Theoretical Physics
Prof. Ruiz, UNC Asheville, doctorphys on YouTube
Chapter I Notes. Quantum Mechanics

I1. Quantization. Starting in 1900, experimental results started forcing physicists to quantize physical quantities that are continuous in classical physics.

1, Quantizing Oscillator Energy (1900)

Max Planck (1858-1947)
Courtesy School of Mathematics and Statistics
University of St. Andrews, Scotland

Planck quantized the energy levels in atomic harmonic oscillators to explain radiation emitted from a glowing mass. His energy levels are given by

$$E_n = nhf \ ,$$

where n = 0, 1, 2, … The n refers to the n^{th} state of vibration, f is the frequency of the lowest energy state, h is a constant called the Planck constant, and E_n is the energy of the n^{th} level of vibration.

Later, the formal calculation from quantum mechanics gave

$$E_n = (n + \frac{1}{2})hf \ .$$

Planck postulated his equation. He did not derive it and he got it right except for the ground-state reference energy $E_0 = \frac{1}{2}hf$. Planck had zero for that, but the spacing of the energy levels agree:

$$\Delta E_{adjacent} = E_{n+1} - E_n = hf \ .$$

You are going to do for homework the calculation that won Planck the Nobel Prize in 1918. You will use our statistical methods and the partition function.

In classical physics an oscillator can have any energy. Energy is continuous. But to make things work in the microscopic world, Planck had to quantize energy.

PI1 (Practice Problem). What are the dimensions for h?

2. Quantizing Light (1905)

Albert Einstein (1873-1943)
Courtesy School of Mathematics and Statistics
University of St. Andrews, Scotland

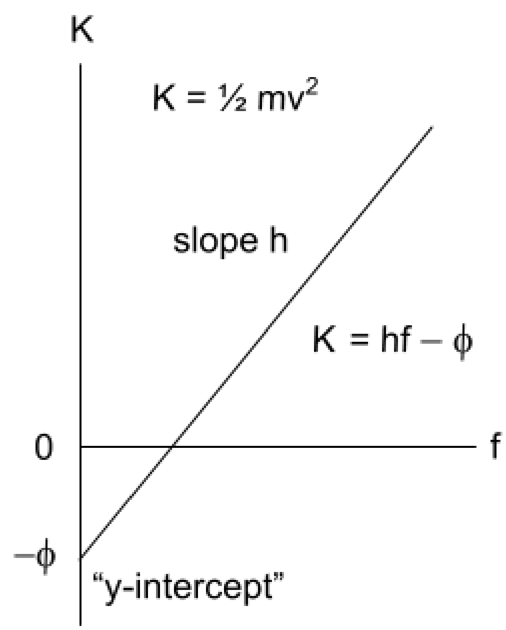
Einstein, taking Planck seriously, stated that light carries off a quantum of energy should the oscillator drop from one level to another. So Einstein related light frequency to light energy.

$$\Delta E_{adjacent} = E_{n+1} - E_n = hf$$

$$E_{photon} = hf$$

He used this idea to explain the photoelectric effect. When light shines on a metal, if the frequency reaches a threshold, the light pops off electrons from the metal.

The experimental graph is shown here where you plot the kinetic energy of the ejected electrons as a function of the frequency of the light hitting the metal.



You need to reach a threshold frequency for K = 0, i.e., electron just pops off. Then higher frequencies kick the electron out where the electron moves. Einstein quantized light energy according to Planck's formula.

He then obtained a straight line to fit the data, where the slope is the Planck constant.

Einstein called his quantized light the light quantum ("das lichtquant"). The chemist Gilbert Lewis coined the name "photon" in 1926, which has been used ever since. Lewis was inspired by Greek. The Greek word for light is "phos" and the Greek word for "of light" is photos. The word photography is also derived from Greek, along with the Greek word for writing.

3. Quantizing Angular Momentum (1913)

Niels Bohr (1885-1962)
Courtesy School of Mathematics and Statistics
University of St. Andrews, Scotland

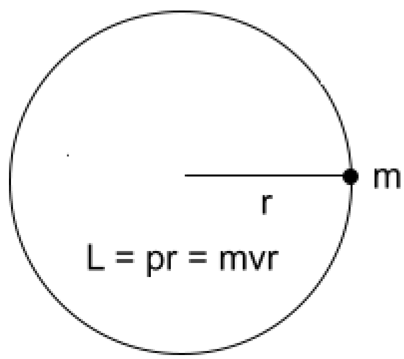
To understand the discrete wavelengths emitted from the excited hydrogen atom as it dropped to lower energy states Bohr quantized the angular momentum.

