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## A DFT study of dodecahedral beryllium silicide cage clusters

Silvina Fioressi<sup>a</sup>, Daniel E. Bacelo<sup>b,c,\*</sup>, R.C. Binning Jr.<sup>b</sup><sup>a</sup> Facultad de Ciencias Exactas y Naturales, Universidad de Belgrano, Villanueva 1324, CP 1426 Buenos Aires, Argentina<sup>b</sup> Department of Sciences and Technology, Universidad Metropolitana, P.O. Box 21150, San Juan, PR 00928-1150, USA<sup>c</sup> Dpto. de Química, FCN, Universidad Nacional de la Patagonia San Juan Bosco, Km. 4, 9000 Comodoro Rivadavia, Chubut, Argentina

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## ABSTRACT

Density functional theory calculations have been conducted on 20- and 32-atom dodecahedral and face-capped dodecahedral cage clusters of beryllium and silicon. Stable  $\text{Be}_{24}\text{Si}_8$ ,  $\text{Be}_{12}\text{Si}_8$  and  $\text{Be}_{12}\text{Si}_{20}$  cages are described, as is a stuffed cluster consisting of dodecahedral  $\text{Si}_{20}$  with an endohedral icosahedral  $\text{Be}_{12}$ . Especial stability is associated with clusters in which faces are capped by silicon atoms, acting as electron donors to beryllium atoms.

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## 1. Introduction

Cage clusters are pursued as sources of novel structural, electronic and chemical properties on the nanometer scale. Research in the area is active, spurred initially by the discovery of an allotrope of carbon in the form of a truncated icosahedron, or fullerene, cage [1] with atoms positioned at each of 60 vertices. Theoretical exploration has since unearthed a great variety of stable cage structures [2]. The research described herein is a computational inquiry into cage clusters of beryllium and silicon.

Silicon is the second-row atom in the carbon group, the most important elemental high band gap semiconductor, and its clusters have been intensely examined experimentally [3] and theoretically [2]. Silicon has been found to favor collapsed structures, the search for exact silicon analogs to  $\text{C}_{60}$  and other fullerenes has foundered, yet techniques by which stable silicon cages may be constructed are avidly sought [4,5]. Computational studies have produced a variety of examples, most constructed around endohedral metals [6], nonmetals [7] and additional Si atoms [8]. Beryllium is among the dopants employed to stabilize silicon clusters. Originally seen merely as a capping atom for dangling bonds, the role of beryllium has evolved to one in which it is added to attain specific features in clusters and nanostructures [6,9,10]. Beryllium has not been studied as intensely as silicon, but clusters of as many as 20 atoms have been examined [11–13].

The present study is an extension of a survey of the isomers of  $\text{Be}_n\text{Si}_m$  and  $\text{Be}_{2n}\text{Si}_n$  ( $n = 1–4$ ) [14], clusters in which beryllium is not a dopant but a major component. Density functional theory (DFT) was employed to optimize geometries, and G3XMP2 theory [15]

then ordered the isomers energetically. The two elements were found to be compatible in forming mixed clusters. The ranges of lengths of Be–Be and Be–Si bonds overlap and the similarity abets mixed cluster formation. For example  $\text{Be}_2\text{Si}$  was found to be nearly equilateral triangular, with a Be–Be bond length of 2.04 Å and Be–Si 2.11 Å, following the structure of equilateral  $\text{Be}_3$  [11], not of isosceles  $\text{Si}_3$  [16]. The most stable isomer of the largest cluster,  $\text{Be}_8\text{Si}_4$ , was found to be a cage,  $D_{2h}$  in overall symmetry, with atoms arranged at the vertices of a nearly regular icosahedron.

In general Si atoms were found to stabilize Be–Si clusters, but Si–Si bonds are stronger and longer than Be–Si, and clusters in which silicons bonded primarily to each other generally produced less symmetrical and less stable small clusters. On the other hand in the  $D_{2h}$   $\text{Be}_8\text{Si}_4$  icosahedral isomer mentioned above pairs of bonded Si atoms appeared at the periphery of the cluster, and did not destabilize it, for it was the global minimum energy isomer. Most of the clusters were small enough that there was no clear distinction between inner and peripheral atoms, and thus an examination of the roles of Be and Si in larger clusters was indicated.

