CHEM 26100 (Quantum Mechanics) Notes

Steven Labalme

December 1, 2021

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 $500 - 600\,^{\circ}\mathrm{C}$, 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:
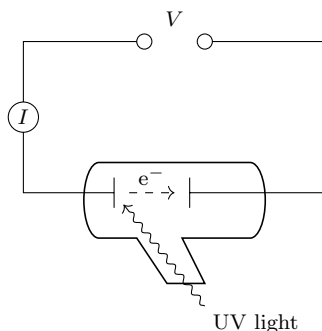
Figure 1.2: Photoelectric effect experiment.

– 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.

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

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 $364.7\,\text{nm}$.

- **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	$2, 3, 4, \ldots$	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

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

  - It follows that we should have

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

  which we indeed do.

Week 2

The Schrödinger Equation

2.1 Particle-Wave Duality and Uncertainty Relations

10/4:
- 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:

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

- 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?

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

  - 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:

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

– Adding/subtracting the two equations yields

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

– 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 $\rightarrow$ II.
    - If $E_0 > V$, the particle *always* passes from I $\rightarrow$ 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:

$$\psi_{\mathrm{I}}(x) = Ae^{i\alpha x} + Be^{-i\alpha x} \qquad\qquad \psi_{\mathrm{II}}(x) = Ce^{i\beta x} + De^{-i\beta x}$$

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

---

[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.

■ 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:

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

where $\beta_2 > 0$ by definition.
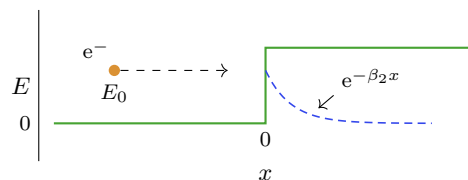
Figure 2.2: Quantum tunneling.

- 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

From McQuarrie and Simon (1997).

10/10:
- "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 $0 \leq N_j \leq N$ implies that $0 \leq p_j \leq 1$ 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*

$$\langle x \rangle = \sum_{j=1}^{n} x_j p_j = \sum_{j=1}^{n} x_j p(x_j)$$
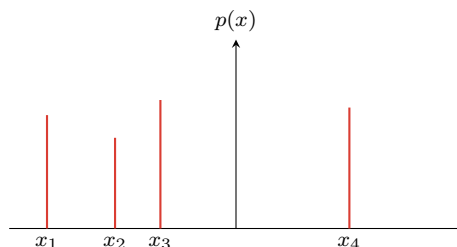
Figure 2.3: The discrete probability frequency function.

  - 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

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

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

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

  - 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

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

  - 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

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

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

From McQuarrie and Simon (1997).

- **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*

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

- **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.

10/12:
- Calculating the variance σ_p^2 of the momentum of a particle in a box.

  $$\langle p^2 \rangle = \int \psi_n^* \hat{P}_x^2 \psi_n(x)\,\mathrm{d}x$$
  $$= \frac{n^2\pi^2\hbar^2}{a^2}$$

  – It follows that $\sigma_p = n\pi\hbar/a$.

- **Root-mean-square momentum**: The square root of $\langle p^2 \rangle$.

- "Because the variance σ^2, and hence the standard deviation σ, is a measure of the spread of a distribution about its mean value, we can interpret σ as a measure of the uncertainty involved in any measurement" (McQuarrie & Simon, 1997, p. 89).

  – For the simple situation of a particle in a box, we can calculate *exact* uncertainties in position and momentum σ_x, σ_p.

    ■ We can see from these exact formulae that σ_x is directly proportional to the length a of the box, and σ_p is inversely proportional to the length a of the box.

    ■ This means that as the box gets bigger, it becomes harder to know where the particle is but its momentum becomes more certain, and vice versa as the box gets smaller.

  – From the above, it is clear that σ_x and σ_p have a reciprocal relation.

- Indeed, taking the product $\sigma_x \sigma_p$ yields the **Heisenberg Uncertainty Principle**

$$\sigma_x \sigma_p = \frac{\hbar}{2} \sqrt{\frac{\pi^2 n^2}{3} - 2}$$
$$> \frac{\hbar}{2}$$

- **Free particle**: A particle that is allowed to range over the entire x-axis.

  - "A free particle has a definite momentum, but its position is completely indefinite" (McQuarrie & Simon, 1997, p. 90).

- The Uncertainty Principle also says that the minimum product of the two uncertainties is on the order of Planck's constant.

- The particle in a three-dimensional box:

  - If the box (a rectangular parallelepiped) has sides of length a, b, c, then the Schrödinger equation for this case is

  $$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) = E\psi(x, y, z)$$

  where $0 \leq x \leq a$, $0 \leq y \leq b$, and $0 \leq z \leq c$.

    - An alternate form is

    $$-\frac{\hbar^2}{2m} \nabla^2 \psi = E\psi$$

  - Boundary conditions:

    - $\psi(0, y, z) = \psi(a, y, z) = 0$ for all y, z.
    - $\psi(x, 0, z) = \psi(x, b, z) = 0$ for all x, z.
    - $\psi(x, y, 0) = \psi(x, y, c) = 0$ for all x, y.

  - Invoke the method of separation of variables, i.e., suppose

  $$\psi(x, y, z) = X(x)Y(y)Z(z)$$

  - Then

  $$-\frac{\hbar^2}{2m} \frac{1}{X(x)} \frac{\mathrm{d}^2 X}{\mathrm{d}x^2} - \frac{\hbar^2}{2m} \frac{1}{Y(y)} \frac{\mathrm{d}^2 Y}{\mathrm{d}y^2} - \frac{\hbar^2}{2m} \frac{1}{Z(z)} \frac{\mathrm{d}^2 Z}{\mathrm{d}z^2} = E$$

  - It follows since each of the three terms contains only one of the variables and hence each of the terms can be varied independently that each term must equal a constant. The sum of the three constants will be E.

  - But dividing the above equations into three smaller equations gives us cases entirely analogous to the one-dimensional particle in a box, meaning that

  $$X(x) = A_x \sin \frac{n_x \pi x}{a} \qquad Y(y) = A_y \sin \frac{n_y \pi y}{b} \qquad Z(z) = A_z \sin \frac{n_z \pi z}{c}$$

  for $n = 1, 2, 3, \ldots$.

  - Therefore, the solution is

  $$\psi(x, y, z) = A_x A_y A_z \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c}$$

  - The normalization constant then turns out to be

  $$1 = \int_0^a \int_0^b \int_0^c \psi^*(x, y, z)\psi(x, y, z) \, \mathrm{d}x \, \mathrm{d}y \, \mathrm{d}z$$
  $$A_x A_y A_z = \sqrt{\frac{8}{abc}}$$

– We can now also obtain the following formula for the energies by plugging the full solution back into the original Schrödinger equation.

$$E_{n_x n_y n_z} = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

– McQuarrie and Simon (1997) does calculations to show that $\langle x \rangle = (a/2, b/2, c/2)$ and $\langle p \rangle = 0$.

– Note that we have the following 3D operators:

  ■ Position operator:
$$\hat{\mathbf{R}} = \hat{X}\mathbf{i} + \hat{Y}\mathbf{j} + \hat{Z}\mathbf{k}$$

  ■ Momentum operator:
$$\hat{\mathbf{P}} = -i\hbar \left(\mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z} \right)$$

– Consider the special case where $a = b = c$. Then only one set of values n_x, n_y, n_z corresponds to the lowest energy level, but *three degenerate ones* correspond to the second energy level (211, 121, 112).

  ■ Note that the degeneracy is introduced by the symmetry of the box and is lifted when the box becomes no longer symmetric.

- **Laplacian operator**: The operator ∇^2.

- **Separable** (operator): An operator that is the sum of multiple variably independent terms.

Week 3

Vibrational Motion and the Harmonic Oscillator

3.1 Vibrational Motion and the Harmonic Oscillator

10/11:

- Suppose we have an attractive force F proportional to the displacement x from the center of a system

$$F = -kx$$

  - Then we also have an associated potential energy

$$V(x) = \frac{1}{2}kx^2$$

  - Recall that $F = -\partial V/\partial x$.

- Thus, we have a harmonic (or parabolic) potential well.

(a) Harmonic (parabolic) well. (b) Approximating a potential well.

Figure 3.1: Parabolic potential wells.

  - However, because this is a quantum system, the attainable energy levels will be quantized (see Figure 3.1a).
  - We can use a parabolic well to approximate the minimum of the potential well (see Figure 3.1b).

- **Reduced mass**: For two objects of mass m_A, m_B, the quantity

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

  - We can map the two body problem of two atoms being drawn together and pulled apart onto the one body problem of a single harmonic oscillator of reduced mass μ at the center of mass of the diatomic system.

Labalme 26

- The Taylor series expansion of the Moiré Potential about $x = a$ where a is the minimum potential:

$$W(x) = W(a) + (x-a)W'(a) + \frac{1}{2!}(x-a)^2 W''(a) + \cdots$$

$$= W(a) + \frac{1}{2}(x-a)^2 W''(a)$$

$$= \frac{1}{2}kx^2$$

  - We reduce by noting that $W'(a) = 0$ at the minimum of the potential well, we can let $W(a) = 0$, we can set $a = 0$ to be the origin of our coordinate system, and we can let $k = W''(a)$.

- The Schrödinger equation describing this system is

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + \frac{1}{2}m\omega^2 x^2 \psi(x) = E\psi(x)$$

  - Note that since $\omega = \sqrt{k/m}$, we substituted $k = m\omega^2$.

- If we let $x = y\sqrt{\hbar/m\omega}$ and $E = \omega\hbar\epsilon/2$, then we can simplify the above to the form

$$\frac{d^2}{dy^2}\psi(y) + (\epsilon - y^2)\psi(y) = 0$$

- Asymptotic solution: In the limit of large y, the finite value of ϵ becomes negligible, that is

$$\frac{d^2}{dy^2}\psi(y) - y^2\psi(y) = 0$$

- General form solution:

$$\psi(y) = y^p e^{-y^2/2}$$

  - This is the Gaussian exponential.
  - p is any integer.

- Because the sign of the exponential must be negative for the wave function to be bounded, we have the form
$$\psi(y) = e^{-y^2/2}H(y)$$
where $H(y)$ are polynomials.

- Hermite equation:

$$\frac{d^2}{dy^2}H(y) - 2y\frac{d}{dy}H(y) - (\epsilon - 1)H(y) = 0$$

  - Whenever $H(y)$ solves this equation, it yields a full solution.

- What are the correct polynomials?

  - The polynomials that are even about the origin will give us the even solutions, and vice versa for the odd ones.
  - Even solution: Because the potential has a definite parity (even-ness or odd-ness), we know that the solution to the polynomials must be even or odd.
  - Expanding in an infinite power series:

$$H(y) = \sum_{j=0}^{\infty} c_j y^{2j}$$

- This is the power series solution to differential equations. We have to plug into the differential equation and get a recursion relation.

  - Upon substitution,

$$\sum_{j=0}^{\infty} \left(2j(2j-1)c_j y^{2j-2} + (\epsilon - 1 - 4j)c_j y^{2j}\right) = 0$$

  - The indices are arbitrary, so

$$\sum_{j=0}^{\infty}(2(j+1)(2j+1)c_{j+1} + (\epsilon - 1 - 4j))y^{2j} = 0$$

  - Recursion relation: The whole coefficient above must equal 0 for all j, but that gives us a relationship between c_j and c_{j+1}! Explicitly,

$$c_{j+1} = \frac{4j + 1 - \epsilon}{2(j+1)(2j+1)}c_j$$

- How do we know when to stop?

  - If the recursion never stops, then the ratio is approximately equal to

$$\frac{c_{j+1}}{c_j} = \frac{1}{j}$$

  - But this means that asymptotically, the boundary conditions will be violated because it will keep expanding. The probability of finding the particle will actually diverge (infinite probability at infinite distances). Thus, the expansion procedure *must* terminate.
  - The truncation of this expansion requires us to pick a particular energy ϵ (in particular, one such that $\epsilon = 4j + 1$).

- Test on Friday:

  - 5 questions. Each question is approximately 20 points.
  - There will be a formula page in the back with formulas and constants.
  - There will be a periodic table provided.
  - Topics: Everything in problem sets 1-2. BB radiation, Photoelectric effect, SG experiment, particle-wave duality, Heisenberg uncertainty relations, Gaussian wave packets and their role in the Heisenberg uncertainty, de Broglie formula, free particles, particle in a box, potential step, and a bit of the harmonic oscillator.
  - Study for it by going back to the problem sets and seeing which ones might be doable in a 50 minute test.
  - Go back to your notes and review some of the key highlights of each of the topics in the topic list.
  - You're allowed to use a calculator. The test won't be too calculator-heavy though.
  - Deriving vs. understanding and applying: Emphasis on applying and getting answers.

3.2 Harmonic Oscillator (cont.)

10/13:
- Assume that the $(n+1)^{\text{th}}$ coefficient vanishes by the recurrence relation; this causes the energy to be quantized.

  - Therefore, $\epsilon = 4n + 1$.

- For each value of n, there is an even Hermite polynomial[1].

    - Thus, our even solutions include $H_0(y) = 1$, $H_2(y) = 4y^2 - 2$, $H_4(y) = 16y^4 - 48y^2 - 2$, for example.

- Odd solutions:

    - Let

    $$H(y) = \sum_{j=0}^{\infty} d_j y^{2j+1}$$

    - Our recurrence relation works out to be

    $$d_{j+1} = \frac{4j + 3 - \epsilon}{2(j+1)(2j+3)} d_j$$

    - Again, if it does not terminate, $d_{j+1}/d_j \approx 1/j$, so the solutions will blow up at the edges due to the high powers of y. Therefore, the series must truncate.
    - If the coefficient at n exists but the next one will vanish, it must be true that $4n + 3 = \epsilon$.
    - Example odd solutions: $H_1(y) = 2y$, $H_3(y) = 8y^3 - 12y$, $H_5(y) = 32y^5 - 160y^3 + 120y$.
        - Note that you can make the coefficients pretty much of any scale because they will be normalized later as part of the wave function.

- Energies and wave functions:

    - The energy levels are $\epsilon_n = 2n + 1$ for $n = 0, 1, 2, \ldots$ or $E_n = (n + \frac{1}{2})\hbar\omega$ for $n = 0, 1, 2, \ldots$.
    - It follows that if $\psi(y) = N_y e^{-y^2/2} H_n(y)$, where

    $$N_y = \frac{1}{\sqrt{2^n n! \sqrt{\pi}}}$$

    - In terms of x, we get

    $$N_x = \sqrt[4]{\frac{\omega m}{\hbar}} N_y$$

    - Observations:
        1. The energy levels are quantized (discrete).
        2. The energy levels are equally spaced apart where $\Delta E = h\nu$.
        3. The energy levels are non-degenerate.
        4. The zero-point energy is equal to $\hbar\omega/2$. (Recall that the finite energy is there due to the Uncertainty Relation.)
        5. Similar to the levels discovered by Max Planck.

- Classical harmonic oscillator:

    - Position: $x = x_0 \sin(\omega t)$.
    - Velocity: $v = \cos x_0 \sin(\omega t)$.
    - Energy: $E = m\omega^2 x_0^2/2$.
    - Turning point: $x_0 = \sqrt{2E/m\omega^2}$.
    - Probability of the oscillator being at x:

    $$P(x)\,\mathrm{d}x = \frac{\frac{2\mathrm{d}x}{v}}{T} = \frac{\mathrm{d}x}{\pi\sqrt{x_0^2 - x^2}}$$

---

[1]So named because they were studied by the mathematician Charles Hermite before they were utilized in Quantum Mechanics.

