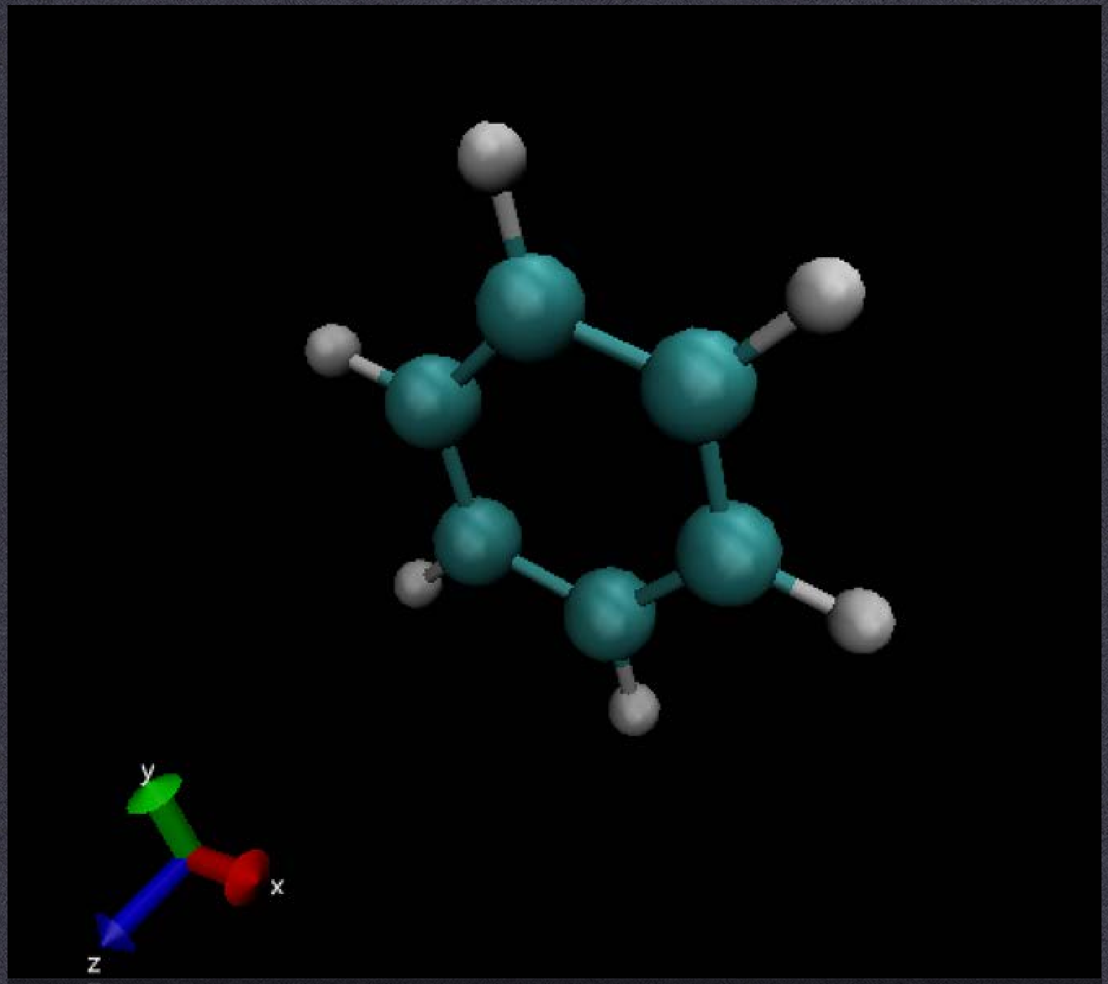

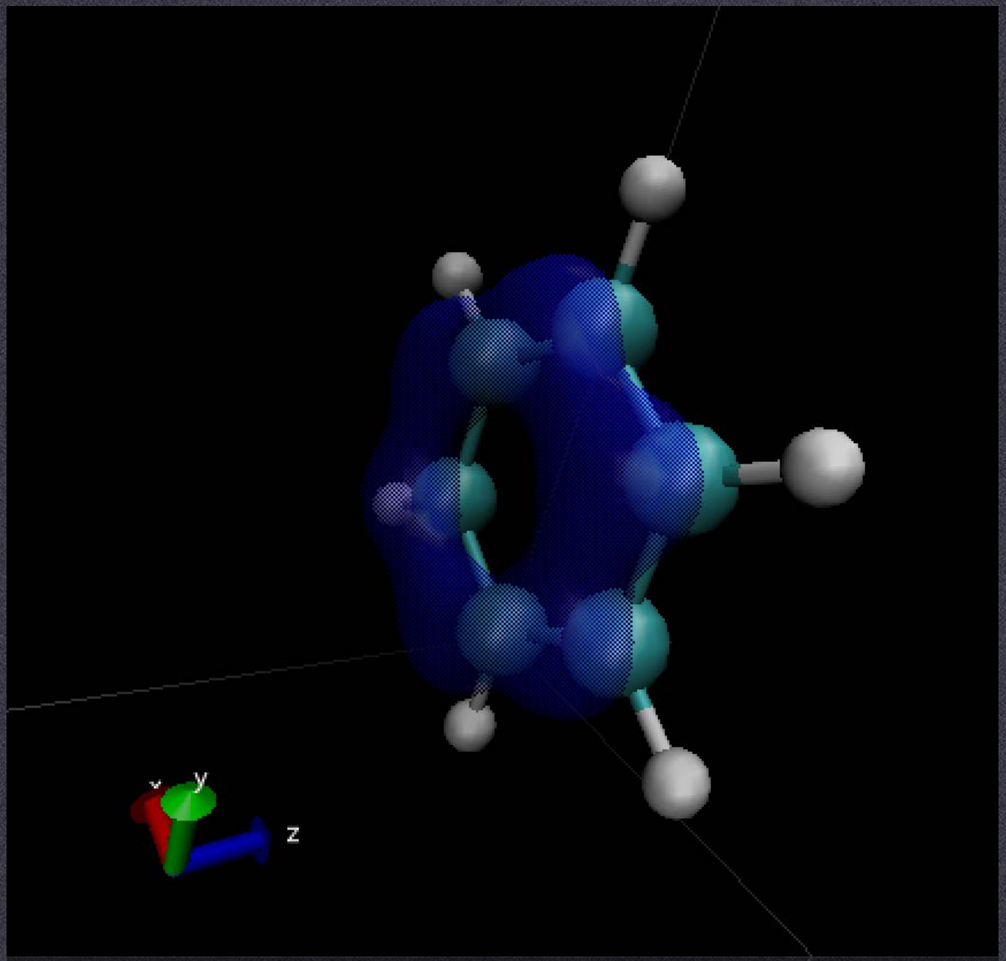

DENSITY FUNCTIONAL THEORY CALCULATIONS OF MOLECULAR ORBITAL EVOLUTION DURING CHEMICAL REACTIONS

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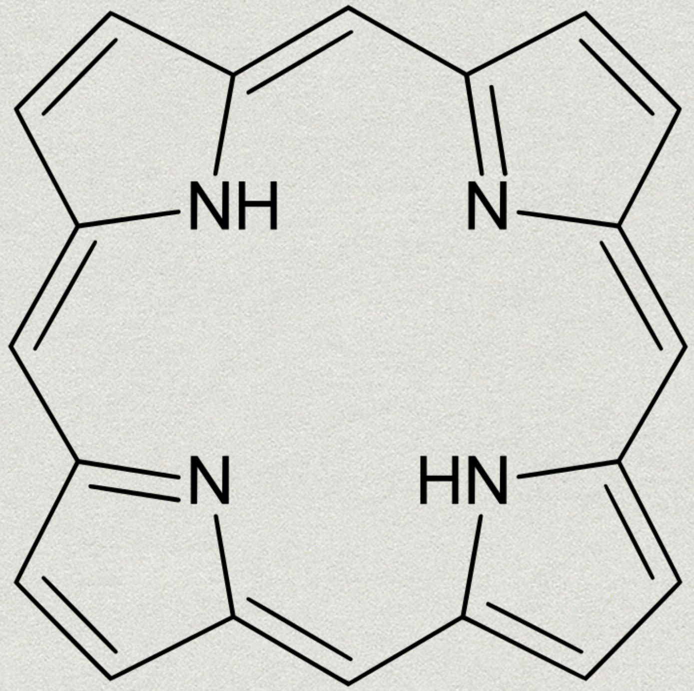
Outline

- The problem: Molecular orbitals and DFT
- Simulation methods
- Results: Visualizing molecular orbital structures
- Results: Visualizing chemical reactions
- Conclusions

Goals

- The calculation and visualization of molecular orbitals and their transformation during reactions.
- We modeled molecular structures and chemical reactions to learn about the behavior of valence electrons.
- Studied orbitals of porphyrin and reactions of smaller molecules.
- Ultimately we want a better understanding of what really goes on in chemical reactions! This involves exploring a large solution space, so is well-suited for HPC.



How do we model it?

- The ASE (Atomic Simulation Environment) and Projector Augmented Wave (GPAW) Python packages for calculating orbitals and molecular geometries
- Visual Molecular Dynamics (VMD) for visualization
- Avogadro (molecule editor) for modeling molecules

