

Molecular Modeling

COSMOS

18-Jul-2008

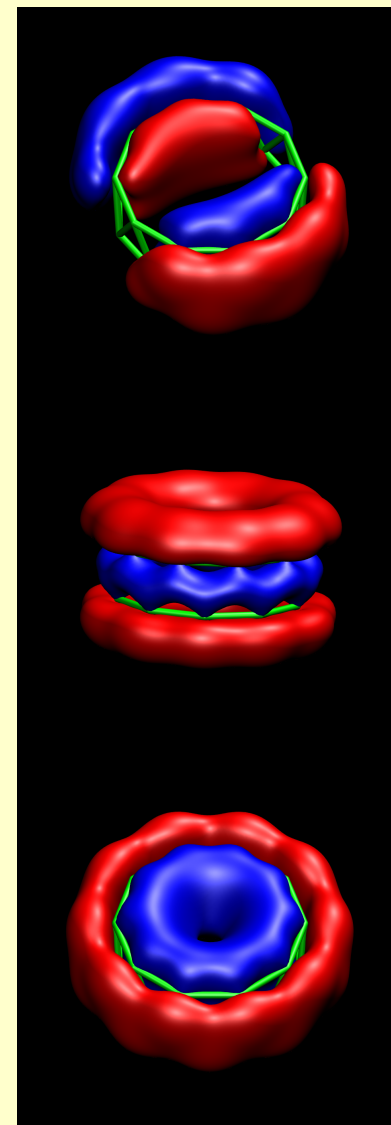
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Modeling Facility



What is Molecular Modeling?

- Simulate molecule-sized pieces of reality with calculations
- Application of physical laws: a mixture of classical and quantum mechanics
- Impose conditions and observe how simulation responds
- Use computation to predict and explain experimental results



MOs of B₁₂

What Information Does It Give?

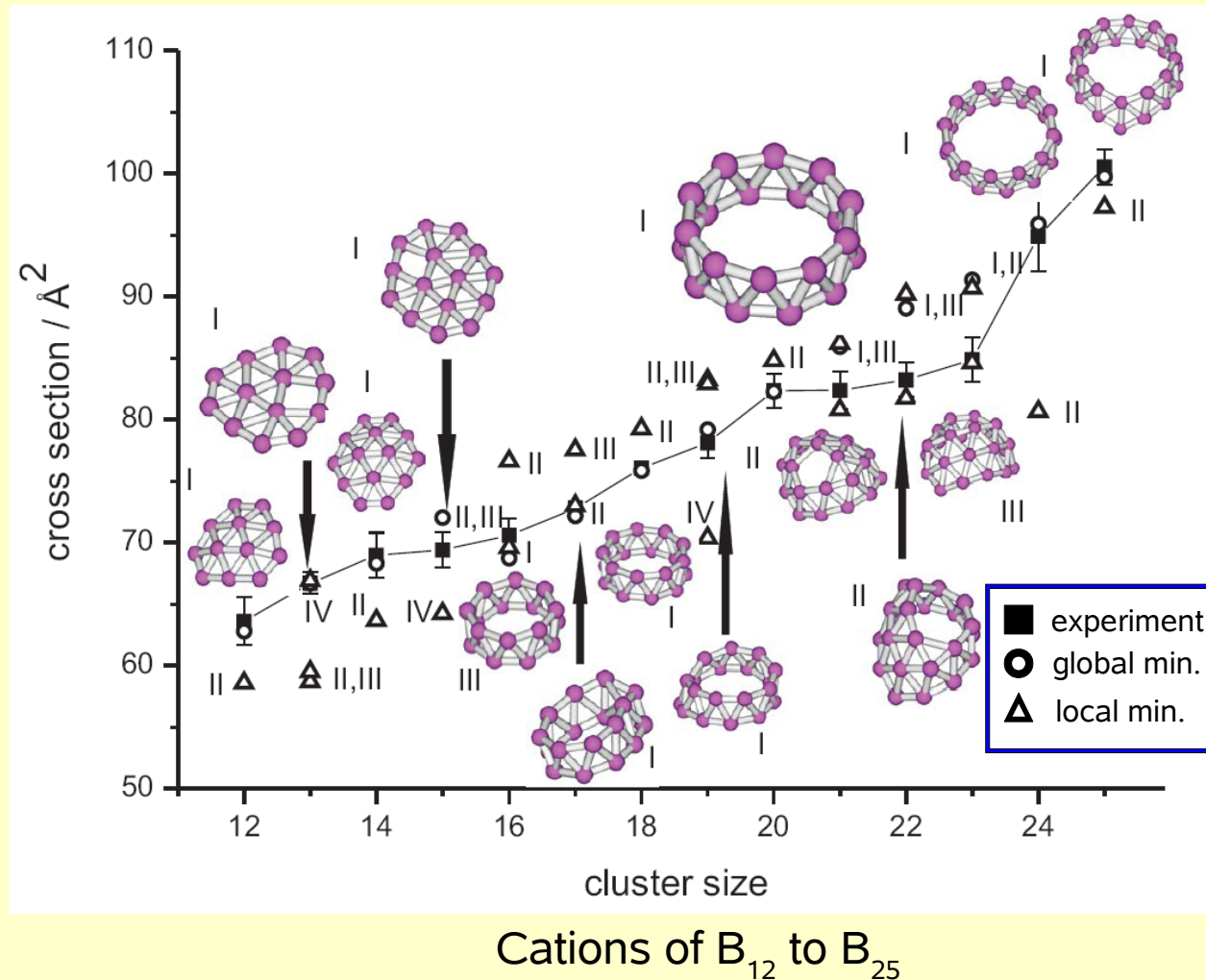
- Energies
 - Of isomers, reaction intermediates, excited states
- Molecular structures
- Molecule behavior over time (MD)
- Reactivity
- Spectroscopic properties
 - Vibrational (IR, Raman), electronic (UV-Vis, PES), Magnetic (NMR, EPR), etc.
- Molecule need not exist!

Why Model?

