Physics 224: Discoveries and Inventions of Modern Physics

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LECTURE 1: Energy Levels in Quantum Mechanics

Discuss Syllabus. This course is a bird's eyeview of some of the most interesting and important phenomena of physics. This includes atomic physics, condensed matter physics, high energy physics, and astrophysics. We will cover such topics as the basics of atomic and molecular physics, how a laser works, Bose–Einstein condensation, superconductivity, semiconductors, magnetism, quarks and leptons, and the Big Bang. These are not disparate phenomena. There are common concepts and themes which reappear again and again. For example, understanding black body radiation was crucial to the birth of quantum mechanics, but it also reappears as the remnant of the Big Bang. The emphasis of the course will be on qualitative phenomena and intuitive concepts rather than on analytical derivations which are covered in other courses.

Before we can really start exploring these topics, we need to have a basic understanding of some of the fundamentals of quantum mechanics and statistical physics. One of the essential ingredients of quantum mechanics is the fact that energy can be discretized as opposed to being continuous. For example, in an atom electrons occupy certain energy levels and their wavefunctions constitute atomic orbitals. Perhaps you have heard of s, p, and d orbitals. We'll talk more about this later. Another example is a particle in a box. As long as the box if finite in size, the energy levels will be discrete. It turns out that the energy of a particle of mass m in a box of size a can only have the values given by:

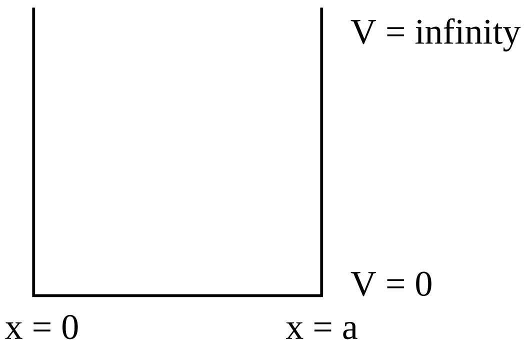
$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \tag{1}$$

where $n = 1, 2, 3, ...$ These are the only values a particle can have. Nothing in between is allowed.

Let's take a moment to derive this. (If this all looks foreign to you, don't worry about it. Just remember that the energy levels are quantized.) We start with Schroedinger's equation:

$$H\psi = E\psi \tag{2}$$

where E is the energy and H is the Hamiltonian operator. H is the sum of the kinetic and potential energies. Given H one can solve for the eigenfunction or wavefunction ψ and the energy eigenvalue E.



Let's consider a particle in a one dimensional box. The box goes from 0 to a and the walls are infinitely high. So the wavefunction goes to zero at $x = 0$ and at $x = a$. Inside the box the potential $V = 0$. The kinetic energy is $p^2/2m$ where p is the momentum. p and H are operators. One way to represent them is with derivatives. Derivatives do an operation on a function. So

$$\hat{p} = \frac{\hbar}{i}\frac{d}{dx} \tag{3}$$

where $i = \sqrt{-1}$. I put a hat on $\hat{p}$ to indicate that it is an operator. When p doesn't have a hat, it's the eigenvalue of the momentum, i.e., it's a scalar value representing the momentum. We could write $\hat{p}\psi = p\psi$. Notice that the momentum operator measures the slope or gradient of a wavefunction. This may seem strange if you haven't seen it before. It will be derived in the quantum mechanics course, so I don't want to go through the derivation here. But what this says is that if the wavefunction has no slope, it has no momentum. If you had a perfectly flat function that was the same everywhere, i.e., $\psi(x) = \text{const}$, then it wouldn't have any momentum. A wavefunction has to change spatially in order to have momentum. The more it changes, the more momentum it has.

The Hamiltonian is

$$\hat{H} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \tag{4}$$

Notice that the Hamiltonian has the square of a gradient. This means that if the wavefunction wiggles a lot spatially, then it represents a particle with a lot of kinetic energy. So Schroedinger's equation (2) becomes

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \tag{5}$$

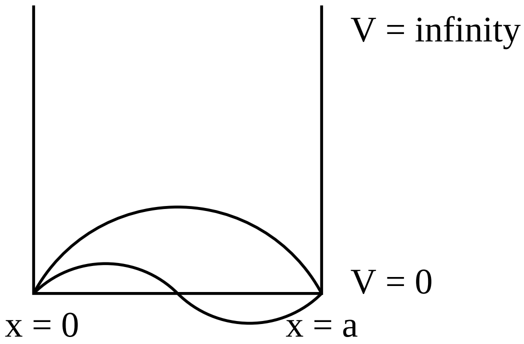
Here the wavefunction represents the particle ψ. This is an example of wave–particle duality for which quantum mechanics is famous. The probability that the particle is at site x is given by $|\psi(x)|^2$. We can rewrite (5) as

$$\frac{d^2\psi}{dx^2} = -\frac{p^2}{\hbar^2}\psi \tag{6}$$

where $p^2 = 2mE$. This is a second order differential equation. The solution has the form

$$\psi(x) = A\sin(px/\hbar) + B\cos(px/\hbar) \tag{7}$$

where A and B are constant coefficients. You can check this solution by plugging it into (6).



