Time Independent Schrödinger Equation for Multi-electron Systems

MERCURY Workshop 2025

Exact Methods

Time-Independent Schrödinger Equation

Hamiltonian $\longrightarrow$ $$\widehat{H}\Psi = E\Psi$$ $\longleftarrow$ Wavefunction

Systems differ definition of Hamiltonian

e.g. H-atom

$$\widehat{H} = \widehat{T}_e + \widehat{V}_{Ne}$$

Electron Kinetic Energy   **Nuclear-Electronic Potential**

$$= \frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

Exact Methods

Solve differential equation

$$\left(\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} \right) \Psi_{nlm}(r,\theta,\phi) = E_n \Psi_{nlm}(r,\theta,\phi)$$

$$E_n = \frac{-e^2}{8\pi\varepsilon_0 a_0 n^2}$$

$$\Psi_{n\ell m}(r,\theta,\phi) = R_{nl}(r) Y_\ell^m(\theta,\phi)$$

Potentially messy but possible for 1 electron systems

From exact to approximate in one electron

- One electron systems can usually be solved exactly

  ⇒ Particle in a box
  ⇒ Particle on a ring
  ⇒ Particle on a sphere
  ⇒ Hydrogen and hydrogen-like atoms

- ≥2 electrons create a system that cannot be solved exactly

  ⇒ He
  ⇒ H_2
  ⇒ Almost anything else

Multi-electron systems

Time-Independent Schrödinger Equation

Hamiltonian →

$$\widehat{H}\Psi = E\Psi$$

← Wavefunction

$$\widehat{H} = \widehat{T}_N + \widehat{T}_e + \widehat{V}_{NN} + \widehat{V}_{Ne} + \widehat{V}_{ee}$$

Nuclear Kinetic Energy	Electron Kinetic Energy	Nuclear Potential	Nuclear-Electronic Potential	Electron-Electron Potential
$-\sum_I^N \frac{1}{2M_I}\nabla_I^2$	$-\frac{1}{2}\sum_i^n \nabla_i^2$	$\sum_{I,J>I}^N \frac{Z_I Z_J}{\|R_I - R_J\|}$	$\sum_i^n \sum_I^N \frac{Z_I}{\|r_i - R_I\|}$	$\sum_{i,j>i}^n \frac{1}{\|r_i - r_j\|}$

Atomic Units:
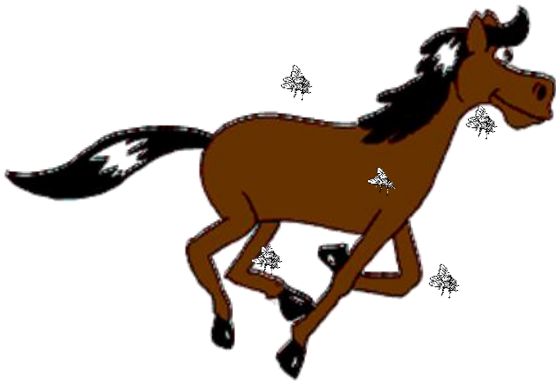$e = \hbar = m_e = 4\pi\varepsilon_0 = 1$
Energy = 1 E_h = 27.21 eV
Distance = 1 a_0 = 0.52 Å

