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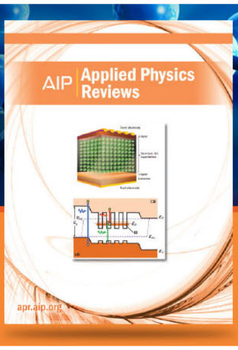

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The nature of the chemical bond in Be_2^+, Be_2, Be_2^-, and Be_3

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The present study focuses on the Be_2^+, Be_2, Be_2^-, and Be_3 species with the aim to unveil their bonding pattern. The ground states of the above molecules are examined mainly through multi reference configuration interaction methods using an aug-cc-pVQZ basis set. Previous work is scrutinized with an eye to the instability problems inherent in various Hartree-Fock schemes. Under this point of view, we rationalize previous findings and put them in a unified context of what and why should be done in similar hard to crack cases. In all the above species, the covalently bound ground states are formed just because the Be atom is found in its first excited ^{3}P($2s^12p^1$) state. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4967819]

I. INTRODUCTION

Heitler-London's quantum mechanical description of the H_2 molecule[1] came as a full support to Lewis' electronic theory of valence[2] that is too much alive nowadays as it was 100 years ago and provides the building principles that help us to make the transition from atoms to molecules. The directionality of the chemical bond dating back from the mid 19th century seems to be absent in the delocalized, symmetry adapted, canonical one electron functions of the molecular orbital theory, although transformations into localized bond and lone pair orbitals are quite feasible without altering the Hartree-Fock (HF) wavefunction. Unfortunately, this reconciliation did not prevail and the canonical orbitals are considered to be the building blocks of the chemical bond instead of the valence electrons, a situation quite paradoxical considering the fact that we all draw lines/bonds between the valence electrons. But it is these valence electrons responsible for the "chemical glue" that keeps the atoms together, distributed in so many ways that give rise to the ground and excited atomic states. Consequently, all these atomic states should be considered as the chemical ingredients for the molecular formation. One simple example is the quadrivalency of carbon in the methane molecule due to the electronic promotion $2s^22p^2$(^{3}P) to $2s^12p^3$(^{5}S).[3]

A remedy to the above situation was provided by Coulson and Fischer through a work of major significance on the ground state of H_2.[4] It is the first work that shows the HF instability due to the double occupancy in the molecular case[5] and second it underpins the localized character of the "chemical bond" by quantum mechanical means; the molecular orbitals are not point group symmetry adapted as in the "usual" HF theory. The physics contained in the Coulson-Fischer wavefunction was generalized by Hurley, Lennard-Jones, and Pople in their pair function model[6] while its structure can be considered as a precursor of the Generalized Valence Bond[7] (GVB) and Spin-Coupled[8] (SC) wavefunctions (see also Ref. 9 for similar work on the GVB/SC formalism). This new approximate wavefunction is better than the Restricted (R) or Unrestricted (U) HF schemes not only on energetic grounds but also in terms of properties' expectation values.[10] The resulting molecular orbitals are not point group symmetry orbitals while the atomic orbitals are not in general l^2 eigenfunctions. The latter seems to be surprising at first sight but it is theoretically founded on the existence of another constant of motion known as the Laplace-Runge-Lenz (LRL) vector[11] measuring the eccentricity of elliptical orbits in the Kepler problem. This is also an expedient rationalization of the so-called "*s*–*p*" resonance (or near degeneracy)[12] or singlet instability[13] problem; the terminology depends on our scientific appetite. The fact that the atomic orbitals are not l^2 eigenfunctions, in compliance with the LRL constant of motion, is clearly manifested in the form of the atomic GVB/SC one electron functions; see also Ref. 14

This instability problem, viewed under Sinanoğlu's spirit,[6(a,b)] shows that the HF wavefunction, being an unstable point in the functional space, is a bad starting point for any correlation treatment. The most spectacular example is the catastrophic behavior upon dissociation. By taking into account double excitations,[6] the electrons are placed into different spatial orbitals and the resulting wavefunction is a restricted form of a GVB/SC type known as Perfect-Pairing GVB (GVB-PP); see also Ref. 10 for some unexpected pitfalls of the restricted GVB-PP form. Moreover, the molecular orbitals are of semi localized nature while their evolution along the reaction coordinate offers an insightful view on the formation of the chemical bond.

There is an upsurge of interest lately for the description of the chemical bond through a GVB/SC analysis.[15] The Dunning group in its quest to explain hypervalency has introduced the concept of recoupled pair bonds[15(a)] and recoupled pair bond dyads,[15(b)] being in essence an evolution of the different spin functions during bond formation, and attributed to them the status of an "essential new unifying concept in chemistry."[14] Although not explicitly stated in their work, it is the excited states of the constituent fragments that "do" the job and explain the concept.[16] The role of the excited states is also apparent in the so-called "democracy principle" enunciated some

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20 years ago by Cooper *et al.*[17] and states that any valence electron can participate in chemical bonding if provided with sufficient energetic incentive. Thus we believe that the introduction of new terminologies/concepts[15(a,b)] is misleadingly unnecessary.

The above discussion shows that the HF description of both atoms and molecules should be replaced by a properly constructed GVB/SC or by the Complete Active Space Self Consistent Field (CASSCF) function mainly due to instability problems. The above problems or intricacies of the R(O)HF equations are not a mere theoretical curiosity of academic character but complications that appear in all quantum chemists' everyday life. Perhaps, the most deleterious example of such a sneaky behavior is the seemingly "innocent" Be atom. With only 4 electrons two of which ($\sim 1s^2$) are core ones, the Be atom appears to be the most insidious case in the periodic table exclusively due to the long standing myth around the bonding mechanism of its homonuclear $Be_2(X^1\Sigma_g^+)$ species. These two valence electrons traditionally denoted as $(\sim)2s^2$ and apparently chemically different from the He $(\sim)1s^2$ e^- are responsible for a tremendously large body of scientific publications on Be_2 since the early 1960s. Since then, more than 100 papers have been published aiming at deciphering the bonding mechanism and obtaining an accurate value for its binding energy ($\sim$1000 cm^{-1}).

The present work should be considered as an effort to unravel the "secrets" of its bonding mechanism. To this end, we will critically present the pertinent work not only on the target molecule but also on other simple Be diatomics like BeH, BeHe, BeLi, and BeB in order to isolate that "binding force" in Be containing molecules.

II. THE Be_2 SAGA

Probably the very first *ab initio* work is the RHF calculation by Fraga and Ransil in 1962.[18] The ground $X^1\Sigma_g^+$ state is repulsive but numerical data for the bound $^3\Sigma_u^+$ state are given at a limited Configuration Interaction (CI) level. Since then numerous papers on the ground Be_2 state have been published; see, e.g., Ref. 19. The great interest on this molecule is also manifested by the number of publications during the last few years; there are at least two in 2016,[20] five in 2015,[19(h,i),21] while the latest revision of the experimental binding energy was published just in 2014.[22] Although there are computational works of unprecedented accuracy (see, e.g., Refs. 19(c), 19(f), 19(h), and 23) the nature of the chemical bond is still an open question. In what follows we will review only those papers we think they advance our understanding on what keeps together these two closed shell Be atoms.

A major breakthrough, perhaps the most important, in the Be literature is Watson's "Approximate Wave Functions for Atomic Be"[24(a)] published in July 1960 followed by Weiss's "Configuration Interaction in Simple Atomic Systems"[24(b)] published in June 1961 being essentially similar to Watson's work. Watson's paper contains all the physics we should understand for the ground Be state. It is perhaps the first paper showing explicitly the inappropriateness or instability problems of the HF theory by treating the so-called orbital degeneracy problem. It precipitates, at the computational level, the HF instability analysis[13] and Sinanoğlu's[6(a,b)] theoretical foundation of the double excitations out of a HF wavefunction.

It is Watson's paper that paved the way to the first successful description of $Be_2(X^1\Sigma_g^+)$ by Liu and McLean[25] almost twenty years after Fraga and Ransil's HF treatment.[18] Based on a MCSCF + 1 + 2/$[7s5p4d2f]_{STO}$ wavefunction that dissociates into two Be($c_1 1s^2 + c_2 2p^2$) atoms they obtained a $D_e = 0.10 \pm 0.01$ eV (=806.55 ± 80.66 cm^{-1}) at $r_e = 2.49 \pm 0.02$ Å in clear contrast to all previous works. Soon after, Blomberg, Siegbahn, and Ross[26] published ground state potential curves based on several methods and basis sets. Their best estimate for the binding energy is D_e = 2.0 kcal/mol (=700 cm^{-1}) at r_e = 4.9 bohrs (=2.59 Å). The most important point of their paper is that it shows explicitly for the first time a shoulder in the potential curve. A full-CI (FCI)/$[8s5p2d1f]$ calculation on Be_2 by Harrison and Handy[27] yields a D_e = 1.86 kcal/mol (=650 cm^{-1}) and r_e = 4.75 bohrs (=2.51 Å). A FCI calculation is certainly an achievement, especially back in the 1980s, but the most important lesson we get out of their work is that linked triple and quadruple excitations out of HF are necessary in order to obtain a physically meaningful curve since singles and doubles are just insufficient. That was also the spirit of the work in Ref. 25.