- Experiment may give unambiguous results, but may leave *how?* and *why?* unclear
 - Nature of reaction intermediates
 - Importance of environmental effects
- Experiment has several possible interpretations
 - Simulate possible explanations and choose best
- Predict exp. results – avoid problem areas
- Real experiment too dangerous, or impossible to do on Earth

Theory and Experiment

- Laser vaporization of boron
 - Exp. gives mass and cross section
 - Theory gives geometry and energy
- Need both to remove ambiguity

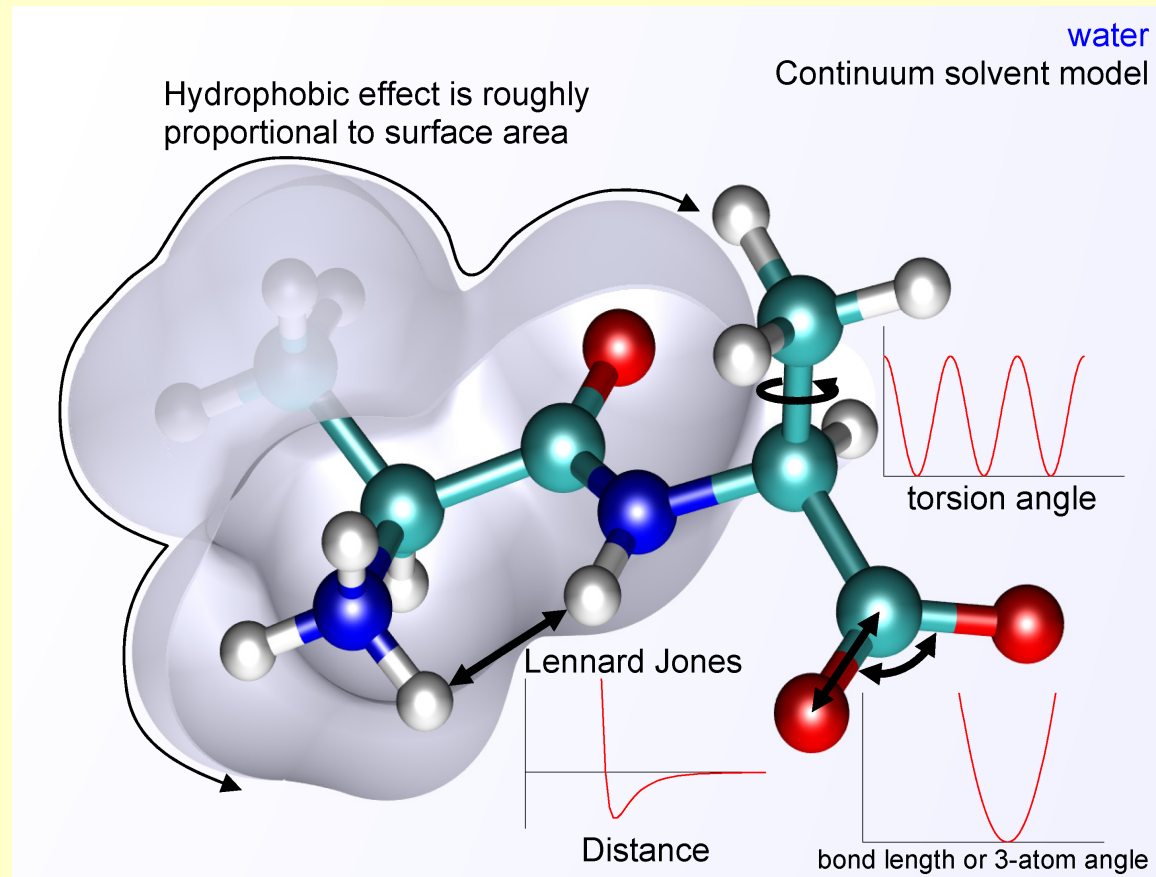


Molecular Mechanics

- Simple model
 - Uses atoms and point charges, no electrons
 - Newtonian (Classical) mechanics
 - Computationally cheap
- Atoms separated into types
 - Types based on connectivity, oxidation state, etc.
 - Model parameters taken from experiment & theory
- Can give excellent results
 - If carefully applied to molecules similar to those that parameters taken from

