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The optimized geometries and binding energies for the linear and triangular isomers of the beryllium trimer have been obtained through benchmark multireference averaged quadratic coupled cluster (AQCC) calculations using very large complete active space SCF (CASSCF) references (12 active electrons in 13 and 14 orbitals). Geometries were optimized with the cc-pV5Z basis, while the binding energies (including counterpoise correction) were obtained with the significantly larger aug-cc-pV5Z basis set. The binding energies (27.3 and 16.3 kcal/mol for the equilateral and linear isomers, respectively) are larger than the previous full CI benchmark values, while the corresponding Be-Be equilibrium distances of 4.101 and 4.088 a.u. are smaller. In view of the near-size consistency character of the CASSCF + AQCC method, the fact that all 12 electrons are fully correlated, the active reference space includes 14 orbitals, and the very large basis set used here, we propose to consider these results as reference data for Be₃. Using the electron pair localization function obtained at the CASSCF(12,15) level, it is clearly illustrated that the 2p orbitals lying in the molecular plane play a dominant role in the bonding pattern for the equilateral isomer. © *2011 American Institute of Physics*. [doi:10.1063/1.3635403]

I. INTRODUCTION

The structure and binding energies of the beryllium dimer and trimer have been widely studied,[1–36] both theoretically and experimentally. The dimer is experimentally known to be very weakly bound and, since it contains only eight electrons, the accurate theoretical description of its ground (singlet) state potential surface has been the subject of many works since the early days of quantum chemistry. A large number of studies have shown that the bonding in the dimer is actually due to contributions of the hybridization of the 2s and 2p orbitals, and the non-dynamic correlation effects that arise are, therefore, crucial to properly define zeroth-order electronic wavefunctions. Many electronic structure methods ranging in complexity (perturbational up to fourth order, single- and multi-reference variational CI, density functional theory (DFT)-based, coupled cluster, and even full CI (FCI)) have been applied to study Be₂ (Refs. [3–5, 8–10, 17, 18, 21, 24–26]) and Be₃ (Refs. [4, 5, 8, 10–13, 15, 20–24, 27, 28]) using, also, many types of atomic basis sets. In the case of the Be dimer, a number of quantum Monte Carlo (QMC) approaches have also been used (see Refs. [30–36]). Since Be exists in the bulk as a metallic solid, it is natural to raise the question of the evolution of the binding energy (BE) per atom as the number of atoms grows. For larger Be clusters, it has been found that, in spite of the fact that no d orbitals are involved in the bond shells, as mentioned by Junquera *et al.*,[23] the presence of the unoccupied 2p orbitals, which are quasi-degenerate with

the 2s orbitals, allows the formation of Be clusters by this sp2 hybridization process. Actually, it has been shown that this hybridization grows with the number of Be atoms in the cluster.[5] Kaplan *et al.*[21] have argued that the binding in Be₃ has a mixed physical (van der Waals) and chemical (non-additive exchange) nature, while the 2s-2p quasi-degeneracy leads to strong multiconfigurational character in the description of the wavefunctions for both dimer and trimer (see, for instance, Refs. [8, 12, 13, 18, 19, 24]). Lee *et al.*[11] made a careful comparison of the electronic description at the MRCI and CCSD levels for Beₙ (n = 3–5) clusters. They concluded that the coupled cluster approach restricted to single and double excitations is not capable of quantitative accuracy in the description of the electronic structure for Be clusters, since this method underestimates the dissociation energies.

For the Be₂ van der Waals dimmer, it is well known, both theoretically[3–5, 8–10, 16–18, 21, 24–26, 30–36] and experimentally,[6, 7, 14, 19, 29] that the interaction energy is quite small, around 2.4 kcal/mol, while the Be-Be distance is rather large, around 2.4 Å. This rather small binding energy for the dimer is in contrast with the non-negligible binding energy per bond (around 13 kcal/mol) for the bulk.[11] So, it has been proposed that the existence of Be in the bulk can be explained through an increase of the BE for larger Beₙ clusters. Based on the previous idea, density functional techniques were applied to address beryllium clusters Beₙ (n = 2–8) by Beyer *et al.*,[20] using a large 6-311++G(3df) basis set to study the structural and energetic properties as functions of cluster size and to determine their convergence towards metallic beryllium.

