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Effect of molecular bending and foreign molecules on electronic properties of molecular junctions

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ABSTRACT

We have investigated the charge transport properties of molecular junction using density functional theory in combination with the non-equilibrium Green's function. The charge transport behaviour and change in electronic properties of the molecular junctions formed by bending CNTs is explained by analysing molecular projected self-consistent Hamiltonian, projected density of state, transmission eigen channel, and transmission spectra. The system we used for investigation is consisting of CNTs (3, 3), & (3, 0) with conducting electrodes of Au. Because of the gradual loss in overlapping of the molecular orbitals due to bending processes the conductance decreases. The work also reveals that H_2O significantly affects the conductance of the bent CNTs by interacting with the orbitals of the CNTs and shifting orbital energies, closer to the Au Fermi energy.

1. Introduction

Remarkable advancement has been made in modeling and design of molecular junctions [1,2], electronics of nano-devices [3,4], and molecular devices [5–8] over recent years. Since then, quantitative conformity amid different techniques i.e. theoretical and experiment has remained hard to pin down differences; and the main reason for this vagueness is “difficulty in controlling processes and measuring of binding configuration and observation” of the contact geometry, and molecule junctions or devices [9,10].

Thus theoretical modeling is necessary for calculations and designing, therefore large numbers of theoretical studies have been focused on how charge is transported, how the binding configurations, contact geometries, morphology and environment impinge on the charge transport behaviour, and effect of electric field on electrical properties of molecular junctions or devices [11–16]. From these reports we found that changes in molecular/electrode configuration, interface geometry, morphology of molecular device and environment resulting in multiple conductance values (Experimentally measured) for a single-molecule junction because, it has not been possible to control the exact experimental conditions at molecular level [17–20]. However, performing experiments at molecular level is time consuming and need sophisticated instruments so to study such systems theoretical analysis is one of the best solution, here we are computing charge transport properties and effect of electrical field on of molecular system using the density functional theory (DFT) in combination with non-equilibrium Green's function (NEGF) theory. Since the electronic behaviour of molecular system depends on the structure of molecular core, the characteristics of interface due to metal-molecule interaction, and surrounding environment. In this paper we focus on how the charge moves in presence of electric field in a carbon nano tube alone, effect of electrodes, surrounding environment, and effect on bending CNT's which is of prime importance for creating devices from molecules based on Bottom-up approach and helps to explain phenomena of charge transport in many molecular systems [4,5]. We have used single workstation to perform calculations.

2. Computational details

Our system is consisting of CNT (3,3) & (3,0) (Shown in Fig. 1) as a molecular core sandwiched between two metallic electrodes. We had optimized the extended molecule using the maximum force of 0.04 eV/Å (SIESTA package [22]). Further for describing the core electrons present in molecular core we used Troullier-Martins type non-conserving pseudo-potentials. To compute the transport properties of molecular junctions [23–25] we further used the generalized gradient approximation (GGA) to calculate exchange-correlation function.

