3.23 Electrical, Optical, and Magnetic Properties of Materials
Fall 2007


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# Last time: Wave mechanics

1. Time-dependent Schrödinger equation
2. Separation of variables – stationary Schrödinger equation
3. Wavefunctions and what to expect from them
4. Free particle and particle in a 1-d, 2-d, 3-d box
5. Scanning tunnelling microscope
6. (Applets)

## Good news

- Study material: Prof Fink QM notes (uploaded on Stellar)



## First postulate

- All information of an ensemble of identical physical systems is contained in the ket $|\Psi\rangle$ (usually a wavefunction Ψ(x,y,z,t), which is complex, continuous, finite, and single-valued, square-integrable $\left(\text{i.e. } \int \|\Psi\|^2 d\vec{r} \text{ is finite}\right)$

- The ket can also be a geometrical vector (e.g. spin); in truth, wavefunctions are objects that satisfy vector algebra, and the space of wavefuncitons is a Hilbert space (instead of being 3-d, it's infinite-d)

# Normalization, scalar products



# Second Postulate

- For every physical observable there is a corresponding Hermitian operator

# From classical mechanics to operators

- Total energy is T+V (Hamiltonian is kinetic + potential)

  $T = p^2/2m$

- classical momentum $\vec{p}$ → 
  → gradient operator $-i\hbar\vec{\nabla}$

- classical position $\vec{r}$ → 
  → multiplicative operator $\hat{r}$



# Operators and operator algebra

- Examples: derivative, multiplicative

$$\psi(\vec{r})$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r})$$

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## Linear and Hermitian

- $\hat{A}[\alpha|\varphi\rangle + \beta|\psi\rangle] - \alpha\hat{A}|\varphi\rangle + \beta\hat{A}|\psi\rangle$

$$\vec{\nabla}[\alpha\,\varphi(\vec{r}) + \beta\,\psi(\vec{r})] =$$
$$= \vec{\nabla}[\alpha\,\varphi(\vec{r})] + \vec{\nabla}[\beta\,\psi(\vec{r})] =$$
$$= \alpha\,\vec{\nabla}\varphi(\vec{r}) + \beta\,\vec{\nabla}\psi(\vec{r})$$

- $\langle\varphi|\hat{A}\psi\rangle = \langle\hat{A}\varphi|\psi\rangle$

$$\int \varphi^*(\vec{r})\left(\hat{A}\,\psi(\vec{r})\right)d\vec{r} = \int \left(\hat{A}\,\varphi(\vec{r})\right)^* \psi(\vec{r})\,d\vec{r}$$



## Examples: ~~(d/dx)~~ $\hat{A}$ and i(d/dx)

$$\langle\varphi|A\psi\rangle = \langle A\varphi|\psi\rangle$$

$$\int_{-\infty}^{\infty} \varphi^* \frac{d\psi}{dx}\,dx = \int_{-\infty}^{\infty} \left(\frac{d\varphi}{dx}\right)^* \psi\,dx$$

$$\int d(\varphi^*\psi) = \int \varphi^* d\psi + \int \psi\,d\varphi^*$$

$$\left[\varphi^*\psi\right]_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \psi \frac{d\varphi^*}{dx}\,dx$$

