Lecture 24. Hermitian Operators

What properties must operators that correspond to observables have? For oen thing, we want its eigenvalues to be all real. We will show that Hermitian opeators have the desired properties. Definition: An operator $\hat{A}$ is Hermitian if

$$\int f^* \left(\hat{A}g\right) d\tau = \int \left(\hat{A}f\right)^* g\, d\tau$$

Example: $\hat{A} = -i\hbar \frac{d}{dx}$

$$\int_{-\infty}^{\infty} f^* \left(-i\hbar \frac{dg}{dx}\right) dx = -i\hbar f^* g\Big|_{-\infty}^{\infty} + i\hbar \int_{-\infty}^{\infty} \frac{df^*}{dx} g\,dx = \int_{-\infty}^{\infty} \left(-i\hbar \frac{df}{dx}\right)^* g\,dx$$

In the first step we integrated by parts:

$$u = f^*, dv = -i\hbar \frac{dg}{dx} dx$$

$$du = \frac{df^*}{dx} dx, v = -i\hbar g$$

In the second step we assumed that f and g vanish at $\pm\infty$.

Properties of Hermitian operators:

1) Their eigenvalues are real.

Let $f = \psi_m$ and $g = \psi_n$ be eigenfunctions of $\hat{A}$. Then the Hermition property of $\hat{A}$ tells us that

$$\langle m|\hat{A}|n\rangle = \langle n|\hat{A}|m\rangle^*$$

But by assumption,

$$\hat{A}|n\rangle = a_n|n\rangle$$
$$\hat{A}|m\rangle = a_m|m\rangle$$

It follows that

$$a_n\langle m|n\rangle = a_m^*\langle n|m\rangle$$

For m = n, $a_n = a_n^*$.

Note: $\langle n|n\rangle = \int \psi_n^* \psi_n d\tau = \langle n|n\rangle^*$

Eigenfunctions belonging to different eigenvalues of a Hermitian operator are orthogonal.

$$\langle m|\hat{A}|n\rangle = a_n \langle m|n\rangle$$
$$\langle n|\hat{A}|m\rangle^* = a_m^* \langle n|m\rangle^* = a_n \langle m|n\rangle$$

Note: $\langle n|m\rangle^* = \left[\int \psi_n^* \psi_m d\tau\right]^* = \int \psi_m^* \psi_n d\tau = \langle m|n\rangle$

But $\langle m|\hat{A}|n\rangle = \langle n|\hat{A}|m\rangle^*$

Therefore:

$$(a_n - a_m)\langle m|n\rangle = 0$$
$$a_n \neq a_m \Rightarrow \langle m|n\rangle = 0$$

2) If $\hat{A}$ and $\hat{B}$ are Hermitian and do not commute, then $[\hat{A},\hat{B}] = i\hat{C}$, where $\hat{C}$ is also Hermitian.

Claim: $\int \psi^* \hat{A}\hat{B}\phi d\tau = \int \left(\hat{A}\psi\right)^* \hat{B}\phi d\tau = \int \left(\hat{B}\hat{A}\psi\right)^* \phi d\tau$

Therefore, $\int \psi^* \left(\hat{A}\hat{B} - \hat{B}\hat{A}\right)\phi d\tau = \int \left[\left(\hat{B}\hat{A} - \hat{A}\hat{B}\right)\psi\right]^* \phi d\tau$

$$\int \psi^* [\hat{A},\hat{B}]\phi d\tau = \int \left[[\hat{B},\hat{A}]\psi\right]^* \phi d\tau = -\int \left[[\hat{A},\hat{B}]\psi\right]^* \phi d\tau$$

Set $[\hat{A},\hat{B}] = i\hat{C}$

Therefore,

$$\int \psi^* i\hat{C}\phi d\tau = -\int \left(i\hat{C}\psi\right)^* \phi d\tau = i\int \left(\hat{C}\psi\right)^* \phi d\tau$$
$$\int \psi^* \hat{C}\phi d\tau = \int \left(\hat{C}\psi\right)^* \phi d\tau$$

It follows that $\hat{C}$ is Hermitian.

Examples:

$$[\hat{x},\hat{p}] = i\hbar$$
$$[\hat{L}_x,\hat{L}_y] = i\hbar\hat{L}_z$$

We can use these theorems to derive the Uncertainty Principle.

Definition of the uncertainty:

$$(\Delta A)^2 = \left\langle \hat{A}^2 \right\rangle - \left\langle \hat{A} \right\rangle^2$$

Can $\Delta A = 0$? Yes, for an eigenstate!

