CHEM 26100 (Quantum Mechanics) Notes

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Weeks

List of Figures

List of Tables

Week 1

From Classical to Quantum Mechanics

1.1   Blackbody Radiation

- The surface of a hot body emits energy in the form of EM radiation.

- Changes that occur with temperature:
  - If less than $500\,^{\circ}\mathrm{C}$, we have IR Radiation (heat).
  - If $500\,^{\circ}\mathrm{C}$ to $600\,^{\circ}\mathrm{C}$, we have visible radiation (a glowing body).
  - If $5000\,^{\circ}\mathrm{C}$, 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 $\sigma \approx 5.67 \times 10^{-8}\,\mathrm{W\,m^{-2}\,K^{-4}}$ 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 $b = 2.898 \times 10^{-3}\,\mathrm{m\,K}$ is **Wien's displacement constant**. *Also known as* **Wien's displacement law**.
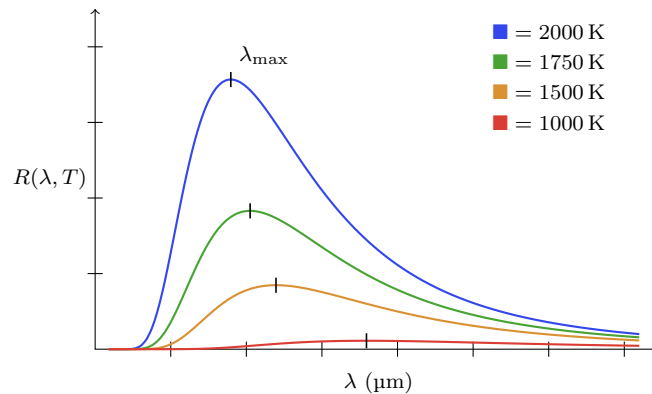

Figure 1.1: Wien's 1st Law.

- 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

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

    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 $\lambda \to 0$. 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 acacdemy 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,

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

- Thus,

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

- 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.
  - $\lambda_{\mathrm{max}} = 7.35\,\mathrm{cm}$.
  - Isotropic radio signal, that comes form everywhere.
  - From this, you can workout the temperature of the universe from Wien's first law.
  - Thus, the whole universe is a blackbody with a temperature of approximately $3\,\mathrm{K}$.

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.
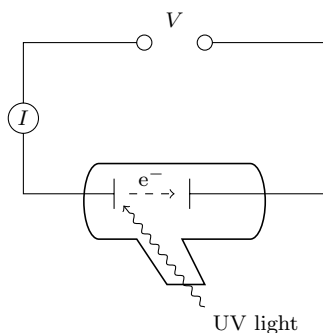
- Experimental setup:

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.

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

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

    - When $KE \to 0$, 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).

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

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

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

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

• With respect to potential energy, we also have

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

• It follows that the total energy E is given by

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

• 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 Rhydberg constant (observed by Rhydberg 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

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

  where $\rho_\nu(T)\,\mathrm{d}\nu$ is the "radiant energy density between the frequencies ν and $\nu + \mathrm{d}\nu$" (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 $h = 6.626 \times 10^{-34}\,\mathrm{J\,s}$, then this equation gives excellent agreement with the experimental data for all frequencies and temperatures.

- **Planck distribution law for blackbody radiation**: The equation

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

  - 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 $\mathrm{d}\nu = -c/\lambda^2\,\mathrm{d}\lambda$), we can write the Planck distribution law in terms of wavelength, as well.

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

- 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 $\lambda_{\max}$. 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 amplidude/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 $n \to \infty$, 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 $\boldsymbol{R_H}$.*

- 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	$2, 3, 4, \ldots$	Ultraviolet
Balmer	2	$3, 4, 5, \ldots$	Visible
Paschen	3	$4, 5, 6, \ldots$	Near infrared
Bracket	4	$5, 6, 7, \ldots$	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

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

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

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

■ Thus, the radii of the allowed **Bohr orbits** are quantized.

