Computational Chemistry

Guido Falk von Rudorff, University of Kassel


ferchault


@ferchault


nablachem.org

What is this course about?

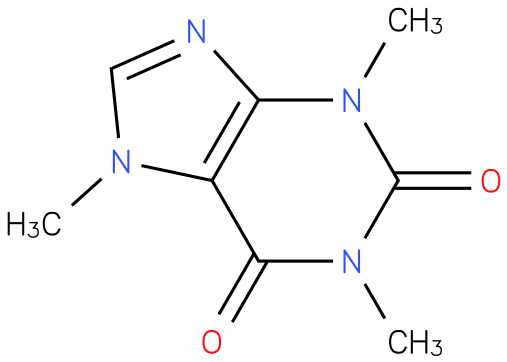
Computational Chemistry

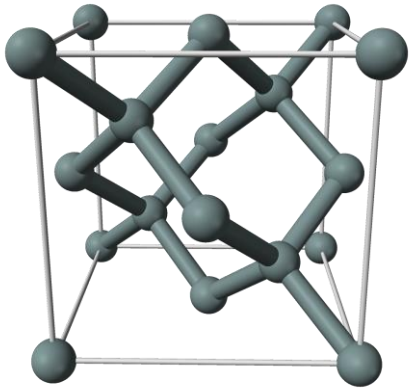
1. Start from Schrödinger equation

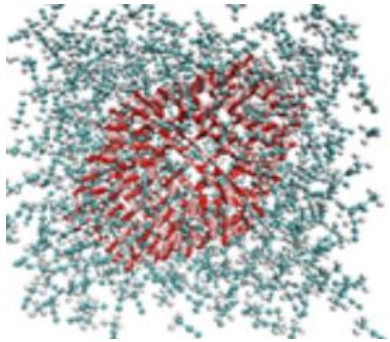
2. Realise it is impractical to solve exactly

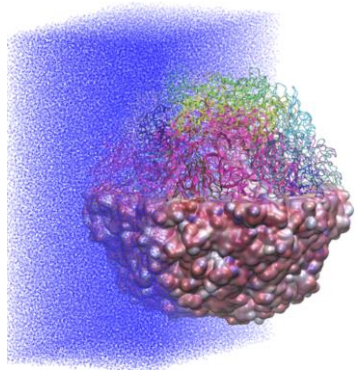
3. Neglect effects: build, explain and justify approximations
   - Force fields, Density Functional Theory
   - Degree of electron correlation
   - …

4. For each system, find appropriate approximations

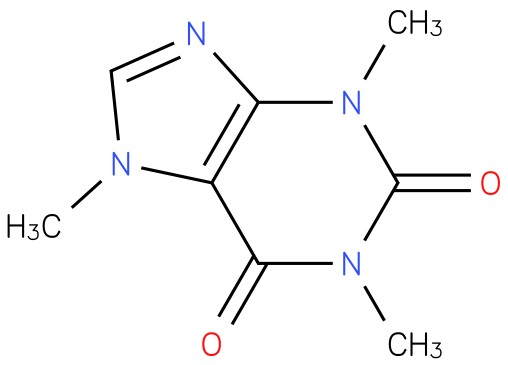


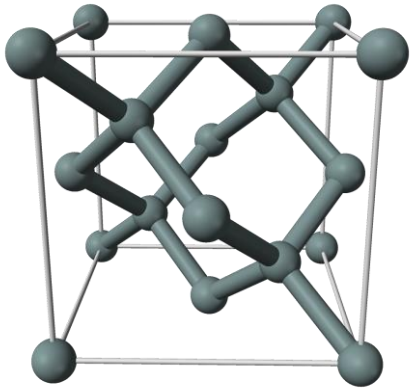


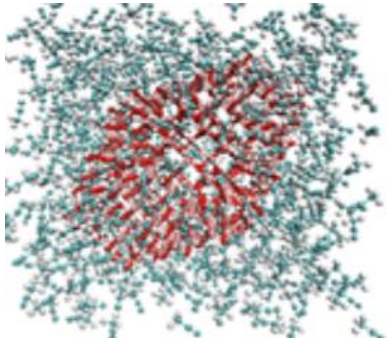


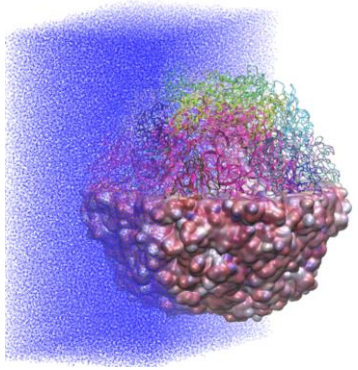


What is this course about?