Density Functional Theory

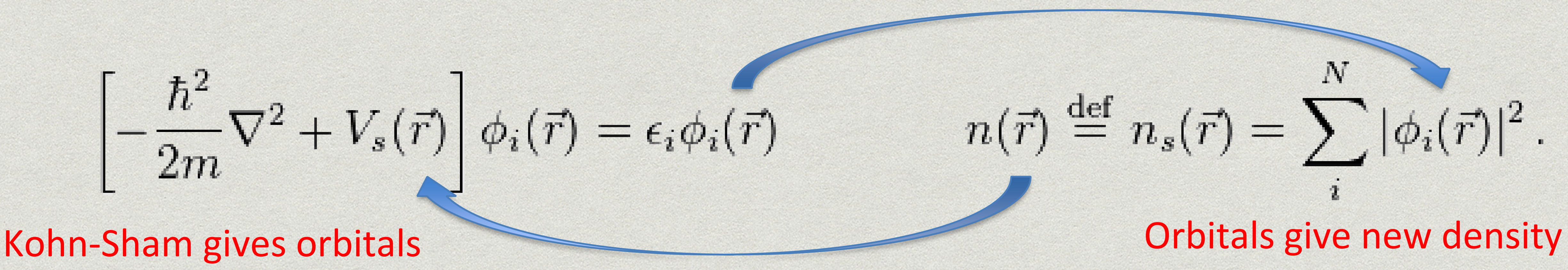
- Goal: Numerical approximation of physical properties of a many-body quantum system in its ground state.
- All information about the state of the system is expressed in the wave function, which satisfies the Schrödinger equation:

$$\hat{H}\Psi = \left[\hat{T} + \hat{V} + \hat{U}\right]\Psi = \left[\sum_{i}^{N}\left(-\frac{\hbar^2}{2m_i}\nabla_i^2\right) + \sum_{i}^{N} V(\vec{r}_i) + \sum_{i<j}^{N} U(\vec{r}_i, \vec{r}_j)\right]\Psi = E\Psi$$

- We can rewrite the wave function as an expression in terms of the electron density:

$$n(\vec{r}) = N \int \mathrm{d}^3 r_2 \cdots \int \mathrm{d}^3 r_N \Psi^*(\vec{r}, \vec{r}_2, \dots, \vec{r}_N)\Psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N).$$

- Thus the electron density tells us everything about the system, but it is a function of a single three-vector and is much more tractable to approximate.
- We make an initial guess for the density by assuming no interaction between electrons. Then we refine our guess by iteratively solving the Kohn-Sham equations:



$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_s(\vec{r})\right]\phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r})$$

$$n(\vec{r}) \overset{\text{def}}{=} n_s(\vec{r}) = \sum_{i}^{N} |\phi_i(\vec{r})|^2 .$$

Kohn-Sham gives orbitals

Orbitals give new density

Kohn-Sham equations

- Variational principle:

$$\min E[\rho] = T_s[\rho] + \int v_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_H[\rho] + E_{xc}[\rho]$$

(kinetic) (external) (Coloumb) (exchange-correlation)

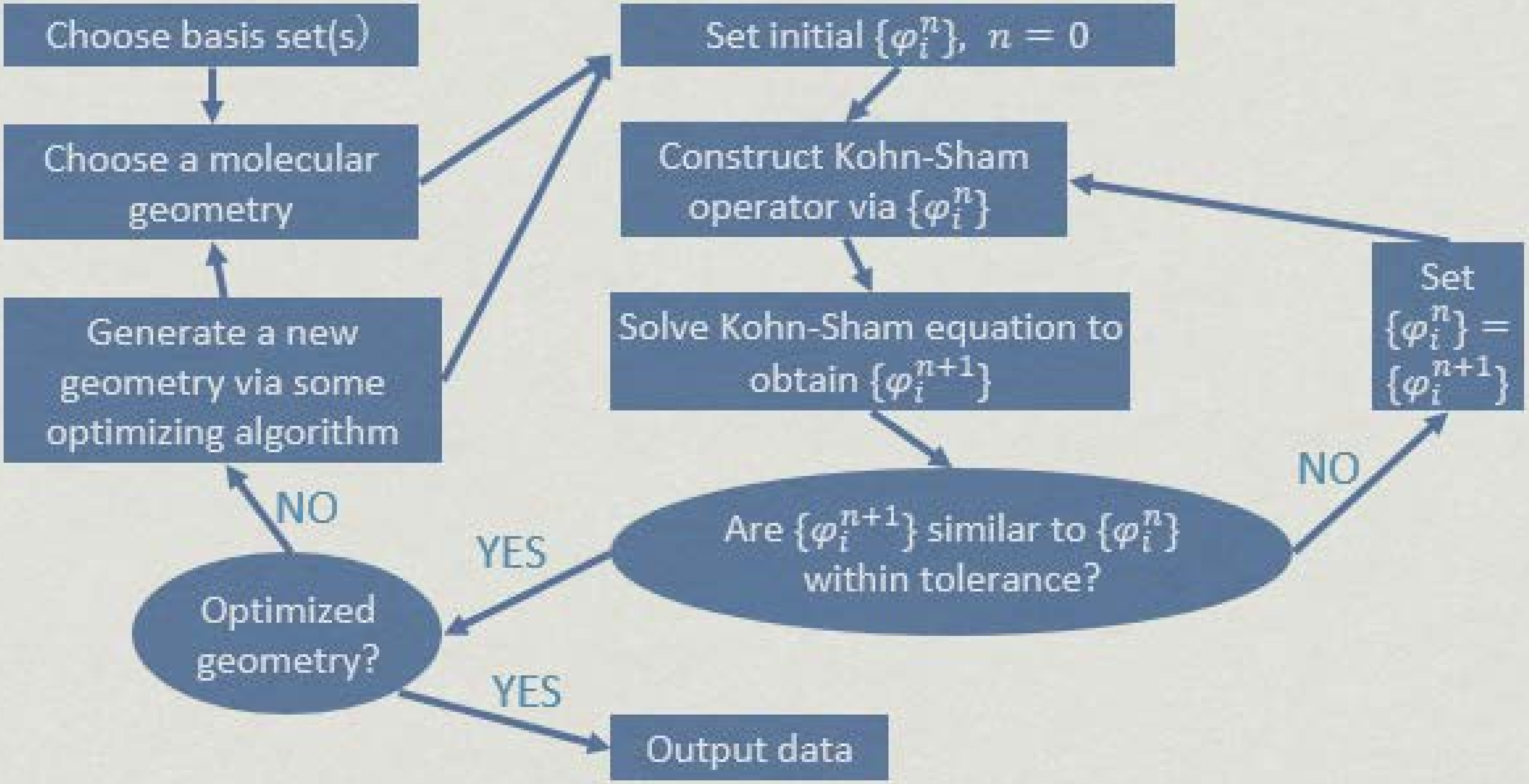
with $\rho[\mathbf{r}] = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2$, subject to $\int \varphi_i^*(\mathbf{r})\varphi_j(\mathbf{r})d\mathbf{r} = \delta_{ij}$

