THEOREMS OF QUANTUM MECHANICS

In order to develop methods to treat many-electron systems (atoms & molecules), many of the theorems of quantum mechanics are useful.

Useful Notation

The matrix element A_{mn} is defined by

$$A_{mn} = \int \phi_m{}^* A \, \phi_n \, d\tau$$

$$= <\phi_m | A | \phi_n> \qquad \text{bracket notation}$$

$$= (\phi_m | A | \phi_n)$$

$$= <m | A | n>$$

The overlap integral between two functions is

$$\int \phi_m{}^* \phi_n \, d\tau = <\phi_m | \phi_n> = <m | n>.$$

The complex conjugate of the overlap integral is

$$[\int \phi_m{}^* \phi_n \, d\tau]^* = \int \phi_n{}^* \phi_m \, d\tau = <n | m>$$

$$= [<m | n>]^*$$

Also $<m | m>^* = <m | m>$.

Theorems

The average value of a physical quantity must be a real number.

Let A be the linear operator for the property A. So if A is real, then

$$<A> = <A>^*$$

and A is said to be a **_Hermitian Operator._** For a Hermitian Operator:

$$<A> = \int \psi^* A\psi \, d\tau = <A>^* = (\int \psi^* A\psi \, d\tau)^*$$

$$= \int \psi (A\psi)^* \, d\tau$$

Using the above relation, prove $\int f^* Ag \, d\tau = \int g (Af)^* \, d\tau$.

If $\psi = f + cg$ & A is a Hermitian operator, then

$$\int (f + cg)^* A(f + cg) \, d\tau = \int (f + cg)[A(f + cg)]^* \, d\tau.$$

Left-hand side $= \int (f + cg)^* A(f + cg) \, d\tau$

$$= \int (f^* + c^*g^*) A(f + cg) \, d\tau$$

$$= \int (f^* + c^*g^*) Af \, d\tau + \int (f^* + c^*g^*) Acg \, d\tau$$

$$= \int f^* Af d\tau + c^* \int g^* Af d\tau + c \int f^* Ag \, d\tau + cc^* \int g^* Ag \, d\tau$$

By symmetry, the right-hand side

$$= \int f(Af)^* d\tau + c \int g(Af)^* d\tau + c^* \int f(Ag)^* d\tau + cc^* \int g(Ag)^* \, d\tau$$

Since A is Hermitian

$$\& \int f^* Af d\tau = \int f(Af)^* d\tau \ \& \ \int g^* Ag \, d\tau = \int g(Ag)^* \, d\tau,$$

then, from the left- & right-hand sides:

$$c^* \int g^* A f d\tau + c \int f^* A g \, d\tau = c \int g (Af)^* d\tau + c^* \int f(Ag)^* d\tau.$$

Since this must hold for all c's, it must hold for c=i or 1. Set c=1 to give one eqn., set c=i to give a second eqn. Then add.

c=1: $\int g^* A f d\tau + \int f^* A g \, d\tau = \int g (Af)^* d\tau + \int f(Ag)^* d\tau$

c=i: $-\int g^* A f d\tau + \int f^* A g \, d\tau = \int g (Af)^* d\tau - \int f(Ag) d\tau$; i* = -i

Add eqns. $\Rightarrow \int f^* A g \, d\tau = \langle \phi_i | A | \phi_j \rangle = \langle \phi_j | A | \phi_i \rangle^* = \int g (Af)^* d\tau.$

So for a Hermitian operator,

$$\langle \phi_i | A | \phi_j \rangle = \langle \phi_j | A | \phi_i \rangle^* \text{ or } \langle i | A | j \rangle = \langle j | A | i \rangle^*$$

or $A_{ij} = A_{ji}^*$

What Operators Are Hermitian?

Is V(x), the potential energy operator, Hermitian?

$$\langle \phi_j | V(x) | \phi_i \rangle^* = \int_{-\infty}^{\infty} \phi_j (V\phi_i)^* \, dx$$

$V^* = V$ & V is just a multiplicative operator (no square roots, etc). So

$$\int_{-\infty}^{\infty} \phi_j V^* \phi_i^* \, dx = \int_{-\infty}^{\infty} \phi_j V \phi_i^* \, dx = \int_{-\infty}^{\infty} \phi_i^* V \phi_j \, dx$$

$$\langle \phi_i | V(x) | \phi_j \rangle \qquad \qquad \text{Hermitian}$$

Is $p_x = -i\hbar \partial/\partial x$ Hermitian? ($p_x^* = i\hbar \partial/\partial x$)

$$\langle \phi_i | p_x | \phi_j \rangle = \int_{-\infty}^{\infty} \phi_i^* (-i\hbar \partial/\partial x) \phi_j \, dx = -i\hbar \int_{-\infty}^{\infty} \phi_i^* \phi_j' \, dx$$

