

TAMING THE ENERGY SURFACE AND SPECTROSCOPY OF BERYLLIUM DIMER IN ITS GROUND ELECTRONIC STATE

Uttam Sinha Mahapatra¹ Sudip Chattopadhyay² and Dhananjay Roy^{3*}

¹Department of Physics, Maulana Azad College, Kolkata 700013, India

E-mail: uttam.mahapatra@linuxmail.org

²Department of Chemistry, Indian Institute of Engineering Science and Technology, Shibpur, Howrah 711103, India, **E-mail: sudip@chem.iiests.ac.in**

³Department of Physics, Barasat Government College, North 24 Parganas-700124, India

***Email: dhananjay1964@rediffmail.com**

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Abstract

The bonding potential energy surface (PES) of the ground state of Be₂ is rather flat and very sensitive to the level of electron correlation employed. For the Be₂, methods that do not handle these effects in an accurate and democratic manner generally underestimate dissociation energy and can fail to locate the minimum on the PES. We present, here, the investigation of the structure and the energetics of Be₂ using our recently proposed single-reference based coupled-cluster (CC) method. The quality of the computed PES has been checked by extracting spectroscopic constants and comparing our estimates with the recent state-of-the-art theoretical and experimental results. Our calculated PES has a minimum at 2.461 Å and a well depth of 816.8 cm⁻¹ with vibrational frequency 258.9 cm⁻¹. The corresponding experimental estimates are 2.453 Å, 929.7 cm⁻¹ and 270.7 cm⁻¹ respectively. We have also numerically solved the vibrational Schrodinger equation to provide vibrational eigenvalues which show good agreement with the experiment values especially for a few low lying levels, reflecting the goodness of the computed PES and hence efficacy of our CC method.

Introduction

In the last few decades, aided by the remarkable advances in computational hard-ware, *many-body (ab initio)* methods have been developed and matured to a sophisticated level capable of providing useful answers to questions of chemical interest[1]. However, there are certain classes of fairly simple molecules that can pose considerable challenge for quantum chemical calculations. With just eight electrons, the beryllium dimer (Be₂) is one such celebrated example. Despite tremendous lot of investigations using various currently available methods, it is still difficult to provide a simple, yet satisfactory picture, of the bond formation in Be₂. The electronic excited states of Be₂ were also the subject of many experimental and theoretical studies [2-5]. The ground state of Be atom with its 1s² 2s² configuration has a closed 2s shell and no unpaired electrons. Be₂ has a formal bond order of zero, and the HF (Hartree-Fock) potential energy surface (PES) is purely repulsive. However, Be₂ turns out to be only

slightly bound, with a dissociation energy $D_e = 2.658 \pm 0.006$ kcal/mol and eleven bound vibrational levels. The special bound nature of Be_2 in the ground state emerges from the easy accessibility to an entirely empty valence \mathbf{p} shell. This vacant \mathbf{p} shell can invite bonding motif in two ways: (i) by \mathbf{sp} hybridization, i.e., mixing \mathbf{p} -character into the doubly occupied \mathbf{s} -orbitals of RHF (restricted HF) function, and (ii) by a strong near-degeneracy correlation effect through the double excitation $\mathbf{s}^2 \rightarrow \mathbf{p}^2$. Although 2s-2p hybridization certainly occurs in Be_2 , closed-shell RHF calculations still yield a repulsive energy surface. Moreover, the full valence space multi-configuration self-consistent field (MCSCF) wave function (8 orbitals provided by the nearly-degenerate 2s, 2p shells, which are occupied by 4 valence electrons) also yields a repulsive PES, which is in fact closely parallel to the RHF surface. Consequently, a highly unusual bond between two Be atoms is contingent on the changes of the dramatic influence of both dynamical and non-dynamical correlation effects. It should be emphasized here that Be_2 is not a *van der Waals* molecule. Actually, many calculations show that near the harmonic region (equilibrium zone) the bond can be classified as a conventional covalent bond (hybridization of 2s and 2p orbitals), whereas it can be described as *van der Waals* type because in the Be atom, the 2p orbitals as well as the 2s orbitals are energetically accessible to the two valence electrons) in the long range regime (anharmonic zone). Therefore, a substantial change must occur in the slope of the ground state potential-well [at around 3.2 Å], which allows one to distinguish an ‘inner well’ (i.e. covalent) region from an ‘outer well’ (i.e. dispersive) region. This ‘two distinct regions’ energy surface can be viewed as an indirect proof that the *van der Waals* interaction alone is not sufficient to completely characterize the PES. Be_2 is unique in this respect as the related dimers of closed-shell metal atoms Mg_2 , Ca_2 , Zn_2 , and Hg_2 exhibit typical *Morse* and/or *van der Waals* type potentials. Schmidt *et al.* [3] argued that the formation of the unusual Be_2 bond should be attributed exclusively to dynamical correlation that is defined with respect to the (2s, 2p) active space associated with the Be ^1S ground state. Kerkines and Nicolaides [5], on the other hand, argued that the origin of the weak Be_2 bond is to be found in nondynamical-type correlations. From the foregoing discussion it is evident that Be_2 is much more complicated than the conventional diatoms. In our recent work [4] we stated that bonding in Be_2 comes from the interplay of both correlation effects over the entire range of interaction, which calls for higher dynamical correlations; indeed the $3\mathbf{d}$ orbitals, in particular, determine the quantitative details of the PES.

