PHYSICAL REVIEW B VOLUME 50, NUMBER 23 15 DECEMBER 1994-I

Energetics and structure of toroidal forms of carbon

J. Karl Johnson,* Brian N. Davidson, Mark R. Pederson, and Jeremy Q. Broughton
Complex Systems Theory Branch, Naval Research Laboratory, Washington, D.C. 20375-5345

(Received 25 July 1994)

Total-energy calculations for 13 different fullerene clusters, including 8 toroidal fullerenes, are performed using a parametrized tight-binding functional, and in select cases, an all-electron first-principles local-density functional. The tori considered here are composed of graphitelike six-membered rings, with five-membered rings on the outer surface of the torus providing positive Gaussian curvature, and seven-membered rings on the inner toroidal surface providing negative Gaussian curvature. Comparisons are made with energies calculated from a Stillinger-Weber–type potential for graphite, which is found to be inadequate for addressing relative energetic stability among the tori. Two empirical strain relations are tested against our tight-binding energy calculations. A simple elastic theory is found to give reasonably good energy orderings. Charge-density calculations on the tori reveal that electron density is enhanced for atoms in five-membered rings, and depleted for atoms in seven-membered rings. First-principles total-energy calculations indicate that a single potassium atom is bound to the center of a C_{144} torus by 0.5 eV. It is proposed that atoms with higher orbital angular momentum (e.g., Zr, etc.) may bond more tightly to the torus, and thus facilitate formation of C_{120} or similar tori.

I. INTRODUCTION

The discovery of the C_{60} fullerene[1] marked the beginning of research into a family of graphenelike pure carbon molecules with virtually endless variety. Many different fullerene forms of carbon have been observed experimentally, while others have been proposed theoretically. Experimentally realized fullerenes range in size from C_{28},[2] which is stabilized by encapsulating metal atoms such as U and Zr,[2–5] to giant fullerenes[6] containing on the order of 10^6 atoms.[7] Other structures have been observed in addition to the spherical and nearly-spherical fullerenes. These include fullerene tubules, first observed as multiwalled structures.[8] It is thought that the multiwalled tubules are composed of concentric shells, but recent work[9] has suggested that many such nanostructures may be described by a model of highly defective "paper mache" graphitic sheets. Single-walled tubules have been synthesized in the presence of metal catalysts such as Fe, Co, Ni, and Gd.[10–12] Conical fullerenes have been observed as caps to multi-walled tubules[13] and as individual fullerene cones.[14] While spherical fullerenes are composed entirely of hexagons and pentagons, heptagons are thought to play an important role in tubule caps and turn-around regions.[13,15]

Theoretically proposed structures include periodic minimal surfaces,[16–18] networks of cages,[19] small diameter capped tubules,[20] large single and multishelled fullerene cages,[21,22] toroidal fullerenes,[23–28] and helical carbon structures.[29]

In this paper we concentrate on the energetic, structural, and electronic properties of several different toroidal fullerenes. We address the relative energetic stabilities of eight different toroidal forms of carbon, most of which have been previously proposed but three of which are new. Part of our motivation for performing this work is to check the results of previous empirical classical potential calculations on fullerene tori.[24–27] We also compare empirical strain expressions for the energy of tori with our total-energy calculations. Finally, we calculate the binding of a single metal atom at the center of a torus and discuss the modified electronic structure.

II. TOROIDAL CARBONS

Dunlap was the first to propose the torus as a stable form of graphitic carbon.[23] He proposed constructing toroidal fullerenes by joining two tubules of different radii, and repeating this structure twelve times to form a torus. Such a procedure introduces five-membered rings (pentagons) on the outer surface of the torus, and seven-membered rings (heptagons) on the inner surface of the torus, which provides the needed curvature to close the torus on itself. Note that Euler's theorem for toroidal fullerenes containing only five-, six-, and seven-membered rings dictates that the number of five- and seven-membered rings must be equal.[28] Dunlap proposed two different tori constructed in this manner. Both of these tori have D_{6h} symmetry; the smaller torus contains 540 atoms, and the larger 576 atoms. The structure (relaxed bond lengths) and cohesive energies for the two tubules were calculated using an accurate empirical manybody chemical bonding potential for carbon,[30] while electronic properties were calculated from a tight-binding formalism. Itoh and co-workers[24–26] have proposed the largest number of toroidal carbon forms, with molecules ranging in size from 80 to 1920 atoms. They used a Stillinger-Weber–type potential,[31] with parameters optimized for graphite.[32] We will refer to this as

0163-1829/94/50(23)/17575(8)/$06.00

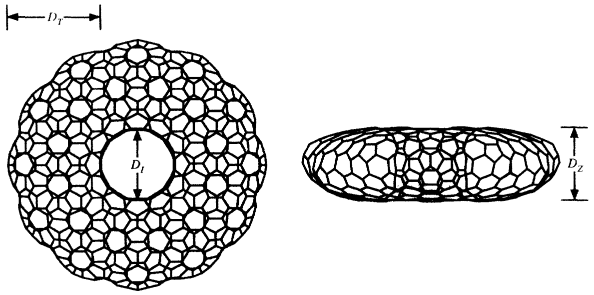

FIG. 1. Definitions of the inside torus diameter, D_I, the top projection tube diameter, D_T, and the Z direction tube diameter, D_Z, for a torus. The Z axis passes through the center of the torus and coincides with the axis of highest rotational symmetry (the C_6 axis in this case). The torus shown here is the C_{600} torus.

the graphite-Stillinger-Weber (GSW) potential throughout this paper. Gal'pern *et al.*[28] proposed four toroidal carbon clusters containing from 200 to 408 atoms. The electronic structures were calculated from topological arguments.