Integration by parts: $\int uv' = uv - \int vu'$

So $-i\underline{h}\int_{-\infty}^{\infty}\phi_i{}^*\phi_j{}'\ dx = -i\underline{h}[\phi_i{}^*\phi_j\big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty}\phi_j(\phi_i{}^*)'\ dx]$

Assume ϕ_i & ϕ_j are well-behaved (i.e. =0) at $\pm\infty$, so that the first term on the right equals 0. Then

$$<\phi_i\,|p_x\,|\phi_j> = i\underline{h}\int_{-\infty}^{\infty}\phi_j(\phi_i{}^*)'\ dx = \int_{-\infty}^{\infty}\phi_j(\,i\underline{h}\,\partial/\partial x)\phi_i{}^*\ dx$$

$$= \int_{-\infty}^{\infty}\phi_j(p_x)^*\phi_i{}^*\ dx = <\phi_j\,|p_x\,|\phi_i>^* \qquad \text{Hermitian}$$

(Prove: T, the kinetic energy operator, is Hermitian).

Then $H = T + V$ is Hermitian.

PROVE: The eigenvalues of a Hermitian operator are real. (This means they represent a physical quantity.)

For $A\,\phi_i = b\,\phi_i$, show that $b = b^*$ (b is real).

If A is Hermitian, then $\int \phi_i{}^*A\phi_i\ d\tau = \int \phi_i(A\phi_i)^*\ d\tau$.

Or, $\qquad \int \phi_i{}^*b\phi_i\ d\tau = \int \phi_i(b\phi_i)^*\ d\tau = \int \phi_i b^*\phi_i{}^*\ d\tau$

Then $\qquad b\int \phi_i{}^*\phi_i\ d\tau = b^*\int \phi_i\phi_i{}^*\ d\tau = b^*\int \phi_i{}^*\phi_i\ d\tau$

So $b = b^*$

PROVE: The eigenfunctions of a Hermitian operator can be chosen to be orthogonal.

Show that, if $B\,F = s\,F$ & $B\,G = t\,G$ & t is not equal to s, then $<F\,|\,G> = 0$.

Since B is Hermitian

$$\langle F \mid B \mid G \rangle = \langle G \mid B \mid F \rangle^*$$

Or $\quad \langle F \mid t \mid G \rangle = \langle G \mid s \mid F \rangle^*$

So $\quad t \langle F \mid G \rangle = s^* \langle G \mid F \rangle^* = s^* \langle F \mid G \rangle = s \langle F \mid G \rangle$

$$(t-s) \langle F \mid G \rangle = 0$$

t not equal to s $\Rightarrow \langle F \mid G \rangle = 0$

The requirement that t is not equal to s means that F & G are independent eigenfunctions that have different eigenvalues (i.e. they are non-degenerate)

PROVE: That in the case of degenerate eigenfunctions, we can construct from these eigenfunctions a new eigenfunction that will be orthogonal.

Remember: We have shown that any linear combination of degenerate eigenfunctions corresponding to the same eigenvalue is also an eigenfunction with the same eigenvalue.

Let $\quad$ B F = s F & B G = s G

Let $\quad \phi_1$ & ϕ_2 be the new eigenfunctions that will be orthogonal.

Set $\phi_1 = F$, $\phi_2 = G + c$ F. Find c such that $\langle \phi_1 \mid \phi_2 \rangle = 0$.

Procedure: Schmidt Orthogonalization

$$\langle \phi_1 \mid \phi_2 \rangle = \langle F \mid G + cF \rangle = \langle F \mid G \rangle + c \langle F \mid F \rangle$$

If $\langle \phi_1 \mid \phi_2 \rangle = 0$, then $c = - \langle F \mid G \rangle / \langle F \mid F \rangle$

(Unless otherwise noted, assume all eigenfunctions are orthogonal & normalized: $\langle \phi_i | \phi_j \rangle = \delta_{ij} = 0$ unless $i = j$; $\delta_{ii} = 1$)

Expansion in terms of eigenfunctions:

We can use the eigenfunctions of a Hermitian operator to describe an arbitrary well-behaved function. We can expand the arbitrary function in terms of all (or a **complete set**) of eigenfunctions of the operator.

