Handouts:
1. administrative structure
2. narrative
3. Last year's lecture titles (certain to be modified)
4. Gaussian and FT
5. PS #1 Due 9/13

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

Administrative Structure

20% In-class 5 minute Quizzes.
Exercise concepts immediately after they are introduced.

~10 Problem Sets
40% Difficult, mostly computer based problems
group consultation encouraged

TAs (grade problem sets)
some help with computer programs

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

Optional Recitation! R. Field - answer questions about Problem Sets
How about: Wednesdays, 5:00PM

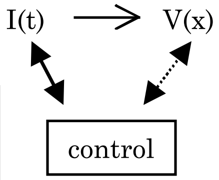
40% Take home Exam
no group consultation about methods of solution,
OK for clarification of meaning of the questions.

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

Course Outline

increasingly complex, mostly time-independent problems



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

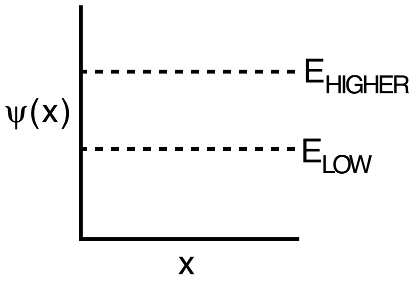
- spectrum $\{E_n\} \leftrightarrow$ potential V(x)

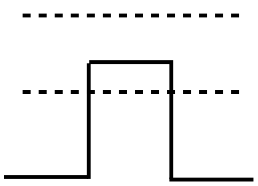
central problem in Physical Chemistry until recently

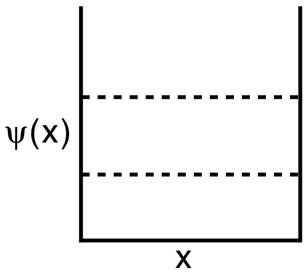
- femtochemistry: wavepackets exploring V(x), information about V(x) from timing experiments.
  How is a wavepacket encoded for x_c, Δx, p_c, Δp?(c = center)

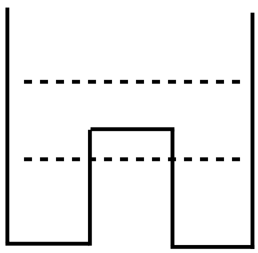
- stationary phase
  - evaluate integrals
  - interpret information contained in $\psi(x)$ with respect to expectation values and transition probabilities

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









* Matrix Picture

- $\psi(x)$ replaced by collections of numbers called "matrix elements"

- tools: **perturbation theory**
  - * small distortions from exactly solved problems
  - * f(quantum numbers) ↔ F(potential parameters)

representation of spectrum

representation of potential

e.g. Dunham Expansion

Vibration-Rotation Energy Levels:

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

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

- 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".

* 3D Central Force - 1 particle

radial, angular factorization

specific

universal, exactly soluble

ANGULAR MOMENTUM

map one problem surprisingly onto others

symmetry classification of operators → matrix elements

"reduced matrix elements"

* Many Particle Systems

- many electron atoms
- Slater determinants satisfy antisymmetrization requirement for Fermions
- Matrix elements of Slater determinantal wavefunctions
- orbitals → configurations → states ("terms")
- spectroscopic constants for many electron systems ↔ orbital integrals

* Many-Boson systems: coupled vibrations:

Intramolecualr Vibrational Redistribution (IVR)

* Periodic Lattices -band structure of metals

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.
$$\left(\hat{H} - E\right)\psi = 0$$

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

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

$$\frac{d^2\psi}{dx^2} = \pm\underbrace{\boxed{\left(E - V_0\right)\frac{2m}{\hbar^2}}}_{\text{call this } k^2}\psi$$

k real if E ≥ V_0

k imaginary if E < V_0 (classically forbidden region)

$$\psi(x) = A \;\; e^{ikx} + Be^{-ikx}$$ 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? $$k = \left[\left(E - V_0\right)\frac{2m}{\hbar^2}\right]^{1/2}$$ but

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

$$\hat{p}e^{ikx} = \frac{\hbar}{i}\frac{d}{dx}e^{ikx} = \underbrace{\enclose{circle}{\hbar k}}_{\text{eigenvalue}}\overbrace{\enclose{circle}{e^{ikx}}}^{\text{eigenfunction}}$$

of $\hat{p}$

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

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.

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

advance x by one full oscillation cycle ≡ λ wavelength

k is # of waves per 2π unit length

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

travels to left?

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

travels to right?

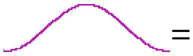
simplify:

$$x = \mathrm{Re}(x) + i\,\mathrm{Im}(x)$$
$$2\,\mathrm{Re}(A^*B) = A^*B + AB^*$$
$$2i\,\mathrm{Im}(A^*B) = A^*B - AB^*$$
$$e^{\pm i\alpha} = \cos\alpha \pm i\sin\alpha$$

$$\psi^*\psi = \underbrace{|A|^2 + |B|^2}_{\substack{\text{constant} \\ \text{(delocalized particle)}}} + \underbrace{\underbrace{2\,\mathrm{Re}(A^*B)\cos 2kx + 2\,\mathrm{Im}(A^*B)\sin 2kx}_{\substack{\text{wiggly - only present if both} \\ \text{A and B are nonzero}}}}_{\text{standing wave, real not complex or imaginary}}$$

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 = superpositon 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).]

Dave Lahr to talk here about use of computers.