

Tuning the electronic properties of boron nitride nanotubes with transverse electric fields: A giant dc Stark effect

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Ab initio calculations show that the band gap of boron nitride (BN) nanotubes can be greatly reduced by a transverse electric field. This gap reduction arises from a mixing of states within the highest occupied molecular orbital and lowest unoccupied molecular orbital complexes and leads to a spatial separation of electrons and holes across the tube diameter. The gap modulation increases with tube diameter and is nearly independent of chirality. For BN nanotubes of diameters of 5 nm or more, a sizable gap reduction should be achievable with laboratory fields. This effect provides a possible way to tune the band gap of BN tubes for various applications.

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Since its discovery, carbon nanotubes have been a subject of great interest due to their unique electrical and mechanical properties as well as their potential for applications. Following this, there has also been a search for noncarbon nanotubes and, drawing on an analogy between hexagonal boron nitride and graphite, the existence of boron nitride nanotubes was predicted theoretically in 1994¹ and synthesized experimentally shortly after.² However, different from their carbon analogues, boron nitride nanotubes are wide-gap semiconductors with a quasiparticle band gap of ~ 5.5 eV independent of their radii and helicities.³ The range of applications (e.g., in optoelectronic devices) of these boron nitride nanotubes would be greatly extended if their band gap can be tuned to desired values in a controlled way. In this work, we apply a first-principles methodology to investigate the possibility of and the mechanism for achieving such a tuning of the electronic properties of the BN nanotubes by means of an electric field applied perpendicular to the tube axis.

The basic idea is that, through the Stark effect, the electric field mixes the nearby subband states in the valence band complex and separately it mixes the nearby subband states in the conduction band complex. The “fanning” out of the mixed states then leads to a reduction in the band gap. Although not analyzed within this mechanism, this effect has in fact been seen in previous calculations on carbon nanotubes.⁴ In this work, we elucidate the mechanism and show that, for boron nitride nanotubes, the effect is more dramatic and interesting due to a reduced screening of the electric field. We show that the reduction in the band gap involves the formation of new states with wave functions separated across the tube diameter.

Practically, a nanotube on an insulating substrate can be subjected to a strong transverse electric field through an applied gate voltage. Such systems are prototype nanoscale field effect transistors. For BN nanotubes, if the band gap were tuned from ~ 5 eV to less than 2.0 eV, interesting electronic properties may be realizable. Finally, the spatial separation of charge carriers (see below) in such field-induced semiconducting BN nanotube should give rise to interesting effects in transport measurements.

Our calculations were performed using the *ab initio* pseudopotential density-functional method,⁵ within the

generalized gradient approximation (GGA) for exchange-correlation,⁶ and norm-conserving pseudopotentials.⁷ The basis set is a linear combination of numerical pseudoatomic orbitals of finite range.⁸ We carried out the calculations employing the SIESTA computer code⁹ and used a double-zeta basis set (8 orbitals per atom). The range of the orbitals were determined by fixing the energy shift due to the confinement of the basis orbitals to be 0.005 Ry as described in Ref. 9. In general, use of atom-centered localized orbitals only as basis functions may give an inaccurate description of states with wave function extended away from the atoms. To overcome this difficulty, we augmented our basis set with additional atomic basis orbitals centered on concentric cylinders about the nanotube axis. These orbitals are s-like and the cylinders on which they reside have radii given by $R + nd$, where R is the nanotube radius, d is the distance between the nanotube walls and nearly free electron NFE states obtained from previous work,¹ and n is an integer. By varying n , we fit as many cylinders as allowed inside the nanotube and introduce two cylinders outside. The spacing between orbital centers along the circumferential direction goes from 3 to 6 Å and the orbital positions are chosen to best preserve the symmetries of the nanotube. Along the axial direction, we have one layer of orbitals per unit cell in armchair nanotubes, two layers in zigzag tubes, and three layers in the (16,4) nanotube. With this scheme, we were able to reproduce band structures obtained with a plane wave basis set. All geometries were optimized by minimizing the forces on the atoms.