The work of Itoh *et al.*[24–26] provides the most systematic look at toroidal carbon forms. They chose to use the GSW potential to obtain relaxed structures and total energies. One of the purposes of their work was to assess the energetic stability of various tori relative to C_{60}. Calculations from the GSW potential indicate that toroidal forms of carbon with as few as 120 atoms have a lower energy per atom than the C_{60} fullerene. This is surprising because the proposed C_{120} torus has a tubule diameter (D_T) and an inside torus diameter (D_I) of about 4 Å (see Fig. 1), both of which are considerably smaller than the C_{60} diameter of about 7 Å. One would expect the C_{120} to have a higher energy per atom than C_{60} because it is more highly curved. However, the argument was made that the seven-membered rings on the inside of the torus act to relieve the strain in the torus and lower its energy relative to C_{60}. On the other hand, it is possible that the surprising stability of the C_{120} torus is an artifact of the GSW potential. It is also surprising to note that the GSW potential predicts that the smaller of the two tori proposed by Dunlap[23] has a lower energy per atom than the larger. This contradicts the results from the many-body potential calculations,[23] which indicate that the larger torus is about 0.07 eV/atom more stable than the smaller torus. This may also be due to limitations of the GSW potential. In this paper we will clarify these issues of relative energetic favorability by performing calculations using both essentially exact *ab initio* and accurate parametrized tight-binding functional (PTBF) methods.

III. COMPUTATIONAL METHODS

Selected cluster calculations were performed using an accurate all-electron Gaussian-orbital local-density approximation (LDA) code developed by Pederson and Jackson at the Naval Research Laboratory.[33,34] We used a double zeta quality basis set, with five s-type and four p-type orbitals for carbon. This basis set has been well tested on hydrocarbons, diamond, and fullerene-based materials and has been found to be accurate for energy differences and cohesive energies. LDA calculations were carried out for the C_{60} and C_{70} fullerenes and the C_{120} and C_{144} tori.

For studying the larger molecules, the all-electron LDA method is computationally prohibitive because of the large number of inequivalent atoms involved. For calculations on clusters larger than the C_{144} torus we have adopted a PTBF for carbon,[35] which was generated from a simultaneous fit to the LDA energies of three phases of carbon: diamond, graphite and linear chains. This approach still retains electronic structure information, but is faster than *ab initio* methods without much loss in accuracy. The total-energy functional uses a parametrized tight-binding Hamiltonian matrix to generate the electronic levels and a pairwise function, $E_{\rm rep}$, to model the remaining repulsive terms. The total energy is written as

$$E_{\rm total} = E_{\rm rep} + E_{\rm bs} + E_{\rm charge} . \qquad (1)$$

The band-structure energy, $E_{\rm bs}$ is a sum of the occupied eigenvalues of an orthogonal sp^3 basis Hamiltonian. A repulsive, Hubbard-like charge term, $E_{\rm charge}$, is added to account for charge transfer. The functional forms for these terms, along with the parameters used, are described in detail in Ref. 35. This energy expression has been previously applied to the dynamics of C_{60}[36] and the energetics of various fullerene clusters.[37–40]

The PTBF method is known to reproduce accurately the bond lengths for C_{60} and C_{70} from LDA calculations.[40] As a further test of the accuracy of the PTBF method, we compare the relative energies for the C_{70}, C_{120}, and C_{144} fullerene clusters with LDA calculations in Table I. Note that both methods predict a lower energy per atom for C_{70} than C_{60} and that the PTBF energies are in very good agreement with LDA calculations. All the structures in Table I were relaxed using PTBF. The energies and forces of the final structure were calculated using the all-electron LDA method. The LDA forces were calculated as the proper total-energy derivatives, including the Pulay–basis-set corrections.[34] The magnitude of these forces were found to be small (less than 0.5 eV/Å), and we would not expect the LDA method to yield relaxed geometries substantially different from those obtained with the PTBF code (note that the

TABLE I. Energies/atom relative to C_{60} from LDA and PTBF calculations. Highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) gaps from LDA are also listed. All energies are in eV.

System	$E - E(C_{60})$		HOMO-LUMO
	LDA	PTBF	LDA
C_{60}	0	0	1.8
C_{70}	-0.04	-0.04	1.8
C_{120} (torus)	0.13	0.12	1.3
C_{144} (torus)	0.11	0.09	1.3

energy is correct to the square of the Hellmann-Feynman forces).

The CPU intensive operation of a PTBF calculation is the band-structure term, which requires the sum of the occupied eigenvalues of the electronic Hamiltonian. Canonical diagonalization techniques scale superlinearly with the size of the basis, limiting the number of atoms that can be considered. To overcome this limitation, we have used an "order N" electronic structure technique proposed independently by Li, Nunes, and Vanderbilt[41] and Daw,[42] which scales linearly with the number of atoms in the system (thus "order N"). Since we need the sum of the eigenvalues to evaluate E_{bs}, rather then each eigenvalue itself, we can consider a solution to the equation,

$$E_{\mathrm{bs}} = \mathrm{Tr}[H\rho], \tag{2}$$

where ρ is the electron density matrix and $\mathrm{Tr}[H\rho]$ means the trace of the product of $H\rho$, where H is the Hamiltonian. Li, Nunes, and Vanderbilt[41] and Daw[42] described a method for finding the elements of ρ by minimizing a function of ρ, while retaining the constraint of idempotency, $\rho = \rho^2$. For an insulator or closed shell molecule, the elements of the density matrix ρ decay exponentially to zero with distance. If we assume that the elements of the density matrix representing interactions beyond a defined cutoff are zero, then the number of unknowns in the density matrix scales linearly with the size of the system, and therefore evaluating E_{bs} becomes an order N computation. As larger clusters with more atoms are considered, this method eventually becomes significantly faster over conventional diagonalization.