■ Thus, classically, the oscillator spends most of its time at the turning points (this makes intuitive sense because a pendulum slows down at the turning points, spending more time there).

■ In quantum mechanics, we don't have a hard turning point the way we do classically.

■ Classical limit of quantum theory: In higher and higher order Hermite polynomials, the probability gets pushed to the edges.

3.3 Chapter 4: Some Postulates and General Principles of Quantum Mechanics

From McQuarrie and Simon (1997).

10/19:
- **Dynamical variable**: A quantity dealt with by classical mechanics, e.g., position, momentum, angular momentum, and energy.

- **Observable**: A measurable dynamical variable.

- "The classical-mechanical state of a particle at any particular time is specified completely by the three position coordinates (x, y, z) and the three momenta (p_x, p_y, p_z) or velocities (v_x, v_y, v_z) at that time. The time evolution of the system is governed by Newton's equation" $F = ma$ applied separately in each dimension (McQuarrie & Simon, 1997, p. 115).

- **Trajectory** (of a classical particle): The three-dimensional path of the particle described by the initial conditions and Newton's laws.

  - A particle's trajectory completely describes its state.

- However, since the Uncertainty Principle decrees that we cannot specify the position and momentum of a *microscopic*[2] particle to any desired precision, we have our first postulate of quantum mechanics.

  Postulate 1. *The state of a quantum-mechanical system is completely specified by a function $\psi(x)$ that depends upon the coordinate of the particle. All possible information about the system can be derived from $\psi(x)$. This function, called the wave function or the state function, has the important property that $\psi^*(x)\psi(x)\,\mathrm{d}x$ is the probability that the particle lies in the interval $\mathrm{d}x$, located at the position x.*

  - We will use one-dimensional notation, but note that what is stated in the postulates is equally applicable to two or three dimensions.

  - "If there is more than one particle, say two, then $\psi^*(x_1, x_2)\psi(x_1, x_2)\,\mathrm{d}x_1\,\mathrm{d}x_2$ is the probability that particle 1 lies in the interval $\mathrm{d}x_1$ located at x_1, and that particle 2 lies in the interval $\mathrm{d}x_2$ located at x_2" (McQuarrie & Simon, 1997, p. 116).

- **Normalizable** (function): A function $\psi(x)$ for which the following integral converges.

$$\int_{\text{all space}} \psi^*(x)\psi(x)\,\mathrm{d}x$$

- **Well-behaved** (function): A function $\psi(x)$ such that it and its first derivative are single-valued, continuous, and finite.

- Every state function must be normalizable and well-behaved.

- We now formalize the notion that classical mechanical quantities have analogous linear operators in quantum mechanics.

  Postulate 2. *To every observable in classical mechanics, there corresponds a linear Hermitian operator in quantum mechanics.*

OBSERVABLE		OPERATOR	
Name	**Symbol**	**Symbol**	**Operation**
Position	x	$\hat{X}$	Multiply by x
	$\mathbf{r}$	$\hat{\mathbf{R}}$	Multiply by $\mathbf{r}$
Momentum	p_x	$\hat{P}_x$	$-i\hbar\dfrac{\partial}{\partial x}$
	$\mathbf{p}$	$\hat{\mathbf{P}}$	$-i\hbar\left(\mathbf{i}\dfrac{\partial}{\partial x}+\mathbf{j}\dfrac{\partial}{\partial y}+\mathbf{k}\dfrac{\partial}{\partial z}\right)$
Kinetic energy	K_x	$\hat{K}_x$	$-\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2}$
	K	$\hat{K}$	$-\dfrac{\hbar^2}{2m}\nabla^2$
Potential energy	$V(x)$	$\hat{V}(\hat{x})$	Multiply by $V(x)$
	$V(x,y,z)$	$\hat{V}(\hat{x},\hat{y},\hat{z})$	Multiply by $V(x,y,z)$
Total energy	E	$\hat{H}$	$-\dfrac{\hbar^2}{2m}\nabla^2+V(x,y,z)$
Angular momentum	$L_x=yp_z-zp_y$	$\hat{L}_x$	$-i\hbar\left(y\dfrac{\partial}{\partial z}-z\dfrac{\partial}{\partial y}\right)$
	$L_y=zp_x-xp_z$	$\hat{L}_y$	$-i\hbar\left(z\dfrac{\partial}{\partial x}-x\dfrac{\partial}{\partial z}\right)$
	$L_z=xp_y-yp_x$	$\hat{L}_z$	$-i\hbar\left(x\dfrac{\partial}{\partial y}-y\dfrac{\partial}{\partial x}\right)$

Table 3.1: Classical-mechanical observables and their corresponding quantum-mechanical operators.

- Note that we derive the expressions for L_x, L_y, L_z in Table 3.1 from $\mathbf{r}\times\mathbf{p}$.

- If an eigenvalue problem is two-fold degenerate with linearly independent solutions ϕ_1, ϕ_2, then any linear combination of ϕ_1, ϕ_2 is also a solution.

- Although each observable has a corresponding operator by Postulate 2, only eigenvalues of our operators are actually observable.

  Postulate 3. *In any measurement of the observable associated with the operator $\hat{A}$, the only values that will ever be observed are the eigenvalues a_n, which satisfy the eigenvalue equation*

$$\hat{A}\psi_n = a_n\psi_n$$

- We now formally introduce the method for finding the average values of observables.

  Postulate 4. *If a system is in a state described by a normalized wave function ψ, then the average value of the observable corresponding to $\hat{A}$ is given by*

$$\langle a\rangle = \int_{all\ space}\psi^*(x)\hat{A}\psi(x)\,\mathrm{d}x$$

- Note that we can prove from Postulate 4 that σ for any observable is zero, i.e., that we *can* only observe the eigenvalues.

- We now postulate the time-dependent Schrödinger equation[3].

---

[2]Note that classical mechanics still describes *macroscopic* bodies perfectly well.
[3]Note that just like Newton's laws, we cannot derive this — we can only show that data is consistent with it.

Postulate 5. *The wave function (or state function) of a system evolves in time according to the time-dependent Schrödinger equation*

$$\hat{H}\psi(x,t) = i\hbar\frac{\partial\psi(x,t)}{\partial t}$$

- Relating the time-dependent and time-independent Schrödinger equations.

    - Consider a system where $\hat{H}$ does not explicitly contain time.
    - In such a case, we may use separation of variables and let

    $$\psi(x,t) = \psi(x)f(t)$$

    - Substituting in the above and dividing by $\psi(x)f(t)$ allows us to fully separate the variables:

    $$\hat{H}\psi(x)f(t) = i\hbar\frac{\mathrm{d}\psi(x)f(t)}{\mathrm{d}t}$$
    $$f(t)\hat{H}\psi(x) = i\hbar\psi(x)\frac{\mathrm{d}f(t)}{\mathrm{d}t}$$
    $$\frac{1}{\psi(x)}\hat{H}\psi(x) = \frac{i\hbar}{f(t)}\frac{\mathrm{d}f(t)}{\mathrm{d}t}$$

    - But if two functions of entirely different variables are equal, the individual functions must both be constant. If we let the constant they are both equal to be E, then we obtain

    $$\frac{1}{\psi(x)}\hat{H}\psi(x) = E \qquad\qquad \frac{i\hbar}{f(t)}\frac{\mathrm{d}f(t)}{\mathrm{d}t} = E$$
    $$\hat{H}\psi(x) = E\psi(x) \qquad\qquad \frac{\mathrm{d}f(t)}{\mathrm{d}t} = \frac{1}{-i^{-1}\hbar}Ef(t)$$
    $$= -\frac{i}{\hbar}Ef(t)$$
    $$f(t) = \mathrm{e}^{-iEt/\hbar}$$

    - The left equation above is the time-independent Schrödinger equation, and the right equation allows us to define the general form of a time-dependent wave function as follows.

    $$\psi(x,t) = \psi(x)f(t)$$
    $$= \psi(x)\mathrm{e}^{-iEt/\hbar}$$

- Note, however, that even the time-*dependent* Schrödinger equation gives stationary-state probability densities and averages:

$$\psi_n^*(x,t)\psi_n(x,t)\,\mathrm{d}x = \psi^*(x)\mathrm{e}^{iE_nt/\hbar}\psi_n(x)\mathrm{e}^{-iE_nt/\hbar}\,\mathrm{d}x$$
$$= \psi_n^*(x)\psi_n(x)\,\mathrm{d}x$$

- **Stationary-state** (wave function): The $\psi_n(x)$ in the above equation.

- It follows from postulate 3 that the eigenvalues of quantum mechanical operators must be real (not complex) if they are to, indeed, to be observable.

    - A consequence of this is that any two eigenfunctions $\psi_m(x), \psi_n(x)$ where $m \neq n$ of quantum-mechanical operators are **orthogonal**.

- **Orthogonal** (wave functions): Two wave functions $\psi_m(x), \psi_n(x)$ such that

$$\int_{-\infty}^{\infty} \psi_m^*(x)\psi_n(x) = 0$$

- **Orthonormal** (set of wave functions): A set of wave functions that are both normalized and mutually orthogonal.

  - In other words, a set $\psi_1, \ldots, \psi_n$ of wave functions is orthonormal iff

  $$\int_{-\infty}^{\infty} \psi_i^* \psi_j \, \mathrm{d}x = \delta_{ij}$$

  for all $1 \leq i, j \leq n$.

- Note that if a quantum-mechanical operator $\hat{A}$ is to have real eigenvalues, it must satisfy the equation

  $$\int_{\text{all space}} f^*(x) \hat{A} g(x) \, \mathrm{d}x = \int_{\text{all space}} g(x)[\hat{A}f]^*(x) \, \mathrm{d}x$$

  where f, g are any two state functions.

  - McQuarrie and Simon (1997) does a worked example of applying the above equation to the momentum operator in the context of the solutions to the one-dimensional harmonic oscillator problem.

- **Hermitian** (operator): An operator that satisfies the previous equation.

- **Commutator** (of $\hat{A}, \hat{B}$): The operator defined as follows. *Denoted by* $[\boldsymbol{\hat{A}}, \boldsymbol{\hat{B}}]$. *Given by*

  $$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

  - We can show that $\hat{A}$ and $\hat{B}$ commute iff the commutator is equal to the zero operator.

- Relating the Uncertainty Principle and the commutator (without proof):

  - Consider two operators $\hat{A}, \hat{B}$ and the standard deviations σ_a, σ_b corresponding to the uncertainties in the observed values of their respective physical quantities.
  - It follows from the fact that

  $$\sigma_a^2 = \langle A^2 \rangle - \langle A \rangle^2 = \int \psi^*(x) \hat{A}^2 \psi(x) \, \mathrm{d}x - \left[\int \psi^*(x) \hat{A} \psi(x) \, \mathrm{d}x \right]^2$$

  (and similarly for σ_b) that

  $$\sigma_a \sigma_b \geq \frac{1}{2} \left| \int \psi^*(x) [\hat{A}, \hat{B}] \psi(x) \, \mathrm{d}x \right|$$

- Results from the above.

  - If $\hat{A}, \hat{B}$ commute, there is no restriction on the uncertainties in the measurements of a and b.
  - If $\hat{A}, \hat{B}$ do not commute, there will be a restriction on the precision to which we can measure a and b, namely that as our measurements of one get more precise, our measurements of the other necessarily get less precise.
  - In particular, if we consider the case of $\hat{X}, \hat{P}_x$ (the operators corresponding to the standard uncertainty relation), we have that

  $$\hat{P}_x \hat{X} \psi(x) = \left(-i\hbar \frac{\mathrm{d}}{\mathrm{d}x} \right) x \psi(x) \qquad\qquad \hat{X} \hat{P}_x = x \left(-i\hbar \frac{\mathrm{d}}{\mathrm{d}x} \right) \psi(x)$$

  $$= -i\hbar \psi(x) - i\hbar x \frac{\mathrm{d}\psi}{\mathrm{d}x} \qquad\qquad\qquad = -i\hbar x \frac{\mathrm{d}\psi}{\mathrm{d}x}$$

so the corresponding commutator is

$$[\hat{P}_x, \hat{X}] = \hat{P}_x \hat{X} - \hat{X} \hat{P}_x$$

$$= \left[-i\hbar \hat{I} - i\hbar x \frac{d}{dx} \right] - \left[-i\hbar x \frac{d}{dx} \right]$$

$$= -i\hbar \hat{I}$$

so

$$\sigma_p \sigma_x \geq \frac{1}{2} \left| \int \psi^*(x)(-i\hbar \hat{I})\psi(x)\, dx \right|$$

$$= \frac{1}{2} \left| -i\hbar \int \psi^*(x)\psi(x)\, dx \right|$$

$$= \frac{1}{2} \left| -i\hbar \cdot 1 \right|$$

$$= \frac{\hbar}{2}$$

which is the typical formulation of the Heisenberg Uncertainty Relation.

3.4 MathChapter D: Spherical Coordinates

From McQuarrie and Simon (1997).

- We can integrate products of multiple variables one at a time and multiply the results instead of taking a traditional triple integral.

- Example:

  - To find the volume of a sphere of radius a with a triple integral, we'd traditionally do the following.

$$V = \int_0^{2\pi} \int_0^{\pi} \int_0^{a} r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$= \int_0^{2\pi} \int_0^{\pi} \frac{a^3}{3} \sin\theta \, d\theta \, d\phi$$

$$= \int_0^{2\pi} \frac{a^3}{3} \cdot 2 \, d\phi$$

$$= \frac{4}{3}\pi a^3$$

  - However, we can alternatively do the following.

$$V = \int_0^{2\pi} \int_0^{\pi} \int_0^{a} r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$= \frac{a^3}{3} \int_0^{2\pi} \int_0^{\pi} \sin\theta \, d\theta \, d\phi$$

$$= \frac{a^3}{3} \cdot 2 \int_0^{2\pi} d\phi$$

$$= \frac{a^3}{3} \cdot 2 \cdot 2\pi$$

$$= \left(\int_0^{a} r^2 \, dr \right) \left(\int_0^{\pi} \sin\theta \, d\theta \right) \left(\int_0^{2\pi} d\phi \right)$$

- In fact, to generalize, we can express an integral of the form

$$I = \int_0^\infty \int_0^\pi \int_0^{2\pi} F(r, \theta, \phi) r^2 \sin\theta \, \mathrm{d}r \, \mathrm{d}\theta \, \mathrm{d}\phi$$

  as an operator

$$I = \int_0^\infty \mathrm{d}r \, r^2 \int_0^\pi \mathrm{d}\theta \sin\theta \int_0^{2\pi} \mathrm{d}\phi \, F(r, \theta, \phi)$$

  where we understand each integral to act on everything that lies to its right, i.e., "we first integrate $F(r, \theta, \phi)$ over ϕ from 0 to 2π, then multiply the result by $\sin\theta$ and integrate over θ from 0 to ϕ, and finally multiply the result by r^2 and integrate over r from 0 to ∞" (McQuarrie & Simon, 1997, p. 150).

- If our integrand is spherically symmetric, i.e., $F(r, \theta, \phi) = f(r)$, then

$$I = \int_0^\infty \mathrm{d}r \, r^2 \int_0^\pi \mathrm{d}\theta \sin\theta \int_0^{2\pi} \mathrm{d}\theta \, f(r) = \int_0^\infty f(r) 4\pi r^2 \, \mathrm{d}r$$

  - In other words, we take a one-dimensional integral, but multiply the integrand by a factor of $4\pi r^2 \, \mathrm{d}r$, which is the volume of a spherical shell of radius r and thickness $\mathrm{d}r$.

- On the other hand, we can also hold r constant and integrate over the surface of a sphere of unit radius.

  - In this case, we sum pieces of differential surface area

$$\mathrm{d}A = \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi$$

- **Solid angle**: The solid enclosed by the surface that connects the origin and the area $\mathrm{d}A$.

