

MATHEMATISCHES FORSCHUNGSINSTITUT OBERWOLFACH

Report No. 32/2011

DOI: 10.4171/OWR/2011/32

Mathematical Methods in Quantum Chemistry

Organised by
Gero Friesecke, München
Peter Gill, Canberra

June 26th – July 2nd, 2011

ABSTRACT. The field of quantum chemistry is concerned with the analysis and simulation of chemical phenomena on the basis of the fundamental equations of quantum mechanics. Since the 'exact' electronic Schrödinger equation for a molecule with N electrons is a partial differential equation in $3N$ dimension, direct discretization of each coordinate direction into K gridpoints yields K^{3N} gridpoints. Thus a single Carbon atom ($N = 6$) on a coarse ten point grid in each direction ($K = 10$) already has a prohibitive 10^{18} degrees of freedom. Hence quantum chemical simulations require highly sophisticated model-reduction, approximation, and simulation techniques.

The workshop brought together quantum chemists and the emerging and fast growing community of mathematicians working in the area, to assess recent advances and discuss long term prospects regarding the overarching challenges of

- (1) developing accurate reduced models at moderate computational cost,
- (2) developing more systematic ways to understand and exploit the multi-scale nature of quantum chemistry problems.

Topics of the workshop included:

- wave function based electronic structure methods,
- density functional theory, and
- quantum molecular dynamics.

Within these central and well established areas of quantum chemistry, the workshop focused on recent conceptual ideas and (where available) emerging mathematical results.

Mathematics Subject Classification (2000): 81Q05 (81V55, 65Y20).

Introduction by the Organisers

The field of quantum chemistry is concerned with the analysis and simulation of chemical phenomena on the basis of the fundamental equations of quantum mechanics. While mathematical thinking (by physicists and chemists) has always played a large role in this field, in the past years a growing and very active community of mathematicians working in the area has also emerged. The workshop was interdisciplinary, bringing together quantum chemists and mathematicians to assess the state of the art and discuss recent conceptual ideas and emerging mathematical results.

The Oberwolfach institute and format (of fewer talks than standard conferences) provided an ideal venue. It stimulated not just lively discussions (by no means limited to the explicit 10-minutes discussion slot allocated after each morning lecture). The Oberwolfach format also proved a fertile ground for cultural cross-fertilization. A clear proof that the latter was taking place was that by Wednesday morning, the first quantum chemist (Alexander Auer) was ready to spontaneously give up his planned laptop presentation for a blackboard talk.

Recurring themes of the meeting were (1) the continuing search for accurate computational methods with feasible computational cost, (2) the need for developing more systematic ways to understand and exploit the multiscale nature of quantum chemical systems, (3) new examples of quasi-exactly soluble many-electron systems.

As regards theme (1), the ‘exact’ electronic Schrödinger equation for an atom or molecule with N electrons is a partial differential equation in $3N$ dimensions, so direct discretization of each coordinate direction into K gridpoints yields K^{3N} gridpoints; thus the unreduced equation for a single Carbon atom ($N = 6$) on a coarse ten point grid in each direction ($K = 10$) already has a prohibitive 10^{18} degrees of freedom. The computational cost of the best wave function based methods, such as multiply-excited Configuration-Interaction methods or Coupled Cluster theory, while no longer exponential, still scales like an unphysically steep power of the particle number. By contrast, density functional theory, which replaces the linear many-electron Schrödinger equation in $3N$ dimensions by a nonlinear system of partial differential equations in 3 dimensions, is applicable up to thousands of atoms (and hence the method of choice in most applications in materials science, molecular biology, and nanotechnology), but its modelling approximations have proven hard to systematically understand or improve despite great effort over many years.

