Chapter III

Atomic Physics and Chemistry

Day 1 Early Models of the Atom and the Cathode Ray Tube

Section 27-1

Early Models of the Atom

Democritus - $\alpha\tau o\mu o\varsigma$ - indivisible
Dalton - Billiard ball model
Thompson - Raisin bun model
Rutherford - Planetary model
Bohr - Quantum Model

The Cathode Ray Tube

Late 1800's, scientists were experimenting with vacuum tubes fitted with electrodes. If high voltage were pumped across these tubes, a dark area seemed to extend from the cathode and caused a glow at the other end. These "rays" were called cathode rays. It was speculated that these were like light rays, but further experimentation revealed that the rays could be bent by electric and magnetic fields, implying that they were, in fact, charged particles.

J. J. Thomson, 1897, measured the ratio of the charge of the particle to the mass of the particle directly using his cathode ray tube. (See Figure 27-2 in your text.) If only an electric field were present, the beam would go one way, and if only a magnetic field were present, the beam would go the other. By having the electric field and magnetic field provide an equal force. . .

$F = eE = evB$, so $v = E/B$, where e is the charge of the particle.

But the magnetic force $F = evB$, in the absence of the electric field would cause the particle to move in a circle of radius r, i.e.,

$$evB = \frac{mv^2}{r}$$

or

$$\frac{e}{m} = \frac{v}{Br}.$$

This radius can be measured, then have the electric field applied, so

$$\frac{e}{m} = \frac{E}{B^2 r} \tag{3.1}$$

Notice that E, B and r are all measurable. The accepted value is $\dfrac{e}{m} = 1.76 \times 10^{11}\ \dfrac{\mathrm{C}}{\mathrm{kg}}$

Thomson is credited with the discovery of the electron, and the “raisin bun” model of the atom.

The charge of the electron was measured precisely by Robert Millikan using his (in)famous oil-drop experiment. By balancing electrical forces with gravity, he was able to determine the charge on the electron to be 1.6×10^{-19} C. This, combined with the charge to mass ratio give us the mass of the electron to be $m_e = 9.11 \times 10^{-31}$ kg.

Day 2 Blackbodies, Planck and the Photoelectric Effect

Sections 27-2 to 27-3

Blackbodies and Planck

A blackbody is an idealized object that absorbs all EM radiation that hits it. The radiation it would emit when hot (and therefore luminous) is called blackbody radiation. Wilhelm Wien discovered that blackbodies (which stars approximate very closely) radiate frequencies which are proportional to their Kelvin temperatures.

Wien determined that the peak of the spectrum was related to the temperature by Wien's law:

$$\lambda_p T = 2.90 \times 10^{-3}\ \mathrm{m} \cdot \mathrm{K}. \tag{3.2}$$

So, hotter objects radiate shorter wavelengths and therefore higher frequencies. Also, the cooler an object is, the lower the overall intensity.

In late 1900, Planck determined an empirical formula that fit experimental curves, to fit the curve of black-body radiation. It was ugly (we aren't going to use it):

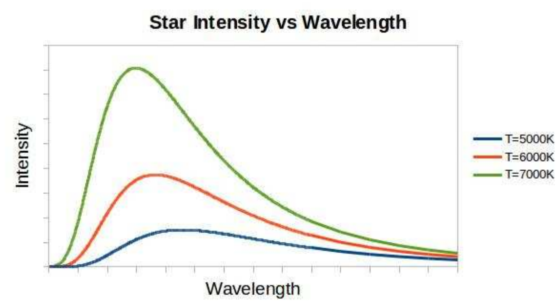

Figure 3.1: Blackbody Radiation.

$$E(\lambda, T) = \frac{2hc^2}{\lambda^5}\frac{1}{e^{hc/\lambda kT} - 1}$$

where k is Bolzmann's constant and h is Planck's constant ($h = 6.626 \times 10^-34$ Js). He then set about trying to determine a physical reason why this equation should work, and to explain the existence of this new constant, h. By assuming that the energy distributed among the molecules was not continuous, but discrete, he could explain the formula. That is that

$E_{min} = hf$, where f is the frequency of oscillation of the electric charges.

It then follows that the energy of oscillation can only be a multiple of E_{min}, or

$$E = nhf. \tag{3.3}$$

Einstein took this a step further and said, by conservation of energy, if the molecules oscillate with an energy nhf and drop to a lower state $(n-1)hf$, then by conservation of energy, the light emitted must have energy

$$E = hf \tag{3.4}$$

where f is now the frequency of the light.

The Photoelectric Effect

The photoelectric effect (as it is no known) was originally conducted in 1899 by Julius Elster and Hans Geitel. The experiment was set up as shown in Figure 3.2. When light of sufficient frequency is shone on the metal plate, electrons are released from the metal plate. This was confirmation that light had the ability to do work. However, it also was an indicator of the particle-like behaviour of light. With the discovery of interference of light by Thomas Young in 1802, it was solidly believed that light was a wave. Einstein's interpretation of the photoelectric effect revolutionized our thoughts on light.

