

Nonadiabatic relativistic correction in two-electron molecules

Thanks to the development of modern measuring techniques, the precision with which modern spectroscopy allows us to determine the energy of dissociation and the energy of transitions between the levels in the hydrogen molecule and its isotope variations has exceeded the threshold of 10^{-4} cm^{-1} . So precise measurements are sensitive to small quantum relativistic and electrodynamic effects. To understand and quantify the origin of these effects, a parallel development of theoretical methods is necessary to explain the observed phenomena. The need for theory and experiment to keep pace with each other in terms of the precision obtained, results also from the fact that many atomic and molecular parameters and physical constants have been determined by collating the results from both of these fields of science. Then, the least precise component decides on the final precision of the result.

Research project objectives Contrary to the experiment, the theoretical dissociation energy of a given energy level of a molecule consists of several items. The dominant of them is non-relativistic energy, which needs to be augmented with small corrections from quantum relativistic and electrodynamic effects. This project is devoted to the relativistic correction to rotation-vibration levels in light two-electron molecules such as the hydrogen molecule and its isotopic varieties or the hydrohelium cation. A characteristic feature of this proposal is the focus on full coverage of the finite nuclear mass effect on this correction. The commonly used Born-Oppenheimer approximation related to the separation of electron and nuclear motion will not be used in the planned calculations, thanks to which the precision of calculations of this correction will increase even 10,000 times compared to that currently obtained.

Research methodology The relativistic correction will be taken as the expectation value of the relativistic Hamiltonian. In order to successfully perform such calculations, it will be necessary to find a new, previously unknown class of integrals. The most difficult and time-consuming part of the project will be devoted to this task. In the further part of the research, the most accurate currently known non-adiabatic exponential wave functions will be employed. For the intended effects it will be necessary to use matrices with sizes up to half a million. In order to achieve the planned results in a reasonable time, the use of advanced programming methods allowing effective parallelization of calculations will be required.

Expected impact of the research project on the development of science The obtained results will make it possible to practically eliminate the relativistic effects from the total error budget. Comparison of theoretical and experimental results will be a critical test of the theory developed and applied to various molecular systems. The obtained results can be used for interpretation, or even correction of existing results coming from ultra-precise spectroscopic measurements, contributing to a better understanding of the mechanisms of the formation of spectral line shapes. Moreover, the implementation of this project will be a strong motivation to carry out the new experiments. The most accurate results ever obtained for diatomic molecules will serve as reference values for research in various areas of chemistry and physics, and even to search for new phenomena going beyond the Standard Model. Implementation of the research planned in this project, in combination with new experimental results, will enable, in the future, determination of molecular properties (e.g. electric or magnetic) with a precision higher than available today. The proposed project is a milestone in a long-term expansion plan of increasing the accuracy of theoretical predictions for the hydrogen molecule and other two-electron molecules.