An Introduction to Quantum Chemistry and Potential Energy Surfaces

Benjamin G. Levine

This Week's Lecture

- Potential energy surfaces
  - What are they?
  - What are they good for?
  - How do we use them to solve chemical problems?

What do quantum chemists do?

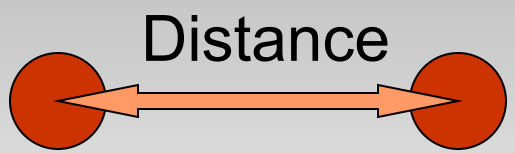
- Approximate the electronic structures of molecules
- Extract useful chemical information from them

Potential energy surface (PES) defined

- The PES, $E(R)$, is the energy of a molecule as a function of the locations of its nuclei, R.

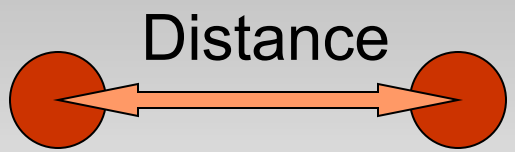
Potential energy surface (PES) defined

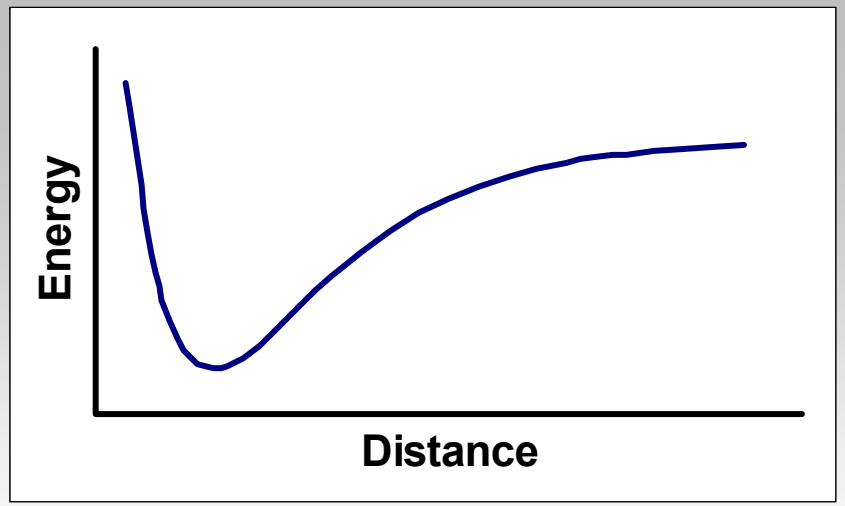
- The PES, $E(R)$, is the energy of a molecule as a function of the locations of its nuclei, R.



Potential energy surface (PES) defined

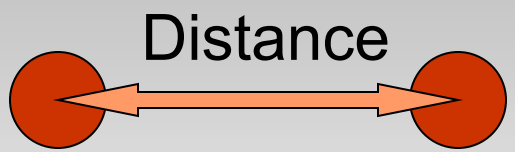
- The PES, $E(R)$, is the energy of a molecule as a function of the locations of its nuclei, R.

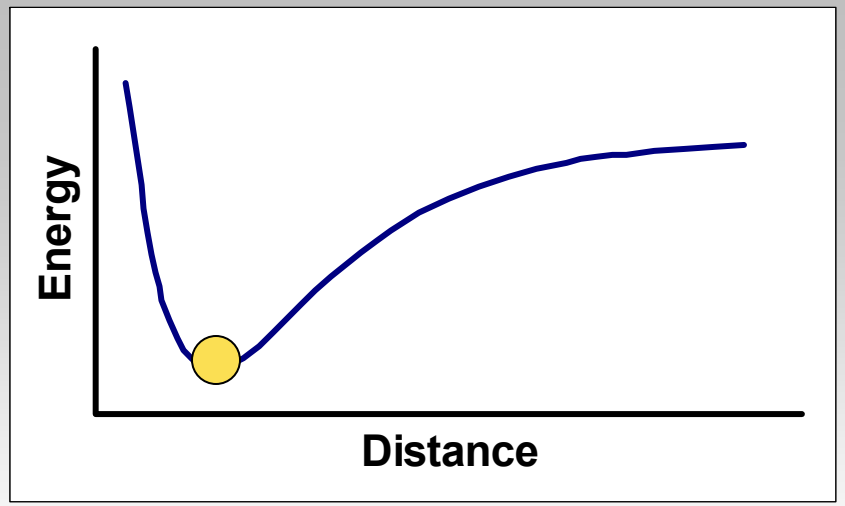




Potential energy surface (PES) defined

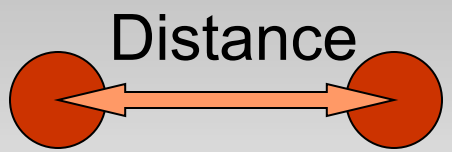
- The PES, $E(R)$, is the energy of a molecule as a function of the locations of its nuclei, R.

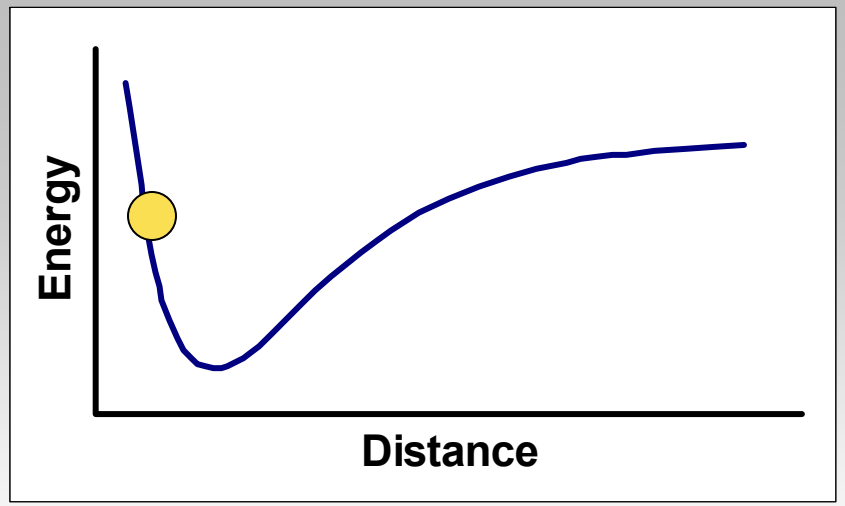




Potential energy surface (PES) defined

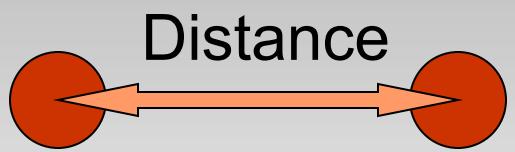
- The PES, $E(R)$, is the energy of a molecule as a function of the locations of its nuclei, R.

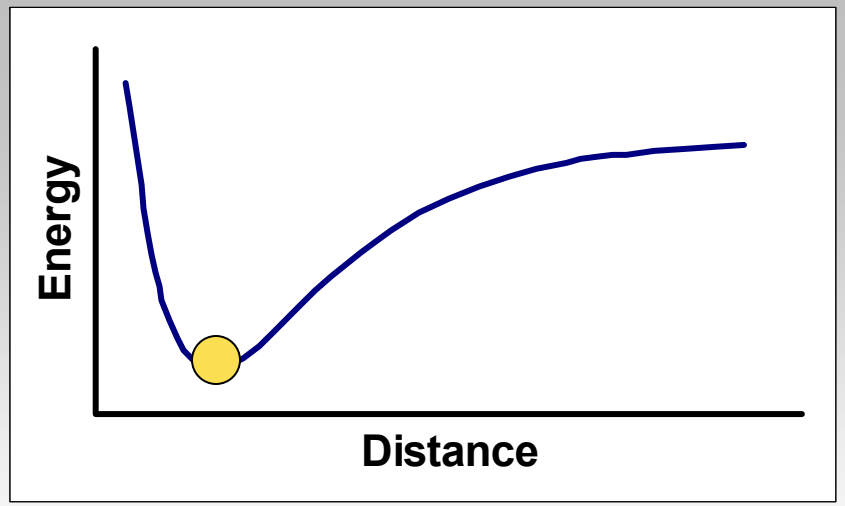




Potential energy surface (PES) defined

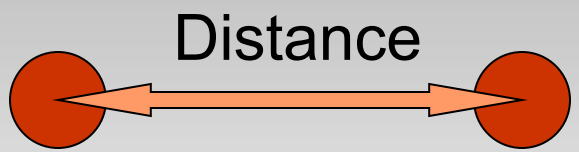
- The PES, $E(R)$, is the energy of a molecule as a function of the locations of its nuclei, R.

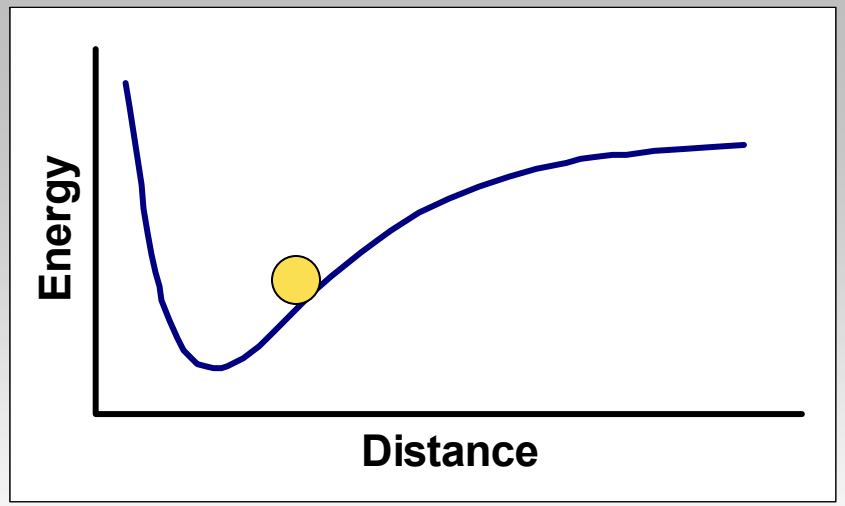




Potential energy surface (PES) defined

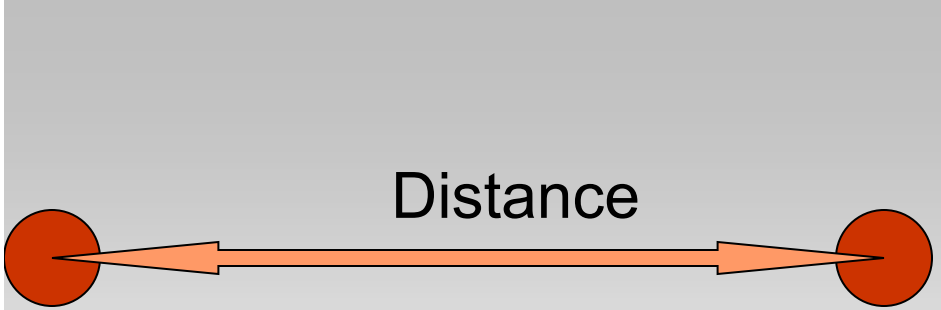
- The PES, $E(R)$, is the energy of a molecule as a function of the locations of its nuclei, R.

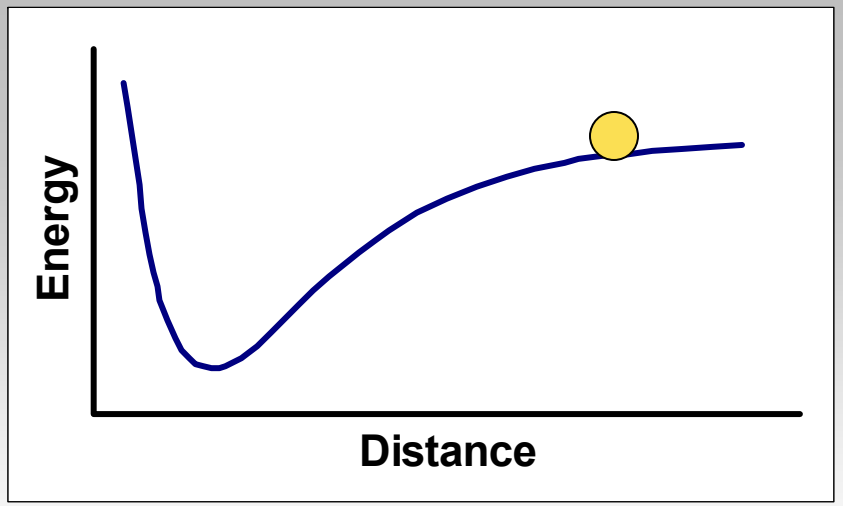




Potential energy surface (PES) defined

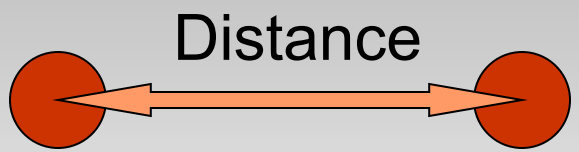
- The PES, $E(R)$, is the energy of a molecule as a function of the locations of its nuclei, R.

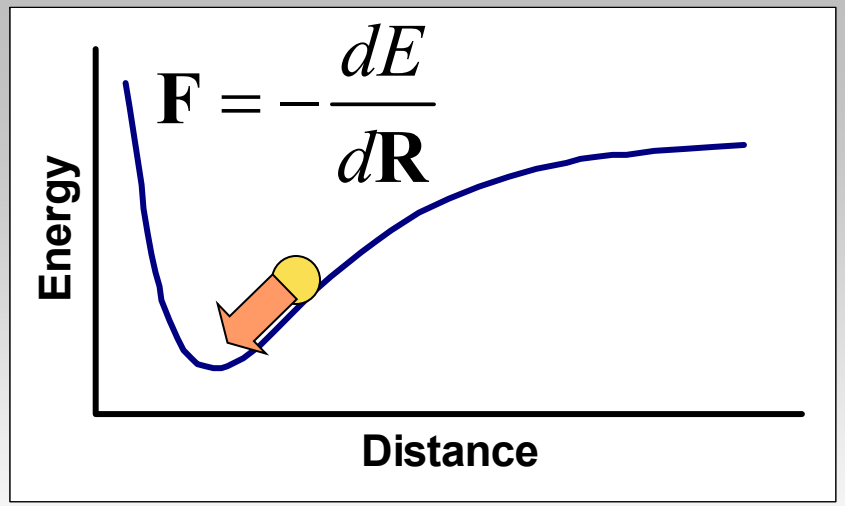




Potential energy surface (PES) defined

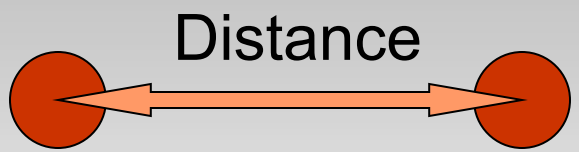
- The PES, $E(R)$, is the energy of a molecule as a function of the locations of its nuclei, R.

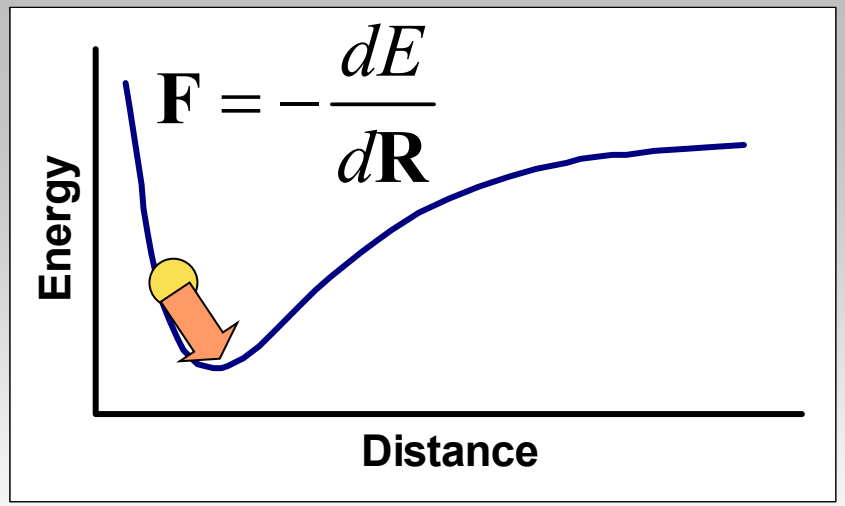




Potential energy surface (PES) defined

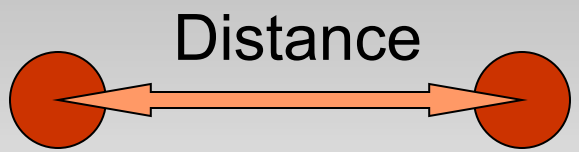
- The PES, $E(R)$, is the energy of a molecule as a function of the locations of its nuclei, R.

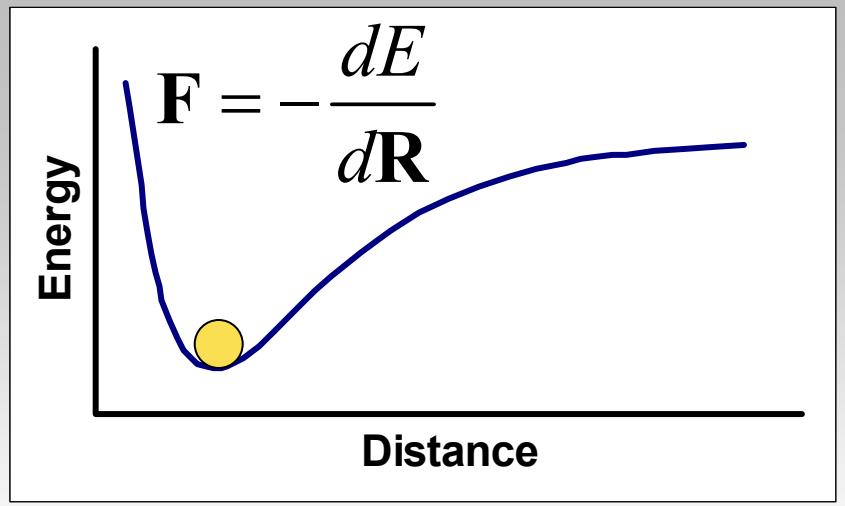




Potential energy surface (PES) defined

- The PES, $E(R)$, is the energy of a molecule as a function of the locations of its nuclei, R.





Using the PES

- Many important chemical question can be rephrased in terms of the PES
- We rarely calculate the whole PES, but instead explore and describe it in a variety of ways
- The PES can be calculated in many ways which vary in
  - Accuracy
  - Computational cost
  - The portions of the PES which they are capable of describing

The PES is approximate

The PES idea comes from the approximate solution of the full molecular time-independent Schrodinger equation

$$\hat{H}\Psi(\mathbf{R},\mathbf{r}) = E\Psi(\mathbf{R},\mathbf{r})$$

The PES is approximate

The PES idea comes from the approximate solution of the full molecular time-independent Schrodinger equation

$$\hat{H}\Psi(\mathbf{R},\mathbf{r}) = E\Psi(\mathbf{R},\mathbf{r})$$

Nuclear coordinates

Electronic coordinates

The PES is approximate

The molecular Hamiltonian is

$$\hat{H} = -\sum_I \tfrac{1}{2m_I} \nabla_I^2(\mathbf{R}) - \tfrac{1}{2}\sum_i \nabla_i^2(\mathbf{r}) + \sum_I \sum_J \frac{q_I q_J}{r_{IJ}} - \sum_I \sum_i \frac{q_I}{r_{Ij}} + \sum_i \sum_j \frac{1}{r_{ij}}$$

The PES is approximate

The molecular Hamiltonian is

$$\hat{H} = -\sum_I \frac{1}{2m_I} \nabla_I^2(\mathbf{R}) - \frac{1}{2}\sum_i \nabla_i^2(\mathbf{r}) + \sum_I \sum_J \frac{q_I q_J}{r_{IJ}} - \sum_I \sum_i \frac{q_I}{r_{Ij}} + \sum_i \sum_j \frac{1}{r_{ij}}$$

I and *J* index nuclei

i and *j* index electrons

The PES is approximate

The molecular Hamiltonian is

$$\hat{H} = -\sum_I \frac{1}{2m_I} \nabla_I^2(\mathbf{R}) - \frac{1}{2}\sum_i \nabla_i^2(\mathbf{r}) + \sum_I \sum_J \frac{q_I q_J}{r_{IJ}} - \sum_I \sum_i \frac{q_I}{r_{Ij}} + \sum_i \sum_j \frac{1}{r_{ij}}$$

m is represents mass

r represents distance

q represents charge

The PES is approximate

The molecular Hamiltonian is

$$\hat{H} = -\sum_I \frac{1}{2m_I} \nabla_I^2(\mathbf{R}) - \frac{1}{2}\sum_i \nabla_i^2(\mathbf{r}) + \sum_I \sum_J \frac{q_I q_J}{r_{IJ}} - \sum_I \sum_i \frac{q_I}{r_{Ij}} + \sum_i \sum_j \frac{1}{r_{ij}}$$

Nuclear Kinetic Energy

Electronic Kinetic Energy

The PES is approximate

The molecular Hamiltonian is

$$\hat{H} = -\sum_I \frac{1}{2m_I} \nabla_I^2(\mathbf{R}) - \frac{1}{2}\sum_i \nabla_i^2(\mathbf{r}) + \sum_I \sum_J \frac{q_I q_J}{r_{IJ}} - \sum_I \sum_i \frac{q_I}{r_{Ij}} + \sum_i \sum_j \frac{1}{r_{ij}}$$

Nuclear Kinetic Energy

Electronic Kinetic Energy

Nuclear Repulsion

Electron-Nuclear Attraction

Electron-Electron Repulsion

The PES is approximate

The molecular Hamiltonian is

$$\hat{H} = -\sum_I \tfrac{1}{2m_I} \nabla_I^2(\mathbf{R}) - \tfrac{1}{2}\sum_i \nabla_i^2(\mathbf{r}) + \sum_I \sum_J \frac{q_I q_J}{r_{IJ}} - \sum_I \sum_i \frac{q_I}{r_{Ij}} + \sum_i \sum_j \frac{1}{r_{ij}}$$

Atomic Units

$$\hbar = 1$$

$$e = 1$$

$$m_e = 1$$

$$1/(4\pi\varepsilon_0) = 1$$

The PES is approximate

Separate the nuclear and electronic problems (Born-Oppenheimer Approx.)

$$\Psi(\mathbf{R},\mathbf{r}) = \chi(\mathbf{R})\psi(\mathbf{r};\mathbf{R})$$

Nuclear Wavefunction

Electronic Wavefunction (which depends parametrically on the nuclear coordinates)

The PES is approximate

Separate the nuclear and electronic problems (Born-Oppenheimer Approx.)

$$\Psi(\mathbf{R},\mathbf{r}) = \chi(\mathbf{R})\psi(\mathbf{r};\mathbf{R})$$

The PES is approximate

Separate the nuclear and electronic problems (Born-Oppenheimer Approx.)

$$\Psi(\mathbf{R},\mathbf{r}) = \chi(\mathbf{R})\psi(\mathbf{r};\mathbf{R})$$

$$\hat{H}_{elec}\psi(\mathbf{r};\mathbf{R}) = V(\mathbf{R})\psi(\mathbf{r};\mathbf{R})$$

$$\hat{H}_{elec} = -\tfrac{1}{2}\sum_i \nabla_i^{\,2}(\mathbf{r}) + \sum_I\sum_J \frac{q_I q_J}{r_{IJ}} - \sum_I\sum_j \frac{q_I}{r_{Ij}} + \sum_i\sum_j \frac{1}{r_{ij}}$$

The PES is approximate

Separate the nuclear and electronic problems (Born-Oppenheimer Approx.)

$$\Psi(\mathbf{R},\mathbf{r}) = \chi(\mathbf{R})\psi(\mathbf{r};\mathbf{R})$$

$$\hat{H}_{elec}\psi(\mathbf{r};\mathbf{R}) = V(\mathbf{R})\psi(\mathbf{r};\mathbf{R})$$

$$\hat{H}_{elec} = -\tfrac{1}{2}\sum_i \nabla_i^2(\mathbf{r}) + \sum_I\sum_J \frac{q_I q_J}{r_{IJ}} - \sum_I\sum_j \frac{q_I}{r_{Ij}} + \sum_i\sum_j \frac{1}{r_{ij}}$$

$V(\mathbf{R})$ is the (adiabatic) potential energy surface

The PES is approximate

Separate the nuclear and electronic problems (Born-Oppenheimer Approx.)

$$\Psi(\mathbf{R},\mathbf{r}) = \chi(\mathbf{R})\psi(\mathbf{r};\mathbf{R})$$

$$\hat{H}_{elec}\psi(\mathbf{r};\mathbf{R}) = V(\mathbf{R})\psi(\mathbf{r};\mathbf{R})$$

$$\hat{H}_{elec} = -\tfrac{1}{2}\sum_i \nabla_i^2(\mathbf{r}) + \sum_I\sum_J \frac{q_I q_J}{r_{IJ}} - \sum_I\sum_j \frac{q_I}{r_{Ij}} + \sum_i\sum_j \frac{1}{r_{ij}}$$

$V(\mathbf{R})$ is the (adiabatic) potential energy surface

This is the electronic structure problem

The PES is approximate

Separate the nuclear and electronic problems (Born-Oppenheimer Approx.)

$$\Psi(\mathbf{R},\mathbf{r}) = \chi(\mathbf{R})\psi(\mathbf{r};\mathbf{R})$$

$$\hat{H}_{elec}\psi(\mathbf{r};\mathbf{R}) = V(\mathbf{R})\psi(\mathbf{r};\mathbf{R})$$

$$\hat{H}_{elec} = -\tfrac{1}{2}\sum_i \nabla_i^{\,2}(\mathbf{r}) + \sum_I\sum_J \frac{q_I q_J}{r_{IJ}} - \sum_I\sum_j \frac{q_I}{r_{Ij}} + \sum_i\sum_j \frac{1}{r_{ij}}$$

$$\hat{H}_{nuc}\chi(\mathbf{R}) = E\chi(\mathbf{R})$$

$$\hat{H}_{nuc} = -\sum_I \tfrac{1}{2m_I}\nabla_I^{\,2}(\mathbf{R}) + V(\mathbf{R})$$

The PES is approximate

- The Born-Oppenheimer Approximation (BOA) neglects couplings between electronic and nuclear motions
- These missing terms are called nonadiabatic or vibronic coupling terms
- The BOA is a good approximation when electronic states are not near each other in energy (ground states of stable molecules with simple electronic structures)
- Electronic states **are** near each other in energy sometimes:
  - Some transition states (nonadiabatic reaction dynamics)
  - Excited states/photochemistry
  - Jahn-Teller systems

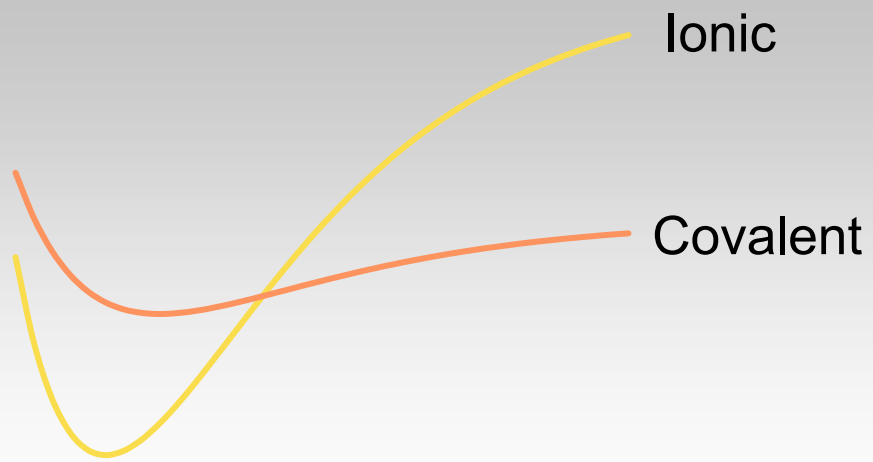
The BOA is valid for the majority of problems you see in the literature and in this course

Adiabatic vs Diabatic PES

- Adiabatic PES are the solution to the electronic Schrodinger equation
- Diabatic PES are defined according to state character (e.g. covalent vs ionic)