The fact that the solution has sine and cosine functions represents the fact that the particle is represented by a wave function whose nodes are at the walls of the box. We want the wavefunction to vanish at the walls because there is no way the particle can get through infinitely high walls. This gives us the boundary conditions: $\psi(x=0)=0$ and $\psi(x=a)=0$. The first condition $\psi(x=0)=0$ leads to $B=0$. The second condition $\psi(x=a)=0$ implies that

$$\frac{pa}{\hbar} = n\pi \tag{8}$$

where the integer $n = 1, 2, 3, ...$ Note that for $n = 0$, $\psi = 0$. We can solve for p

$$p = \frac{n\pi\hbar}{a} \tag{9}$$

We can use this to get the energy eigenvalues:

$$E_n = \frac{p^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2} \tag{10}$$

Each value of n corresponds to a different eigenvalue of the energy E_n. Notice that the energy levels are not equally spaced; they get farther apart as you go up in energy. Each value of n also corresponds to a different wavefunction

$$\psi_n(x) = A\sin(px/\hbar) = A\sin\left(\frac{n\pi x}{a}\right) \tag{11}$$

Notice that the more nodes there are, the more wiggles there are, and the higher the energy is. The coefficient A is determined by the normalization condition that says that there is only one particle in the box.

$$\int_0^a dx|\psi(x)|^2 = 1 \tag{12}$$

Can you figure out what A should be?

A harmonic oscillator is another example. This is just the quantum mechanical case of a mass attached to a spring. In this case the potential is a parabola rather than being a square well. A particle of mass m in this potential oscillates with frequency ω. The Hamiltonian is

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 \tag{13}$$

You will learn how to solve this in your quantum mechanics course. Let me just write down the result. The energy eigenvalues are

$$E_n = (n + \frac{1}{2})\hbar\omega \tag{14}$$

where $n = 0, 1, 2, 3, ...$ Notice once again that the energy levels are quantized. In this case they are evenly spaced by an amount $\Delta E = \hbar\omega$.

Electromagnetic radiation is also quantized. Light can be described as waves or as particles called photons. A photon has energy $h\nu$ where ν is the frequency of the electromagnetic wave. Recall that $\omega = 2\pi\nu$ and that $\nu = c/\lambda$ where c is the speed of light. Often one speaks in terms of the wavenumber $k = 2\pi/\lambda$. If we make it a vector quantity $\vec{k}$, then we call it a wavevector. This is related to the momentum by $\vec{p} = \hbar\vec{k}$ and to the frequency by $\omega = ck$. So if the electromagnetic wave has a short wavelength, it has a high frequency and the photon carries a lot of energy. Once again we see that lots of wiggles means lots of energy. Photons are massless and they travel at the speed of light. So the basic message is that energy is quantized and that there are discrete energy levels.

Quantum Statistical Mechanics

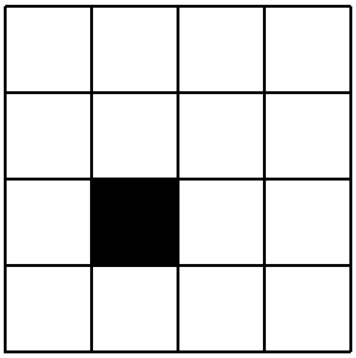
Counting States

In the example of a particle in a box we saw that the energy levels are quantized. Each energy level is associated with a mode or eigenfunction. It is often useful to be able to count the number of modes in a box that have energies between E and $E + dE$. This is because statistical mechanics deals with many particle systems. Life would be boring if we only dealt with one particle.

Suppose we have a 3 dimensional box whose walls are parallel to the x, y, and z axes with lengths L_x, L_y, and L_z. Thus the volume is $V = L_xL_yL_z$. We can solve this in much the same way as we did the particle in a box problem. Inside the box the potential is zero. The eigenmodes are waves. Let's choose boundary conditions such that the solution of Schroedinger's equation (2) are wavefunctions that are plane waves:

$$\Psi = A\exp[i(\vec{k}\cdot\vec{r} - \omega t)] = \psi(\vec{r})\exp(-i\omega t) \tag{15}$$

This is a propagating wave that is never reflected. So our box can't have hard walls. Rather let's imagine that our box is embedded in an infinite set of similar boxes in each of which the physical situation is exactly the same. In other words, each of these boxes is a repeat of the original box.



