

# Simulating chemistry

Enabling novel approaches for modelling the  
electronic structure of molecules

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# Contents

- 1 Why “computer chemistry”?
- 2 Top to bottom
  - Sketching models and equations
- 3 A platform to try things
  - `molsturm`



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- 1 Why “computer chemistry”?
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# Why “computer chemistry”?

- Experiments are expensive (money, people, time)
  - 1 droplet water<sup>1</sup>:  $1.7 \cdot 10^{21}$  particles
  - Experiments only measure averages
  - Sometimes hard to link to physical laws
- ⇒ Cooperative research of experiment and theory
- ⇒ Standard practice in industry and research

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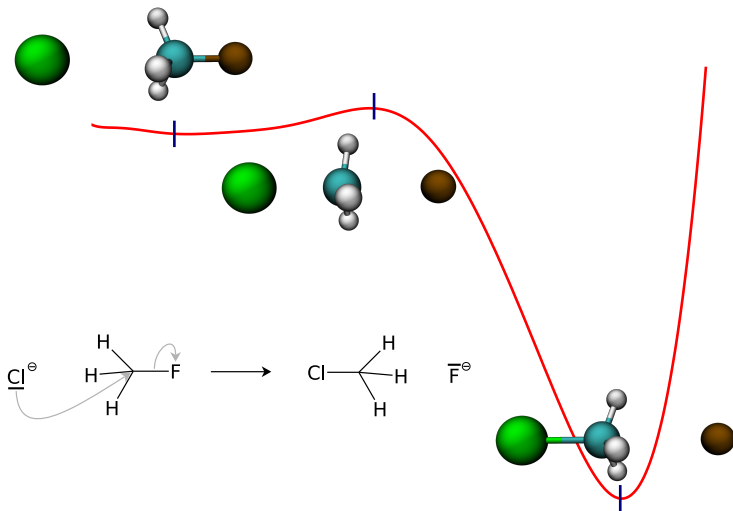
<sup>1</sup>Assume 0.05 ml.

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# Describing chemistry



# Quantum chemistry

- Goal: Describing chemical reactivity / properties
- Physics at the atomic level: Quantum physics
- Quantum physics + chemistry → quantum chemistry

⇒ **Electronic** Schrödinger equation:

$$\hat{\mathcal{H}}\Psi_i = E_i\Psi_i$$

- Defines energy  $E_i$
- Solving allows to probe arbitrary properties via  $\Psi_i$

# Electronic Schrödinger equation

- Electronic Schrödinger equation:

$$\hat{\mathcal{H}}\Psi_i = E_i\Psi_i$$

- Hamiltonian  $\hat{\mathcal{H}}$ : Contains physics and molecular structure
  - State  $\Psi_i \in H^2(\mathbb{R}^{3N}, \mathbb{C})$  ( $N$ : Number of electrons)
  - Energy  $E_i \in \mathbb{R}$ : Eigenvalue corresponding to  $\Psi_i$
  - Most important: Ground state energy  $E_0$  and  $\Psi_0$
  - One  $\hat{\mathcal{H}}$  for each structure
- ⇒ Many equations to solve



# Solving the Schrödinger equation: How hard can it be?

- Main ingredient: Min-max principle<sup>1</sup>:

$$E_0 \leq \min_{\Psi \in S} \mathcal{E}(\Psi) = \min_{\Psi \in S} \frac{\langle \Psi | \hat{\mathcal{H}} \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

where  $S \subset H^1(\mathbb{R}^{3N}, \mathbb{C})$  and  $L^2(\mathbb{R}^{3N}, \mathbb{C})$  inner product  $\langle \cdot | \cdot \rangle$

- Discretisation: **Curse of dimensionality**:
  - $\langle \cdot | \cdot \rangle$  involves integral over  $3N$ -dim. space
  - Assume 2 quadrature points only
  - Chloromethane:  $N = 26 \Rightarrow 2^{78} \approx 3 \cdot 10^{23}$  quadrature points

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<sup>1</sup>Because of technical details we can use  $H^1$  instead of  $H^2$ .

