Lecture 1 (revised): Course Outline. Free Particle. Motion?

Quantum Mechanics is cruel. We cannot look directly at either intramoleclar structure or dynamics. But, as chemists or physicists, we seek and build beautiful detailed pictures of structure, dynamics, and mechanism.

How do we do this? How do we get what we want (more than mere description) from experiment or calculation? $\boxed{\text{Reductionist.}}$

5.73: Quantum Mechanics for **use**, not admiration, history, or philosophical challenges.

Insight and Intuition

Confidence to make free-hand drawn pictures (cartoons) of ψ and level structure (matrix structure) and wavepacket motion.

What are we allowed to know and how are we allowed to measure (or calculate) it?

Tricks for evaluating integrals
Tricks for reducing Quantum Mechanics to Classical Mechanics
The Periodic Table re-emerges.

Course Outline

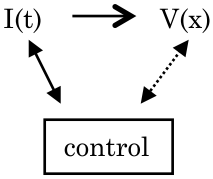
increasingly complex, mostly time-independent problems

* 1-Dimensional in $\psi(x)$ picture (Schrödinger)

- spectrum $\{E_n\} \leftrightarrow$ potential $V(x)$

central problem in Physical Chemistry, until recently

- femtochemistry: wavepackets exploring V(x), information about V(x) from timing experiments.

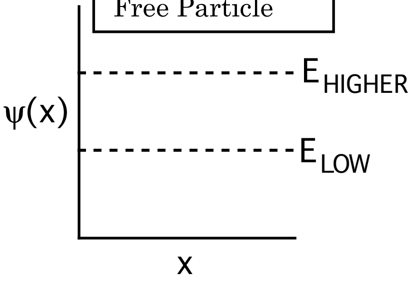


How is a wavepacket encoded for x_c, Δx, p_c, Δp? (c = center) What to look for?

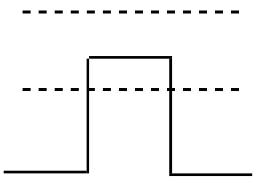
- stationary phase
  - trick to evaluate integrals
  - where does stuff "happen"

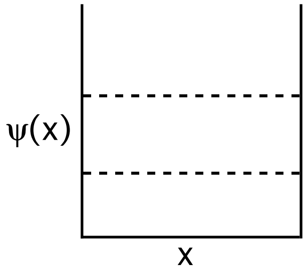
- Confidence to draw cartoons of $\psi(x)$, even for problems that you have solved once but no longer remember the details.

Free Particle

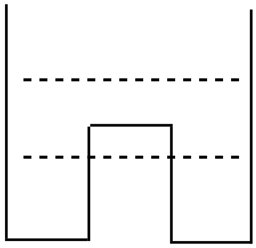


Transmission through a Barrier





Particle in a Box



Tunneling in a Well

Semi-classical: WKB. Connection of ψ across E = V(x) turning point. Quantization condition, RKR [Wentzel, Kramers, Brillouin, and Rydberg, Klein, Rees]

* Matrix Picture (Linear algebra)

- $\Psi(x)$ replaced by a large collection of numbers called "matrix elements"
- Main tool: **perturbation theory**
  - * small distortions from exactly solved problems
  - * f(quantum numbers) ↔ F(potential parameters)

representation of spectrum

representation of potential

Vibration-Rotation Energy Levels:

e.g. Dunham Expansion

$$E_{vJ} = \sum_{\ell,m} Y_{\ell m}\left(v+\frac{1}{2}\right)^{\ell}\left[J(J+1)\right]^{m}$$

$$V(\xi) = \sum_{n=0} a_n \xi^n \qquad \xi \equiv \frac{R-R_e}{R_e}$$

The $\{a_n\}$ determine the $\{Y_{\ell m}\}$. Energy levels determine the potential energy curve.

- Linear Algebra: "Diagonalization" ↔ Eigenvalues and Eigenvectors
- How to set up and "read" a matrix.
- **Density Matrices**: specify general state of system (**ρ**) and operators (**Op**) that correspond to a specific type of measurement, "populations" and "coherences".

***Problems in Three Dimensions**

- Central Forces: Radial x Angular factorization

  Specific Problem Universal Symmetry, exactly soluble
- The Hydrogen Atom: eigenstates and perturbations
- Rigid Rotor, $\mathbf{J}^2$, $\mathbf{J}_z$, $\mathbf{J}_\pm$ matrix elements and selection rules
- Vector Model
- Transformation between "coupled" and "uncoupled" basis sets
- Scattering : quantum mechanics for processes that involve unbound states.