To describe this situation, we use periodic boundary conditions which we can write as

$$\begin{aligned}\psi(x+L_x,y,z) &= \psi(x,y,z)\\ \psi(x,y+L_y,z) &= \psi(x,y,z)\\ \psi(x,y,z+L_z) &= \psi(x,y,z)\end{aligned}$$

If we require our traveling wave solution

$$\psi(\vec{r}) = \exp(i\vec{k}\cdot\vec{r}) = \exp[i(k_x x + k_y y + k_z z)] \tag{16}$$

to satisfy these boundary conditions, then we must require that

$$k_x(x+L_x) = k_x x + 2\pi n_x \tag{17}$$

where n_x is an integer. We can rewrite this as

$$k_x = \frac{2\pi}{L_x} n_x \tag{18}$$

Similarly,

$$\begin{aligned}k_y &= \frac{2\pi}{L_y} n_y\\ k_z &= \frac{2\pi}{L_z} n_z\end{aligned}$$

Here the numbers n_x, n_y, and n_z are any set of integers– positive, negative, or zero.

We can use $p = \hbar k$ and $E = p^2/2m$ to deduce that

$$E(n_x, n_y, n_z) = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) = \frac{2\pi^2\hbar^2}{m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \tag{19}$$

Once again we see that the energy levels are quantized. Notice that for any kind of macroscopic volume where L_x, L_y, and L_z are large, the energy levels are very closely spaced.

Now we want to count the number of modes or waves that have wavevectors between $\vec{k} = (k_x, k_y, k_z)$ and $\vec{k} + d\vec{k} = (k_x + dk_x, k_y + dk_y, k_z + dk_z)$. For given values of k_y and k_z, it follows from (18) that the number Δn_x of possible integers n_x for which k_x lies in the range between k_x and $k_x + dk_x$ is equal to

$$\Delta n_x = \frac{L_x}{2\pi} dk_x \tag{20}$$

We see that if L_x is very large, a lot of states can be in the small interval dk_x. The same holds true for dk_y and dk_z. So the number of states that lie between $\vec{k}$ and $\vec{k} + d\vec{k}$ is

$$\rho d^3k = \Delta n_x \Delta n_y \Delta n_z = \left(\frac{L_x}{2\pi}dk_x\right)\left(\frac{L_y}{2\pi}dk_y\right)\left(\frac{L_z}{2\pi}dk_z\right) = \frac{L_x L_y L_z}{(2\pi)^3} dk_x dk_y dk_z \tag{21}$$

or

$$\rho d^3k = \frac{V}{(2\pi)^3} d^3k \tag{22}$$

where $d^3k \equiv dk_x dk_y dk_z$ is an element of volume in "k space." Notice that the number of states ρ is independent of $\vec{k}$ and proportional to the volume V under consideration. So the "density of states", i.e., the number of states per unit volume, lying between $\vec{k}$ and $\vec{k} + d\vec{k}$ is $d^3k/(2\pi)^3$ which is a constant independent of the magnitude or shape of the volume V.

Using the relation $\vec{p} = \hbar\vec{k}$, we can also deduce that the number of states $\rho_p d^3p$ in the momentum range between $\vec{p}$ and $\vec{p} + d\vec{p}$ is

$$\rho_p d^3p = \rho d^3k = \frac{V}{(2\pi)^3}\frac{d^3p}{\hbar^3} = V\frac{d^3p}{h^3} \tag{23}$$

where $h = 2\pi\hbar$ is the ordinary Planck's constant.

If k–space is isotropic, i.e., the same in every direction, then the number of states in a spherical shell lying between radii k and $k + dk$ is

$$\rho_k dk = \rho d^3k = \frac{V}{(2\pi)^3}(4\pi k^2 dk) = \frac{V}{2\pi^2}k^2 dk \tag{24}$$

If we are considering photons for which $\omega = ck$, then we can plug $k = \omega/c$ into (24) to get the number of states lying between ω and $\omega + d\omega$.

$$\rho_\omega d\omega = 2\frac{V}{2\pi^2 c^3}\omega^2 d\omega \tag{25}$$

The factor of 2 comes from the fact that there are 2 photon polarizations. The polarization refers to the direction of the electric field vector $\vec{E}$ in the electromagnetic radiation. Since $\vec{E}$ must be perpendicular to $\vec{k}$, there are 2 polarization directions. We will use (25) in deriving blackbody radiation in lecture 4. Sometimes the term “density of states” for photons is used to refer to the number of states per unit volume per unit energy:

$$N(\omega) = \frac{2}{2\pi^2 c^3}\omega^2 = \frac{1}{\pi^2 c^3}\omega^2 \tag{26}$$