Theorems of QM

Chem 2430

Nomenclature:

$$\int f_m^* \hat{A} f_n d\tau = \langle f_m | \hat{A} | f_n \rangle = \langle m | \hat{A} | n \rangle = A_{mn}$$

A_{mn} is called a matrix element

$$\left(\int \psi_m^* \psi_n d\tau\right)^* = \int \psi_n^* \psi_m d\tau$$

$$\Rightarrow \langle m | n \rangle^* = \langle n | m \rangle$$

Hermitian operators

For QM operators that correspond to observables

$\langle A \rangle = \langle A \rangle^*$ the average must be real

$$\Rightarrow \int \psi^* \hat{A} \psi d\tau = \int \psi \left(\hat{A}\psi\right)^* d\tau$$

If this holds the operator is Hermitian

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

is sometimes uses as a definition of a Hermitian operator let $\psi = f + cg$, c is a constant

From the definition of Hermitian operators

$$\int (f + cg)^* \hat{A}(f + cg)\, d\tau = \int (f + cg)\left[\hat{A}(f + cg)\right]^* d\tau$$

$$\int (f^* + c^* g^*)\hat{A} f d\tau + c\int (f^* + c^* g^*)\hat{A} g d\tau =$$

$$\int (\boldsymbol{f} + \boldsymbol{cg})\left(\hat{A}f\right)^* d\tau + c^*\int (f + cg)\left(\hat{A}g\right)^* d\tau$$

$$\int f^*\hat{A} f d\tau + c^*\int g^*\hat{A} f d\tau + c\int f^*\hat{A} g d\tau + c^* c\int g^*\hat{A} g d\tau$$

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

This reduces to

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

$$\rightarrow \int f^*\hat{A} g d\tau = \int g\left(\hat{A}f\right)^* d\tau \quad \Rightarrow \langle m|\hat{A}|n\rangle = \langle n|\hat{A}|m\rangle^* = A_{mn} = A_{nm}^*$$

Implications for matrix representation. If one has two basis functions ψ_1 and ψ_2, the Hamiltonian matrix becomes

$$\underline{\underline{H}} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}$$

To find the eigenvalues of the matrix, we have to solve

$$\begin{vmatrix} H_{11}-\lambda & H_{12} \\ H_{21} & H_{22}-\lambda \end{vmatrix} = 0$$

$$\left(H_{11}-\lambda\right)\left(H_{22}-\lambda\right) - H_{12}H_{21} = 0$$

$$\lambda^2 - \lambda\left(H_{11}+H_{22}\right) + H_{11}H_{22} - H_{12}H_{21} = 0$$

$$\lambda = \frac{H_{11}+H_{22}}{2} \pm \frac{1}{2}\sqrt{\left(H_{11}+H_{22}\right)^2 + 4\left(-H_{11}H_{22}+H_{21}H_{12}\right)}$$

$$\lambda = \frac{H_{11}+H_{22}}{2} \pm \frac{1}{2}\sqrt{\left(H_{11}-H_{22}\right)^2 + 4H_{12}H_{21}}$$

let $\underline{\underline{H}} = \begin{pmatrix} 1 & 2 \\ 2 & 2 \end{pmatrix}, \lambda = \frac{3}{2} \pm \frac{1}{2}\sqrt{1+16}$

let $\underline{\underline{H}} = \begin{pmatrix} 1 & 2i \\ 2i & 2 \end{pmatrix}, \lambda = \frac{3}{2} \pm \frac{1}{2}\sqrt{1-16}$

Not real

let $\underline{\underline{H}} = \begin{pmatrix} 1 & 2i \\ -2i & 2 \end{pmatrix}, \lambda = \frac{3}{2} \pm \frac{1}{2}\sqrt{1+16}$

real

Note $H_{12}{}^* = H_{21}$ in the first and third examples.

Suppose the operator $\hat{A}$ is real

$$\int \psi_m{}^* \hat{A}\psi_n\, dx \stackrel{?}{=} \int \psi_n \left(\hat{A}\psi_m\right)^* dx \quad = \int \psi_n \hat{A}\psi_m{}^*\, dx$$

If $\hat{A}$ is an operator such as x or a potential V(x) then the order does not matter ,so the equality obviously holds.

What if $\hat{A} = \frac{\hbar}{i}\frac{\partial}{\partial x}$

does $\int \psi_m{}^* \frac{\hbar}{i}\frac{\partial}{\partial x}\psi_n dx \stackrel{?}{=} \int \psi_n \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\psi_m\right)^* dx$

Equivalent to $\int \psi_m{}^* \frac{\partial}{\partial x}\psi_n dx \stackrel{?}{=} -\int \psi_n \left(\frac{\partial}{\partial x}\psi_m\right)^* dx$

Lets check using integration by parts

$$\int_a^b u\,dv = uv\Big|_a^b - \int v\,du$$

let $u = \psi_m{}^*, dv = \frac{d\psi_n}{dx}dx$

$v = \psi_n$

$$\int_{-\infty}^{\infty} \psi_m{}^* \frac{d\psi_n}{dx} dx = \psi_m{}^* \psi_n \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \psi_n \frac{d\psi_m{}^*}{dx} dx$$

