

CHEM 26100 (Quantum Mechanics) Notes

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Chapter 1

From Classical to Quantum Mechanics

1.1 Blackbody Radiation

9/27: • The surface of a hot body emits energy in the form of EM radiation.

• Changes that occur with temperature:

- If less than 500 °C, we have IR Radiation (heat).
- If 500 °C to 600 °C, we have visible radiation (a glowing body).
- If 5 000 °C, we have a “white hot” body (short wavelength).

• As a body gets hotter, it emits shorter wavelength radiation.

• **Stefan-Boltzmann law:** The the total emissive power R (recall that power is en / time) of a blackbody (BB) is given by

$$R(T) = \sigma T^4$$

where $\sigma \approx 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ is **Stefan’s constant**.

- Work done by Stefan and Boltzmann (c. 1870 / 1884, respectively).

• **Wien’s 1st Law:** The wavelength for maximum emissive power obeys the equation

$$\lambda_{\text{max}} T = b$$

where $b = 2.898 \times 10^{-3} \text{ m K}$ is **Wein’s displacement constant**. *Also known as Wien’s displacement law.*

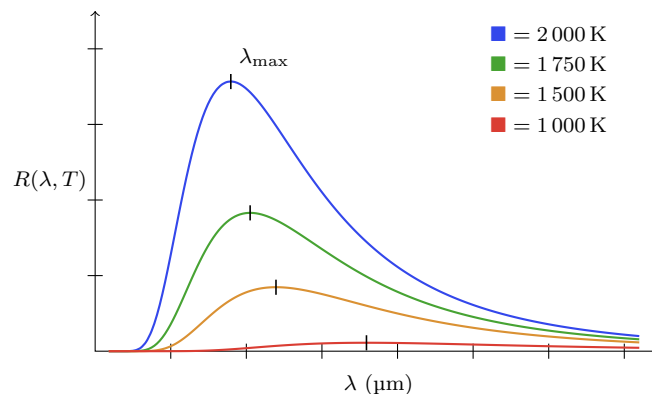


Figure 1.1: Wein’s 1st Law.

- Area under the curve (found with integration) is the total emissive power.
- We now change variables from emissive power R to energy density ρ in the BB cavity.

$$\rho(\lambda, T) = \frac{4}{c} R(\lambda, T)$$

- Wien's 2nd Law (1893): The energy density must have a functional relationship with the following form.

$$\rho(\lambda, T) = \frac{f(\lambda T)}{\lambda^5}$$

– $f(\lambda T)$ cannot be determined from thermodynamics. Thus, something else is needed!

- Lord Rayleigh and his graduate student Jeans (1899) propose a solution.
 - EM: The thermal radiation within a cavity must exist in the form of standing waves.
 - RJ showed that the number n of standing waves per unit volume, per wavelength has the following form.

$$n(\lambda) = \frac{8\pi}{\lambda^4}$$

– If $\bar{\epsilon}$ is the average energy in the mode with wavelength λ , then

$$\rho(\lambda, T) = \frac{8\pi}{\lambda^4} \bar{\epsilon}$$

- Waves come from atoms in the walls of the BB cavity, which act as linear harmonic oscillators at a frequency $\nu = c/\lambda$.
- Assuming thermal equilibrium, we obtain

$$\begin{aligned} \bar{\epsilon} &= \frac{\int_0^\infty \epsilon e^{-\epsilon/kT} d\epsilon}{\int_0^\infty e^{-\epsilon/kT} d\epsilon} \\ &= -\frac{\partial}{\partial \beta} \ln \left(\int_0^\infty e^{-\beta \epsilon} d\epsilon \right) \\ &= \frac{1}{\beta} \\ &= kT \end{aligned}$$

where k is the Boltzmann constant.

- Basically, we sum all energies ϵ , weighted by the probability $e^{-\epsilon/kT}$ of the energy existing, and divided by the total energy.
- The first equation is equivalent to the second with $\beta = 1/kT$.
- Therefore,

$$\rho(\lambda, T) = \frac{8\pi kT}{\lambda^4}$$

- UV catastrophe: Rayleigh's formula diverges from the experimental data for short wavelength.
 - The above formula diverges to $+\infty$, driven by the λ^4 term in the denominator, as $\lambda \rightarrow 0$. However, the amount of radiation of shorter wavelengths should decrease past a point, as seen in Figure 1.1.
- Max Planck comes in, proposes an idea to the German academy that's so radical, they think he's insane, but he's actually right and it lays a key idea for quantum mechanics.
- Planck's key insight: The energy levels of the oscillators are not continuous, but are quantized.