The near degeneracy of 2s and 2p orbitals in the isolated atoms that can give the dimer’s ground state significant MR or multiconfigurational character is mainly responsible for the poor performance of the SR-based CC methods to yield PES of the system[2-5]. It is worth mentioning that the single reference (SR) coupled cluster (CC) theory has been well established for describing the ground-state electronic structures of molecules [1]. Although the standard SRCC approaches with higher body cluster operators, such as ‘gold-standard’ CCSD(T) approximation, or the predecessor of CCSD(T) abbreviated as CCSD+T(CCSD) or CCSD[T], in which one corrects the CCSD energy for the dominant effects due to triply excited clusters are very successful for most molecules near their equilibrium geometries, they have difficulties with capturing nondynamical electron correlations characterizing reaction profiles involving bond breaking and biradicals. To

tackle this problem, various modified CCSD schemes to incorporate the nondynamical effects have been suggested over the years [1]. Full-blown inclusion of three body cluster operator in a blanket manner is not useful yet for routine application because the computational cost of the resulting method CCSDT scales as N^8 (N is the total number of basis functions). To reduce the computational cost, a number of approximate triples correction schemes have emerged. As with the structural flexibility of CC theory, one has the freedom in choosing to define connected triples corrections to CCSD. This freedom allows exploration of different choices of connected triples excitations, which yield different corrections to the energy and can lead to qualitatively different behavior for the methods [1].

Mahapatra and Chattopadhyay [4] very recently have proposed a new iterative triples correction for the CCSD (termed as CCSDT-1a+d) where only a subset of triple excitations is included in such a way that the computational cost for triples correction is dramatically reduced (compared to the cost of CCSDT). Preliminary results demonstrated that the CCSDT-1a+d method represents a very good approximation to the CCSDT method for the entire bond breaking process in some closed-shell molecules [4]. In this paper, we report its applications to study the bond breaking potential energy surface (PES) of Be_2 in the ground state with the modern basis set. The results will be compared with the recent advanced MRCI calculations due to Kerkines and Nicolaides [5] and other methods currently in vogue. As pointed out by several authors, large basis sets are needed to obtain accurate results for Be_2 and to account fully for electron correlations; the results have been reviewed nicely in Figure 2 (reported in ref. [3]) by Schmidt *et al.* [3]. The present study is an attempt in this direction. To assess the quality of the resulting PES we have extracted some selective spectroscopic constants. With the computed PES, the vibrational energy levels of Be_2 have been derived via the corresponding vibrational Schrödinger equation and we have compared them with the experimental values.

Results and Discussion:

(α) Energy surface:

It is quite useful to illustrate how a number of popular *ab initio* methods available via currently widely used quantum chemistry packages, perform or fail to do so for Be_2 in order to illustrate the difficulty in computing PES of this system successfully. For a consistent and reliable comparison, we use the same large basis set, cc-pVQZ (taken from EMSL Basis Set Library [6]), for the different methods considered here [such as hybrid DFT (B3LYP), MRCI, and CCSDT-1a+d] and present our results in Figure 1. In our present application we have used the frozen-core approximation scheme. From the previous works [2-5], it is evident that for the correct description of very weak bonds like in the ground state of Be_2 , the CC approach must be applied at a level which is higher than the “gold standard” CCSD(T). One fact which emerges from the comparison of the data in Figure 1 is that the results of CCSDT-1a+d is closer to the advanced size-extensive-corrected CASSCF(4,8)-based MRCI data [5]. The deepest potential well has been obtained from DFT calculations and hence DFT potentials dramatically over-bind. It is generally accepted that DFT wave functions do not reflect dispersion effects. The *van*

