

**Peer review of the doctoral thesis**

***“A model of resonant collisions of electrons with molecules and molecular ions”***

**submitted by Martin Váňa**

in July 2017 at the Faculty of Mathematics and Physics, Charles University, Prague  
(work performed under supervision of RNDr. K. Houfek, Ph.D., Inst. of Theoretical Physics)

**Reviewer:** prof. RNDr. Pavel Cejnar, DSc.

Inst. of Particle and Nuclear Physics, Faculty of Mathematics and Physics, Charles University,  
V Holešovičkách 2, Praha 8, 18000, Email: cejnar@ipnp.troja.mff.cuni.cz

The Ph.D. thesis of Mr. Váňa is devoted to a theoretical description of resonant collisions of electrons with diatomic molecules with the aid of a simple model based on a local two-dimensional potential  $V(r,R)$ , where  $r$  is the electron distance from the molecular center of mass and  $R$  is the distance of nuclei within the molecule. In spite of its strictly reduced number of degrees of freedom, the model exhibits rather complex modes of dynamics. It was proposed in 2006 by the thesis supervisor & collaborators with the aim to provide a testing platform for various approximation methods in the simulation of some processes induced by electron-molecule collisions, particularly (a) vibrational molecular excitations and (b) dissociative electron attachments. The present author considerably extended the earlier work by elaborating the time-dependent approach to the above processes (in contrast to the stationary approach used earlier) and also by studying an additional process of (c) dissociative recombination of molecular ions by incoming electrons.

The general methods and numerical programs developed in the Thesis were applied to vibrational-excitation and dissociative-attachment processes for three types of molecules ( $N_2^-$ ,  $NO^-$  and  $F_2^-$ -like models) and to dissociative recombination of the  $H_2^+$  ions (with an additional long-range electric potential term). This required nontrivial analytical and numerical efforts (the use of several sophisticated numerical methods). The aim of this work was not to directly compare the calculated results with experimental data, but rather to test the consistency of various evaluation techniques within the model (including its time-independent formulation) and to set limits to the local complex potential approximation, which is a method commonly used in the present-day theoretical description of electron-induced vibrational excitations of molecules. Indeed, the calculations show discrepancies (large in some cases) between the exact results and outcomes of the time-independent approach and mainly those of the local complex potential approximation. Moreover, the precise dynamical simulations provide deep insight into the complicated interplay of electronic and nuclear degrees of freedom during the electron-molecule collision. It turned out that oscillatory cross sections of electron-molecule interactions often result from a coherent combination of multiple contributions. Simulations of dissociative recombination of  $H_2^+$  ions disclosed a peculiar mechanism involving repeated transitions between Rydberg states in the attractive electronic potential. These findings demonstrate high complexity of the above processes and falsify attempts of their description by some oversimplified models.

In my opinion, the Thesis represents a valuable and important contribution to a highly actual research area. Detailed understanding of electron-molecule collision mechanisms is essential in fundamental physics (like astrophysics) as well as in various branches of applied science (e.g., in the physics behind the nuclear fusion technology). The relevance of the work was proven by the publication of its essential part in a recent extensive paper of M. Váňa and K. Houfek in *Physical Review A* (vol. 95, article 022714, 17 pages).

The other part of the Thesis, which contains still unpublished material (mainly the work on the dissociative recombination), certainly deserves publication in an equally prestigious journal.

The Thesis is well structured and written in good English (as far as I can judge). I found a minimal amount of typos. Even the previously published material is presented not just as a reprint, but in a consistent way and with more details than in the publication. An attached CD contains neat animations (results of the dynamical calculations) that clearly illustrate the complexity of processes described in the text. The Thesis will certainly serve as a valuable source of information for future students in the field.

I have also a critical comment, but it concerns mostly the formal, or rather pedagogical aspect of the Thesis. I really missed a non-technical introduction into the field. Chapter 1 jumps immediately to formal mathematical derivations which are not clear without properly explaining a wider physical background. For example, the diatomic molecule is already a complex system containing several nuclear and electronic degrees of freedom – why it is justified to isolate just its single nuclear vibrational degree of freedom? And further, why the electron-nuclear potential  $V(r,R)$  takes the specific forms given by Eqs.(1.12)-(1.18) and (1.74)? Why the numerical solution of a mere 2D problem is so complicated? (I see that it is but it deserves some explaining words.) What is the basis for the three methods used for the evaluation of the S-matrix elements (Secs.1.4.1-1.4.3)? The Thesis looks like a self-contained text, but in reality a number of formulas and statements remain unexplained. The clarity of the text is not improved by the use of many (maybe too many) abbreviations (the list at the end of the Thesis contains only a fraction of them).

I have a few questions:

- (i) The author mentioned on page 9 of the Thesis that it would be straightforward to generalize the model in order to include also the rotational excitations of the molecule. But is it really so? I do not doubt that the inclusion of the nuclear centrifugal term would not be too difficult, but as far as I can see, the description of rotational excitations would require to increase the number of degrees of freedom or to consider a coupled system of individual rotational channels.
- (ii) In connection with question (i), is it possible to specify the physical conditions under which the molecular rotational motions can be decoupled from vibrational ones and neglected in the description of electron-molecule collisions?
- (iii) What is the reason for the particular choice of the model parameters in Tables 1.1 and 1.2? The text contains only a partial explanation. The differences in the shape of the electron-molecule potential for the four processes (Figs. 3.1, 3.8, 3.15 and 4.1) play a crucial role in the observed dynamical differences, but they are not adequately supported.
- (iv) Why the electron-molecule interaction potential has the different forms (1.14) for a neutral molecule and (1.74) for an ionized molecule?

In spite of the few critical remarks given above, I consider the doctoral thesis of Mr. Váňa as an excellent piece of work, which brings an important and relevant contribution to an active research area. It proves the capability of the author to carry independent scientific research. I recommend to accept the Thesis and to grant Mr. Váňa the Ph.D. degree.

Pavel Cejnar

In Prague, August 29, 2017