– We now consider the total energy of the electron in an atom:

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

■ 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 $52.92\,\text{pm}$. *Denoted by $\boldsymbol{a_0}$.*

• **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:

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

- **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

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

  - It follows that we should have

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

  which we indeed do.

Week 2

The Schrödinger Equation

2.1 Particle-Wave Duality and Uncertainty Relations

- Particle-wave duality (de Brogelie's original formulation):

$$\lambda\nu = c \qquad\qquad E = h\nu \qquad\qquad p = \frac{h}{\lambda}$$

- **Angular frequency**: The quantity $\omega = 2\pi r$.

- **Wavenumber**: The quantity $k = 2\pi/\lambda$.

- We can create a symmetrical formulation of the de Broglie relation using these new quantities:

$$E = \hbar\omega \qquad\qquad\qquad p = \hbar k$$

- What is the wave that we might associate with a de Broglie particle?

$$\psi(x) = A\mathrm{e}^{ikx - i\omega t}$$

- Probability:

  - Classically, such a wave might be associated with EM radiation hitting a surface with intensity $I = |\psi(x)|^2 = \psi(x)\psi^*(x)$.

  - As soon as we associate a particle (photon) with the wave, the intensity may be re-interpreted as the number of particles reaching the surface or the probability of a particle being at the surface.

  - Thus, the probability of finding a particle at the surface becomes $|\psi(x)|^2$, as well.

- Following de Broglie, we also associate waves with particles such as electrons.

  - With the association of light as a particle, the particle wave duality leads to the appearance of probability.

- What is the probability of finding the particle at the origin?

$$Pr = \left|A\mathrm{e}^{ik\cdot 0}\right|^2$$
$$= |A|^2$$

  - Since the probability is not dependent on position, it is the same everywhere.

  - We also run into issues **normalizing** this unbounded wavefunction.

- – We know this particle's momentum exactly, but we know nothing about its position.

- **Normalizing** (a wavefunction): Guaranteeing that the integral for the entire wavefunction is equal to 1.

- **Free particle**: A particle that does not have constraints on where it is more likely to be.

- Heisenberg's uncertainty relations are formalized in terms of matrix mechanics.

    - – We can Fourier transform the wave function of particle to convert it from a function of position to a function of momentum.
    - – The Fourier transform will yield one spike at $\hbar k$ and will be 0 everywhere else — just like the Dirac delta function.
    - – Thus,

$$\psi(p) = \delta(p - \hbar k)$$

- Consider a Gaussian wave packet at $p = 0$. Then

$$\phi(p) = C\mathrm{e}^{-\frac{p^2}{2(\Delta p)^2}}$$

    - – Δp is the standard deviation of the Gaussian/width of the distribution. It is a constant such that the probability drops to $1/\mathrm{e}$ of its maximum at $p = 0$.

- With the Fourier Transform of $\psi(p)$, we obtain

$$\psi(x) = D\mathrm{e}^{-\frac{(\Delta p)^2 x^2}{2\hbar^2}}$$

    - – Thus, a Gaussian quantum function produces a Gaussian position function via an FT as well, i.e.,

$$\psi(x) = D\mathrm{e}^{-\frac{x^2}{2(\Delta x)^2}}$$

- Now if we set the last two equations equal to each other, we get

$$\frac{(\Delta p)^2}{2\hbar^2} = \frac{1}{2(\Delta x)^2}$$
$$(\Delta p)^2(\Delta x)^2 = \hbar^2$$
$$\Delta p \Delta x = \hbar = \frac{h}{2\pi}$$

    - – This implies that the spread of the Gaussian in momentum times the spread of the Gaussian in position is a constant.
    - – If we make one Gaussian wave packet more specific, the other gets more spread out, and vice versa.
    - – Note that the above equality does *satisfy* the Heisenberg uncertainty principle, but it is not it itself.

