Review of thesis proposal

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Thesis title: Modeling the dissociative recombination of light ions
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In his thesis *Modeling the dissociative recombination of light ions* Dávid Hvizdoš compares three different theoretical methods to model dissociative recombination in diatomic ions, and applies the developed techniques to two benchmark molecular ions: H_2^+ and HeH^+. The first method is a fully numerical. The second one is based on the approximation of vibrational frame transformation, initially proposed by Chang and Fano, and later extended by Gao and Greene. The third method is an R-matrix method in two dimensions of the electronic coordinate and the coordinate of internuclear distance in the molecular ion.

The approximation of vibrational frame transformation is employed a lot in theoretical modeling of different processes involving collisions between molecular ions and electrons. However, its accuracy has often been questioned due to the assumption of the approximation about a rapid scattering on the electron when it is close to the ion. This assumption is similar to the sudden approximation in the perturbation theory. The accuracy of the vibrational frame transformation is difficult to quantify. The only way to do this is to perform numerically accurate calculations solving the Schrodinger equation explicitly for the electronic and vibrational degrees of freedom and compare with the results obtained with the vibrational frame transformation. This long-standing problem is resolved in Dávid Hvizdoš' thesis. The work performed in the thesis comparing the three methods is extremely valuable for the community working on modeling collisions between molecular ions and electrons. Below, I give more details on the work performed in the thesis.

In the first chapter, Dávid Hvizdoš briefly discusses the work he made in his Master thesis, devoted to the problem of DR in H_2^+ (accounting for singlet ungerade symmetry of the $H_2^+ + e^-$ system only), where the DR cross section was obtained from wave functions computed directly solving the Schrödinger equation for an electron incident on the vibrating molecular ion. The Schrödinger equation is solved using the method of exterior complex scaling in the electronic and the internuclear-distance coordinates to account for outgoing fluxes in the two coordinates. Only a few details about the approach are provided in the thesis. A detailed discussion was published in Dávid's Master thesis and Refs. [A,3]. No results of calculations using the approach are given in this chapter, they are discussed in following chapters.

Chapter 2 "DR by frame transformation" is devoted to the method of vibrational frame transformation. First, the author gives a list of basic assumptions of the method and briefly reviews them. I would comment on the assumption, mentioned first in the list, the one on Born-Oppenheimer quantum defects. Indeed, in many studies, in which the FT method was employed, one used the Born-Oppenheimer quantum defects, but it is not always the

case. Even in very early studies using the FT method, non-Born-Oppenheimer couplings were accounted for. It is done typically, by non-adiabatic couplings represented by quantum-defect matrices. One can cite such authors as Ch. Jungen, I. Schneider, C. H. Greene. Myself, I account for certain (not all!) non-Born-Oppenheimer effects in DR studies of polyatomic ions. Maybe, the relevant discussion in the thesis could be slightly corrected.

After discussing the assumptions of the FT method, Dávid Hvizdoš gives a derivation of the formula for the FT in the basis of Siegert states. I might be wrong, but I have some doubt about the claim that the derivation of Eq. (2.14) is more rigorous than the derivation given in earlier studies by Greene and even earlier work by Tolstikhin. For example, the statement of Eq. (2.6) come without a proof or an argument.

Following the derivation of the FT formula, the author develops the rest of theoretical DR theory based on Siegert states, developed in earlier studies. In Section 2.2 of Chapter 2 Dávid Hvizdoš compares the DR cross sections obtained by the two methods – the FT method and the one discussed in Chapter 1. The agreement is very good. In Section 2.3 Dávid analyses sources of remaining disagreement between the results.

Chapter 3 is devoted to the solution of the problem of DR in H_2^+ using a purely-numerical two-dimensional R-matrix approach, without using the vibrational frame transformation. The results are compared with the results obtained using the Born-Oppenheimer approximation separating the full solution of the problem in two steps: First, electronic molecular states are obtained, then an R-matrix approach along the internuclear distance is applied.

In Chapter 4, the approximation of frame transformation is analyzed and compared with the exact numerical solution. For the frame transformation, instead of the vibrational Siegert states, Dávid employs vibrational states, obtained by the method of exterior complex scaling (ECS). The spectra of Siegert and ECS states are compared and briefly discussed. In addition, it was attempted to include energy-dependent quantum defects in order to account for the energy-dependence of the body-frame scattering matrix. It was found that the frame transformation using the energy-dependent quantum defects yields non-symmetric reaction matrix. The only way to solve this problem was to symmetrize the matrix artificially.

The second half of Chapter 4 is devoted to the idea of backpropagation frame transformation, which is based on a discovery that one can find correct and converged quantum defects at some larger electronic radius (for fixed geometries) and then propagate the electronic solution to some smaller electronic radius, where the vibrational transformation can be applied reducing the error associated with the neglected part of the non-Born-Oppenheimer couplings. The backpropagation frame transformation gives an excellent agreement with the numerically accurate DR and vibrational excitation cross sections. Given such an excellent agreement, the idea of the backpropagation frame transformation appears to be a major achievement of the thesis.

I do have a small suggestion about the discussion of the backpropagation frame transformation. To me it is not completely clear what the "interaction free" back propagation means. Given the importance of the results presented in this part of the thesis, I would suggest that some more details be given about the technical aspects of the procedure in Sections 4.3 and 4.4.

Chapter 5 is devoted to the study of DR in HeH+, for which experimental data exist. The calculation were based on the quantum-defect matrix obtained using the UK R-matrix code. The linear dependence with energy of the quantum defect was accounted for. The obtained theoretical results are in an excellent agreement with high-resolution experimental data from the CSR storage ring. The agreement is probably the best that theory has ever

achieved interpreting DR experiments. This is indeed a remarkable result.

In Chapter 6, Dávid Hvizdoš discusses an extension of the two-dimensional R-matrix model to treat the direct mechanism in dissociative recombination, applying it to the DR in H_2^+ (accounting for singlet gerade symmetry of $H_2^+ + e^-$). First, he discusses the molecular model, in which $s-, p-$, and $d-$waves in the $H_2^+ + e^-$ scattering are included and then he evaluates the accuracy of the model comparing with experimental data. Preliminary DR cross sections are presented at the end of the chapter.

Chapter 7 summarizes the results of the thesis.

Overall, the thesis presents an important advance in theory of dissociative recombination (as well as vibrational excitation) of diatomic ions. In particular, I believe that the following two results are very valuable to the community working on theory and experiment of dissociative recombination (1) the direct and accurate assessment of accuracy of vibrational frame transformation, used extensively in many previous studies, and (2) the development of the technique that is able to describe and interpret in great details experimental cross sections for DR in HeH^+.

I recommend enthusiastically to accept the thesis proposal.

I am not sure if this document is meant to be published or it should be considered just as a supporting document for the proposal defense. If it is to be published, I have a couple of editing suggestions.

Conclusions, at least, very brief, for each chapter would make the thesis easier to understand.

Lines in certain figures are so thin that it is difficult to distinguish the lines by their color. For example, in Fig 3.5, blue and black dashed lines look almost identical. Increasing the thickness of lines in figures would certainly help.

In Orlando, March 25, 2021.

Viatcheslav Kokoouline