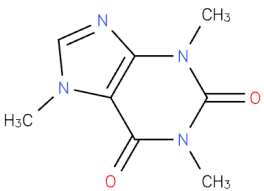
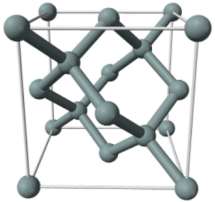
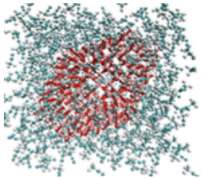
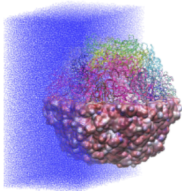
Introduction









Molecules

Solids

Nanoparticles

Bio systems

10^0 10^1 10^2 10^3 10^4 10^5 10^6

Number of Atoms

Reactions



What is this course about?

Computational Chemistry

- Start from Schrödinger equation
- Realise it is impractical to solve exactly
- Neglect effects: build, explain and justify approximations
  - Force fields, Density Functional Theory
  - Degree of electron correlation
  - ...
- For each system, find appropriate approximations

What is this course about?

Potential Energy Surfaces
Which compounds are stable? Which reactions take place?

Molecular mechanics
How do atoms move?

Machine Learning models
How can one automate approximations?

Electronic structure calculations
Which methods have predictive power?

Simulation of molecules, materials, and interfaces
How to get started?

Perturbation Theory
How does the system react to changes?

Differentiable Chemistry
How can one get derivatives conveniently?

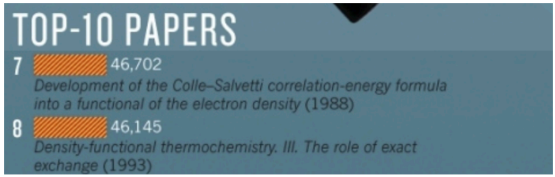
Where can I use this knowledge?

Direct

- Molecular / Materials design: Guide experiment
- Bio / Medical applications: Understand chemical process
- Method development: Widen applicability

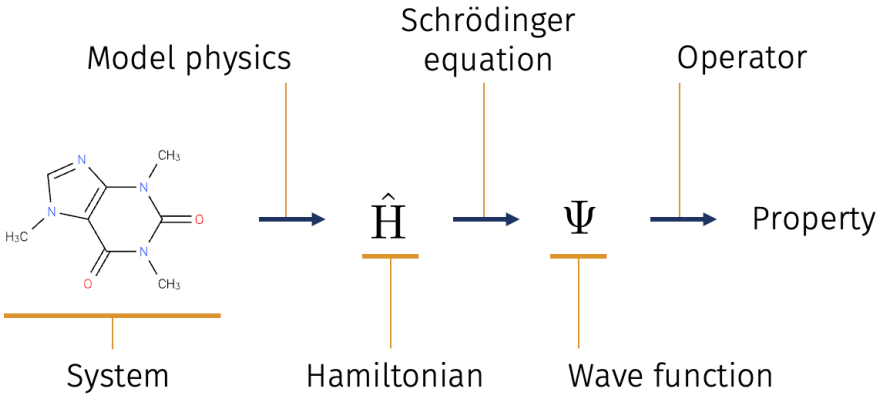
Indirect

- Machine learning: Data-driven approximations
- Data science: Extract and manage large databases
- Research in general: Strategies and methods



R. Van Noorden, B. Maher, R. Nuzzo, Nature, 2014.

Born-Oppenheimer Approximation


Model physics
Schrödinger equation
Operator
$\hat{H}$
Ψ
Property
System
Hamiltonian
Wave function

$$\text{Chemical system} \longrightarrow \hat{H}(\mathbf{r}_i, \mathbf{R}_I) \longrightarrow \Psi(\mathbf{r}_i, \mathbf{R}_I) \tag{1}$$

$$\hat{H}(\mathbf{r}_i, \mathbf{R}_I) = \hat{T}_{\mathrm{n}}(\mathbf{R}_I) + \hat{T}_{\mathrm{e}}(\mathbf{r}_i) + \hat{V}_{\mathrm{ee}}(\mathbf{r}_i) + \hat{V}_{\mathrm{en}}(\mathbf{r}_i, \mathbf{R}_I) + \hat{V}_{\mathrm{nn}}(\mathbf{R}_I) + \hat{V}_{\mathrm{ext}} \tag{2}$$