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?

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?

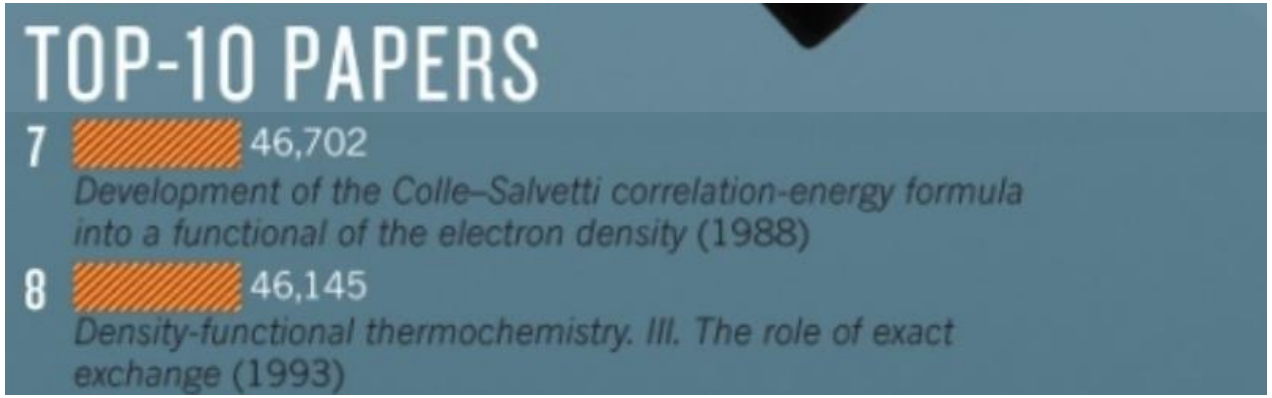
Where can I use this knowledge?

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.

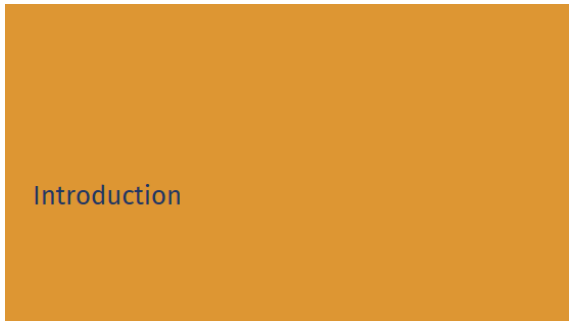
Lecture

Questions anytime
lecture, moodle, vonrudorff@uni-kassel.de, …

Live recording: POLYGLOTT

Slides and notes as PDF after the lecture

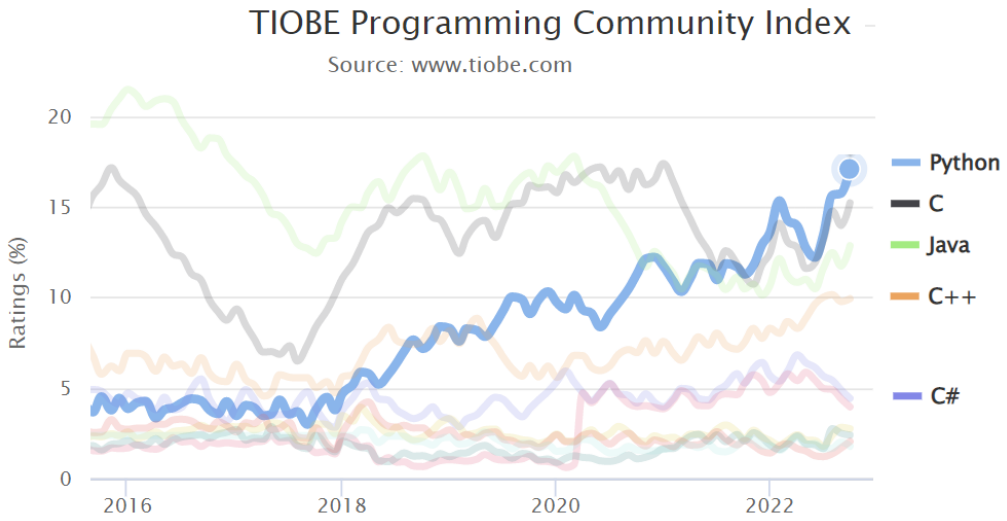
Related: Machine Learning (summer term)