The current study samples dodecahedral and face-capped dodecahedral clusters, larger clusters but simple enough to limit the number of structures that must be examined. Earlier results suggest the pentagon motif of the faces of a dodecahedron. The low-energy form of  $\text{Be}_4\text{Si}_2$  is a nearly regular  $\text{Be}_3\text{Si}_2$  pentagon capped by a Be [14]. In fact the low-energy form of  $\text{Be}_8\text{Si}_4$  may be viewed as a sandwich of two opposed  $\text{Be}_4\text{Si}_2$  face-capped pentagons ringed by a belt of ten triangles. The stability of mixed composition of a dodecahedral surface is one focus of the present study.

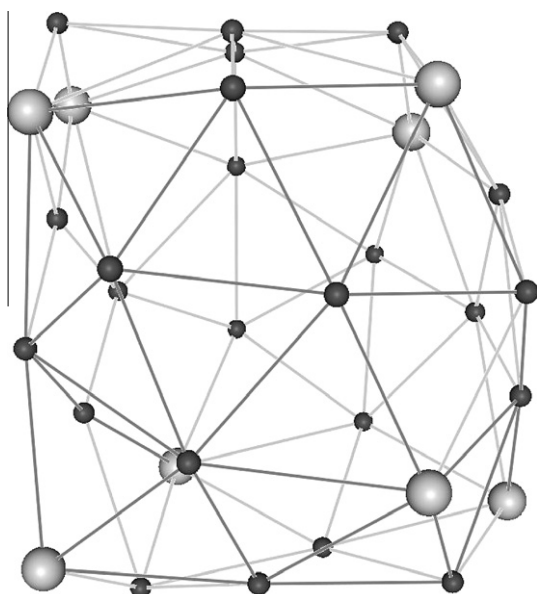
Twenty-atom dodecahedral and 32-atom face-capped dodecahedral clusters were examined. Clusters in which a mixture of beryllium and silicon formed the dodecahedral surface were constructed, with the silicons isolated. These were compared with clusters in which a dodecahedron composed of 20 atoms of one element, with faces capped by 12 atoms of the other. These were

\* Corresponding author at: Department of Sciences and Technology, Universidad Metropolitana, P.O. Box 21150, San Juan, PR 00928-1150, USA. Fax: +1 787 759 7663.

E-mail addresses: [um\\_dbacelo@suagm.edu](mailto:um_dbacelo@suagm.edu) (D.E. Bacelo), [binningrc@yahoo.com](mailto:binningrc@yahoo.com) (R.C. Binning Jr.).

**Table 1**  
Total energies (a.u.) and zero-point energies (kcal/mol) of silicon, beryllium and beryllium silicide clusters.

	Figure	BPW91/DNP	$E_{ZP}$	B3LYP/6-31 + G*	$E_{ZP}$	B3LYP/6-31(2df)	$E_{ZP}$
Be( <sup>1</sup> S)		-14.65934		-14.67075		-14.66894	
Si( <sup>3</sup> P)		-289.38543		-289.37286		-289.37199	
Si <sub>8</sub> ( <sup>1</sup> A <sub>g</sub> )		-2316.06745	7.1	-2315.86667	7.2	-2315.89742	7.2
Si <sub>12</sub> ( <sup>1</sup> A <sub>g</sub> )		-3474.14821	11.1	-3473.83441	11.2	-3473.88126	11.3
Be <sub>12</sub> ( <sup>1</sup> A <sub>1g</sub> )		-176.81487	20.5	-176.85145	20.6	-176.85486	20.7
Be <sub>20</sub> ( <sup>3</sup> A)	5a	-294.94276	34.8	-294.96931	35.2	-294.97886	35.6
Be <sub>32</sub> ( <sup>1</sup> A <sub>g</sub> )	6	-472.07882	57.8	-472.12128	58.7	-472.13590	58.6
Be <sub>12</sub> Si <sub>8</sub> ( <sup>3</sup> A <sub>1</sub> )	2	-2493.28720	31.4	-2493.08907	31.3	-2493.10510	31.2
Be <sub>24</sub> Si <sub>8</sub> ( <sup>3</sup> A)	1	-2670.53365	53.8	-2670.26393	55.6	-2670.28634	55.5
Be <sub>20</sub> Si <sub>12</sub> ( <sup>5</sup> A <sub>1g</sub> )	4	-3769.60723	48.8	-3769.28816	48.8	-3769.31682	48.8
Be <sub>12</sub> Si <sub>20</sub> ( <sup>5</sup> A <sub>1</sub> )	3	-5967.72166	43.6	-5967.13230	43.4	-5967.18446	43.1
Si <sub>20</sub> ( <sup>1</sup> A)	5b	-5790.31344	19.5	-5789.81039	21.1	-5789.87716	20.7



