

# Lecture 1

# Elementary Quantum Mechanics

Potential-energy surface; wavefunction; Schrödinger equation; 1-D particle in a box

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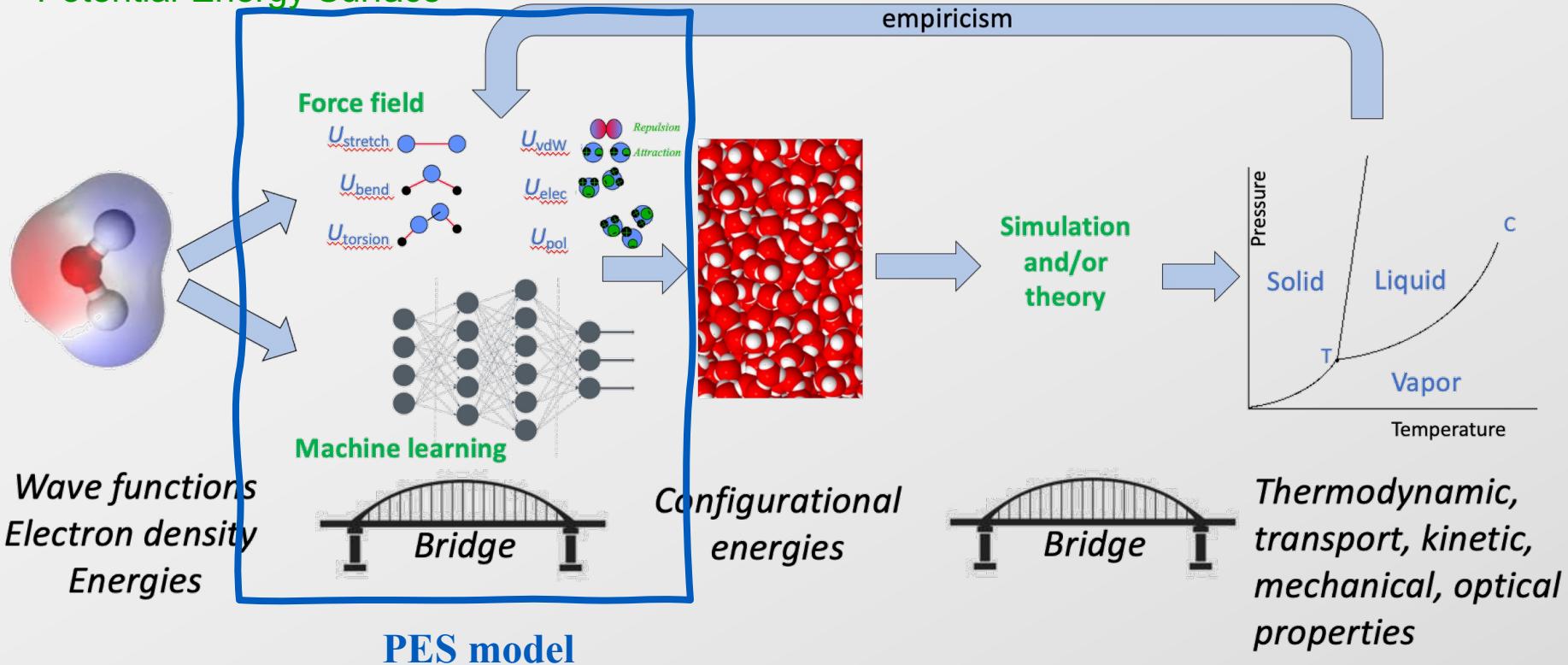
*CE 500 – Modeling Potential-Energy Surfaces*

