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Large electron correlation effect leading to Be–Be bond<sup>☆</sup>

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## ARTICLE INFO

## Article history:

Received 31 May 2011

Accepted after revision 16 August 2011

Available online 19 September 2011

## Keywords:

Chemical bonding

Electron correlation

Potential energy curves

Spectroscopic constants

Excited states

## Mots clés :

Liaison chimique

Corrélation électronique

Courbes d'énergie potentielle

Constantes spectroscopiques

États excités

## ABSTRACT

The bonding of the beryllium diatomic molecule ( $\text{Be}_2$ ) in the ground state is exclusively made from the electron correlation effect. Unlike the ordinary van der Waals bond, where the electron correlation of the dispersion type makes weak bond energy ( $D_e$ ) at large bond distance ( $R_e$ ), the Be–Be bond is surprisingly strong with  $D_e = 830 \text{ cm}^{-1}$  and  $R_e = 245 \text{ pm}$ . This paper presents in an analytical way the different electron correlation effects with the corresponding spectroscopic data.

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## R É S U M É

La liaison chimique de la molécule diatomique de béryllium ( $\text{Be}_2$ ) dans l'état fondamental est entièrement faite de l'effet de corrélation électronique. Tandis que la liaison du type van der Waals où la corrélation électronique du type dispersion donne en général de très faible énergie de liaison ( $D_e$ ) et de grande distance d'équilibre ( $R_e$ ), celle de Be–Be est étonnamment forte avec  $D_e = 830 \text{ cm}^{-1}$  et  $R_e = 245 \text{ pm}$ . Cet article présente d'une manière analytique les différents effets de corrélation électronique avec les constantes spectroscopiques correspondantes.

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## 1. Introduction

The bonding of the beryllium diatomic molecule ( $\text{Be}_2$ ) in the ground state has attracted many researchers in the past. The spectroscopic study by Bondybey [1] reported the bond energy ( $D_e$ ) of  $790 \pm 30 \text{ cm}^{-1}$  and the bond length ( $R_e$ ) of 245 pm. Petersson and Shirley [2] have reported the vibrational constant ( $\omega_e$ ) fitted on the observed data of  $275.8 \text{ cm}^{-1}$ . Considering the compact closed-subshell structure of the ground atomic state ( $1s^2 2s^2$ ), this bond can be regarded as astonishingly strong with relatively short equilibrium distance. The neighbour lithium atom which has an open-subshell ( $1s^2 2s^1$ ) makes much stronger bond in the dimer  $\text{Li}_2$  with  $D_e = 8516.61 \text{ cm}^{-1}$  according to the experimental data [3]

while the best *ab initio* calculation gave  $8353 \text{ cm}^{-1}$  [4]. In this case, there exists an effective chemical bond made with both the covalent and resonant ionic contributions. In comparison, the magnesium dimer  $\text{Mg}_2$  has the bond energy less the zero-vibration energy ( $D_0$ ) of  $404.1 \pm 0.5 \text{ cm}^{-1}$  and  $\omega_e = 51.12 \text{ cm}^{-1}$  with  $R_e = 389 \text{ pm}$  according to the spectroscopic study of Li and Stwalley [5]. So, it appears that the  $\text{Mg}_2$  has the smallest metal-metal bond energy. The calcium dimer  $\text{Ca}_2$  has been observed and given  $D_e = 1102.08(9) \text{ cm}^{-1}$  [6,7] and  $R_e = 428 \text{ pm}$ ,  $\omega_e = 64.92 \text{ cm}^{-1}$ . The bond energy increase between  $\text{Mg}_2$  and  $\text{Ca}_2$  can be understood in terms of the increasing polarizability of the atoms. However, the singular data for  $\text{Be}_2$  cannot be explained in the same framework.

A recent paper by Røeggen and Almlöf [8] showed a long list of the experimental and theoretical studies on  $\text{Be}_2$  made in the past. To name only relatively recent quantum chemical studies, Evangelisti et al. [9] have made a full valence configuration interaction calculation with a basis set including *f* and *g* polarization functions and have shown

<sup>☆</sup> Paper for the special issue: "Polyoxometalates, metal wires, and other polymeric complexes: structures, properties, theoretical modelling. A tribute to Marie-Madeleine Rohmer".