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Unlike Be_2, to the best of our knowledge, for the trimer there are no experimental values to compare with. However, there is a large number of theoretical works using many types of electronic structure methods.[4,5,8,10–13,15,20–24,27,28] All these studies highlight the importance of an accurate treatment of both dynamic and non-dynamic correlation effects, coupled to the use of extended atomic basis sets including higher l-angular momentum orbitals. For Be_3, both the geometry and the binding energy are known to be strongly dependent on such factors. Here, our goal is to present the results of new benchmark-type multireference variational calculations for the linear and triangular isomers of Be_3 using the largest augmented correlation-consistent Gaussian atomic basis sets defined for the beryllium atom. Section II deals with the theoretical method and the computational details, including the treatment of the basis set superposition error (BSSE) which is known to be important for the binding energy. In the same section, we recall the fundamentals of the electron pair localization function (EPLF) we will be using to study the binding pattern of the equilateral isomer. In Sec. III, we present the structural and energetic results compared with previous values. Finally, Sec. IV presents the conclusions and some perspectives.

II. METHOD AND COMPUTATIONAL DETAILS

A. Basis sets and non-dynamic/dynamic correlation treatments

Since we are interested in improving the most accurate values of the binding energy presently available for the Be trimer, some important aspects must be taken into account. First, in view of the strong dependence of the binding energy on the largest l-angular momentum atomic functions used, the highest-quality available basis sets have to be chosen. Thus, we have employed two of the most sophisticated atomic Gaussian basis sets existing for this atom, namely, the cc-pV5Z and aug-cc-pV5Z (AV5Z) basis sets of Dunning *et al.*[37,38] The latter correlation-consistent $15s9p5d4f3g2h$ basis set is contracted to $[7s6p5d4f3g2h]$ and leads here to a molecular basis of 381 orbitals for 12 electrons in Be_3. Second, as stressed by many authors, both non-dynamic and dynamic correlation effects are crucial to properly describe the atomic interactions in Be_3 (see, for instance, Refs. 8, 11, 12, 23, 24, 27, 28). In particular, the Be-Be bonds in Be_3 must be described using a zeroth-order wavefunction that includes, at least, the $2p$ orbitals that lie in the molecular plane. It is well known that the core-valence correlation effects are crucial to study this system;[8,17,24,27,28] therefore, we have used the complete active space self-consistent field (CASSCF) approach to build zeroth-order wavefunctions considering four active electrons per atom, thus including all 12 active electrons of the trimers. Since the $2p$ shells are nearly degenerate with the $2s$ one, the ideal chemically relevant active space would consist of five orbitals per atom ($1s$, $2s$, $2p_x$, $2p_y$, and $2p_z$), thus leading to reference wavefunctions built from CASSCF(12,15) calculations. However, with the present basis set, this ideal active orbital space yields zeroth-order wavefunctions containing more than 1.6×10^6 configuration state functions (CSFs) in

the D_{3h} case; this reference space leads to computationally intractable MRCI calculations involving more than 9×10^{10} uncontracted CSFs. Therefore, we have used a two-step procedure that will be explained below. The CASSCF wavefunctions were used as references to perform averaged quadratic coupled cluster (AQCC) (Ref. 39) calculations which, by construction, yield size-consistent energies. Here, it is crucial to highlight that this method has been shown to yield potential energy surfaces parallel to FCI ones with a much reduced computational cost.[17]

B. Geometry optimizations at the CASSCF(12,12) + AQCC level

In order to perform the geometry optimizations, since the Be-Be bonding occurs mainly in the plane defined by the three atoms (here chosen as the xy plane), a reasonable choice is to exclude the three $2p_z$ orbitals from the active space, thus obtaining CASSCF(12,12) references for both trimers. For the triangular molecule, the geometry optimizations have been performed under the C_{2v} point group (which includes the more symmetric D_{3h} group). The optimizations of the linear cluster ($D_{\infty h}$ structure) have been performed in the D_{2h} finite group. The geometries of both trimers were optimized using the automatic numerical algorithm at the AQCC level using the CASSCF(12,12) references and the cc-pV5Z basis set[44] with the MOLPRO-2006.1 code.[40] Note that even with this basis set, which yields 273 molecular orbitals, the AQCC calculations include 4 024 119 522 (27 890 603) uncontracted (contracted) CSFs. Therefore, using as starting point, the optimized geometries reported by Junquera *et al.*[23] for the triangular cluster and from Vetere *et al.*[24] for the linear isomer, the CASSCF(12,12) + AQCC/cc-pV5Z optimizations required each more than a week of CPU time allocating up to 18 GB of RAM.

