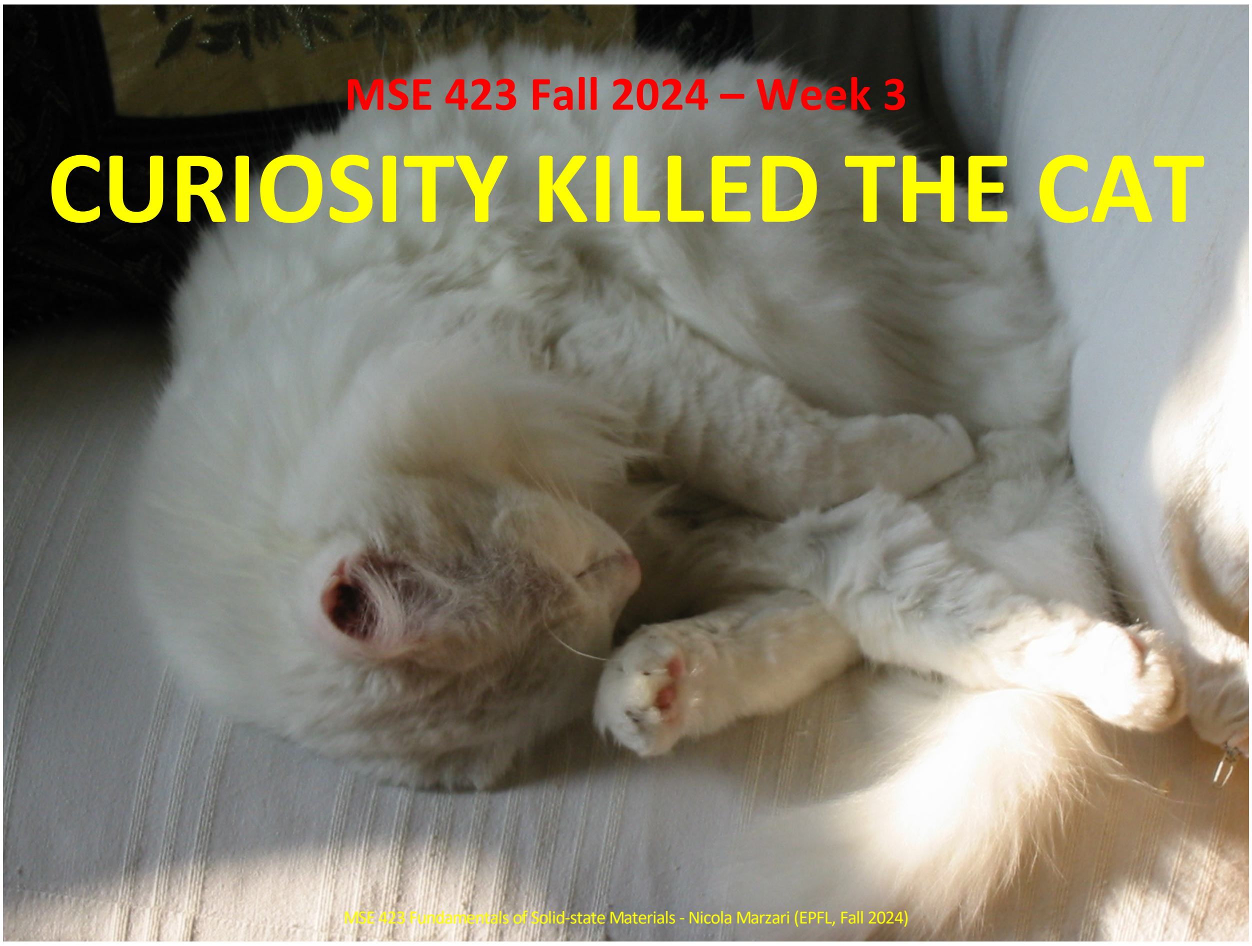


$A e^{i(\vec{k}\cdot\vec{r}-\omega t)}$

Last week: First steps

$\hat{H}$ $\quad \psi(\vec{r},t) = \varphi(\vec{r}) f(t)$

1. Stationary and time-dependent Schroedinger eq.
2. Eigenvalue equations $\left[-\frac{\hbar^2}{2m}\nabla^2+V\right]\varphi_\ell = \varepsilon_\ell \varphi_\ell$
3. Free particle, and particle in a 1D, 2D, 3D box.
4. Metal surfaces and STM $\quad V=0 \quad V=V_0$
5. Quantum applets on osscar.org
6. Operators, eigenvalues, eigenfunctions, expectation values $\varphi_\ell \Rightarrow \int \varphi_\ell^* \cdot \underbrace{\left[-\frac{\hbar^2}{2m}\nabla^2+V\right]\varphi_\ell}_{\varepsilon_\ell \varphi_\ell} = \varepsilon_\ell \underbrace{\int \varphi_\ell^* \varphi_\ell}_{=1}$
7. Dirac notations, <bra|ket>

$\hat{H}|\varphi_\ell\rangle = \varepsilon_\ell |\varphi_\ell\rangle$

$\varepsilon_\ell = \langle\varphi_\ell|\hat{H}|\varphi_\ell\rangle$

$\varphi_\ell(\vec{r}) = |\varphi_\ell\rangle$

$\varphi_\ell^*(\vec{r}) = \langle\varphi_\ell|$

Physical Observables from Wavefunctions

Eigenvalue equation:

$$\hat{H}|\varphi\rangle = \varepsilon|\varphi\rangle$$

(EIGENVALUE EQ. FOR THE ENERGY ⟺ $\hat{H}$ IS THE SCH. EQ.)

Expectation values for the operator (energy)

$$\varepsilon = \langle\varphi|\hat{H}|\varphi\rangle$$

4 concepts

- Operators
- Eigenvalues
- Eigenfunctions
- Expectation values

Operators: Linear, Hermitian

WAVEFUNCTIONS (KETS)

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