**Figure 1.** B3LYP/6-31G(2df) optimized structure of Be<sub>24</sub>Si<sub>8</sub>. Silicon atoms are represented as larger and lighter; beryllium are smaller and darker.

in turn compared with clusters composed of the pure atoms. The isomers of the 20- and 32-atom clusters of silicon have been exhaustively studied, and these required no more than cursory study, but the beryllium atomic clusters are not as extensively catalogued, and a full set of calculations on Be<sub>20</sub> and Be<sub>32</sub> was conducted. This minimal sample of clusters was examined for guiding principles in constructing cage clusters, insight into the structural roles of silicon and beryllium and ideas for larger and more complex cluster constructions.

The goal of the previous study of small Be–Si clusters was to enumerate the isomers of each cluster and accurately order their relative energies. To this end the G3XMP2 method [15] was employed. Geometry determinations in the G3X family are determined by B3LYP/6-31G(2df,p) calculations. G3X has been calibrated by comparison with test sets of several hundred experimental values [17], and there is thus reason to be confident in geometries determined with the method. However, effective exploration of larger clusters will require rapid screening of isomers, and more efficient computational methods, that retain essential accuracy, are needed. To this end B3LYP/6-31G(2df) results were compared to those obtained with two more computationally efficient methods. The first of these, B3LYP/6-31 + G\*, simply reduces the size of the basis sets employed. The second reduces the size of the basis sets still further by introducing numerical basis sets that are of double numerical plus

polarization (DNP) quality, and replaces the hybrid B3LYP functional with the generalized gradient approximation (GGA) BPW91 functional.

## 2. Methods

Initial geometry optimizations were done in spin-unrestricted density functional theory calculations employing the BPW91 gradient-corrected functionals [18,19] and numerical basis sets of double-zeta plus polarization quality (DNP). Calculations were carried out with the DMOL<sup>3</sup> program [20,21]. Additional geometry optimizations were conducted with the B3LYP functionals [22,23] with the GAUSSIAN function 6-31 + G\* and 6-31G(2df) basis sets. These calculations employed the GAUSSIAN 03 programs [24]. Harmonic frequency analysis, conducted by diagonalization of the full Hessian, was performed at each stationary point to test for the absence of imaginary frequencies and guarantee that a true minimum was located. Stability testing was done on the final B3LYP/6-31 + G\* wavefunctions and, where instability was found, reoptimization of the wavefunctions obtained with each method was done.

## 3. Results and discussion

Calculated energies of optimized clusters appear in Table 1. The initial cluster was one in which mixed Be and Si atoms occupied the vertices of a regular dodecahedron, the number of Si atoms being a maximum such that no two were adjacent. This amounts to constructing the dodecahedral surface from twelve Be<sub>3</sub>Si<sub>2</sub> pentagonal units, discussed above. These assemble into a Be<sub>12</sub>Si<sub>8</sub> dodecahedron, and adding twelve Be face caps produces a Be<sub>24</sub>Si<sub>8</sub> face-capped dodecahedral cluster with T<sub>h</sub> symmetry. Upon optimization the Be<sub>24</sub>Si<sub>8</sub> cluster undergoes considerable distortion. The molecule is closed-shell so the distortion is not Jahn–Teller [25] in origin. The final structure is a cage, but an unsymmetrical C<sub>1</sub> structure (Figure 1) probably with numerous conformational isomers. During optimization the silicon atoms gravitate to the periphery of the cluster, and the Be<sub>3</sub>Si<sub>2</sub> structures are not evident in the final structure, though Be-capped Be<sub>4</sub>Si and Si-capped Be<sub>5</sub> pentagons are, as well as some buckled capped hexagons.