- Applying Lagrangian multipliers:

$$(\frac{\hbar^2}{2}\Delta + v_{ext}(\mathbf{r}) + e^2\int \frac{\rho(\mathbf{r}')}{|r-r'|}d\mathbf{r}' + \frac{\delta E_{xc}[\rho]}{\delta\rho})\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r})$$

- Two main difficulties:
  1. Last two terms depend on ρ, iteration needed
  → Self-consistent field (SCF) procedure
  2. No explicit form of exchange-correlation term
  → Approximations (LDA, PBE, RPBE etc.)

Illustration of SCF procedure



Choose basis set(s)

Choose a molecular geometry

Generate a new geometry via some optimizing algorithm

Set initial $\{\varphi_i^n\}$, $n = 0$

Construct Kohn-Sham operator via $\{\varphi_i^n\}$

Solve Kohn-Sham equation to obtain $\{\varphi_i^{n+1}\}$

Are $\{\varphi_i^{n+1}\}$ similar to $\{\varphi_i^n\}$ within tolerance?

Set $\{\varphi_i^n\} = \{\varphi_i^{n+1}\}$

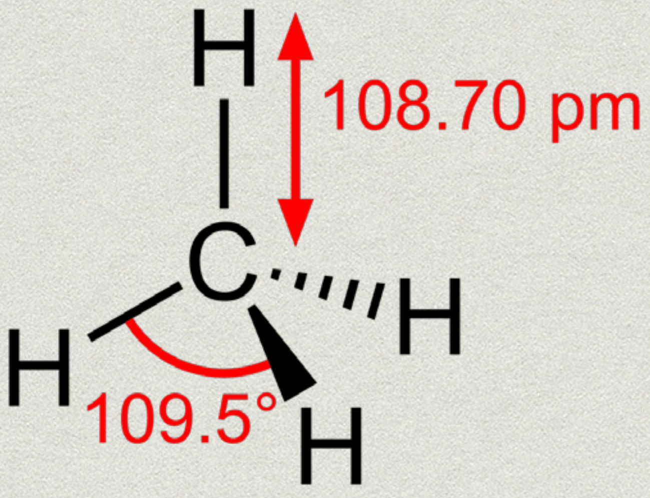
Optimized geometry?