Can $\Delta A = \Delta B = 0$? Let $\left[\hat{A}, \hat{B}\right] = i\hat{C}$. We will prove that

$$\Delta A \cdot \Delta B \geq \frac{1}{2}\left|\left\langle \hat{C} \right\rangle\right|$$

The proof is based on a theorem known as the Schwarz inequality:

$$\int |f|^2 d\tau \cdot \int |f|^2 d\tau \geq \left| \int f^* g d\tau \right|^2$$

The equality holds only if $f \propto g$. A simple geometric interpretation of this inequality is based on the "angle" between two state vectors:

$$\cos\theta = \frac{\left|\langle f \mid g \rangle\right|}{\sqrt{\langle f \mid f \rangle \langle g \mid g \rangle}} \leq 1$$

Choose:

$$f = \left(\hat{A} - \langle A \rangle\right)\psi$$
$$g = \left(\hat{B} - \langle B \rangle\right)\psi$$

Schwarz' inequality tells us that

$$(\Delta A)^2 (\Delta B)^2 \geq \left| \int \psi^* \left(\hat{A} - \langle A \rangle\right)\left(\hat{B} - \langle B \rangle\right)\psi d\tau \right|^2$$

Prove the following:

$$\left(\hat{A} - \langle A \rangle\right)\left(\hat{B} - \langle B \rangle\right) = \frac{1}{2}\hat{F} + \frac{i}{2}\hat{C}$$

where

$$\hat{F} = \{(\hat{A} - \langle A \rangle)(\hat{B} - \langle B \rangle) + (\hat{B} - \langle B \rangle)(\hat{A} - \langle A \rangle)\}$$
$$\hat{C} = i[\hat{A}, \hat{B}]$$

Also prove that $\hat{F}$ is Hermitian.

It then follows that

$$\int \psi^* (\hat{A} - \langle A \rangle)(\hat{B} - \langle B \rangle)\psi d\tau = \langle F \rangle + \frac{i}{2}\langle C \rangle$$

where $\langle F \rangle, \langle C \rangle$ are both real.

The absolute value squared of this integral is

$$\langle F \rangle^2 + \frac{1}{4}\langle C \rangle^2 \geq \frac{1}{4}\langle C \rangle^2$$

Q.E.D.

Lecture 25. Matrix Mechanics

State vectors

Basis set:

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ . \\ . \\ . \end{pmatrix},$$

$$|2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \\ . \\ . \\ . \end{pmatrix}$$

$$|3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ . \\ . \\ . \end{pmatrix}$$

Addition of basis vectors:

$$\begin{pmatrix} 1 \\ 0 \\ 0 \\ . \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ 1 \\ . \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 1 \\ . \end{pmatrix}$$

Scalar multiplication of basis vectors:

$$a\begin{pmatrix}1\\0\\0\\.\end{pmatrix}=\begin{pmatrix}a\\0\\0\\.\end{pmatrix}$$

State expansion:

$$|a\rangle=\sum_i a_i|i\rangle=a_1\begin{pmatrix}1\\0\\0\\.\end{pmatrix}+a_2\begin{pmatrix}0\\1\\0\\.\end{pmatrix}+a_3\begin{pmatrix}0\\0\\1\\.\end{pmatrix}+\cdots=\begin{pmatrix}a_1\\a_2\\a_3\\.\end{pmatrix}$$

Vector addition:

$$|a\rangle+|b\rangle=\begin{pmatrix}a_1\\a_2\\a_3\\.\end{pmatrix}+\begin{pmatrix}b_1\\b_2\\b_3\\.\end{pmatrix}=\begin{pmatrix}a_1+b_1\\a_2+b_2\\a_3+b_3\\.\end{pmatrix}$$

Scalar multipluication:

$$\lambda|a\rangle=\lambda\begin{pmatrix}a_1\\a_2\\a_3\\.\end{pmatrix}=\begin{pmatrix}\lambda a_1\\\lambda a_2\\\lambda a_3\\.\end{pmatrix}$$

Dual or adjoint vectors:

$$|a\rangle^{\perp}=\left\{\sum_i a_i|i\rangle\right\}^{\perp}=\sum_i\langle i|a_i^{*}=\begin{pmatrix}a_1\\a_2\\a_3\\.\end{pmatrix}^{\perp}=\begin{pmatrix}a_1^{*} & a_2^{*} & a_3^{*} & \cdot\end{pmatrix}$$

Note: The symbol for an adjoint is a dagger, but because I don't have that font, I used $\perp$ instead.