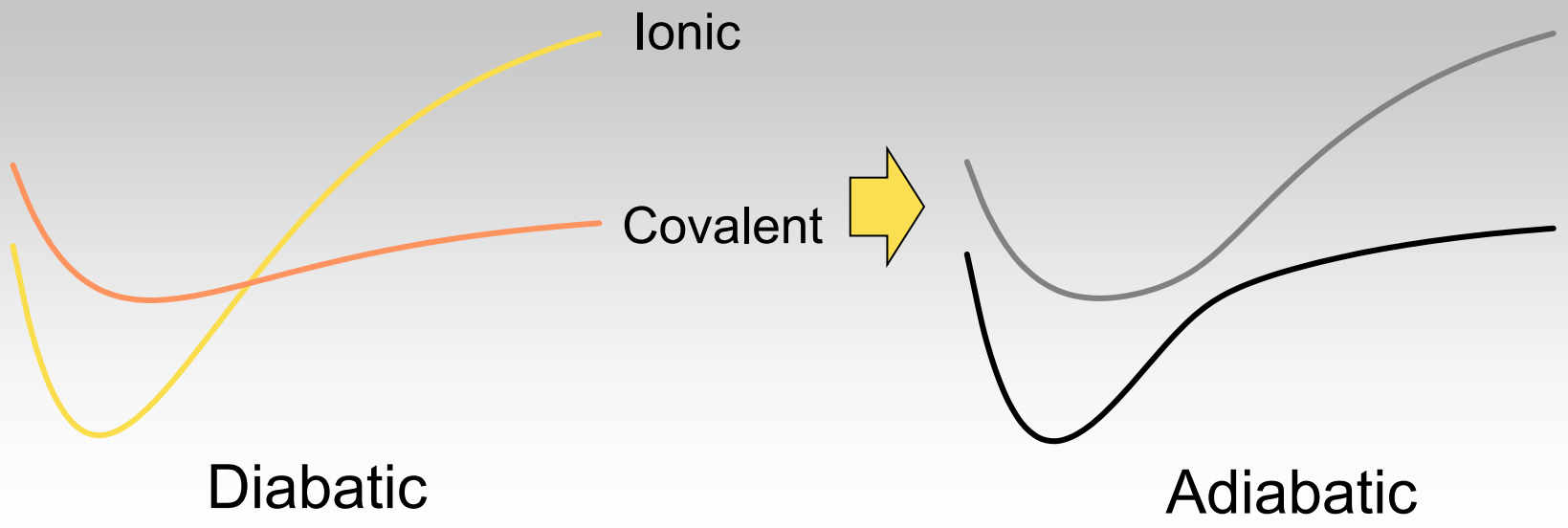
Adiabatic vs Diabatic PES

- Adiabatic PES are the solution to the electronic Schrodinger equation
- Diabatic PES are defined according to state character (e.g. covalent vs ionic)



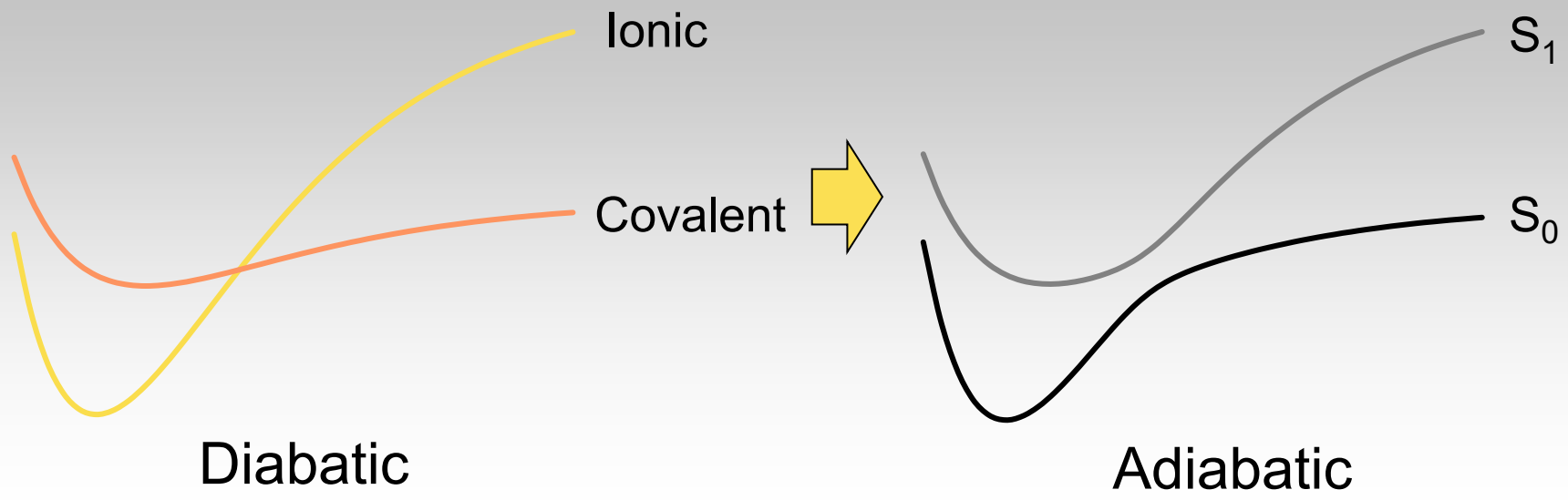
Adiabatic vs Diabatic PES

- Adiabatic PES are the solution to the electronic Schrodinger equation
- Diabatic PES are defined according to state character (e.g. covalent vs ionic)



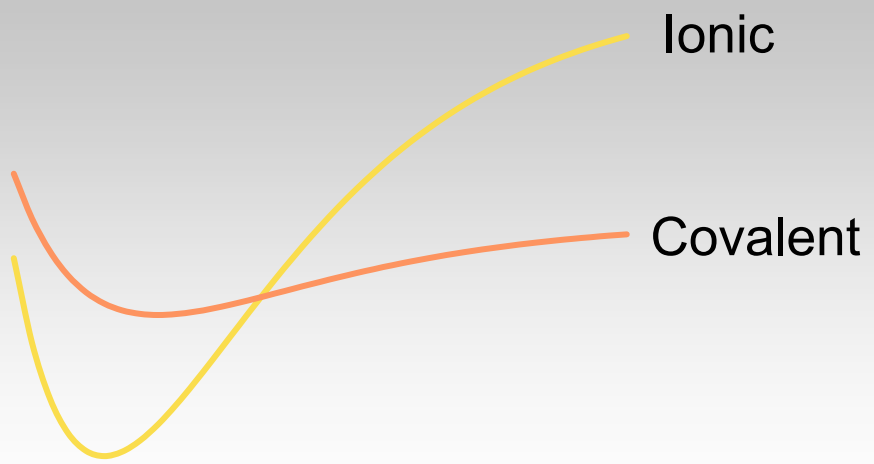
Adiabatic vs Diabatic PES

- Adiabatic PES are the solution to the electronic Schrodinger equation
- Diabatic PES are defined according to state character (e.g. covalent vs ionic)



Diabatic PES

- Diabats are conceptually convenient
- There is no unique way to define diabats
- Diabats can be very strongly coupled over a broad range of configuration space



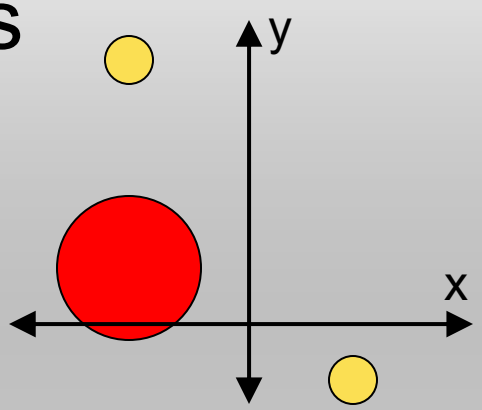
The PES is many-dimensional

- Each atom is a point in a 3-D space – the PES is 3*N* dimensional (where *N* is the number of atoms)
- The molecular geometry (configuration, structure) can be represented many ways
  - Cartesian coordinates
  - Internal Coordinates (e.g. Z-matrix)

Cartesian Coordinates

- Also known as XYZ coordinates

```
O   -0.464    0.177    0.0
H   -0.464    1.137    0.0
H    0.441   -0.143    0.0
```



- Used in various common storage formats: .xyz, .pdb

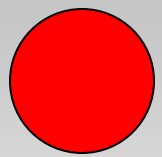
Z-Matrix Coordinates

- Define bond lengths, angles, dihedrals

Z-Matrix Coordinates

- Define bond lengths, angles, dihedrals

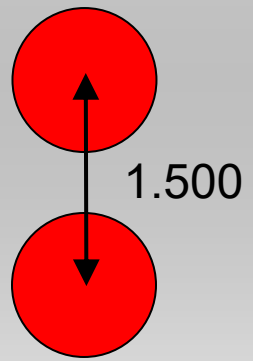
0



Z-Matrix Coordinates

- Define bond lengths, angles, dihedrals

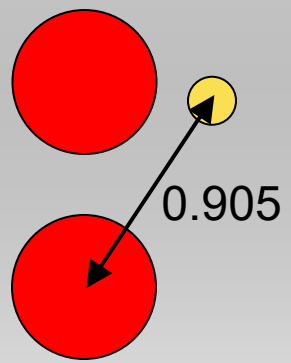
```
O
O, 1, 1.500
```



Z-Matrix Coordinates

- Define bond lengths, angles, dihedrals

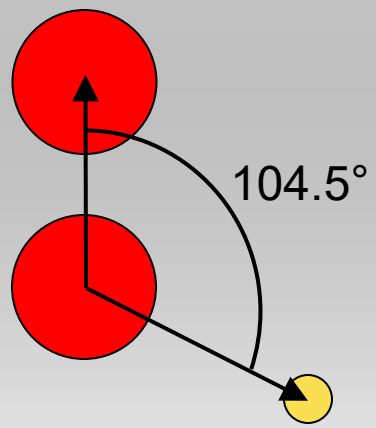
```
O
O, 1, 1.500
H, 1, 0.905
```



Z-Matrix Coordinates

- Define bond lengths, angles, dihedrals

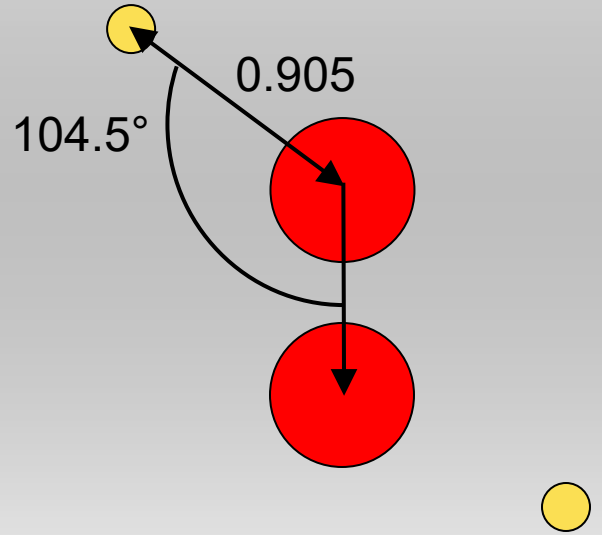
```
O
O, 1, 1.500
H, 1, 0.905, 2, 104.5
```



Z-Matrix Coordinates

- Define bond lengths, angles, dihedrals

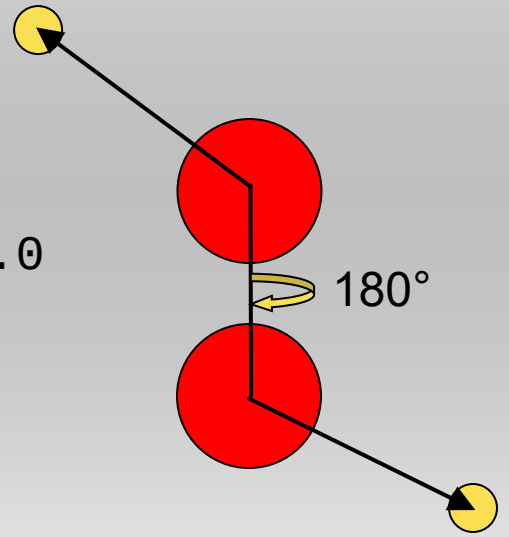
```
O
O, 1, 1.500
H, 1, 0.905, 2, 104.5
H, 2, 0.905, 1, 104.5
```



Z-Matrix Coordinates

- Define bond lengths, angles, dihedrals

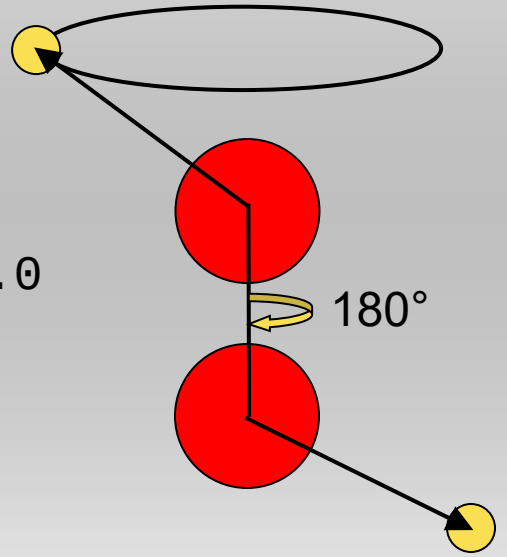
```
O
O, 1, 1.500
H, 1, 0.905, 2, 104.5
H, 2, 0.905, 1, 104.5, 3, 180.0
```



Z-Matrix Coordinates

- Define bond lengths, angles, dihedrals

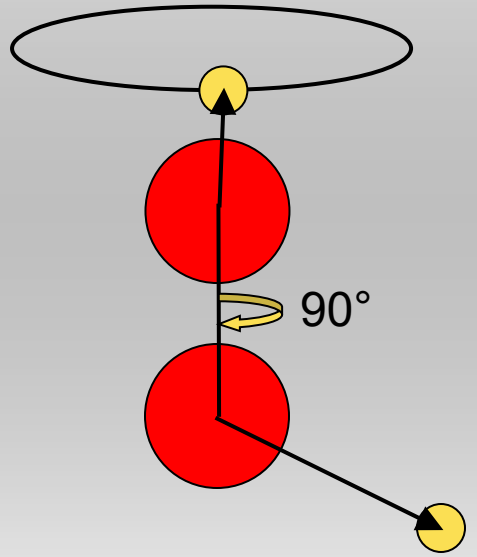
```
O
O, 1, 1.500
H, 1, 0.905, 2, 104.5
H, 2, 0.905, 1, 104.5, 3, 180.0
```



Z-Matrix Coordinates

- Define bond lengths, angles, dihedrals

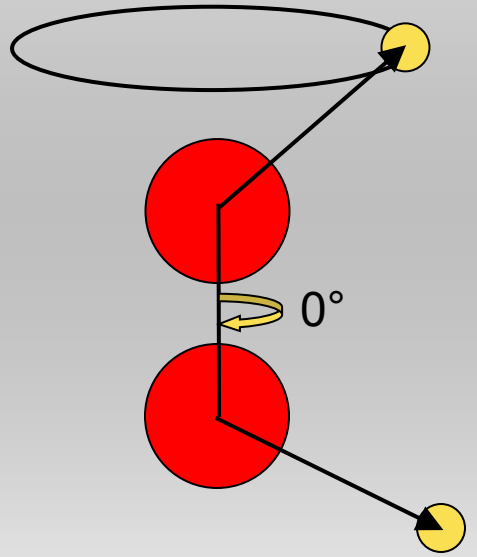
```
O
O, 1, 1.500
H, 1, 0.905, 2, 104.5
H, 2, 0.905, 1, 104.5, 3, 90.0
```



Z-Matrix Coordinates

- Define bond lengths, angles, dihedrals

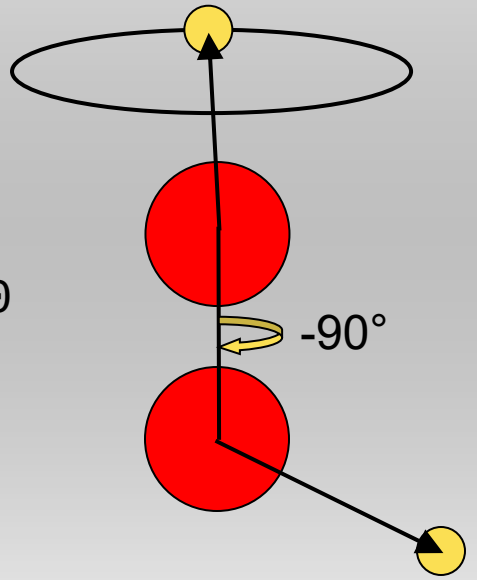
```
O
O, 1, 1.500
H, 1, 0.905, 2, 104.5
H, 2, 0.905, 1, 104.5, 3, 0.0
```



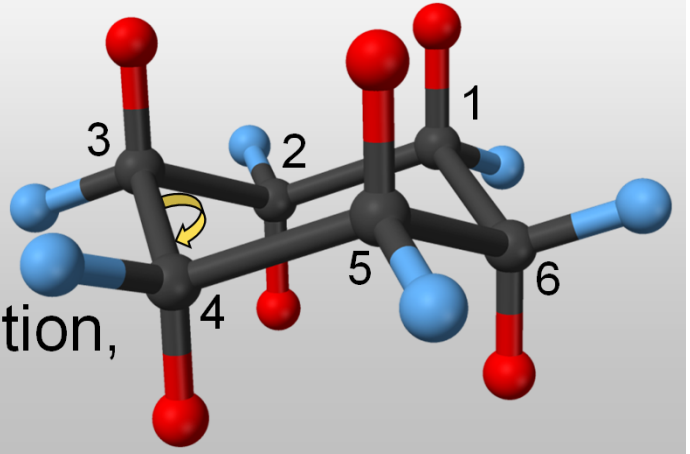
Z-Matrix Coordinates

- Define bond lengths, angles, dihedrals

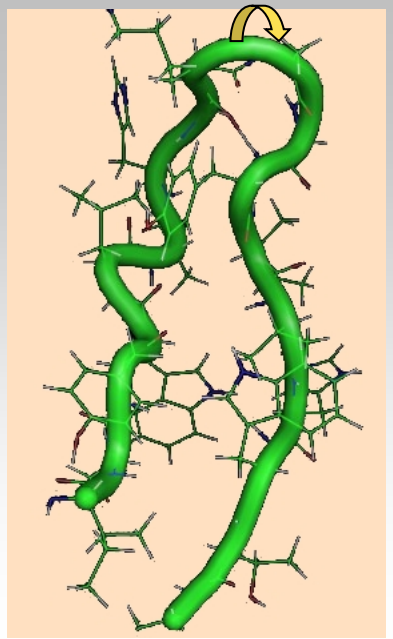
```
O
O, 1, 1.500
H, 1, 0.905, 2, 104.5
H, 2, 0.905, 1, 104.5, 3, -90.0
```



Z-Matrix Coordinates



- Advantages
  - Chemically intuitive
  - Non-redundant (eliminates translation, rotation)
- Disadvantages
  - For large or cyclic molecules the geometry can be very sensitive to small changes in the parameters
  - Equations of motion/geometry optimization are more nature in Cartesians.

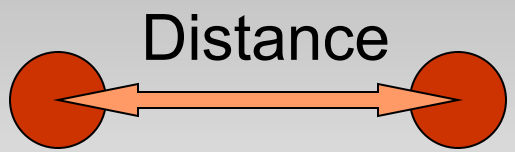


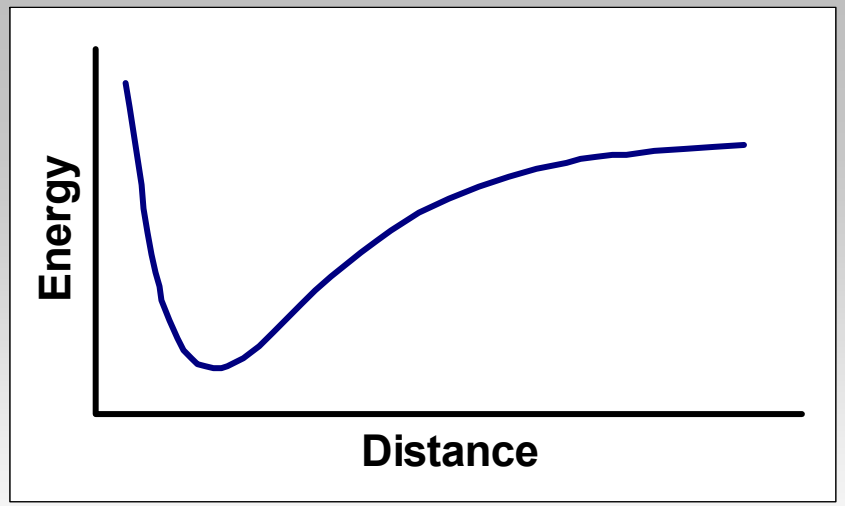
Local Minima Correspond to Stable Structures

- At reasonable temperatures molecules tend to spend most of their time at low energy points on the PES

Local Minima Correspond to Stable Structures

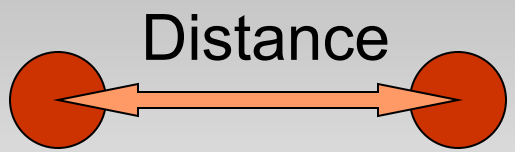
- At reasonable temperatures molecules tend to spend most of their time at low energy points on the PES

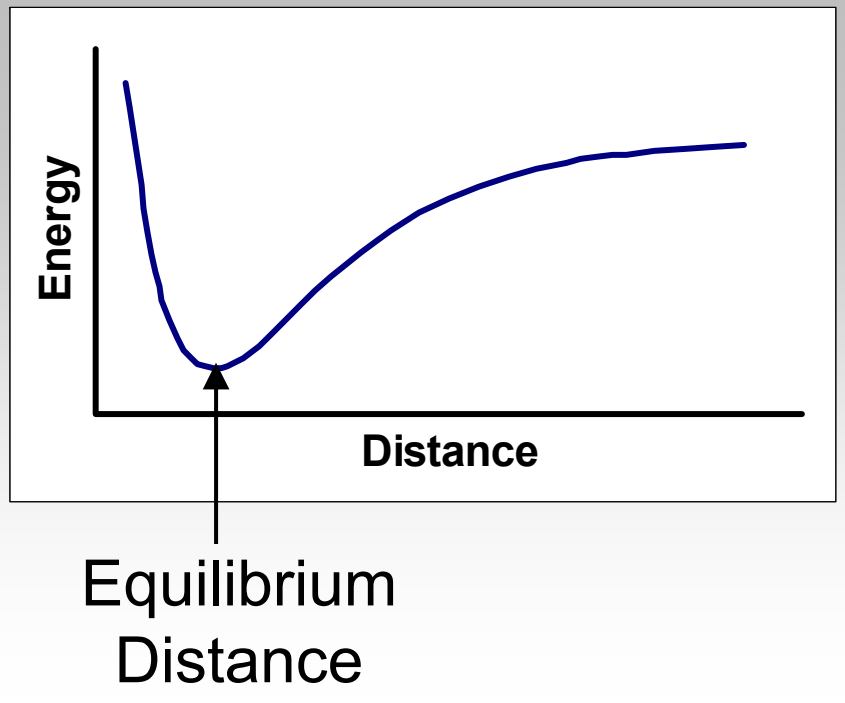




Local Minima Correspond to Stable Structures

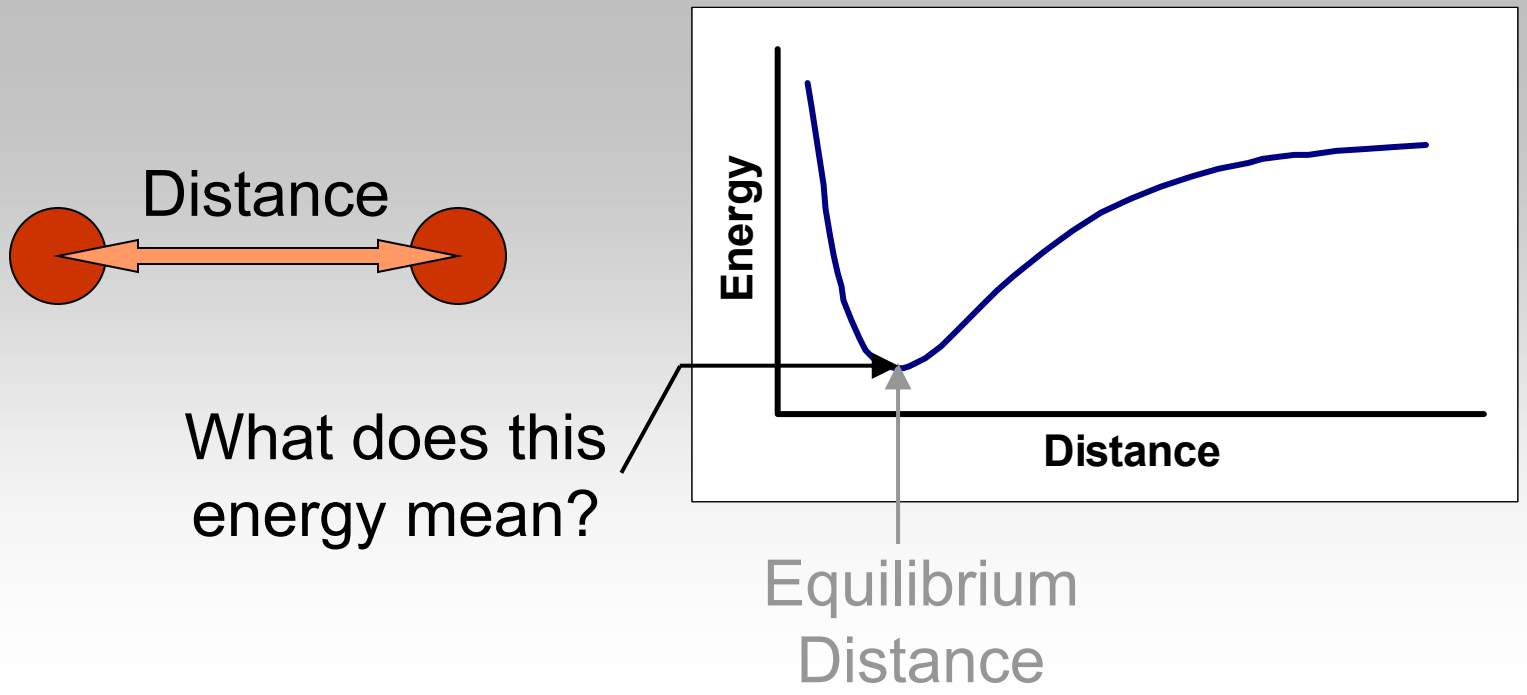
- At reasonable temperatures molecules tend to spend most of their time at low energy points on the PES





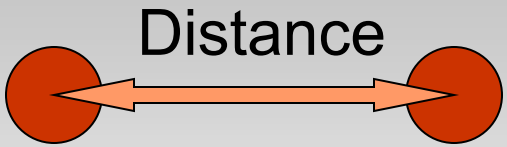
Local Minima Correspond to Stable Structures

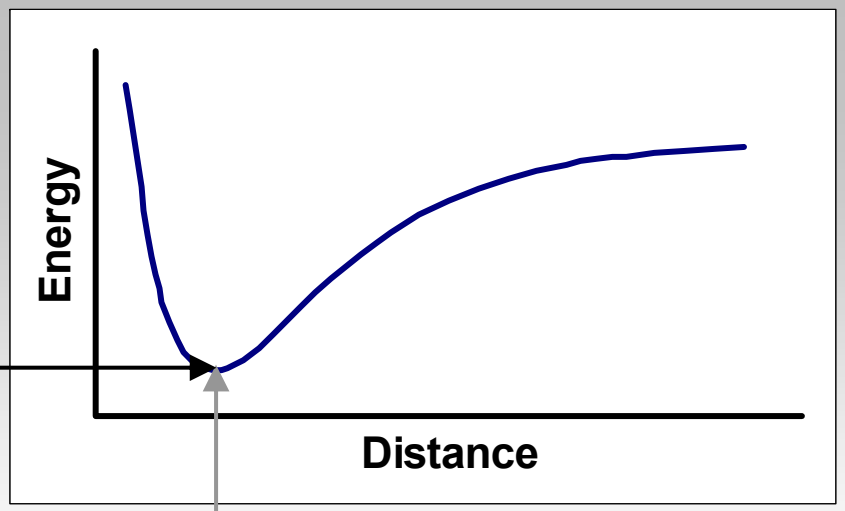
- At reasonable temperatures molecules tend to spend most of their time at low energy points on the PES



Local Minima Correspond to Stable Structures

- At reasonable temperatures molecules tend to spend most of their time at low energy points on the PES





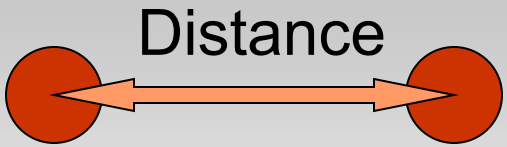
What does this energy mean?

