Ab-Initio Calculations of Materials Properties

RLE Group
ab-initio Physics Group

Academic and Research Staff
Professor John D. Joannopoulos
Professor Marin Soljacic

Graduate Students
K.C. Huang
Matthew Evans

Postdoctoral Fellows
Evan Reed

Technical and Support Staff
Margaret O'Meara

Introduction

Predicting and understanding the properties and behavior of real materials systems is of great importance both from technological and academic points of view. The theoretical problems associated with these systems are, of course, quite complex. However, we are currently at the forefront of beginning to overcome many of these problems. Our research is devoted to creating a realistic microscopic quantum mechanical description of the properties of real material systems. In the past, theoretical attempts to deduce microscopic electronic and geometric structure have been generally based on optimizing a geometry to fit known experimental data. Our approach is more fundamental: predicting geometric, electronic, and dynamical structure, *ab-initio* — that is, given *only* the atomic numbers of the constituent atoms as experimental input. Briefly, our method makes it possible to accurately and efficiently calculate the total energy of a solid by the use of density functional theory, pseudopotential theory and a conjugate gradients iterative minimization technique for relaxing the electronic and nuclear coordinates. *Ab-initio* investigations are invaluable because they make possible theoretical calculations or simulations that can stand on their own. They may complement experimental observations but need not be guided by experimental *interpretations*. Our objective is to obtain a fundamental, microscopic understanding of various physical and chemical phenomena of real materials systems.

The Nature of Boron Nanotubes

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Project Staff
Matthew Evans and J. Joannopoulos

Boron, carbon's first-row neighbor, has only three valence electrons. Its natural crystalline structure is a rhombohedral lattice with 12-atom icosahedral clusters at each lattice site.[1] Nevertheless, there are some intriguing similarities with carbon. Boron's three electrons could in principle form sp^2 hybrid orbitals that might lead to planar and tubular structures similar to those

formed by carbon. Since carbon nanotubes and fullerenes[2] are metastable structures, formed only under kinetically constrained conditions,[3] one might envision analogous boron structures. Indeed, initial resuts by Boustani *et al.*[4,5] have demonstrated the possibility of such metastable structures with relatively low energy cost. Crystalline[6] and amorphous[7] boron nanowires with diameters as small as 20 nm have recently been fabricated, suggesting that boron nanotubes may already be within the range of experimental possibility.
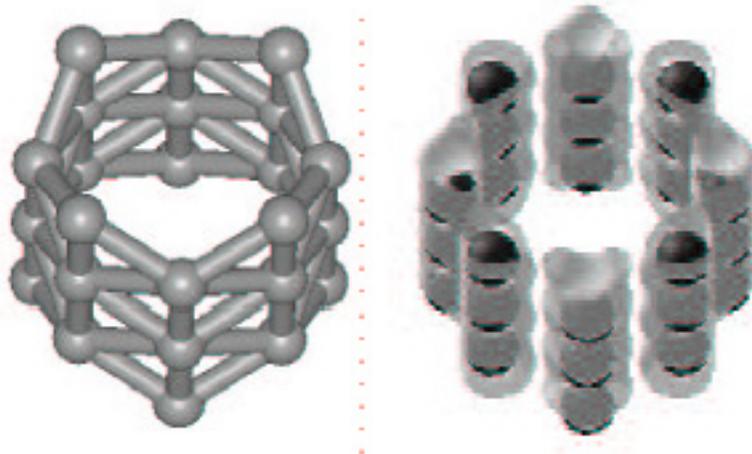

Figure 1. The (4,4) boron nanotube. (a) Ball and stick structural model. (b) A valence electron density isosurface of 0.67 electrons/A^3. The ion cores are shown as dark spheres.

There is an intriguing and potentially significant difference between carbon and boron however. Boron has only three valence electrons, so that in sp^2-bonded planar or tubular boron structures the relative occupations of the sp^2- and the π-bonded bands depend on the energetic positions and dispersions of the two bands, perhaps opening up a broader range of possibilities.