Let f be an arbitrary well-behaved function *that obeys the same boundary conditions as the complete set ϕ_i*

$$f = \sum_i a_i \phi_i \qquad a_i \text{ is an expansion coefficient}$$

To find a_i (formal solution):

$$\langle \phi_j | f \rangle = \langle \phi_j | \sum_i a_i \phi_i \rangle = \sum_i a_i \langle \phi_j | \phi_i \rangle = \sum_i a_i \delta_{ji} = a_j$$

$$\text{Or } f = \sum_i \langle \phi_i | f \rangle \phi_i$$

So, the eigenfunctions of a Hermitian operator form a complete orthonormal set with real eigenvalues

Eigenfunctions of Commuting Operators:

In Chapter 5 we stated that a wavefunction can be simultaneously an eigenfunction of two different operators if those operators commute. Or, more exactly, a necessary condition for the existence of a complete set of simultaneous eigenfunctions of two operators is that the operators commute with each other. *This means that the physical properties associated with the operators can be measured simultaneously.*

<u>PROVE: If there exists a common complete set of eigenfunctions for two linear operators, then the operators commute.</u>

Let ϕ_i be the complete set of eigenfunctions of the operators A & B.

$A\,\phi_i = s_i\phi_i$ & $B\,\phi_i = t_i\phi_i$

Show that $[A,B] = 0$ or $(AB - BA)f = 0$ where f is an arbitrary function.

We can expand f in terms of the complete set of eigenfunctions of A & B:

$$f = \sum_i c_i\,\phi_i$$

So $(AB - BA)\,f = (AB - BA)\sum_i c_i\,\phi_i = \sum_i c_i(AB - BA)\,\phi_i$

$$= \sum_i c_i(AB\phi_i - BA\phi_i) = \sum_I c_i(A\,t_i\,\phi_i - B\,s_i\,\phi_i)$$

$$= \sum_i c_i(t_i\,A\,\phi_i - s_i\,B\,\phi_i) = \sum_i c_i(t_i\,s_i\,\phi_i - s_i\,t_i\,\phi_i)$$

$$= \sum_i c_i t_i\,s_i\,(\phi_i - \phi_i) = 0$$

The important point here is that both operators must have a common complete set of eigenfunctions. The existence of just one eigenfunction in common is not enough to guarantee that $[A,B] = 0$.

Look over the proofs for:

If A & B commute, we can select a common complete set of eigenfunctions for them.

If A is a Hermitian operator with eigenfunction ϕ_i such that $A\phi_i = s_i\phi_i$ & $[A,B] = 0$, then $B_{ij} = <\phi_i | B | \phi_j> = 0$ (s_i not $= s_j$).

PARITY OPERATOR - a quantum mechanical operator that has no classical mechanical equivalent

$$\Pi f(x,y,z) = f(-x,-y,-z)$$

The parity operator, Π, replaces the Cartesian coordinates with their negative values.

Example: $\Pi (x^2 - z\, e^{Ay}) = (x^2 + z\, e^{-Ay})$

[In Cartesian coordinates, $\Pi (x,y,z) = (-x,-y,-z)$. What about spherical polar coordinates? The allowed ranges for the variables are:

$$0 \le r \le \infty,\ 0 \le \theta \le \pi,\ 0 \le \phi \le 2\pi$$

To move into the quadrant of (-x,-y,-z),

$$r \rightarrow r,\ \phi \rightarrow \pi + \phi,\ \theta \rightarrow \pi - \theta]$$

Find the eigenvalues of the parity operator:

$$\Pi\, g_i = c_i\, g_i$$

First, find Π^2:

$$\Pi^2\, f(x,y,z) = \Pi\, [\Pi\, f(x,y,z)] = \Pi\, f(-x,-y,-z) = f(x,y,z)$$

So $\Pi^2 = 1$ (unit operator)

Then $\Pi^2\, g_i = \Pi\, [\Pi g_i] = \Pi\, c_i\, g_i = c_i\, \Pi\, g_i = c_i\, c_i\, g_i = c_i{}^2 g_i$

So $c_i{}^2 = 1$ & $c_i = \pm 1$

Find the eigenfunctions of the parity operator:

$$\Pi\, g_i = c_i\, g_i$$

Or $\Pi\, g_i\,(x,y,z) = \pm\, g_i\,(x,y,z)$

And $\Pi\, g_i\,(x,y,z) = g_i\,(-x,-y,-z)$

If $c_i = +1$, $g_i\,(x,y,z) = g_i\,(-x,-y,-z)$ & g is an even function
If $c_i = -1$, $g_i\,(x,y,z) = -g_i\,(-x,-y,-z)$ & g is an odd function

So the eigenfunctions of Π are all the possible well-behaved even & odd functions.