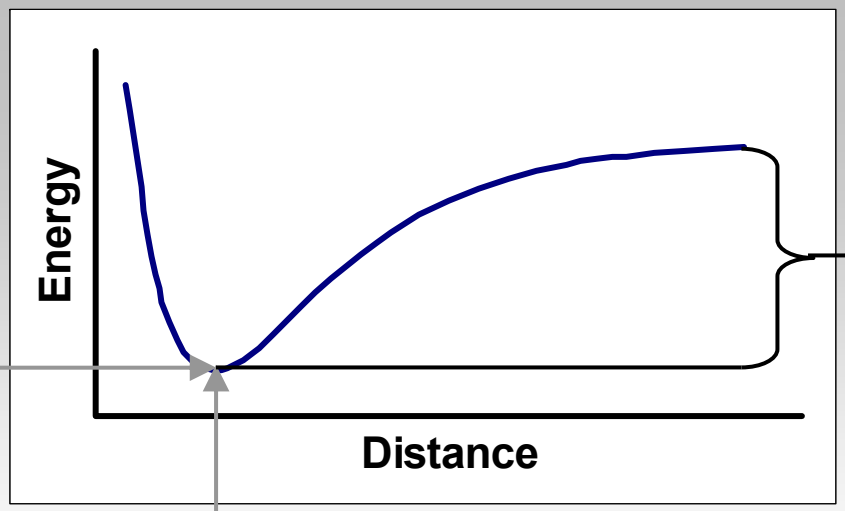
NOTHING!

Equilibrium Distance

Local Minima Correspond to Stable Structures

- At reasonable temperatures molecules tend to spend most of their time at low energy points on the PES





What does this energy mean?

NOTHING!

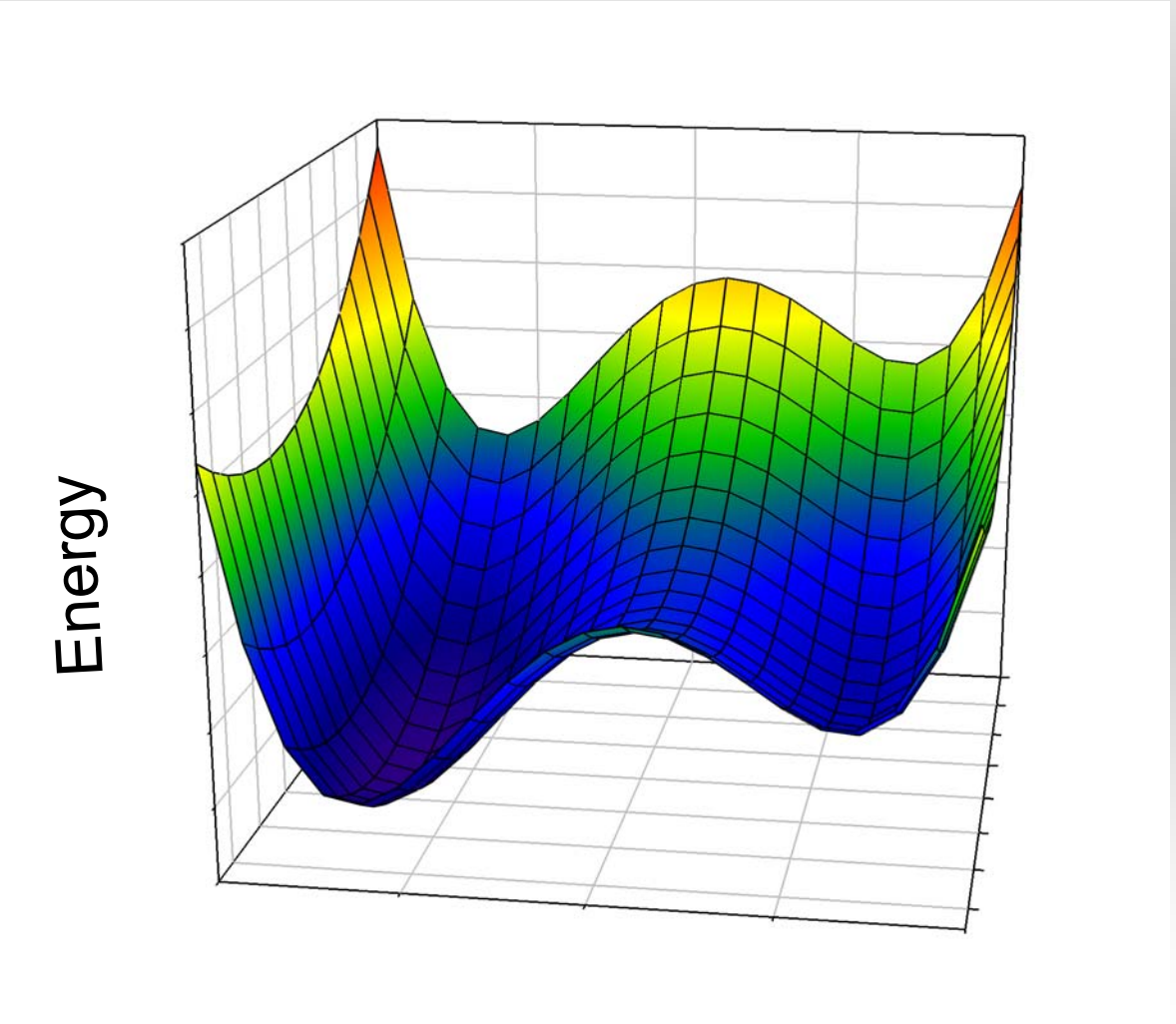
Equilibrium Distance

Dissociation Energy

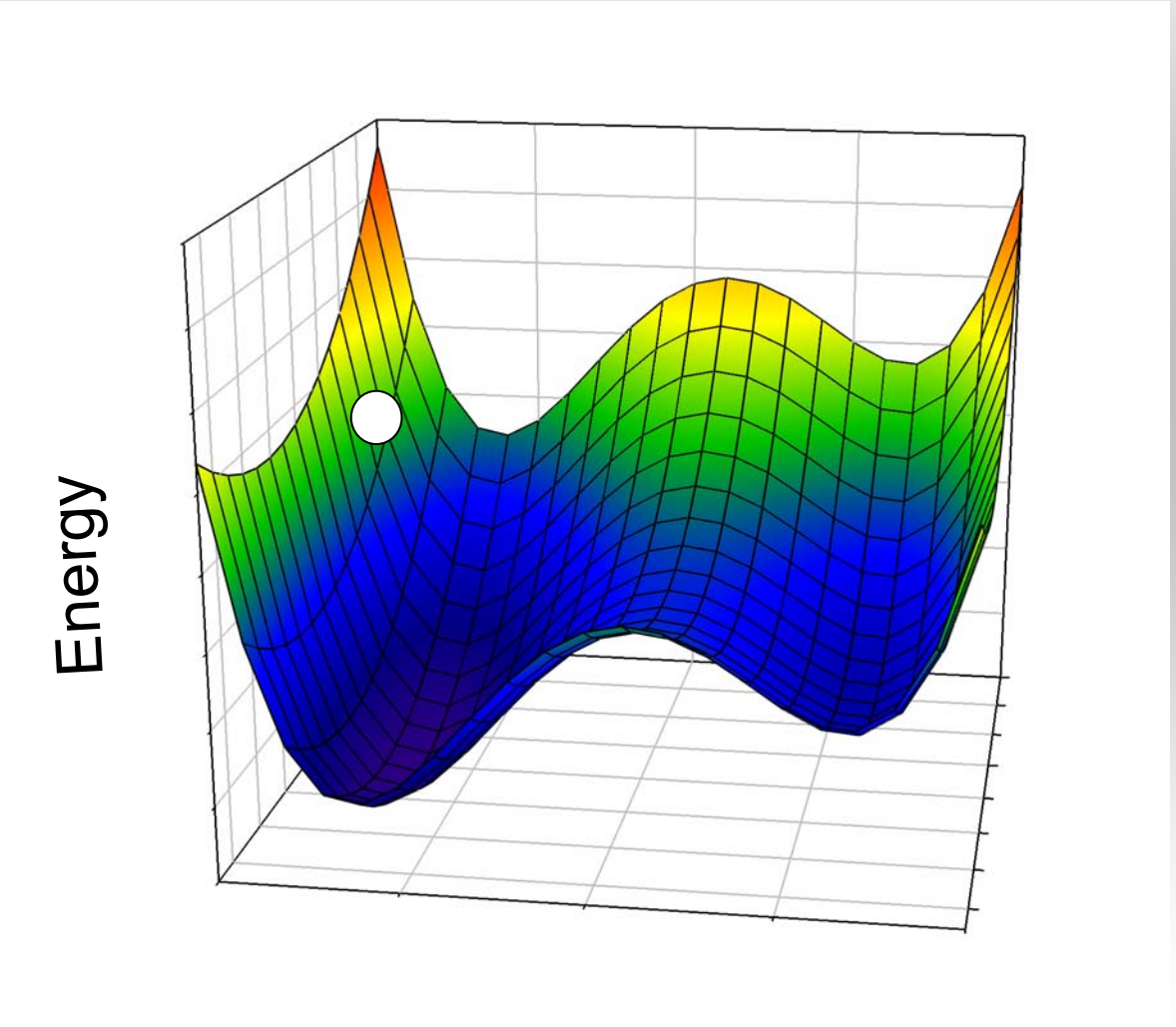
A Good Minimum is Hard to Find

- In many-dimensional systems we use geometry optimization algorithms
- Iterative process
  - Calculate gradient of the PES (AKA forces)
  - Update geometry
  - Check for convergence
  - Repeat if necessary