- Sections of 15-20min
- Largely self-contained
- Ask questions at latest then: new train of thought

Exercise

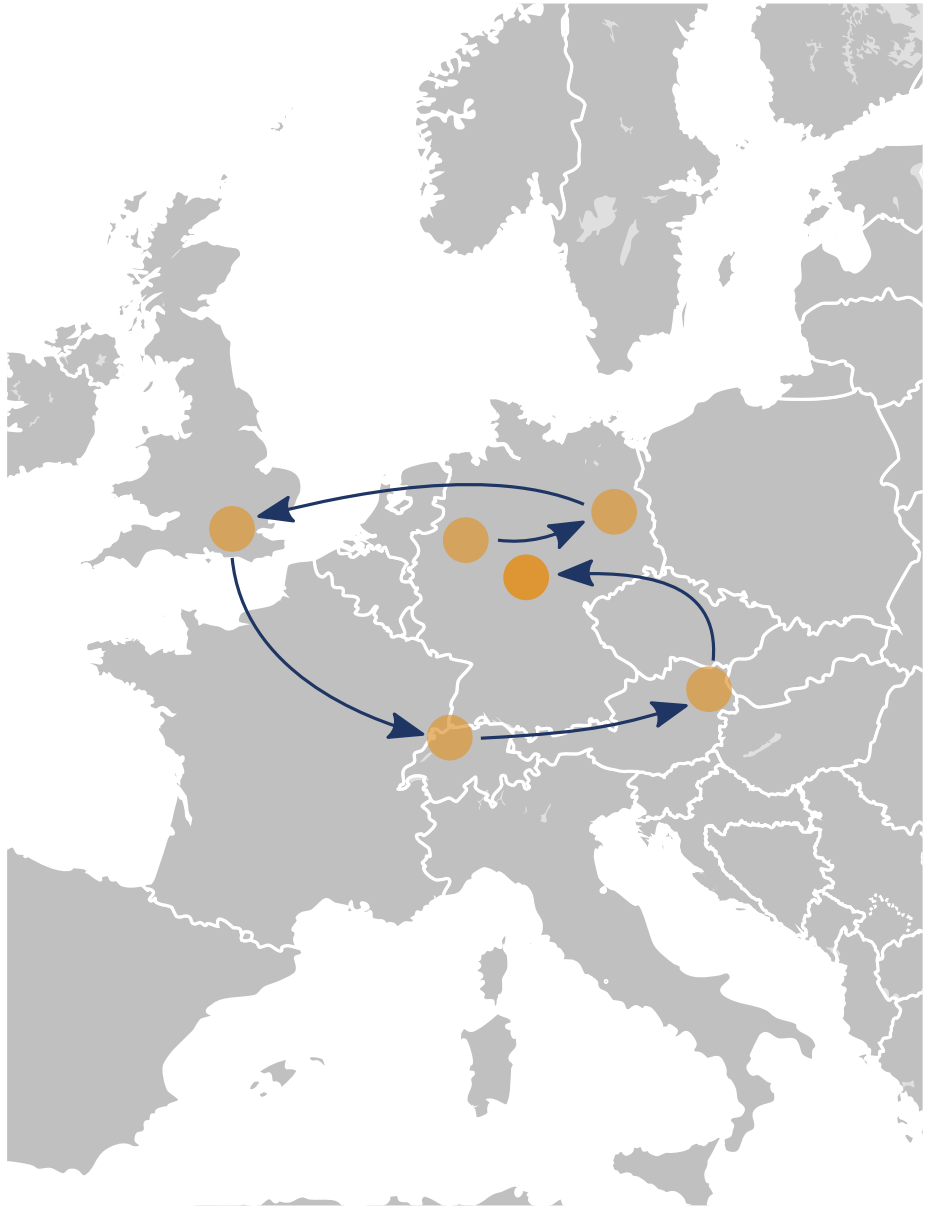
Python-based: the language of data science and glue code



Weekly assignments:

