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Accurate electrical and spectroscopic properties of $X\,^1\Sigma^+$ BeO from coupled-cluster methods

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Summary. This paper reports a series of coupled-cluster (CC) calculations through CCSDT on the theoretically challenging ground state of the BeO molecule. Along with CC methods, quadratic configuration interaction (QCI) approximations to CC theory have been used (QCISD and QCISD(T)), which show several dramatic failings. Equilibrium electrical properties (μ, α_{xx}, and α_{zz}) and basic spectroscopic properties (r_e, ω_e, D_e, and infrared intensity (I)) have been computed. Basis set and electron correlation effects are analyzed in order to arrive at accurate values of the dipole moment and polarizability, which are not known experimentally. For the dipole moment, we obtain a value of 6.25 D, with an uncertainty of about 0.1 D. For α_{xx} and α_{zz}, we suggest respective values of 32 and 36 atomic units (a.u.) and error bars of about 1 and 2 a.u. With extended basis sets, the spectroscopic properties r_e, ω_e, and D_e are reproduced to high accuracy, which is the first time this has been achieved for this species by *ab initio* methods. At the highest calculation levels, I is predicted to be very small. Although I has not been measured, some support for this prediction comes from a recent infrared study of BeO–rare gas complexes. The QCI methods are shown to be much more sensitive to basis set, and even with large basis sets yield values of α_{zz} and I which differ from CC results by an order of magnitude and three orders of magnitude, respectively. These differences doubtless arise from the importance of single excitations (T_1) for this molecule, as several terms involving T_1 are neglected in the QCISD approximation compared with CCSD. We also report CC calculations with Brueckner orbitals, which yield results similar to those obtained with restricted Hartree–Fock orbitals.

Key words: BeO molecule – Coupled-cluster calculations – Quadratic configuration interaction – Spectroscopy

1. Introduction

The $X\,^1\Sigma^+$ state of BeO has long been known to be a challenge to *ab initio* calculations [1], and it has been studied on several occasions. It is a highly ionic

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species, and its high polarity makes a significant contribution to the stability of complexes such as He–BeO [2], Ne–BeO [3], CO–BeO [4], and N_2 BeO [4], as well as the existence of a dipole-bound anion [5], all of which have been predicted by theoretical calculations. Complexes of BeO with Ar, Kr, and Xe have recently been synthesized [6].

Early theoretical calculations [7, 8] were performed at the SCF level and were unable to predict the correct ordering of the low-lying electronic states. Using first-order CI methods and double-zeta plus polarization Slater basis sets, Schaefer and coworkers [1, 9] obtained the correct ordering of electronic states and quite accurate spectroscopic constants for the difficult ground state. Combining single reference CI data with some experimental data, Langhoff et al. [10] obtained an accurate dissociation energy. In a study of the ability of single reference coupled-cluster (CC) methods to describe BeO, Scuseria et al. [11] used a small Gaussian basis set, computed r_e and ω_e with three CC methods, and compared with the results given by CI with all single, double, triple, and quadruple excitations (CISDTQ). Multi-reference CI calculations with a modest basis set have been performed by Irisawa and Iwata [12].

Electrical properties of BeO are important for understanding the dipole bound anion [5] and the intermolecular complexes [2–4]. Some of these have been computed by Yoshioka and Jordan [13], Pyykko et al. [14], and by Diercksen et al. [15].

As well as spectroscopic and electrical properties, miscellaneous other properties of BeO have been computed, including magnetic properties [16] and full CI transition moments [17]. The molecule has also been used as a test case for MCSCF wavefunction construction [18] and convergence [19]. Solid state calculations have also been performed [20].

In this paper we report results of a study of electrical and spectroscopic properties of BeO using CC methods and extended basis sets. There are several reasons for this study.

First, although electrical properties of BeO are needed for several reasons, not even the dipole moment has been measured experimentally. A number of papers have quoted a value of 7.1 ± 0.3 D, but this is not an experimental value; it was arrived at by Yoshimine [8] by decreasing the Hartree–Fock dipole moment of BeO by a value determined from examining the errors of Hartree–Fock dipole moments of some other molecules. Explicit calculations of the dipole moment with correlated methods [13, 15] have indicated that the correction applied by Yoshimine is too small, and that the true dipole moment is below the suggested range. At the same time, it should be said that no previous calculation is of sufficient accuracy to make this conclusion certain. Consequently, there is a need for a thorough investigation of this issue using accurate methods and large basis sets. Similarly, there are no experimental data for the dipole moment as a function of internuclear distance, infrared intensity, or polarizability.