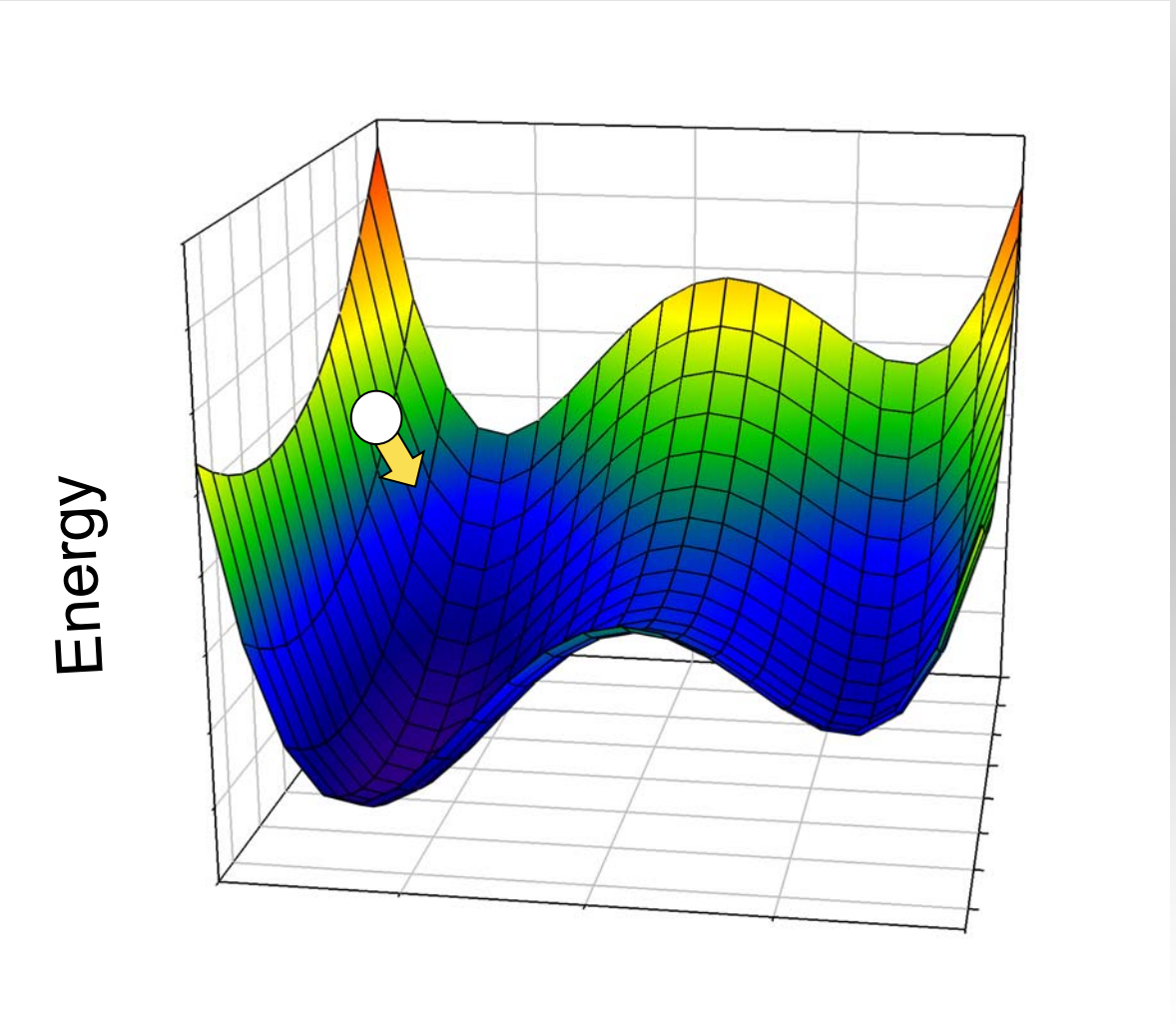
A Good Minimum is Hard to Find



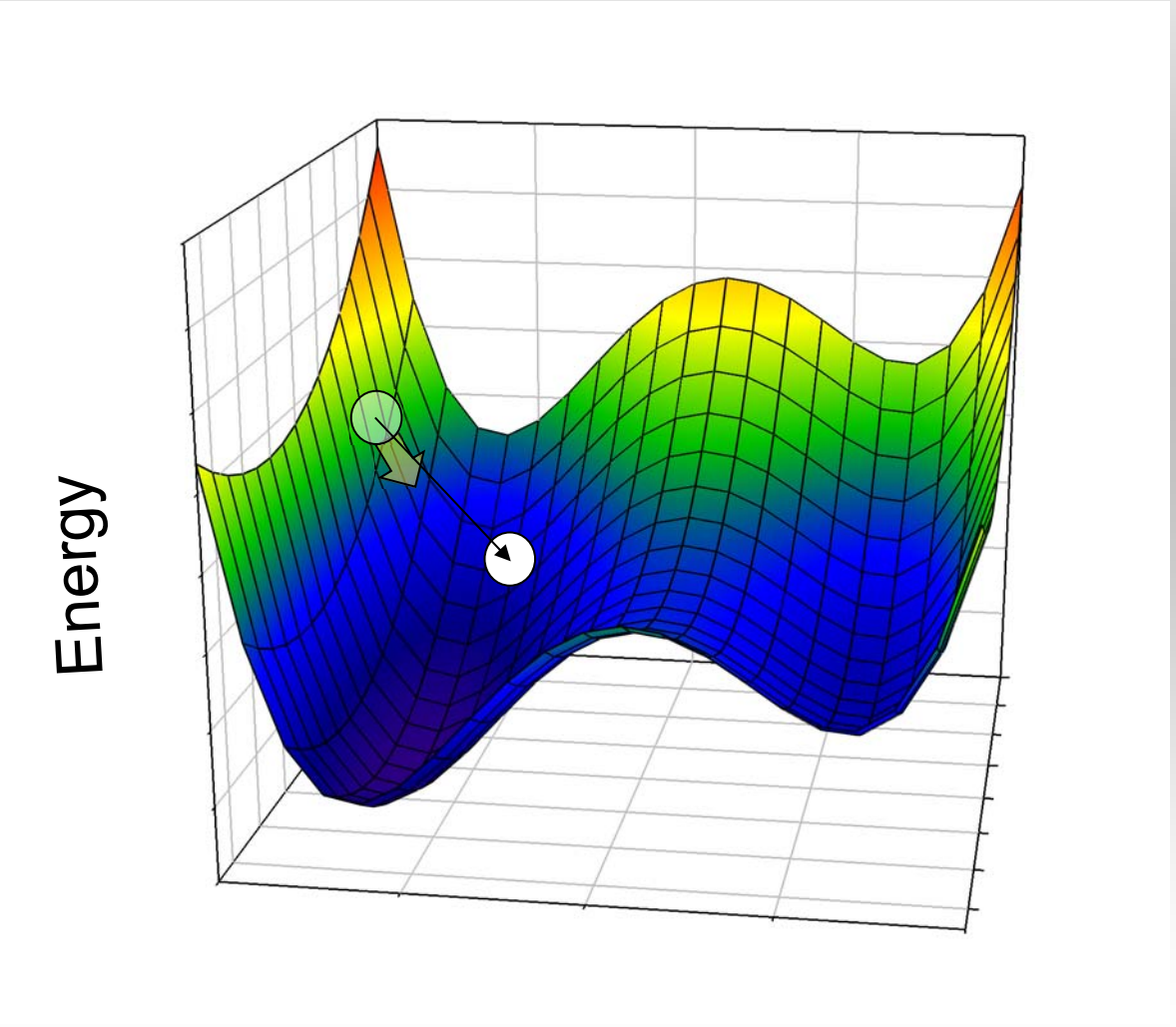
A Good Minimum is Hard to Find



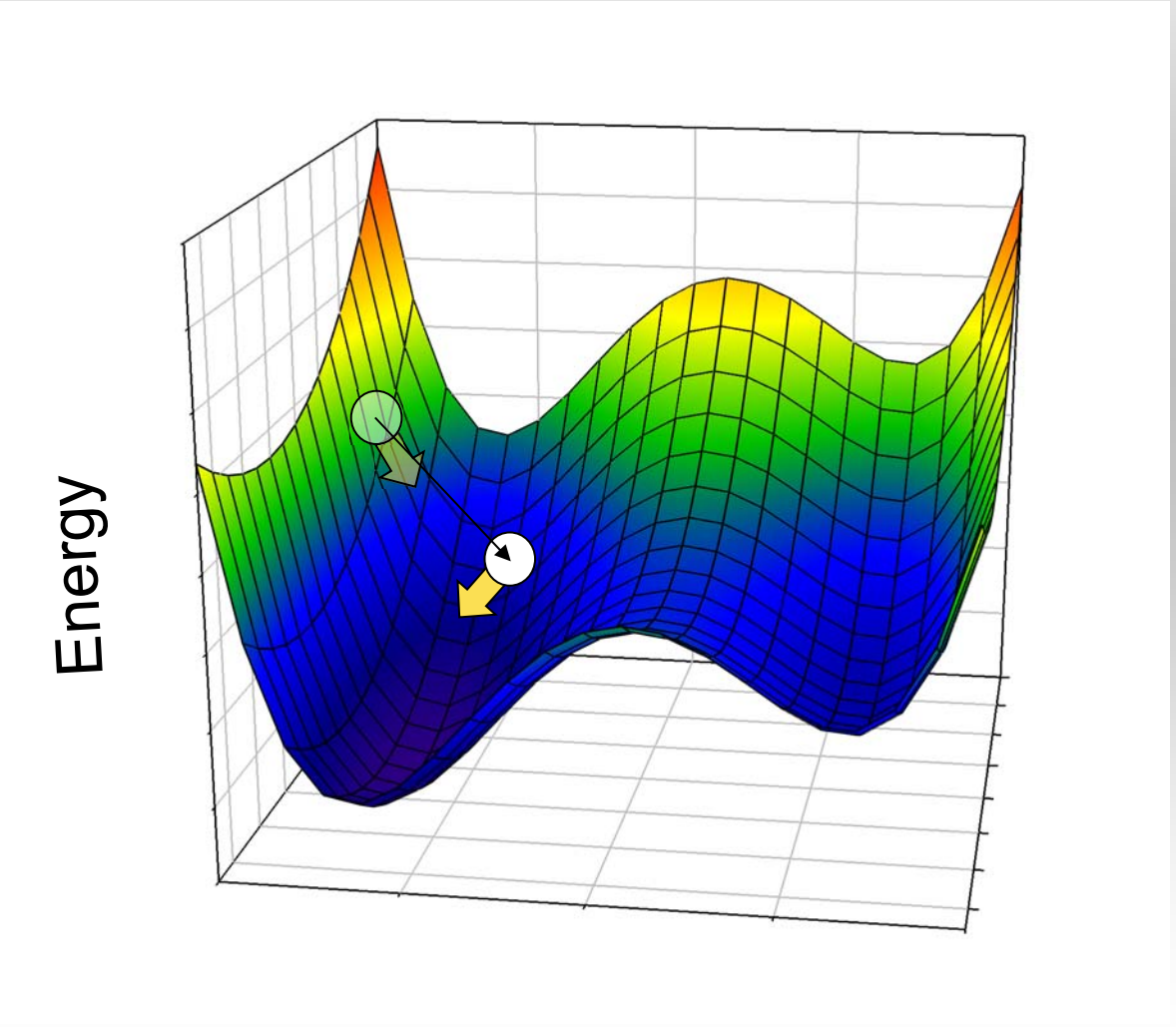
A Good Minimum is Hard to Find



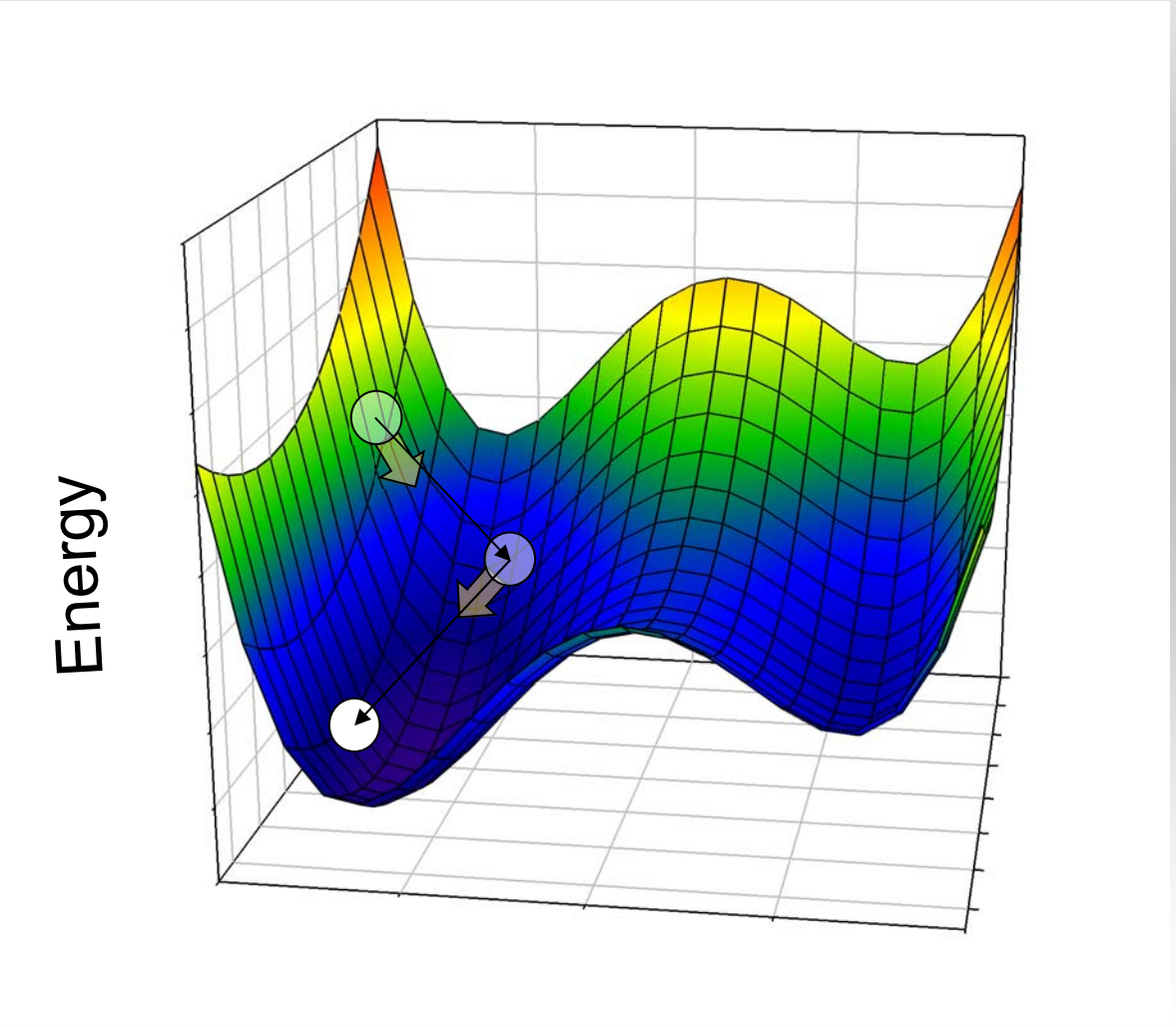
A Good Minimum is Hard to Find



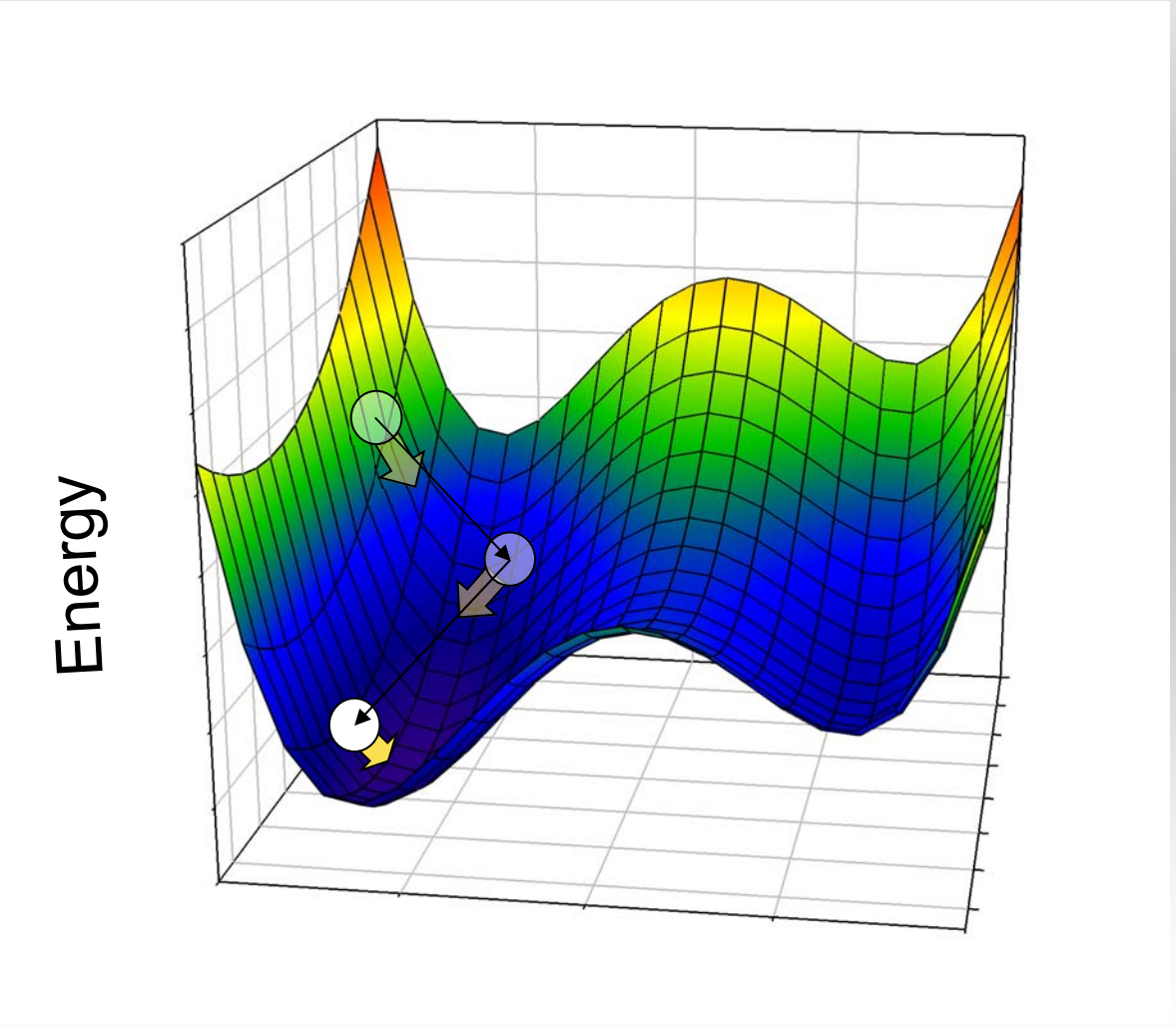
A Good Minimum is Hard to Find



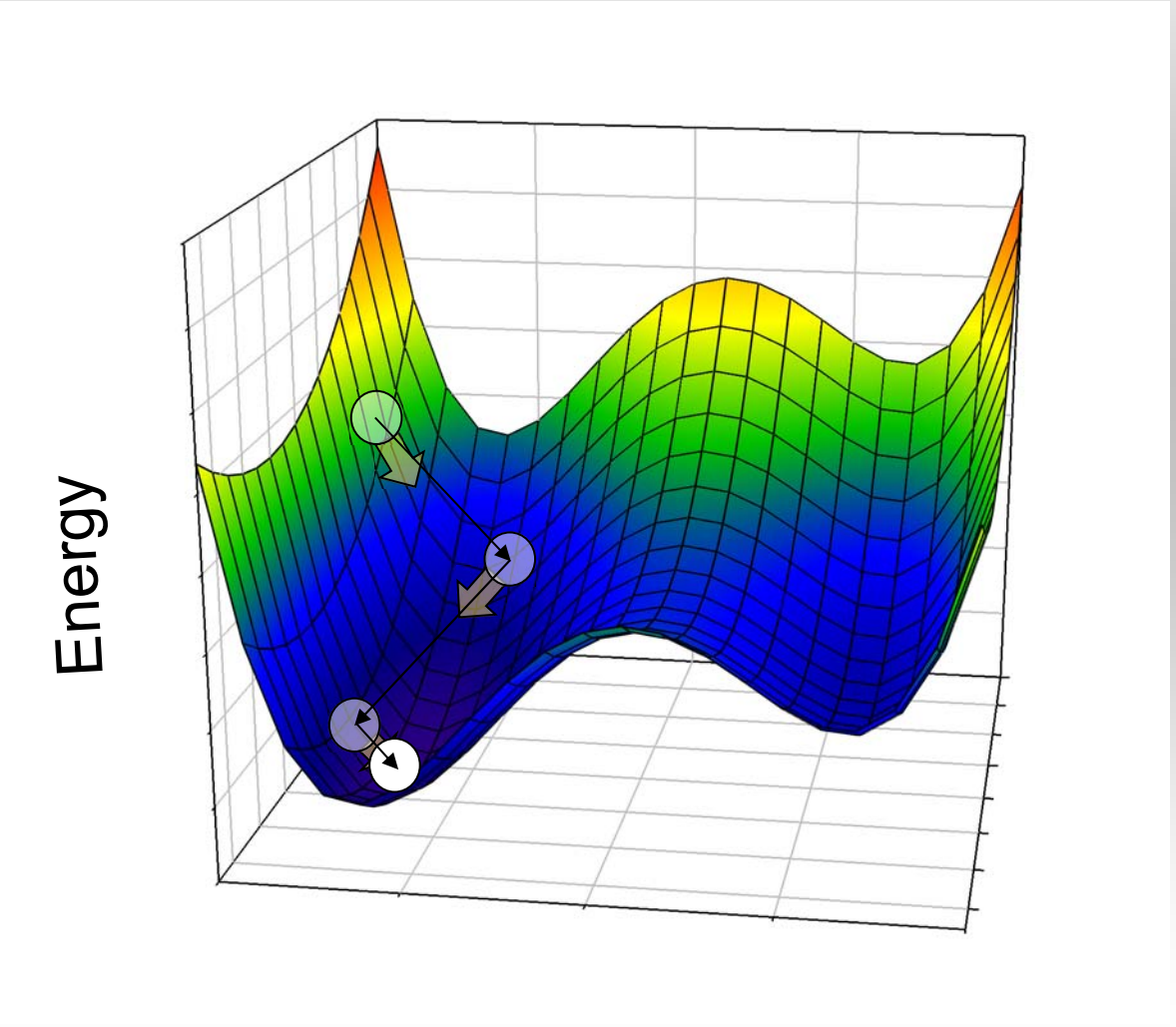
A Good Minimum is Hard to Find



A Good Minimum is Hard to Find



A Good Minimum is Hard to Find



A Good Minimum is Hard to Find

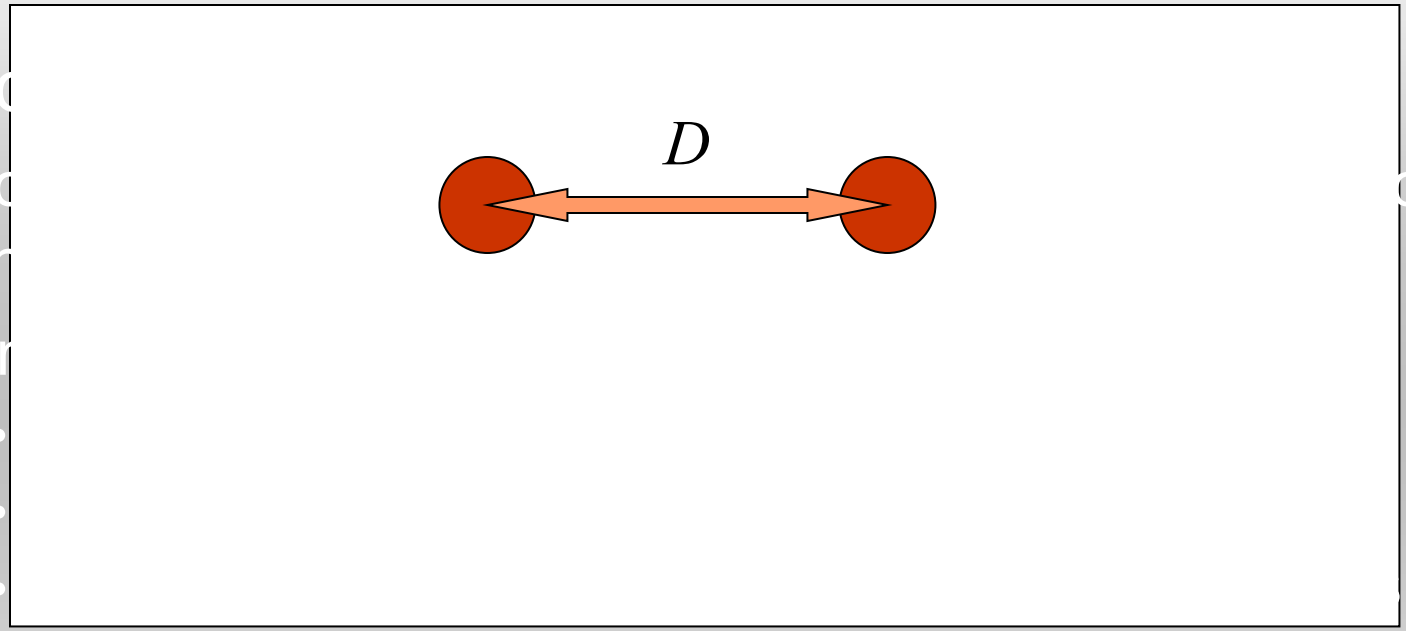
- Convergence criteria
  - The gradient (force) is below a threshold
  - The change in geometry from the previous step is below a threshold
  - The change in energy from the previous step is below a threshold

A Good Minimum is Hard to Find

- A word on forces
  - Forces are a 3*N*-dimensional vector (x, y, and z force on each atom)
  - Analytical forces
    - Actually differentiate
    - (Computational) cost is similar to calculating energy
    - Available for most simpler methods of calculating the PES
  - Numerical forces
    - Compute derivative by finite difference
    - Cost is at least 3*N* times the cost of calculating the energy
    - Available for all methods of calculating the PES

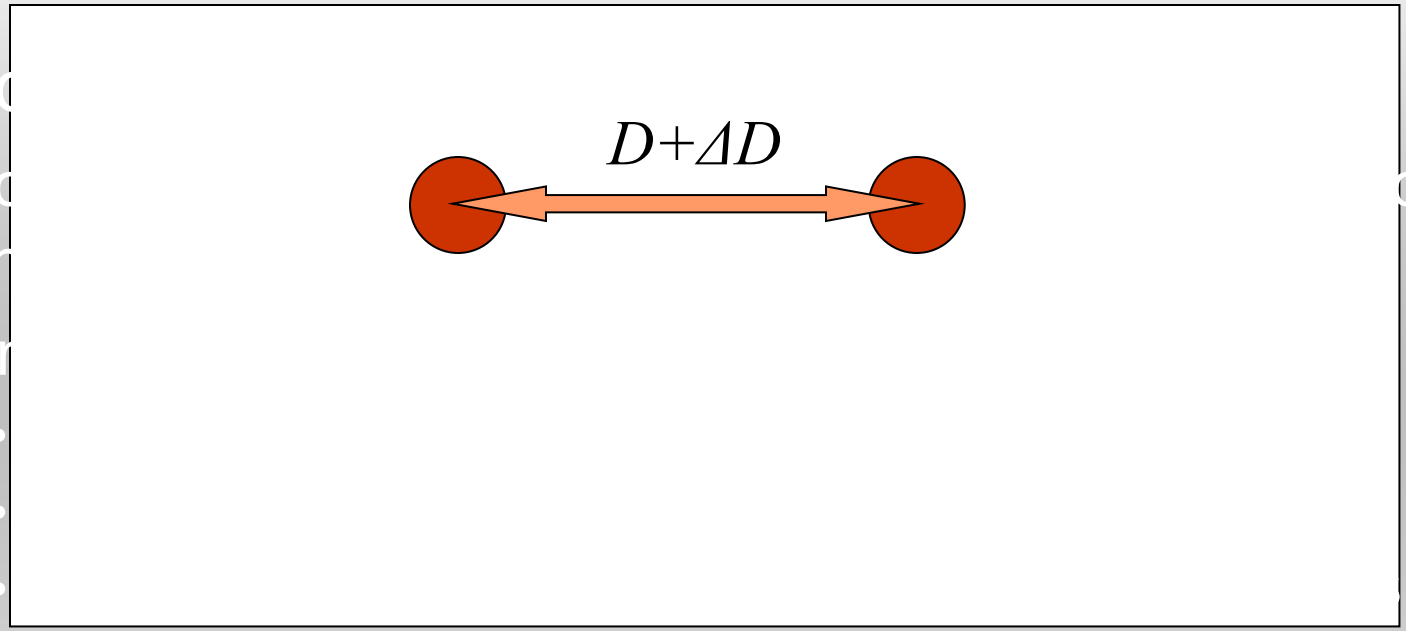
A Good Minimum is Hard to Find

- A wo
  - Fo ce
    or
  - Ar
    -
    -
    -
  - Numerical forces
    - Compute derivative by finite difference
    - Cost is at least 3*N* times the cost of calculating the energy
    - Available for all methods of calculating the PES



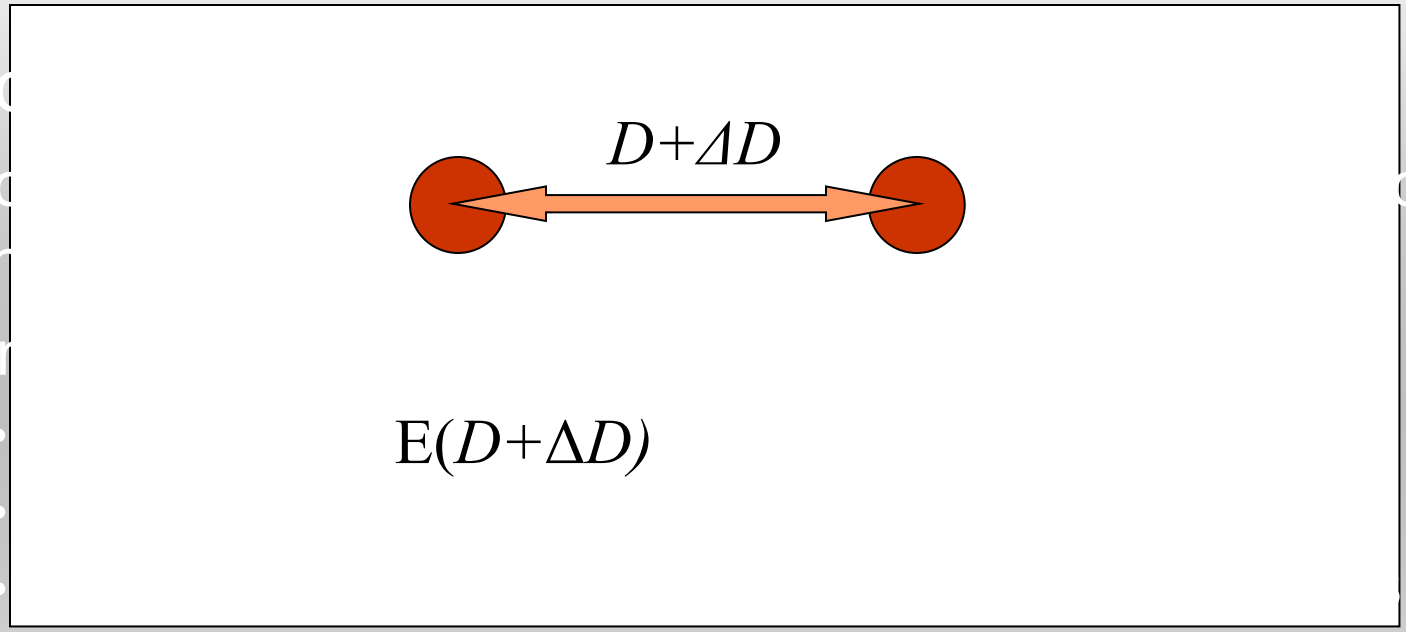
A Good Minimum is Hard to Find

- A wo
  - Fo ce
    or
  - Ar
    -
    -
    -
  - Numerical forces
    - Compute derivative by finite difference
    - Cost is at least 3*N* times the cost of calculating the energy
    - Available for all methods of calculating the PES



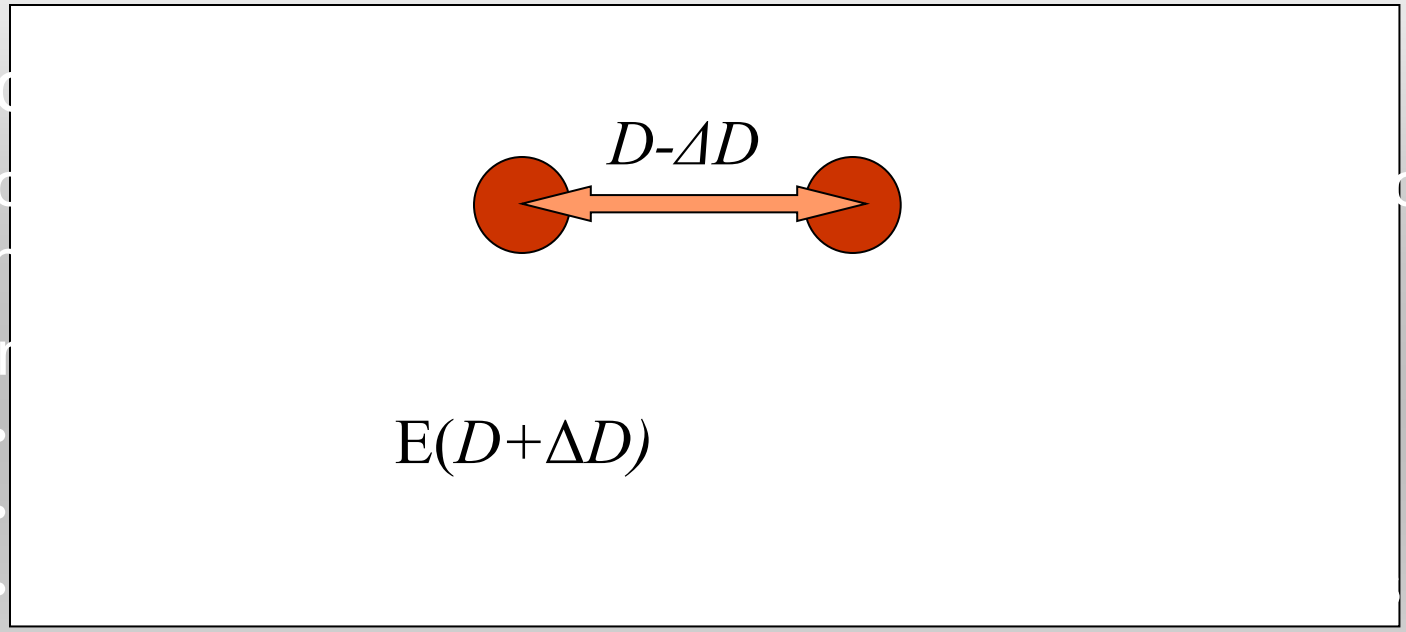
A Good Minimum is Hard to Find

- A wo
  - Fo ce
    or
  - Ar
    -
    -
    -
  - Numerical forces
    - Compute derivative by finite difference
    - Cost is at least 3*N* times the cost of calculating the energy
    - Available for all methods of calculating the PES



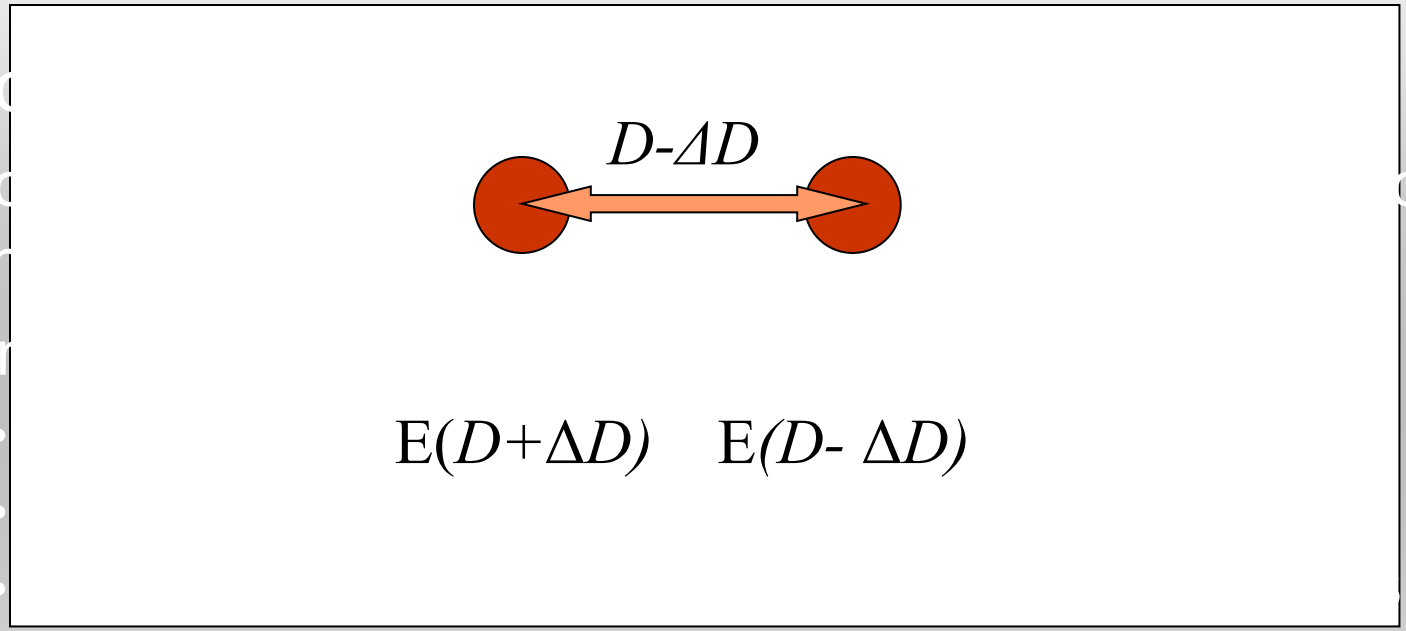
A Good Minimum is Hard to Find

- A wo
  - Fo ce
    or
  - Ar
    -
    -
    -
  - Numerical forces
    - Compute derivative by finite difference
    - Cost is at least 3*N* times the cost of calculating the energy
    - Available for all methods of calculating the PES



A Good Minimum is Hard to Find

- A wo
  - Fo ce on
  - An
    -
    -
    -
  - Numerical forces
    - Compute derivative by finite difference
    - Cost is at least 3*N* times the cost of calculating the energy
    - Available for all methods of calculating the PES



A Good Minimum is Hard to Find

- A wo
  - Fo ce on
  - An
    -
    -
    -
  - Numerical forces
    - Compute derivative by finite difference
    - Cost is at least 3*N* times the cost of calculating the energy
    - Available for all methods of calculating the PES

$$-F = \frac{E(D+\Delta D) - E(D-\Delta D)}{2\Delta D}$$

A Good Minimum is Hard to Find

- A wo
  - Fo ce on
  - An
    -
    -
    -
  - Numerical forces
    - Compute derivative by finite difference
    - Cost is at least 3*N* times the cost of calculating the energy
    - Available for all methods of calculating the PES

Central finite difference

$$-F = \frac{E(D+\Delta D) - E(D-\Delta D)}{2\Delta D}$$

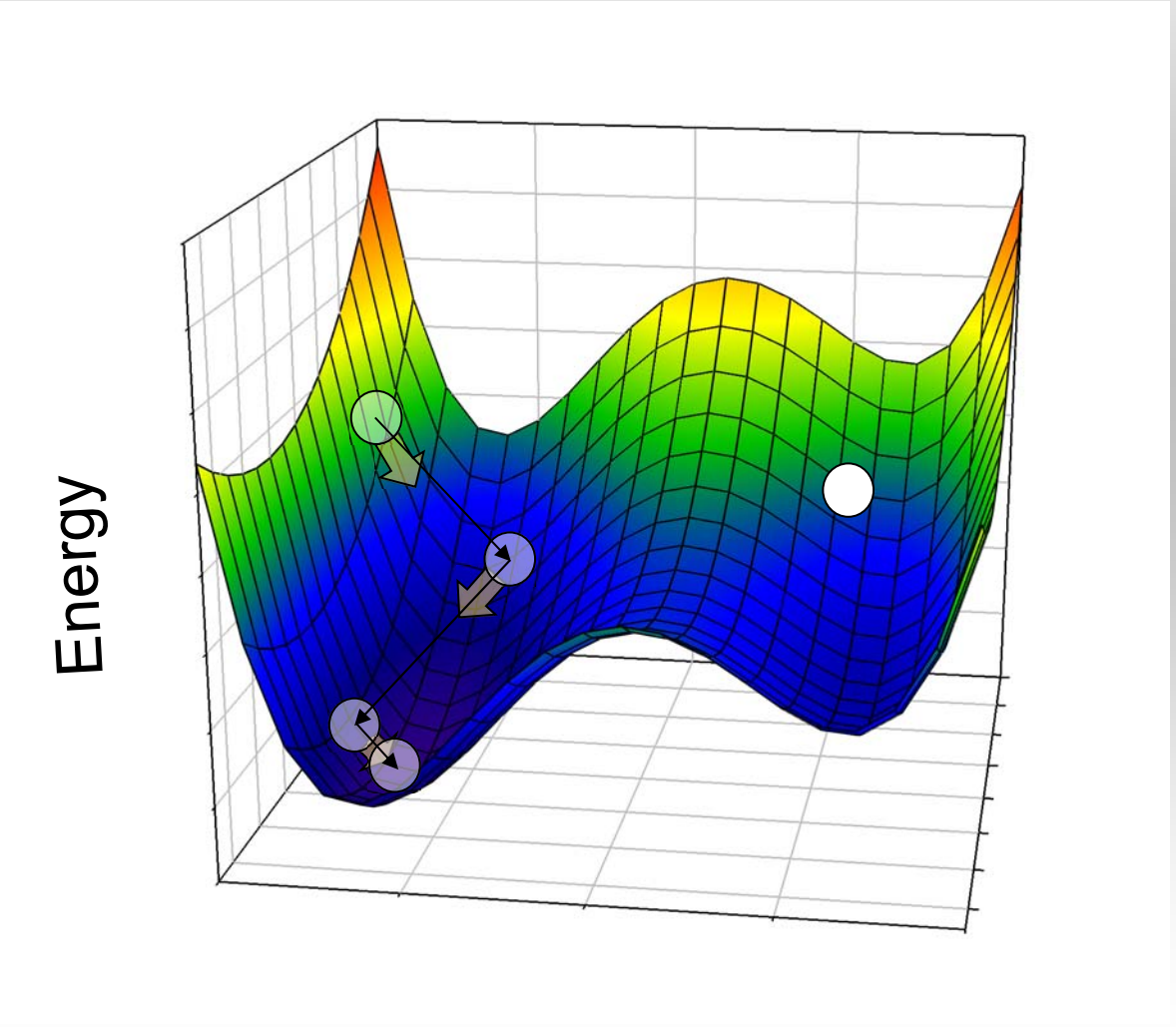
A Good Minimum is Hard to Find

- A wo
  - Fo ce on
  - An
    -
    -
    -
  - Numerical forces
    - Compute derivative by finite difference
    - Cost is at least 3*N* times the cost of calculating the energy
    - Available for all methods of calculating the PES