  - In the same way that a complete angle of the unit circle is 2π, a complete solid angle is 4π.
  - We often denote a complete solid angle by $\mathrm{d}\Omega$. Thus, we can write

$$\int_{\text{sphere}} \mathrm{d}\Omega = 4\pi$$

- The quantum theory of the hydrogen atom frequently involves angular integrals of the form

$$I = \int_0^\pi \mathrm{d}\theta \sin\theta \int_0^{2\pi} \mathrm{d}\phi \, F(\theta, \phi)$$

3.5 Chapter 5: The Harmonic Oscillator and the Rigid Rotator — Two Spectroscopic Models

From McQuarrie and Simon (1997).

- **Hooke's law**: The equation describing the motion of a spring whose restoring force is directly proportional to its displacement from equilibrium. *Given by*

$$f = -kx$$

- **Force constant** (of a spring): The positive proportionality constant k in the Hooke's law description of the spring.

- The general solution to $ma = f = -kx$ is

$$x(t) = c_1 \sin\omega t + c_2 \cos\omega t$$

  where $\omega = \sqrt{k/m}$.

- This solution can be rewritten in the form

$$x(t) = A \sin(\omega t + \phi)$$

- Thus, the displacement oscillates sinusoidally, or harmonically, with a natural frequency ω, an amplitude A, and a phase angle ϕ.

- Additionally, since $f = -\,\mathrm{d}V/\mathrm{d}x$ where V is the potential energy of the system, we have that

$$-\frac{\mathrm{d}V}{\mathrm{d}x} = -kx$$

$$V(x) = \frac{1}{2}kx^2 + C$$

where C is an arbitrary constant used to fix the zero energy.

- Kinetic and potential energy:

  - If $x(t) = A \cos \omega t$, then

$$K = \frac{1}{2}m\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)^2 \qquad\qquad V = \frac{1}{2}k[x(t)]^2$$

$$= \frac{1}{2}m\omega^2 A^2 \sin^2 \omega t \qquad\qquad = \frac{1}{2}kA^2 \cos^2 \omega t$$

  - It follows that the total energy is

$$E = K + V$$

$$= \frac{1}{2}m\omega^2 A^2 \sin^2 \omega t + \frac{1}{2}kA^2 \cos^2 \omega t$$

$$= \frac{1}{2}kA^2(\sin^2 \omega t + \cos^2 \omega t)$$

$$= \frac{1}{2}kA^2$$

  - Since the total energy is constant, the system is **conservative**.

- **Conservative system**: A system in which the total energy is conserved.

- We now analyze a harmonic oscillator classically.

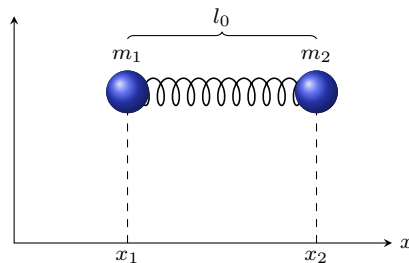Figure 3.2: Harmonically oscillating diatomic molecule.

- We have two equations of motion, one for each mass.

$$m_1 \frac{\mathrm{d}^2 x_1}{\mathrm{d}t^2} = k(x_2 - x_1 - l_0) \qquad\qquad m_2 \frac{\mathrm{d}^2 x_2}{\mathrm{d}t^2} = -k(x_2 - x_1 - l_0)$$

- If we add them, we get the equation

$$\frac{d^2}{dt^2}(m_1 x_1 + m_2 x_2) = 0$$

which tells us that the center of mass of the system is not accelerating.

- Thus, the motion of the two-body system must depend only on the relative separation of the two masses, or on the **relative coordinate**

$$x = x_2 - x_1 - l_0$$

- Indeed, subtracting the initial two equations and substituting for both the relative coordinate and **reduced mass**

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

gives us

$$\frac{d^2 x_2}{dt^2} - \frac{d^2 x_1}{dt^2} = -\frac{k}{m_2}(x_2 - x_1 - l_0) - \frac{k}{m_1}(x_2 - x_1 - l_0)$$

$$\frac{d^2}{dt^2}(x_2 - x_1) = -k\left(\frac{1}{m_1} + \frac{1}{m_2}\right)(x_2 - x_1 - l_0)$$

$$\mu\frac{d^2 x}{dt^2} + kx = 0$$

- Conclusion: The kinematics of a diatomic harmonic oscillator are identical to those of a single ball on a spring except with the reduced mass and relative coordinate.

- "Generally, if the potential energy depends upon only the *relative* distances between two bodies, then we can introduce relative coordinates such as $x_2 - x_1$ and reduce a two-body problem to a one-body problem" (McQuarrie & Simon, 1997, p. 163).

- Note that while the harmonic oscillator potential may be a terrible approximation of the exponential curve of bond energy overall, it is a very good approximation in the region of the minimum, which is the physically important region for many molecules at room temperature. In particular, the approximation works well for oscillators of small amplitude.

- **Equilibrium bond length**: The bond length at the minimum potential energy of a molecule.

- McQuarrie and Simon (1997) goes through the Taylor series derivation of Hooke's law for diatomic molecules.

  - Additional result: The force constant is equal to the curvature of $V(l)$ at the minimum.

- **Anharmonic term**: A term in the Taylor series expansion of a potential energy curve about the minimum of degree greater than two.

- **Morse potential**: An approximation of an intermolecular potential energy curve. *Given by*

$$V(l) = D(1 - e^{-\beta(l - l_0)})^2$$

  - D is the dissociation energy of the molecule measured from the minimum of $V(l)$.
  - β is a measure of the curvature of $V(l)$ at its minimum.
  - McQuarrie and Simon (1997) derives from the Taylor series expansion of the Morse potential about $V(l_0)$ that the force constant $k = 2D\beta^2$.

- We are now ready to discuss a quantum-mechanical harmonic oscillator.

- Because of our prior simplification of a two-body harmonic oscillator to a single particle of reduced mass μ moving in a potential field described by $V(x) = kx^2/2$, we have that the Schrödinger equation for a one-dimensional harmonic oscillator is

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

$$\frac{d^2\psi}{dx^2} + \frac{2\mu}{\hbar^2}\left(E - \frac{1}{2}kx^2\right)\psi(x) = 0$$

  - This differential equation does not have constant coefficients, so we need a new, custom method to solve it.
  - Indeed, when solved, well-behaved solutions can be obtained only if the energy is restricted to the quantized values

$$E_v = \hbar\omega\left(v + \frac{1}{2}\right) = h\nu\left(v + \frac{1}{2}\right)$$

  where $\omega = \sqrt{k/\mu}$, $\nu = \omega/2\pi$, and $v = 0, 1, 2, \ldots$.
  - Note that these energy levels are equally spaced apart (see Figure 3.1a).
  - Note the nonzero zero-point energy — since $E = p^2/2\mu + kx^2/2$, we cannot have $E = 0$ as this would imply that $0 = 0 \cdot 0 = (\Delta x)(\Delta p) < \hbar/2$, violating the Uncertainty Principle.

- **Selection rule**: A criterion that narrows the states between which a quantum system can move.

- McQuarrie and Simon (1997) will later prove that the harmonic oscillator model allows transitions only between adjacent energy states.

  - Thus, the only frequency absorbed or emitted by a diatomic harmonic oscillator should be

$$\begin{aligned}
\nu_{\text{obs}} &= \frac{\Delta E}{h} \\
&= \frac{E_{v+1} - E_v}{h} \\
&= \frac{h\nu}{h} \\
&= \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}
\end{aligned}$$

  - We can convert to wavenumbers by dividing the above by c.

- **Fundamental vibration frequency**: The single frequency absorbed or emitted by a diatomic molecule.

  - We can use the fundamental vibration frequency and the above equation to calculate the force constant of the attraction.

- McQuarrie and Simon (1997) will later prove that the dipole moment of the molecule must change as the molecule vibrates in order for it to absorb infrared radiation.

- As a last note, be aware that although deviations from the prediction do crop up, they can be systematically corrected for.

- Harmonic oscillator wave functions:

$$\psi_v(x) = N_v H_v(\sqrt{\alpha}x)e^{-\alpha x^2/2}$$

– We have

$$\alpha = \frac{\sqrt{k\mu}}{\hbar} \qquad\qquad N_v = \frac{1}{\sqrt{2^v v!}} \sqrt[4]{\frac{\alpha}{\pi}}$$

where N_v is a normalization constant and $H_v(\sqrt{\alpha}x)$ is the vth-degree **Hermite polynomial** in $\sqrt{\alpha}x$.

- **Hermite polynomials**: A classical orthogonal polynomial sequence. *Examples*

$H_0(\xi) = 1$	$H_1(\xi) = 2\xi$
$H_2(\xi) = 4\xi^2 - 2$	$H_3(\xi) = 8\xi^3 - 12\xi$
$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12$	$H_5(\xi) = 32\xi^5 - 160\xi^3 + 120\xi$

Table 3.2: The first few Hermite polynomials.

- The polynomials in Table 3.2 allow us to generate the first few wave functions.

$\psi_0(x) = \sqrt[4]{\dfrac{\alpha}{\pi}}e^{-\alpha x^2/2}$	$\psi_1(x) = \sqrt[4]{\dfrac{4\alpha^3}{\pi}}xe^{-\alpha x^2/2}$
$\psi_2(x) = \sqrt[4]{\dfrac{\alpha}{4\pi}}(2\alpha x^2 - 1)e^{-\alpha x^2/2}$	$\psi_3(x) = \sqrt[4]{\dfrac{\alpha^3}{9\pi}}(2\alpha x^3 - 3x)e^{-\alpha x^2/2}$

Table 3.3: The first few harmonic-oscillator wave functions.

- When graphed, the above wave functions and their corresponding probabilities look like the following.

Figure 3.3: Harmonic-oscillator wave functions and probability densities.

– Notice how the probability distributions are slowly converging to the classical limit of a parabola of peaks.

- McQuarrie and Simon (1997) proves that a couple of the given wave functions satisfy the relevant Schrödinger equation, are normalized, and are orthogonal.

- Hermite polynomials are even functions if v is even and odd functions if v is odd.

  – Thus, ψ_v is even when v is even, and odd when v is odd.
  – It follows that ψ_v^2 is even for any v (since the square of either an odd or even function is even).

- Consequently, since $x\psi_v^2(x)$ is odd, we have that

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_v(x) x \psi_v(x) \, dx = 0$$

  for a harmonic operator

- Similarly, since the derivative of an even function is odd and the product of an even and odd function is odd, we have that

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi_v(x) \left(-i\hbar \frac{d}{dx} \right) \psi_v(x) \, dx = 0$$

  for a harmonic operator.

Problems

10/26: **3-28.** The Schrödinger equation for a particle of mass m constrained to move on a circle of radius a is

$$-\frac{\hbar^2}{2I} \frac{d^2\psi}{d\theta^2} = E\psi(\theta)$$

where $I = ma^2$ is the moment of inertia and $0 \le \theta \le 2\pi$ is the angle that describes the position of the particle around the ring. Show by direct substitution that the solutions to this equation are

$$\psi(\theta) = Ae^{in\theta}$$

where $n = \pm\sqrt{2IE}/\hbar$. Argue that the appropriate boundary condition is $\psi(\theta) = \psi(\theta + 2\pi)$ and use this condition to show that

$$E = \frac{n^2\hbar^2}{2I}$$

where $n = 0, \pm 1, \pm 2, \ldots$. Show that the normalization constant A is $1/\sqrt{2\pi}$. Discuss how you might use these results for a free-electron model of benzene.

Answer. We have that

$$
\begin{aligned}
E(Ae^{in\theta}) &= -\frac{\hbar^2}{2I} \frac{d^2}{d\theta^2} \left(Ae^{in\theta} \right) \\
&= \frac{An^2\hbar^2}{2I} e^{in\theta} \\
&= \frac{2IEA\hbar^2}{2\hbar^2 I} e^{in\theta} \\
&= EAe^{in\theta}
\end{aligned}
$$

so the given wave wave function is a solution to the given Schrödinger equation, as desired.

Since the free space is a 2D ring into which all wave functions must "fit," i.e., align in phase, it is necessary that $\psi(\theta) = \psi(\theta + 2\pi)$. Substituting in our solutions, we have that

$$
\begin{aligned}
Ae^{in\theta} &= Ae^{in(\theta+2\pi)} \\
&= Ae^{in\theta}e^{2\pi in} \\
e^{2\pi in} &= 1 \\
n &= 0, \pm 1, \pm 2, \ldots
\end{aligned}
$$

as desired.

As for the normalization constant, we have that

$$1 = \int_0^{2\pi} \psi^*(\theta)\psi(\theta)\,\mathrm{d}\theta$$

$$= \int_0^{2\pi} (A\mathrm{e}^{-in\theta})(A\mathrm{e}^{in\theta})\,\mathrm{d}\theta$$

$$= A^2 \int_0^{2\pi} 1\,\mathrm{d}\theta$$

$$A = \frac{1}{\sqrt{2\pi}}$$

as desired.

This could potentially be used for a free-electron model of benzene by looking at the energy levels and associated probability densities and overlaying them on the benzene ring. □

3.6 Harmonic Oscillator Energy Derivation

From Dudik (2004).

11/17:
- The one-dimensional time-independent Schrödinger equation governing the motion of the harmonic oscillator is
$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2\psi = E\psi$$
as derived from the sum of the quantum kinetic energy operator and classical potential for a harmonic oscillator.

- To find the wave functions and eigenenergies of this second-order differential equation, we use the power series method.

- To begin, introduce the dimensionless variable
$$y = \sqrt{\frac{m\omega}{\hbar}}\,x$$
and perform a change of variables as follows.
$$0 = \frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + \left(\frac{2mE}{\hbar^2} - \frac{m^2\omega^2}{\hbar^2}x^2\right)\psi(x)$$

$$= \frac{\mathrm{d}}{\mathrm{d}y}\left(\frac{\mathrm{d}\psi(y)}{\mathrm{d}y}\cdot\frac{\mathrm{d}y}{\mathrm{d}x}\right)\cdot\frac{\mathrm{d}y}{\mathrm{d}x} + \left[\frac{2mE}{\hbar^2} - \frac{m^2\omega^2}{\hbar^2}\left(\sqrt{\frac{\hbar}{m\omega}}y\right)^2\right]\psi(y)$$

$$= \frac{\mathrm{d}}{\mathrm{d}y}\left(\frac{\mathrm{d}\psi(y)}{\mathrm{d}y}\cdot\sqrt{\frac{m\omega}{\hbar}}\right)\cdot\sqrt{\frac{m\omega}{\hbar}} + \left(\frac{2mE}{\hbar^2} - \frac{m\omega}{\hbar}y^2\right)\psi(y)$$

$$= \frac{\mathrm{d}^2\psi(y)}{\mathrm{d}y^2} + \left(\frac{2E}{\hbar\omega} - y^2\right)\psi(y)$$

- If we let $\epsilon = 2E/\hbar\omega$ as well, we obtain
$$\frac{\mathrm{d}^2\psi(y)}{\mathrm{d}y^2} + (\epsilon - y^2)\psi(y) = 0$$
as a fully simplified version of the original differential equation.

- We now perform an asymptotic analysis.

- In the limit as $y \to \infty$, the constant ϵ becomes negligible in comparison to the y^2 term. Thus, our differential equation becomes

$$\frac{\mathrm{d}^2\psi(y)}{\mathrm{d}y^2} - y^2\psi(y) = 0$$

11/18:
- The general solution is

$$\psi(y) = H(y)\mathrm{e}^{-y^2/2}$$

where $H(y)$ is some function.