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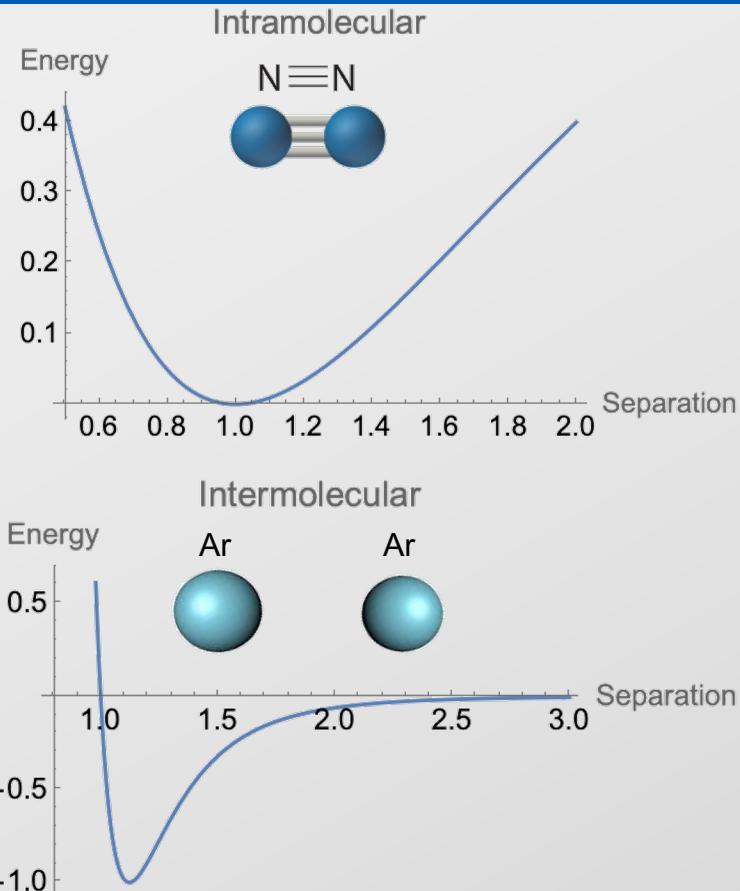
# The PES is the crux of any attempt to understand or predict behavior of material systems

Potential-Energy Surface



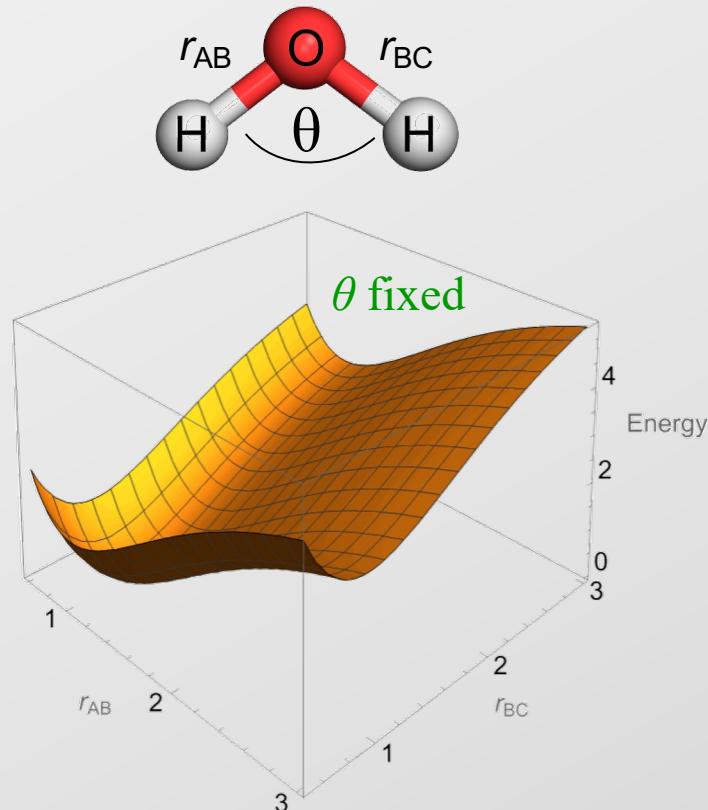
# The PES is a function, or surface, in a high-dimensional space

- Potential energy as a function of nuclear positions:  $E(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots)$ 
  - Electronic contributions are averaged out
  - Nuclei may be treated classically or quantum-mechanically
  - Can visualize up to at most two coordinates
  - Choice of how to define coordinates can be important
  - Often focus is on minima and saddle points, but we will need more than this



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# Quantum chemistry is the application of quantum mechanics to electrons and nuclei

- In principle, the PES can be computed from physical laws
- QM is needed because particles are very light in mass
- We will discuss the basic formalism and principles of quantum chemistry first, to lay a foundation to understand the behavior qualitatively
- Later we will go into detail about methods of computational chemistry that are used to compute the PES accurately
- Let's get started...

