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PAPER

The ground-state potential energy function of a beryllium dimer determined using the single-reference coupled-cluster approach

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The accurate ground-state potential energy function of the beryllium dimer, Be_2, has been determined from large-scale *ab initio* calculations using the single-reference coupled-cluster approach in conjunction with the correlation-consistent core–valence basis sets up to septuple-zeta quality. Results obtained with the conventional and explicitly-correlated coupled-cluster methods were compared. The scalar relativistic and adiabatic (the diagonal correction) effects were also discussed. The vibration–rotation energy levels of Be_2 were predicted and found to be as accurate as those determined from the empirical potential energy function [J. M. Merritt *et al.*, *Science*, 2009, **324**, 1548]. The potential energy function of Be_2 was determined in this study to have a minimum at 2.444 Å and the well depth of 935 cm^{-1}.

1 Introduction

The beryllium dimer, Be_2, has been the subject of numerous theoretical studies over the years;[1–15] this list is by no means exhaustive, and for earlier references, the reader is referred to Table I of ref. 1. In the first calculation at the Hartree–Fock (HF) level of theory by Fraga and Ransil,[16] the potential energy function of Be_2 in its ground electronic state $X\,^1\Sigma_g^+$ was shown to be purely repulsive. The inclusion of electron correlation *via* the limited single-reference configuration interaction did not change the character of the potential energy function.[16,17] However, in more extensive single-reference configuration interaction calculations,[18,19] the beryllium dimer was found to be weakly bound, with the binding energy of about 50 cm^{-1} and the equilibrium internuclear distance of about 5 Å. In the full configuration interaction (FCI) calculation involving the four valence electrons of Be_2, Harrison and Handy[20] predicted the binding energy to be substantially larger. Using the [8s5p2d1f] basis set, the potential energy function of Be_2 was calculated to have a minimum at 2.51 Å and the well depth of 650 cm^{-1}. This indicated that high-order excited configurations (triple and quadruple), with larger bonding character than low-order configurations (single and double), play an important role in determining the electronic wave function of the beryllium dimer. A similar conclusion emerged from the studies applying the single-reference coupled-cluster (CC) approach. At the CCD/[7s3p2d] level of theory, the binding energy of Be_2 was predicted by Chiles and Dykstra[21] to be only about 90 cm^{-1}. Upon accounting for the effects of connected triple excitations,[5,12,15,22] the binding energy was calculated to range from 200 to 800 cm^{-1}, depending on the basis

set used and the way of including the contributions of triple excitations. By applying the CCSD(T) method with the valence active space, Martin[5] predicted the binding energy of Be_2 to be 587 cm^{-1} using the cc-pV5Z basis set. In a similar calculation by Patkowski *et al.*,[12] the binding energy was found to be 614 cm^{-1} using the aug-cc-pV5Z basis set extended with a (3s3p2d2f1g) set of midbond functions. Martin[5] showed that the effects of high-order excited configurations, beyond the CCSD(T) level of approximation, increased the binding energy of Be_2 by as much as 240 cm^{-1}. As shown by Liu and McLean,[23] the source of problems when using the single-reference methods is the near-degeneracy of the 2s and 2p orbitals of the beryllium atom. As a result, the ground-state electronic wave function of Be_2 has strong multi-reference character. Using the multi-reference configuration interaction (MRCI) approach, Liu and McLean[23] predicted the potential energy function of Be_2 to have a minimum at 2.49 Å and the well depth of 810 cm^{-1}. In the subsequent studies using various MRCI-type methods,[2–4,7,13,14,24,25] the well depth was calculated to range from 300 to 1000 cm^{-1}, depending on the basis set, the reference space, and the type of the MRCI method used.

As pointed out by several authors, to determine the reliable ground-state potential energy function of Be_2, it is necessary to use large basis sets and to account fully for electron correlation. The present study is an attempt in this direction. The molecular parameters of the beryllium dimer are determined here by using highly-correlated wave functions calculated with large correlation-consistent core–valence basis sets up to septuple-zeta quality.

2 Method of calculation

The one-particle basis sets employed in this study were the augmented correlation-consistent core–valence basis sets up to septuple-zeta quality, aug-cc-pCVnZ (n = D–7). The basis sets