COMPLEX NUMBER

$\hat{A}$ IS HERMITIAN IF $\forall f,g \Rightarrow \langle \underbrace{f}_{\text{VECTOR}}|\underbrace{\hat{A}g}_{\text{VECTOR}}\rangle=\langle Af|g\rangle$

$\langle\ |\ \rangle$ IS THE SCALAR PRODUCT

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

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

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

$$d[fg]=df\,g+dg\,\cancel{df}$$
$$\int d[fg]-\int df\,g=\int dg\,\cancel{df}$$
$$fg\Big|_{-\infty}^{+\infty}-\int df\,g=\int f\,dg$$

$$\underbrace{[f^*g]_{-\infty}^{+\infty}}_{0}-\underbrace{\int_{-\infty}^{+\infty}i\frac{df^*}{dx}g}$$

$$\boxed{\int\|f\|^2=A}$$

$$f\to\frac{1}{\sqrt{A}}f$$

$$\int\frac{1}{A}\|f\|^2=1$$

Product of operators, and commutators

2x3

2·3

2*3

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

COMMUTATOR OF $\hat{A}$ AND $\hat{B}$

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

$\rightarrow 0$ $\hat{A}$ AND $\hat{B}$ COMMUTE

$\rightarrow \neq 0$ $\hat{A}$ AND $\hat{B}$ DO NOT COMMUTE

Hermitian Operators

(NON DIAGONAL OPERATORS)

1. The eigenvalues of a Hermitian operator are real

$$\hat{A}|\varphi\rangle = a|\varphi\rangle \qquad a \in \mathbb{R}$$

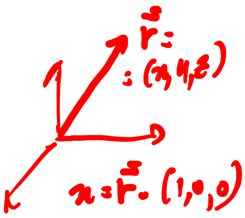
TRY TO PROVE

2. Two eigenfunctions corresponding to different eigenvalues are orthogonal

$$\hat{A}|\varphi_1\rangle = a_1|\varphi_1\rangle \qquad a_1 \neq a_2 \Rightarrow \langle\varphi_1|\varphi_2\rangle = 0$$
$$\hat{A}|\varphi_2\rangle = a_2|\varphi_2\rangle$$

