SMALL BERYLLIUM CLUSTERS:
Be_2, Be_4, AND Be_5

by

PETER N. ASCIK

(Under the direction of Henry F. Schaefer III)

ABSTRACT

With the exception of the dimer, the small clusters of beryllium have yet to be successfully characterized by spectroscopy. In this study, the geometries and dissociation energies of Be_4 and Be_5 are computed using highly accurate coupled-cluster methods. Dunning's correlation consistent polarized-valence basis sets are employed, and the energies computed for the tetramer are extrapolated to the complete basis set (CBS) limit. The importance of triple and quadruple excitations from the zeroth-order wavefunction are assessed for both clusters. Triples are found to be essential to describing the clusters, but quadruples are found to be of only minor importance. Computations on the challenging Be_2 molecule are reported for the purpose of benchmarking our results. For the tetramer, fundamental vibrational frequencies and rotational constants are obtained by applying second-order vibrational perturbation theory (VPT2) to a full quartic force field computed at the c∼CCSDT(Q)/CBS level of theory.

INDEX WORDS: Be2, Be4, Be5, beryllium tetramer, beryllium pentamer, beryllium dimer, beryllium clusters, CCSDT(Q), quartic force field

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PETER N. ASCIK

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PETER N. ASCIK

Approved: July 22, 2011

Major Professor: Henry F. Schaefer III

Committee: Nigel Adams
Geoffrey Smith

Electronic Version Approved:

Dean's Name Here
Dean of the Graduate School
The University of Georgia
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Chapter 1

Introduction

The unique properties of small beryllium clusters present challenges for both theory and experiment. Of the series Be_n (n = 2, 3, 4, 5), only Be_2 has been observed by experiment, and full spectroscopic characterization of the bonding curve was accomplished only recently. In 2009, Merritt, Bondybey, and Heaven[1] obtained rotationally resolved spectra of Be_2 via stimulated emission pumping, settling years of controversy about the molecule's ground-state parameters. They reported a dissociation energy $D_\mathrm{e} = 2.658 \pm 0.006$ kcal mol^{-1} and eleven bound vibrational levels. Further *ab initio* studies predict the existence of a twelfth vibrational level.[2] The more strongly bound ($D_\mathrm{e} = 47.00$ kcal mol^{-1}) Be_2^+ molecule has also excited experimental interest,[3] as have small oxides of Be such as BeOBe.[4] Heaven *et al.* report that they are currently engaged in "systematic spectroscopic studies"[5] of small beryllium clusters, but to date no spectroscopic information on Be_3, Be_4, or Be_5 has appeared. Theory predicts significant jumps in the dissociation energy for the next two clusters, with $D_\mathrm{e} = 17.2$ kcal mol^{-1}[6] for Be_3 and a D_e for Be_4 of 80-90 kcal mol^{-1}. The dissociation energy of the Be_5 cluster is thought to lie above 100 kcal mol^{-1}.

1.1 Be_2 and Be_4

Small beryllium clusters are a challenge for quantum chemical computations.[7] The difficulty lies in correctly describing the dramatic influence of both dynamical and static correlation on the bonding of these molecules. The $2s$ and $2p$ orbitals in atomic beryllium are nearly degenerate, and this can give the clusters significant multiconfiguration character. The bonding potential energy surfaces for small Be clusters are also rather flat and very sensitive to the level of electron correlation employed. For the dimer, methods that do not include the effects of triple and quadruple excitations from the Hartree-Fock (HF) wavefunction generally underestimate D_{e} and can fail to locate the minimum on the potential surface.[8, 9, 10, 11, 12, 13, 14] Finally, the dissociation energy shows a strong basis set dependence, with significant contributions from *d*, *f*, and *g* polarization functions.[15, 10, 13, 14]

The ground state of Be_2 was a subject of controversy until the recent experiments of Merrit, Bondybey, and Heaven.[1] The dimer has a formal bond order of zero, and the HF potential curve is purely repulsive.[16, 17, 18, 19, 20, 21, 22] Early treatments of the electron correlation [17, 18, 19, 23, 24, 25, 26, 27, 28, 22, 29] gave inconclusive results, with many studies failing to predict any bonding beyond a shallow van der Waals minimum. The lone spectroscopic observation of the species was of an excited electronic state.[30] A series of extrapolated full configuration interaction (FCI) computations were the first to offer definitive information on the bonding behavior of Be_2 by predicting a bond length of 2.49 Å and a dissociation energy of around 2 kcal mol^{-1}.[31, 15, 8] These findings were substantiated by some preliminary experimental studies of ground state Be_2 by Bondybey *et al.*[32, 33, 34]

Bondybey's experiments indicated that the ground state of the dimer was bound at a shorter bond length (~2.45 Å) than would be expected for a van der Waals complex.[35] However, they were unable to characterize the full potential curve, especially in the anharmonic region. A new wave of theoretical studies sought to fill in the gaps in experimental information and to account for the failure of many-body perturbation theory (MBPT) and coupled-cluster (CC) methods to correctly describe the system in earlier studies.[36, 10, 37, 38, 39, 11, 13, 40, 41] Estimates of the dissociation energy steadily increased with larger basis sets and more extensive correlation treatments.[42, 43, 14, 44, 45, 46, 47, 41, 48, 49, 50, 51, 52, 53, 54, 2] Despite the application of high-level theoretical methods and large basis sets, some uncertainty about the nature of the Be_2 bond remained until the extensive experimental characterization of the molecule in 2009 by Merritt, Bondybey, and Heaven.[1] Given the level of experimental detail now available, the dimer can serve as a useful benchmark to evaluate the performance of theoretical methods in predicting the structures, dissociation energies, and vibrational frequencies of small beryllium clusters.

While bonding in the dimer and the trimer is entirely due to correlation effects, the tetramer is already bound at the HF level by 35-45 kcal mol^{-1}, depending on the basis set size.[55, 21, 56, 57, 38, 58] The tetrahedral T_d structure is the lowest energy geometry.[29] Study of Be_4 was originally motivated by the prediction of *ab initio* computations that it would form the smallest significantly bound beryllium cluster.[59, 55] When the tetramer is treated at a sufficiently high level of theory, correlation effects can double the predicted dissociation energy relative to HF theory.[23, 57, 29, 38, 60, 58] The dissociation energy also shows a large basis set dependence. The configuration interaction method with singles and doubles (CISD) gives a bonding energy of 39-41 kcal mol^{-1} in double- or triple-zeta plus polarization (DZP or TZP) basis sets.[38] This increases to 59-65 kcal mol^{-1} when a simple correction for the effect of disconnected quadruples is included.[57, 38] Second-order Møller-Plesset perturbation theory (MP2) gives $D_\mathrm{e} = 97.6$ in a TZP basis, while fourth-order Møller-Plesset perturbation theory [MP4(SDTQ)] gives $D_\mathrm{e} = 85.3$ kcal mol^{-1} in the same basis.[58] The optimized bond length increases with the correlation method, although this effect is small compared to the change in D_e.