The parity relationships are useful in constructing variational wavefunctions & molecular wavefunctions (later chapters).

If Π & H commute, we can select a common set of eigenfunctions.

$$H = -\underline{h}^2/(2m)\,(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial y^2) + V$$

$$[H, \Pi] = -\underline{h}^2/(2m)[\partial^2/\partial x^2, \Pi]\ -\underline{h}^2/(2m)[\partial^2/\partial y^2, \Pi]$$

$$-\,\underline{h}^2/(2m)[\partial^2/\partial z^2, \Pi] + [V, \Pi]$$

Consider $[\partial^2/\partial x^2, \Pi] = \partial^2/\partial x^2\, \Pi - \Pi\, \partial^2/\partial x^2$:

$$\Pi \, \partial^2/\partial x^2 \phi(x,y,z) = \partial/\partial(-x) \, \partial/\partial(-x) \, \phi(-x,-y,-z)$$

$$= [-\partial/\partial x][-\partial/\partial x] \, \phi(-x,-y,-z)$$

$$= \partial^2/\partial x^2 \, \phi(-x,-y,-z) = \partial^2/\partial x^2 \, \Pi \, \phi(x,y,z)$$

So $[\partial^2/\partial x^2, \Pi] = 0 = [\partial^2/\partial y^2, \Pi] = [\partial^2/\partial z^2, \Pi]$

Consider $[V, \Pi] = V\Pi - \Pi V$

$$\Pi V(x,y,z) \, \phi(x,y,z) = V(-x,-y,-z) \, \phi(-x,-y,-z)$$

If V is an even function, $V(x,y,z) = V(-x,-y,-z)$

$$\Pi V(x,y,z) \, \phi(x,y,z) = V(x,y,z) \, \phi(-x,-y,-z)$$

$$= V(x,y,z) \, \Pi\phi(x,y,z); \ V \ \& \ \Pi \ \text{commute.}$$

Otherwise they don't commute.

So $[H, \Pi] = 0$ if V is an even function. When V is even, we can choose the ψ so that they are even or odd, i.e. have definite parity. This is used in the Variation Method to construct the appropriate wavefunction.

MEASUREMENT & SUPERPOSITION OF STATES:

The basic method is a scheme for calculating the probabilities of various possible outcomes of a measurement.

Example: If the state function, $\Psi(x,t)$ is known, the probability of finding the particle between x & x+dx is $|\Psi(x,t)|^2 dx$.

In general, consider the property, G: How can we calculate the probability for each possible result of the measurement of G? (Assume there are N particles & three coordinates; Let q represent the position coordinates.)

$$G \, \phi_i(q) = g_i \, \phi_i(q)$$

The eigenfunctions of any Hermitian operator form a complete set (i.e. they are all the linearly independent eigenfunctions). The ϕ_i form a complete set, so we can expand any arbitrary wavefunction in terms of them:

$$\Psi(q,t) = \sum_i c_i(t)\phi_i(q)$$

Require

$$\int \Psi^*\Psi \, d\tau = 1,$$

where $d\tau$ is the volume element for the spatial coordinates (not time). Then

$$1 = \int \sum_i c_i^*(t)\phi_i^*(q) \, \sum_j c_j(t)\phi_j(q) \, d\tau$$

$$= \sum_i c_i^* \sum_j c_j \int \phi_i^*(q)\phi_j(q) \, d\tau$$

$$= \sum_i c_i^* \sum_j c_j \delta_{ij}$$

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

Choose the c_i's so that $1 = \sum_i |c_i|^2$

Since $\Psi(q,t)$ is a normalized state function, we can write the average value of G as

$$<G> = \int \Psi(q,t)^* \, G \, \Psi(q,t) \, d\tau$$

$$= \int \sum_i c_i^*(t)\phi_i^*(q) \, G \, \sum_j c_j(t)\phi_j(q) \, d\tau$$

$$= \sum_i c_i^* \sum_j c_j \int \phi_i^*(q) \, G \, \phi_j(q) \, d\tau$$

$$= \sum_i c_i^* \sum_j c_j \int \phi_i^*(q) \, g_j \, \phi_j(q) \, d\tau$$

$$= \Sigma_i c_i^* \Sigma_j c_j g_j \int \phi_i^*(q) \, \phi_j(q) \, d\tau$$

$$= \Sigma_i c_i^* \Sigma_j c_j g_j \, \delta_{ij}$$

$$= \Sigma_i |c_i|^2 g_i$$

We have previously defined the average value in terms of the probability of getting one of the eigenvalues, g_i, when G is measured (i.e. When a property is measured, we can only get one of the eigenvalues as a result.   No other numbers are possible.)