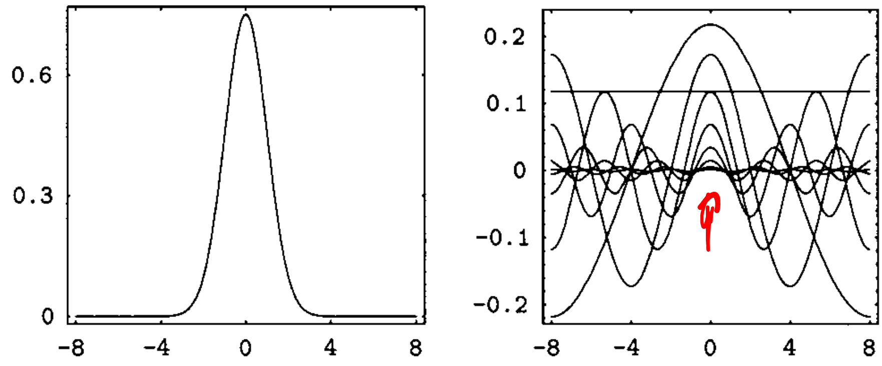
3. The set of eigenfunctions of a Hermitian operator is complete

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



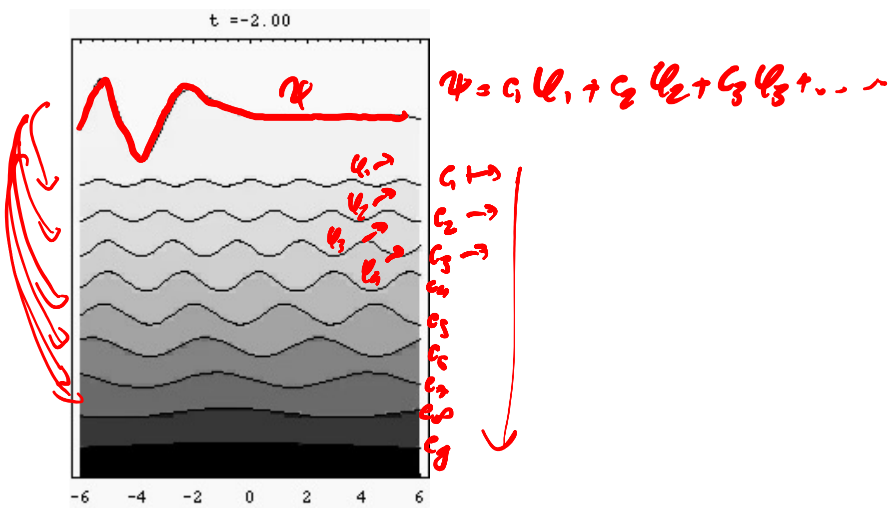
4. Commuting Hermitian operators have a set of common eigenfunctions

The set of eigenfunctions of a Hermitian operator is complete



(a) (b)

The set of eigenfunctions of a Hermitian operator is complete



$\psi = c_1 \varphi_1 + c_2 \varphi_2 + c_3 \varphi_3 + \ldots$

Commuting Hermitian operators have a set of common eigenfunctions

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

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

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

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

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

I DISCOVERED THAT $\hat{B}|f_i\rangle$ IS AN EIGENFUNCTION OF $\hat{A}$

(3) $\hat{B}|f_i\rangle = \gamma_i|f_i\rangle$

First postulate: wavefunctions

- All information of an ensemble of identical physical systems is contained in the ket $|\Psi\rangle$ (usually a wavefunction $\Psi(x,y,z,t)$, 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); 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

$\forall \varphi, \psi$:

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

From classical mechanics to operators

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

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

$\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) \cdot \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$

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

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

$= -\frac{\hbar^2}{2m} \nabla^2$

$E = \frac{p^2}{2m} + V$

$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \hat{V}(r)$, $\hat{L} = \vec{r} \times \vec{p}$

