Relativistic nonadiabatic corrections to the ground state of molecular hydrogen

Paweł Czachorowski

Abstract

The hydrogen molecule (H_2) is a classic example of a research subject of the interdisciplinary field between physics and chemistry. It is complex enough to be considered a chemical molecule, yet its simplicity allows us to calculate its properties – such as rovibrational transition energies or the dissociation energy – with high-accuracy (e.g. $\sim 10^{-5}\,\mathrm{cm}^{-1}$ for the dissociaton energy of H_2) fundamental methods typical for physics. Availability of experimental results of similar accuracy allows not only to check consistency of our understanding of physics, but also to potentially determine physical quantities and constants: the proton charge radius, electron-proton mass ratio, the Rydberg R_∞ constant. To achieve the level of accuracy needed to perform this, not only the finite-nuclear-mass effects (adiabatic and nonadiabatic) have to be included, but also relativistic and quantum-electrodynamical (QED) too. To apply all these corrections systematically, nonrelativistic quantum electrodynamics (NRQED) and nonadiabatic perturbation theory (NAPT) methods can be employed.

The thesis reviews those approaches and shows how to combine them to calculate the titular relativistic nonadiabatic effects for H_2 and its isotopomers. Neglect of said effects was responsible for the widespread disagreement between theory and experiment among the dissociation energies and rovibrational transitions of the hydrogen isotopomers, which occured in 2017. Methods of regularisation of the arising operators and of handling the nuclear gradients are presented in detail, as well as an extensive comparison with experimental data for H_2, HD, D_2, DT, and T_2 is included.

Although the calculations of the nonadiabatic relativistic correction presented here involve a Gaussian basis set (explicitly correlated, ECG) to represent the wave function, application of explicitly correlated exponential (ECE) functions has also been studied. The thesis contains the expressions needed to perform calculations in such a basis, methods to solve certain numerical problems which then arise, and a tentative comparison to ECG calculations.

When working within the NAPT framework, it is relatively easy to calculate all possible rovibrational transitions for all the isotopomers of H_2 in a given electronic state, if only the various energy components (e.g. nonrelativistic, relativistic, QED) are available in a form of internuclear-distance-dependent potentials for this electronic state. Previous works of our research group, as well as this one, have yielded such potentials as their result. For that reason, the `H2spectr` 'black box' computer program was created. It allows the user to rapidly obtain energies of rovibrational levels and transitions. It is described in detail in this thesis.

The results of the thesis help to reconcile theory and experiment again, being the next step at the path leading to the determination of the proton charge radius from molecular spectroscopy and – more generally – a further improvement of the theory.