Orthonormality: $\langle i | j \rangle = \delta_{ij}$

$$\begin{pmatrix} 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = 1$$

$$\begin{pmatrix} 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = 0$$

Dot product:

$$\langle b | a \rangle = \begin{pmatrix} b_1^* & b^* & b_3^* \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} = b_1^* a_1 + b_2^* a_2 + b_3^* a_3 = \sum_i b_i^* a_i$$

Normalization:

$$\langle a | a \rangle = \begin{pmatrix} a_1^* & a_2^* & a_3^* \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} = \sum_i |a_i|^2 \geq 0.$$

Lecture 26. Matrix Representations of Linear Operators

A linear operator is a linear vector transformation: $\hat{T}|a\rangle = |b\rangle$
Consider the clockwise rotation of a vector in the *xy* plane by an angle θ.

$$\hat{R}_\theta \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} \cos\theta \\ -\sin\theta \end{pmatrix}$$

$$\hat{R}_\theta \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} \sin\theta \\ \cos\theta \end{pmatrix}$$

$$\hat{R}_\theta \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = a_1 \hat{R}_\theta \begin{pmatrix} 1 \\ 0 \end{pmatrix} + a_2 \hat{R}_\theta \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} a_1 \cos\theta + a_2 \sin\theta \\ -a_1 \sin\theta + a_2 \cos\theta \end{pmatrix}$$

This last result prompts us to write $\hat{R}_\theta$ as a matrix:

$$\hat{R}_\theta = \begin{pmatrix} R_{11} & R_{12} \\ R_{21} & R_{22} \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}$$

Transformation of a basis sate:

$$\hat{R}_\theta \begin{pmatrix}1\\0\end{pmatrix} = \begin{pmatrix}R_{11} & R_{12}\\ R_{21} & R_{22}\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = \begin{pmatrix}R_{11}\\R_{21}\end{pmatrix} = \sum_i R_{i1}|i\rangle$$

$$\hat{R}_\theta \begin{pmatrix}0\\1\end{pmatrix} = \begin{pmatrix}R_{11} & R_{12}\\ R_{21} & R_{22}\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} = \begin{pmatrix}R_{12}\\R_{22}\end{pmatrix} = \sum_i R_{i2}|i\rangle$$

$$\hat{R}_\theta |n\rangle = \sum_i R_{in}|i\rangle$$

Transformation of an arbitrary state:

$$\hat{R}_\theta |a\rangle = \hat{R}_\theta \sum_j a_j | j\rangle = \sum_j a_j \hat{R}_\theta | j\rangle = \sum_j a_j \left[\sum_i R_{ij}|i\rangle\right] = \sum_i \left[\sum_j R_{ij} a_j\right]|i\rangle = \sum_i b_i |i\rangle = |b\rangle$$

$$b_i = \sum_j R_{ij} a_j$$

Successive operations: $\hat{C} = \hat{B}\hat{A}$

Let

$$| f\rangle = \sum_i f_i |i\rangle$$

$$\hat{A}| f\rangle = |g\rangle = \sum_i g_i |i\rangle$$

$$\hat{B}|g\rangle = |h\rangle = \sum_i h_i |i\rangle$$

But we already proved that

$$h_i = \sum_k B_{ik} g_k$$

$$g_k = \sum_j A_{kj} g_j$$

Putting the pieces together,

$$h_i = \sum_k \sum_j B_{ik} A_{kj} f_j$$

$$|h\rangle = \sum_i \left[\sum_{jk} B_{ik} A_{kj} f_j\right]|i\rangle = \sum_i h_i |i\rangle$$

But it is also true that

$$|h\rangle = \hat{C}| f\rangle = \sum_j f_j \hat{C}| j\rangle = \sum_j f_j \sum_i C_{ij}|i\rangle = \sum_i \left[\sum_j C_{ij} f_j\right]|i\rangle = \sum_i h_i |i\rangle$$

Equating these two results,

$$\sum_j C_{ij} f_j = \sum_j \left[\sum_k B_{ik} A_{kj} f_j \right]$$
$$C_{ij} = \sum_k B_{ik} A_{kj}$$

This is matrix multiplication.

How do we calculate A_{ij}?

$$\hat{A}| j\rangle = \sum_k A_{kuj} |k\rangle$$
$$\langle i [\hat{A}| j\rangle] = \langle i | \sum_k A_{kj} |k\rangle = \sum_k A_{kj} \langle i | k\rangle = \sum_k A_{kj} \delta_{ik} = A_{ij}$$

It follows that

$$A_{ij} = \langle i | \hat{A} | j\rangle = \int \psi_i^* \hat{A} \psi_j d\tau$$

Lecture 27. Hermitian Matrices.

