Structural Deformation and Intertube Conductance of Crossed Carbon Nanotube Junctions

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We present a first-principles study of the structure and quantum electronic conductance of junctions consisting of two crossed (5, 5) single-walled carbon nanotubes. The structures are determined by constrained minimization of total energy at a given force between the two tubes, simulating the effects of substrate-tube attraction or an applied force. We find that the intertube contact distance is very sensitive to the applied force in the range of 0–10 nN. The intertube conductance is sizable for realistic deformation expected from substrate interaction. The results explain the recent transport data on crossed nanotubes and show that these systems may be potentially useful as electromechanical devices.

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Carbon nanotubes have drawn intense research efforts due to their unique structural and electronic properties since their discovery about a decade ago [1]. For example, nanotubes have high material strength and extraordinary flexibility [2], and they are metallic or semiconducting depending sensitively on their radii and chiralities [3–5]. Because of their unusual strength and electrical properties, carbon nanotubes have been proposed as molecular electronic devices such as field-effect transistors [6,7], single-electron-tunneling transistors [8,9], and rectifiers [10–13]. In addition, they may be used as molecular wires which interconnect molecular-scale objects. For example, a topological defect consisting of a 5-atom ring and 7-atom ring pair can join two different half-tubes to form metal-semiconductor, semiconductor-semiconductor, or metal-metal junctions [10,14]. The electronic properties of such on-tube junctions have already been studied theoretically [10,15,16], and the existence of these junctions has been experimentally verified [11,12].

Recently, crossed carbon nanotube junctions have been made and shown to exhibit properties potentially applicable for molecular electronic devices [13]. This type of junction is formed by single-walled carbon nanotubes (SWNTs) crossing each other on a substrate, and easier to fabricate than the on-tube [10,14–16], T [17], or Y junctions [18]. In crossed-tube junctions, one can control intertube distances by applying a pressure using, for example, an atomic force microscope (AFM) tip. The intertube conductance is expected to change with varying intertube distance, which may be useful for application in electromechanical devices. A junction under pressure would result in a change in the overlap of wave functions and structural deformation. A large overlap of wave functions will favor intertube tunneling, but a large structural deformation may reflect back the incident current because such deformation would act as a strong scatterer.

To address these issues, a first-principles study of both the structure and the conductance of the system is necessary. The structure needs to be accurate, since the interatomic distance between carbon atoms across the different tubes will play a key role in determining the intertube conductance. First-principles calculations are desirable because accurate wave functions and Hamiltonian matrix elements are required to describe quantitatively the small intertube and large intratube conductances simultaneously.

We calculate the crossed-tube junction conductance employing an *ab initio* pseudopotential density functional approach with a linear combination of atomic orbitals (LCAO) basis [19]. We use norm-conserving pseudopotentials [20] in the Kleinman-Bylander form [21]. An exchange correlation functional in the generalized gradient approximation (GGA) is used [22]. We expand the wave functions in a double zeta basis set with an energy cutoff (for real space mesh points) of 70 Ry for structural relaxations and in a single zeta basis set with an energy cutoff of 80 Ry for conductance calculations. Test calculations show that the basis set is able to reproduce accurately the bond length of graphene as well as the interlayer distance between the graphite planes. The calculated binding energy of graphite within the GGA is 6.9 eV per carbon atom as compared to the experimental value of 7.4 eV per atom.

We consider a resistive junction region and four perfect regions (metallic leads) composed of semi-infinite perfect carbon nanotubes. The LCAO Hamiltonian matrix elements for each region are obtained from *ab initio* calculations, and matched at the boundaries. Incident electrons are described by Bloch eigenstates of a perfect carbon nanotube. After the Hamiltonian matrix elements between basis orbitals at the resistive junction regions and semi-infinite perfect regions are determined, we set up the inhomogeneous linear equations for scattering states. Scattering-state solutions at a given energy are used to determine the desired transmission coefficients used in the conductance calculation within the Landauer-Büttiker formalism [23,24]. The junction is modeled to consist of two (5, 5) SWNTs crossing at a 90° angle.

