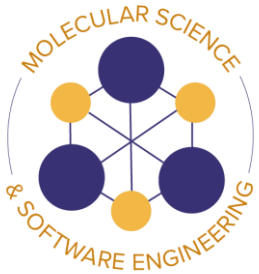
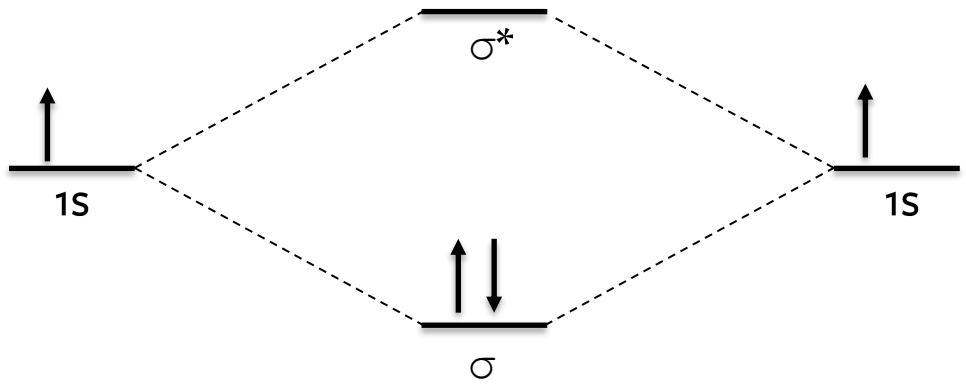
Electronic Structure Theory