Left and right operations:

Compare $\langle a | \cdot (\hat{A} | b\rangle) = \int \psi_a^* (\hat{A} \psi_b) d\tau$ with $(\langle a | \hat{A}) \cdot | b\rangle = \int (\hat{A} \psi_a)^* \psi_b d\tau$. Are they equal? Not necessarily! For this reason we define the Hermitian adjoint of $\hat{A}$.

$$\int (\hat{A}^{\perp} \psi_b)^* \psi_a d\tau = \int \psi_b^* (\hat{A} \psi_a) d\tau$$

What are the matrix elements of $\hat{A}^{\perp}$? Look at how it operates on the basis functions, ϕ_i. By the definition of the adjoint,

$$\int (\hat{A}^{\perp} \phi_i)^* \phi_j d\tau = \int \phi_i^* (\hat{A} \phi_j) d\tau$$

By the definition of a matrix operator,

$$\hat{A}^{\perp} | i\rangle = \sum_l A_{li}^{\perp} | l\rangle$$

The LHS of the integral therefore gives

$$\int \left(\hat{A}^{\perp}\phi_i\right)^* \phi_j d\tau = \int \left(\sum_l A_{li}^{\perp}\phi_l\right)^* \phi_j d\tau = \sum_l A_{li}^{\perp *}\left\langle l \middle| j \right\rangle = A_{ji}^{\perp *}$$

The RHS of the integral gives

$$\int \phi_i^* \hat{A}\phi_j d\tau = \int \phi_i^* \sum_l A_{lj}\phi_l d\tau = \sum_l A_{lj}\left\langle i \middle| l \right\rangle = A_{ij}$$

Conclusion:

$$A_{ji}^{\perp *} = A_{ij}$$
$$A_{ji}^{\perp} = A_{ij}^{*}$$
$$\hat{A}^{\perp} = \hat{A}^{t*}$$

where we have defined the transpose of $\hat{A}$:

$$A_{ij}^{t} = A_{ji}$$

Illustration:

$$\hat{A} = \begin{pmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{pmatrix}$$
$$\hat{A}^{\perp} = \begin{pmatrix} A_{11}^* & A_{21}^* & A_{31}^* \\ A_{12}^* & A_{22}^* & A_{32}^* \\ A_{13}^* & A_{23}^* & A_{33}^* \end{pmatrix}$$

Definition: A Hermitian operator is self-adjoint: $\hat{A} = \hat{A}^{\perp}$

The third theorem that we proved above is that

$$\left[\hat{A}, \hat{B}\right]^{\perp} = -\left[\hat{A}, \hat{B}\right]$$

where $\hat{A}$ and $\hat{B}$ are Hermitian. The commutator of two Hermitian operators is Hermitian only if it is zero. On the other hand, you can prove that the "anti-commutator" is always Hermitian,

$$\left[\hat{A}\hat{B} + \hat{B}\hat{A}\right]^{\perp} = \hat{A}\hat{B} + \hat{B}\hat{A}$$

Some simple examples of Hermitian operators.

Hamiltonian for the harmonic oscillator (for 3 levels):

$$\hat{H} = \hbar\omega \begin{pmatrix} 1/2 & 0 & 0 \\ 0 & 3/2 & 0 \\ 0 & 0 & 5/2 \end{pmatrix}$$

Angular momentum operators for $l = 1$

$$\hat{L}^2 = 2\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\hat{L}_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$\hat{L}_x$ and $\hat{L}_y$ are trickier to get. Remember that

$$\hat{L}_x = \frac{1}{2}\left(\hat{L}_+ + \hat{L}_-\right)$$

$$\hat{L}_y = \frac{1}{2i}\left(\hat{L}_+ - \hat{L}_-\right)$$

So let’s investigate the ladder operators.

We know that

$$\hat{L}_+ \left| lm \right\rangle = \sqrt{l(l+1) - m(m+1)}\hbar \left| l, m+1 \right\rangle$$

$$\hat{L}_- \left| lm \right\rangle = \sqrt{l(l+1) - m(m-1)}\hbar \left| l, m-1 \right\rangle$$

It follows that for $l = 1$,

$$\hat{L}_+ = \sqrt{2}\hbar \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\hat{L}_- = \sqrt{2}\hbar \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$

where the rows and columns are labeled in the order $m = 1, 0, -1$.

