Some (important) problems in Quantum Chemistry

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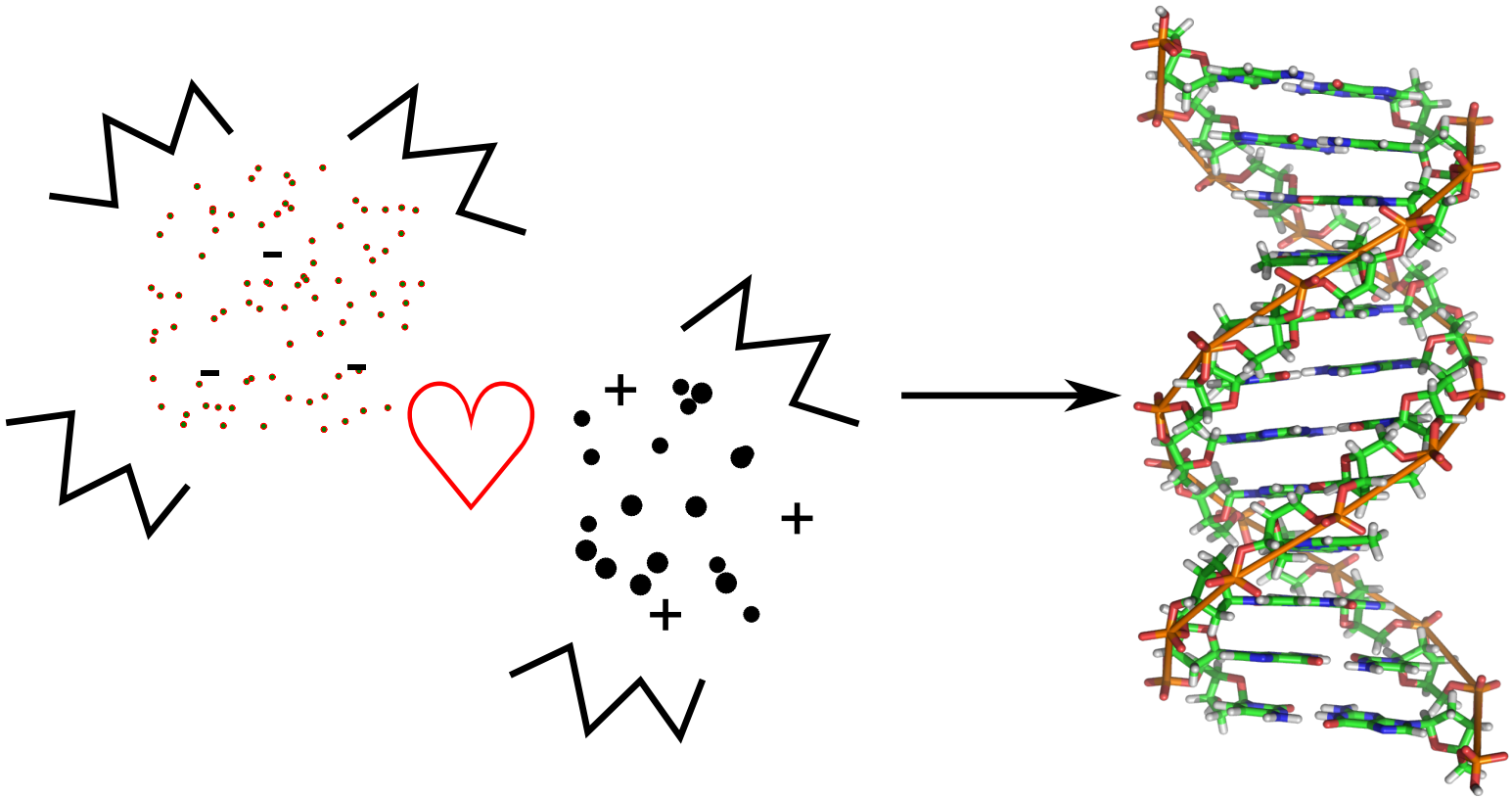
What is Quantum Chemistry?

