Nanotube-Metal Junctions: 2- and 3-Terminal Electrical Transport

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We address the quality of electrical contact between carbon nanotubes and metallic electrodes by performing first-principles calculations for the electron transmission through ideal 2- and 3-terminal junctions, thus revealing the physical limit of tube-metal conduction. The structural model constructed involves surrounding the tube by the metal atoms of the electrode as in most experiments; we consider metallic (5,5) and n-doped semiconducting (10,0) tubes surrounded by Au or Pd. In the case of metallic tubes, the contact conductance is shown to approach the ideal $4e^2/h$ in the limit of large contact area. For three-terminals, the division of flux among the different transmission channels depends strongly on the metal material. A Pd electrode has nearly perfect tube-electrode transmission and therefore turns off the straight transport along the tube. Our results are in good agreement with some recent experimental reports and clarify a fundamental discrepancy between theory and experiment.

Carbon nanotubes (CNTs) have received extensive experimental attention for more than a decade1,2, and are considered a possible basis for nanoelectronic technology independent of silicon. A major issue is the quality of CNT/metal contacts: obtaining the minimum contact resistance is critical to access the intrinsic electric properties of CNTs. Despite extensive experimental effort to improve the contact transparency and reveal the relevant factors behind it – metal material, contact structure, and type of tube, for instance – a clear picture is still not available.

On the theoretical side, it is highly desirable to be able to simulate from the first principles the electron transport through CNT/metal junctions and thus improve our understanding of this important issue. So far, first-principles studies of the contact transparency between metallic CNTs and metals have been carried out [(3,3), (4,4), or (5,5) tubes with Al, Au, or Ti, for instance]3,4,5,6,7. The results are, however, quite scattered, and agreement between theory and experiment has not yet been achieved: For Al electrodes, an equilibrium conductance of $\sim 1 G_0 (= 2e^2/h$, the conductance quantum) was found by some calculations8,9, while $\sim 2 G_0$ was found by another. For Ti electrodes, 1.7 $G_0$ was obtained by one calculation10,11 and $\sim 1.2 G_0$ by another12, while experiment found $\sim 2 G_0$. For Au electrodes, a recent calculation13 showed $\sim 1 G_0$ while a value of 1.5 $G_0$ was found experimentally14. On the other hand, a model calculation15 using a jellium model for the electrode even showed that the ideal CNT/metal conductance will not be larger than 1 $G_0$. With regard to the metal used, it was found theoretically that Ti is better than either Au or Al for contact transparency. On the other hand, experimentally, Pd, for which no theoretical calculation is available, was found superior to Ti16.

It has been unclear how to explain these discrepancies. One possible reason, as is supported by this work, is the difference in contact structure between theory and experiment. In all these calculations, simplified contact models were adopted due to computational cost or methodology: On the carbon side, the tube-metal connection is made by either straight $\sigma$-bonds from the tube end or $\pi$-bonds from the side of the tube, while the metal is modeled by a thin nanowire or small cluster. However, in most experimental situations, a tube is surrounded by metal atoms12,13,14,15,16,17. As the contact structure and quality changes from case to case, experimental results are also scattered. In such a situation, the key contribution to be made by theory is to reveal the physical limit to which experimental measurement may approach by improving the contact quality.

Furthermore, compared to metallic CNTs, semiconducting CNTs are much more important for potential electronic applications. This naturally raises the issue of contact transparency between doped semiconducting tubes and metal junctions. In addition, electron transport through multi-terminal structures is a key property in moving toward applications. Neither of these fundamental issues has been tackled previously, to the best of our knowledge, using first-principles calculations.

In this paper, we first construct a better structural model of an ideal contact, as shown in Fig. 1 for the device region, in which an infinitely long tube is surrounded by metal atoms of an electrode. We use this structural model, first, to investigate the two-terminal tube-metal transparency, $T_{\text{2-term}}$, (from terminal 1 to 3), obtaining the physical limit of tube-metal conductance for an ideal contact. Second, we then study three-terminal electron transport by including explicitly the self-energies of all the leads shown in Fig. 1. Specifically, we investigate the division of current among transmission straight-through the junction, probability to turn the corner, and reflection. In both 2- and 3-terminal cases, we consider...
consider the dependence on the contact quality (simulated by the width of the metal electrode), the metal material, and the type of tube (metallic or semiconducting).

