1 Lecture 3: Operators in Quantum Mechanics

1.1 Basic notions of operator algebra.

In the previous lectures we have met operators:

$$\hat{x} \qquad \text{and} \qquad \hat{p} = -i\hbar\nabla$$

they are called "fundamental operators".
Many operators are constructed from $\hat{x}$ and $\hat{p}$; for example the Hamiltonian for a single particle:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{x})$$

where $\hat{p}^2/2m$ is the K.E. operator and $\hat{V}$ is the P.E. operator. This example shows that we can add operators to get a new operator. So one may ask what other algebraic operations one can carry out with operators?
The product of two operators is defined by operating with them on a function.
Let the operators be $\hat{A}$ and $\hat{B}$, and let us operate on a function $f(x)$ (one-dimensional for simplicity of notation). Then the expression

$$\hat{A}\hat{B}f(x)$$

is a new function. We can therefore say, by the definition of operators, that $\hat{A}\hat{B}$ is an operator which we can denote by $\hat{C}$:

$$\hat{C} \text{ is the product of operators } \hat{A} \text{ and } \hat{B}.$$

The meaning of $\hat{A}\hat{B}f(x)$ should be that $\hat{B}$ is first operating on $f(x)$, giving a new function, and then $\hat{A}$ is operating on that new function.

Example: $\hat{A} = \hat{x}$ and $\hat{B} = \hat{p} = -i\hbar d/dx$, then we have

$$\hat{A}\hat{B}f(x) = \hat{x}\hat{p}f(x)$$

We can of course also construct another new operator:

$$\hat{p}\hat{x}$$

Then, by definition of the operator product,

$$\hat{p}\hat{x}f(x)$$

means that $\hat{x}$ is first operating on $f(x)$ and then $\hat{p}$ is operating on the function $\hat{x}f(x)$.
Compare the results of operating with the products $\hat{p}\hat{x}$ and $\hat{x}\hat{p}$ on $f(x)$:

$$(\hat{x}\hat{p} - \hat{p}\hat{x})f(x) = -i\hbar\left(x\frac{df(x)}{dx} - \frac{d}{dx}(xf(x))\right)$$

and hence by the product rule of differentiation:

$$(\hat{x}\hat{p} - \hat{p}\hat{x})f(x) = i\hbar f(x)$$

and since this must hold for any differentiable function $f(x)$, we can write this as an operator equation:

$$\hat{x}\hat{p} - \hat{p}\hat{x} = i\hbar$$

Thus we have shown that the operator product of $\hat{x}$ and $\hat{p}$ is non-commuting.

Because combinations of operators of the form

$$\hat{A}\hat{B} - \hat{B}\hat{A}$$

do frequently arise in QM calculations, it is customary to use a short-hand notation:

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

and this is called the commutator of $\hat{A}$ and $\hat{B}$ (in that order!).
If $[\hat{A}, \hat{B}] \neq 0$, then one says that $\hat{A}$ and $\hat{B}$ do not commute,
if $[\hat{A}, \hat{B}] = 0$, then $\hat{A}$ and $\hat{B}$ are said to commute with each other.
An operator equation of the form of

$$[\hat{A}, \hat{B}] = \text{something}$$

is called a commutation relation.

$$[\hat{x}, \hat{p}] = i\hbar$$

is the fundamental commutation relation.

1.2 Eigenfunctions and eigenvalues of operators.

We have repeatedly said that an operator is defined to be a mathematical symbol that applied to a function gives a new function.

Thus if we have a function $f(x)$ and an operator $\hat{A}$, then

$$\hat{A}f(x)$$

is a some new function, say $\phi(x)$.

Exceptionally the function $f(x)$ may be such that $\phi(x)$ is proportional to $f(x)$; then we have

$$\hat{A}f(x) = af(x)$$

where a is some constant of proportionality. In this case $f(x)$ is called an eigenfunction of $\hat{A}$ and a the corresponding eigenvalue.

Example: Consider the function $f(x,t) = e^{i(kx-\omega t)}$.
This represents a wave travelling in x direction.
Operate on $f(x)$ with the momentum operator:

$$\begin{aligned} \hat{p}f(x) &= -i\hbar\frac{d}{dx}f(x) = (-i\hbar)(ik)e^{i(kx-\omega t)} \\ &= \hbar k f(x) \end{aligned}$$

and since by the de Broglie relation $\hbar k$ is the momentum p of the particle, we have

$$\hat{p}f(x) = pf(x)$$

Note that this explains the choice of sign in the definition of the momentum operator!

1.3 Linear operators.

An operator $\hat{A}$ is said to be linear if

$$\hat{A}(cf(x)) = c\hat{A}f(x)$$
and
$$\hat{A}(f(x)+g(x)) = \hat{A}f(x)+\hat{A}g(x)$$

where $f(x)$ and $g(x)$ are any two appropriate functions and c is a complex constant.
Examples: the operators $\hat{x}$, $\hat{p}$ and $\hat{H}$ are all linear operators. This can be checked by explicit calculation (Exercise!).