It now follows that

$$\hat{L}_x = \frac{\sqrt{2}\hbar}{2} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

$$\hat{L}_y = \frac{\sqrt{2}\hbar}{2} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}$$

Examples of non-Hermitian operators are $\hat{L}_+$ and $\hat{L}_-$ They are in fact Hermitian adjoints of each other:

$$\int f^* \hat{L}_+ g d\tau = \int f^* \hat{L}_x g d\tau + i \int f^* \hat{L}_y g d\tau$$

$$\int \left(\hat{L}_- f\right)^* g d\tau = \int \left(\left[\hat{L}_x - i\hat{L}_y\right] f\right)^* g d\tau = \int \left(\hat{L}_x f\right)^* g d\tau + i \int \left(\hat{L}_y f\right)^* g d\tau = \int f^* \hat{L}_x g d\tau + i \int f^* \hat{L}_y g d\tau$$

Having identified the matrix representation of an operator, we next inquire after its eigenvalues and eigenvectors. The simplest case is that of a diagonal matrix.

Consider a two state problem with the Hamiltonian

$$H = \begin{pmatrix} H_{11} & 0 \\ 0 & H_{22} \end{pmatrix}$$

Clearly,

$$\begin{pmatrix} H_{11} & 0 \\ 0 & H_{22} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = H_{11} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\begin{pmatrix} H_{11} & 0 \\ 0 & H_{22} \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = H_{22} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Lecture 28. Diagonalizing the Hamiltonian

What happens if the matrix is not in diagonal form? This might happen, for example, if the Hamiltonian consists of two terms, $H = H_0 + H_{1,}$ where

$$H_0 = \begin{pmatrix} H_{11} & 0 \\ 0 & H_{22} \end{pmatrix},$$
$$H_1 = \begin{pmatrix} 0 & H_{12} \\ H_{21} & 0 \end{pmatrix},$$
$$H = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}$$

The matrix element $H_{12} = H_{21} = \varepsilon$ is called a coupling term because it mixes the eigenfunctions of H_0 (the "zero-order" Hamiltonian) to create a new set of orthogonal eigenfunctions that are superpositions of the old ones. When it written this way, the suggestion is that ε is small, but there is nothing so far that requires this. Later we may choose to make such an assumption, but here we will solve the problem exactly. Our goal is to find the eigenfunctions and eigenvalues of *H*.

$$\begin{pmatrix} H_{11} & \varepsilon \\ \varepsilon & H_{22} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \lambda \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$
$$\begin{pmatrix} H_{11} - \lambda & \varepsilon \\ \varepsilon & H_{22} - \lambda \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

This corresponds to a pair of homogeneous linear equations,

$$(H_{11} - \lambda)c_1 + \varepsilon c_2 = 0$$
$$\varepsilon c_1 + (H_{22} - \lambda)c_2 = 0$$

We have three unknowns and only two equations. The third equation is

$$c_1^2 + c_2^2 = 1$$

Let's try to solve the equations:

$$c_1 = -\frac{\varepsilon c_2}{H_{11} - \lambda}$$
$$-\frac{\varepsilon^2 c_2}{H_{11} - \lambda} + (H_{22} - \lambda)c_2 = 0$$
$$(H_{11} - \lambda)(H_{22} - \lambda) - \varepsilon^2 = 0$$

In other words, we have to solve a determinental equation

$$\left|Det(H-\lambda)\right| = 0$$

In the 2x2 problem, the equation is

$$\lambda^2 - \lambda(H_{11}+H_{22}) + H_{11}H_{22} + 4\varepsilon^2 = 0$$
$$\lambda = \frac{1}{2}\left\{(H_{11}+H_{22}) \pm \left[(H_{11}+H_{22})^2 - 4H_{11}H_{22} + 4\varepsilon^2\right]^{1/2}\right\}$$
$$= \frac{1}{2}\left\{(H_{11}+H_{22}) \pm \left[(H_{11}-H_{22})^2 + 4\varepsilon^2\right]^{1/2}\right\}$$

This is an exact result. We can simplify it if $\varepsilon^2 << (H_{11}-H_{22})^2$

$$\left[(H_{11}-H_{22})^2 + 4\varepsilon^2\right]^{1/2} = (H_{11}-H_{22})\sqrt{1+\frac{4\varepsilon^2}{(H_{11}-H_{22})^2}} \approx (H_{11}-H_{22})\left[1+\frac{2\varepsilon^2}{(H_{11}-H_{22})^2}\right]$$
$$= (H_{11}-H_{22}) + \frac{2\varepsilon^2}{(H_{11}-H_{22})}$$
$$\lambda = \frac{1}{2}\left[(H_{11}-H_{22}) \pm \left(H_{11}-H_{22}+\frac{2\varepsilon^2}{(H_{11}-H_{22})}\right)\right]$$
$$\lambda_+ = H_{11} + \frac{\varepsilon^2}{(H_{11}-H_{22})}$$
$$\lambda_- = H_{22} - \frac{\varepsilon^2}{(H_{11}-H_{22})}$$

What are the eigenfunctions?

