Centre for Theoretical and Computational Chemistry

Trygve Helgaker

Centre for Theoretical and Computational Chemistry

Department of Chemistry, University of Oslo

Opening of CTCC

September 19, 2007

Auditorium Tabletten, School of Pharmacy

Experimental vs. theoretical chemistry

- Chemistry is an experimental science!
- Computation provides numbers but no understanding!

"Every attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational. If mathematical analysis should ever hold a prominent place in chemistry—an aberration which is happily impossible—it would occasion a rapid and widespread degradation of that science."

August Comte, 1748–1857

- Quantum chemistry is built on a deep understanding of chemical systems!

"The more progress sciences make, the more they tend to enter the domain of mathematics, which is a kind of center to which they all converge. We may even judge the degree of perfection to which a science has arrived by the facility with which it may be submitted to calculation."

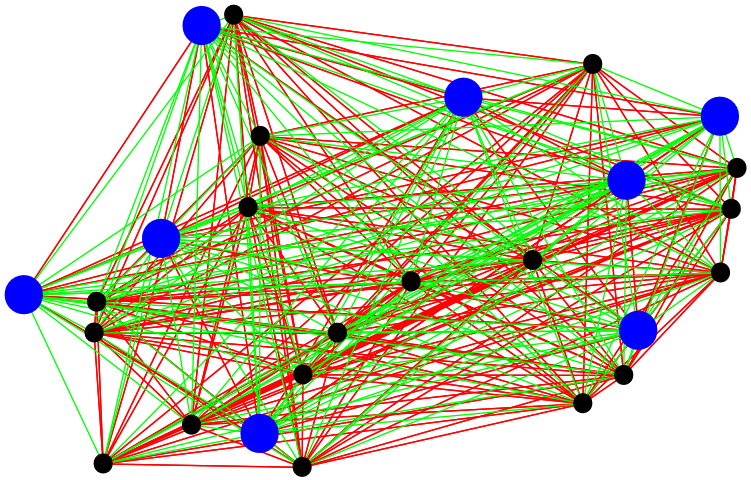
Adolphe Quetelet, 1796–1874

Quantum mechanics and the many-body problem

- Chemistry became physics with the introduction of QM in the 1920s
- Dirac's statement:

  "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble."

- The complication lies only in the large number of particles: the many-body problem



- The quantitative application of QM to problems of chemical interest seemed hopeless

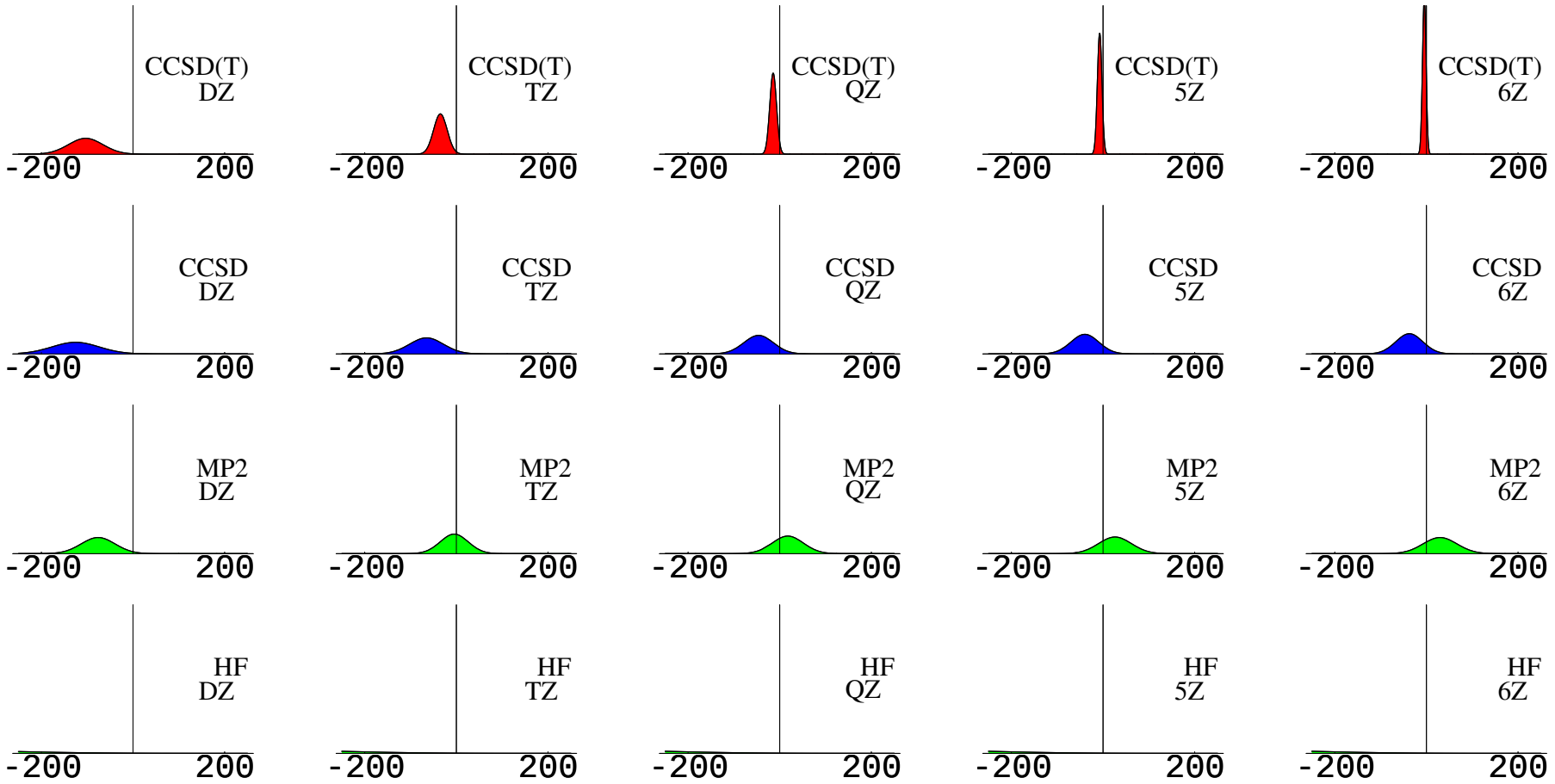
The electronic computer—the quantum chemist's tool

