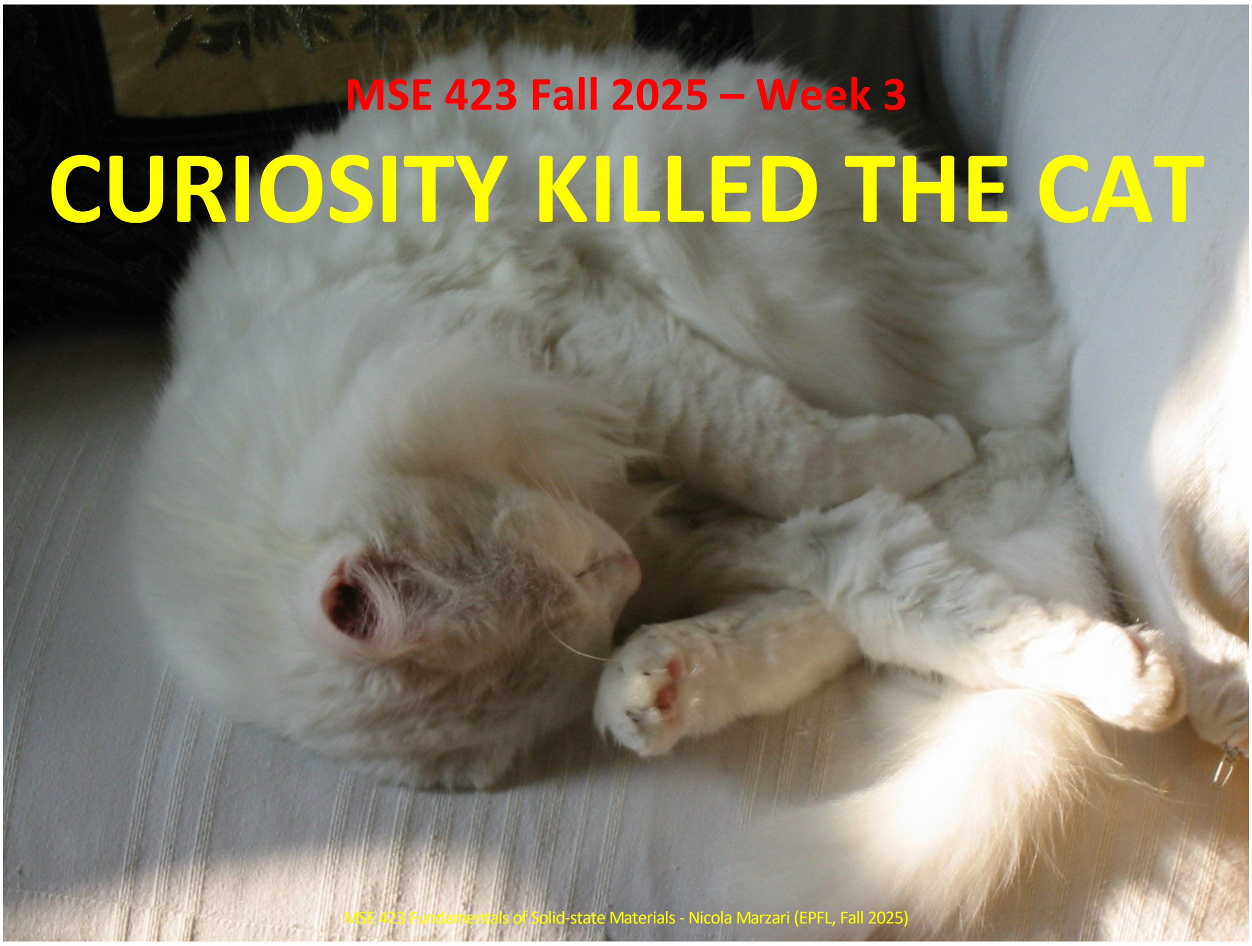
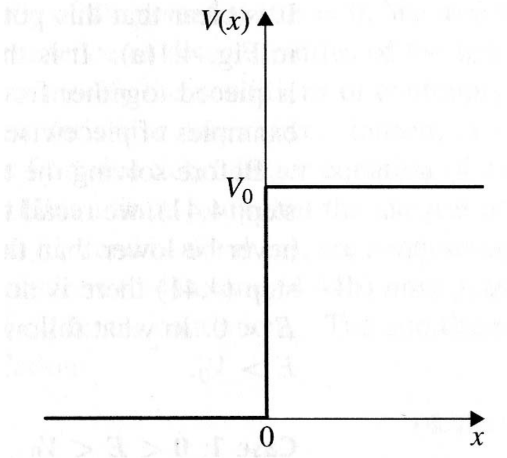