Born-Oppenheimer Approximation

Separate nuclear and electronic motion

Treat electrons and nuclei separately
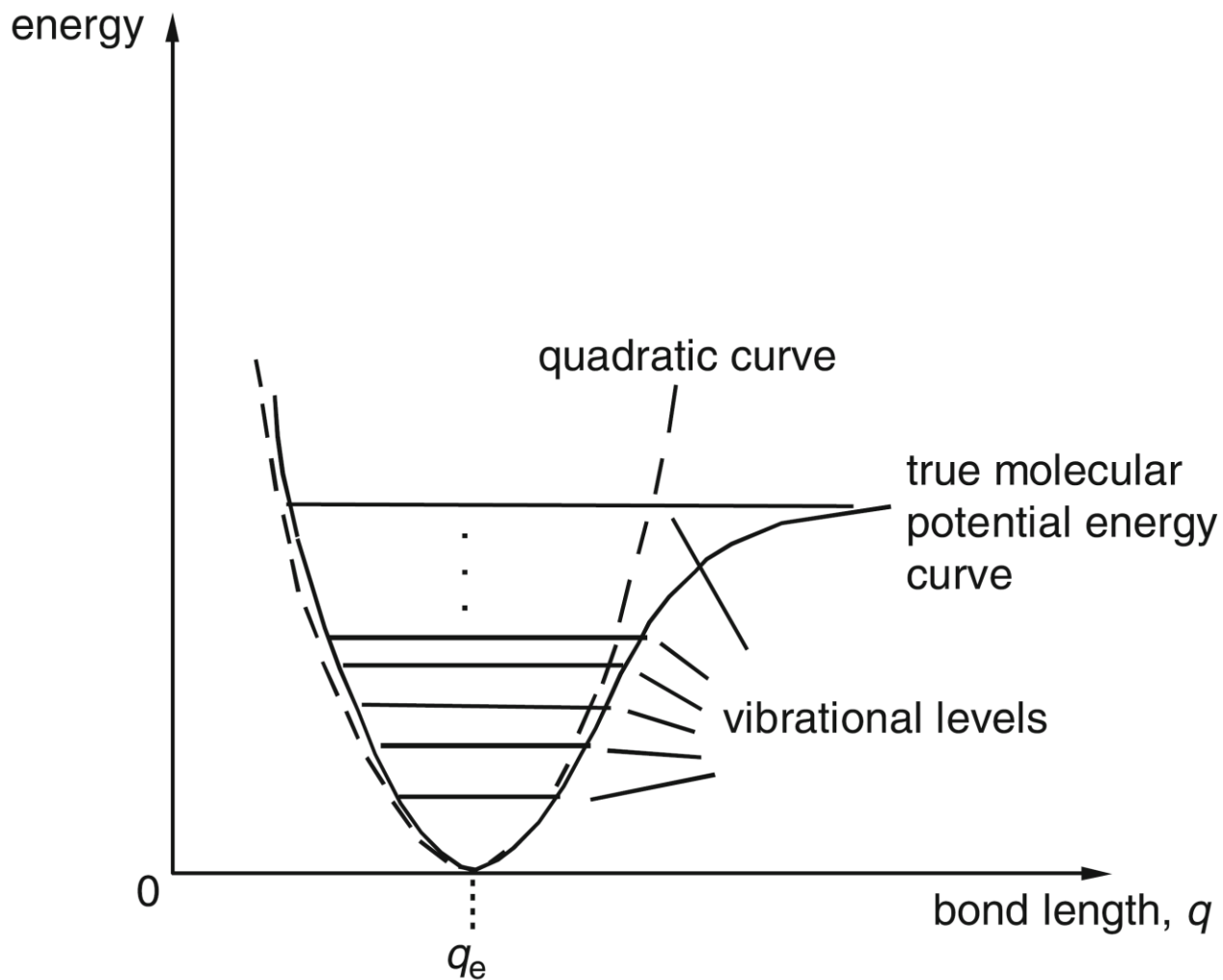 ⇒ Quantum electrons
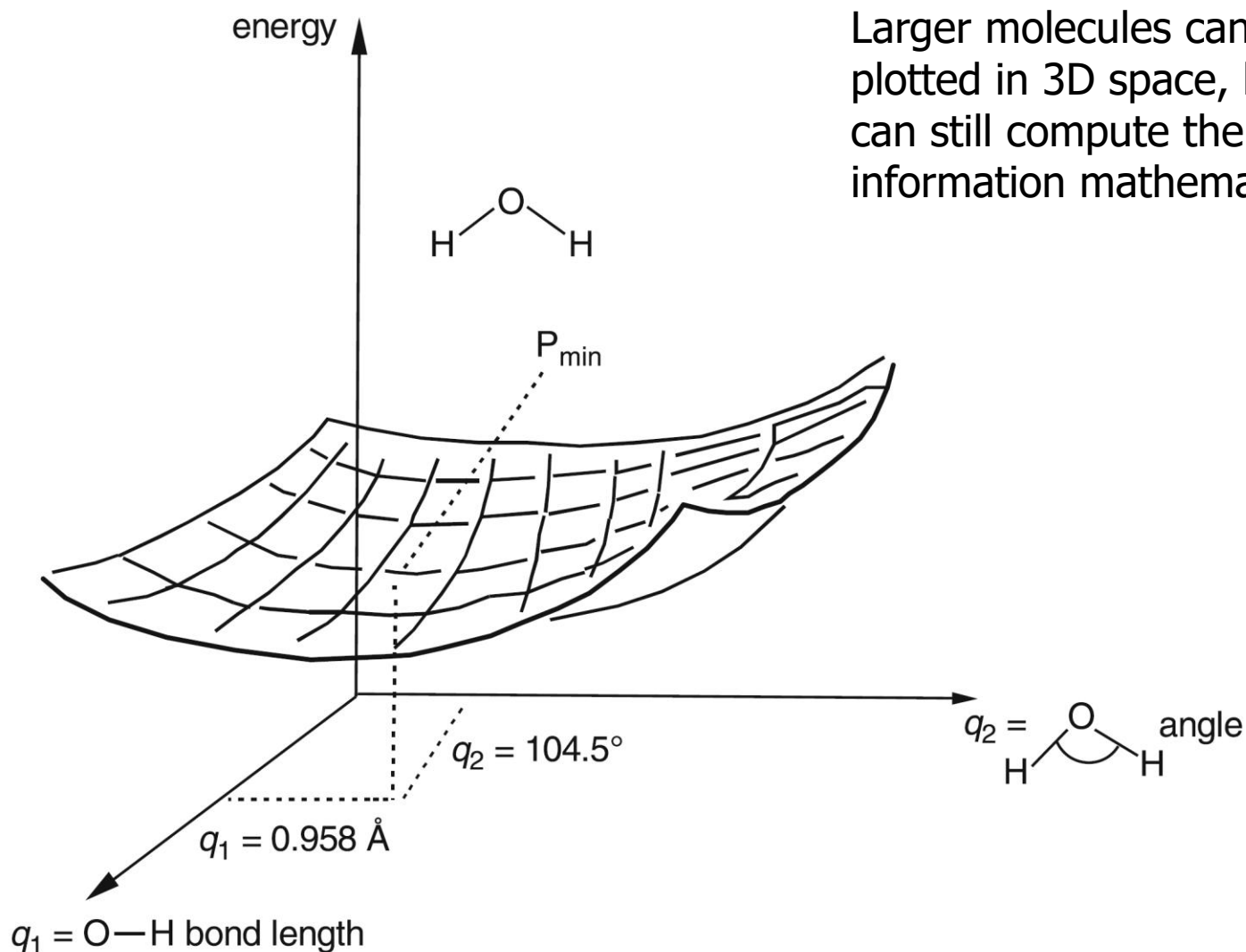 ⇒ Classical nuclei

