1. PHD PROJECT DESCRIPTION

Project title:

Effective inclusion of the nonrigidity of molecules in the inelastic scattering calculations.

1.1. Project goals

In the present project we will study how to take into account intramolecular degrees of freedom in description of inelastic collisions of molecules. Since in most cases quantum-mechanical treatment of the problem involving all degrees of freedom is not possible, our main goal is to obtain an algorithm how to prepare the effective surface of reduced dimensionality without losing the essential physical information. The resulting cross sections or rate coefficients are expected to be of the accuracy of the best experiments. As the result, we will provide also the most reliable interaction energy surfaces for a few complexes of astrochemical relevance, including the hydrogen molecule as one of the interaction partners. For these systems scattering calculations will be performed and rate coefficients for rotational transitions will be set.

1.2. Outline

In recent years one can observe a tremendous progress in accuracy of experiments in low-energy scattering of small molecules [1-3]. This progress is stimulated mainly by two factors: astrochemical applications and cold chemistry. In the former case the energies of a few Kelvin has to be considered, while in the latter one even sub-Kelvin energies are probed. In such conditions quantum nature of processes is pronounced and a new challenge has been established for theory to keep pace with experiment. Until very recently, in most of the theoretical applications, the quantum scattering calculations were performed within the rigid-rotor approximation, i.e., assuming that the molecules in the complex are rigid. This widely used approximation is well physically motivated, since the internal vibrations of interaction molecules are much more energetic than the intermolecular modes. Going beyond that model is very rare and limited only to small molecules [4]. The main reason of this limitation is the curse of dimensionality: quantum-mechanical treatment of the problem involving all degrees of freedom of the complex is not possible. Thus, we need to work out some procedures to solve the problem in an approximate way. Some time ago we have proposed an approach, called the Taylor expansion (TE) method, to take into account the nonrigidity effects by the proper averaging of the interaction energy surface over the vibration of the molecules [5]. This method turned out to be very successful in prediction of bound-state spectra of small complexes [6]. Also applications to the selected scattering problems performed by us [7,8] have shown a great prospects of the method. In the present project we want to perform systematic studies of the TE method applied for complexes of H2 with: 1) a diatom with large amplitude vibrational motion (HF), 2) a triatomic molecule with soft bending mode (H_2S), or 3) a simple organic molecule also

with a soft mode (acetylene). All such complexes are potentially sensitive for the nonrigidity effects. The TE methods will be further developed to fit demands of larger complexes. At each stage the theoretical results will be verified by comparison with their best experimental counterparts.

1.3. Work plan

At first, the student will be asked to test the whole planned procedure for the relatively simple diatom-diatom case, e.g. H_2-HF. It will be opportunity to acquire theoretical background and practical skills needed to obtain full-dimensional potential energy surface [9], to prepare the approximate (averaged) energy surfaces, to test them in the bound-state calculations, to perform scattering calculations [10], and finally to analyze the results. This first, introductory stage should be finished after 12-16 months. The system to study will be chosen in such a way that the results will be well publishable.

In the next step we will aim a more complex system, e.g. H_2-H_2S. Adding one atom to the considered complex, one can expect much more work and complexity. There are also more models to be tested, for instance by selective freezing of vibrational modes, starting from the most energetic stretching ones, through the soft bending one, up to all of them.

Depending on the progress and assuming smooth work, we can consider more complex systems, like H_2-HCCH. Interaction of H_2 with organic molecules is now of great interest for astrochemistry.

1.4. Literature

[1] A. Klein et al., Nature Phys. 13, 35 (2017);
[2] T. de Jongh et al., Science 368, 626 (2020);
[3] C. Nauline et al., Int. Rev. Phys. Chem. 33, 427 (2014);
[4] N. Balakrishnan, J. Chem. Phys. 145, 150901 (2016);
[5] P. Jankowski, J. Chem. Phys. 121, 1655 (2004);
[6] P. Jankowski et al., Science 336, 1147 (2012);
[7] A. Faure et al., Sci. Rep. (Nature) 6, 28449 (2016);
[8] M. Pawlak et al., J. Chem. Theory Comput. 16, 2450 (2020);
[9] M. P. Metz et al., J. Chem. Theory Comput. 16, 2317 (2020);
[10] J. Hutson et al., Computer Physics Communications 241, 9 (2019);

1.5. Required initial knowledge and skills of the PhD candidate

- Master degree in theoretical chemistry or physics;
- Basic knowledge of electronic structure methods;
- Some experience in using packages for advanced molecular electronic structure calculations (like Molpro, Cfour, or similar);
- Experience in using Linux;
- Knowledge of programming in at least one of the following languages: Fortran, C++, or Python.

1.6. Expected development of the PhD candidate's knowledge and skills

- solid knowledge of quantum chemistry methods, especially those related to the theory of the van der Waals interactions;
- knowledge of the theory of bound-state and scattering calculations and related numerical codes;
- proficiency in programming, including parallelization and optimization of codes;
- knowledge of selected numerical methods;
- some skills in preparing publications;
- adequate experience in presentation of scientific results in international conferences