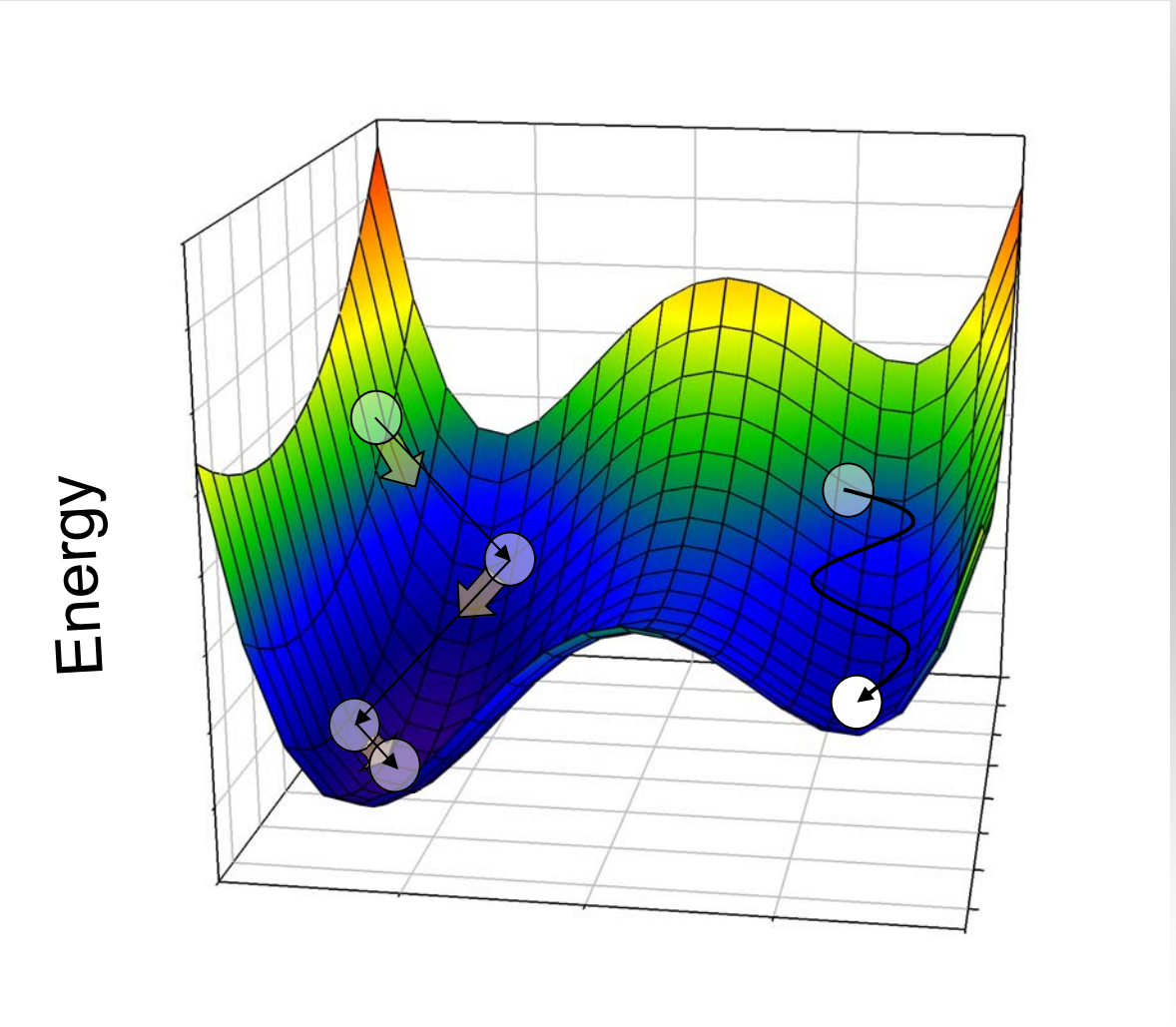
Forward finite difference

$$-F = \frac{E(D+\Delta D) - E(D)}{2\Delta D}$$

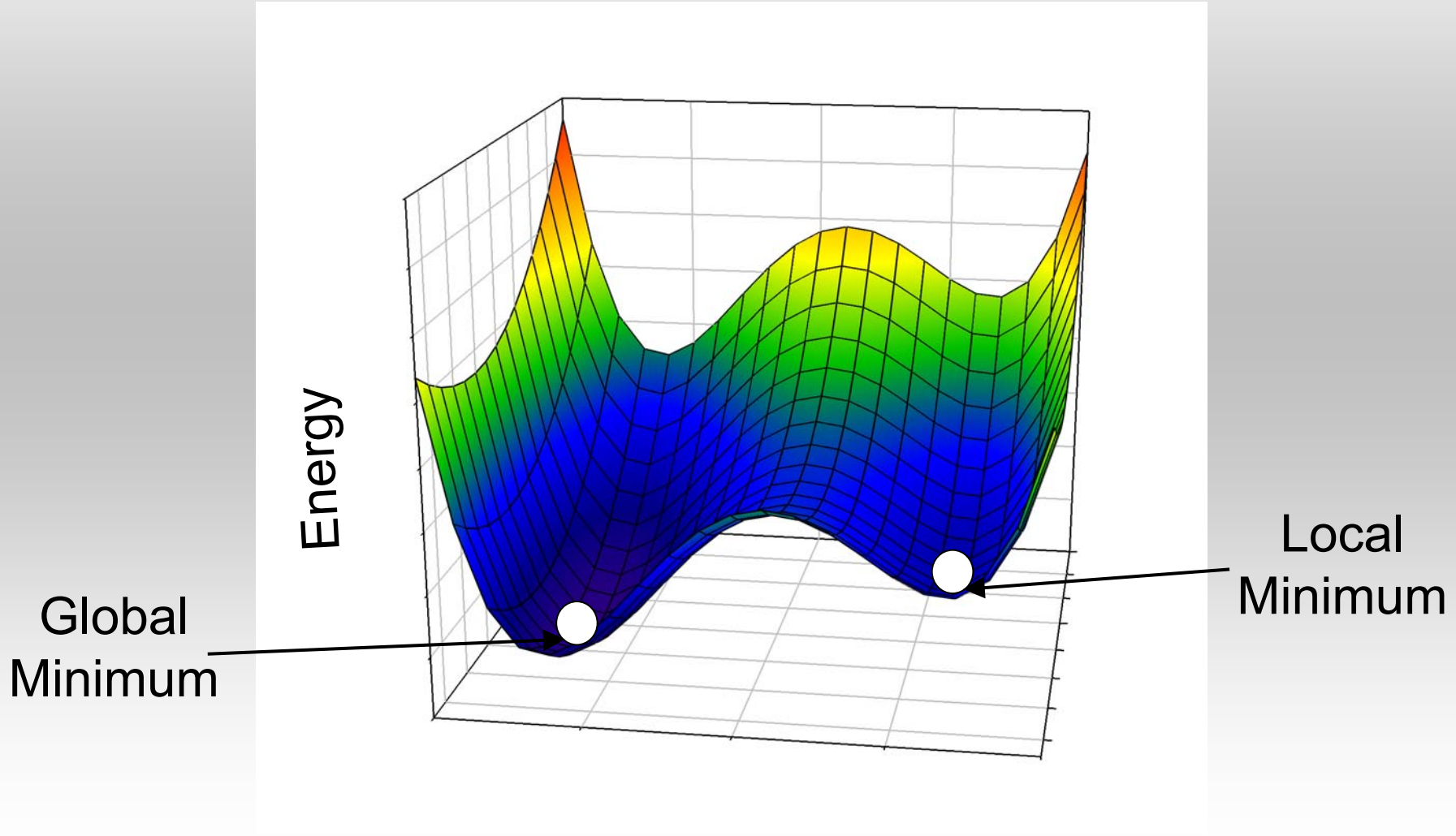
A Good Minimum is Hard to Find



A Good Minimum is Hard to Find

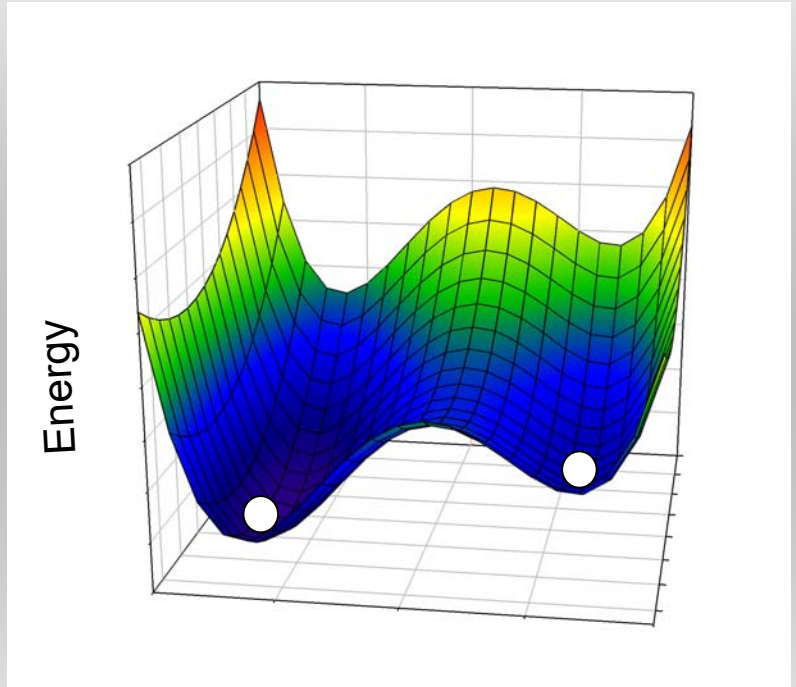


A Good Minimum is Hard to Find



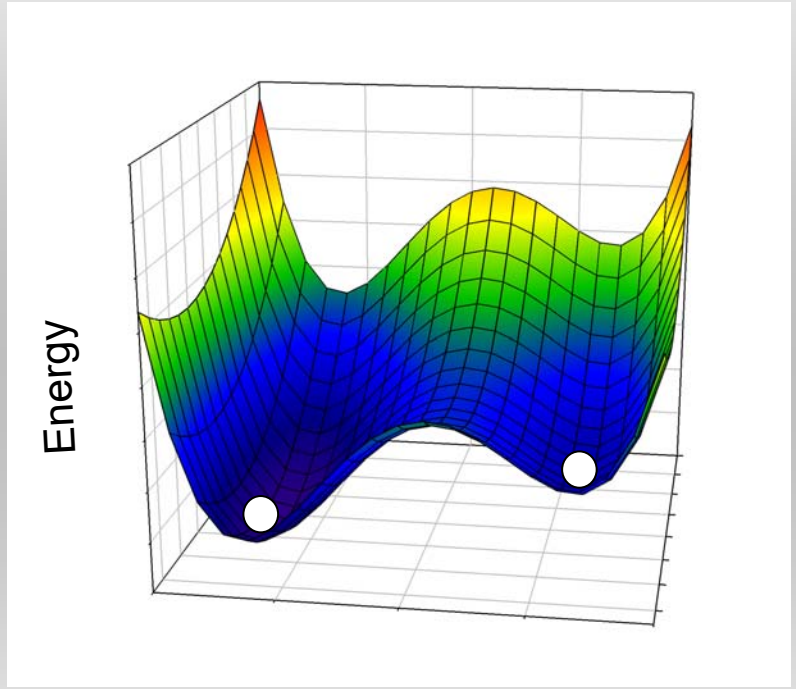
A Good Minimum is Hard to Find

- How do you know you've found the global minimum?



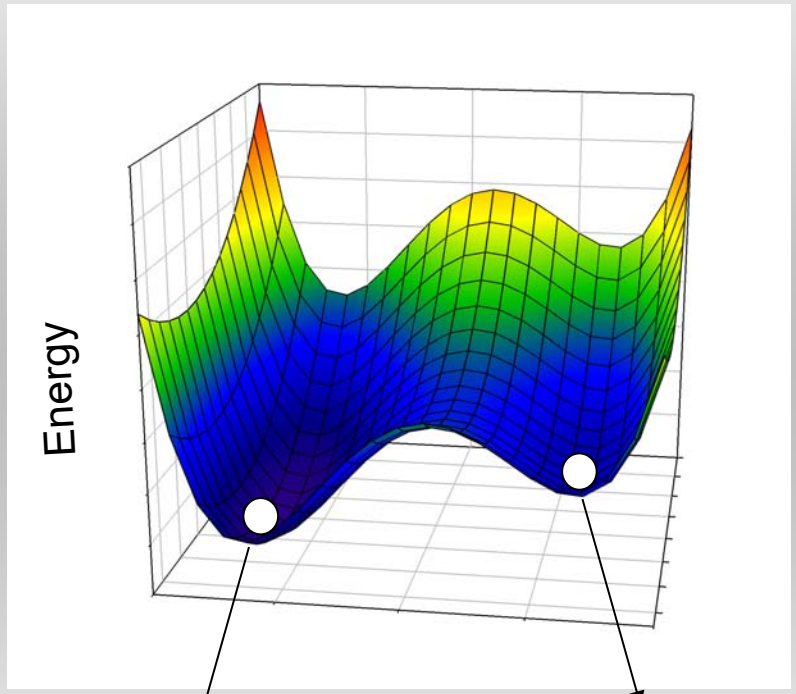
A Good Minimum is Hard to Find

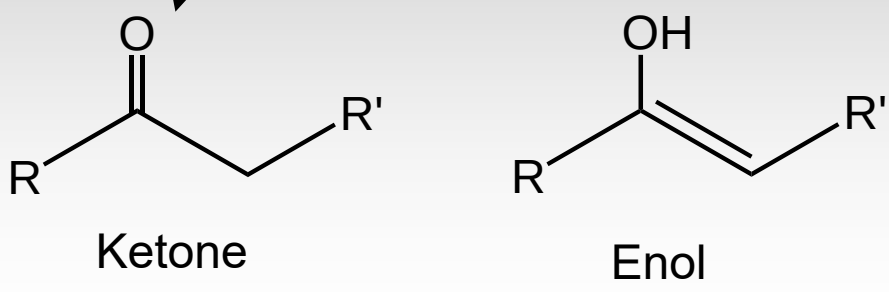
- How do you know you've found the global minimum?
- Which minimum do you want?



A Good Minimum is Hard to Find

- How do you know you've found the global minimum?
- Which minimum do you want?



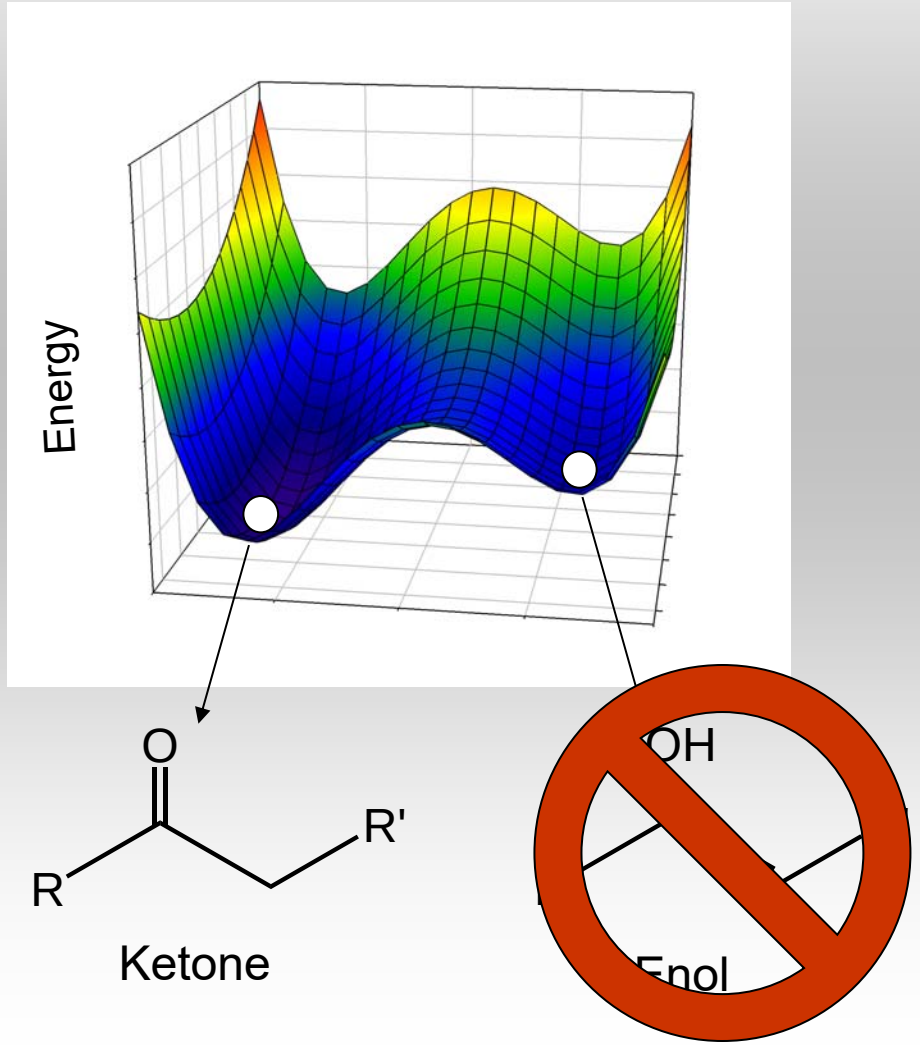


Ketone

Enol

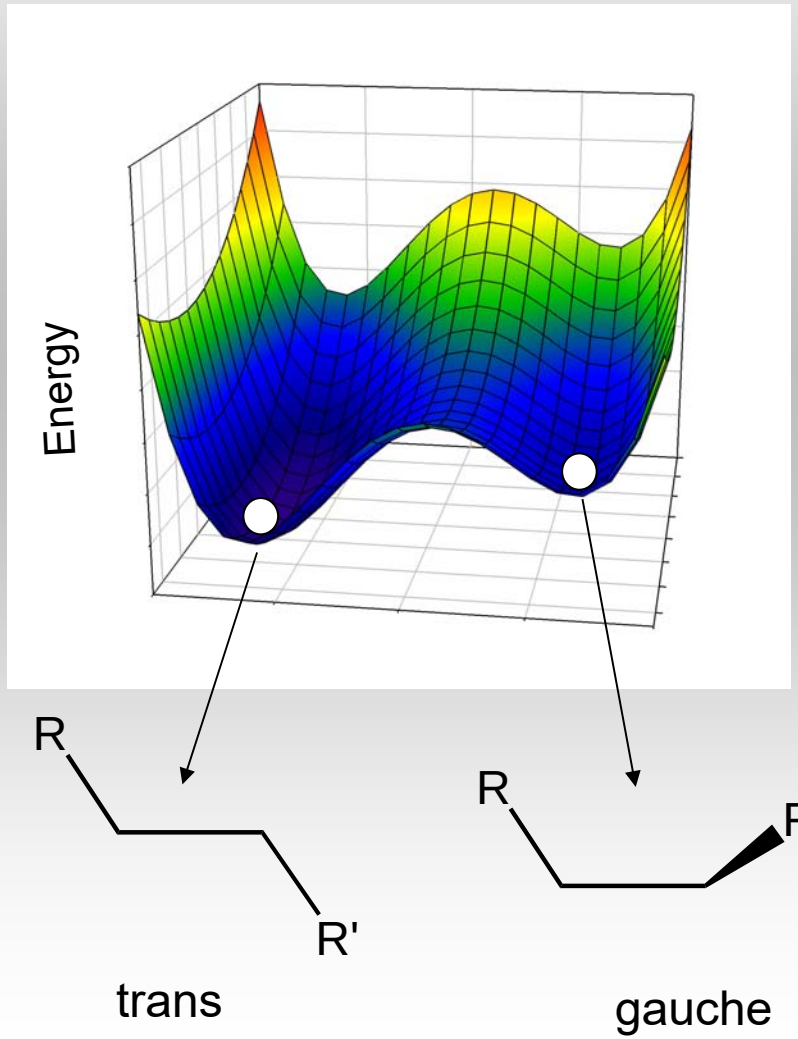
A Good Minimum is Hard to Find

- How do you know you've found the global minimum?
- Which minimum do you want?



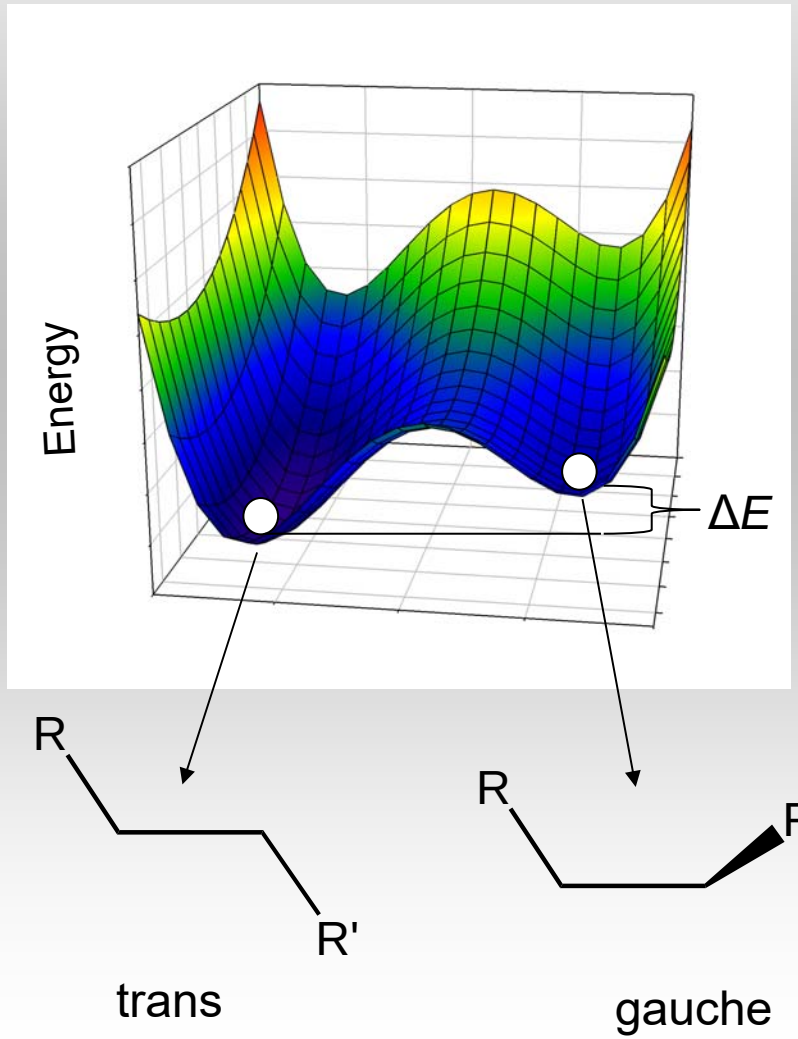
A Good Minimum is Hard to Find

- How do you know you've found the global minimum?
- Which minimum do you want?



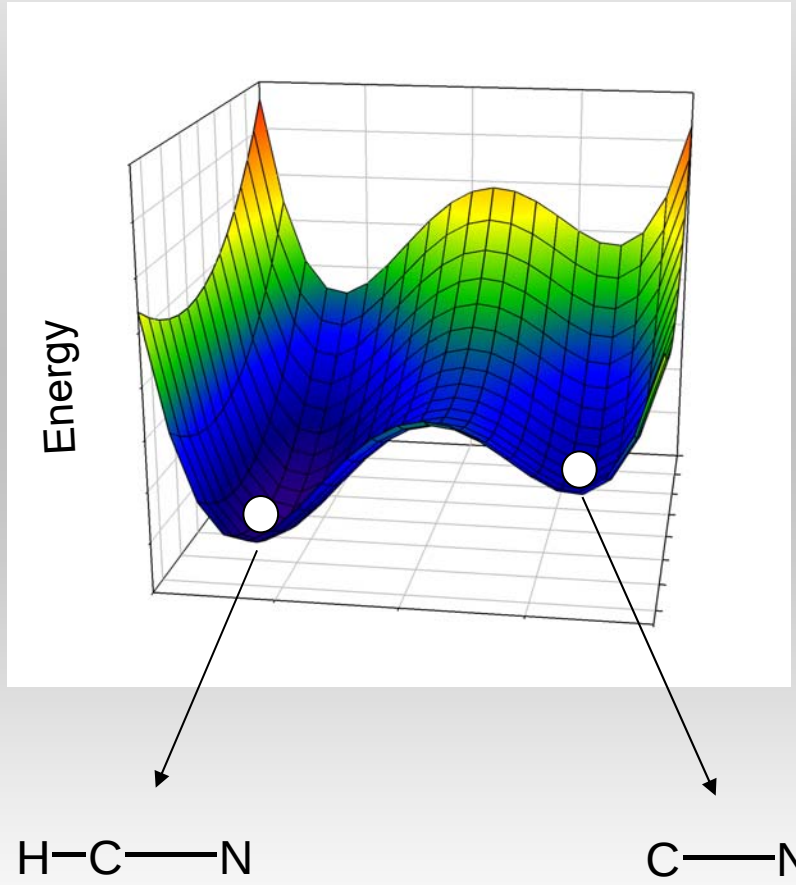
A Good Minimum is Hard to Find

- How do you know you've found the global minimum?
- Which minimum do you want?



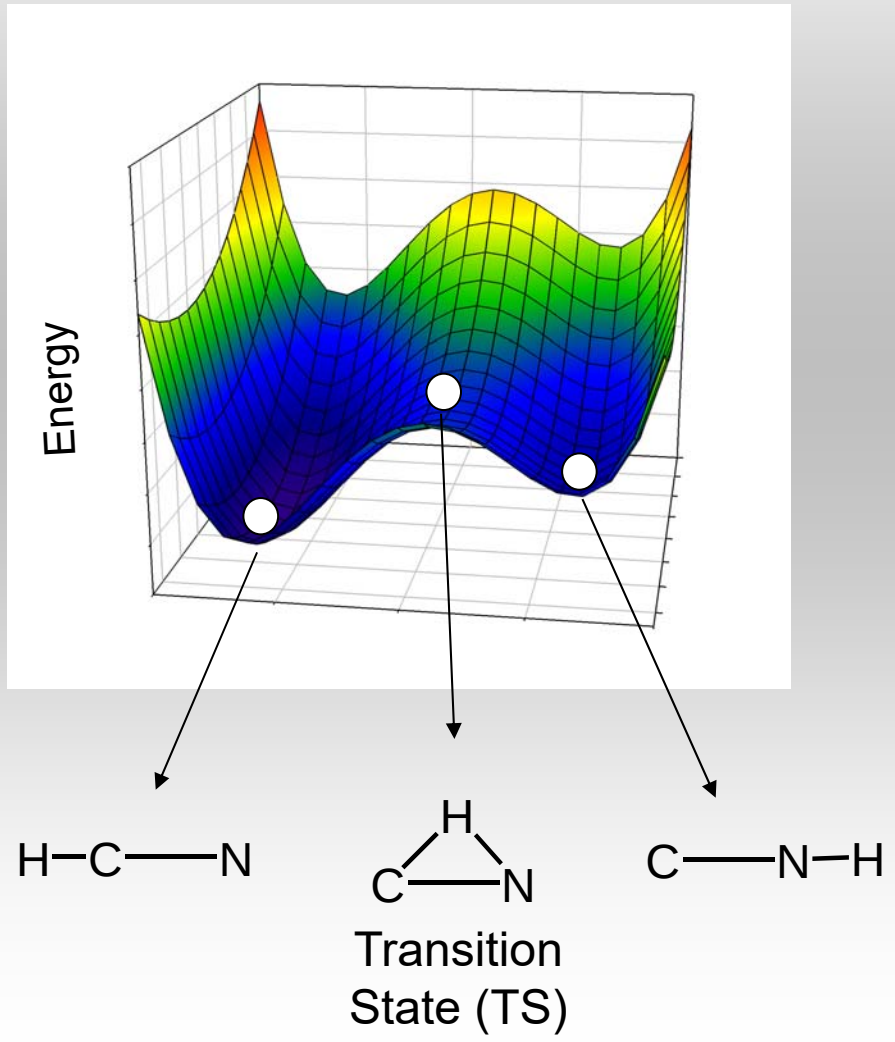
A Good Minimum is Hard to Find

- How do you know you've found the global minimum?
- Which minimum do you want?



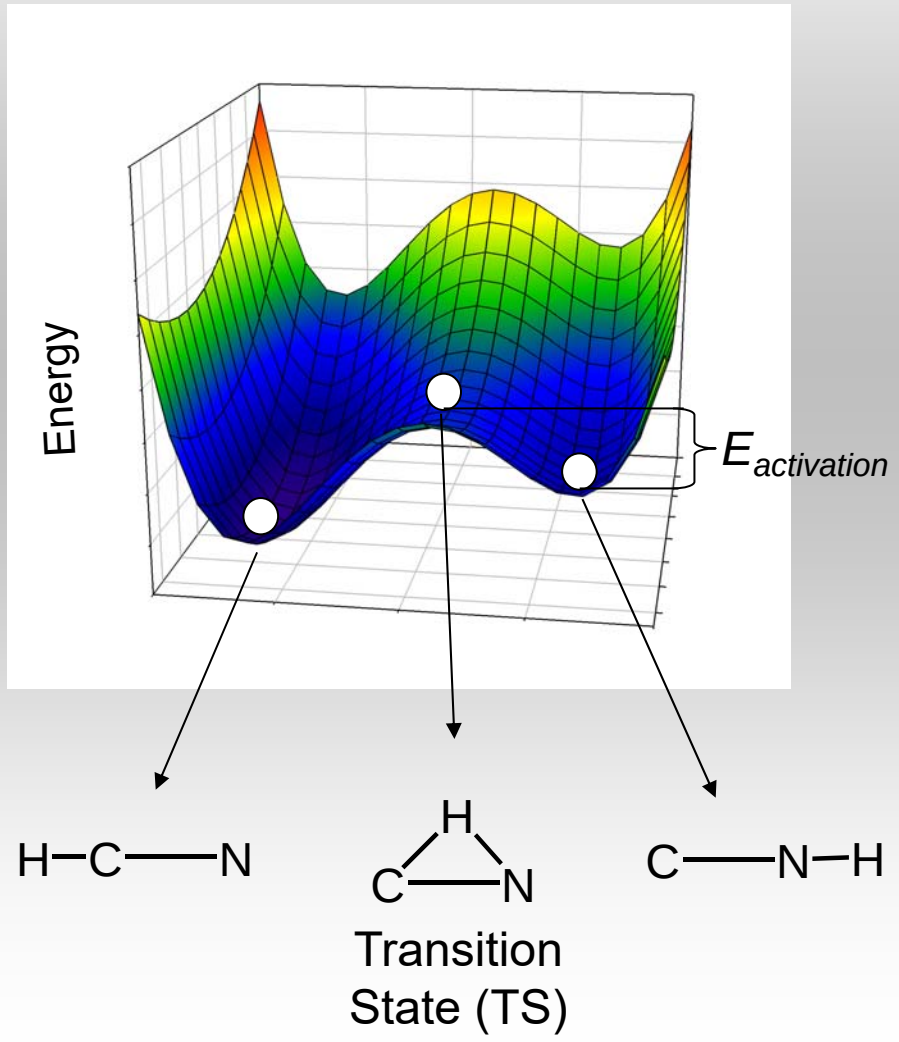
A Good Minimum is Hard to Find

- How do you know you've found the global minimum?
- Which minimum do you want?



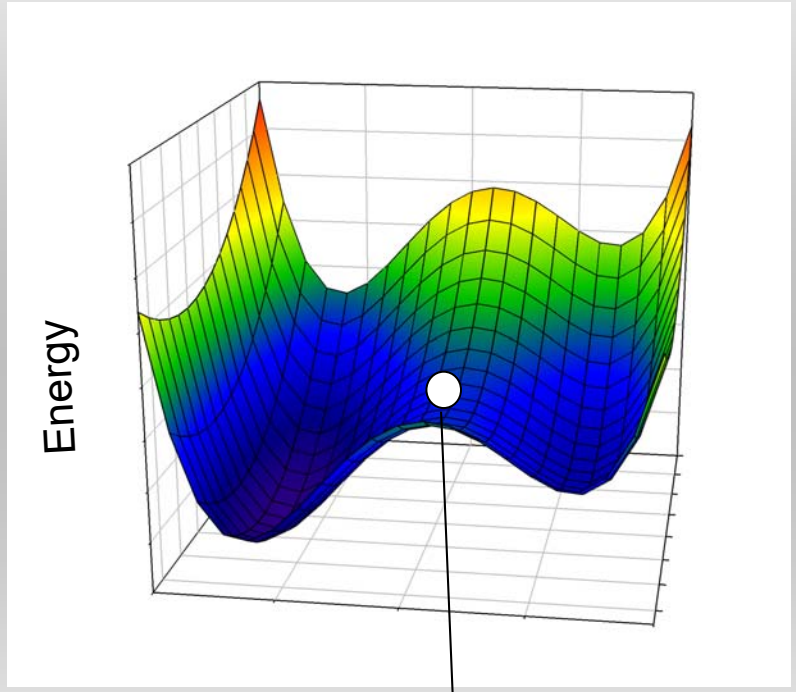
A Good Minimum is Hard to Find

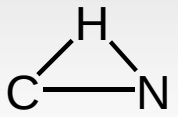
- How do you know you've found the global minimum?
- Which minimum do you want?