- The solution came in an unexpected manner, with the emergence of the computer: ENIAC (Electronic Numerical Integrator and Computer) (1946)
- Over the last 50 years, computers have developed in a spectacular fashion, as expressed by Gordon Moore's law (1964):

  the capacity of computers double every two years, at no extra cost

  – computers are now 10000 more powerful than one generation ago
- With this amazing tool at their disposal, chemists have diligently developed new computational techniques: quantum chemistry
  – the development of refined models of chemical electronic systems
  – their solution using advanced methods of numerical analysis
  – their implementation on the latest computer hardware
- The exact solution is beyond reach but can be approached systematically
  – the "insoluble" problem is being solved every day—by nonspecialists!

Atomization energies (kJ/mol)

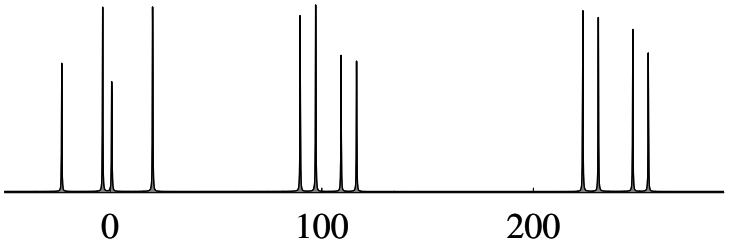


Reaction Enthalpies (kJ/mol)

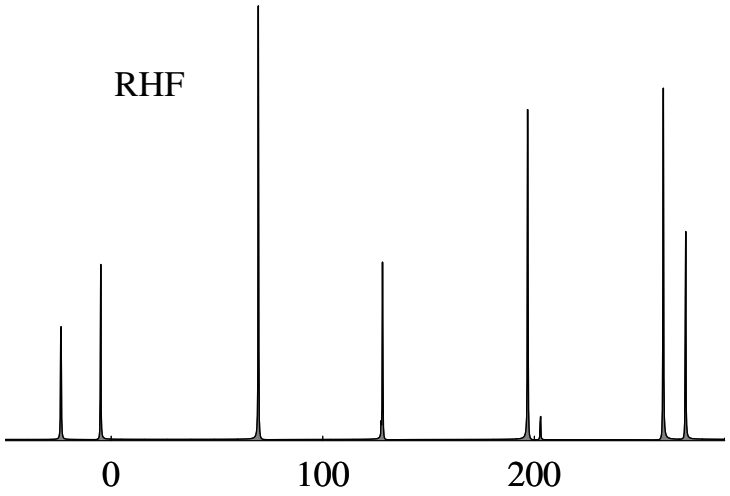
	B3LYP	(56)	exp.
$CH_2 + H_2 \rightarrow CH_4$	−543	−543	−544(2)
$C_2H_2 + H_2 \rightarrow C_2H_4$	−208	−206	−203(2)
$C_2H_2 + 3H_2 \rightarrow 2CH_4$	−450	−447	−446(2)
$CO + H_2 \rightarrow CH_2O$	−34	−23	−21(1)
$N_2 + 3H_2 \rightarrow 2NH_2$	−166	−165	−164(1)
$F_2 + H_2 \rightarrow 2HF$	−540	−564	−563(1)
$O_3 + 3H_2 \rightarrow 3H_2O$	−909	−946	−933(2)
$CH_2O + 2H_2 \rightarrow CH_4 + H_2O$	−234	−250	−251(1)
$H_2O_2 + H_2 \rightarrow 2H_2O$	−346	−362	−365(2)
$CO + 3H_2 \rightarrow CH_4 + H_2O$	−268	−273	−272(1)
$HCN + 3H_2 \rightarrow CH_4 + NH_2$	−320	−321	−320(3)
$HNO + 2H_2 \rightarrow H_2O + NH_2$	−429	−446	−444(1)
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	−211	−244	−244(1)
$2CH_2 \rightarrow C_2H_4$	−845	−845	−844(3)

