

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

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

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

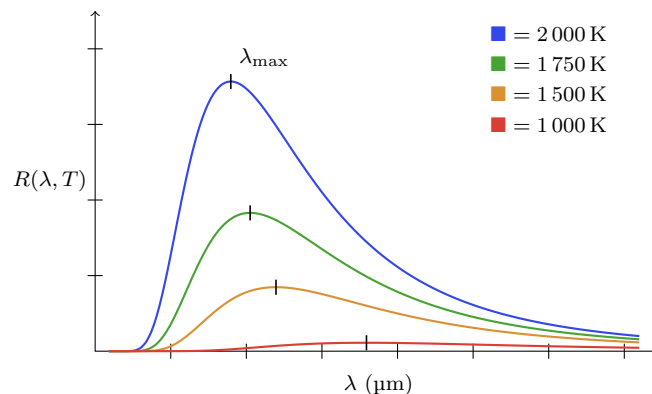


Figure 1.1: Wien’s 1st Law.

- 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,

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

- 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:

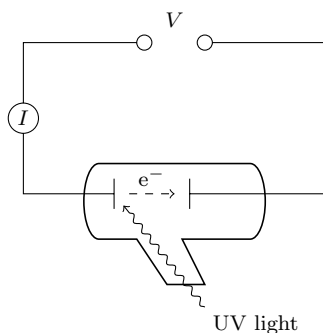


Figure 1.2: Photoelectric effect experiment.

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

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

- 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:

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

10/3:

- **Photoelectric effect:** The ejection of electrons from the surface of a metal by radiation.
- Classical predictions vs. experimental data.
 - Classical mechanics: Intensity is proportional to the amplitude squared of the incident light. Thus, the electrons at the surface of the metal should oscillate along with the field, and when they are oscillating violently enough, they should break away from the surface with a kinetic energy that depends on the amplitude/intensity (specifically, *not* the frequency).
 - Experimental observation: KE of the ejected electrons is independent of intensity and linearly dependent on the frequency.
 - Classical mechanics: The photoelectric effect should occur for any frequency of light as long as the intensity is sufficiently high.
 - Experimental data: There exists a threshold frequency ν_0 , characteristic of the metallic surface, below which no electrons are ejected, regardless of intensity.
- **Work function:** The minimum energy required to remove an electron from the surface of the particular metal. Denoted by ϕ . Units eV.
 - The work function of the metal is analogous to the ionization energy of an isolated atom.
- Bright line spectra: “For many years, scientists had tried to find a pattern in the wavelengths or frequencies of the lines in the hydrogen atom spectrum. Finally, in 1885, an amateur Swiss scientist, Johann Balmer, showed that a plot of the frequency of the lines versus $1/n^2$ ($n = 3, 4, 5, \dots$) is linear” (McQuarrie & Simon, 1997, p. 10).
- **Balmer’s formula:** The equation

$$\tilde{\nu} = 109\,680 \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \text{cm}^{-1}$$

for $n = 3, 4, 5, \dots$, where $\tilde{\nu}$ denotes wavenumber.

- **Balmer series:** The series of lines predicted by Balmer’s formula as n takes on the values $3, 4, 5, \dots$, notably those occurring in the visible and near ultraviolet regions of the hydrogen atomic spectrum.
- **Series limit:** The wavelength of the “last” line in the Balmer series, as $n \rightarrow \infty$, of value 364.7 nm.
- **Rydberg formula:** The equation

$$\tilde{\nu} = \frac{1}{\lambda} = 109\,680 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{cm}^{-1}$$

for $n_1, n_2 \in \mathbb{N}$ such that $n_2 > n_1$.

- The Rydberg formula accounts for all the lines in the hydrogen atomic spectrum.
- **Rydberg constant:** The constant $109\,677.57 \text{cm}^{-1}$. Denoted by R_H .
- The first four series of lines composing the hydrogen atomic spectrum are described in Table 1.1.
- Rydberg found approximate empirical laws for many series of lines in many different atoms throughout the 1890s.
- **Ritz combination rule:** The empirical laws for all the observed lines can be expressed as the difference between terms such as those in the Rydberg formula.
- **de Broglie wavelength:** The wavelength $\lambda = h/(mv)$ corresponding to a particle of mass m moving with velocity v .

Series name	n_1	n_2	Region of spectrum
Lyman	1	2, 3, 4, ...	Ultraviolet
Balmer	2	3, 4, 5, ...	Visible
Paschen	3	4, 5, 6, ...	Near infrared
Bracket	4	5, 6, 7, ...	Infrared

Table 1.1: Hydrogen spectral series.

