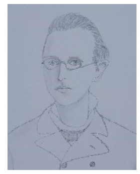
Modern Physics

Notes on Quantum Mechanics



Why quantum mechanics?

It was clear at the beginning of the 20th century that Classical Physics does not work well at the microscopic level. Among the phenomena that are in conflict we have:

Planck's radiation law: It was found that to make sense of the spectrum emitted by a blackbody, the energy in electromagnetic waves cannot be any continuous value, rather it has to be an integer number of quanta (quanta is the plural of quantum) given by the equation $E = nhf$, where E is the energy, n is an integer, f is the frequency and h is a constant of nature that we now call Planck's constant.

$h = 6.62607015\times10^{-34}$ Js

Photoelectric Effect: If you illuminate the surface of a metal with light of short-enough wavelength the surface ejects electrons whose kinetic energy can be measured in an experiment. Typically, you detect the ejected electrons as a tiny electric current going from the metal to a capturing electrode. By making the potential of the electrode negative you can stop all the photoelectrons and estimate their maximum kinetic energy.

This experiment posed several questions, for example,

Why is it that photoelectrons are emitted immediately and not after the surface absorbs enough energy?
Because each quantum comes as a bundle, like a bullet.

Why is it that there has to be a short-enough wavelength, why can't we just increase the intensity of the light to get photoelectrons?
Because the energy of a quantum is hf, it is not dependent on the intensity.

Rutherford Model of the atom. After the atomic nucleus was discovered, a picture of the atom emerged, similar to a solar system, where the electrons are the planets and the nucleus the sun, but classical physics tells us that the electrons will emit energy and collapse on the nucleus. That is obviously not right, otherwise we would not be here to ask the questions!
Now we know that a confinement like that would require an enormous amount of energy and transitions are only allowed for good quantum numbers.

Quantized wavelengths: The light emitted by atoms and molecules consists of discrete, separated wavelengths, not a continuous spectrum. This hints that the energy levels in atoms are discrete (quantized), not continuous.

Compton Effect: Light can behave as a particle, scattering off of electrons and transferring linear momentum to them (kicking them). But light is a wave, right? Yes, but we know now that it is absorbed and emitted in packets (quanta).

Electron diffraction: Electrons also have wavelengths and they can show interference. More recent experiments have shown that even C_{60} with its massive 720 Daltons shows wave qualities.

Heat capacity of diamond: It was found that at low temperatures the heat capacity of diamond is not $3R$ anymore! The reason, explained by Einstein, is that vibrations are also quantized. You cannot shake an atom with any old amplitude or energy. The increments in energy have to be multiples of hf once again, and the total energy is $(n + 1/2)\, hf$.

Frank-Hertz experiment: When electrons collide with atoms, they only lose energy if they can transfer enough of it to excite the atom to an available state. This experiment also demonstrates a principle of quantum mechanics: If you cannot reach an available state, nothing happens. I like to compare this to superconductivity: to slow down an electron you need to break a Cooper pair and that will not happen if the collision does not have enough energy to do so.

Stern-Gerlach experiment: Silver atoms have a single valence electron whose orbital angular momentum is zero, but their spin is $\sqrt{3}h/4\pi$. There is a magnetic moment anti-aligned with the spin angular momentum, and when it was measured, it was found that it would only show as "up" or "down" with respect to the applied magnetic field. The magnitude of the projection of the angular momentum has the magnitude $h/4\pi$, never zero and never a different fraction.

Old quantum mechanics

There was a period when physicists thought of using Planck's constant in a theory that explained the experiments: quantization of energies, waves of matter and quantization of angular momentum. Bohr's atom model, for example, assumes that the orbital angular momentum is quantized in the hydrogen atom and it gets the energies, radius, velocities, ionization potentials, wavelengths, etc. almost right. However, this was not enough to explain all the new phenomena and eventually people realized that a more radical theory was necessary.

"*Your theory is crazy, but not crazy enough to be true*"

Niels Bohr

Quantum Mechanics

"*Nature isn't classical, dammit!*"

Richard P. Feynman

We give up the idea that we can describe the position of a particle with a vector $\vec{r}(t)$, instead we have this 1st postulate of quantum mechanics:

The properties of a quantum system are completely defined by its wavefunction ψ.

If there is only one particle in one dimension the wavefunction is given by $\psi(x,t)$. The wavefunction is interpreted in the sense that its magnitude squared indicates the probability of finding the particle in a small interval in the vicinity of *x* at time *t*. The units of the wavefunction should be $m^{-1/2}$ in that case. Also, since the particle must be somewhere, the wavefunction must satisfy:

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2 \, dx = 1$$

A wavefunction for one particle in 3 dimensions has the form $\psi(x,y,z,t)$ or in spherical coordinates $\psi(r,\theta,\phi,t)$. The interpretation is the same, the square of its magnitude indicates the probability of finding the particle in a small volume in the vicinity of (*x, y, z*), so it has units of $m^{-3/2}$ and it must satisfy:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\psi(x,y,z,t)|^2 \, dxdydz = 1$$

The 2nd postulate of quantum mechanics concerns the calculation of probabilities or expected values. Given that we want the expected value of a quantity *u*, we find it using the prescription:

$$\langle u \rangle = \int_{-\infty}^{\infty} \psi^*(x,t) u \psi(x,t) dx$$

The 3rd postulate of quantum mechanics asserts that for every physical quantity *A*, there is an operator that acts on all possible states ψ and any measurement of that quantity can only give as a result an eigenvalue of the operator.

The 4th postulate of quantum mechanics establishes the evolution of the wavefunction which is dictated by the Schrödinger equation:

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

The operator *H* in the equation is the Hamiltonian of the system. In most cases it is the kinetic energy plus the potential energy operators, so:

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\psi + V\psi$$

The equation had the great success of solving the problem of the hydrogen atom, obtaining the energies, radius and angular momenta, but it has proven to be too difficult for multi-electron atoms or for molecules. Alternative methods have been invented to advance our knowledge of nature by using approximations, perturbation theory, density functionals and other human creations.