Last week: First steps

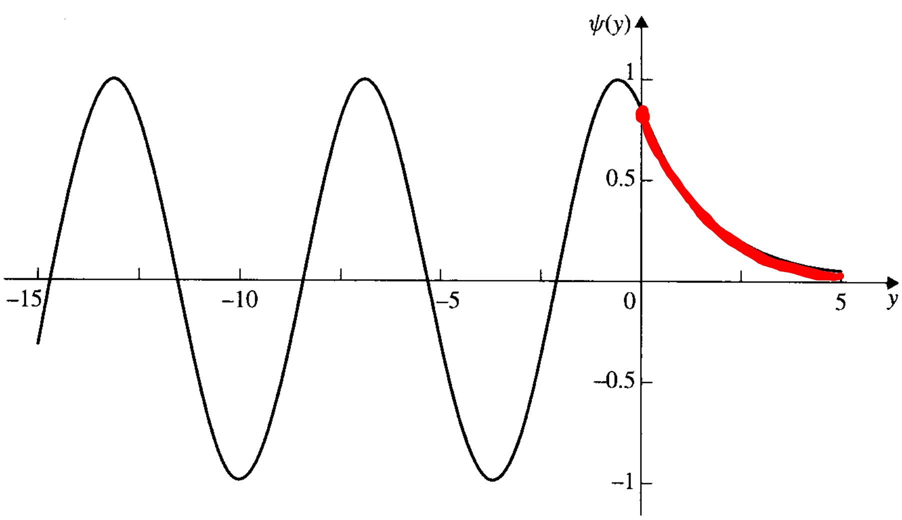
1. From one time-dependent Schroedinger eq. to two eqs.: stationary Schr. Eq. for $\varphi(\vec{r})$, and one for *f(t)*
2. Recovering the free particle, plane wave solution
3. Particle in a 1D, 2D, 3D box.
4. Potential step/metal surfaces
5. Quantum applets on osscar.org

Metal Surfaces (I)

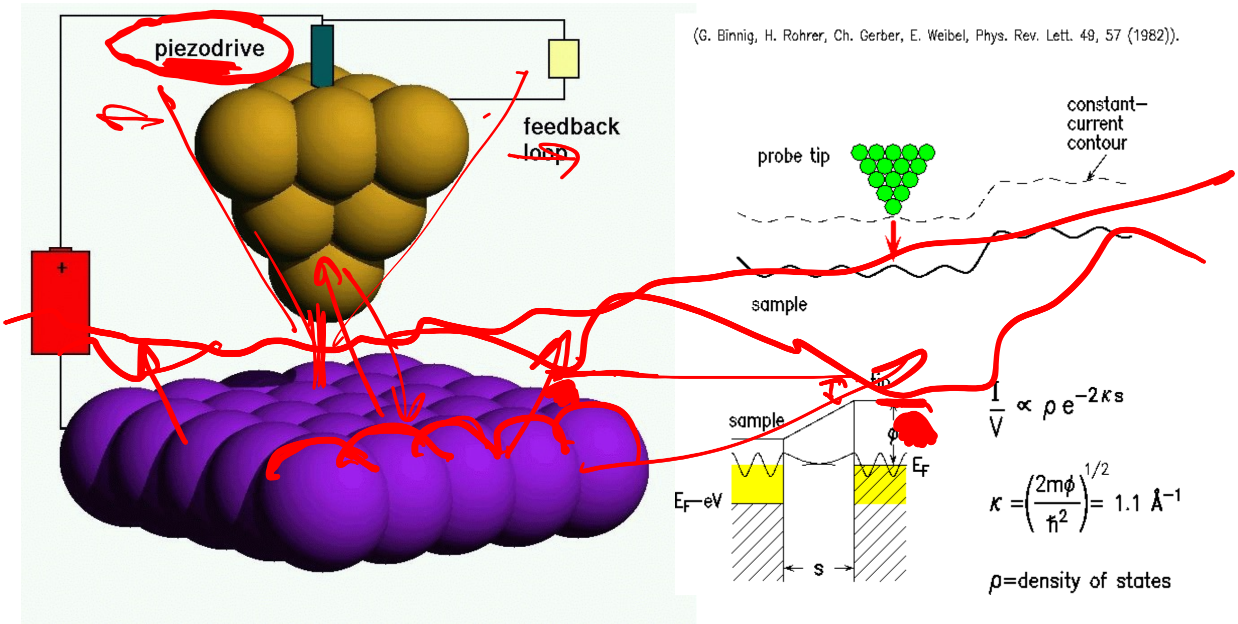
$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\varphi(x)=E\varphi(x)$$



