Introduction to Electronic Structure Theory

Mikael Johansson

Goals

- To get familiarised with the, subjectively chosen, most important concepts of electronic structure theory from a computational chemistry viewpoint
- After the QC lectures, the student will have at least a rudimentary exposure to different approximations to the molecular Schrödinger equation, and the alternative theory of density functionals

What is quantum chemistry?

- "Simply", the application of quantum mechanics in chemistry
- Based largely on solving the Schrödinger equation (1926):

$$\nabla^2\psi + \frac{2m}{K^2}\left(E + \frac{e^2}{r}\right)\psi = 0$$

- Or even more condensed:

$$\mathrm{H}\psi = E\psi$$

- The central creature is the ***wave function Ψ***

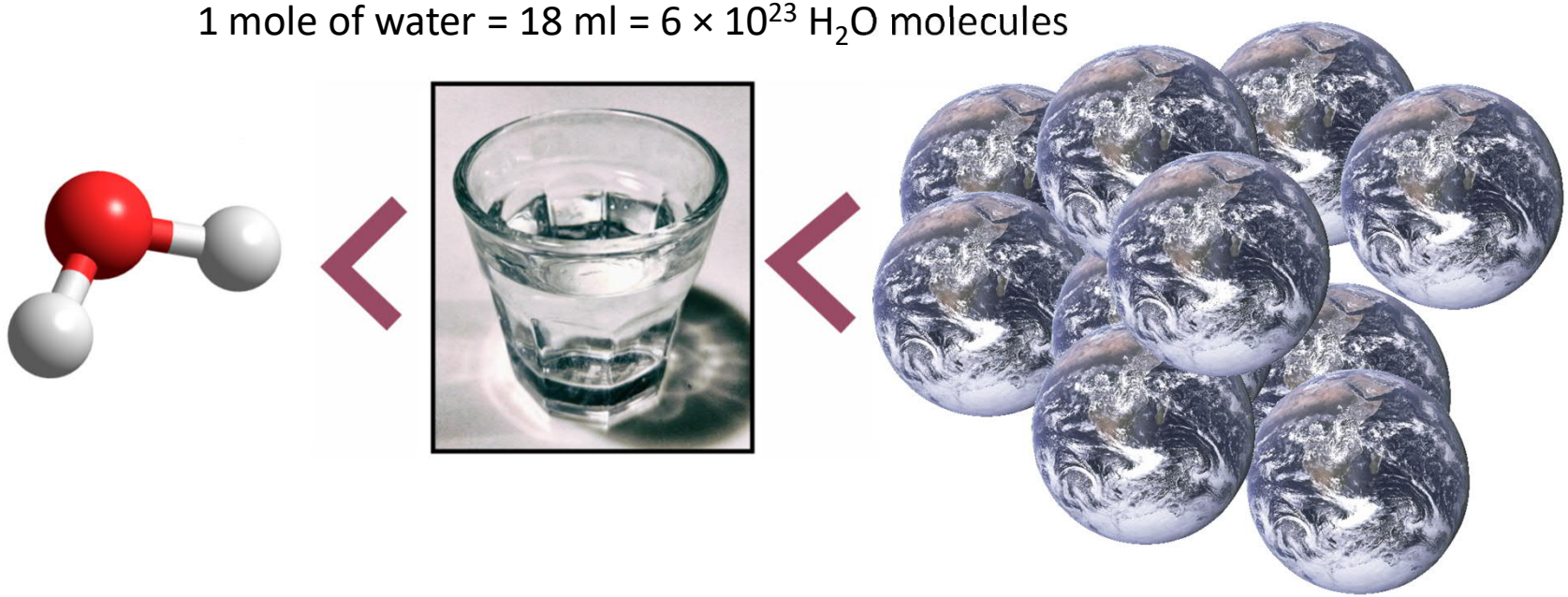
The Schrödinger equation

- The Schrödinger wave function Ψ implies that particles can *and should* be described as waves
- Molecules *are* small, electrons even smaller (or are they!)

Small molecules, even smaller electrons(?)