200 MHz NMR spectra of vinyllithium

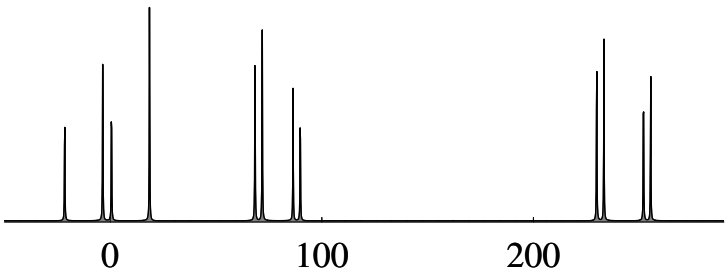
experiment



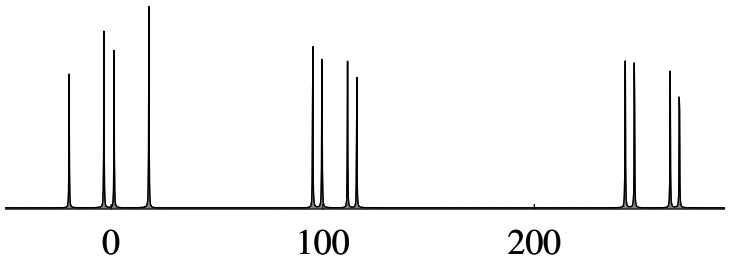
RHF



MCSCF



B3LYP

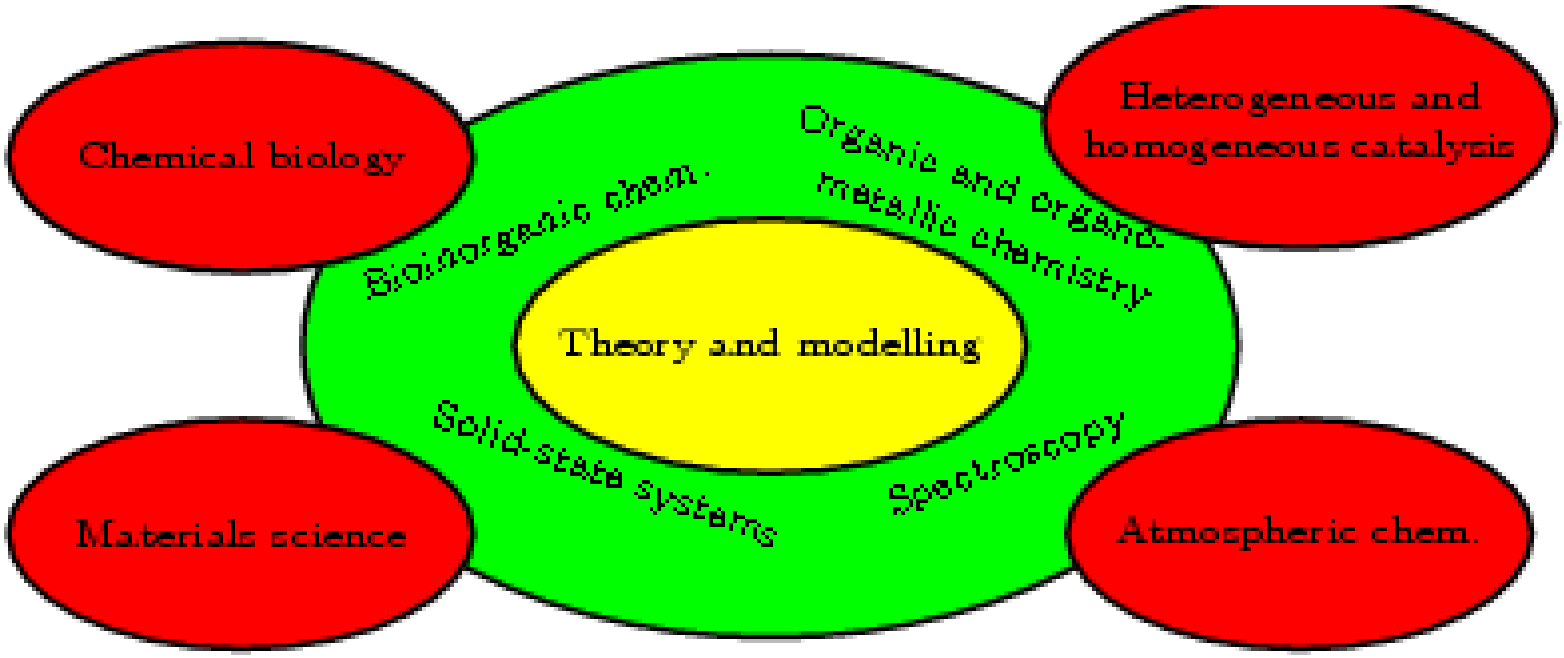


New Challenges

- Today quantum chemistry has become an integral part of modern chemistry
  - used by specialists and nonspecialists alike
  - for prediction, elucidation, explanation and confirmation
  - Computational Science has become an important area of modern science
- But, chemistry itself is in constant change
  - biochemistry
  - materials science
- This development provides ever new challenges to quantum chemistry
