The Bohr-de Broglie-Sommerfeld analysis of the hydrogen spectrum

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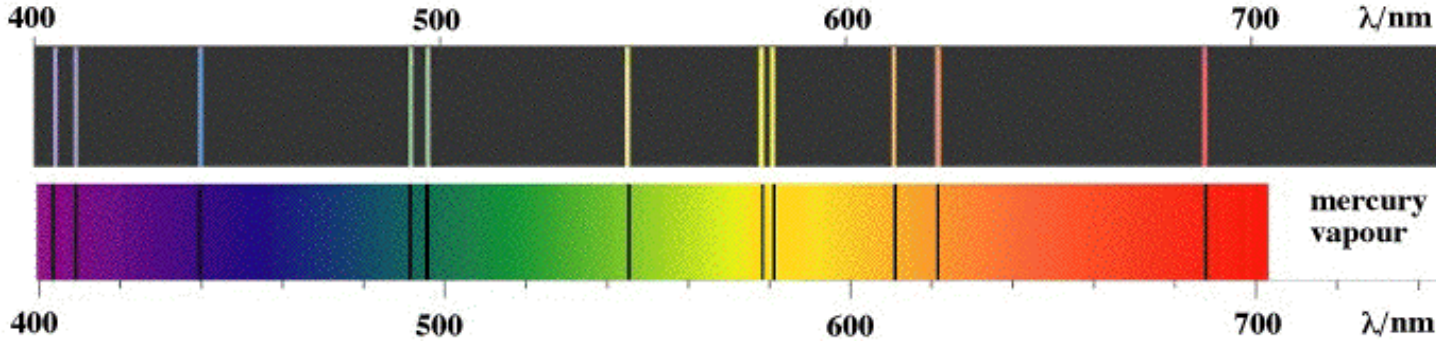
What follows are some notes on the Bohr-de Broglie-Sommerfeld model and their explanation of the spectrum. I am not a historian, so these do not address the historical points raised by some students. I shall present them as an attempt to answer a series of questions. (In fact these are the questions that I asked as a child, and this is essentially the path that led me to encounter quantum physics for the first time.) There are a few equations, but the equations are all simple. They may have several factors in them, but they are mainly just products and ratios, so do be intimidated by them.

The first question in the series is a simple one, and one that you have probably asked yourself in the past. Why is grass green? Why is blood red? ***Why are things coloured****?* In many cases, this is because molecules absorb or emit only certain frequencies. Atomic gases are the simplest cases, and here are representations of the emission and absorption spectra for mercury vapour.



But that leads us to ask: ***why does an atom or molecule absorb or emit certain frequencies, and not others?***

We can go one level further using Einstein's observation that the energy of light (and other EM radiation) is quantised. Each photon has an energy

$$E = hf = \frac{hc}{\lambda} \qquad \text{so} \qquad \begin{matrix}\text{particular}\\ \text{colours}\end{matrix} \quad \begin{matrix}\text{sometimes}\\ \Leftrightarrow\end{matrix} \quad \begin{matrix}\text{particular}\\ \text{f or } \lambda\end{matrix} \quad \Leftrightarrow \quad \begin{matrix}\text{particular}\\ \text{energies}\end{matrix}$$

So, if electrons in atoms or molecules have only certain values of energy (we say their *energies are quantised*), then they would only lose or gain energy with certain discrete values ΔE giving certain colours $f = \Delta E/h$. But that leads us to ask: ***Why are electron energies quantised?***

Bohr's answer is that electrons orbit nuclei, and that only certain orbits are allowed. But ***why are only certain orbits allowed?***

Here we try to explain this for the simple case of the hydrogen atom. But a little background first. Bohr had it easy, in the sense that the answer (if not the explanation, was already known. In the early 20th century, a purely *empirical* formula was known for the hydrogen spectrum: it gives the frequency f and wavelength λ of EM radiation either absorbed or emitted by the hydrogen atom. It is

$$f = \frac{c}{\lambda} = \text{constant}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \text{or} \qquad \frac{1}{\lambda} = R.\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where n_1 and n_2 are integers and the constants are purely empirical. Empirical means that they were determined experimentally, and there existed no theory to explain either the form of the equation or the value of the constant. In the second version of the equation, R is called Rydberg's constant. This is the answer that we want to be able to derive from a physical argument.

Rutherford's contribution (Bohr was his student) was the 'solar system' model: the proton is so massive that its motion is neglected (*cf* sun) and the electron 'orbits in circles' (*cf* planet). I have put the scare quotes on 'orbits in circles' because we now know that this phrase is not merely untrue, but doesn't have a meaning for an electron.

In this classical model, the electron energy is kinetic plus electric potential

$$E = \left(\frac{1}{2}mv^2\right) + \left(-k\frac{e^2}{r}\right) \qquad (1)$$

where m is the electron mass, v its (tangential) velocity, k is Coulomb's constant, and r the 'orbit' radius. To go further, we need to eliminate a variable. Now, we know that the centripetal force F is provided by the electrostatic attraction, so from Newton's second law:

$$\frac{mv^2}{r} = F = k\frac{e^2}{r^2}$$

so substitution gives the classical result (which looks much like that in planetary mechanics):

so $$rv^2 = \frac{1}{4\pi\varepsilon_o}\frac{e^2}{m} \qquad (2)$$

Now we introduce de Broglie's contribution, but it requires a little background. In the 19th century, classical electromagnetism (Maxwell's equations) gave the momentum p of light as