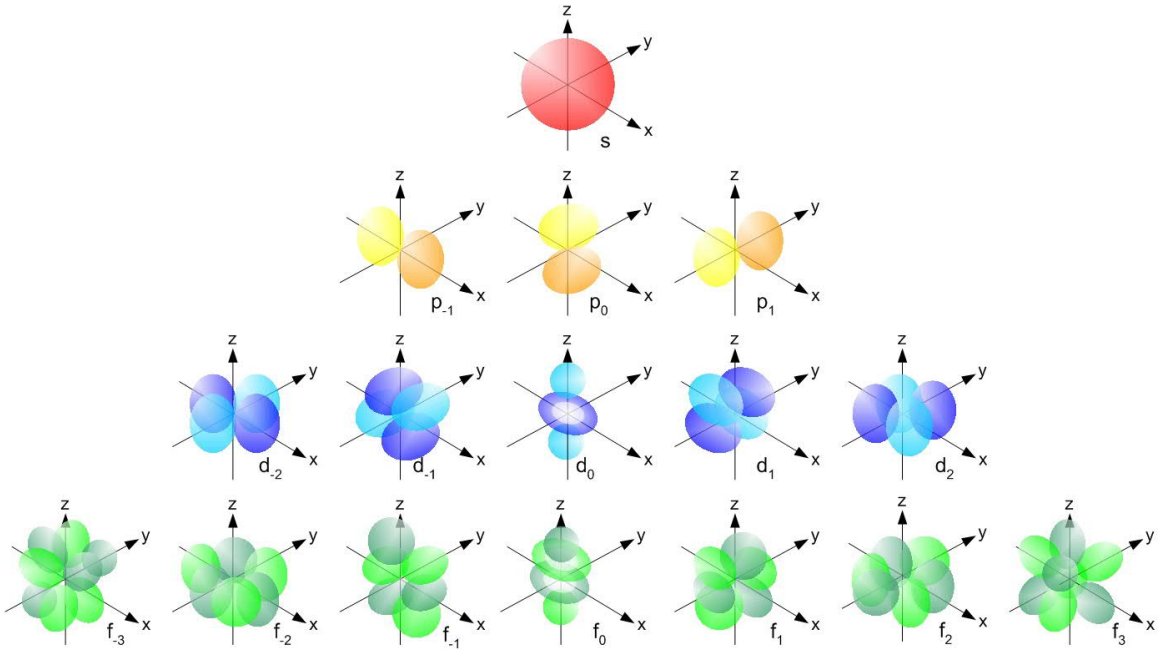
- Small, light particles can *and should* be described as waves
- Molecules are small, electrons even smaller... Or at least lighter

1 mole of water = 18 ml = 6×10^{23} H_2O molecules



The Schrödinger equation

- For one-electron systems, the Schrödinger equation is simple to solve
- The resulting wave-functions Ψ are the hydrogen-like atomic orbitals:



The Schrödinger equation

- For more than two particles, the SE *cannot be solved analytically*

Quantum Mechanics of Many-Electron Systems.

By P. A. M. Dirac, St. John's College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received March 12, 1929.)

§ 1. *Introduction.*

■ ■ ■

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.

Computational quantum chemistry

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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. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

Computational quantum chemistry

$$\zeta = (Z - s)/n \qquad (11.17)$$

where Z is the atomic number, n is the orbital's principal quantum number, and s is a screening constant calculated by a set of rules (see Problem 15.79). A Slater orbital replaces the polynomial in r in a hydrogenlike orbital with a single power of r. Hence a single Slater orbital does not have the proper number of radial nodes and does not represent well the inner part of an orbital.

A great deal of computation is required to perform a Hartree–Fock SCF calculation for a many-electron atom. Hartree did several SCF calculations in the 1930s, when electronic computers were not in existence. Fortunately, Hartree's father, a retired engineer, enjoyed numerical computation as a hobby and helped his son. Nowadays computers have replaced Hartree's father.