We start the discussion by examining the (22,22) BN nanotube, which has a diameter of about 30 Å. Its band structure is shown in Fig. 1(a) with the origin of the energy scale set at midgap. As found in previous calculations, this material is a widegap semiconductor with a Kohn-Sham gap of 4.5 eV within the GGA approximation. (As found in all semiconductors, the Kohn-Sham gap underestimates the true value of the gap.¹⁰) The bottom of the conduction band complex is consisted of two subbands that are close in energy but of very different nature. As shown in Fig. 2, the nearly-free-electron-like state close to the Γ point is a tubulelike state that exists inside the nanotube, and it corresponds to the interlayer state of the hexagonal boron nitride sheet in a band folding picture. The state at the direct gap conduction band

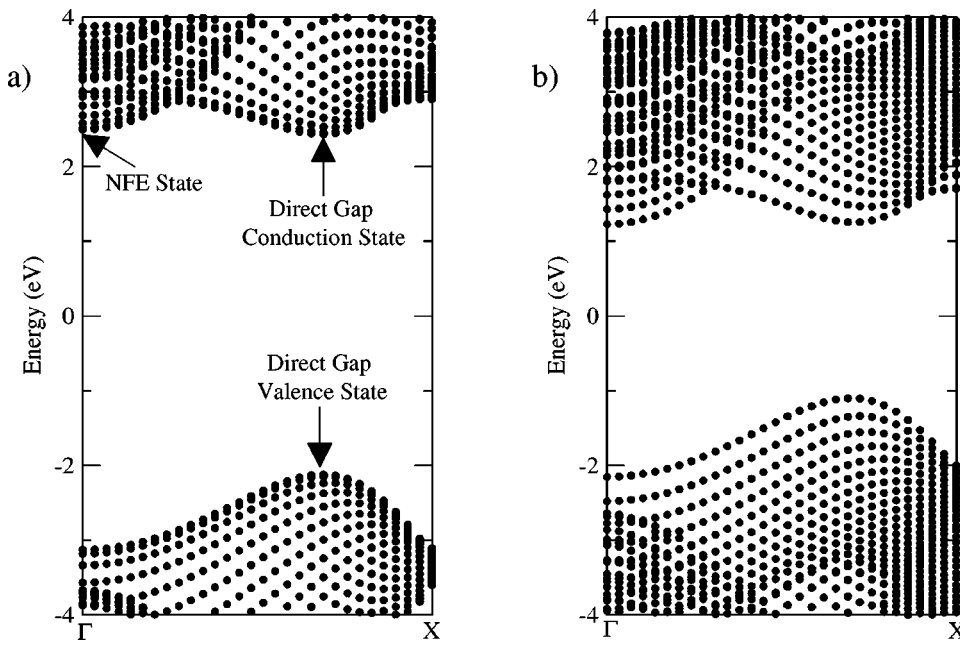


FIG. 1. Calculated band structures of (22,22) BN nanotubes under (a) zero and (b) 0.1 V/Å transverse electric field.

minimum, on the other hand, is consisted of π -like orbitals uniformly distributed along the circumference of the nanotube with large amplitudes on the boron atoms. Based on these electron distributions, one expects the NFE states to be more loosely bound as it is not localized on the atomic cores, and this has important consequences in terms of band gap modulation by electric fields. The valence band maximum also is made up of π -like orbitals uniformly distributed along the circumference but centered on the nitrogen instead of boron atoms.

To simulate the effect of a uniform transverse electric field, we apply a sawtooth potential along the direction perpendicular to the nanotube axis in a supercell geometry. Structural relaxation under the perturbation produces a displacement of boron atoms in and of nitrogen atoms against the direction of the applied field, respectively. This is consistent with the fact that there is a slight charge transfer from the boron atom to the nitrogen atom due to the nitrogen atom's larger electronegativity. For example, the relative dis-

placement of the atoms is of the order of 0.005 a.u. for a field of 0.1 V/Å on a (10,10) BN nanotube.

