Electron transport in molecular systems

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Abstract. Large-scale quantum electronic structure calculations coupled with non-equilibrium Green function theory are employed for determining quantum conductance on practical length scales. The combination of state-of-the-art quantum mechanical methods, efficient numerical algorithms, and high performance computing allows for realistic evaluation of properties at length scales that are routinely reached experimentally. Two illustrations of the method are presented. First, quantum chemical calculations using up to $10^4$ basis functions are used to investigate the amphoteric doping of carbon nanotubes by encapsulation of organic molecules. As a second example, we investigate the electron transport properties of a Si/organic-molecule/Si junction using a numerically optimized basis.

1. Introduction

Present day semiconductor devices are approaching their physical limits, prompting a growing number of researchers across multiple disciplines to attempt to devise innovative ways for decreasing the size and increasing the performance of microelectronic circuits. One possible route is based on the idea of using molecules and molecular structures as functional electronic devices. This research and development field, known as molecular electronics, promises to substantially decrease the size and improve the performance of electronic devices by taking advantage of the intrinsic size of molecules and quantum mechanical effects that dominate at the nanometer scale.

We have coupled large-scale quantum electronic structure calculations with a Green’s function formulation for determining the quantum conductance at the nanoscale. The difficulty associated to the study of open systems is tackled using two different approaches. The first technique is based on recasting all-electron quantum chemistry calculations on finite systems into infinite, non-periodic systems, thereby mimicking actual working devices (Sect. 2). The second technique is based on multigrid-based periodic calculations employing a real-space grid as a basis (Sect. 3). In this case, the electron-ion interactions are represented by nonlocal, norm-conserving pseudopotentials. Both approaches have in common to allow for large scale calculations in terms of number of atoms or basis functions and therefore allow for realistic evaluation of properties at length scales that are routinely reached experimentally.
Figure 1. Electronic properties (density of states and quantum conductance, respectively) of pristine (10,10) single-walled nanotube ((a) and (d)), and n-doped TDAE ((b) and (e)) and n-doped TTF ((c) and (f)) molecules encapsulated in a (10,10) nanotubes.

2. Transport properties of doped carbon nanotubes
While electronic transport in carbon nanotubes has been shown to be ballistic, practical realizations of new nanotube-based electronic devices hinge on a number of outstanding problems, such as the capability of achieving large-scale air-stable and controlled doping. Recent experimental evidence [1] suggests that amphoteric doping of single-walled carbon nanotubes (SWCNTs) might be achieved by encapsulating organic molecules possessing different electron affinities and ionization energies.

All-electron density function theory (DFT) calculations of hydrogen terminated (10,10)-SWCNTs with encapsulated organic molecules were performed using NWChem [3] within the local density approximation (LDA). A number of different atom centered, contracted Gaussian basis sets were used along with charge density fitting of the Coulomb potential during the calculation of the self-consistent solution. The initial starting geometries for the different SWCNT-based systems were obtained by first optimizing the geometry of the individual molecules using DFT (LDA) followed by optimizing their orientation inside a fixed (10,10) SWCNT geometry using molecular mechanics and a suitable potential. Organic molecules studied are TTF (Tetrathiafulvalene), F4TCNQ (Tetrafluorotetracyano-p-quinodimethane), and TDAE (Tetrakis(dimethylamino)ethylene). The ionization energies for these molecules are, 6.4, 9.5, and 5.4 eV, respectively. It is clear that molecules possessing the lower ionization energies (TDAE, TTF) tend to increase the Fermi energy (compared to that of a bare (10,10) tube) while
that with the highest ionization energy tends to decrease it. These changes correspond to the well-known effect related to n- and p-type doping, respectively. We verified that the observed trends are consistent with increasing basis set size and with orientation of the molecule [2].

In addition, we have computed the transmission properties of electrons coming from a perfect semi-infinite tube through a doped nanotube section and further down another semi-infinite nanotube. Density of states and quantum conductance through a nanotube n-doped with a TDAE molecule are shown on Figs. 1(b) and (e), respectively. Corresponding information for a TTF n-doped nanotube is shown on Figs. 1(c) and (f). Interestingly, we see that the conductance spectra, in each case, still display the same overall shape that the one of a pristine tube with a noticeable slight reduction of the plateau at Fermi energy. This reduction arises from partial reflection, by the physisorbed molecule, of the two Bloch states originating in the nanotube lead. It is however small enough to infer that we keep a good conductor. The robustness of the eigenchannels originating from a defect-free tube and passing through the modified region constitutes a clear indication of the possibility of realizing complex carbon nanotube based nano-electronics by using organic molecules as dopants.

These results complement the experimental evidence provided by Takenobu et al [1] by showing how the electronic structure of a carbon nanotube can be manipulated by encapsulating organic molecules. Charge transfer processes induced by encapsulated organic molecules can lead to efficient n- and p-type doping of a single-walled carbon nanotube. It is promising that, even though a molecule can induce p- and n-doping, it has a minor effect on the transport properties of the doped tube when compared to a non-encapsulated one. This type of doping therefore preserves the most of the intrinsic properties of the pristine tube as a exceptional electron conductor.