# Now what?

- Need a suitable **inexact** model
- Plenty have been developed
- Our focus: **Hartree-Fock** approximation
  - Single-particle functions:  $\psi_i \in H^1(\mathbb{R}^3, \mathbb{R})$
  - Slater-determinant:

$$\Phi = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \psi_1(\underline{\mathbf{r}}_1) & \psi_2(\underline{\mathbf{r}}_1) & \cdots & \psi_N(\underline{\mathbf{r}}_1) \\ \psi_1(\underline{\mathbf{r}}_2) & \psi_2(\underline{\mathbf{r}}_2) & \cdots & \psi_N(\underline{\mathbf{r}}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\underline{\mathbf{r}}_N) & \psi_2(\underline{\mathbf{r}}_N) & \cdots & \psi_N(\underline{\mathbf{r}}_N) \end{pmatrix}$$

- Subspace  $S$ : Choose the best single-determinant subspace

# Hartree-Fock approximation

- For trial determinant  $\tilde{\Phi}$  made up of  $\{\tilde{\psi}_i\}_i$ :

$$E_0 \leq E_0^{\text{HF}} \leq \mathcal{E}^{\text{HF}}(\tilde{\Phi})$$

⇒ Minimisation problem for  $\{\tilde{\psi}_i\}_i$

- Unique minimising set  $\Theta^0 = \{\psi_i^0\}_i$  exists!
- Euler-Lagrange equations:

$$\hat{\mathcal{F}}_{\Theta^0} \psi_i^0 = \varepsilon_i \psi_i^0 \qquad \langle \psi_i^0 | \psi_j^0 \rangle = \delta_{ij}$$

- Fock operator  $\hat{\mathcal{F}}_{\Theta^0}$  depends on solution

⇒ Self-consistent field problem

# The standard approach

- Note: HF is in single-particle space, i.e. 3D

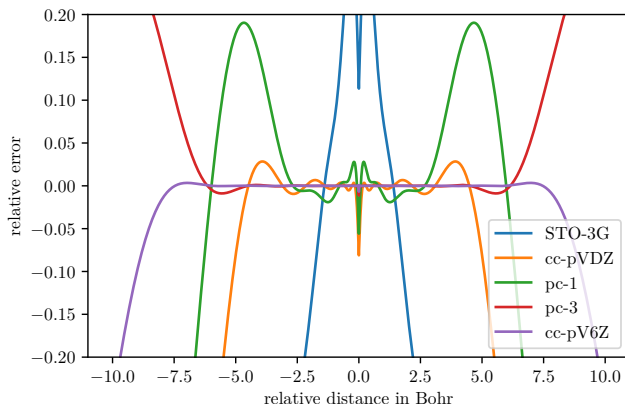
- Discretise  $\hat{\mathcal{F}}_{\Theta^0}$  in a basis  $\{\varphi_\mu\}_\mu$

⇒ Problem now: Find the lowest-energy  $\{\psi_i^0\}_i$ , built from  $\{\varphi_\mu\}_\mu$

- Self-consistent field procedure:
  - 1 Guess trial coefficients  $\mathbf{C}^{(0)}$
  - 2 Build trial Fock matrix  $\mathbf{F}^{(0)}$
  - 3 Solve Euler-Lagrange equations ⇒ New  $\mathbf{C}^{(1)}$
  - 4 Build next Fock matrix  $\mathbf{F}^{(1)}$
  - 5 Repeat

# The standard basis: Gaussian-type basis sets

$$\varphi_{\mu}^{\text{GTO}}(\underline{\mathbf{r}}) = r^{\mathbf{l}_{\mu}} \sum_i^{N_{\text{contr}}} c_{\mu,i} \exp(-\alpha_{\mu,i} r^2) \cdot Y_{\mathbf{l}_{\mu}}^{m_{\mu}}(\hat{\mathbf{r}})$$



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# Alternatives

- Gaussians: Not physical, but cheap
  - Tuned to be good in the regions where chemistry happens
- ⇒ Implicit assumptions:
- Electron is close to the nucleus
  - Valence region
- 
- There are cases where these are violated!
  - How about alternatives?