2.2   The Schrödinger Equation and Particle in a Box

10/6:
- Review:

    - – de Broglie describes an electron as a free particle.

$$\psi(x) = A\mathrm{e}^{ikx}$$

    - – We can only observe the real part, but being able to access the complex part is important in quantum mechanics.

- Schrödinger was on vacation in the Swiss Alps with his mistress when he derived the wave equation.

  - Schrödinger realized that

$$\frac{\mathrm{d}\psi(x)}{\mathrm{d}x} = Aik\mathrm{e}^{ikx}$$

$$-i\hbar\frac{\mathrm{d}\psi(x)}{\mathrm{d}x} = Ap\mathrm{e}^{ikx}$$

$$= p\psi(x)$$

  - Let's introduce operators in quantum mechanics and let $\hat{p}$ be an operator that when it acts on $\psi(x)$, it gives the above. In other words,

$$\hat{p} = -i\hbar\frac{\mathrm{d}}{\mathrm{d}x}$$

  - Thus,

$$\hat{p}\psi(x) = p\psi(x)$$

  - But energy is more important than momentum, so let's introduce an energy operator $\hat{T}$ related to $\hat{p}$ by

$$\hat{T} = \frac{\hat{p}^2}{2m} = \frac{-\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$$

  since $E = mv^2/2 = p^2/(2m)$.

  - Thus, we have

$$\hat{T}\psi(x) = \frac{p^2}{2m}\psi(x)$$

  - It follows from classical physics that the total energy operator $\hat{H}$ (the Hamiltonian) is the sum of the kinetic and potential energy operators, i.e., $\hat{H} = \hat{T} + \hat{V}$. Therefore, we must have

$$\hat{H}\psi(x) = E\psi(x)$$

  and that is the Schrödinger equation.

- The particle in a box is like a single electron in a one-dimensional chamber that runs from $-a$ to a with $L = 2a$ (Schrödinger figured this out a few days later, still in the Swiss Alps).

  - The walls are infinite and have infinite potential.
  - We need the boundary condition, though, to be able to solve a differential equation like the Schrödinger equation.
    - Fortunately, we know that at $|x| = a$, we have $\psi(\pm a) = 0$.
    - Another important point is that $\mathrm{d}\psi(x)/\mathrm{d}x$ at a is discontinuous.
  - So we have that

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi_n(x) = E_n\psi_n(x)$$

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi(x) = -k^2\psi(x)$$

  where

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

  - The solution of the differential equation will be of the form

$$\psi(x) = A\cos(kx) + B\sin(kx)$$

– Boundary conditions 1 and 2, respectively:

$$0 = \psi(a)$$
$$\qquad = A\cos(ka) + B\sin(ka)$$

$$0 = \psi(-a)$$
$$\qquad = A\cos(ka) - B\sin(ka)$$

– Adding/subtracting the two equations yields

$$A\cos(ka) = 0 \qquad\qquad\qquad B\sin(ka) = 0$$

– We satisfy these equations with either of 2 classes of nontrivial solutions (the trivial solution being $a = 0$).

1. $B = 0$ and $\cos(ka) = 0$, i.e., $k_n = \frac{n\pi}{2a}$ for $n \in 2\mathbb{N} + 1$.
2. $A = 0$ and $\sin(ka) = 0$, i.e., $k_n = \frac{n\pi}{2a}$ for $n \in 2\mathbb{N}$.

– Thus, either

$$\psi_n(x) = \frac{1}{\sqrt{a}}\cos\left(\frac{n\pi x}{2a}\right)$$

for $n \in 2\mathbb{N} + 1$ are the **even solutions** (because cosine is an even function), and

$$\psi_n(x) = \frac{1}{\sqrt{a}}\sin\left(\frac{n\pi x}{2a}\right)$$

for $n \in 2\mathbb{N}$ are the **odd solutions** (because sine is an odd function).