Second, the theoretical studies of intermolecular complexes of BeO have used rather modest basis sets and low-order many-body perturbation theory. Considering the complexity of the ground state of BeO, the reliability of these treatments must be questioned. High-level calculations on BeO can be used as benchmarks for more approximate calculations. For example, in order to compute accurate binding energies for the intermolecular complexes, it will be necessary for a method to provide accurate electrical properties of BeO. Likewise, the BeO stretching frequency of the complex will only be computed accurately if the frequency of the diatomic is calculated accurately.

Third, spectroscopic properties (e.g. r_e, ω_e, D_e, and infrared intensity) also warrant a more careful study than has hitherto been done. Despite the fact that there have been many calculations on BeO, the most basic spectroscopic properties have not been computed with high accuracy. In particular, it should be noted that the accurate D_e for the ground state obtained by Langhoff et al. [10] was obtained from a calculation of D_e for an excited state and the observed excitation energy.

Another aspect of this work is methodological. This study uses a wide variety of CC methods, including the "quadratic configuration interaction" (QCI) approximation. The ground state of BeO has large T_1 amplitudes and therefore offers a critical test for QCI methods since they neglect many nonlinear terms involving T_1. Comparisons of the different methods shows some dramatic failings of the QCI methods, indicating that the QCI truncation is not justified in the present case and is unlikely to be satisfactory in other systems with large T_1 amplitudes. As T_1 is large, we have also performed CC calculations with Brueckner orbital reference determinants [21–23], which make an interesting comparison with those based on a closed-shell restricted Hartree-Fock (RHF) reference determinant. Finally, we critically address the $\mathscr{T}_1$ diagnostic [24, 25] as an indicator of limitations of CC methods.

2. Computational details

A variety of Gaussian basis sets have been used in this work.

(*a*) A double-zeta plus polarization (DZP) set [11]. The Be DZP basis set is the $3s2p$ set from Dunning and Hay [26], augmented with a d function with exponent 0.6 [11], while the O DZP basis set is Dunning's $4s2p$ set [27], augmented with a d function with exponent 0.85 [26].

(*b*) The $5s3p2d$ polarized basis set is that of Sadlej [28]. This is a medium-sized basis set which was designed to be sufficiently flexible in the valence region to describe electrical properties such as the dipole moment and dipole polarizability quite well.

(*c*) The 6-311 + G($3df$) basis set [29], which in terms of numbers of contracted functions is $5s4p3d1f$.

(*d*) The $10s7p2d1f$ (O) and $8s5p2d1f$ (Be) basis set of Diercksen et al. [15].

(*e*) The [$5s4p3d2f$] and [$7s7p4d3f$] generally contracted, atomic natural orbital (ANO) sets of Widmark et al. [30].

Apart from the DZP set, all basis sets used spherical harmonic d and f functions.

A variety of single reference determinant CC methods have been used in this work, including some with the QCISD and QCISD(T) methods. Most calculations have been based on the closed-shell RHF reference determinant, while some have used a Brueckner orbital reference determinant. All calculations were performed with the ACES II program system [31].

Two series of calculations have been performed. In the first series, the dipole moment and parallel (z) and perpendicular (x) components of the dipole polarizability have been computed at the experimental equilibrium internuclear separation [32]. In the second, the equilibrium bond length has been obtained, and the harmonic frequency, dissociation energy, and dipole moment have been determined at this bond length.

For methods for which analytical derivatives are available in ACES II [33] (namely CCSD, CCSD + T(CCSD), CCSD(T), QCISD, and QCISD(T)), gradients and dipole moments have been calculated analytically, and harmonic frequencies, infrared intensities, and polarizabilities have been computed from appropriate finite differences of gradients and dipole moments. For other methods, differentiations have been performed numerically from energies.

3. Results and discussion

We begin this section by reviewing the methods used. Following this we consider the demands which BeO places on a theoretical method. We then present results of calculations of the dipole moment, dipole polarizability, and spectroscopic properties, each time calibrating methods with complete CCSDT. Finally, we compare QCISD and QCISD(T) with CCSD and CCSD(T).

