Review of PhD thesis by the thesis advisor

Thesis author: Ivan A. Pshenichnyuk
Title of thesis:
Interaction of electrons with vibrating molecules: molecular electronics applications

The main topic of the thesis is the theoretical description of the steady vibrational state of a molecule connected to two metallic electrodes subjected to the mutual voltage bias. The vibrational dynamics of the system is described with a model, assuming one electronic state available for the transport through the junction and coupled to one vibrational mode. The dynamics is studied for a standard model with harmonic vibrations and for two groups of models with anharmonic vibrations and coupling amplitudes depending on vibrational coordinates. These two generalizations represent a highly nontrivial generalization of the standard model for coupling of the current and localized phonon mode. They furthermore allow to study "the motor effect", i.e. the correlation of the voltage applied to the junction with the angular momentum of the molecular bridge (the vibrational mode of interest is torsional mode allowing full 2π rotation).
The subject of molecular conduction and the interaction of the current with the molecular vibrations, in particular, are the extremely difficult subject of research with many open questions. The full treatment of the correlated (with vibrations) electron transport is extremely difficult, if not impossible. Ivan Pshenichnyuk selected two approximate approaches to the subject. First is the description of the current conduction as a sequence of electron scattering events and the second, master equation treatment, in which the molecule-metal coupling is treated perturbatively. The former approach treats both the molecule-metal and electron-vibrational couplings in exact way but does not take fully coherently into account the many-particle nature of the problem and the later approach assumes the second order expansion of the Liouville equation in terms of the molecule-metal coupling. Author compares both approaches for simple models and decides to use master-equation approach for the treatment of the most complicated (i.e. most interesting) model. The master equation method had to be extended beyond standard treatment of harmonic vibrations. He finds many interesting phenomena including negative differential conductance, cooling of vibrations by current and the "motor effect". The last phenomenon is the key topic of the thesis and it is furthermore studied considering the variations of the model parameters and the symmetries of the models.

There is no doubt that the studied topic is timely and that a significant amount of new scientific results were obtained. On the formal side: the thesis is carefully written and is well arranged. The second chapter reviews and introduces the tight binding model of the leads and both the scattering and master equation approach in a pedagogical way and can be used as a study material for his successors. The studied models are introduced in the third chapter. The chapters 4 and 5 represent the core of the thesis. The implementation of the methods for the studied systems and the results are presented there. Ivan Pshenichnyuk is not a native English speaker and the language of the thesis is not perfect, but the language imperfections do not exceed the acceptable level and the presentation of the ideas is clear.

Ivan Pshenichnyuk joined our theoretical group four years before after finishing his thesis in experimental physics. His former work was in electron-molecule collisions in vacuum. He started his PdD project by learning the theory of inelastic electron-molecule collisions. He contributed to this subject by calculating the cross sections for creation of metastable H_2^- ions in electron-molecule and ion-atom collisions (this work is not included as a part of thesis, the paper is in press). He then repeated some of our earlier calculations for electron conduction

through molecules using the electron-molecule scattering theory. After we decided to use the master equation approach he showed a large degree of independence and ability to learn both new theories and numerical methods. It was further complicated by the fact that I started to learn this subject at the same time and for some periods of time he had little support on my side. I genuinely believe that by finishing this thesis and by obtaining the interesting and scientifically relevant results he proved his scientific qualities.

To conclude I think that Ivan Pshenichnyuk showed his ability to work as an independent scientist and I fully recommend this thesis as a PhD thesis

In Prague October 25, 2010

Doc. RNDr Martin Čížek, PhD
Thesis advisor