# The wavefunction is the full description of the (micro)state of a QM system

- Example: a single particle in a 3-D space

$$\Psi(x, y, z, t)$$

- An alternative formulation can be given in terms of momenta

$$\tilde{\Psi}(p_x, p_y, p_z, t)$$

- This contains information equivalent to  $\Psi(x, y, z, t)$

- $\Psi, \tilde{\Psi}$  are related as Fourier transforms

- We will work exclusively with the “position representation”

# Beware of different role of coordinates in classical-mechanics formulation

- Position and momentum define the state of a classical particle  $x, y, z, p_x, p_y, p_z$ 
  - These are functions of time
- Do not confuse with same quantities used in the wavefunction  $\Psi(x, y, z, t)$ 
  - Here,  $x, y, z$  are *parameters* that specify where the wavefunction is evaluated. They are not themselves state variables

# For a many-particle system, wavefunction depends simultaneously on all coordinates

$$\Psi(x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_N, y_N, z_N, t) \equiv \Psi(\tau, t)$$

- In chemistry applications, the particles are electrons and nuclei
  - Spin is also an important parameter, to be discussed later
- Evaluation of wavefunction of a macroscopic system is hopelessly difficult
- We focus on evaluation of  $\Psi$  for the electrons in a set of molecules with a total of 10 or so atoms

# Wavefunction relates to the probability to find the particle(s) at the specified coordinates

- Wavefunction is a complex number
  - i.e. having real and imaginary parts
- Its magnitude is a probability density
  - $\Psi^* \Psi d\tau$  probability to observe system in volume  $d\tau$  at coordinate  $\tau$

- Wavefunction is normalized to unity

$$\int \Psi^* \Psi d\tau \equiv \int |\Psi|^2 d\tau \equiv \langle \Psi^* | \Psi \rangle = 1$$

“bra-ket” notation

- Average, or expectation value of an operator  $\hat{M}$

$$\langle \Psi^* | \hat{M} | \Psi \rangle = \int \Psi^* \hat{M} \Psi d\tau$$

# The Schrödinger equation describes the time evolution of the wavefunction

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$

- $\hat{H}$  is the Hamiltonian operator
  - Total-energy operator. Sum of kinetic- and potential-energy operators:

$$\hat{H} \equiv -\frac{\hbar^2}{2m} \nabla^2 + V = -\frac{\hbar^2}{2m} \sum_{\nu} \frac{\partial^2}{\partial \tau_{\nu}^2} + V(\tau)$$

- We consider only time-independent Hamiltonians (e.g., no EM field)
- We will soon do some simple examples that demonstrate how this equation is applied. First, a few more developments...

# Separation of variables is applied to generate the time-independent Schrödinger equation

- The SE derivatives include separate time and position terms

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$

Time derivative                          Position derivatives

- This suggests attempting a solution of the form

$$\Psi(\tau, t) = \psi(\tau)\chi(t)$$

- Let's work through the math...

SE

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi$$

postulate

$$\psi(\vec{x}, t) = \Psi(\vec{\tau}) \chi(t)$$

insert

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{\tau}) \chi(t) = \hat{H} \Psi(\vec{\tau}) \chi(t)$$

separate

$$\Psi(\vec{\tau}) i\hbar \frac{\partial}{\partial t} \chi(t) = \chi(t) \hat{H} \Psi(\vec{\tau})$$

$$\frac{1}{\chi(t)} i\hbar \frac{\partial}{\partial t} \chi(t) = E$$

$\frac{1}{i} = -i$

$$\frac{1}{\chi(t)} i\hbar \frac{\partial}{\partial t} \chi(t) = \frac{1}{\Psi(\vec{\tau})} \hat{H} \Psi(\vec{\tau})$$

function of only  $t$       function of only  $\vec{\tau}$

For both sides to be equal for all  $t, \vec{\tau}$ ,  
both must be a constant, designated  $E$ .

$$\frac{1}{\Psi(\vec{\tau})} \hat{H} \Psi(\vec{\tau}) = E$$

$$\boxed{\chi(t) = e^{-\frac{i}{\hbar} Et}}$$

$$\boxed{\hat{H} \Psi(\vec{\tau}) = E \Psi(\vec{\tau})}$$

# The time-independent Schrödinger equation is the central formula in quantum chemistry

$$\hat{H}(\tau)\psi(\tau) = \psi(\tau)E$$

- This is an eigenvalue equation. Solutions are “stationary states”
- Eigenvalues  $E$  are the energies accessible to the system described by  $\hat{H}$ . Both  $\psi$  and  $E$  are important.
- The full time dependence of stationary states is easily obtained if  $\psi$  is known