Apply quantum theory to problems in chemistry (Schrödinger, Slater, Löwdin ...)

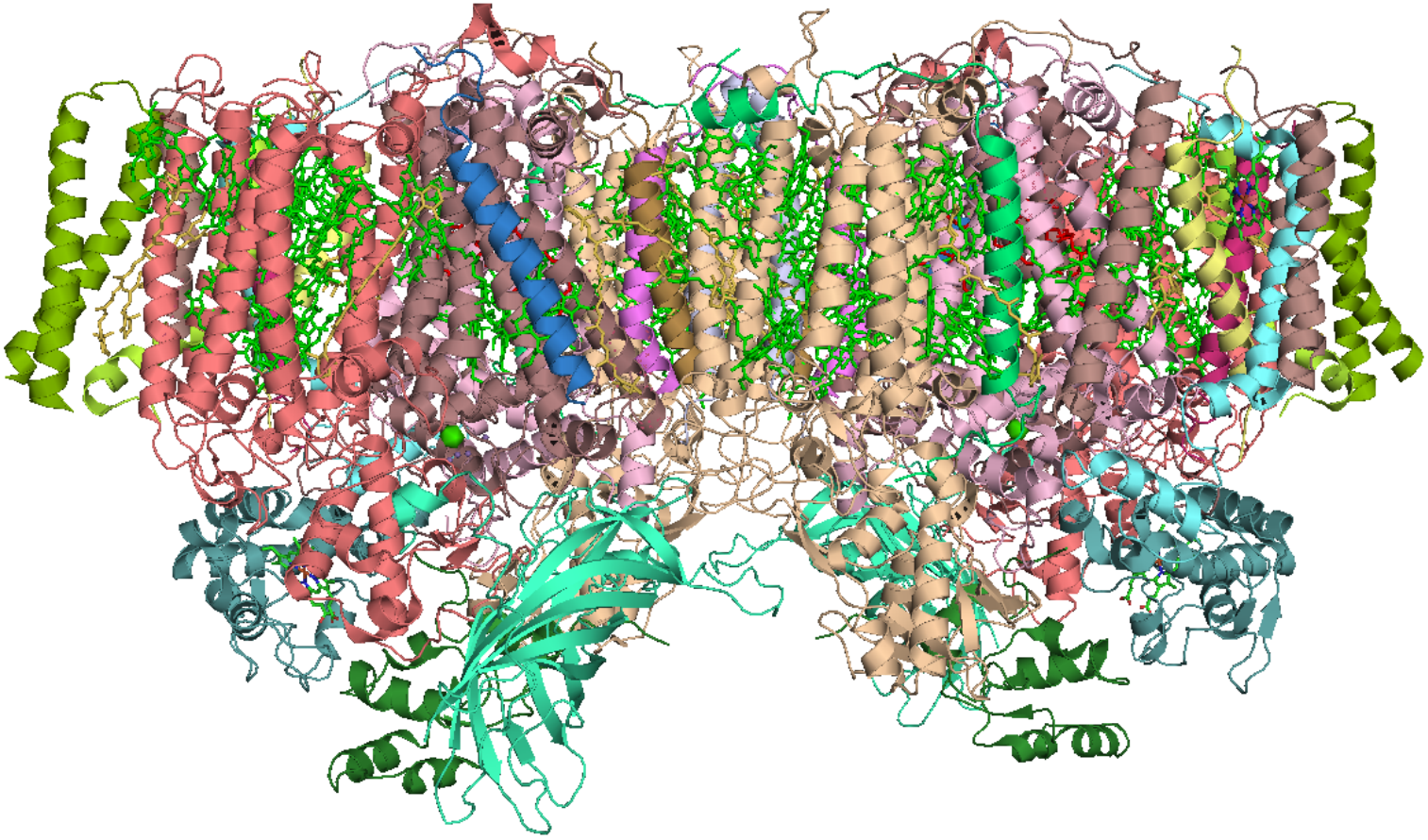
- Optical properties of molecules (spectroscopy)
- What is a chemical bond?
- Determine molecular structure (optimization)
- Chemical reaction mechanisms and rates
- Dynamical properties of electrons and atoms

Structure determination



Electron dynamics and Photochemistry

Photosystem II:



How can photosynthesis be so efficient? Quantum energy transport. 10^5 atoms..

