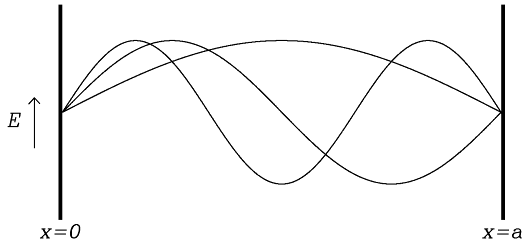


3.4 blackbody radiation

While there are many problems with the Bohr model, at least it gives some understanding of spectra of hydrogen, why its made up of distinct lines rather than a continuous spectrum.

But there are big problems understanding continuous spectra as well!

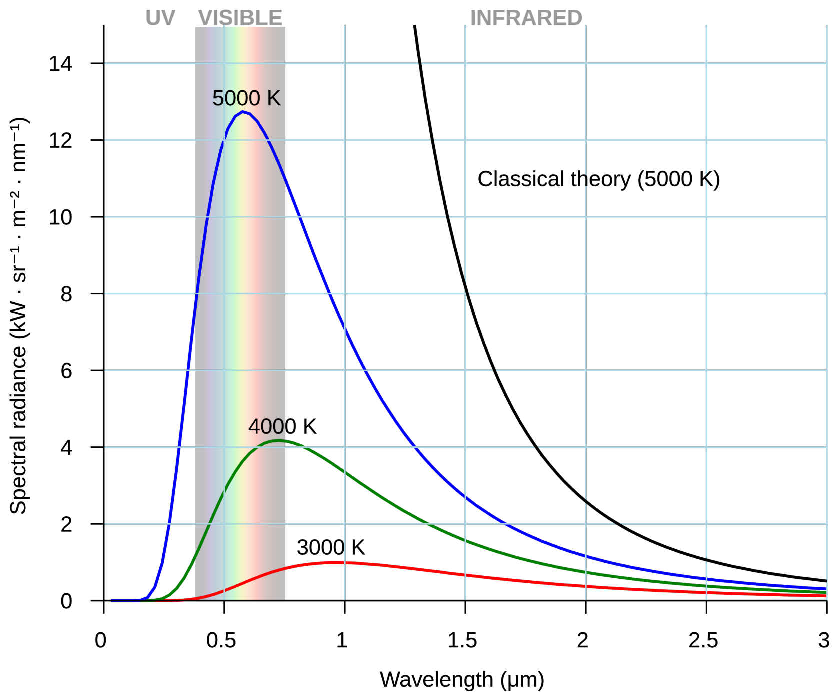
Blackbody radiation is made by electron vibrating in the walls of a box because they are hot. as they vibrate, they emitt e/m waves which are then absorbed elsewhere in the box, making those electrons vibrate. when everything is in equilibrium, the rate of energy emitted by electrons in e/m waves and the rate they absorb energy as e/m waves are exactly the same - this is called blackbody radiation and unlike the spectral lines it depends only on temperature of the material not on which material we use.

The full derivation is nasty, but you can get physical intuition quite easily. We know that the E/M waves must fit inside the box - their wavelength must be an integer multiple of the length of the box - as electrons are conductors so the wave must go to zero. So how many waves can fit in a cubic box of length L?

we can have one standing wave in the x-direction of a box with wavelength $\lambda = 2L$, and another with $\lambda = L$ and another with $\lambda = 2L/3$.... so we can get n_x separate waves with $\lambda = 2L/n_x$

and similarly for y and z directions. multiply them together and divide by L^3 to get the number density of waves in the 3D box as $n \propto \lambda^{-3}$

but then we want their distribution with wavelength - number density of



waves per unit wavelength is $dn/d\lambda \propto \lambda^{-4}$

in thermodynamic equilibrium, the probability of the electron having energy E at temperature T is $P(E) \propto e^{-E/kT}$. The average energy $< E >= \int EP(E)dE / \int P(E) = kT$

The energy per unit volume per unit wavelength is $< E > dn/d\lambda = kTdn/d\lambda \propto kT/\lambda^4$. This was Rayleigh's result for the intensity of radiation seen escaping from a small hole in the box $I(\lambda) \propto kT/\lambda^4$.

but then if we want to know how much energy comes out then we integrate over all wavelength $\int I(\lambda)d\lambda \rightarrow \infty$!!

Planck's 'act of desperation' was to say that the average energy of the wave modes was NOT made by averaging over a continuum of energies but quantised with $E = nh\nu$ where n is an integer. so then the distribution is $P(E) \propto e^{-E/kT} \propto e^{-nh\nu/kT}$. Then the average energy expression is a sum rather than an integral. After some more nasty maths it gives

$$< E >= \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

This goes $\rightarrow kT$ for $h\nu \ll kT$ but $\rightarrow h\nu e^{-\frac{h\nu}{kT}}$ for $h\nu \gg kT$.

This gives us the blackbody radiation law as observed!

$$I(\lambda) = \frac{2\pi hc^2}{\lambda^5}\left[\frac{1}{e^{\frac{hc}{\lambda kT}} - 1}\right]$$

this does NOT go to ∞: integrating over all wavelength now gives an integrated flux (luminosity per unit area) of a blackbody of $L/A = \sigma T^4$ where σ is the stephan boltzman constant.

this peaks at $\lambda = 2.90 \times 10^{-3}/T$ m $= 2.90 \times 10^6/T$ nm

The spectrum of the sun peaks at 500 nm so its temperature is $2.9 \times 10^6/500 =$ 5800 K

4 Quantum mechanics

What we've been doing so far is some horrid mixture of classical and quantum concepts (particles and waves). and its been wildly sucessful in getting the transition energies in hydrogen and blackbody radiation and describing the photoelectric effect and ....