Let’s recast the problem for any Hermetian 2x2 matrix:

$$\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \lambda\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$
$$\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}\begin{pmatrix} 1 \\ x \end{pmatrix} = \lambda\begin{pmatrix} 1 \\ x \end{pmatrix}$$

Once λ is known, we can solve for x.

$$A_{11} + A_{12}x = \lambda,$$
$$A_{21} + A_{22}x = \lambda x;$$
$$x = \frac{\lambda - A_{11}}{A_{12}},$$
$$x = \frac{A_{21}}{\lambda - A_{22}}$$

These formulas are necessarily equivalent; use whichever is more convenient.

Numerical example:

Find the eigenvalues and eigenfunctions of $\begin{pmatrix} 1 & 4 \\ 9 & 1 \end{pmatrix}$

$$\begin{vmatrix} 1-\lambda & 4 \\ 9 & 1-\lambda \end{vmatrix} = 0$$
$$(1-\lambda)^2 - 36 = 0$$
$$1-\lambda = \pm 6$$
$$\lambda = 7, -5$$

Eigenvector for $\lambda = 7$:

$$\begin{pmatrix} 1 & 4 \\ 9 & 1 \end{pmatrix}\begin{pmatrix} 1 \\ x \end{pmatrix} = 7\begin{pmatrix} 1 \\ x \end{pmatrix}$$
$$1 + 4x = 7$$
$$x = 3/2$$

Normalization constant = $\left[1 + \left(\frac{3}{2}\right)\right]^{1/2} = \frac{\sqrt{13}}{2}$

Eigenvector = $\frac{2}{\sqrt{13}}\begin{pmatrix} 1 \\ 3/2 \end{pmatrix}$

Eigenvector for $\lambda = -5$: $\frac{2}{\sqrt{13}}\begin{pmatrix} 1 \\ -3/2 \end{pmatrix}$

Returning to the two state problem above, define $\Delta = H_{11} - H_{22}$

You can plug into the two equations for x to get for the two eigenfunctions:

$$x_+ = \frac{\lambda - H_{11}}{H_{12}} = -\frac{\varepsilon}{\Delta}$$
$$|+\rangle \equiv |1\rangle = \begin{pmatrix} 1 \\ -\varepsilon/\Delta \end{pmatrix}$$
$$x_- = \frac{H_{21}}{\lambda - H_{22}} = \frac{\Delta}{\varepsilon}$$
$$|-\rangle \equiv |2\rangle = \begin{pmatrix} 1 \\ \Delta/\varepsilon \end{pmatrix} \sim \begin{pmatrix} \varepsilon/\Delta \\ 1 \end{pmatrix}$$

These eigenvectors are orthogonal. They still need to be normalized. The fraction of stat mixing is just $(\varepsilon/\Delta)^2$. If the coupling is weak, or if the states are very far apart, there is little mixing. The zero-order eigenfunctions (without the coupling term) are

$$|1\rangle_0 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$
$$|2\rangle_0 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

This effect is important in spectroscopy, where coupling terms, such as the spin-orbit interaction or configuration interaction, mix nominal states together, for example, to add Π character to a Σ state. It is also important in making forbidden transitions become allowed, by mixing in some oscillator strength into a state that otherwise has the wrong symmetry (e.g., parity).

Lecture 29. The Coordinate Representation

It is possible to expand a state vector in any complete basis set. Each basis set gives a unique representation of the state. The basis set itself is a complete set of eigenfunctions of some operator, $\hat{A}$, and an expansion in that basis is called the “A-representation.” For example, expansion in the eigenfunctions of the Hamiltonian is called the energy representation.

What does the coordinate representation look like?

For any operator, the eigenvalue equation has the form

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

or

$$\left(\hat{A} - a\right)|a\rangle = 0$$

The same equation applies to the position operator,

$$\left(\hat{x} - a\right)|a\rangle = 0$$
$$\left(x - a\right)|a\rangle = 0$$

This equation implies that $|a\rangle = 0$ everywhere except at x = a. At x = a the function must be infinite so that its normalization integral is finite. Such a singular function is called a Dirac delta function, and is written as $\delta(x-a)$. It has the following properties:

$$\delta\left(x - x_0\right) = 0 \text{ for } x \neq x_0$$
$$\delta\left(x - x_0\right) = \infty \text{ for } x = x_0$$

It has many other very useful properties, including the following:

$$\delta(x) = \delta(-x)$$
$$\delta(x-a) = \delta(a-x)$$

The reason for this is that $\delta(x)$ is an even function. If it were odd, we would have $\delta(0) = -\delta(0) = 0$.