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consisted of the valence cc-pVnZ basis sets augmented with sets of diffuse (aug) and tight (C) functions. The valence cc-pVnZ basis sets up to quintuple-zeta quality were developed by Prascher *et al.*[26] The largest basis set for beryllium, cc-pV5Z, consists of a (14s8p4d3f2g1h)/[6s5p4d3f2g1h] set. In the study on the potential energy surface of BeH$_2$,[27] the cc-pV6Z basis set was developed, consisting of a (16s9p5d4f3g2h1i)/[7s6p5d4f3g2h1i] set. The cc-pV7Z basis set was developed for this study, consisting of a (20s13p6d5f4g3h2i1k)/[8s7p6d5f4g3h2i1k] set.† The exponents of the *s* primitive functions were determined in the HF calculation for the beryllium atom in its ground electronic state ^{1}S. Using the (14s), (16s), and (20s) sets (for cc-pVnZ with n = 5, 6, and 7, respectively), the HF total energies for ^{1}S Be was calculated to be −14.57301207, −14.57302078, and −14.57302304, respectively. The latter value is by just 0.13 μE_h larger than the numerical HF limit energy of −14.57302317.[28] The exponents of the *p* primitive functions were determined in the spin-restricted HF calculation for the first triplet excited state ^{3}P. The exponents of the higher angular momentum functions were determined using the configuration interaction method, with single and double excitations (CISD), by minimizing the total CISD energy for ^{1}S Be. These calculations were performed using the MOLPRO–2010 package of *ab initio* programs.[29] Because the MOLPRO package cannot handle the k functions, the exponent of this function was determined using the coupled-cluster method including single and double excitations and a perturbational correction due to connected triple excitations, CCSD(T). These calculations were performed using the DALTON package of *ab initio* programs.[30] Only the spherical harmonic components of the d through k polarization functions were used.

For accurately describing electron distribution at large distances, the basis sets were augmented with diffuse functions, aug-cc-pVnZ. One primitive diffuse function was added for each angular symmetry present in the valence cc-pVnZ basis set. For the basis sets up to quintuple-zeta quality, Prascher *et al.*[26] determined the exponents of the diffuse functions in the HF and CISD calculations for the BeH$^-$ anion. In this study, for the aug-cc-pV6Z and aug-cc-pV7Z basis sets, the customary even-tempered exponents were calculated by multiplying the exponent of the outermost primitive function of a given angular symmetry in the valence basis set by a factor of 0.4.

To account for the correlation effects of the 1s core electrons of the beryllium atom, the basis sets were further augmented with tight functions, aug-cc-pCVnZ. Groups of the primitive tight functions were added to the valence cc-pVnZ basis set. Prascher *et al.*[26] determined the largest core–valence basis set cc-pCV5Z for beryllium by augmenting the cc-pV5Z basis set with a (4s4p3d2f1g) set. The exponents of the tight functions were determined in the CISD calculations with either the valence active space or with all electrons correlated, both calculations performed with the same core–valence basis set. The exponent values were adjusted to maximize the absolute sum of the calculated core–core and core–valence correlation energies. The same strategy was adopted in this study. The cc-pV6Z and cc-pV7Z basis sets were augmented with the

(5s5p4d3f2g1h) and (6s6p5d4f3g2h1i) sets, respectively. Using the CCSD(T) method with all electrons correlated, the ground-state total energy of the beryllium atom was calculated to be −14.666511, −14.666883, and −14.667050 E_h for the aug-cc-pCV5Z, aug-cc-pCV6Z, and aug-cc-pCV7Z basis sets, respectively. The latter value is by 305 μE_h larger than the nonrelativistic energy of −14.667355 E_h calculated variationally by Komasa *et al.*[31] using a large basis set of explicitly-correlated Gaussian functions.

To determine the vibration–rotation energy levels of Be$_2$, the potential energy function was written as a polynomial expansion using the Simons–Parr–Finlan coordinate.[32] The expansion coefficients were determined from a least-squares fit of the polynomial expansion to the computed total energies. The vibration–rotation energy levels of Be$_2$ were then calculated using the Numerov–Cooley method.[33] The energy levels were calculated using the atomic mass of beryllium.‡

3 Results and discussion

To determine the shape of the potential energy function of Be$_2$, the total energies were calculated at the CCSD(T)/aug-cc-pCVnZ (n = Q–7) level of theory, with all electrons correlated, at 39 internuclear distances ranging from 1.8 to 20 Å. The calculated molecular parameters of $X\ ^1\Sigma_g^+$ Be$_2$ are given in Table 1. The parameters quoted include the equilibrium internuclear distance r_e, the total energy at minimum, the binding energy D_e, the vibrational fundamental wavenumber ν, and the ground-state vibrationally-averaged (effective) rotational constant B_0. For a given vibrational state, the effective rotational constant B_v was determined by fitting the predicted rotation energies with a power series in $J(J + 1)$, where J is the rotational quantum number. The predicted values of the molecular parameters are compared with the experimental values reported recently by Merritt *et al.*[34] and derived from the analysis of the stimulated emission pumping spectrum $A\ ^1\Pi_u \to X\ ^1\Sigma_g^+$ of Be$_2$. As could be expected from the previous theoretical studies, the molecular parameters of Be$_2$ predicted at this level of theory differ significantly from those derived from the experimental data. The predicted values tend clearly to converge with enlargement of the basis set. The accuracy of the predicted values can be estimated by applying various extrapolation schemes to the calculated total energies. The following exponential,[35] exponential/Gaussian,[36] and two Schwartz-type[37,38] formulas were considered here:

$$E = E_\infty + a*\exp[-b*(n - 2)] \qquad (1)$$

$$E = E_\infty + a*\exp[-(n - 1)] + b*\exp[-(n - 1)^2] \qquad (2)$$

$$E = E_\infty + a/(n + 0.5)^b \qquad (3)$$

$$E = E_\infty + a/n^3 \qquad (4)$$

where E is the total energy computed with the aug-cc-pCVnZ basis set, E_∞ is the total energy at the complete-basis-set (CBS) limit, a and b are adjustable parameters. Because extrapolation

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† The cc-pCV6Z and cc-pCV7Z basis sets for Be are available on request from the author.