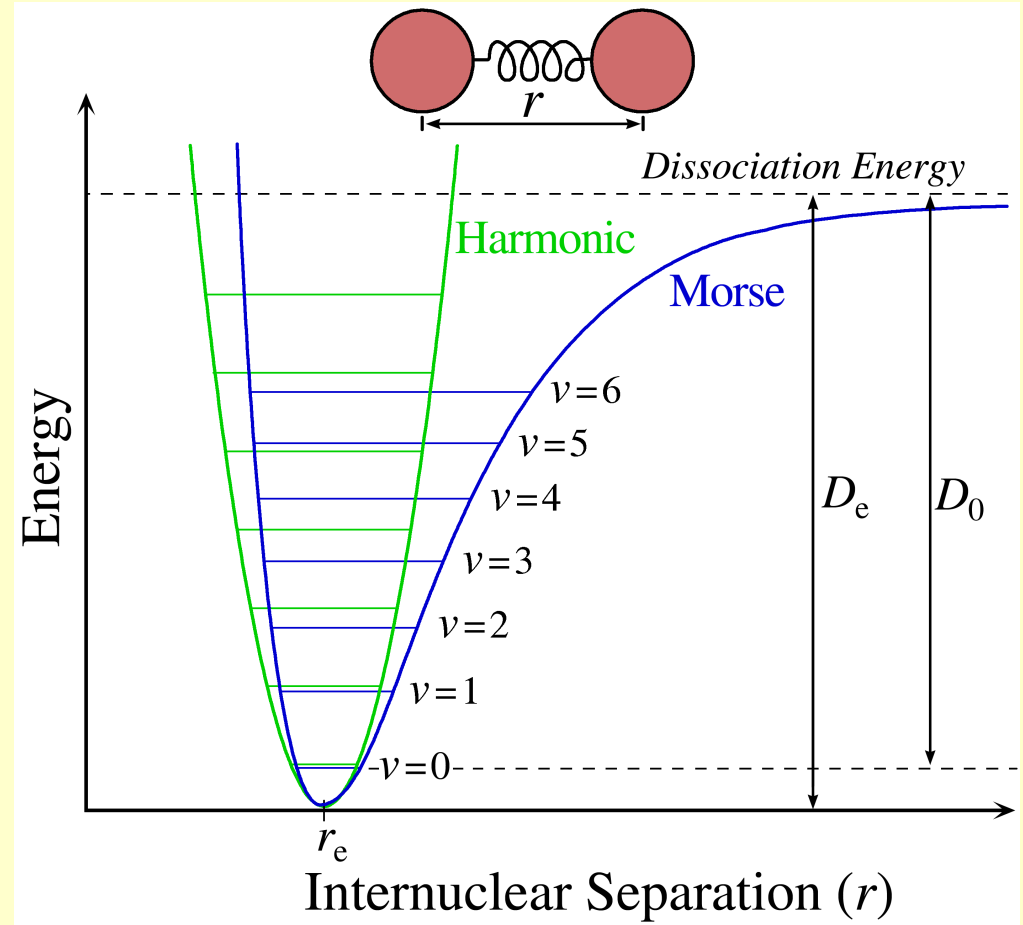
Force Field Energy

- MM potential energy model is a combination of easily computed analytical functions
- With n atom types, need many params.
 - Bonds: n^2
 - Angles: n^3
 - Torsions: $3n^4/2$
- Most force fields make do with thousands rather than millions



Bond Lengths and Angles

- Bonds stretch in a Morse-like potential
- Harmonic oscillator is much simpler (faster)
- Bond angles treated similarly
- Good approx. near equilibrium geometry
- Fails at extremes

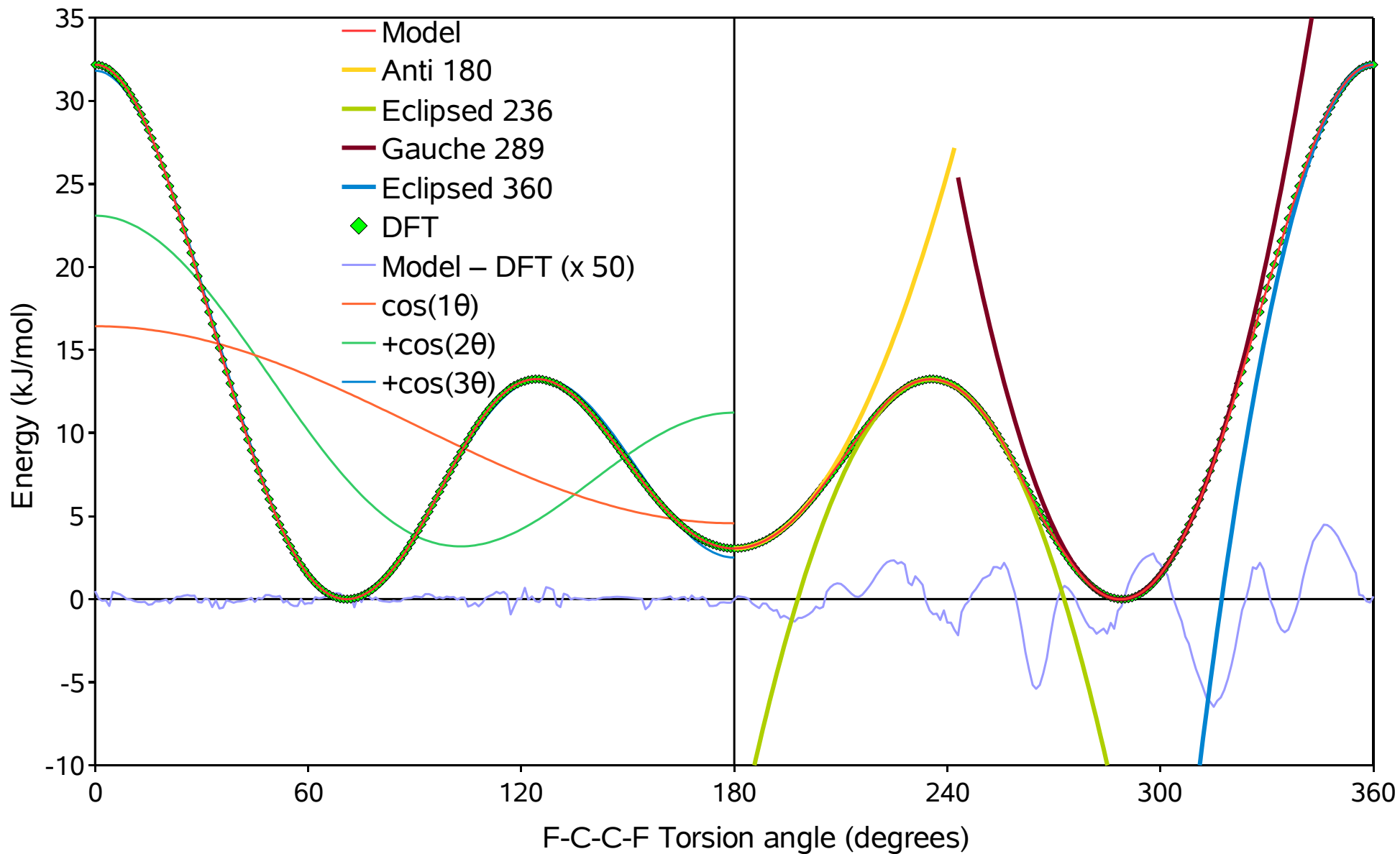


Morse and harmonic oscillator potentials for a diatomic molecule

Author: Mark Somoza (Wikipedia)