By having a variable voltage source, we can reverse the voltage. If the electron "kicked off" by the light has sufficient energy, it will still overcome the voltage and hit the electrode. By adjusting the voltage so that the current is (just) zero, we can determine the maximum KE of the electrons:

$$\mathrm{KE_{max}} = \mathrm{eV_0}, \tag{3.5}$$

where V_0 is known as the stopping voltage or potential.

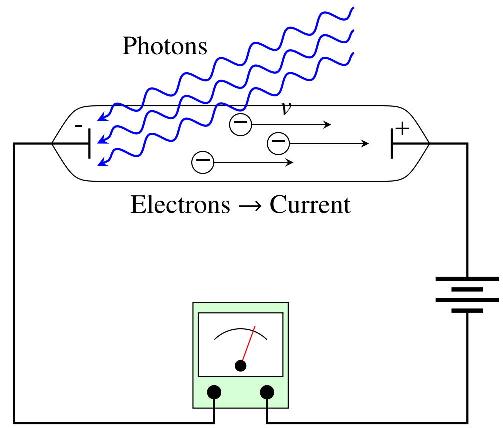

Figure 3.2: The Photoelectric Effect

The EM wave theory of light predicts that:

1. an increase in intensity means more energy, so more electrons and a greater $\mathrm{KE_{max}}$ can be obtained by these electrons.
2. frequency should not affect the KE of the electrons

The photon theory of light (a particle theory) predicts that:

1. an increase in intensity means more photons, so more electrons, but same $\mathrm{KE_{max}}$.
2. if the frequency of light increases, maximum energy increases linearly, $\mathrm{KE_{max}} = \mathrm{hf} - \mathrm{W_0}$, where W_0 is the minimum energy required to get the electron through the surface of the metal, known was the work function.
3. if the frequency is less than the cutoff frequency, f_0, no electrons will be emitted al all (i.e., $hf_0 = W_0$).

Careful experimentation by Millikan in 1913-14 supported the photon theory of light rather than the EM wave theory.

Day 3 Photon Interactions, Compton Effect, Pair Production

Section 27-4

Compton Effect

From Einstein, the energy of a photon is $E = hf$. By substituting for frequency using the wave equation $c = f\lambda$, we get

$$E = \frac{hc}{\lambda}. \tag{3.6}$$

The rest mass of a photon, according to Einstein must be 0, since the relativistic mass of a particle, $m = \frac{m_0}{\sqrt{1-\frac{v^2}{c^2}}}$ (otherwise mass of photon would be infinite and would have infinite energy).

The momentum of a particle is $p = mv$, so the *effective mass* of a photon, $m_{eff} = \frac{p}{c}$ Substituting this into Einstein's famous equation $E = mc^2$ we get the momentum of a photon to be

$$\begin{aligned} p &= \frac{E}{c} && (3.7) \\ &= \frac{h}{\lambda}. && (3.8) \end{aligned}$$

Compton found that when a photon hits an electron, part of the energy of the photon is transferred to the electron, resulting in a lengthening of wavelength of the photon. The new wavelength of the photon is

$$\lambda' = \lambda + \frac{h}{m_0 c}(1 - \cos\varphi) \tag{3.9}$$

where φ is the angle at which the photon is scattered, m_0 is the rest mass of the particle off which the scattering occurs (e.g an electron) and λ' is the scattered photon's wavelength. (You will derive this result in one of the homework problems).

This is in fact what is observed, however, the EM theory of light predicts no such thing (in fact it would predict that the light would cause the electron to oscillate and emit the same wavelength of light).

Photon (γ) Interactions

There are four possible interactions of a photon with matter:

1. scattered off a particle (Compton effect),
2. photoelectric effect (absorption and displacement of an electron),
3. absorption causing electron to go to an excited state, but is insufficient to displace the electron,
4. pair production: a photon with sufficient energy (and a nucleus or heavy particle nearby) can create a particle-antiparticle pair (e.g. e^- and e^+). If matter and antimatter collide, they annihilate releasing 2 gamma rays.

Day 4 Wave-Particle Duality

Sections 27-5 to 27-6

We have come to accept the reality that sometimes light behaves like a particle and sometimes like a wave. That does not actually say it is either, only that it behaves like both. Typically, high energy light has more particle-like behaviour (e.g., X-rays, γ-rays) and lower energy light has more wave-like behaviour (e.g. visible light, IR, microwave, radio wave).

In 1923, Louis de Broglie suggested that particles could also behave like waves. Using Einstein's $E = mc^2$, we derived $p = h/\lambda$. De Broglie suggested that this could apply to particles as well. For a particle, $p = mv$, so $mv = \dfrac{h}{\lambda}$ or

$$\lambda = \frac{h}{mv}. \tag{3.10}$$

This is known as the de Broglie wavelength for a particle.

What evidence exists for wave behaviour of particles?

1. A diffraction pattern of a beam of electrons through a crystal is very similar to that found by shining X-rays through the same crystal. Interestingly enough, the de Broglie wavelength of particles travelling at about 1/100th the speed of light are very similar to the wavelengths of X-rays!
2. Consider an experiment where a beam of electrons is fired through two sharp edged slits (like Young's experiment). Since electrons are particles, we expect to see most particles grouped together behind each slit. Instead, we see an interference pattern like we expect from waves!