C. CASSCF + AQCC/aug-cc-pV5Z calculations

Once the optimal geometries were determined at the CASSCF(12,12) + averaged coupled pair functional (ACPF)/cc-pV5Z level, we proceeded to perform single point calculations using the larger aug-cc-pV5Z basis set considering the largest possible active reference space that our computational resources allowed, i.e., 12 electrons in 13 and 14 active MOs. In the latter case, this means that only one of the molecular orbitals involving the $\{2p_z(1), 2p_z(2), 2p_z(3)\}$ set of AOs was excluded from the optimal reference space, thus having the lowest natural occupation number in the CASSCF(12,15) calculation. Although there are several variational CI-based studies for Be_3,[8,23,24,27] we note that the largest FCI calculations done to date are those reported in 2009 by Vetere *et al.*,[24] where the dimension of their CI spaces was 344 545 308 Slater determinants with the $5s3p2d$ atomic natural orbital (ANO) basis set (with 72 molecular orbitals for Be_3), but these authors kept the six $1s$ core electrons frozen and only studied the linear trimer. The final variational space of the present AQCC/AV5Z calculation using the CASSCF(12,14) reference includes 46 667 364 646 (240 820 790) uncontracted (contracted) CSFs for the D_{3h}

TABLE I. Details of the CASSCF and ACPF calculations for the $^1A_1$ state of triangular Be₃ with the aug-cc-pV5Z basis set. The numbers in parentheses correspond to the A_1, B_1, B_2, and A_2 irreps of the C_{2v} group, respectively.

	CASSCF(12,13)	CASSCF(12,14)
Active orbitals	13 (7 5 1 0)	14 (7 5 2 0)
Slater determinants	740 720	2 262 121
CSFs in reference	198 598	545 857
Averaged quadratic coupled cluster calculations with CASSCF references		
Internal configs	198 598	545 857
Contracted configs	94 763 087	240 820 790
Uncontracted configs	19 875 254 627	46 667 364 646

cluster. For the linear isomer, the CASSCF(12,14) includes 277 697 CSFs, which generate variational AQCC spaces with 23 268 073 773 (120 696 813) uncontracted (contracted) CSFs. Note that CI energy convergence to 10^{-6} a.u. took 10 CPU days allocating 32 GB of RAM for the D_{3h} isomer. Table I presents the details of the CASSCF and AQCC variational spaces for this isomer.

As has been noted before, both the dimer[17] and the trimer,[8,23,24,27] are strongly multiconfigurational due to the fact that the nearly degenerate $2p$ orbitals play an important role in the bonding pattern of these species. As an example of this, Table II presents the composition of the optimized CASSCF(12,15)/AV5Z wavefunction of the D_{3h} trimer, where a rather large number of CSFs appear with CI coefficients larger than 0.05 in absolute value; in particular, note the very low 0.86*0.86 = 0.79 weight of the HF configuration.

TABLE II. List of CSF in second quantized notation with CI coefficients larger than 0.05 in the CASSCF(12,15) wavefunction of Be₃ (D_{3h}) at the equilibrium geometry.

C₂ᵥ Irreps				CI coefficient
A_1	B_1	B_2	A_2	
2222000	22000	000	0	0.8650686
2222200	20000	000	0	− 0.1771835
2220020	22000	000	0	− 0.1265278
2222000	20200	000	0	− 0.1015432
2220000	22200	000	0	− 0.0951988
2220200	22000	000	0	− 0.0948863
222bb00	2aa00	000	0	− 0.0938290
222aa00	2bb00	000	0	− 0.0938290
2220ba0	22000	000	0	0.0904947
2220ab0	22000	000	0	− 0.0904947
2220000	22000	200	0	− 0.0887784
2222ba0	20000	000	0	− 0.0883776
2222ab0	20000	000	0	0.0883776
222ab00	2ba00	000	0	0.0863489
222ba00	2ab00	000	0	0.0863489
2222020	20000	000	0	− 0.0762465
2202000	22000	200	0	− 0.0728661
2220220	20000	000	0	0.0593958
2220200	20200	000	0	0.0568272
22ba000	22000	ab0	0	− 0.0552713
22ab000	22000	ba0	0	− 0.0552713
222a0b0	2ab00	000	0	− 0.0545349
222b0a0	2ba00	000	0	− 0.0545349