– Note that we derive the $1/\sqrt{a}$ coefficient by normalizing $\psi(x)$ with

$$\int_{-a}^{a} |\psi(x)|^2 \, \mathrm{d}x = \int_{-a}^{a} \psi^*(x)\psi(x) = 1$$

– The energies come out to

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2}{8m} \cdot \frac{\pi^2 n^2}{a^2}$$

with the substitution $k_n = \frac{n\pi}{2a}$.

■ Note that this means that the particle becomes more discrete the smaller the box gets (as uncertainty in position goes down, it acts more and more quantum mechanically).

2.3   Potential Step

10/8:   • Particle in a box:

– For $n = 1$, the potential is defined by one hump of a sine wave.
– For $n = 2$, the potential is defined by two humps.
– The number of nodes is equal to the principal quantum number minus 1.
– We have

$$E_n = \frac{\hbar^2}{8m}\frac{\pi^2 n^2}{a^2}$$

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

– By the Heisenberg uncertainty relationship, we must have $E_1 > 0$. In other words, the **zero-point energy** arises from the UR.
– Trend wrt. a: As $a \to \infty$, all of the energies become degenerate.
– Trend wrt. m: As $m \to \infty$, $E_n \to 0$ as well.

■ In other words, as $m \to \infty$, the particle behaves more classically!
■ The zero-point energy also disappears as $a \to \infty$.

- **Zero-point energy**: The lowest possible energy a quantum mechanical system may have.

- All of that information comes from the Schrödinger equation, so we now know much more than we used to.

- Free particle vs. particle in a box:

  - For a free particle, we have $\psi(x) = e^{ikx}$. Boundary condition was a circle (as per the Bohr model).
  - In the particle in a box, we weed out all of the free particle solutions that don't match the boundary conditions. And the only solutions that match the boundary conditions are the ones that have integers for the quantum number n.
  - The only constraint is that you can retain more particles the bigger the box gets; this is why the particle gets more quantum mechanical as you shrink the box.

- **Potential step**: Let the energy E be 0 up until the origin, where it steps up to potential V_0.
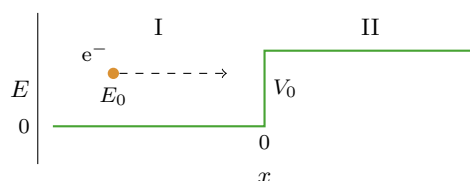

Figure 2.1: Potential step.

  - We shoot a particle at a potential wall with energies varying from below the top to above the top.

- In classical mechanics, we have
$$E = \frac{p^2}{2m} + V$$

  - In region I, there's no potential, so the total energy is all kinetic. The particle is moving with momentum $p_{\mathrm{I}} = \sqrt{2mE}$.
  - In region II, the particle is moving with momentum $p_{\mathrm{II}} = \sqrt{2m(E-V)}$.
    - If $E_0 < V$, the particle *never* passes from region I $\to$ II.
    - If $E_0 > V$, the particle *always* passes from I $\to$ II, but has less KE in II than I[1].

- Quantum particle motion:
$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi(x) + V(x)\psi(x) = E\psi(x)$$
$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi(x) + k^2\psi(x) = 0$$

where $k = \sqrt{2m(E-V)/\hbar^2}$.

  - The total wave function will be the sum of the LCAOs that fit the boundary condition.
  - Our general solution has two parts:
$$\psi_{\mathrm{I}}(x) = Ae^{i\alpha x} + Be^{-i\beta x} \qquad\qquad \psi_{\mathrm{II}}(x) = Ce^{i\alpha x} + De^{-i\beta x}$$

  - Two energy cases: $E > V_0$ and $E < V_0$.

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[1]Note that the classical resolution to the case $E = V_0$ is that the particle never has $E_0 = V$; it always has energy ϵ above or ϵ below V. However, in some sense, there *is* another answer: Classical mechanics is not an "accurate" reflection of reality, and this is a place where it shows. Indeed, we *need* quantum mechanics to treat this case.