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the importance of high angular momentum functions in the basis. Stärck and Meyer [10] have made a multi-reference configuration interaction calculation including the core-valence interaction with an effective core potential, with *f* and *g* polarization functions, obtaining the bond energy ( $D_e$ ) of  $893\text{ cm}^{-1}$ . The most recent theoretical study by Røeggen and Veseth [11] with an extended geminal model reported the bond energy ( $D_e$ ) of  $945 \pm 15\text{ cm}^{-1}$ . Those studies attempted to better understand the meaning of such strong bond between two compactly closed shell atoms.

In this paper, I report quantum chemical calculations on this state using different atomic basis sets and *ab initio* methods of different variational approximations. One might ask why another calculation would be necessary while there are already so many reported works, so it is necessary to explain the reason why. Indeed, past theoretical calculations were made in different times by different research groups using diverse methods. Although the essential conclusion drawn from those works should remain qualitatively valid, one may not easily compare the different compositions of the electron correlation quantitatively. Here, I tried to use a coherent set of bases and methods to study the interatomic interaction in a more systematic way than before to analyze quantitatively the different results obtained from them, so that one might clearly distinguish different levels of the electron correlation effect.

In experimental point of view, the highest lying vibrational energy levels are not reported yet, although a large number of levels were determined. The past experimental and theoretical data are also compared in this paper to estimate the most accurate spectroscopic data.

## 2. Method of calculation

Here, the atomic basis sets are generated in a systematic way to avoid unwanted basis set superposition errors and allow progressively higher angular momentum components. The molecular energy is calculated using the multi-reference single and double configuration interaction (MRCI) method, which is one of the mostly tested variational methods where the result is generally known to be reliable. The Gaussian type orbitals (GTO) are used for the atomic basis functions where the exponents of *s*- and *p*-type orbitals were determined from the Hartree-Fock (HF) calculation of the ground state beryllium atom using a program derived from ATOM [12]. At first, a set of 15 *s*-type GTOs were obtained to minimize the HF energies of the ground state ( $2s^2, ^1S$ ) and the excited state  $2s3s (^3S)$ , which thus includes diffuse functions. Then 8 *p*-type GTOs were obtained to minimize the  $2s2p (^3P^o$  and  $^1P^o)$  states. These 15 $s8p$  GTOs constitute the smallest basis set common to all other bases. To this, various numbers of the polarization and correlation functions (*d*, *f*, *g*, *h*) were added, including 5*d* GTOs for the ( $2s3d, ^3D$  and  $^1D$ ) states. Then molecular energy calculated in the MRCI was minimized with given polarization and correlation basis functions. The details about the choice of basis set will be explained in the result section. For the molecular calculations, the MOLCAS program suite [13] was used. The  $D_{2h}$  point-group symmetry was used for the HF and CI calculations.

The largest basis set used was 15 $s8p5d3f2g1h$ , which makes in all 228 molecular orbitals, and where no orbital was discarded from the multi-reference HF and CI calculations. The CI involved the valence electron correlation by the MRSDCI scheme and the core-valence electron correlation by including as supplementary all single excitations from the core electrons. The largest CI calculation, which could be done with given computational conditions involved more than five million configuration state functions (CSF) for the ground state. Both the valence-only CI (VCI) and core-valence CI (CVCI) were performed. In the latter case, only all possible single excitations from the core electron ( $1s^2$ ) but not the core-core type double excitations were allowed in constructing the configuration state functions.

Similar *ab initio* calculation on the ground state of  $Li_2$ , mentioned in above [4], gave 98.1% of the experimentally determined dissociation energy where the experimental value is considered as very accurate. It seems that the best experimental bond energy of  $Be_2$  known today [1], where the observed vibrational levels were extrapolated, has not the same degree of accuracy as in the  $Li_2$  case [3]. One might assume that the *ab initio* calculation presented in this work for  $Be_2$  would have the similar accuracy as in the  $Li_2$  case, with the error in the bond energy of about 2%.