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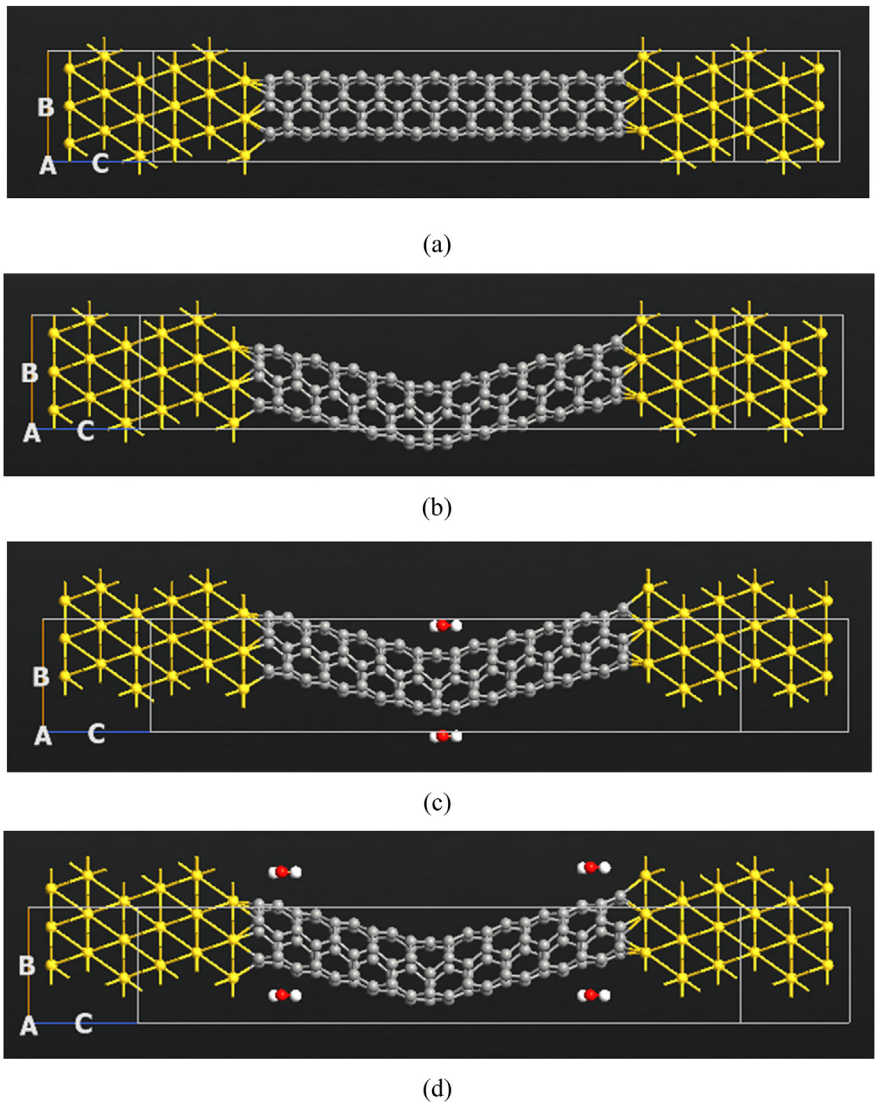

Fig. 1. CNT's (3,3) anchored between Gold electrodes (a) Without Bending (b) Bent at 30° (c) H_2O molecule at centre, (d) H_2O molecule at end of CNTs.

For Gold atoms we used single-ζ plus single polarization (SZP) set while for Carbon, Hydrogen and Oxygen atom we used double-ζ plus single polarization (DZP) basis sets. To find the (local) energy minima we perform geometry optimization [21] each time after bending of CNTs (as shown in Fig. 1) in the direction perpendicular to the surface. Using finite difference method vibrational frequencies is calculated. Further applying the force for displacing each of the atoms in CNTs in all three directions by a factor of 0.02 we compute the dynamical matrix (Hessian) for the finite vibrational region. Further using the derivative of the Hamiltonian (H) at the vibrational modes ($v^{(\lambda)}$), the electron–phonon couplings ($M^{(\lambda)}$) is defined by

$$M_{ij}^{(\lambda)} = \sum_{\alpha} \sqrt{\frac{\hbar}{2m_\alpha \omega_\lambda}} i \left| \frac{\partial H}{\partial R_\alpha} \right| j v_\alpha^{(\lambda)} \tag{1}$$

where the basis set is defined by $\{|i\}$, R_α, is the nuclear coordinate of atom having mass m_α having angular frequency ω_λ at mode λ. Further using finite difference method [2] to calculate the derivatives of the Hamiltonian. To simplify & ease the calculation, it is assumed that the interaction outside the boundary lines of subspace defining device is negligible, for the electron–phonon coupling (as shown in Fig. 1, the electron–phonon coupling is assumed to be limited to the central molecular cluster only).

Further assuming that non-interacting charge carriers coupling with molecular vibration in our model, the current through the molecular junction [26–30] is given by

$$I = \frac{2e}{h} \int \mathrm{d}\omega (f_L(\omega) - f_R(\omega)) ImTr\{\Gamma(\omega) G^r(\omega)\} \tag{2}$$

Here $\Gamma = \Gamma_L \Gamma_R / (\Gamma_L + \Gamma_R)$ defines the fermi distribution for non-interacting left and right electrodes. The retarded Green function of core as a result of interactions within itself, and electrode coupling G^r is defined [27,29] by

$$G^r(\omega) = \left[\omega - \varepsilon_o - \sum_{\{o\}}^{r} (\omega) - \sum_{eph}^{r} (\omega) \right]^{-1} \tag{3}$$

where $\sum_{eph}^{r}(\omega)$ represents self energy due to electron-phonon interaction within the boundary lines of subspace of molecule, $\sum_{\{o\}}^{r}(\omega)$ gives electrodes self energy within molecular core. We