In a very enlightening paper, Lepetit and Malrieu[28] proposed that the "problematic" Be_2 bond is due to the Be($2s^1 2p^1$; ^{3}P) state. Their whole work is triggered by a dramatic UHF instability that leads to a weakly bound system (by ~6 kcal/mol at 4.3 bohrs). Although this computational level cannot provide quantitative results, it provides invaluable insights into the nature of the chemical bond but quite unfortunately their work did not have any substantial impact. The same conclusion is stated in Ref. 29 based on a private communication between the authors and the late Joseph Gerratt. We read "... No bonding is expected between two $1s^2 2s^2$ beryllium atoms, but an avoided crossing occurs between this nonbonding state and an excited bound state in which the constituent beryllium atoms have had an s electron promoted into the p manifold.[63]" In a FCI study by Evangelisti *et al.*,[30] we read that "linked triple and quadruple excitations play an essential role in the description of the bond even if the exact mechanism is not yet clear" and that "... d orbitals are needed in order to have even a qualitatively correct description of the bond; f and g orbitals together account for about one half of the exact dissociation energy." Although both of these statements appear to be rather of practical value, they will help us to unveil the nature of the chemical bond.

Sometime later Stärck and Meyer[31] reached the same conclusions as Lepetit and Malrieu[28] did; the minimum interaction is due to the interaction of two triplet valence states of *sp* hybrid orbitals. In 2010 Schmidt *et al.*,[32] in a *tour de force* study on Be_2 stated that "... the attraction between them results entirely from changes in the dynamic electron correlations." while a bit later they say "... the binding in Be_2 is contingent on the effects of dynamical electron correlation, which is uncommon and therefore of considerable interest." The upshot of their analysis is that orbitals arising from the $3d$ shell are responsible for the bond in Be_2 since they provide the most important angular correlation to the $2p$ admixture into the HF orbitals due to the $2s$-$2p$ degeneracy problem. Moreover, the $3d_\pi$ orbitals are related to the marked change in the slope of the curve at 3.2 Å (see also Ref. 26).

An important advance in our understanding of the Be_2 conundrum is Nicolaides' work[33] that appeared just a year after Ref. 32. Based on the state-specific "Fermi sea" wavefunctions for the Be(^1S, $^3P^0$, $^1P^0$, ^1D, and ^3P) atomic states,[34] he concluded that the d orbitals play a primary role in the description of the zeroth order excited Be states (see our discussion in Section I) which are responsible for the binding in Be_2. In his own words "By asserting that the formation of the bond at about 2.5 Å is influenced by the interactions involving excited states, I point to the corresponding significance in zeroth-order ("Fermi-sea") not only of p waves but also of d waves whose origin is in the valence-Rydberg state mixing of the lowest ^1D and $^1P^0$ states of Be." He explicitly pointed out the participation of the excited Be states in the ground Be_2 molecule, and he clearly attributed the importance of the d functions in their correct description, although we would not agree with the role of the ^1D and $^1P^0$ excited states in the bond formation (see below). This point of view is also shared by Helal *et al.*[35] who, based on a FCI/[$7s6p5d4f3g2h1i$] calculation, concluded that "... as pointed out by Nicolaides [21], the static correlation plays a crucial role in the formation of the bound state of the beryllium dimer." Similarly, El Khatib *et al.*[36] based on multireference CI (MRCI) and FCI results concluded that "... Be_2, even if weakly bounded, shows the typical behavior of a covalent molecule ..." and that "... the present work could be considered as an attempt to define a new type of chemical bond based on nondynamical correlation." In Ref. 19(i), the authors attributed the origin of the chemical bond to a mutual interplay of dynamical and nondynamical correlations. Finally, in the most recent work,[20(a)] the authors concluded that there is a "particular type of weak bond."

What we know about the potential curve of the ground Be_2 state is that it presents a rather weird change of slope at ~3.2 Å, a potential minimum of <1000 cm^{-1} at ~2.5 Å, and that there is a universal vague consensus that Be_2 is not a van der Waals (vdW) molecule but there is somehow a particular type of covalent bond of an unclear origin.

Although the ground state of Be_2 is surrounded by a chemical "haze," the situation is much transparent concerning its excited states; see Ref. 37.

From an experimental point of view, Be_2 has also an intriguing story. It was detected for the first time in 1984 by Bondybey[38(a)] and Bondybey and English.[38(b)] They reported a D_e = 790 ± 30 cm^{-1}, r_e = 2.45 Å, ω_e = 275.8 cm^{-1}, and $\omega_e x_e$ = 26.0 cm^{-1}.[38(a)] A new experiment performed a quarter of a century later gave a D_e value of 929.7 ± 2.0 cm^{-1} and r_e = 2.453 Å,[39] while 11 vibrational levels have been characterized.[40] Soon after a 12th vibrational level was found by "morphing" several *ab initio* potentials fitted to experimental data.[41] The new level lies 0.41–0.44 cm^{-1} below the dissociation limit and supports two excited rotational states. The latest experimental value[22] for the binding energy is D_e = 934.9 ± 0.4 cm^{-1} at r_e = 2.445(5) Å. It resulted from a direct potential fit of the experimental data reported in Ref. 39, and it is in excellent accord with the theoretical value of D_e = 935(10) cm^{-1} and r_e = 2.444(10) Å by Koput.[19(f)]

Despite its only four valence electrons, Be_2 has been the source of numerous theoretical studies and also a test case for state of the art computational methods. The purpose of the present paper is to shed light on the still mysterious chemical pattern that keeps together two closed shell atoms or to quote Kutzelnigg[42] "... if one has understood this bond, one has the basis for understanding more interesting features about the chemical bond in general."

III. RESULTS AND DISCUSSION

In our quest to unravel the intricacies of the titled species, we have used primarily the multi reference CI (MRCI) method coupled with the Dunning augmented correlation consistent polarized valence quadruple (aug-cc-pVQZ) basis set.[43] For the description of the Be atom in all Be containing molecules except Be_3, we employed an active space that would correlate adiabatically to functions of $2s$, $2p$, $3s$, $3p$, and $3d$ angular momenta. For Be_3, the zeroth order wavefunction is deployed on the functions of the valence space, a choice based on the fact that the MRCI results founded on either the plain valence or an augmented active space for all Be_2 species are practically the same, so we did not want to make the calculations unnecessarily intractable; see also Ref. 25. For the description of the H, Li, and B atoms, their usual valence space has been employed. All of our calculations have been done with the MOLPRO 2012.1 suite of programs[44] under D_{2h} and C_{2v} symmetry and equivalence constraints.

In Section III A, we will study the ground states of $Be_2{}^+$, Be_2, and Be_2^-, in Section III B, we will present some of the presently studied excited states of the neutral species, and finally in Section III C, the ground state of the trimer Be_3 will be discussed.

A. $Be_2{}^+(X^2\Sigma_u^+)$, $Be_2(X^1\Sigma_g^+)$, and $Be_2{}^-(X^2\Pi_u)$

There are too many vdW molecules but the most emblematic ones are Rg_2 (Rg = He, Ne, Ar, Kr, and Xe). Their ground electronic states are extremely loosely bound not only because the ground atomic states are of closed shell character but also because of the large excitation energy to their first open shell excited state. For example, the interaction energies (IE in cm^{-1}) of Rg_2 and the first excitation energy (ΔE in eV) of Rg are (IE, ΔE) = $(7.26, 19.8)_{He}$, $(16.29, 16.6)_{Ne}$, $(84.76, 11.6)_{Ar}$, $(126.63, 10.0)_{Kr}$, and $(185.51, 8.3)_{Xe}$.[45] The $(934.9, 2.725)_{Be}$ couple of values does not fit in the above sequence. The IE is too large for a vdW molecule and too little for a traditional covalent bond. Although Rg_2 are traditionally thought of as vdW molecules, they can form covalently bound molecular states due to their excited atomic states; see, for example, Ref. 45(b). So, in the case of closed shell atoms, it is the energetic proximity of their excited open shell states that "drive" the atoms to form chemical bonds; this is the energetic "incentive" enunciated long ago by Cooper *et al.*[17]

Let us now examine the Be atom, the second lightest closed shell atom of the periodic table, and consider the BeH system. One should not expect a chemical bond to be formed