- So we can't actually take an integral as Rayleigh did; we have to take an infinite series.
- In reality,

$$\bar{\epsilon} = \frac{\sum_{n=0}^{\infty} n\epsilon_0 e^{-\beta n\epsilon_0}}{\sum_{n=0}^{\infty} e^{-\beta n\epsilon_0}} = \frac{\epsilon_0}{e^{\beta\epsilon_0} - 1}$$

- Thus,

$$\rho(\lambda, T) = \frac{8\pi\epsilon_0}{\lambda^4(e^{\epsilon/kT} - 1)}$$

- But to satisfy Wien's 2nd law, we must let $\epsilon_0 \propto 1/\lambda$. More specifically, $\epsilon_0 = hc/\lambda = h\nu$, where h is Planck's constant.
 - This setup allowed us to get an accurate value for Planck's constant for the first time in history.
- Planck's theory predicts the data of Figure 1.
- A perfect blackbody absorbs and emits radiation at all frequencies.
 - A star is pretty close to a blackbody. The graphite in a pencil is 97% a blackbody. We are all blackbodies.
 - The entire universe can be viewed as a blackbody.
- Princeton and Bell Labs telescopes find **Cosmic Background Radiation** (A. A. Penzias and R. W. Wilson, 1964).
 - Background radiation from the universe itself.
 - $\lambda_{\max} = 7.35$ cm.
 - Isotropic radio signal, that comes from everywhere.
 - From this, you can work out the temperature of the universe from Wein's first law.
 - Thus, the whole universe is a blackbody with a temperature of approximately 3 K.

1.2 Photoelectric Effect and Bohr Atom

- 9/29:
- In 1887, Hertz shines UV light at electrodes and observes a spark.
 - In 1900, Lenard shows that electrons are ejected from the metal surface of the electrodes.
 - Experimental setup:

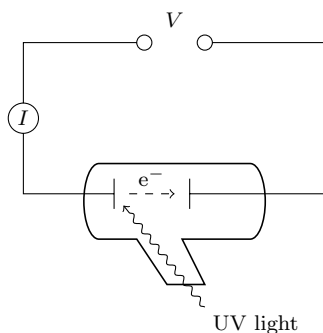


Figure 1.2: Photoelectric effect experiment.

- Shine UV light through a quartz crystal window so that it impinges on the left plate.
- This causes an electron to be ejected from the illuminated plate and cross the potential difference (recall that they didn't know about electrons at the time; they just knew something was happening).
- Increase the external potential until the spark goes away (gives some data about the energy of the electron).
- Odd features:
 1. There is a threshold frequency of radiation required to eject the electrons.
 - You can shine as much light as you want below a certain frequency and nothing will happen.
 - However, as soon as you reach that frequency, you get a spark.
 2. The maximum kinetic energy (KE necessary to overcome the voltage PE???) depends linearly upon the frequency and is independent of the intensity.
- Einstein (1906) proposes that light consists of quanta called photons.
- If you assume this, Max KE obeys the following form.

$$\frac{1}{2}mv_{\max}^2 = h\nu - W$$

where the work function W is the energy required to remove the photon from the metal.

- When $KE \rightarrow 0$, we obtain the threshold frequency

$$\nu_{\text{th}} = \frac{W}{h}$$

required to remove an electron from the metal.

- Millikan (1914-1917), hot off the success of the oil drop experiment, experimentally corroborates Einstein's theory at UChicago in Ryerson.
 - Noting that $KE = eV$ as well where e is the charge of an electron and V is the stopping voltage, Millikan obtains

$$V = \frac{h}{e}\nu - \frac{W}{e}$$
 - The slope of this linear data plot is h/e , and Millikan definitely knows the charge of the electron (!), so he can also measure Planck's constant this way.
 - When Millikan gets the same value Planck got a different way, he corroborates Einstein's theory.
- Thus, this quantization is not just one result, but is fundamental to our understanding of radiation.
- Bohr (1913) makes assumptions.
 1. Circle orbits of electrons about the nucleus.
 2. Only certain stationary orbits are allowed.
 3. The electron radiates energy only during a transition between orbits.
 4. The orbital angular momentum is quantized: $L = \frac{nh}{2\pi}$ where $n \in \mathbb{N}$ is a quantum number.
- Assumption 1 is wrong.
- Two equations:

- Equation one: Coulomb attraction of the electron and proton (nucleus) is balanced by a centripetal acceleration.

$$\frac{Ze^2}{4\pi\epsilon_0 r^2} = \frac{mv^2}{r}$$

where Z is the charge of the nucleus, and e is the charge of an electron.

- This follows exactly from classical mechanics.

- Equation two: Quantization of the orbital angular momentum:

$$mvr = \frac{nh}{2\pi} = n\hbar$$

where $\hbar = h/2\pi$.

- This is a new development from quantum mechanics.