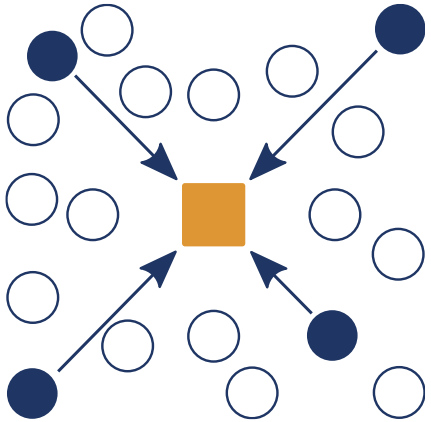
- At first: concepts / programming
- Later: computational chemistry
- End: modern research problems
- Typically: 2 regular tasks + one harder one if you consider research in this area

About me

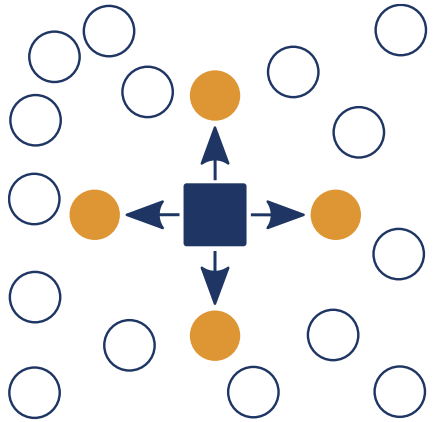


BSc/MSc Physics	Berlin	Force fields
PhD Physics	London	Quantum chemistry
PostDoc	Basel, Vienna	Machine Learning & Alchemy