In the experimental devices [13], we expect that the strong adhesion of the SWNTs to the SiO_2 substrate

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generates a significant contact force between the two crossed SWNTs. For a crossed junction composed of SWNTs of the experimental diameter of 1.4 nm, this contact force has been estimated to be about 5 nN [25]. To mimic a similar deformation for our (5, 5) crossed-tube junction, one would need a contact force about 15 nN [26]. We have performed a complete study of the conductance as a function of the contact force. In our calculation, the junction geometry is determined by performing a constrained total energy minimization in a supercell, in which we fully relax the position of the atoms near the junction while fixing the center-to-center intertube distance at the boundaries to produce the desired contact force. To establish a reference, we first calculate the conductance of a crossed-nanotube junction in free space, where the walls of the SWNTs at the closest point of contact are at the van der Waals distance (3.34 Å) away from each other. To obtain the geometry for the finite force case, we reduce the center-to-center intertube distance until the relaxed structure has a given contact force between the two SWNTs. For example, at a contact force of 15 nN, the closest atomic separation between the two (5, 5) SWNTs is reduced by 20% from the van der Waals distance.

Figure 1 shows the relaxed structure of a (5, 5) crossed-tube junction with a center-to-center intertube distance of 7.4 Å which produces a contact force of 15 nN. In the calculation for the junction geometry, we include 320 atoms in the supercell, corresponding to two segments of the SWNT, each containing 160 atoms, and relax the 240 atoms closest to the junction area. In Fig. 2, the calculated contact force and contact distance are plotted as functions of the center-to-center intertube distance. The contact distance is defined to be the shortest distance between atoms at different tubes.

As in graphite, the tubes repel each other at the junction area when the contact distance is below 3.34 Å. In the experiment [13], this repulsive force is balanced by the attractive force between the tube and the substrate. For the (5, 5) crossed-tube junction, our results show that the contact distance saturates at near 2.5 Å for contact force exceeding 10 nN. (See Fig. 2.) This arises because, below a critical contact distance, the repulsive part of the interlayer potential behaves "hard-wall"-like, as in any closed-shell system. The junction responds to any further increase in applied force by flattening the tube over a large area of deformation rather than reducing the contact distance. Hence, although the contact distance is a steep function of the contact force (or center-to-center intertube distance) in the range of 1–10 nN, it becomes rather insensitive to the force afterwards.

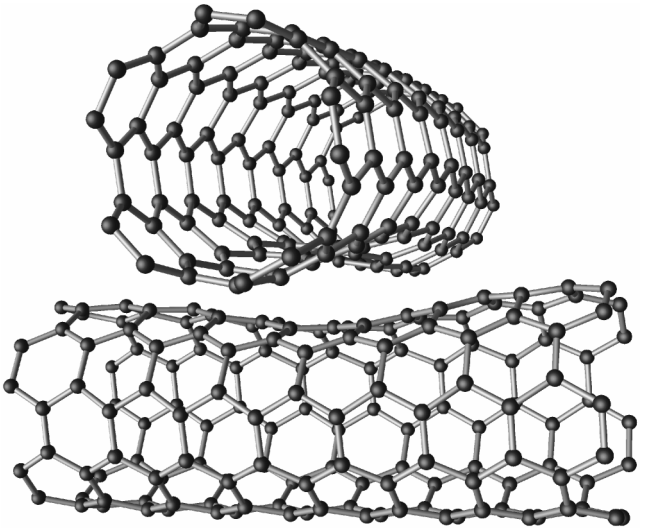

FIG. 1. Structural relaxation of a (5, 5) crossed carbon nanotube junction with a 15 nN contact force.

Once the structure is known, the calculated self-consistent Hamiltonian matrix elements may be used to calculate the linear-response conductance of the crossed-tube junction by using the Landauer-Büttiker formula [23,24]. The intertube and the intratube conductance is calculated as a function of the energy of an incident electron for a 4-terminal device in a 4-terminal 4-probe measurement setup. If we denote the lead pairs of single tubes by (1, 2) and (3, 4), respectively (see Fig. 3), then the 4-terminal 4-probe intertube conductance can be written in the following manner:

$$G_{13,24}(\text{4-terminal 4-probe, intertube}) = \frac{I_1}{V_2 - V_4} = \frac{\alpha_{11}(\{T_{ij}\})\alpha_{22}(\{T_{ij}\}) - \alpha_{12}(\{T_{ij}\})\alpha_{21}(\{T_{ij}\})}{\alpha_{21}(\{T_{ij}\})}, \quad (1)$$