- Substituting this general solution back into the simplified differential equation yields a condition that the function(s) $H(y)$ must satisfy.

$$
\begin{aligned}
0 &= \frac{\mathrm{d}^2}{\mathrm{d}y^2}(\psi(y)) - y^2\psi(y) \\
&= \frac{\mathrm{d}}{\mathrm{d}y}\left(\frac{\mathrm{d}}{\mathrm{d}y}\left(H(y)\mathrm{e}^{-y^2/2}\right)\right) + (\epsilon - y^2)H(y)\mathrm{e}^{-y^2/2} \\
&= \frac{\mathrm{d}}{\mathrm{d}y}\left(\frac{\mathrm{d}H(y)}{\mathrm{d}y}\mathrm{e}^{-y^2/2} - yH(y)\mathrm{e}^{-y^2/2}\right) + (\epsilon - y^2)H(y)\mathrm{e}^{-y^2/2} \\
&= \frac{\mathrm{d}}{\mathrm{d}y}\left(\frac{\mathrm{d}H(y)}{\mathrm{d}y}\mathrm{e}^{-y^2/2}\right) + \frac{\mathrm{d}}{\mathrm{d}y}\left(-yH(y)\mathrm{e}^{-y^2/2}\right) + (\epsilon - y^2)H(y)\mathrm{e}^{-y^2/2} \\
&= \left(\frac{\mathrm{d}^2H(y)}{\mathrm{d}y^2}\mathrm{e}^{-y^2/2} - y\frac{\mathrm{d}H(y)}{\mathrm{d}y}\mathrm{e}^{-y^2/2}\right) + \left(-H(y)\mathrm{e}^{-y^2/2} - y\frac{\mathrm{d}H(y)}{\mathrm{d}y}\mathrm{e}^{-y^2/2} + y^2H(y)\mathrm{e}^{-y^2/2}\right) + (\epsilon - y^2)H(y)\mathrm{e}^{-y^2/2} \\
&= \frac{\mathrm{d}^2H(y)}{\mathrm{d}y^2}\mathrm{e}^{-y^2/2} - 2y\frac{\mathrm{d}H(y)}{\mathrm{d}y}\mathrm{e}^{-y^2/2} + (\epsilon - 1)H(y)\mathrm{e}^{-y^2/2} \\
&= \frac{\mathrm{d}^2H(y)}{\mathrm{d}y^2} - 2y\frac{\mathrm{d}H(y)}{\mathrm{d}y} + (\epsilon - 1)H(y)
\end{aligned}
$$

  – Note that the last line above is the Hermite equation.

- To solve the second-order differential equation above, suppose

$$H(y) = \sum_{n=0}^{\infty} c_n y^n$$

- Then we have

$$
\begin{aligned}
0 &= \frac{\mathrm{d}^2}{\mathrm{d}y^2}(H(y)) - 2y\frac{\mathrm{d}}{\mathrm{d}y}(H(y)) + (\epsilon - 1)H(y) \\
&= \frac{\mathrm{d}^2}{\mathrm{d}y^2}\left(\sum_{n=0}^{\infty} c_n y^n\right) - 2y\frac{\mathrm{d}}{\mathrm{d}y}\left(\sum_{n=0}^{\infty} c_n y^n\right) + (\epsilon - 1)\sum_{n=0}^{\infty} c_n y^n \\
&= \sum_{n=2}^{\infty} c_n n(n-1)y^{n-2} - 2y\sum_{n=1}^{\infty} c_n n y^{n-1} + (\epsilon - 1)\sum_{n=0}^{\infty} c_n y^n \\
&= \sum_{n=0}^{\infty} c_{n+2}(n+2)(n+1)y^n - 2y\sum_{n=0}^{\infty} c_{n+1}(n+1)y^n + (\epsilon - 1)\sum_{n=0}^{\infty} c_n y^n \\
&= \sum_{n=0}^{\infty}\left(c_{n+2}(n+2)(n+1)y^n - 2c_{n+1}(n+1)y^{n+1} + (\epsilon - 1)c_n y^n\right) \\
&= \sum_{n=0}^{\infty}\left(c_{n+2}(n+2)(n+1)y^n - 2c_n n y^n + (\epsilon - 1)c_n y^n\right)
\end{aligned}
$$

$$= \sum_{n=0}^{\infty} ((n+2)(n+1)c_{n+2} + (\epsilon - 1 - 2n)c_n)y^n$$

- For this equality to hold, the coefficient of each power of y on the right hand side of the above equation must equal zero, i.e., we must have

$$(n+2)(n+1)c_{n+2} + (\epsilon - 1 - 2n)c_n = 0$$
$$(n+2)(n+1)c_{n+2} = (2n + 1 - \epsilon)c_n$$
$$c_{n+2} = \frac{2n + 1 - \epsilon}{(n+1)(n+1)}c_n$$

- The above equation is a "series representation of all the expansion coefficients in terms of c_0 for the power series solution" to the Hermite equation (Dudik, 2004).

- However, there is a problem: For large values of y, if n keeps increasing indefinitely, $H(y)$ will keep increasing indefinitely. Thus, to have a physically meaningful solution over the whole number line, the Taylor series must contain only a finite number of terms.

- It follows that at some point, $a_{n+2} = 0$. But this happens if and only if the numerator of the recursion relation equals zero, i.e., if

$$0 = 2n + 1 - \epsilon$$
$$\frac{2E}{\hbar \omega} = 2n + 1$$
$$E = \hbar \omega \left(n + \frac{1}{2} \right)$$

Week 4

The Hydrogen Atom and Angular Momentum

4.1 Rotational Motion

• Consider the diatomic molecule AB at a distance r_0 apart rotating about its center of mass.
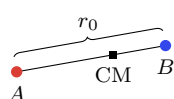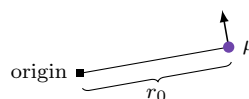
(a) Diatomic. (b) An equivalent system.

Figure 4.1: Diatomic rotation.

  – To simplify the problem, replace the two particles rotating about the center of mass with one particle of reduced mass μ rotating about the center of mass with lever arm r_0.

• Classically, the kinetic energy of the translational motion is

$$T = \frac{L^2}{2I}$$

where $I = \mu r_0^2$ and $L = p \times r_0 = pr_0$ (for this kind of rotation; see Figure 4.1b).

• To further talk about this problem, we should introduce **spherical coordinates**.

• **Spherical coordinates**: The coordinate system (r, θ, ϕ) related to the Cartesian coordinates (x, y, z) by

$$x = r \sin\theta \cos\phi \qquad y = r \sin\theta \sin\phi \qquad z = r \cos\theta$$

• Classically, we will have

$$H = \frac{1}{2\mu}(p_x^2 + p_y^2 + p_z^2) + V(x, y, z)$$

in Cartesian coordinates.

• In spherical coordinates, this becomes

$$H = \frac{1}{2\mu}\left(p_r^2 + \frac{L^2}{r^2}\right) + V(r)$$

- Thus, in quantum mechanics, we get

$$\hat{H} = \frac{1}{2\mu}(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) + V(x, y, z)$$

$$= \frac{1}{2\mu}\left(\hat{p}_r^2 + \frac{\hat{L}^2}{r^2}\right) + V(r)$$

- Thus, we have in spherical coordinates that

$$\hat{T}\psi = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi\right) + \frac{1}{r^2\sin\theta}\left(\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\psi\right)\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\psi\right]$$

- 2D rigid rotor:

  - Let the system from Figure 4.1b be confined to rotating in two dimensions.
  - This simplifies the problem since both the $\partial/\partial r$ and $\partial/\partial\theta$ terms in the kinetic energy operator disappear (since, respectively, the particle is at a fixed distance from the center of mass and it cannot move out of the 2D plane).
  - Thus, our Schrödinger equation for this system is

$$-\frac{\hbar^2}{2\mu r_0^2}\frac{\partial^2}{\partial\phi^2}\psi(\phi) = E\psi(\phi)$$

  - Solution: Let $\psi(\phi) = e^{im\phi}$; then

$$E_m = \frac{\hbar^2 m^2}{2\mu r_0^2}$$

    - $m = 0, 1, 2, \ldots$ is a new quantum number.
    - m doesn't go to infinity because $|m|$ is bounded by l (the total angular momentum).
  - Remembering our original restriction, we have that this math describes the system from Figure 4.1a but confined to rotate in the xy plane with angular momentum in the z direction.

    - Thus, for example, the energies of the system from Figure 4.1a are dependent on m and $I = \mu r_0^2$.
  - Such a system occurs in physical reality when we put the diatomic in an external field, or attach to it a big functional group.
  - Zero point energy: $m = 0$ does not violate the UR since we still have $\Delta L \Delta\theta \geq \hbar/2$ (as everything is still rotating in the sense that we have equal probability of the particle being everywhere [as opposed to more localized/normal rotation with higher values of m]).

- 3D rigid rotor:

  - Assume that the potential energy is zero on the surface of the sphere (so we basically have a particle on a sphere).
  - Then

$$\hat{H} = \frac{\hat{L}^2}{2\mu r_0^2} = \frac{\hat{L}^2}{2I}$$

  - Solving $\hat{H}\psi = E\psi$ asserts that the eigenfunctions of the Hamiltonian are the spherical harmonics $Y_{lm}(\theta, \phi)$.
  - Energy:

$$E_l = \frac{\hbar^2}{2I}l(l + 1)$$

    where $l = 0, 1, 2, \ldots$.
  - Recall that m corresponds to the projection of angular momentum onto the z-axis, so that

$$m = -l, \ldots, +l$$

4.2   Hydrogen Atom

10/20:
- Microwaves (for food) excite the rotational motion of water molecules.

- Spherical harmonics: The solution of $\psi_{lm}(\theta, \phi) = Y_{lm}(\theta, \phi)$, where l, m are quantum numbers.

- $E_l = \hbar^2/2I \cdot l(l+1)$ for $l = 0, 1, 2, \dots$.

- Form of the spherical harmonics:
$$Y(\theta, \phi) = P_{lm}(\cos\theta)e^{im\phi}$$
  where $P_{lm}(cos\theta)$ is a polynomial.

- The polynomials $P_{lm}(\cos\theta)$ are the associated Legendre polynomials.

- When $m = 0$, we have the Legendre polynomials.

  - The differential equation describing these is

$$\frac{\mathrm{d}}{\mathrm{d}x}\left((1-x^2)\frac{\mathrm{d}}{\mathrm{d}x}P_l(x) + l(l+1)P_l(x)\right) = 0$$

  - The Legendre polynomials converge very quickly to functions on $[-1, 1]$.
  - People map these polynomials onto other domains, too, to solve a variety of problems.
  - Legendre polynomials have more of their roots at the boundaries — since the boundary conditions are the most important part of solving a differential equation, it makes sense that accurate representations would sample near the boundary more.
  - Examples:

$$P_0(x) = 1 \qquad\qquad\qquad P_1(x) = x$$
$$P_2(x) = \frac{3}{2}x^2 - \frac{1}{2} \qquad\qquad P_3(x) = \frac{5}{2}x^3 - \frac{3}{2}x$$

- Consider HCl.

  - For it,
$$\frac{\hbar^2}{2I} = 1.3 \times 10^{-3}\,\mathrm{eV}$$

  - Rotational spectral lines may arise from different values of the quantum number l.
  - The molecule vibrates in harmonic oscillation with spacings $\approx 0.1\,\mathrm{eV}$ (it's not strictly rigid).
  - Rovibrational spectra includes both forms of movement.
    - Very high precision.
    - Very big in the 90s.
  - Electronic spectra: A few electron volts.

- The hydrogen atom.

  - Two generalizations of the 3D rigid rotor combine to treat the hydrogen atom:
    1. An addition of the kinetic energy in the radial direction $\hat{r}$.
    2. An addition of the Coulomb potential.

– Schrödinger equation:

$$\hat{H}\psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$$

where

$$\hat{H} = \frac{1}{2\mu}\left(\hat{p}_r^2 + \frac{\hat{L}^2}{r^2}\right) + V(r)$$

$$\hat{p}_r^2 = -\frac{\hbar^2}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\psi(r)\right)$$

$$V(r) = -\frac{e(eZ)}{4\pi\epsilon_0 r}$$

– Because the particle has spherical symmetry (that it, does not depend on θ or ϕ), the wave function is separable, that is, it may be written as a product

$$\psi(r, \theta, \phi) = R_n(r)Y_{lm}(\theta, \phi)$$

– Note that there is no analytic solution to the Schrödinger equation in Cartesian coordinates — we need spherical coordinates to take advantage of the spherical symmetry.

– Substitution into the Schrödinger equation yields

$$\left(\frac{1}{2\mu}\left(\hat{p}_r^2 + \frac{\hat{L}^2}{r^2}\right) + V(r)\right)R(r)Y(\theta, \phi) = ER(r)Y(\theta, \phi)$$

where μ is the reduced mass of the electron and the nucleus (which is approximately the mass of the electron).

– But since

$$\frac{1}{2\mu r^2}\hat{L}^2 Y_{lm}(\theta, \phi) = \frac{l(l+1)}{2\mu r^2}\hbar^2 Y_{lm}(\theta, \phi)$$

we have that

$$\frac{1}{2\mu}\left(\hat{p}_r^2 + \frac{l(l+1)\hbar^2}{r^2} + V(r)\right)R_n(r) = E_n R_n(r)$$

∎ We have reduced the three-dimensional case of the hydrogen atom to a one-dimensional differential equation.

4.3 Hydrogen Atom (cont.)

10/22:
- We want to solve the SE $\hat{H}\psi_n = E\psi_n$ for the hydrogen atom.

- To exploit the spherical symmetry of the hydrogen atom, we use (r, θ, ϕ).

- Thus, our Hamiltonian is equal to

$$\hat{H} = \frac{1}{2\mu}\left(\hat{p}_r^2 + \frac{\hat{L}^2}{r^2}\right) + V(r)$$

– Since V is just a function of r, the wave function is separable: $\psi(r, \theta, \phi) = R_n(r)Y_{l,m}(\theta, \phi)$.

– "Whenever you have a separation of variables additively in the Hamiltonian, you have a separation of variables multiplicatively in the wave function."

- Substitute the wave function into the Schrödinger equation:

$$\left(\frac{1}{2\mu}\left(\hat{p}_r^2 + \frac{\hat{L}^2}{r^2}\right) + V(r)\right)R_n(r)Y_{lm}(\theta,\phi) = ER_n(r)Y_{lm}(\theta,\phi)$$

$$\left(\frac{1}{2\mu}\left(\hat{p}_r^2 + \frac{l(l+1)\hbar^2}{r^2}\right) + V(r)\right)R_n(r)Y_{lm}(\theta,\phi) = ER_n(r)Y_{lm}(\theta,\phi)$$

$$\left(\frac{1}{2\mu}\left(\hat{p}_r^2 + \frac{l(l+1)\hbar^2}{r^2}\right) + V(r)\right)R_n(r) = E_{nl}R_n(r)$$

- Noting that we only care about the behavior of the differential equation on $[0,\infty)$, specifically at really large distances, we perform an asymptotic analysis.

$$\lim_{r\to\infty}\left(\frac{1}{2\mu}\hat{p}_r^2\right)R(r) = ER(r)$$

- Plugging in the value of the momentum operator, we have that

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}r^2}R(r) = ER(r)$$

$$R(r) = \mathrm{e}^{-\alpha r}$$

where $\alpha = i\hbar/\sqrt{2\mu E}$.

- But we want to multiply $\mathrm{e}^{-\alpha r}$ by some type of polynomial. Namely, **Laguerre polynomials**.

  - These polynomials may be found by expanding a power series.
  - Let

$$L\left(\frac{\alpha r}{n}\right) = \sum_{j=0}^{\infty}c_j\left(\frac{\alpha r}{n}\right)^j$$

  - A recursion relation may be found.
  - The quantization of energy in the hydrogen atom again arises from the truncation of the polynomials.

