

5.73 Lecture #1

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- Handouts:
1. administrative structure
 2. narrative
 3. Last year's lecture titles (certain to be modified)
 4. Gaussian and FT
 5. PS #1 Due 9/12

Read CTDL, pages 9-39, 50-56, 60-85

Administrative Structure

15% In-class 5 minute Quizzes.
Exercise concepts immediately after they are introduced.

~10 Problem Sets
35% Difficult, mostly computer based problems
group consultation encouraged
Vladimir Petrovic and Serhan Petrovic, TAs (grade problem sets)
some help with computer programs

TROY AND I WILL DEAL WITH THE QM, NOT THE COMPUTER PROGRAMS!

Optional Recitation! R. Field - answer questions about Problem Sets

How about: Wednesdays, 5:00PM, Room 2-151

20% Take home mid-term exam

30% Take home final exam

no group consultation about methods of solution,
OK for clarification of meaning of the questions.

CTDL - formal, elegant, analytic

Handouts - other texts and Herschbach

Lecture Notes - provide tools for solving increasingly complex problems

NO PHILOSOPHY, NO PREACHING TO THE CONVERTED

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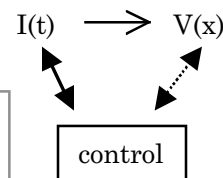
Course Outline

increasingly complex, mostly time-independent problems

* 1D in $\psi(x)$ picture

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

central problem in Physical Chemistry until recently

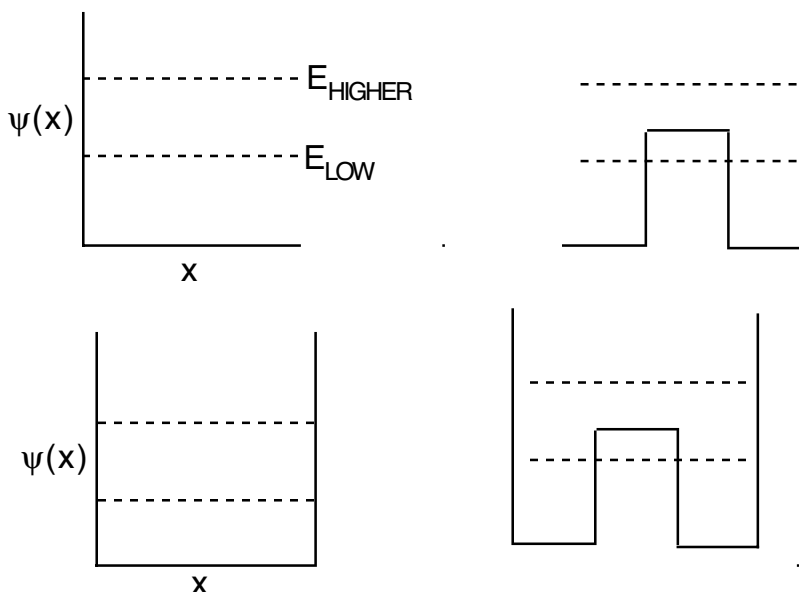


- femtochemistry: wavepackets exploring $V(x)$, information about $V(x)$ from timing experiments.

How is a wavepacket encoded for $x_c, \Delta x, p_c, \Delta p$? ($c =$ center)

- stationary phase $\left\{ \begin{array}{l} \text{evaluate integrals} \\ \text{interpret information contained in } \psi(x) \text{ with respect to expectation values and transition probabilities} \end{array} \right.$

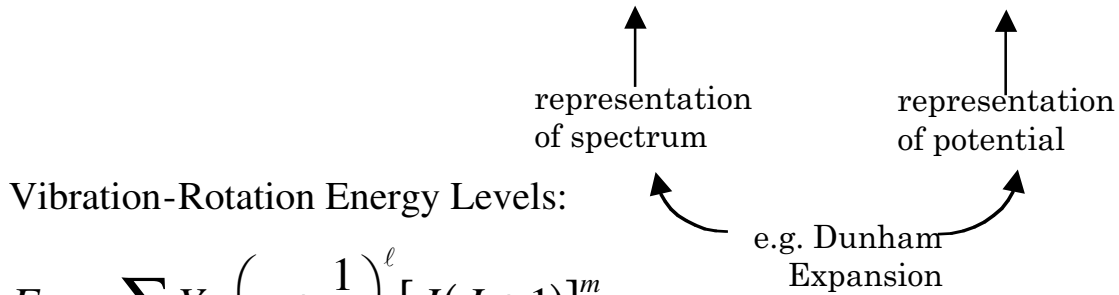
Confidence to draw cartoons of $\psi(x)$, even for problems you have solved once but no longer remember the details.



