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, 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.

Keywords: Be$_2^+$ potential curves, ab initio calculations, long range coefficients
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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 $1\sigma_g^21\sigma_u^22\sigma_g^22\sigma_u$ reference, but the B $^2\Sigma_g^+$ state has a multi-reference character, as previously discussed by Fischer et al. [10]. In this paper 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, 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.

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 \(1\sigma_1^2 \tau_1^2 2\sigma_g^2 \sigma_u^2\). While at large separation it becomes \(1\sigma_1^2 \pi_0^2 \pi_u^2 \pi_g^2\). 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 \(2^2\Sigma_g^+\) state at the SCF curve crossing (see Fig. 3). 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-pV5Z 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]:

\[
E^{corr}_{XY} = \frac{X^3 E^{corr}_{XY} - Y^3 E^{corr}_{XY}}{X^3 - Y^3},
\]

where \(X, Y\) are 4, 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 calculations done with Martin’s MTsmall basis set [15]. The MTsmall basis set consists of a completely uncontracted cc-pVTZ basis set augmented 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 \(2^2\Sigma_u^+\) and \(2^2\Sigma_g^+\) states by \(\sim 40\ \text{cm}^{-1}\), however \(D_0\) for the outer well in the \(2^2\Sigma_g^+\) state was unchanged. Scalar relativistic corrections were estimated to be \(\sim 10\ \text{cm}^{-1}\) and are neglected.

The FCI calculations were done using the MOLPRO 2009.1 [17] and PS13 [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 M. Källay. Le Roy’s LEVEL program [20] has been used to calculate the bound vibrational levels, Frank-Condor factors and Einstein A coefficients. Using these Einstein A coefficients we were able to calculate the lifetimes of all vibrational levels of the \(2^2\Sigma_g^+\) state.

**Results and Discussions**

**Potential Curves and Spectroscopic Constants**

Fig. 3 shows the \textit{ab initio} potential curves for the lowest \(2^2\Sigma_u^+\) and \(2^2\Sigma_g^+\) states of Be\(_2^+\) dimer. We have used a standard Dunham analysis [21] to calculate the spectroscopic constants (Table 1).

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\[\text{Table 1: Calculated spectroscopic constants of Be}_2^+\]

| State          | \(r_i\) (Å) | \(B_i\) (cm\(^{-1}\)) | \(\omega_\nu\) (cm\(^{-1}\)) | \(\omega_{\nu,\chi}\) (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)             |
| \(B^2\Sigma_u^+\) (In) | 2.123        | 0.829                   | 547.452                       | 11.681                        | 2550                  |
| \(B^2\Sigma_u^+\) (Out) | 7.106        | 0.074                   | 33.703                        | 3.548                         | 69                    |

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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.
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 transition moment for electric dipole transitions is defined as,

$$\mu_{XB}(R) = \langle B | er | X \rangle,$$

where $|X\rangle$ and $|B\rangle$ are the electronic wave functions corresponding to the states X $^2\Sigma_u^+$ and B $^2\Sigma_g^+$ when the two Be cores are separated 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 transition moment $\mu_{XB}$ asymptotically follows the classical dipole behavior, $\mu_{XB} \sim R/2$. The curve shows a zero-crossing at around 5.5 bohrs which is approximately the same distance at which the dominant molecular orbital configuration changes from $(1\sigma_g^2 1\sigma_u^2 2\sigma_u^2 3\sigma_g)$ to $(1\sigma_g^2 1\sigma_u^2 2\sigma_u^2 2\sigma_u^2)$ in the B $^2\Sigma_g^+$ state of Be$_2^+$ (Fig. 1).

The calculated potential curves and the electronic transition dipole moments were used as input to Le Roy’s LEVEL program to 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 are extremely long-lived ($\sim 10^{-7}$ s) in comparison to the levels in the inner well ($\sim 10^{-3}$ s). Our results for $\nu' = 0$ - 3 agree well with the results of Fischer et al. [10].

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

Long Range Coefficients

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

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

Figure 4: [COLOR ONLINE] The figure shows a plot of the computed electronic dipole transition moment $\mu_{XB}$ coupling the B $^2\Sigma_g^+$ to the X $^2\Sigma_u^+$ state. The dotted line (in blue) shows a plot of R/2.
where $E_{\text{exch}}$ is the exchange energy contribution and $V_{\text{in}}$ is the energy of the atomic asymptote (which we have set to zero). Note that $\alpha_1$ is the static dipole polarizability, $\alpha_2$ is the quadrupole polarizability and $C_6$ is the dispersion coefficient. $E_{\text{exch}}$ is repulsive (plus sign in Eq. (3)) for the $2\Sigma_u^+$ state and attractive (minus sign in Eq. (3)) for the $2\Sigma_u^-$ state.

All the parameters in Eq. (3) are common for both the X $2\Sigma_u^+$ and B $2\Sigma_u^+$ states. Neglecting higher order terms in Eq. (3), if we add the potentials for both states, the exchange term cancels and we get,

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

Table 3 lists the values of the long-range coefficients that we obtained from fitting our long-range data to Eq. 4. We get $\alpha_1 = 38.12$ a.u. which is in excellent agreement with previous results [23]. 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 $C_6 = 124.23$. This is in good agreement with unpublished results of Mitroy [24].

### Concluding Remarks

Accurate ab initio calculations have been performed on the X $2\Sigma_u^+$ and B $2\Sigma_u^+$ states of the Be$^+$ dimer. Since the $2\Sigma_u^+$ state has a shallow well near 13.4 bohr, 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 $2\Sigma_u^+$ state has not been experimentally observed we were unable to confirm our theoretical values for dissociation energies or spectroscopic constants [24]. However there are recent experimental results for the bond dissociation energy and $\omega_\infty$ for the $2\Sigma_u^+$ state which are respectively $16072 \pm 40$ cm$^{-1}$ and $498 \pm 20$ cm$^{-1}$. These values compare well with our calculated results of $16172$ cm$^{-1}$ and $525$ cm$^{-1}$.

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