Metal Surfaces (II)



Scanning Tunnelling Microscopy



Eigenvalue equation and expectations

Schrödinger equation: operator, eigenvalues

$$-\frac{\hbar^2}{2m}\nabla^2\varphi(\vec{r}) + V(\vec{r})\varphi(\vec{r}) = E\varphi(\vec{r})$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\varphi(\vec{r}) = E\varphi(\vec{r})$$

E can be obtained as an "expectation value"

$$\int \|\varphi\|^2 = 1$$

$$\underbrace{\int \varphi^* [\quad] \varphi}_{\text{EXP. VAL.}} = \underbrace{\int \varphi^*(\vec{r})\, E\, \varphi(\vec{r})} = E\int \varphi^*\varphi = E\int \|\varphi\|^2$$

Dirac notation

Dirac's <bra|kets> (elements of vector space)

$\varphi^*(\vec{r}) = \langle \varphi |$ KET $\varphi(\vec{r}) = | \varphi \rangle$

$\langle \varphi | \varphi \rangle = \int \varphi^*(\vec{r})\, \varphi(\vec{r})\, d\vec{r} = \int \| \varphi(\vec{r}) \|^2 d\vec{r}$

Scalar product (induces a metric → Hilbert space)

$\langle f | g \rangle = \int f^* g \, d\vec{r}$ $\vec{a} \cdot \vec{b} = a_x b_x + a_y b_y + a_z b_z$

SCALAR PRODUCT

$\vec{a} \cdot \vec{a} = \| a \|^2$

Eigenvalue equation and expectations

Schrödinger equation: operator, eigenvalues

$\hat{H} = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right]$ $\hat{H} | \varphi \rangle = E | \varphi \rangle$

E can be obtained as an "expectation value"

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

$\langle \varphi | E | \varphi \rangle = E \langle \varphi | \varphi \rangle = E$

4 concepts

- Operators $\rightsquigarrow \hat{H}$
- Eigenvalues $\rightsquigarrow E$
- Eigenfunctions $\rightsquigarrow |\varphi\rangle$
- Expectation values $\rightsquigarrow \langle\varphi|\hat{H}|\varphi\rangle$

Operators: Linear, Hermitian

$$\hat{A}(\alpha|f\rangle + \beta|g\rangle) =$$
$$= \alpha\hat{A}|f\rangle + \beta\hat{A}|g\rangle$$

$\forall\ |g\rangle,\ \langle f|$

$$\langle f|\hat{A}g\rangle = \langle\hat{A}f|g\rangle$$

$\hat{A}$ IS HERMITIAN

NOT HERMITIAN HERMITIAN

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

$$\langle f | i\frac{d}{dx} g \rangle \overset{?}{=} \langle i\frac{df}{dx} | g \rangle$$

$$= \int_{-\infty}^{+\infty} f^*(x)\, i\frac{dg(x)}{dx}\, dx \overset{?}{=} \int_{-\infty}^{+\infty} -i\frac{df^*(x)}{dx}\, g(x)\, dx$$

$$\cancel{\left[f^*(x)g(x)\right]_{-\infty}^{+\infty}} - \int_{-\infty}^{+\infty} i\frac{df^*}{dx} g(x)\, dx$$

$$d[fg] = df\, g + f\, dg$$

Hermitian Operators

1. The eigenvalues of a Hermitian operator are real

$$\hat{A}|f\rangle = a|f\rangle$$

2. Two eigenfunctions corresponding to different eigenvalues are orthogonal

$$\hat{A}|f_1\rangle = a_1|f_1\rangle \qquad a_1 \neq a_2 \Rightarrow \langle f_1|f_2\rangle$$