11.2 ORBITALS AND THE PERIODIC TABLE

The orbital concept and the Pauli exclusion principle allow us to understand the periodic table of the elements. An orbital is a one-electron spatial wave function. We have

Ira N. Levine, *Quantum Chemistry*

Computational quantum chemistry

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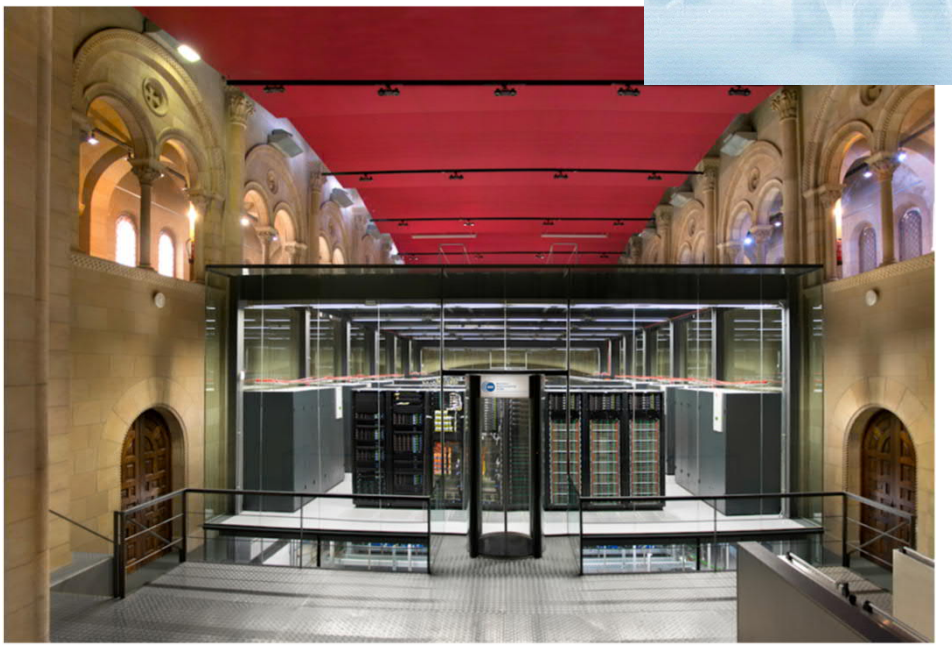
Computational quantum chemistry

Lumi, CSC, Kajaani

coming in 2021

former paper mill

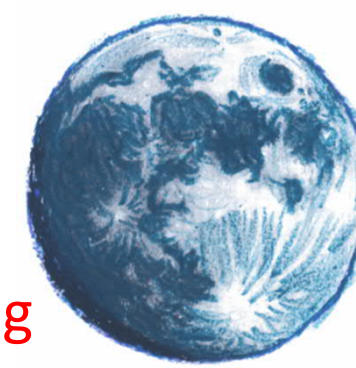


MareNostrum,

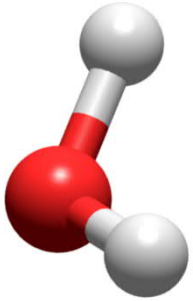
BSC, Barcelona

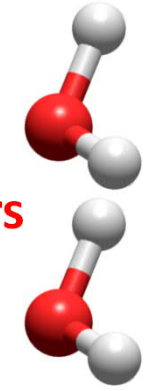
former chapel

Computational quantum chemistry



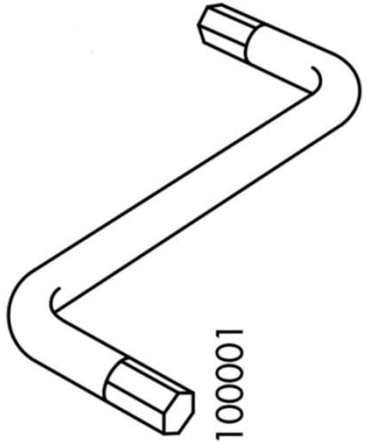
- In a world where everything seems instant, it can be difficult to perceive that *computers can actually be slow*
  - A microwave is more powerful than the Apollo Guidance Computer…
- Even supercomputers are too weak for accurately approximating the Schrödinger equation!
- CCSD(T), the "golden standard" of QC
  - scales as ~N^7 with system size N
  - 1 water molecule: 1 second
  - 10 water molecules: 100 days
  - 100 water molecules: **3 million years**