der Waals interactions in the alkaline-earth dimers present a stringent test of density functional methods. The agreement between CCSDT-1a+d and MRCISD PESs is good. It is worth noticing that the CCSD(T) PES has a similar shape but is significantly shallower indicating the need for a better treatment of correlation energies. The CCSD(T) method seriously underestimates the binding energy of Be₂. At the CCSDT-1a+d level of theory, the binding energy, D_e of Be₂ is only about 816.8 cm⁻¹ at equilibrium distance R_e= 2.461 Å with harmonic vibrational frequency ω_e = 258.9 cm⁻¹. MRCI analysis yielded D_e = 792.6 cm⁻¹, R_e =2.479 Å, and ω_e 245.0= cm⁻¹. The experimental results for the challenging Be₂ molecule reported by Merritt *et al.* can also allow us to evaluate the accuracy of our theoretical treatment: D_e = 929.7 cm⁻¹, R_e =2.4536 Å, and ω_e =270.3 cm⁻¹. From these values, it appears that the results for CCSDT-1a+d are in excellent agreement with that of MRCI and experimental estimates. Therefore, Be₂ has a considerably more stable minimum than its helium homologue. The gap between experimental data and our values is not really disappointing, as it has been noted many times by several workers that to reach very high accuracy, besides the basis-set convergence, one has to include full-blown triples-quadruples (and higher) excitations as well as non-adiabatic effects in conjunction with relativistic ones. The basis set presented here is not large enough to come close to the basis set limit.

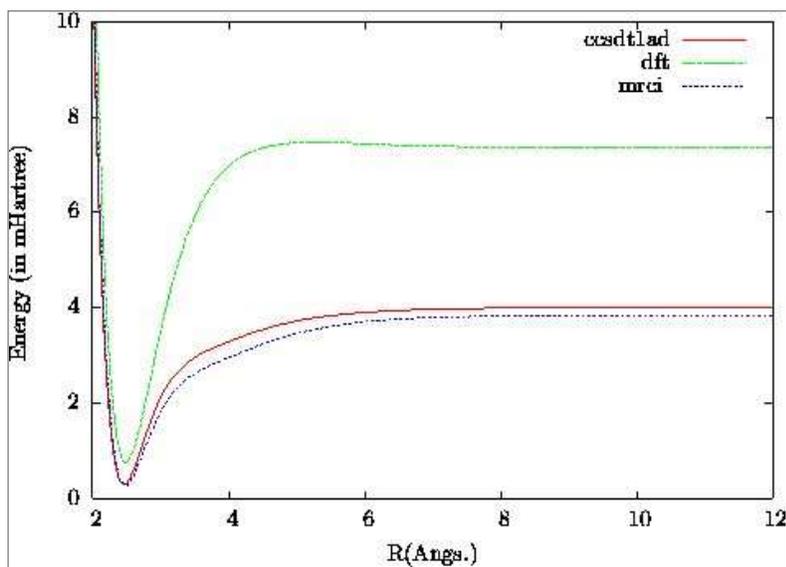


Fig. 1: PES of 1Σ state of Be₂ with different methods.

(β) Vibrational levels:

At this point, we examine the quality of the CCSDT-1a+d potential for Be₂ as obtained via the vibrational energy level calculations. Such computations provide the most rigorous test of the method designed to compute PESs. This is so since the results depend on the accuracy and the correctness of the computed PES. In fact, for modern structural computations using the state-of-the-art techniques, theoretical computation of vibrational energies along with frequencies has become almost ‘a must’ for elucidating experimental results, as it helps to interpret and assign experimental infrared or Raman spectra, especially in difficult and questionable cases. It is also worth stressing that the vibrational spectra of diatomic molecules probably furnish the most precise data available for probing energy changes along the entire reaction path. They therefore present good tests for *ab initio* methods that aim at describing reaction paths.