$$\delta(ax) = \frac{1}{|a|}\delta(x)$$

$$\delta\left(a(x-b)\right) = \frac{1}{|a|}\delta(x-b)$$

We can prove this be defining $\delta(x)$ as a limit of a well-behaved function:

$$\delta(x) = \frac{1}{\sqrt{\pi}}\lim_{\varepsilon \to 0}\frac{1}{\sqrt{\varepsilon}}e^{-x^2/\varepsilon}$$

$$\delta(ax) = \frac{1}{\sqrt{\pi}}\lim_{\varepsilon \to 0}\frac{1}{\sqrt{\varepsilon}}e^{-a^2x^2/\varepsilon}$$

$$\frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty} e^{-a^2x^2/\varepsilon}\frac{dx}{\sqrt{\varepsilon}} = \frac{1}{\sqrt{\pi}|a|}\int_{-\infty}^{\infty} e^{-y^2/\varepsilon}dy = \frac{1}{|a|}$$

$$\delta\big(g(x)\big) = \sum_n \frac{1}{|g'(x_n)|}\delta(x - x_n)$$

In this equation, x_n are the roots of g(x). It can be derived by writing

$$\begin{aligned} g(x) &= (x - x_n)h(x) \\ g'(x) &= h(x) + (x - x_n)h'(x) \\ g'(x_n) &= h(x_n) \end{aligned}$$

Invoking the previous result and summing over all the roots gives the desired result.

Other properties include:

$$x\delta(x) = 0$$
$$f(x)\delta(x-a) = f(a)\delta(x-a)$$
$$\int f(x)\delta(x-a)dx = f(a)$$
$$\int \delta(y-x)\delta(x-a)dx = \delta(y-a)$$
$$\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ikx}dk$$
$$\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i(k-k')x}dx = \delta(k-k')$$

The last equation provides the normalization for a free particle.

How do we transform from a discrete basis to the coordinate basis? Let's start with the general procedure. Suppose we wish to expand $|\psi\rangle$ in a basis set $|i\rangle$. We do this by the usual Fourier expansion technique:

$$|\psi\rangle = \sum_i |i\rangle\langle i|\psi\rangle$$

The quantity $\langle i|\psi\rangle$ is the projection (probability amplitude) of $|\psi\rangle$ on $|i\rangle$. You may also think of $|i\rangle\langle i|$ as a projection operator and

$$\sum_i |i\rangle\langle i| = 1$$

as a closure relationship.

Now let's do this with the coordinate representation:

$$|\psi\rangle = \int |x\rangle dx \langle x|\psi\rangle$$

The amplitude $\langle x|\psi\rangle$ is the probability amplitude of finding the particle at x. It is called a wave function, and is written as

$$\psi(x) = \langle x|\psi\rangle$$

The closure relation is

$$\int |x\rangle dx \langle x| = 1.$$

Lecture 30. Recovery of wave mechanics

Evaluation of overlap integrals:

In a discrete representation,

$$\langle\psi_2|\psi_1\rangle = \sum_i \sum_j \langle\psi_2|i\rangle\langle i|j\rangle\langle j|\psi_1\rangle = \sum_i \langle\psi_2|i\rangle\langle i|\psi_1\rangle$$

In a continuous representation

$$\langle\psi_2|\psi_1\rangle = \iint \langle\psi_2|x''\rangle dx'' \langle x''|x'\rangle dx' \langle x'|\psi_1\rangle = \iint \langle\psi_2|x''\rangle dx'' \delta(x''-x') dx' \langle x'|\psi_1\rangle = \int_{-\infty}^{\infty} \psi_2^*(x)\psi_1(x)dx$$

What do operators look like in the coordinate representation? Think of the coordinates as an infinite square matrix, with indices x' and x''. The only non-zero elements lie along the diagonal, and are proportional to delta functions. That is,

$$\langle x''|f(x)|x'\rangle = f(x')\delta(x'-x'')$$

This is analogous to saying that in the energy representation the Hamiltonian has matrix elements $H_{ij}\delta_{ij}$.