1.4 Hermitian operators.

The operator $\hat{A}^\dagger$ is called the hermitian conjugate of $\hat{A}$ if

$$\int \left(\hat{A}^\dagger\psi\right)^* \psi dx = \int \psi^* \hat{A}\psi dx$$

Note: another name for "hermitian conjugate" is "adjoint".

The operator $\hat{A}$ is called hermitian if

$$\int \left(\hat{A}\psi\right)^* \psi\, dx = \int \psi^* \hat{A}\psi\, dx$$

Examples:
(i) the operator $\hat{x}$ is hermitian. Indeed:

$$\int (\hat{x}\psi)^* \psi\, dx = \int (x\psi)^* \psi\, dx = \int \psi^*\, x\psi\, dx = \int \psi^*\, \hat{x}\psi\, dx$$

(ii) the operator $\hat{p} = -i\hbar d/dx$ is hermitian:

$$\begin{aligned}\int (\hat{p}\psi)^* \psi\, dx &= \int \left(-i\hbar \frac{d\psi}{dx}\right)^* \psi\, dx \\ &= i\hbar \int \left(\frac{d\psi}{dx}\right)^* \psi\, dx\end{aligned}$$

and after integration by parts, and recognizing that the wfn tends to zero as $x \to \infty$, we get on the right-hand side

$$-i\hbar \int \psi^* \frac{d\psi}{dx}\, dx = \int \psi^* \hat{p}\psi\, dx$$

(iii) the K.E. operator $\hat{T} = \hat{p}^2/2m$ is hermitian:

$$\begin{aligned}\int \left(\hat{T}\psi\right)^* \psi\, dx &= \frac{1}{2m}\int \left(\hat{p}^2\psi\right)^* \psi\, dx \\ &= \frac{1}{2m}\int (\hat{p}\psi)^* \hat{p}\psi\, dx \\ &= \frac{1}{2m}\int \psi^* \hat{p}^2\psi\, dx \\ &= \int \psi^* \hat{T}\psi\, dx\end{aligned}$$

(iv) the Hamiltonian is hermitian:

$$\hat{H} = \hat{T} + \hat{V}(\hat{x})$$

here $\hat{V}$ is a hermitian operator by virtue of being a function of the hermitian operator $\hat{x}$, and since $\hat{T}$ has been shown to be hermitian, so $\hat{H}$ is also hermitian.

Theorem: The eigenvalues of hermitian operators are real.
Proof: Let ψ be an eigenfunction of $\hat{A}$ with eigenvalue a:

$$\hat{A}\psi = a\psi$$

then we have

$$\int \left(\hat{A}\psi\right)^* \psi \, dx = \int (a\psi)^* \psi \, dx = a^* \int \psi^* \psi \, dx$$

and by hermiticity of $\hat{A}$ we also have

$$\int \left(\hat{A}\psi\right)^* \psi \, dx = \int \psi^* \hat{A}\psi \, dx = a \int \psi^* \psi \, dx$$

hence

$$(a^* - a) \int \psi^* \psi \, dx = 0$$

and since $\int \psi^* \psi \, dx \neq 0$, we get

$$a^* - a = 0$$

The converse theorem also holds: an operator is hermitian if its eigenvalues are real.
The proof is left as an exercise.

Note: by virtue of the above theorems one can define a hermitian operator as an operator with all real eigenvalues.

Corollary: *The eigenvalues of the Hamiltonian are real.*
In fact, since by definition the Hamiltonian has the dimension of energy, therefore the eigenvalues of the Hamiltonian are the energies of the system described by the wave function.

1.5 Expectation values.

Consider a system of particles with wave function $\psi(x)$
(x can be understood to stand for all degrees of freedom of the system; so, if we have a system of two particles then x should represent
$\{x_1, y_1, z_1;\, x_2, y_2, z_2\}$).