The structural model (Fig. 1) can be regarded as an ideal CNT-metal junction because of three features: (1) The tube is perfect and infinitely long, thus eliminating the quantization in the transport direction which bedevils calculations using a short CNT segment. (2) The tube is surrounded by metal atoms, as is usual in experiments. (3) The large active region around the contact ensures that the tube-metal interaction is fully included.

Contact quality will depend experimentally on the number of good carbon-metal connections, which is essentially determined by whether the metal wets the CNT surface. If the metal (like Au) does not wet the CNT surface, there will be few connections even though the electrode is large. In our models, because of the ideal structure, the number of good carbon-metal connections is substantial even for a small electrode (Fig. 1 top view). As a proxy, we change the number of good carbon-metal connections by adjusting the contact width, in this way simulating the changing contact quality.

We consider three widths for the metal electrodes – 3, 5, and 7 atomic layers (denoted by 3L, 5L, and 7L) – and two kinds of metals – Au and Pd. The electronic states of the two electrodes are very different: Au has active s states while Pd has only d states. We consider three kinds of CNTs: (5,5), (10,0), and Na-doped (10,0) – denoted Na@(10,0) hereafter – in which dopant Na atoms are adsorbed periodically on the inner surface of the tube. [The adsorption position is determined by minimizing the atomic force on the Na atom and is found to be slightly off the tube axis and approximately above one of the C atoms.] The concentration is one Na atom per 40 C atoms. Because of the large charge transfer from Na to the tube (∼0.7 electrons per Na atom by Mulliken population analysis), the (10,0) tube is therefore heavily n-doped.

The electronic structure of the junctions is calculated by density functional theory (DFT) using periodic boundary conditions and a localized basis set with a finite range. In the device region, as shown in Fig. 1 the number of atoms included is ∼350 – 500, depending on the metal width and material. The large dimensions (see Fig. 1 (top view)) ensure that the separation among the tube and its images is larger than 12Å which is much larger than the range of the basis functions used. As a result, a good convergence with respect to the lateral dimensions can be expected. The convergence with respect to the length of the tube in the device region is also found good, as will be discussed later.

We adopt a DFT supercell which is larger than the device region shown in Fig. 1 for all the different systems: ∼500 – 700 atoms are included, depending on the electrode width and material. To avoid too expensive computational cost, a single-zeta plus polarization basis set (SZP) is adopted for all atomic species. Our test calculation for a small system shows that the use of SZP results in only minor differences from results using a higher-level double-zeta plus polarization basis set. We use optimized Troullier-Martins pseudopotentials for the atomic cores and the PBE version of the generalized gradient approximation for the electron exchange and correlation. The contact atomic structure is optimized by eliminating the atomic forces on the atoms around the contact region, i.e., the carbon atoms underneath the metal and the metal atoms contacting the tube. The relaxation is found quite small (see Fig. 1 (top view) for the (5,5)-Au system) because of the choices of the tubes, (5,5) and (10,0), and the orientation of the metals, (001).

Electron transport through the CNT-metal junction is calculated using a Green function method in which the device region and the leads (not shown in Fig. 1) are treated exactly on the same footing. The retarded Green function of the device region, $G_D(E)$, is determined by the Hamiltonian given by DFT [$H_D$] combined with the self-energies for the semi-infinite leads [$\Sigma_i(E)$]:

$$G_D(E) = \left[ E S_D - H_D - \sum_{i=1}^{N_t} \Sigma_i(E) \right]^{-1} ,$$

where $N_t$ is the number of leads or terminals. The transmission at any energy, $T(E)$, is calculated from the Green function, and the conductance, $G$, then follows from a Landauer-type relation. We adopt the following notation: $T_{2\text{term}}$, is the two-terminal transmission between tube and metal (terminals 1 and 3) without electrode 2 attached, which means that the tube on the right side of Fig. 1 (side view) is somehow terminated and all the electron wave entering that part of tube will be totally reflected. $T_{\text{straight}}$ is the transmission straight through the junction from tube to tube, $T_{\text{turn}}$ is the tube-to-metal transmission with the presence of electrode 2, and $R$ is reflection from the tube back to itself.