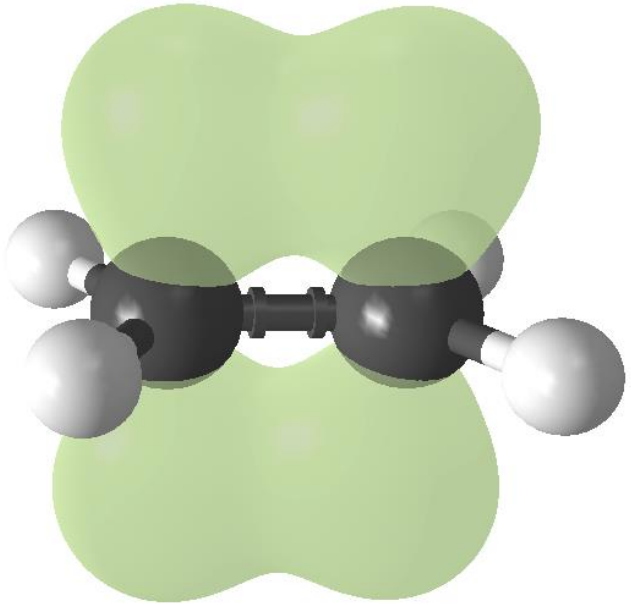
Berkeley
UNIVERSITY OF CALIFORNIA



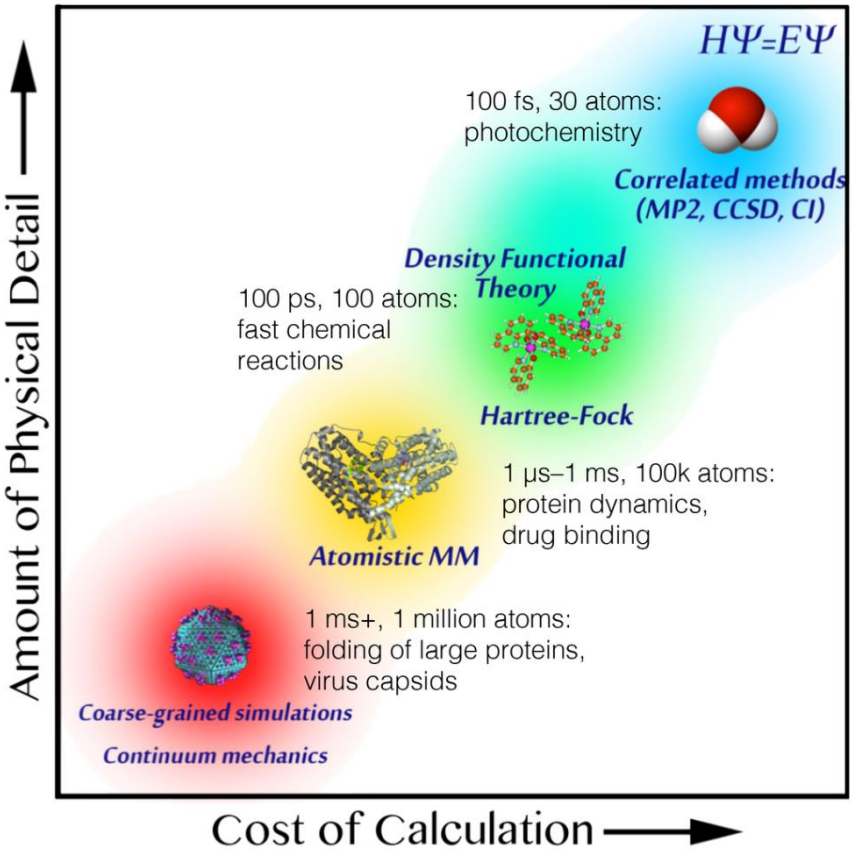
What is Electronic Structure Theory

- Determination of location and structure of electrons within a molecule

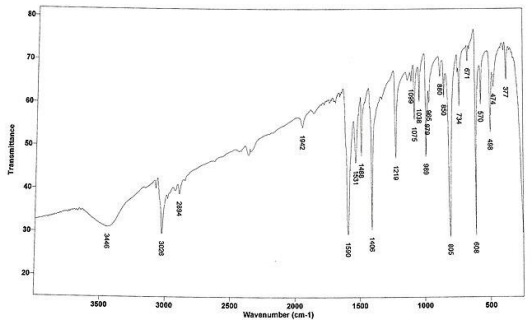


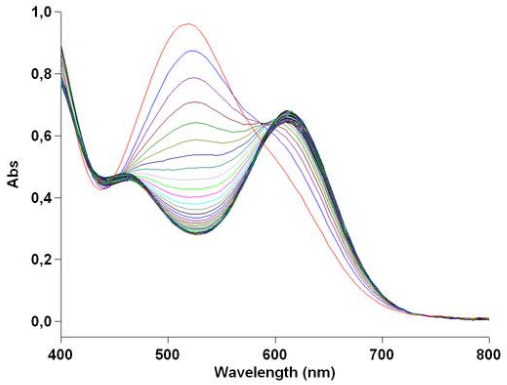


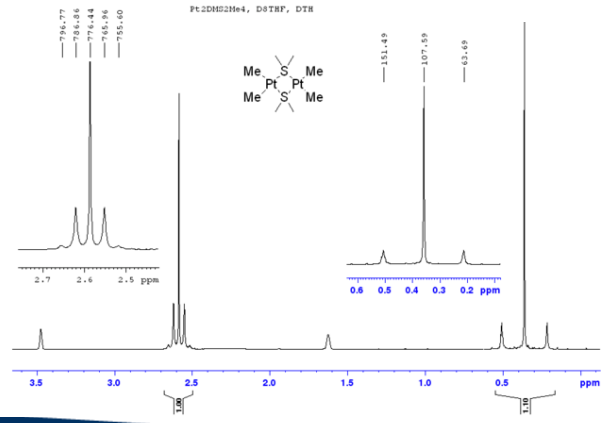
Vs Classical Calculations

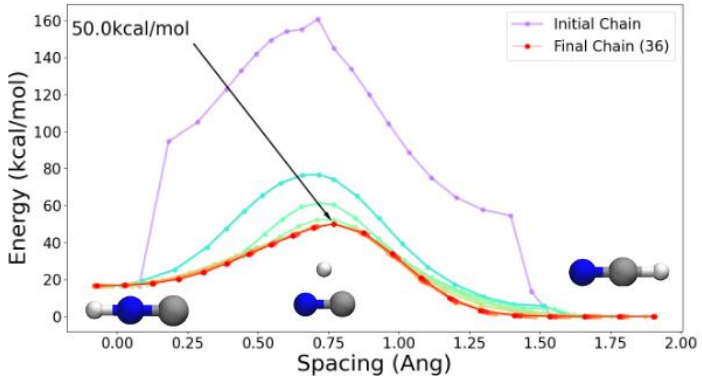


Singlepoint Calculations



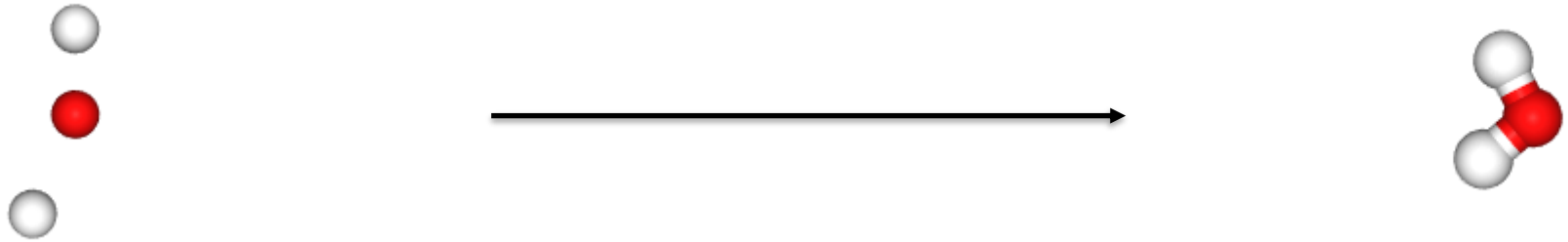






- Calculation on a single fixed geometry
- Electronic properties:
  - UV/Vis, IR, CD spectra
  - NMR/Magnetic susceptibility
  - Bonding information
  - Reaction energies/Transition states

Geometry Optimization