The expectation value of an operator $\hat{A}$ that operates on ψ is defined by

$$\langle \hat{A} \rangle \equiv \int \psi^* \, \hat{A}\psi \, dx$$

If ψ is an eigenfunction of $\hat{A}$ with eigenvalue a, then, assuming the wave function to be normalized, we have

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

Now consider the rate of change of the expectation value of $\hat{A}$:

$$\begin{aligned}\frac{d\langle\hat{A}\rangle}{dt} &= \int \frac{\partial}{\partial t}\left(\psi^* \hat{A}\,\psi\right) dx \\ &= \int \left\{\frac{\partial\psi^*}{\partial t}\hat{A}\psi + \psi^*\frac{\partial\hat{A}}{\partial t}\psi + \psi^*\hat{A}\frac{\partial\psi}{\partial t}\right\} dx \\ &= \left\langle\frac{\partial\hat{A}}{\partial t}\right\rangle + \frac{i}{\hbar}\int\left\{\left(\hat{H}\psi\right)^*\hat{A}\psi - \psi^*\hat{A}\hat{H}\psi\right\} dx\end{aligned}$$

where we have used the Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi$$

Now by hermiticity of $\hat{H}$ we get on the r.h.s.:

$$\begin{aligned}&\frac{i}{\hbar}\int\left\{\psi^*\hat{H}\hat{A}\psi - \psi^*\hat{A}\hat{H}\psi\right\} dx \\ =\; &\frac{i}{\hbar}\int \psi^*\left(\hat{H}\hat{A} - \hat{A}\hat{H}\right)\psi\, dx\end{aligned}$$

hence

$$\frac{d\langle\hat{A}\rangle}{dt} = \left\langle\frac{\partial\hat{A}}{\partial t}\right\rangle + \frac{i}{\hbar}\langle[\hat{H},\hat{A}]\rangle$$

Of particular interest in applications are linear hermitian operators that do not explicitly depend on time, *i.e.* such that

$$\partial\hat{A}/\partial t = 0$$

For this class of operators we get the following equation of motion:

$$i\hbar\frac{d\langle\hat{A}\rangle}{dt} = \langle[\hat{A},\hat{H}]\rangle$$

Here the expectation values are taken with arbitrary square integrable functions. Therefore we can re-write this equation as an operator equation:

$$i\hbar\frac{d\hat{A}}{dt} = [\hat{A},\hat{H}]$$

If in particular $\hat{A}$ is an observable that commutes with $\hat{H}$, *i.e.* if $[\hat{A},\hat{H}] = 0$, then

$$\frac{d\hat{A}}{dt} = 0$$

i.e. $\hat{A}$ is a <u>conserved</u> observable.

We can also prove the following theorem:
if two operators $\hat{A}$ and $\hat{B}$ commute, then they have common eigenfunctions.
<u>Proof:</u> Let ψ be an eigenfunction of $\hat{A}$ with eigenvalue a:

$$\hat{A}\psi = a\psi$$

operating on both sides with $\hat{B}$ we get

$$\hat{B}(\hat{A}\psi) = a\hat{B}\psi$$

on the l.h.s. we can write $\hat{B}\hat{A}\psi$, and then since by assumption $\hat{A}$ and $\hat{B}$ commute, we get

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

thus $\hat{B}\psi$ is an eigenfunction of $\hat{A}$ with the same eigenvalue as ψ; therefore $\hat{B}\psi$ can differ from ψ only by a constant factor, *i.e.* we must have

$$\hat{B}\psi = b\psi$$

i.e. ψ is also an eigenfunction of $\hat{B}$.

The converse theorem is also true but not as useful; I shall therefore omit the proof.

1.6 Angular momentum.

Often operators can be constructed by taking the corresponding dynamical variable of classical mechanics, which is expressed in terms of coordinates and momenta, and replacing x by $\hat{x}$, p by $\hat{p}$ etc. That was in fact the way we have constructed the Hamiltonian.

Now we apply this prescription to angular momentum.
In classical mechanics one defines the angular momentum by

$$\vec{L} = \vec{r} \times \vec{p}$$

We get the angular momentum operator by replacing the vector $\vec{r}$ by the vector operator $\hat{r} = (\hat{x},\, \hat{y},\, \hat{z})$ and the momentum vector by the momentum vector operator

$$\hat{p} = -i\hbar\nabla = -i\hbar(\partial_x,\, \partial_y,\, \partial_z)$$

where $\partial_x = \partial/\partial x$ etc.

The complete fundamental commutation relations of the coordinate and momentum operators are

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

and

$$[\hat{x}, \hat{p}_y] = [\hat{x}, \hat{p}_z] = \ldots = [\hat{z}, \hat{p}_y] = 0$$

It will be convenient to use the following notation:

$$\hat{x}_1 = \hat{x}, \quad \hat{x}_2 = \hat{y}, \quad \hat{x}_3 = \hat{z}$$

and

$$\hat{p}_1 = \hat{p}_x, \quad \hat{p}_2 = \hat{p}_y, \quad \hat{p}_3 = \hat{p}_z$$

we can then summarize the fundamental commutation relations by

$$[\hat{x}_i,\, \hat{p}_j] = i\hbar\delta_{ij}$$

where δ_{ij} is the Kronecker symbol:

$$\delta_{ij} = \begin{cases} 1 & \text{if} \quad i = j \\ 0 & \text{if} \quad i \neq j \end{cases}$$

We can now find the commutation relations for the components of the angular momentum operator. To do this it is convenient to get at first the commutation relations with $\hat{x}_i$, then with $\hat{p}_i$, and finally the commutation relations for the components of the angular momentum operator.