Recent ideas to directly attack the curse of dimensionality of electronic wavefunctions which were presented at the workshop included: the derivation and implementation of symmetry-projected Hartree-Fock-Bogoliubov theory for molecular electronic structure problems (talk by Gustavo Scuseria); design of a stochastic ‘game’ of life, death and annihilation in Slater determinant space (talks by Ali Alavi and Alex Thom); the recently developed general mathematical format of truncation and low-rank approximation of tensors (talk by Wolfgang Hackbusch); quantum-chemical versions of the density matrix renormalization group algorithm

and its analysis in the context of the matrix product state alias TT tensor format (talk by Reinhold Schneider); the recent proof of high mixed regularity of Schrödinger electronic wavefunctions and its implications for efficient approximability in sparse bases (talk by Harry Yserentant); a sophisticated combination of coupled-cluster theory and low-rank approximation of tensors (talk by Alexander Auer); use of a Jastrow ansatz with prefactor optimization via a quantum Monte Carlo approach (talk by Heinz-Jürgen Flad), efficient iterative symmetry decomposition for large atoms (talk by Christian Mendl); hierarchical decomposition of total molecular energies into contributions from different bond orders (Fredrik Heber); and use of a Smolyak grid and an efficient quadrature scheme built from nested 1D quadratures to solve the vibrational Schrödinger equation (talk by Tucker Carrington).

Another important aspect in computational cost reduction is the structure of the underlying single-particle basis sets. Werner Kutzelnigg presented sophisticated results on completeness and convergence rates for Gaussian and exponential bases, Lin Lin presented novel adaptive local basis sets for efficient density functional theory calculations in solids, and Peter Pulay gave a quantum chemist's view on basis sets based on his own more than 40 years of work in the area.

Volker Bach gave an overview over old and new mathematical results in Hartree-Fock theory, Thomas Oestergaard Soerensen explained his recent work on local analyticity of Schrödinger wavefunctions in the interparticle positions and distances, and Thorsten Rohwedder and Saber Trabelsi presented rigorous analyses of the coupled cluster equations respectively the multi-configuration time-dependent Hartree-Fock equations. Heinz Siedentop derived and analyzed a mathematical model for interacting Dirac Fermions in graphene quantum dots.

Progress related to multiscale aspects of many-electron systems included the derivation, analysis and implementation of a governing equation for the distortion in electronic structure caused by a defects in a solid (opening talk by Eric Cancès). Note that in an approximating N -particle system the total energy is order N , but the desired energy contribution is order 1, and one needs to pass to the limit $N \rightarrow \infty$. Similar scale issues (with small parameter being the reciprocal of the number of particles) appear when one is interested in the energy required to perturb the density of a Fermi gas (talk by Mathieu Lewin) and the distortion of electronic structure in a solid by elastic deformation (talk by Jianfeng Lu). Another important small parameter appears in quantum molecular dynamics, namely the ratio between electronic and nuclear mass; this parameter is traditionally exploited both by adiabatic decoupling of electronic and nuclear motion (Born-Oppenheimer approximation) and semiclassical approximation of the nuclear motion. Subtle ways of exploiting this smallness even when the traditional assumptions of the Born-Oppenheimer approximation (namely uniform gaps between electronic energy levels) are violated were presented by Caroline Lasser (numerical approximations of quantum molecular dynamics) and Volker Betz (asymptotic analysis of quantum dynamics at avoided crossings of electronic

levels). George Hagedorn explained his recent derivation and analysis (and ensuing predictions) of non-classical Born-Oppenheimer-type approximations for the vibrational Schrödinger equation for hydrogen-bonded systems; here one exploits the smallness of the mass of the hydrogen nucleus compared to the other nuclear masses.

New examples of quasi-exactly soluble many-electron models were presented by Jerzy Cioslowski (electrons in spherical confining potentials), Pierre-Francois Loos (electrons restricted to hyperspheres), and Ben Goddard (highly charged atomic ions).

Another highlight of the workshop was a very well attended Thursday evening session with short presentations by the graduate students Virginie Ehlacher, Robert Lang, Stefan Kühn, André Uschmajew, Fabian Hantsch, and Stefan Handschuh, which – just like the daytime lectures – were followed by lively discussion.