This order N approach is used to relax the geometries of the fullerenes with more than 360 carbon atoms. We initially relaxed the geometries using a steepest descent approach from forces that were obtained with a 3-Å density matrix cutoff. A more precise relaxation was then obtained by extending the density matrix cutoff to 6 Å. According to our comparisons for smaller clusters, a 6-Å cutoff in the density matrix for sp^2 bonded carbon yields an accuracy in the band-structure energies of better than 0.01%. For a 360 atom torus the 6-Å cutoff is accurate to better than 0.09% in band-structure energy. The final energies of the large clusters were calculated with an exact diagonalization of the Hamiltonian.

IV. RESULTS

We have computed the relaxed bond lengths and total energies for 14 different systems, including graphite, using our PTBF formalism. In Table II we list the systems studied, along with their symmetries and cohesive energies. Both tubules listed in Table II (120 and 360 atoms) have about the same diameter as C_{60} and are capped with C_{60} hemispheres. The tubules correspond to capped $A(10,5)$ tubules in the notation of Hamada, Sawada, and Oshiyama[43] or [5,5] tubules in the notation of Robertson *et al.*[44] Infinite tubules of this type are conductors[43–45] but PTBF calculations show that the capped, finite length tubules are insulators. The approximate dimensions of the toroidal carbons are given in Table III. We define three diameters to quantify the curvature in the tori. These are the inside torus diameter, D_I, the tube diameter from a top projection, D_T, and the tube diameter in the Z direction, D_Z. See Fig. 1 for a schematic representation of these three dimensions.

TABLE II. Structures and cohesive energies in eV/atom as calculated from PTBF. N is the number of atoms in the molecule and the symbols in parentheses indicate the point group.

N	Structure	Energy
60	Sphere (I_h)	-8.008
70	Ellipsoid (D_{5h})	-8.044
120	Torus (D_{5d})	-7.892
120	Tubule (S_{10})	-8.129
144	Torus (D_{6d})	-7.915
240	Torus (D_{5d})	-7.989
240	Sphere (I_h)	-8.261
360	Torus (D_{5d})	-8.190
360	Torus (D_{6d})	-8.068
360	Tubule (S_{10})	-8.208
540	Torus (D_{6h})	-8.015
576	Torus (D_{6h})	-8.138
600	Torus (D_{6d})	-8.242
—	Graphite	-8.407

Calculations using the GSW potential performed for 8 of the structures in Table II were reported by Itoh and co-workers.[24–27] In Table IV we compare the cohesive energies per atom for these clusters relative to C_{60} as calculated from PTBF and the GSW models. The GSW calculations predict that the 120- and 240-atom tori have the same energy per atom, and are both 0.04 eV/atom lower in energy than C_{60}. In contrast, the PTBF calculations show that the C_{120} and C_{240} tori are 0.12 eV/atom and 0.02 eV/atom higher in energy than C_{60}, respectively.

The C_{120} torus is highly curved, with inside and tubule diameters close to 4 Å (see Table III). From strain considerations one would expect the energy per atom to be higher for this structure than for C_{60}, which has a diameter of about 7 Å. We have evaluated two different em-

TABLE III. Approximate dimensions of the toroidal fullerenes used in this study. The inside torus diameter, D_I, the top projection tube diameter, D_T, and the tube diameter in the Z direction, D_Z are given in Å, and are depicted graphically in Fig. 1.

N	Structure	D_I	D_T	D_Z
120	Torus (D_{5d})	4.0	3.8	4.5
144	Torus (D_{6d})	4.8	4.3	4.1
240	Torus (D_{5d})	6.3	3.9	8.0
360	Torus (D_{5d})	6.8	7.0	7.8
360	Torus (D_{6d})	14.7	5.0	4.8
540	Torus (D_{6h})[a]	28	4	4.5
576	Torus (D_{6h})[a]	20	6	5.3
600	Torus (D_{6d})	7.7	10.0	8.0

[a] Average diameters used.

TABLE IV. Energies in eV/atom relative to C_{60} from PTBF, GSW, and the Tersoff elastic theory (TET) of Eq. (4). N is the number of atoms in the molecule and the symbols in parentheses indicate the point group. $\Delta E = E - E(C_{60})$.