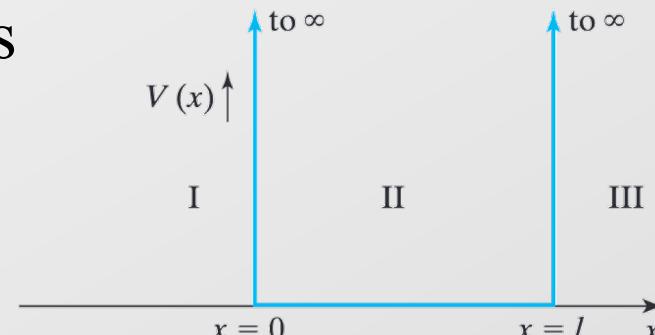
$$\Psi(\tau, t) = \psi(\tau)e^{-\frac{i}{\hbar}Et}$$

- Used when examining time-dependent perturbations
- Not of interest in this course

# Particle-in-a-box model exhibits many important qualitative features of interest to us

- Particle moves within fixed boundaries in a 1D space
- No force acts ( $V = 0$ ) except at boundaries, where  $V = \infty$
- Can show that solutions in regions I and III are  $\psi = 0$
- In region II, we solve

$$\hat{H}\psi(x) = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} = \psi(x)E$$



Credit: Levine, 7th ed.

- For continuous  $\psi$ , we have B.C.  $\psi = 0$  at  $x = 0, l$

# Demonstrate solving in Mathematica

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} = \psi(x)E$$

```
In[3435]:= DSolve[{-\frac{\hbar^2}{2m} \psi''[x] == \psi[x] \epsilon, \psi[0] == 0, \psi[l] == 0}, \psi[x], x]
```

```
Out[3435]=
```

$$\left\{ \begin{array}{l} \psi[x] \rightarrow \begin{cases} c_1 \sin\left[\frac{\sqrt{2}\sqrt{m}\sqrt{\epsilon}}{\hbar}x\right] & \sin\left[\frac{\sqrt{2}l\sqrt{m}\sqrt{\epsilon}}{\hbar}\right] = 0 \\ 0 & \text{True} \end{cases} \end{array} \right\}$$

Use this  $\epsilon$  symbol instead of E because the latter is predefined to mean the constant e

This indicates that a non-trivial solution is found only for  $\sin\left[\frac{\sqrt{2}l\sqrt{m}\sqrt{\epsilon}}{\hbar}\right] = 0$ . This happens when

$$\frac{\sqrt{2}l\sqrt{m}\sqrt{\epsilon}}{\hbar} = n\pi, \text{ or}$$

$$\epsilon = \frac{n^2\pi^2\hbar^2}{2ml^2} = \frac{n^2\hbar^2}{8ml^2} \text{ for which } \psi(x) = c \sin\left(\frac{n\pi x}{l}\right)$$

The constant is determined by normalization  $\int \psi^* \psi d\tau = 1$

```
In[3449]:= Simplify[Integrate[Sin[\frac{n\pi x}{l}] Sin[\frac{n\pi x}{l}], {x, 0, l}], Assumptions \rightarrow n \in Integers]
```

```
Out[3449]=
```

$$\frac{l}{2}$$

$$\text{So } c = \left(\frac{2}{l}\right)^{1/2}$$

# PiaB model demonstrates discretization of energies

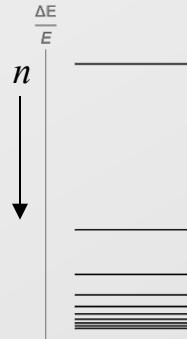
$$E_n = \frac{n^2 h^2}{8ml^2}, \quad n = 1, 2, 3, \dots \quad \text{“quantum number”}$$

Lowest possible energy is not zero!

- Relative difference vanishes with increasing  $n$ :

$$\frac{\Delta E}{E} = \frac{(n+1)^2 - n^2}{n^2} \frac{h^2/8ml^2}{h^2/8ml^2} = \frac{2}{n} + \frac{1}{n^2}$$