Torsional Interactions

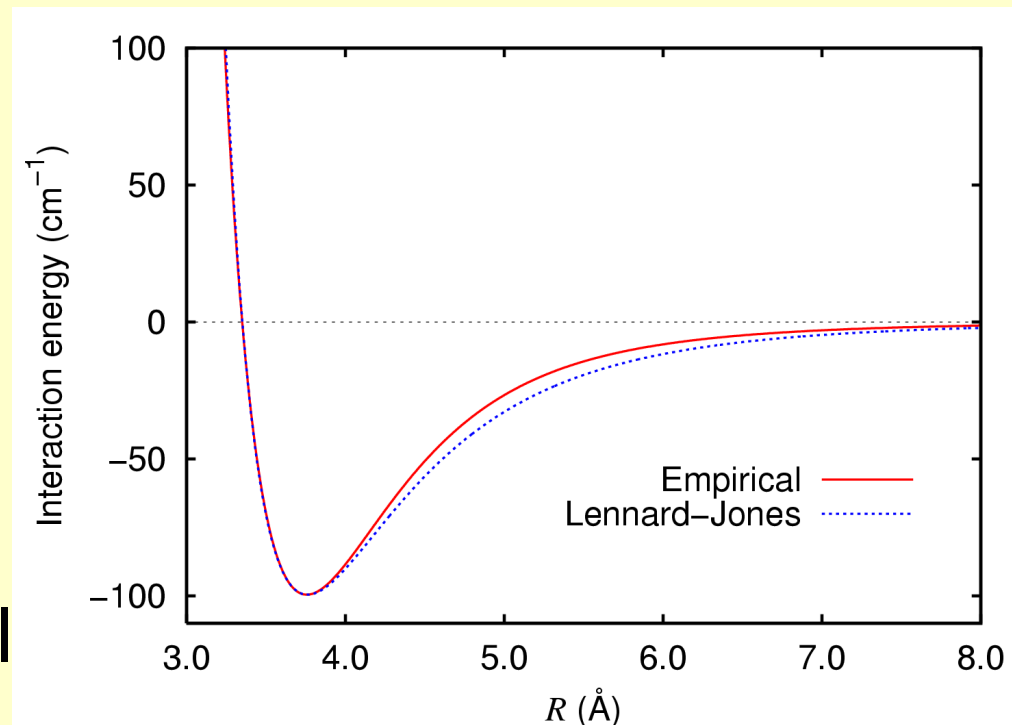
Torsion about C-C in 1,2-difluoroethane



Non-bonded Interactions

- Coulombic forces $V(r_{AB}) = \frac{q_A q_B}{r_{AB}}$
 - Partial charges assigned by atom type
- Van der Waals / Pauli
 - static and dynamic multipole – multipole interactions
 - electron spin
 - Lennard-Jones potential

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$



Ar-Ar potential

Author: Poszwa (Wikipedia)

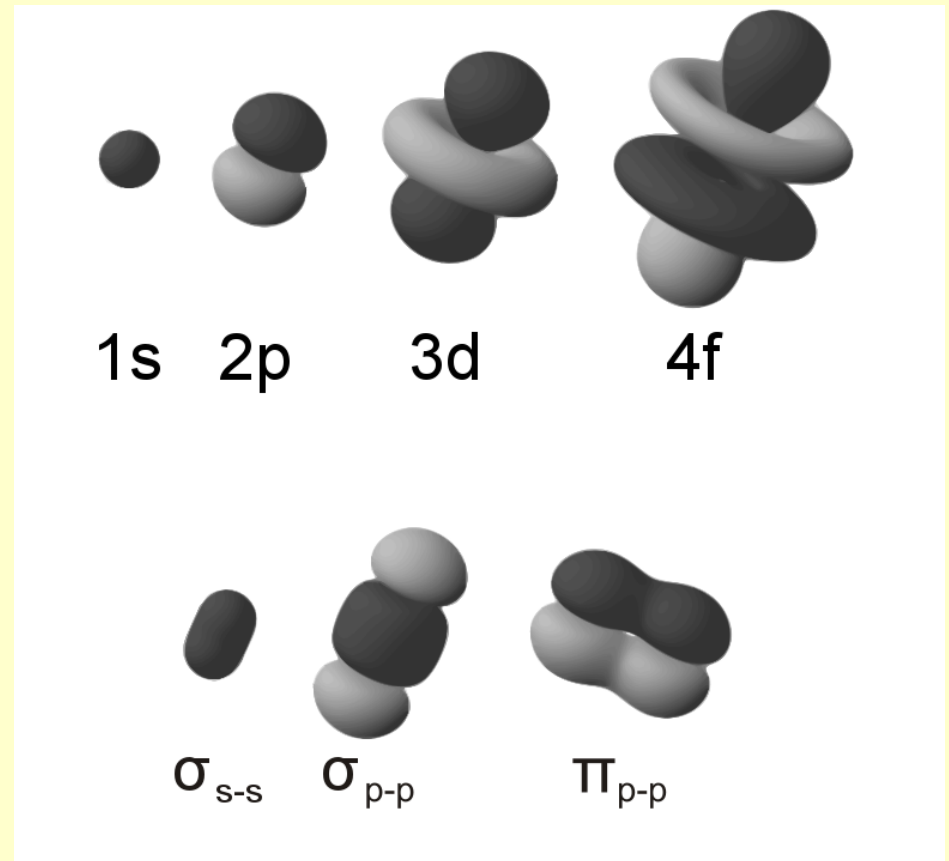
Modeling Quantum Mechanics

$$E \Psi(x) = \hat{H} \Psi(x) = -\frac{\hbar^2}{2m} \nabla^2 \Psi(x) + V(x) \Psi(x)$$

- Can't ignore the electrons forever
- Too small and quick (and only probably there)
- QM allows calculation from first principles (*ab initio*), avoiding need to determine empirical parameters
- Semi-empirical methods use QM framework, but substitute experimentally derived parameters for some expensive parts

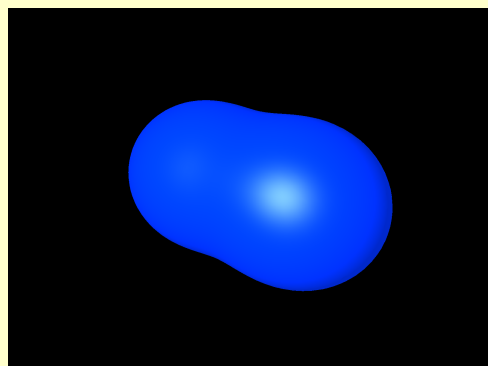
MO-LCAO

- Not possible to solve exactly with more than a single electron
- Can use hydrogenic AOs as a *basis set* to build more complex answers
- QM programs use a large number of AO-like basis functions from all atoms in molecule to create an MO