N	Structure	ΔE PTBF	ΔE GSW	ΔE TET
120	Torus (D_{5d})	0.12	-0.04	0.17
240	Torus (D_{5d})	0.02	-0.04	-0.25
240	Sphere (I_h)	-0.25	-0.11	-0.46
360	Torus (D_{5d})	-0.18	-0.12	-0.39
540	Torus (D_{6h})	-0.01	-0.11	-0.19
576	Torus (D_{6h})	-0.13	-0.10	-0.34
—	Graphite	-0.40	-0.15	-0.67

pirical strain energy models in an effort to quantify the role of strain energy in these structures. The first model is the π-orbital axis vector analysis method, which has been useful for fullerenes.[46] In this analysis, one defines the π-orbital axis as that vector which makes equal angles with the three σ bonds. The energy per atom relative to graphite is estimated by[47]

$$\Delta E = \frac{a}{N}\sum_{i=1}^{N}(\theta_i - \pi/2)^2 + b, \tag{3}$$

where N is the number of atoms, θ_i is the angle (in radians) made by the π-orbital axis with the σ bonds for atom i, and a and b are constants. Equation (3) works reasonably well for fullerenes with only six-membered rings and isolated five-membered rings, i.e. systems with only positive Gaussian curvature. We have compared calculations from Eq. (3) with the PTBF cohesive energies of Table II and found that Eq. (3) does not correctly describe the energies of clusters with negative Gaussian curvature (i.e., systems with seven-membered rings). Further, the 120- and 144-atom tori both have fused (adjacent) seven-membered rings that are probably not correctly accounted for in the form of Eq. (3). The second approach we tried for predicting the strain energy is the elastic theory due to Tersoff.[48] We have combined the three separate equations that Tersoff gives for tubules, spherical fullerenes (with only five-membered ring disclinations), and negative curvature periodic surfaces (with only seven-membered ring disclinations). The energy per atom relative to graphite is given as

$$\Delta E = \frac{1}{N}\left\{\frac{1}{2}c_0\kappa^2 A + N_5\left[\lambda_5 + \frac{11}{60}\pi c_0 \ln(N/60)\right] + N_7\left[\lambda_7 + 1.14 c_0 \ln(N/168)\right]\right\}, \tag{4}$$

where N is the total number of atoms, c_0 is the elastic constant for curvature out of the graphite plane, κ is the inverse radius of curvature, A is the area of curvature, N_5 and N_7 are the number of five- and seven-membered rings, respectively, and λ_5 and λ_7 are constants. We have used the values of the parameters reported by Tersoff,[48] namely, $c_0 = 1.2$ eV, $\lambda_5 = 3.36$ eV, and $\lambda_7 = 0.75$ eV. We use the average radius of curvature of the torus tubule to define the inverse radius of curvature,

$$\kappa = \frac{1}{D_T} + \frac{1}{D_Z}, \tag{5}$$

where D_T and D_Z are reported in Table III. Thus we assume that the energy required to bend a graphite sheet into a tube is accounted for by the first term on the right-hand side of Eq. (4), while the five- and seven-membered rings provide the positive and negative Gaussian curvature required to close the tube on itself in the form of a torus. We have chosen the area of the tubule curvature, A, to be the number of six-membered rings times the area of a planar hexagon with bond lengths equal to 1.42 Å. We have used Eq. (4) to calculate the energies of C_{60} and the structures in Table IV, and have reported the energy differences along with the PTBF and GSW results in the same table. The elastic theory of Eq. (4) is surprisingly accurate for predicting the trends in energetic stability, even though the energy differences are not in quantitative agreement with PTBF calculation. With the exception of the C_{240} torus, the elastic theory energy orderings are in agreement with the PTBF calculations for the structures in Table IV.

The GSW potential gives a different energy ordering for the C_{540} and C_{576} tori than the empirical many-body potential calculations of Dunlap.[23] The PTBF and elastic theory calculations agree with the many-body potential calculations in placing the C_{576} torus at a lower energy per atom than the C_{540} torus. We also note from Table IV that the GSW potential underestimates the relative stability of the spherical C_{240} fullerene by a substantial 0.24 eV/atom, and erroneously places the 360-atom D_{5d} torus lower in energy than the spherical C_{240}.

The graphite-C_{60} energy difference is almost a factor of 3 greater when calculated by PTBF compared to the GSW calculations. The PTBF value of −0.40 eV/atom compares well with the experimental estimate of −0.44 eV/atom.[49] The fact that the GSW potential severely underestimates the graphite-C_{60} energy difference was not initially noted because the cohesive energy for C_{60} from GSW was compared to *ab initio* calculations, while the cohesive energy for graphite from GSW was compared to experiment.[25]

Table II lists two different structures containing 120 atoms, two different structures containing 240 atoms, and three different structures containing 360 atoms. It is interesting to see the effect of structure on clusters of the same number of atoms and bonds. The C_{120} tubule has a much lower cohesive energy than the torus. This is to be expected because the radius of the tubule ($\sim$ 7 Å) is about twice that of the torus (D_T = 3.8 Å) and hence there is much less strain energy associated with the tubule. Elastic theory calculations with Eq. (4) show the 120-atom tubule to be 0.39 eV/atom lower in energy than the C_{120} torus. The C_{240} icosahedral fullerene is 0.27 eV/atom lower in energy than the 240-atom torus from PTBF calculations, and 0.21 eV/atom lower from the elastic theory computations. The three 360-atom clusters consist of a tubule, a D_{5d} torus, and a D_{6d} torus. The tubule is slightly lower in energy than the D_{5d} torus, which is substantially lower in energy than the D_{6d} torus. The diameter of the tubule is about 7 Å, which is roughly the same as the tubule diameter of the D_{5d} torus. The tube diameter of the D_{6d} torus is about 5 Å. The elastic theory gives energies relative to graphite for the tubule, the D_{5d} and D_{6d} tori as 0.28, 0.29 and 0.44 eV/atom, respectively. The fact that the D_{6d} torus is higher in energy than the D_{5d} torus is a result of the higher strain energy for wrapping the tubule into a smaller diameter and also the added defect energy of including 12 pairs of five- and seven-membered rings, rather than the 10 pairs in the D_{5d} structure.