- We now solve the two equations for our two unknowns (the velocity and radius).

$$v = \frac{Ze^2}{4\pi\epsilon_0 \hbar n} \qquad r = \frac{4\pi\epsilon_0 \hbar^2 n^2}{Zme^2}$$

- It follows that the translational kinetic energy T is given by

$$\begin{aligned} T &= \frac{1}{2}mv^2 \\ &= \frac{m}{2\hbar} \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2} \end{aligned}$$

- This is the origin of the $1/n^2$ in the Bohr model.

- With respect to potential energy, we also have

$$\begin{aligned} V &= -\frac{Ze^2}{4\pi\epsilon_0 r} \\ &= -\frac{m}{\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2} \end{aligned}$$

- It follows that the total energy E is given by

$$\begin{aligned} E_n &= T + V \\ &= -\frac{m}{\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2} \end{aligned}$$

- Thus, the reason we have discrete transitions is because the atom has discrete energy levels.
- Indeed, energy transitions are described by the following.

$$E_b - E_a = hcR_0 \left(\frac{1}{n_b^2} - \frac{1}{n_a^2} \right)$$

where R_0 , the Rhydborg constant (observed by Rhydborg and his spectral lines far before Bohr, but applicable here), is all of the other constants swept together.

- Note that

$$R_0 = \frac{m \left(\frac{e^2}{4\pi\epsilon_0} \right)^2}{4\pi c \hbar^3}$$

- Thus, quantum mechanics exactly describes the spectral transitions experimentally described earlier.
- Limitations of the Bohr model:
 1. Assumption 1.
 2. Cannot be generalized to many electron atoms and models.
 3. No reliable way to predict the time dependence of events like the electron transitions.
- So the Bohr model brings us to the brink of being able to predict chemistry, but we still need to go a bit further.

1.3 Chapter 1: The Dawn of the Quantum Theory

From McQuarrie and Simon (1997).

- 9/28:
- **Blackbody:** A body which absorbs and emits all frequencies. *Also known as ideal body.*
 - “Many theoretical physicists tried to derive expressions consistent with these experimental curves of intensity versus frequency [see Figure 1.1], but they were all unsuccessful. In fact, the expression that is derived according to the laws of nineteenth century physics is” as follows (McQuarrie & Simon, 1997, p. 3).
 - **Rayleigh-Jeans law:** The equation

$$d\rho(\nu, T) = \rho_\nu(T) d\nu = \frac{8\pi k_B T}{c^3} \nu^2 d\nu$$

where $\rho_\nu(T) d\nu$ is the “radiant energy density between the frequencies ν and $\nu + d\nu$ ” (McQuarrie & Simon, 1997, p. 3).

- The ultraviolet catastrophe is so named because the frequency increases as the radiation enters the ultraviolet region.
- Planck’s solution:
 - Rayleigh and Jeans assumed (as does classical physics) that the energies of the electronic oscillators responsible for the emission of the radiation could have any value whatsoever.
 - However, Planck assumed discrete oscillator energies proportional to an integral multiple of the frequency: $E = nh\nu$, where $n \in \mathbb{Z}$.
 - Using this quantization energy and ideas from statistical thermodynamics (see Chapter 17), Planck derived the **Planck distribution law for blackbody radiation**.
 - The only undetermined constant in the above equation was h , and Planck showed that if we let $h = 6.626 \times 10^{-34}$ J s, then this equation gives excellent agreement with the experimental data for all frequencies and temperatures.
- **Planck distribution law for blackbody radiation:** The equation

$$d\rho(\nu, T) = \rho_\nu(T) d\nu = \frac{8\pi h}{c^3} \frac{\nu^3 d\nu}{e^{h\nu/k_B T} - 1}$$

- Note that for small frequencies, the Planck distribution law and Rayleigh-Jeans law converge, but they diverge for large frequencies, as expected.
- Because ν and λ are related by $\lambda\nu = c$ (and subsequently by $d\nu = -c/\lambda^2 d\lambda$), we can write the Planck distribution law in terms of wavelength, as well.

$$d\rho(\lambda, T) = \rho_\lambda(T) d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{hc/\lambda k_B T} - 1}$$

- Differentiating $\rho_\lambda(T)$ with respect to λ gives an alternate formulation for b :

$$\lambda_{\max}T = \frac{hc}{4.965k_B}$$

- Astronomers use the theory of blackbody radiation to estimate the surface temperatures of stars.
 - We can measure the electromagnetic spectrum of a star (which will follow a curve similar to one of the ones in Figure 1.1).
 - Then we can find λ_{\max} . From here, all that's necessary is to plug into Wien's displacement law:

$$T = \frac{b}{\lambda_{\max}}$$

References

McQuarrie, D. A., & Simon, J. D. (1997). *Physical chemistry: A molecular approach*. University Science Books.