We will watch the final 2 clips from the *Wave-Particle Duality* series.

Day 5 Atomic Spectra and the Bohr Model

Sections 27-8 to 27-10

The spectrometer will be set up for viewing either this day or the next work day. We will observe some atomic spectra using diffraction gratings and discharge tubes.

Atomic Spectra

If we shine sunlight through a prism, we see (nearly) the full rainbow or spectrum of colours. In general, light from heated solids, or dense gases (like stars) provide continuous spectra. If a continuous spectrum is passed through a gas, we get an absorption spectrum (some lines are missing where frequencies of light are absorbed).

If we intensely heat a gas, we get an emission spectrum – only single lines (representing particular frequencies) are visible. This spectrum is effectively a fingerprint for a particular element. By analyzing spectra, we can identify elements present in the atmosphere, a heated gas, etc.

Hydrogen, having only 1 electron produces the simplest spectrum. In 1885, J. J. Balmer showed that the lines in the visible spectrum of H, with $\lambda = 656$ nm, 486 nm, 434 nm and 410 nm fit the equation:

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right),$$

where $n = 3, 4, 5$ or 6, and $R =$ Rydberg constant $= 1.097 \times 10^7\ \text{m}^{-1}$. This became known as the Balmer series and was later found to extend up to about 365 nm (where $n = \infty$).

Further series of lines were found known as the Lyman series ranging from 91 to 121 nm given by

$$\frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right),$$

and the Paschel series in the IR spectrum given by

$$\frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{n^2}\right),$$

Rutherford's model was unable to explain this, and this required a quantum understanding of the atom.

The Bohr Model of the Atom

Bohr argued that electrons could only lose energy in discrete amounts, by performing quantum "jumps". Furthermore, an electron is in defined energy states or orbits and can move in the orbit without radiating energy. Light is emitted when an electron goes from one stationary state to a lower one.

$$E = hf = E_u - E_l$$

Bohr had the Balmer series for a reference and realized his theory would agree if he used angular momentum as the quantum condition:

$L = mvr = n\hbar$, where $\hbar = \dfrac{h}{2\pi}$.

For an atom with Z protons, the attractive force of the nucleus on an electron is

$F_{el} = \dfrac{kZe^2}{r^2}$.

Equating this with the centripetal force gives
$\dfrac{kZe^2}{r^2} = \dfrac{mv^2}{r}$, but $v = \dfrac{n\hbar}{mr_n}$ giving

$r_n = \frac{kZe^2}{mv^2} = \frac{kZe^2 {r_n}^2}{n^2\hbar^2}$. Solving for r_n:

$$r_n = \frac{n^2\hbar^2}{mkZe^2} = \frac{n^2}{Z}{r_1}^2, \tag{3.11}$$

where r_1 is the smallest possible orbit for an electron and is given by

$$r_1 = \frac{\hbar^2}{mke^2} \tag{3.12}$$

and is known as the Bohr radius. Note that for a hydrogen atom, $Z = 1$ and $r_1 = 0.529$ Å and $r_n = n^2 r_1$.

For potential energy, the zero point is defined as an infinite distance away and all other PE's are negative. The energy of the n$^{\text{th}}$ orbit can be determined from kinetic energies and electrical potentials:
$E_n = \frac{1}{2}mv^2 - \frac{kZe^2}{r_n}$, substituting r_n and v from above gives

$$E_n = -\frac{Z^2 e^4 mk^2}{2\hbar^2}\frac{1}{n^2} = \frac{Z^2}{n^2}E_1 \tag{3.13}$$

and E_1 can be calculated to be -13.6 eV for hydrogen and is known as the ground state.

Note: $\frac{1}{\lambda} = \frac{1}{hc}(E_n - E_{n'})$ for a photon emitted, so we can find compare Bohr's constant with Rydberg's constant and they agree experimentally.

Day 6 Heisenberg Uncertainty Principle

Sections 28-3

The important concept here is that in order to observe something, we must interact with it. Specifically, to see something, a photon must interact with it. If that is the case, then there are limitations on how well we know certain things:

1. Position: If a photon strikes a particle (say an electron), then we know the photon will impart energy to the electron, causing a change in the electron's position. The limit to which we know this position depends upon the photon's wavelength. At best, we can know the position as accurately as the wavelength of the photon we are using to measure it. In general, $\Delta x \approx \lambda$.
2. Momentum: Likewise, the accuracy to which we can measure the momentum of a particle is dependent upon the momentum of the photon with which we "bombard" it. That is, $\Delta p \approx \frac{h}{\lambda}$.

Combining 1 and 2 gives us

$$\Delta x \Delta p \approx h.$$

In reality, with more careful calculations and assumptions, we have

$$\Delta x \Delta p \geq \hbar, \tag{3.14}$$

however, the derivation becomes much more complicated than the one here.

Notice that this is not the same as experimental error in the classical sense, but rather implies a physical limit with regards to measurement accuracy.