where $\alpha_{lm}(\{T_{ij}\})$'s are defined in Ref. [24]. Intertube conductance refers to the 4-terminal 4-probe intertube conductance throughout this paper unless otherwise stated. When there is no magnetic field, $\alpha_{ij} = \alpha_{ji}$, and $G_{ij} = G_{ji}$, with $G_{ij} = \frac{2e^2}{h}\,\mathrm{Tr} t_{ij}^{\dagger} t_{ij} = \frac{2e^2}{h} N_j T_{ij}$. Here G_{ij}, t_{ij}, and T_{ij} denote the 2-terminal conductance, transmission coefficient, and average transmission probability from terminal j to terminal i in a multichannel configuration, respectively, and N_j is the number of channels in terminal j not including spin degeneracy. Since the 2-terminal intratube conductance is expected to be much greater than the 2-terminal intertube conductance G_{ij}, the 4-terminal 4-probe intertube conductance can be approximated to first order by the sum of four 2-terminal intertube conductances determined by transmission coefficients. That is, when the 2-terminal intertube conductances (G_{13}, G_{14}, G_{23}, and G_{24}) in Fig. 4 are small compared to the 2-terminal intratube conductances (G_{12}, G_{34}), the following relation holds to first order for the 4-terminal 4-probe intertube conductance:

$$G_{13,24}(\text{4-terminal 4-probe, intertube}) \approx G_{13} + G_{14} + G_{23} + G_{24}. \quad (2)$$

Figure 3 gives the calculated 4-terminal 4-probe intertube conductance for the (5, 5) crossed-tube junction. The

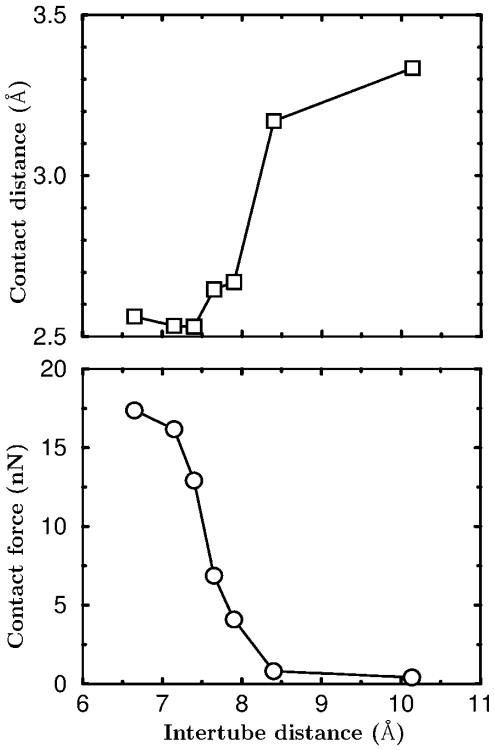

FIG. 2. Calculated contact distance and contact force as functions of the center-to-center intertube distance for a (5, 5) crossed-tube junction.

4-terminal 4-probe conductances calculated in different configurations (i.e., between 1 and 3 or 1 and 4) are essentially the same [27]. In Fig. 3, the average of the absolute values of the 4-terminal 4-probe conductances [Eq. (1)] of different configurations and the results from the approximation above [Eq. (2)] are compared. The agreement between the two curves in Fig. 3 near the Fermi level shows that the 4-terminal 4-probe intertube conductance near the Fermi level can be sizable even though the 2-terminal intertube conductances are small.