‡ If the nuclear mass of beryllium (9.0099879 u) was used instead of the atomic mass (9.0121822 u), the vibrational fundamental wavenumber ν and the effective rotational constant B_0 of Be$_2$ were calculated to be larger by about 0.02 and 0.0001 cm^{-1}, respectively.

Table 1 Molecular parameters of $X\ ^1\Sigma_g^+$ Be$_2$ determined at the CCSD(T)/aug-cc-pCVnZ level of theory

	$n = Q$	$n = 5$	$n = 6$	$n = 7$	Exp.[a]
$r_e{}^b$/Å	2.4732	2.4675	2.4645	2.4632	2.4536
$E + 29^c$/hartree	−0.334196	−0.336080	−0.336901	−0.337272	
$D_e{}^d$/cm^{-1}	632	671	688	696	929.7
ν^e/cm^{-1}	186.1	192.1	194.5	195.8	222.6
$B_0{}^f$/cm^{-1}	0.5877	0.5913	0.5930	0.5938	0.609

[a] The experimental values, ref. 34. [b] The equilibrium internuclear distance. [c] The total energy at a minimum. [d] The binding energy. [e] The vibrational fundamental wavenumber. [f] The ground-state effective rotational constant.

Table 2 Extrapolated CCSD(T)/CBS values of the molecular parameters[a] of $X\ ^1\Sigma_g^+$ Be$_2$

Method[b]	r_e	$E + 29$	D_e	ν	B_0
{$n = $ Q,5,6}					
(1)	2.4618	−0.337534	701	196.2	0.5945
(2)	2.4629	−0.337379	698	195.9	0.5940
(3)	2.4599	−0.337937	709	197.2	0.5955
(4)	2.4606	−0.338029	711	197.7	0.5953
{$n = $ 5,6,7}					
(1)	2.4620	−0.337580	705	197.0	0.5946
(2)	2.4624	−0.337489	701	196.5	0.5943
(3)	2.4614	−0.337742	709	197.8	0.5950
(4)	2.4609	−0.337905	711	197.9	0.5952

[a] See Table 1. [b] See eqn (1)–(4).

to the infinite basis set may be hazardous, the formulas quoted were used first to predict the CCSD(T)/aug-cc-pCVnZ energy for $n = 7$ using the energies computed for $n = $ Q, 5, and 6. Extrapolation with the two-point formula (4) involved the $n = 5$ and 6 data only. For the internuclear distance of 2.45 Å, close to the experimental equilibrium distance of $X\ ^1\Sigma_g^+$ Be$_2$, the total energy extrapolated using formulas (1), (2), (3), and (4) differs from the directly computed value by -14, -70, $+36$, and $+46$ μE_h, respectively. The incremental change between the total energies directly computed for $n = 6$ and 7 is 372 μE_h. Thus, the extrapolation relative error is: (1) -4%, (2) -19%, (3) $+10\%$, and (4) $+12\%$. The total energies predicted with formulas (1) and (3) most closely bracket the directly computed value and, therefore, their mean value can be taken as the best estimate. The extrapolated potential energy function of Be$_2$ was calculated using formulas (1)–(4). For each of these functions, the molecular parameters quoted in Table 1 were then determined. The results are given in Table 2. The CBS limit values were determined using the {$n = $ Q, 5, 6} and {$n = $ 5, 6, 7} data set. Using these values, the changes in the CCSD(T) calculated equilibrium distance r_e and the binding energy D_e beyond the aug-cc-pCV7Z basis set are estimated to be about 0.002 Å and 10 cm^{-1}, respectively. The analogous changes in the vibrational fundamental wavenumber ν and the effective rotational constant B_0 are estimated to be about 1 and 0.001 cm^{-1}, respectively. The CCSD(T)/CBS energy of $X\ ^1\Sigma_g^+$ Be$_2$ at minimum is estimated to be -29.3377 ± 0.0001 E_h. A comparison of the total energy values extrapolated using the best data set {$n = $ 5,6,7} is somewhat disappointing. The extreme values, calculated using formulas (2) and (4), are by more than 400 μE_h apart, whereas lowering of the total energy from the aug-cc-pCV7Z basis set to the CBS limit is estimated to be essentially of the same order.