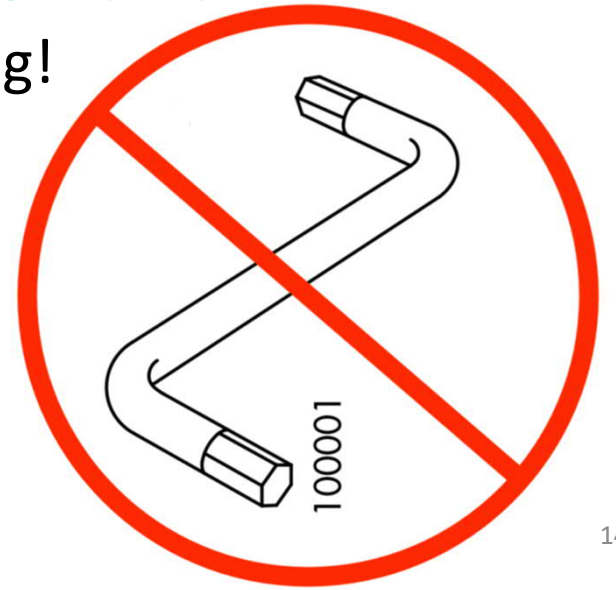
What is quantum chemistry?

- **Designing and solving *approximations* to the Schrödinger equation**
- The number of different approximations is humongous
  - Hartree-Fock, MP2, Full CI, B3LYP, …
- The challenge is to find the ***right tool for the right purpose***

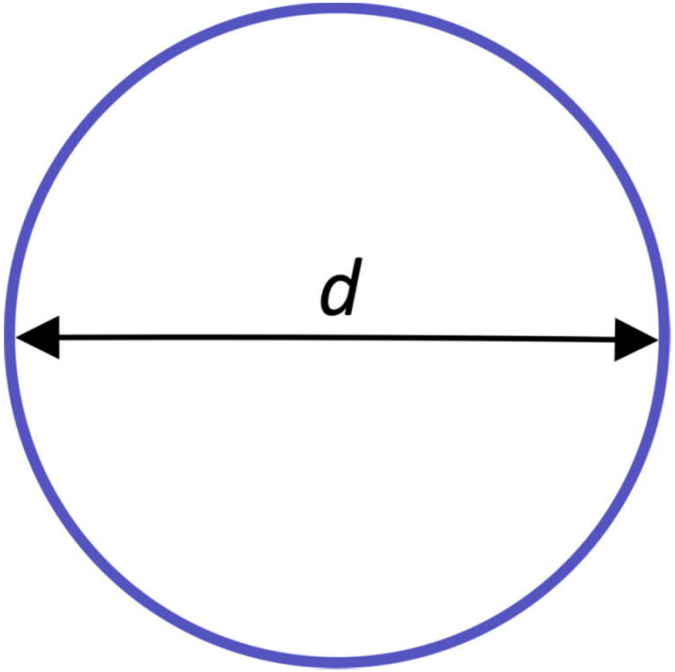


What is quantum chemistry?

- **Designing and solving *approximations* to the Schrödinger equation**
- The number of different approximations is humongous
  - RASPT2, quantum Monte Carlo, revTPSS, DLPNO-CCSD(T)-F12, …
- The challenge is to find the ***right tool for the right purpose***
- There is no single tool that works for everything!