  - we must prepare ourselves for tomorrow's important problems
- Quantum chemistry is an interdisciplinary science
  - theory, experiment, computation
  - chemistry, physics, mathematics, computer technology
- The future of quantum chemistry requires knowledge of all these areas!

CTCC: Theory and Modeling

- CTCC has therefore been established as a collaborative effort



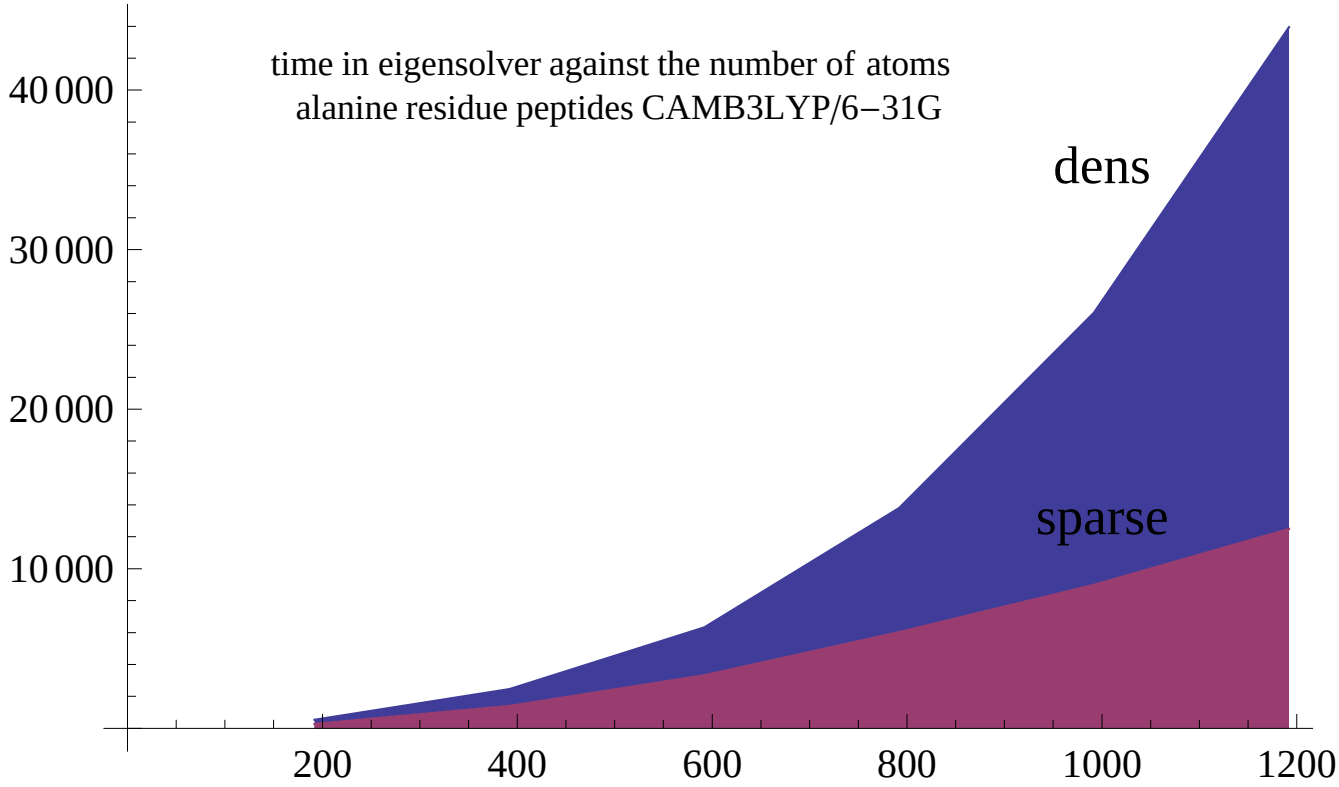
  - five senior researchers from the University of Tromsø
  - five senior researchers and two affiliated from the University of Oslo
  - experimentalists and theorists from chemistry, physics, and mathematics