To address the question of the basis-set-superposition error (BSSE), the interaction energy of the beryllium atoms was calculated at the CCSD(T)/aug-cc-pCVnZ ($n = 5$–7) level of theory, with all electrons correlated, using the counterpoise method.[39] At the internuclear distance of 2.45 Å, the counterpoise correction to the interaction energy was determined to be 4.0, 1.5, and 0.7 cm^{-1} for $n = 5$, 6, and 7, respectively. In the vicinity of the equilibrium configuration of $X\ ^1\Sigma_g^+$ Be$_2$, the BSSE at the CCSD(T)/aug-cc-pCV7Z level is by the order of magnitude smaller than the estimated uncertainty in the binding energy D_e. At the highest level of theory used in this study, the counterpoise corrections to the potential energy function of Be$_2$ were thus found to be insignificant and, therefore, were not included.

The results obtained using the conventional CCSD(T) method can be compared with those obtained using the explicitly-correlated coupled-cluster methods including exponential geminal basis functions, CCSD(T)-F12x ($x = $ a, b)[40] and CCSD(T)(F12).[41] The latter method is implemented in the MOLPRO package[29] and denoted there CCSD(T)-F12c. The methods were used in conjunction with the correlation-consistent core–valence basis sets cc-pCVnZ-F12 developed by Hill and Peterson,[42] along with the corresponding auxiliary basis sets OptRI. The largest basis set (available in the literature) of quadruple-zeta quality, cc-pCVQZ-F12, was employed. For general computational details of the calculations, the reader is referred to ref. 42. The potential energy function of Be$_2$ was determined in the present study at the CCSD(T)-F12x/cc-pCVQZ-F12 ($x = $ a, b, c) level of theory, with all electrons correlated. The derived molecular parameters of $X\ ^1\Sigma_g^+$ Be$_2$ are given in Table 3. Because the results of calculations with the explicitly-correlated methods are known to depend on the geminal exponent β,[10] the CCSD(T)-F12x/cc-pCVQZ-F12 calculations were performed first using the exponent $\beta = 1.5$, recommended by Hill and Peterson.[42] Then, two different exponent values were employed: $\beta_v = 1.0$ for describing valence correlation and $\beta_c = 1.5$ for describing core–core and core–valence correlation. The exponent $\beta_v = 1.0$ was recommended by Peterson *et al.*[43] as optimal for explicitly-correlated calculations with the correlation-consistent valence basis sets cc-pVnZ-F12. This value was also found by Tew and Klopper[10] to be optimal for recovering the valence correlation energy of Be$_2$ using the explicitly-correlated second-order Møller–Plesset method, MP2-F12/2B, with the aug-cc-pVnZ basis sets. A comparison of the results given in Tables 3 and 1 shows that the molecular parameters of $X\ ^1\Sigma_g^+$ Be$_2$ obtained at the CCSD(T)-F12b/cc-pCVQZ-F12 level are comparable to those obtained at the conventional CCSD(T)/aug-cc-pVnZ level with $n = 6$ and 7. In particular, the total energy of Be$_2$ at minimum is

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Phys. Chem. Chem. Phys., 2011, **13**, 20311–20317 | 20313

Table 3 Molecular parameters[a] of $X\,^1\Sigma_g^+$ Be$_2$ determined at the CCSD(T)-F12x/cc-pCVQZ-F12 level of theory

	r_e	$E + 29$	D_e	ν	B_0
$\beta = 1.5$					
$x = a$	2.4627	−0.338555	701	196.6	0.5942
$x = b$	2.4635	−0.336993	695	196.3	0.5938
$x = c$	2.4670	−0.336822	676	193.1	0.5917
$\beta_v = 1.0$, $\beta_c = 1.5$					
$x = a$	2.4626	−0.338548	705	197.0	0.5943
$x = b$	2.4633	−0.336799	700	196.9	0.5940
$x = c$	2.4674	−0.336585	677	193.0	0.5915

[a] See Table 1.

determined to be near the CCSD(T)/aug-cc-pV6Z value. Note that the change in the exponent β_v from 1.5 to 1.0 affects the CCSD(T)-F12b/cc-pCVQZ-F12 total energy of Be$_2$ by nearly 200 μE_h. The CCSD(T)-F12a method tends to substantially overestimate the correlation energy of Be$_2$. However, the binding energy D_e and the vibrational fundamental ν determined with this method differ by only about 5 and 0.2 cm^{-1}, respectively, from the corresponding CCSD(T)-F12b values. This suggests that the CCSD(T)-F12a correlation energy is uniformly overestimated on going from the separated beryllium atoms to the beryllium dimer. This is in contrast with the results obtained using the CCSD(T)-F12c method. The binding energy D_e and the vibrational fundamental ν were determined at the CCSD(T)-F12c/cc-pCVQZ-F12 level to be by about 20 and 3.6, respectively, lower than the corresponding CCSD(T)-F12b/cc-pCVQZ-F12 values.