Population analysis places charges of +0.55 to +0.8 on each Si, and –0.15 to –0.4 on each Be. The stabilizing influence of Si on the cluster may therefore be attributed to its transfer of charge to electron-deficient Be. Beryllium in the clusters behaves not as an alkaline earth ion, rather its bonding is polar covalent. Similar charge transfer was seen in each of the binary clusters studied.

Be<sub>12</sub>Si<sub>8</sub> also undergoes significant distortion, to a modified hexagonal prism of beryllium atoms (Figure 2). The beryllium hexagons are not planar but in chair conformation. The top, bottom and each vertical face are capped by silicon atoms. Pairs of the vertical face caps are near enough to bond (Si–Si 2.62 Å). It is an

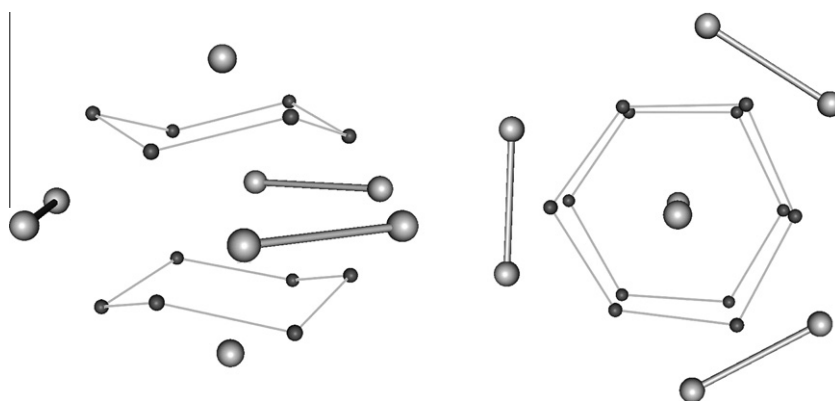


Figure 2. Two views of  $\text{Be}_{12}\text{Si}_8$ ,  $C_{2v}$  point group.

interesting  $C_{2v}$  cage structure that may also be viewed as a construction of four  $\text{Be}_4\text{Si}$  pentagons, each capped by a silicon.

In  $\text{Be}_{12}\text{Si}_{20}$  (Figure 3) the vertices of the dodecahedron are occupied by silicons, while beryllium atoms cap the faces. During optimization the twelve Be atoms migrate to the interior of the  $\text{Si}_{20}$  dodecahedron, where they become interior face caps in an icosahedral  $\text{Be}_{12}$ . Si–Si distances on the dodecahedral surface range from 2.53 to 2.67 Å. The overall cluster has a  $D_{5d}$  saddle point, but the true minimum is  $C_{5v}$ , each pentagon discernible within the structure being regular but with a slightly different Be–Be distance, lengths varying from 2.09 to 2.14 Å. Again the cluster has a closed-shell electronic structure, and the observed distortion is not Jahn–Teller. The cluster joins the great variety of silicon cages stabilized by endohedral structures [6–8], and by endohedral beryllium specifically [4].

The  $\text{Be}_{12}$  and  $\text{Si}_{20}$  moieties within  $\text{Be}_{12}\text{Si}_{20}$  were optimized separately to test their individual stabilities.  $\text{Be}_{12}$  in  $I_h$  symmetry is an open-shell molecule with an outer electron configuration of  $g_u^4$ . As a nonlinear molecule in a degenerate electronic state, it is subject to Jahn–Teller distortion, eventually optimizing to a  $D_{3d}$  complex similar to the distorted icosahedra noted in previous studies of  $\text{Be}_{12}$  [12,13].