The matrix element of f(x) for two states, $|\Psi_1\rangle$ and $|\Psi_2\rangle$, is given by

$$\langle\Psi_2|f(x)|\Psi_2\rangle = \iint \langle\Psi_2|x''\rangle dx'' \langle x''|f(x)|x'\rangle dx' \langle x'|\Psi_1\rangle = \iint \langle\Psi_2|x''\rangle dx'' f(x)\delta(x'-x'')\langle x'|\Psi_1\rangle$$
$$= \int \Psi_2^*(x'') f(x'')\Psi_1(x'')dx''$$

The key to unraveling the entire problem is to find the corresponding results for functions of the momentum operator. To do this we need to know the properties of the derivative of the delta function, which we obtain by integrating by parts.

$$\int_{-\infty}^{\infty} f(x)\delta'(x)dx = f(x)\delta(x)|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} f'(x)\delta(x)dx = -f'(0)$$

$$\int_{-\infty}^{\infty} x\delta'(x)dx = -1$$

$$x\delta'(x) = -\delta(x)$$

We will use this last relation to obtain the matrix element of p in the coordinate representation.

First, we have to make a crucial assumption. We postulate that $[\hat{x}, \hat{p}] = i\hbar$.
Next we unpeel the matrix element of the commutator:

$$\langle x''|\hat{x}\hat{p} - \hat{p}\hat{x}|x'\rangle = \langle x''|\hat{x}\hat{p}|x'\rangle - \langle x''|\hat{p}\hat{x}|x'\rangle = i\hbar\delta(x'' - x')$$

But $\langle x''|\hat{x} = \langle x''|x''$ and $\hat{x}|x'\rangle = x'|x'\rangle$. It follows that

$$\langle x''|\hat{x}\hat{p}|x'\rangle = x''\langle x''|\hat{p}|x'\rangle$$
$$\langle x''|\hat{p}\hat{x}|x'\rangle = x'\langle x''|\hat{p}|x'\rangle$$

$$\langle x''|\hat{x}\hat{p} - \hat{p}\hat{x}|x'\rangle = (x'' - x')\langle x''|\hat{p}|x'\rangle = i\hbar\delta(x'' - x')$$

$$\langle x''|p|x'\rangle = i\hbar\frac{\delta(x'' - x')}{x'' - x'} = -i\hbar\frac{\partial}{\partial x''}\delta(x'' - x')$$

Next we generalize this result for any power of p.

$$\langle x''|p^2|x'\rangle = \int\langle x''|p|x'''\rangle dx'''\langle x'''|p|x'\rangle = \int\left(\frac{\hbar}{i}\frac{\partial}{\partial x''}\right)\delta(x'' - x''')\left(\frac{\hbar}{i}\frac{\partial}{\partial x'''}\right)\delta(x''' - x')dx''' = \left(\frac{\hbar}{i}\frac{\partial}{\partial x''}\right)^2\delta(x'' - x')$$

For any power of p,

$$\langle x''|p^n|x'\rangle = \left(\frac{\hbar}{i}\frac{\partial}{\partial x''}\right)^n\delta(x'' - x')$$

and for any power series in p,

$$\langle x''|f(p)|x'\rangle = f\left(\frac{\hbar}{i}\frac{\partial}{\partial x''}\right)\delta(x''-x')$$

The matrix element for arbitrary states is given by

$$\langle \Psi_2|f(p)|\Psi_1\rangle = \iint \langle \Psi_2|x''\rangle dx'' \langle x''|f(p)|x'\rangle dx' \langle x'|\Psi_1\rangle = \int \Psi_2^*(x'')\, f\left(\frac{\hbar}{i}\frac{\partial}{\partial x''}\right)\Psi_1(x'')dx''$$

Now finally we can recover the Schrodinger equation. We will use as an illustration the harmonic oscillator:

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2$$
$$H|E\rangle = E|E\rangle$$
$$\left(\frac{p^2}{2m} + \frac{1}{2}kx'^2\right)|E\rangle = \frac{1}{2m}\int |x'\rangle\left(-\hbar^2\frac{\partial^2}{\partial x'^2}\right)\psi_E(x')dx' + \frac{k}{2}\int |x'\rangle x'^2 \psi_E(x')dx'$$
$$= E\int |x'\rangle \psi_E(x')dx'$$

Equating the integrands gives

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{k}{2}x^2\right)\psi_E(x) = E\psi_E(x)$$

These results can also be derived in the momentum representation. The wave function for a state with definite p is given by

$$\psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}}e^{ikx'} = \frac{1}{\sqrt{2\pi\hbar}}e^{ip'x'/\hbar} = \langle x'|p'\rangle$$

We can derive all of the equivalent results in the momentum representation:

$$\hat{p}|p'\rangle = p'|p'\rangle$$
$$\langle p''|f(\hat{p})|p'\rangle = f(p')\delta(p''-p')$$
$$\langle p''|\hat{x}|p'\rangle = i\hbar\frac{\partial}{\partial p'}\delta(p''-p')$$
$$\langle p''|f(\hat{x})|p'\rangle = f\left(i\hbar\frac{\partial}{\partial p'}\right)\delta(p''-p')$$