To estimate the effects of valence-electron correlation beyond the CCSD(T) level of approximation, full-configuration-interaction (FCI)[44] calculations were performed with the aug-cc-pVDZ through aug-cc-pVQZ basis sets. At each point of the potential energy function of Be$_2$, the total energy was calculated using the FCI and CCSD(T) methods, both with the aug-cc-pVnZ (n = D, T, Q) basis set and valence electrons correlated. A difference between the FCI and CCSD(T) total energies was then added to the total energy of Be$_2$ computed previously at the CCSD(T)/aug-cc-pCV7Z level. Because for the beryllium dimer, the valence FCI approach is equivalent to the CCSDTQ approach, this difference corrects the perturbative treatment of connected triple excitations and it accounts additionally for the effects of connected quadruple excitations. For each of the corrected potential energy functions of Be$_2$, the molecular parameters were then determined. The results are given in Table 4. As could be expected from the previous theoretical studies, the high-order valence correlation effects appeared to be essential. The predicted values of the molecular

Table 4 High-order valence-electron correlation effects on the molecular parameters[a] of $X\,^1\Sigma_g^+$ Be$_2$ determined at the FCI/aug-cc-pVnZ level of theory[b]

	r_e	$E + 29$	D_e	ν	B_0
$n = D$	2.4375	−0.338519	970	227.8	0.6104
$n = T$	2.4404	−0.338461	957	225.5	0.6087
$n = Q$	2.4431	−0.338380	939	223.4	0.6072

[a] See Table 1. [b] The total energy is calculated as a sum of the CCSD(T)/aug-cc-pCV7Z energy and the FCI/aug-cc-pVnZ correction (see the text).

parameters of $X\,^1\Sigma_g^+$ Be$_2$ tend to converge to the experimental values[34] with increasing quality of the basis set. For the best FCI correction (n = Q), the binding energy D_e and the vibrational fundamental ν were found to differ from the corresponding experimental values by 9 and 0.8 cm^{-1}, respectively. Note that the total energy of Be$_2$ calculated at the CCSD(T)/aug-cc-pCVnZ level approaches its CBS limit from above, whereas the FCI corrected energy approaches its CBS limit from below. The correlation energy of Be$_2$ calculated at the CCSD(T)/aug-cc-pCVnZ level is underestimated, whereas the valence FCI correction to the correlation energy is overestimated. In a similar manner, the binding energy D_e and the vibrational fundamental ν calculated at the CCSD(T)/aug-cc-pCVnZ level approach their CBS limits from below, whereas the FCI corrected parameters approach these limits from above.

The potential energy function including the best FCI correction, referred further to as 'CV + F', was used to determine all bound vibration–rotation energy levels of $X\,^1\Sigma_g^+$ Be$_2$. The calculated vibrational term values E_v and the effective rotational constants B_v are given in Table 5. The predicted values are compared with the experimental values reported by Merritt et al.[34] The experimental data include eleven vibrational levels up to v = 10. The question of the twelfth vibrational state of $X\,^1\Sigma_g^+$ Be$_2$, suggested recently by Patkowski et al.,[45] will be discussed later. Experimental uncertainties in the vibrational term values and the effective rotational constants were estimated by Merritt et al.[34] to be ± 0.5 and ± 0.005 cm^{-1}, respectively. Although the fundamental term value E_1 is predicted to be within 1 cm^{-1}, the differences between the predicted and experimental values (Δ) increase substantially with v, reaching as much as 4.4 cm^{-1} for v = 10. The root-mean-square (rms) deviation $\bar{\Delta}$ for the vibrational term values E_v is 3.3 cm^{-1}. In contrast, the effective rotational constants B_v are all predicted to be within the experimental error bar, except for the v = 2 state. The rms deviation $\bar{\Delta}$ is here 0.003 cm^{-1}.

The potential energy function of Be$_2$ was further corrected for the scalar relativistic effects. These effects were investigated using the second-order Douglas–Kroll–Hess (DKH) one-electron Hamiltonian.[46,47] The relativistic contributions to the total energy were calculated using the CCSD(T) method with the uncontracted aug-cc-pCVQZ basis set, and with all electrons correlated. At each point of the potential energy function of Be$_2$, the relativistic correction was determined as the difference in the total energy calculated using either the DKH or nonrelativistic Hamiltonian. The inclusion of the scalar relativistic effects lowers the total energy of Be$_2$ by about 5.1 mE_h. In the test calculation at the fourth order of decoupling of the Dirac Hamiltonian, the relativistic energy of Be$_2$ appeared to be converged to better than 1 μE_h. To test the importance of the multi-reference effects, the another test calculation at the MRCI + Q/aug-cc-pCVQZ(uncontracted) level of theory was performed (see below for the details). Differences between the CCSD(T) and MRCI + Q relativistic corrections were found to vary by about 1 μE_h along the potential energy function of Be$_2$. In comparison to the FCI correction, the relativistic correction is nearly constant over the large range of the internuclear distance. This is illustrated by Fig. 1. The relativistic corrections were added to the CV + F potential energy function of Be$_2$, and this function is referred further to