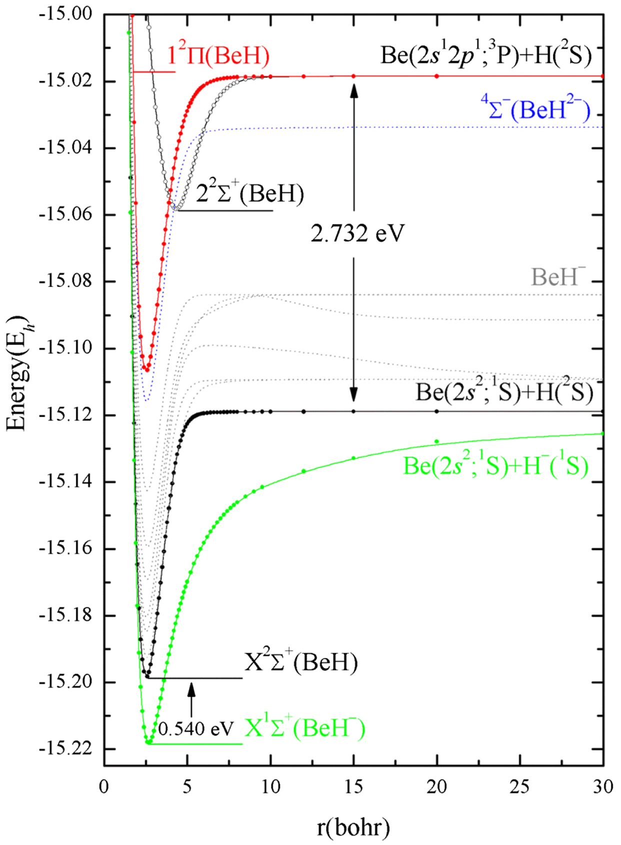


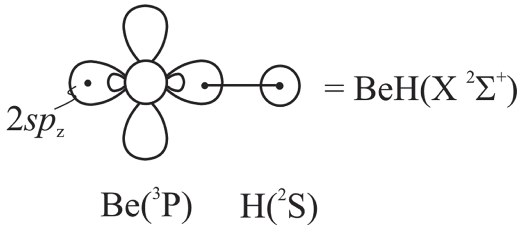
FIG. 1. MRCI potential energy curves of BeH ($X^2\Sigma^+$, $1^2\Pi$, and $2^2\Sigma^+$) and BeH$^-$($X^1\Sigma^+$). Dotted line curves display the "excited" BeH$^-$ (in grey color) and the BeH^{2-}($^4\Sigma^-$) (in blue color) states; no physical significance can been attributed to these curves but they are plotted in order to show the *in situ* excited ^{3}P Be state (see text for details).

but the BeH ground $X^2\Sigma^+$ state is bound by 49.8(50.0) kcal/mol with r_e = 1.348(1.3426) Å [MRCI(exp)[45(b)]]. In Fig. 1, we display the MRCI curves of the $X^2\Sigma^+$ (dissociating adiabatically to Be(^{1}S)+H(^{2}S)) state and the $1^2\Pi$ and $2^2\Sigma^+$ (correlating to Be(^{3}P)+H(^{2}S)) states, along with the $X^1\Sigma^+$ state of BeH$^-$. The minimum of the $X^2\Sigma^+$ BeH curve has Mulliken atomic distributions $2s^{1.08}2p_z^{0.68}/_{\mathrm{Be}}1s^{1.17}/_{\mathrm{H}}(q_{\mathrm{Be}} = +0.19)$ that unequivocally point to the participation of the Be($2s^12p^1$; ^{3}P) atomic state (just 2.725 eV[45(a)] above the ground ^{1}S state) in the chemical bond. This is also evident by the shape of its curve which at ∼5.5 bohrs suffers a strong interaction with the $2^2\Sigma^+$ state coming from the first excited asymptotic channel. The electronic characteristics of the $X^2\Sigma^+$ BeH state can be pictorially represented by the following valence bond Lewis structure; see Scheme 1.

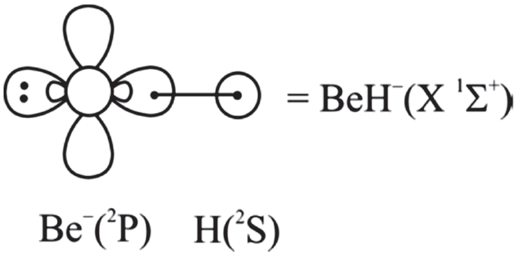
The spin defining electron, pointing to the rear of the Be atom, is available for another bond and this is indeed the case. The addition of a second H(^{2}S) atom gives rise to the linear HBeH($X^1\Sigma_g^+$) species; see Ref. 46 for an experimental characterization and Ref. 47 for a theoretical study. This is also the case when we add another BeH($X^2\Sigma^+$) unit creating the linear HBeBeH($X^1\Sigma_g^+$) species. Its dissociation energy with respect to two BeH($X^2\Sigma^+$) fragments is D_e = 74.9 kcal/mol[48] due to a sigma bond between the two *sp* hybrid orbitals located in Be and pointing away from the H atoms.

Most interestingly is the addition of another electron creating BeH$^-$. The ground state of the Be atom ^{1}S($2s^2$) has naturally a zero electron affinity (EA) while the hydrogen atom has a value of EA = 0.754 19 eV.[49] Approaching these two closed shell atoms, i.e., Be(^{1}S) + H$^-$(^{1}S), we would not certainly expect a chemically bound molecular system. Nevertheless, the reality is completely different, see Fig. 1. The BeH$^-$($X^1\Sigma^+$) exists with an experimental value of EA = 5600 ± 800 cm^{-1} (=0.694 ± 0.099 eV)[50] while its computed curve has a well depth of 58 kcal/mol at a r_e = 1.419 Å. Based on the valence bond scheme of BeH($X^2\Sigma^+$), it is not hard to understand the formation of BeH$^-$($X^1\Sigma^+$). The additional electron is singlet coupled to the already existent electron in the 2*sp* hybrid orbital, see Scheme 2, corroborated also by its Mulliken populations $2s^{1.41}2p_z^{1.09}2p_x^{0.06}2p_y^{0.06}(d^{0.10})/_{\mathrm{Be}}1s^{1.25}/_{\mathrm{H}}(q_{\mathrm{Be}} = -0.72)$. The ground state of BeH$^-$ exists just because the Be atom in the neutral BeH system is *in situ* in its ^{3}P state with respect to which the Be atom has a non-zero EA value (see below). It is interesting to mention that the placement of this additional electron in a $2p_\pi$ Be orbital leads to strongly bound curves of $^{1,3}\Pi$ (BeH$^-$) symmetry (see grey color dotted line curves in Fig. 1). Even the addition of a second electron to the remaining vacant $2p_\pi$ Be orbital giving rise to a $^4\Sigma^-$ BeH^{2-} curve (see blue color dotted line curve in Fig. 1) is strongly bound, although all these potential curves lack of any physical significance. Having said that the additional charge(s) does not disturb the equilibrium distance of the ground BeH species; see Fig. 1. The upshot of the above discussion is the participation of the Be($2s^12p^1$; ^{3}P) atomic state in the ground molecular state of BeH. Under this point of view, the anionic BeH$^-$ species is not an unconventional system and it has no surprising electronic structure as stated by Verdicchio *et al.*,[51] who concluded that the mechanism of the bond formation is the result of the quasi degeneracy of 2*s* and 2*p* and the low electron affinity of hydrogen.

The BeHe is an interesting system. The first excitation energy of the He atom is prohibitively high [ΔE(^{3}S ← ^{1}S) = 19.82 eV][45(a)] so there cannot be a chemical bond with the Be(^{1}S) atom. But the doubly excited Be($2p^2$, ^{3}P) state, just 7.40 eV[45(a)] above its ground ^{1}S state, is the perfect candidate



SCHEME 1.



SCHEME 2.

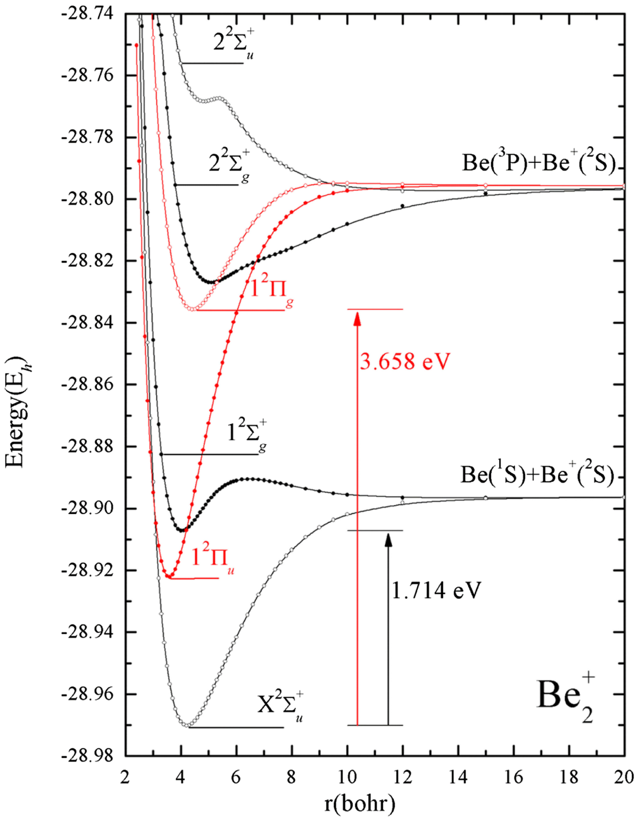


FIG. 2. MRCI potential energy curves of the cationic system Be_2^+ ($X^2\Sigma_u^+$, $1^2\Pi_u$, $1^2\Sigma_g^+$, $1^2\Pi_g$, $2^2\Sigma_g^+$, and $2^2\Sigma_u^+$).

for a putative bond. Indeed, the Be($2p_x 2p_y$, ^{3}P, $M_L = 0$)·He(^{1}S) [$^3\Sigma^-$] is bound by 6251 cm^{-1} through a putative sigma bond; see Fig. 1 and Table II of Ref. 52.

The situation is similar in both the BeLi($X^2\Sigma^+$) and BeB($X^2\Pi$) states. Both of them are bound by 6.84 and 21.15 kcal/mol, respectively, with the Mulliken populations showing a heavy participation of the Be(^{3}P) state.

In all the above cases, the Be atom is excited into its first (or second) ^{3}P state in order to form a chemical bond. Based on that, we should expect the same to happen in the $X^1\Sigma_g^+$ Be_2 state.