It is known that the GSW potential produces relaxed fullerene structures with bond lengths on average about 10% larger than experimental bond lengths.[24] We test here the GSW potential to see if it is capable of producing the correct trends in bond lengths as a function of the bond environment. The C_{120} torus has eight inequivalent atoms and 12 distinct bonds, the rest of the atoms and bonds are equivalent by D_{5d} symmetry. In Fig. 2 we enumerate eight distinct atoms; we use this set of atoms in Table V to label the 12 distinct bonds. The bonds listed in Table V are sorted in order of increasing bond length as calculated from the PTBF relaxed structure. The bond lengths as computed from the GSW relaxed structure (for the same bonds) are also listed in the table. It is evident from Table V that the GSW relaxed bond lengths do not follow the correct trend, and hence we conclude that the GSW potential incorrectly responds to the bond environment.

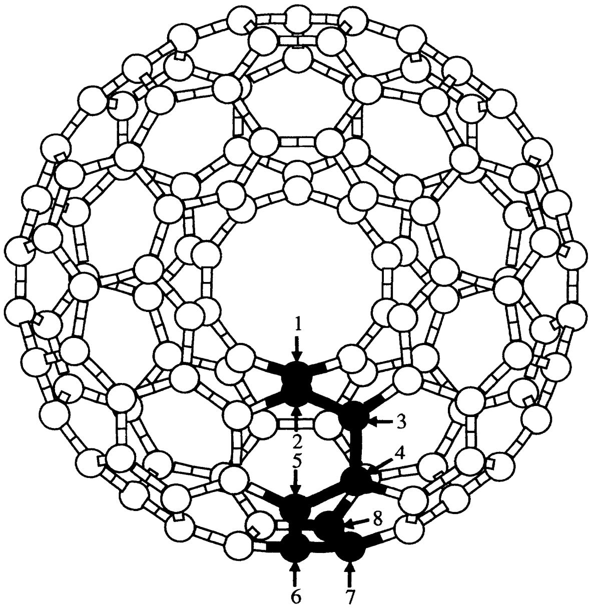

FIG. 2. The eight inequivalent atoms of the D_{5d} C_{120} torus.

TABLE V. The 12 inequivalent bond lengths for the C_{120} torus from the PTBF and GSW relaxed structures. All lengths are given in Å. The bonds are listed in order of increasing PTBF bond length. See Fig. 2 for a definition of the atom labels associated with each bond.

Bond	PTBF	GSW
C_1-C_2	1.3781	1.5947
C_3-C_3	1.3876	1.5822
C_7-C_7	1.3929	1.5858
C_5-C_6	1.4059	1.6002
C_4-C_8	1.4246	1.6249
C_3-C_4	1.4293	1.5844
C_1-C_1	1.4579	1.5838
C_7-C_8	1.4593	1.5998
C_8-C_8	1.4614	1.6266
C_6-C_7	1.4623	1.6042
C_4-C_5	1.4693	1.6006
C_2-C_3	1.4696	1.5745

The PTBF used in this work assumes a localized basis set which enables us to calculate a charge associated with each atom in the cluster. We have calculated the charge density for the atoms in each of the eight tori considered in this work. In general we find that electrons migrate to the five-membered rings in the tori. We also find that at least 5 of the atoms in the seven-membered rings in each torus are electron deficient, indicating that some of the electrons are donated from the seven-membered rings to the five-membered rings. On average, the five-membered rings have a total of about 0.3 more electrons, and the seven-membered rings have about 0.2 fewer electrons than required for charge neutrality.

We have computed the electronic density of states (DOS) for the C_{60} fullerene, and the C_{120} and C_{144} tori from our LDA calculations. In Fig. 3 we plot the 0.2-eV Lorentzian broadened DOS for these three clusters. All three systems lead to clusters with reasonably large gaps and should be expected to be inert at low temperatures.

The relative complexity of fullerene tori is expected to make their fabrication significantly more difficult than fullerenes which are topologically equivalent to a sphere, e.g., C_{60}, C_{70}, tubules, etc. By analogy with C_{28}, which is only produced when stabilized by endohedral atoms such as U and Zr, we here examine the electronic and geometrical structure associated with the C_{144} torus and discuss whether fabrication could be facilitated by placing an atom at the center of the structure. Aside from the possibility of enabling fabrication, the resulting structure could be useful as a binary storage device if there is a double-well potential associated with the added atom, and an applied field is capable of moving the atom from one well to the other.[50] From the standpoint of enhanced fabrication, it is interesting to compare