Work Packages

- WP1: Large periodic and nonperiodic systems (T. Helgaker)
- WP2: Fragment approach for large systems (I. Røggen)
- WP3: Multiscale methods with wavelets (T. Flå)
- WP4: Properties and Spectroscopy (L. Frediani)
- WP5: Dynamics and time development (E. Uggerud)
- WP6: Bioinorganic chemistry (A. Ghosh)
- WP7: Catalysis and organometallic chemistry (M. Tilset)
- WP8: Gas-phase reactions and photochemistry (C. J. Nielsen)
- WP9: Clusters, surfaces and solids (K. Fægri jr.)

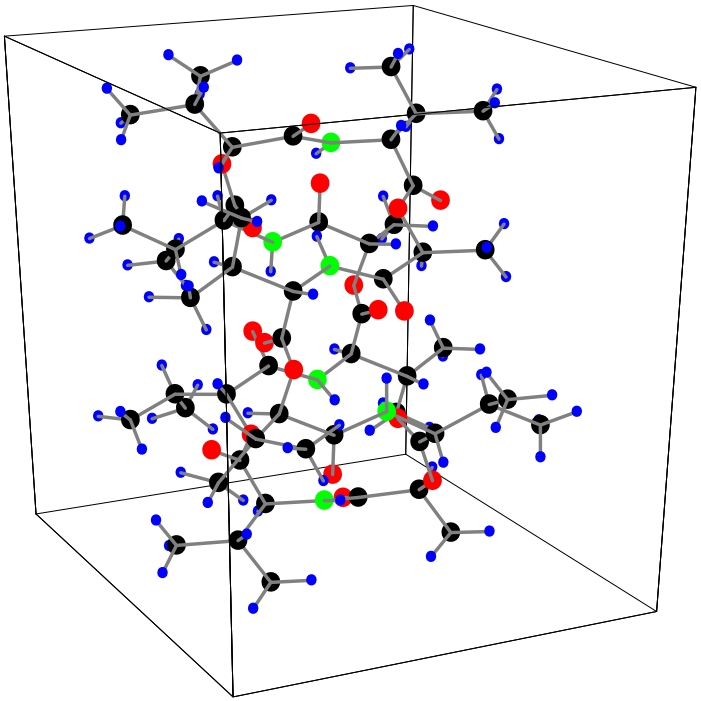
WP1: Large periodic and nonperiodic systems

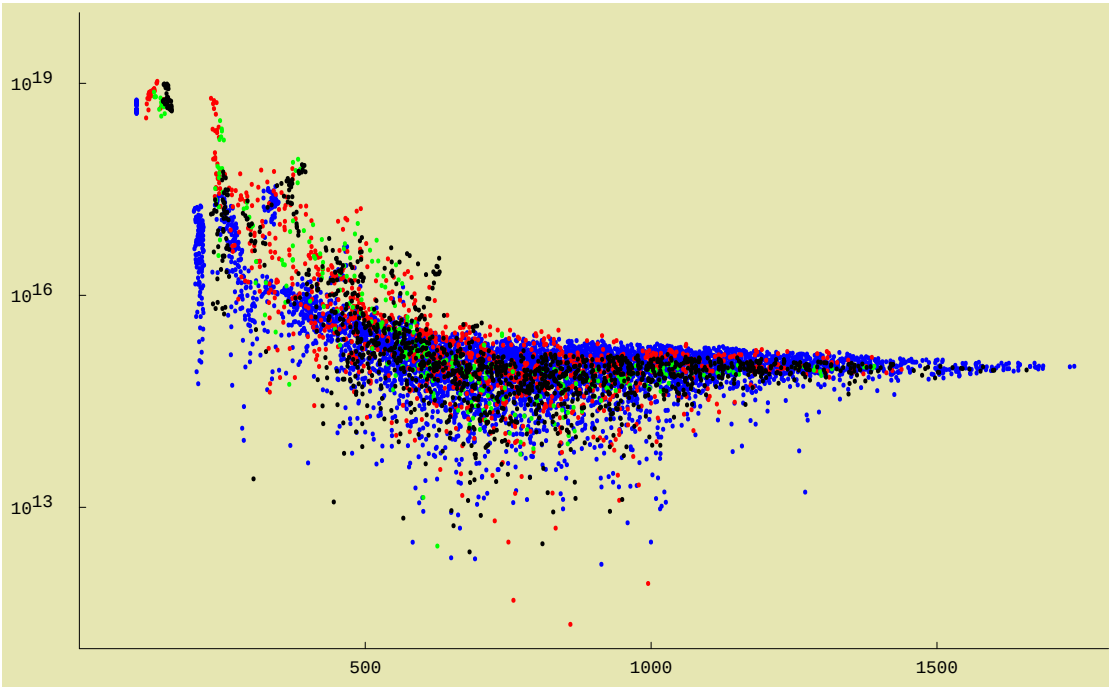
- Large systems demand new computational methods
  - steep increase in cost with increasing system size
- The ultimate goal: linear scaling of cost for large systems
  - example: cost of evaluating excitation energies