- Thus, the general solution of $R_{nl}(r)$ is

$$R_{nl}(r) = \left(\frac{\alpha r}{n}\right)^l L_{n+1,2l+1}\left(\frac{\alpha r}{n}\right)\mathrm{e}^{-\alpha r/2n}$$

- Energy levels:

$$E_n = -\frac{\mu}{2\hbar^2}\left(\frac{(Ze)e}{4\pi\epsilon}\right)^2\frac{1}{n^2}$$

  - These are the discrete energies of Bohr!

- But now we also have the electron's probability distributions, i.e., the ground state wave function is

$$\psi(r,\theta,\phi) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\mathrm{e}^{-Zr/a_0}$$

- Thus, we can now take a look at the probabilities. *picture*

  - The probability is

$$\mathrm{Pr} = |\psi(r,\theta,\phi)|^2 r^2\sin\theta$$

– The radial probability is

$$\Pr(r) = r^2 |R_{nl}(r)|^2$$

■ The radial probability peaks at a_0, the **Bohr radius**.
■ Thus, the Bohr radius (the radius of the circular orbit of Bohr's hydrogen electron) is just the most probable distance from the nucleus!

• The average distance from the nucleus (the expectation value of r) is

$$\langle r \rangle = \int_0^\infty \Pr(r) r \, dr$$
$$= \int_0^\infty \psi^*(r) r \psi(r) \, dr$$

– Note we also find that $\langle \hat{H} \rangle = E$, so there is no uncertainty in the energy.

• Note that in some ways, quantum mechanics is more certain than classical mechanics since, for instance, in quantum we know the energy exactly.

4.4 Chapter 5: The Harmonic Oscillator and the Rigid Rotator — Two Spectroscopic Models

From McQuarrie and Simon (1997).

10/19:
• **Rigid-rotator model**: Two point masses m_1 and m_2 at fixed distances r_1 and r_2 from their center of mass.

– Since the vibrational amplitude of a rotating molecule is small compared to its amplitude, this is a good model.

• Kinetic energy of the rigid rotator:

$$K = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2$$
$$= \frac{1}{2}(m_1 r_1^2 + m_2 r_2^2)\omega^2$$
$$= \frac{1}{2} I \omega^2$$

– Note that

$$I = m_1 r_1^2 + m_2 r_2^2$$
$$= \mu r^2$$

(see Problem 5-29).

• It follows that we the two-body problem of the rigid rotator is equivalent to the one-body problem of a single body of mass μ rotating at a distance r from a fixed center.

• Since there are no external forces on the rigid rotator (we're not applying any electric or magnetic fields), the energy of the molecule is solely kinetic (i.e., there is no potential energy term in the Hamiltonian).

– Thus, for a rigid rotator,

$$\hat{H} = \hat{K} = -\frac{\hbar^2}{2\mu} \nabla^2$$

- Since this particle has a natural center of spherical symmetry, we opt for spherical coordinates. However, this necessitates expressing ∇^2 as the following.

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)_{\theta,\phi} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)_{r,\phi} + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)_{r,\theta}$$

  - See Problem 5-32 for a derivation.

- With respect to the rigid rotator, r is constant. Thus,

$$\nabla^2 = \frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2}\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

$$\hat{H} = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right]$$

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right]$$

  - Note that since both θ and ϕ are unitless, the units of angular momentum for quantum system are $\hbar$.

- Rigid-rotator wave functions are customarily denoted by $Y(\theta,\phi)$.

- In solving $\hat{H}Y(\theta,\phi) = EY(\theta,\phi)$, it will be useful to multiply the original Schrödinger equation by $\sin^2\theta$ and let $\beta = 2IE/\hbar^2$ to obtain the partial differential equation

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{\partial^2 Y}{\partial\phi^2} + (\beta\sin^2\theta)Y = 0$$

  - The solutions to the above equation are intimately linked to those for the hydrogen atom.
  - Solving the above equation yields the condition that $\beta = J(J+1)$ for $J = 0, 1, 2, \ldots$. Therefore,

$$E_J = \frac{\hbar^2}{2I}J(J+1)$$

for $J = 0, 1, 2, \ldots$.
  - Each energy level has a degeneracy $g_J = 2J+1$ as well.

- Once again, electromagnetic radiation can cause a rigid rotator to undergo transitions from one state to another subject to the selection rules that only transitions between adjacent states are allowed and the molecule must possess a permanent dipole moment.

- As before, we can calculate

$$\Delta E = \frac{h^2}{4\pi^2 I}(J+1)$$

and the frequencies at which absorption transitions occur are

$$\nu = \frac{h}{4\pi^2 I}(J+1)$$

for $J = 0, 1, 2, \ldots$.

- It follows from reduced mass, bond length, and moment of inertia data that the frequencies typically lie in the microwave region.

- **Microwave spectroscopy**: The direct study of rotational transitions.

- **Rotational constant** (of a molecule): The following quantity. *Given by*

$$B = \frac{h}{8\pi^2 I}$$

- We often write the absorption frequencies as $\nu = 2B(J + 1)$.

- The spacing of lines in a microwave spectrum is $2B$.

- Like IR spectroscopy can be used to determine the force constants of molecular attractions in diatomics, microwave spectroscopy can be used to determine the bond lengths of diatomics.

Problems

5-29. Show that the moment of inertia for a rigid rotator can be written as $I = \mu r^2$ where $r = r_1 + r_2$ (the fixed separation of the two masses) and μ is the reduced mass.

Answer. First, note that $m_1 r_1 = m_2 r_2$ for such a rotation about the center of mass. Then

$$
\begin{aligned}
I &= \mu r^2 \\
&= \frac{m_1 m_2}{m_1 + m_2}(r_1 + r_2)^2 \\
&= \frac{m_1 m_2 r_1}{m_1 r_1 + m_2 r_1}(r_1 + r_2)^2 \\
&= \frac{m_1 m_2 r_1}{m_2 r_2 + m_2 r_1}(r_1 + r_2)^2 \\
&= \frac{m_1 r_1}{r_2 + r_1}(r_1 + r_2)^2 \\
&= m_1 r_1 (r_1 + r_2) \\
&= m_1 r_1^2 + m_1 r_1 r_2 \\
&= m_1 r_1^2 + m_2 r_2^2
\end{aligned}
$$

as desired.   □

5-30. Consider the transformation from Cartesian coordinates to plane polar coordinates where

$$
x = r \cos \theta \qquad\qquad\qquad r = \sqrt{x^2 + y^2}
$$
$$
y = r \sin \theta \qquad\qquad\qquad \theta = \tan^{-1}\left(\frac{y}{x}\right)
$$

If a function $f(r, \theta)$ depends upon the polar coordinates r and θ, then the chain rule of partial differentiation says that[1]

$$
\left(\frac{\partial f}{\partial x}\right)_y = \left(\frac{\partial f}{\partial r}\right)_\theta \left(\frac{\partial r}{\partial x}\right)_y + \left(\frac{\partial f}{\partial \theta}\right)_r \left(\frac{\partial \theta}{\partial x}\right)_y
$$

and that

$$
\left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial f}{\partial r}\right)_\theta \left(\frac{\partial r}{\partial y}\right)_x + \left(\frac{\partial f}{\partial \theta}\right)_r \left(\frac{\partial \theta}{\partial y}\right)_x
$$

For simplicity, we will assume that r is constant so that we can ignore terms involving derivatives with respect to r. In other words, we will consider a particle that is constrained to move on the circumference of a circle. This system is sometimes called a **particle on a ring**. Using the above equations, show that

$$
\left(\frac{\partial f}{\partial x}\right)_y = -\frac{\sin \theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r \qquad\qquad\qquad \left(\frac{\partial f}{\partial y}\right)_x = \frac{\cos \theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r
$$

---

[1]Note that the subscript means that the subscripted variable is held constant.

for r fixed. Now apply the above equations again to show that

$$\left(\frac{\partial^2 f}{\partial x^2}\right)_y = \left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial x}\right)_y\right]$$

$$= \left[\frac{\partial}{\partial \theta}\left(\frac{\partial f}{\partial x}\right)_y\right]_r \left(\frac{\partial \theta}{\partial x}\right)_y$$

$$= \left\{\frac{\partial}{\partial \theta}\left[-\frac{\sin \theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r\right]\right\}_r \left(-\frac{\sin \theta}{r}\right)$$

$$= \frac{\sin \theta \cos \theta}{r^2}\left(\frac{\partial f}{\partial \theta}\right)_r + \frac{\sin^2 \theta}{r^2}\left(\frac{\partial^2 f}{\partial \theta^2}\right)_r$$

for r fixed. Similarly, show that

$$\left(\frac{\partial^2 f}{\partial y^2}\right)_x = -\frac{\sin \theta \cos \theta}{r^2}\left(\frac{\partial f}{\partial \theta}\right)_r + \frac{\cos^2 \theta}{r^2}\left(\frac{\partial^2 f}{\partial \theta^2}\right)_r$$

and that

$$\nabla^2 f = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} \longrightarrow \frac{1}{r^2}\left(\frac{\partial^2 f}{\partial \theta^2}\right)_r$$

both for r fixed. Now show that the Schrödinger equation for a particle of mass m constrained to move on a circle of radius r (see Problem 3-28) is

$$-\frac{\hbar^2}{2I}\frac{\partial^2 \psi(\theta)}{\partial \theta^2} = E\psi(\theta)$$

where $I = mr^2$ is the moment of inertia and $0 \leq \theta \leq 2\pi$.

Answer. We have that

$$\left(\frac{\partial \theta}{\partial x}\right)_y = \frac{\partial}{\partial x}\left(\tan^{-1}\left(\frac{y}{x}\right)\right) \qquad\qquad \left(\frac{\partial \theta}{\partial y}\right)_y = \frac{\partial}{\partial y}\left(\tan^{-1}\left(\frac{y}{x}\right)\right)$$

$$= \frac{1}{\left(\frac{y}{x}\right)^2 + 1}\cdot y \cdot -\frac{1}{x^2} \qquad\qquad = \frac{1}{\left(\frac{y}{x}\right)^2 + 1}\cdot\frac{1}{x}$$

$$= -\frac{y}{x^2 + y^2} \qquad\qquad\qquad\qquad = \frac{x}{x^2 + y^2}$$

$$= -\frac{r\sin \theta}{r^2} \qquad\qquad\qquad\qquad = \frac{r\cos \theta}{r^2}$$

$$= -\frac{\sin \theta}{r} \qquad\qquad\qquad\qquad = \frac{\cos \theta}{r}$$

This combined with the fact that r is constant yields

$$\left(\frac{\partial f}{\partial x}\right)_y = \left(\frac{\partial f}{\partial r}\right)_\theta\left(\frac{\partial r}{\partial x}\right)_y + \left(\frac{\partial f}{\partial \theta}\right)_r\left(\frac{\partial \theta}{\partial x}\right)_y \qquad \left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial f}{\partial r}\right)_\theta\left(\frac{\partial r}{\partial y}\right)_x + \left(\frac{\partial f}{\partial \theta}\right)_r\left(\frac{\partial \theta}{\partial y}\right)_x$$

$$= 0\cdot\left(\frac{\partial r}{\partial x}\right)_y + \left(\frac{\partial f}{\partial \theta}\right)_r\cdot -\frac{\sin \theta}{r} \qquad\qquad = 0\cdot\left(\frac{\partial r}{\partial y}\right)_x + \left(\frac{\partial f}{\partial \theta}\right)_r\frac{\cos \theta}{r}$$

$$= -\frac{\sin \theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r \qquad\qquad\qquad = \frac{\cos \theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r$$

as desired.

The rest of the differential equation derivations follow fairly easy with simple calculus rules.

As for the Schrödinger equation, we know that there is no potential field for this particle. Additionally, although we could choose to express ψ as a function of x, y, owing to the radial symmetry, we choose to express it as a function of r, θ. In fact, we need only express ψ as a function of θ since r is invariant throughout the chosen free space. Thus, expanding from the general form, we get

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

$$\left(-\frac{\hbar^2}{2m}\nabla^2\right)\psi(\theta) = E\psi(\theta)$$

$$-\frac{\hbar^2}{2m} \cdot \frac{1}{r^2}\left(\frac{\partial^2\psi(\theta)}{\partial\theta^2}\right)_r = E\psi(\theta)$$

$$-\frac{\hbar^2}{2I}\frac{\partial^2\psi(\theta)}{\partial\theta^2} = E\psi(\theta)$$

as desired. $\qquad\square$

5-31. Generalize Problem 5-30 to the case of a particle moving in a plane under the influence of a central force; in other words, convert

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$$

to plane polar coordinates, this time without assuming that r is constant. Use the method of separation of variables to separate the equation for this problem. Solve the angular equation.

Answer. We have

$$\frac{\partial r}{\partial x} = \frac{1}{2\sqrt{x^2+y^2}} \cdot 2x \qquad\qquad\qquad \frac{\partial r}{\partial y} = \frac{1}{2\sqrt{x^2+y^2}} \cdot 2y$$
$$= \frac{x}{r} \qquad\qquad\qquad\qquad\qquad = \frac{y}{r}$$
$$= \cos\theta \qquad\qquad\qquad\qquad\qquad = \sin\theta$$

Thus

$$\frac{\partial f}{\partial x} = \cos\theta\frac{\partial f}{\partial r} - \frac{\sin\theta}{r}\frac{\partial f}{\partial\theta} \qquad\qquad \frac{\partial f}{\partial y} = \sin\theta\frac{\partial f}{\partial r} + \frac{\cos\theta}{r}\frac{\partial f}{\partial\theta}$$

Also note that

$$\frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial x}\right)$$
$$= \frac{\partial}{\partial\theta}\left(\frac{\partial f}{\partial x}\right)\frac{\partial\theta}{\partial x} + \frac{\partial}{\partial r}\left(\frac{\partial f}{\partial x}\right)\frac{\partial r}{\partial x}$$

The rest of the expansions are routine, leading to

$$\nabla^2 f = \frac{\partial^2 u}{\partial r^2} + \frac{1}{r}\frac{\partial u}{\partial r} + \frac{1}{r^2}\frac{\partial^2 u}{\partial\theta^2}$$

$\qquad\square$

5-32. Using Problems 5-30 and 5-31 as a guide, convert ∇^2 from three-dimensional Cartesian coordinates to spherical coordinates.

4.5   Chapter 6: The Hydrogen Atom

From McQuarrie and Simon (1997).

10/29:
- Idealize the hydrogen atom to a proton fixed at the origin and an electron of mass m_e interacting with the proton through a Coulombic potential

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

- Because of the spherical geometry of the model, we opt for spherical coordinates.

- The appropriate Hamiltonian is thus

$$\hat{H} = -\frac{\hbar}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

- Expressing the Laplacian in spherical coordinates gives us

$$\left\{ -\frac{\hbar^2}{2m_e}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 \psi}{\partial \phi^2} \right] - \frac{e^2}{4\pi\epsilon_0 r} \right\} \psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

  as the Schrödinger equation for the hydrogen atom.

