Molecular Dynamics Investigation of Electron Transport Through Single Molecule Junctions

Dávid P. Jelenfi, Attila Tajti, Péter G. Szalay

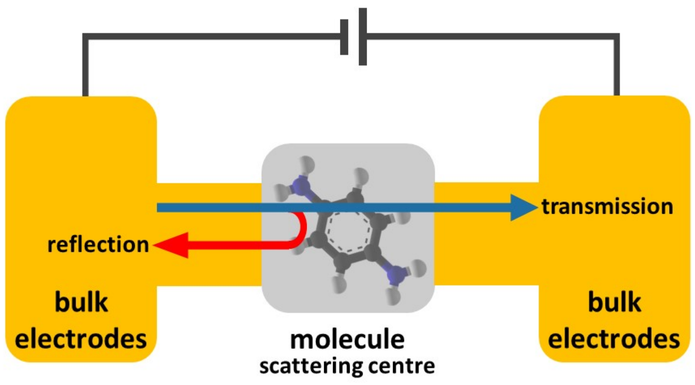
Institute of Chemistry, ELTE Eötvös Loránd University, Budapest, Hungary

Introduction

Understanding the **charge transport** properties of molecules is of fundamental importance for molecular-scale electronics and biochemical processes. Research in this area was spectacularly boosted in the past two decades, in particular by experimental realisation of so-called **single molecular junctions** (SMJs). In these systems, a single molecule is trapped between two metallic electrodes, allowing the examination of the electrical properties of single molecules measuring, for example, their conductivity.

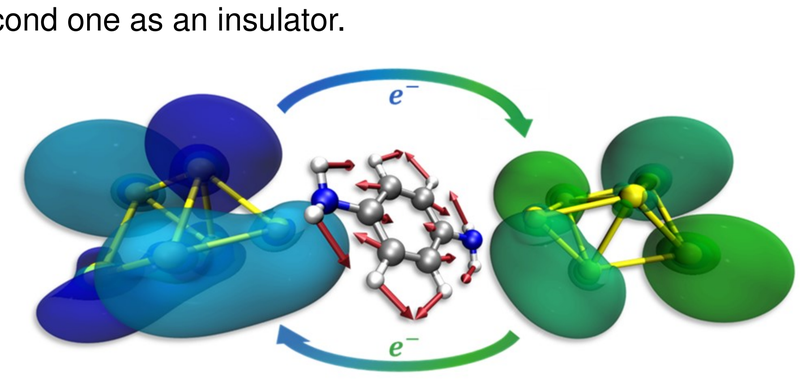
Physicist's conduction model

The majority of theoretical investigations of transport on SMJs are based on the **Landauer approach**. In this model the electrical conduction through SMJs is described as a scattering process, in which the molecule is a scattering centre in a bulk conductor. The charge transport properties of the molecule are calculated from the electron's **transmission probability** through the molecule, which in this picture depends only the molecular orbitals, usually sourced from density functional theory (DFT) calculations.

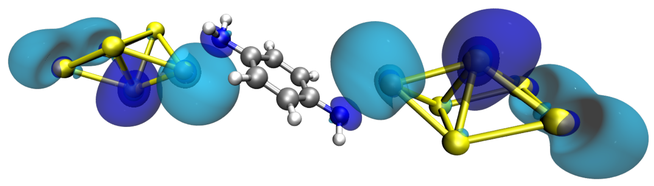


Chemists' conduction model

Here we take a different interpretation of the electron transport through the SMJs assuming that the vibrations of the molecule can cause a transition between different electronic states or change the localisation of the electron, therefore an incoming electron can move through the molecule. For this reason, ***ab initio* quantum-classical molecular dynamics** [1] simulations are performed for the electron attached (EA) states which are calculated with CC2 and ADC(2) methods using TURBOMOLE [2] the continuum orbital strategy [3]. We study two model systems, built from the benzene-1,4-diamine (BDA) and the 1,4-diazabicyclo[2.2.2]octane (DABCO) molecules and gold clusters, the first molecule being known as a good conductor, while the second one as an insulator.

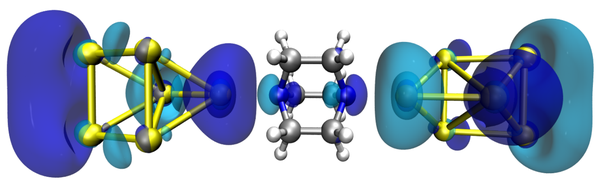


BDA
(Conductor)



Electrode state 6

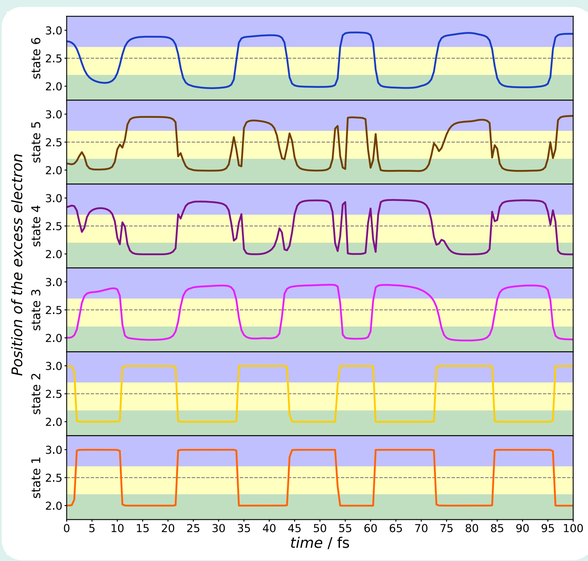
DABCO
(Insulator)