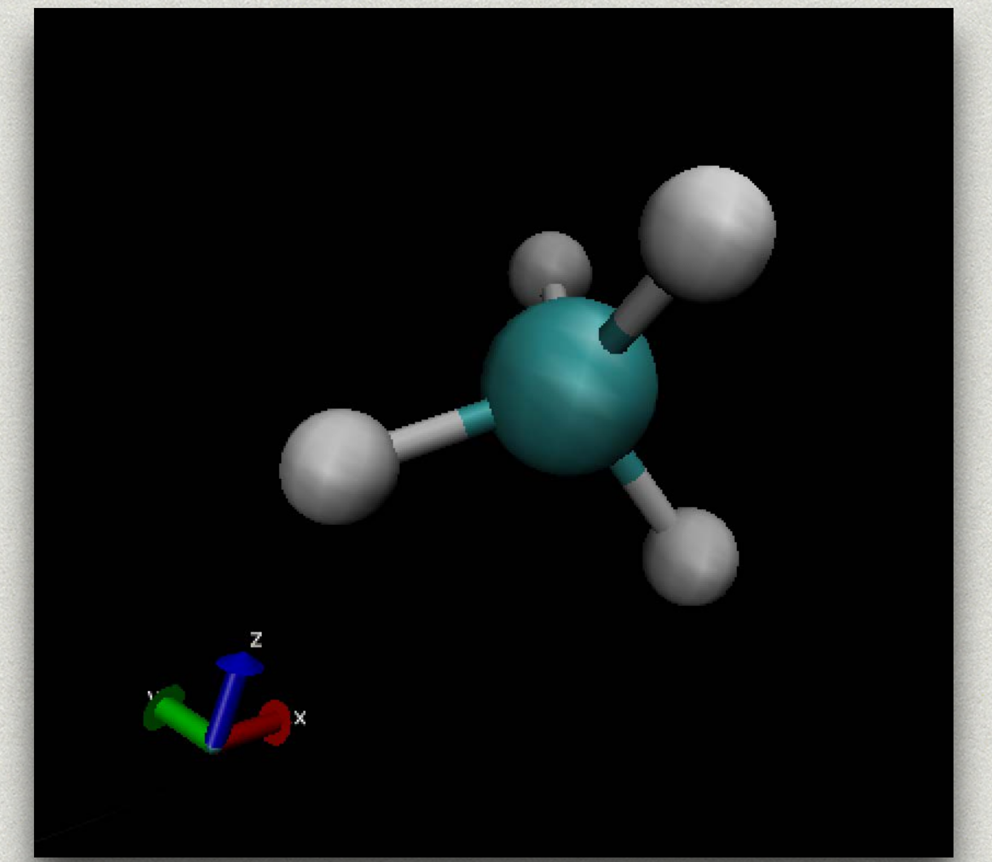
Output data

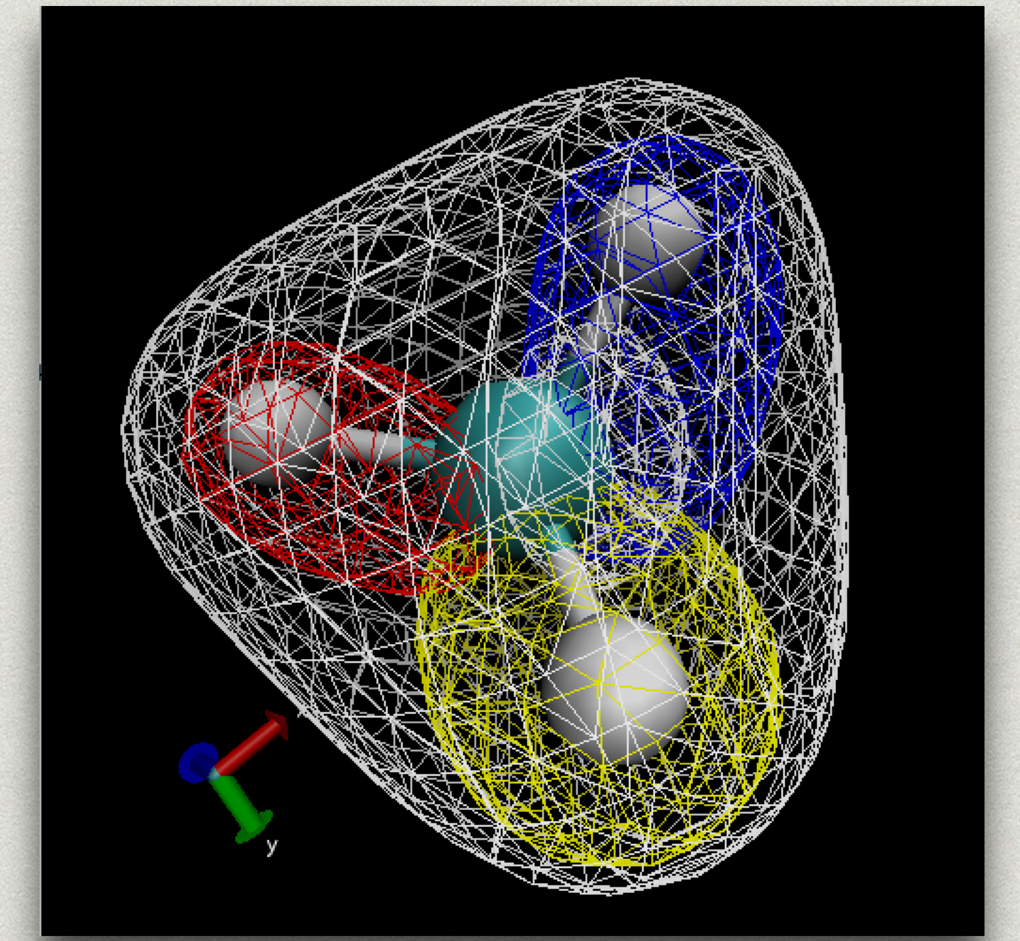
Paw method: a technique using pseudo wavefunctions, improving computational efficiency → implemented in python package GPAW