0

So we have proven that $\frac{\hbar}{i}\frac{d}{dx}$ is Hermitian

Theorems

1. Eigenvalues of Hermitian operators are real

$$\int g_i * \hat{A} g_i d\tau = \int g_i \left(A g_i \right) * d\tau$$

$$a_i \int g_i * g_i d\tau = a_i * \int g_i * g_i d\tau$$

$$\Rightarrow \left(a_i - a_i * \right) \int g_i * g_i d\tau = 0 \Rightarrow a_i = a_i *$$

2. The eigenfunctions of a Hermitian operator are orthogonal

$$\hat{A} f = sf, \quad \hat{A} g = tg$$

$$\langle f \mid g \rangle = ?$$

$$\langle f \mid \hat{A} \mid g \rangle = \langle g \mid \hat{A} \mid f \rangle *$$

$$t \langle f \mid g \rangle = s * \langle g \mid f \rangle * \quad \Longrightarrow \quad \left(s - t \right) \langle f \mid g \rangle = 0$$

If $s = t$ (degenerate eigenvalues), we can always form eigenfunctions that are $\perp$

Let $g_1 = f, \quad g_2 = g + cf$

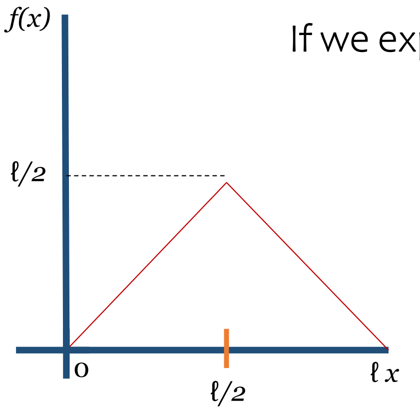
$$\langle g_1 \mid g_2 \rangle = \langle f \mid g \rangle + c \langle f \mid f \rangle$$

Require this to = 0

$c = -\langle f \mid g \rangle / \langle f \mid f \rangle$ makes g_1 and g_2 $\perp$

3. A set of functions $\{g_i\}$ is a complete set if any function in the same space can be written as

$$f = \sum_i a_i g_i, \quad a_i = \langle g_i \mid f \rangle$$



If we expand this in terms of particle-in-the-box eigenfunctions

$$f(x) = \frac{4\ell}{\pi^2} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{1}{(2n-1)^2} \sin\left[(2n-1)\frac{\pi x}{\ell}\right]$$

$$f\left(\frac{\ell}{2}\right) = \frac{4\ell}{\pi^2}\left[1 + \frac{1}{3^2} + \frac{1}{5^2} + \frac{1}{7^2} + \ldots\right]$$

Note: $\pi^2 = 8[1 + 1/9 + 1/25 + 1/49 + \ldots]$

If we use the eigenfunctions of the H atom as a basis, we need to use both the bound states and the continuum.

$$f(r,\theta,\phi) = \sum_n \sum_\ell \sum_m a_{n\ell m} \psi_{n\ell m}(r,\theta,\phi) + \sum_\ell \sum_m \int a_{\ell m}(E) \psi_{E\ell m}(r,\theta,\phi)\, dE$$

Suppose we use the eigenfunctions of p_x as a basis

$$f(x) = \int_{-\infty}^{\infty} a(k) e^{ikx/\hbar} dk$$

Essentially a Fourier transform

If $\hat{A} g_i = a_i g_i, \quad \hat{B} g_i = b_i g_i$ then $\left[\hat{A}, \hat{B}\right] = 0$

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

But we can expand f in terms of the g_i which enables us to see that $\left[\hat{A}, \hat{B}\right] = 0$

Theorem: if g_m and g_n are eigenfunctions of $\hat{A}$ (Hermitian)

and If $\hat{B}$ commutes with $\hat{A}$ then $\left\langle g_n \,|\, \hat{B} \,|\, g_m \right\rangle = 0$

$\hat{A} g_m = a_m g_m$ and $\hat{A} g_n = a_n g_n$, and $g_m \neq g_n$

$$\left\langle g_n \,|\, \hat{B}\hat{A} \,|\, g_m \right\rangle = \left\langle g_n \,|\, \hat{A}\hat{B} \,|\, g_m \right\rangle$$

$$\left\langle g_n \,|\, \hat{A}\hat{B} \,|\, g_m \right\rangle = \left\langle g_n \,|\, \hat{A} \,|\, \hat{B} g_m \right\rangle = \left\langle \hat{B} g_m \,|\, \hat{A} \,|\, g_n \right\rangle *$$

$$a_m \left\langle g_n \,|\, \hat{B} \,|\, g_m \right\rangle = a_n * \left\langle \hat{B} g_m \,|\, g_n \right\rangle * = a_n * \left\langle g_n \,|\, \hat{B} \,|\, g_m \right\rangle$$

but $a_n * = a_n$

$$\left(a_m - a_n\right) \left\langle g_n \,|\, \hat{B} \,|\, g_m \right\rangle \Rightarrow \left\langle g_n \,|\, \hat{B} \,|\, g_m \right\rangle = 0$$

Parity operator : $\hat{\pi} f(x,y,z) = f(-x,-y,-z)$

$\hat{\pi} g_i = c_i g_i$ | What are c_i and g_i?