Thus consider the commutator $[\hat{x}, \hat{L}_x]$: we have $\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y$, and hence by the fundamental commutation relations

$$[\hat{x}, \hat{L}_x] = 0$$

Next consider $[\hat{x}, \hat{L}_y]$: we have

$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z$$

hence

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

and similarly

$$[\hat{x}, \hat{L}_z] = -i\hbar\hat{y}$$

etc. We can summarize the nine commutation relations:

$$[\hat{x}_i, \hat{L}_j] = i\hbar\varepsilon_{ijk}\hat{x}_k$$

where

$$\varepsilon_{ijk} = \begin{cases} 1 & \text{if} \quad (ijk) = (1,2,3) \text{ or } (2,3,1) \text{ or } (3,1,2) \\ -1 & \text{if} \quad (ijk) = (1,3,2) \text{ or } (3,2,1) \text{ or } (2,1,3) \\ 0 & \text{if} \quad i = j \text{ or } i = k \text{ or } j = k \end{cases}$$

and summation over the repeated index k is implied.

Similarly one can show

$$[\hat{p}_i, \hat{L}_j] = i\hbar\varepsilon_{ijk}\hat{p}_k$$

after which it is straight forward to deduce:

$$[\hat{L}_i, \hat{L}_j] = i\hbar\varepsilon_{ijk}\hat{L}_k$$

The important conclusion from this result is that *the components of angular momentum have no common eigenfunctions.*

Of course, we must also show that the angular momentum operators are hermitian. This is of course plausible (reasonable) since we know that the angular momentum is a dynamical variable in classical mechanics. The proof is left as an exercise.

We can construct one more operator that commutes with all components of $\hat{L}$: define the square of $\hat{L}$ by

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

then

$$\begin{aligned} [\hat{L}_x, \hat{L}^2] &= [\hat{L}_x, \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2] \\ &= [\hat{L}_x, \hat{L}_y^2] + [\hat{L}_x, \hat{L}_z^2] \end{aligned}$$

Now there is a simple technique to evaluate a commutator like $[\hat{L}_x, \hat{L}_y^2]$: write down explicitly the known commutator $[\hat{L}_x, \hat{L}_y]$:

$$\hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x = i\hbar \hat{L}_z$$

multiply this on the left by $\hat{L}_y$, then multiply on the right by $\hat{L}_y$:

$$\begin{aligned} \hat{L}_y \hat{L}_x \hat{L}_y - \hat{L}_y^2 \hat{L}_x &= i\hbar \hat{L}_y \hat{L}_z \\ \hat{L}_x \hat{L}_y^2 - \hat{L}_y \hat{L}_x \hat{L}_y &= i\hbar \hat{L}_z \hat{L}_y \end{aligned}$$

and if we add these commutation relations we get

$$\hat{L}_x \hat{L}_y^2 - \hat{L}_y^2 \hat{L}_x = i\hbar (\hat{L}_y \hat{L}_z + \hat{L}_z \hat{L}_y)$$

and similarly

$$\hat{L}_x \hat{L}_z^2 - \hat{L}_z^2 \hat{L}_x = -i\hbar (\hat{L}_y \hat{L}_z + \hat{L}_z \hat{L}_y)$$

hence

$$[\hat{L}_x, \hat{L}^2] = 0$$

and similarly

$$[\hat{L}_y, \hat{L}^2] = [\hat{L}_z, \hat{L}^2] = 0$$

Finally one can also show that the components of $\hat{L}$ and $\hat{L}^2$ commute with $\hat{p}^2$, and therefore also with the K.E. operator $\hat{T}$, and that they commute with r and hence with any function of r.

The latter statement is most easily shown by working in spherical polar coordinates (r, θ, φ), where θ is the polar angle and φ the azimuth. If we choose the polar axis along the cartesian z direction, then we get after some tedious calculation the following expressions for the angular momentum components:

$$\begin{aligned} \hat{L}_x &= i\hbar \left(\sin\varphi \frac{\partial}{\partial\theta} + \cot\theta \, \cos\varphi \frac{\partial}{\partial\varphi} \right) \\ \hat{L}_y &= i\hbar \left(-\cos\varphi \frac{\partial}{\partial\theta} + \cot\theta \, \sin\varphi \frac{\partial}{\partial\varphi} \right) \\ \hat{L}_z &= -i\hbar \frac{\partial}{\partial\varphi} \end{aligned}$$

We can therefore conclude that the angular momentum operators commute with the Hamiltonian of a particle in a central field, for example a Coulomb field, and that implies that $\hat{L}^2$ and one of the components can be chosen to have common eigenfunctions with the Hamiltonian.