Let us now consider the cationic Be_2^+ species. Although it has been extensively studied in the past,[53] we will be presently concerned with its connection to the bonding pattern of the Be_2($X^1\Sigma_g^+$) state. In Fig. 2, we display the ground $X^2\Sigma_u^+$ along with some of its low lying excited states. The first excited state is of $^2\Pi_u$ symmetry ($T_e = 1.306$ eV) and the second excited state of $^2\Sigma_g^+$ symmetry ($T_e = 1.714$ eV). The most important point of Fig. 2 is that within an energy range of ~3 eV there are only three electronic states. Their MRCI equilibrium characteristics are synopsized below (only valence e$^-$ are shown):

$$\left|X^1\Sigma_u^+\right\rangle \cong 0.95\left|1\sigma_g^2 1\sigma_u^1\right\rangle,\ 2s^{1.19}2p_z^{0.25}2p_x^{0.02}2p_y^{0.02},$$

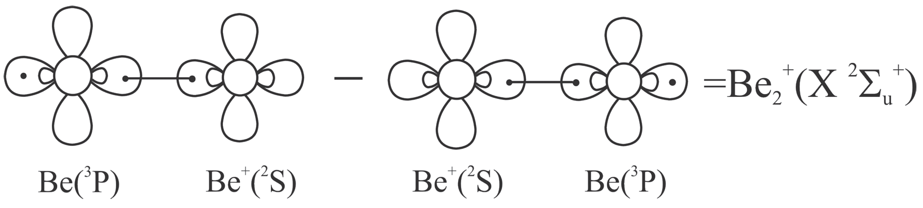
$$\left|1^2\Pi_u\right\rangle \cong 0.95\left|1\sigma_g^2 1\pi_u^1\right\rangle,\ 2s^{0.81}2p_z^{0.32}2p_x^{0.96}2p_y^{0.03},$$

$$\left|2^2\Sigma_g^+\right\rangle \cong 0.90\left|1\sigma_g^2 2\sigma_g^1\right\rangle - 0.35\left|1\sigma_g^1 1\sigma_u^2\right\rangle,$$
$$2s^{0.92}2p_z^{0.52}2p_x^{0.01}2p_y^{0.01}.$$

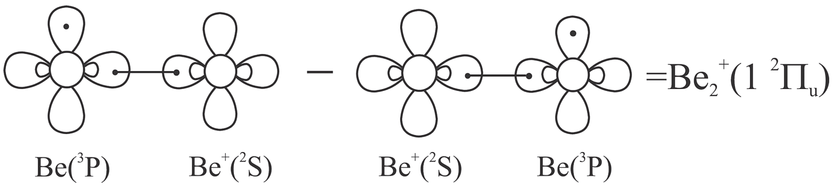
It is more than clear that the Be atoms are found in the excited ^{3}P state. Pictorially the above wavefunctions are represented by the valence bond Schemes 3, 4, and 5. Considering these structures as the founding stones for the neutral Be_2($X^1\Sigma_g^+$) state, the additional electron can be placed in either a sp_z hybrid orbital along the σ-frame or in a p_π orbital of the π-frame rendering the resonance structure (see Scheme 6) quite plausible for its chemical description and indeed the MRCI equilibrium character of the Be_2($X^1\Sigma_g^+$) state adheres to this conjecture, i.e.,

$$\begin{aligned}\left|X^1\Sigma_g^+\right\rangle \cong &\left|1\sigma_g^2(0.89\times 1\sigma_u^2 - 0.26\times 2\sigma_g^2)\right\rangle\\ &-0.10\left|1\sigma_g^2(1\pi_{u,x}^2 + 1\pi_{u,y}^2)\right\rangle\\ &+0.15\left[\left|1\sigma_g^1 1\pi_{u,x}^1 1\bar{\sigma}_u^1 1\bar{\pi}_{g,x}^1\right\rangle + \left|1\sigma_g^1 1\pi_{u,y}^1 1\bar{\sigma}_u^1 1\bar{\pi}_{g,y}^1\right\rangle\right],\end{aligned}$$

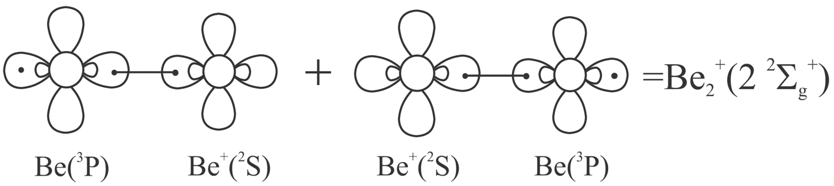
with corresponding Mulliken equilibrium distributions $2s^{1.64}2p_z^{0.25}2p_x^{0.05}2p_y^{0.05}$. The first two configurations (0.89 and −0.26) with a total weight of 0.87 are pictorially represented by the first of the resonance structures of Scheme 6 featuring two nominally sigma bonds between two excited ^{3}P($2s^1 2p^1$) Be atoms through two $2s2p_z$ hybrid orbitals pointing oppositely on each center. Based on the traditional definition of hypervalency the ground Be_2 species is the lightest hypervalent molecule since its real (2) valence is different than its nominal one (0). Our valence bond picture is practically identical with the density difference contour map given by Bader *et al.*; see Fig. 4 of Ref. 54. The above is also consistent with the equilibrium atomic populations, with the structure of the parental Be_2^+($X^2\Sigma_u^+$) species, with the electronic structure of the HBeBeH($X^1\Sigma_g^+$) molecule,[48] and the existence of the anionic Be_2^- system (see below). If there was no covalent bond in the ground state of Be_2, we would not expect the formation of the two sigma bonds between a vdW molecule and two incoming H(^{2}S) atoms. The latter, i.e., H(^{2}S)+H(^{2}S), can be coupled to either a $^1\Sigma_g^+$ or $^3\Sigma_u^+$ symmetry forming a $^1\Sigma_g^+$ HBeBeH species when combined with a $^1\Sigma_g^+$ or $^3\Sigma_u^+$ Be_2 system, respectively. $^3\Sigma_u^+$ is the first excited Be_2 state (see Section III B) featuring a single sigma bond and two symmetry defining electrons triplet coupled. Figure 3 shows the interaction curves between Be_2($^1\Sigma_g^+$ or $^3\Sigma_u^+$) with H(^{2}S) + H(^{2}S) ($^1\Sigma_g^+$ or $^3\Sigma_u^+$).



SCHEME 3.



SCHEME 4.



SCHEME 5.

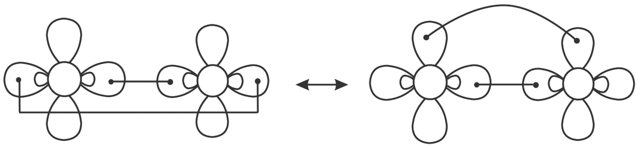
The ground $^1\Sigma_g^+$ HBeBeH state connects diabatically to the H(^{2}S) + Be$_2$($^3\Sigma_u^+$) + H(^{2}S) channel, or in other words the formation of the two H–Be$_2$ sigma bonds between the covalently bonded Be$_2$($X^1\Sigma_g^+$) state and the incoming H(^{2}S) atoms proceeds through a spin rearrangement (or decoupling mode) via the Be$_2$($^3\Sigma_u^+$) state giving rise to a strong interaction between the two curves at around 6.5 bohr.

Finally, the diabatic bond strength of Be$_2$($X^1\Sigma_g^+$) is 2.30 kcal/mol + 2 × ΔE(^{3}P←^{1}S) = 128 kcal/mol; see Table I. At this point, we should also comment on why the cationic Be$_2^+$ species (D$_e$ = 46.3 kcal/mol; similar in bond strength with the BeH($X^2\Sigma^+$) system) is much more bound than the neutral one (D$_e$ = 2.3 kcal/mol); see Table I. This is entirely due to the fact that in the cation only one Be should get excited to ^{3}P while in the neutral both of the Be atoms should get excited, so the energy "penalty" is doubled.

Let us now consider the Be$_2^-$ anionic system largely studied since the mid 1970s.[55] If the ground Be$_2$ state was a vdW molecule then the incoming electron would not "stick" to the diatom. For example, He$_2$ is a vdW molecule, He$_2^-$ does not exist. But this is not the case here. Not only Be$_2^-$ is bound but it also has an excited state. As clearly shown in Figure 4, the ground Be$_2^-$ state is of $^2\Pi_u$ symmetry while its first and only excited state, of $^2\Sigma_g^+$ symmetry, is just 0.14 eV above it. If we consider the first valence bond picture of the neutral molecule, we clearly see that the additional electron can be hosted by either a sp_z hybrid orbital creating a $^2\Sigma_g^+$ state or by a p_π orbital giving rise to a $^2\Pi_u$ state. Evidently, the charge distribution of $^2\Pi_u$ is energetically more favorable as being less congested than in the $^2\Sigma_g^+$ case and retains the second sigma bond. Their MRCI equilibrium characteristics,

$$|X^2\Pi_u\rangle \cong |1\sigma_g^2(0.88\times 1\sigma_u^2 - 0.26\times 2\sigma_g^2)1\pi_u^1\rangle,$$
$$2s^{1.39}2p_z^{0.50}2p_x^{0.50}2p_y^{0.05},$$
$$|1^2\Sigma_g^+\rangle \cong 0.90\,|1\sigma_g^2 2\sigma_g^1 1\sigma_u^2\rangle,$$
$$2s^{1.70}2p_z^{0.62}2p_x^{0.06}2p_y^{0.06},$$

mirror the excited ^{3}P($2s^12p^1$) (Be) and ^{2}P($2s^22p^1$) or ^{4}P($2s^12p^2$) (Be$^-$) states of the constituent atoms; needless to say that the configurations of the $X^2\Pi_u$ state mirror those of the Be$_2$($X^1\Sigma_g^+$) one. All the above are visually synopsized by Schemes 7 and 8. It may seem completely paranoiac to



SCHEME 6.