What do we know?

- We know the relevant laws of physics, very very well (too well). Schrödinger equation with Hamiltonian

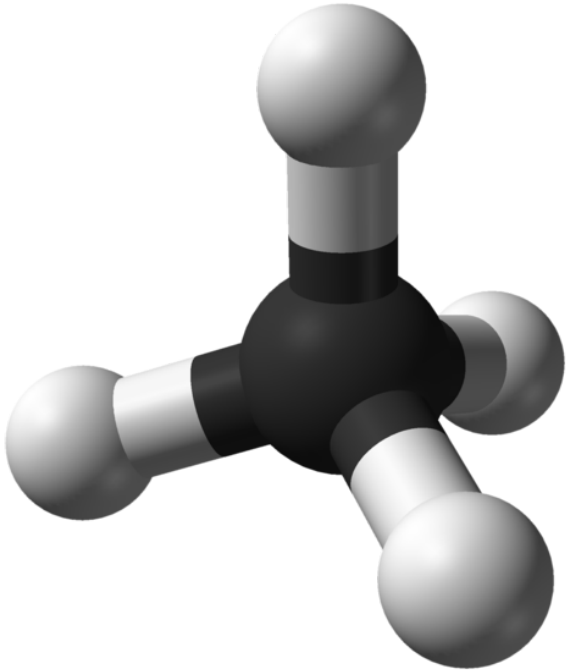
$$H = \sum_k -\frac{\nabla^2}{2m_k} + \sum_{i \neq k} \frac{q_i q_k}{r_{ik}}$$

- We can easily solve the problem for *one* particle:

$$H\Psi = \left[-\frac{\nabla^2}{2m} + V(r) \right] \Psi = E\Psi$$

Problem One

Space and Time



10^1-10^5 particles
Times 10^{-15}-10^{-12} s

10^{23} particles
Times $10^{-3} - 10^{6}$ s

Brute force is impossible. We need clever connections between micro and macro.

Electron Correlation

- Quantum N-body problem
- Quantum calms down chaos, but
- Wave function complexity N^N

$$\Psi = \Psi(r_1, r_2, \ldots r_N)$$

- Nevertheless, chemistry is full of concepts: Atoms, bonds, functional groups
- Suggests approximate theories!
- (Counter-example: Spin glasses)

Density Functional Theory (DFT)

- Kohn and {Hohenberg,Sham}: "$\Psi(r_1, r_2, \ldots)$ is too much"
- Observable properties come from the electron density $\rho(r)$!
- Proof that $E = E[\rho]$, but no closed form.

	WFT	DFT
Variable	$\Psi(r_1, r_2, \ldots r_N)$	$\rho(r)$
Energy	Trivial	Complicated Unknown (kernel trick?)
Formal Scaling	N^N	N
Practical Scaling	N^6–N^8	N^2–N^3
Nr atoms	$1 - 20$	$100 - 1000$

Approximate DFT consumes a majority of Swedish supercomputer time!

Density Functional Theory in practice

DFT Energy:

$$E_{\text{DFT}} = E_{\text{Kinetic}} + E_{\text{Electrostatic}} + \int_{\mathbb{R}^3} \epsilon_{XC}(\rho(r))dV$$

Only approximate $\epsilon_{XC}(\rho)$ are known.