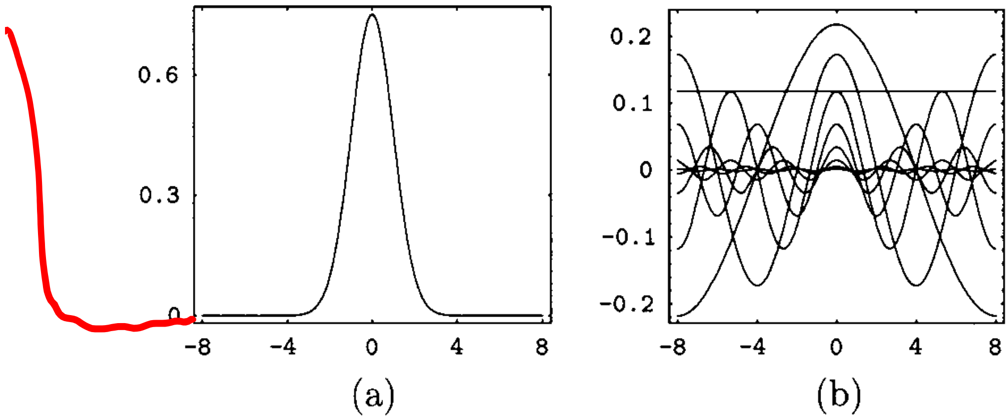
$$\hat{A}|f_2\rangle = a_2|f_2\rangle \qquad = \langle f_2|f_1\rangle = 0$$

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

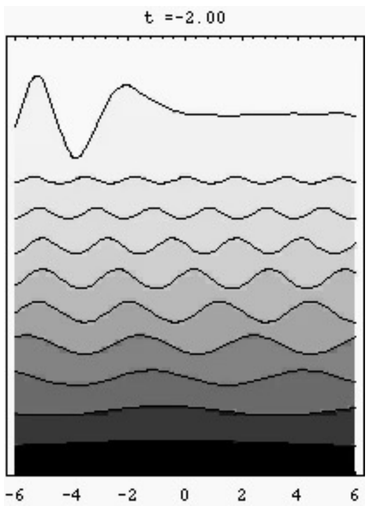
$$\hat{A}|f_i\rangle = a_i|f_i\rangle$$

4. Commuting Hermitian operators have a set of common eigenfunctions

The set of eigenfunctions of a Hermitian operator is complete



The set of eigenfunctions of a Hermitian operator is complete



Product of operators, and commutators

$$\hat{A} \cdot \hat{B} = \hat{A}\hat{B} \qquad \hat{A}\left(\hat{B}\,|f\rangle\right)$$

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

COMMUTATOR

$\hat{A}$ AND $\hat{B}$ COMMUTE $[\hat{A},\hat{B}] = 0$

Commuting Hermitian operators have a set of common eigenfunctions

(I) $\hat{A}\,|f_i\rangle = a_i\,|f_i\rangle$

(II) $\hat{B}\,|g_i\rangle = b_i\,|g_i\rangle$

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

$$\hat{A}\hat{B} = \hat{B}\hat{A}$$

$$\underbrace{\hat{B}\hat{A}\,|f_i\rangle}_{\parallel} = \underbrace{\hat{B}\,a_i\,|f_i\rangle}_{\parallel}$$

$$\hat{A}\left(\hat{B}\,|f_i\rangle\right) = a_i\left(\hat{B}\,|f_i\rangle\right)$$

$\hat{B}\,|f_i\rangle$ IS AN EIGENSTATE OF $\hat{A}$

$$\hat{B}\,|f_i\rangle = \gamma_i\,|f_i\rangle$$

First postulate: wavefunctions

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

- The ket can also be a geometrical vector (e.g. spin); 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)

Second postulate: operators

- For every physical observable there is a corresponding Hermitian operator

$$\left\langle \varphi \middle| \hat{A}\psi \right\rangle = \left\langle \hat{A}\varphi \middle| \psi \right\rangle$$

From classical mechanics to operators

- classical momentum $\vec{p}$ → $-i\hbar\vec{\nabla}$
  → gradient operator $-i\hbar\vec{\nabla}$
- classical position $\vec{r}$ →
  → multiplicative operator $\hat{r}$