He was then able to build on Einstein's concept of light quanta. The exited hydrogen atom "relaxes" as the electron drops from a higher energy level to a lower one, giving off a photon with energy given by the difference in energy levels.

$$\Delta E = E_{final} - E_{initial} = hf$$

Bohr's model, light the others, is semiclassical. Here an electron is in a circular orbit. Assign the electron mass m and speed v. Then the momentum is

$$p = mv \; .$$



The angular momentum is defined as the tangential momentum times the radius from the reference point. In this case, we use the center of the orbit. The angular momentum L is then

$$L = pr = mvr$$

Bohr had to first postulate that the orbiting electron does not radiate if it stays in the same orbit. This postulate contradicts electromagnetic theory since a circular path means acceleration and changing electric fields. The changing electric field should produce a changing magnetic field and so on so that energy is radiated away in the form of electromagnetic waves. The electron would then lose energy and spiral into the center. So classical physics indicates that atoms don't exist and "you do not exist."

Bohr's 1st postulate stops this, his 2nd postulate quantizes angular momentum, and his 3rd is the energy-photon equation above. He derived the correct hydrogen spectrum.

PI2 (Practice Problem). Show that the dimensions of h are also angular momentum.

Bohr's quantization of angular momentum is given below.

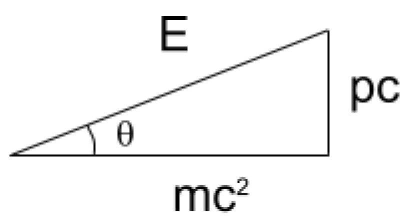
$$L = n\frac{h}{2\pi} \equiv n\hbar$$

Angular momentum is not continuous as in classical physics. Angular momentum comes in lump units related to the Planck constant. The unit is

$$\frac{h}{2\pi} \equiv \hbar,$$

i.e., the Planck constant divided by 2π. We refer to this unit as h-bar.

I2. Modern Physics Revisited. We return to the Einstein formula that relates energy, momentum, and mass.



$$E^2 = m^2c^4 + p^2c^2$$

Light travels at the speed of light. Therefore, according to the relativistic energy equation, the energy is all pc as the angle swings up to 90°.

$$E = pc$$ (for light from relativity, Einstein)

But we also have

$$E = hf$$ (for light from the photoelectric effect, Einstein)

Therefore,

$$E = pc = hf$$

For a moment, consider

$$E = \frac{mc^2}{\sqrt{1-\frac{v^2}{c^2}}} = pc = hf$$

We are including here the general energy equation for a particle with mass m. Note what happens to the denominator if the particle goes the speed of light. We are in trouble. But if the numerator conspires to give zero for light particles, then we have an indeterminate form and the energy can be anything. And indeed, photons can have all kinds of energy given by hf. Mathematics here guides us again. For photons, the mass of the particles must be zero.

But light is a wave. So light satisfies the wave relation

$$c = \lambda f$$

In addition to our

$$E = pc = hf \; .$$

We can substitute for c to arrive at

$$E = p\lambda f = hf \; .$$

We then find a formula that relates the momentum to the wavelength through the Planck constant.

$$p\lambda = h$$

Let's write this in the following form.

$$\boxed{\lambda = \frac{h}{p}}$$

Louis de Broglie (1892-1987)
Courtesy School of Mathematics and Statistics
University of St. Andrews, Scotland

Matter Waves (1924). Louis de Broglie postulated that the above equations also apply to matter where p = mv.

$$\lambda = \frac{h}{p}$$

The Two Big Surprises

1: Light, which was thought to be a wave classically is also a particle.

2: A particle, which was thought to be matter classically is also a wave.

So we pick this de Broglie relation as our simple key equation in the panel below for the physics of the microscopic world.

Classical, Modern Physics, and Dirac

Speed		
Fast	"x = ct"	Dirac
Slow	F = ma	"λ = h/p"
	Large	Small

Size (Getting Smaller)

Modern Physics

"x = ct"

"λ = h/p"

I3. Wave Properties. We step back to look at basic properties of waves as we will be needing wave concepts for our study of matter waves.

We can illustrate all the basic properties using a sine wave.