A Good Transition State is *Really* Hard to Find

- A TS
  - is defined as the highest point along the lowest energy path between reactant and product
  - is a stable point (**F**=0)
  - has a single "imaginary frequency" (one normal mode in which the second derivative is negative)

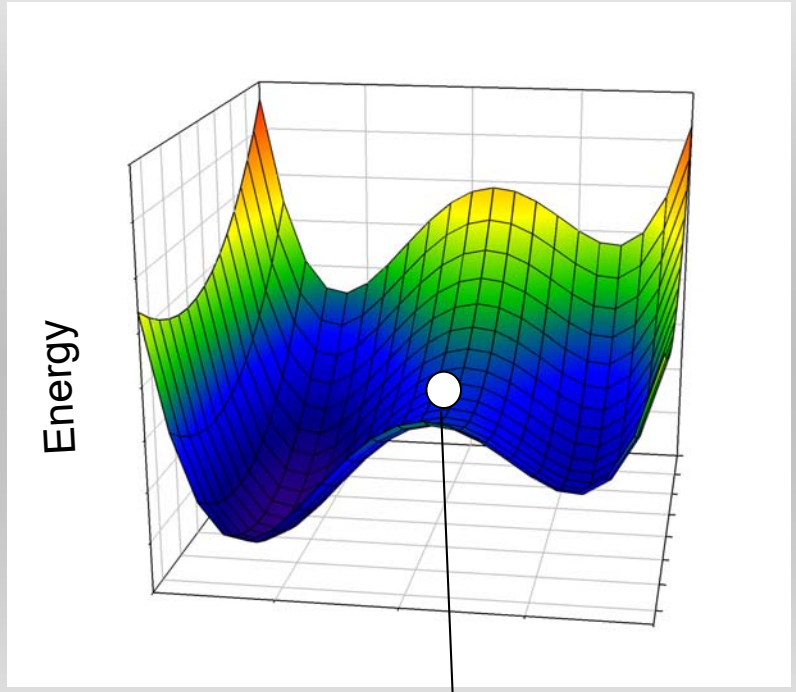


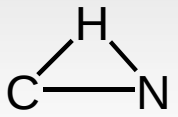


Transition State (TS)

A Good Transition State is *Really* Hard to Find

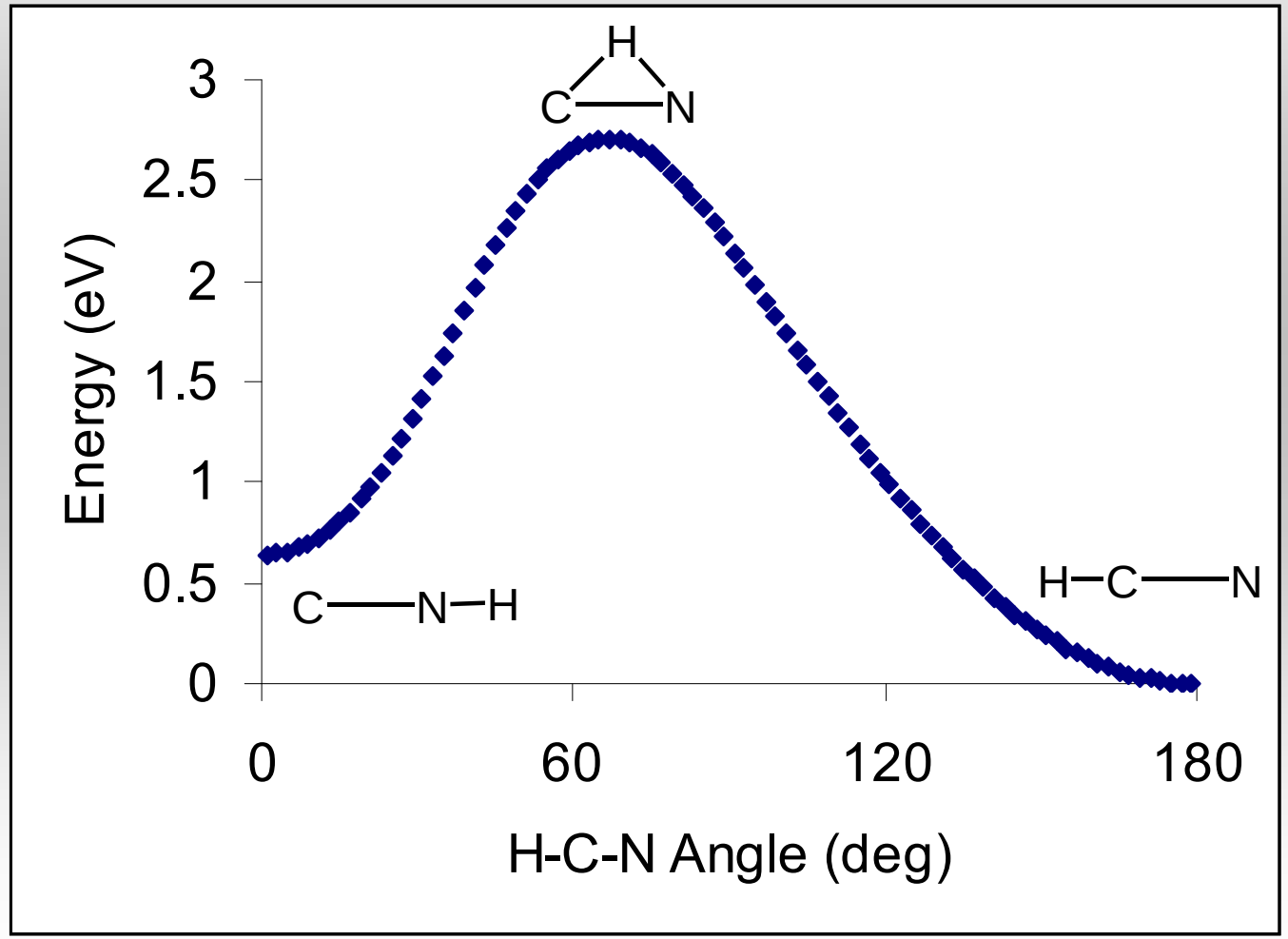
- A TS can be found
  - using one of the TS optimization algorithms available in most quantum chemistry codes
  - by a series of constrained optimizations *with only a single reaction coordinate is constrained*



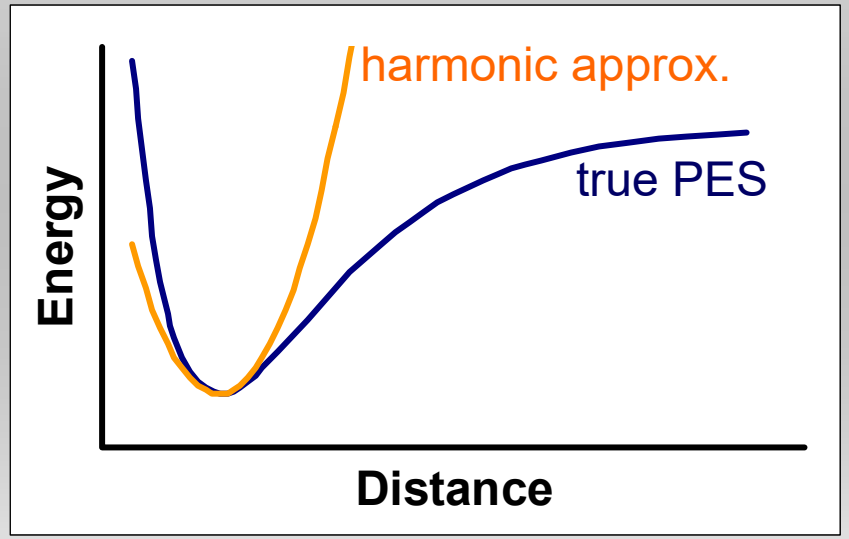


Transition State (TS)

A Good Transition State is *Really* Hard to Find



Calculating Vibrational Frequencies



- Calculate the second derivative matrix (Hessian):

$$\frac{d^2E}{d\mathbf{R}^2}$$

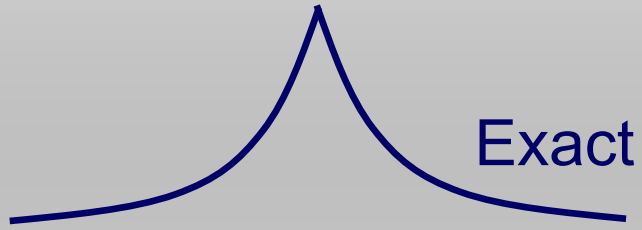
  at the minimum
- Diagonalize mass weighted hessian to get "normal modes"
- Calculate frequencies according to the well known solution of the harmonic oscillator problem

Energy Differences and Errors

- Two types of errors
  - Constant error – an error that is the same for all points on the PES
  - Non-parallelity error – an error that varies from point to point of the PES

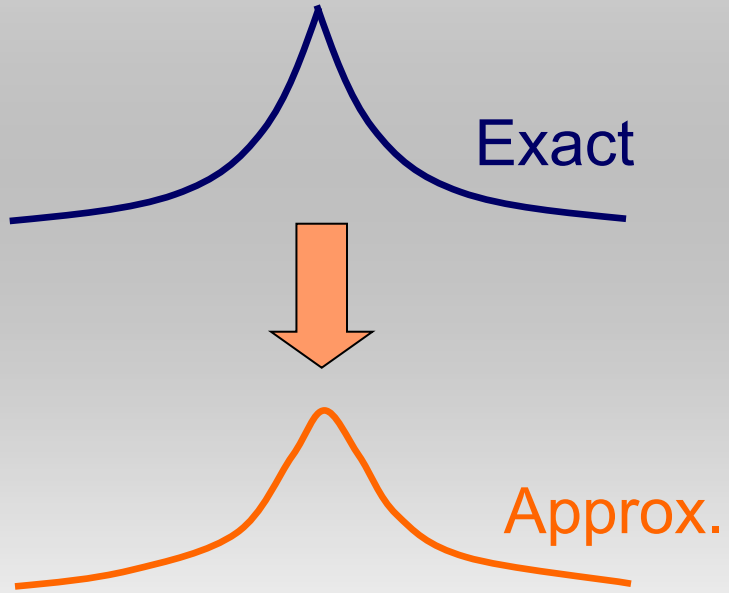
Energy Differences and Errors

- Constant Error



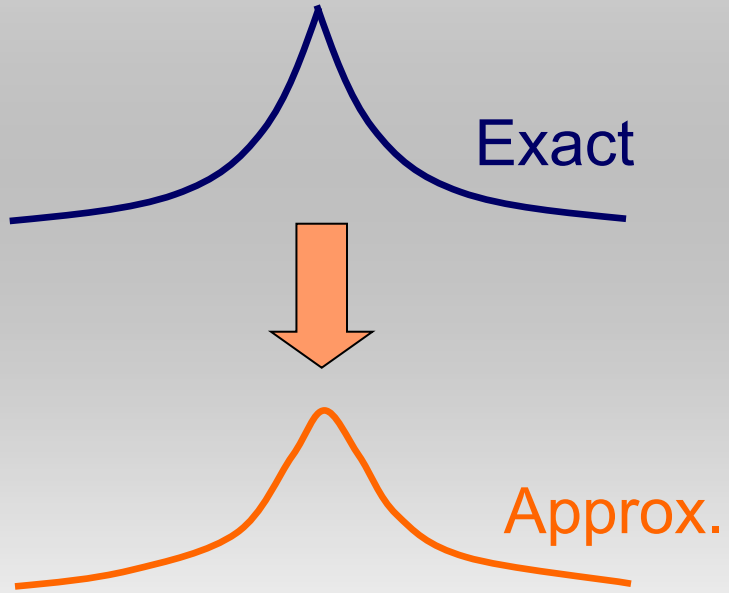
Energy Differences and Errors

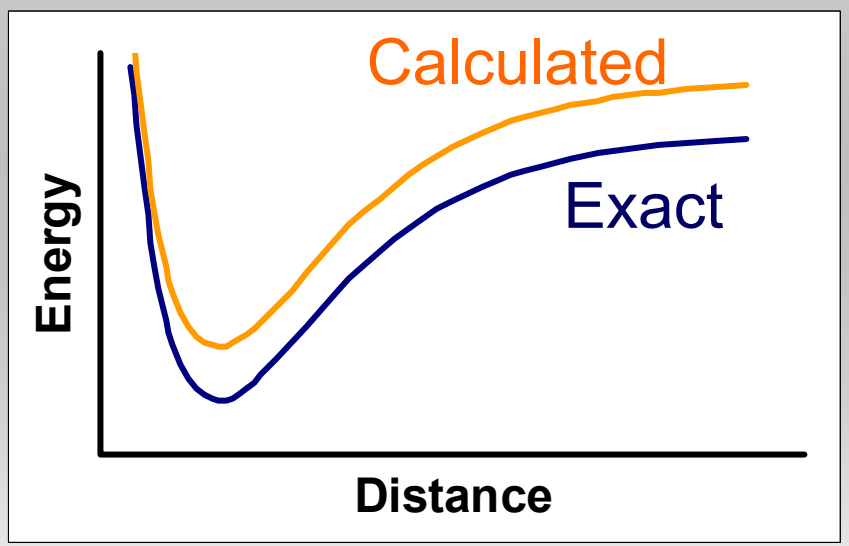
- Constant Error



Energy Differences and Errors

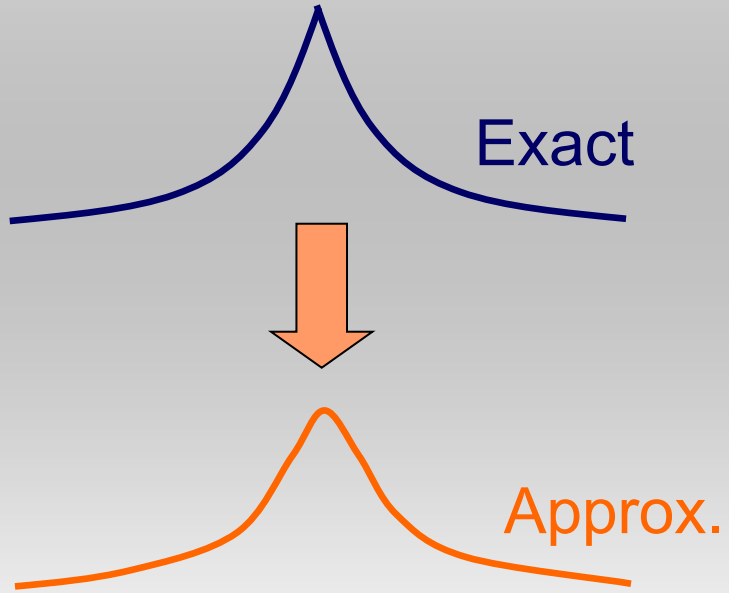
- Constant Error

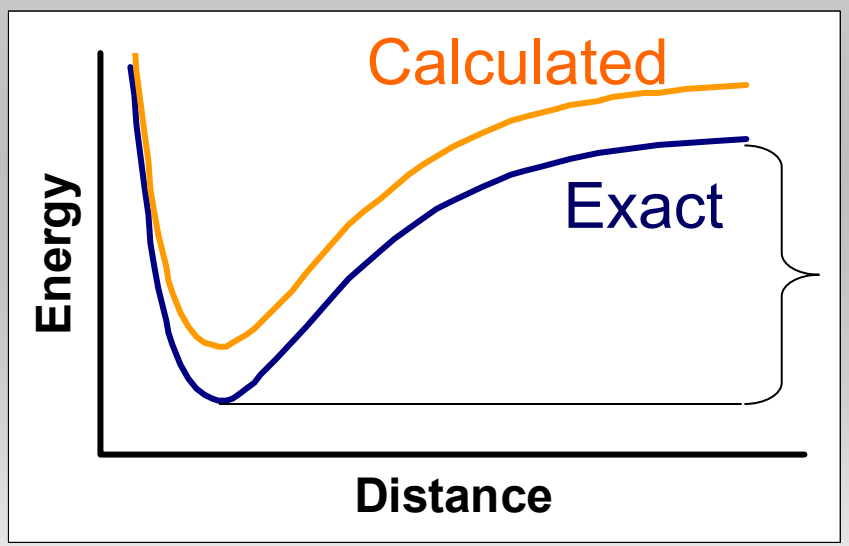




Energy Differences and Errors

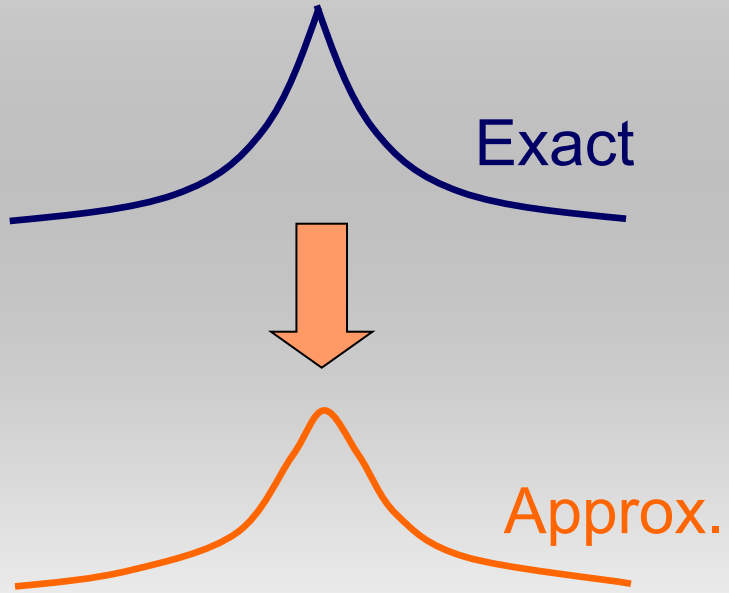
- Constant Error

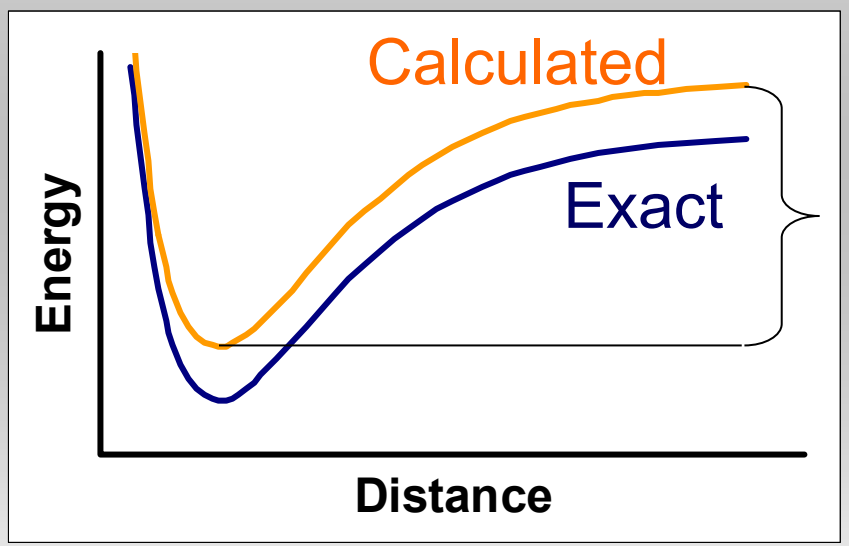




Energy Differences and Errors

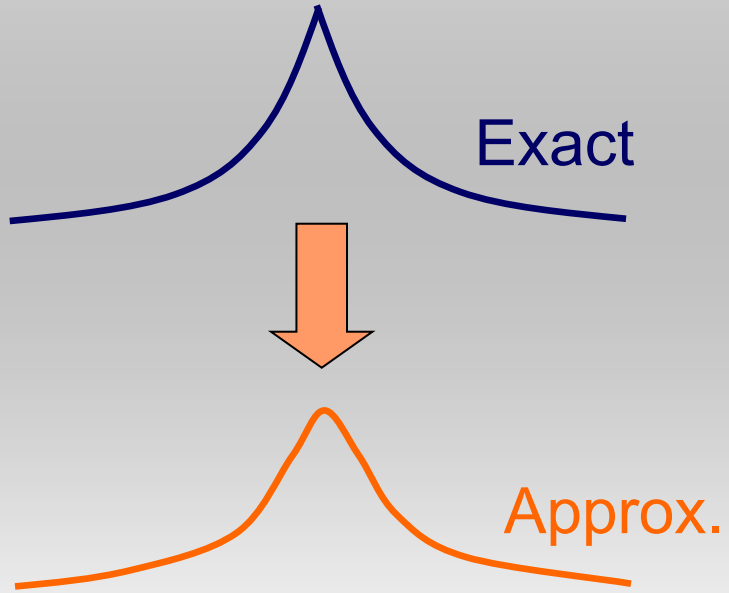
- Constant Error

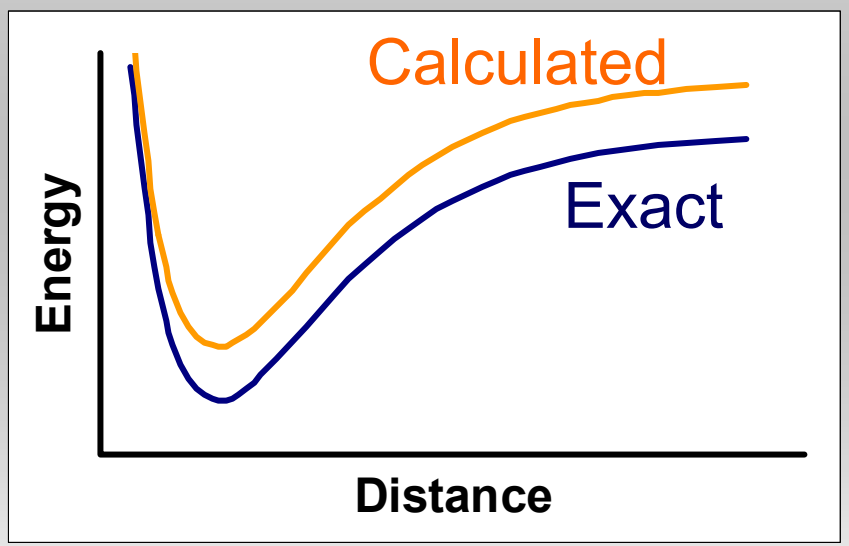




Energy Differences and Errors

- Constant Error

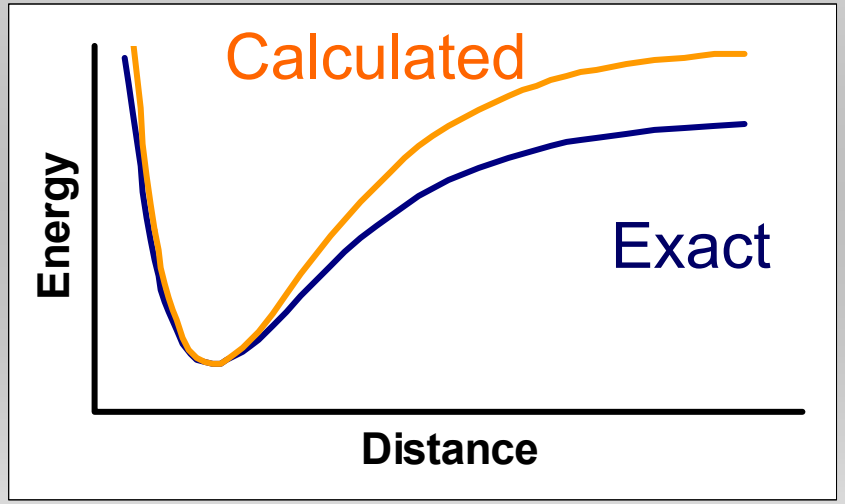




Constant errors in energy *usually* don't matter

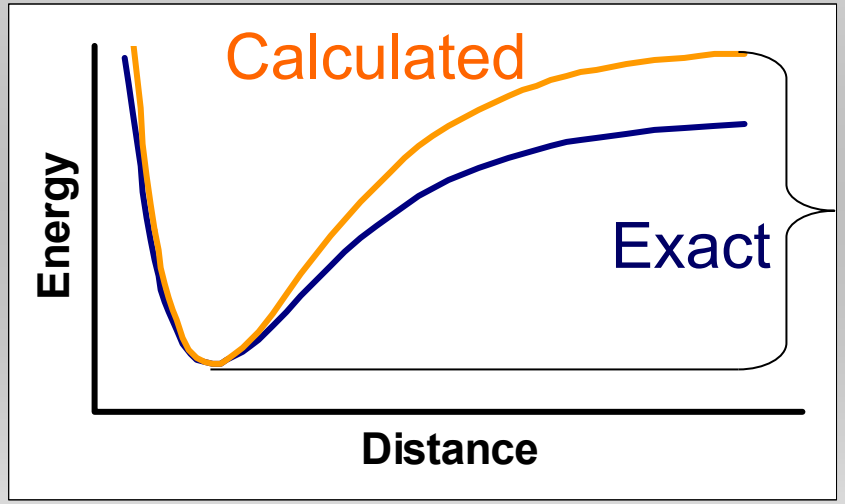
Energy Differences and Errors

- Non-parallelity Error



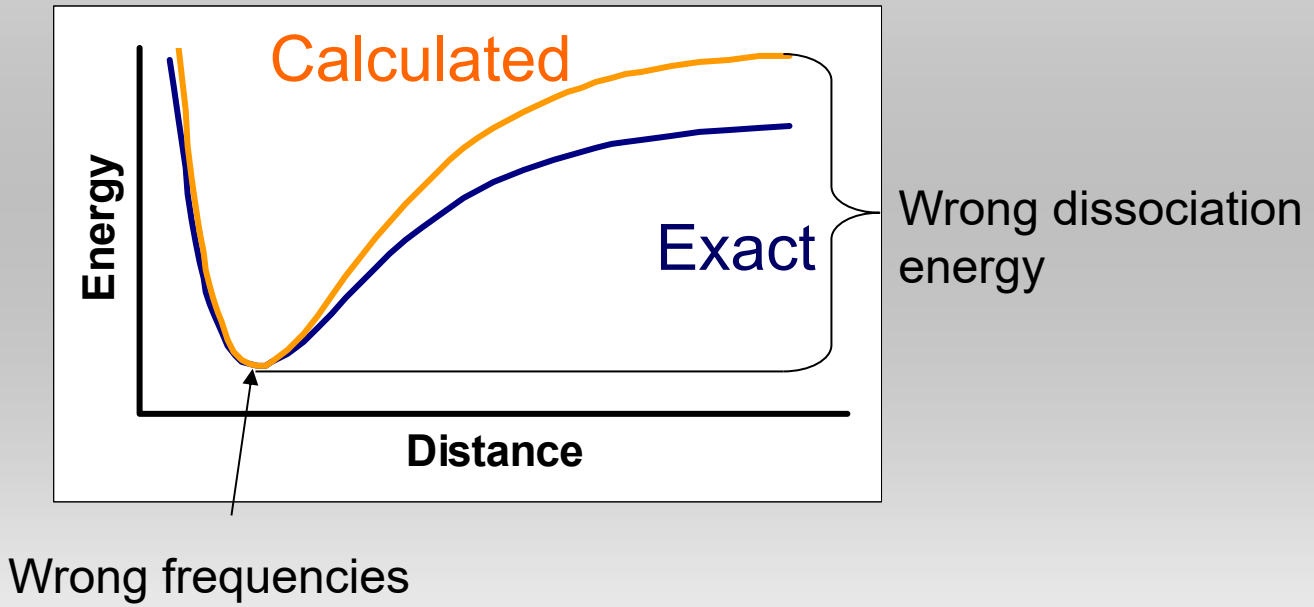
Energy Differences and Errors

- Non-parallelity Error



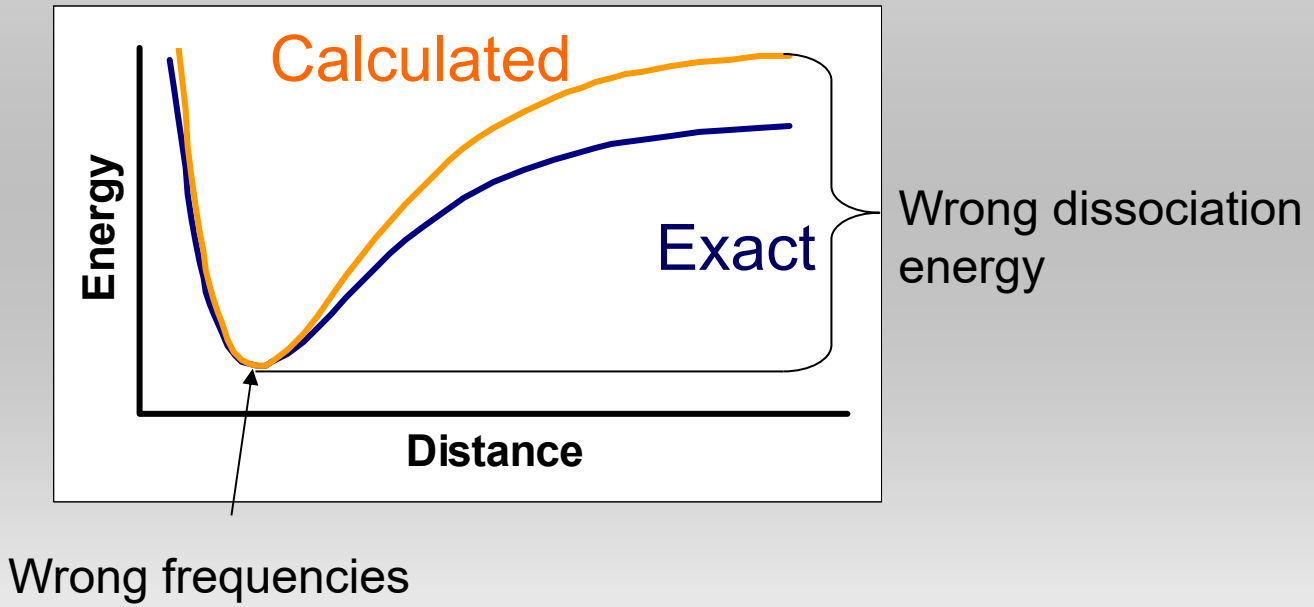
Energy Differences and Errors

- Non-parallelity Error



Energy Differences and Errors

- Non-parallelity Error

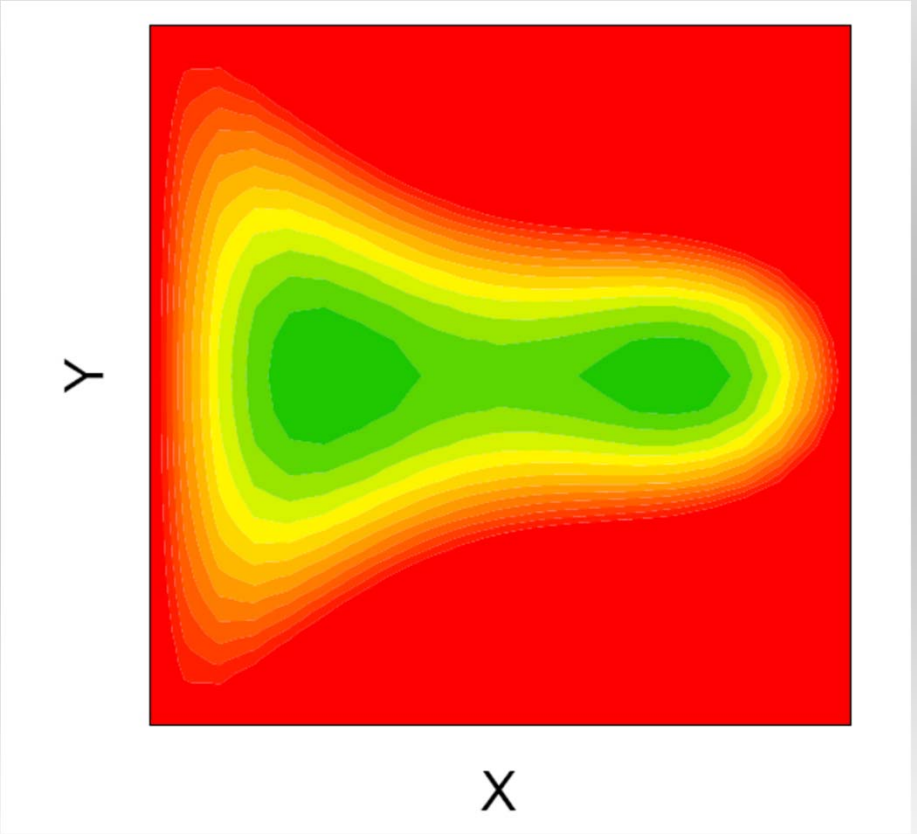


Non-parallelity errors matter!