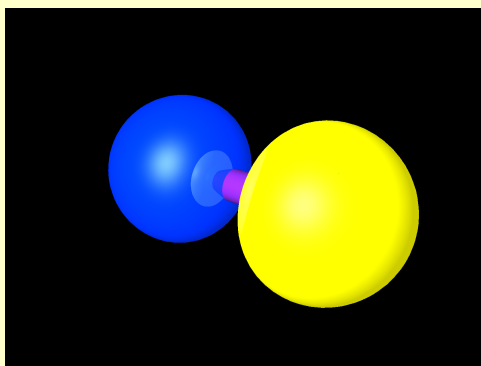


Eigenvalues and Eigenvectors

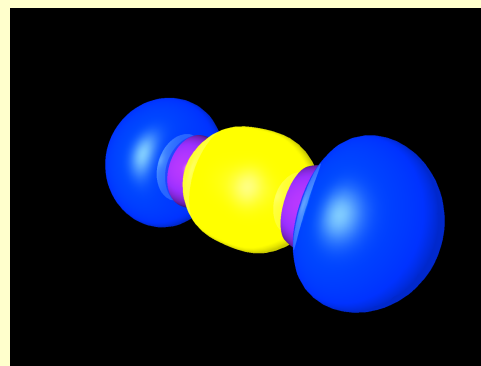
- When squared and integrated, each MO is one e^- worth of the total electron density
- They are a set of functions (eigenvectors) that are unchanged by the hamiltonian operator, except by multiplication by a corresponding energy (eigenvalue)



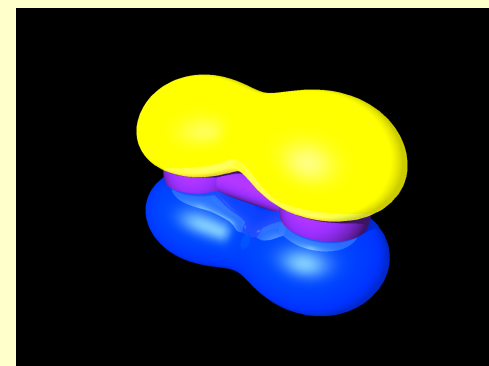
-34.268 eV



-26.064 eV



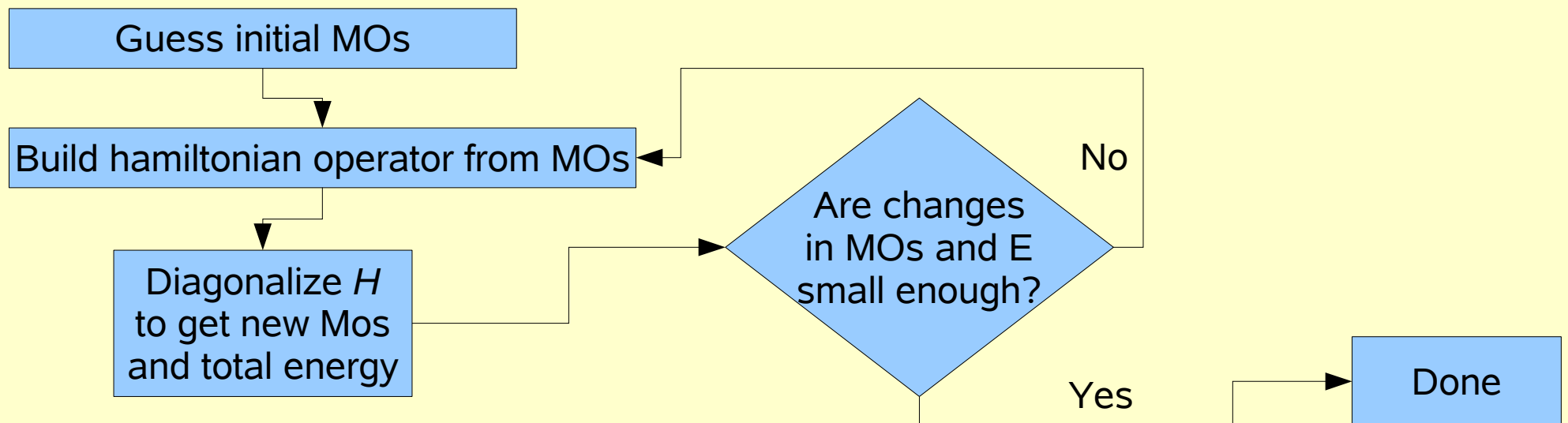
-15.221 eV



-12.594 eV

Self-Consistent Field (SCF)

- Getting A solution to the Schrödinger Eqn. relatively easy
- Finding the best, lowest energy solution is work
- The $V(x)$ part of H depends on the MOs, which depend on $H...$