Full Potential Energy Surface

Solve electronic Schrödinger equation at ALL possible nuclear coordinates

- Gives relationship of molecule energy to its geometry

- Fix R, compute electronic structure

- Usually not feasible
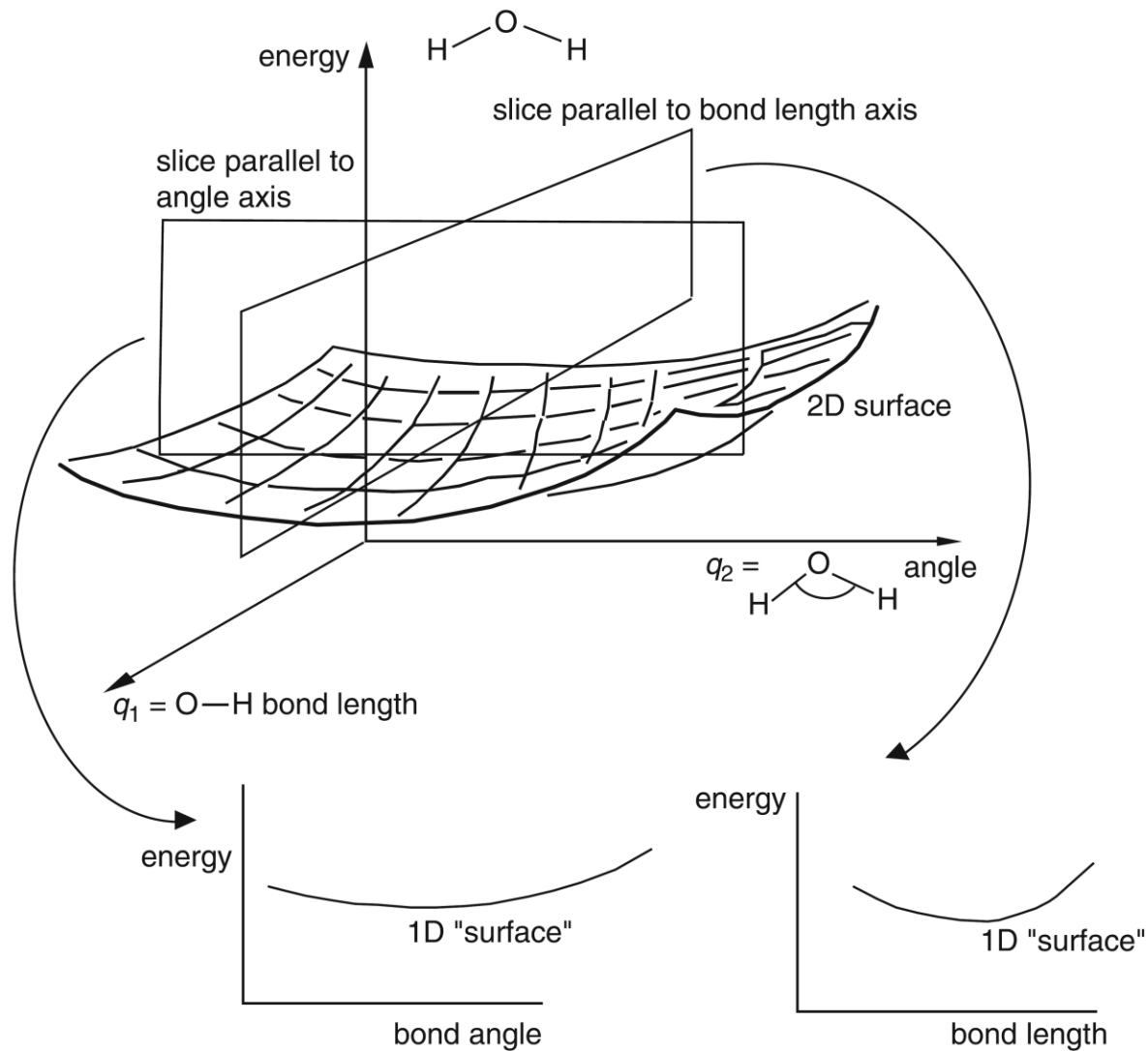
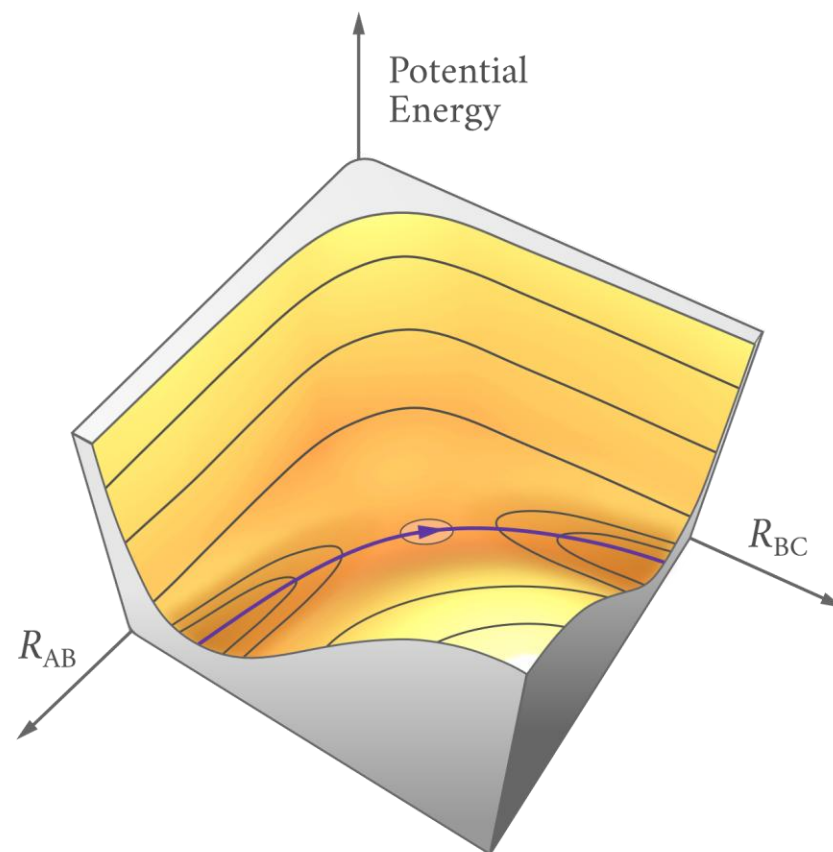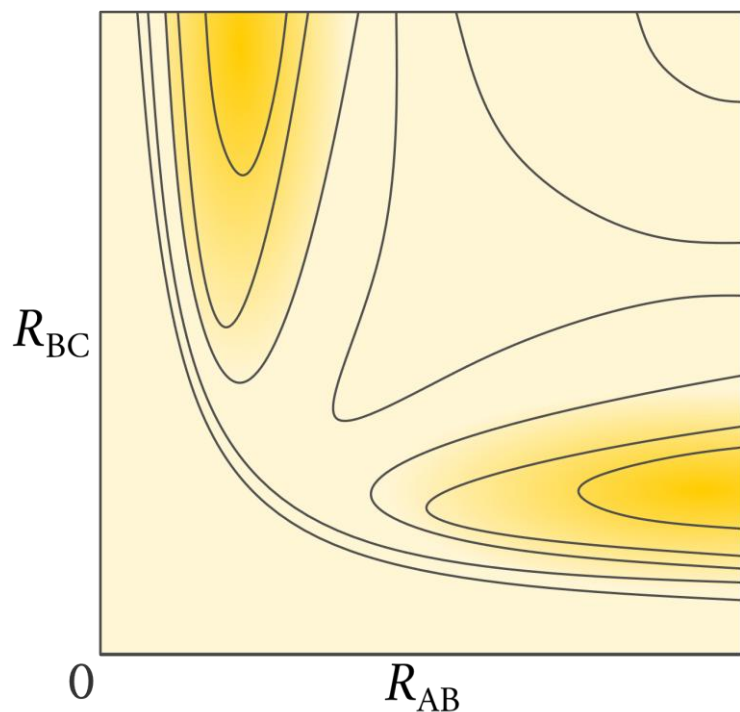 ⇒ 3N-5 or 6 (N=number of atoms) nuclear coordinates