The application of coupled-cluster methods to the study of Be_4 has established the importance of including triple excitations in the correlated wavefunction.[9, 11, 61, 62, 63, 64, 65, 12] Rendell, Lee, and Taylor found that coupled-cluster theory with singles and doubles (CCSD) gave $D_\mathrm{e} = 63.5$ kcal mol^{-1} in a $[5s\ 3p\ 2d\ 1f]$ basis, but this increased to 79.5 kcal mol^{-1} when a perturbative estimate of connected triples was included [CCSD(T)].[65, 64] A correction of that size suggests that static correlation could play a significant role in the cluster, which would indicate that higher-order corrections will influence the dissociation energy.[66] Quadruple excitations are known to be important to the description of the dimer, but their influence on the tetramer has not been established. Our study presses beyond CCSD(T) to include the effect of connected quadruples in an effort to provide a definitive estimate of the structure, energetics, and vibrational frequencies of Be_4. The focal point approach is used to systematically examine the effects of correlation treatment and basis set size on the dissociation energy of the molecule.

1.2 Be_5

The beryllium pentamer adopts a number of geometries, but the trigonal bipyramidal D_3h structure has been consistently found to be lowest in energy.[67, 68, 69, 70] The HF bonding energy is only slightly higher than that of Be_4. Lee, Rendell, and Taylor obtained $D_\mathrm{e} = 49.3$ kcal mol^{-1} based on a HF calculation in the $7s3p2d$ basis set.[63] However, as in the tetramer, correlation dramatically affects the energetics of the molecule. The same authors reported a CCSD dissociation energy of 82.3 kcal mol^{-1}, almost 20 kcal mol^{-1} above the value they calculated for the tetramer at that level of theory. They recognized that as is the case for the tetramer, the neglect of triple excitations in CCSD likely leads to an energy that is too low. Another study employed the quadratic configuration interaction method with singles, doubles, and perturbative triples [QCISD(T)] and found $D_\mathrm{e} = 103.8$ kcal mol^{-1}.[71] Application of perturbation theory to the clusters gives dissociation energies that are even higher. Fourth-order perturbation theory (MP4/6-311+G*) gives D_e = 122.1 kcal mol^{-1}, while second-order perturbation theory (MP2/6-311+G*) gives 145.9 kcal mol^{-1}.[71] The erratic predictions of previous *ab initio* studies emphasize the need for a systematic study of correlation and basis set effects in Be_5.

Chapter 2

Theoretical Methods

2.1 Coupled-Cluster Theory

Quantum chemical studies begin by solving the electronic Schrödinger equation (2.1) for the system under investigation.

$$H|\Psi >= E|\Psi > \tag{2.1}$$

The electronic wavefunction (Ψ) in principle holds all the information about the chemical system. Once described in a tractable form, it can be used to evaluate the matrix elements of any quantum mechanical operator to obtain physical properties of the system. *Ab initio* methods compute the electronic energy by applying the exact Hamiltonian operator (H) to an approximate wave function. The wavefunction is represented as a single determinant or linear combination of determinants expanded in a basis set of one-electron functions. The exact representation varies with the level of theory employed, hence choosing a level of theory that adequately describes the electronic wavefunction is of paramount importance.

Methods based on coupled-cluster theory employ an exponential ansatz to describe the wavefunction. The best variational single-configuration description of the wavefunction (Φ_0) is multiplied by an exponential excitation operator, called the cluster operator, as shown in Eqation 2.2.[72] The cluster operator is expanded as a power series, generating a linear combination of determinants with excited configurations.

$$\Psi = e^{\hat{T}}\Phi_0 \tag{2.2}$$

The cluster operator is itself a sum of individual operators ($\hat{T} = \hat{T}_1 + \hat{T}_2 + ... + \hat{T}_N$), each of which describe the excitation of a certain number of electrons from the ground-state configuration. If the operator is not truncated, the exponential expansion generates all possible excitations from the ground state, and is equivalent to the full configuration interaction (CI) treatment.[73] In practice, excitations higher than the first few orders are rarely physically important, and a truncated sum of excitation operators is used.

Coupled-cluster methods are labeled according to the highest level of excitation included in the truncated cluster operator. Coupled-cluster with singles and doubles ($\hat{T} = \hat{T}_1 + \hat{T}_2$) is known as CCSD, coupled-cluster with singles, doubles, and triples ($\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$) is denoted CCSDT, the analogous method with quadruples included is CCSDTQ, etc.[72] The inclusion of certain higher levels of excitation can be approximated by computing the energy at a lower excitation level and then adding a perturbation theory estimate of the contribution from the higher excitation. The level of excitation estimated by perturbation theory is enclosed by parentheses when labeling the method. For instance, CCSD(T) refers to a coupled-cluster with singles and doubles computation followed by the addition of a perturbative estimate of the effect of triples.

The explicit inclusion of a certain level of excitation in the cluster operator (triples, for instance) is accomplished by including the excitation operator (in this case $\hat{T}_3$) that corresponds to that level of excitation. However, the power series expansion of the exponential operator introduces multiplicative powers of each excitation operator included in the expansion. For instance, if the cluster operator is truncated at doubles ($\hat{T} = \hat{T}_1 + \hat{T}_2$) the expression in Equation 2.2 can be expanded as a power series to obtain the expression:[72]

$$\Psi = (1 + \hat{T}_1 + \frac{1}{2!}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2!}\hat{T}_2^2 + ...). \tag{2.3}$$

In Equation 2.3, the product of the $\hat{T}_1$ and $\hat{T}_2$ operators indirectly introduces triple excitations into the wavefunction. Such contributions are said to be disconnected, whereas the excitation levels explicitly included in the cluster operator are said to be connected.[72] Hence, even methods that formally truncate at a certain level of excitation will indirectly include effects from higher levels of excitation that arise from the products of lower-level operators.