Leads to a *one particle* eigenvalue problem

$$H_{KS}\psi_i = \left[-\frac{\nabla^2}{2m} + V(r)\right]\psi_i = E_i\psi_i$$

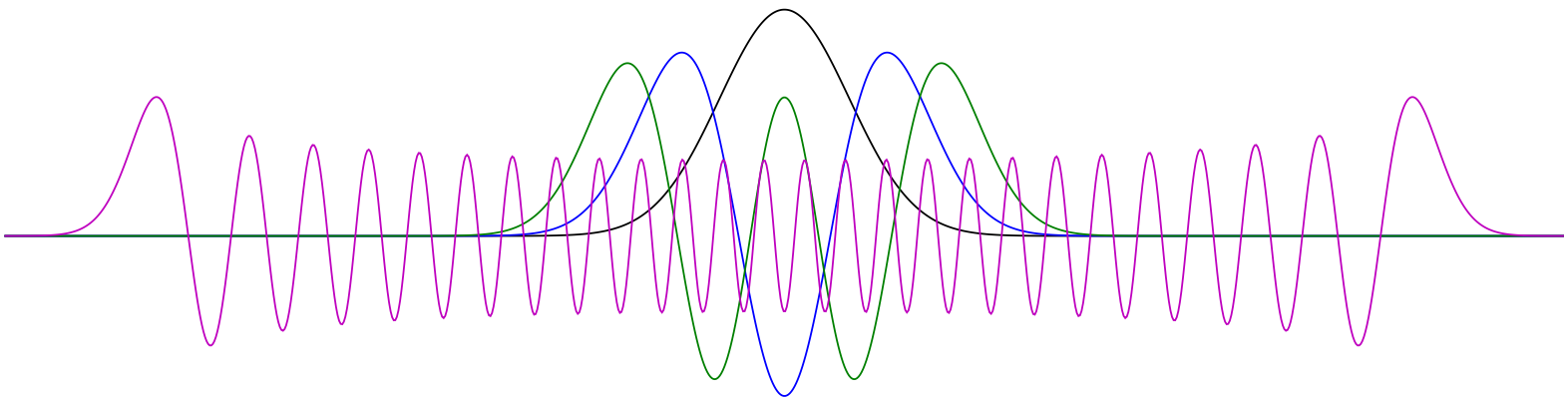
Reduction from $\mathcal{O}(N^N)$ to $\mathcal{O}(N)$! But ϵ_{XC} is very difficult to work with.

Introducing a Basis

To solve

$$H_{KS}\psi_i = \left[-\frac{\nabla^2}{2m} + V(r)\right]\psi_i = E_i\psi_i$$

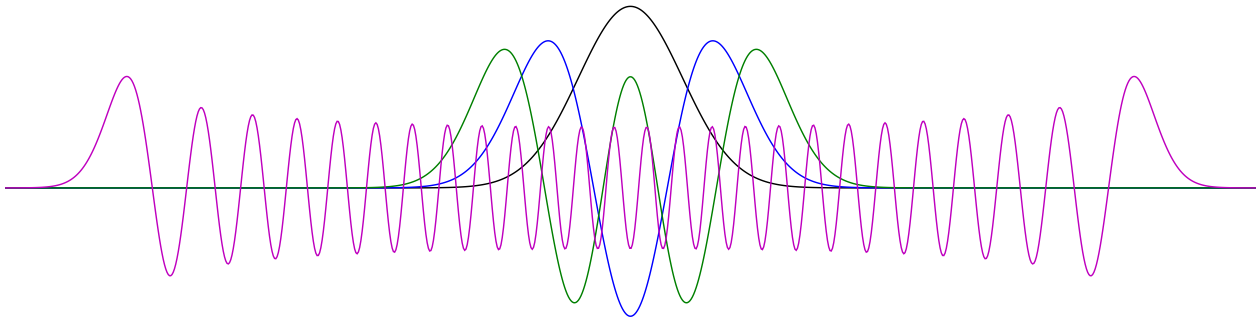
don't discretize in real space! Use a problem specific basis!



Atom centered Gaussian Type Orbitals.

Generating functions

We can generate a basis



with derivatives!

$$\varphi_n(r) = \frac{\partial^n}{\partial R^n} e^{-\alpha(r-R)^2}$$

Perfect for AD! Here $e^{-\alpha(r-R)^2}$ is the *Generating Function*.

Generating functions are very powerful for combinatorics (look it up)