2-Atom PES
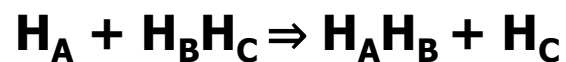

Figure from Computational Chemistry E. Lewars

3-Atom PES (H_2O symmetric bonds)

Larger molecules cannot be plotted in 3D space, but we can still compute the information mathematcially

Figure from Computational Chemistry E. Lewars

3-Atom PES (H$_2$O symmetric bonds)

Figure from Computational Chemistry E. Lewars

3-Atom PES (reaction)

$$H_A + H_BH_C \Rightarrow H_AH_B + H_C$$

https://chem.libretexts.org/@go/page/14571
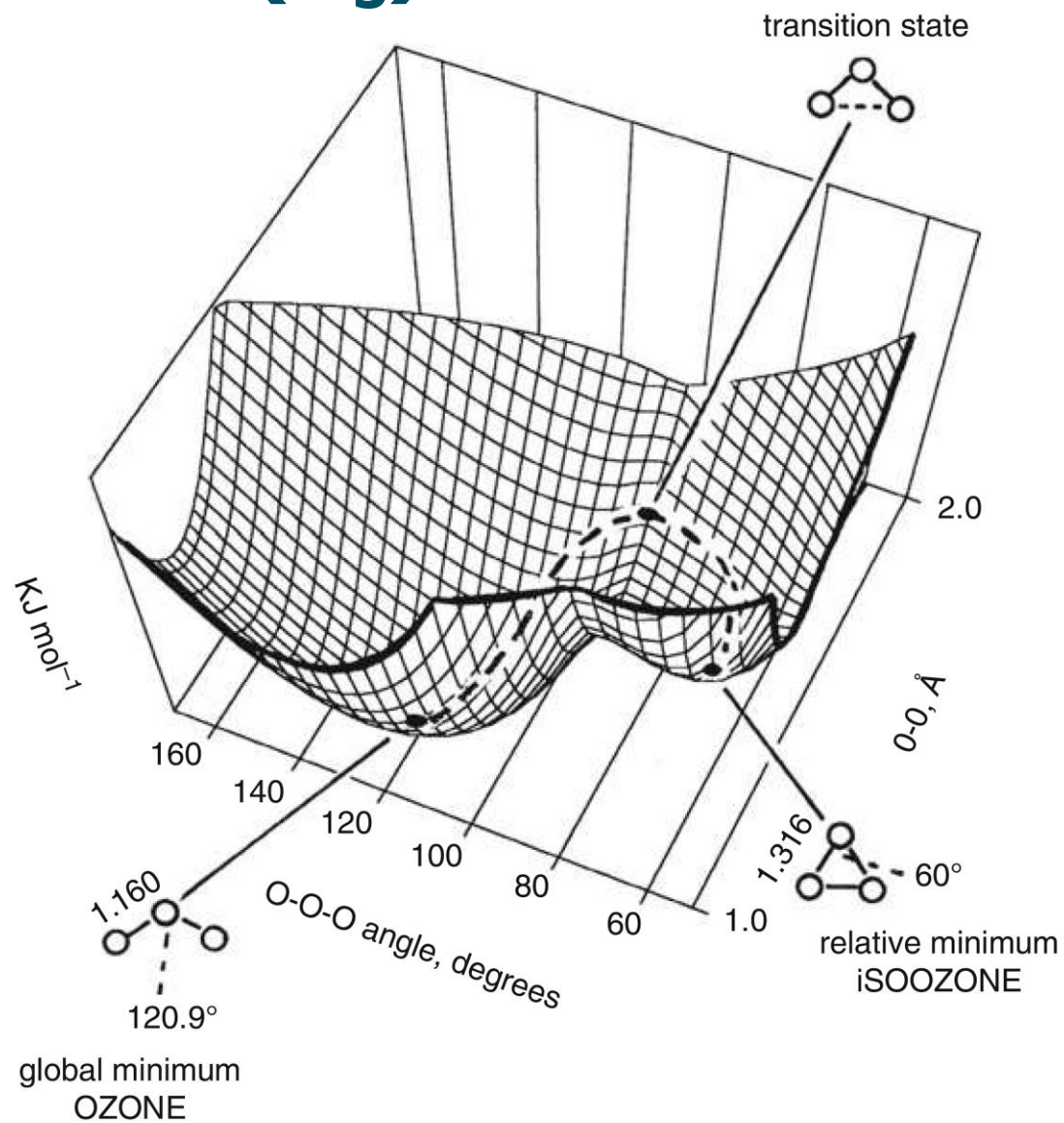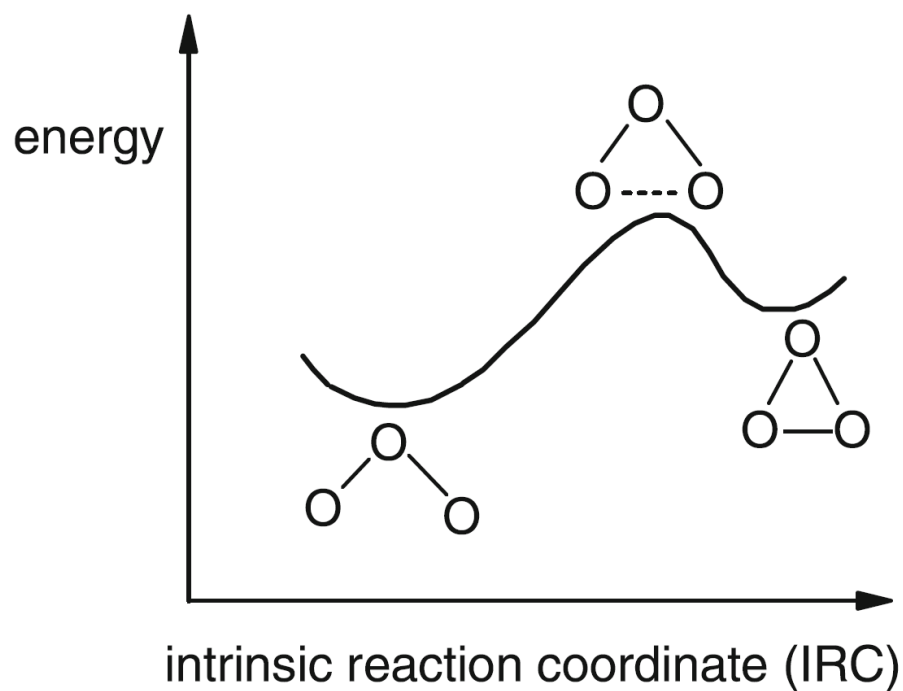
3-Atom PES (O₃)