The variation in the value of the calculated band gap with respect to the applied E field is plotted in Fig. 3(a) for various armchair nanotubes. The band gap varies quadratically for small electric fields and becomes linear once the drop in the perturbing potential across the diameter becomes comparable to the spacing of the energy levels. In analogy to the Stark effect in atomic physics, the field dependence of the band gap in the small field regime is quadratic as the lowest conduction band and the highest valence band are nondegenerate. For larger electric fields that produce potentials comparable to the energy level spacings within the conduction and valence subband complexes, the perturbation then causes extensive mixing among subband states within each complex, giving rise to a linear field dependence for the band edge states. In this regime, an electric field has a very strong effect on the wave function of the band edge states, as shown by the electron charge density plots in Fig. 2 for a (22,22)

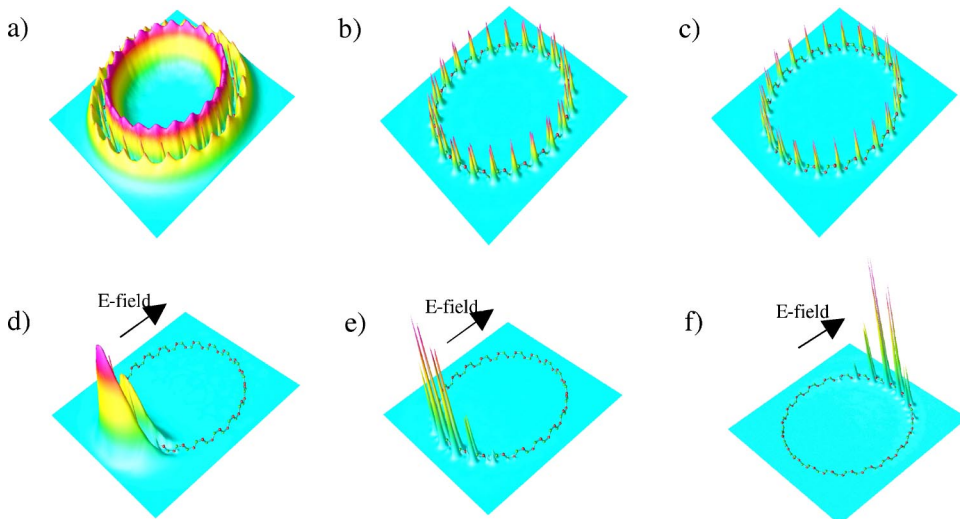


FIG. 2. (Color online) Electronic densities under zero electric field for (a) NFE state, (b) direct gap conduction state, and (c) direct gap valence state, and under $E=0.1$ V/Å for (d) NFE state, (e) direct gap conduction state, and (f) direct gap valence state.

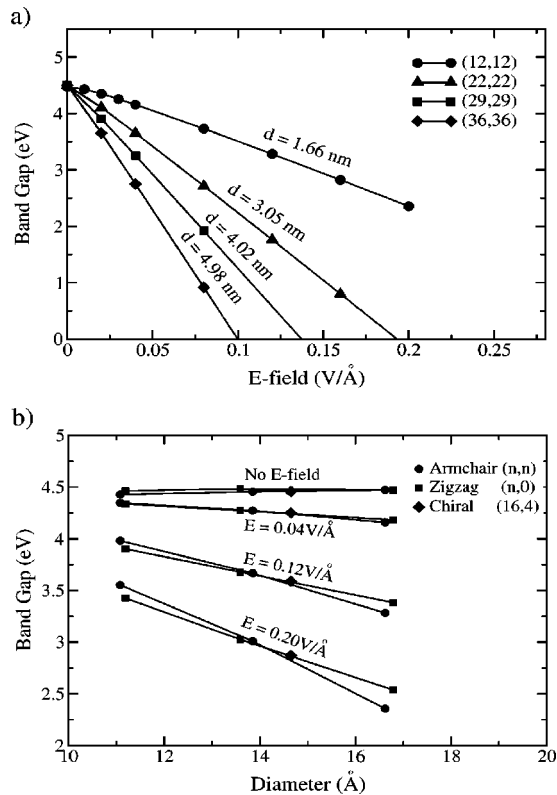


FIG. 3. (a) Calculated direct band gap vs E field for various armchair BN nanotubes. (b) Calculated direct band gap vs nanotube diameter for nanotubes of different chiralities.

nanotube in a 0.1 V/\AA field. Indeed, the charge density corresponding to the bottom of the conduction band state is moved in the direction opposite to the electric field and it is highly localized on one side of the tube. The charge density of the valence band maximum state, on the other hand, is moved along the direction of the electric field and it is highly localized on the other side of the tube. While paying some kinetic energy in localizing the wave function across the tube axis, the conduction band edge lowers its energy in response to the electric field as the charge is accumulated in regions of higher electrical potential. Similarly, the valence band edge state moves up in energy since its charge is accumulated in regions of low electrical potential. The combined effect gives rise to a reduced band gap.