D. The binding energies and inclusion of the counterpoise correction

It is well known that in order to obtain accurate binding energies for Be$_n$ clusters, the counterpoise (CP) correction[41] has to be taken into account, since the basis set superposition error plays a very important role.[17] Therefore, we shall report BE obtained with and without the CP corrections (with respect to 3Be) for both trimers. The CP correction can be automatically calculated using the Molpro algorithm; however, for the present case, there is a technical limitation that arises due to the high symmetry of these Be₃ isomers. With the MOLPRO program, it is not possible to make the CP correction for symmetry-equivalent ghost atoms, so we had to reduce the symmetry from C_{2v} to use the C_s point group by using slightly modified geometries involving changes of 10^{-4} a.u. in the optimized x-y coordinates of both isomers. For methodological coherence, the CP-corrected binding energies were calculated using the CASSCF(4,13/14) + AQCC CP-corrected atomic reference energies and the energies of the optimized trimers at the CASSCF(12,13/14) + AQCC/AV5Z level, with the usual definition, BE(D_{3h}) = E(D_{3h}) − 3 E(Be) for the equilateral isomer and BE(linear) = E(linear) − 2 E(Be*) − E(Be^c), where Be^c and Be* are the central and end atoms of the linear isomer, respectively. For instance, the CP-corrected atomic energies are −14.6476853 and −14.6476855 a.u. at the CASSCF(4,13) + AQCC and CASSCF(4,14) + AQCC levels using the optimized D_{3h} geometry for the ghosts. For comparison, the atomic CP-uncorrected AQCC/AV5Z energy is −14.646173 a.u. using the $1s,2s,2p_x,2p_y,2p_z$ orbitals as active in the CASSCF(4,5) atomic reference; this energy was used to obtain the CP-uncorrected BE for the trimers at the CASSCF(12,13) + AQCC and CASSCF(12,14) + AQCC levels.

E. The electron pair localization function

Let us briefly present the electron pair localization function. The EPLF is a local scalar function defined in the ordinary 3D space, bounded above and below, which focuses essentially on the localization of electron *pairs*. It is a good descriptive tool for chemical bonds, since pairs of electrons play a central role in our everyday interpretation of chemical structure and reactivity (Lewis model, VSEPR). The original framework proposed to calculate such a localization function is that of quantum Monte Carlo approaches,[42]

$$\text{EPLF}(\mathbf{r}) = \frac{d_{\sigma\sigma}(\mathbf{r}) - d_{\sigma\bar{\sigma}}(\mathbf{r})}{d_{\sigma\sigma}(\mathbf{r}) + d_{\sigma\bar{\sigma}}(\mathbf{r})}, \qquad (1)$$

where

$$d_{\sigma\sigma}(\mathbf{r}) = \langle\psi|\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i)\min_{j\neq i;\sigma_i=\sigma_j}r_{ij}|\psi\rangle \qquad (2)$$

is the average of the shortest distance between two electrons with the same spin, one "reference" electron being located at $\mathbf{r}$, and

$$d_{\sigma\bar{\sigma}}(\mathbf{r}) = \langle\psi|\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i)\min_{j;\sigma_i\neq\sigma_j}r_{ij}|\psi\rangle \qquad (3)$$