# Hermitian Operators $\hat{A}$

1. The eigenvalues of a Hermitian operator are real

$$\hat{A}|\psi_n\rangle = a_n|\psi_n\rangle$$

2. Two eigenfunctions corresponding to different eigenvalues are orthogonal

$$\langle\psi_i|\psi_j\rangle = \delta_{ij}$$

3. The set of eigenfunctions of a Hermitian operator is complete

$$\varphi(x) = \sum_n c_n|\psi_n\rangle$$

4. Commuting Hermitian operators have a set of common eigenfunctions



# The set of eigenfunctions of a Hermitian operator is complete

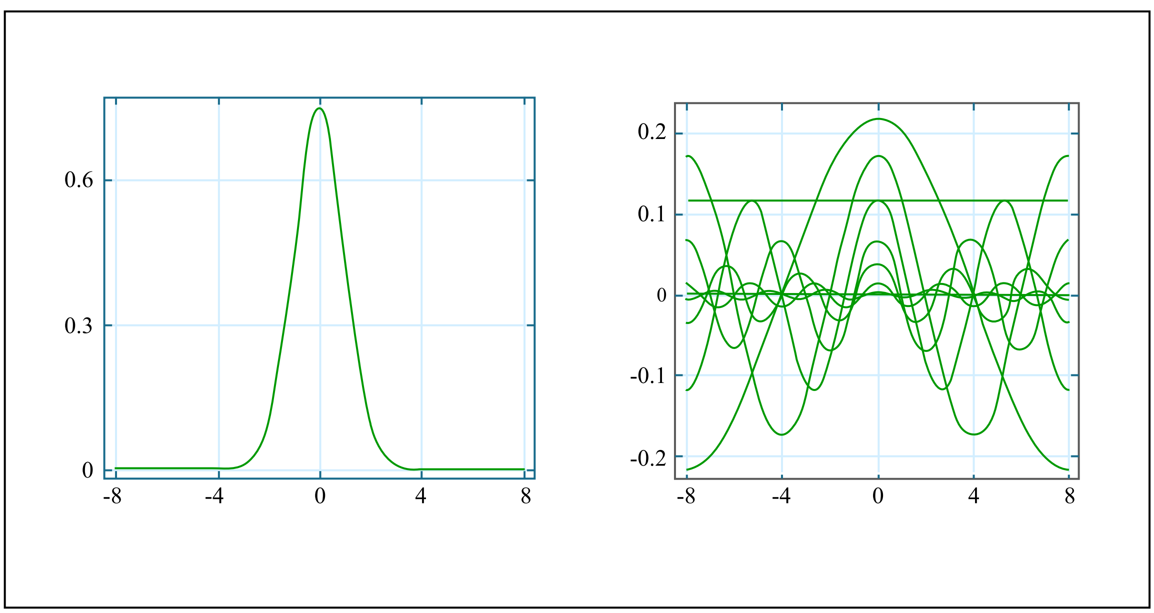


Figure by MIT OpenCourseWare.

## The set of eigenfunctions of a Hermitian operator is complete

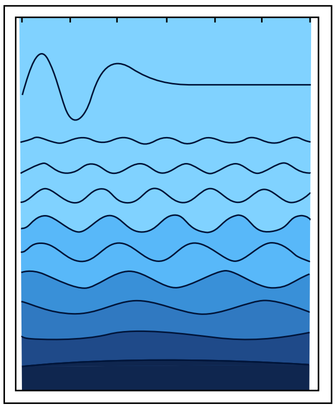

Figure by MIT OpenCourseWare.

$\leftarrow \psi(t=0) = \sum_{n=1}^{\infty} c_n \sin(k_n(x))$

$\Downarrow$

$\sin(k_n(x)) \cdot e^{\frac{E}{i\hbar}t}$



## Product of operators, and commutators

- $\hat{A}\hat{B}$  $\quad \hat{A}(\hat{B}\psi) = \hat{B}(\hat{A}\psi)$
- $\left[\hat{A},\hat{B}\right]$  $\quad \hat{A}\hat{B}\psi = \hat{B}\hat{A}\psi$

$[\hat{A}\hat{B} - \hat{B}\hat{A}]\psi = 0$

$[\hat{A}, \hat{B}]$

- $\left[x, \frac{d}{dx}\right] = -1$  $\quad \left(\frac{d}{dx} \rightarrow -i\hbar\frac{d}{dx}\right)$

$x\frac{d}{dx}f \stackrel{?}{=} \frac{d}{dx}(xf) \rightarrow x\frac{df}{dx} + f$

$[x, p_x] = i\hbar$

# Third Postulate

- In any single measurement of a physical quantity that corresponds to the operator A, the only values that will be measured are the eigenvalues of that operator.