- Multiply through by $2m_e r^2$ and move all terms over to the lefthand side of the equality to get the above equation into the following separable form.

$$\left\{ -\hbar^2 \left(\frac{\partial}{\partial r}r^2\frac{\partial \psi}{\partial r} \right) - \hbar^2 \left[\frac{1}{\sin\theta}\left(\frac{\partial}{\partial \theta}\sin\theta\frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2\theta}\frac{\partial^2 \psi}{\partial \phi^2} \right] - 2m_e r^2 \left[\frac{e^2}{4\pi\epsilon_0 r} + E \right] \right\} \psi(r,\theta,\phi) = 0$$

- Since all the θ, ϕ dependence occurs within the large square brackets, assume that

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

- Substituting into the differential equation and separating terms (dividing by $R(r)Y(\theta,\phi)$) yields

$$-\frac{\hbar^2}{R(r)}\left[\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r} \right) + \frac{2m_e r^2}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) R(r) \right] - \frac{\hbar^2}{Y(\theta,\phi)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial \phi^2} \right] = 0$$

- All terms containing r are in the first set of square brackets, and all terms containing θ, ϕ are in the second set of square brackets. Since the above equation must hold for all r, θ, ϕ, and r, θ, ϕ are independent variables, we must have that varying r while holding θ, ϕ constant does not change the r term of the above equation (as this would violate the equality). Similarly, changing θ, ϕ must not change the θ, ϕ term. Therefore, we may let

$$-\beta = -\frac{1}{R(r)}\left[\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r} \right) + \frac{2m_e r^2}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) R(r) \right]$$

$$\beta = -\frac{1}{Y(\theta,\phi)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial \phi^2} \right]$$

  where β is a **separation constant** into which we have incorporated $\hbar^2$.

- **Radial equation**: The first equation above.

- **Angular equation**: The second equation above after having been multiplied by $\sin^2\theta Y(\theta,\phi)$. *Given by*

$$\sin\theta\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial Y}{\partial \theta} + \frac{\partial^2 Y}{\partial \phi^2} + \beta\sin^2\theta Y \right) = 0$$

- – Note that this is identical to the partial differential equation derived in Chapter 5 for the rigid rotator.
  - – Thus, the angular parts of hydrogen atomic orbitals are also rigid-rotator wave functions.
- **Spherical harmonic**: A wave function of the rigid rotator.
- We now solve the angular equation.
- Invoking separation of variables again with $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$ yields

$$\frac{\sin\theta}{\Theta(\theta)} \frac{\mathrm{d}}{\mathrm{d}\theta} \left(\sin\theta \frac{\mathrm{d}\Theta}{\mathrm{d}\theta} \right) + \beta\sin\theta + \frac{1}{\Phi(\phi)} \frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} = 0$$

- We now introduce a new separation constant (written in a form that predicts future algebraic manipulations) to get

$$\frac{\sin\theta}{\Theta(\theta)} \frac{\mathrm{d}}{\mathrm{d}\theta} \left(\sin\theta \frac{\mathrm{d}\Theta}{\mathrm{d}\theta} \right) + \beta\sin^2\theta = m^2$$

$$\frac{1}{\Phi(\phi)} \frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} = -m^2$$

- Solving the bottom equation above gives solutions

$$\Phi(\phi) = A_m \mathrm{e}^{im\phi} \qquad\qquad \Phi(\phi) = A_{-m}\mathrm{e}^{-im\phi}$$

  where the constants A_m, A_{-m} may depend on the value of m.

- From the domain of ϕ, we have the boundary condition $\Phi(\phi + 2\pi) = \Phi(\phi)$.

- This yields

$$A_m \mathrm{e}^{im(\phi+2\pi)} = A_m \mathrm{e}^{im\phi} \qquad\qquad A_{-m}\mathrm{e}^{-im(\phi+2\pi)} = A_{-m}\mathrm{e}^{-im\phi}$$

$$\mathrm{e}^{i2\pi m} = 1 \qquad\qquad \mathrm{e}^{-i2\pi m} = 1$$

  from which it follows that we must have

$$1 + 0i = 1$$
$$= \mathrm{e}^{\pm i2\pi m}$$
$$= \cos(2\pi m) \pm i\sin(2\pi m)$$

- Therefore, $m = 0, \pm 1, \pm 2, \dots$.

- It follows that we can express the solutions to the bottom angular equation in the more compact form

$$\Phi_m(\phi) = A_m \mathrm{e}^{im\phi}$$

  where $m = 0, \pm 1, \pm 2, \dots$.

- Normalizing gives us the coefficient A_m:

$$1 = \int_0^{2\pi} \Phi_m^*(\phi)\Phi_m(\phi)\,\mathrm{d}\phi$$
$$= \int_0^{2\pi} (A_m\mathrm{e}^{-im\phi})(A_m\mathrm{e}^{im\phi})\,\mathrm{d}\phi$$
$$= A_m^2 \int_0^{2\pi} 1\,\mathrm{d}\phi$$
$$A_m = \frac{1}{\sqrt{2\pi}}$$

- Thus, the normalized wave functions of $\Phi(\phi)$ are

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi}$$

  for $m = 0, \pm 1, \pm 2, \ldots$.

- We now direct our attention to solving the differential equation containing $\Theta(\theta)$.

- Let $x = \cos\theta$ and $P(x) = \Theta(\theta)$. Substituting, we have (see Problem 6-2)

$$(1 - x^2)\frac{d^2 P}{dx^2} - 2x\frac{dP}{dx} + \left[\beta - \frac{m^2}{1 - x^2}\right]P(x) = 0$$

  where $m = 0, \pm 1, \pm 2, \ldots$.

  - Note that since $x = \cos\theta$, $0 \le \theta \le \pi$, the range of x is $-1 \le x \le 1$.

- Solving the above equation gives **Legendre's equation**.

- **Legendre's equation**: The following equation. *Given by*

$$(1 - x^2)\frac{d^2 P}{dx^2} - 2x\frac{dP}{dx} + \left[l(l+1) - \frac{m^2}{1 - x^2}\right]P(x) = 0$$

  - The key difference between Legendre's equation and the previous one is that solving the previous one finds β equal to $l(l+1)$ with $l = 0, 1, 2, \ldots$ and $|m| \le l$ if the solutions are to remain finite.

- **Legendre polynomials**: The solutions to Legendre's equation when $m = 0$. *Denoted by* $\boldsymbol{P_l(x)}$.

$P_0(x) = 1$
$P_1(x) = x$
$P_2(x) = \frac{1}{2}(3x^2 - 1)$
$P_3(x) = \frac{1}{2}(5x^3 - 3x)$
$P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3)$

Table 4.1: The first few Legendre polynomials.

  - Notice that $P_l(x)$ is an even function if l is even and an odd function if l is odd.
  - The factors in front of $P_l(x)$ are chosen such that $P_l(1) = 1$.
  - The Legendre polynomials are orthogonal: If $l \ne n$, then

$$\int_{-1}^{1} P_l(x)P_n(x)\,dx = 0$$

  - We have that

$$\int_{-1}^{1} [P_l(x)]^2 \,dx = \frac{2}{2l+1}$$

  for each l, so the normalization constant of $P_l(x)$ is

$$\sqrt{\frac{2l+l}{2}}$$

- **Associated Legendre functions**: The solutions to Legendre's equation when $m \ne 0$. *Denoted by* $\boldsymbol{P_l^{|m|}(x)}$. *Given by*

$$P_l^{|m|}(x) = (1 - x^2)^{|m|/2}\frac{d^{|m|}}{dx^{|m|}}P_l(x)$$

10/30:

Function	x-coordinates	θ-coordinates
$P_0^0(x)$	1	1
$P_1^0(x)$	x	$\cos\theta$
$P_1^1(x)$	$\sqrt{1-x^2}$	$\sin\theta$
$P_2^0(x)$	$\frac{1}{2}(3x^2-1)$	$\frac{1}{2}(3\cos^2\theta-1)$
$P_2^1(x)$	$3x\sqrt{1-x^2}$	$3\cos\theta\sin\theta$
$P_2^2(x)$	$3(1-x^2)$	$3\sin^2\theta$
$P_3^0(x)$	$\frac{1}{2}(5x^2-3x)$	$\frac{1}{2}(5\cos^2\theta-3\cos\theta)$
$P_3^1(x)$	$\frac{3}{2}(5x^2-1)\sqrt{1-x^2}$	$\frac{3}{2}(5\cos^2\theta-1)\sin\theta$
$P_3^2(x)$	$15x(1-x^2)$	$15\cos\theta\sin^2\theta$
$P_3^3(x)$	$15\sqrt{1-x^2}$	$15\sin^2\theta$

Table 4.2: The first few associated Legendre functions.

- – Note that only the magnitude of m is present because m^2 is the only form of m present in Legendre's equation.

- Relating the normalization and orthogonality conditions back to the variable of interest (θ), we have (for the Legendre polynomials) that

$$\int_0^\pi P_l(\cos\theta)P_n(\cos\theta)\sin\theta\,\mathrm{d}\theta = \frac{2\delta_{ln}}{2l+1}$$

- Similarly, for the associated Legendre functions, we have that

$$\int_0^\pi P_l^{|m|}(\cos\theta)P_n^{|m|}(\cos\theta)\sin\theta\,\mathrm{d}\theta = \frac{2}{2l+1}\frac{(l+|m|)!}{(l-|m|)!}\delta_{ln}$$

  - – Thus, the normalization constant for the associated Legendre functions is

$$N_{lm} = \sqrt{\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}}$$

- Thus, the normalized wave functions of $\Theta(\theta)$ are

$$\Theta(\theta) = N_{lm}P_l^{|m|}(\cos\theta)$$

  for $l = 0,1,2,\dots$ and $m = 0,\pm1,\dots,\pm l$.

- **Spherical harmonics**: The orthonormal set of angular wave functions of the hydrogen atom. *Given by*

$$Y_l^m(\theta,\phi) = \Theta(\theta)\Phi(\phi) = \sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}P_l^{|m|}(\cos\theta)\mathrm{e}^{im\phi}$$

  - – Note that $l = 0,1,2,\dots$ and $m = 0,\pm1,\dots,\pm l$.
  - – The orthonormality condition:

$$\int_0^\pi \mathrm{d}\theta\sin\theta \int_0^{2\pi} \mathrm{d}\phi\, Y_l^m(\theta,\phi)^* Y_n^k(\theta,\phi) = \delta_{ln}\delta_{mk}$$

$$Y_0^0 = \frac{1}{\sqrt{4\pi}} \qquad\qquad Y_2^1 = \sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{i\phi}$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta \qquad\qquad Y_2^{-1} = \sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{-i\phi}$$

$$Y_1^1 = \sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi} \qquad\qquad Y_2^2 = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{2i\phi}$$

$$Y_1^{-1} = \sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi} \qquad\qquad Y_2^{-2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{-2i\phi}$$

$$Y_2^0 = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$$

Table 4.3: The first few spherical harmonics.

10/31: • Recalling the definition of $\hat{L}^2$ from Chapter 5, we have that

$$\beta = -\frac{1}{Y_l^m(\theta,\phi)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y_l^m(\theta,\phi)}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y_l^m(\theta,\phi)}{\partial\phi^2}\right]$$

$$\hbar^2 l(l+1)Y_l^m(\theta,\phi) = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y_l^m(\theta,\phi)$$

$$\hat{L}^2 Y_l^m(\theta,\phi) = \hbar^2 l(l+1)Y_l^m(\theta,\phi)$$

  – Implication: The spherical harmonics are eigenfunctions of $\hat{L}^2$.
  – Additionally, the square of the angular momentum L^2 can only have the values given by $\hbar^2 l(l+1)$ for $l = 0, 1, 2, \dots$.
  – We can also adapt the above to reflect energy with $\hat{H} = \hat{L}^2/2I$.

11/1: • We can apply partial differentiation to convert the expressions for $\hat{L}_x, \hat{L}_y, \hat{L}_z$ in Table 3.1 to spherical coordinates.

  – Doing so yields complex expressions for $\hat{L}_x$ and $\hat{L}_y$, but a simple expression for $\hat{L}_z$:

$$\hat{L}_z = -i\hbar\frac{d}{d\phi}$$

• The spherical harmonics are eigenfunctions of $\hat{L}_z$:

$$\hat{L}_z Y_l^m(\theta,\phi) = -i\hbar\frac{d}{d\phi}\left(N_{lm}P_l^{|m|}(\cos\theta)e^{im\phi}\right)$$

$$= -i\hbar N_{lm}P_l^{|m|}(\cos\theta)\frac{d}{d\phi}\left(e^{im\phi}\right)$$

$$= m\hbar N_{lm}P_l^{|m|}(\cos\theta)e^{im\phi}$$

$$= m\hbar Y_l^m(\theta,\phi)$$

  – It follows that L_z is quantized by $m\hbar$.
  – This implies that $\hbar$ is a fundamental measure of the angular momentum of a quantum mechanical system.
  – Note that the spherical harmonics are not eigenfunctions of $\hat{L}_x$ or $\hat{L}_y$.

• The last two results imply that we can determine precise values of L^2 and L_z simultaneously, and that $\hat{L}^2, \hat{L}_z$ commute.

- Proving that $|m| < l$.

  - We have that

  $$\hat{L}_z^2 Y_l^m(\theta, \phi) = m^2 \hbar^2 Y_l^m(\theta, \phi) \qquad \hat{L}^2 Y_l^m(\theta, \phi) = l(l+1)\hbar^2 Y_l^m(\theta, \phi)$$

  - Subtracting and substituting $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ yields

  $$(\hat{L}^2 - \hat{L}_z^2) Y_l^m(\theta, \phi) = [l(l+1) - m^2]\hbar^2 Y_l^m(\theta, \phi)$$
  $$(\hat{L}_x^2 + \hat{L}_y^2) Y_l^m(\theta, \phi) = [l(l+1) - m^2]\hbar^2 Y_l^m(\theta, \phi)$$

  - It follows since $m, l \in \mathbb{Z}$ that

  $$0 \leq L_x^2 + L_y^2 = [l(l+1) - m^2]\hbar^2$$
  $$0 \leq l(l+1) - m^2$$
  $$m^2 \leq l(l+1)$$
  $$|m| \leq l$$

  as desired.

- Consider the case $l = 1$.

  - In this case, $L^2 = 2\hbar^2$ and $L_z = -\hbar, 0, \hbar$.
  - It follows from the first condition that $|L| = \sqrt{L^2} = \sqrt{2}\hbar$, i.e., the magnitude of the angular momentum vector is $\sqrt{2}\hbar$.
  - Since L and L_z have differing magnitudes, their vectors cannot point in the same direction.
  - Since $\hat{L}^2$ commutes with each of $\hat{L}_x, \hat{L}_y, \hat{L}_z$ individually but the three directional components don't commute among themselves, it is possible to measure the values of L^2 and any directional component simultaneously to any precision, but this leads to complete uncertainty in the other two directional components.
  - This combined with the fact that $\langle L_x \rangle = \langle L_y \rangle = 0$ leads to this nice interpretation: Imagine **L** processing around a cone whose axis is the z-axis. We know that the height of **L** (its z-coordinate) never changes, but the x, y-coordinates could be anywhere.

- Solving the radial equation.

  - Energy is quantized by

  $$E_n = -\frac{m_e e^4}{8\epsilon_0^2 h^2 n^2} = -\frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2} = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2}$$

  for $n = 1, 2, \ldots$ where a_0 is the Bohr radius.

    - Note that these energies are identical to those predicted by the Bohr model, even though the electron here is not restricted to sharply defined circular orbits but rather is described by $\psi(r, \theta, \phi)$.
  - We also have the condition
  $$0 \leq l \leq n - 1$$

  on the quantum number n.