```
O   0.0000    0.0000    0.0000
H   0.0000    1.5875    0.0000
H   0.7938   -1.8521    0.0000
```

```
O  -0.1282   -0.1662    0.0000
H   0.3142    0.6933    0.0000
H   0.7087   -0.7918    0.0000
```

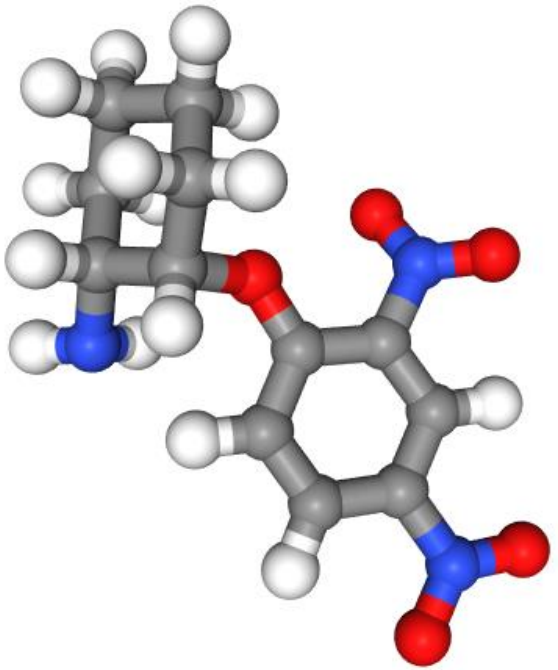
QM Model Selection

- Molecular Orbitals (MOs) are expanded in the basis of Atomic Orbitals (AOs). These AOs are defined by your *basis set*
- Your *method* defines how you are calculating those MOs (what approximations)
- Combined, these are referred to as your *model*, *model chemistry*, or *level of theory*
- Often written together with a slash, with the method first

`hf/sto-3g` `b3lyp/6-31g*` `pbe0/def2-SVP` `ccsd(t)/aug-cc-pvdz`

Why not use QM for everything?