WP1 example: NMR spin–spin coupling constants

- Indirect nuclear spin–spin coupling constants in valinomycin
  - requires a flexible description of the electronic system
  - reveals a rich structure of couplings





WP2: Fragment approach for large systems

- Large molecular systems constructed from accurately calculated subsystems
  - Perturbed Atoms in Molecules and Solids (PATMOS)
- Prof. Inge Røeggen,
  Department of Physics, University of Tromsø

- electron correlation
- intramolecular interactions
- computational chemistry
- chemical bonding

WP3: Multiscale methods with wavelets

- Different regions of space treated at different resolutions and accuracies
  - use of scaling and detail (wavelet) functions
- Prof. Tor Flå,
  Department of Mathematics, University of Tromsø

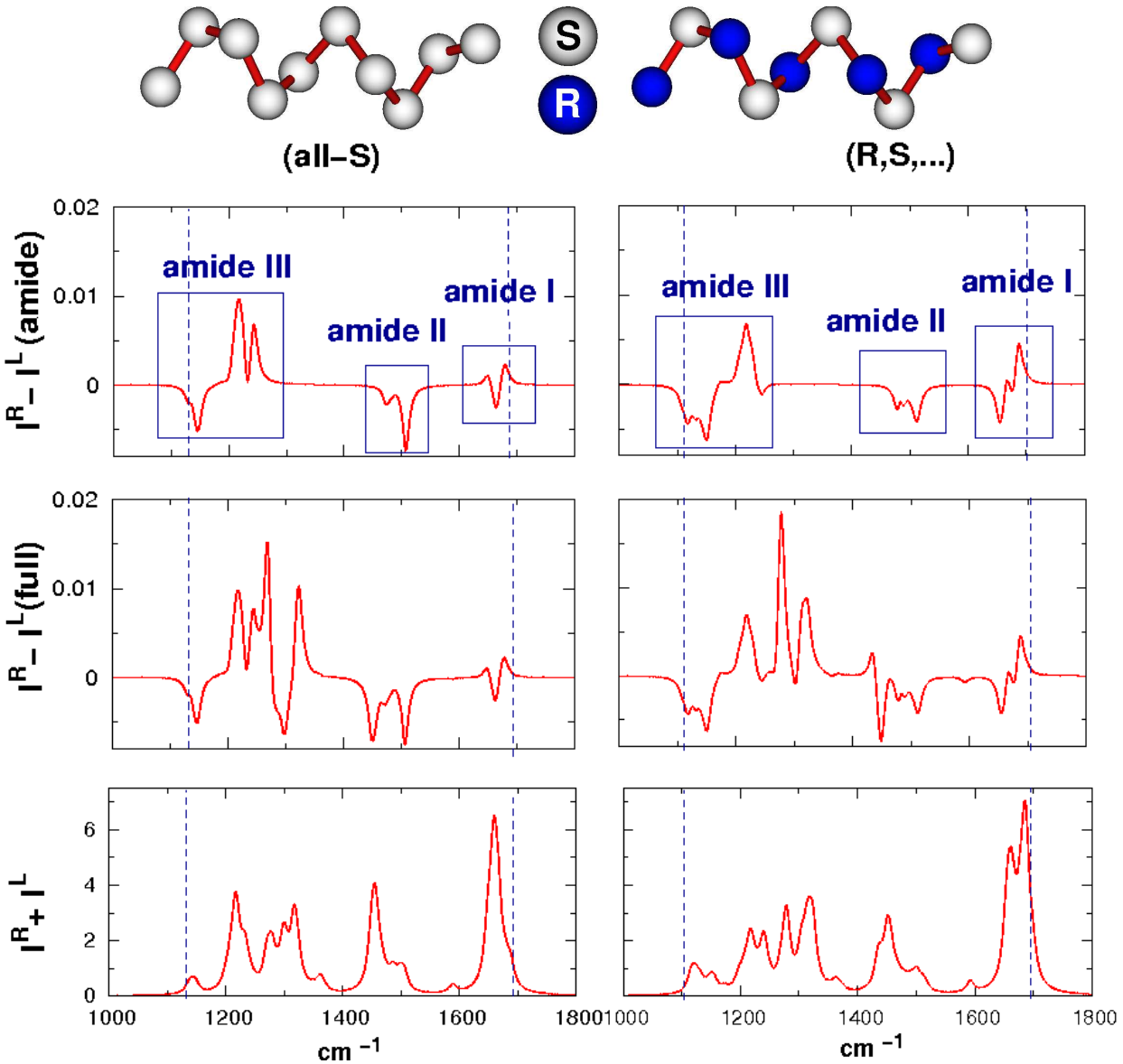
- density-functional theory
- wavelets
- bioinformatics