The total energy of the system

- Kinetic energy ~~K~~ T

T

$\downarrow$

$$\frac{p^2}{2m} \rightarrow -\frac{\hbar^2}{2m}\nabla^2$$

- Potential energy V

$$\hat{V}(\vec{r})$$

$$E = T + V = \frac{p^2}{2m} + V$$

$\downarrow$

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

Third postulate: measurements

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

Position and probability

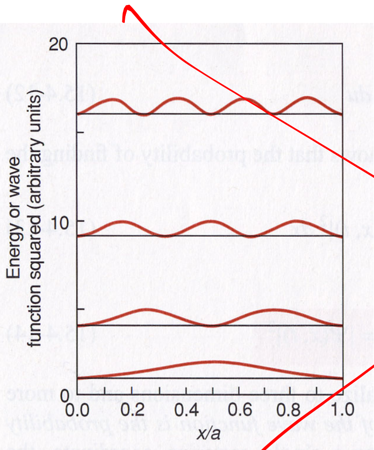


Figure 15.2. The Probability Density for Positions of a Particle in a One-Dimensional Hard Box. This diagram shows the squares of the energy eigenfunctions (probability densities) for the first four states of a particle in a one-dimensional hard box.

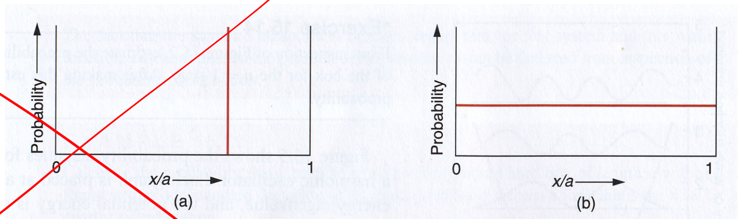


Figure 15.3. The Probability Density for Positions of a Particle in a One-Dimensional Hard Box according to Classical Mechanics. (a) **The instantaneous probability.** At a given time, there is no uncertainty about the position of the particle. (b) **The probability averaged over a long time.** The average probability density is uniform, with all parts of the box equally probable.

Fourth postulate: expectation values and probabilities

If a series of measurements is made of the ~~dynamical~~ PHYSICAL variable A CORRESPONDING TO THIS OPERATOR on an ensemble described by Ψ, the average ("expectation") value is

$$\langle \hat{A} \rangle = \frac{\langle \Psi | \hat{A} | \Psi \rangle}{\underbrace{\langle \Psi | \Psi \rangle}_{=1}} = \frac{\int \psi^* \hat{A} \psi}{\underbrace{\int \psi^* \psi}_{=1}}$$

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

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

$$\langle \varphi_5 | \underbrace{\Psi}\rangle = \frac{1}{\sqrt{2}}\langle\varphi_5|\varphi_1\rangle + \frac{1}{\sqrt{2}}\langle\varphi_5|\varphi_3\rangle$$

$$\langle \Psi|\Psi\rangle = \left(\frac{1}{\sqrt{2}}\langle\varphi_1| + \frac{1}{\sqrt{2}}\langle\varphi_3|\right)\left(\frac{1}{\sqrt{2}}|\varphi_1\rangle + \frac{1}{\sqrt{2}}|\varphi_3\rangle\right)$$

$|\varphi_1\rangle$ AND $|\varphi_3\rangle$ ARE EIGENSTATES OF PARTICLE IN THE BOX.

$$\frac{1}{2}\underbrace{\langle\varphi_1|\varphi_1\rangle}_{=1} + \frac{1}{2}\cancel{\langle\varphi_3|\varphi_1\rangle} + \frac{1}{2}\cancel{\langle\varphi_1|\varphi_3\rangle} + \frac{1}{2}\underbrace{\langle\varphi_3|\varphi_3\rangle}_{=1}$$

$= 1$

$$\langle\varphi_i|\varphi_j\rangle = \delta_{ij}$$

$\hat{x}$ $\hat{y}$ $\hat{z}$

$(1,0,0)$ $(0,1,0)$ $(0,0,1)$

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

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

$\hat{A}$ IS HERMITIAN $\Rightarrow$ IS COMPLETE

$$\frac{\langle\psi|\hat{A}|\psi\rangle}{\langle\psi|\psi\rangle} = \langle\hat{A}\rangle = \frac{\sum_n \|C_n\|^2 a_n}{\sum_n \|C_n\|^2}$$

$\|C_n\|^2$

$$|\Psi\rangle = \sum_n C_n|\varphi_n\rangle$$

$$(\ \cdots\ )\ \underbrace{\|\langle\varphi_n|\psi\rangle\|^2}_{\text{PROB. OF } a_n}$$