$\text{Si}_{20}$  has been extensively examined, but the structure optimized from the dodecahedral configuration within  $\text{Be}_{12}\text{Si}_{20}$  seems not to have been hitherto reported.  $\text{Be}_{20}$  was also optimized from an initially dodecahedral geometry and the two are compared in Figure 4.  $\text{Be}_{20}$  initially optimizes by distorting from dodecahedral to a  $D_{6h}$  capped hexagonal prism that subsequently Jahn–Teller distorts, ending in a structure in which one of the end caps on the prism moves inside a stack of three regular hexagons, then to a  $C_1$  structure.  $\text{Be}_{20}$  has been studied [12,13], but the structure reported here is unlike the minimum energy structure, which is also rather spherical but collapsed, and may be viewed as interwoven icosahedra.  $\text{Si}_{20}$  forms a  $C_1$  cage cluster in which the original dodecahedron is considerably distorted. Si–Si distances lie in the range 2.33–2.54 Å. The global minimum energy  $\text{Si}_{20}$  cluster has been shown to be a collapsed composite of two  $\text{Si}_6$  clusters and an  $\text{Si}_8$  [26].

In  $\text{Be}_{20}\text{Si}_{12}$  the vertices of the dodecahedron are occupied by beryllium atoms, the faces are capped by silicons and this essential configuration is maintained throughout optimization. The complex optimizes to a  $D_{5d}$  saddle point, then Jahn–Teller distorts to a  $C_{2h}$  (Figure 5) cluster that is still not much different from the initial structure. Si atoms acting as face caps effectively stabilize the beryllium dodecahedron. The minor skeletal displacements leave the Be–Be distances in a tight range of 2.12–2.16 Å, apical Si–Si distances are 7.35–7.55 Å and Be–Si distances lie in the range 2.18–2.30 Å.

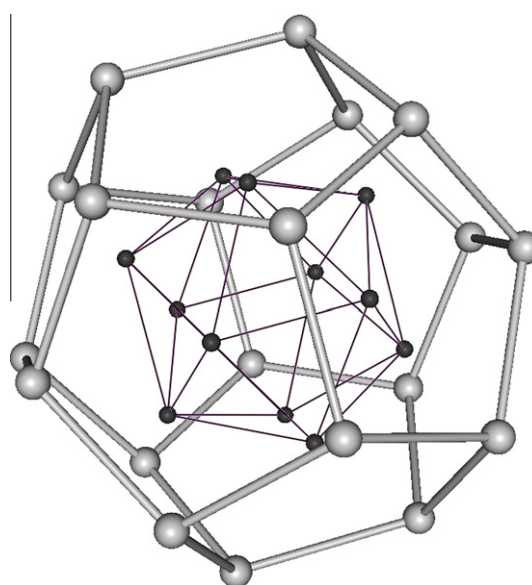


Figure 3.  $C_{5v}$   $\text{Be}_{12}\text{Si}_{20}$ , a slightly distorted  $\text{Be}_{12}$  icosahedron within a slightly distorted  $\text{Si}_{20}$  dodecahedron.

$\text{Be}_{32}$  and  $\text{Si}_{32}$  face-capped dodecahedra were also examined.  $\text{Si}_{32}$  has been exhaustively studied, and calculations were done only to confirm that it collapses to a previously reported structure. However, stable  $\text{Si}_{32}$  cage clusters of the fullerene type may be formed with two or four endohedral Si atoms [8].  $\text{Be}_{32}$  collapses to an interesting  $C_{2h}$  structure that contains two endohedral Be atoms (Figure 6). The two inner atoms are bonded (Be–Be 2.10 Å) and neither atom lies within 2.25 Å of any other. The Be face caps present in the initial configuration prove not to be as effective as Si in stabilizing dodecahedral  $\text{Be}_{20}$ .