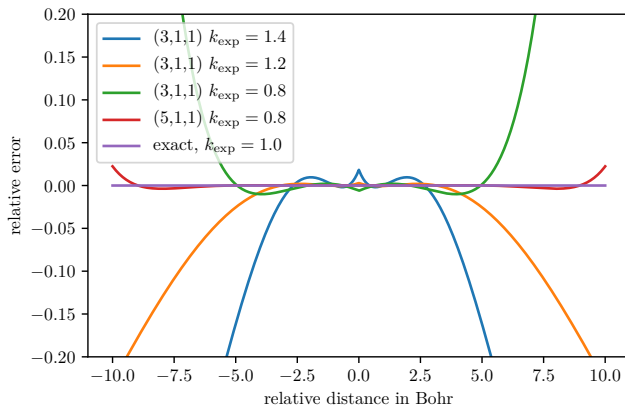
# Alternatives

- Gaussians: Not physical, but cheap
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- ⇒ Implicit assumptions:
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  - Valence region
- 
- There are cases where these are violated!
  - How about alternatives?
  - Many exist!

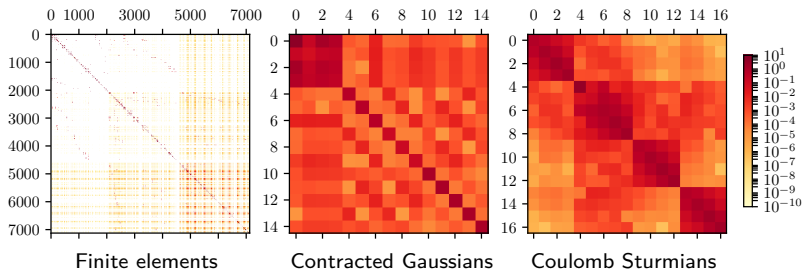


# Alternatives: Coulomb-Sturmians

$$\varphi_{\mu}^{\text{CS}}(\underline{\mathbf{r}}) = P_{nl}(r) \exp(-kr) \cdot Y_l^m(\hat{\mathbf{r}})$$



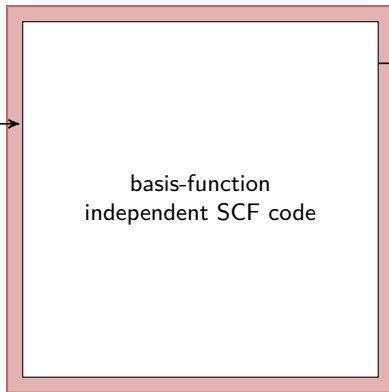
# Challenge: Deviating Fock matrix structures



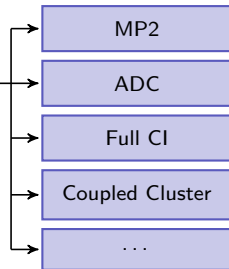
- Required numerical procedures differ
- Details should be hidden from SCF

