DOCTORAL THESIS ABSTRACT

Accurate calculations of binding energies of the ground and excited states of the hydrogen molecule

The hydrogen molecule is a fascinating system, located at the intersection of simplicity hydrogen atom, an exactly solvable quantum mechanical (QM) problem, for which many subtle effects beyond QM, due to finite nuclear mass and quantum electrodynamics has been deeply studied, and large chemical molecules with additional rich structure due to rotational and vibrational degrees of freedom.

Although here we study just this one particular physical system, main results of the thesis address three substantially different aspects. Firstly, armed with the recently developed efficient method of evaluating molecular integrals in the two-center two-electron exponential basis we pursue the decades long controversy concerning the functional form of the long-range asymptotics of the exchange energy in the two lowest states $X^1\Sigma_g^+$ and $b^3\Sigma_u^+$, which is an exponentially small effect due to Pauli exclusion principle.

Secondly, the most recent spectroscopic measurements of rovibrational transitions in HD molecule are determined with an unprecedented sub-ppb accuracy. Those are at least an order of magnitude more accurate than the current best theoretical predictions, yet the theoretical values are systematically by $1.4 - 1.9\sigma$ too small. It is currently unclear, what is the source of this discrepancy and whether the deficiency of theoretical model can be attributed to unaccounted-for, purely heteronuclear effects. To address this issue, we evaluate the leading order QED correction to the rovibrational spectra of hydrogen molecule isotopologues in its electronic ground state. Our new results do not resolve the discrepancy, but remove the uncertainty due to QED effects from the uncertainty budget of theoretical predictions and hint toward the significance of the finite nuclear mass QED effects on the order of a few MHz.

Thirdly, we address the scarcity of accurate theoretical predictions for excited states of hydrogen molecule. Even though experimental results concerning those states are plentiful, theoretical knowledge about excited states is limited to roughly about a two dozen of potential energy curves for Σ^+ symmetry and about a few less for the Π symmetry. Crucially, the accuracy of previous calculations is uncertain and those obtained concurrently by other methods are by far insufficient in view of meaningful confrontation with the modern experimental data. For symmetries corresponding to even larger angular momentum projections (Λ) our knowledge was virtually limited to two lowest ${}^{1,3}\Delta_g$ states.

With our computational method we demonstrate that trial basis sets of Kołos-Wolniewicz type still find a niche in high-accuracy variational calculations of excited states of a diatomic two-electron molecules and as a result we deliver a set of nearly one hundred highly-accurate Born-Oppenheimer potentials for Σ, Π, Δ, and Φ symmetry, typically with a relative accuracy better than 1 ppb. The successfulness of our method originates from a concentrated effort, summarized in a series of works lead by Prof. K. Pachucki (Supervisor of this thesis), towards efficient and versatile approach to evaluation of molecular integrals in exponential basis of two-electron diatomics.

Our results find an immediate application to the MQDT-assisted Rydberg spectroscopy of f electrons and lastly they shall provide a valuable benchmark for other computational methods. With these results we reconcile with all the previous *ab initio* calculations of Born-Oppenheimer potentials of H_2 by elucidating the lack of accuracy of the former calculations. Numerical uncertainty of Born-Oppenheimer potentials has been alleviated from a level of a few to the millionth parts of cm^{-1}. Resultantly, we pave the way towards evaluation of higher-order corrections to the energy levels, as their absence currently hinders the comparison with state-of-the-art spectroscopic results.

Michał Siłkowski