Results for small molecules

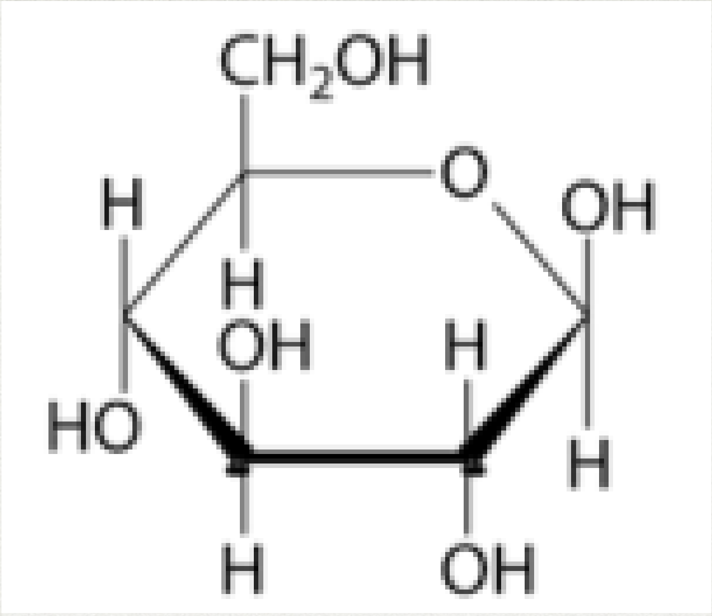
- Example of small molecule: CH4, Methane
- Visualization of orbitals shows how tetrahedral structure is formed

