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Prof. Dr. Zdeněk Doležal
proděkan pro vědu a zahraniční styky
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Praha

Věc: Oponentský posudek habilitační práce Dr. Zdeňka Futery

Habilitation Thesis "*Computational Approaches to Electron Transfer Processes: From Ionic Solutions to Nanobioelectronic Devices*" submitted by Dr. Futera proves that the author is an accomplished scientist whose research covers several important aspects of charge transport processes. It is mostly, but not exclusively, focused on theory of electron transfer (ET) in biomolecules (proteins) in solution as well as at metal and semiconductor interfaces, addressing two main underlying mechanisms – coherent tunneling and incoherent hopping. Besides that, his work deals with ionic conductivity (in ice) and electron transfer between small metal complexes in solution. Simulating effects of electric fields at electrode surfaces on the structure of the double layer and adsorbate behavior is another important research direction. Candidate's contribution is two-fold: (i) He has developed and/or improved the theoretical background and computational methodology needed to simulate ET, and (ii) Using this novel methodology, he has carried out high-level theoretical analyses and simulations of various charge-transport processes, thereby obtaining new important mechanistic insights and understanding. Importantly, his theoretical research is linked to experimental results either from the literature or carried out by his collaborators.

Electron transfer processes are ubiquitous in biology where they play crucial roles in bioenergetics (photosynthesis, respiration) as well as in many enzymatic substrate transformations, RNA biosynthesis, etc.. They also are essential artificial light (solar) energy conversion and storage, batteries, electrocatalysis, as well as in the emerging field of bioelectronics whereby various electronic and sensory functions, traditionally performed by solid-state devices, are carried out by ET-active biomolecules. Progress in these directions hinges on detailed understanding and theoretical description of underlying ET steps. In addition to its fundamental importance, candidate's research is thus highly relevant to potential applications and he rightly stresses these links in his papers. This is especially the case of bioelectronics (ET through protein films and single molecules at electrodes) and (photo)electrochemical water splitting at TiO_2 and Fe_2O_3 (hematite) facilitated by electric field.

In the first two chapters (2 and 3), the candidate discusses ET theories and various computational approaches in general, with an emphasis on biomolecular systems, long-range ET in redox chains, interfaces between a protein and an electrified electrode, electron transport through single molecules, etc.. This is a very clear text that shows convincingly that theory and simulations are essential for correct interpretation of experimental data. These two chapters could

easily serve as an educational text and an entry to the extensive ET-related literature. In chapter 4, the candidate outlines his own contributions to the development of computational methodology, which are presented within a broader context. One can stress, among others, the development of the double QM/MM method that treats the two redox sites jointly, implementation of the projector-operator based diabatization method to calculate electronic coupling in (bio)molecular systems, or a methodology to include static as well as oscillatory electric fields in nonequilibrium molecular dynamics simulations to reveal changes in water ordering and vibrations. Chapter 5 describes applications to several important and well-chosen cases of biological ET. The reviewer found especially interesting the examination of ergodicity in cytochrome *c* ET reaction, where previous claims of nonergodic behavior were convincingly disproved. Accompanying discussion of conditions that could lead to nonergodicity is enlightening, since this is the mechanism to consider when designing ultrafast ET processes for light energy conversion. Explanation of the much faster ET in azurin- than in four-heme cytochrome protein junctions by tunneling through delocalized heme and amino-acid states is another fascinating result. Qualitatively, one would expect hopping in the latter case, but the candidate's work showed that hopping sets in only at long distances (>7 nm). Chapter 6 then summarizes results of simulations and theoretical analyses of several other important systems. In the case of ferro/ferricyanide redox couple, a good use was made of candidate's novel implementation of the projector-operator based diabatization approach. In this (and some other) cases computationally demanding polarizable force fields have been used. Especially important are simulations of electric field effects on water solvation layers at metal oxides, which has shown that electrochemical water oxidation to produce oxygen can be promoted by electric fields in particular orientations. Hydrogen-bond lifetimes in water, proton diffusivity, as well as intra- and intermolecular water vibrations were found to be affected. This work has important implications for (photo)electrocatalyzed water splitting. Of great interest for electrochemistry is the work on boron-doped diamond electrodes, where it was shown how the electrode surface changes between hydrophobic and hydrophilic, depending on the electrode preparation and pretreatment.

Results presented in the thesis provide a clear evidence that the candidate has made important contributions to the theory of charge-transport processes, both in methodology development and applications to particular systems and processes. Results of his work amount to important scientific achievements. This is further documented by the 14 selected high-profile journal articles that are included in the thesis. It should be stressed that these papers present only a part of his publication outcome – overall, there are 33 references to his papers in the thesis. It's also important to note that some of his papers were published jointly with experimentalists; and these links between theory and experiments make his work especially relevant and impactful.

Finally, it is concluded that the submitted dissertation meets all the requirements for habilitation thesis. Neither Turnitin nor my reading of the thesis indicated any signs of plagiarism. I do recommend Dr. Futera's dissertation to be accepted for the continuation of his habilitation procedure.

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