In Fig. 2 we show the transmission $T_{2\text{term}}(E)$ for the (5,5)-Au and (5,5)-Pd junctions with different widths of the metal.
FIG. 3: Three-terminal transmission functions $T_{\text{straight}}(E)$, $T_{\text{turn}}(E)$, and $R(E)$ for (5,5)-Au [first column, (a)-(c)] and (5,5)-Pd [second column, (d)-(f)]. The width of the metal electrode is indicated in the legends. Also plotted is the transmission function of a pure (5,5) tube as a comparison (dashed). The Pd traces converge much more quickly than those for Au.

...electrodes. As a comparison, $T(E)$ for the pure (5,5) tube is also plotted; it shows, as expected, perfect steps and two channels around the Fermi energy. Note that throughout this work the position of the Fermi energy is set to be exactly the same as in the pure tube. This is required since very far from the device region the tube (lead) is completely charge neutral.

In Fig. 2 the dependence of $T_{\text{term}}(E)$ on the electrode width for the two metals is clear: For Au, the dependence is strong. In contrast, for Pd the dependence is much weaker: the overall shape of $T_{\text{term}}(E)$ for the three widths is similar, and the result is nearly the same for 5L and 7L. This result for Pd also indicates that in our calculation the convergence with respect to the length of the tube included in the device region is good. Despite the difference in width dependence, the equilibrium conductance, $G$, of both systems increases with increasing electrode width: for the thinnest, hence poor quality, electrode $G \sim G_0$, while it approaches the physical limit of $2G_0$ for the widest electrode.

Even the widest electrode (7L) considered here is, of course, still much thinner than those used in experiments. However, our calculation bears on real experimental situations because the number of good carbon-metal connections may be similar in that the contact structure considered here is perfect while in real experimental situations it is usually far from perfect. For example, Au is thought not to wet the tube surface but rather will form nanoparticles near the surface. As a result, although the Au electrode can be very wide, the tube will pass through the space between these Au nanoparticles with very few good C-Au connections formed. In this case increasing the diameter of the tube will improve the contact quality as more C-Au connections will be formed and, therefore, increase the conductance. In fact, a recent experiment using tubes with different diameters shows that a larger diameter yields a larger conductance. Obviously, increasing the electrode width here is similar to increasing the tube diameter: both increase the number of C-Au connections and so increase the conductance. A key result here is that for good contact quality, the equilibrium conductance approaches the physical limit of $2G_0$ for both Au and Pd. This finding differs from a previous first-principles calculation which used a short segment of tube contacted by two Au electrodes through several carbon-$\pi$ bonds, and also differs from a previous model calculation which shows that CNT/metal conductance will not be larger than $G_0$, but is consistent with recent experiments.

The three-terminal transmission in the (5,5)-metal case is shown in Fig. 3 for the different metal widths. [Note that reflection $R(E) = T_{\text{tube}}(E) - T_{\text{straight}}(E) - T_{\text{turn}}(E).$] For the
For the undoped (10,0)-Au system, the Fermi energy is at the Na@(10,0) tube alone and for the undoped (10,0)-Au system. First, electrode material than Au. The electronic states: The Pd electrode dominates. This feature is in very good agreement with a recent experimental showing that a Pd electrode suppresses inner electron transport through the tube. For Au, $T_{\text{turn}}$ is also larger than $T_{\text{straight}}$ but they are still comparable and the latter is not turned off.

In Figs. 3, we see that for Au the apportioning of transmission among the different components depends significantly on the electrode width: For small width, $T_{\text{straight}}(E)$ and $T_{\text{turn}}(E)$ are comparable around the Fermi energy, while for the widest electrode (7L), $T_{\text{turn}}(E)$ begins to dominate due to the improved contact quality. In the Pd system, the convergence as a function of width is much faster (as for the two-terminal case Fig. 2); indeed, one sees only minor changes between the curves. This quick convergence indicates that the carrier injection takes place mainly at the very edge of the junction, being consistent with the experimental observation. Thus for Pd, the contact quality is already good (i.e., the width is large enough) even though the junction is very thin. Since the contact structure is the same, this difference between Au and Pd electrodes is due to their different electronic states: The Pd d states have stronger interaction with C p states than Au s-d states. As a result, Pd is a better electrode material than Au.

Two additional features of Figs. 3 are worth comments. First, $T_{\text{turn}}(E)$ is always smaller than the two-terminal result $T_{\text{2term}}(E)$ of Fig. 2. This is reasonable since in the three-terminal case some of the initial flux escapes into electrode 2 while for two terminals that flux will be totally reflected. Second, the reflection increases in all cases near the energies where more modes start to propagate in the pure tube. These are examples of threshold singularities.