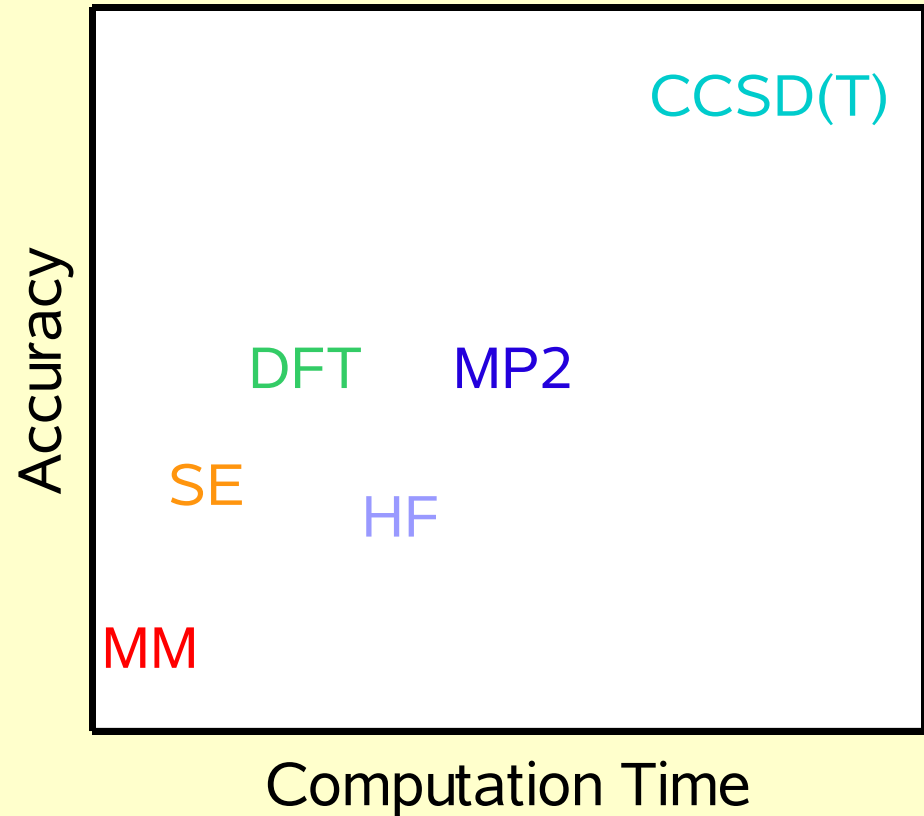


What Use is Having Ψ ?

- With the exact wavefunction, the molecular system is fully determined
- Applying mathematical operators other than H can give you properties other than the energy
- Every observable property has (in principle) a corresponding operator, although actually implementing them may be difficult

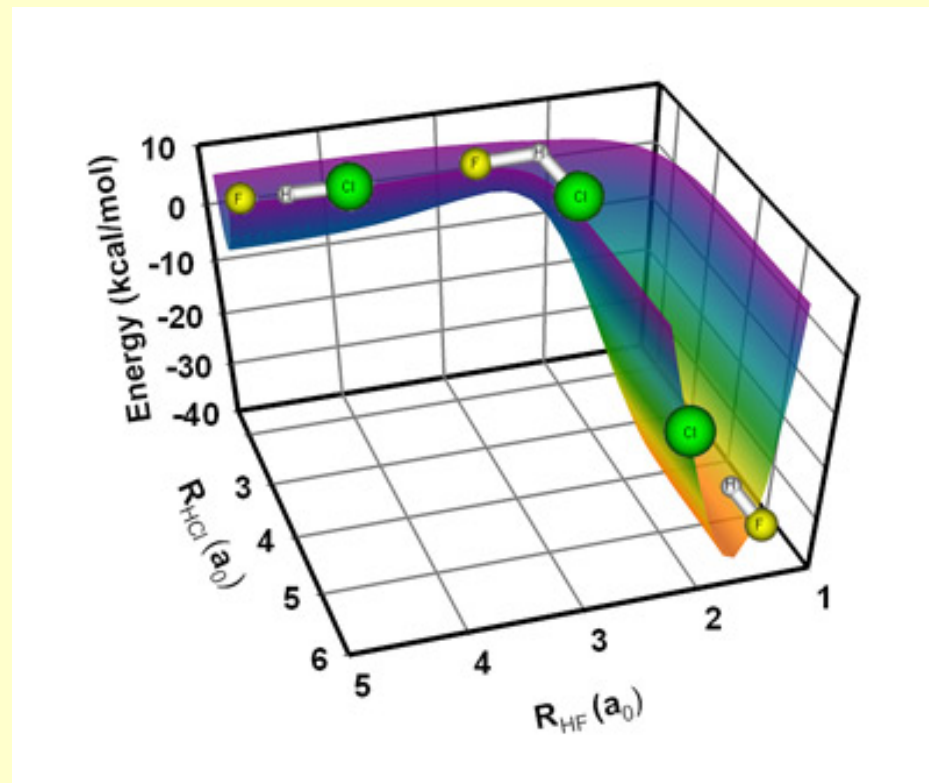
Hierarchy of Methods

- Molecular mechanics
- Semi-empirical
- HF
- DFT/MP2
- CCSD(T)