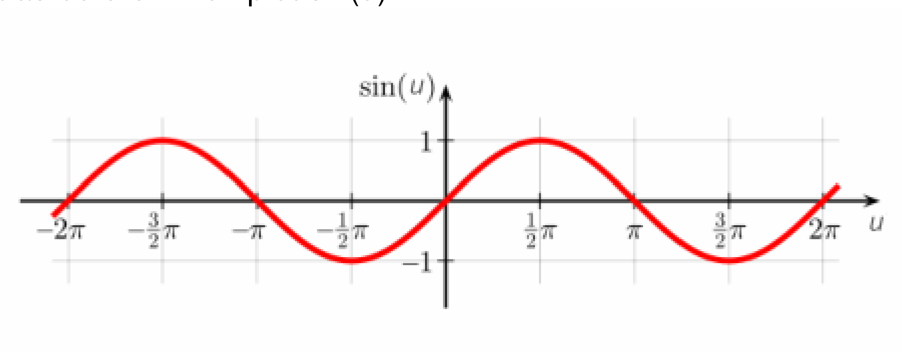
$$\psi(x,t) = A\sin\left[k(x - vt)\right]$$

Remember our general wave traveling to the right?

$$\psi(x,t) = f(x - vt)$$

Note the importance of the constant k as you cannot take the sine of meters. So the k is necessary to make the argument in the sine function dimensionless. What is the meaning of this k?

Let u = x –vt as before. Then plot sin(u).



Courtesy Wikimedia

1. The Wave Number k. Take a snapshot at t = 0 to get a frozen wave. Then

$$\psi(x,t) = A\sin\left[k(x - vt)\right] \text{ becomes } \psi(x,0) = A\sin(kx).$$

If you now march from $u = 0$ to $u = 2\pi$ along the u axis, you walk a wavelength $x = \lambda$ along the associated x axis. Remember, $u = kx$ when $t = 0$. Therefore,

$$k\lambda = 2\pi \quad \text{and} \quad k = \frac{2\pi}{\lambda}.$$

The parameter k is called the wave number. It tells you how many wavelengths there are in an extent of 2π. If the actual x-wavelength happens to be 2π, then $k=1$. If the wavelength is π, then the wave number $k=2$ and so on.

2. The Angular Velocity. Now freeze yourself in space and watch the wave at x = 0.

$$\psi(x,t) = A\sin\left[k(x-vt)\right] \text{ becomes } \psi(0,t) = A\sin(-kvt).$$

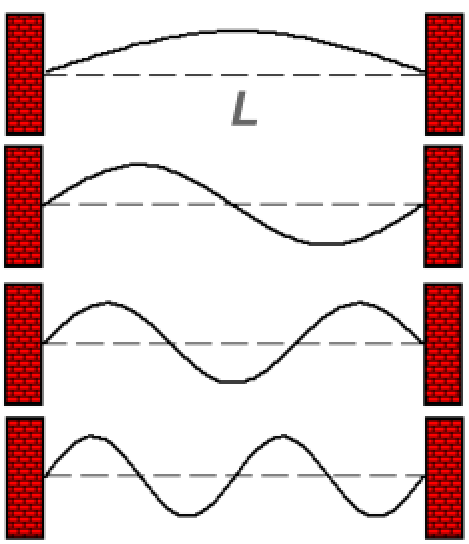
We must have $kvT = 2\pi$, where T is the period, i.e., time for one cycle.

Then $kv = \dfrac{2\pi}{T} = 2\pi f \equiv \omega$, the angular velocity.

I4. The "Back Door" to Quantum Mechanics.

The back door into quantum mechanics from classical mechanics is through the rare occurrence in classical physics of quantization. We have here a key to unlock the door to the new from the old.

Let There Be Music!



The secret path to quantum mechanics from classical mechanics is from the harmonics!

$$n\frac{\lambda}{2} = L$$

The above equation is our "fitting" equation. We fit n half-waves to L for the nth harmonic where n = 1, 2, 3 ,,,

$$\lambda = \frac{2L}{n}$$

These are the allowed wave patterns - nothing in between. Now it is time for de Broglie.

$$p = \frac{h}{\lambda}$$

We let our wave patterns apply to a particle trapped between the walls bouncing off them as it goes right, then left, then right again, etc. The energy is all kinetic:

$$E = \frac{1}{2} m v^2$$

We want to replace the velocity with momentum.

$$E = \frac{1}{2}\frac{m^2 v^2}{m} = \frac{p^2}{2m}$$

This latter form is nice to memorize as it saves time to just write it down.