is the average of the shortest distance between two electrons with opposite spins, one "reference"electron being located at **r**. By definition, the EPLF takes its values within the interval $[-1, 1]$. It gives a local indicator of electron pairing as follows. In regions of space where electrons are unpaired, the average shortest distance between spin-like and spin-unlike electrons are similar, and the EPLF goes to zero. When antiparallel electrons are paired, EPLF takes positive values and when parallel electrons are paired, EPLF takes negative values. We have used this approach with great success to study the bonding in tetraoxygen[43] and the complex intermolecular interaction of a lithium atom with a thiophene ring.[44] Quite recently, an approximation of Eqs. (2) and (3) has been proposed in order to allow the analytical evaluation of the EPLF for the standard forms of wavefunctions employed in computational chemistry without resorting to QMC simulations.[45] It has been shown that the modified EPLF leads to nearly identical shapes when compared to the original EPLF with the advantage of having much faster calculations while avoiding the presence of statistical noise inherent to any Monte Carlo method. The modified formula can be implemented with HF-, CASSCF-, or DFT-based representations by employing any type of basis set. The new EPLF form is based on the following modified definition of the average of the shortest distances:

$$d_{\sigma\sigma}(\mathbf{r})$$

$$= \sqrt{-\frac{1}{\gamma(\mathbf{r})} \ln \langle \psi | \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i) \sum_{j \neq i; \sigma_i = \sigma_j}^{N} e^{-\gamma(\mathbf{r})|\mathbf{r}_i-\mathbf{r}_j|^2} | \psi \rangle}$$

$$d_{\sigma\bar{\sigma}}(\mathbf{r})$$

$$= \sqrt{-\frac{1}{\gamma(\mathbf{r})} \ln \langle \psi | \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i) \sum_{j; \sigma_i = \sigma_j}^{N} e^{-\gamma(\mathbf{r})|\mathbf{r}_i-\mathbf{r}_j|^2} | \psi \rangle}$$

$$\text{(4)}$$

where $\gamma(\mathbf{r})$ is an **r**-dependent exponent directly related to the local electronic density (see details in Ref. 45). In order to study the bonding pattern of the lowest energy isomer of Be_3, we have calculated the EPLF using the most dominant part of our best reference wavefunction, namely, the function issued from the CASSCF(12,15) calculation. The construction of the EPLF used all the determinants (around 30 000) whose CI coefficients are larger than 10^{-5}. A discussion of the 3D plots of the EPLF will be presented below.

III. RESULTS AND DISCUSSION

A. Structures of both Be_3 isomers

We start by noting the dramatic effect on the reduction of the Be-Be distances when the $1s$ core electrons are included in the reference space as active; for instance, the optimal Be-Be distance of the linear isomer goes from 4.16 to 4.09 a.u., while for the triangular structure it is reduced from 4.17 to 4.10 a.u. at the CASSCF(12,12) + AQCC/cc-pV5Z level. Table III presents the optimized geometries for the linear and triangular trimers along with previous results at different levels of theory, most of which kept the $1s$ core elec-

TABLE III. Be_3 optimized AQCC/cc-pV5Z geometries (a.u.) and AQCC/aug-cc-pV5Z energies (a.u.). Binding energies in kcal/mol. BE(CP) means counterpoise corrected values. Energies are reported using the CASSCF(12,13) and CASSCF(12,14) reference spaces (see text). Previous values in parentheses. BE are calculated using the CASSCF(4,5) + AQCC atomic energy; for details on the CP corrections see the text.

	CASSCF(12,13)	CASSCF(12,14)
D_{3h}	R_e = 4.101 (4.20[b], 4.21[c], 4.29[d], 4.22[e], 4.38[f], 4.08[g], 4.20[h])	
E(CASSCF)	−43.825969	−43.841233
E(AQCC)	−43.984548	−43.985563 (−43.882330[b])
BE	28.88	29.51
BE(CP)	26.67	27.29 (22.5[b], 20.4[c], 17.2[d], 19[e], 13.9[f], 21.2[h])
Linear	R_e = 4.088 (4.220[a], 4.26[b], 4.16[h])	
E(CASSCF)	−43.832138	−43.838818
E(AQCC)	−43.966717	−43. 967047 (−43.874507[a], −43.868969[b])
BE	17.69	17.90
BE(CP)	16.10	16.32 (11.4[a], 8.84[b], 12.63[h])

[a]From Ref. 24, FCI with [5s3p2d] ANO basis.
[b]From Ref. 12, MRCI/[5s3p2d1f].
[c]From Ref. 12, CCSD(T)/[5s3p2d1f].
[d]From Ref. 23, FCI with [3s2p1d] ANO basis set.
[e]From Ref. 8, MRCI/[7s4p2d].
[f]From Ref. 13 MRCI/[4s2p1d].
[g]From Ref. 20 B3LYP/6-311++G(3*df*).
[h]From Ref. 27, active space CCSDt/cc-pVTZ.

trons frozen. For the latter case, we note that even though the optimizations were done within the more general C_{2v} group, the optimal structure turned out to be an equilateral triangle (D_{3h} point group), as found before using other methods, like MP2, MP4, MRCI, and FCI. We can compare the present equilibrium distances with previous results. Sudhakar *et al.*[15] report an equilibrium MP2/6-3ll+G* bond length of 4.23 a.u. for the D_{3h} isomer. Using a larger basis set, Harrison and Handy[8] obtained a Be-Be distance of 4.22 a.u. through the MRCI/[7*s*4*p*2*d*] method. Junquera *et al.*[23] using FCI with the [3*s*2*p*1*d*] ANO basis set obtained an equilibrium distance of 4.29 a.u. for the equilateral isomer. Rendell *et al.*[12] reported much shorter bond lengths of 4.22 a.u. [CCSD(T)] and 4.20 a.u. at the MRCI level, but note that their basis set (5*s*3*p*2*d*1*f*) already includes one f function. The same authors have stressed that both basis set improvements and electron correlation (coupled-cluster, MRCI) shorten the bond length and increase the binding energy. The shortest Be-Be distance reported for this isomer, 4.08 a.u., was obtained by Beyer *et al.*[20] with a DFT-based approach, using the B3LYP/6-311++G(3*df*) method. Lee *et al.*[11] obtained R_e = 4.199 a.u. by MRCI with a [5*s*3*p*2*d*1*f*] basis set and their MRCI calculations used a threshold of 0.025 for the CI coefficient of the reference configurations.

More recently we note the active space CCSDt and MRCI calculations of Ref. 27, performed in bases cc-pVTZ and cc-pVQZ, respectively. The active-space CCSDt calculations were an extension of an earlier study[28] and reproduce quite well the FCI results of Junquera *et al.*;[23] in particular, they report a Be-Be distance of 4.20 a.u for the equilateral isomer. However, in comparison with our 5-active orbital per atom procedure, we stress that they kept the $1s$ core orbitals frozen, thus neglecting all the core-core and core-valence correlation effects.

For the linear isomer, there are far fewer studies; however, we point out the recent work by Vetere *et al.*[24] using the FCI method to address linear beryllium chains. For the linear Be$_3$ cluster, they obtained an equilibrium distance of 4.22 a.u. with the 5s3p2d ANO basis. However, note here that with the 4s3p1d basis set, the FCI distance is significantly longer (4.28 a.u.), thus revealing the very strong dependence of the equilibrium distance on the basis set quality. The newest highly correlated results come from Klos *et al.*,[27] where they obtain a Be-Be distance of 4.15 a.u. for the linear isomer at the CCSDt/cc-pVTZ level but, again, neglecting all the core-core and core-valence correlation effects. The present CASSCF(12,12)+AQCC/cc-pV5Z optimized geometry yields R$_e$ = 4.088 a.u. and it was obtained with a significantly larger basis set including much higher l-angular momentum functions up to 3f2g1h. The crucial factor here is that our reference CASSCF wavefunctions were built considering the six 1s core electrons as active, while in the calculations of Refs. 23, 27, and 28 these were kept frozen, i.e., the three lowest MO are doubly occupied in all the configurations of their FCI and CCSDt expansions.

B. Binding energies

The abundant literature on Be$_3$ shows that the binding energy is extremely dependent upon the type of correlation treatment and the quality of the basis sets employed. Let us first begin with the triangular isomer. Sudhakar and Lammertsma[15] reported a detailed analysis with the 6-31G* and 6-31+G* basis sets at various levels of electronic correlation using coupled cluster (CC) and Möller-Plesset theories; their dissociation energies were 31.4 kcal/mol at MP2/6-31G* and 18.7 kcal/mol at MP4/6-31G* which illustrate a large overestimation of correlation effects with MP2, while their 21.6 kcal/mol value at MP4/6-311+G* shows the dependence on basis set quality. Rendell *et al.*[12] report a D$_e$ of 22.5 kcal/mol at the MRCI/[5321] level and 20.6 kcal/mol after correction for harmonic zero-point vibrational energy contributions. They found a much smaller binding energy of 11.3 kcal/mol at the CCSD level with the same basis set, but a value of 20.4 kcal/mol when the triple excitations are included at the CCSD(T) level. Watts *et al.*[13] reported 16.2, 11.3, and 13.9 kcal/mol values using fourth-order many-body perturbation theory (MBPT)(4), CCSD(T), and MRCI respectively, all using a 4s2p1d ANO basis set. However, their MRCI calculations used the CASSCF reference that arises with the 2s and 2p orbitals as active, keeping the three 1s orbitals frozen, thereby excluding all the core-valence correlation effects. Harrison and Handy[8] calculated a MRCI value of 19 kcal/mol with a 7s4p2d basis set, but they estimated a true binding energy of 24 $\pm$ 2 kcal/mol by including extrapolation of higher excitations and basis set extensions. Junquera *et al.*,[23] through full CI calculations using the 3s2p1d ANO basis set, reported a value of 17.2 kcal/mol; however, they also kept the three 1s orbitals frozen (doubly occupied) in all the determinants of their FCI wavefunction. The newest estimations of the binding energy for Be$_3$ come from the active space CCSDt/cc-pVTZ calculations of Klos

et al.[27] where they report BE of 21.2 and 12.63 kcal/mol for the equilateral and linear isomers, respectively; however, we emphasize that they also kept the 1s core orbitals frozen, thereby neglecting the core-core and core-valence correlation effects. Our CASSCF(12,14)+AQCC/AV5Z binding energy is 29.5 kcal/mol but, as expected, the BSSE is non-negligible (around 10% of the BE) so that when the CP correction is applied, a value of 27.3 kcal/mol is obtained. This new benchmark value is larger than all previous estimates, but it remains close to the upper limit of the prediction made by Harrison and Handy[8] twenty-five years ago concerning the exact binding energy.

For the linear cluster, Rendell *et al.*[12] report an MRCI dissociation energy of 8.8 kcal/mol with the [5s3p2d1f] basis set. Vetere *et al.*[24] performed systematic FCI calculations using increasingly larger ANO basis sets. They found that the smaller basis sets lead to dissociative potential curves and that only the largest basis sets yield stable linear Be$_3$ clusters. Their FCI/[5s3p2d] dissociation energy is 11.4 kcal/mol[46] without taking into account the basis set superposition error, but we recall that their FCI calculations kept the 1s orbitals frozen.

Our CASSCF(12,14)+AQCC/AV5Z dissociation energy is 17.9 kcal/mol and, even when the CP correction is applied, it remains slightly larger (16.3 kcal/mol) than previous estimates.

C. Analysis of the bonding pattern in the equilateral isomer through the EPLF

Since the EPLF is a scalar field in ordinary space, there are two easy ways to visualize it. The first one is to plot the points in space where the EPLF takes on a specified value (called the threshold in what follows). Of course the shape and extension of the resulting isosurface will change with varying thresholds. Figures 1 and 2 show the surfaces of the EPLF obtained with two isosurface values. In both isosurfaces, the three 1s^2 couples of spin-paired electrons appear as spheres centered around each nucleus. However, it is quite interesting to note that the first isosurface (at 0.011) also reveals a larger "ring" which completely surrounds the nuclear skeleton and has three radial arms between each couple of Be atoms. If the threshold is slightly increased to 0.0113, the isosurface varies, the surrounding ring disappears, and the regions between the Be atoms become more dominant.