- $E > V_0$:
  - ■ We must maintain the continuity of the $\psi(x)$ and $\mathrm{d}\psi(x)/\mathrm{d}x$ at $x = 0$. This yields

$$A + B = C + D \qquad\qquad i\alpha(A - B) = i\beta(C - D)$$

  - ■ It follows that

$$A = \frac{C(\alpha + \beta)}{2\alpha} + \frac{D(\alpha - \beta)}{2\alpha} \qquad\qquad B = \frac{C(\alpha - \beta)}{2\alpha} + \frac{D(\alpha + \beta)}{2\alpha}$$

  - ■ Assume that the particles only travel from left to right in II, i.e., $D = 0$.
  - ■ The flux of the particle: The probability of the particle going left to right in region I is $|A|^2$. Thus, since the incident flux factors in the speed v_I of the particle, the incident flux is $v_\mathrm{I}|A|^2$. Similarly, the transmitted flux of the particle is $v_\mathrm{II}|C|^2$.
  - ■ Consequently, the reflected flux of the particles is

$$R = \frac{c|B|^2}{c|A|^2} = \frac{|B|^2}{|A|^2} = \frac{(\alpha - \beta)^2}{(\alpha + \beta)^2}$$

  Note that the speed of the particle (the speed of light, c) is the same in both regions.
  - ■ Conclusion: There is a probability of reflection *even when* $E_0 > V_0$, disagreeing with classical mechanics.
  - ■ Fraction of transmitted particles:

$$T = \frac{v_\mathrm{II}}{v_\mathrm{I}} \frac{|C|^2}{|A|^2} = \frac{4\alpha\beta}{(\alpha + \beta)^2}$$

- $E < V_0$:
  - ■ The continuity of $\psi(x)$ and $\psi'(x)$ at $x = 0$ again gives us

$$A + B = C + D \qquad\qquad i\alpha(A - B) = i\beta(C - D)$$

  - ■ But since we have

$$\beta = \frac{\sqrt{2m(E - V_0)}}{\hbar}$$

  and $E - V_0 < 0$, β will be a complex number.
  - ■ Thus, to treat the real and complex portions of β separately, we define β_2 to be a real number.
  - ■ Consequently, we may write

$$R = \frac{|B|^2}{|A|^2} = \frac{|\alpha - \beta|^2}{|\alpha + \beta|^2} = \frac{|\alpha - i\beta_2|^2}{|\alpha + i\beta_2|^2} = \frac{\alpha^2 + \beta_2^2}{\alpha^2 + \beta_2^2} = 1$$

  - ■ Conclusion: When the energy of the particle is less than the energy of the potential, even quantum mechanics predicts total reflection. However, there's still something subtle happening.
  - ■ Let's look at the wave function in region II:

$$\psi_\mathrm{II} = Ce^{i\beta x} = Ce^{i(i\beta_2)x} = Ce^{-\beta_2 x}$$

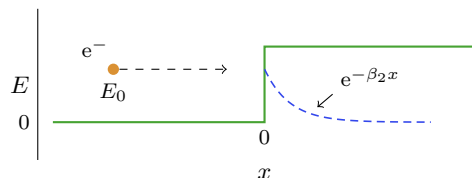 where $\beta_2 > 0$ by definition.

Figure 2.2: Quantum tunneling.

  - ■ Thus, even though the particle is reflected 100%, it has some probability of going through the step, namely a probability that decays exponentially the farther you go into the wall.
  - ■ This is **quantum tunneling**.
  - ■ The particle can't ever get to ∞, so that's why $T = 0$, but it can go into the wall for a little bit, just a sec.

2.4   MathChapter B: Probability and Statistics

- "Consider some experiment, such as the tossing of a coin or the rolling of a die, that has n possible outcomes, each with probability p_j, where $j = 1, 2, \ldots, n$" (McQuarrie & Simon, 1997, p. 63).