WP4: Properties and spectroscopy

- Modeling of spectroscopic techniques by computation
  - linear and nonlinear optics, effects of solvation
- Ass. Prof. Luca Frediani,
  Department of Chemistry, University of Tromsø

- linear and nonlinear molecular properties
- solvation
- multiwavelets

WP4 example: Raman Optical Activity



WP5: Dynamics and time development

- The modeling of chemical reactions by on-the-fly dynamics
  - application to metal clusters, water clusters and organic reactions
- Prof. Einar Uggerud,
  Department of Chemistry, University of Oslo

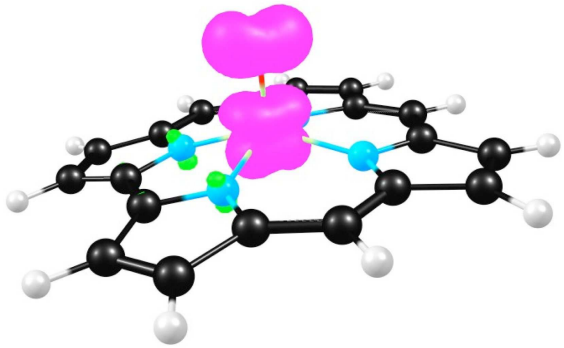
- mass spectroscopy
- computational chemistry
- reaction mechanisms
- molecular clusters

WP6: Bioinorganic chemistry

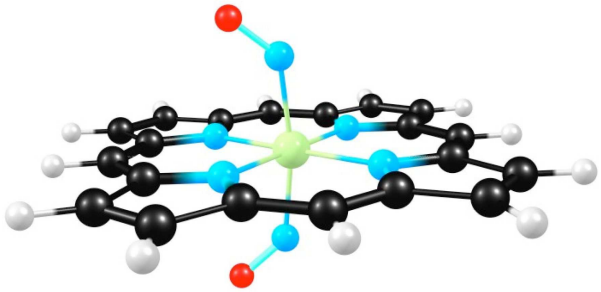
- Applications of quantum chemistry to problems in metallobiochemistry
  - in conjunction with experimental work in synthesis, spectroscopy and electrochemistry
- Prof. Abhik Ghosh,
  Department of Chemistry, University of Tromsø

- computational chemistry
- bioinorganic chemistry
- porphyrin chemistry
- metal complexes

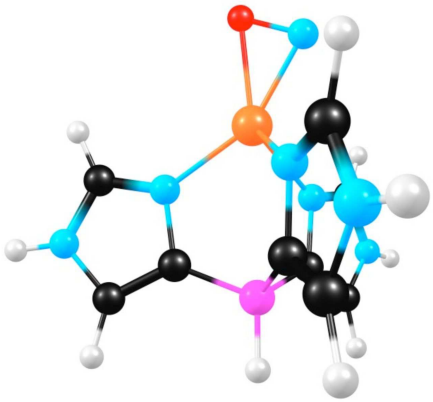
WP6 example: transition metal complexes



Spin density profile for Fe^{V}(Cor)(O): Energetics of alternative spin states?



Dinitrosylheme: An open-shell singlet? Why *cisoid* NO's?



$\{CuNO\}^{11}$ copper nitrite reductase: Energetics of side-on NO binding?

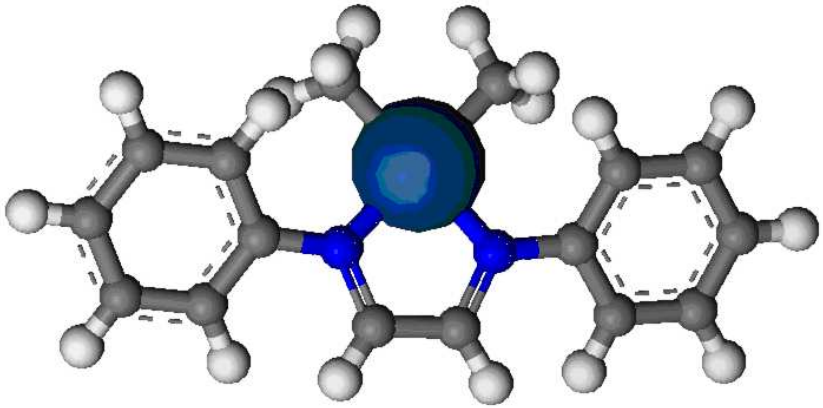
– transition metal complexes of relevance for catalysis of metal enzymes