Table 5 Vibrational term values (E_v) and effective rotational constants (B_v) (in cm^{-1}) of $X\ {}^1\Sigma_g^+$ Be_2

	Exp.[a]		CV + F[b]				CV + F + R[b]				F12b + F + R[b]			
v	E_v	B_v	E_v	Δ^c	B_v	Δ^c	E_v	Δ^c	B_v	Δ^c	E_v	Δ^c	B_v	Δ^c
0	0.0	0.609	0.0		0.6072	−0.002	0.0		0.6069	−0.002	0.0		0.6068	−0.002
1	222.6	0.562	223.4	0.8	0.5613	−0.001	222.7	0.1	0.5608	−0.001	223.1	0.5	0.5609	−0.001
2	397.1	0.509	398.3	1.2	0.5015	−0.008	396.8	−0.3	0.5006	−0.008	397.9	0.8	0.5010	−0.008
3	518.1	0.424	520.2	2.1	0.4242	−0.000	517.8	−0.3	0.4231	−0.001	519.3	1.2	0.4233	−0.001
4	594.8	0.355	597.7	2.9	0.3532	−0.002	594.7	−0.1	0.3524	−0.003	596.1	1.3	0.3520	−0.003
5	651.5	0.306	654.8	3.3	0.3089	−0.003	651.6	0.1	0.3084	−0.002	652.8	1.3	0.3080	−0.002
6	698.8	0.272	702.2	3.4	0.2732	−0.001	698.9	0.1	0.2728	−0.001	699.9	1.1	0.2723	0.000
7	737.7	0.237	741.5	3.8	0.2381	−0.001	738.0	0.3	0.2377	−0.001	738.8	1.1	0.2369	0.000
8	768.2	0.196	772.3	4.1	0.2002	−0.004	768.6	0.4	0.1997	−0.004	769.2	1.0	0.1986	−0.003
9	789.9	0.153	794.2	4.3	0.1567	−0.004	790.4	0.5	0.1560	−0.003	790.6	0.7	0.1541	−0.001
10	802.6	0.102	807.0	4.4	0.1058	−0.004	803.1	0.5	0.1050	−0.003	802.7	0.1	0.1017	0.000

[a] The experimental values, ref. 34. [b] The values predicted using the CV + F, CV + F + R, and F12b + F + R potential energy functions (see the text). The zero-point energies were calculated to be 127.1, 126.8, and 126.9 cm^{-1}, respectively. [c] A difference between the predicted and experimental values.
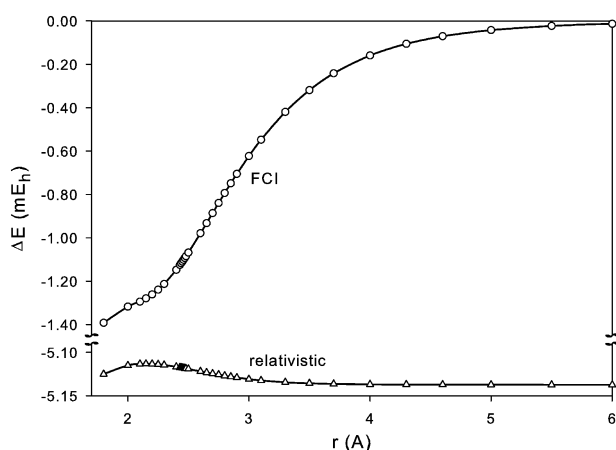

Fig. 1 The FCI (circles) and relativistic (triangles) corrections ΔE to the total energy of $X\ {}^1\Sigma_g^+$ Be_2 as functions of the internuclear distance r. Note that the ΔE axis for the relativistic correction (below the break) is stretched by a factor of 4 compared to that for the FCI correction.

as 'CV + F + R'. The molecular parameters of $X\ {}^1\Sigma_g^+$ Be_2 determined with this function are given in Table 5. Upon the inclusion of the scalar relativistic corrections, all of the vibrational term values of $X\ {}^1\Sigma_g^+$ Be_2 were predicted to be within the experimental error bar. The rms deviation $\bar\Delta$ is just 0.3 cm^{-1}. The scalar relativistic corrections appeared to have very little impact on the predicted values of the effective rotational constants.

The another potential energy function of Be_2 was obtained by adding the FCI and relativistic corrections to the total energies calculated at the CCSD(T)-F12b/cc-pCVQZ-F12 ($\beta = 1.5$) level of theory. The molecular parameters thus determined are given in Table 5, in the column headed 'F12b + F + R'. The rms deviation $\bar\Delta$ for the vibrational term values of $X\ {}^1\Sigma_g^+$ Be_2 is found to be 1.0 cm^{-1}. Although it is by a factor of 3 larger than that determined with the CV + F + R potential energy function of Be_2, this level of theory seems to be very promising in view of larger van der Waals complexes. Surprisingly enough, the analogous potential energy function of Be_2 calculated with two different exponent values, $\beta_v = 1.0$ and $\beta_c = 1.5$, appeared to be significantly worse for the higher excited vibrational states. Comparing both these functions, the vibrational fundamental wavenumber ν was found to differ by only 0.4 cm^{-1}, whereas the vibrational term value E_v for $v = 10$ was found to differ by as much as 4.7 cm^{-1}.

To account for the adiabatic effects, the diagonal Born–Oppenheimer correction (DBOC) was calculated using the HF and CCSD methods[48,49] with the aug-cc-pCVTZ basis set, and with all electrons correlated. The calculations were performed using the CFOUR package of *ab initio* programs.[50] In the vicinity of the equilibrium configuration of Be_2, the DBOC was determined to be 390 and 404 cm^{-1} with the HF and CCSD methods, respectively. Although the DBOC is quite sizable, it was found to be essentially constant as a function of the internuclear distance, varying by less than 2 cm^{-1} (10 μE_h) along the potential energy function of Be_2. Therefore, the effect of the DBOC on the molecular parameters of $X\ {}^1\Sigma_g^+$ Be_2 is negligible.

Relative energies of the CV + F + R potential energy function of $X\ {}^1\Sigma_g^+$ Be_2 are given in Table 6. This potential energy function is a significant improvement over the *ab initio* potential energy function V_{vdW} determined by Patkowski *et al.*[12,45] Using the V_{vdW} function, the vibrational term values of $X\ {}^1\Sigma_g^+$ Be_2 (given in Table 5) were predicted with the rms deviation $\bar\Delta$ of 3.4 cm^{-1}.[45] This is by the order of magnitude larger than the rms deviation $\bar\Delta$ of 0.3 cm^{-1} determined in this study with the CV + F + R function. In fact, the CV + F + R function is of a similar quality as the empirical function derived by Merritt *et al.*[34] from the analysis of the experimental data and as the two- and three-parameter morphed functions, $\tilde V_{vdW}^{(2)}$ and $\tilde V_{vdW}^{RPC(3)}$, determined by Patkowski *et al.*[45] Using these potential energy functions, the vibrational term values of $X\ {}^1\Sigma_g^+$ Be_2 were predicted with the rms deviation $\bar\Delta$ of 0.6, 0.4, and 0.4 cm^{-1}, respectively.[34,45] Following the study by Špirko,[51] the morphed potential energy functions of Be_2 were constructed from the *ab initio* potential energy function V_{vdW} by introducing some empirical parameters. The parameter values were then adjusted in a least-squares fit of the calculated vibrational term values to the experimental ones. For the best morphed function $\tilde V_{vdW}^{RPC(5)}$ determined by Patkowski *et al.*,[45] five empirical parameters were adjusted using the ten

Table 6 Relative energies[a] of the CV + F + R potential energy function of $X\ ^1\Sigma_g^+$ Be$_2$

$r/\text{Å}$	Energy	$r/\text{Å}$	Energy
1.80	6016.27	2.85	−610.55
2.00	1333.85	2.90	−566.80
2.10	185.61	3.00	−490.14
2.15	−193.96	3.10	−428.22
2.20	−473.61	3.30	−341.44
2.25	−671.80	3.50	−287.34
2.30	−804.45	3.70	−249.45
2.40	−925.41	4.00	−203.94
2.43	−934.27	4.30	−163.38
2.44	−935.09	4.60	−127.05
2.45	−934.97	5.00	−87.42
2.46	−933.91	5.50	−52.84
2.47	−932.02	6.00	−31.59
2.48	−929.34	7.00	−11.82
2.50	−921.83	8.00	−4.95
2.60	−852.76	10.00	−1.19
2.65	−806.46	12.00	−0.38
2.70	−756.90	15.00	−0.10
2.75	−706.63	20.00	−0.02
2.80	−657.43		

[a] In cm^{-1}, relative to the total energy of the separated beryllium atoms.

Table 7 Molecular parameters[a] of $X\ ^1\Sigma_g^+$ Be$_2$ determined at the MRCI + Q/aug-cc-pCVnZ level of theory

	r_e	$E + 29$	D_e	ν	B_0
$n = 5$	2.4470	−0.337323	906	220.3	0.6049
$n = 6$	2.4450	−0.338120	920	221.8	0.6061
$n = 7$	2.4443	−0.338457	923	222.2	0.6064

[a] See Table 1.

experimental vibrational term values listed in Table 5; these were reproduced with the rms deviation $\bar\Delta$ smaller than 0.1 cm^{-1}. The CV + F + R potential energy function has a minimum at 2.4436 Å and the well depth of 935.1 cm^{-1}. The corresponding parameters were found previously to be 2.4536 Å and 929.7 cm^{-1} from the empirical function of Merritt et al.,[34] and 2.438 Å and 934.6 cm^{-1} from the five-parameter morphed function $\tilde{V}_{vdW}^{RPC(5)}$ of Patkowski et al.[45] The theoretical binding energy D_e of $X\ ^1\Sigma_g^+$ Be$_2$ is then determined in this study to be 935 ± 10 cm^{-1}, being slightly larger than the experimental value[34] of 929.7 ± 2.0 cm^{-1} and essentially equal to the best semi-empirical value[45] of 934.6 cm^{-1}. In view of a near coincidence with the latter value of D_e, the estimated theoretical error of ±10 cm^{-1} seems to be a bit conservative. Furthermore, the convergence characteristic of the CCSD(T)/aug-cc-pCVnZ total energy and the FCI/aug-cc-pVnZ energy correction (discussed above) indicates that the errors associated with these quantities tend to cancel each other with increasing n. Using the CV + F + R potential energy function, the dissociation energy D_0 of $X\ ^1\Sigma_g^+$ Be$_2$ is determined to be 808.3 cm^{-1}.

Patkowski et al.[45] predicted the existence of the twelfth ($v = 11$) vibrational state of $X\ ^1\Sigma_g^+$ Be$_2$, lying just about 0.4 cm^{-1} below the dissociation limit. Using the CV + F + R potential energy function, the vibrational term value E_{11} and the effective rotational constant B_{11} were predicted in this study to be 807.9 and 0.0465 cm^{-1}, respectively. Therefore, the $v = 11$, $J = 0$–2 vibration-rotation energy levels are all confirmed here to lie below the dissociation limit of $X\ ^1\Sigma_g^+$ Be$_2$.

Finally, it is interesting to compare the potential energy function of Be$_2$ determined using the single-reference coupled-cluster approach with that determined using the multi-reference configuration interaction approach. The calculations performed in this study consisted of the complete-active-space self-consistent-field (CASSCF) step followed by the internally-contracted multi-reference configuration interaction (MRCI) step.[52,53] As shown by Martin,[5] the usual full-valence active space, consisting of the 2s- and 2p-like orbitals of the beryllium

atoms, appeared to be not adequate. Therefore, it was extended with the 3s- and 3p-like orbitals. The CASSCF wave function of Be$_2$ included thus all excitations of 4 valence electrons in 16 molecular orbitals. The reference function for the MRCI calculation consisted of the CASSCF orbitals, resulting in 816 reference configuration state functions for the $X\ ^1\Sigma_g^+$ state. The 1s-like orbitals of the beryllium atoms were kept doubly occupied in all reference configuration state functions, however, all of these orbitals were correlated through single and double excitations. To account approximately for the contributions of higher-order excitations, the Davidson correction (MRCI + Q) was applied.[54] The calculations were performed using the MOLPRO–2010 package.[29] The molecular parameters of $X\ ^1\Sigma_g^+$ Be$_2$ determined at the MRCI + Q/aug-cc-pCVnZ ($n = 5$–7) level of theory are given in Table 7. Because the MOLPRO package cannot handle the k functions, these were omitted in the calculations with the aug-cc-pCV7Z basis set. The predicted molecular parameters tend to approach those determined with the best coupled-cluster potential energy function CV + F (see Tables 4 and 5). The best potential energy function, determined at the MRCI + Q/aug-cc-pCV7Z(i) level, appeared to be softer than the CV + F function. The well depth was predicted to be 16 cm^{-1} smaller than that of the CV + F function. The vibrational term values E_v were calculated to be systematically lower than the corresponding CV + F values, the difference being −1.2 cm^{-1} for $v = 1$ and reaching as much as −15.0 cm^{-1} for $v = 10$. It is interesting to note that the binding energy D_e of $X\ ^1\Sigma_g^+$ Be$_2$ determined at the MRCI + Q/aug-cc-pCVnZ ($n = 5$–7) level is larger than the nonrelativistic value of 903 cm^{-1} determined by Gdanitz[6] using the explicitly-correlated multi-reference averaged coupled-pair functional method, r_{12}-MR-ACPF, with a large uncontracted (19s11p6d4f3g2h) basis set. The nonrelativistic binding energy D_e of 915.5 cm^{-1} determined recently by Schmidt et al.[13] using a composite configuration interaction approach is midway between the $n = 5$ and 6 MRCI + Q values.

In conclusion, the accurate potential energy function of the beryllium dimer in its ground electronic state $X\ ^1\Sigma_g^+$ was determined in the direct ab initio calculations, without invoking any extrapolation or morphing procedures. "Spectroscopic accuracy" was achieved, as the vibrational term values and the effective rotational constants of Be$_2$ were predicted to be within the corresponding experimental error bars.

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