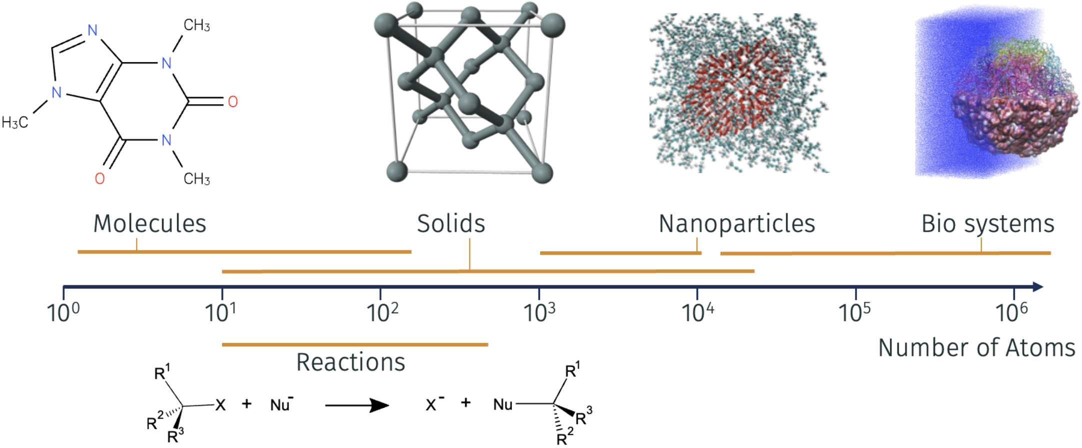
Introduction

Systems



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?

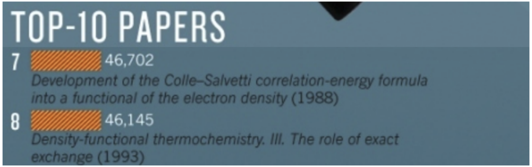
Where can I use this knowledge?

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



TOP-10 PAPERS

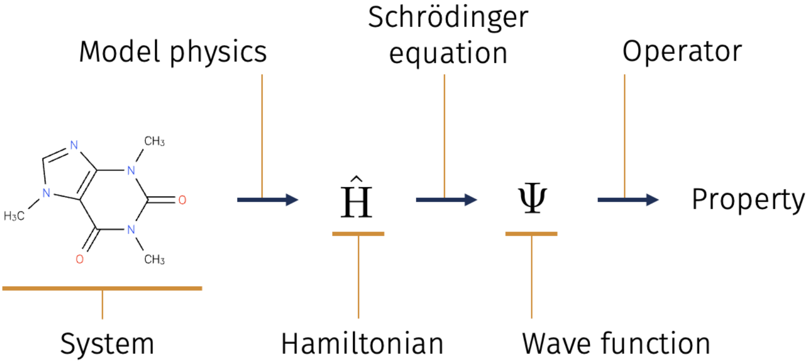
7 46,702
Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density (1988)

8 46,145
Density-functional thermochemistry. III. The role of exact exchange (1993)

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

Born-Oppenheimer Approximation

Basic terms



Model physics

Schrödinger equation

Operator

$\hat{\mathrm{H}}$ → Ψ → Property

System

Hamiltonian

Wave function

Formal picture

$$\text{Chemical system} \longrightarrow \underbrace{\hat{H}}_{\text{Hamiltonian}}(\mathbf{r}_i, \mathbf{R}_I) \longrightarrow \underbrace{\Psi}_{\text{Wavefunction}}(\overbrace{\mathbf{r}_i}^{\text{Coordinates of } n \text{ electrons}}, \overbrace{\mathbf{R}_I}^{\text{Coordinates of } N \text{ nuclei}})$$

$$\hat{H}(\mathbf{r}_i, \mathbf{R}_I) = \underbrace{\hat{T}_{\text{n}}}_{\text{Kinetic energy of nuclei}}(\mathbf{R}_I) + \underbrace{\hat{T}_{\text{e}}}_{\text{Kinetic energy of electrons}}(\mathbf{r}_i) + \underbrace{\hat{V}_{\text{ee}}}_{\text{Electronic repulsion}}(\mathbf{r}_i) + \underbrace{\hat{V}_{\text{en}}}_{\text{Electron-nuclei attraction}}(\mathbf{r}_i, \mathbf{R}_I) + \underbrace{\hat{V}_{\text{nn}}}_{\text{Nuclear repulsion}}(\mathbf{R}_I) + \underbrace{\hat{V}_{\text{ext}}}_{\text{External potential}}$$

Equipartition theorem

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

$$\underbrace{E_{\text{kin,n}}}_{\text{Kinetic energy of the nuclei}} \approx \underbrace{E_{\text{kin,e}}}_{\text{Kinetic energy of the electrons}} \quad \Rightarrow \quad \overbrace{m_n}^{\text{Mass nucleus}}\underbrace{v_n}_{\text{Speed nucleus}}{}^2 \approx \overbrace{m_e}^{\text{Mass electron}}\underbrace{v_e}_{\text{Speed electron}}{}^2$$

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

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).

$$f(\underbrace{x}_{\text{Argument (changeable)}}|\underbrace{b}_{\text{Parameter (static)}}) = f_b(x)$$

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

Born-Oppenheimer Approximation

Full picture

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

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

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

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.

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

Electronic molecular Hamiltonian

System defines molecular Hamiltonian

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

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

Simplifies wave function

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

Wave functions

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] $\simeq \exp(n)/2$

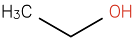
Methane

CH_4

N_2

$N \equiv N$

Ethanol



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[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