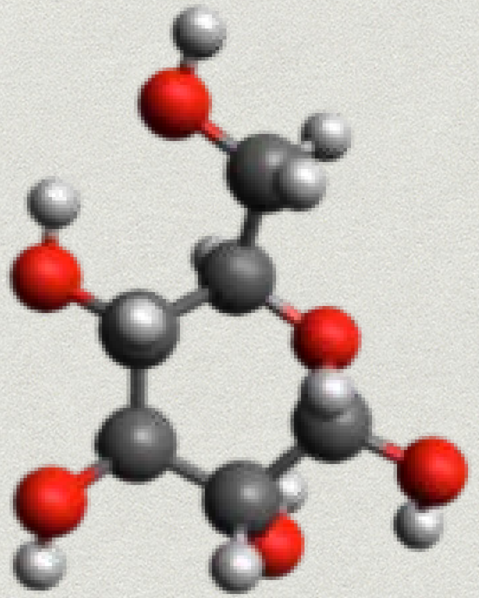




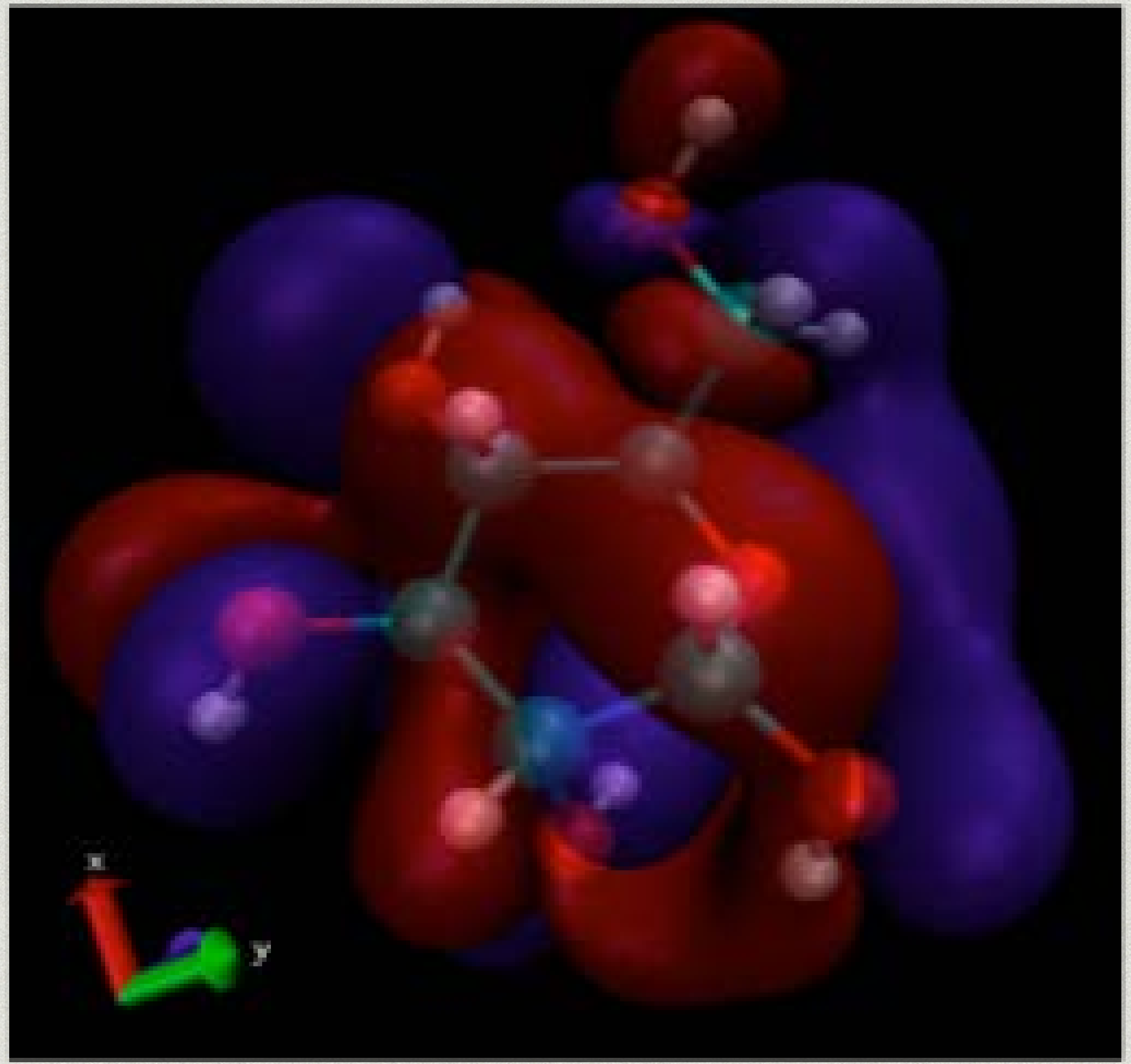


Results for bigger molecules —Glucose

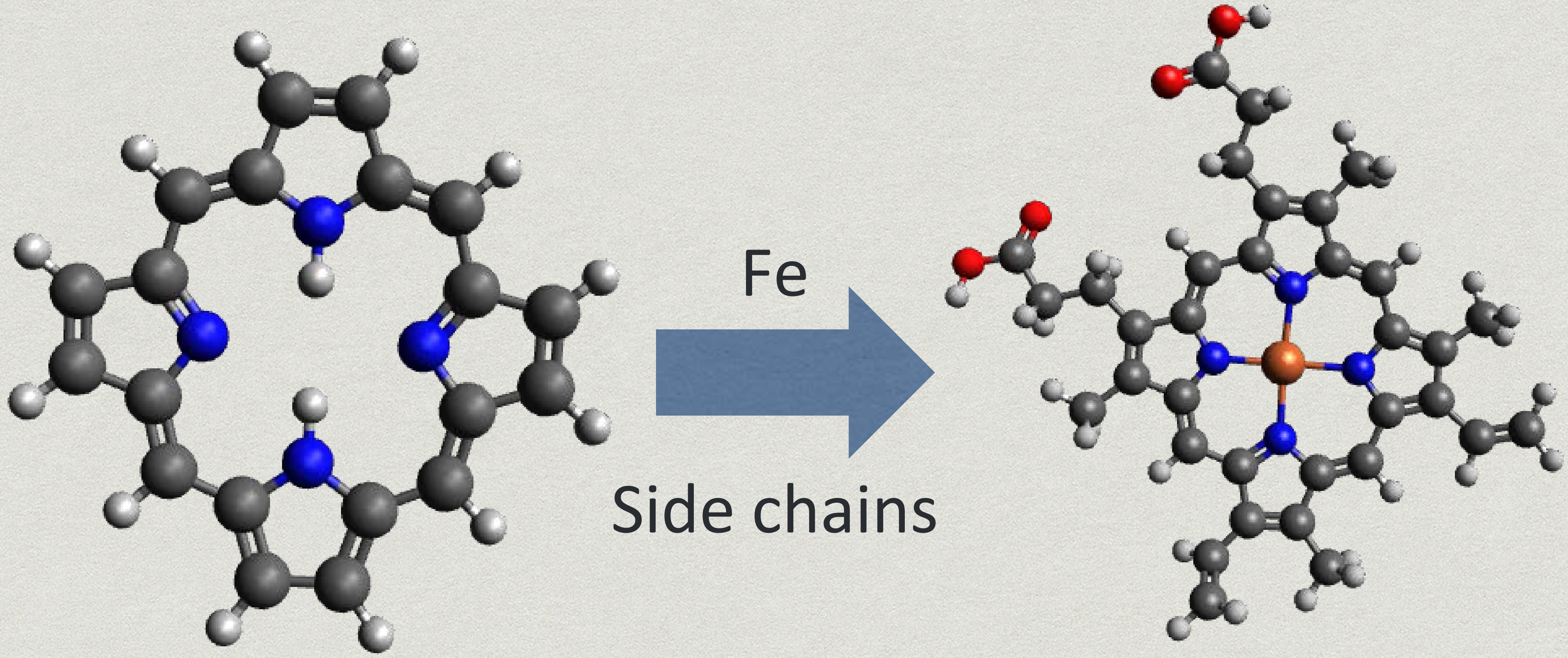




Highest occupied molecular orbital (HOMO):



