Mathematisches Forschungsinstitut Oberwolfach

Report No. 13/2018

DOI: 10.4171/OWR/2018/13

Mathematical Methods in Quantum Chemistry

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18 March – 24 March 2018

Abstract. The field of quantum chemistry is concerned with the modelling and simulation of the behaviour of molecular systems on the basis of the fundamental equations of quantum mechanics. Since these equations exhibit an extreme case of the curse of dimensionality (the Schrödinger equation for N electrons being a partial differential equation on $\mathbb{R}^{3N}$), the quantum-chemical simulation of even moderate-size molecules already requires highly sophisticated model-reduction, approximation, and simulation techniques. The workshop brought together selected quantum chemists and physicists, and the growing community of mathematicians working in the area, to report and discuss recent advances on topics such as coupled-cluster theory, direct approximation schemes in full configuration-interaction (FCI) theory, interacting Green's functions, foundations and computational aspects of density-functional theory (DFT), low-rank tensor methods, quantum chemistry in the presence of a strong magnetic field, and multiscale coupling of quantum simulations.

Mathematics Subject Classification (2010): 81Q05 (81V55, 65Y20).

Introduction by the Organisers

Originally developed for a small number of atoms, quantum-chemical or "ab initio" simulations are nowadays essential tools not just in chemistry but also in materials science, solid-state physics, nanoscience, and molecular biology. A key bottleneck is the computation of the electronic ground or excited states of the system. Since the "exact" electronic Schrödinger equation for a molecule with N electrons is a partial differential equation in $3N$ dimensions, it exhibits an extreme case of the curse of dimensionality: direct simulation on a grid or in standard approximation

subspaces is prohibitive already for a few electrons. Quantum-chemical simulations therefore require highly sophisticated model-reduction, approximation, and simulation techniques. This interdisciplinary workshop brought together quantum chemists, mathematicians, and physicists, focusing on recent conceptual and methodological ideas and (where available) mathematical results.

The contributions by Fabian Faulstich, Heinz-Jürgen Flad, Simen Kvaal, Thomas Bondo Pedersen, and Chao Yang are devoted to the coupled-cluster method, which has been a benchmark method in quantum chemistry for accurate simulation of systems of up to a few dozen electrons for quite some time. Nevertheless, novel understanding – for instance, of its "bi-variational" structure, its singularities at coalescence points, and some subtle numerical challenges – is only now emerging in current research.

The contributions by Jürgen Gauss and Harry Yserentant discuss direct approximability of many-body Schrödinger equation, or FCI wave functions, via, respectively, Gauss–Hermite functions and many-body expansion in the virtual orbital space.

Another, very general and ultimately nonlinear, strategy to capture functions depending on a large number of variables is low-rank tensor approximation. Applications of this strategy – for instance, to the simulation of stationary electronic states and optical spectra – are discussed in the contributions by Venera Khoromskaia and Boris Khoromskij. Christian Lubich summarizes how to carry out robustly dynamical low-rank approximation in the presence of small singular values.

For large systems, the method of choice has for many years been DFT, in which the numerical approximation of the high-dimensional wave function is replaced by a drastic model reduction, focusing on the single-particle density as the key variable. The contributions by Andre Laestadius, Robert van Leeuwen, and Aihui Zhou revisit foundational issues in time-dependent and static DFT. What is rigorously known regarding the existence of the density-to-potential mapping? How can one overcome the lack of functional differentiability of the constrained-search Levy–Lieb functional via functional analytic (Moreau–Yosida) regularization? Computational aspects of DFT – in particular, how to project out an ambient bath and how to compute the exchange–correlation energy efficiently in the random-phase approximation (RPA) – are discussed by Leonardo Zepeda-Núñez and Kyle Thicke, respectively.

Interacting Green's function methods are discussed in the contributions by Michael Lindsey, Lucia Reining, and Reinhold Schneider.

In periodic systems, a highly nontrivial correspondence between the topology and Chern number of the Bloch bundle and the existence of Wannier function is described in the contribution by Gianluca Panati. Antoine Levitt and Anil Damle report on recent advances in the computation of Wannier functions.

Sometimes – for instance in the presence of magnetic fields – it is important to

incorporate effects beyond standard DFT, or even beyond the standard (Born–Oppenheimer–)Schrödinger equation. Andrew Teale discusses recent advances in current-DFT, Erik Tellgren reports on the magnetic Schrödinger–Maxwell model, and Trond Saue discusses the X2C Hamiltonian, which is isospectral to the positive part of the Dirac Hamiltonian despite sacrificing the "small" components of Dirac spinors.

Another important aspect discussed in this report is multiscale coupling of quantum mechanics to molecular mechanics or molecular dynamics. Christoph Ortner discusses electronic relaxation at material defects at the tight-binding level of theory, Benjamin Stamm reports on the effective simulation of solvents, and the contribution by Caroline Lasser is devoted to the emulation of quantum dynamics by stochastic surface hopping.

The richness and diversity of mathematical topics in quantum chemistry presented in this report is rounded off by the contributions by Virginie Ehrlacher, on the inverse problem of designing periodic potentials giving rise to a desired band structure, by Geneviève Dusson, on a-posteriori estimation and post-processing methods for nonlinear eigenvalue problems, by Mathieu Lewin, on the mathematical and physical meaning of critical points of the Hartree–Fock functional, and by Michael Herbst, on a novel basis set for molecular electronic-structure theory, the Coulomb-Sturmians.

Acknowledgement: The MFO and the workshop organizers would like to thank the National Science Foundation for supporting the participation of junior researchers in the workshop by the grant DMS-1641185, "US Junior Oberwolfach Fellows".

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