From a physical standpoint, the inclusion of excitations from the ground-state configuration in the wavefunction describes the instantaneous repulsion of electrons of opposite spin. This is referred to as dynamical correlation, and is distinguished from static correlation, which is important in systems where the ground state itself cannot adequately be described by a single configuration wavefunction. Single excitations describe orbital relaxation effects, while doubles account for the interaction of electron pairs, triples the interaction of three electrons, etc.[73] The inclusion of double excitations is usually the most chemically important effect, and the inclusion of even a perturbative estimate of triples via the CCSD(T) method is often sufficient to achieve chemical accuracy. However, in systems with strong correlation effects, it may be necessary to include full triples (CCSDT) or even quadruples for an adequate description of the molecule. Previous work on the beryllium clusters under investigation in this study has indicated that the correlation in these molecules is not adequately described unless such higher-order excitations are taken into account.

2.2 Basis Set Effects

An accurate description of a chemical system requires inclusion of sufficient levels of excitation from the ground-state configuration in the wavefunction. However, in order to express the wavefunction in a form that is convenient for computations, it must also be expanded in a basis of one-electron functions. An exact description of the wavefunction would require a basis set of infinite size. As this is impossible, the basis set must be truncated at a finite number of functions. This limits the accuracy of the wavefunction description of the system, which in turn limits the accuracy of computed properties such as the dissociation energy. One approach to overcoming this basis-set incompleteness problem is the use of extrapolation formulas to remove errors due to incompleteness of the basis set. This allows computations to closely approximate complete basis set (CBS) limit properties. A series of extrapolation formulas have been developed for the Dunning correlation-consistent polarized-valence basis sets employed in this study. We use these formulas, which are described in Equations 2.6 and 2.7, to essentially remove the basis set error from our correlated computations.

2.3 Molecular Vibrations

The atoms in molecules vibrate about their equilibrium positions in a potential field generated by the electronic potential energy of the molecule. When a proper coordinate system is used, the vibrational, rotational, and electronic contributions to the wavefunction can be treated separately.[74] This allows us to obtain the electronic wavefunction and then use it to solve for the frequencies of these vibrations. The energy is expanded in a Taylor series as shown in Equation 2.4.[75]

$$E(\mathbf{x}) = E_0 + \sum_i F_i x_i + \sum_{ij} F_{ij} x_i x_j + \sum_{ijk} F_{ijk} x_i x_j x_k + \sum_{ijkl} F_{ijkl} x_i x_j x_k x_l + \ldots \quad (2.4)$$

Here the variables $x_{i,j,\ldots}$ are a set of internal coordinates and the $F_{i,j,\ldots}$ are the force constants obtained from successively higher-order derivatives of the electronic wavefunction with respect to the coordinate system. The Taylor series can be truncated at different orders to obtain a hierarchy of approximations to the potential energy surface. For a quartic force field, fourth derivatives are computed to obtain the fourth-order force constants F_{ijkl}. Once the force field is defined, the second-order vibrational perturbation theory (VPT2) equations can be applied to obtain fundamental frequencies of vibration.

2.4 Computational Details

Geometry optimizations and single-point energy computations were carried out using various levels of coupled cluster theory with all electrons correlated. These include coupled cluster with single and double excitations (CCSD),[76, 77, 78, 79] CCSD with perturbative triple excitations [CCSD(T)],[80, 81, 82, 83] full triples (CCSDT),[84, 85, 62, 86] and perturbative quadruple excitations [CCSDT(Q)].[87, 88] All correlated computations were based on a restricted Hartree-Fock (RHF) reference wavefunction. The Dunning correlation-consistent polarized-valence basis sets were employed, denoted cc-pVXZ (X = D, T, Q, 5).[89, 90] The augmented (aug-cc-pVXZ),[89] core-valence (cc-pCVXZ),[89, 90, 91] and augmented core-valence (aug-cc-pCVXZ)[89, 90] extensions to these basis sets are also used. Computations were performed using MOLPRO 2009.1 [92] and the Mainz-Austin-Budapest (MAB) version of the ACESII program suite.[93, 94] The MRCC program written by Kállay[88, 95] was utilized for the CCSDT(Q) computations.

At the center of this study are investigations of the effect of quadruple excitations on the spectroscopic constants and dissociation energy of Be_4. A multilevel composite computation denoted c$\sim$CCSDT(Q)/CBS is employed for this purpose. Quadruples are included in this computation as an additive correction, and the energy is extrapolated to the complete basis set (CBS) limit. The use of a composite computation allows us to obtain accurate single-point energies while bypassing the prohibitive computational expense of directly calculating CCSDT(Q) energies in large basis sets. The components of the computation are shown in Eq. (2.5).

$$E^{\mathrm{AE}}_{\mathrm{c{\sim}CCSDT(Q)}} = E^{\mathrm{CBS}}_{\mathrm{CCSD(T)}} + E^{\mathrm{cc-pCVDZ}}_{\mathrm{CCSDT(Q)}} - E^{\mathrm{cc-pCVDZ}}_{\mathrm{CCSD(T)}}. \tag{2.5}$$

The acronym AE indicates that all electrons are correlated in the computation, and CBS indicates that the energy is extrapolated to the complete basis set limit. The CCSD(T) basis set limit energy is obtained from extrapolation formulas applied to single-point energies calculated at the CCSD(T) level using the cc-pCVQZ and cc-pCV5Z basis sets. The Hartree-Fock energy is extrapolated using the equation[96]

$$E_{\mathrm{HF}}(X) = E^{\infty}_{\mathrm{HF}} + a(X+1)e^{-9\sqrt{X}}, \tag{2.6}$$

and the all-electron correlation energy is extrapolated using[97]

$$E_{\mathrm{Corr}}(X) = E^{\infty}_{\mathrm{Corr}} + aX^{-3}, \tag{2.7}$$

where the symbol X denotes the cardinal number of the basis set. The sum of Eqs. (2.6) and (2.7) give the CBS energy at the desired level of theory.

The equilibrium geometry was obtained at the c∼CCSDT(Q)/CBS level of theory. The T_{d} symmetry of Be_4 allowed us to optimize the geometry using a fifth-order polynomial fit of the energy as a function of the bond length. The analytic minimum of this function was taken to be the equilibrium bonding distance. A focal point table[98, 99, 100, 101, 102] was constructed to monitor the dependence of D_{e} on the basis set and correlation treatment. In this approach, the dissociation energy is computed at successively higher levels of theory and basis sets. The increments in D_{e} with increasing completeness in the correlation treatment are tabulated and monitored for convergence towards the full CI limit. The basis set error is essentially removed by extrapolating the D_e increments for all theories lower than CCSDT using Eqs. (2.6) and (2.7). The CCSDT/CBS correction is computed by adding the the CCSDT/cc-pCVTZ D_e increment to the CCSD(T)/CBS value, and the CCSDT(Q)/CBS correction comes from the sum of the CCSDT(Q)/cc-pCVDZ increment and the CCSDT/CBS value. Our final estimates of D_e and D_0 include corrections for auxiliary effects. The diagonal Born-Oppenheimer correction (DBOC)[103, 104] is computed at the HF/aug-cc-pVQZ level of theory,[105, 106, 107] and relativistic effects are included via the one-electron Darwin and mass-velocity terms,[108, 109, 110, 111, 112] computed at the CCSD(T)/aug-cc-pCVQZ level of theory.

