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Theoretical Analysis for a Molecular Resonant Tunneling Diode

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1. Introduction

The remarkable miniaturization trend in semiconductor industry drives new technological schemes to be developed for the use in nano-scale dimensions. Molecular scale electronics that offer single molecules to function as the key component in future electronic devices. Thus it is evident that a change in the technology is necessary in near future to supplement the solid state based microelectronics. The immediate importance of replacing semiconductor (usually Silicon) based micro-electronics by molecular scale electronics is evident from a larger number articles appeared in the most popular journals during past two-three years [1-3].

Finite size of atoms, molecules and clusters offer advantage to design tailor made materials to perform desired functions by exploiting the quantum mechanical phenomenon of electrons in a confined space. For example, to construct a molecular wire we need an elongated molecule through which electrons can flow easily from one end to other. The incoming electrons move from one end to other through the unoccupied orbital, which is dispersed throughout the molecule. A typical empty, low-energy electron orbital is known as π orbital. Normally conjugated system provides the path where electron clouds are overlapped between molecular components so that electrons can hop from one to other. Therefore, a molecular wire is constructed by combining π-conjugated molecular units. The task of a molecular electronics engineer is to design a molecule whose orbital characteristics achieve the desired kind of electronic control.

A diode is a two terminal switch consisting of source and drain where it can turn a current on and off depending the direction of flow. For a resonant tunneling diode, current can flow equally in both directions. However, to switch the current in "on & off " position it takes the advantage of molecular discrete energy levels for the resonant tunneling of electrons across the molecule at specific bias voltage. Recently in an experimental demonstration Chen *et al.* [4] has shown that a single molecule (*shown in fig. 1a*) could behave like a *resonant tunneling diode* or a device with negative differential molecular impedance. The resonance effect for tunneling the electrons has been observed at 2.1V bias voltage with a peak current of 1 nA. The molecule consists of three benzene rings connect each other by acetylene group. The central benzene ring is substituted by NO_2 and NH_2 group on opposite sides. This asymmetrical configuration leads the molecule susceptible to change its configuration under perturbation. In the present work we have performed a first-principles electronic structure calculations to understand the electronic transport for this molecule, reported to behave like a resonant tunneling diode.

Computational details:

All calculational have been performed using Gaussian-98 software [5]. The 6-311G valence triple zeta basis set augmented with polarization functions, was used. All geometries have been optimized using Hartree-Fock level of theory. To obtain accurate electronic structure, single point energy calculation have been carried out using B3PW91 level of theory. It can be noted that for single point energy calculations we have used the optimized geometry from HF method.

Results and Discussion:

Figure 1 shows the initial and optimized geometries of the resonant tunneling diode (RTD) molecule mentioned above. It is seen that one of benzene rings is twisted by 35° with respect to the central ring after optimization. This conformational change is attributed due to the assymetrical nature of the central ring and responsible for showing resonant tunneling behavior in this molecule. It is believed that the lowest unoccupied molecular orbital (LUMO), which should be spatially connected from one end of the molecule to the other, is responsible for the electron transport. Accordingly, the unoccupied molecular orbitals were plotted to understand their shape. It is seen from the spatial extent of the unoccupied molecular orbitals (*shown in fig.2*) that while LUMO and LUMO+1 are localized to two benzene rings, the LUMO+2 state is delocalized and spans the length of the molecule. In a first approximation, the barrier for electron transport through a molecule will be half of HLG (HOMO-LUMO). For the present RTD (shown in fig.1) molecule, the HLG has been calculated to be 3.66 eV. However, from the orbital analysis it is seen that instead of LUMO level, LUMO+2 level is delocalized across the molecule and the difference between LUMO and LUMO+2 energy level is calculated to be 4.95 eV. Therefore the required bias voltage for the electron transport through this molecule is predicted to be 2.475 V, which is slightly higher than obtained in experiment [4]. This small difference is predicted due to the influence of metal tips connected to this molecule, which has not been accounted here.

In order to obtain a qualitative understanding on the effect of metallic tips on the molecular system we have calculated the electronic structure of the RTD molecule connected with Au nano-clusters as shown in fig3. We have taken Au, Au_3, Au_4 and Au_{10} clusters as model tips for the calculation. These calculations were performed using B3PW91 level of theory as lanl2dz basis set. It is observed that the HLG value decreases significantly in presence of Au atoms, indicating less bias voltage required as compared to the free molecule to tunnel electron from one end to other.

The geometrical and electronic structure of this molecule is expected to change under bias voltage due to the presence of an excess electron. We plan to present the optimized geometries of the neutrals and anions along with analyses of the molecular orbitals for the highest occupied and lowest unoccupied states, which can lead to an understanding of the electronic transport through this molecule.

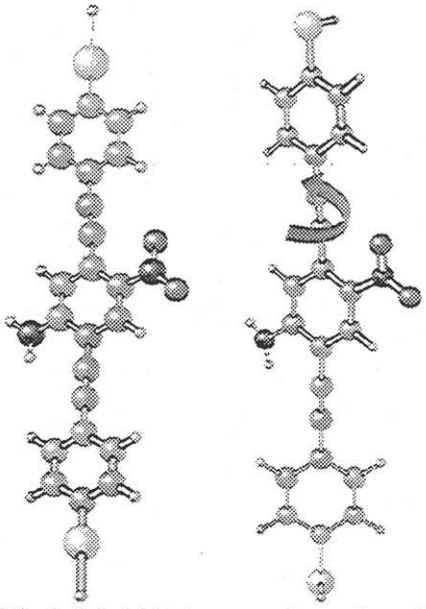
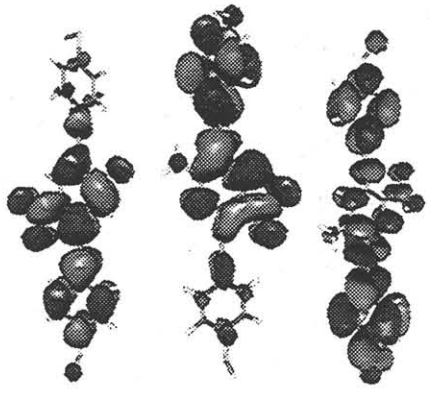


Fig.1 a) Initial planer configuration of the RTD molecule. b) Optimized geometry. The top benzene ring is twisted by 35° with respect to the central benzene ring.



LUMO LUMO+1 LUMO+2

Fig.2 Orientation plot for lowest unoccupied orbitals. LUMO+2 level is delocalized from one end to other.

Conclusion:

We have performed quantum chemical calculation for a molecule experimentally demonstrated to behave like resonant tunneling diode. The effect of Au clusters modeled as tip materials has been included in this study. The electron transport through conjugated molecules is determined from the electronic energy levels and their corresponding orbital spatial nature.

Acknoledgement:

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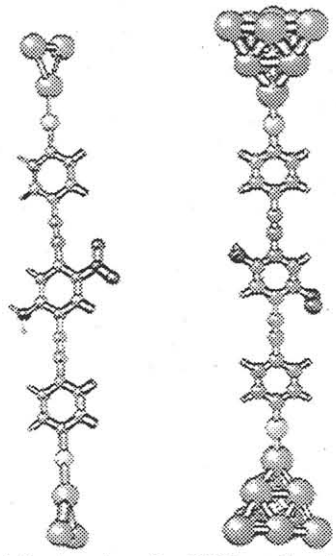

Fig.3 Geometric structure for RTD molecule connected with Au_3 and Au_{10} cluster.