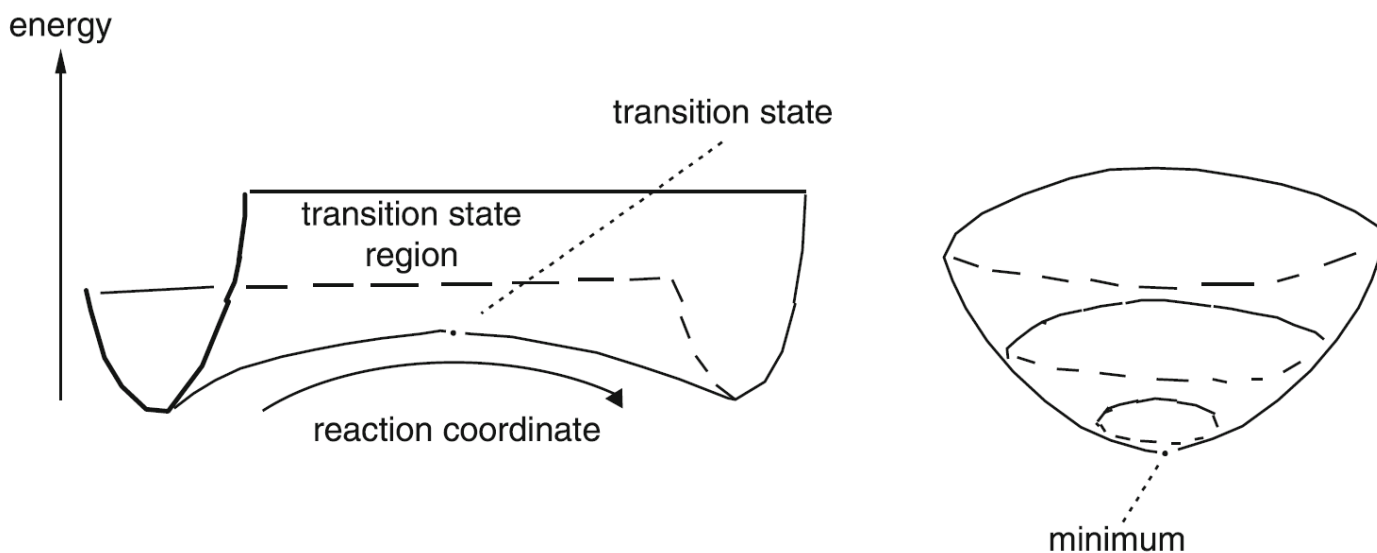Figure from Computational Chemistry E. Lewars
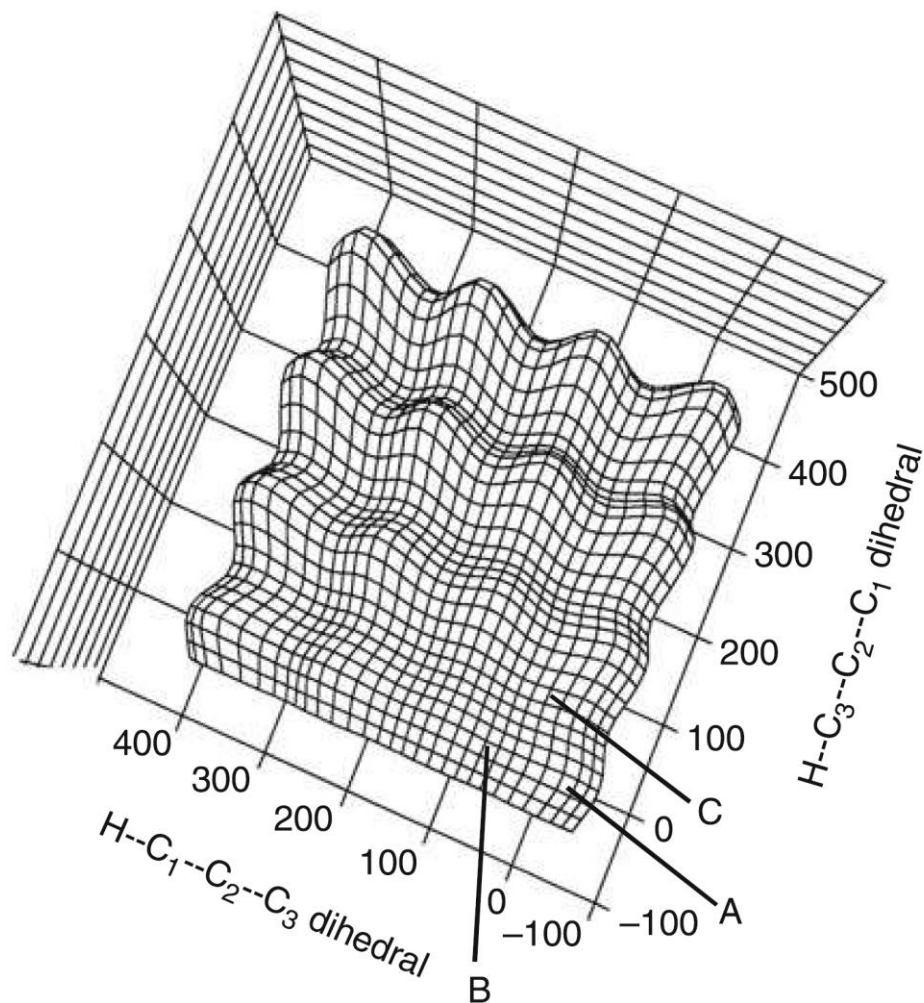
3-Atom PES (O₃)

PES Extrema

What is the difference in these points mathematically?