The spectroscopic constants with anharmonic corrections were obtained from a full quartic force field calculated at the c∼CCSDT(Q)/CBS level of theory described above. The force field was generated using the code GRENDEL++.[113] The energy was expanded in terms of simple internal coordinates in a Taylor series around the equilibrium geometry. The internal coordinates were chosen as the six Be-Be bond distances within the tetrahedral structure; this allowed us to reduce the required number of displacements to 33 by using the equivalence of displaced geometries in full tetrahedral symmetry. The total energies were converged to $10^{-12}E_h$. Second-order perturbation theory[114, 115, 116, 117, 118, 119, 120, 121] (VPT2) was applied to the force field in order to obtain vibrational frequencies and spectroscopic constants. The force constants were transformed to Cartesian space using INTDER2005,[122, 123, 124, 125, 126] and the transformation to normal coordinate representation and subsequent VPT2 analysis was carried out using the program ANHARM.[127, 125] The final VPT2 values were checked by introducing a negligible change to the atomic mass of the atoms in the tetramer. This allowed us to obtain fundamental frequencies using both the symmetric and asymmetric top formalisms, and these methods were found to agree exactly.

Chapter 3

Results and Discussion

3.1 Beryllium Dimer

The experimental results for the challenging Be_2 molecule reported by Merritt and co-workers [1] allow us to evaluate the accuracy of our theoretical treatment. Computed properties for the dimer are shown in Table 4.1. The importance of connected triples and quadruples to the description of this molecule is immediately apparent. The CCSD/CBS potential energy surface gives only a shallow long-range minimum, and the VPT2 analysis at this level of theory gives spectroscopic constants that are not even qualitatively correct. The inclusion of a perturbative estimate of connected triples via the CCSD(T) method gives a PES that is much closer to experiment, however the relative error in the spectroscopic constants is still significant. In the cc-pCVQZ basis set the error in (r_e, ω_0) is (+0.0187 Å, -29.1 cm^{-1}), and little improvement is seen in the cc-pCV5Z basis set, which retains an error of (+0.0132 Å, -25.2 cm^{-1}). Extrapolation to the CBS limit improves agreement with the experimental bond length to (+0.0085 Å), but misses ω_0 by a considerable (-21.6 cm^{-1}). Agreement with the experimental D_e is also poor. Though the difference is small in absolute terms, the CCSD(T)/CBS dissociation energy fails to account for almost 30% of the total bonding energy of Be_2.

Application of the c∼CCSDT(Q)/CBS method (Eq. 2.5) to Be_2 improves agreement with experiment to (+5 cm^{-1}) for ω_0 and brings the predicted dissociation energy to within 3% of the experimental value. The c∼CCSDT(Q)/CBS method represents a twofold improvement over CCSD(T). The additive correction accounts for the effects of an iterative treatment of triple excitations and introduces connected quadruple excitations to the expansion. The full iterative inclusion of connected triples has been shown to be decisive in correctly describing the Be_2 potential curve within the coupled-cluster ansatz, and quadruples have also been shown to make a noticeable contribution to the energy.[][36, 11, 61, 12] These findings are consistent with our results, which indicates that our additive correction for full triples and perturbative quadruples is an accurate representation of these effects. Our computations on Be_2 at this level of theory achieve an accuracy that has previously been recovered only by extensive FCI studies. This underscores the importance of treating higher-order excitations in the dimer beyond the perturbative triples correction in CCSD(T).

3.1.1 Static Correlation in the Dimer and the Tetramer

Further insight into the soundness of our method is gained by directly estimating the degree of multireference character in the clusters. The T_1 diagnostic[128] and the largest T_2 amplitudes from the coupled-cluster wavefunction can be used to assess the influence of static correlation on chemical systems. These diagnostics were computed for Be_2 and Be_4 at the CCSD(T)/cc-pCVQZ level of theory. The results (Table 4.2) confirm that the tetramer has significantly less multireference character than the dimer. The T_1 diagnostic is larger for Be_2 than Be_4 and the largest T_2 amplitude is an order of magnitude larger in the dimer than in the tetramer. The dimer has fourteen T_2 amplitudes that are greater than 0.02. In contrast, the tetramer has only six amplitudes that exceed this cutoff. The excellent performance of our single-reference c∼CCSDT(Q)/CBS method in describing the multireference character of the dimer indicates that any lingering static correlation effects in the tetramer will be adequately treated by our theoretical approach.

3.2 Beryllium Tetramer

3.2.1 Bond Length

There are no experimental data available for Be_4; however, the excellent agreement between the c∼CCSDT(Q)/CBS and experimental parameters for Be_2 gives us confidence that the same methods will yield highly accurate results when applied to Be_4. Table 4.3 shows results for r_e computed at various levels of theory. All-electron correlation shortens the bond length relative to valence-only computations. The CCSD(T) computation gives a bond length that is ∼0.01 Å longer than the CCSD value in the cc-pCVQZ basis set. However, full iterative triples give a bond length ∼0.02 Å shorter than the CCSD(T) result. The c∼CCSDT(Q)/CBS computation allows us to pinpoint the Be-Be bond length in the tetramer at 2.043 Å. The overall variation in the magnitude of r_e from HF to CCSDT(Q) occurs within an interval of (−0.035 Å), which is moderate compared to the variation in D_e values among these levels.

3.2.2 Dissociation Energy

Dissociation energies computed at various levels of theory are shown in Table 4.3. It is apparent from these results that MP2 theory overestimates the bonding energy by nearly 20 kcal mol^{-1}. This tendency has been previously noted by Klopper and Almlöf.[40] In contrast, CCSD underestimates D_e significantly. This has been attributed to the persistent multireference character of beryllium clusters, a character which is not accounted for by the inclusion of single and double excitations.[63] The CCSD(T) method appears to provide a reasonable approximation to D_e; however, it does not completely account for the effects of higher excitations. The move from perturbative triples in CCSD(T) to full iterative triples in CCSDT adds approximately 1 kcal mol^{-1} to the dissociation energy. This positive correction contrasts with the negative correction to atomization energies typically seen when moving from perturbative to iterative triples.[129] The combined effect of the CBS extrapolation and the perturbative estimate of quadruples in the c$\sim$CCSDT(Q)/CBS method adds an additional 1.5 kcal mol^{-1}. The importance of all-electron correlation to the dissociation energy is also apparent. All-electron correlation increases the bonding energy by 2-3 kcal mol^{-1} over the valence-only computations at the different levels of theory.