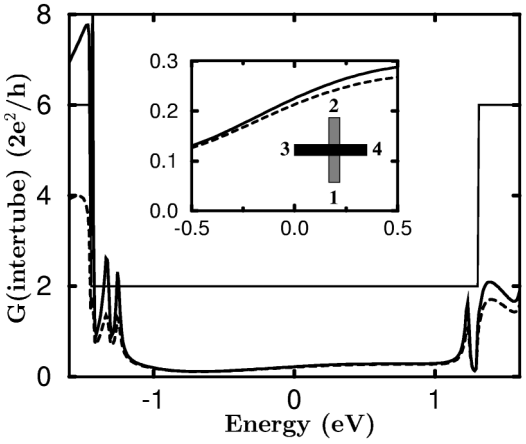

FIG. 3. Calculated intertube conductance of a (5, 5) crossed-tube junction with a center-to-center intertube distance of 7.4 Å as a function of the energy of the incident electron. The thin solid line indicates the intratube conductance of a single perfect tube. The thick solid line is the 4-terminal 4-probe intertube conductance from the Landauer-Büttiker formula. The dashed line is calculated from the sum of four intertube transmission coefficients (see text). The inset shows an expanded view of conduction near the Fermi level and terminal indices.

So far, we have presented the results with relaxed geometries starting from a specific initial configuration in which one carbon atom of one tube is located directly on top of an atom of the other tube, defining the contact point and the contact distance. We have also calculated relaxed geometries and conductance starting from a different initial orientation in which the center of a hexagon of one tube is directly over the center of a hexagon of the other tube. No significant difference has been found between the two sets of calculations.

For contact forces considered in Fig. 4, our calculated intertube conductance is of the same order as those measured for the experimental metallic junctions [13]. For the zero-force junction, we find an intertube conductance of approximately 2 orders of magnitude lower than the observed conductance, showing the importance of the junction deformation. The intertube conductance also has a nontrivial dependence on the contact force or distance. For example, as shown in Fig. 4, a smaller contact distance results in a larger intertube conductance, as expected from a larger overlap of wave functions; however, the dependence is not exponential. The junction conductance is a consequence of an interplay between intratube and intertube transmissions, both of which depend on the entire

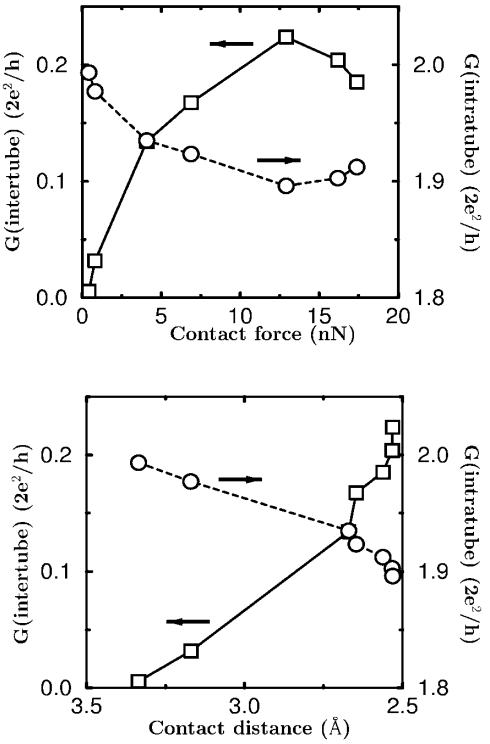

FIG. 4. Calculated intertube and intratube conductances as a function of contact force or contact distance for a (5, 5) crossed nanotube junction. Solid (dashed) lines and left (right) y-axis indicate intertube (intratube) conductances.

deformation region at the junction. One interesting potential application of these systems is that one can tune the intertube conductance mechanically by applying a force on the junction area. This may be realized, for example, with AFM tips. The junctions may then be used as nanoscale electromechanical devices.

Another interesting result from the calculations is that, for the relaxed structures considered, the intertube currents are found to be larger than the backscattered currents for states near the Fermi level. The implication is that, at a moderate contact force, electrons can easily tunnel from one SWNT to the other, whereas backscattering by the junction is more or less suppressed. The suppressed backscattering is consistent with the findings in Ref. [28].

In summary, we have presented a first-principles study of the intertube conductance of crossed carbon nanotube junctions. The electronic and geometric structures for a fixed contact force (or center-to-center intertube distance) are determined self-consistently by using a constrained total energy minimization approach. The intertube conductance is found to depend globally on the overall structural deformation of the junction. For moderate contact forces, a smaller contact distance corresponds to a greater intertube conductance. Thus, the role of the tube-substrate interaction is important in understanding the recent experimental results on the crossed-tube junctions. The sensitivity of the junction conductance to the contact force makes these crossed-tube structures potentially useful for nanoscale electromechanical devices.

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