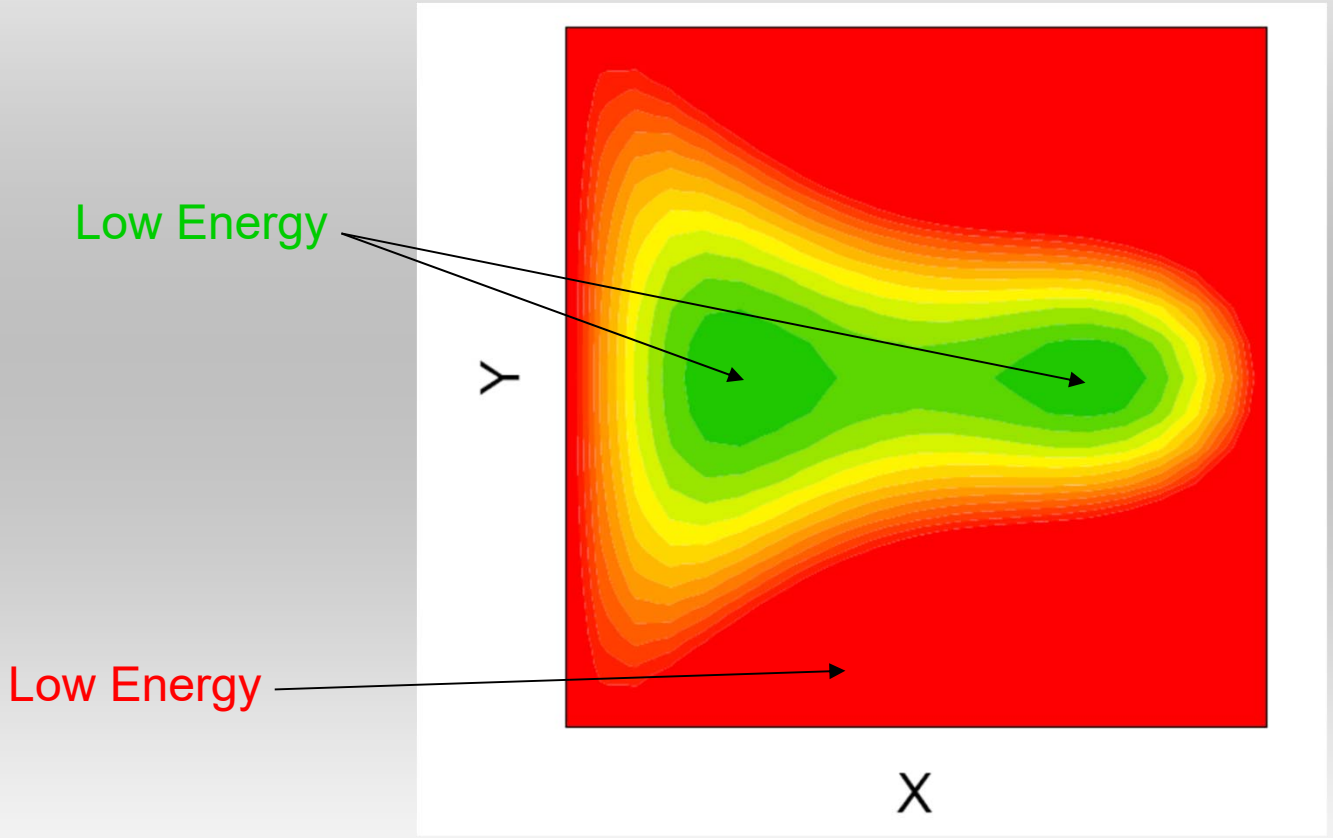
Energy v. Free Energy

- Free energies, not energies, determine the probability of being in a specific state at finite temperature
- The energy of a molecule at a specific geometry is an energy, NOT a free energy!
- Some additional work is required to get a free energy
  - estimate from frequencies
  - RRKM theory – estimate reaction rates from frequencies at the reactant and transition state
  - molecular dynamics

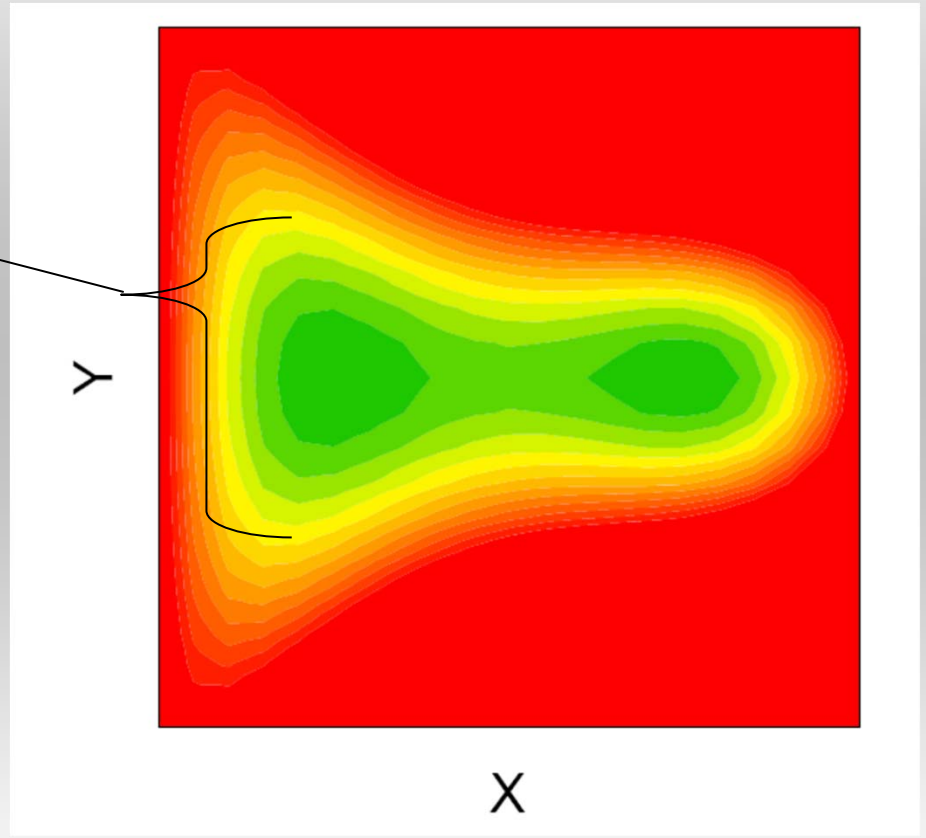
Energy v. Free Energy



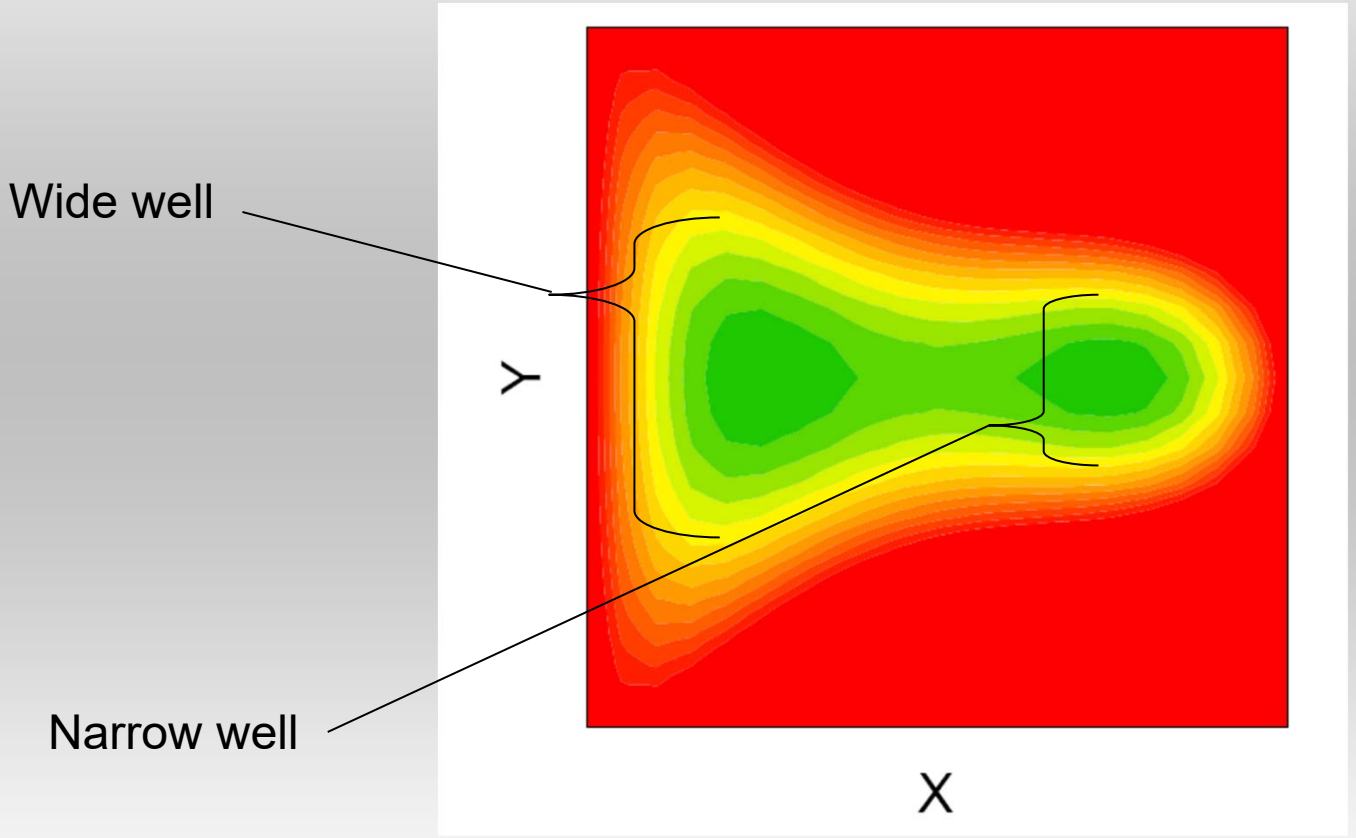
Energy v. Free Energy



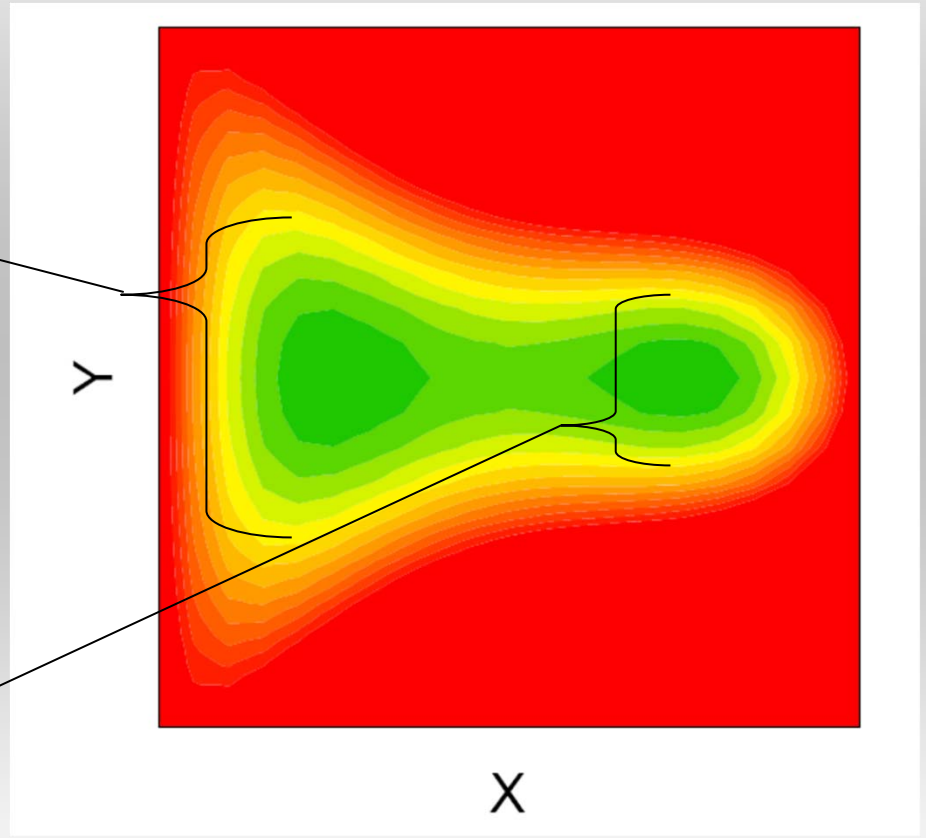
Energy v. Free Energy



Energy v. Free Energy



Energy v. Free Energy

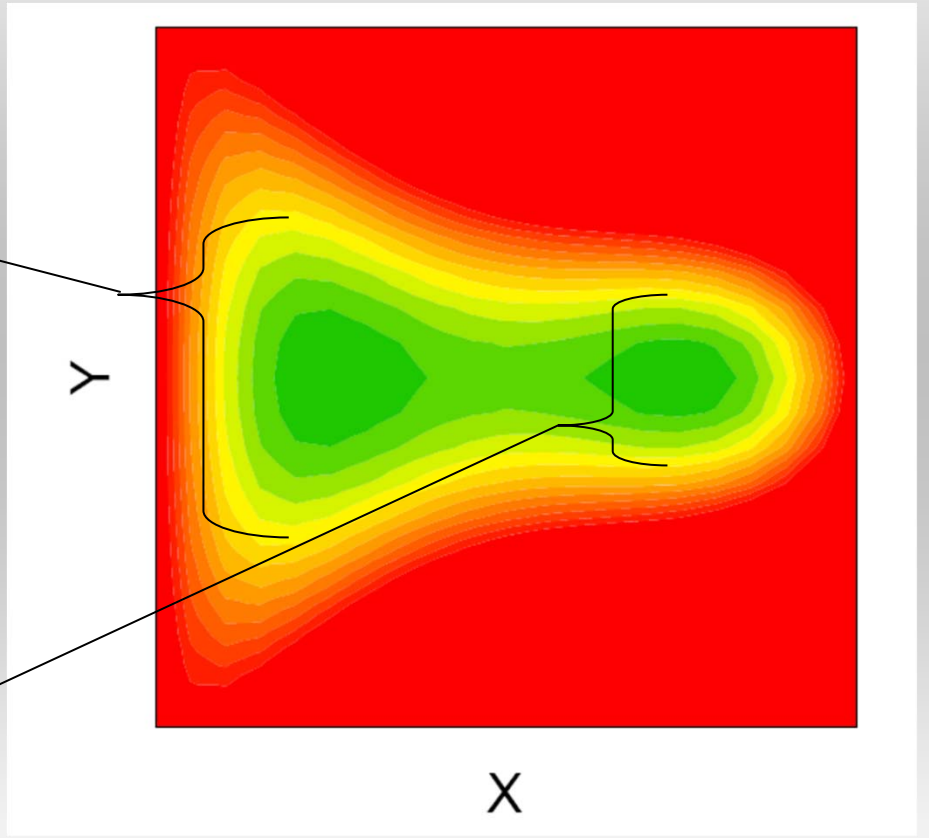


Energy v. Free Energy

Wide well

Higher Entropy

Lower Free Energy

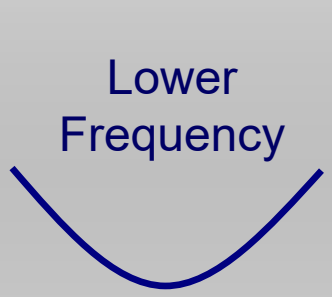


Narrow well

Lower Entropy

High Free Energy

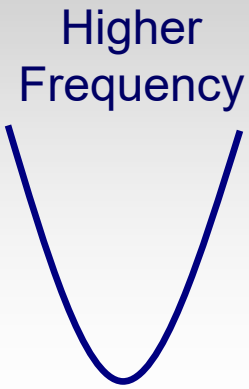
Energy v. Free Energy



Wide well

Higher Entropy

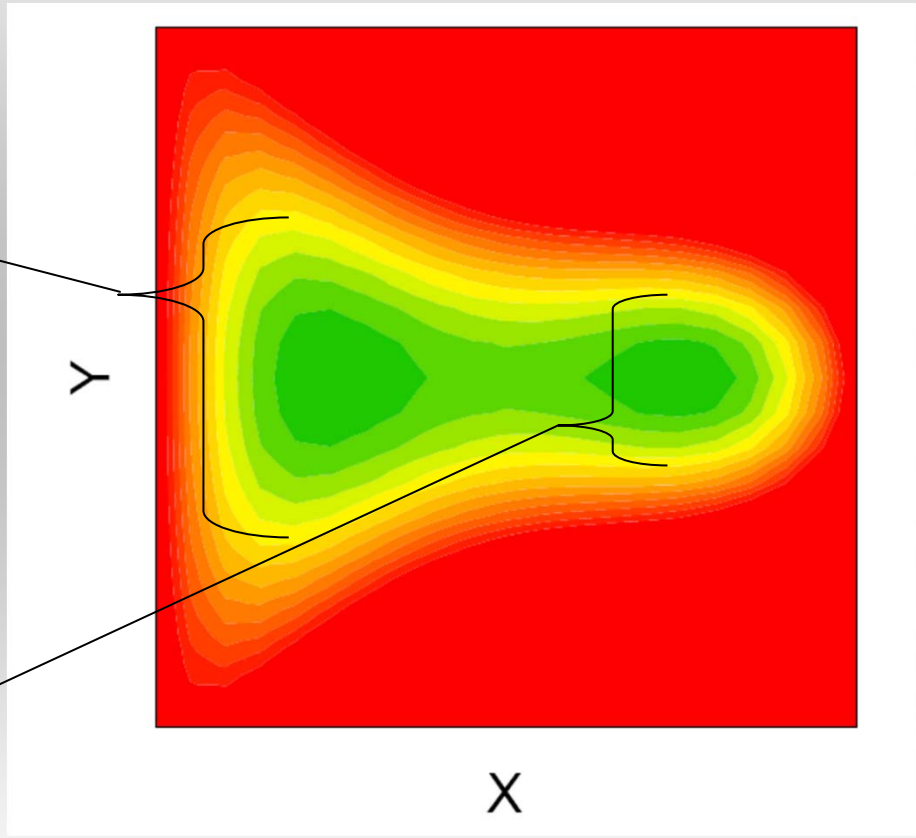
Lower Free Energy



Narrow well

Lower Entropy

High Free Energy



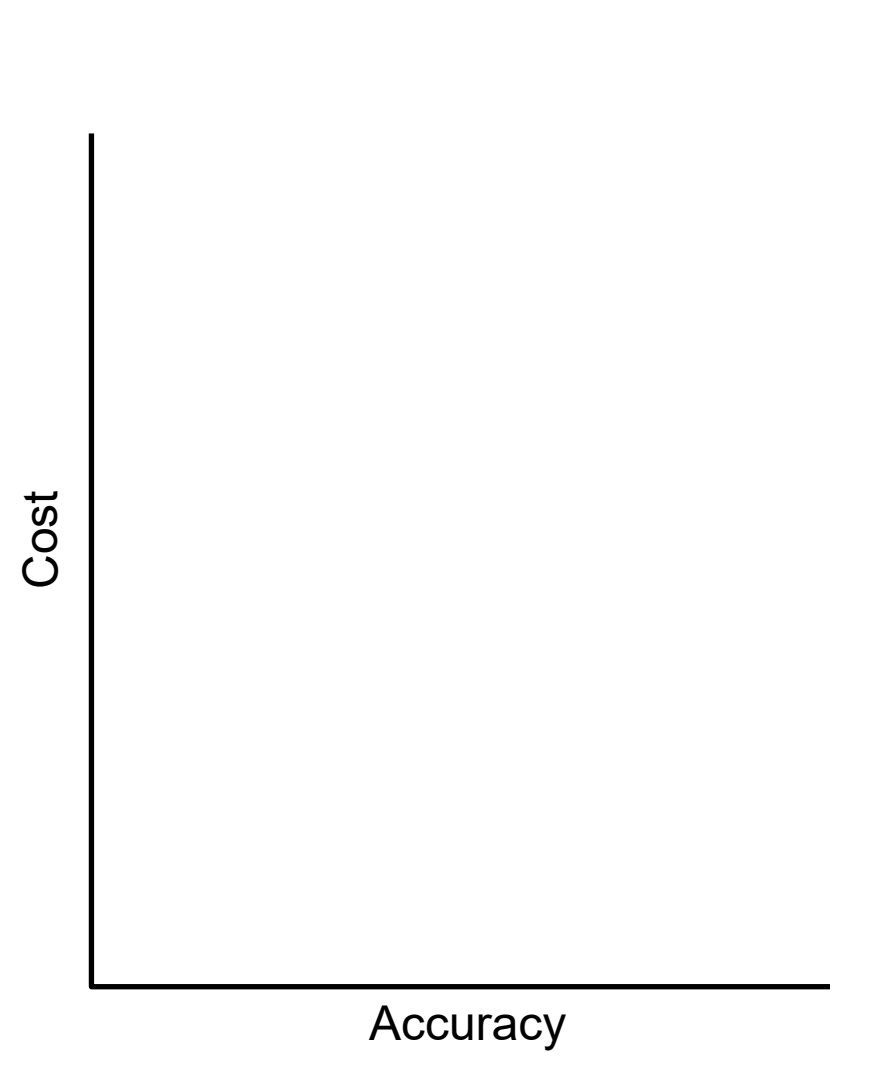
The PES isn’t everything

- Electronic properties can be calculated from the wavefunction
  - Dipole, quadrupole… moments
  - Atomic charges
  - Polarizabilities
  - IR intensities
  - NMR chemical shifts

Summary

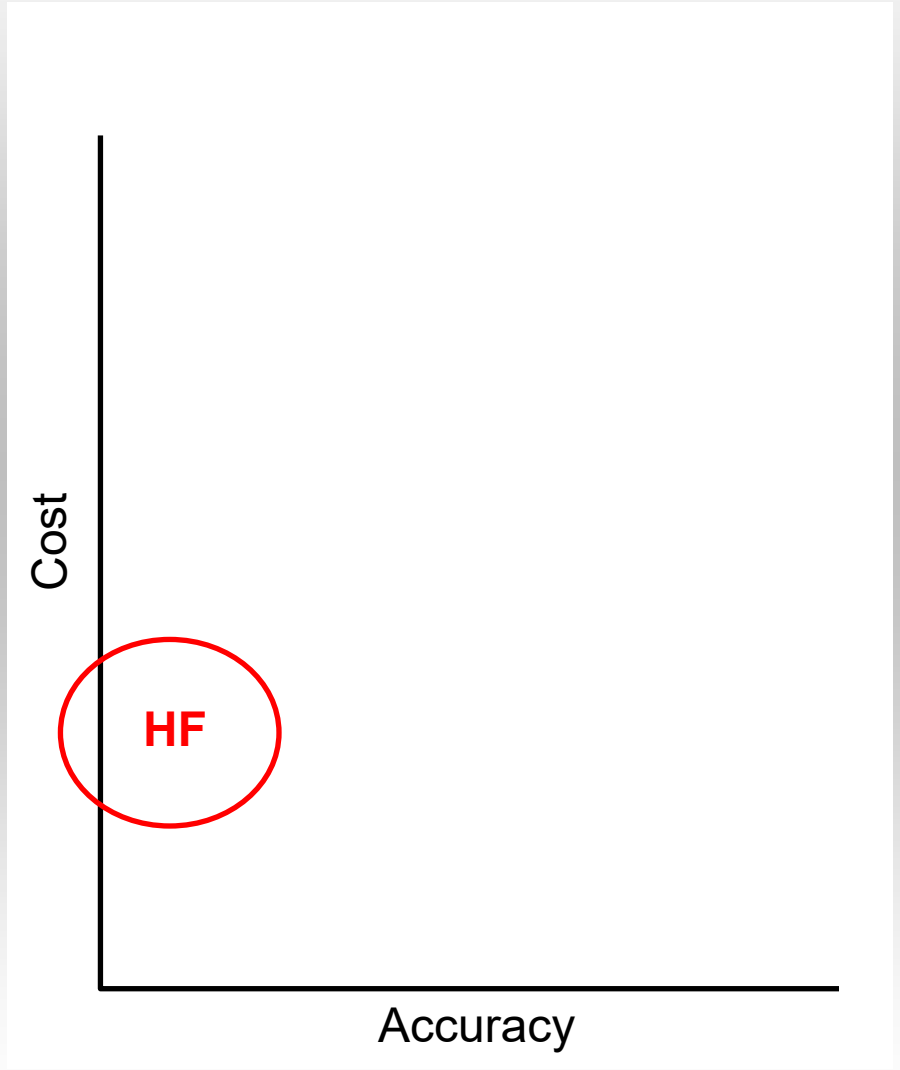
- The PES is the energy as a function of the location of the nuclei
- Stationary points (F=0) on the PES are representative of stable structures and transition states
- Non-parallelity error in the PES is bad; error cancellation is your friend
- We can calculate electronic properties from the wavefunction