***Many Particle Systems**

- many-electron atoms
- Slater determinants satisfy anti-symmetrization requirement for Fermions
- matrix elements of Slater determinantal wavefunctions
- orbitals→configurations→states (“terms”): L–S–J states
- molecular constants for many-electron systems↔orbital integrals

[Periodicity “recovered”]

* Many-Boson systems: anharmonically coupled vibrations
Intramolecular Vibrational Redistribution (IVR)
* Periodic Lattices: band structure of metals

Some warm-up exercises

Particle in a constant V(x)

* standard Quantum Mechanics problem ~ warm up

* practice with complex numbers

* building of intuition – “encoding” of motion

Hamiltonian $$\mathrm{H} = \mathrm{T} + \mathrm{V} = \frac{\mathrm{p}^2}{2\mathrm{m}} + \mathrm{V}(\mathrm{x})$$ Classical Mechanics

special QM prescription $$\hat{\mathrm{p}}_{\mathrm{x}} = \frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial \mathrm{x}}$$ Why? Could have started with $\left[\hat{x}, \hat{p}_x\right] = i\hbar$

$$\hat{\mathrm{H}} = -\frac{\hbar^2}{2\mathrm{m}} \frac{\partial^2}{\partial \mathrm{x}^2} + \mathrm{V}(\mathrm{x})$$

Schrödinger Equation $$\left(\hat{\mathrm{H}} - \mathrm{E}\right)\psi = 0$$

Free particle in constant V(x)

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V_0 - E\right)\psi = 0$$ Schrödinger Equation

What kind of Ψsatisfies this differential equation?

$$\frac{d^2\psi}{dx^2} = -\left[\left(E - V_0\right)\frac{2m}{\hbar^2}\right]\psi$$

call this k^2

k real if $E \geq V_0$

k imaginary if $E < V_0$ (classically forbidden region)

Thus $k = \left[\left(E - V_0\right)\frac{2m}{\hbar^2}\right]^{1/2}$

general solution (more general than sin kx and cos kx)

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

Two cases:

$E > V_0$ Classicallly allowed

$E < V_0$ Forbidden. $k \equiv i\kappa$ $\kappa = \left[\left(V_0 - E\right)\frac{2m}{\hbar^2}\right]$ real

General solutions:

$$E > V_0 \quad \psi(x) = Ae^{ikx} + Be^{-ikx} \quad k \text{ real}$$

oscillatory

$$E < V_0 \quad \psi(x) = ce^{\kappa x} + De^{-\kappa x} \quad \kappa \text{ real}$$

exponential

Neat! form of $\psi(x)$ depends on sign of $E - V_0$

Some refresher for complex numbers:

$$z = \overset{\text{Re}(z)}{\overset{\searrow}{x}} + \underset{\underset{i^2=-1}{\nearrow}}{i}\overset{\text{Im}(z)}{\overset{\searrow}{y}}$$

$z^* = x - iy$

$2\text{Re}(z) = (z + z^*)$

$2i\text{Im}(z) = (z - z^*)$

$|z|^2 = zz^* = x^2 + y^2$ real and positive

$e^{\pm ikx} = \cos kx \pm i \sin kx$

$$\cos kx = \frac{1}{2}\left[e^{ikx} + e^{-ikx}\right]$$

$$\sin kx = \frac{1}{2i}\left[e^{ikx} - e^{-ikx}\right]$$

What happens when we apply $\hat{p}$ to e^{ikx}?

$$\hat{p}e^{ikx} = \frac{\hbar}{i}\frac{d}{dx}e^{ikx} = \underbrace{\boxed{\hbar k}}_{\text{eigenvalue of }\hat{p}}\boxed{e^{ikx}} \quad \text{eigenfunction of } \hat{p}$$

$\hbar k = \underset{\uparrow}{p}$

a number, not an operator

$p = +\hbar k$ motion in $+x$ direction

$p = -\hbar k$ motion in $-x$ direction

OK, we have some connection to Classical Mechanical motion. We want to ask: how is motion encoded in $\Psi(x)$?

* Intuition

* <u>Before</u> we get to the TDSE $\hat{H}\Psi(x,t) = i\hbar\frac{\partial\Psi}{\partial t}$ (mostly in 5.74)

How is $\psi(x)$ $\boxed{\textbf{encoded}}$ for motion?