3.1. Methodological review

The CCSD method [34] includes all effects of single (T_1) and double (T_2) excitation cluster operators and is exact for two electrons. The different CCSDT-*n* methods are *iterative* approximations to the complete CC single, double, and triple excitation method (CCSDT) [35]. The latter includes all effects of the T_1, T_2, and T_3 cluster operators and is exact for three electrons. CCSDT-1a [36] includes the lowest-order term ($W_N T_2$) in the T_3 equation and then $W_N T_3$ in the T_1 and T_2 equations, while CCSDT-1b [37] is the same as CCSDT-1a except that it also has the $W_N T_1 T_3$ term in the T_2 equation. CCSDT-2 [38] extends CCSDT-1b by adding the $W_N T_2^2/2$ term to the T_3 equation, and CCSDT-3 [38] includes all terms in the T_3 equation which do not include T_3. The other methods all include T_3 *noniteratively*, i.e. T_1 and T_2 are not influenced by T_3, and in this sense may be considered less theoretically complete than their iterative counterparts, although they sometimes give "better" results due to a balance of errors. These methods correspond to noniterative approximations to CCSDT-1a. The CCSD + T(CCSD) method [37] adds the fourth-order triples energy term of many-body perturbation theory (MBPT), evaluated with the converged CCSD T_2 amplitudes, to the CCSD energy. CCSD(T) [39] extends CCSD + T(CCSD) by also introducing the converged CCSD T_1 amplitudes by the addition of the fifth-order $E_{\mathrm{ST}}^{[5]}$ term [40]. Through fifth-order MBPT CCSD(T) is equivalent to the CCSDT-1 approximation. When using Brueckner orbitals [21–23], $T_1 = 0$, so CCSD becomes B-CCD, and CCSD(T) becomes B-CCD(T).

The QCISD method [41] is a truncation of CCSD. It neglects all nonlinear terms except for the $T_2^2/2$ term in the T_2 equation and the $T_1 T_2$ term redundant in the T_1 equation. The QCISD(T) method incorporates triple excitations in the same manner as CCSD(T), but it has an additional $E_{\mathrm{ST}}^{[5]}$ term in order to account for the $T_1 T_2$ term in the T_2 equation, which is not included in the QCISD method. Through fifth-order of MBPT, QCISD(T) is equivalent to CCSD(T) and CCSDT-1.

3.2. Electron correlation in $X\,{}^1\Sigma^+$ BeO

We now consider, within the realm of single reference CC theory, what methods are likely to provide a reliable account of the electron correlation in BeO. To do this we

Table 1. Largest T_1 and T_2 amplitudes of CCSD wavefunction for $X\,^1\Sigma^+$ BeO at internuclear separation of 1.331 Å. The basis set is ANO-5*s*4*p*3*d*2*f*. All electrons were correlated and all virtual orbitals included. The diagnostic $\mathscr{T}_1$ is 0.033. The orbital labelling includes the core orbitals

Amplitude description	Value
T_1 ($4\sigma \rightarrow 5\sigma$)	-0.089
T_1 ($4\sigma \rightarrow 6\sigma$)	-0.030
T_2 ($1\pi_x^2 \rightarrow 2\pi_x^2$)	-0.040
T_2 ($1\pi_y^2 \rightarrow 2\pi_y^2$)	-0.040

investigate the CCSD wavefunction. Using the ANO-5*s*4*p*3*d*2*f* basis set, we have performed a CCSD calculation at the experimental internuclear separation of 1.331 Å. The largest amplitudes are shown in Table 1. It is seen that the dominant secondary determinants are singly excited relative to the reference, while doubly excited ones are much less important. Therefore, an excellent approximation should be provided by the complete CCSDT wavefunction, since it includes all single and double excitations from the most important secondary determinants. Moreover, by virtue of the exponential ansatz, the disconnected parts of quadruple excitations (from $T_2^2/2$), which in most molecules are numerically much more important than the connected parts (i.e. T_4), are also included.

Unfortunately, an extensive study with large basis sets with the CCSDT method, while not impossible, is rather expensive. Therefore, we must consider whether more economical, approximate treatments of triple excitations, particularly noniterative procedures such as CCSD + T(CCSD) and CCSD(T), are sufficiently accurate. As we shall show, CCSD(T) does indeed reproduce the full CCSDT results very well, and so in conjunction with large basis sets, should provide accurate properties.

There is some confusion regarding the proposed $\mathscr{T}_1$ diagnostic [24, 25], which takes the Euclidean norm of the T_1 amplitudes subject to Hartree–Fock orbitals and normalizes them:

$$\mathscr{T}_1 = \sqrt{\sum_{a,i} (t_i^a)^2/N}, \tag{1}$$

where a and i refer, respectively, to virtual and occupied orbitals and N is the number of correlated electrons. It is clear from many older papers [42–44] that large T_1 amplitudes in CCSD indicate that the orbitals are in some sense less suited to the description of a problem, as new orbitals can be introduced by incorporating the T_1 occupied-virtual amplitudes into their form, and this has been done [45]. This is an orbital relaxation phenomenon, that is largely introduced automatically in CCSD and its extensions, as any single determinant ϕ can be rotated to another Φ, viz., $\Phi = \exp(T_1)\phi$. Though restricting to HF orbitals limits the relaxation to occupied and virtual blocks, obviously, the $\mathscr{T}_1$ expression provides some measure of the importance of single excitations and their repeated products.