Note $\hat{\pi}^2 f = \hat{\pi}(\hat{\pi} f) \Rightarrow \hat{\pi}^2 = \hat{I}$

$$\hat{\pi} g_i = c_i g_i \rightarrow \hat{\pi}^2 g_i = c_i \hat{\pi} g_i$$

$$\hat{I} g_i = c_i^2 g_i$$

$$\hat{I} = c_i^2 \Rightarrow c_i = \pm 1$$

The eigenfunctions of $\hat{\pi}$ are all possible even and odd functions

even: $g_i(-x,-y,-z) = g_i(x,y,z)$

odd: $g_i(-x,-y,-z) = -g_i(x,y,z)$

If $\left[\hat{\pi}, \hat{H}\right] = 0,$ e.f.'s of $\hat{H}$ can be chosen to be e.f.'s of $\hat{\pi}$

$$\left[\nabla^2, \hat{\pi}\right] = 0$$

So the question is whether V commutes with $\hat{\pi}$

It does if it is even (Do you see this?)

$$\int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} g\left(x, \ldots, z_n\right) dx_1 \ldots dz_n = 0, \text{ if g is odd}$$

Suppose the g_i are eigenfunctions from $\hat{B}g_i = b_i g_i$ and

$$\Psi = \sum_i c_i(t) g_i$$

$$\int \Psi^* \Psi d\tau = 1 \quad = \int \sum_i c_i^* g_i^* \sum_j c_j g_j d\tau = \sum_i \sum_j c_i^* c_j \langle g_i | g_j \rangle$$

$$= \sum_i |c_i|^2$$

$$\int \Psi \hat{B} \Psi d\tau = \int \sum_i c_i^* g_i \hat{B} \sum_j c_j g_j d\tau =$$

$$\sum_i \sum_j c_i^* c_j \langle g_i | \hat{B} | g_j \rangle = \sum_i \sum_j c_i^* c_j b_j \delta_{ij} \quad = \sum_i |c_i|^2 b_i$$

Careful how you treat degeneracy.

Position eigenfunctions

$$xg_a(x) = ag_i(x)$$

$$(x-a)g_a(x) = 0$$

$g_a(x) = 0$ if $x \neq a$

$g_a(x) \neq 0$ if $x = a$

We have already mentioned that $g_a(x) = \delta(x-a)$

Heaviside function

$$H(x) = \begin{cases} 1 & x > 0 \\ 0 & x < 0 \\ 1/2 & x = 0 \end{cases}$$

$$\delta(x) = \frac{dH(x)}{dx}$$

$H(x-a) = 1 \quad x > a$

$H(x-a) = 0 \quad x < a$

$H(x-a) = 1/2 \quad x = a$

$$\delta(x-a) = \frac{dH(x-a)}{dx}$$

$\delta(x) = \infty$ at $x = 0$

$$\int_{-\infty}^{\infty} f(x)\delta(x-a)\,dx = f(a)$$

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

If H is independent of time we have $\Psi(q,t) = e^{-iEt}\psi(q)$ If Ψ is an eigenfunction of H

satisfies time-indep SE

If Ψ is not an eigenfunction of H

$$\Psi = \sum c_n e^{-iE_n t/\hbar}\psi_n(q)$$

If $\hat{H} = \hat{H}^o + \hat{H}'(t)$, the c_n's in the expansion depend on *t*.

Measurement: read this discussion in the text

Two important philosophical issues are

Measurement: collapse of the wave function

Action at a distance (faster than the speed of light)

Hidden variable interpretation (Bohm)

Bohm – nonlocal deterministic hidden variable theory. (particle moves in potential *V* + *Q* where *Q* is determined from the wave function)

Matrices

Given $\boldsymbol{A}(m \times n)$, $\boldsymbol{B}(n \times p)$

$$\boldsymbol{C} = \boldsymbol{AB},\ c_{ij} = \sum_k a_{ik} b_{kj} \quad \text{(row x column)}$$

We are especially interested in square matrices

$$Tr\boldsymbol{A} = \sum a_{ii}$$

$$\boldsymbol{I} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$, Identity matrix of order 3

Given a basis $|f_i\rangle$, the matrix representation of an operator $\hat{A}$ is

$$\begin{pmatrix} \langle f_1 | \hat{A} | f_1 \rangle & \langle f_1 | \hat{A} | f_2 \rangle \ldots \\ \langle f_2 | \hat{A} | f_1 \rangle & \langle f_2 | \hat{A} | f_2 \rangle \ldots \end{pmatrix} = \begin{pmatrix} A_{11} & A_{12} \ldots \\ A_{21} & A_{22} \ldots \end{pmatrix}$$

If the basis consists of eigenfunctions of $\hat{A}$, then the matrix is diagonal.