- If the experiment is repeated indefinitely, we intuitively expect that for each $j = 1, \ldots, n$

$$p_j = \lim_{N \to \infty} \frac{N_j}{N}$$

  where N_j is the number of times that the event j occurs and N is the total number of repetitions of the experiment.

- The fact that $0 \le N_j \le N$ implies that $0 \le p_j \le 1$ by the above condition.

- **Certainty**: An event j such that $p_j = 1$.

- **Impossibility**: An event j such that $p_j = 0$.

- **Normalization condition**: The result that

$$\sum_{j=1}^{n} p_j = 1$$

  - This follows from the fact that $\sum_{j=1}^{n} N_j = N$ and the above.
  - The normalization condition expresses the idea that "the probability that some event occurs is a certainty" (McQuarrie & Simon, 1997, p. 64).

- **Average** (of x): The following quantity, where we associate some number x_j with each outcome j. *Also known as* **mean** (of x). *Denoted by* $\langle \boldsymbol{x} \rangle$. *Given by*

$$\langle x \rangle = \sum_{j=1}^{n} x_j p_j = \sum_{j=1}^{n} x_j p(x_j)$$
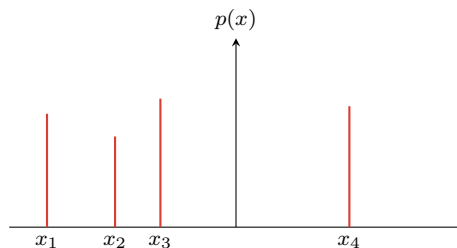

Figure 2.3: The discrete probability frequency function.

  - It is helpful to interpret a probability distribution like p_j as a distribution of a unit mass along the x-axis in a discrete manner such that p_j is the fraction of mass located at the point x_j.
  - According to this interpretation, the average value of x is the center of mass of this system.

- **Second moment** (of the distribution $\{p_j\}$): The following quantity.

$$\langle x^2 \rangle = \sum_{j=1}^{n} x_j^2 p_j$$

   - Note that $\langle x^2 \rangle \neq \langle x \rangle^2$.
   - Analogous to the moment of inertia.

- The next quantity is physically more interesting than the second moment.

- **Second central moment**: The following quantity. *Also known as* **variance**. *Denoted by* $\boldsymbol{\sigma_x^2}$. *Given by*

$$\sigma_x^2 = \langle (x - \langle x \rangle)^2 \rangle = \sum_{j=1}^{n} (x_j - \langle x \rangle)^2 p_j$$

   - $\sigma_x^2 \geq 0$ because it is a sum of positive terms.
   - An alternate form of σ_x^2:

$$\begin{aligned}
\sigma_x^2 &= \sum_{j=1}^{n} (x_j - \langle x \rangle)^2 p_j \\
&= \sum_{j=1}^{n} (x_j^2 - 2\langle x \rangle x_j + \langle x \rangle^2) - p_j \\
&= \sum_{j=1}^{n} x_j^2 p_j - 2\langle x \rangle \sum_{j=1}^{n} x_j p_j + \langle x \rangle^2 \sum_{j=1}^{n} p_j \\
&= \langle x^2 \rangle - 2\langle x \rangle \cdot \langle x \rangle + \langle x \rangle^2 \cdot 1 \\
&= \langle x^2 \rangle - \langle x \rangle^2
\end{aligned}$$

   - If $\sigma_x^2 = 0$ or $\langle x \rangle^2 = \langle x^2 \rangle$, then we must have $x_j = \langle x \rangle$ for all j, i.e., the event is not really probabilistic because the event j occurs on every trial.

- **Standard deviation**: The positive square root of the variance. *Denoted by* $\boldsymbol{\sigma_x}$.

- Both the standard deviation and the variance are measures of the spread of the distribution about its mean.

- We now step into continuous probability distributions.

- **Linear mass density**: The quantity $\rho(x)$ defined by

$$\mathrm{d}m = \rho(x)\,\mathrm{d}x$$

   where $\mathrm{d}m$ is the fraction of the mass lying between x and $x + \mathrm{d}x$.