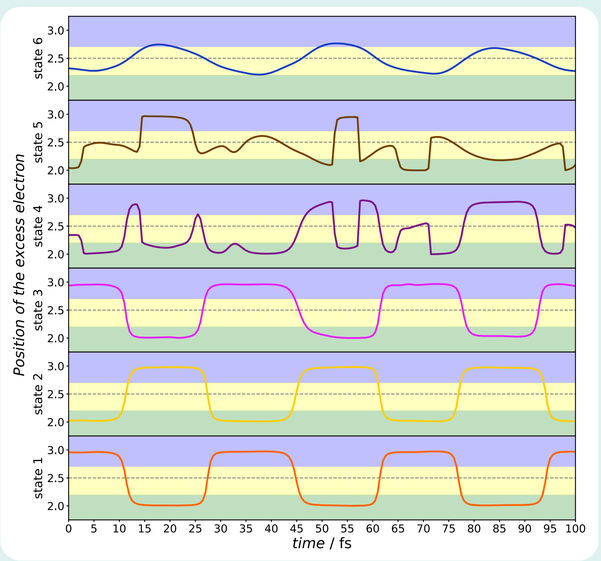


Electrode state 6

Typical trajectories of the two systems

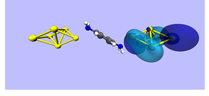
Change of the excess electron's position in the first six EA states:



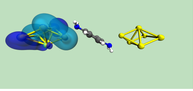


Where is the excess electron?

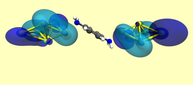
Right side



Left side

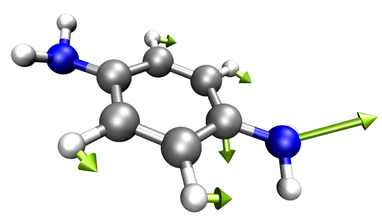


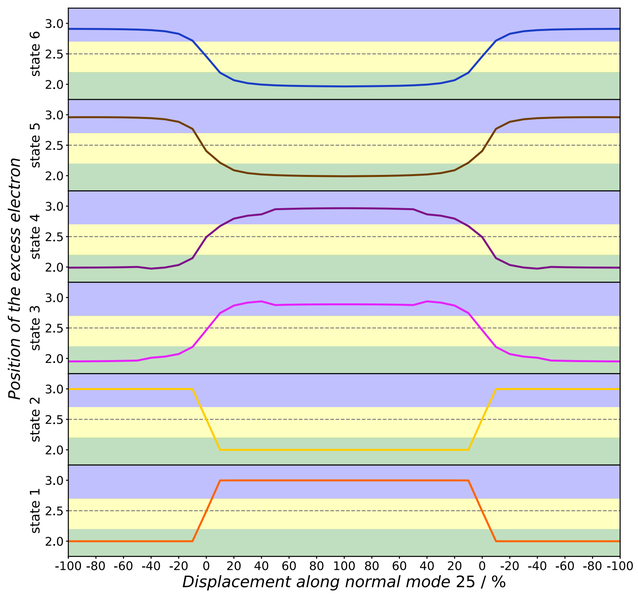
Delocalised

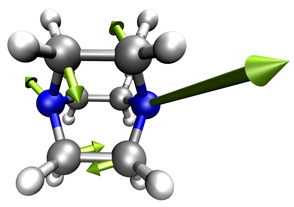


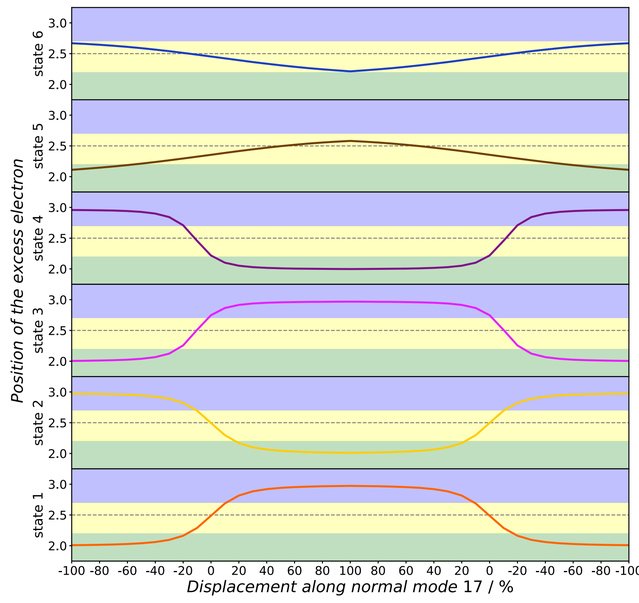
Role of molecular vibrations

The connection with molecular vibrations can be investigated via normal mode analysis, allowing the identification of the vibrations which cause the oscillation:









Conclusions

The **excess electron oscillates** between the two sides of the system as a result of the molecular vibrations. [4] The vibrations which cause this oscillation are identified. In both systems these have the same character, dominated by the two **amine groups' opposite displacements** towards the electrodes. **Conductor and insulator molecules can be distinguished** by the parameters of the oscillation. In a conductor more charge is oscillating, and the oscillations are more frequent.

References

[1] M. Barbatti, et al. *WIREs Comput. Mol. Sci* 4, 26 (2014).

[2] TURBOMOLE V7.3 2018, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.

[3] J.F. Stanton and J. Gauss, *J. Chem. Phys* 111, 8785 (1999).

[4] D. P. Jelenfi, A. Tajti and P. G. Szalay *Mol. Phys.* 119, 21 (2021).

Acknowledgment

The authors appreciate the computational resources provided by the ELTE IIG High-Performance Computing facility.

CPLT2022