- Behavior is more continuum-like at large  $n$



Energy-level diagram

Energy

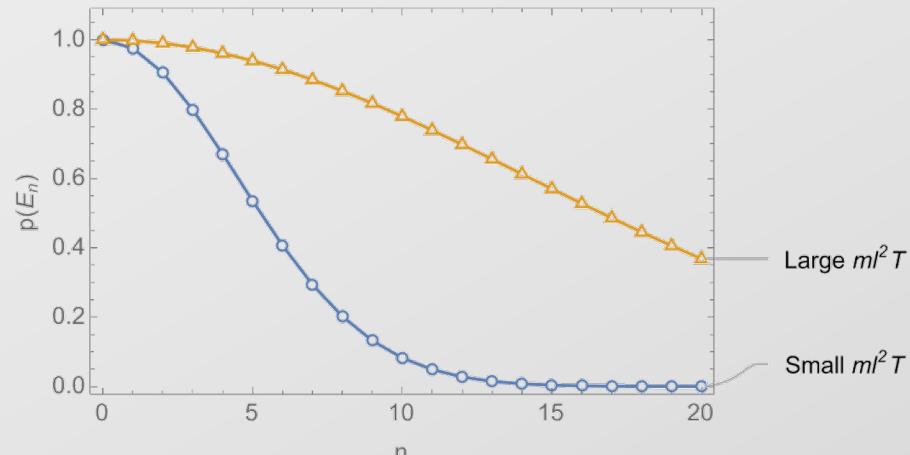


# Behavior is more continuum-like (classical) for large mass, size, and/or temperature

- From statistical mechanics, energy-level probability follows a Boltzmann distribution

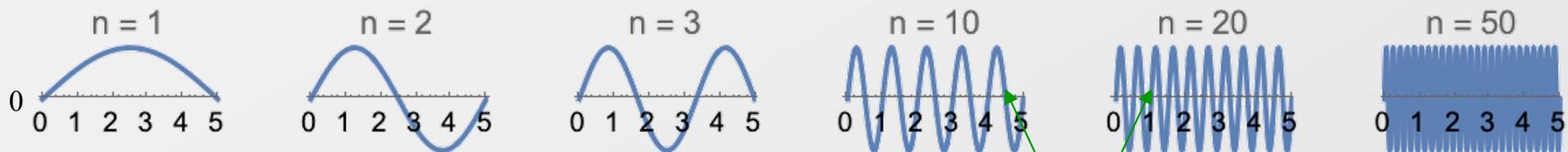
$$p(E_n) = \exp\left(-\frac{E_n}{k_B T}\right) = \exp\left(-\frac{n^2 h^2}{8ml^2 k_B T}\right)$$

- Large  $m$ ,  $l$ , or  $T$  increases importance of states at larger  $n$ 
  - Behavior is more classical



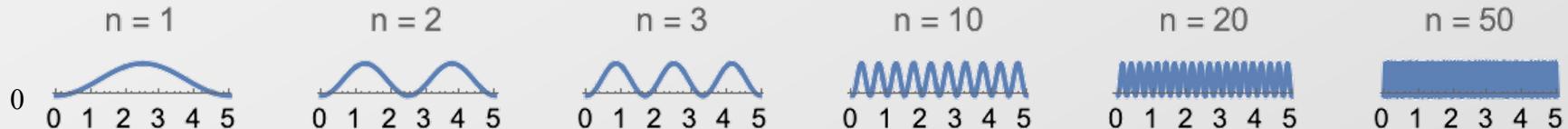
# PiaB model demonstrates nodal structure of wavefunction

- Wavefunction,  $\psi_n(x)$



- Probability density,  $\psi_n^*(x) \psi_n(x)$

Higher-energy wavefunctions have more nodes  
Larger curvature = larger kinetic energy



- For a given state, some positions have zero probability
- Continuum limit approached for large  $n$  (changes too fast to resolve)

# Piab wavefunctions are orthogonal and normalized (orthonormal)

$$\int \psi_m^*(\tau) \psi_n(\tau) d\tau = \delta_{mn} \equiv \begin{cases} 0 & m \neq n \\ 1 & m = n \end{cases}$$

Kronecker delta function

- Integral is analogous to dot product, in an infinite-dimensional space

$$x^T y = \sum_i x_i y_i$$

- Each  $\tau$  value in integral is a different “index”

Mathematica evaluation of integral

```
In[3593]:= psi[x_, n_, l_] := Sqrt[2/l] Sin[n Pi x/l]

In[3594]:= Integrate[psi[x, m, l] * psi[x, n, l], {x, 0, l}]
Simplify[%, Assumptions -> {n ∈ Integers, m ∈ Integers}]
Integrate[psi[x, n, l] * psi[x, n, l], {x, 0, l}]
Simplify[%, Assumptions -> {n ∈ Integers}]

Out[3594]=
2 n Cos[n π] Sin[m π] - 2 m Cos[m π] Sin[n π]
────────────────────────────────────────────────────────
m² π - n² π

Out[3595]=
0

Out[3596]=
1 - Sin[2 n π]
──────────────────
2 n π

Out[3597]=
1
```

# Suggested Reading/Viewing

- Autschbach Chs. 3,4,5
- Levine Chs. 1,2,3
- Cramer, Videos 2.01, 2.02