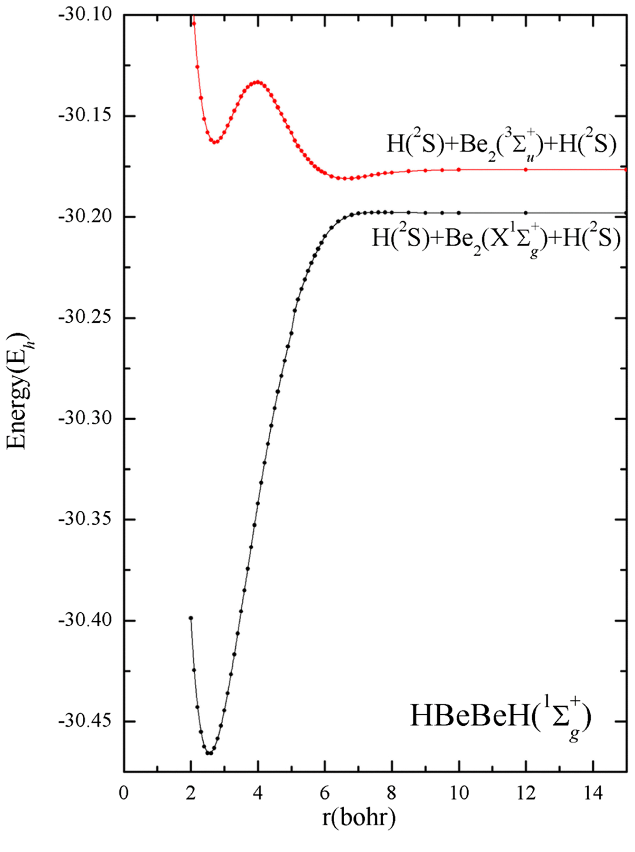


FIG. 3. CASSCF potential energy curves of two $^1\Sigma_g^+$ HBeBeH states along the linear attack of two H(^{2}S) atoms to Be$_2$($X^1\Sigma_g^+$ and $1^3\Sigma_u^+$).

TABLE I. Energies E(E_h), bond distances r_e(Å), harmonic frequencies ω_e(cm^{-1}), anharmonic corrections $\omega_e x_e$(cm^{-1}), adiabatic dissociation energies D_e(kcal/mol), and separation energies $\Delta E = |(E_{Be_2^{+/-}} - E_{Be_2(X^1\Sigma_g^+)})|$ (eV) of the $Be_2(X^1\Sigma_g^+)$, $Be_2^+(X^2\Sigma_u^+)$, and $Be_2^-(X^2\Pi_u$ and $1^2\Sigma_g^+)$ states at the MRCI/aug-cc-pVQZ computational level; experimental results in square brackets.

State	-E	r_e	ω_e	$\omega_e x_e$	D_e	ΔE
$Be_2(X^1\Sigma_g^+)$	29.241 580	2.477 [2.445(5)][a]	247.8 [275.8][b]	23.28 [26.0][b]	2.30 [2.67][a]	0.0
$Be_2^+(X^2\Sigma_u^+)$	28.970 168	2.235	521.2 [498(20)][c]	4.58	46.3 [45.95(0.11)][c]	7.386 [7.418(5)][c]
$Be_2^-(X^2\Pi_u)$	29.259 908	2.223	443.8	8.32		0.499
$Be_2^-(1^2\Sigma_g^+)$	29.254 885	2.418	346.2	6.57		

[a] Reference 22.

[b] Reference 38(a).

[c] Reference 37(e).

explain the existence of $Be_2^-(X^2\Pi_u$ or $1^2\Sigma_g^+)$ based on an atomic anion (Be^-) that does not exist. As already stated the EA of Be is zero *but* with respect to its ground ^1S state. The Be atom *has* an experimental EA value of 290.99 ± 0.10 meV[56] *but* with respect to its excited $2s^12p^1$, ^3P state or in other words $Be^-(2s^12p^2, {}^4P)$ is lower in energy than $Be(2s^12p^1, {}^3P)$ by 290.99 ± 0.10 meV. The same is also true for the $2s^22p^1$, ^2P Be^- state, it is stabler than $Be(^3P)$ notwithstanding its resonance character with respect to the $Be(^1S)$ state; see below. In simple words, the Be atom is "trapped" in its ^3P excited state within the $Be_2(X^1\Sigma_g^+)$ molecule with respect to which the $Be^-(2s^12p^2, {}^4P)$ and $Be^-(2s^22p^1, {}^2P)$ are "bound" states and not resonances. The electronic structure of $Be_2^-(^2\Sigma_g^+)$ is so clear that the linear addition of an $H(^2S)$ atom creates the $^-BeBeH(^1\Sigma^+)$ state that is bound with respect to $Be_2(X^1\Sigma_g^+) + H^-(^1S)$.[55(f)]

In all the above cases, the Be atom is found in its excited ^3P state. But in order to describe correctly this excited atomic state at the zeroth order level, the active space should be enlarged beyond the valence $2s$ and $2p$ space (see Section I and Refs. 33 and 34) and in particular to add orbitals of d angular momentum. This is also true for the Be^- case. The presence of d orbitals is what prompted Schmidt *et al.*[32] to state that "... the orbitals that arise from the $3d$ shell are the ones that account for the presence of the bond in Be_2, as the MCSCF(4, 20) + $3d$ curve is the first to exhibit binding as well as the inner and the outer sections of the potential curve." The HF/CISD energies of the $Be(2s^12p^1; {}^3P)$ and $Be^-(2s^12p^2; {}^4P)$ states are −14.511 411/−14.518 560 E_h and −14.507 992/−14.527 586 E_h, respectively. We see that only at the CISD (=FCI for Be and near FCI for Be^-) level, they are correctly described with an EA value of 0.246 eV. When our zeroth order wavefunction goes beyond the HF level (or active space) and includes the necessary $3s$, $3p$, and $3d$ functions the CASSCF/MRCI energies are now −14.518 148/−14.518 560 E_h and −14.525 963/−14.528 287 E_h, respectively, with an EA value of 0.213/0.265 eV. So, the problem of the chemical bond in Be_2 is not a matter of dynamic correlation energy but a problem of correctly describing the zeroth order level, a description that is pathologically inappropriate at the RHF level and not sufficiently accounted for at the RHF + 1 + 2 level. In order to elaborate the importance of the d functions, we have constructed potential energy curves at the coupled cluster CCSD(T) level with different subsets of the aug–cc–pVQZ basis set, see Fig. 5. At the CCSD(T)/[$6s$] level, the interaction of two $Be(^1S)$ atoms is purely repulsive. The addition of p functions result in a small interaction of ∼20 cm^{-1} (CCSD(T)/[$6s5p$]). The introduction of d functions clearly results into big changes. There are clearly two potential minima, one of vdW nature of ΔE ∼ 105 cm^{-1} and another one of non–vdW or covalent character of ∼160 cm^{-1} with a sharp change of slope at 6.0 bohrs (=3.2 Å[26]). Our vdW interaction energy is very close to the ∼90 cm^{-1} value given by Sheng *et al.*[57] modeled after the $V_{vdW}(r) = V_{HF}^s(r) + V_{corr}(r)$ formula. The d functions are necessary for the correct description of the $Be(^3P)$ state which is the building stone for the Be_2 ground $X^1\Sigma_g^+$ state. The f and g functions (CCSD(T)/[$6s5p4d3f2g$]) smooth the sharp change of slope conferring a soft shoulder like appearance at the CI interaction between the vdW curve between two $Be(^1S)$ atoms and the genuinely covalently bound curve arising from the $Be(^3P) + Be(^3P)$ channel.