With

$$\lambda = \frac{2L}{n} \qquad \frac{1}{\lambda} = \frac{n}{2L} \qquad p = \frac{h}{\lambda} \qquad E = \frac{p^2}{2m}$$

we find

$$E = \frac{p^2}{2m} = \frac{1}{2m}\frac{h^2}{\lambda^2} = \frac{1}{2m} h^2 \left[\frac{n}{2L}\right]^2 = \frac{n^2 h^2}{8mL^2}$$

Discrete energies! The energy is quantized.

$$E_n = \frac{n^2 h^2}{8mL^2}$$

This is often written in terms of h-bar as

$$E_n = \frac{n^2 h^2}{8mL^2} = \frac{n^2 (2\pi\hbar)^2}{8mL^2} = \frac{n^2 4\pi^2\hbar^2}{8mL^2} = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

The energy levels for a particle in a one dimensional box of width L is

$$E_n = \frac{n^2 h^2}{8mL^2} \quad \text{or} \quad E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} .$$

The standing waves for our harmonics are oscillating sine waves. We can write

$$\psi(x,t) = A\sin(kx)\cos(\omega t) .$$

We are now in search of a differential equation for our "matter" wave.

You can also consider two sine waves, one moving to the left and one to the right on our string. We choose A/2 for the amplitude for each wave.

$$\psi = \psi_R + \psi_L = \frac{A}{2}\sin(kx - \omega t) + \frac{A}{2}\sin(kx + \omega t)$$

Now use trig identifies which we derived earlier in our course.

$$sin(\alpha - \beta) = \sin\alpha\cos\beta - \sin\beta\cos\alpha$$

$$sin(\alpha + \beta) = \sin\alpha\cos\beta + \sin\beta\cos\alpha$$

Then

$$\psi = \frac{A}{2}\left[\sin(kx - \omega t) + \sin(kx + \omega t)\right]$$

$$\psi = \frac{A}{2}\left[\sin(kx)\cos(\omega t) - \sin(\omega t)\cos(kx)\right]$$

$$+\frac{A}{2}\left[\sin(kx)\cos(\omega t) + \sin(\omega t)\cos(kx)\right]$$

$$\psi(x,t) = A\sin(kx)\cos(\omega t)$$

This is the result we simply wrote down earlier. A superposition of two identical sine waves reflecting off the waves produces a pattern we call a "standing wave." These standing waves form the harmonics. Note that k in our "wave function" can't just be anything. The waves must be "fitted" to length L giving wavelengths 2L/n.

Discrete wavelengths lead to discrete k values. Discrete wavelengths also lead to discrete momenta via de Broglie, which in turn require a discrete energy spectrum.

$$E_n = \frac{n^2 h^2}{8mL^2}$$

I5. The Schrödinger Equation. We are in search of a differential equation for our "wave function" developed in the previous section.

Erwin Schrödinger (1887-1961)
Courtesy School of Mathematics and Statistics University of St. Andrews, Scotland

Here is our "wave function" from the last section.

$$\psi(x,t) = A\sin(kx)\cos(\omega t)$$

We also have conditions to be met. These involve the energies that go with our wave function. To emphasize this, we can write

$$\psi_n(x,t) = A\sin(k_n x)\cos(\omega t)$$

$$k_n = \frac{2\pi}{\lambda_n} \qquad \lambda_n = \frac{2L}{n} \qquad p_n = \frac{h}{\lambda_n} \qquad E_n = \frac{n^2 h^2}{8mL^2} = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

Let's dwell on this some more. We state that for both light and matter, we can write

$$p = \frac{h}{\lambda} \qquad\qquad E = hf$$

The de Broglie relation can also be expressed using the wave number k.

$$p = \frac{h}{\lambda} = h\frac{k}{2\pi} = \hbar k$$

For energy, since $\omega = 2\pi f$, we have $f = \dfrac{\omega}{2\pi}$ and $E = hf = \hbar\omega$

The following are elegant: $E = \hbar\omega$ and $p = \hbar k$

Since, $E = \dfrac{p^2}{2m}$ in our "bouncing-off-the-walls" scenario, we can use $E = \hbar\omega$ and $p = \hbar k$ to obtain

$$\hbar\omega = \frac{\hbar^2 k^2}{2m}$$

Summary: We want a differential equation for which

$$\psi(x,t) = A\sin(kx)\cos(\omega t)$$

Is a solution, with the condition

$$\hbar\omega = \frac{\hbar^2 k^2}{2m}.$$

Let's get started by taking a derivative or two. We can get that k-squared by taking two derivatives with respect to x.

$$\frac{\partial^2\psi}{\partial x^2} = -k^2\psi$$

To get the linear term in omega, we take one time derivative

$$\frac{\partial\psi}{\partial t} = -\omega A\sin(kx)\sin(\omega t).$$

Big Problem! We did not get the function back again. This is not good.