- Geometry optimization of this molecule took **7 hours** on two cores (psi4, ωB97x/6-31G*)

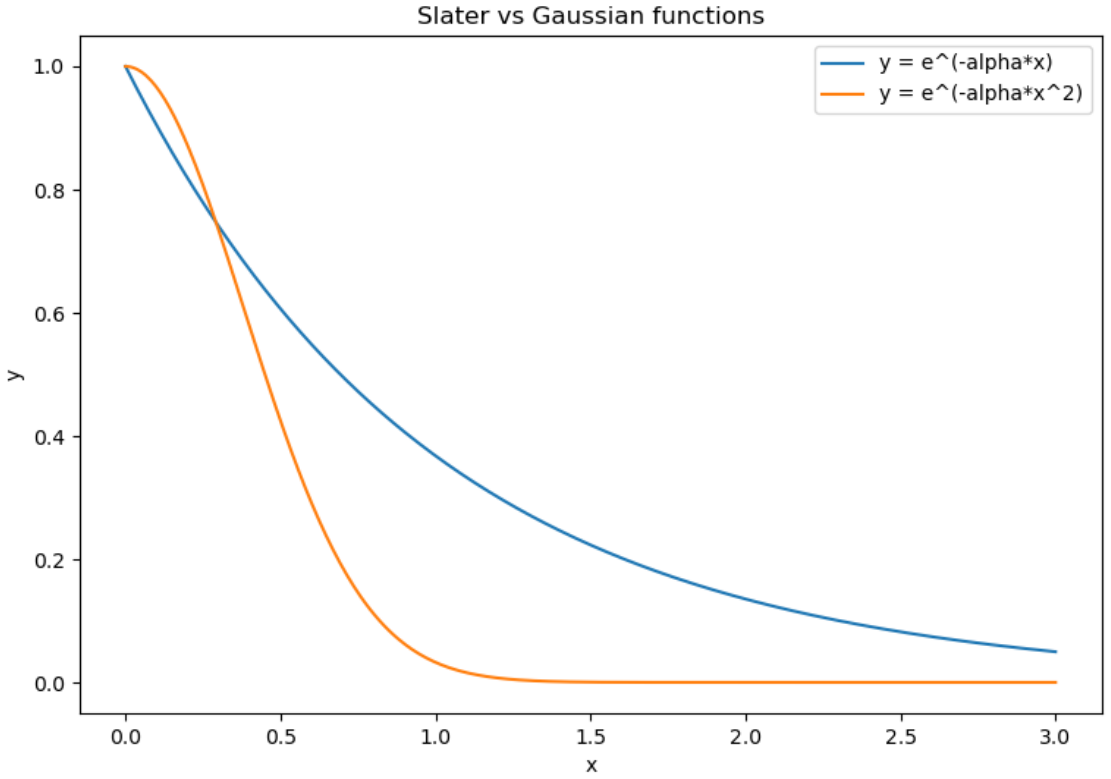


Method Hierarchy

- There is a zoo of methods, all with their strengths and weaknesses
- Hartree-Fock (HF) – very basic, but inaccurate relative to others (lacks correlation)
- Møller–Plesset perturbation theory (MP2, MPn) – Adds correlation
- Coupled Cluster (CCS, CCSD, CCSD(T)) – Very accurate, very expensive
- Density Functional Theory (DFT) – Very good balance between accuracy and cost
  - Walter Kohn – 1998 Nobel Prize in Chemistry for the development of DFT

Basis Sets

- Two common types of functions in basis sets
- Slater: $e^{-\alpha x}$
- Gaussian: $e^{-\alpha x^2}$
- Most atom centered codes use gaussian
- *In general*, larger basis sets are more accurate (but more expensive of course)



Molecules

- In QM, we generally only care about:
  - Element (number of protons)
  - Coordinates
  - Charge & multiplicity (unpaired electrons)
- **Bonds do not exist in the QM world**

- Two units of distance
  - Angstrom (Å, 10^{-10}m)
  - bohr ($5.291\,772 \times 10^{-11}$m or 0.5291772 Å)

```
O     1.548014347149     0.000000000000     0.060071441686
H     0.548241218221     0.000000000000     0.038771425885
H     1.819295099755     0.000000000000    -0.902428819751
```