The incremented focal point table computed with all electrons correlated is shown in Table 4.4. The c$\sim$CCSDT(Q)/CBS optimized Be-Be distance of 2.0427 Å was used for these computations. The dissociation energy is labeled ΔE, and incremental corrections to this energy computed using correlated methods are denoted by the symbol δ. Improving the correlation treatment beyond CCSD(T) to full iterative triples (CCSDT) yields an increment of +0.36 kcal mol^{-1} in the cc-pCVDZ basis set. When perturbative quadruples [CCSDT(Q)] are included, the increment is -0.14 kcal mol^{-1} in the cc-pCVDZ basis set, and this value is used for all basis sets at the CCSDT(Q) level of theory. The validity of this assumption for CCSDT(Q) effects was tested by computing the CCSDT/CCSDT(Q) increment using frozen-core single-point computations in the cc-pVDZ and cc-pVTZ basis sets. The CCSDT(Q)/cc-pVTZ increment was found to be -0.16 kcal mol^{-1}, in close agreement with the CCSDT(Q)/cc-pCVDZ increment reported in the focal point table. This gives strong evidence that the CCSDT(Q) increment can be modeled in the small cc-pCVDZ basis set.

Table 4.4 highlights the high basis set dependence observed in D_e for the tetramer, indicating a need for care in extrapolating to the CBS limit. While the HF energy converges quickly once the cc-pCVTZ basis is reached, correlated methods show a more persistent variation with basis set size. A large increase of 1.41 kcal mol^{-1} is gained by moving from cc-pCVDZ to cc-pCVTZ at the CCSD(T) level. Further increases in the basis set size reduce this dependence however, and convergence is observed at cc-pCVQZ and above. The cc-pCVTZ/cc-pCVQZ change is only 0.34 kcal mol^{-1}, and the cc-pCVQZ/cc-pCV5Z difference shrinks to 0.14 kcal mol^{-1}. The extrapolated difference between the highest explicit energy and the CBS limit at the CCSD(T) level is 0.16 kcal mol^{-1}. This closely mirrors the difference between cc-pCVQZ and cc-pCV5Z, indicating that basis set effects have stabilized. Explicit computations at the CCSDT level give a difference of 0.24 kcal mol^{-1} between the cc-pCVDZ and cc-pCVTZ basis sets. While not insignificant, this is much smaller than the cc-pCVDZ/cc-pCVTZ gap of 1.41 kcal mol^{-1} observed at the CCSD(T) level. By analogy to the behavior observed with CCSD(T), further increases in the basis set size at CCSDT should yield very similar changes in D_e. Based on this assumption, the change for larger basis sets at this level of theory is estimated to be the same as the cc-pCVTZ difference of 0.12 kcal mol^{-1}.

After inclusion of the diagonal Born-Oppenheimer correction and relativistic effects, our final estimate for the dissociation energy is $D_\mathrm{e} = 89.7$ kcal mol^{-1} and $D_0 = 84.9$ kcal mol^{-1}. It is apparent from the focal point analysis that a complete treatment of triples and quadruples in calculating D_e is less important for the tetramer than for the dimer. The sum of the CCSDT and CCSDT(Q) correlation increments from the focal point table modifies the CCSD(T)/CBS dissociation energy by only -0.02 kcal mol^{-1}. This is consistent with the findings of Lee, Rendell, and Taylor (LRT), who reported that the CCSD(T) method gave good results for the dissociation energy when compared to MRCI computations. They obtained $D_\mathrm{e} = 79.5$ kcal mol^{-1} for Be_4 from a CCSD(T) computation with the $[5s\ 3p\ 2d\ 1f]$ basis set,[65] and $D_\mathrm{e} = 77.3$ kcal mol^{-1} using the MRCI method in the same basis set.[63] Our CCSD(T)/cc-pCVQZ dissociation energy is 87.8 kcal mol^{-1}. However, LRT noted deficiencies in their basis set and correlation treatment and estimated that the true dissociation energy would be 80-85 kcal mol^{-1}.[63]

Klopper and Almlöf added complete basis set corrections computed using MP2 theory with linear r_{12} terms (MP2-R12) to LRT's MRCI result.[40] They estimated D_e = 87.9 kcal mol^{-1} for the tetramer, which is close to our CCSD(T)/cc-pCVQZ result, but about 2 kcal mol^{-1} less than our final prediction for D_e. J.S. Lee reported D_e = 89.7 kcal mol^{-1} for Be_4 based on a CCSD(T) computation extrapolated to the CBS limit.[53] This agrees well with our CCSDT(Q)/CBS estimate of D_e = 89.9 kcal mol^{-1} before auxiliary corrections are applied, and indicates that a perturbative estimate of triples can obtain reasonable energetics for this cluster. However, our initial VPT2 results for Be_2 and Be_4 suggest that quadruples may exert a more noticeable influence on the curvature of the bonding potential surface. The best value of ω_0 predicted for the dimer at the CCSD(T) level was qualitatively different from the experimental value. Close agreement was not obtained until quadruples were appended via the c$\sim$CCSDT(Q)/CBS method. These results motivate our investigation of the importance of quadruples in computing spectroscopic parameters for the tetramer.

3.2.3 Vibrational Frequencies

The vibrational frequencies for Be_4 obtained from the full quartic force field in simple internal coordinates are shown in Table 4.5. The cubic and quartic force constants, transformed to the symmetry coordinate representation employed by Rendell, Lee, and Taylor[64] are reported in Table 4.6. The force constants we compute are found to obey the same dependency relationships reported by those authors. We report B_e = 0.448 cm^{-1} and values for the fundamental frequencies of 666.3 (a_1), 467.8 (e), and 570.9 (t_2) in units of cm^{-1}. The anharmonicity corrections obtained from the force field are less than 5% of the magnitude of the fundamentals, validating our use of VPT2 theory to describe this system. In addition, no Fermi resonances are predicted. The spectroscopic constants we report should serve as a guide to experimental efforts to observe this elusive molecule.

Some insight into the importance of quadruple excitations in computing accurate vibrational frequencies for the tetramer may be gained by comparing the harmonic frequencies obtained numerically from our c∼CCSDT(Q) force field with harmonic frequencies computed at the CCSD(T) level using analytic derivatives. Computations at the CCSD(T)/cc-pVTZ level with core electrons frozen gave values of 662.9 (a_1) 469.1 (e), and 570.2 (t_2) cm^{-1} for the harmonic frequencies. These values disagree with our c∼CCSDT(Q) frequencies by [-21.6 cm^{-1} (a_1)], [-13.1 cm^{-1} (e)], and [-19.4 cm^{-1} (t_2)]. Computations at the CCSD(T)/cc-pCVTZ level with all electrons correlated gave harmonic frequencies of 671.3 (a_1), 476.2 (e), and 580.4 (t_2), improving agreement with the c∼CCSDT(Q) values to [-13.2 cm^{-1} (a_1)], [-6.0 cm^{-1} (e)], and [-9.2 cm^{-1} (t_2)]. Given these results, it seems that all-electron correlation and basis set size are more significant factors than perturbative quadruples in computing accurate vibrational frequencies for the tetramer. This differs from the results found for the dimer, where quadruples play an essential role in computing accurate parameters.

An earlier study by Rendell, Lee, and Taylor at the CCSD(T) level found values of 639 (a_1), 455 (e), and 682 (t_2) for the fundamental frequencies of Be_4.[64] Quartic force fields computed at the CCSD(T) level have also been reported for the tetrahedral alkaline earth clusters Mg_4 and Ca_4 by Lee, Rendell, and Taylor,[130, 131] and for tetrahedral P_4 by Persson, Taylor, and Lee.[132] Their studies found small cubic force and quartic force constants for each of these molecules, giving small negative anharmonic corrections to each of the vibrational modes. These findings are consistent with our results. However, in their study of Be_4, LRT found a large positive anharmonic correction of +111 cm^{-1} in the triply-degenerate t_2 mode. This result is due to the contribution of the quartic force constants they computed for Be_4, which were an order of magnitude larger than those obtained for the Mg_4 and Ca_4 clusters. Our quartic force constants are significantly smaller than those reported by LRT, and as a result we find a t_2 correction of -18.8 cm^{-1} (a 3.2 % correction). The size of our quartic force constants and the anharmonic correction for this mode are consistent with the results reported for other X_4 molecules with comparable bonding energies.

3.3 Beryllium Pentamer

3.3.1 Bond Lengths

Table 4.7 shows the optimized bond lengths for D_3h Be$_5$ computed at various levels of theory. The trends shown are very similar to those observed in the tetramer. Correlating all the electrons again shortens the bond length relative to the valence-only computations. For the pentamer, however, the CCSD(T) bond lengths are slightly longer than the CCSD results, which is the reverse of the effect seen in the tetramer when moving between the two levels. The CCSD(T)/cc-pCVQZ equatorial Be-Be bond length of 2.00 Å is shorter than the value of 2.03 Å obtained by Lee, Rendell, and Taylor (LRT) at the CCSD level of theory, and even shorter than the value of 2.04 Å obtained by Sudhakar and co-workers at the MP2 level.[63, 71] The CCSD(T)/cc-pCVQZ axial-equatorial bond length of 2.06 is also shorter than LRT's value of 2.08 Å and the value of 2.09 Å obtained by Sudhakar *et al.* The inclusion of a perturbative estimate of triples offers a noticeable improvement over the CCSD bond lengths. Based on the results of tetramer, it is unlikely that optimization at higher levels of theory would change the CCSD(T) result significantly. Thus we can consider the CCSD(T) result highly accurate.

3.3.2 Static Correlation in the Pentamer

Table 4.8 lists the results of the T_1 diagnostic[128] and the largest T_2 amplitudes from the coupled-cluster wavefunction for Be$_5$. These values are computed at the CCSD(T)/cc-pCVQZ level of theory. The T_1 diagnostic shows that the level of static correlation in the pentamer is almost identical to that of the tetramer. The pentamer's T_2 amplitudes are larger than those of the tetramer, however both clusters have significantly less multireference character than the dimer. The similar levels of static correlation in Be$_4$ and Be$_5$ and the closeness of the energetic predictions of CCSD(T) and higher levels of theory for the tetramer indicate that it is appropriate to treat Be_5 at this level of theory.

3.3.3 Dissociation Energy

The dissociation energy computed at various levels of theory is reported in Table 4.7. The importance of correlating all the electrons in the cluster is apparent, as improvements of 4-5 kcal mol^{-1} are seen in D_e upon moving from valence-only computations to full-core at all levels of theory. We obtain an SCF/cc-pCVQZ bonding energy of 51.6 kcal mol^{-1}, which is close to the value of 49.3 kcal mol^{-1} obtained by LRT at the SCF/$7s3p2d$ level. Both values are approximately 10 kcal mol^{-1} higher than the Be_4 SCF dissociation energy. The MP2 dissociation energies shown in Table 4.7 are even higher than earlier perturbation theory estimates for this cluster. Sudhakar and co-workers obtained D_e = 145.9 kcal mol^{-1} at the MP2/6-311+G* level and 122.1 kcal mol^{-1} using MP4 in the same basis.[71] Their MP4 value is quite close to our CCSD(T)/cc-pCVQZ result of 124.0 kcal mol^{-1}. The authors suggested that the Møller-Plesset expansion might give better results for the pentamer than for the tetramer. However, our MP2/cc-pCVQZ result of D_e = 158.6 kcal mol^{-1} suggests that, as in the tetramer, second-order perturbation theory estimates of D_e overshoot the true value.

Our CCSD/cc-pCVQZ result of D_e = 99.7 kcal mol^{-1} is significantly higher than LRT's CCSD value of 82.3 kcal mol^{-1}, which they computed in a much smaller basis set.[63] This indicates that the dissociation energy in the pentamer shows the same strong basis set dependence observed in the tetramer. The CCSD(T) method has not been previously applied to Be_5. We find D_e = 124.0 kcal mol^{-1} in the cc-pCVQZ basis set at this level of theory. The close agreement in the CCSD(T) and c∼CCSDT(Q) dissociation energies observed for Be_4 gives us confidence that there would be little change in D_e for the pentamer between these two levels of theory. Given the similar levels of static correlation in the two clusters, it is reasonable to assume that the CCSD(T) value reported in Table 4.7 is within 1-2 kcal mol^{-1} of the true value.

3.4 Trends in Bonding Energy for Small Beryllium Clusters

The rigorous *ab initio* predictions of the properties of Be_4 and Be_5 presented in this work, combined with the experimental data on Be_2[1] and the extensive FCI treatment of Be_3 by Junquera and co-workers[6], allow us to make observations about the energetic trends present in this series of molecules. The dimer is very weakly bound, with $D_{\mathrm{e}} = 2.66$ kcal mol^{-1}. Dramatic increases in D_{e} are seen for the next two clusters, with Be_3 bound by 17.2 kcal mol^{-1} and Be_4 by 89.7 kcal mol^{-1}. A more modest increase in the dissociation energy is seen when moving from Be_4 to Be_5, which is bound by 124.0 kcal mol^{-1}. It is clear that the clusters Be_2, Be_3, and Be_4 each exhibit significantly different bonding behavior, but the more modest energetic difference between Be_4 and Be_5 suggests that these clusters share similar bonding behavior. The bonding motif can be illustrated more clearly when the dissociation energies are divided into binding energies per atom (BEPA). The BEPA value for Be_2 is 1.33 kcal mol^{-1} per atom, which increases to 5.7 kcal mol^{-1} for Be_3 and then jumps to 22.4 kcal mol^{-1}for Be_4. After Be_4, the trend seems to stabilize; the BEPA value for Be_5 is 24.8 kcal mol^{-1}, a much smaller increase per atom than that observed in the previous clusters. The BEPA assessment distributes the bonding energy evenly over the cluster, but a more focused look at the energetic gains of adding a fifth Be atom to Be_4 can be gained from the energy of the reaction that removes one Be atom from the pentamer. Table 4.7 lists this value as ΔE. The energy change is only 8.3 kcal mol^{-1} at the SCF level, however this increases to 36.2 kcal mol^{-1} at CCSD(T)/cc-pCVQZ. The bonding energy of this fifth atom is greater than the dissociation energy of the entire Be_3 cluster, emphasizing the presence of a much stronger pattern of chemical bonding in the tetramer and the pentamer than that observed in the smaller clusters.

Chapter 4

Conclusions

The geometry, dissociation energy, and vibrational frequencies with anharmonic corrections for the tetrahedral molecule Be_4 have been computed using highly accurate coupled-cluster theory including quadruple excitations [c∼CCSDT(Q)] with complete basis set (CBS) extrapolations. Fundamental frequencies were obtained from a full quartic force field computed at the c∼CCSDT(Q)/CBS level of theory. The importance of a complete treatment of triple and quadruple excitations in describing the beryllium dimer suggests that they would have a similar influence on the tetramer. However, after accounting for all-electron correlation and errors due to incompleteness of the basis set, the correction to the CCSD(T) bonding energy obtained by moving to the c∼CCSDT(Q) method is found to be small. Full triples and perturbative quadruples have only a minor effect on the the spectroscopic parameters of the molecule.

Benchmarking computations were performed on the more challenging molecule Be_2. The c∼CCSDT(Q)/CBS results are in excellent agreement with experiment for the dimer, despite the strong influence of static correlation on this system. Static correlation is somewhat reduced in the tetramer, and thus we are confident that our theoretical approach provides an adequate description of the ground state potential energy surface of Be_4.

The reliability of the predictions reported in this study may aid the experimental detection of this molecule. The detection of Be_4 should be possible by mass spectrometry, but laboratory detection via vibrational or electronic spectroscopy would be more desirable. We hope that all three avenues of observation will open. A note of caution might be raised concerning the non-observation to date of the tetrahedral N_4 molecule, which should also be kinetically viable.[133, 134] However, we have higher hopes for Be_4, which is predicted to be not only kinetically but also thermodynamically stable.

The geometry and dissociation energy of trigonal bipyramidal Be_5 have been computed using coupled-cluster theory with singles, doubles, and perturbative triples [CCSD(T)] in large basis sets. Triples are found to have a significant effect on the bonding energy, and should be considered essential to a proper description of this molecule. Full triples and perturbative quadruples were found to have very little effect on the energetics of Be_4. Given the similar levels of static correlation in Be_4 and Be_5, this gives us confidence that our CCSD(T) dissociation energy for Be_5 is very close to the true value. The increase in D_e gained when moving from Be_4 to Be_5 is found to be modest, in sharp contrast to the large differences seen between Be_2, Be_3, and Be_4. This points to the onset of chemical bonding patterns in Be_4 that distinguish the larger clusters of beryllium from the dimer and the trimer.

Table 4.1: Benchmark[a] equilibrium bond lengths (Å), vibrational band origins (cm-1), rotational constants (cm-1) and dissociation energies (kcal mol-1) for Be_2.

	r_e	ω_0	B_0	D_e
Be_2				
CCSD/CBS	4.3625	2.9	0.194	0.05
CCSD(T)/cc-pCVQZ	2.4723	193.5	0.590	1.75
CCSD(T)/cc-pCV5Z	2.4668	197.4	0.593	1.84
CCSD(T)/CBS[b]	2.4621	201.0	0.596	1.92
c∼CCSDT(Q)/CBS[c]	2.4385	227.6	0.611	2.73
Experiment[d]	2.4536	222.6	0.609	2.66

[a] The parameters reported in this table were obtained by applying VPT2 to a five-point potential energy surface computed at the indicated level of theory.

[b] Energies extrapolated according to Eqs. (2.6) and (2.7).

[c] Composite approximation, see text for details.

[d] Ref. Merritt09.

Table 4.2: Diagnostics for static correlation (a.u.) at the CCSD(T)/cc-pCVQZ level of theory.

	T_1 diagnostic	Largest T_2 amplitudes
Be_2	0.023	0.225
		0.082
Be_4	0.022	0.062
		0.061

Table 4.3: Optimized Be-Be bond lengths^a and dissociation energies for tetrahedral Be_4.

Method	AO basis	Be-Be (Å)	D_{e} (kcal mol^{-1})
SCF	cc-pCVQZ	2.0698	42.3
MP2$^{(FC)}$	cc-pVQZ	2.0632	106.0
CCSD$^{(FC)}$	cc-pVQZ	2.0487	68.7
CCSD(T)$^{(FC)}$	cc-pVQZ	2.0592	85.1
MP2$^{(AE)}$	cc-pCVQZ	2.0490	108.1
CCSD$^{(AE)}$	cc-pCVQZ	2.0345	72.1
CCSD(T)$^{(AE)}$	cc-pCVQZ	2.0449	87.8
c∼CCSDT$^{(AE)}$	cc-pCVQZ	2.0432	88.4
c∼CCSDT(Q)$^{(AE)}$	CBS	2.0427	89.9

^{a} The optimized bond lengths preceded by the symbol "c∼" were obtained by a numerical fit to a fifth-order polynomial. The other bond lengths reported in this table were optimized using analytic gradients.