## 3. Result and discussion

When only the 15 *s* and 8*p* GTOs are used in the VCI, a very weak long-range potential well of the van der Waals nature is obtained with  $R_e = 503\text{ pm}$  and  $D_e = 26\text{ cm}^{-1}$  as can be seen in Table 1 and Fig. 1. The addition of the core-valence electron correlation effect through CVCI does not change the result. In the second calculation was added one *d*-type GTO for more polarization and correlation effects. The best exponent, *i.e.* which gives the lowest total energy, depends slowly upon the internuclear distance (*R*). It is 2.5 at  $R = 4.5$

**Table 1**  
Bond energy ( $D_e$ , in  $\text{cm}^{-1}$ ) and bond distance ( $R_e$ , in pm) of  $Be_2$  in the ground state calculated using different basis sets and valence configuration interaction (VCI) and core-valence configuration interactions (CVCI).

Basis sets	Methods	$D_e$ ( $\text{cm}^{-1}$ )	$R_e$ (pm)
15 $s8p$	VCI	26	503
	CVCI	27	502
15 $s8p1d^a$	VCI	240	256
	CVCI	226	255
15 $s8p5d$	VCI	392	255
	CVCI	413	252
15 $s8p5d1f$	VCI	690	250
	VCI	716	250
15 $s8p5d3f$	CVCI	747	247
	VCI	789	248
15 $s8p5d3f2g$	CVCI	825	246
	VCI	784	248
15 $s8p3f2g1h$	CVCI	833	244
	Experimental <sup>b</sup>	$790 \pm 30$	245

<sup>a</sup> Inner well, see text.

<sup>b</sup> From Bondybey [1].

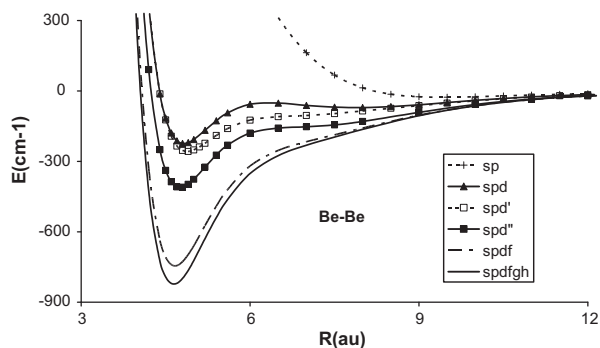


Fig. 1. Potential energy curves of the ground state of  $\text{Be}_2$  calculated with the configuration interactions.

bohr (atomic unit) and 2.8 at infinity. When one  $d$ -type GTO with 2.5 was used for all  $R$ , the potential energy curve presented two minima, the lowest one at short distance and the higher one at large distance ( $spd$  in Fig. 1). In 1970s, this brought about a dispute about the origin of these double minima. When the exponent of the  $d$ -type GTO was varied as a function of  $R$ , the large-distance minimum disappeared leaving still a non-typical curve ( $spd'$  in Fig. 1). The minimum around 255 pm gave somewhat larger bond energy,  $240 \text{ cm}^{-1}$  in VCI and  $226 \text{ cm}^{-1}$  in CVCI.

When five  $d$ -type GTOs were used ( $15s8p5d$  basis,  $spd''$  in Fig. 1), the bond distance changed little but the bond energy increases significantly to  $392 \text{ cm}^{-1}$  (VCI) and  $413 \text{ cm}^{-1}$  (CVCI). It is interesting that the core-valence electron correlation effect increases in this case the bond energy, contrary to the  $15s8p1d$  case.

One  $f$ -type GTO which minimizes the total energy at 4.5 bohr was found to have exponent 0.28. Addition of this atomic basis function furthermore increases the bond significantly to  $690 \text{ cm}^{-1}$  in VCI. This function was split into three functions according to the well-tempered way, that is, by multiplying and dividing by a given factor. The best factor appeared to be 1.8, so three  $f$ -type GTO with exponents of respectively 5.04, 2.8 and 1.556 were used, making the  $15s8p5d3f$  basis. This basis gave the bond energy of  $716 \text{ cm}^{-1}$  (VCI) and  $747 \text{ cm}^{-1}$  (CVCI) at respectively 250 pm (VCI) and 247 pm (CVCI).