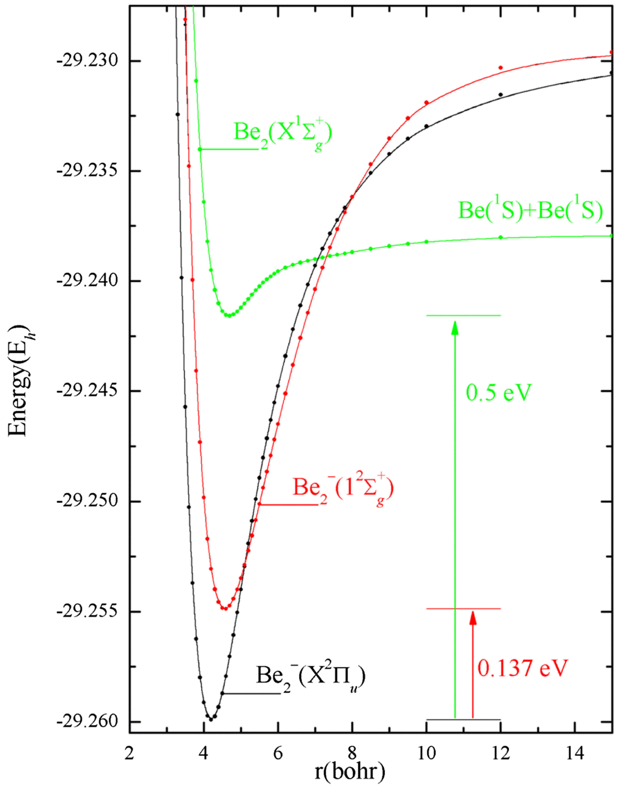
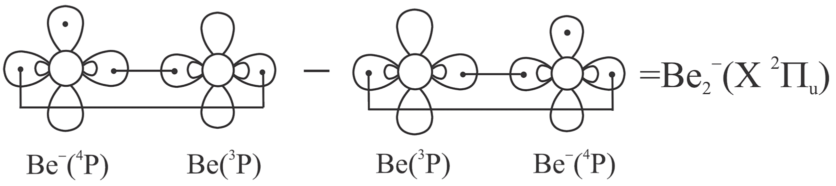
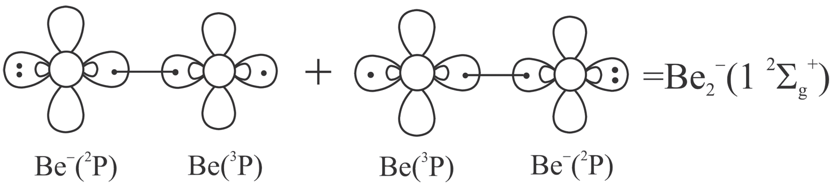


FIG. 4. MRCI potential energy curves of Be_2^- ($X^2\Pi_u$ and $1^2\Sigma_g^+$) and Be_2 ($X^1\Sigma_g^+$).



SCHEME 7.



SCHEME 8.

In Table I, we report the molecular constants of $Be_2(X^1\Sigma_g^+)$, $Be_2^+(X^2\Sigma_u^+)$, and $Be_2^-(X^2\Pi_u$ and $1^2\Sigma_g^+)$. It is interesting to notice that the equilibrium distance of $Be_2(X^1\Sigma_g^+)$, similar to the equilibrium distance of $Be_2^-(1^2\Sigma_g^+)$, is longer than the equilibrium distance of $Be_2^-(X^2\Pi_u)$ by 0.25 Å. The charge of the anionic system in its ground $X^2\Pi_u$ state is in a p_π orbital and not along the σ frame as in the $1^2\Sigma_g^+$ state; additionally it polarizes the sp_z hybrid orbitals and makes the σ bond shorter. This is also the reason that the bond distance in $Be_2^-(1^2\Sigma_g^+)$ is slightly shorter (by ~0.06 Å) than the equilibrium distance of $Be_2(X^1\Sigma_g^+)$.

B. Be_2 (excited states)

The lion's share in the Be_2 literature is on the ground $X^1\Sigma_g^+$ state but some work is also devoted to its excited states; see Ref. 37. We have constructed potential energy curves for 39 molecular states; see Figure 6 and Table II. In what follows, we will comment upon the bonding characteristics of only some of them.

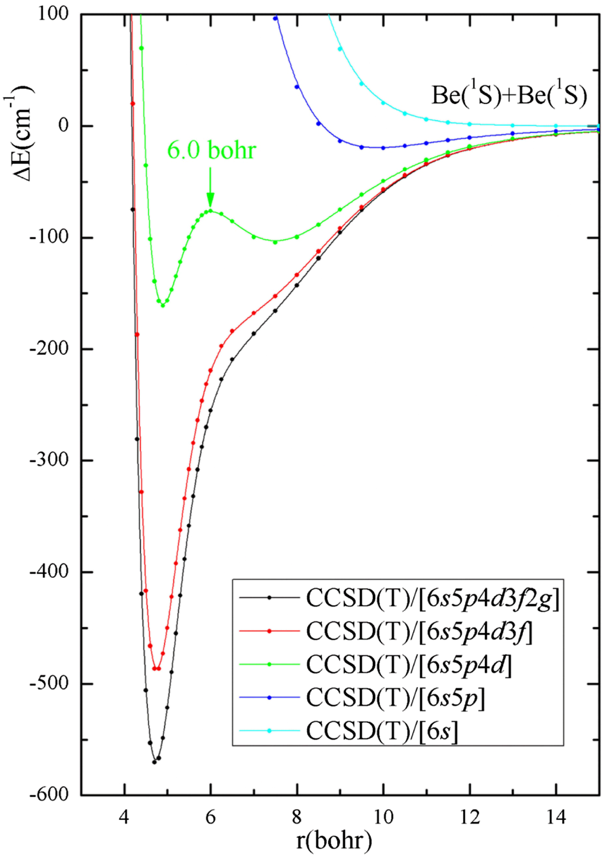


FIG. 5. CCSD(T) potential energy curves of Be_2 $(X^1\Sigma_g^+)$ with various subsets of the aug-cc-pVQZ basis set (see text for details).

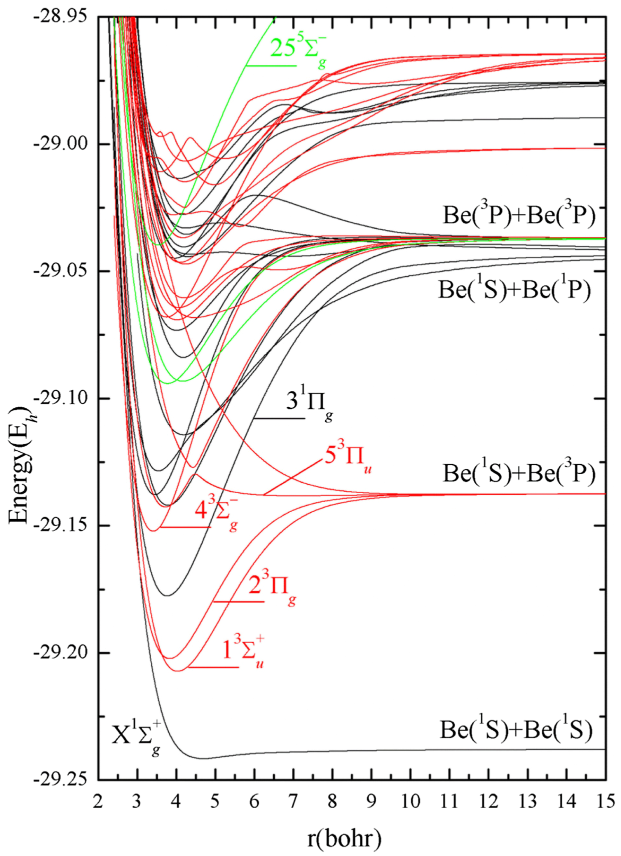


FIG. 6. MRCI potential energy curves of all 39 Be_2 states presently studied. Singlet spin states are shown in black, triplet spin states in red, and quintet spin states in green.

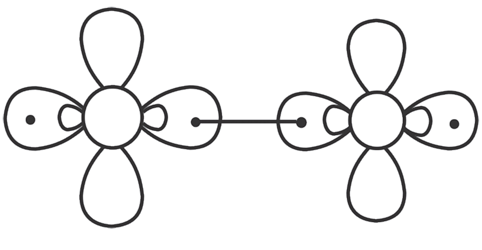
TABLE II. Energies E(E_h), bond distances r_e(Å), harmonic frequencies ω_e(cm^{-1}), anharmonic corrections $\omega_e x_e$(cm^{-1}), adiabatic dissociation energies D_e(kcal/mol), and excitation energies T_e (cm^{-1}) of all the Be_2 states studied presently at the MRCI/aug-cc-pVQZ computational level; experimental results in square brackets