However, the $\mathscr{T}_1$ diagnostic has not always been viewed solely as a measure of orbital relaxation, but instead as a measure of "multi-reference effects" [46, 47] or "nondynamical correlation effects" [25]. We quote: "$\mathcal{T}_1$ is investigated for several systems which exhibit a range of multi-reference behavior and is shown to be an excellent measure of the importance of nondynamic electron correlation" [25]. Or "It has been advocated that a large $\mathcal{T}_1$ ($\geqslant 0.02$) is an indication that nondynamical electron correlation effects are very important" [48].[1] Reference [25] itself emphasizes the orbital relaxation aspect, being primarily a single excitation effect, and the principal example of CuH falls into this category. However, "multi-reference" and "nondynamical correlation" usually refer to more than single excitations. Classic examples like bond breaking require at least two determinants (GVB) differing by a double excitation, as does a description of open-shell singlets or the prototype multireference examples O_3 and $^1A_1$ CH_2. Consequently, our best indicator as a basis for such multi-reference character is not $\mathcal{T}_1$, but the size of the largest T_2 cluster amplitudes, as has been used by us since the initial CCD work [50].

We can illustrate the misuse of $\mathcal{T}_1$ by comparing the isoelectronic series $X\,^1\Sigma^+$ BeO, $X\,^1\Sigma_g^+$ C_2, and $a\,^1\Sigma^+$ BN. The $\mathcal{T}_1$ for BeO from the calculation described at the beginning of this section is 0.033 (with frozen core electrons it is 0.041), the largest T_2 is -0.04. The dominant amplitudes are shown in Table 1. C_2 has quite large single excitation amplitudes and one particularly large double excitation amplitude: with the ANO-$5s4p3d2f$ basis set and an internuclear distance of 1.243 Å, the CCSD $\mathcal{T}_1$ is actually smaller, 0.032 (frozen core value is 0.039), and the largest CCSD amplitude is $T_2(2\sigma_u^2 \rightarrow 3\sigma_g^2) = -0.274$. We have recently studied $X\,^1\Sigma_g^+$ C_2 with the CCSD(T) method [51], and despite the large T_2, found that very good results were obtained for r_e, ω_e, and D_e. The energy difference between this state and the first excited state ($a\,^3\Pi_u$) was not so well reproduced owing to the large multi-reference character of the ground state. $a\,^1\Sigma^+$ BN has significantly larger T_1 amplitudes than both BeO and C_2, and it also has one particularly large T_2: with the ANO-$5s4p3d2f$ basis and an internuclear distance of 1.28 Å, the CCSD $\mathcal{T}_1$ is 0.059 (frozen core value is 0.073), and the largest CCSD amplitude is $T_2(4\sigma^2 \rightarrow 5\sigma^2) = 0.211$. This system was recently studied by Martin et al. [52], who found that CCSD(T) was unable to reproduce r_e and ω_e satisfactorily, with the CCSD(T) results differing significantly from CCSDT and multi-reference CI. Not surprisingly, there were also difficulties with T_e. C_2 and BN both have much larger T_2 amplitudes than BeO, while BN also has larger T_1 amplitudes. As single excitation (orbital relaxation) effects are nearly always going to be handled by CCSD and higher approximations, the success of CCSD(T) for C_2 ground state properties further justifies the application of CCSD(T) to BeO. Since BN has much more multi-reference, double excitation character than BeO, the problems encountered with BN *should* not be encountered with BeO. Incidentally, we have recently observed that CCSD(T) results for some properties of BN are significantly improved by using Brueckner orbitals ($T_1 = 0$) [53], further eliminating any single excitation effects. A final word on the differences between BeO and C_2 and BN is that C_2 and BN also have very small $^1\Sigma^+ - {}^3\Pi$ separations, while that of BeO is much larger.

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[1] Reference [25] stated "if $\mathcal{T}_1$ is greater than 0.02, then single-reference-based electron correlation methods are probably unreliable, and will certainly not yield highly accurate results". This statement apparently refers to CCSD, and not to CC methods which include connected triple excitations: Bowman et al. [49] have recently stated that "the CCSD(T) method has given very good results for diagnostic values up to 0.08".

Table 2. Calculated dipole moment of $X\,{}^1\Sigma^+$ BeO at experimental equilibrium internuclear separation with $5s3p2d$ basis set. Atomic units are used. All electrons were correlated and all virtual orbitals included

	Energy	μ
SCF	– 89.429153	2.95
MBPT(2)	– 89.708986	2.48
CCSD	– 89.703870	2.56
CCSD + T(CCSD)	– 89.718657	2.26
CCSD(T)	– 89.714159	2.43
CCSDT-1b[a]	– 89.687982	2.27
CCSDT-3	– 89.717046	2.29
CCSDT	– 89.715237	2.40
B-CCD	– 89.701190	2.64
B-CCD(T)	– 89.714589	2.42

[a] O(1*s*) electrons not correlated (Ref. [15]).