Machine Learning

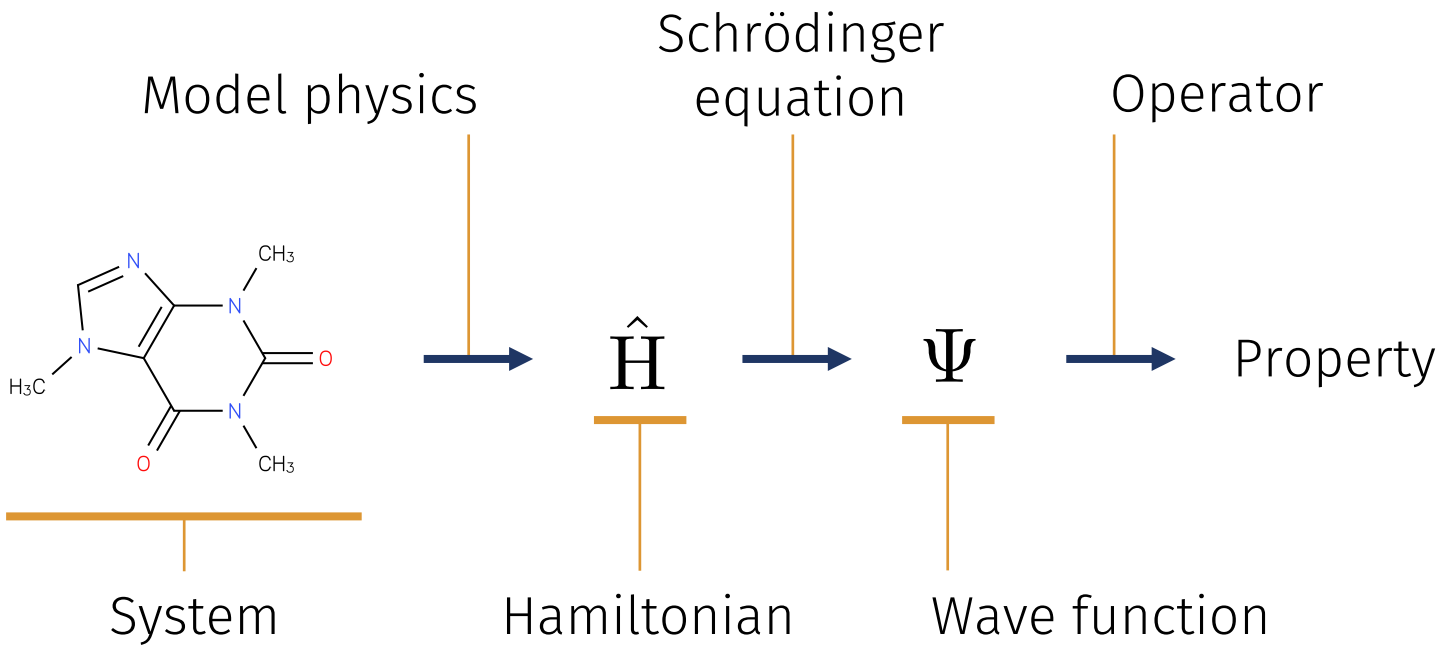


Quantum Alchemy

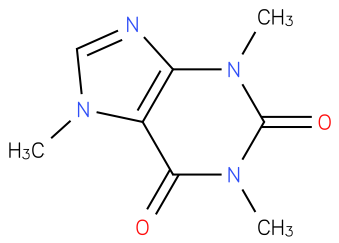


Born-Oppenheimer Approximation

Basic terms


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

Formal picture



$$\hat{\mathrm{H}}(\mathbf{r}_i, \mathbf{R}_I) \longrightarrow \Psi(\mathbf{r}_i, \mathbf{R}_I)$$

$\mathbf{r}_i$: Coordinates of n electrons

$\mathbf{R}_I$: Coordinates of N nuclei

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

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

Formal picture

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

What if Hamiltonian would be separable into electronic and nuclear parts?

Equipartition theorem (thermodynamics):

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

$$\begin{aligned} E_{\mathrm{kin,n}} &\approx E_{\mathrm{kin,e}} \\ \Rightarrow m_n v_n^2 &\approx m_e v_e^2 \\ \Rightarrow \frac{v_e}{v_n} &\approx \sqrt{\frac{m_n}{m_e}} \end{aligned} \qquad \frac{m_n}{m_e} \approx 1800$$

Separation: slow nuclei and fast electrons live on different time scales.

Born-Oppenheimer approximation

Approximation: Hamiltonians and wave functions of the two are separable by time scales.

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

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

$$f(x|b) = f_b(x) \equiv \log_b x$$

Parameter (static)

Argument (changeable)

1. Consider nuclei fixed (and potentially classically).
2. Solve Schrödinger equation for electrons only.

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

Electronic molecular Hamiltonian

System defines molecular Hamiltonian $\hat{\mathrm{H}}$

$$\hat{\mathrm{H}} = \hat{\mathrm{T}} + \hat{\mathrm{V}} = \hat{\mathrm{T}}_{\mathrm{e}} + \hat{\mathrm{V}}_{\mathrm{en}} + \hat{\mathrm{V}}_{\mathrm{ee}} + \hat{\mathrm{V}}_{\mathrm{nn}} + \hat{\mathrm{V}}_{\mathrm{ext}}$$

$$= -\sum_i \frac{\hbar^2}{2m_e} \nabla^2_{\mathbf{r}_i}$$ Kinetic energy of the electrons

$$-\sum_{i,j} \frac{Z_i e^2}{4\pi\varepsilon_0 |\mathbf{R}_i - \mathbf{r}_j|}$$ Coulomb interaction electrons-nuclei

$$+\sum_{i,j>i} \frac{e^2}{4\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|}$$ Coulomb interaction electrons-electrons

$$+\sum_{i,j>i} \frac{Z_i Z_j e^2}{4\pi\varepsilon_0 |\mathbf{R}_i - \mathbf{R}_j|}$$ Coulomb interaction nuclei-nuclei

Wave function $\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_n)$

Wave function

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

Impractical:
- 3n dimensions for n electrons
- Almost always no closed form expression
- Numerical solution: discretisation in basis functions