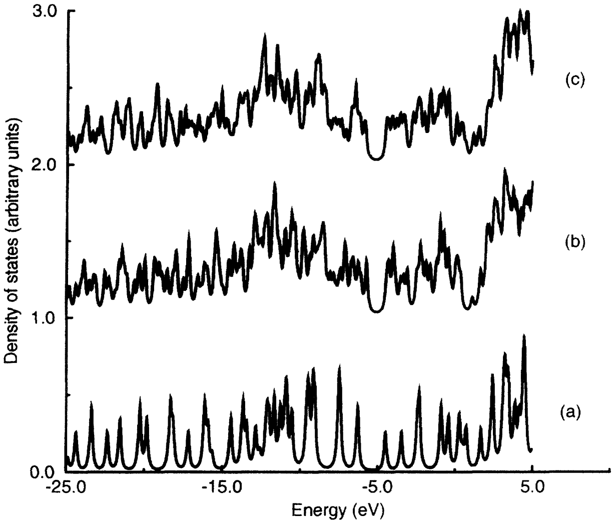

FIG. 3. Density of states for (a) the C_{60} fullerene, (b) the C_{120} torus (shifted up by 1 ordinate unit), and (c) the C_{144} torus (shifted up by 2 ordinate units). In each case, the density of states has been Lorentzian broadened by 0.2 eV. The HOMO is located at −6.3 eV for C_{60}, at −5.7 eV for C_{120}, and at −5.8 eV for C_{144}.

the electronic and geometrical structure to the small gapless C_{28} molecule,[2–5] which forms strong covalent interactions with endohedral atoms, and the large wide-gap C_{60} molecule which forms weak ionic bonds with endohedral atoms. With respect to size, the center of the C_{28} molecule and C_{144} torus (D_I) both have diameters of approximately 4.8 Å. In contrast, the C_{60} molecule is significantly larger with a diameter of 7.1 Å. Size considerations suggest that the center of C_{144} torus could very well accommodate the addition of an atom. However, in contrast to the C_{28} molecule, the C_{144} torus has a gap of 1.3 eV which is not significantly smaller than the C_{60} molecule (1.8 eV). While it is now known that C_{60} can dimerize,[51] the dimerization energy is on the order of 1.0 eV per pair, which is significantly smaller than the Zr-C bonding in C_{28} of approximately 12.6 eV per Zr atom.[4]

These considerations suggested that ionic bonding between an alkali atom and a fullerene torus might be the first type of interaction to investigate. We have performed LDA calculations with a potassium atom at the center of a C_{144} torus. We find that the potassium atom is bound by 0.5 eV. Analysis of the electronic densities shows that the potassium 4*s* state is unoccupied when placed at the center of the torus. The empty torus has a LUMO that transforms like a p_z state and two more states slightly above that transform in an *e* representation. Upon introduction of the K atom, the p_z LUMO level is repelled upward by the occupied K 3*p* levels and the *e* representation is pulled downward to accept the K 4*s* electron. While we have not addressed the question from first principles, we note that it is possible that the K-C_{144} system may exhibit a double-well potential because of repulsive interactions between the K atom and the closest C atoms on the torus, even though the C-K distance of 2.47 Å in the toroidal-potassium system is larger than the combined ionic radii of the K ion and the carbon atom (2.1 Å). For example, in K_6C_{60}, experimental geometry and theoretical cluster calculations show that the potassium atoms arrange themselves to maximize their distance from carbon atoms.[52] This suggests that for distances smaller than 3.1 Å, the K-C interaction should be repulsive[53] which allows for the possibility of a double well in the K-C_{144} system. In analogy to the C_{28} molecule, which forms covalent interactions[3–5] with valence levels of orbital angular momentum $\ell \geq 2$, it appears that this particular torus may also bond with high angular momentum atomic valence states (e.g., Zr, etc.). Since the presence of K-3*p* semicore states pushes up some of the valence levels, it seems most appropriate to look for a tetravalent atom that has a tightly bound lower core of *p* states.

V. CONCLUSIONS

In this paper we have presented total-energy calculations from a PTBF formalism for 13 fullerene clusters and graphite. We have compared selected PTBF energy differences and relaxed structures to accurate LDA calculations and have found very good agreement. The PTBF method is deemed to be an accurate and relatively fast approach for calculating the electronic and structural properties of graphene systems.

We have specifically addressed the issue of the energetic stabilities of fullerene tori. Previous calculations[24–26] indicate that even small toroidal fullerenes with as few as 120 carbon atoms have a lower energy per atom than C_{60}. Our more accurate PTBF calculations show that this is probably an artifact of using the Stillinger-Weber–like empirical potential. We have found that a simple elastic theory due to Tersoff[48] gives energy orderings in good agreement with the PTBF calculations. The GSW potential is less accurate for predicting energy orderings than the elastic theory. The GSW potential gives an energy difference between C_{60} and graphite that is too small by almost a factor of 3 when compared to both PTBF calculations and experiment.

We have compared energies of tori, tubules, and spherical fullerenes. We find that tubules have lower energies per atom than tori of similar tube radius. However, this does not mean that it is impossible to form toroidal fullerenes. Growth kinetics, reaction pathways, and Gibbs free-energy driving forces play important roles in determining the products of any chemical reaction. While assessment of these factors is beyond the scope of this work, we have calculated the binding energy of a single potassium atom in the center of a 120-atom torus in order to assess whether fabrication of tori would be facilitated by metal atoms. We found that the K atom forms a stable, moderately strong bond at the center of the torus. Further studies are needed to see if this torus will bind more strongly with atoms of higher orbital angular momentum.

Charge densities for the tori from our PTBF calculations show that the five-membered rings on the outer surface of the torus have enhanced electron densities. Atoms that are part of the inner surface seven-membered rings are generally electron deficient. We conclude that atoms in seven-membered rings may donate electrons to the atoms of the five-membered rings.

ACKNOWLEDGMENTS

We thank A. A. Quong for helpful discussions. We are grateful to S. Itoh and S. Ihara for providing coordinates for the C_{360} D_{5d} torus, and B. I. Dunlap for providing the coordinates of his C_{540} and C_{576} tori. We thank A. Maiti and E. G. Gal'pern for providing manuscripts prior to publication. J. K. Johnson and B. N. Davidson acknowledge financial support from the National Research Council fellowships at the Naval Research Laboratory.

---

[*] Permanent address: Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261.

[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Nature **318**, 162 (1985).

[2] T. Guo, M. D. Diener, Y. Chai, M. J. Alford, R. E. Haufler, S. M. McClure, T. Ohno, J. H. Weaver, G. E. Scuseria, and R. E. Smalley, Science **257**, 1661 (1992).

[3] B. I. Dunlap, O. D. Häberlen, and N. Rösch, J. Phys. Chem. **96**, 9095 (1992); N. Rösch, O. D. Häberlen, and B. I. Dunlap, Angew. Chem. Int. Ed. Engl. **32**, 108 (1993).

[4] M. R. Pederson and N. Laouini, Phys. Rev. B **48**, 2733 (1993).

[5] K. Jackson, E. Kaxiras, and M. R. Pederson, Phys. Rev. B **48**, 17 556 (1993).

[6] D. Ugarte, Nature **359**, 707 (1992).

[7] H. W. Kroto, Nature **359**, 670 (1992).

[8] S. Iijima, Nature **354**, 56 (1991).

[9] O. Zhou, R. M. Flemming, D. W. Murphy, C. H. Chen, R. C. Haddon, A. P. Ramirez, and S. H. Glarum, Science **263**, 1744 (1994).

[10] S. Iijima and T. Ichihashi, Nature **363**, 603 (1993).

[11] D. S. Bethune, C. H. Kiang, M. S. de Vries, G. Gorman, R. Savoy, J. Vazques, and R. Beyers, Nature **363**, 605 (1993); C. H. Kiang, W. A. Goddard III, R. Beyers, J. R. Salem, and D. S. Bethune, J. Phys. Chem. **98**, 6612 (1994).

[12] S. Subramoney, R. S. Ruoff, D. C. Lorents, and R. Malhotra, Nature **366**, 637 (1993).

[13] S. Iijima, T. Ichihashi, and Y. Ando, Nature **356**, 776 (1992).

[14] M. Ge and K. Sattler, Chem. Phys. Lett. **220**, 192 (1994).

[15] S. Iijima, P. M. Ajayan, and T. Ichihashi, Phys. Rev. Lett. **69**, 3100 (1992).

[16] A. L. Mackay and H. Terrones, Nature **352**, 762 (1991).

[17] T. Lenosky, X. Gonze, M. Teter, and V. Elser, Nature **355**, 333 (1992); S. J. Townsend, T. J. Lenosky, D. A. Muller, C. S. Nicols, and V. Elser, Phys. Rev. Lett. **69**, 921 (1992).

[18] D. Vanderbilt and J. Tersoff, Phys. Rev. Lett. **68**, 511 (1992).

[19] L. A. Chernozatonskii, Phys. Lett. A **172**, 173 (1992).

[20] M. S. Dresselhaus, G. Dresselhaus, and R. Saito, Phys. Rev. B **45**, 6234 (1992); R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Appl. Phys. Lett. **60**, 2204 (1992).

[21] A. Maiti, C. J. Brabec, and J. Bernholc, Phys. Rev. Lett. **70**, 3023 (1993); A. Maiti, C. J. Barbec, and J. Bernholc, Mod. Phys. Lett. B **7**, 1883 (1993).

[22] D. York, J. P. Lu, and W. Yang, Phys. Rev. B **49**, 8526 (1994).

[23] B. I. Dunlap, Phys. Rev. B **46**, 1933 (1992).

[24] S. Itoh, S. Ihara, and J. Kitakami, Phys. Rev. B **47**, 1703 (1993).

[25] S. Ihara, S. Itoh, and J. Kitakami, Phys. Rev. B **47**, 12 908 (1993).

[26] S. Itoh and S. Ihara, Phys. Rev. B **48**, 8323 (1993).

[27] S. Itoh and S. Ihara, Phys. Rev. B **49**, 13 970 (1993).

[28] E. G. Gal'pern, I. V. Stankevich, A. L. Chistyakov, and L. A. Chernozatonskii, Full. Sci. Technol. **2**, 1 (1994).

[29] S. Ihara, S. Itoh, and J. Kitakami, Phys. Rev. B **48**, 5643 (1993).

[30] D. W. Brenner, Phys. Rev. B **42**, 9458 (1990).

[31] F. H. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5262 (1985).

[32] F. F. Abraham and I. P. Batra, Surf. Sci. **209**, L125 (1989).

[33] M. R. Pederson and K. A. Jackson, Phys. Rev. B **41**, 7453 (1990); **43**, 7312 (1991).

[34] K. A. Jackson and M. R. Pederson, Phys. Rev. B **42**, 3276 (1990).

[35] C. H. Xu, C. Z. Wang, C. T. Chan, and K. M. Ho, J. Phys. Condens. Matter **4**, 6047 (1992).

[36] C. H. Xu and G. E. Scuseria, Phys. Rev. Lett. **72**, 669 (1994).

[37] B. L. Zhang, C. Z. Wang, and K. M. Ho, Chem. Phys. Lett. **193**, 225 (1992).

[38] B. L. Zhang, C. Z. Wang, K. M. Ho, C. H. Xu, and C. T. Chan, J. Chem. Phys. **97**, 5007 (1992).

[39] C. Z. Wang, B. L. Zhang, and K. M. Ho, Chem. Phys. Lett. **200**, 35 (1992).

[40] C. Z. Wang, C. T. Chan, and K. M. Ho, Phys. Rev. B **46**, 9761 (1992).

[41] X.-P. Li, R. W. Nunes, and David Vanderbilt, Phys. Rev. B **47**, 10 891 (1993).

[42] M. S. Daw, Phys. Rev. B **47**, 10 895 (1993).

[43] N. Hamada, S. I. Sawada, and A. Oshiyama, Phys. Rev. Lett. **68**, 1579 (1992).

[44] D. H. Robertson, D. W. Brenner, and J. W. Mintmire, Phys. Rev. B **45**, 12 592 (1992); C. T. White, D. H. Robertson, and J. W. Mintmire, Phys. Rev. B **47**, 5485 (1993).

[45] J. W. Mintmire, B. I. Dunlap, and C. T. White, Phys. Rev. Lett. **68**, 631 (1992).

[46] R. C. Haddon, Science **261**, 1545 (1993).

[47] D. Bakowies and W. Thiel, J. Am. Chem. Soc. **113**, 3704 (1991); D. Bakowies, A. Gelessus, and W. Thiel, Chem. Phys. Lett. **197**, 324 (1992).

[48] J. Tersoff, Phys. Rev. B **46**, 15 546 (1992).

[49] H. D. Beckhaus, S. Verevkin, C. Rüchart, F. Diederich, C. Thilgen, H. U. ter Meer, H. Mohn, and W. Müller, Angew. Chem. **33**, 996 (1994).

[50] The potential observed by an added atom on the torus Z axis is symmetric with respect to reflections through the torus center. For tori with large inner diameters, the potential will have a minimum at the center of the torus. However, for tori with sufficiently small inner diameters, kinetic-energy repulsions between the torus carbon atoms and the added atom will lead to an energy barrier, and thus a double-well potential. For an example of kinetic repulsions between open carbon rings and external moieties, see M. R. Pederson and J. Q. Broughton, Phys. Rev. Lett. **69**, 2689 (1992).

[51] A. M. Rao, P. Zhou, K. A. Wang, G. T. Hager, J. M. Holden, Y. Wang, W. T. Lee, X. X. Bi, P. C. Eklund, D. S. Cornett, M. A. Duncan, and I. J. Amster, Science **259**, 955 (1993); O. Chauvet, G. Oszlànyi, and L. Forro, Phys. Rev. Lett. **72**, 2721 (1994); M. Menon and K. R. Subbaswamy, Phys. Rev. B **49**, 13 966 (1994); M. R. Pederson and A. A. Quong (unpublished).

[52] O. Zhou, J. E. Fischer, N. Coustel, S. Kycia, Q. Zhu, A. R. McGhie, W. J. Romanow, J. P. McCauley, A. B. Smith, and D. E. Cox, Nature **351**, 426 (1991); M. R. Pederson, S. C. Erwin, W. E. Pickett, K. A. Jackson, and L. L. Boyer, in *Physics and Chemistry of Finite Systems: From Clusters to Crystals,* edited by P. Jena *et al.* (Kluwer Academic Publishers, The Netherlands, 1992), Vol. II, p. 1323.

[53] A subtle point related to the K_6C_{60} structure is that there are *two* energetically degenerate structures *if the fullerene molecules are spherical.* These structures can be determined by placing potassium atoms at the positions that are equivalent to $(0.0, d, 0.5)a_0$ and $(0.0, 0.5 - d, 0.5)a_0$, respectively. Since the fullerene molecule is not spherical, the energetic degeneracy of these two structures is broken. Since all C-C and K-K distances are equivalent in both structures, and since the the smallest C-K interactions is maximized for the experimental value of d, the C-K interaction should be repulsive for the distances found here. See Ref. 52.

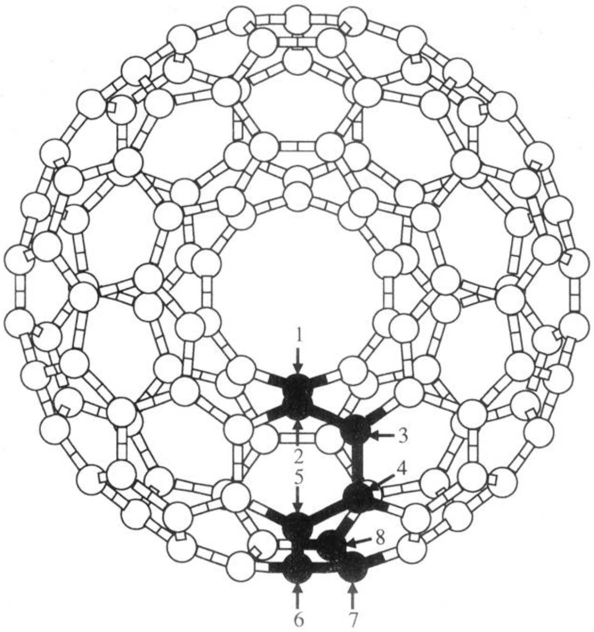

FIG. 2. The eight inequivalent atoms of the D_{5d} C_{120} torus.