- An electron moving at 1.00% the speed of light has a de Broglie wavelength comparable to those of X-rays. Thus, electrons should act like X-rays to an extent.
- **X-ray diffraction:** The scattering of a beam of X-rays directed at a crystalline surface, characteristic of the atomic structure of the crystalline surface.
 - Occurs because the interatomic spacings in the crystal are about the same as the wavelength of the X-rays.
- The scattering of X-rays and electrons at such crystalline surfaces are very similar.
- The wavelike property of electrons is used in electron microscopes.
 - “The wavelength of the electrons can be controlled through an applied voltage, and the small de Broglie wavelengths attainable offer a more precise probe than an ordinary light microscope. In addition, in contrast to electromagnetic radiation of similar wavelengths (X-rays and ultraviolet), the electron beam can be readily focused by using electric and magnetic fields, generating sharper images” (McQuarrie & Simon, 1997, p. 18).
- The Bohr model:
 - The hydrogen atom has a central, rather massive nucleus with one associated electron. Because the nucleus is so much more massive than the electron, we can approximate it as fixed with the electron revolving around it.
 - The force f holding the electron in a circular orbit is supplied by the Coulombic force of attraction between the proton and the electron:

$$f = \frac{e^2}{4\pi\epsilon_0 r^2}$$

- The Coulombic force is balanced by the centrifugal force

$$f = \frac{m_e v^2}{r}$$

- Since $\sum f_c = 0$ for a stable circular orbit, we have

$$\frac{e^2}{4\pi\epsilon_0 r^2} = \frac{m_e v^2}{r}$$

- However, according to classical mechanics, an electron under these conditions is constantly accelerating (centripetally), so it should emit EM radiation, lose energy, and spiral into the nucleus. Thus, we make two nonclassical assumptions:
 1. Stationary electronic orbits exist.
 2. The de Broglie waves of the orbiting electron must be in phase, as the electron makes one complete revolution.

- For the wave pattern around an orbit to be stable, we must have that the circumference of the orbit is equal to an integral number of wavelengths, i.e.,

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

where $n \in \mathbb{N}$.

- Substituting the de Broglie wavelength formula into the above gives

$$\begin{aligned} 2\pi r &= n \cdot \frac{h}{m_e v} \\ m_e v r &= \frac{nh}{2\pi} \\ m_e v r &= n\hbar \end{aligned}$$

where $n \in \mathbb{N}$.

- Since $m_e v r$ is the angular momentum of the electron, another interpretation of the above (and the one more commonly attributed to Bohr) is that the angular momentum of the electron about the proton must be quantized.
- Solving for r by substituting out v yields

$$r = \frac{\epsilon_0 \hbar^2 n^2}{\pi m_e e^2}$$

- Thus, the radii of the allowed **Bohr orbits** are quantized.
- We now consider the total energy of the electron in an atom:

$$\begin{aligned} E &= \text{KE} + V(r) \\ &= \frac{1}{2} m_e v^2 - \frac{e^2}{4\pi\epsilon_0 r} \\ &= \frac{1}{2} \cdot \frac{e^2 r}{4\pi\epsilon_0 r^2} - \frac{e^2}{4\pi\epsilon_0 r} \\ &= -\frac{e^2}{8\pi\epsilon_0 r} \\ &= -\frac{m_e e^4}{8\epsilon_0^2 \hbar^2} \cdot \frac{1}{n^2} \end{aligned}$$

- The negative sign in this equation indicates that the energy states are bound states; the energies given are less than when the proton and electron are infinitely separated.
- **First Bohr orbit:** The Bohr orbit corresponding to $n = 1$, having radius 52.92 pm. Denoted by a_0 .
- **Ground state energy:** The lowest energy, corresponding to $n = 1$ in the total energy equation.
- **Excited state:** The states of higher energy, i.e., those other than the ground state.
 - Generally unstable with respect to the ground state.
 - At ordinary temperatures, hydrogen atoms as well as other atoms and molecules are found almost exclusively in their ground states.
 - An atom in an excited state will usually relax back to the ground state and give off the energy as electromagnetic radiation.
- With respect to spectral lines, Bohr assumed that the observed spectrum of the hydrogen atom is due to transitions from one allowed energy state to another:

$$\Delta E = \frac{m_e e^4}{8\epsilon_0^2 \hbar^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = h\nu$$

- **Bohr frequency condition:** The above equation, specifically the relation $\Delta E = h\nu$.
 - Implies that as the electron falls from one level to another, the energy evolved is given off as a photon of energy $E = h\nu$.
 - Making the substitution $h\nu = hc\tilde{\nu}$, we can make the theoretical prediction that spectral lines will be of wavenumber

$$\tilde{\nu} = \frac{m_e e^4}{8\epsilon_0^2 ch^3} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

- It follows that we should have

$$R_\infty = \frac{m_e e^4}{8\epsilon_0^2 ch^3}$$

which we indeed do.

References

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