We now turn from metallic tubes to discussing the doped (10,0) semiconducting tube. The doping is achieved by adding Na atoms periodically on the inner surface of the (10,0) tube with a high concentration as described earlier. For comparison, the transmission is shown for two additional cases: $T_{\text{2term}}(E)$ for the Na@(10,0) tube alone and for the undoped (10,0)-Au system. For the undoped (10,0)-Au system, the Fermi energy is at the middle of the gap because one of the leads is the semiconducting (10,0) tube. After the tube is n-doped, its Fermi energy enters the conduction band, and the transmission through the Na@(10,0) tube in the absence of any metal has a value of 2 around the Fermi energy. As in the metallic case, here the Pd electrode results in a larger two-terminal conductance $(0.79 \, G_0)$ than the Au electrode $(0.56 \, G_0)$. Both are smaller than the two-terminal conductance of the (5,5) systems.

An interesting feature of the results in Fig. 4 is that $T_{\text{2term}}(E)$ for the doped Na@(10,0)-Au case is approximately a constant shift of that for the undoped (10,0)-Au system. Thus the role of the dopants is mainly to give electrons to the tube, and therefore to shift its Fermi energy, without noticeably altering the electronic structure of the tube. Our calculations indicate this is a general rule of thumb. Following this idea, we can approximately get the two-terminal conductance of a p-doped (10,0)-metal junction by simply shifting the Fermi energy slightly into the valence band (to around $-1$ eV in Fig. 4). For a Pd electrode, this p-type conductance is about $1 \, G_0$ which is in good agreement with a recent experimental report where the Fermi energy of a semiconducting CNT contacted by Pd electrodes was shifted into the valence band by applying a back gate [see Fig. 1 (c) in Ref. 24].

The three-terminal transmission functions for the semiconducting tubes cases are shown in Fig. 5. For Na@(10,0)-Au, the straight-through and tube-metal transmission around the Fermi energy are comparable, just like for the corresponding (5,5) system [Fig. 2(b)]. Both of them are, however, much smaller than the reflection because the Fermi energy now is at the edge of the gap. For a Pd electrode, on the other hand, $T_{\text{turn}}$ is comparable to the reflection, near the Fermi energy, and both of them are much larger then the straight-through transport. Therefore, for an n-doped semiconducting (10,0) tube, the Pd electrode turns off conduction through the tube, just like for the metallic (5,5) tube.

FIG. 4: Two-terminal transmission, $T_{\text{2term}}(E)$, with semiconducting tubes: (a) Na@(10,0)-Au and (b) Na@(10,0)-Pd systems with an electrode width of 5L. The transmission function of the bare Na@(10,0) tube is shown in each panel for comparison; in addition, (a) includes $T_{\text{2term}}(E)$ for the undoped (10,0)-Au system.

widest case (7L) (see Figs. 3(a) and (d)) a striking feature of the result for Pd is that the straight-through transmission is almost turned off while transmission into the metal electrode dominates. This feature is in very good agreement with a recent experimental showing that a Pd electrode suppresses inner electron transport through the tube. For Au, $T_{\text{turn}}$ is also larger than $T_{\text{straight}}$ but they are still comparable and the latter is not turned off.
In summary, we have calculated transmission through both 2- and 3-terminal CNT-metal junctions using an ideal structure in which the tube is surrounded by a Au or Pd electrode. In this way we have established the physical limit to which experiments will approach by improving the contact quality.

The main quantities studied are the contact transparency in the case of two-terminal systems and the division among the different transmission coefficients for three-terminals. The two main findings are:

1. For two-terminal junctions, when the tube is metallic the conductance will approach $2G_0$ as the contact quality improves, while for the doped semiconducting tube systems, the conductance is about $1G_0$. In both cases, Pd is better than Au for contact transparency.

2. For three terminal junctions, the relative magnitude of the different types of transmission depends significantly on the metal material. The “better” Pd electrode yields near perfect transmission between the tube and electrode and, therefore, turns off the straight transport through the tube for both the (5,5) and Na @(10,0) tubes.

Our results are in good agreement with recent experiments and clarify a fundamental discrepancy between theory and experiment.

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