Figure from Computational Chemistry E. Lewars

$Minimum: \dfrac{\partial^2 E}{\partial q_i^2} > 0$

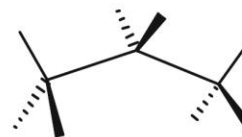$Transition\ State: \dfrac{\partial^2 E}{\partial q_i^2} > 0,\ except\ along\ the\ reaction\ coordinate$

Propane PES

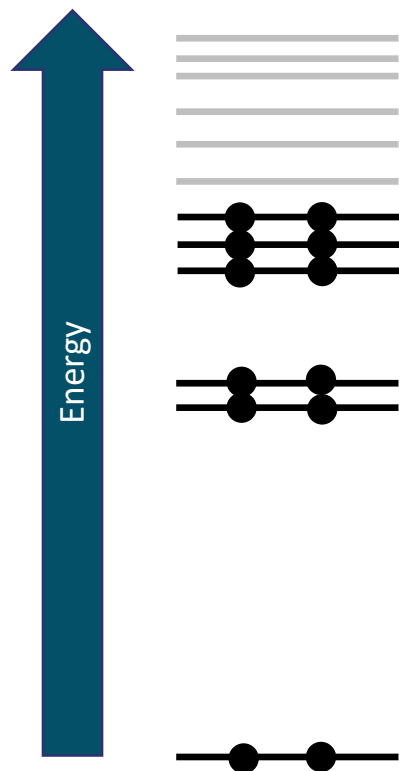Figure from Computational Chemistry E. Lewars

Ground State

Minimum energy for Schrödinger equation at a given set of coordinates
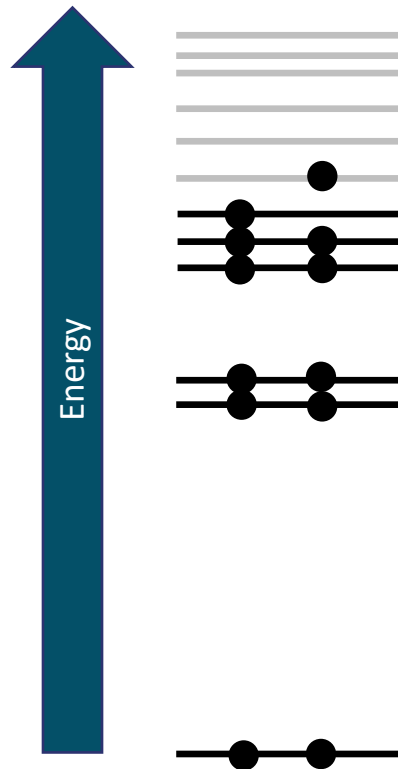
$$\widehat{H}\Psi_0 = E_0\Psi_0$$

Energy

"Add" energy of individual occupied orbitals to get total energy
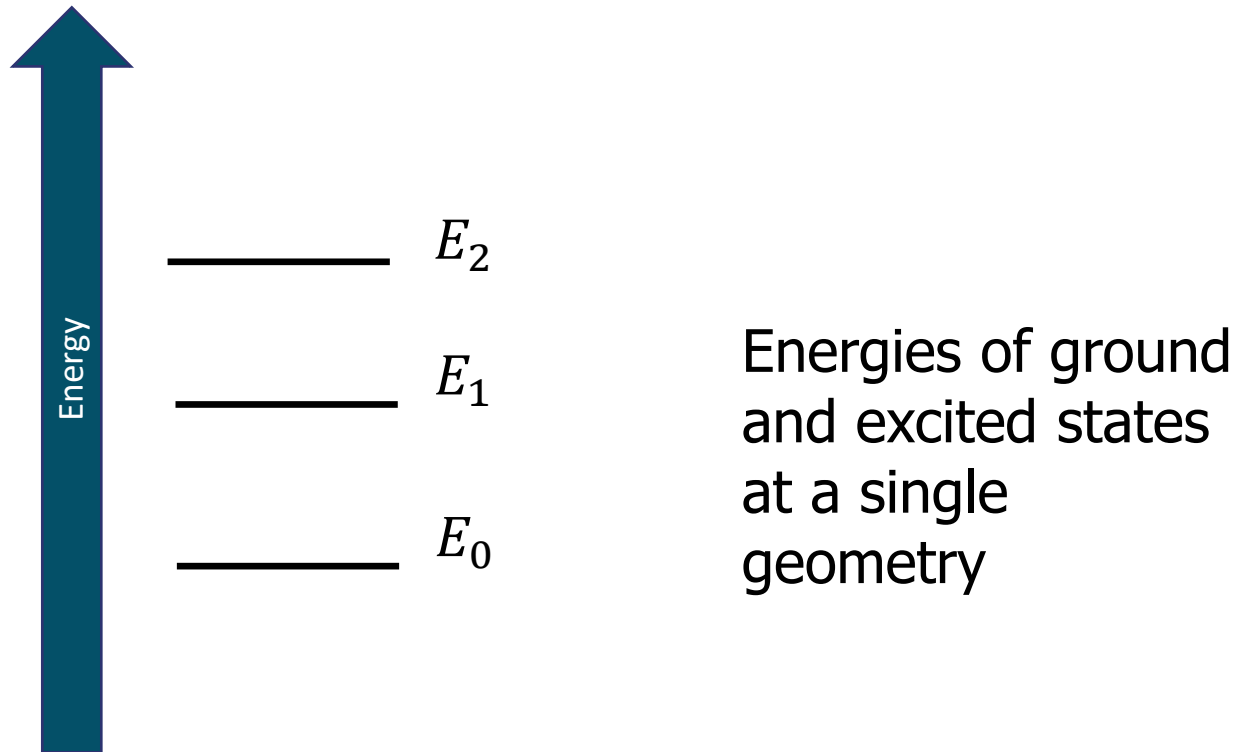
Excited States