Using an *ab-initio* total-energy density functional approach we have examined in detail the electronic structure and relative stabilities of planar and tubular boron structures. We find that boron does form a stable sp^2-bonded hexagonal graphene-like sheet, but a planar triangular lattice has an even larger cohesive energy, though still smaller than that of the bulk α-rhombohedral structure. The triangular planar structure has an unusual property. It is essentially a homogeneous electron gas system with a threefold-degenerate ground state. This degeneracy makes the flat triangular plane unstable with respect to buckling, which breaks the symmetry and introduces a preferred direction defined by strong σ bonds. When rolled into a tube, this preferred direction, which is not present in carbon nanotubes, defines the chirality and controls the electron density, cohesive energy, and elastic response of boron nanotubes. The properties of the (n,0) tubes arise from the flat plane and are very similar to carbon nanotubes. The properties of the (n,n) boron nanotubes are derived from the buckled plane and contrast sharply with carbon nanotube structures. As a result of the buckling, the curvature energies of (n,n) tubes are lower than those of (n,0) tubes and show a nonmonotonic plateau structure as a function of n. The contrast in the electron densities of the buckled and flat triangular planes also explains the differing elastic responses of the (n,n) and (n,0) tubes.

We define the chirality of a boron nanotube based on a triangular lattice. An (m,n) tube is constructed by rolling a triangular plane such that the head of the lattice vector m**a** + n**b** meets its tail; **a** and **b** are the primitive vectors of the triangular lattice.

Consider first the case of an (n,n) nanotube, shown in Figure 1(a). Here, the σ bond direction can be chosen to lie along the length of the tube. Given this possibility, the boron atoms will form σ bonds running along the nanotube, as the electron density isosurface in Figure 1(b) shows. The strong longitudinal bonds allow the tube to buckle laterally, emulating the buckled plane structure.

Instead of the circular cross section seen in carbon nanotubes, the (8,8) tube has a square cross section. The sides of the square are sections of the buckled plane, and the corners have only a slight distortion. In contrast, the cross section of the (6,6) tube shows no buckling. With only four atoms on each side, it is not possible to buckle the sides without distorting the topology of the corners. A "buckled" structure of the (6,6) tube breaks the mirror symmetries of the actual (6,6) and (8,8) structures.

Table I. Summary of the cohesive energy E_{coh}, the curvature energy with respect to the buckled plane E_{curv}, the equilibrium diameter d, the modified Young's modulus Y_s (see Equation 1), and the Poisson ratio σ for boron nanotubes.

Chirality	E_{coh} (ev)	E_{curv} (eV)	D(Å)	Y_s (Tpa nm)	σ
(4,4)	6.71	0.08	4.34	0.29	0.5
(6,6)	6.65	0.14	5.65	0.15	0.4
(8,8)	6.76	0.03	8.48	0.22	0.1
(7,0)	6.36	0.43	3.99	0.49	0.2
(8,0)	6.39	0.40	4.62	0.49	0.1

Larger diameter tubes sharing the favorable buckled structure of the (8,8) tube can be constructed by adding atoms to the sides of the square in pairs. This implies that among the (n,n) boron nanotubes, (4n,4n) tubes should have lower curvature energies and be more stable. This trend is suggested by the cohesive and curvature energies summarized in Table I. In the table, the curvature energy is defined as the difference in cohesive energy between the tube and the

plane: $E_{curve} \equiv E_{coh}^{tube} - E_{coh}^{plane}$

An (n,0) nanotube cannot align σ bonds longitudinally (see Figure 2(a)). Although buckling and selecting a σ bond direction proves energetically favorable in the (n,n) tubes, it is not required by symmetry. Buckling is necessary to break the symmetry of the flat plane, but rolling up the plane into an achiral tube breaks the degeneracy automatically. The threefold planar degeneracy reduces to a twofold degeneracy (spiraling σ bonds related by chiral symmetry) and a nondegenerate state (σ bonds running longitudinally or laterally). It is possible for σ bonds to run along the circumference of an (n,0) tube, but the electron density of an (8,0) nanotube, shown in Figure 2(b), shows no such bonds. Instead, the density of (n,0) boron nanotubes is nearly uniform, exhibiting the free electron character of the flat triangular plane. The energetic consequences are apparent. The curvature energies of (n,0) boron nanotubes lie 0.25 – 0.4 eV above those of the (n,n) tubes; this is roughly the same as the 0.26 eV cohesive energy difference between the flat and buckled triangular planes. Between the achiral limits, there may be a critical chiral angle at which boron nanotubes switch from the σ bond dominated electronic structure of the buckled plane to the free-electron-like structure of the flat plane. This could have important consequences for the behavior of boron nanotubes under torsion.

