5.73 Lecture #1

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
increasingly complex, mostly time-independent problems

* 1D in \( \psi(x) \) picture
  - spectrum \( \{E_n\} \leftrightarrow \text{potential } V(x) \) 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 \( x_c, \Delta x, p_c, \Delta p? (c = \text{center}) \)
  - 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
  - \( f(\text{quantum numbers}) \leftrightarrow F(\text{potential parameters}) \)

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

Vibration-Rotation Energy Levels:

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

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

* **3D Central Force - 1 particle**

  - radial, angular factorization
  - specific \( \rightarrow \) universal, exactly soluble

**ANGULAR MOMENTUM**

- map one problem surprisingly onto others
- symmetry classification of operators \( \rightarrow \) 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:
  Intramolecular 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. \[ (\hat{H} - E)\psi = 0 \]

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

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

Call this \( k^2 \)

\( k \) real if \( E \geq V_0 \)
\( k \) imaginary if \( E < V_0 \) (classically forbidden region)

\[ \psi(x) = A e^{ikx} + Be^{-ikx} \]

General solution

Complex Numbers:
\( i^2 = -1 \)
\( z = x + iy, \quad z^* = x - iy \)
\( e^{\pm ikx} = \cos kx \pm i \sin kx \)

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

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

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

\( \hbar k = p \)

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

- in 3-D get $e^{i \mathbf{k} \cdot \mathbf{r}}$ where $\mathbf{k}$ points in direction of motion
- $e^{i(kx+2\pi)} = e^{ikx}$ periodic
- $e^{ik(x+\lambda)} \equiv e^{ikx}$ \[ \therefore \quad k\lambda = 2\pi \quad \Rightarrow \quad k = \frac{2\pi}{\lambda} \]

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

$k$ is # of waves per $2\pi$ unit length

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

probability distribution \[ \psi \ast \psi = |A|^2 + |B|^2 + A \ast Be^{-2ikx} + AB \ast e^{2ikx} \]

simplify:

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

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

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

$e^{\pm i\alpha} = \cos \alpha \pm i \sin \alpha$
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, \( \delta \)-function potential, start wavepackets).]

Dave Lahr to talk here about use of computers.