But If we alter the wave function to have an imaginary component, we will get the desired result. **A subtitle of this section could be "Why We Need the Imaginary Number i in Quantum Mechanics."**

If $\psi(x,t) = A\sin(kx)e^{-i\omega t}$, then $\dfrac{\partial \psi}{\partial t} = -i\omega\psi$

You might ask why we didn't use $\psi(x,t) = A\sin(kx)e^{+i\omega t}$ with the plus in front of the omega. The answer there is that if we promote the spatial part to an exponential with the plus and minus on the k, then we get

$$\psi_R(x,t) \sim e^{+ikx}e^{-i\omega t} = f(kx - \omega t),$$

$$\psi_L(x,t) \sim e^{-ikx}e^{-i\omega t} = g(kx + \omega t),$$

where the one to the right is e^{+ikx}, which is the standard convention.

Summary. So far we have

$$\psi(x,t) = A\sin(kx)e^{-i\omega t} \qquad \frac{\partial^2\psi}{\partial x^2} = -k^2\psi \qquad \frac{\partial \psi}{\partial t} = -i\omega\psi$$

To get

$$\hbar\omega = \frac{\hbar^2 k^2}{2m}$$

we note

$$i\hbar\frac{\partial \psi}{\partial t} = \hbar\omega\psi \qquad \text{and} \qquad -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = \frac{\hbar^2 k^2}{2m}\psi$$

The differential equation must then be

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

If we include the general case with potential energy, then $E = \frac{p^2}{2m} + V$ and

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

The "F=ma" of quantum mechanics!

This is the time-dependent Schrödinger equation in one dimension. For time independent potentials V(x,t) = V(x), We have the "standing matter waves."

$$\psi(x,t) = \psi(x)e^{-i\omega t}$$

Then,

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

becomes

$$i\hbar \frac{\partial \left[\psi(x)e^{-i\omega t}\right]}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \left[\psi(x)e^{-i\omega t}\right]}{\partial x^2} + V(x)\psi(x)e^{-i\omega t}$$

$$i\hbar(-i\omega)\psi(x)e^{-i\omega t} = -e^{-i\omega t}\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)e^{-i\omega t}$$

You can put everything on one side, factor out the exponential and use the arbitrary argument that everything multiplying it must be zero. Or in this case you can simply divide by the exponential since it can never be zero.

$$\hbar\omega\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)$$

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)$$

This is the time-independent Schrödinger equation in 1 dimension. It is often written as follows.

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)=E\psi(x)}$$

The time-dependent form is

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

We can easily get the three-dimensional case by recalling

$$\nabla^2 \equiv \nabla\cdot\nabla = \left[\frac{\partial}{\partial x}\hat{i}+\frac{\partial}{\partial y}\hat{j}+\frac{\partial}{\partial z}\hat{k}\right]\cdot\left[\frac{\partial}{\partial x}\hat{i}+\frac{\partial}{\partial y}\hat{j}+\frac{\partial}{\partial z}\hat{k}\right]$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

The corresponding equations in three dimensions are

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi+V\psi=E\psi}$$

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

where now the wave function ψ and potential V can in general depend on x, y, z, and t. Remember your physics as a check here. We want

$$\frac{\hbar^2 k_x^{\ 2} + \hbar^2 k_y^{\ 2} + \hbar^2 k_z^{\ 2}}{2m} = \hbar\omega$$

Here is a quick way to remember the Schrödinger equation

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

There is a convention to make the following assignments, where we promote energy and momentum to derivative operators.

$$E \rightarrow i\hbar\frac{\partial}{\partial t} \quad \text{and} \quad \vec{p} \rightarrow -i\hbar\nabla\ .$$

Then

$$\left[\frac{p^2}{2m} + V\right]\psi = E\psi$$

gets you the Schrödinger equation.