Thermodynamics: The time-averaged kinetic energy in a degree of freedom only depends on the temperature.

$$E_{\text{kin,n}} \approx E_{\text{kin,e}} \quad \Rightarrow \quad m_n v_n^2 \approx m_e v_e^2 \tag{3}$$

$$\frac{v_e}{v_n} \approx \sqrt{\frac{m_n}{m_e}} \approx \sqrt{1800} \tag{4}$$

Here: Allows separation, since nuclei are slow and electrons are fast.

Notation for function arguments and parameters

Distinction between general dependence (parameters) and functional dependence (arguments).

$$f(x|b) = f_b(x) \tag{5}$$

Conceptually, parameters are considered frozen for a given application. Read: *f of x given b*. Example: $\log_b(x)$.

Full picture

- Hamiltonian as sum (interactions are additive)
- Wavefunction as product (needed for combination of variables)

$$\hat{H}(\mathbf{r}_i, \mathbf{R}_I) \equiv \hat{H}_\mathrm{e}(\mathbf{r}_i \mid \mathbf{R}_I) + \hat{H}_\mathrm{n}(\mathbf{R}_I) \tag{6}$$

$$\Psi(\mathbf{r}_i, \mathbf{R}_I) \equiv \Psi_\mathrm{e}(\mathbf{r}_i \mid \mathbf{R}_I)\, \Psi_\mathrm{n}(\mathbf{R}_I) \tag{7}$$

Approximation

- Hamiltonians and wave functions of the two are separable by time scales.
- Consider nuclei fixed (and potentially classically).
- Solve Schrödinger equation for electrons only.

$$\hat{H}_\mathrm{e}(\mathbf{r}_i \mid \mathbf{R}_I)\, \Psi(\mathbf{r}_i \mid \mathbf{R}_I) = E\, \Psi(\mathbf{r}_i \mid \mathbf{R}_I) \tag{8}$$

Electronic molecular Hamiltonian

System defines molecular Hamiltonian

$$\hat{H} = -\sum_i \frac{\hbar^2}{2m_e}\nabla^2_{\mathsf{r}_i} - \sum_{I,j} \frac{Z_I e^2}{4\pi\varepsilon_0|\mathsf{R}_I - \mathsf{r}_j|} + \sum_{i,j>i} \frac{e^2}{4\pi\varepsilon_0|\mathsf{r}_i - \mathsf{r}_j|} + E_{\mathsf{NN}} \tag{9}$$

$$E_{\mathsf{NN}} = \sum_{I,J>I} \frac{Z_I Z_J e^2}{4\pi\varepsilon_0|\mathsf{R}_I - \mathsf{R}_J|} \tag{10}$$

Simplifies wave function

$$\Psi = \Psi(\mathsf{r}_1, \mathsf{r}_2, \mathsf{r}_3, \ldots, \mathsf{r}_n) \tag{11}$$

Impractical:

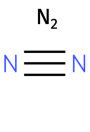
- $3n$ dimensions for n electrons
- Almost always no closed form expression
- Numerical solution: discretisation in basis functions
- Costly[1]:
  [s] $\simeq \exp(2n)/10^4$ [MB] $\simeq \exp(n)/2$

Methane

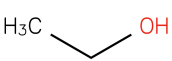
CH_4



N_2



Ethanol





1| https://gist.github.com/ferchault/1e6009e78310200673969ef96c9dad1d

Summary

Formal picture

Properties could be done arbitrarily accurately, but that is too expensive

Practical side: Approximations

- Electrons feel static nuclei and nuclei feel averaged electrons: *Born-Oppenheimer*
- Finite accuracy of wave function / numerics: *Discretisation*

Mental picture

Static atoms and electron density