3.3. *Dipole moment*

Table 2 shows the dipole moment of BeO computed with the $5s3p2d$ basis set and a variety of methods. The purpose of these data is to compare more approximate methods with CCSDT. It is seen that electron correlation significantly decreases μ, and that triple excitations decrease the CCSD value. The magnitude of the triples correction varies somewhat with method. Of the various methods that include triple excitations, it is seen that CCSD(T) best approximates CCSDT. The closeness of the CCSD(T) results gives us confidence in using this more economical method with larger basis sets, the results of which we consider below. Before doing so, we consider the effect of using Brueckner rather than Hartree–Fock orbitals. Table 2 shows that the results differ little from the closed-shell RHF CC results, illustrating once again the effective orbital invariance of CC methods [54, 55]. Some Brueckner orbital property calculations have recently been performed by Kobayashi et al. [56]. For the systems investigated (Ne, Be, CH^+, BH, NNO, and CO), small differences were observed between the Brueckner and Hartree–Fock-based results.

We now consider the large basis set results (Table 3). With all four basis sets, the Hartree–Fock limit dipole moment is obtained, and all four basis sets give similar results with correlated methods. In view of this uniformity, it is most likely that these basis sets saturate the *spdf* space for this property. Therefore, considering the reliability of the CCSD(T) method, the true dipole moment of BeO is 6.25 D, with an uncertainty of about 0.1 D. This lies outside of the range suggested by Yoshimine [8], but this is not surprising since correlation effects in BeO are unlikely to be extrapolated reliably from those of other molecules.

There have been few previous correlated estimates of the dipole moment of BeO. With the CCSD + T(CCSD) method and a large segmented basis set, Diercksen et al. [15] obtained 5.87 D, which differs slightly from our CCSD + T(CCSD) results with the same basis set because the oxygen core electrons were not correlated. As we showed above, the CCSD + T(CCSD) method

Table 3. Calculated dipole moment of $X\,^1\Sigma^+$ BeO using extended basis sets at the experimental internuclear separation. All electrons are correlated and all virtual orbitals included

Basis set	Method	Energy [a.u]	μ [a.u.]	μ [D]
ANO-5*s*4*p*3*d*2*f*	SCF	− 89.451158	2.96	7.52
ANO-5*s*4*p*3*d*2*f*	MBPT(2)	− 89.789073	2.49	6.33
ANO-5*s*4*p*3*d*2*f*	CCSD	− 89.778404	2.60	6.61
ANO-5*s*4*p*3*d*2*f*	CCSD + T(CCSD)	− 89.798763	2.33	5.92
ANO-5*s*4*p*3*d*2*f*	CCSD(T)	− 89.795540	2.46	6.25
ANO-7*s*7*p*4*d*3*f*	CCSD(T)	− 89.848125	2.46	6.25
6-311 + G(3*df*)	CCSD(T)	− 89.791260	2.46	6.25
10*s*7*p*2*d*1*f* (O) 8*s*5*p*2*d*1*f* (Be)	CCSD(T)	− 89.824254	2.46	6.25

Table 4. Calculated values of α_{xx} and α_{zz} for $X\,^1\Sigma^+$ BeO at experimental equilibrium internuclear separation with 5*s*3*p*2*d* basis set. Atomic units are used. All electrons were correlated and all virtual orbitals included

	α_{xx}	α_{zz}
SCF	22.4	19.7
MBPT(2)	32.3	29.3
CCSD	31.3	29.8
CCSD + T(CCSD)	38.7	45.9
CCSD(T)	35.1	34.4
CCSDT-1b[a]	35.3	45.5
CCSDT-3	35.0	44.9
CCSDT	34.3	36.0
B-CCD	31.3	24.8
B-CCD(T)	33.5	34.5

[a] O(1*s*) electrons not correlated (Reference [15])

appears to underestimate the dipole moment. Using somewhat smaller basis sets and the MBPT(2) method, Yoshioka and Jordan obtained a value of 6.40 D.

We also investigated the sensitivity of the dipole moment to geometry by computing it at the equilibrium geometries given by some of the methods with the ANO-5*s*4*p*3*d*2*f* basis set. The results were insignificantly different than the results obtained at the experimental equilibrium bond length, since the calculated bond lengths are very close to the experimental one (see below).

3.4. Dipole polarizability

For this property we have also performed calibration calculations with the 5*s*3*p*2*d* basis set, and the results are shown in Table 4.

Table 5. Calculated α_{xx} and α_{zz} of $X\,^1\Sigma^+$ BeO at the experimental equilibrium internuclear separation using extended basis sets. Atomic units are used. All electrons were correlated and all virtual orbitals included

Basis	Method	α_{xx}	α_{zz}
ANO-5*s*4*p*3*d*2*f*	SCF	21.9	20.4
ANO-5*s*4*p*3*d*2*f*	MBPT(2)	31.0	30.3
ANO-5*s*4*p*3*d*2*f*	CCSD	28.9	28.3
ANO-5*s*4*p*3*d*2*f*	CCSD + T(CCSD)	34.7	42.8
ANO-5*s*4*p*3*d*2*f*	CCSD(T)	32.6	34.4
ANO-7*s*7*p*4*d*3*f*	CCSD(T)		34.0
6-311 + G(3*df*)	CCSD(T)	32.6	34.1
10*s*7*p*2*d*1*f* (O) 8*s*5*p*2*d*1*f* (Be)	CCSD(T)		35.0

α_{xx}, the perpendicular component, is increased significantly by the inclusion of electron correlation, with triple excitations increasing it by varying degrees. With the exception of CCSD + T(CCSD), the results from the CC methods including triple excitations lie in an interval of about 2 a.u. The CCSDT value is quite well approximated by CCSD(T) and CCSDT-3. With a Brueckner orbital reference, the CCSD result is unchanged, but the CCSD(T) value is decreased by 1.6 a.u.

In contrast to what is found for α_{xx}, the behavior of α_{zz} is somewhat erratic. Taking the CCSDT result as the reference point, satisfactory results are given by the CCSD(T) method, but CCSD + T(CCSD), CCSDT-1b, and CCSDT-3 all overestimate this quantity significantly. Using a Brueckner reference, the CCSD value of α_{zz} is decreased by 5 a.u., but the CCSD(T) result is essentially unchanged.

Table 5 shows the value of α_{xx} and α_{zz} obtained with several methods and extended basis sets. The numerical results and trends are similar to those found with the smaller 5*s*3*p*2*d* basis set. If we examine the results for a particular method as a function of basis set, we see a small variation, indicating that extension of the *spdf* space is unlikely to change the results for this property. Considering the difference between the CCSD(T) and CCSDT results in Table 4, the true values for α_{xx} are close to 32 and 36 a.u. respectively. Basing their estimates on the CCSD + T(CCSD) method, Diercksen et al. [15] estimated higher values of 36 and 44 a.u., while MBPT(2) calculations with smaller basis sets yielded a value of about 30 a.u. for both components [13]. Our estimated anisotropy is about midway between the values obtained in previous studies [13, 15].

3.5. *Spectroscopic properties*

For spectroscopic properties we have used the DZP basis set for calibration of methods. Computed bond lengths, harmonic vibrational frequencies, dissociation energies, and dipole moments are shown in Table 6. These data are a substantial extension of the results presented earlier [11]. For this small basis set, the appropriate reference point is the CISDTQ data. It was found that while CCSDT gave results very close to CISDTQ, the CCSDT-1b method showed a rather large

Table 6. Calculated spectroscopic properties of $X\,^1\Sigma^+$BeO. DZP basis set. (O(1*s*) electrons not correlated and highest virtual orbital discarded)

	Energy	r_e [A]	ω_e [cm^{-1}]	D_e [eV]
SCF	− 89.423222	1.312	1690	1.27
CCSD	− 89.655281	1.351	1511	3.39
CCSD + T(CCSD)	− 89.671190	1.386	1301	3.79
CCSD(T)	− 89.664881	1.367	1406	3.62
CCSDT-1a	− 89.672263	1.403	1131	3.82
CCSDT-1b	− 89.672091	1.400	1164	3.82
CCSDT-2	− 89.667867	1.378	1335	3.70
CCSDT-3	− 89.669674	1.388	1268	3.75
CCSDT	− 89.666290	1.368	1413	3.66
CISDTQ[a]	− 89.665616	1.367	1419	

[a] Reference [11]

Table 7. Calculated spectroscopic properties of $X\,^1\Sigma^+$BeO, using the ANO-5*s*4*p*3*d*2*f* basis set. All electrons are correlated and all virtual orbitals included

	Energy	r_e [A]	ω_e [cm^{-1}]	μ [D]	I [km mol^{-1}]	D_e [eV]
CCSD	− 89.778655	1.315	1591	6.59	27.5	4.26
CCSD(T)	− 89.795543	1.329	1496	6.25	0.02	4.62
B-CCD	− 89.776541	1.311	1609	6.73	44.9	4.21
B-CCD(T)	− 89.795787	1.330	1496	6.23	0.005	4.62
Experiment[a]		1.331	1487			4.69

[a] Reference [32]

deviation. The present data allow us to assess a wider range of methods for including triple excitations. We consider first the iterative approximations to CCSDT, namely CCSDT-1a, CCSDT-1b, CCSDT-2, and CCSDT-3. The CCSDT-1 methods yield bond lengths which are significantly greater than the CISDTQ results and correspondingly smaller frequencies. The CCSDT-2 method yields greatly improved results, but the CCSDT-3 method reverses the trend. Overall, none of the iterative T_3 approximations considered reproduces the complete CCSDT results satisfactorily. We turn now to the noniterative approximations, CCSD + T(CCSD) and CCSD(T). The results of the former display the same failings as CCSDT-1, although to a smaller extent. The CCSD(T) method, on the other hand, gives results in excellent agreement with CCSDT, despite the fact that it differs from CCSD + T(CCSD) by a single fifth-order energy contribution, and through fifth-order is equivalent to CCSDT-1. Clearly, then, the agreement must again be regarded as somewhat fortuitous, but must now be regarded as an established fact [48, 51, 54, 55] with the one exception being potential energy curves at large separation where CCSDT-1 results are qualitatively better [55].

We now consider results with the ANO-5*s*4*p*3*d*2*f* basis set. These are shown in Table 7. Using the CCSD(T) method, the calculated bond length, frequency, and dissociation energy are in very good agreement with experiment. For CCSD(T), Brueckner orbital calculations give essentially the same results as those based on a closed-shell RHF reference determinant, while for CCSD the differences are somewhat larger. In a recent comparison of Brueckner and RHF CC results [57], it was found that the infrared intensity was somewhat sensitive to the reference determinant. This is true in this case for the CCSD and B-CCD results, but there is a small difference in absolute values between the CCSD(T) and B-CCD(T) results, although there is a significant percentage difference.

The calculated infrared intensity of BeO is of some interest. Based on SCF data, Yoshimine [8] discussed the question of whether the maximum in the dipole moment curve occurs before or after the minimum in the potential energy curve of the alkaline earth monoxides. The predictions were that for BeO the dipole maximum occurred at greater distance than R_e, but that as one went down the group the difference in distances became smaller, with the oxides of the heavier elements having a maximum in the dipole moment curve at a smaller internuclear distance than R_e. Our best calculations (CCSD(T) and B-CCD(T) with the ANO-5*s*4*p*3*d*2*f* basis set) for BeO indicate that the turning points are almost coincident, i.e. the infrared intensity is very small, in disagreement with Yoshimine's data and some of our data for other methods. However, although we are not aware of any measurement of the infrared intensity of BeO, a recent experiment may indicate that it is small. Thus, we recently received a preprint from Thompson and Andrews describing the synthesis and infrared characterization of Ar, Kr, and Xe complexes with BeO, yet no band at the diatomic BeO stretching frequency was obtained in the spectra [6].

3.6. *A comparison of CC and QCI methods*

The QCISD and QCISD(T) methods were introduced by Pople and coworkers in 1987 [41]. QCISD may be viewed as an intermediate method between CISD and CCSD, and can either be derived by adding terms to CISD to remove unlinked diagrams, or by removing most of the nonlinear terms from the CCSD equations and removing the $T_1^2/2$ term from the energy expression. CCSD and QCISD have the same rate determining steps, as do CCSD(T) and QCISD(T), so computationally there is little gain in using the QCI approximation. Unlike CC and general CI methods, QCI was only formulated for the case of canonical Hartree–Fock orbitals. As QCISD omits many nonlinear terms involving T_1, it was immediately anticipated [54] that CCSD and QCISD were likely to differ when T_1 was large. Clear numerical demonstration of this has been lacking, however. One obvious reason is the restriction of QCISD to canonical Hartree–Fock orbitals, since these usually do not lead to large T_1 amplitudes. Lee et al. [46] compared QCI and CC methods for a variety of systems, and obtained only moderate differences. More significant differences were reported by Martin et al. for the $a\,{}^1\Sigma^+$ state of BN [52].[2] As the ground state of BeO has quite large T_1 amplitudes, if offers a critical comparison of CC and QCI methods.

CC and QCI electrical properties are shown in Table 8. For the dipole moment, there are large differences between the CC and QCI results with the smaller basis set, but these are substantially reduced for the larger basis set. α_{xx} is not very

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[2] Recently, Rico and Head-Gordon [58] compared QCISD and CCSD equation-of-motion (EOM) (or CC linear response) techniques [59] for the calculation of excitation energies and found differences of about 0.4 eV in some cases, causing the QCISD excitation energies to have large errors. It should be emphasized that these large differences are for excitation energies, but not for ground state energies. Compare also [59] for EOM-QCI

Table 8. Comparison of CC and QCI electrical properties. Atomic units are used. All electrons correlated and all virtual orbitals included

Basis	Method	Energy	μ	α_{xx}	α_{zz}
5*s*3*p*2*d*	CCSD	− 89.703870	2.56	31.3	29.8
5*s*3*p*2*d*	CCSD(T)	− 89.714159	2.43	35.1	34.4
5*s*3*p*2*d*	QCISD	− 89.713586	1.86	31.5	109.1
5*s*3*p*2*d*	QCISD(T)	− 89.711318	3.30	36.7	− 162.0
ANO-5*s*4*p*3*d*2*f*	CCSD	− 89.778404	2.60	28.9	28.3
ANO-5*s*4*p*3*d*2*f*	CCSD(T)	− 89.795540	2.46	32.6	34.4
ANO-5*s*4*p*3*d*2*f*	QCISD	− 89.784333	2.24	29.9	66.9
ANO-5*s*4*p*3*d*2*f*	QCISD(T)	− 89.796818	2.54	32.7	3.7

Table 9. Calculated spectroscopic properties of $X\,^1\Sigma^+$ BeO. All electrons correlated and all virtual orbitals included

	Energy	r_e/[A]	ω_e [cm^{-1}]	μ [D]	I [km mol^{-1}]	D_e [eV]
DZP basis set						
CCSD	− 89.669675	1.351	1513	6.00	9.7	3.40
CCSD(T)	− 89.679314	1.367	1407	5.60	10.5	3.63
QCISD	− 89.684605	1.389	1405	3.27	68.6	3.80
QCISD(T)	− 89.671954	1.338	1530	9.72	2679.2	3.43
ANO-5*s*4*p*3*d*2*f* *basis set*						
CCSD(T)	− 89.795543	1.329	1496	6.25	0.02	4.62
QCISD(T)	− 89.696818	1.330	1496	6.46	41.5	4.65
Experiment[a]		1.331	1487			4.69

[a] Reference [32]

sensitive to method, and there are only small differences between the CC and QCI results. α_{zz},however, is quite a different story, and the difficulties QCI has for μ are propagated. With the 5*s*3*p*2*d* basis set, both QCISD and QCISD(T) give unreasonable values. The triple excitations attempt to correct the behavior of QCISD, but being based on the QCISD amplitudes, they overcorrect. The situation is similar for the ANO-5*s*4*p*3*d*2*f* basis set, although the magnitude is now reduced some what.

The CC and QCI spectroscopic properties are shown in Table 9. With the DZP basis set, the QCI results are particularly poor. The triples correlation to the energy is positive, and triples lead to a bond length decrease and frequency increase, contrary to the usual behavior. Not surprisingly, μ and I (proportional to the square of $\mathrm{d}\mu/\mathrm{d}R$, where R is the internuclear distance) also differ a lot from the CC values. With the ANO-5*s*4*p*3*d*2*f* basis set, the deviations are considerably reduced, with CC and QCI giving virtually identical results for r_e and ω_e, and comparable values for D_e and μ, but not for I.

While significant differences between CC and QCI methods might have been anticipated from the presence of large amplitudes, the strong basis set dependence

Table 10. Comparison of CCSD and QCISD values of largest T_1 amplitude ($4\sigma \rightarrow 5\sigma$ excitation) and $\mathscr{T}_1$

		$5s3p2d$	ANO-$5s4p3d2f$
QCISD	T_1 ($4\sigma \rightarrow 5\sigma$)	-0.29	-0.19
	$\mathscr{T}_1$	0.093	0.063
CCSD	T_1 ($4\sigma \rightarrow 5\sigma$)	-0.11	-0.09
	$\mathscr{T}_1$	0.039	0.033

of the difference is an additional subtlety. The large basis set effects likely originate from the difficulty the one-particle basis set has in describing the charge distribution in this highly polar molecule. With a small one-particle basis set one obtains a set of MOs which do not describe the charge distribution well. Consequently, this poor reference determinant places severe demands on the correlation treatment. Since the CCSD method retains the full e^{T_1} operator, it is better able to effect on orbital rotation and recover from poor initial orbitals, whereas since QCISD only includes T_1 approximately, it is less able to recover. With the larger basis set, the MOs are better and therefore less demands are placed on the correlation treatment, and the differences between the methods are reduced. The sizes of the principal CCSD and QCISD amplitudes and $\mathscr{T}_1$ for the different basis sets are instructive in this regard (Table 10). The largest amplitude is for the $4\sigma \rightarrow 5\sigma$ single excitation. The values of this amplitude are shown in Table 10. It is seen that the QCISD values are significantly larger than the CCSD ones, and also that the magnitude of the QCISD values is reduced significantly on going from $5s3p2d$ to ANO-$5s4p3d2f$.

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