Higher energy for Schrödinger equation at a given set of coordinates

$$\hat{H}\Psi_1 = E_1\Psi_1$$

Energy

Excited States

Higher energy for Schrödinger equation at a given set of coordinates

Energy

$$E_2$$ _____

$$E_1$$ _____

$$E_0$$ _____

Energies of ground and excited states at a single geometry
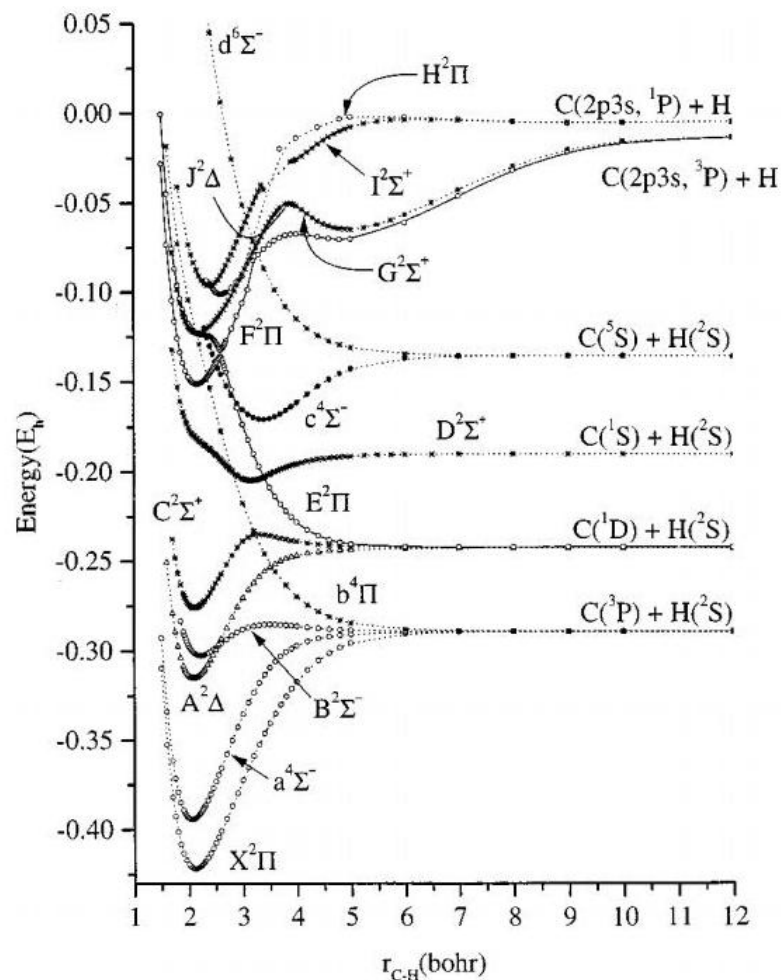
Potential energy of ground and excited states for CH

FIG. 1. Potential energy curves of the lowest 11 valence and 4 Rydberg states of CH. All energies have been shifted by +38.00 hartree.

A. Kalemos, A. Mavridis, A. Metropoulos, J. Chem. Phys. **111**, 9536 (1999)

Quantum Chemistry Calculations

Types

- **Single point calculation: Evaluate energy at a given set of atomic coordinates**

- **Geometry Optimization: Locate minimum on PES**

- Saddle Point Search: Locate transition state on PES

Dependent on starting point, gives closest minimum
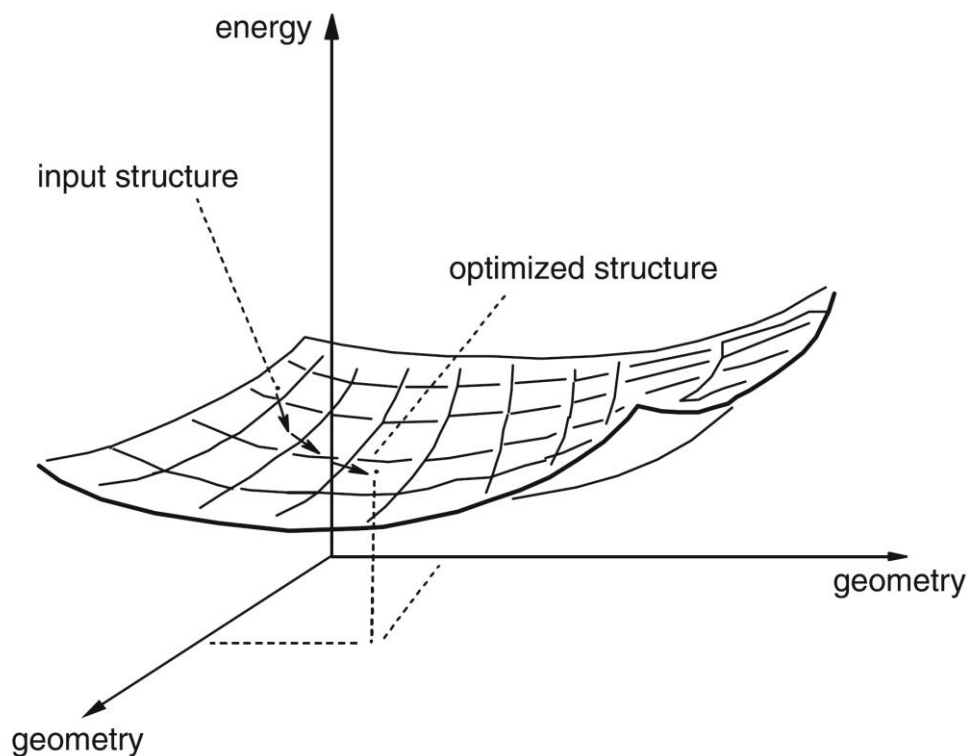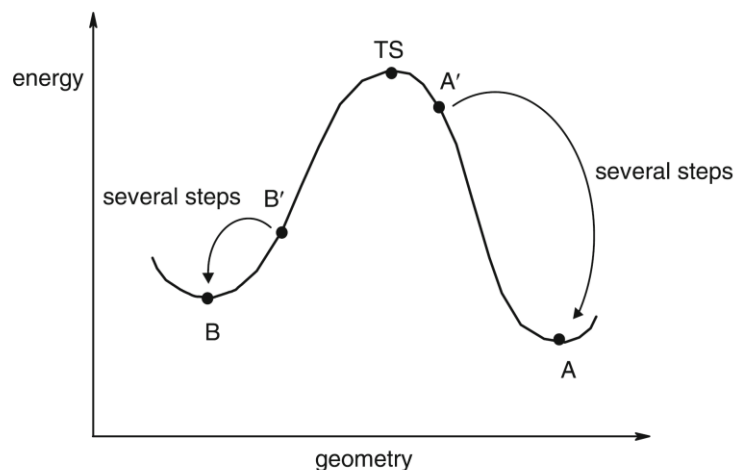
Quantum Chemistry Calculations

