

CHEM 26100 (Quantum Mechanics) Notes

Steven Labalme

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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 **Wien’s displacement constant**. *Also known as Wien’s displacement law.*

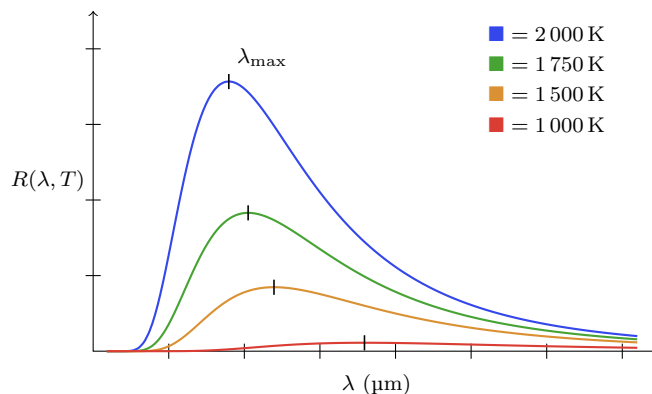


Figure 1.1: Wien’s 1st Law.

- 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 Wien'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:

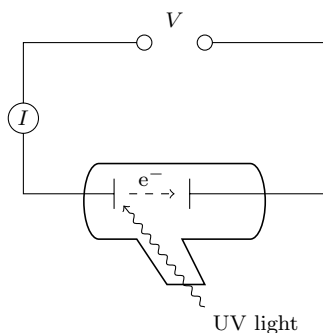


Figure 1.2: Photoelectric effect experiment.

- 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 Stern-Gerlach Experiment

10/1:

- Measurement of the magnetic dipole moment of atoms.
- Nobel-prize winning experiment done by Otto Stern and W. Gerlach (1922). Stern was Gerlach's grad student.
- **Magnetic dipole moment:** Think about an electron moving in a circle with velocity v . Then the charge creates a magnetic field M perpendicular to the plane of the circle.
- Thus, we want to detect the magnetic moment of atoms. They will measure this by measuring the deflection of the atoms by an **inhomogeneous** field.
- **Inhomogeneous** (magnetic field): Because they're not setting up the magnetic field so that its equal everywhere in space through which the beam travels.
- They put the atoms in an "oven" to get them hot, and then shoot them through a beam. The beam passes through a magnet, and if the beam has a magnetic moment, it will break up. There is a collection plate at the far end.
- Effect of the \vec{B} field: $PE = -\vec{M} \cdot \vec{B} = W$.
- It follows that $F = -\nabla W$.
- Additionally,

$$F_z = M_z \frac{\partial B_z}{\partial z}$$
- Classical expectation: Every value of M_z would occur, that is, $|M_z| \leq M$. Would lead to one continuous pile on the collection plate with a Gaussian proportionality.
- Stern and Gerlach expect it to be discrete/quantized. Focused on Ag atoms. Thought two discrete lines would be formed symmetrically about the center. Thought they would see similar results for Na, Cs, K, H.
- Didn't see anything at first.
- Smoked some cigars, released sulfate, and AgSO_4 (black) showed up on the collection plate in 2 discrete piles.
- Bohr quantization (varies from $-\ell$ to $+\ell$, where ℓ is orbital angular momentum). $L = \ell\hbar$ (approximately), $L_z = m\hbar$.
- Actual quantum mechanics gives us $L = \sqrt{\ell(\ell+1)}\hbar$.
- But this does not explain the Stern-Gerlach experiment. According to this theory...
 - If $\ell = 0$ and $m = 0$, then we'll observe just 1 spot.

- If $\ell = 1$ and $m = -1, 0, +1$, then we'll observe 3 spots.
- But, of course, they only saw 2 spots.
 - The first case corresponds to silver with $\ell = 0$.
 - They were actually seeing electron spin.
- Electron spin is later understood by S. Goudsmit and G. E. Uhlenbeck (1925).
 - Able to show that the splitting of spectral lines when atoms are placed in \vec{B} fields. The electron must have an intrinsic spin (magnetic moment M_1) where two values are allowed: $M_1 = \pm \frac{1}{2}$.
 - They postulate that this is a form of intrinsic angular momentum of spin: $S = \sqrt{s(s+1)}\hbar$.
- Total angular momentum: The vector addition of all angular momentum of the part.
 - The angular momentum of the nuclei may be neglected. Addition of the orbital and spin angular momentum of the electrons.
- Stern and Gerlach:
 - The orbital angular momentum of Ag atoms is zero.
 - The net spin angular momentum is $\frac{1}{2}$.
 - Thus, the total angular momentum $m = \pm \frac{1}{2}$. Thus, we expect two spots on the plate.
- Note that this relates to the Pauli exclusion principle (spin implies no more than 2 electrons together), first posited in 1926.
- Particle-wave duality (by Louis de Broglie): Introduces matter waves (1923-24).
 - Einstein says $E = h\nu$. Additionally, momentum of a photon is $p = h\nu/c = h/\lambda$. Thus, this formula relates the particle (momentum) and wave (wavelength) natures of the photon.
- de Broglie: Turns in a 4 page thesis, Paris committee will fail him, but they write to Einstein who recognizes this is really important.
 - de Broglie defines a frequency and a wavelength for material particles $\nu = E/h$. It follows that $\lambda = h/p$. Thus, electrons have a wavelength, too.
- **de Broglie's relationship:** The equation

$$\lambda = \frac{h}{mv}$$

for a nonrelativistic particle.

- Explanation of the Bohr atom:
 - For the electron's orbit to be stable, an integer number of wavelengths must match the circumference of the orbit.
 - This is why the orbits are quantized!
 - Thus, $n\lambda = 2\pi r$ and $L = rp$ (from classical physics), so

$$L = \frac{n\lambda p}{2\pi} = \frac{nh}{2\pi} = n\hbar$$

as desired.

1.4 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 $h = 6.626 \times 10^{-34}$ Js, 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 :

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

- 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.