Recent spectroscopic measurements [2] on Be₂ characterized the molecule’s ground electronic state with sufficient resolution to distinguish 10 vibrational levels. Patkowski *et al.* [2] have recently shown that the twelfth vibrational state of beryllium dimer can be positively identified from *ab initio* calculations. To estimate vibrational levels the Fourier Grid Hamiltonian method [7] has been used in the present work. In this approach the vibrational equation has been transcribed into an eigenvalue problem in the eigenbasis of position operator \mathbf{x} , and for numerical purpose, we have considered a finite domain of L^2 which is valid in the present context as we are interested in bound states of the vibrational Hamiltonian. If the one dimensional coordinate space of vibration is divided into equispaced grid points defined by $R_i=i\Delta R$ where $i= 1,\dots,(N+1)$ and $\Delta R = (R_{N+1} - R_1)/ N$



with

$$\mathcal{T} = \frac{\hbar^2}{2\mu} \left(\frac{d}{dx} \right)^2 \quad \text{and } 2n = N-1, \quad \Delta k = 2\pi/N\Delta R.$$

In Figure 2 we have presented the vibrational eigen energies resulting from the numerical solution of the vibrational equation. The vibrational eigenvalues are reported in Table 1, where the CCSDT-1a+d and MRCI results, are reported, and where the experimental results are also added for comparison. Other spectroscopic data show good agreement with advanced MRCI and the experimental values reflect the quality of our computed surface. While, in general, it is a non-trivial task to reliably judge the accuracy of theoretical computations, we expect that there is strong ground for high reliability when the estimates of various advanced-level methods coincide. The quality of vibrational spacings for the lowest five vibrational levels is very good and matches well with experimental findings as compared to MRCI. It turns out that our computed PES supports seven vibrational levels, although the recent state-of-the-art studies support 12 levels. Therefore, we conclude that our CCSDT-1a+d PES is not as good as the best published, but adequate for our purpose. We express the hope that our method in conjunction with our present results will foster new efforts in obtaining reliable spectroscopic data on the ground states of Be-containing systems such as BeMg[8].

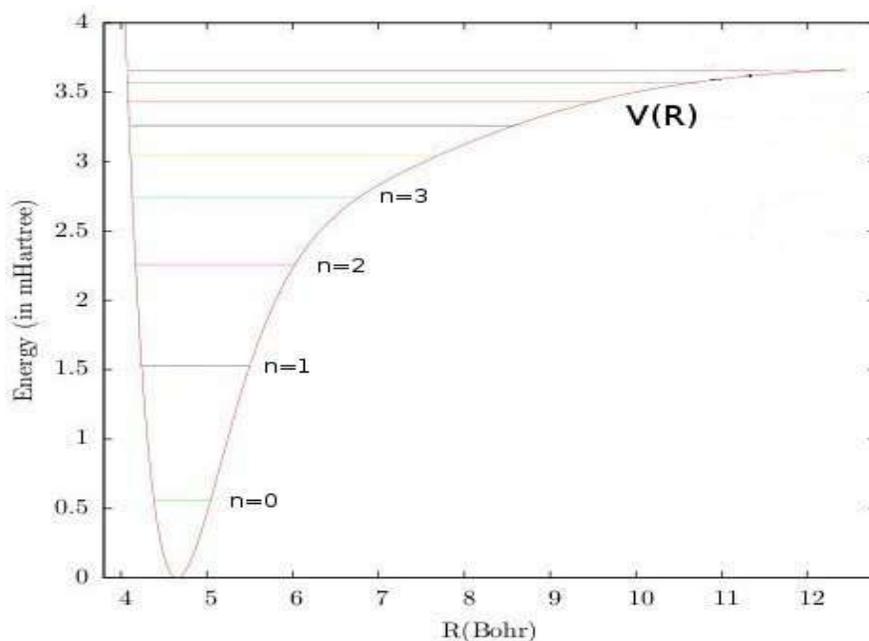


Fig.2 Vibrational eigenvalues

Table 1: Comparison between experimental and *ab initio* calculated vibrational energy level differences $G(v) = G_v - G_0$ in the electronic ground state of Be_2 (in cm^{-1}). Experimental data have been taken from *Science*, **324**, 1548 (2009).

v	CCSDT-1a+d	MRCISD	Experiment
0	0.00	0.00	0.00
1	212.00	199.05	222.6
2	372.09	345.09	397.1
3	478.31	437.86	518.1
4	543.75	498.21	594.8
5	591.52	517.24	651.5
6	629.81	547.19	698.8

Conclusion:

Computation of complete Be-Be interaction potential can be deemed as a benchmark for tests of high-level theoretical methods tailored to treat the effects of configurational mixing and electron-electron correlations. The electronic ground state of the notoriously “difficult” system Be_2 has been studied via non-perturbative quantum mechanical many-particle method. It has been found that the main challenge in computing Be-Be interaction emerges from the quite different character of the wave function in the equilibrium region and in the asymptotic zone. This fact indicates that even small errors in the energy calculation can lead to qualitatively incorrect estimates.