State	−E	r_e	ω_e	$\omega_e x_e$	D_e	T_e
$X^1\Sigma_g^+$	29.241 580	2.477	247.8	23.3	2.30	0.0
		[2.445(5)][a]	[275.8][b]	[26.0][b]	[2.67][a]	
$1^3\Sigma_u^+$	29.207 369	2.133	614.9	4.4	43.8	7508
		[2.127][c]				[7406][c]
$2^3\Pi_g$	29.202 379	2.026	657.2	6.3	40.7	8604
$3^1\Pi_g$	29.177 758	1.993	708.2	4.2	84.7	14 007
			[726 ± 25][d]	[4.4][d]	[84.90 ± 0.09][d]	[13 711 ± 30][d]
$4^3\Sigma_g^-$	29.152 387	1.801	874.3	5.6	72.3	19 576
$5^3\Pi_u$	29.142 776	1.966	701.3	6.0	3.3	21 685
$6^1\Pi_u$	29.142 121	2.003	677.2	4.7	62.5	21 829
		[1.997][c]	[685.86][c]	[4.951][c]	[62.7][d]	[21 468.11][c]
$7^1\Delta_g$	29.138 051	1.827	851.9	9.5	63.3	22 722
$8^1\Sigma_g^+$	29.128 672	1.871	743.3	14.2	54.1	24 780
$9^1\Sigma_u^+$	29.114 373	2.218	508.0	5.0	44.8	27 919
		[2.199][d]	[511.2][d]	[4.69][d]	[44.79][d]	[27 738][d]
$10^5\Sigma_u^-$	29.094 252	1.996	599.1	5.2	35.9	32 335
$11^5\Pi_g$	29.093 306	2.204	495.8	4.2	35.3	32 542
$12^1\Sigma_g^+$	29.084 023	2.212	652.4	5.6	29.4	34 580
$13^1\Sigma_u^-$	29.073 361	2.122	552.1	6.8	22.7	36 920
$14^3\Delta_u$	29.069 187	2.122	535.6	7.2	20.1	37 836
$15^3\Pi_g$	29.068 273	2.363	342.4	15.5	19.5	38 036
		[2.352][c]	[323.5][c]			[37 906][c]
$16^3\Sigma_u^-$	29.068 144	1.986	651.6	3.8	65.1	38 065
$17^3\Sigma_u^+$	29.064 365	2.155	512.2	3.5	17.1	38 894
$18^3\Sigma_u^+$	29.060 581	2.222	516.0	12.8	14.7	39 725
$19^3\Sigma_g^+$	29.047 297	2.240	503.5	3.5	28.9	42 640
$20^3\Pi_u$	29.046 593	2.168	539.8	4.6	28.5	42 795
$21^1\Delta_u$	29.044 999	2.101	586.9	3.9	43.5	43 145
$22^1\Sigma_u^+$	29.044 392	2.273	458.2	3.4	34.6	43 278
$23^1\Pi_g$	(Two loosely bound minima appear in the potential curve)					
$24^1\Sigma_g^+$	29.040 509	2.219	523.2	5.9	2.1	44 130
$25^5\Sigma_g^-$	29.039 871	1.868	746.2	4.8	110.2	44 270
$26^3\Pi_g$	29.036 922	2.205	529.4	4.7	108.4	44 917
		[2.186][c]	[541.1][c]	[5.4][c]		[44 177][c]
$27^1\Pi_g$	29.035 672	2.256	571.1	7.0	37.6	45 192
$28^1\Pi_u$	(Loosely bound minima appear in the potential curve)					
$29^3\Sigma_u^+$	29.032 491	2.981	544.4	26.6	19.6	45 890
$30^1\Sigma_u^+$	29.027 808	2.205	560.0	5.4	32.7	46 918
$31^3\Sigma_u^+$	(Highly interacting with the $30^1\Sigma_u^+$ state; a minimum is located at 4.2 bohr with a $T_e = 47\,351$ cm^{-1})					
$32^3\Pi_g$	29.016 102	2.634	511.5	7.4	32.4	49 487
$33^3\Pi_u$	29.014 927	2.233	516.1	6.9	31.7	49 745
$34^1\Pi_u$	29.013 578	2.157	421.7	4.2	23.8	50 041
$35^3\Sigma_g^-$	29.005 787	2.773	347.5		26.0	51 751
	29.011 043	1.904	713.0	4.6	29.3	50 597
$36^3\Sigma_g^+$	29.006 802	2.241	480.6	7.7	26.1	51 528

[a] Reference 22.
[b] Reference 38(a).
[c] Reference 37(e).
[d] Reference 37(c).

The first excited state is $1^3\Sigma_u^+$ just 0.93 eV above the ground state. It derives from the mixed asymptote Be(^{1}S) + Be(^{3}P), while its equilibrium characteristics are $\left|1^3\Sigma_u^+\right\rangle \cong 0.95\left|1\sigma_g^2 2\sigma_g^1 1\sigma_u^1\right\rangle$ and $2s^{1.23}2p_z^{0.71}2p_x^{0.02}2p_y^{0.02}$. It is evident that there is a single sigma bond and two electrons triplet coupled pointing outwards from each Be atom, see Scheme 9. Its equilibrium distance is shorter than the one of the ground state by 0.344 Å due to the spin/space symmetry that dislocates completely the triplet coupled electrons decongesting the sigma frame.

The second excited state, $2^3\Pi_g$, arises from the same asymptotic channel as the $1^3\Sigma_u^+$ one. Its MRCI equilibrium characteristics $\left|2^3\Pi_g\right\rangle \cong 0.92\left|1\sigma_g^2 1\sigma_u^1 1\pi_u^1\right\rangle$ and $2s^{1.21}2p_z^{0.25}2p_x^{0.50}$ point to a chemical pattern synopsized in



SCHEME 9.

Scheme 10 and can be considered as a $\sigma_g \rightarrow \pi_u$ transition from the $1^3\Sigma_u^+$ state with $\Delta r = (r_e(1^3\Sigma_u^+) - r_e(2^3\Pi_g)) = 0.107$ Å due to the decongestion of the sigma frame. The Be(^{1}S) + Be(^{3}P) channel generates four states, $^3\Sigma_u^+$, $^3\Pi_g$, $^3\Pi_u$, and $^3\Sigma_g^+$, the first two being attractive while the latter two are repulsive. The question of why this happens naturally arises. If we have a look at the electronic structure of these repulsive states,

$$\left|^3\Sigma_g^+\right\rangle \cong 0.85\left|1\sigma_g^1 2\sigma_g^1 1\sigma_u^2\right\rangle \text{ and}$$
$$\left|^3\Pi_u\right\rangle \cong 0.70\left|1\sigma_g^2 1\sigma_u^1 1\pi_g^1\right\rangle + 0.60\left|1\sigma_g^1 1\sigma_u^2 1\pi_u^1\right\rangle,$$

we realize that the triplet coupled electrons are put in the same neighborhood of space and therefore naturally repel each other.

The third excited state is $3^1\Pi_g$ and dissociates adiabatically to Be(^{1}S) + Be(^{1}P). It is the singlet analogue of the $2^3\Pi_g$ state as mirrored in its equilibrium characteristics $\left|3^1\Pi_g\right\rangle \cong 0.90\left|1\sigma_g^2 1\bar{\sigma}_u^1 1\pi_u^1\right\rangle$ and $2s^{1.14}2p_z^{0.31}$ $2p_x^{0.50}$. The fourth excited state is of $4^3\Sigma_g^-$ symmetry $\left(\left|4^3\Sigma_g^-\right\rangle \cong 0.93\left|1\sigma_g^2 1\pi_{u,x}^1 1\pi_{u,y}^1\right\rangle \text{ and } 2s^{0.87}2p_z^{0.12}2p_x^{0.50}2p_y^{0.50}\right)$ and is the first excited state correlating adiabatically to Be(^{3}P) + Be(^{3}P). The Σ^- symmetry dictates its bonding pattern which is visualized in Scheme 11.

Just above the $4^3\Sigma_g^-$ state, there are two quasidegenerate states, the $5^3\Pi_u$ and $6^1\Pi_u$. The $5^3\Pi_u$ state dissociates adiabatically to Be(^{1}S) + Be(^{3}P) but only due to a severe avoided crossing with a state coming directly from Be(^{3}P) + Be(^{3}P). It is of multireference character $\left(\left|5^3\Pi_u\right\rangle \cong 0.85\left|1\sigma_g^2 2\sigma_g^1 1\pi_u^1\right\rangle - 0.33\left|1\sigma_g^1 1\sigma_u^2 1\pi_u^1\right\rangle + 0.24\left|1\sigma_g^2 1\sigma_u^1 1\pi_g^1\right\rangle\right)$ but clearly displays the ^{3}P character of its excited atoms ($2s^{1.0}2p_z^{0.50}2p_x^{0.50}$). The quasi degenerate $6^1\Pi_u$ state stems from Be(^{1}S) + Be(^{1}P) instead and is also of multireference nature.

There are three singlet states above the couple of quasi degenerate $5^3\Pi_u$ and $6^1\Pi_u$, the $7^1\Delta_g$ (dissociating to Be(^{3}P) + Be(^{3}P)), $8^1\Sigma_g^+$, and $9^1\Sigma_u^+$ (both of them dissociating to Be(^{1}S) + Be(^{1}P)). The $7^1\Delta_g$ state is a clear cut case as evidenced from its equilibrium configurations $\left(\left|7^1\Delta_g\right\rangle \cong 0.65\left|1\sigma_g^2\left(1\pi_{u,x}^2 - 1\pi_{u,y}^2\right)\right\rangle\right)$ and atomic populations ($2s^{0.86}2p_z^{0.12}2p_x^{0.50}2p_y^{0.50}$). The two Be(^{3}P) atoms are bound together by σ and π bonds. The $8^1\Sigma_g^+$ state is the first excited state having the same symmetry as the ground one. Its potential energy curve is initially repulsive, as it should, but at ∼9.0 bohr it suffers an avoided crossing with a state arising from Be(^{3}P) + Be(^{3}P). Its equilibrium features σ and π bonds as the previously discussed $7^1\Delta_g$, i.e., $\left|8^1\Sigma_g^+\right\rangle \cong 0.60\left|1\sigma_g^2(1\pi_{u,x}^2 + 1\pi_{u,y}^2)\right\rangle - 0.32\left|1\sigma_g^2 2\sigma_g^2\right\rangle$ with $2s^{0.87}2p_z^{0.21}2p_x^{0.45}2p_y^{0.45}$. The $9^1\Sigma_u^+$ state can be viewed as the singlet analogue of the $1^3\Sigma_u^+$ state. Its electronic character is mirrored in the following data: $\left|9^1\Sigma_u^+\right\rangle \cong \left|1\sigma_g^2(0.81 \times 2\sigma_g^1 - 0.37 \times 3\sigma_g^1)1\bar{\sigma}_u^1\right\rangle$, with corresponding Mulliken distributions $2s^{1.50}2p_z^{0.37}2p_\pi^{0.10}$.