$\hat{T} + \hat{V} = \hat{H}|\psi\rangle = E|\psi\rangle$

The total energy of the system =

$= K + V$

- Kinetic energy K =

$\vec{p}\cdot\vec{p}$

$K = \frac{1}{2}m\vec{v}^2 = \frac{\vec{p}^2}{2m} \mapsto \frac{(-i\hbar\vec{\nabla})\cdot(-i\hbar\vec{\nabla})}{2m} = -\frac{\hbar^2}{2m}\vec{\nabla}\cdot\vec{\nabla} =$

$\vec{p} = m\vec{v}$

$\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)\cdot\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) = -\frac{\hbar^2}{2m}\nabla^2$

- Potential energy V

$V(\vec{r})$

Third postulate: measurements

- 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.

Position and probability

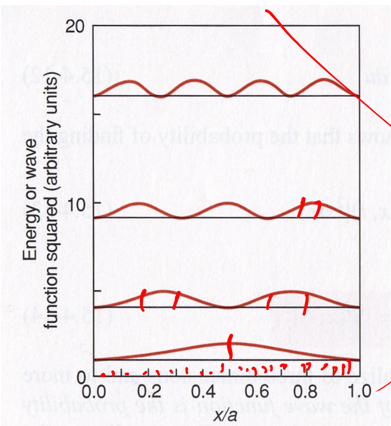


Figure 15.2. The Probability Density for Positions of a Particle in a One-Dimensional Hard Box. This diagram shows the squares of the energy eigenfunctions (probability densities) for the first four states of a particle in a one-dimensional hard box.

Fourth postulate: expectation values and probabilities

If a series of measurements is made of the dynamical variable A on an ensemble described by $|\Psi\rangle$, the average ("expectation") value is

$$\langle \hat{A} \rangle = \frac{\langle \Psi | \hat{A} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

i.e. the probability of obtaining an eigenvalue a_n is

$$\underline{P(a_n)} = (p_n)^2 = \left| \underline{\langle \varphi_n | \Psi \rangle} \right|^2$$

$$\hat{A}\,|\varphi_n\rangle = a_n\,|\varphi_n\rangle$$

$$|\psi\rangle = \sum_i c_i\,|\varphi_i\rangle$$

$$\langle \varphi_{27} | \psi \rangle = \sum_i c_i \underbrace{\langle \varphi_{27} | \varphi_i \rangle}_{\delta_{27,i}} = c_{27}$$

HERMITIAN:
a_n POSSIBLE EIGENV. RESULTS OF A MEASUREMENT.
THEY ARE REAL
$\{|\varphi_n\rangle\}$ IS COMPLETE
$\{\ \ \}$ ARE ORTHOGONAL
" ORTHONORMAL

$$(x,y,z) = \vec{r} = x\,\hat{x} + y\,\hat{y} + z\,\hat{z}$$

$$\stackrel{!}{=} x(1,0,0) + y(0,1,0) + z(0,0,1)$$

$$(1,0,0)\cdot\vec{r} = x$$

$$\langle \hat{A} \rangle = \frac{\langle \psi | \hat{A} | \psi \rangle}{\langle \psi | \psi \rangle}$$

$$\langle \psi | \psi \rangle = \sum_{i,j} c_j^* c_i \langle \varphi_j | \varphi_i \rangle$$ 1 ys NORMALIZED

$$= \sum_i \langle \psi | \hat{A} | \varphi_i \rangle c_i$$

$$= \sum_{i,j} c_j^* c_i \langle \varphi_j | \underbrace{\hat{A} | \varphi_i \rangle}_{a_i | \varphi_i \rangle}$$

$$= \sum_{i,j} c_j^* c_j \langle \varphi_j | a_i | \varphi_i \rangle = \sum_{i,j} a_i c_j^* c_i \langle \varphi_j | \varphi_i \rangle$$

$$= \sum_\ell a_\ell \| c_\ell \|^2$$

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

$$| \psi \rangle = \sum_i c_i | \varphi_i \rangle$$

$$c_i = \langle \varphi_i | \psi \rangle$$

$$\langle \psi | = \sum_j c_j^* \langle \varphi_j |$$

$$\int (\dots) \hat{A} (\dots)$$