Lecture 2: Early QM - Quantization and Wave-Particle Duality

Here we will go through three early developments that helped define attributes of the theory that Schroedinger would later capture in his wave equation. These observations were in addition to some we have already mentioned, such as the regular but discrete patterns of lines in photoabsorption or photoemission processes on atoms.

Raleigh-Jeans Formula and the Stefan-Boltzmann law: A black body consists of a cavity in which electromagnetic standing waves in the cavity interior have reached thermal equilibrium with the cavity walls. The walls are perfect absorbers, absorbing all incident radiation regardless of frequency, and perfect emitters, radiating energy isotropically in a spectrum we discuss below. Physics has some remarkable examples of black bodies, with the cosmic microwave background left over from the Big Bang one of the most spectacular, as the spectral deviations from a perfect black body are on the order of one part in a million (and extremely interesting from the perspective of what they tell us about structure in the universe when it was just 370,000 years old). One can envision probing the radiation by making a pin-prick in the cavity in order to monitor the radiation

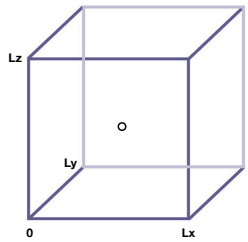

Figure 1: A cubic cavity with walls held at temperature T, and with a volume L^3. The walls perfectly absorb all incident energy, then readmit that radiation, maintaining an equilibrium between the contained radiation and the walls characteristic of T.

The Stefan-Boltzmann law was deduced experimentally in the late 19th century: the power P radiated per unit surface area A of a black body (of course, summed over all wavelengths) is

$$\text{Stefan} - \text{Boltzmann Law}: \quad P/A = \sigma T^4 \quad \text{where } \sigma \sim 5.6710^{-8} \text{ Watts/m}^2\text{K}^4$$

This law nicely reproduces observations on systems that range from heated filament in the laboratory to the surfaces of stars.

Raleigh and Jeans attempted to derive this law – and thus obtain an expression for the Stefan-Boltzmann constant σ – from first principles, by explicitly summing over the electromagnetic standing waves in a box. This requires one to calculate the number of standing electromagnetic modes in the box of volume L^3. Electromagnetic waves satisfy Laplace's equation which in Cartesian coordinates is

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+k^2\psi=0$$

One writes $k^2=k_x^2+k_y^2+k_z^2$ and separates the equation into a product of solutions in the x, y, z directions, each of which must vanish at the boundaries at 0 and L. The solutions are

$$\psi[n_x,n_y,n_z]=N\sin\left(\frac{\pi n_x}{L}x\right)\sin\left(\frac{\pi n_y}{L}y\right)\sin\left(\frac{\pi n_z}{L}x\right)\qquad k^2=\frac{\pi^2}{L^2}\left(n_x^2+n_y^2+n_z^2\right)$$

where (n_x,n_y,n_z) are positive integers. We want to count how many modes (n_x,n_y,n_z) there are, and we can do that by switching to spherical coordinate and integrating over k, while assuming a large volume. Taking into account that $k_i/(\pi/L)=n_i$, in the large volume limit we have

$$N(k)dk=\frac{1}{8}\times 2\times\frac{4\pi k^2dk}{(\pi/L)^3}=\frac{Vk^2dk}{\pi^2}\qquad V=L^3$$

where the factor of $\frac{1}{8}$ is needed as we only want the fraction of the sphere where all $n_i>0$, and where the factor of 2 is needed because each standing wave supports both transverse electric and transverse magnetic projections.

One can use a classical Boltzmann distribution calculate the average energy per cavity mode. One finds

$$\bar{E}=\frac{\int_0^\infty Ee^{-E/k_BT}dE}{\int_0^\infty e^{-E/k_BT}dE}=k_BT$$

This result applies separately to the light quanta of the same frequency in a black body cavity. We can then fold this with the expression for the number of standing wave modes, derived above, to get the energy density,

$$\frac{E}{V}=k_BT\int\frac{k^2dk}{\pi^2}=k_BT\int\frac{8\pi\nu^2d\nu}{c^3}=k_BT\int\frac{8\pi d\lambda}{\lambda^4}$$

where we have used the relationships between wave number, frequency, and wave length $k=\frac{2\pi\nu}{c}=\frac{2\pi}{\lambda}$ to write equivalent formulas.

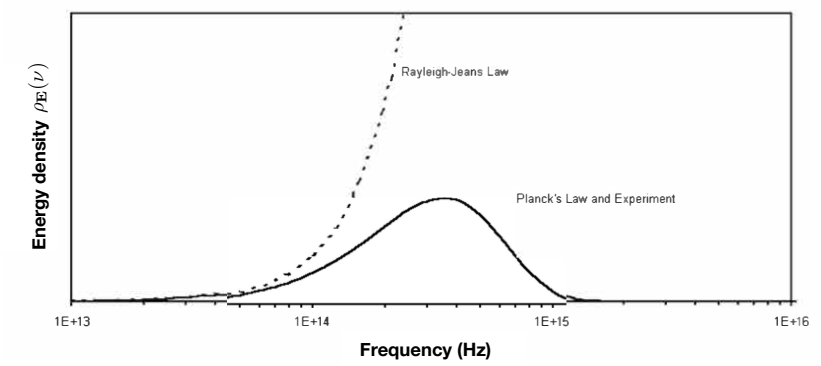

Figure 2: Comparison of the .differential black-box energy densities of the Raleigh-Jeans and Planck formulas, the latter agreeing with experiment.