Elastic properties of boron nanotubes exhibit a strong chirality dependence as well. Among the most important characteristics of a cylindrical object is the Young's modulus Y_s, defined for single walled tubes as:

$$Y_s = \frac{1}{S_0}\left(\frac{\partial^2 E}{\partial \varepsilon^2}\right)_{\varepsilon=0} \tag{1}$$

where S_0 is the equilibrium surface area, E is the total energy, and ε is the longitudinal strain. Since the walls of our boron nanotube are only a single atom thick, it is not possible to define the tube volume, and we must use this modified Young's modulus. For the (n,n) tubes with square cross sections, we define the diameter as the diagonal of the square, and we ignore buckling in calculating the surface area.
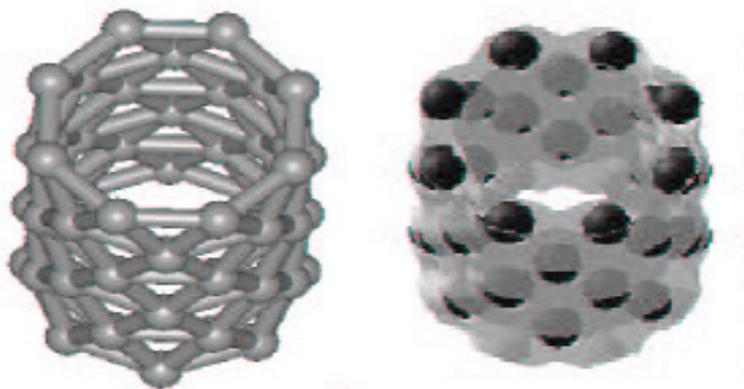

Figure 2. The (8,0) boron nanotube. (a) Ball and stick structural model. (b) A valence electron density isosurface of 0.67 electrons/A^3. The ion cores are shown as dark spheres

Another important elastic property of a tube is the Poisson ratio σ:

$$\frac{d - d_{eq}}{d_{eq}} = -\sigma\varepsilon \qquad (2)$$

where d is the tube diameter at strain ε, and d_{eq} is the equilibrium tube diameter. The Poisson ratio measures the change in the tube's radius as it is strained longitudinally. The combination of the Young's modulus and the Poisson ratio provides information about the strength of both the longitudinal and lateral bonds of the nanotube.

We have calculated the Young's modulus Y_s and Poisson ratio σ for the (n,n) and (n,0) boron nanotubes discussed above. As with the binding energy, chirality plays a crucial role in determining these properties. As is clear from the electron density isosurface in Figure 1b, the strength of the (n,n) boron nanotubes arises from the bonds running along the length of the tube. Since the lateral bonds are comparatively weak, we would expect that an (n,n) nanotube will be able to expand and contract circumferentially to relieve stress, leading to a high Poisson ratio and a low Young's modulus. This is indeed the case for the small-diameter (4,4) and (6,6) tubes. For the (4,4) tube, Y_s = 0.29 TPa nm and σ = 0.5. The Young's modulus is comparable to boron nitride nanotubes and roughly half that of carbon nanotubes, while the Poisson ratio is nearly twice as large as the value for either carbon or boron nitride nanotubes.

For the (8,8) boron nanotube, however, structural dynamics play a more important role. Using the previous definition of the Poisson ratio, we find that σ = 0.1, considerably smaller than the Poisson ratio of the (4,4) and (6,6) tubes. The diameter of the (8,8) tube does not change significantly with strain, but there is considerable lateral relaxation that results in a low Young's modulus. The simple square cross sections of the (4,4) and (6,6) tubes, as well as the circular cross sections of the (n,0) tubes, permit only uniform lateral dilation and contraction if the symmetry of the structure is to be maintained. The buckled sides of the (8,8) (and larger (4n,4n) tubes, as discussed previously) permit tube walls to relax without changing the overall square structure.

Although the (8,8) boron nanotube does not change its diameter under longitudinal strain, the comparatively weak lateral bonds do allow for relaxation of the buckled tube sides. Buckling introduces a third dimension into the planar structure, enabling strain to be relaxed in an internal degree of freedom that does not break the planar symmetry. As the buckled plane is stretched, atoms can move perpendicular to the plane to relieve stress, an option that is forbidden by symmetry in flat planar structures. This is analogous to the fundamental difference between the phonon modes of a monatomic Bravais lattice and those of a lattice with a basis: in the latter, optical modes are present that allow relative motion without a net translation of the crystal.

In contrast to the (n,n) nanotubes, the (n,0) tubes have no dominant bonding direction. Straining the tube stresses bonds both laterally and longitudinally, making it difficult for the tube to expand or contract circumferentially. An increased Young's modulus and a decreased Poisson ratio reflect this cost. For the (8,0) boron nanotube, Y_s = 0.49 Tpa nm and σ = 0.1. Although the radius of the (8,0) tube is only 6% larger than that of the (4,4) tube, the Young's modulus is 68% larger. This is in sharp contrast to carbon nanotubes, where tubes of similar radius have Young's moduli that differ by only a few percent.

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