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Electronic structure theory meets precision measurements

Haase, Pi

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Electronic structure theory meets precision measurements

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Nikhef

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Electronic structure theory meets precision measurements

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 and in accordance with
 the decision by the College of Deans.

This thesis will be defended in public on

Thursday 23 December 2021 at 16:15

by

Pi Ariane Bresling Haase

born on 16 March 1990
 in Copenhagen, Denmark

Supervisors

Prof. A. Borschevsky

Prof. R. G. E. Timmermans

Assessment Committee

Prof. S. Faraji

Prof. P. Schwerdtfeger

Prof. R. Berger

Abstract

Electronic structure theory and precision measurements go hand in hand. Reliable predictions of atomic and molecular properties are often very useful and sometimes strictly necessary in order to design the best possible experimental setups and to interpret the measured results. This thesis is motivated by the search for new physics with molecules, where symmetry breaking molecular enhancement factors are crucial for the interpretation of measurements. Such enhancement factors should be provided by theoretical methods and the main question of this thesis is: How accurate can electronic structure methods be and how to quantify this accuracy?

To answer this question, the performance of the state-of-the-art relativistic coupled-cluster method for predicting molecular properties was thoroughly examined. In addition, a scheme for estimating the uncertainty of the obtained results from first principles was investigated. This scheme was benchmarked using both ground and excited state hyperfine structure (HFS) constants. Comparison between the calculated and experimental HFS constants showed excellent agreement within the estimated uncertainty, demonstrating the reliability of the relativistic coupled-cluster method and, more importantly, the scheme for estimating the uncertainty for predicting core-like properties.

The relativistic coupled-cluster method could consequently be used to determine the more exotic symmetry breaking molecular enhancement factors, where no experiment is available. Accurate values of these properties and, equally important, reliable uncertainty estimates will be crucial in the interpretation of the, yet to come, first measurements of symmetry breaking effects in molecules. Such measurements will have a large impact on the development of new physics theories.

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List of Publications

Throughout this thesis, publications that I have co-authored will be referenced, along with my contributions, according to list presented here. The publications marked with **bold** have been included as chapters.

- Paper 1** S. Sami, P. A. B. Haase, R. Alessandri, R. Broer, and R. W. A. Havenith, *Can the Dielectric Constant of Fullerene Derivatives Be Enhanced by Side-Chain Manipulation? A Predictive First-Principles Computational Study*, J. Phys. Chem. A, vol. 122, no. 15, pp. 3919-3926, 2018.
- Paper 2** P. Aggarwal, H. L. Bethlem, A. Borschevsky, M. Denis, K. Esajas, P. A. B. Haase, Y. Hao, S. Hoekstra, K. Jungmann, T. B. Meijknecht, M. C. Mooij, R. G. E. Timmermans, W. Ubachs, L. Willmann, and A. Zapara, *Measuring the electric dipole moment of the electron in BaF*, Eur. Phys. J. D, vol. 72, no. 11, p. 197, Nov. 2018.
- Paper 3** M. Denis, P. A. B. Haase, R. G. E. Timmermans, E. Eliav, N. R. Hutzler, and A. Borschevsky, *Enhancement factor for the electric dipole moment of the electron in the BaOH and YbOH molecules*, Phys. Rev. A, vol. 99, no. 4, p. 42512, 2019.
- Paper 4** C. G. Pech, P. A. B. Haase, N. Galland, A. Borschevsky, and R. Maurice, *Relevance of effective bond orders in heterodiatom molecules and role of the spin-orbit coupling in the AtX (X=At-F) series*, Phys. Rev. A, vol. 100, no. 3, pp. 1-8, 2019.
- Paper 5** P. A. B. Haase, E. Eliav, M. Iliaš, and A. Borschevsky, *Hyper-fine Structure Constants on the Relativistic Coupled Cluster Level with Associated Uncertainties*, J. Phys. Chem. A, vol. 124, no. 16, pp. 3157-3169, Apr. 2020. (Chapter 4)
- Paper 6** C. G. Pech, P. A. B. Haase, D.-C. Sergentu, A. Borschevsky, J. Pilmé, N. Galland, and R. Maurice, *Quantum chemical topology at the spin-orbit configuration interaction level: Application to astatine compounds*, J. Comput. Chem., vol. 41, no. 23, pp. 2055-2065, 2020.
- Paper 7** P. A. B. Haase, D. J. Doeglas, A. Boeschoten, E. Eliav, M. Iliaš, P. Aggarwal, H. L. Bethlem, A. Borschevsky, K. Esajas, Y. Hao,

S. Hoekstra, V. R. Marshall, T. B. Meijknecht, M. C. Mooij, K. Steinebach, R. G. E. Timmermans, A. P. Touwen, W. Ubachs, L. Willmann and Y. Yin (NL-eEDM Collaboration), *Systematic study and uncertainty evaluation of P, T -odd molecular enhancement factors in BaF* , J. Chem. Phys., vol. 155, no. 3, p. 034309, Jul. 2021. (Chapter 5)

Paper 8 M. Denis, P. A. B. Haase, M. C. Mooij, P. Aggarwal, H. L. Bethlem, A. Boeschoten, A. Borschevsky, S. Hoekstra, V. R. Marshall, T. B. Meijknecht, R. G. E. Timmermans, A. P. Touwen, W. Ubachs, and L. Willmann (NL-eEDM Collaboration), *Magnetic hyperfine interaction in the ground and excited states of BaF* , in preparation. (Chapter 6)

Paper 9 T. L. C. Janssen, P. A. B. Haase, A. Borschevsky, *Molecular Dynamics of ordered domains in methylammonium lead iodine and the effect of polarizability*, in preparation.

Paper 10 M. Fiechter, P. A. B. Haase, et al., *Towards detection of the molecular parity violation in chiral $Ru(acac)_3$ and $Os(acac)_3$* , in preparation.

Paper 11 Anne de Vries, P. A. B. Haase, E. Eliav, A. Borschevsky, *Magnetic hyperfine structure constants in the excited states of ^{133}Cs and ^{137}Ba* , in preparation.

Paper 12 J. De Wit, P. A. B. Haase, L. Pasteka, S. Hoekstra, A. Borschevsky, *Static polarizabilities in the excited states of BaF* , in preparation