Then $<G> = \Sigma_i P_{g_i} g_i$,

where P_{g_i} is the probability of finding the eigenvalue g_i. So

$$P_{g_i} = |c_i|^2$$

We can predict the result of the measurement of G with certainty only if all the c_i's except one are 0:

$c_i = 0$, i not equal to k; c_k not equal to zero.

Then $|c_k|^2 = 1$ & the result of the measurement will be g_k &

$\psi_k = \phi_k$ since all the other c's are 0.

So $\Psi(q,t) = \Sigma_i c_i(t)\phi_i(q)$

gives the state function as a superposition of eigenstates, ϕ_i, of G. The coefficient, c_i, of ϕ_i in the expansion is related to the probability of finding the eigenvalue g_i when G is measured (i.e.

The larger the contribution of ϕ_i in the expansion - indicated by the magnitude of c_i - the larger the probability of measuring that eigenvalue).

Calculate c_i:

$$\Psi(q,t) = \sum_i c_i(t)\phi_i(q)$$

$$\int \phi_j^*(q)\ \Psi\ d\tau = \int \phi_j^*(q)\ [\sum_i c_i(t)\phi_i(q)]\ d\tau$$

$$= \sum_i c_i(t) \int \phi_j^*(q)\ \phi_i(q)\ d\tau$$

$$= \sum_i c_i(t)\ \delta_{ji} = c_j = <\phi_j\ |\ \Psi> = \text{probability amplitude}$$

So the probability of measuring g_j as a value of G is:

$$|\ c_j\ |^2 = |<\phi_j\ |\ \Psi>|^2 = |\int \phi_j^*(q)\ \Psi\ (q,t)\ d\tau|^2$$

So, if we know Ψ, we can predict the outcome of the measurement of G.

Example: $G = p_x$ linear momentum

$$\phi_i = e^{ik_i x/\underline{h}}; \qquad g_i = k_i$$

We previously found the general form for the wavefunction for a free particle in one dimension:

$$\Psi = a_1\, e^{-iEt/\underline{h}}\, e^{i\sqrt{(2mE)}\ x/\underline{h}} + a_2\, e^{-iEt/\underline{h}}\, e^{-i\sqrt{(2mE)}\ x/\underline{h}}$$

$$= c_1\, e^{ik_1 x/\underline{h}} + c_2\, e^{ik_2 x/\underline{h}},$$

where $c_1 = a_1\, e^{-iEt/\underline{h}}$, $c_2 = a_2\, e^{-iEt/\underline{h}}$, $k_1 = \sqrt{(2mE)}$, $k_2 = -\sqrt{(2mE)}$.

So $\left| c_1 \right|^2 = \left| a_1 e^{-iEt/\hbar} \right|^2 = \left| a_1 \right|^2 e^{iEt/\hbar} e^{-iEt/\hbar} = \left| a_1 \right|^2$

= the probability of getting k_1 when measuring G.

And $\left| c_2 \right|^2 = \left| a_2 \right|^2$

= the probability of getting k_2 when measuring G.

The probability of getting any other number when measuring G is zero.

So $\Psi_n(q,t) = e^{-iE_n t/\hbar} \psi_n(q)$ is a *stationary state*

& $H\psi_n(q) = E_n \psi_n(q)$

For a stationary state, the probability density does not depend on time:

$\left| \Psi_n(q,t) \right|^2 = \left| \psi_n(q) \right|^2$ is independent of t.

If we take a superposition of stationary states, Ψ_n,

$\Psi = \sum_n c_n \Psi_n = \sum_n c_n e^{-iE_n t/\hbar} \psi_n$

is not an eigenfunction of H, but is an eigenfunction of the time-dependent Schrödinger Eq.

$[-i\hbar \, \partial/\partial t + H] \Psi = 0$

Ψ doesn't have a definite energy because it is a combination of the ψ_n, each with energy E_n. The probability of getting E_n when the energy is measured is

$$\left|\, c_n \, e^{-iE_n t/\hbar} \,\right|^2 = \left|\, c_n \,\right|^2.$$

Ψ is a nonstationary state because the probability density depends on t due to cross terms of the form

$$e^{-iE_n t/\hbar} \; e^{iE_{n'} t/\hbar}$$

Physical example: If a system that is in a stationary state is exposed to radiation (i.e. a laser field whose potential varies with time) the state changes to a nonstationary state.