1 Scientific Report

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3 Purpose of the visit

Our group is collaborating with the group of Dr. Čížek for several years. During that time, a scheme to compute transport characteristics for realistic models of molecular junctions from first-principles electronic structure calculations was developed[2, 1]. One aim of this visit was to develop this scheme further, especially for the use of larger basis sets (like a double- or triple-zeta basis set).
Vibrationally coupled charge transport through single-molecule junctions is typically described in terms of scattering theory[3], density matrix approaches[8], or non-equilibrium Green's function theory[5, 7, 8]. Most of the approaches, however, are constructed for harmonic oscillators, especially the ones that can handle vibrational degrees of freedom that are driven far from thermal equilibrium. We wanted to explore the possibility to go beyond the harmonic approximation, and further, to discuss the possibility of contact-induced vibrational effects. Contact-induced vibrational degrees of freedom may drive a molecular motor, which is one of the main research topics in the group of Dr. Čížek.

4 Work carried out

In order to update ourselves on the current status of our research, we have been discussing results that are already published[8] and that serve as a basis to compare our methods, especially our density matrix approaches, and of course, results that we are going to publish. That way, minor discrepancies between our results could be resolved very quickly.
Furthermore, Dr. Čížek introduced me and his students to his approach of calculating the self energy terms for the $Au(111)$-cluster that we use in our DFT(density functional theory)-based transport simulations. These terms come into play, once we truncate the infinite system of a molecular junction, consisting of a left lead, a bridging molecule, and a right lead, to a finite system, where the left and the right lead are modelled e.g. by a finite cluster of ≈ 32 gold (Au) atoms. We have been discussing the possibility to extend this approach for the use of larger basis sets, which may involve also f-orbitals (right now we are restricted to the use s-,p- and d-orbitals), different electrode materials like silver (Ag) or platinum (Pt), by which experiments are carried out as well, and different orientations of the cluster's surface like a (110)- or (101)-surface.
Primarily, I was focusing on the possibility to describe anharmonic effects in molecular transport junctions in terms of nonequilibrium Green's function theory. Anharmonicities may arise on the molecular bridge itself (e.g. in describing current-induced reactions of the bridging molecule) as well as in the contact area between the molecular bridge and the leads (e.g. in models of a quantum shuttle, or a molecular motor). The idea of Dr. Čížek was to use Green's functions that are based on projection operators. Following the guidlines of Dr. Čížek, I was deriving the respective equations of motion for this set of correlation functions, and I was able to close this set of equations. In contrast to a harmonic degree of freedom, which may be described just by a single Green's function[5], we need to employ N_{vib}^2 correlation functions (N_{vib} denotes the number of vibrational states that we like to take into account). Similar approaches have been described previously[6, 4]. However, these approaches build up a set of N_{vib}^4 correlation functions instead of N_{vib}^2 correlation functions.

Finally, Dr. Čížek organized a meeting with Dr. Novotný (Charles University), who has been working on the field of quantum shuttles in the past. We have had a very interesting and fruitful discussion about projection operator based Green's functions, and Dr. Novotný pointed out some interesting references to us.

5 Main results

The main result of my visit in Prague is the derivation of the following set of equations:

$$\begin{aligned} G^{\mathrm{r}}_{nv}(E) &= g^{\mathrm{r}}_{\epsilon_v-\epsilon_n}(E)\rho_{nv} \\ &\quad - \sum_{k,n',v'} |V_k|^2(1-n_k)\langle v|n'\rangle\langle v'|n\rangle \left(g^{\mathrm{r}}_{\epsilon_v-\epsilon_n}(E)\left[g^{\mathrm{r}}_{\epsilon_k+\epsilon_{n'}-\epsilon_n}(E) - g^{\mathrm{r}}_{\epsilon_k+\epsilon_v-\epsilon_{v'}}(E)\right]\right) G^{\mathrm{a}}_{n'v'}(\epsilon_k) \\ &\quad -\frac{i}{2}\sum_{K,n',v'} \Gamma_K(1-f_K(E-\epsilon_{n'}+\epsilon_n))\langle v|n'\rangle\langle n'|v'\rangle g^{\mathrm{r}}_{\epsilon_v-\epsilon_n}(E)G^{\mathrm{r}}_{nv'}(E) \\ &\quad -\frac{i}{2}\sum_{K,v',n'} \Gamma_K f_K(E-\epsilon_v+\epsilon_{v'})\langle v'|n\rangle\langle n'|v'\rangle g^{\mathrm{r}}_{\epsilon_v-\epsilon_n}(E)G_{n'v}(E) \end{aligned}$$

which represents a closed set of linear equations for the retarded real-time projection of the projection operator based Green's functions G_{nv}. Within the wide-band approximation, which is a valid approximation for the systems we like to study, these correlation functions suffice to compute the current-voltage characteristic and the vibrational excitation of a molecular junction comprising a single electronic state that is coupled to an anharmonic vibrational degree of freedom.

6 Future collaboration

In the next months we like to explore the derived nonequilibrium Green's function approach in more depth, and we are going to adopt it in our spectrum of transport calculations. In combination with our DFT-based scheme, this is going to bring us closer to a complete description of charge transport through single-molecule junctions.

References

[1] C. Benesch, M. Cizek, J. Klimes, M. Thoss, and W. Domcke. Vibronic effects in single molecule conductance: First-principles description and application to benzenealkanethiolates between gold electrodes. *J. Phys. Chem. C*, 112:9880, 2008.

[2] C. Benesch, M. Cizek, M. Thoss, and W. Domcke. *Chem. Phys. Lett.*, 430:355, 2006.

[3] M. Cizek, M. Thoss, and W. Domcke. *Phys. Rev. B*, 70:125406, 2004.

[4] K. Flensberg. Tunneling broadening of vibrational sidebands in molecular transistors. *Phys. Rev. B*, 68:205323, 2003.

[5] M. Galperin, A. Nitzan, and M. A. Ratner. *Phys. Rev. B*, 73:045314, 2006.

[6] M. Galperin, A. Nitzan, and M. A. Ratner. Inelastic transport in the coulomb blockade regime within a nonequilibrium atomic limit. *Phys. Rev. B*, 78:125320, 2008.

[7] R. Härtle, C. Benesch, and M. Thoss. Multimode vibrational effects in single-molecule conductance: A nonequilibrium green's function approach. *Phys. Rev. B*, 77:205314, 2008.

[8] R. Härtle, C. Benesch, and M. Thoss. Vibrational nonequilibrium effects in the conductance of single molecules with multiple electronic states. *Phys. Rev. Lett.*, 102:146801, 2009.