCSD	[531]	-798.604727	(6.102)	8.1
CASSCF	[531]	-798.579605	(6.102)	-2.9
MRCI(0.025)	[531]	-798.616000	(6.102)	16.2
CCSD	[7631]	-798.615505	(6.102)	13.6
CISD+Q[a]	DZP		6.02	11.9
Mg_5				
SCF	6s5p2d	-998.020131	(5.967,6.667)	-9.1
CCSD	6s5p2d	-998.223515	5.967,6.667	13.1

a. Reference 3.

Table 5

Best estimates of D_e for the Be_n and Mg_n (n=3-5) clusters.

D_e/atom and D_e/bond are also given.

All values in kcal/mole.

Cluster	D_e	D_e/atom	D_e/bond
Be_3	24	8.0	8.0
Be_4	83	20.8	13.8
Be_5	110	22.0	12.2
Bulk	-	78	13
Mg_3	9	3.0	3.0
Mg_4	31	7.8	5.2
Mg_5	41	8.2	4.6
Bulk	-	35	5.8