3. Quantum transport in Si/organic molecule/Si
Several experimental and theoretical investigations of the transport properties of various organic molecules on Si surfaces have been reported recently [4, 5, 6]. These systems have a number of advantages compared to the traditional molecule-metal junctions. First, the organic molecules can be patterned on the Si surface [7, 8], because of the thermodynamic and kinetic stability of the Si-C bond. Second, the bonding between organic molecules and Si surface atoms is well understood [7, 8, 9, 10], which should allow for straightforward comparisons between theoretical and experimental results on exactly the same atomic configuration. Third, there is a tremendous potential for applications combining Si microelectronics with organics-based structures, e.g., porphyrins on Si(001) are promising candidates for molecular memories [11]. As a paradigmatic example, we investigate the transport properties of 1,4-diethynylbenzene connected between two hydrogenated Si(111) surface fragments. In this paradigmatic geometry, the bonding to Si is well-defined [7, 8], thereby avoiding the ambiguity of the contact geometry of metal-connected molecules.

Two different ballistic transport calculations are performed with the applied bias, with and without self-consistent iterations. In both cases, the charge density in the leads is fixed and the electrostatic potentials are shifted to match their chemical potentials. For the active region, the initial charge density is chosen from zero-bias DFT calculation and a linear potential drop across the conductor region is added to the electrostatic potential. In the non-SCF (non-self-consistent-field) calculations, the Hamiltonian matrix and the transmission coefficients are evaluated from the initial potentials. In the self-consistent calculations, the charge density and the potentials in the conductor region are determined iteratively, with the transmission coefficients obtained using the relaxed potentials and the updated matrix elements.

The I-V curves are calculated by integrating the transmission in the bias windows. They are shown in Fig. 2(b). From Fig. 2(b), it is clear that when the bias is smaller than 1.4 V, the non-SCF calculations result in very similar I-V characteristics to those of SCF calculations.
Figure 2. (a) Optimized geometry of the Si(111)-1,4-diethynylbenzene-Si(111) junction. The large, medium and small balls represent Si, C, and H atoms, respectively. The molecules are arranged periodically on the (111) surface with one molecule per (4x3) unit cell, with the Si-C bond length equal to 1.82 Å. Semi-infinite Si(111) on both sides of the molecule mimic the presence of the leads. (b) Self-consistent transmission coefficients through 1,4-diethynylbenzene connected to hydrogenated Si(111) leads. Bias windows are shown as dashed lines. The energy zeros are chosen to be at the center of each bias window. (c) I-V curve for 1,4-diethynylbenzene between Si(111) leads. The squares and circles represent results from non-self-consistent and self-consistent calculations, respectively.

In this bias region, the current exponentially increases with the applied bias, as expected for a system with a gap. However, when the bias is larger than 1.5 V, self-consistency becomes very important. A very small shoulder appears at 1.6 V in the non-SCF calculation, while a current valley, i.e., a negative differential resistance, is observed in SCF calculations. This underlines the importance of performing fully self-consistent calculations at large biases, when the device is far from equilibrium and the complex interplay between enhanced broadening of molecular levels and their rearrangement with respect to semiconductor band edges at both sides of the molecule. In the present system, resonant tunnelling occurs when the LUMO matches the conduction band edge of the negative lead, leading to negative differential resistance when this orbital drops below the band edge. As the bias is further increased, resonant tunnelling occurs between the broadened HOMO and the valence band edge of the positive lead, resulting in a significant increase in transmission [12].

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References
[1] T. Takenobu et al. Nature Materials, 2(10):683–688, 2003.
[2] V. Meunier and B. G. Sumpter. J. Chem. Phys., in press 2005.
[3] R. A. Kendall, et al. Computer Physics Communications, 128(1-2):260–283, 2000.
[4] N. P. Guisinger, M. E. Greene, R. Basu, A. S. Baluch, and M. C. Hersam. Nano Lett., 4(1):55, 2004.
[5] N. P. Guisinger, R. Basu, A. S. Baluch, and M. C. Hersam. Nanotechnology, 15:S452, 2004.
[6] T. Rakshit, G. C. Liang, A. W Ghosh, and S. Datta. Nano Lett., 4(10):1803, 2004.
[7] R. J. Hamers, J. S. Hovis, S. Lee, H. Liu, and J. Shan. J. Phys. Chem. B, 101:1489, 1997.
[8] P. T. Hurley, A. E. Ribbe, and J. M. Buriak. J. Am. Chem. Soc., 125(37):11334, 2003.
[9] W. C. Lu, W. G. Schmidt, and J. Bernholc. Phys. Rev. B, 68(11):115327, 2003.
[10] J. Cho and L. Kleinman. Phys. Rev. B, 64:235420, 2001.
[11] Z. Liu, A. A. Yasseri, J. S. Lindsey, and D. F. Bocian. Science, 302:1543, 2003.
[12] W. C. Lu, V. Meunier, and J. Bernholc. to be published, 2005.