Costly: $[\mathrm{s}] \simeq \exp(2n)/10^4$ $[\mathrm{MB}] \simeq \exp(n)/2$

Methane

CH_4

N_2

$N \equiv N$

Ethanol

H_3C — OH

https://gist.github.com/ferchault/1e6009e783102006739 69ef96c9dad1d

Summary

1. In principle, properties could be done arbitrarily accurately, but that is too expensive.

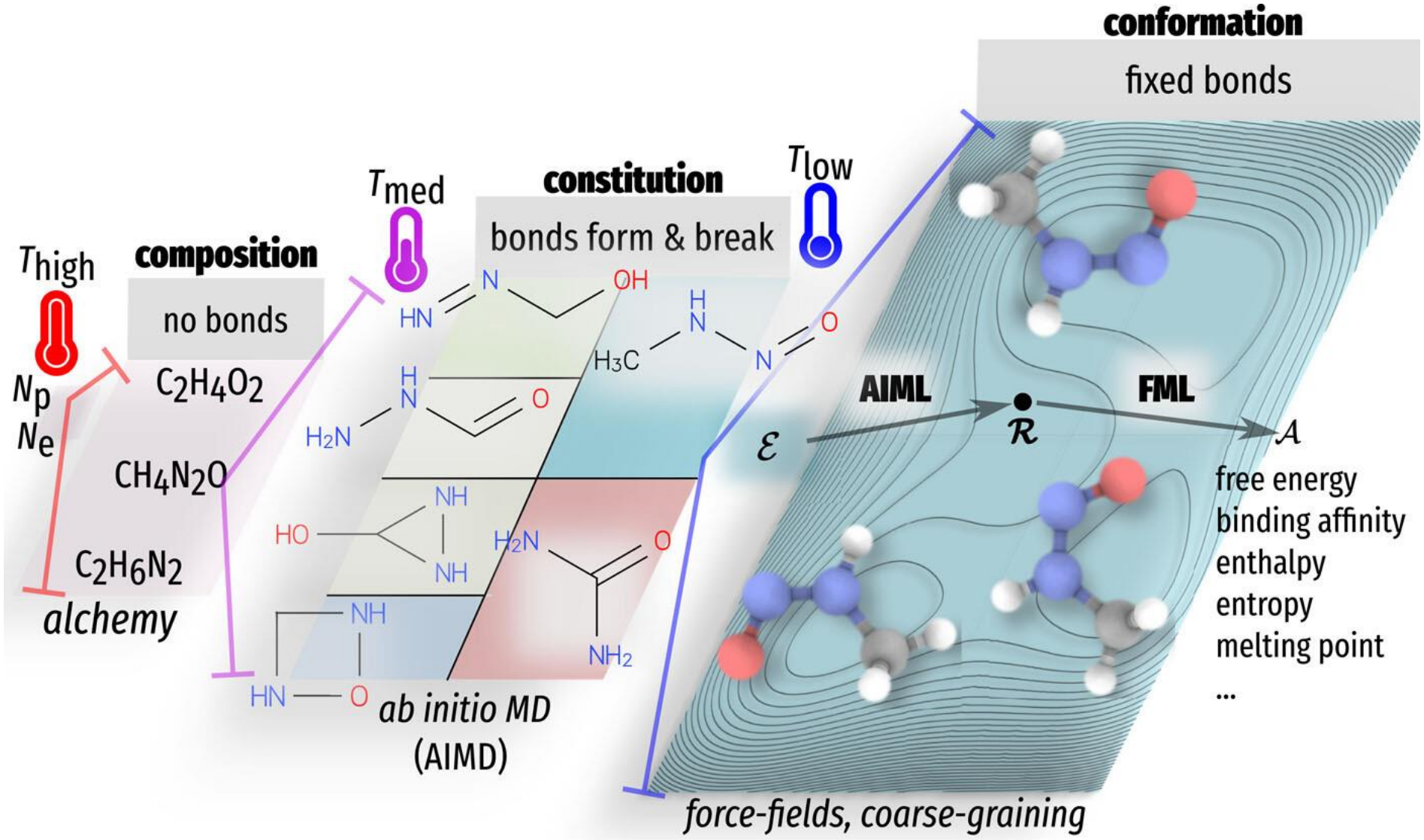
2. Two core approximations:
   Electrons feel static nuclei and nuclei feel averaged electrons. (“Born-Oppenheimer”)

   Finite accuracy of wave function / numerics. (“Discretisation”)

3. Mental picture: static atoms and electron density.

Chemical Space

Hierarchies



https://doi.org/10.1063/5.0095674

Scaling

Scaling with chemical diversity

Elements	# atoms	# sum formulas	# graphs [1]	#confomers
CONF	5	169	4,715	16,797[2]
CONFS	5	349	9,917	51,710
CONFSP	5	757	31,550	
CONFSPCl	5	1,142	37,908	
CONFSPClBr	5	1,647	45,132	
CONFSPClBrI	5	2,291	53,285	328,591[2]

Scaling with number of heavy atoms

Elements	# atoms	# sum formulas	# graphs	#confomers [2]
CONF	1	4	4	
CONF	2	19	19	
CONF	3	49	94	
CONF	4	97	621	
CONF	5	169	4,715	
CONF	6	276	42,087	
CONF	7	425	417,923	7,039,390
CONFS	1	5	5	
CONFS	2	28	28	
CONFS	3	82	160	
CONFS	4	180	1,161	
CONFS	5	349	9,917	
CONFS	6	625	97,607	
CONFS	7	1,050	1,064,343	23,016,417

https://gist.github.com/ferchault/9ae958b637a255475b502fc63c652835