As seen in Fig. 3(a), the gap reduction for a given transverse electric field strength is larger for larger diameter nanotubes, as the charge densities of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) states are separated further from each other in the potential field upon mixing [see Fig. 3(b)]. An extrapolation of these calculated data allows one to estimate the electric fields needed for a direct band gap closure. For example, it is about 0.14 V/\AA and 0.10 V/\AA for the (29,29) and (36,36) BN nanotubes, respectively. The value of such closure fields would be greatly reduced for larger diameter tubes, and of course, tuning of the gap to the 2–3 eV range for these large diameter tubes would only need a field which is a fraction of the closure field strength, bringing it to within the reach of laboratory fields.

As discussed above, one would expect the NFE state also play a role in determining the band gap in BN nanotubes as it is close to the band edge. In particular, for very large value of the electric field, there is a threshold beyond which the NFE state is ionized (i.e., detached from the tube). This behavior is characterized in our calculations by a tendency of the charge density associated with the NFE state to move as far away as possible from the nanotube walls in the direction opposite to the applied field. We estimate the threshold ionization field to be larger than 0.10 V/\AA for nanotubes that we have studied and it increases slightly with decreasing nanotube diameter. However, this is not an issue for the larger diameter BN nanotubes (which are the most abundantly produced ones) since the values for significant modification of the gap would be well below this threshold.

We have also addressed the issue of the dependence of the effect of transverse electric fields on nanotubes with different chiralities. Figure 3(b) depicts our results from calculations on the (14,0), (17,0) and (21,0) zigzag nanotubes as well as the (16,4) chiral nanotube. The results are organized in the figure as band gap versus nanotube diameter for various electric fields, and we have included the results of armchair nanotubes for comparison. It can be seen that the band gap decreases linearly with increasing diameter for a given electric field, and this behavior is quite independent of the chirality of the nanotube. The states near the band gap for the zigzag and chiral tubes also exhibits charge redistribution similar to that of armchair nanotubes under strong transverse E fields depicted in Fig. 2. These results demonstrate the insensitivity of the band gap modulation effect on the chirality of the nanotube, which would greatly enhance the utility of the approach for tuning the electronic properties of the BN nanotubes.

One may also raise the question of the possibility of electron field emission under electric field strengths required for significant band gap reduction. Experimentally, it has been shown, using electron holography techniques, that the onset of field emission for a carbon nanotube occurs with a local electric field of about 0.064 V/\AA .¹¹ If we extend these observations to boron nitride nanotubes, we see that only the fields calculated for band gap closure in BN nanotubes below 5 nm in diameter are comparable to the above field emission threshold. But the field needed for gap closure drops with increasing nanotube diameter and one can stay well below the field emission threshold by going to larger nanotubes. For example, by extrapolating the linear dependence of the band gap in nanotube diameter for a fixed E field, we predict that a 10 nm diameter nanotube can have band gap closure under a transverse E field of 0.04 V/\AA . Importantly, we expect that the most useful application of such modulation would be to reduce the BN nanotube gaps to normal semiconductor range, which would required proportionally smaller transverse field strength. Due to the spatial separation in the electronic density of the band edge states of the HOMO and LUMO complexes induced by the transverse E field, electrons and holes are localized on distinct regions of the BN nanotube, and this may give rise to interesting transport and thermoelectric properties. The spatial separation of the states

also causes the optical matrix elements between conduction and valence states near the gap to be small.

In summary, we have performed first-principles calculations on BN nanotubes in the presence of a transverse electric field and found that these systems exhibit dramatic decrease in band gap when subject to strong fields. We show that the band gap narrowing arises from a Stark effect among the states which form the HOMO and LUMO subband complexes. With the development of synthesis techniques in mass-producing BN nanotube samples,¹² the effects discussed in this article should be realizable experimentally for the large diameter BN nanotubes, and they may be of impor-

tance as an avenue for tuning the band gap of BN nanotubes for practical applications.

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