- It follows that the probability that, for example, a particle lies between positions x and $x + \mathrm{d}x$ in a box is

$$\mathrm{Prob}(x, x + \mathrm{d}x) = p(x)\,\mathrm{d}x$$

- Therefore,

$$\mathrm{Prob}(a \leq x \leq b) = \int_{a}^{b} p(x)\,\mathrm{d}x$$

- Furthermore, the continuous normalization condition becomes

$$\int_{-\infty}^{\infty} p(x)\,\mathrm{d}x = 1$$

- We may also analogously define

$$\langle x \rangle = \int_{-\infty}^{\infty} x p(x) \, \mathrm{d}x \qquad \langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 p(x) \, \mathrm{d}x \qquad \sigma_x^2 = \int_{-\infty}^{\infty} (x - \langle x \rangle)^2 p(x) \, \mathrm{d}x$$

- **Gaussian distribution**: The most commonly occuring and the most important continuous probability distribution. *Given by*

$$p(x) \, \mathrm{d}x = c \mathrm{e}^{-x^2/2a^2} \, \mathrm{d}x$$

  - Note that the normalization condition implies that

  $$c = \frac{1}{\sqrt{2\pi a^2}}$$

  - We can also prove that

  $$\sigma_x = a$$

  - Thus, the standard notation for a normalized Gaussian distribution function is

  $$p(x) \, \mathrm{d}x = \frac{1}{\sqrt{2\pi\sigma_x^2}} \mathrm{e}^{-x^2/2\sigma_x^2} \, \mathrm{d}x$$

  - Note that as σ_x gets smaller, the bell curves become narrower and taller, and vice versa as it gets larger.
  - A more general form (one that accounts for a center at $x = \langle x \rangle$ as opposed to just $x = 0$) is

  $$p(x) \, \mathrm{d}x = \frac{1}{\sqrt{2\pi\sigma_x^2}} \mathrm{e}^{-(x-\langle x \rangle)^2/2\sigma_x^2} \, \mathrm{d}x$$

2.5 Chapter 3: The Schrödinger Equation and a Particle In a Box

- **Schrödinger equation**: The fundamental equation of quantum mechanics. A differential equation whose solution $\psi(x)$ describes a particle of mass m moving in a potential field described by $V(x)$. *Given by*

$$-\frac{\hbar^2}{2m} \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x)\psi(x) = E\psi(x)$$

- **Wave function**: A solution to the Schrödinger equation. A measure of the amplitude of the matter wave. *Denoted by* $\boldsymbol{\psi(x)}$

- **Stationary-state wave function**: A solution to the time-independent Schrödinger equation.

- **Particle in a box**: A system consisting of a free particle of mass m that is restricted to lie along a one-dimensional interval of length a.

- **Spatial amplitude** (of a wave): The function $\psi(x)$ of position that serves as a coefficient to a time-dependent wave function.

- **Operator**: A symbol that tells you to do something to whatever follows the symbol. *Denoted by* a capital letter with a carat over it.

- **Linear operator**: An operator $\hat{A}$ such that

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x)$$

where c_1, c_2 are possible complex constants.

- **Eigenvalue problem**: The problem of determining $\phi(x)$ and a given $\hat{A}$ such that

$$\hat{A}\phi(x) = a\phi(x)$$

- **Eigenfunction**: The function $\phi(x)$ in an eigenvalue problem.

- **Eigenvalue**: The constant a in an eigenvalue problem.

- **Hamiltonian operator**: The following operator. *Denoted by $\bar{\boldsymbol{H}}$. Given by*

$$\bar{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)$$

- The substitution of the Hamiltonian operator into the Schrödinger equation allows us to formulate the Schrödinger equation as an eigenvalue problem.

  - The wave function then becomes the eigenfunction and the energy, the eigenvalue of the Hamiltonian operator.