  - Thus, the radial wave functions depend on the quantum numbers n and l as follows.

  $$R_{nl}(r) = -\sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}} \left(\frac{2}{na_0}\right)^{l+3/2} r^l e^{-r/na_0} L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$$

11/2:

$n = 1$	$l = 0$	$L_1^1(x) = -1$
$n = 2$	$l = 0$	$L_2^1(x) = -2!(2 - x)$
	$l = 1$	$L_3^3(x) = -3!$
$n = 3$	$l = 0$	$L_3^1(x) = -3!(3 - 3x + \frac{1}{2}x^2)$
	$l = 1$	$L_4^3(x) = -4!(4 - x)$
	$l = 2$	$L_5^5(x) = -5!$
$n = 4$	$l = 0$	$L_4^1(x) = -4!(4 - 6x + 2x^2 - \frac{1}{6}x^3)$
	$l = 1$	$L_5^3(x) = -5!(10 - 5x + \frac{1}{2}x^2)$
	$l = 2$	$L_6^5(x) = -6!(6 - x)$
	$l = 3$	$L_7^7(x) = -7!$

Table 4.4: The first few associated Laguerre polynomials.

■ The $L_{n+l}^{2l+1}(2r/na_0)$ are the **associated Laguerre polynomials**.
■ The combinatorial factors in Table 4.4 just guarantee that the $R_{nl}(r)$ are normalized.

• We can now construct the complete hydrogen atomic wave functions as

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_l^m(\theta, \phi)$$

$n = 1$	$l = 0$	$m = 0$	$\psi_{100} = \dfrac{1}{\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} e^{-\sigma}$
$n = 2$	$l = 0$	$m = 0$	$\psi_{200} = \dfrac{1}{\sqrt{32\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2}(2 - \sigma)e^{-\sigma/2}$
	$l = 1$	$m = 0$	$\psi_{210} = \dfrac{1}{\sqrt{32\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2}\sigma e^{-\sigma/2}\cos\theta$
	$l = 1$	$m = \pm 1$	$\psi_{21\pm 1} = \dfrac{1}{\sqrt{64\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2}\sigma e^{-\sigma/2}\sin\theta e^{\pm i\phi}$
$n = 3$	$l = 0$	$m = 0$	$\psi_{300} = \dfrac{1}{81\sqrt{3\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2}(27 - 18\sigma + 2\sigma^2)e^{-\sigma/3}$
	$l = 1$	$m = 0$	$\psi_{310} = \dfrac{\sqrt{2}}{81\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2}(6\sigma - \sigma^2)e^{-\sigma/3}\cos\theta$
	$l = 1$	$m = \pm 1$	$\psi_{31\pm 1} = \dfrac{1}{81\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2}(6\sigma - \sigma^2)e^{-\sigma/3}\sin\theta e^{\pm i\phi}$
	$l = 2$	$m = 0$	$\psi_{320} = \dfrac{1}{81\sqrt{6\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2}\sigma^2 e^{-\sigma/3}(3\cos^2\theta - 1)$
	$l = 2$	$m = \pm 1$	$\psi_{32\pm 1} = \dfrac{1}{81\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2}\sigma^2 e^{-\sigma/3}\sin\theta\cos\theta e^{\pm i\phi}$
	$l = 2$	$m = \pm 2$	$\psi_{32\pm 2} = \dfrac{1}{162\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2}\sigma^2 e^{-\sigma/3}\sin^2\theta e^{\pm 2i\phi}$

Table 4.5: The first few complete hydrogenlike atomic wave functions.

– Note that in Table 4.5, Z is the atomic number of the nucleus and $\sigma = Zr/a_0$ where a_0 is the Bohr radius.

– The orthonormality condition is

$$\int_0^\infty \mathrm{d}r\, r^2 \int_0^\pi \mathrm{d}\theta \sin\theta \int_0^{2\pi} \mathrm{d}\phi\, \psi^*_{n'l'm'}(r,\theta,\phi)\psi_{nlm}(r,\theta,\phi) = \delta_{nn'}\delta_{ll'}\delta_{mm'}$$

- **Principal quantum number**: The quantum number n.

  – $n = 1, 2, \ldots$.
  – The energy of the hydrogen atom depends on n.

- **Angular momentum quantum number**: The quantum number l.

  – $l = 0, 1, \ldots, n-1$.
  – The angular momentum of the electron about the proton is determined by l through $|L| = \hbar\sqrt{l(l+1)}$.
  – When $l = 0, 1, 2, 3$, it is customary to denote the value of l with the letters s, p, d, f, respectively.
    - After 3, we continue alphabetically past f.
    - The origin of s, p, d, f is historic from the designation of the observed spectral lines of atomic sodium; s, p, d, f stand for sharp, principal, diffuse, and fundamental, respectively.
  – A wave function with $n = 1$ and $l = 0$ is called a $1s$ wave function; a wave function with $n = 2$ and $l = 0$ is called a $2s$ wave function, and so on and so forth.

- **Magnetic quantum number**: The quantum number m.

  – $m = 0, \pm 1, \pm 2, \ldots, \pm l$.
  – So named because "the energy of a hydrogen atom in a magnetic field depends on m" (McQuarrie & Simon, 1997, p. 209).

- **Zeeman effect**: In the absence of a magnetic field, energy levels are $2l + 1$-fold degenerate; in the presence of a magnetic field, however, the energy levels split.

  – In the magnetic field case, E is a function of both n and m.

- Since the radial wave functions are normalized, we have that

$$\int_0^\infty [R_{nl}(r)]^2 r^2\, \mathrm{d}r = 1$$

  – It follows that the probability that the nl electron lies between r and $r + \mathrm{d}r$ is

$$\mathrm{Prob} = [R_{nl}(r)]^2 r^2\, \mathrm{d}r$$

  – Alternatively, we can consider the full wave functions to learn that

$$\mathrm{Prob} = r^2\, \mathrm{d}r \int_0^\pi \mathrm{d}\theta \sin\theta \int_0^{2\pi} \mathrm{d}\phi\, \psi^*_{nlm}(r,\theta,\phi)\psi_{nlm}(r,\theta,\phi)$$

  – For any specific example, these two equations will be in agreement.

- The number of radial nodes is equal to $n - l - 1$.

- **Orbital**: An atomic wave function.

- The above radial probability functions can be used to calculate average values of r via

$$\langle r \rangle_{nl} = \int_0^\infty r R^*_{nl}(r) R_{nl}(r)\, \mathrm{d}r$$

- Using general properties of the associated Laguerre polynomials, we can show that

$$\langle r \rangle_{ns} = \frac{3}{2}a_0 n^2$$

- We can calculate the most probable value of r for an nl wave function by differentiating the probability function and setting it equal to zero and then maximizing over the possible values.

- p orbitals.

  - Considers the p_z orbital corresponding to Y_1^0, which is real.
  - Covers tangent sphere picture, probability density plot, and contour map representations of atomic orbitals.
  - When $m \neq 0$, the angular wave functions $Y_1^{\pm 1}$ are complex.
  - To make them real, note that $|Y_1^1|^2 = |Y_1^{-1}|^2$, so the probability densities and hence energies are the same.
  - It follows that any linear combination of these two wave functions is another energy eigenfunction with the same energy, so take

$$p_x = \frac{1}{\sqrt{2}}(Y_1^1 + Y_1^{-1}) \qquad\qquad p_y = \frac{1}{\sqrt{2}i}(Y_1^1 - Y_1^{-1})$$

- d orbitals.

  - We can take analogous linear combination to find real solutions (see Table 4.6).

- "There is no fundamental reason to choose these linear combinations of spherical harmonics over the spherical harmonic themselves, but most chemists use the five d orbitals given... because the functions... are real and have directional properties consistent with molecular structures" (McQuarrie & Simon, 1997, p. 218).

- The Schrödinger equation of the helium atom is

$$\left(-\frac{\hbar^2}{2M}\nabla^2 - \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2\right)\psi(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2)$$
$$+ \left(-\frac{2e^2}{4\pi\epsilon_0|\mathbf{R} - \mathbf{r}_1|} - \frac{2e^2}{4\pi\epsilon_0|\mathbf{R} - \mathbf{r}_2|} + \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_1 - \mathbf{r}_2|}\right)\psi(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2) = E)\psi(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2)$$

  - $\mathbf{R}$ is the position of the helium nucleus.
  - $\mathbf{r}_1, \mathbf{r}_2$ are the positions of the two electrons.
  - M is the mass of the nucleus.
  - m_e is the electronic mass.
  - ∇^2 is the Laplacian operator with respect to the position of the nucleus.
  - ∇_1^2, ∇_2^2 are the Laplacian operators with respect to the positions of the electrons.

- The above Schrödinger equation describes a three body problem and thus is not solveable.

- By fixing the nucleus at the center of a spherical coordinate system (as is justifiable since $M >> m_e$), we can simplify the Schrödinger equation to

$$-\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2)\psi(\mathbf{r}_1, \mathbf{r}_2) - \frac{2e^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)\psi(\mathbf{r}_1, \mathbf{r}_2) + \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_1 - \mathbf{r}_2|}\psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2)$$

- **Interelectronic repulsion term**: The $e^2/4\pi\epsilon_0|\mathbf{r}_1 - \mathbf{r}_2|$ term in the Schrödinger equation of the helium atom.

  - This term makes it so that even this equation is still not solveable.

$$n = 1 \quad l = 0 \quad m = 0 \qquad \psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma}$$

$$n = 2 \quad l = 0 \quad m = 0 \qquad \psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (2 - \sigma)e^{-\sigma/2}$$

$$l = 1 \quad m = 0 \qquad \psi_{2p_z} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \cos\theta$$

$$l = 1 \quad m = \pm 1 \quad \psi_{2p_x} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \sin\theta \cos\phi$$

$$\psi_{2p_y} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \sin\theta \sin\phi$$

$$n = 3 \quad l = 0 \quad m = 0 \qquad \psi_{3s} = \frac{1}{81\sqrt{3\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (27 - 18\sigma + 2\sigma^2)e^{-\sigma/3}$$

$$l = 1 \quad m = 0 \qquad \psi_{3p_z} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (6\sigma - \sigma^2)e^{-\sigma/3} \cos\theta$$

$$l = 1 \quad m = \pm 1 \quad \psi_{3p_x} = \frac{1}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (6\sigma - \sigma^2)e^{-\sigma/3} \sin\theta \cos\phi$$

$$\psi_{3p_y} = \frac{1}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (6\sigma - \sigma^2)e^{-\sigma/3} \sin\theta \sin\phi$$

$$l = 2 \quad m = 0 \qquad \psi_{3d_{z^2}} = \frac{1}{81\sqrt{6\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3} (3\cos^2\theta - 1)$$

$$l = 2 \quad m = \pm 1 \quad \psi_{3d_{xz}} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3} \sin\theta \cos\theta \cos\phi$$

$$\psi_{3d_{yz}} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3} \sin\theta \cos\theta \sin\phi$$

$$l = 2 \quad m = \pm 2 \quad \psi_{3d_{x^2-y^2}} = \frac{1}{81\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3} \sin^2\theta \cos 2\phi$$

$$\psi_{3d_{xy}} = \frac{1}{81\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3} \sin^2\theta \sin 2\phi$$

Table 4.6: The first few complete real hydrogenlike atomic wave functions.

Problems

10/29: **6-2.** In terms of the variable θ, Legendre's equation is

$$\sin\theta \frac{\mathrm{d}}{\mathrm{d}\theta} \left(\sin\theta \frac{\mathrm{d}\Theta(\theta)}{\mathrm{d}\theta}\right) + (\beta \sin^2\theta - m^2)\Theta(\theta) = 0$$

Let $x = \cos\theta$ and $P(x) = \Theta(\theta)$. Show that

$$(1 - x^2)\frac{\mathrm{d}^2 P(x)}{\mathrm{d}x^2} - 2x\frac{\mathrm{d}P(x)}{\mathrm{d}x} + \left[\beta - \frac{m^2}{1 - x^2}\right] P(x) = 0$$

Answer. If $\cos\theta = \frac{x}{1}$, then

$$\sin\theta = \sqrt{1 - x^2}$$

Additionally,

$$\frac{\mathrm{d}\Theta}{\mathrm{d}\theta} = \frac{\mathrm{d}P}{\mathrm{d}\theta} = \frac{\mathrm{d}P}{\mathrm{d}x}\frac{\mathrm{d}x}{\mathrm{d}\theta} = -\sin\theta\frac{\mathrm{d}P}{\mathrm{d}x} = -\sqrt{1 - x^2}\frac{\mathrm{d}P}{\mathrm{d}x}$$

Therefore, we have by substitution and simplification that

$$
\begin{aligned}
0 &= \sqrt{1-x^2}\,\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sqrt{1-x^2}\cdot-\sqrt{1-x^2}\frac{\mathrm{d}P}{\mathrm{d}x}\right) + (\beta^2(1-x^2)-m^2)P(x) \\
&= \sqrt{1-x^2}\,\frac{\mathrm{d}}{\mathrm{d}x}\left(-(1-x^2)\frac{\mathrm{d}P}{\mathrm{d}x}\right)\frac{\mathrm{d}x}{\mathrm{d}\theta} + (\beta^2(1-x^2)-m^2)P(x) \\
&= (1-x^2)\frac{\mathrm{d}}{\mathrm{d}x}\left((1-x^2)\frac{\mathrm{d}P}{\mathrm{d}x}\right) + (\beta^2(1-x^2)-m^2)P(x) \\
&= (1-x^2)\left[(1-x^2)\frac{\mathrm{d}^2P}{\mathrm{d}x^2} - 2x\frac{\mathrm{d}P}{\mathrm{d}x}\right] + (\beta^2(1-x^2)-m^2)P(x) \\
&= (1-x^2)\frac{\mathrm{d}^2P}{\mathrm{d}x^2} - 2x\frac{\mathrm{d}P}{\mathrm{d}x} + \left[\beta^2 - \frac{m^2}{1-x^2}\right]P(x)
\end{aligned}
$$

$\square$

Week 5

Approximate Solutions of the Schrödinger Equation

5.1 Approximation Methods

- The **variational method** and **perturbation theory** are two methods of approximating solutions to Schrödinger equations describing systems more complex than the hydrogen atom.

- To begin our investigation of the variational method, we will look at the particle in a box.

  - Consider a Hamiltonian for an electron in a box of length $L = 2$ a.u. centered around $x = 0$.
    - Note that we take the electron as the fundamental mass, $\hbar$ as the fundamental unit of energy time, and the charge of the electron as the fundamental unit of charge, and the Bohr radius as the fundamental unit of length.
  - Our Hamiltonian is
    $$H\psi(x) = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi(x)$$
    or, in atomic units,
    $$H\psi(x) = -\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi(x)$$

- **Variational theorem**: The expectation value of our Hamiltonian with respect to a trial wave function produces an approximate energy. Moreover[1],
  $$E_{\mathrm{approx}} \geq E_{\mathrm{gr.\ st.}}$$

- **Variational method**: Take $\psi_{\mathrm{trial}} = \sum_n a_n \left|\psi_n\right\rangle$ where ψ_n is a trial wave function and the a_j's are parameters of the wave function which we want to optimize to lower E_{trial}.

  - Dirac's ket describes an abstract state of the particle (possibly position, possibly its Fourier transform, momentum).

- Back to the particle in a box:

  - A possible trial wave function (that satisfies the boundary conditions) is
    $$\psi_{\mathrm{tr}} = (1+x)(1-x) = 1 - x^2$$

---

[1] We will prove that the approximate energy is an upper bound on the ground state energy in the homework.

- The energy of ψ_{tr} may be evaluated as follows.

$$\begin{aligned}
E &= \frac{\int \psi_{\text{tr}}^*(x)\hat{H}\psi_{\text{tr}}(x)\,\mathrm{d}x}{\int \psi_{\text{tr}}^*(x)\psi_{\text{tr}}(x)\,\mathrm{d}x} \\[6pt]
&= \frac{\int_{-1}^{1}(1-x^2)\left(-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\right)(1-x^2)\,\mathrm{d}x}{\int_{-1}^{1}(1-x^2)(1-x^2)\,\mathrm{d}x} \\[6pt]
&= \frac{\int_{-1}^{1}(1-x^2)\,\mathrm{d}x}{\int_{-1}^{1}(1-x^2)(1-x^2)\,\mathrm{d}x} \\[6pt]
&= \frac{4/3}{16/15} \\[6pt]
&= \frac{5}{4} \\[6pt]
&= 1.25\,\text{a.u.}
\end{aligned}$$

- From the exact solution to the particle in a box

$$E_1 = 1.23370055 < 1.25 = E_{\text{trial}}$$

so the variational theorem is satisfied.

