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 $\Psi(x,y,z,t)$, which is complex, continuous, finite, and single-valued, square-integrable (i.e. $\int \Psi^* \Psi \, d^3r$ is finite)

- The ket can also be a geometrical vector (e.g. spin); in truth, wavefunctions are objects that satisfy vector algebra, and the space of wavefunctions 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)
  $$T = \frac{p^2}{2m}$$

• classical momentum $\vec{p} \rightarrow \nabla$ \hspace{1cm} gradient operator $-i\hbar \vec{\nabla}$

• classical position $\vec{r} \rightarrow \hat{r}$ \hspace{1cm} multiplicative operator $\hat{r}$

Operators and operator algebra

• Examples: derivative, multiplicative

\[
\Psi(\vec{r}) = \frac{-\hbar^2}{2m} \nabla^2 \Psi(\vec{r})
\]

Linear and Hermitian

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

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

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

  $\int \phi^* (\vec{r}) (\hat{A} \phi (\vec{r})) d\vec{r} = \int (\hat{A} \phi (\vec{r}))^* \phi (\vec{r}) d\vec{r}$

Examples: $(d/dx)$ and $i(d/dx)$

$\langle \psi |(A \phi) = \langle A \phi |\psi\rangle$

$\int \phi^* \frac{d\psi}{dn} = \int (\frac{d\phi}{dn})^* \psi d\phi$

$\int d(\psi \phi) = \int \phi^* d\psi + \int \psi d\phi^*$

$\int \phi^* \psi d\vec{r} = \int \phi^* d\psi + \int \psi d\phi^*$
Hermitian Operators

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
\[ \psi (\mathbf{r}) = \sum \psi_n (\mathbf{r}) \]

4. Commuting Hermitian operators have a set of common eigenfunctions

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The set of eigenfunctions of a Hermitian operator is complete

Figure by MIT OpenCourseWare.

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The set of eigenfunctions of a Hermitian operator is complete

\[ \psi(t=0) = \sum_{n=1}^{\infty} c_n \sin \left( \frac{\hbar_n}{\hbar} x \right) \cdot e^{i \frac{\hbar_n}{\hbar} t} \]

Figure by MIT OpenCourseWare.

Product of operators, and commutators

- \( \hat{A} \hat{B} \) \( \hat{A} \left( \hat{B} \psi \right) = \hat{B} \left( \hat{A} \psi \right) \)
- \( [\hat{A}, \hat{B}] \) \[ [\hat{A} \hat{B} - \hat{B} \hat{A}] \psi = 0 \]
- \( \left[ x, \frac{d}{dx} \right] = -1 \) \[ x \frac{df}{dx} = \frac{d}{dx} (xf) \]

Figure by MIT OpenCourseWare.
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.

Fourth Postulate

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

i.e. the probability of obtaining an eigenvalue $a_n$ is $P(a_n) = |\langle \varphi_n | \Psi \rangle|^2$
Dirac Notation

- Eigenvalue equation:
  \[ \hat{A} |\psi_i\rangle = a_i |\psi_i\rangle \quad \Rightarrow \quad \langle \psi_i | \psi_j \rangle = \delta_{ij} \]

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

Commuting Hermitian operators have a set of common eigenfunctions
Quantum double-slit

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**

Image removed due to copyright restrictions. Please see any experimental verification of the double-slit experiment, such as [http://commons.wikimedia.org/wiki/Image:Doubleslitexperiment_results_Tanamura_1.gif](http://commons.wikimedia.org/wiki/Image:Doubleslitexperiment_results_Tanamura_1.gif)

Image of a double-slit experiment simulation removed due to copyright restrictions. Please see "Double Slit Experiment," in *Visual Quantum Mechanics*.

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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!*”