Analogously, one (with exponent 0.37) and two (exponents  $0.37 \times 1.4$  and  $0.37/1.4$ )  $g$ -type GTOs were added. This addition further increases the bond energy to  $789 \text{ cm}^{-1}$  (VCI) and  $825 \text{ cm}^{-1}$  (CVCI) and shortens the bond distance to 248 pm (VCI) and 246 pm (CVCI).

Finally, one  $h$ -type GTO with the best exponent of 0.45 at  $R = 4.5$  bohr was added. The basis set superposition error, according to the counter-poise method of Boys and Bernardi, has been taken into account here. The total basis set superposition error about the bond distance (4.6 bohr) is less than  $6 \text{ cm}^{-1}$  which is much smaller than the interaction energy. This basis gave the largest bond energy  $784 \text{ cm}^{-1}$  (VCI) and  $833 \text{ cm}^{-1}$  (CVCI) with the bond length of 248 pm (VCI) and 244 pm (CVCI).

As can be seen in Table 1 and Fig. 1, the successive increase of the basis set size deepens the potential well and brings the bond distance to a shorter one, as is the case in

Table 2

Potential energy curve of the ground state of  $\text{Be}_2$  calculated with the  $15s8p3f2g1h$  basis set ( $R$  in bohr i.e. atomic unit and  $E$  in  $\text{cm}^{-1}$ ).

$R$ (au)	$E$ ( $\text{cm}^{-1}$ )
2.5	44562.3
2.6	38151.9
2.7	32060.7
2.8	26538.3
2.9	21519.0
3	17248.2
3.1	13659.6
3.2	10670.1
3.3	8198.5
3.4	6170.3
3.5	4519.5
3.6	3189.0
3.7	2128.0
3.8	1293.4
3.9	647.4
4	157.2
4.1	-205.5
4.2	-464.8
4.3	-641.4
4.4	-752.7
4.5	-813.5
4.6	-836.2
4.7	-830.9
4.8	-806.1
4.9	-768.3
5	-722.8
5.2	-623.8
5.4	-530.2
5.6	-450.3
5.8	-386.0
6	-336.6
6.5	-260.4
7	-218.6
7.5	-187.1
8	-157.5
9	-103.3
10	-62.6
11	-36.7
12	-21.6
13	-13.0
14	-8.1
15	-5.2

general in metal-metal bonding. Except for the basis set too poor in the polarization and correlation functions, i.e. lacking higher angular momentum functions, the core-valence electron correlation also increases the bond energy and shortens the bond distance, as was studied before in the alkali dimers [14]. The potential energy curve obtained by employing the largest basis  $15s8p5d3f2g1h$  and subtracting the basis set superposition errors is reported in Table 2, which could be useful to the spectroscopists and others.

#### 4. Conclusion

This work showed one extreme case of metal-metal bonding where the electron polarization and correlation effects play a crucial role in the bond energy. Another famous case is the chromium dimer ( $\text{Cr}_2$ ) where no quantum chemical method has succeeded in fully reproducing the observed bond properties. In particular, the long distance weak potential well was obtained and there was a historic debate on the possibility of the double

potential wells, while no experimental evidence was reported to support such strangeness. In fact, it is not possible now to make a similar study in the case of Cr<sub>2</sub> as was done in this work due to a larger number of electrons and the necessity of employing a much larger basis.

There was much interest to cool down the alkaline-earth atoms to ultracold temperature. The potential well and the long-range interatomic interaction of the dimers are so important to study that phenomenon [15]. One can find the most recent potential energy curves for the Mg<sub>2</sub>, Ca<sub>2</sub>, Sr<sub>2</sub> and Ba<sub>2</sub> diatomic molecules in the NIST website [16]. The quantum scattering calculation on the ground state Be atom has been reported before [17].

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