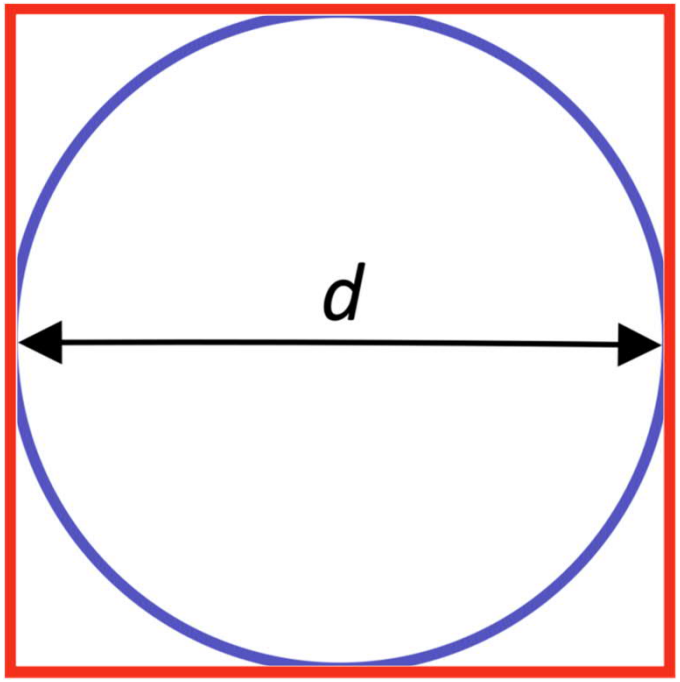


Approximations



$$A = \pi r^2$$

Approximations

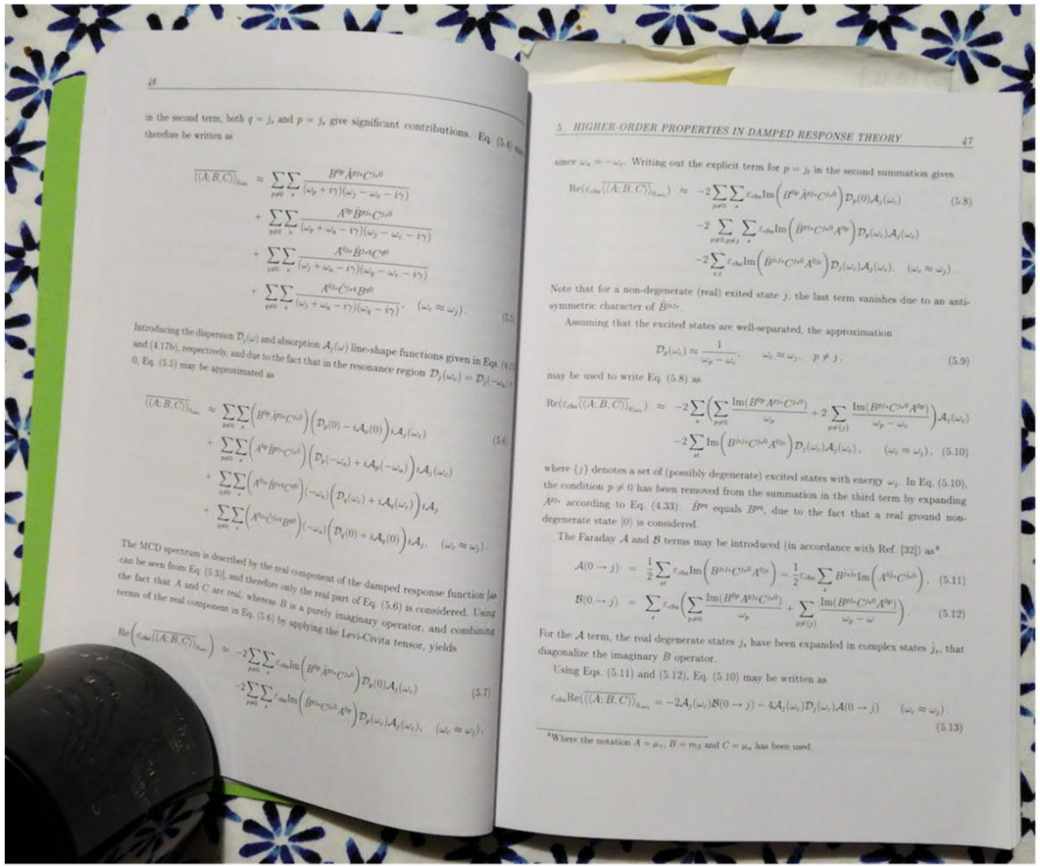


$A = \pi r^2$

$A \approx d^2 = 4r^2$ **27% error**

What is quantum chemistry?