Because of the very different natures of the electronic wave functions at minimum and at dissociation regions, a balanced and accurate treatment of contributions that arise from the orbital motions and the correlation energy over the entire PES is a particularly difficult task. This fact explains why even *state-of-the-art* computations may lead to wrong findings, if the method used does not take into account this issue of the Be₂ molecule. In Be₂ the Be-Be bond does not belong to any one of the classes usually known in chemistry. The topology of the Be₂ PES is quite different from that of a standard Morse like potential, and a simple physical potential such as the Lennard-Jones model. The Be₂ molecule has a bond length that is more characteristic of a conventional covalent interaction. Finally, the vibrational energy levels of Be₂ have been computed via Fourier Grid Hamiltonian method using a PES computed at the CCSDT-1a+d level of theory. The agreement between experimental and the derived CCSDT-1a+d results indicate that the overall vibrational spectrum is accurate enough for us to assert the reliability of the model.

Notes:

1. **'Dynamical' and Nondynamical:** The concept of electrons avoiding each other, is called the dynamical correlation, it is less important at stretched geometries, as the electrons are further apart. There is a more subtle effect called nondynamical or static correlation energy. Nondynamical correlation energy increases with stretching. Systems where static correlation is important are often termed multireference systems. To get a good approximate wave function in this case, both static and dynamical correlation effects have to be taken into account.
2. **Coupled Cluster:** Coupled Cluster methods applied in quantum chemistry reformulate the electronic Schrödinger equation as a nonlinear equation, enabling the computation of size-consistent high-precision approximations of the ground state solution for correlated systems. Size-extensivity is, in fact, a direct result of the exponential parameterization of the CC wave function.
3. **Frozen Core Approximation:** It is quite common in applications of the CI method to invoke the frozen core approximation, in which the lowest-lying molecular orbitals (occupied by the inner-shell electrons) are constrained to remain doubly-occupied in all configurations. The frozen core for Be atom typically consists of the 1s atomic orbital. A justification for this approximation is that the inner-shell electrons of an atom are less sensitive to their environment than are the valence electrons. Thus, the error introduced by freezing the core orbitals is nearly constant for molecules containing the same type of atoms. In fact, it is sometimes *recommended* that one employ the frozen core approximation as a general rule because most of the basis sets commonly used in quantum chemical calculations do not provide sufficient flexibility in the core region to accurately describe the correlation of the core electrons.
4. **GAMESS:** The General Atomic and Molecular Electronic Structure System (GAMESS) is a general *ab initio* quantum chemistry package (a non-commercial package). See www.msg.ameslab.gov/gamess/

References (owing to space limitations, this is a representative sample of the literature rather than an exhaustive review):

1. R. J. Bartlett, and M. Musial, *Rev. Mod. Phys.*, **79**, 291, (2007). Shavitt, I and Bartlett, R. J. *Many-body Methods in Chemistry and Physics* (Cambridge University Press, Cambridge, 2009).
2. V. E. Bondybey, *Science* **227**, 125 (1985). J. S. Lee. *Phys. Rev. E*, **68**, 043201 (2003). J. M. Merritt, V. E. Bondybey, and M. C. Heaven, *Science*, **324**, 1548 (2009). K. Patkowski, V. Špirko, and K. Szalewicz, *Science*, **326**, 1382 (2009).
3. M.W. Schmidt, J. Ivanic and K. Ruedenberg, *J. Phys. Chem. A* **114**, 8687 (2010).
4. U. S. Mahapatra and S. Chattopadhyay, *Mol. Phys.* **110**, 75 (2012); *J. Comput. Chem.* **33**, 1285 (2012).
5. I. Kerkines and C. Nicolaides, *J. Chem. Phys.* **137** 124309 (2012).
6. D. Feller, *J. Comput. Chem.* **17**, 1571 (1996); K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, and T. L. Windus, *J. Chem. Inf. Model.* **47**, 1045 (2007). See www.emsl.pnl.gov/forms/basisform.html
7. C. Clay Marston and G. Balint Kurti *J. Chem. Phys.* **91**, 3571 (1989).
8. U. S. Mahapatra, D. Banerjee, R. K. Chaudhuri, and S. Chattopadhyay, *Mol. Phys.* **113**, 1387 (2015).