Types

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- Saddle Point Search: Locate transition state on PES

Add-Ons

- **IR: Frequency calculation (determine curvature)**

- Thermodynamics: evaluate entropy and free energy

- **UV-vis: Calculate excited states (higher energy PES)**

- NMR: Calculate absolute chemical shifts

- Raman

- ΔH_f

- NBO (natural bonding orbitals)

Multi-electron systems

Time-Independent Schrödinger Equation

Hamiltonian $\longrightarrow$ $\widehat{H}\Psi = E\Psi$ $\longleftarrow$ Wavefunction

$$\widehat{H} = \widehat{T}_N + \widehat{T}_e + \widehat{V}_{NN} + \widehat{V}_{Ne} + \widehat{V}_{ee}$$

$$\widehat{H}_e = \widehat{T}_e + \widehat{V}_{Ne} + \widehat{V}_{ee}$$

Electron Kinetic Energy

Nuclear-Electronic Potential

Electron-Electron Potential

Many-electron wavefunction

- Simple product does not account for anti-symmetry
- Anti-symmetry: wavefuntion changes sign after changing any two electron indices

$$\Psi(r_1, r_2, \ldots, r_n) = -\Psi(r_2, r_1, \ldots, r_n)$$

$$\Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(r_1) & \psi_2(r_1) & \cdots & \psi_n(r_1) \\ \psi_1(r_2) & \psi_2(r_2) & \cdots & \psi_n(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(r_n) & \psi_2(r_n) & \cdots & \psi_n(r_n) \end{vmatrix}$$

$$= |\psi_1 \psi_2 \ldots \psi_n\rangle = |1, 2 \ldots n\rangle$$

Multi-electron systems

Electron-electron interaction makes it unsolvable

- Approximation methods to the rescue!

  ⇒ **Variational Method**
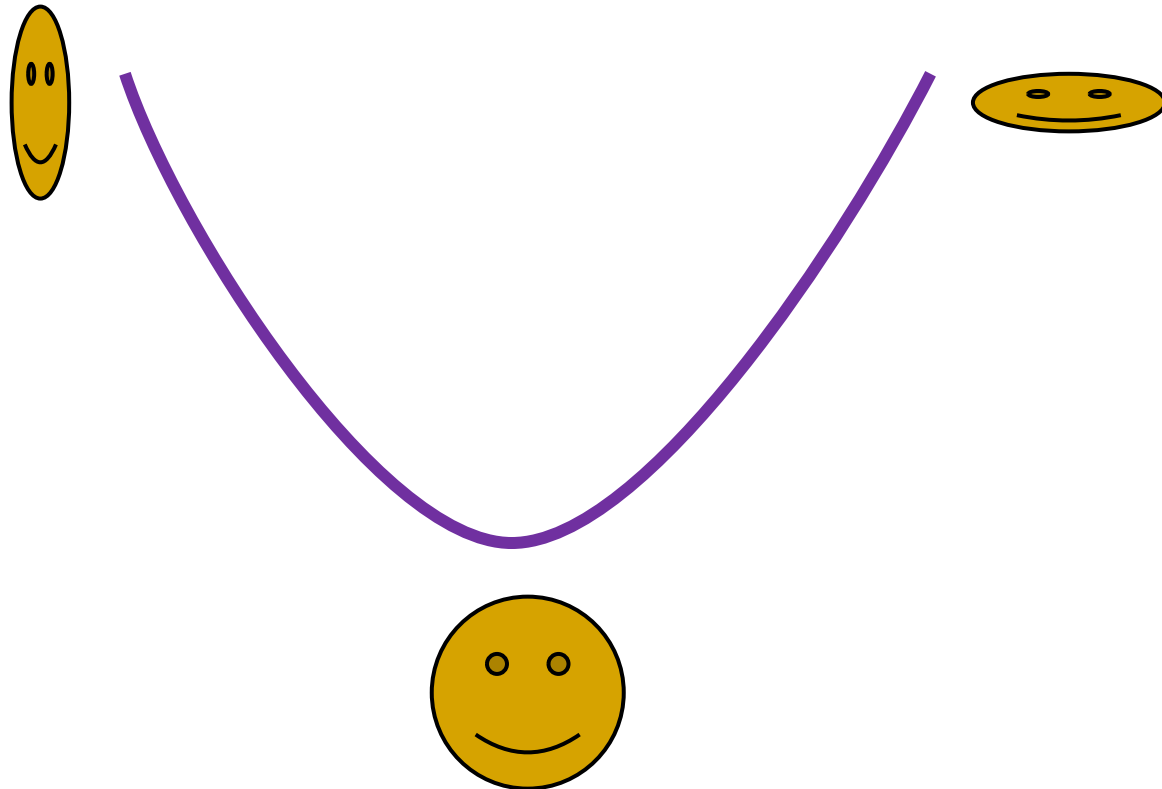
  ⇒ Perturbation Theory

Variational Principle

Any trial function Ψ_{trial} has energy E_{trial} greater than or equal to the true ground state energy E_0

$$E_{trial} \geq E_0$$

Equal only when $\Psi_{trial} = \Psi_0$

Variational Method

- Guess trial function with adjustable parameters
- Optimize parameters to obtain lowest possible energy

Self-Consistent Field (Hartree-Fock) Method

- Method used to find "best" unknown wavefunction
- Computers can solve these types of problems very efficiently