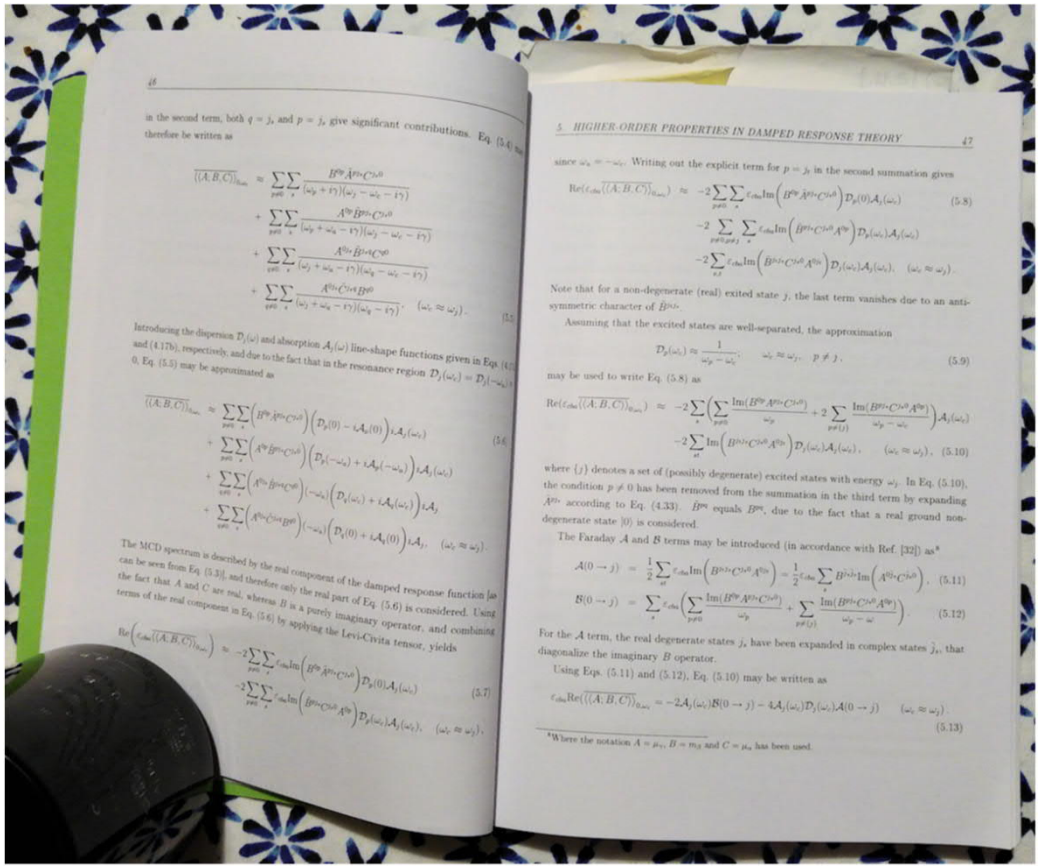
- One branch of quantum chemistry **develops** new methods and algorithms, **equations**, for describing the quantum mechanics of molecules



Joanna Kauczor, PhD thesis, *Damped response theory*

What is quantum chemistry?

- One branch of quantum chemistry **develops** new methods and algorithms, **equations**, for describing the quantum mechanics of molecules
- Another branch **uses, applies the equations** for specific molecular systems



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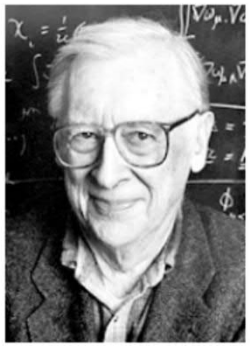
What is quantum chemistry?

The Nobel Prize in Chemistry 1998

Walter Kohn
Prize share: 1/2



John A. Pople
Prize share: 1/2

The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn *"for his development of the density-functional theory"* and John A. Pople *"for his development of computational methods in quantum chemistry"*.

The Nobel Prize in Chemistry 2013

Photo: A. Mahmoud
Martin Karplus
Prize share: 1/3

Photo: A. Mahmoud
Michael Levitt
Prize share: 1/3

Photo: A. Mahmoud
Arieh Warshel
Prize share: 1/3

The Nobel Prize in Chemistry 2013 was awarded jointly to Martin Karplus, Michael Levitt and Arieh Warshel *"for the development of multiscale models for complex chemical systems"*.

What is quantum chemistry?

- **A synthesis of disciplines**
  - Quantum mechanics from physics
  - Concepts and ideas from chemistry (pharma, biochem, nanotech, ...)
  - Formulations from mathematics
  - (Parallell) programming for various architectures (incl. quantum computers) from computer science
  - Aspuru-Guzik, Lindh, Reiher (2018) *The Matter Simulation (R)evolution*: