

Ab initio potential curves for the $X^2\Sigma_u^+$ and $B^2\Sigma_g^+$ states of Be_2^+ : Existence of a double minimum

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ABSTRACT

We report *ab initio* calculations of the $X^2\Sigma_u^+$ and $B^2\Sigma_g^+$ states of the Be_2^+ dimer. Full valence configuration interaction calculations were performed using the aug-cc-pVnZ basis sets and the results were extrapolated to the CBS limit. Core–core and core–valence effects are included at the CCSDT/MTsmall level of theory. Two local minima, separated by a large barrier, are found in the expected repulsive $B^2\Sigma_g^+$ state. Spectroscopic constants have been calculated and good agreement is found with the recent measurements of Merritt et al. Bound vibrational levels, transition moments and lifetimes have also been calculated.

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1. Introduction

In recent years, there has been a lot of interest in ultracold atom–ion scattering [1] in the atomic and molecular physics community. The experimental realization of Bose–Einstein condensation (BEC) has led to numerous applications involving charged atomic and molecular species. The cooling and trapping [2] of such charged gases at sub-Kelvin temperatures is a topic of growing interest. The phenomena of charge transport like resonant charge transfer [3] and charge mobility [4] at ultracold temperatures have also been studied in detail. Other emerging fields of interest include ultracold plasmas [5], ultracold Rydberg gases [6] and systems involving ions in a BEC [7,8].

It is well known that the Be_2 dimer is a difficult problem for computational quantum chemistry, due to the $2s$ – $2p$ near degeneracy in the beryllium atom [9]. This near-degeneracy problem also arises in the less studied Be_2^+ dimer. The ground $X^2\Sigma_u^+$ state is well described by a $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u$ reference, but the $B^2\Sigma_g^+$ state has a multi-reference character, as previously discussed by Fischer et al. [10]. In this Letter we present calculations on the Be_2^+ dimer that should be useful as a starting point for further studies in ultracold atomic and molecular physics.

We begin by describing the methods used in our calculations followed by a discussion of the results which include the potential curves, spectroscopic constants, transition dipole moments, lifetimes of the bound vibrational levels of the $^2\Sigma_g^+$ state and the analysis of long-range behavior and determination of the van der Waals coefficients. The $B^2\Sigma_g^+$ state of Be_2^+ has a double minima instead of a purely repulsive nature as one would expect. We have characterized both the inner (deep) and outer (shallow) well.

2. Methods

As mentioned above, the $B^2\Sigma_g^+$ state cannot be adequately described by a single molecular orbital configuration. At short internuclear separation, the dominant configuration is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 3\sigma_g$ while at large separation it becomes $1\sigma_g^2 1\sigma_u^2 2\sigma_u^2 2\sigma_g$. This behavior is shown in Fig. 1. Preliminary calculations done at the CCSD(T) level of theory find a kink in the potential curve for the $B^2\Sigma_g^+$ state at the SCF curve crossing (see Fig. 2). Valence full configuration interaction (FCI) calculations were found to give a smooth potential curve.

Therefore, our computational approach is to perform valence FCI using the augmented correlation consistent polarized valence n -tuple zeta (aug-cc-pVnZ) basis set of Dunning [11]. We then extrapolated the results from the aug-cc-pVQZ and aug-cc-pV5Z¹ calculations to the complete basis set (CBS) limit. We have used Schwenke's linear formula [12] to extrapolate the SCF energies. For extrapolating the FCI correlation energies we have used the following formula given by Helgaker [13]:

$$E_{XY}^\infty = \frac{X^3 E_X^{\text{corr}} - Y^3 E_Y^{\text{corr}}}{X^3 - Y^3}, \quad (1)$$

where X , Y are 4 and 5 corresponding to the aug-cc-pVQZ and aug-cc-pV5Z basis sets. The total valence energy is the sum of the extrapolated SCF and full CI correlation energies. Core–core (CC) and core–valence (CV) correlations were calculated as the difference between all-electron and frozen core CCSDT [14] calculations done with Martin's MTsmall basis set [15]. The MTsmall basis set consists of a completely uncontracted cc-pVTZ basis set augmented

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¹ The aug-cc-pV5Z basis was created by adding diffuse primitives with the following exponents to the published cc-pV5Z basis: s 0.013777, p 0.007668, d 0.0772, f 0.01375, g 0.174, h 0.225.

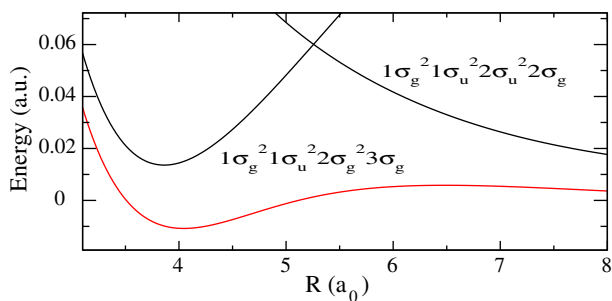


Fig. 1. Dominant molecular orbital configurations in the $B^2\Sigma_g^+$ state. The curves in black shows the SCF curve crossings due to the change of the occupied molecular orbitals, whereas the curve in red shows the calculated FCI potential curve for the $B^2\Sigma_g^+$ state. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

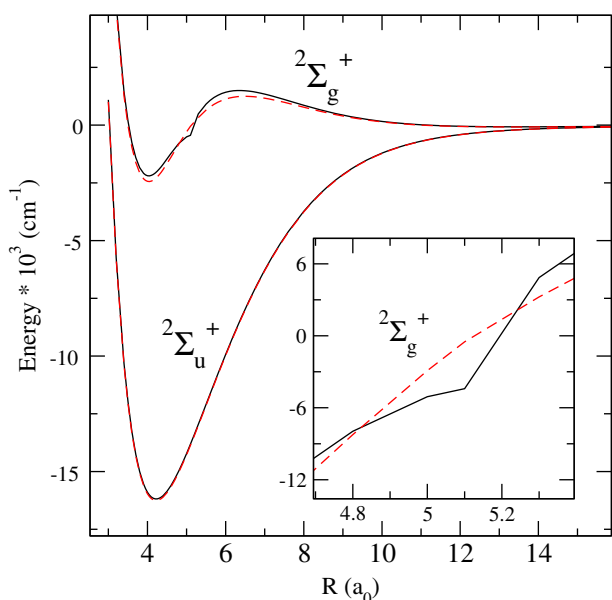


Fig. 2. The curves in black show a CCSD(T) calculation done with aug-cc-pV5Z basis set, whereas the curves in red are a full CI calculation using the same basis set. The inset shows a discontinuity (black line) in the CCSD(T) curve for the $B^2\Sigma_g^+$ state due to the change in reference configuration at larger internuclear separation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

with two tight d and one tight f functions. The calculated potential energy curves are corrected for the effects of basis set superposition error by the counterpoise method of Boys and Bernardi [16]. The CBS extrapolation increased the well depths of the $X^2\Sigma_u^+$ and $B^2\Sigma_g^+$ states by ~ 40 cm^{-1} , however D_0 for the outer well in the $B^2\Sigma_g^+$ state was unchanged. Scalar relativistic corrections were estimated to be ~ 10 cm^{-1} and are neglected.

The FCI calculations were done using the MOLPRO 2009.1 [17] and Psi3 [18] electronic structure programs running on a Linux workstation (2 quad core Intel Xeon E5520 CPU). The core–core and core–valence corrections were done with the multi-reference coupled cluster (MRCC) program [19] of Kállay. All calculations employed restricted open-shell (ROHF) reference wavefunctions.

Le Roy's LEVEL program [20] has been used to calculate the bound vibrational levels, Frank–Condon factors and Einstein A coefficients. Using these Einstein A coefficients we were able to calculate the lifetimes of all vibrational levels of the $^2\Sigma_g^+$ state.

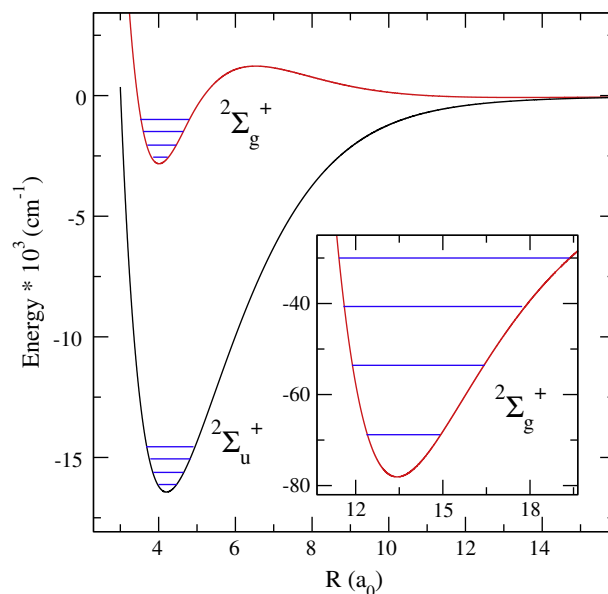


Fig. 3. The figure shows the calculated *ab initio* potential curves of Be_2^+ . The inset is a magnification of the shallow long-range well in the $B^2\Sigma_g^+$ state (in red). The positions of the first four bound vibrational levels are shown (in blue) for both states of Be_2^+ dimer. Note that the energy scale for the inset is in cm^{-1} . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Calculated spectroscopic constants of Be_2^+ .

State	r_e (Å)	B_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_0 (cm^{-1})
$X^2\Sigma_u^+$	2.223	0.756	525.299	4.454	16172
Exp. [22]			498 (20)		16072 (40)
$B^2\Sigma_g^+$ (In)	2.123	0.829	547.452	11.681	2550
$B^2\Sigma_g^+$ (Out)	7.106	0.074	33.703	3.548	69

3. Results and discussion

3.1. Potential curves and spectroscopic constants

Fig. 3 shows the *ab initio* potential curves for the lowest $^2\Sigma_u^+$ and $^2\Sigma_g^+$ states of Be_2^+ dimer. We have used a standard Dunham analysis [21] to calculate the spectroscopic constants (Table 1).

The bond dissociation energy (D_0) is 16172 cm^{-1} is in very good agreement with the experimental data of the Be_2^+ dimer [22]. The $X^2\Sigma_u^+$ state supports approximately 70 bound vibrational levels.

The $B^2\Sigma_g^+$ state which was expected to be repulsive has two minima instead. Both these wells support bound vibrational states. The outer well has 12 bound levels which are long lived (\sim ms).

3.2. Transition moments and lifetimes

To compute the transition moments coupling the $X^2\Sigma_u^+$ and $B^2\Sigma_g^+$ states of Be_2^+ dimer, we have used a 16 orbital complete active space self-consistent field (CASSCF) wavefunction as a reference for performing multi-reference configuration interaction (MRCI) calculations. The electronic dipole transition moment (in atomic units) is given by

$$\mu_{XB}(R) = \langle B_g | z | X_u \rangle, \quad (2)$$

where $|X_u\rangle$ and $|B_g\rangle$ are the electronic wave functions corresponding to the states $X^2\Sigma_u^+$ and $B^2\Sigma_g^+$ when the two Be nuclei are separated

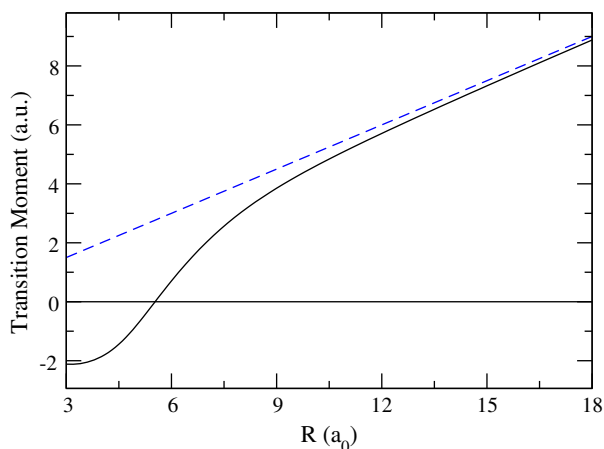


Fig. 4. The figure shows a plot of the computed electronic dipole transition moment μ_{XB} coupling the $B^2\Sigma_g^+$ to the $X^2\Sigma_u^+$ state. The dotted line (in blue) shows a plot of $R/2$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

by the distance R . Fig. 4 shows a plot of the computed electronic dipole transition moment between the $B^2\Sigma_g^+$ and the $X^2\Sigma_u^+$ ground states of Be_2^+ . The curve shows a zero-crossing at around $5.5 a_0$ which is approximately the same distance at which the dominant molecular orbital configuration changes from $(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 3\sigma_g)$ to $(1\sigma_g^2 1\sigma_u^2 2\sigma_u^2 2\sigma_g)$ in the $B^2\Sigma_g^+$ state of Be_2^+ (Fig. 1).

It is well known that the transition moment μ_{XB} asymptotically follows the classical dipole behavior, $\mu_{XB} \sim R/2$ [23,24], and we observe this behavior in the calculated curve (Fig. 4). This result can be understood by writing the electronic wavefunctions in terms of states with the electron centered on A or B, as $|B_g\rangle \sim \frac{1}{\sqrt{2}}(|A\rangle + |B\rangle)$ and $|X_u\rangle \sim \frac{1}{\sqrt{2}}(|A\rangle - |B\rangle)$, from which we find

$$\mu_{XB} = \langle B_g | z | X_u \rangle = \frac{1}{2} [\langle A | z | A \rangle - \langle B | z | B \rangle] \sim \frac{R}{2}. \quad (3)$$

We note that although the transition moment grows linearly with R , the probability of spontaneous transition will tend to zero since it is proportional to ν_{XB}^3 , which vanishes exponentially as $R \rightarrow \infty$.

The calculated potential curves and the electronic transition dipole moments were used as input to Le Roy's LEVEL program to

Table 2
Radiative lifetimes of the vibrational levels of the $B^2\Sigma_g^+$ state (in s).

ν'	$B^2\Sigma_g^+ \rightarrow X^2\Sigma_u^+$
0	0.849×10^{-7}
1	0.937×10^{-7}
2	1.032×10^{-7}
3	1.161×10^{-7}
4	1.423×10^{-7}
5	1.539×10^{-7}
6	2.870×10^{-3}
7	1.861×10^{-3}
8	1.586×10^{-3}
9	1.557×10^{-3}
10	1.992×10^{-3}
11	1.840×10^{-3}
12	2.340×10^{-3}
13	3.382×10^{-3}
14	5.277×10^{-3}
15	10.067×10^{-3}
16	25.718×10^{-3}
17	97.361×10^{-3}

Table 3

Long-range coefficients for both $X^2\Sigma_u^+$ and $B^2\Sigma_g^+$ states (in a.u.).

	α_1	α_2	C_6
This work	38.12	300.01	124.23
Previous [25]	37.755	300.98	
Previous [26]			119.99

calculate the Einstein A coefficients coupling the vibrational bound levels of the $B^2\Sigma_g^+$ state to the $X^2\Sigma_u^+$ state. We have also calculated the radiative lifetimes (Table 2) of the vibrational levels in the $B^2\Sigma_g^+$ state using these Einstein A coefficients. Note that the bound levels in the shallow outer well have long radiative lifetimes ($\sim 10^{-3}$ s) in comparison to the levels in the inner well ($\sim 10^{-7}$ s). Our results for $\nu' = 0-3$ agree well with the results of Fischer et al. [10].

3.3. Long-range coefficients

For large internuclear separations, the standard long-range form of the intermolecular potential is:

$$V_{LR}(R) = V_\infty - \frac{(\alpha_1/2)}{R^4} - \frac{(\alpha_2/2 + C_6)}{R^6} - \dots \pm E_{exch}, \quad (4)$$

where E_{exch} is the exchange energy contribution and V_∞ is the energy of the atomic asymptote (which we have set to zero). Note that α_1 is the static dipole polarizability, α_2 is the quadrupole polarizability and C_6 is the dispersion coefficient. E_{exch} is repulsive (plus sign in Eq. (4)) for the $^2\Sigma_g^+$ state and attractive (minus sign in Eq. (4)) for the $^2\Sigma_u^+$ state.

All the parameters in Eq. (4) are common for both the $X^2\Sigma_u^+$ and $B^2\Sigma_g^+$ states. Neglecting higher order terms in Eq. (4), if we add the potentials for both states, the exchange term cancels and we get,

$$-\frac{(V_g + V_u)}{2} \times R^4 = (\alpha_1/2) + \frac{(\alpha_2/2 + C_6)}{R^2}. \quad (5)$$

Table 3 lists the values of the long-range coefficients that we obtained from fitting our long-range data to Eq. (5). We get $\alpha_1 = 38.12$ a.u. which is in excellent agreement with the previous result [25] of 37.755 a.u. which comes from a correlated basis calculation and is likely accurate to all reported digits. We have also calculated the quadrupole polarizability from a finite-field calculation using MOLPRO which gives $\alpha_2 = 300.01$ a.u. Thus from the fit we were able to extract the value of the dispersion coefficient $C_6 = 124.22$. This is in good agreement with unpublished results of Mitroy [26], which are done by the methods used by Mitroy and Bromley [27] for Be and other alkaline earth dimers. We note that our values for C_4 and C_6 are slightly higher than previous results. This may be due to the omission of higher order terms in our analysis.

4. Concluding remarks

Accurate *ab initio* calculations have been performed on the $X^2\Sigma_u^+$ and $B^2\Sigma_g^+$ states of the Be_2^+ dimer. Since the $^2\Sigma_g^+$ state has a shallow well near $13.4 a_0$, it was necessary to include diffuse functions in the basis sets to describe the well accurately. Large augmented basis sets of the Dunning correlation consistent series were thus chosen and the results were also extrapolated to the complete basis set limit. We have corrected our valence only FCI results for core-core and core-valence effects using CCSDT calculations with both full and frozen core using Martin's MTsmall basis set.

Since the $^2\Sigma_g^+$ state has not been experimentally observed we were unable to compare our theoretical values for dissociation energies or spectroscopic constants [22]. However there are recent experimental results for the bond dissociation energy and ω_e for

the ${}^2\Sigma_u^+$ state which are respectively $16072 \pm 40 \text{ cm}^{-1}$ and $498 \pm 20 \text{ cm}^{-1}$. These values compare well with our calculated results of 16172 cm^{-1} and 525 cm^{-1} .

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