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

$$\langle\psi|\psi\rangle = \sum_{m,n} C_m^* C_n \overbrace{\langle\varphi_m|\varphi_n\rangle}^{\delta_{mn}} = \sum_{m,n} C_m^* C_n \delta_{mn}$$

$\langle\psi| \to \sum_m C_m^*\langle\varphi_m|$

$|\psi\rangle \to \sum_n C_n|\varphi_n\rangle$

$$= \sum_\ell C_\ell^* C_\ell = \sum_\ell \|C_\ell\|^2 =$$

$$= \sum_m \|C_m\|^2 = \sum_n \|C_n\|^2$$

- See lecture video

- See lecture video

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.

Quantum double-slit

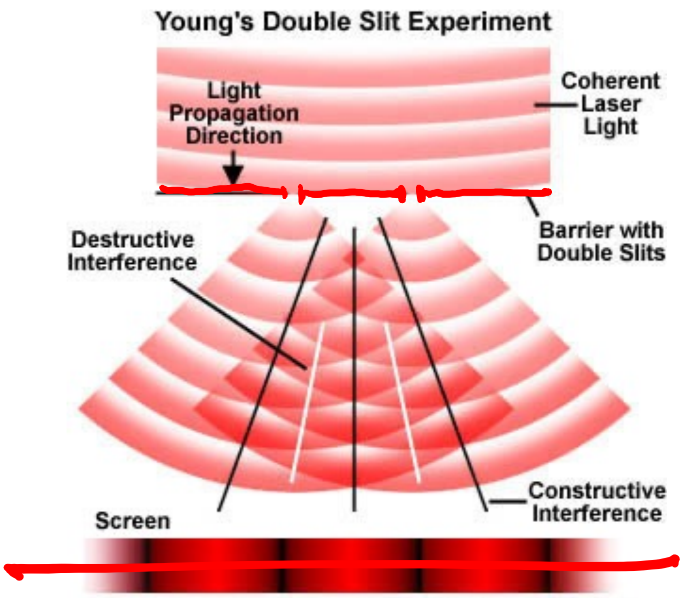
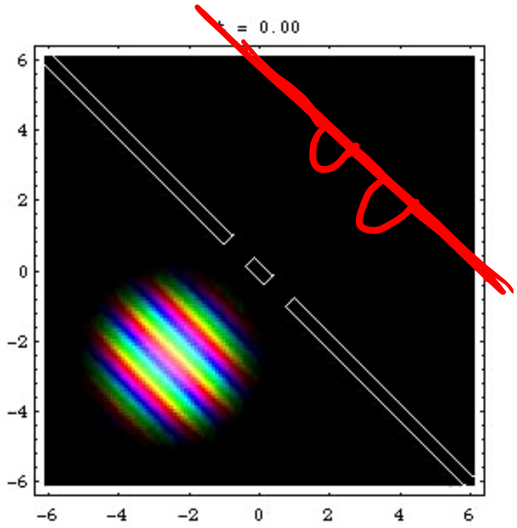
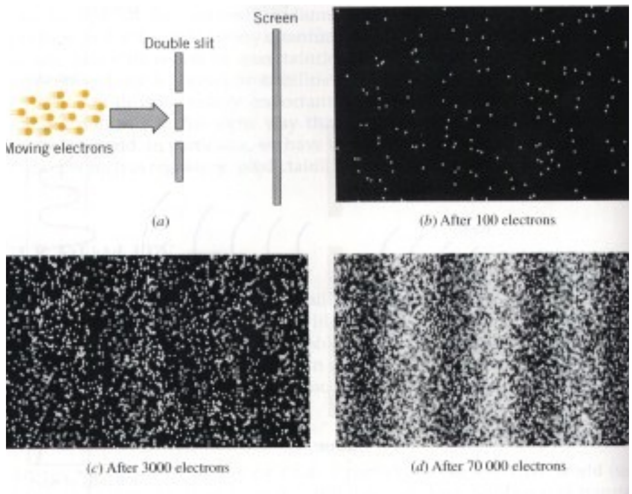


Figure 4

Quantum double-slit





(a)
(b) After 100 electrons
(c) After 3000 electrons
(d) After 70 000 electrons