Results for bigger molecules —Porphin and Heme



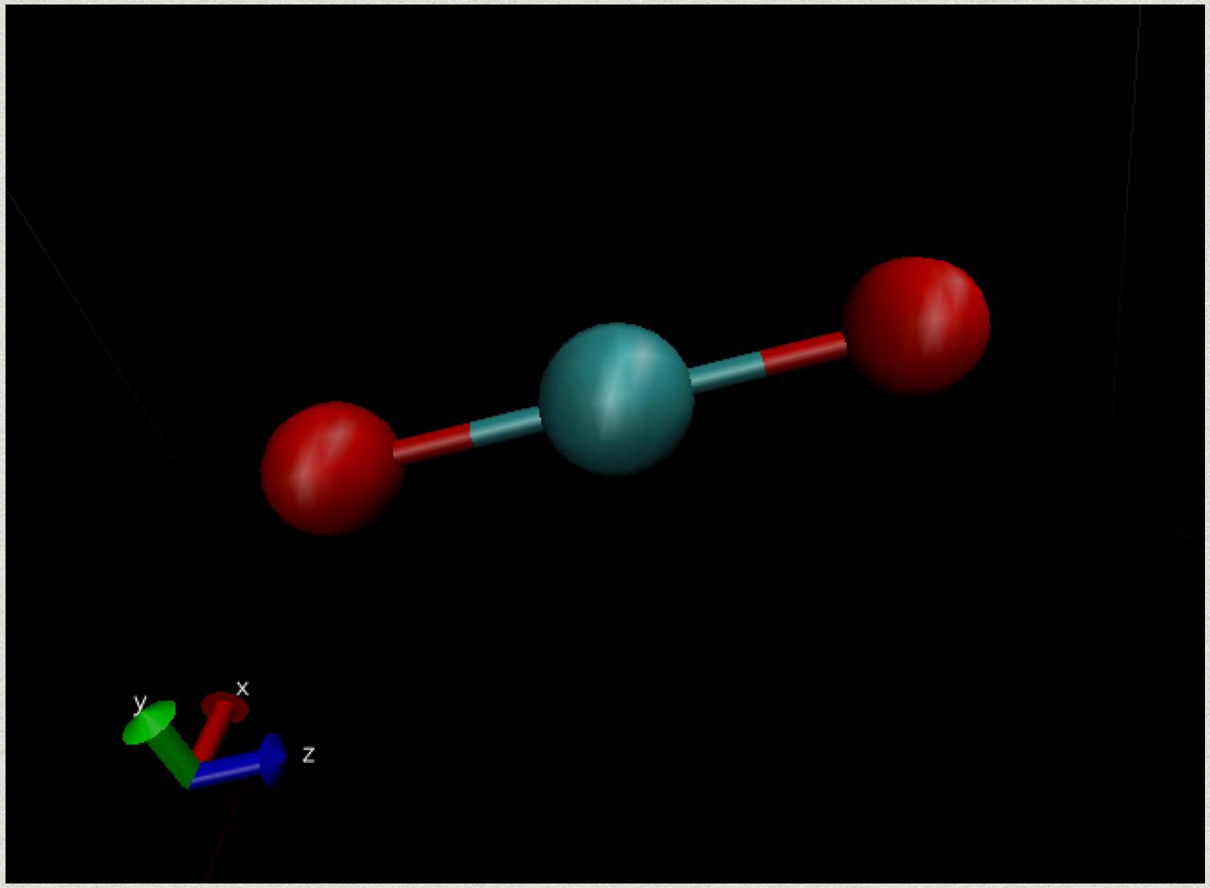
- Iron atom makes a big difference!
- Every SCF step takes long time.
- Geometry can not meet optimization criterion.

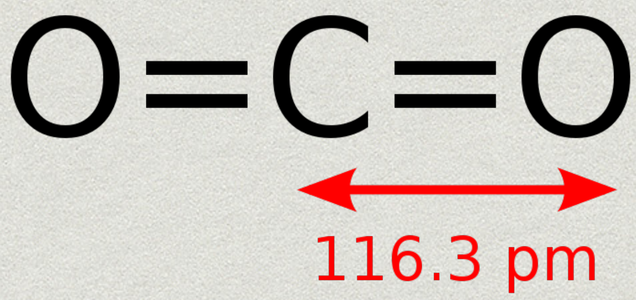
Experiment: Modeling chemical reactions

- Can we learn about the dynamics of chemical reactions by visualizing the transformation of valence electron orbitals?
- Simulation setup: Atoms approach each other from a distance and react to form a compound. Compute and visualize valence orbitals at each time step.
- Even for simple molecules, this is a very resource-intensive computational problem!

Experiment of small molecules reaction

- Example of small molecule: CO2, Carbon dioxide
- Visualizing what will happen when distort molecule position
- Video shows how the molecule go to optimal position(stable position).





Videos!

Conclusions

- DFT and existing tools work well for investigating properties of static molecules.
- Dynamics stretch these techniques beyond their original purposes. It’s a promising direction, but the tools impose some limitations.
    - Black-box objects make solver code difficult to optimize.
    - Existing python modules not designed for parallelization over time steps, have questionable memory management.
    - Video animation requires a lot of hacking.
- For further development, could either use more compute resources or write a new solver designed for dynamics.