There are several $^5\Lambda$ states arising from the Be(^{3}P) + Be(^{3}P) channel but the only bound states are the $10^5\Sigma_u^-$ and $11^5\Pi_g$ ones, while another bound ($25^5\Sigma_g^-$) state, the most bound of all studied states, arises from the Be($2s^12p^1$; ^{3}P)+Be($2p^2$; ^{3}P) channel. Obviously all four valence electrons are highly spin coupled with electronic distributions given by

$$\left|10^5\Sigma_u^-\right\rangle \cong 0.96\left|1\sigma_g^1 1\sigma_u^1 1\pi_{u,x}^1 1\pi_{u,y}^1\right\rangle,\ 2s^{0.80}2p_z^{0.19}2p_x^{0.50}2p_y^{0.50},$$
$$\left|11^5\Pi_g\right\rangle \cong 0.98\left|1\sigma_g^1 2\sigma_g^1 1\sigma_u^1 1\pi_u^1\right\rangle,\ 2s^{0.90}2p_z^{0.57}2p_x^{0.50},$$
$$\left|25^5\Sigma_g^-\right\rangle \cong 0.94\left|1\sigma_g^1 2\sigma_g^1 1\pi_{u,x}^1 1\pi_{u,y}^1\right\rangle,\ 2s^{0.54}2p_z^{0.45}2p_x^{0.50}2p_y^{0.50}.$$

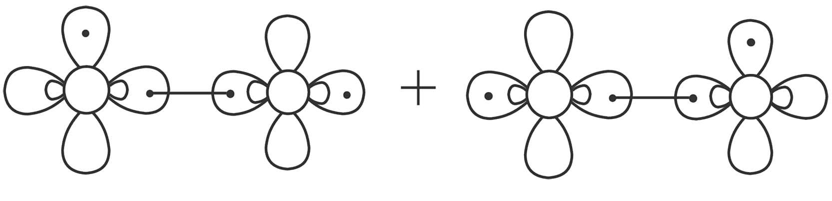
It is quite interesting to visualize the above wavefunctions (see Schemes 12–14). All three quintet states are interconnected through single excitations.

The potential curves of the rest of the states are pretty much congested, and therefore a nonadiabatic analysis should be in order.

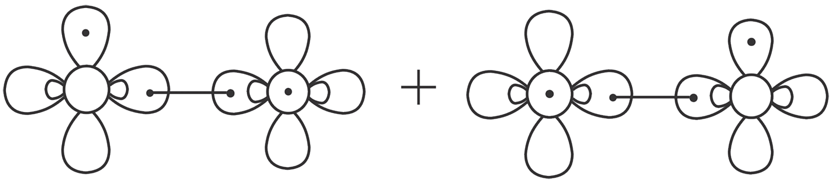
C. Be$_3$ ($\tilde{X}^1A_1'$)

The beryllium trimer has been studied extensively in the past; see Ref. 58 and references therein. Certainly the trimer represents an energetic "singularity" in the case of the Be$_n$ clusters, since the addition of a third Be atom to the rather "unconventional" Be$_2$ dimer (D_e(exp) = 934.9 cm^{-1} (Ref. 22)) creates clearly a chemically bound Be$_3$ system; the three atoms are stabilized overall by ∼30 kcal/mol.[58(i)] Based on the established conviction that Be$_2$ is a vdW system, one cannot understand how Be$_3$ has a completely different chemical pattern, what is that "special something" that every Be atom has in Be$_3$ but not in Be$_2$.

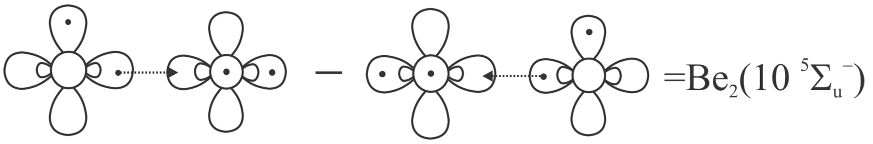
We have scanned (at the CASSCF level) the potential surfaces along the ∠BeBeBe coordinate for all singlet, triplet, and quintet spin states. The ground state of the trimer is



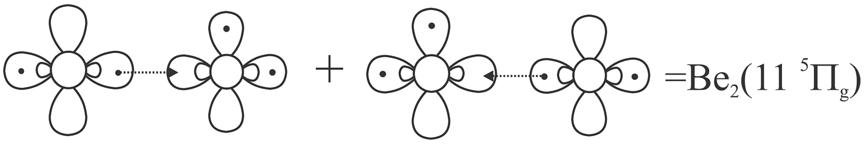
SCHEME 10.



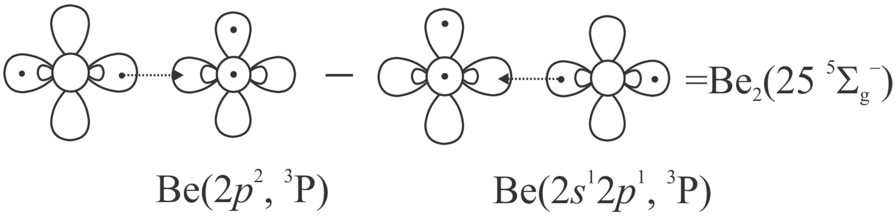
SCHEME 11.



SCHEME 12.

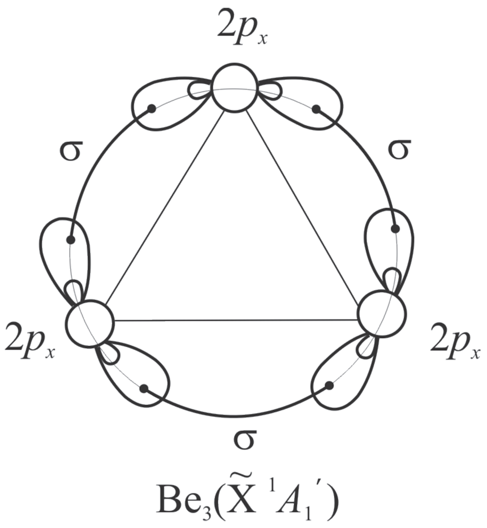


SCHEME 13.



SCHEME 14.

undisputably of singlet spin and D_{3h} equilibrium of $^1A_1'$ symmetry. We have optimized the equilibrium structure of the equilateral Be_3 triangle at both the MRCI (r_e = 2.204 Å, E = −43.897 330 E_h) and CCSD(T) (r_e = 2.213 Å, E = −43.893 794 E_h) computational levels. As already stated, our study does not aim in obtaining the most accurate numerical results but to unveil the secrets of its chemical nature. Based on our analysis of the bonding characteristics of the $Be_2(X^1\Sigma_g^+)$ state, it is not difficult to see that the third Be atom is also excited in its ^{3}P state, as also dictated by its D_{3h} symmetry, and thus three Be atoms are bound together by three sigma bonds. Its equilibrium MRCI wavefunction and Mulliken populations are



SCHEME 15.

$$\left|\tilde{X}^1A_1'\right\rangle \cong 0.85\left|1a_1'^22a_1'^23a_1'^2\right\rangle - 0.12\left|1a_1'^24a_1'^23a_1'^2\right\rangle - 0.12\left|1a_1'^22a_1'^24a_1'^2\right\rangle$$

and

$$2s^{1.35}2p_x^{0.04}2p_y^{0.23}2p_z^{0.32},$$

with its pictorial representation given in Scheme 15. Moreover, we have dissociated the Be_3 trimer by pulling apart all three Be atoms along the totally symmetric D_{3h} breathing mode. The populations evolution shows three Be atoms, initially in their ^{1}S state ($2s^{1.82}2p_x^{0.06}2p_y^{0.06}2p_z^{0.06}$), to gradually getting excited into their ^{3}P state (see the equilibrium populations above) with the synchronous formation of two $2s2p_y2p_z$ hybrids per atom in order to form three strained sigma bonds. This is how the Be_3 trimer is formed. With respect to its diabatic fragments, the $\tilde{X}^1A_1'$ state is stabilized by 25 kcal/mol +3 × $\Delta E(^3P \leftarrow ^1S)_{Be}$ = 214 kcal/mol or ∼71 kcal/mol by bond.

IV. CONCLUSIONS

Molecules are made out of atoms while atoms exist in a variety of excited states being the "chemical ingredients" for the formation of molecular states, both ground and excited.

Restricted HF schemes may be misleading for the description of the above "chemical ingredients" due to their saddle point character in the functional space. When a correct zeroth order wavefunction is considered, the chemical pattern arises naturally. This is the case for the ground Be_2 state.

The two Be atoms, being excited in their ^3P state, are bound covalently through two nominally sigma bonds. The bond has nothing to do with the *s*–*p* near degeneracy problem that is due to the RHF instability of the ground ^1S Be state. Similar stability problems also exist for the excited ^3P state that should be treated correctly, i.e., add orbitals of a higher angular momentum in the active space of the zeroth order wavefunction. This is also connected to the linked triple and quadruple excitations mentioned in previous studies.

In the beryllium trimer, the three Be atoms are also excited in their ^3P state and bound together through three sigma bonds. We strongly believe that this is also the bonding mechanism of larger Be clusters.

We believe that the present study offers a successful bonding description for the beryllium diatomic, and therefore we have successfully fulfilled Kutzelnigg's anticipation.

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