The Hierarchy of Methods



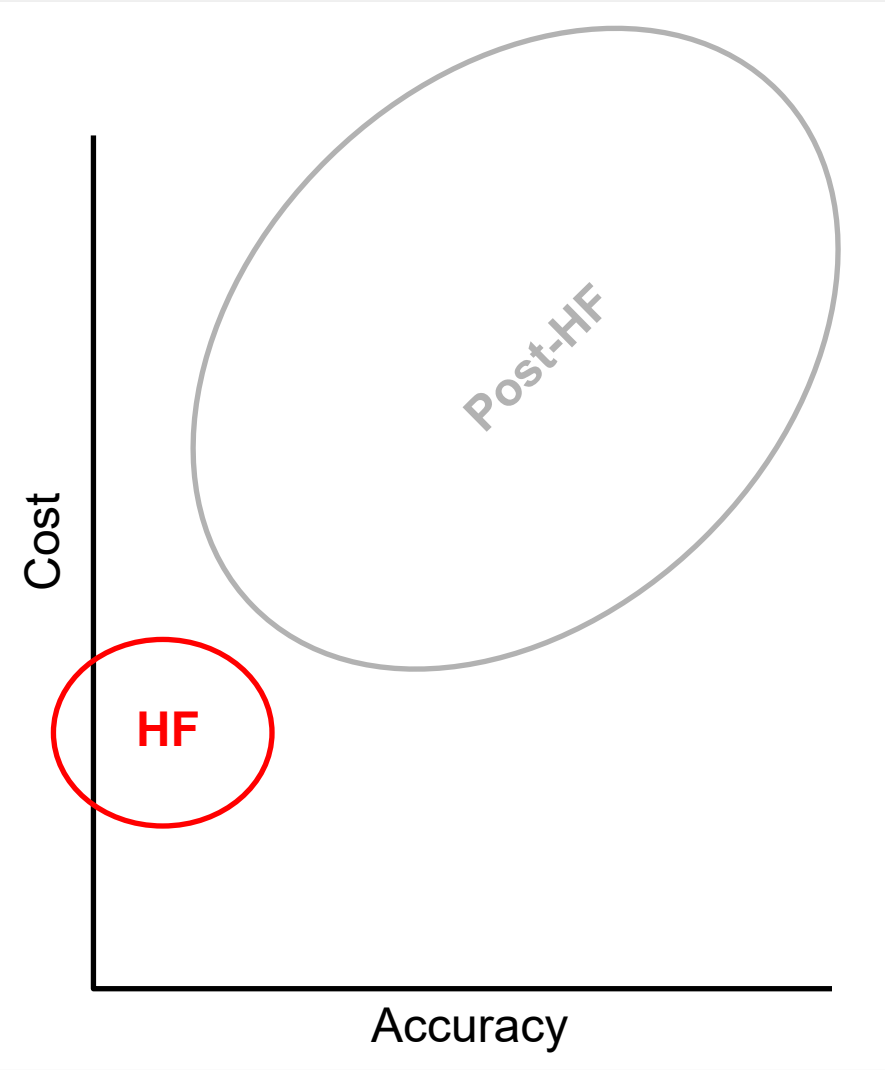
The Hierarchy of Methods

- Hartree-Fock (HF)



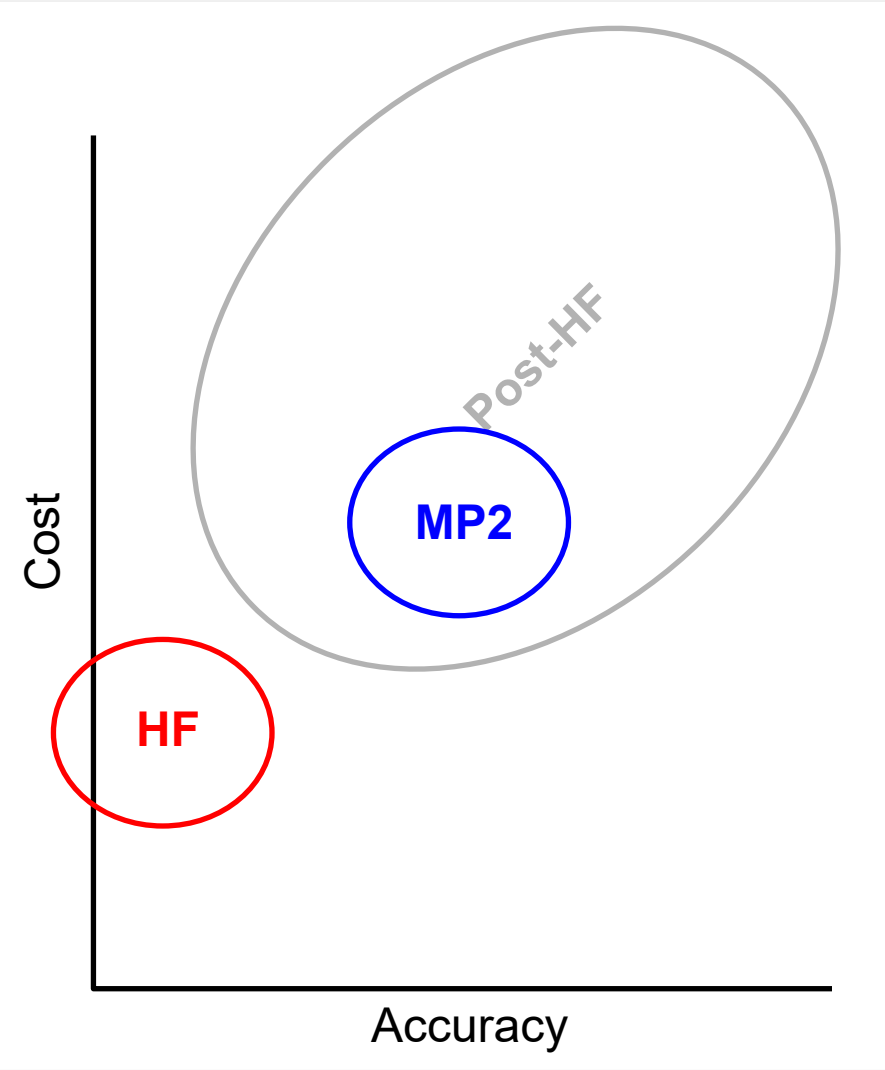
The Hierarchy of Methods

- Hartree-Fock (HF)
- Post-HF



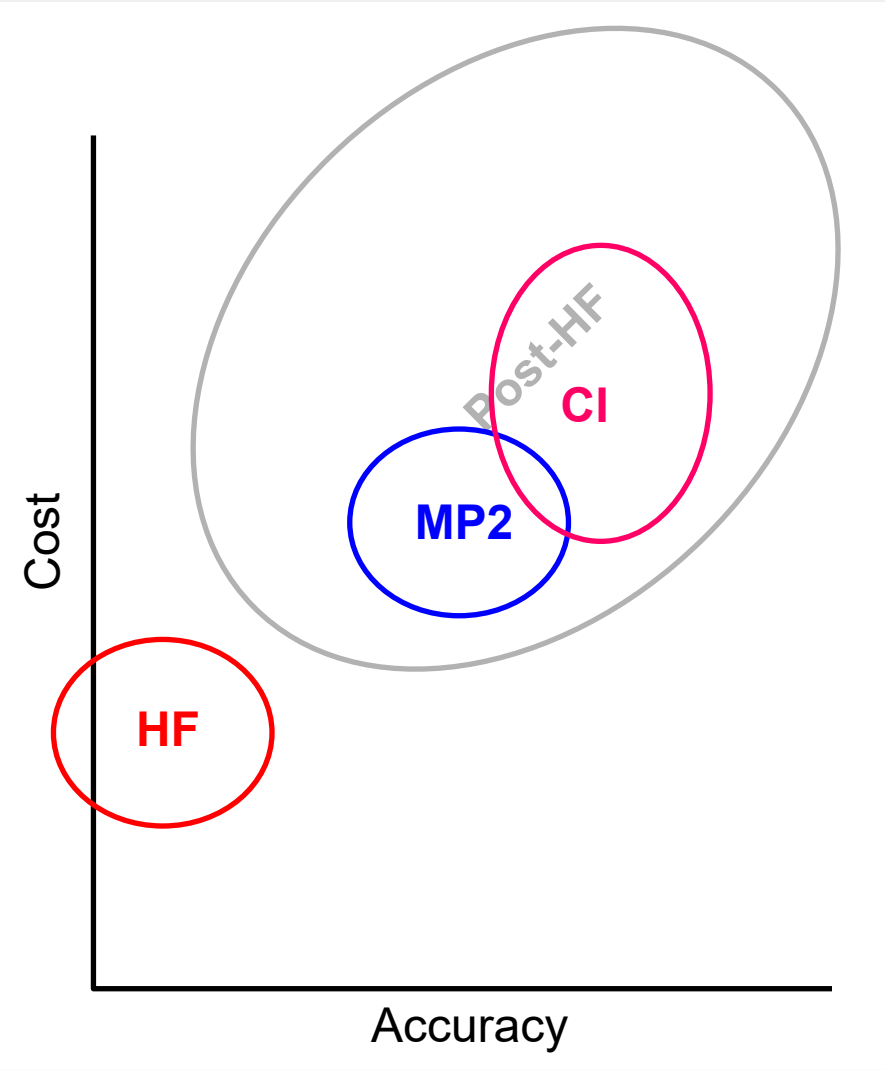
The Hierarchy of Methods

- Hartree-Fock (HF)
- Post-HF
  - Moller-Plesset Perturb. Theory (MP2)



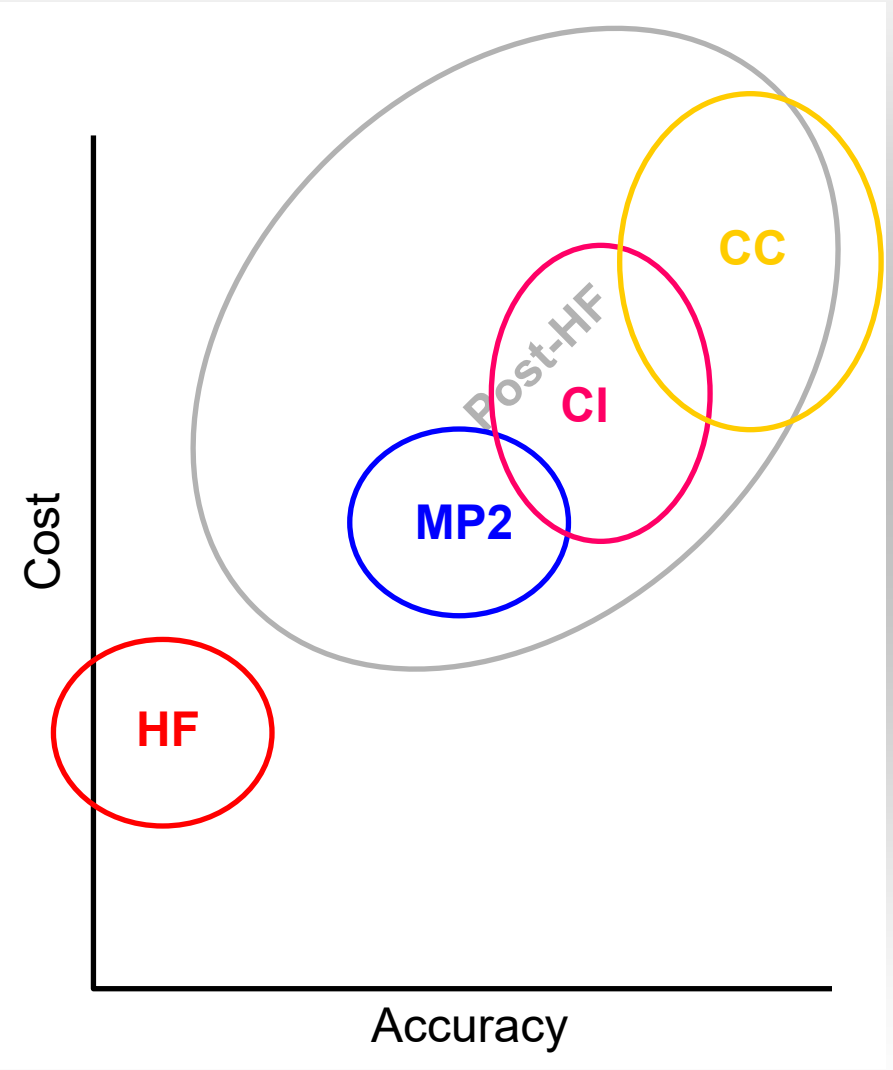
The Hierarchy of Methods

- Hartree-Fock (HF)
- Post-HF
  - Moller-Plesset Perturb. Theory (MP2)
  - Configuration Interaction (CI)



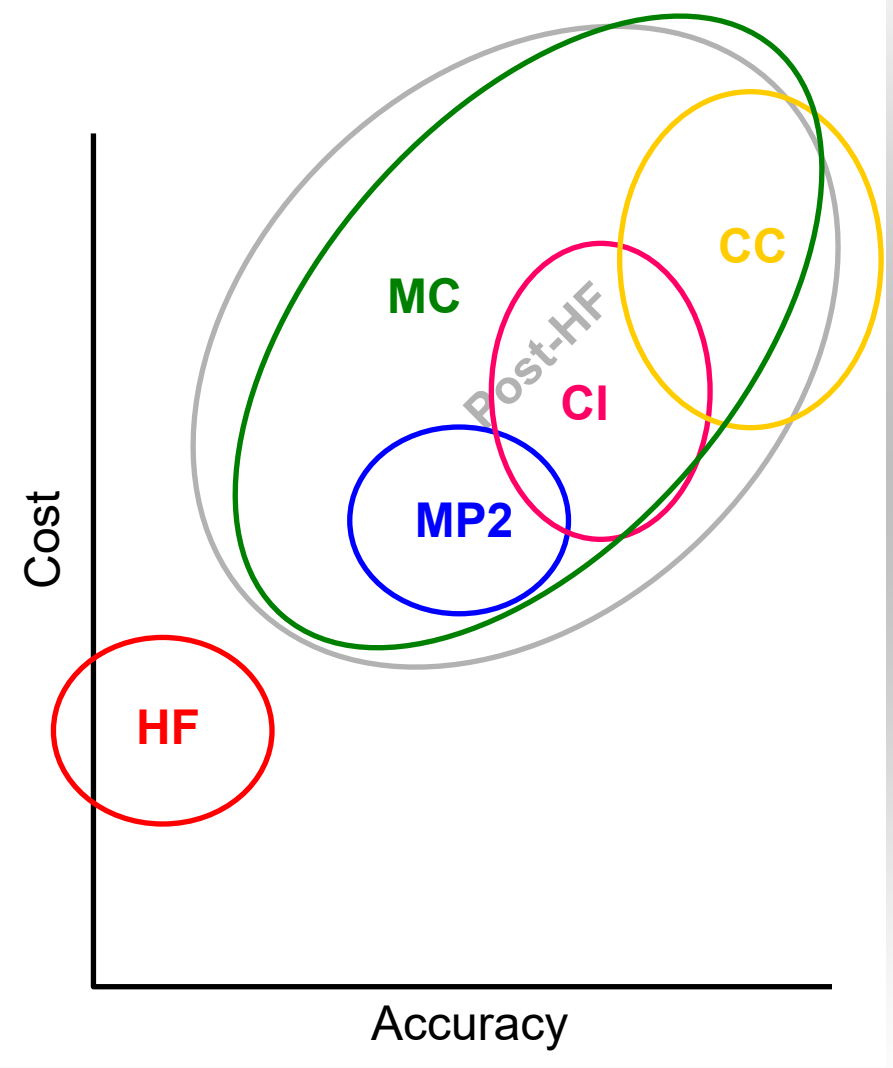
The Hierarchy of Methods

- Hartree-Fock (HF)
- Post-HF
  - Moller-Plesset Perturb. Theory (MP2)
  - Configuration Interaction (CI)
  - Coupled Cluster (CC)



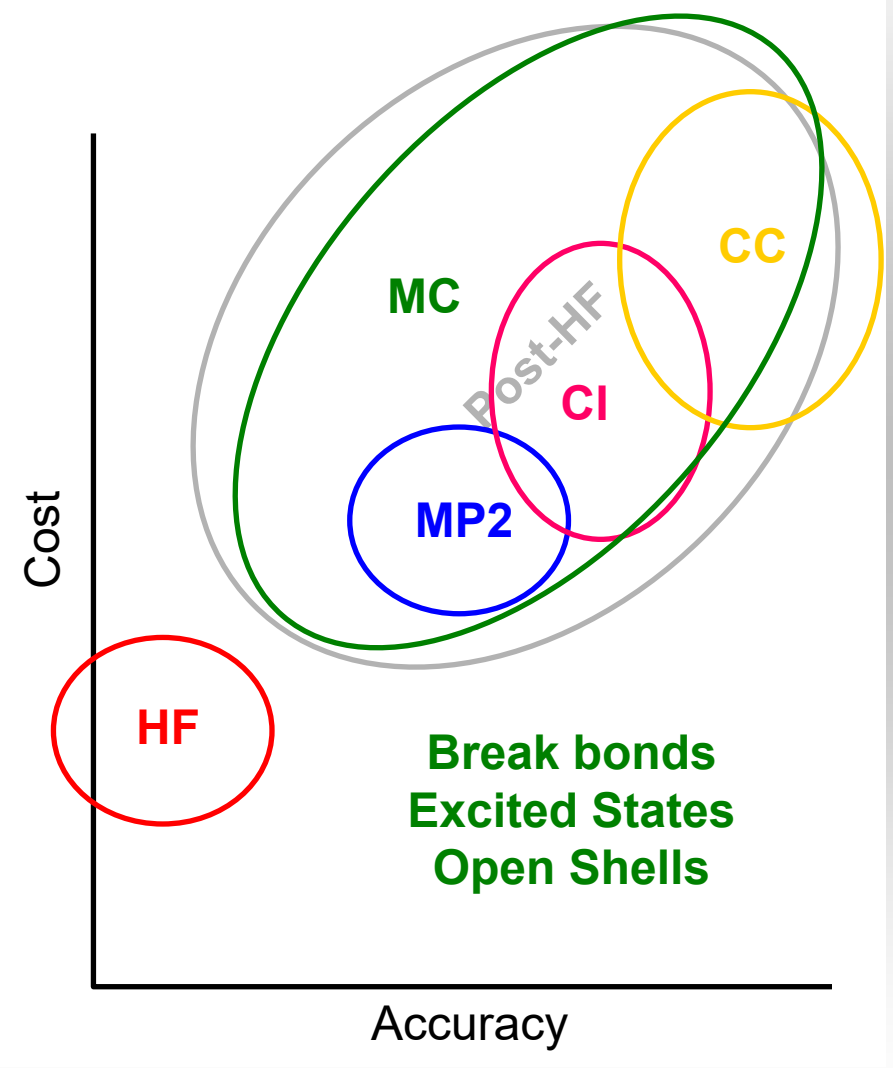
The Hierarchy of Methods

- Hartree-Fock (HF)
- Post-HF
  - Moller-Plesset Perturb. Theory (MP2)
  - Configuration Interaction (CI)
  - Coupled Cluster (CC)
  - Multiconfigurational Methods (MC)



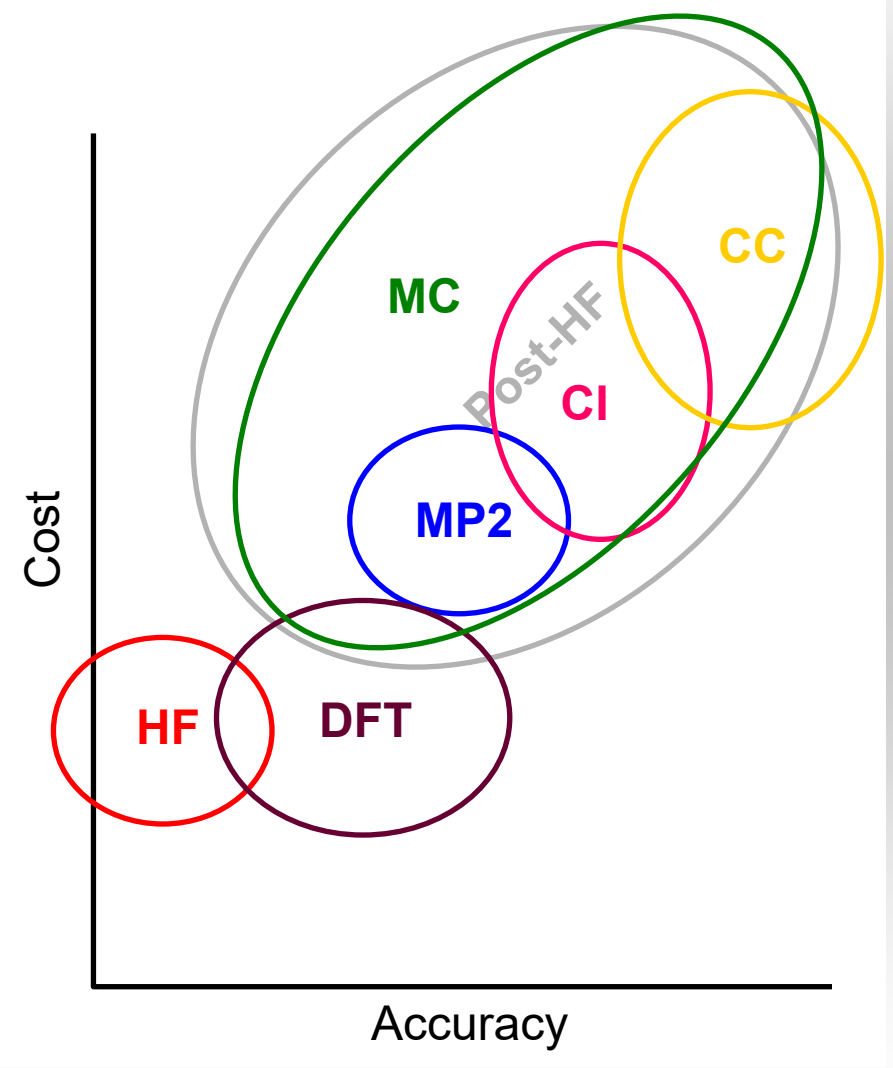
The Hierarchy of Methods

- Hartree-Fock (HF)
- Post-HF
  - Moller-Plesset Perturb. Theory (MP2)
  - Configuration Interaction (CI)
  - Coupled Cluster (CC)
  - Multiconfigurational Methods (MC)



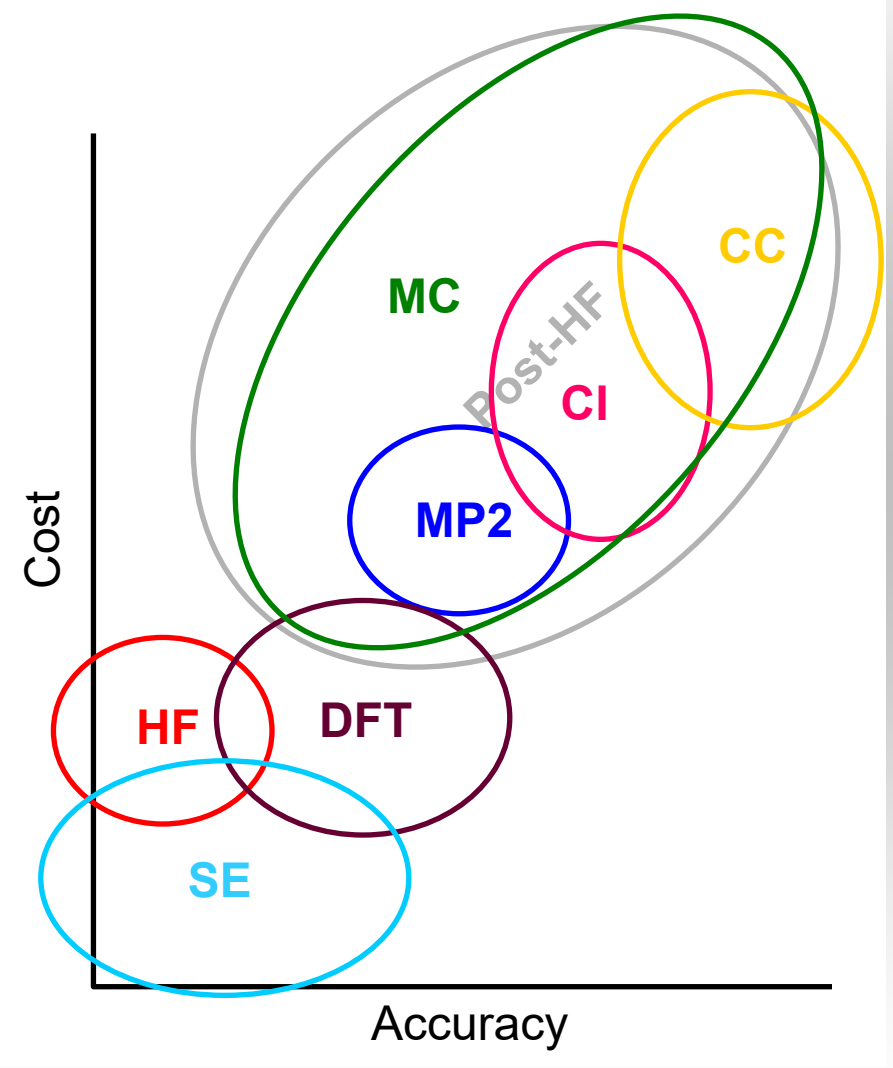
The Hierarchy of Methods

- Hartree-Fock (HF)
- Post-HF
  - Moller-Plesset Perturb. Theory (MP2)
  - Configuration Interaction (CI)
  - Coupled Cluster (CC)
  - Multiconfigurational Methods (MC)
- Density Functional Theory (DFT)



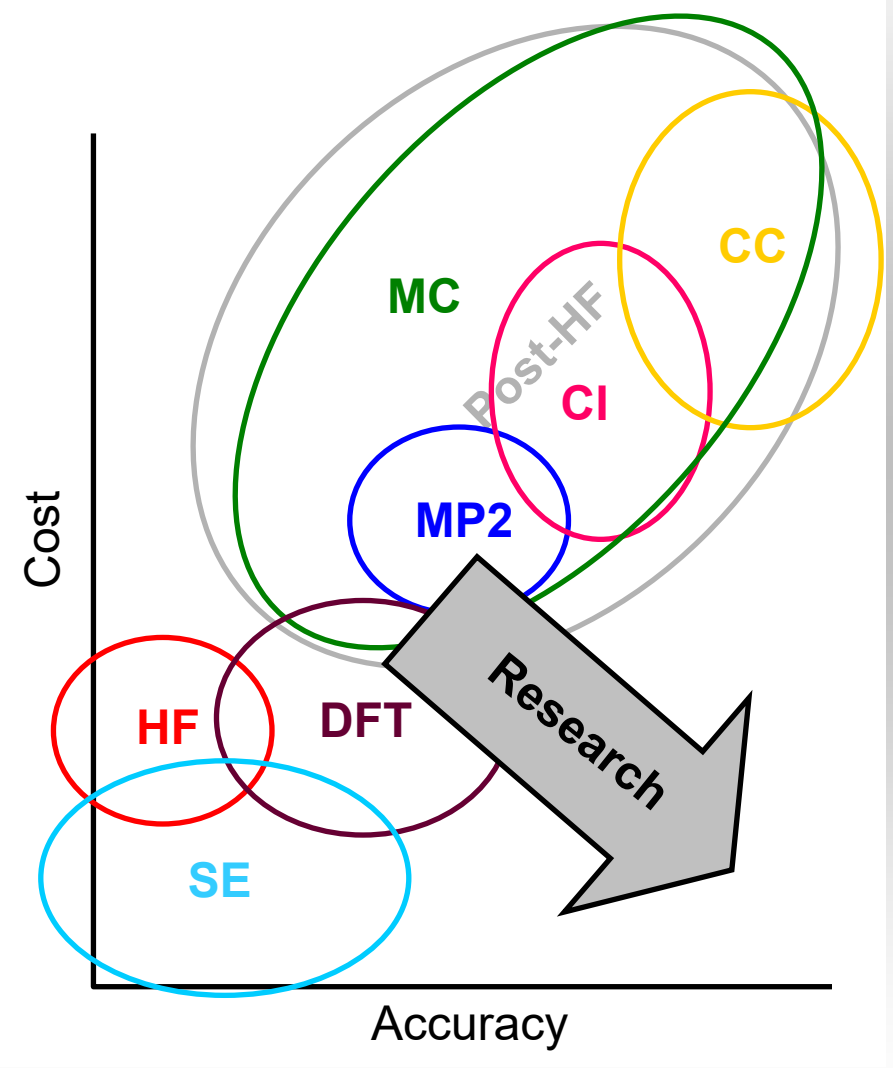
The Hierarchy of Methods

- Hartree-Fock (HF)
- Post-HF
  - Moller-Plesset Perturb. Theory (MP2)
  - Configuration Interaction (CI)
  - Coupled Cluster (CC)
  - Multiconfigurational Methods (MC)
- Density Functional Theory (DFT)
- Semiempirical (SE)



The Hierarchy of Methods

- Hartree-Fock (HF)
- Post-HF
  - Moller-Plesset Perturb. Theory (MP2)
  - Configuration Interaction (CI)
  - Coupled Cluster (CC)
  - Multiconfigurational Methods (MC)
- Density Functional Theory (DFT)
- Semiempirical (SE)



Coming Up Next

- Linear Algebra Review
- Superposition principle
- Variational Principle
- Basis Sets and the relationship between matrices and operators
- Hartree-Fock Approximation
  - What is it?
  - How is it implemented in the computer?
  - When does it fail and why?