But we need a better theoretical framework for handling wave particle duality - we need a wave equation for matter! We'll start from the classical wave equation.

$$\frac{\partial^2 y(x,t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y(x,t)}{\partial t^2}$$

We can write down a solution for sinusoidal waves travelling from left to right:

$$y(x,t) = A\cos(kx - \omega t) + B\sin(kx - \omega t)$$

where $k = 2\pi/\lambda$ (wave number) and $\omega = 2\pi f$ (angular frequency) and $v = \lambda f = \omega/k$. A, B determine the amplitude and phase of the wave.

EM waves: These have $v = c$ irrespective of λ so $f\lambda = c = \omega/k$ i.e. these have $\omega \propto k$.

but now think of them as quantum particles - photons - with $E = hf = \hbar\omega$ and $p = E/c = hf/c = h/\lambda = (h/2\pi)(2\pi/\lambda) = \hbar k$

So $E^2 \propto \omega^2 \propto k^2$.

Then we take our trial solution $y(x,t) = A\cos(kx - \omega t) + B\sin(kx - \omega t)$ where y can be either the electric or magnetic field and put it into the LHS of the classical wave equation

$$\frac{\partial^2 y(x,t)}{\partial x^2} = -Ak^2\cos(kx-\omega t) - Bk^2\sin(kx-\omega t) = -k^2 y(x,t) = -(E^2/\hbar^2)y(x,t)$$

and similarly with the RHS

$$\begin{aligned}\frac{1}{v^2}\frac{\partial^2 y(x,t)}{\partial t^2} &= \frac{1}{c^2}[-A\omega^2\cos(kx-\omega t) - B\omega^2\sin(kx-\omega t)] \\ &= -\omega^2/c^2 y(x,t)\end{aligned}$$

so it all works as $k^2 = \omega^2/c^2$

Matter waves are going to be similar but different. These have $p = mv = h/\lambda$ according to the de Broglie relation. so the velocity is NOT constant with λ. lets go through the relations and see what holds and what doesn't.

we have $p = h/\lambda = hk/(2\pi) = \hbar k$ which was the same as photons. But energy $E = 1/2mv^2 = p^2/(2m) = \hbar^2k^2/(2m)$. So this is $E \propto k^2$ rather than $\propto k$ as for EM waves.

But we still have that the electrons emit and absorb energy in units of $E = hf = \hbar\omega$ in order to get blackbody radiation (Planks desparate measure)

So $E \propto k^2 \propto \omega$. Lets make a trial wavefunction for our matter waves. we are not really sure what is waving so lets just call is Ψ, and we'll try something of the same form so

$$\Psi(x,t) = A\cos(kx - \omega t) + B\sin(kx - \omega t)$$

then we'd get $k^2\Psi$ from $\partial^2\Psi/\partial x^2$ as before but now the time bit is different - we only want one power of ω so we can only take a single derivative

$$\frac{\partial\Psi(x,t)}{\partial t} = \omega[A\sin(kx-\omega t) - B\cos(kx-\omega t)]$$

what we would really like for the term in square brackets to equal $C\Psi$! so if this were true then

$$[A\sin(kx-\omega t) - B\cos(kx-\omega t)] = C[A\cos(kx-\omega t) + B\sin(kx-\omega t)]$$

equating coefficients of sine we get $A = CB$, while for cosine its $-B = CA$. Divide and get $-A/B = B/A$ i.e. $B^2 = -A^2$. so without loss of generality we can set $B = iA$.... our electron wave is COMPLEX!!

$$\Psi(x,t) = A[\cos(kx-\omega t) + i\sin(kx-\omega t)] = Ae^{i(kx-\omega t)}$$

Secondly, we get $C = -B/A = -i$ so $\partial\Psi/\partial t = -iE/\hbar\Psi$. Multiply both sides by $i\hbar$ and get $i\hbar\partial\Psi/\partial t = E\Psi$. We can now put everything together and our wave equation FOR A FREE PARTICLE MOVING IN ONE DIMENSION

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

More generally, energy is both kinetic and potential so we should have considered $E = \hbar\omega = \hbar^2k^2/(2m) + U$. We made the free particle wave into a differential equation using

$$E\Psi = \hbar\omega\Psi = \hbar^2k^2/(2m)\Psi$$

so by analogy the more general case with a potential is

$$E\Psi = \hbar\omega\Psi = (\hbar^2k^2/(2m) + U)\Psi$$

$$\frac{-\hbar^2}{2m}\frac{\partial^2\Psi^2(x,t)}{\partial x^2} + U(x,t)\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t} = E\Psi(x,t)$$

This is the time dependent Schroedinger equation in 1 dimension. it is linear and homogeneous so if Ψ_1 and Ψ_2 are two different solutions of the Schroedinger equation, then their linear sum $\Psi = c_1\Psi_1 + c_2\Psi_2$ is also a solution.