IV. CONCLUSIONS AND PERSPECTIVES

In this work, we have reported the results of benchmark type multireference variational CI calculations. The optimal geometries and binding energies for the linear and triangular isomers of the beryllium trimer have been obtained with very large basis sets and considering the six 1s core electrons as active. The calculations have been done using a two-step procedure. First, starting from the best previously reported geometries, we have reoptimized the geometries of both isomers at the AQCC level using very large complete active space SCF references with 12 active electrons in 12 orbitals with the cc-pV5Z basis set. Then, using these optimized
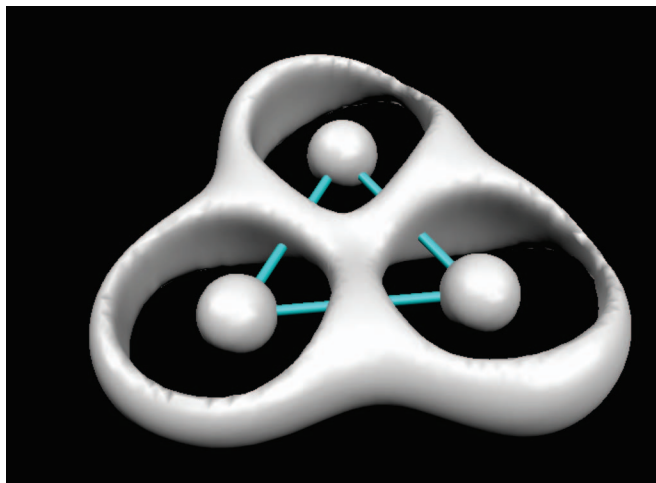
FIG. 1. EPLF of the equilateral Be_3 isomer. EPLF calculated with all the determinants in the CASSCF(12,15) wavefunction whose CI coefficients are larger than 10^{-5}. Isosurface value of 0.011.

geometries, we have performed single-point AQCC/aug-cc-pV5Z calculations using even larger complete active space SCF references with 12 active electrons in 13 and 14 orbitals. The binding energies were counterpoise (CP) corrected to account for the basis set superposition errors. The present CP-corrected binding energies, 27.3 and 16.3 kcal/mol for the equilateral and linear isomers, are larger than the previous FCI benchmark values. The equilibrium distances of 4.101 a.u. for the equilateral isomer and 4.088 a.u. for the linear cluster are slightly shorter than the previous best estimates. These effects are mainly due to the inclusion of the six $1s$ core electrons as active in our AQCC benchmark calculations.

To visualize the nature of the bonding for the D_{3h} isomer, we have calculated the EPLF function and the plots clearly show the crucial role played by the $2p$ orbitals lying in the molecular plane.

Since the AQCC method has been shown to yield parallel potential curves to the FCI ones for Be clusters and since
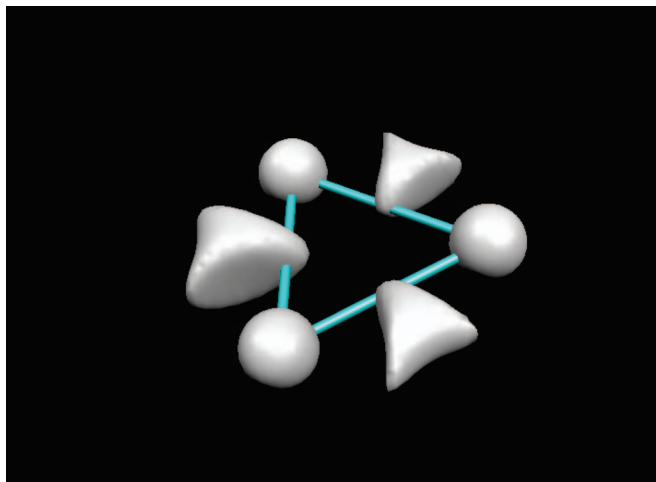
we have included the six $1s$ core electrons as active (which leads to the inclusion of up to 4.7×10^{10} CSFs), we believe that the geometries and energies presented here are the most accurate to date and, thus, should be used as reference data. The MRCI calculations based on the ideal chemically relevant reference space (namely, all 12 electrons in 15 active orbitals) using the very large AV5Z basis set are still unfortunately too large to be feasible with present-day computational resources. Finally, let us note that work is under way to obtain the best estimate of the binding energy for Be_3 through fixed-node diffusion quantum Monte Carlo calculations using the present CASSCF(12,15) reference as trial wavefunction at the optimized geometry with the cc-pV5Z basis set.

ACKNOWLEDGMENTS

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FIG. 2. EPLF of the equilateral Be_3 isomer. EPLF calculated with all the determinants in the CASSCF(12,15) wavefunction whose CI coefficients are larger than 10^{-5}. Isosurface value of 0.0113.

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