$$p = E/c.$$

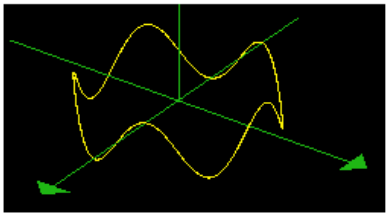
Using Einstein's quantisation of energy E = hf and c = fλ, we get the momentum of a photon

$$p = h/\lambda$$

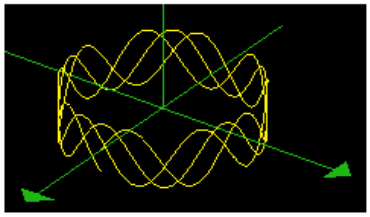
where λ is the wavelength of the light. de Broglie speculated that this formula could hold for an electron also, even though the electron has mass and was, at the time, considered to be a particle. (People wondered what the wavelength of a particle might possibly mean.) Now the electrons in the H atom have sufficiently low energy that we may neglect relativistic effects, so de Broglie's speculation gives us for the electron:

$$mv = \frac{hf}{\lambda f} = \frac{h}{\lambda}.$$

Now if the electron wave is to give constructive interference in a circular orbit, one requires that an integral number n of wavelengths make up a circumference, which gives Sommerfeld's model of the atom:



$2\pi r = n\lambda$
constructive
interference



$2\pi r \neq n\lambda$
destructive
interference

so $$2\pi r = n\lambda = \frac{nh}{p} = \frac{nh}{mv}$$

$$\therefore \quad v = \frac{nh}{2\pi rm} \qquad (3)$$

Let's now solve (2) and (3) for r and v,

$$v = \frac{1}{2\varepsilon_o}\frac{e^2}{nh} \qquad r = \frac{n^2h^2}{\pi m}\frac{\varepsilon_0}{e^2}$$

and substitute in (1) to get the energy of the electron.

$$E = \left(\frac{1}{2}mv^2\right) + \left(-\frac{1}{4\pi\varepsilon_o}\frac{e^2}{r}\right) = -\frac{1}{2}\frac{1}{4\pi\varepsilon_o}\frac{e^2}{r}$$

$$\therefore \quad E = -\left(\frac{me^4}{8\varepsilon_o^2h^2}\right)\frac{1}{n^2}$$

$$\therefore \quad \frac{1}{\lambda} = \frac{\Delta E}{hc} = -R.\left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right)$$

That messy factor $me^4/8\varepsilon_o^2h^2$ (now called R) is the empirical constant in our very first equation. So the energy E of an electron in an orbit that has n waves around the circumference is

$$E(n) = -\text{constant}.\frac{1}{n^2}$$

Now in this model, orbits with non-integral values of n are forbidden, because they correspond to destructive interference of electrons. So energy can only be absorbed or given to photons whose energy is $E(n_2) - E(n_1)$ where n and N are both integers. So we can write the wavelengths L of the emitted or absorbed spectrum as

$$\frac{1}{\lambda} = \frac{\Delta E}{hc} = R\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

where R is called Rydberg's constant.

Now if $n_1 = 1$, the set of lines with different n are called the Lyman series. $n_1 = 2$ gives the Balmer series and $n_1 = 3$ the Paschen series. For example, the lowest energy (longest wavelength) in the Paschen series has

$$\frac{1}{\lambda} = R\left(\frac{1}{4^2} - \frac{1}{3^2}\right) = (1.097\ 10^7)\ m^{-1}\left(\frac{1}{9} - \frac{1}{16}\right) \rightarrow \lambda = 1.9\ \mu m$$

which is in the infrared. But the important thing is that each pair of *integers* gives an energy. n_1 and n_2 are whole numbers, so the spectrum has certain discrete values, rather than a continuum.

By the way, when the electron 'jumps' from one state (n_2) to another (n_1), this was called a quantum jump. It involves a very tiny energy: the energy of just one photon. The modern technical name is a transition.

The Bohr atom (not to mention electron diffraction & much else) shows interference effects produced by massive entities. So, in the case of the electron, we might well ask: ***What is it that waves?***

For the **photon:** wave amplitude is the electric and magnetic field. At any point,

$$\begin{pmatrix}\text{probability of}\\ \text{absorption}\end{pmatrix} \propto \begin{pmatrix}\text{amplitude}\\ \text{of field}\end{pmatrix}^2$$

For **massive particles** ("matter waves")

$$\begin{pmatrix}\text{probability of}\\ \text{collision with it}\end{pmatrix} \propto \begin{pmatrix}\text{amplitude}\\ \text{of wave}\end{pmatrix}^2$$

The amplitude of the electric field can, in some cases, be measured directly. In the case of a single photon, however, we cannot really measure the electric field: we either absorb the photon, and receive its energy, or we don't. The amplitude of a matter wave (called ψ) cannot be measured so directly, so we cannot give you a clear answer. But for an electron, the observation is analogous: either we interact with it or we don't.

Now for the bad news. de Broglie's wave hypothesis is a good one. The electrical potential for the hydrogen nucleus is correct. But a lot of the story that we have just seen, all the analysis based on electrons travelling in circles, is false, even though it gives the correct answer for the H spectrum.

Electrons do not travel in circles in atoms. They do not travel in atoms. The idea of travelling doesn't apply, because of the Heisenberg Uncertainty Principle and for other reasons. To explain the hydrogen spectrum with a physically reasonable model requires solving Schrödinger's equation, and for that one needs more maths than is taught at high school. This is where quantum mechanics begins. Quantum mechanics is a spectacularly successful theory, perhaps the most accurate theory that there has ever been.