$^{(FC)}$ Core electrons frozen in computation .

$^{(AE)}$ All electrons correlated in computation.

Table 4.4: Focal point analysis[a] of the dissociation energy (kcal mol-1) of tetrahedral Be_4.

	ΔE	$+\delta$[MP2]	$+\delta$[CCSD]	$+\delta$[CCSD(T)]	$+\delta$[CCSDT]	$+\delta$[CCSDT(Q)]	ΔE[c∼CCSDT(Q)]
cc-pCVDZ	+39.26	+53.51	−36.36	+14.00	+0.36	−0.14	[+70.63]
cc-pCVTZ	+41.60	+62.22	−35.67	+15.41	+0.12	[−0.14]	[+83.53]
cc-pCVQZ	+42.10	+66.02	−36.06	+15.75	[+0.12]	[−0.14]	[+87.78]
cc-pCV5Z	+42.16	+67.22	−36.38	+15.89	[+0.12]	[−0.14]	[+88.87]
CBS LIMIT	[+42.12]	[+68.47]	[−36.71]	[+16.05]	[+0.12]	[−0.14]	**[+89.91]**
Fit Function	$a + be^{-cX}$	$a + bX^{-3}$	$a + bX^{-3}$	$a + bX^{-3}$	additive	additive	
Points (X)	3,4,5	4,5	4,5	4,5			

ΔE_e (final) = ΔE_e[CBS CCSDT(Q)] + Δ_{rel}[CCSD(T)/aug-cc-pCVQZ] + Δ_{DBOC}[HF/aug-cc-pVQZ]
= 89.91 − 0.24 + 0.04 = **89.71 kcal mol-1**

[a] Computed at $r_e = 2.0427$ Å, the c∼CCSDT(Q)/CBS bond length.

[b] The symbol δ denotes the increment in the relative energy (ΔE_e) with respect to the preceding level of theory in the hierarchy HF→MP2→CCSD→CCSD(T)→CCSDT→CCSDT(Q). Square brackets signify results obtained from basis set extrapolations or additivity assumptions. Final predictions are boldfaced.

Table 4.5: Harmonic and fundamental vibrational frequencies (cm^{-1}) for tetrahedral Be$_4$ computed at the c$\sim$CCSDT(Q)/CBS level of theory.

Mode (Sym.)	ω	ν	ν - ω
ν_1 (a_1)	684.5	666.3	−18.3
ν_2 (e)	482.2	467.8	−14.4
ν_3 (e)	482.2	467.8	−14.4
ν_4 (t_2)	589.6	570.9	−18.8
ν_5 (t_2)	589.6	570.9	−18.8
ν_6 (t_2)	589.6	570.9	−18.8

Table 4.6: Nonzero cubic (aJ/Å^3) and quartic (aJ/Å^4) force constants for Be$_4$.

F_{111}	-1.056
$F_{12a2a} = F_{12b2b}$	-1.541
$F_{13x3x} = F_{13y3y} = F_{13z3z}$	-1.320
$F_{2a2a2a} = -F_{2a2b2b}$	0.943
$F_{2a3z3z} = -2F_{2a3x3x} = -2F_{2a3y3y} = \frac{2}{\sqrt{3}}F_{2b3x3x} = -\frac{2}{\sqrt{3}}F_{2b3y3y}$	2.162
F_{3x3y3z}	-0.099
F_{1111}	1.365
$F_{112a2a} = F_{112b2b}$	1.943
$F_{113x3x} = F_{113y3y} = F_{113z3z}$	1.696
$F_{12a2a2a} = -F_{12a2b2b}$	-1.309
$F_{12a3z3z} = -2F_{12a3x3x} = -2F_{12a3y3y} = -\frac{2}{\sqrt{3}}F_{12b3x3x} = -\frac{2}{\sqrt{3}}F_{12b3y3y}$	-2.713
$F_{13x3y3z}$	-0.001
$F_{2a2a2a2a} = F_{2b2b2b2b} = 3F_{2a2a2b2b}$	0.509
$F_{2a2a3z3z}$	2.873
$F_{2b2b3z3z}$	-0.523
$F_{2a2a3y3y} = F_{2a2a3x3x} = \frac{1}{4}(F_{2a2a3z3z} + 3F_{2b2b3z3z})$	0.326
$F_{2b2b3y3y} = F_{2b2b3x3x} = \frac{1}{4}(3F_{2a2a3z3z} + F_{2b2b3z3z})$	2.024
$F_{2a2b3y3y} = -F_{2a2b3x3x} = \frac{3}{\sqrt{4}}(F_{2a2a3z3z} - F_{2b2b3z3z})$	1.471
$F_{3x3x3x3x} = F_{3y3y3y3y} = F_{3z3z3z3z}$	3.445
$F_{3x3x3y3y} = F_{3x3x3z3z} = F_{3y3y3z3z}$	-0.535

Table 4.7: Optimized Be-Be bond lengths[a] and dissociation energies for trigonal bipyramidal Be_5.

Method	AO basis	Be-Be (eq) (Å)	Be-Be (eq-ax)	D_e (kcal mol^{-1})	ΔE ($Be_5 \rightarrow Be_4$ + Be)
SCF	cc-pCVQZ	2.0265	2.0759	51.6	8.3
MP2$^{(FC)}$	cc-pVQZ	2.0137	2.0697	155.1	49.1
CCSD$^{(FC)}$	cc-pVQZ	2.0096	2.0602	94.8	26.1
CCSD(T)$^{(FC)}$	cc-pVQZ	2.0129	2.0752	119.	34.8
MP2$^{(AE)}$	cc-pCVQZ	1.9998	2.0555	158.6	50.5
CCSD$^{(AE)}$	cc-pCVQZ	1.9969	2.0460	99.7	27.6
CCSD(T)$^{(AE)}$	cc-pCVQZ	2.0000	2.0604	124.0	36.2

[a] The optimized bond lengths reported in this table were obtained using analytic gradients.

$^{(FC)}$ Core electrons frozen in computation.

$^{(AE)}$ All electrons correlated in computation.

Table 4.8: Diagnostics for static correlation (a.u.) at the CCSD(T)/cc-pCVQZ level of theory.

	T_1 diagnostic	Largest T_2 amplitudes
Be_5	0.022	0.126
		0.080

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