Comment on "Curvature effects on electronic properties of small radius nanotube" [Appl. Phys. Lett. 91, 033102 (2007)]

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Zeng *et al.*[1] studied curvature effects in (2,2) and (3,3) carbon nanotubes using the density functional theory/nonequilibrium Green's function (DFT/NEGF) approach. The main conclusions were that due to curvature effects, the (2,2) nanotube is a semiconducting tube with an energy gap of 0.68 eV and the (3,3) tube exhibits a negative differential conductance at a bias of ± 1.8 V.

The purpose of this comment is to demonstrate that a different conclusion about the properties of a (2,2) tube can be reached by choosing a different basis set for the simulations. Also, the length of the electrodes used can significantly affect the results. Further, the use of a polarized basis set for a (3,3) tube indicates an extended range over which there is a negative differential conductance.

Figure 1 in Ref. 1 shows the simulated structures for the two aforementioned tubes in the central region of a two-probe system. Each of the electrodes consists of just one period (0.2463 nm) of each tube. An important assumption in the DFT/NEGF approach is that the electrodes are semi-infinite, meaning that the electrodes are assumed to be repeated infinitely in the transport direction and that they have bulklike properties.[2] The short electrodes described above may well allow an interaction between the central region and the repeated images of the electrodes. To verify this, we simulated the structures with four periods of each tube in the central region and the same short electrodes using the package ATOMISTIX.[3] In Ref. 1, the basis set used is not mentioned so we started with the single-zeta (SZ) basis set (the simplest available basis set in ATOMISTIX) within the local density approximation that was used in Ref. 1. The results for the transmission coefficient as a function of energy are shown in Fig. 1, and the 0.68 eV gap of the (2,2) tube is exactly reproduced. The simulations were repeated with the same basis set but the electrode length was increased to two periods (0.4926 nm). The results are also shown in Fig. 1 and the corresponding gap is only 0.39 eV. Fixing the length of the electrodes and using the double-zeta (DZ) basis set gives a very narrow gap of 0.1 eV. Finally, including polarization by using both the SZ polarized (SZP) and the DZ polarized (DZP) basis sets shows a metallic tube with a zero gap rather than a semiconducting tube with a sizable bandgap, as predicted using the input parameters in Ref. 1. In fact, including polarization in the basis set is essential to accurately describe high-curvature effects.[4] Taking into account all of the above, we suggest that inclusion of polarization in the basis set is necessary for accurate simulation of very small-radius tubes, such as the (2,2).

We note that the DZ set is more complete than the SZP set,[3] and it predicts a small-bandgap tube while the SZP predicts a zero-gap metallic tube, as does the DZP set. This implies that the results of the polarized sets cannot be due to any overcompleteness of the DZP set but rather are a result of the polarization *per se*. Moreover, barring overcompleteness in the basis set, the total energy of the system (E_{tot}) should decrease using a more complete basis set, i.e., E_{tot} is *variational* with the number of basis functions.[5] Indeed, E_{tot} was -1098.188 Ry for the SZ set, -1104.014 Ry for the SZP set, -1107.034 Ry for the DZ set, and -1109.838 Ry for the DZP set. This assures that the DZP set is not overcomplete. We also calculated E_{tot} using the DZ double-polarized (DZDP) basis set and found it to be -1109.143 Ry, i.e., it is larger than that predicted by the DZP basis set. This suggests that the DZDP basis set would be an overcomplete basis set for this system.

Regarding the second conclusion in Ref. 1, performing the current-voltage calculations using a DZP basis set for a 12-unit-cell (3,3) tube does indeed indicate a negative conductance, though it extends over two voltage ranges: -2 to -1.28 and 1.28 to 2 V, instead of the narrow ranges around ± 1.8 V, as mentioned in Ref. 1.

In conclusion, we have demonstrated that the input simulation parameters can have a profound effect on the results of *ab initio* simulations. We suggest that inclusion of the polarization in the basis set is necessary for accurate simulation of very small-radius nanotubes, and we point out that overcompleteness is not a problem with (2,2) tubes when using a DZP basis set.

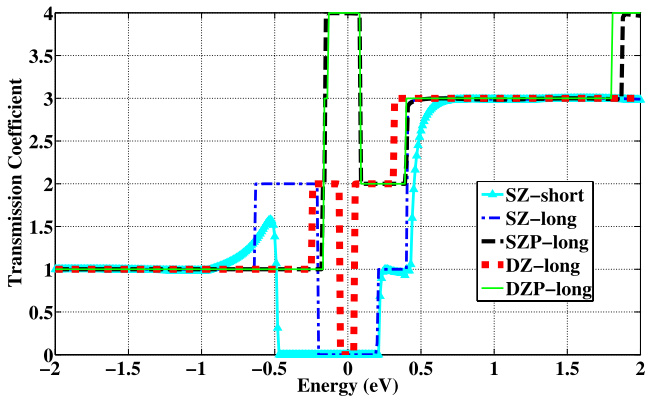

FIG. 1. (Color online) Transmission coefficient vs energy for the (2,2) tube with different basis sets and both short and long electrodes.

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