A Quantum Mechanics Cookbook

The result of the great intellectual struggle of the early 20th century with atomic phenomena was a prescription to take a classical system and turn it into a system following quantum rules. The origin of these rules is mysterious, but they are universal – they apply, not only to atoms, but to photons, quarks, gluons, and everything else we know in nature.

The rules can be summarized simply:

1. For a classical system described by coordinates and momenta, $\vec{x}_i$, $\vec{p}_i$, $i = 1 \ldots N$, there is a quantum system described by a wave function: $\Psi(\vec{x}_1, \ldots \vec{x}_N, t)$. The momenta are represented by operators acting on this wave function, $\vec{p}_i = -i\hbar\vec{\nabla}_i$.

2. The wave function satisfies the Schrodinger equation. This is obtained by writing the energy in terms of the momenta and the coordinates, $E(\vec{p}_i, \vec{x}_i) = H(\vec{p}_i, \vec{x}_i)$ (this is usually called the Hamiltonian). The momenta are interpreted as operators. Then

$$H\Psi = i\hbar\frac{\partial\Psi}{\partial t}.$$

3. For time-independent Hamiltonians, one can write $\Psi = e^{-iEt/\hbar}\psi$, and

$$H\psi = E\psi$$

where E is a number, the energy eigenvalue. In general, the requirement that ψ be normalizable leads to quantization of E, i.e. only discrete values of E are possible.

4. The absolute square of the wave function is the probability density.

Measurement

Measurement is the most interesting and in some ways most troubling aspect of quantum mechanics. We have seen that the probability that a measurement of $\vec{x}$ yields a coordinate in the range $\vec{x} + d\vec{x}$ is $|\psi(\vec{x})|^2 d^3x$. Because of this, the average $\vec{x}$ measured in a very large number of measurements is:

$$< \vec{x} > = \int d^3x |\psi|^2 \vec{x}.$$

This generalizes to other quantities one can measure. With every measurable quantity in quantum mechanics is associated an operator, as in the case of the

momentum:

$$\vec{p}_{op} = -i\hbar\vec{\nabla}.$$

The average result of many measurements of $\vec{p}$ is

$$<\vec{p}> = \int d^3\psi^2 \vec{p}_{op}\psi.$$

Unlike for the coordinate and the momentum, there are times when the measurement of an operator yields a *definite* result. If the wave function satisfies

$$\mathcal{O}\psi = O\psi$$

(where O is just a number) then the wave function ψ is said to be an "eigenfunction" of $\mathcal{O}$ with "eigenvalue" O. We will see examples below, and in our study of the hydrogen atom. But the most ubiquitous example is the energy itself; the energy states are eigenfunctions of the Hamiltonian operator with eigenvalue E. This is just the content of the time-independent Schrodinger equation.

Now from our definition of the average value, and the fact that the wave functions, ψ, are normalized, we see that for a system in an eigenstate of O,

$$<\mathcal{O}> = O$$

i.e. the results of any measurement yield a definite value of the observable.

Some Simple – and Important – Situations

Free Particle

The Hamiltonian for a free particle in three dimensions is

$$H = \frac{\vec{p}^2}{2m}$$

so the Schrodinger equation is:

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\psi(\vec{x}) = E\psi(\vec{x}).$$

This equation is solved by plane waves,

$$\psi = e^{i\frac{\vec{p}\cdot\vec{x}}{\hbar}}.$$

These wave functions are "eigenfunctions" of the momentum operator:

$$\vec{p}_{op}\psi = -i\hbar\vec{\nabla}\psi = \vec{p}\psi.$$

According to the rules of quantum mechanics, when a system is in a state which is an eigenfunction of an operator, a measurement of that operator yields the

corresponding "eigenvalue", in this case $\vec{p}$. The problem here is that the state ψ is not normalizable. The probability of finding the system at any point in all of space is infinite, since $|\psi|^2 = 1$.

To understand this, let's compare with a particle in a box. We can think here of a cubic box with sides L. The potential outside of the box we take to be infinite, so that the wave function must vanish outside of the box. As explained in your text, the solutions are labeled by three integers,

$$\vec{n} = (n_x, n_y, n_z).$$

They are given by

$$\psi_{\vec{n}}(\vec{x}) = A_{\vec{n}} \sin(\frac{n_x \pi x}{\ell}) \sin(\frac{n_y \pi y}{\ell}) \sin(\frac{n_z \pi z}{\ell}).$$

Excercise For $\ell = 1$ meter, and the particle an electron, what is the energy of the lowest state? What is the energy of one of the first excited states?

Because the splitting of the states is so tiny, it doesn't really matter, from a mathematical point of view, what boundary conditions we take on the wave functions. Rather than take the wave functions to vanish on the boundary, it is simpler to use wave functions which are *periodic* in $\vec{x}$:

$$\psi(x + \ell, y, z) = \psi(x, y + \ell, z) = \psi(x, y, z + \ell) = \psi(x, y, z).$$

The solutions of the Schrodinger equation with these boundary conditions are just plane waves:

$$\psi = e^{i\vec{p} \cdot \vec{x}/\hbar}$$

but for particular values of $\vec{p}$

$$\vec{p} = \frac{2\pi \vec{n}}{\ell}.$$

The energies are:

$$E = \frac{\vec{p}^2}{2m} = \frac{(2\pi\hbar)^2 \vec{n}^2}{2m}.$$

Now these states are states of definite momentum, so if we can somehow prepare the system in one of these states, any subsequent measurement of the momentum will yield precisely $\vec{p}$. Because the splitting in energies between states, as seen from this exercise, is extremely tiny, it is, however, very difficult to prepare a

state of definite momentum. Instead, any state will be a *superposition* of different momentum states:

$$\psi(\vec{x}) = \sum_{\vec{p}} c(\vec{p}) e^{i\vec{p}\cdot\vec{x}/\hbar}.$$

Now the probability of measuring a value $\vec{p}$ for the momentum is $|c(\vec{p})|^2$.

In general, this wave function is called a "wave packet." It describes a state spread out in space and in momentum. It satisfies the uncertainty principle:

$$\Delta x \Delta p \geq 2\pi\hbar.$$

This is a consequence of properties of Fourier series, which you will learn about in Physics 114a.