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# Fourth Postulate

- If a series of measurements is made of the dynamical variable A on an ensemble described by Ψ, the average ("expectation") value is $\langle A \rangle = \frac{\langle \Psi | \hat{A} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$

  i.e. the probabiliy of obtaining an eigenvalue $a_n$ is $P(a_n) = \left| \langle \varphi_n | \Psi \rangle \right|^2$

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# Dirac Notation

- Eigenvalue equation:

$$\hat{A}\left|\psi_i\right\rangle = a_i\left|\psi_i\right\rangle \qquad \left( \Rightarrow \left\langle \psi_i \middle| \psi_j \right\rangle = \delta_{ij} \right)$$

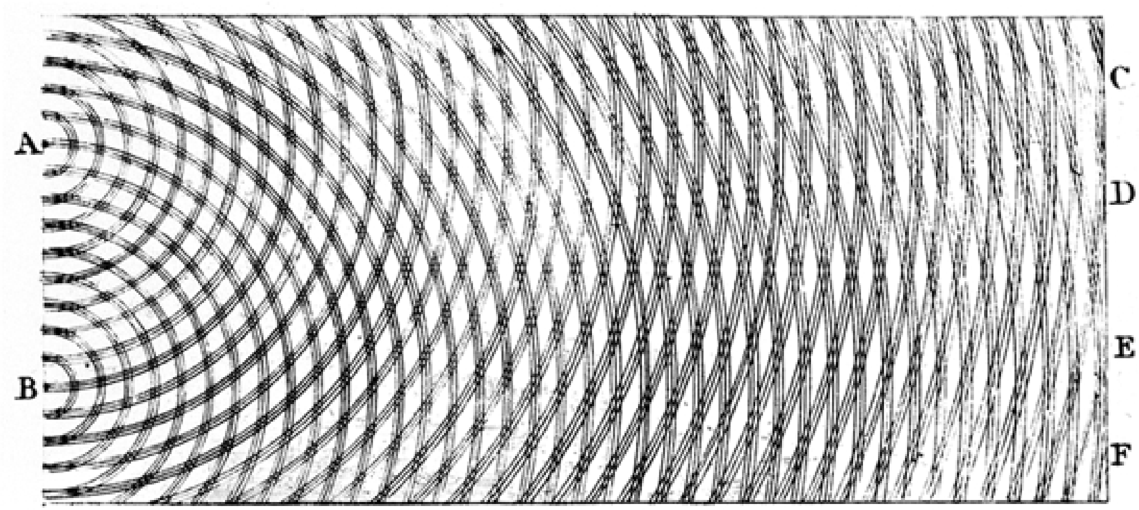
- Expectation values:

$$\left\langle \psi_i \middle| \hat{H}\psi_i \right\rangle = \left\langle \psi_i \middle| \hat{H} \middle| \psi_i \right\rangle = \int \psi_i^*(\vec{r}) \left[ -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \right] \psi_i(\vec{r})\, d\vec{r} = E_i$$



# Commuting Hermitian operators have a set of common eigenfunctions

# Quantum double-slit

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# Fifth postulate

- If the measurement of the physical quantity A gives the result $a_n$ , the wavefunction of the system immediately after the measurement is the eigenvector $|\varphi_n\rangle$

# Position and probability

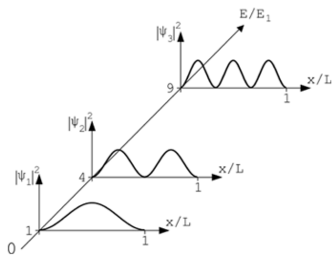


Diagram showing the probability densities of the first 3 energy states in a 1D quantum well of width L.

Graphs of the probability density for positions of a particle in a one-dimensional hard box according to classical mechanics removed for copyright reasons. See Mortimer, R. G. *Physical Chemistry*. 2nd ed. San Diego, CA: Elsevier, 2000, page 555, Figure 15.3.

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# Quantum double-slit

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Please see any experimental
verification of the double-slit experiment, such as
http://commons.wikimedia.org/wiki/Image:Doubleslitexperiment_results_Tanamura_1.gif

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## Deterministic vs. stochastic

- Classical, macroscopic objects: we have well-defined values for all dynamical variables at every instant (position, momentum, kinetic energy…)
- Quantum objects: we have well-defined probabilities of measuring a certain value for a dynamical variable, when a large number of identical, independent, identically prepared physical systems are subject to a measurement.



## Top Three List

- ***Albert Einstein: "****Gott wurfelt nicht!" [God does not play dice!]*
- ***Werner Heisenberg*** *"I myself . . . only came to believe in the uncertainty relations after many pangs of conscience. . ."*
- **Erwin Schrödinger:** *"Had I known that we were not going to get rid of this damned quantum jumping, I never would have involved myself in this business!"*