The result neither reproduces observation nor the Stefan-Boltmann law. The calculation is not self-consistent, as the integrals diverge for large k or large ν, alternatively small λ.

In 1900 Planck revised the Boltmann result for the energy per mode by replacing the classical Boltzmann integral over energy-weighted modes by a discrete sum corresponding to energy quantized as $E = nh\nu,\ n = 0, 1, 2, \ldots$, where h is a new physical constant. This modifies energy/mode calculation in the following way

$$\bar{E} = \frac{\sum_{n=0}^{\infty} nh\nu e^{-nh\nu/k_BT}}{\sum_{n=0}^{\infty} e^{-nh\nu/k_BT}} = -\frac{1}{\sum_{n=0}^{\infty} e^{-nh\nu/k_BT}} \frac{d}{d\frac{1}{k_BT}} \sum_{n=0}^{\infty} e^{-nh\nu/k_BT}$$

As the sum remaining is geometric, it can be done. A bit of algebra yields

$$\bar{E} = \frac{h\nu}{e^{h\nu/k_BT} - 1}$$

and thus Planck obtained (in the frequency form)

$$\begin{aligned} \frac{E}{V} &= \int_0^{\infty} \rho_E(\nu) d\nu \\ \rho_E(\nu) &= \frac{8\pi h}{c^3} \frac{\nu^3}{e^{h\nu/k_BT} - 1} \rightarrow \begin{cases} k_BT \frac{8\pi\nu^2}{c^3} & \frac{h\nu}{k_BT} << 1 \\ \frac{8\pi h}{c^3} e^{-h\nu/k_BT} \nu^3 & \frac{h\nu}{k_BT} >> 1 \end{cases} \end{aligned} \quad (1)$$

The Raleigh-Jeans (classical) result is obtained for small frequencies, so we recognize $h \rightarrow 0$ as the classical limit of Planck's black-body formula. But for high frequencies the energy density as

a function of frequency is now well-behaved, diminishing exponentially, very unlike the classical case.

Photoelectric effect: At about the same period when the issues with black body radiation were confusing physicists, experimental were examined the emission of electrons from metal surface when UV light was focused on the surface. Results from such experiments produced the following

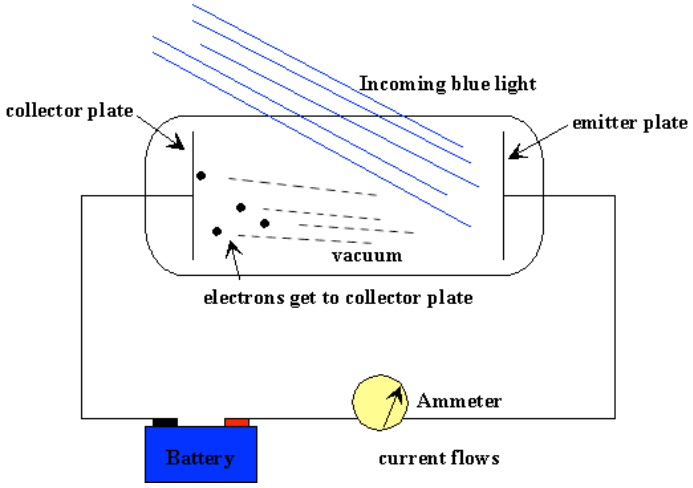

Figure 3: Basics of a photoelectric effect experimental setup.

phenomenology

1. The number but not the energy of the photoelectrons depends on the light intensity;
2. Photoelectrons appear as soon as the light is turned on, even when the light intensity is low; and
3. Photoelectron energy depends on the frequency of the light, with a faint blue light (higher frequency) producing more energetic electrons than an intense red light (lower frequency). If the frequency of the light is too low, no emission is seen.

These results are unexpected in the classical picture of light as a wave. And at the time these experiments were done, there were many verifications of the wave nature of light. In particular, energy from a wave would be absorbed across the metal surface, so that to knock out an electron, one would have to wait until the area immediately around the electron had absorbed enough energy

to make that possible. If the frequency of the light were increased, with all other parameters kept fixed, the necessary period might shorten, but when the threshold for emission is reached, the electrons emitted would be similar in energy to those produced with lower frequency light.