Cluster stabilities as measured by atomization energy per atom (Table 1) indicate that the higher the mole fraction of silicon a cluster is, the more stable it is. Calculations on  $\text{Si}_8$  and  $\text{Si}_{12}$  clusters are included in Table 1 to facilitate comparison of the pure-atom clusters. Atomization per atom was least for  $\text{Be}_{12}$ ,  $\text{Be}_{20}$  and  $\text{Be}_{32}$  and greatest for  $\text{Si}_8$ ,  $\text{Si}_{12}$  and  $\text{Si}_{20}$ , though nearly as great for both  $\text{Be}_{12}\text{Si}_{20}$  and  $\text{Be}_{20}\text{Si}_{12}$ . On the other hand many pure-silicon cage clusters collapse, and the presence of beryllium atoms enables stable cages to form without ‘stuffing’ by endohedral molecules. For each cluster the BPW91/DNP atomization energy is greater than the B3LYP/6-31G(2df), which is in turn greater than that calculated with B3LYP/6-31 +  $G^*$ .

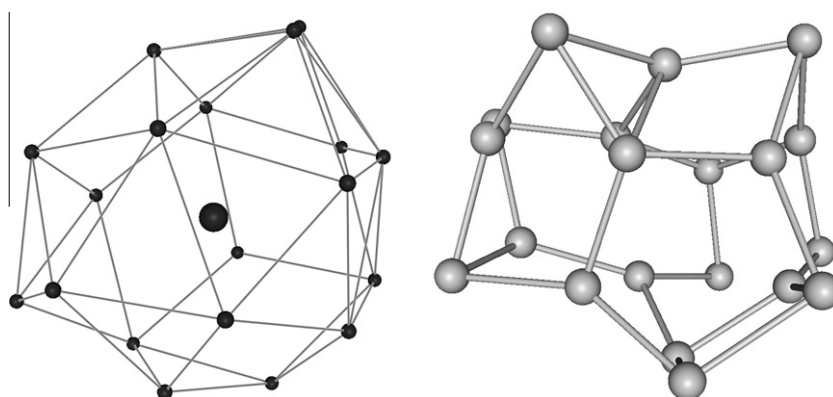


Figure 4.  $\text{Be}_{20}$  (a) and  $\text{Si}_{20}$  (b) clusters optimized from initially dodecahedral configurations.

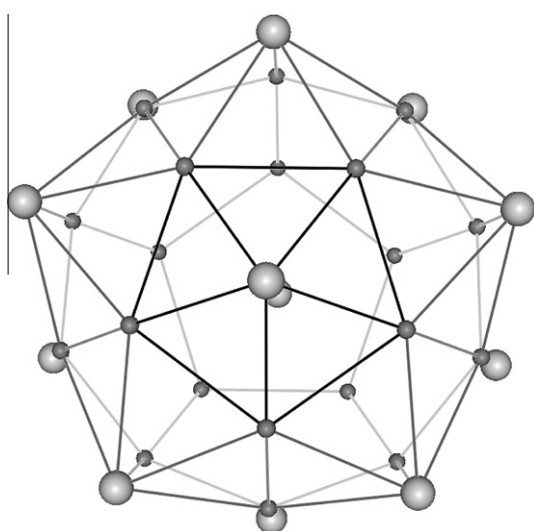


Figure 5.  $\text{Be}_{20}\text{Si}_{12}$ ,  $C_{2h}$ , featuring a slightly distorted  $\text{Be}_{20}$  dodecahedron, each face capped by Si.

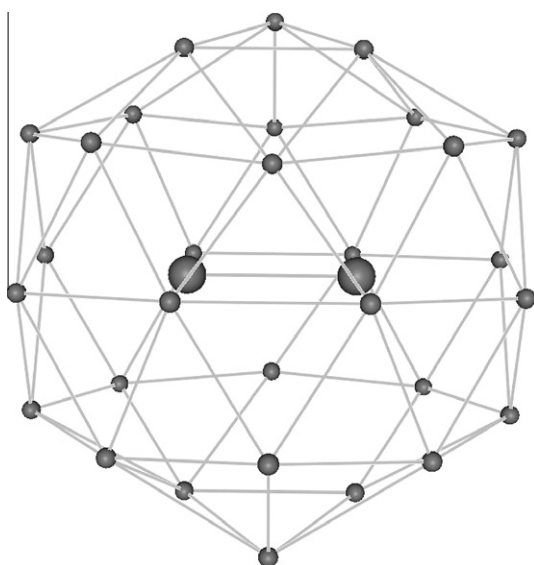


Figure 6.  $C_{2h}$   $\text{Be}_{32}$  optimized from an initially face-capped dodecahedral configuration. There are two endohedral Be atoms, and these are enlarged for emphasis.

