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Subj: Assessment PhD Thesis M. Silkowski

It is my great pleasure to give an assessment of the PhD Thesis by candidate Michal Silkowski. The work, dealing with the quantum mechanical description of the neutral hydrogen molecule at the most fundamental level, is performed in the world leading environment on this subject built by the Thesis advisor. The work involves derivation of the fundamental equations, analysis and computation at the highest level of sophistication, at a point where physics, chemistry, mathematics as well as computer science merge.

The major achievement of the Thesis resides in the novel perspective of computing potential energy curves of electronically excited states in molecular hydrogen. Up to now the Pachucki team, in collaboration with Komasa and Puchalski at Poznan, had entirely focused on the electronic ground state of hydrogen molecular isotopologues, first performing Born-Oppenheimer (BO) curves with adiabatic, nonadiabatic, relativistic and quantum-electrodynamical corrections at ever increasing precision. This Thesis opens a new avenue with precision BO-calculations for over a hundred potential energy curves for excited states. For the $^1\Sigma^+$ states a numerical accuracy of 12-15 digits is obtained for the BO curves, and slightly less for the states of higher electronic angular momenta. Of course, such computations had been done in the past, most notably by Kolos and Wolniewicz, but the precision achieved now is several orders of magnitude better. This achievement requires a wide variety of skills, as mentioned above. These computations form a novel test bed for comparison with experiment. The subject is timely chosen, the community was waiting for it, where experiments on excited states are being performed at increasing precision through laser experiments.

Part of the studies in the Thesis are methodological. In particular, the analysis of ab initio calculations with various basis set approaches is relevant. Detailed comparisons are made by starting out from a Kolos-Wolniewicz (KW) basis with correlated exponential functions, with bases of explicitly correlated Gaussian (ECG) functions. The quantitative comparison between the two methods provides particular insights with relevance for the field of theoretical chemistry.

In addition to that the strive for "well-controlled uncertainties" is important – it used to be uncommon practice in ab initio studies of molecules because uncertainties were so difficult to

assess. The attention given to this particular aspect is novel and worthwhile. For making a comparison between theoretical values with values from precision experiments it is vital, it cannot do without stating an uncertainty. That is the strength of this approach. The computations are made ready for testing in experiment.

In one of the chapters, this Thesis tries to pursue a conundrum of current high-precision experimental work. In the past years several groups in the world have focused on measurements of vibrational spectra of HD, where discrepancies with the most advanced quantum ab initio calculations were found. Even though the discrepancies are only of size 2σ, the consistency of the discrepancy is remarkable. Not only in the HD heteronuclear species, but also for lines in the H_2 and D_2 homonuclear species theoretical values are lower by a similar 2σ. It is very much welcomed that the candidate has tried to tackle this open issue of current experiments to improve the calculation of leading order QED effects in the ground state of molecular hydrogen isotopologues. The study has not resolved the issue, but has contributed to further understanding.

Chapter III forms a remarkable addition, dealing with the exchange energy at very large internuclear distances. In reading this part this reviewer was amazed about the mathematical and computational skills shown by the candidate. The use of efficient parallel versions of "linear algebra in an arbitrary precision arithmetic to fully control the precision" in computing the exchange energy defines a novel advanced level in theoretical chemistry. Here an enormous improvement in the numerical treatment reaching extreme precision in the exchange energy is obtained. This again demonstrates the skills of the candidate. This part also shows where the seminal work of Heitler and London, forming the basis of the chemical bond, needs to be corrected (at very large R).

While this Thesis reaches excellence for the scientific content the question arises whether everything is perfect. Well, there exist some shortcomings in the use of English grammar, tenses, plural and singular, and articles. But that is forgivable for a student having to write a Thesis in a foreign language.

In conclusion this doctoral dissertation shows par excellence the theoretical knowledge of the candidate at the merger point of physics, chemistry, mathematics and computer science.
The problems tackled in the dissertation provide original solutions to a number of problems as discussed in the above.

I confirm, without hesitation, that the candidate deserves the doctor degree for this excellent work. I am not familiar with the Polish system, but in a general sense I would fully support awarding a high degree of distinction associated with the PhD degree bestowed upon him. This work stands in a long tradition of outstanding contributions of Polish scientists involved in quantum analysis of the hydrogen molecule, first pioneered by Kolos, by Wolniewicz. This tradition has now evolved further with the contributions by the team led by Pachucki, of which PhD candidate Silkowski is an excellent pupil.

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