Einstein in 1909 resolved this problem by proposing wave-particle duality – that light sometimes acts as waves, and other times as photons. Following up on Planck, Einstein argued that the the photoelectric effect observations were consistent with a ballistic process in which individual quanta of light of energy $h\nu$ – he used Planck's constant to relate the frequency to the energy of each light quantum – were responsible for knocking out individual electrons from the metal. Energy conservation then yields

$$h\nu = KE_e + h\nu_0$$

Here $h\nu_o$ is the energy required to remove an electron from the metal – the work function, which is a proporty of the specific metal being used – and consequently no photoelectrons are produce if the frequency of light $\nu < \nu_0$. In this picture, provided $\nu > \nu_0$, photoelectrons are expected immediately on illumination, as each photon has the ability to dislodge an electron. If the frequency of the light is increased, the energy of the photoelectrons increases linearly. If the frequency is held fixed but the intensity is double, the photon flux and the number of photoelectron-producing collisions doubles.

This explanation is simple, yet seemed to contradict years of study of light waves interfering and undergoing diffraction. Thus the intellectual leap was the hypothesis of the wave-particle duality of light, that different aspects of light could be manifested in different experimental settings.

de Broglie and the Bohr atom: By the early 1900s, Rutherford had established that atoms had a dense nuclear core, and many experiments had been done observing the absorption and emission of visible and other light from simple atoms, including hydrogen. As the binding energy in hydrogen (neglecting fine structure) is -13.6 eV$/n^2$, where the principal quantum number takes on integer values $n = 1, 2, 3....$, the emission lines correspond to energies

$$E_{n_i} - E_{n_f} = 13.6 \text{ eV } \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right), \quad n_f < n_i$$

Various "series" had been identified

$$\text{Balmer 1885 (visible)}: \quad \Delta E = 13.6 \text{ eV} \left(\frac{1}{2^2} - \frac{1}{n_i^2}\right) \quad n_i > 2$$

$$\text{Lyman } 1906 - 14 \text{ (UV)}: \quad \Delta E = 13.6 \text{ eV} \left(\frac{1}{1^2} - \frac{1}{n_i^2}\right) \quad n_i > 1$$

$$\text{Paschen 1908 (IR)}: \quad \Delta E = 13.6 \text{ eV} \left(\frac{1}{3^2} - \frac{1}{n_i^2}\right) \quad n_i > 3$$

While Rutherford had proposed a model of atoms as electrons orbiting and bound to a nucleus, Bohr attempted to relater this idea to the emerging notion of quantization in a 1913 model. He recognized that the phenomenology above could be reproduced by a classical model of electrons in circular orbits about the nucleus, where

$$|\vec{r} \times \vec{p}| = mvr = \frac{nh}{2\pi} \equiv n\hbar$$

where we have introduced the reduced Planck's constant $\hbar$ – which everyone calls "h bar". If one accepts this hypothesis as a constraint and computes the energies, indeed one reproduces the results above.

The model also got two important matters right

1. Atomic systems can exist only in certain stationary or quantized states, each characterized by a definite energy;

2. Transitions between such states can occur via emission or absorption of radiation with energy $\Delta E = h\nu$, in agreement with how both Planck and Einstein treated radiation.

But there were as many or more unanswered questions as answered ones:

1. Why are the stationary states stationary? Since a classical electron in circular motion radiates, that electron should lose energy, spiraling into the nucleus;

2. And from our modern perspective of quantum mechanics, a classical orbit with a definite radius violates the uncertainty principle of quantum mechanics;

3. Similarly, one might accept this cartoon as a classical analog for s states, but associated with each $n > 1$ are higher angular momentum states that would no natural relation to a classical circular orbit.

In his 1924 thesis de Broglie offered a possible explanation of the Bohr atom that anticipated the quantum mechanics revolution that was about to overtake physics. The details of how his suggestion supported the Bohr atom is not critical – the idea behind it is. Noting that Einstein and Planck had treated electromagnetic waves as particles, de Broglie suggested that perhaps *particles* (the electron in this case) sometimes behave as *waves* – that is quantum mechanics. For a photon

$$p_\gamma = \frac{h\nu}{c} = \frac{h}{\lambda}$$

so perhaps a massive particle satisfies the same relationship

$$p_e = m_e v = \frac{h}{\lambda} \quad \Rightarrow \quad \lambda = \frac{h}{m_e v} \text{ a particle's de Broglie wavelength}$$

If one calculate the de Broglie wavelength of an electron moving at $v/c \sim 0.01$, one finds $\lambda \sim 2$ angstroms – so about the circumference of an atom.

De Broglie was able to account for the Bohr model by assuming that electronic orbits in hydrogen correspond to an integral number of de Broglie wavelengths.

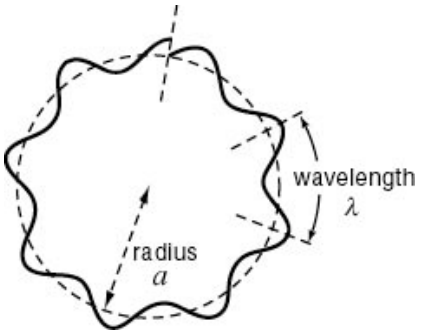

Figure 4: de Broglie propose that atomic orbitals corresponds to an integral number of de Broglie wave lengths. The figure shows a slight mismatch at the top, which means the radius should be adjusted to remove this discontinuity.