My favorite word
in Quantum Mechanics

e^{ikx} is an eigenfunction of $\hat{p}_x$. It is also a complex function of a real variable.

k is called the "wave vector" (or wave number). Why is it called wave vector?

- in 3-D where $e^{i\vec{k}\cdot\vec{r}}$ $\quad$ $\vec{k}$ points in direction of motion
- $e^{i(kx+2\pi)} = e^{ikx}$ $\quad$ e^{ikx} is periodic $x \longrightarrow x+\lambda$
- $e^{ik(x+\lambda)} \equiv e^{ikx}$ $\quad \therefore \quad$ $k\lambda = 2\pi$ $\qquad$ $k = \dfrac{2\pi}{\lambda}$

↑ advance x by one full oscillation cycle $\equiv \lambda$ $\qquad$ "wavelength"

k is # of waves per 2π unit length

Now go back to $\Psi(x)$.

ψ is probability amplitude density $\qquad$ $\psi = Ae^{ikx} + Be^{-ikx}$

travels to left?

probability distribution $\qquad$ $\psi^*\psi = |A|^2 + |B|^2 \left.\begin{array}{l} +A^*Be^{-2ikx} \\ +AB^*e^{2ikx} \end{array}\right\}$ this sum had better be real! Why? It is $\text{Re}(A^*B\,e^{-2ikx})$!

travels to right?

simplify:

$$z = \text{Re}(z) + i\,\text{Im}(z)$$

$$2\,\text{Re}\left(A^*B\right) = A^*B + AB^*$$

$$2i\,\text{Im}\left(A^*B\right) = A^*B - AB^*$$

$$e^{\pm i\alpha} = \cos\alpha \pm i\sin\alpha$$

We know $|\Psi|^2$ is real because it has the form $z + z^*$.

Look at it in more detail. The cross-terms:

$$A^*B(\cos 2kx + i\sin 2kx) + AB^*(\cos 2kx - i\sin 2kx) =$$
$$(A^*B + AB^*)\cos 2kx + (A^*B - AB^*)i\sin 2kx =$$
$$2\mathrm{Re}(A^*B)\cos 2kx + 2\underbrace{i\,\mathrm{Im}(A^*B\,i}_{\boxed{\textbf{note } i \times i = -1}}\sin 2kx) =$$
$$2\mathrm{Re}(A^*B)\cos 2kx - 2\mathrm{Im}(A^*B)\sin 2kx.$$

This is real for all x. It has x-regions of *positive* and *negative* value.

$$|\psi|^2 = \psi^*\psi = \underbrace{|A|^2 + |B|^2}_{\substack{\text{constant} \\ \text{(delocalized particle)}}} + \underbrace{\underbrace{2\mathrm{Re}(A^*B)\cos 2kx + 2\mathrm{Im}(A^*B)\sin 2kx}_{\substack{\text{wiggly – only if both} \\ \text{A and B are nonzero}}}}_{\text{standing wave, real, neither complex nor imaginary}}$$

If |A| > |B| wiggles encode net +x motion. What is fraction $\frac{\text{to right?}}{\text{to left?}}$
A,B are determined by problem-specific boundary conditions.

- Can't directly see any motion in x unless we go to time-dependent Schrödinger Equation
- Need superposition of +k and –k parts in $\Psi(x)$ to get wiggles.

= superpositon of waves with different values of k

= "localization" requires another kind of superposition (wave-packet)

- Motion becomes really clear when we do two things:

  * time-dependent $\Psi(x,t)$

  * create localized states called wavepackets by superimposing several e^{ikx} with *different* |k|'s.

Now for the $E < V_0$ case.

$$e^{\overset{\pm\kappa x}{\underset{E<V}{\uparrow}}}$$ does not have wiggles, no motion in classically forbidden region.

To convince yourself, go back to

$$\psi(x) = Ce^{\kappa x} + De^{-\kappa x}$$

$$|\psi|^2 = |C|^2 e^{2\kappa x} + |D|^2 e^{-2\kappa x} + \underbrace{CD^* + C^* D}_{\substack{\text{real and} \\ \text{independent} \\ \text{of } x}}$$

To *really* see **motion**, need to use time-dependent Schrödinger Equation.

To see **localization**, need superposition of several e^{ikx} with different values of $|k|$.

NEXT LECTURE: CTDL, pages 21-24, 28-31 (motion, infinite box, δ-function potential, scattering off δ-function barrier).

5.73 Quantum Mechanics I
Fall 2018