# Aims of molsturm

## Integral backends



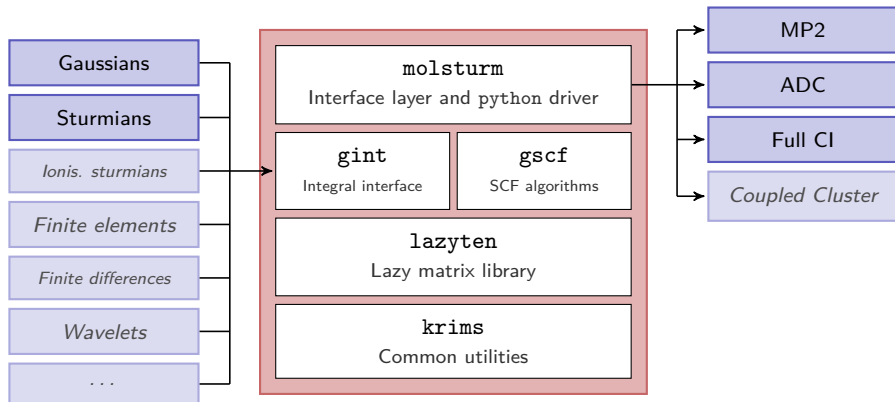
## Post HF methods



# molsturm structure

## Integral backends

## Post HF methods



# Takeaway

- Dimensionality of chemistry is enormous
- Modelling actual experiments: **Approximate** methods
- Sources of error:
  - Method (i.e. Hartree-Fock instead of Schrödinger)
  - Discretisation (i.e. Basis set)
  - Numerics (i.e. convergence tolerance)
- Ideal balancing point strongly dependent on problem

⇒ Need framework to try things

⇒ Main motivation for molsturm

# Acknowledgements



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# Questions?

**Code:** <https://molsturm.org>

**Paper:** <https://michael-herbst.com/molsturm-design.html>

**Thesis:** <https://michael-herbst.com/phd-thesis.html>

**Email:** [michael.herbst@iwr.uni-heidelberg.de](mailto:michael.herbst@iwr.uni-heidelberg.de)

**Blog:** <https://michael-herbst.com/blog>



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# Contents

## 4 Lazy matrices



# Lazy matrix evaluation

- Actual expression in source code

$$\mathbf{D} = \mathbf{A} + \mathbf{B},$$

$$\mathbf{E} = \mathbf{DC},$$

$$\underline{\mathbf{y}} = \mathbf{E}\underline{\mathbf{x}},$$

# Lazy matrix evaluation

- Actual expression in source code

$$\mathbf{D} = \mathbf{A} + \mathbf{B},$$

$$\mathbf{E} = \mathbf{D}\mathbf{C},$$

$$\underline{y} = \mathbf{E}\underline{x},$$

- Performed operation

$$\boxed{\mathbf{D}} = \boxed{\mathbf{A}} + \boxed{\mathbf{B}} = \boxed{\begin{array}{c} + \\ \swarrow \quad \searrow \\ \mathbf{A} \quad \mathbf{B} \end{array}}$$

# Lazy matrix evaluation

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$$\mathbf{D} = \mathbf{A} + \mathbf{B},$$

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- Performed operation

$$\boxed{\mathbf{E}} = \boxed{\mathbf{D}} \cdot \boxed{\mathbf{C}}$$

# Lazy matrix evaluation

- Actual expression in source code

$$\mathbf{D} = \mathbf{A} + \mathbf{B},$$

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- Performed operation

$$\boxed{\mathbf{E}} = \boxed{\begin{array}{c} + \\ \swarrow \quad \searrow \\ \mathbf{A} \quad \mathbf{B} \end{array}} \cdot \boxed{\mathbf{C}} = \boxed{\begin{array}{c} \cdot \\ \swarrow \quad \searrow \\ + \quad \mathbf{C} \\ \swarrow \quad \searrow \\ \mathbf{A} \quad \mathbf{B} \end{array}}$$

# Lazy matrix evaluation

- Actual expression in source code

$$\mathbf{D} = \mathbf{A} + \mathbf{B},$$

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- Performed operation

$$\boxed{\underline{\mathbf{y}}} = \boxed{\mathbf{E}} \boxed{\underline{\mathbf{x}}} = \boxed{\begin{array}{c} \cdot \\ \swarrow \quad \searrow \\ \mathbf{A} + \mathbf{C} \\ \swarrow \quad \searrow \\ \mathbf{B} \end{array}} \boxed{\underline{\mathbf{x}}} = (\mathbf{A} + \mathbf{B}) \mathbf{C} \underline{\mathbf{x}}$$