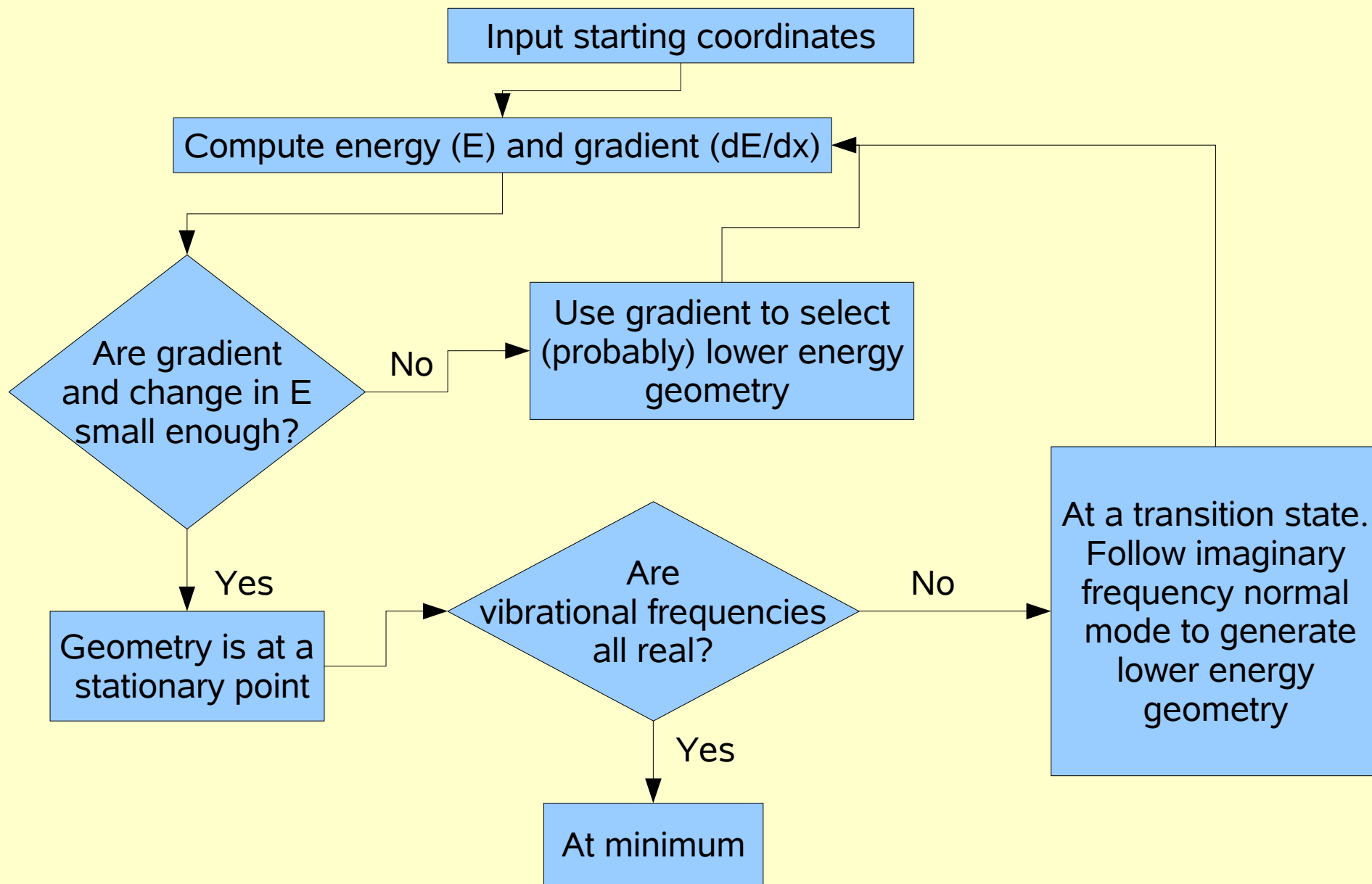
Potential Energy Surface

- Assume electrons respond instantly to nuclear motion
- Molecular energy on $3N-6$ dimension surface
- Change in energy when moving (dE/dx) called gradient – represents force on atoms



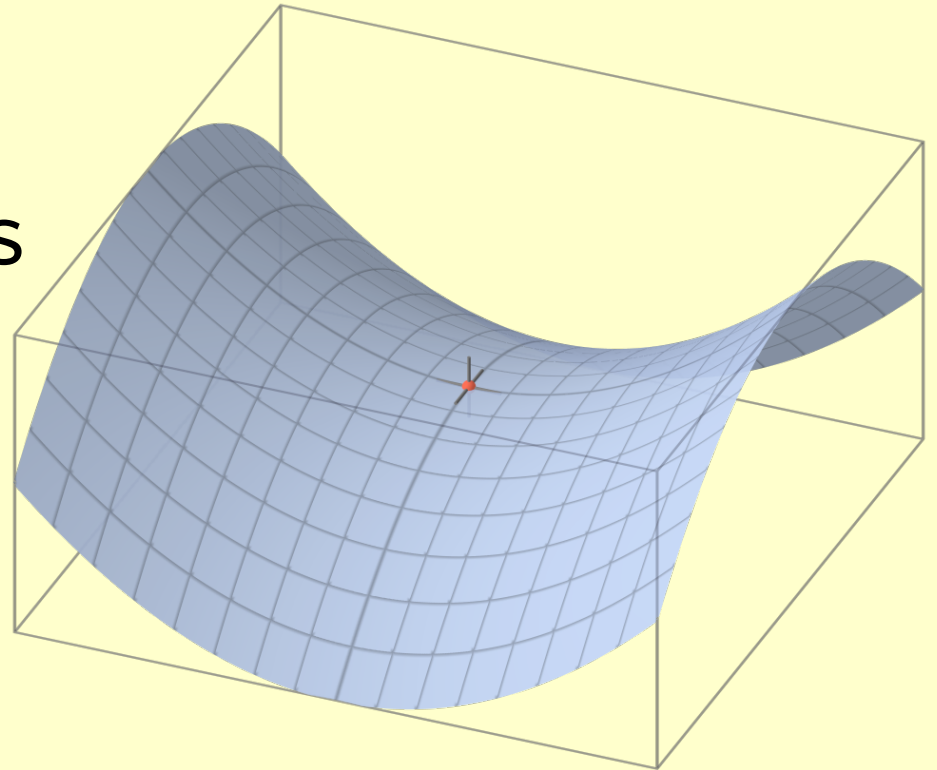
M. P. Deskevich, M. Y. Hayes, K. Takahashi, R. T. Skodje, and D. J. Nesbitt, *J. Chem. Phys.*, 124, 224303 (2006).

