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Report on the dissertation
"Accurate calculations of the ground and excited state energies of the hydrogen molecules"
by
Mr. Michal Kamil Silkowski, University of Warsaw

The dissertation of Michal Silkowski is devoted to the theoretical treatment of molecular hydrogen and to calculations of unprecedented accuracy and completeness of its electronic structure and energy spectrum. The thesis presents in a scholarly manner the latest developments of a long series of theoretical efforts in the group of Professor Krzysztof Pachucki aiming at a complete and quantitatively highly accurate description of this fundamental molecular system. These efforts have a fundamental significance in the physical sciences and can be regarded as one of the most significant recent achievements in theoretical molecular physics. The results presented in the dissertation also form the basis for a rigorous comparison with experimental results and for the development of a quantitative treatment of nonadiabatic interactions in the Rydberg states of molecular hydrogen.

The thesis consists of seven chapters which are complemented, in an extended appendix, by a very extensive set of Born-Oppenheimer potential-energy functions, rescaled mass polarizations, and energy derivatives for the ground and many electronically excited states of Σ, Π, Δ and Φ symmetry of molecular hydrogen.

The first chapter provides a short recapitulation of the general aspects of the Schrödinger equation of molecular hydrogen and its solutions. The Born-Oppenheimer approximation is presented and so are the treatment of nonadiabatic effects through the coupled-equation formalism introduced by Quadrelli, Dressler and Wolniewicz.

The second chapter presents a general discussion of the different sets of basis functions that can be used in calculations of the electronic structure of molecular hydrogen with their merits and shortcomings, Then, the evaluation of integrals involving these functions is presented with mathematical rigor. In particular, practical details are provided on how to best deal with the cusp regions, where the Coulomb interaction diverges.

The third chapter is devoted to an original discussion of the electronic states of molecular hydrogen. It starts with a very interesting discussion of an old controversy concerning the correct asymptotic form of the exchange energy, which could be resolved in the realm of this dissertation by a variational numerical treatment. Then, the results of extremely precise calculations of the Born-Oppenheimer potential-energy functions of the electronic states of Σ^+ symmetry are presented and discussed. The significance of these results, beyond their unprecedented accuracy and completeness, lies in the treatment of numerous highly electronically excited states with n values beyond 7. The main properties of these functions (e.g., the behavior in the united- and separated-atom limits, configuration interactions, avoided crossings, and the

emergence of Rydberg character) are analysed. These calculations and the accompanying discussion are then extended to electronic states of Π, Δ and Φ symmetry and are complemented by the extensive set of numerical results presented in the appendix. The new results are carefully compared with earlier theoretical results and the comparison reveals that the new data are in many cases the accuracy has been improved by several orders of magnitude, which is truly remarkable. This material represents a unique and extremely precious source of information on the electronic spectrum of molecular hydrogen.

Adiabatic and nonadiabatic corrections to energies obtained in the Born-Oppenheimer approximation form the subject of the fourth chapter, including specific effects arising in heteronuclear molecules, e.g., HD. Numerical results are presented for several $^1\Sigma_g^+$ states (EF, GK, HHbar, P and O) and the B $^1\Sigma_u^+$ state. The chapter also shows, with the example of Σ^+ states, how to extract off-diagonal coupling functions needed to treat dense and highly perturbed spectral regions and analyzes the relation between diabatic and adiabatic representations of interacting electronic states.

The fifth chapter extends the treatment presented in the earlier chapters by presenting calculations of relativistic and quantum-electrodynamics corrections and of finite-nuclear-size effects. This chapter combines derivations of the essential equations with numerical calculations, and includes a discussion of the asymptotic behavior of the corrections and of the numerical convergence and accuracy.

The sixth chapter presents a short summary of the discrete-variable-representation procedure, implemented in the programme H2spectre, that can be used to calculate rovibrational energy levels. Because the individual chapters all had an own extensive “discussion and conlcusions” section, the last chapter (Conclusions and outlook) is limited to a rather brief outlook concerning how current (small) discrepancies between experimental and theoretical results might be resolved in the future.

The choice was made in the dissertation to present the procedures to calculate the corrections and illustrate them with numerical results rather than comparing calculated rovibronic energies with experimental results for electronically excited states. In the future, this comparison will be an important task.

The dissertation of Michal Silkowski impresses by the very high quality, the completeness and the significance of the results presented. It represents a document of great value as it documents, with scholarship and numerical accuracy, the current status of the theoretical understanding and description of the simplest molecular system exhibiting all generic features of a chemical bond. Fundamental aspects of molecular structure are addressed with scientific rigor and the more than 240 references illustrate the scholarship of the author. Several small typographical and other very minor errors do not reduce the remarkable quality and value of the dissertation.

I therefore recommend that this excellent thesis be accepted as doctoral dissertation. In my opinion, the quality and scope of the results go far beyond what may be expected of a doctoral thesis and deserve a mark of distinction.

Frédéric Merkt, Professor of Physical Chemitry and member of the Swiss National Research Council
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