$\text{Si}_{20}$  was the only cluster in which the three computational levels employed did not agree in assigning the ground state. In the BPW91 calculation the ground state was found to be a triplet, whereas both B3LYP calculations found it to be singlet. Because the B3 functional admixes a fraction of Hartree–Fock exchange, methods employing it may be expected to favor higher multiplicities. This behavior is observed in  $\text{Be}_2\text{Si}$  [14], in which B3LYP calculation finds a triplet ground state although the actual ground state is singlet. Singlet results are reported in Table 1.

The three computational methods employed, BPW91/DNP, B3LYP/6-31 +  $G^*$  and B3LYP/6-31G(2df) produce cluster geometries that agree closely, and either of the alternatives to the latter should prove satisfactory in screening geometries. All three provided substantial agreement in bond angles and lengths as well as in qualitative cluster form despite the fact that the numerical and GAUSSIAN basis sets differ markedly in their properties. The difference is readily seen in the atomic energies (Table 1), where the GAUSSIAN sets produce lower total energies for beryllium than does the DNP set, but higher for silicon. The DNP set, though it employs a minimal basis for the core, nevertheless fits the 1s cusp well, and the effect on total energy is increasingly noticeable as atomic number increases.

#### 4. Summary and conclusions

The present study adds insight into the roles played by silicon and beryllium in their binary clusters. It is often noted that silicon avoids planar substructures [3], and the observation is borne out in this study, where the one cage with  $\text{Si}_5$  planes must be stabilized by an interior  $\text{Be}_{12}$ . It has been demonstrated that stable, empty beryllium–silicon cage clusters exist, and each of  $\text{Be}_{24}\text{Si}_8$ ,  $\text{Be}_{12}\text{Si}_8$  and  $\text{Be}_{20}\text{Si}_{12}$  is interesting in its own way.  $\text{Be}_{24}\text{Si}_8$  is perhaps most interesting; its structure suggests further study to seek more symmetrical configurations and stabilizing substructures. The study confirms the stabilizing effect of face caps in the binary clusters. Even in clusters undergoing drastic reorganization neither edge nor end caps formed, while face caps persisted in each.

$\text{Be}_{12}\text{Si}_8$  is interesting in its formation of nonplanar hexagonal  $\text{Be}_6$  rings,  $\text{Si}_2$  pairs of face caps and  $\text{Be}_4\text{Si}$  pentagons. The  $\text{Be}_4\text{Si}$  pentagons and nonplanar hexagons containing both Be and Si appear in  $\text{Be}_{24}\text{Si}_8$ . Overall the study discourages the idea of stable mixed binary structures, but it is an idea that may not be dismissed without more extensive examination.  $\text{Be}_{20}\text{Si}_{12}$  features Si face caps, and the role of face cap seems to be one that should be emphasized in larger cages. The example of  $\text{Be}_{12}\text{Si}_8$  indicates that cluster designs in which silicons pair should be explored as well. The isomers of both  $\text{Be}_{12}\text{Si}_8$  and  $\text{Be}_{20}\text{Si}_{12}$  should be explored to find global minima.



The tendency of silicon in its clusters to shun planar structures, in contrast to its first-row relative carbon, is usually laid to the narrow 3s–3p energy gap that discourages  $sp^2$  hybridization [3]. Beryllium has quite a wide 2s–2p gap, so its tendency to favor collapsed clusters may be rationalized by the deficiency of electrons with which to populate the p-shell. The success with which beryllium forms planar pentagonal faces when these are capped by silicon atoms may then be viewed as due to silicon's ability to donate electrons to the beryllium structures. In light of this interpretation the better electron donors in the group, Ge, Sn and Pb, should be examined as face caps on primarily beryllium structures.

The three computational systems employed, BPW91/DNP, B3LYP/6-31 + G\* and B3LYP/6-31G(2df), proved to give geometries that agreed closely. The use of either of the former two to facilitate screening of larger clusters is supported by the results of this study.

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