Geometry Optimization



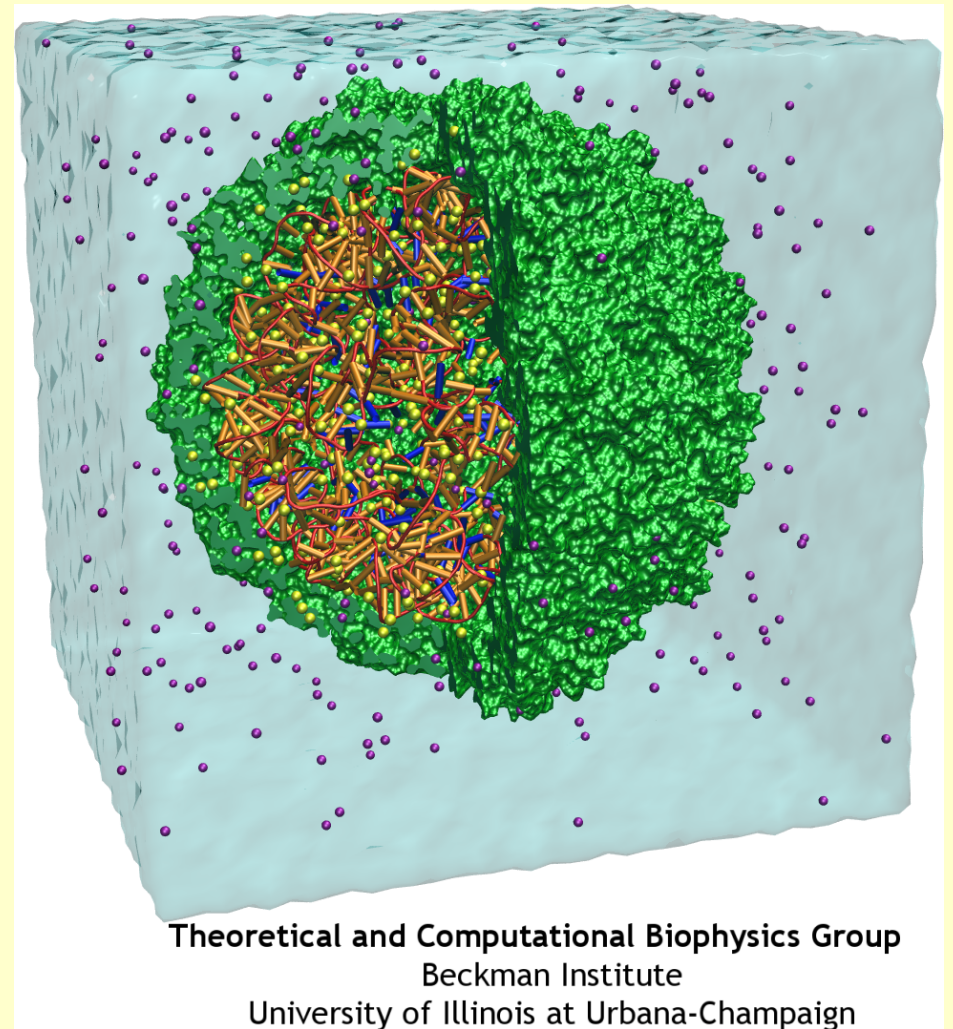
Transition States

- Lowest energy path from reactant to product passes through TS
- All motion *except* towards product or reactant increases energy
- Relative energy of TS is reaction barrier
- Find using same tools as energy minimum, but much trickier



Molecular Dynamics

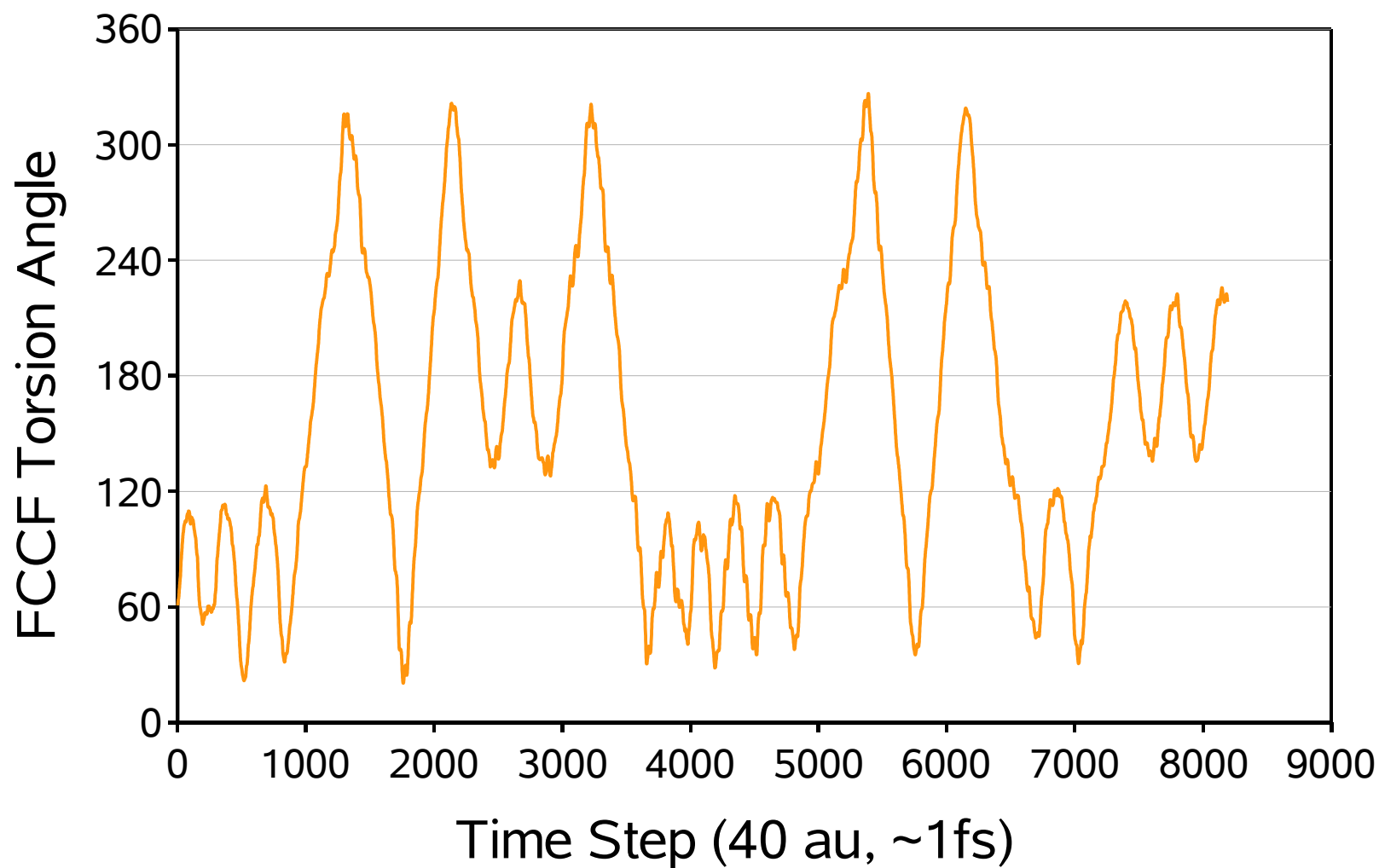
- Like geometry optimization, but with momentum
- Simulate system responding to force from PES
- With big computers and fast MM, whole (small) virus particles can be modeled



A Short MD Trajectory

1,2-difluoroethane

1000K Nosé-Hoover Thermostat



Demonstration Time