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* Matrix Picture

- $\psi(x)$ replaced by collections of numbers called “matrix elements”
- tools: **perturbation theory**
 - * small distortions from exactly solved problems
 - * $f(\text{quantum numbers}) \leftrightarrow F(\text{potential parameters})$



Vibration-Rotation Energy Levels:

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

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

- Linear Algebra: “Diagonalization” → Eigenvalues and Eigenvectors
- How to set up and read a matrix.
- Density Matrices: specify general state of system (**ρ**) vs. an operator (**Op**) that corresponds to a specific type of measurement, “populations” and “coherences”.

*Problems in Three Dimensions

- Central Forces: Radial x Angular factorization
 - Specific
 - Universal Symmetry
- The Hydrogen Atom: eigenstates and perturbations
- Scattering : quantum mechanics for unbound processes

*Many Particles

- Addition of Angular momenta
- Many Electron atoms
- The Born-Oppenheimer approximation
- Molecular bonding
- Insulators, conductors and excitons

Some warm-up exercises

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

special QM prescription $\hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}$

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

Schr. Eqn. $(\hat{H} - E)\psi = 0$

1. Free particle $V(x) = \text{const.} = V_0$

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

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

call this k^2

k real if $E \geq V_0$
 k imaginary if $E < V_0$

(classically forbidden region)

$\psi(x) = A e^{ikx} + B e^{-ikx}$ general solution

Complex Numbers: $i^2 = -1$

$$z = x + iy, z^* = x - iy$$

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

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

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

$$\hat{p} e^{ikx} = \frac{\hbar}{i} \frac{d}{dx} e^{ikx} = \hbar k e^{ikx}$$

$\hbar k = p$
 \uparrow
 a number, not an operator

eigenvalue of \hat{p}

eigenfunction of \hat{p}

This suggests (based on what we know from classical mechanics about momentum) that if $k > 0$ something is “moving” to right (+x direction) and if $k < 0$ moving to left

How do we really know that something is moving? We need to resort to time dependent Schr. Eqn.

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

- in 3 - D get $e^{i\vec{k}\cdot\vec{r}}$ where \vec{k} points in direction of motion

- $e^{i(kx+2\pi)} = e^{ikx}$ periodic

- $e^{ik(x+\lambda)} \equiv e^{ikx} \quad \therefore \quad k\lambda = 2\pi \quad k = \frac{2\pi}{\lambda}$

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

k is # of waves per 2π unit length

ψ is probability amplitude $\psi = Ae^{ikx} + Be^{-ikx}$ travels to left?
↓

probability distribution $\psi^* \psi = |A|^2 + |B|^2 + A^* B e^{-2ikx}$

$+ AB^* e^{2ikx}$
↑
travels to right?

simplify:

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

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

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


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

$$\psi^* \psi = \underbrace{|A|^2 + |B|^2}_{\text{constant}} + \underbrace{2 \operatorname{Re}(A^* B) \cos 2kx + 2 \operatorname{Im}(A^* B) \sin 2kx}_{\substack{\text{wiggly - only present if both} \\ \text{A and B are nonzero}}}$$

(delocalized particle) standing wave, real not complex or imaginary

A,B determined by specific boundary conditions.

- Can't really see any motion unless we go to time dependent Schr. Eq.
- Need superposition of +k and -k parts to get wiggles.
- Wiggles = superposition of waves with different values of k

 = 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.

[NEXT LECTURE: CTDL, pages 21-24, 28-31 (motion, infinite box, δ -function potential, start wavepackets).]