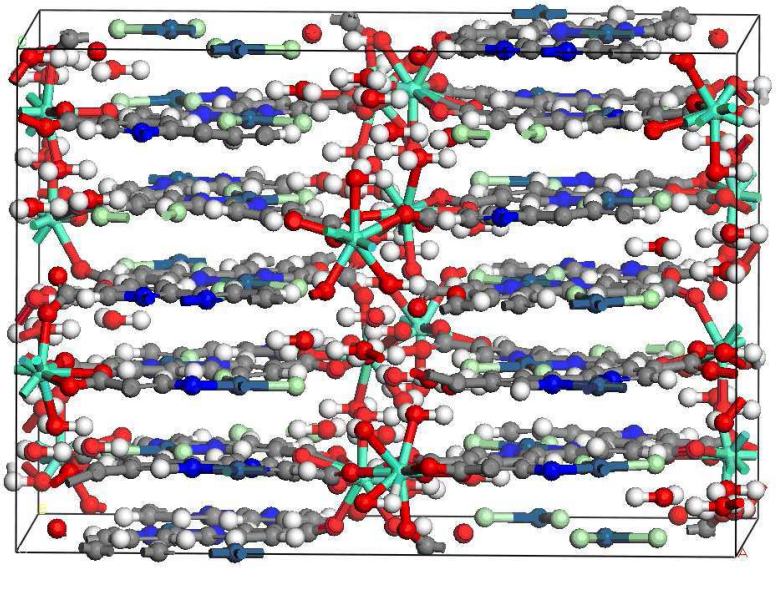
WP7: Catalysis and organometallic chemistry

- Organo- and organometallic catalysis
  - application of methods for large systems and dynamics
- Prof. Mats Tilset,
  Department of Chemistry, University of Oslo

- organometallic chemistry
- reaction mechanisms
- homogeneous catalysis
- C-H activation
- electron transfer

WP7 example: C-H activation





Quantum-chemical calculations help understand C-H activation at metal atoms in molecular complexes

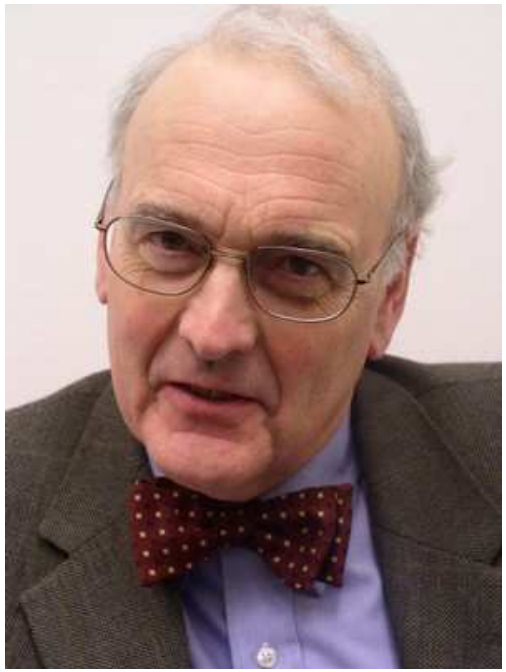
WP8: Gas-phase reactions and photochemistry

- The study of complex gas-phase reactions
  - chemical processes of atmospheric relevance
- Prof. Claus Jørgen Nielsen,
  Department of Chemistry, University of Oslo

- atmospheric chemistry
- spectroscopy
- gas-phase chemistry
- aerosols

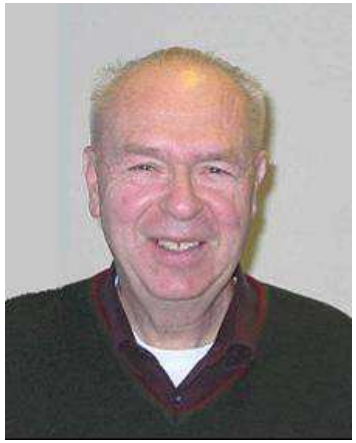
WP9: Clusters, surfaces and solids

- Properties of catalytically important metals in diverse environments
  - metal clusters, molecular complexes
- Prof. Knut Fægri,
  Department of Chemistry, University of Oslo



- relativistic quantum chemistry
- large molecular systems

CTCC affiliates



Prof. Harald Møllendal
-intramolecular hydrogen bonds
-molecular structure
-conformational analysis
-astrochemistry

Prof. Svein Samdal
-molecular structure
-conformational analysis
-computational chemistry