- **Kinetic energy operator**: The following operator. *Denoted by $\hat{\boldsymbol{K}}_{\boldsymbol{x}}$. Given by*

$$\hat{K}_x = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$$

  - Defined by taking $V(x) = 0$ in the Hamiltonian.

- **Momentum operator**: The following operator. *Denoted by $\hat{\boldsymbol{P}}_{\boldsymbol{x}}$.*

$$\hat{P}_x = -i\hbar\frac{\mathrm{d}}{\mathrm{d}x}$$

  - Defined by applying $K = p^2/2m$ to the kinetic energy operator to get

$$\hat{P}_x^2 = -\hbar^2\frac{\mathrm{d}^2}{\mathrm{d}x^2}$$

  and then (noting that we define the square of an operator to be equivalent to applying the same operator successively) factoring the above into

$$\hat{P}_x^2 = \hat{P}_x\hat{P}_x = -\hbar^2\frac{\mathrm{d}^2}{\mathrm{d}x^2} = \left(-i\hbar\frac{\mathrm{d}}{\mathrm{d}x}\right)\left(-i\hbar\frac{\mathrm{d}}{\mathrm{d}x}\right)$$

- **Free particle**: A particle that experiences no potential energy, i.e., a particle for which $V(x) = 0$.

- When solving the particle in a box, we say that $\psi(x)$ represents the the amplitude of the particle in some sense. More specifically, since the intensity of a wave is the square of the magnitude of the amplitude, we write that the "intensity of the particle" is proportional to $\psi^*(x)\psi(x)$.

  - Born, a German physicist working in scattering theory, formalized this by saying that $\psi^*(x)\psi(x)\,\mathrm{d}x$ is the "probability that the particle is located between x and $x + \mathrm{d}x$" (McQuarrie & Simon, 1997, p. 80).

- Schrödinger's quantization of energy arises naturally from his equation and the boundary conditions, as opposed to having to be postulated as in Bohr's model.

- McQuarrie and Simon (1997) use the free-particle model to crudely explain the absorption spectrum of butadiene.

- **Normalized** (wave function): A wave function of the form

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}$$

- "Because the Hamiltonian operator is a linear operator, if ψ is a solution to $\hat{H}\psi = E\psi$, then any constant, say A, times ψ is also a solution, and A can always be chosen to produce a normalized solution to the Schrödinger equation" (McQuarrie & Simon, 1997, p. 84).

- **Correspondence principle**: Quantum mechanical results and classical mechanical results tend to agree in the limit of large quantum numbers.

- Applying the statistical principles to the particle in a box, we can calculate that

$$\langle x \rangle = \frac{a}{2} \qquad \langle x^2 \rangle = \frac{a^2}{3} - \frac{a^2}{2n^2\pi^2} \qquad \sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 \qquad \sigma_x = \frac{a}{2\pi n}\sqrt{\frac{\pi^2 n^2}{3} - 2}$$
$$= \left(\frac{a}{2\pi n}\right)^2 \left(\frac{\pi^2 n^2}{3} - 2\right)$$

- Calculating the average energy or momentum:

  - To calculate the average value of the physical quantity associated with an operator, we sandwich the operator between a wave function $\psi_n(x)$ and its complex conjugate $\psi_n^*(x)$.

  - This will be formalized later, but for now, we assume that

$$\langle s \rangle = \int \psi_n^*(x)\hat{S}\psi_n(x)\,\mathrm{d}x$$

  where $\hat{S}$ is the quantum-mechanical operator associated with the physical quantity s, and $\langle s \rangle$ is the average value of s in the state described for the wave function.

  - For example, the average momentum of a particle in a box in the state described by $\psi_n(x)$ is

$$\langle p \rangle = \int_0^a \left[\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}\right]\left(-i\hbar\frac{\mathrm{d}}{\mathrm{d}x}\right)\left[\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}\right]\mathrm{d}x$$

- Note that the average momentum of a particle in a box is zero.

References

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