- Next step: Trial wave function as a linear combination is $\psi_{\text{tr}}(x) = c_1\psi_1(x) + c_2\psi_2(x)$.
- Plugging this into the SE yields

$$c_1(\hat{H} - E)\psi_1(x) + c_2(\hat{H} - E)\psi_2(x) = 0$$

  ■ ψ_1, ψ_2 span the (Hilbert) space of solutions.

- To solve the above equation, multiply by $\psi_1(x)$ and integrate to obtain

$$c_1\int_{-1}^{1}\psi_1^*(x)(\hat{H}-E)\psi_1(x)\,\mathrm{d}x + c_2\int_{-1}^{1}\psi_1^*(x)(\hat{H}-E)\psi_2(x)\,\mathrm{d}x = 0$$

and multiply by $\psi_2(x)$ an integrate to obtain

$$c_1\int_{-1}^{1}\psi_2^*(x)(\hat{H}-E)\psi_1(x)\,\mathrm{d}x + c_2\int_{-1}^{1}\psi_2^*(x)(\hat{H}-E)\psi_2(x)\,\mathrm{d}x = 0$$

- Substituting, we have

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0 \qquad c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) = 0$$

- In matrix form, the above two equations become

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} - E\begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$
$$\mathbb{H}\vec{c} - E\mathbb{S}\vec{c} = 0$$

  ■ We get a matrix that the same dimension as the size of the expansion (in the first case, we had a 1×1 matrix).
  ■ $\mathbb{S}$ is the overlap matrix because the wave functions aren't normalized.

5.2   Variational Method

10/27:
- Approximating the ground state energy with some trial wave function and applying

$$E_{\text{approx}} = \frac{\int \psi_{\text{tr}}^* \hat{H} \psi_{\text{tr}} \, \mathrm{d}x}{\int \psi_{\text{tr}}^* \psi_{\text{tr}} \, \mathrm{d}x}$$

where

$$\psi_{\text{tr}} = \sum_n c_n \psi_n(x)$$

- Example 2:

- For our second term, we need another even function (since the ground state wavefunction is even). Thus, choose

$$\psi_{\text{tr}}(x) = c_1(1 - x^2) + c_2(1 - x^2)x^2$$

  - Think about this in the context of power series — we have $(1 - x^2)$ times an even power series expansion $(c_1 + c_2 x^2)$.

- To find c_1, c_2, we could plug into the approximation integral and minimize.

- Alternatively, we can use matrices. We essentially project the Schrödinger equation onto the space of the two wave functions.

- Take $\hat{H}\psi = E\psi$ and expand it to $\hat{H}(c_1\psi_1 + c_2\psi_2) = E(c_1\psi_1 + c_2\psi_2)$. In matrix form, $\mathbb{H}\vec{c} = E\mathbb{S}\vec{c}$.

- We have an overlap matrix $\mathbb{S}$ because our wave functions aren't normalized. If the basis *is* orthonormal, $\mathbb{S}$ collapses to the identity matrix.

  - Each s_{ij} equals

$$s_{ij} = \int \psi_i^* \psi_j \, \mathrm{d}x$$

  - If ψ_1, ψ_2 is orthonormal, then $s_{ij} = \delta_{ij}$.

- The elements of the Hamiltonian matrix:

$$H_{11} = \int \psi_1^*(x) \hat{H} \psi_1(x) \, \mathrm{d}x \qquad\qquad H_{12} = \int \psi_1^*(x) \hat{H} \psi_2(x) \, \mathrm{d}x$$

$$= \frac{4}{3} \qquad\qquad\qquad\qquad\qquad = \frac{8}{15}$$

$$H_{21} = \frac{8}{15} \qquad\qquad\qquad\qquad H_{22} = \frac{44}{105}$$

  - Notice that $\mathbb{H}$ is symmetric with $H_{12} = H_{21}$.

- Elements of the overlap matrix:

$$S_{11} = \frac{16}{15} \qquad\qquad\qquad\qquad S_{12} = \frac{32}{105}$$

$$S_{21} = \frac{32}{105} \qquad\qquad\qquad\qquad S_{22} = \frac{16}{315}$$

  - Notice that $\mathbb{S}$ is symmetric with $S_{12} = S_{21}$.

- Note that there are multiple ways to solve $\mathbb{H}\vec{c} = E\mathbb{S}\vec{c}$; McQuarrie and Simon (1997) only teaches one. Thus, you can get computers to do the math and solve far bigger systems than you could by hand.

- Solving $\mathbb{H}\vec{c} = E\mathbb{S}\vec{c}$ with the textbook method:

  - Rewrite as $(\mathbb{H} - E\mathbb{S})\vec{c} = 0$. Find the null space of $\mathbb{H} - E\mathbb{S}$.
  - Since the determinant is the product of the eigenvalues, $\det(\mathbb{H} - E\mathbb{S}) = (E_1 - E)(E_2 - E)$.
  - This determinant is equal to zero only when $E = E_1$ or $E = E_2$.
    - ■ The energy is becoming quantized because of the linear algebra!
  - Now taking $\det(\mathbb{H} - E\mathbb{S})$ gives a characteristic polynomial in E.

$$
0 = \begin{vmatrix} \frac{4}{3} - \frac{16}{15}E & \frac{4}{15} - \frac{16}{105}E \\ \frac{4}{15} - \frac{16}{105}E & \frac{44}{105} - \frac{16}{315}E \end{vmatrix}
$$
$$
= \frac{256}{525} - \frac{2048}{4725}E + \frac{1024}{33075}E^2
$$

  - Solving the quadratic gives us

$$
E = 7 \pm \frac{\sqrt{133}}{2}
$$

  - Thus,

$$
E_1 = 1.233\,718\,705 \text{ a.u.} \qquad\qquad E_2 = 12.766 \text{ a.u.}
$$

  - ■ Notice that the E_1 we found is only *marginally* greater than the real value of E_1. Our value is accurate to four decimal places!
  - Solving for $\vec{c}$ with E_1 gives us

$$
\vec{c}_1 = -0.9764 \qquad\qquad \vec{c}_2 = 0.2156
$$

5.3 Perturbation Theory

10/29:

- Consider the Hamiltonian

$$
\hat{H} = \hat{H}_0 + \lambda\hat{V}
$$

where $\hat{H}_0$ is the reference hamiltonian, $\hat{V}$ is the perturbation, and λ is the perturbation parameter.

- The energy may be expressed as a Taylor series expansion in λ:

$$
E(\lambda) = E(0) + \lambda\frac{\mathrm{d}E}{\mathrm{d}\lambda}\bigg|_0 + \frac{\lambda^2}{2}\frac{\mathrm{d}^2E}{\mathrm{d}x^2}\bigg|_0 + \cdots
$$

  - If λ is sufficiently small, we can get good approximations without resorting to higher order derivatives.

- It follows that our reference energy is

$$
E(0) = \int \psi_0^* \hat{H}_0 \psi_0 \, \mathrm{d}x
$$

- We now have that

$$
E(\lambda) = \int \psi^*(\lambda) \hat{H}(\lambda) \psi(\lambda) \, \mathrm{d}x
$$

- We also have from differentiating that

$$
\frac{\mathrm{d}E}{\mathrm{d}\lambda} = \int \frac{\mathrm{d}\psi}{\mathrm{d}\lambda} \hat{H}\psi(\lambda) \, \mathrm{d}x + \int \psi^*(\lambda)\hat{H}^* \frac{\mathrm{d}\psi}{\mathrm{d}\lambda} \, \mathrm{d}x + \int \psi^* \frac{\mathrm{d}\hat{H}}{\mathrm{d}\lambda} \psi(\lambda) \, \mathrm{d}x
$$

$$= E \int \frac{\mathrm{d}\psi^*}{\mathrm{d}\lambda} \psi(\lambda) \, \mathrm{d}x + E \int \psi^*(\lambda) \frac{\mathrm{d}\psi}{\mathrm{d}\lambda} \, \mathrm{d}x + \int \psi^* \frac{\mathrm{d}\hat{H}}{\mathrm{d}\lambda} \psi(\lambda) \, \mathrm{d}x$$

$$= E \frac{\mathrm{d}}{\mathrm{d}\lambda} \left(\int \psi^*(\lambda) \psi(\lambda) \, \mathrm{d}x \right) + \int \psi^* \hat{H} \psi \, \mathrm{d}x$$

$$= \int \psi^*(\lambda) \frac{\mathrm{d}\hat{H}}{\mathrm{d}\lambda} \psi(\lambda) \, \mathrm{d}x$$

$$= \int \psi^*(\lambda) \hat{V} \psi(\lambda) \, \mathrm{d}x$$

- – Note that the commutativity of $\hat{H}$ follows from the fact that it's a Hermitian operator.

- It follows that

$$\left. \frac{\mathrm{d}E}{\mathrm{d}\lambda} \right|_{\lambda=0} = \int \psi_0^* V \psi_0 \, \mathrm{d}x$$

  - – Richard Feynman worked this out for his undergraduate thesis at MIT. This laid the foundation of quantum electrodynamics, for which he would eventually win the Nobel prize.
  - – This is known as the **Hellmann-Feynman theorem** (1939).
  - – Note that the second derivative of $E(\lambda)$ unfortunately depends on $\mathrm{d}\psi/\mathrm{d}\lambda$.

- Many electron molecules: The Helium atom.

  - – We have $\hat{H}\psi = E\psi$ where

$$\hat{H} = -\frac{1}{2}\hat{\nabla}_1^{\,2} - \frac{1}{2}\hat{\nabla}_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

    - ■ Note that the ∇'s are Laplacians.
    - ■ This equation takes into account the kinetic and potential energy of two electrons, plus the electron-electron repulsion.

  - – Solve using perturbation theory. Our reference Hamiltonian is

$$\hat{H}_0 = \hat{H}_{\mathrm{He}_1^+} + \hat{H}_{\mathrm{He}_2^+} = \underbrace{-\frac{1}{2}\hat{\nabla}_1^2 - \frac{Z}{r_1}}_{\mathrm{He}_1^+} \underbrace{-\frac{1}{2}\hat{\nabla}_2^2 - \frac{Z}{r_2}}_{\mathrm{He}_2^+}$$

    - ■ I.e., it's the sum of the Hamiltonians of two helium ions (one-electron systems like hydrogen).
  - – Since $\hat{V} = +1/r_{12}$, we have that
$$\hat{H}(1) = \hat{H}_0 + \hat{V}$$
    is the hamiltonian of the atom.
  - – Now we look for the solution to $\hat{H}_0 \psi_0 + E_0 \psi_0$.
  - – We know that
$$\psi_0 = \psi_{1s}(r_1\theta_1\phi_1)\psi_{1s}(r_2\theta_2\psi_2)$$
    - ■ The fact that only two electrons fit in an orbital emerges naturally from the quantum mechanics!
  - – We also know that
$$E_0 = -\frac{Z^2}{2n^2} - \frac{Z^2}{2n^2} = -4\,\mathrm{a.u.}$$
  - – Thus, by perturbation theory,

$$\left. \frac{\mathrm{d}E}{\mathrm{d}\lambda} \right|_{\lambda=0} = \int \psi_0^* \hat{V} \psi_0 \, \mathrm{d}\vec{r}_1 \, \mathrm{d}\vec{r}_2$$

$$= \int 1\mathrm{s}^*(1)1\mathrm{s}^*(2)\hat{V}1\mathrm{s}(1)1\mathrm{s}(2) \, \mathrm{d}1 \, \mathrm{d}2$$

$$= \frac{5}{8}Z$$

5.4 Chapter 7: Approximation Methods

From McQuarrie and Simon (1997).

11/2:
- Although the Schrödinger equation cannot be solved exactly for any system more complicated than the hydrogen atom, we can use either the **variational method** or **perturbation theory** to approximate solutions to Schrödinger equations to almost any desired accuracy.

- We begin with the variational method.

- If the ground-state wave function and corresponding energy of some arbitrary system are ψ_0 and E_0, respectively, then

$$\hat{H}\psi_0 = E_0\psi_0$$
$$\psi_0^*\hat{H}\psi_0 = \psi_0^*E_0\psi_0$$
$$\int \psi_0^*\hat{H}\psi_0\,\mathrm{d}\tau = E_0\int \psi_0^*\psi_0\,\mathrm{d}\tau$$
$$E_0 = \frac{\int \psi_0^*\hat{H}\psi_0\,\mathrm{d}\tau}{\int \psi_0^*\psi_0\,\mathrm{d}\tau}$$

where $\mathrm{d}\tau$ represents the appropriate volume element for integrating over all space.

- **Variational principle**: If ϕ is any function, then

$$\frac{\int \phi^*\hat{H}\phi\,\mathrm{d}\tau}{\int \phi^*\phi\,\mathrm{d}\tau} = E_\phi \geq E_0 = \frac{\int \psi_0^*\hat{H}\psi_0\,\mathrm{d}\tau}{\int \psi_0^*\psi_0\,\mathrm{d}\tau}$$

and $E_\phi = E_0$ iff $\phi = \psi_0$[2].

- Essentially, the variational method consists of choosing a trial function ϕ that depends on **variational parameters** (numbers) so that E_ϕ depends on the variational parameters, too, and minimizing E_ϕ over the parameters.

- McQuarrie and Simon (1997) does a worked example with the ground state of the hydrogen atom, comparing answers with the exact solution.

  - Uses the formula for E_ϕ to directly express it in terms of the variational parameter and then differentiates to find the maxima.

  - Applied to a case that can be solved exactly, the variational method with a trial wave function of the appropriate form will give the exact solution.

- Estimating the ground state energy of a helium atom, and deriving effective nuclear charge.

  - Consider the Hamiltonian for helium from the end of Chapter 6.

  - It can be written in the form

$$\hat{H} = \hat{H}_{\mathrm{H}}(1) + \hat{H}_{\mathrm{H}}(2) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}}$$

  where $\hat{H}_{\mathrm{H}}(j)$, $j = 1, 2$, is the Hamiltonian operator for a single electron around a helium nucleus.

  - Ignoring the interelectron repulsion term gives us a separable wave function of the form

$$\phi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)$$

  - We use the above as our trial wave function with Z (see Table 4.6) as our variational parameter.

---

[2] See Problem **??** for a proof of the variational principle.

- – Minimizing gives us $Z_{\min} = 27/16$ and a fairly good $E_{\min}$ value.
  - – Note that $Z_{\min}$ can naturally be interpreted as the **effective nuclear charge**.
  - – Since $Z_{\min} < 2$, we have that each electron partially **screens** the nucleus from the other.

- McQuarrie and Simon (1997) arrives at the two linear algebraic equations Mazziotti did by expanding $\int \phi \hat{H} \phi \, d\tau$ with $\phi = c_1 f_1 + c_2 f_2$, applying the condition that H is Hermitian from Chapter 4 to show that $H_{ij} = H_{ji}$ and $S_{ij} = S_{ji}$, and differentiating the resulting energy function with respect to c_1 and then with respect to c_2.

- **Matrix elements**: The quantities H_{ij} and S_{ij}.

- **Secular determinant**: A determinant of the form

$$
\begin{vmatrix}
H_{11} - ES_{11} & \cdots & H_{1n} - ES_{1n} \\
\vdots & & \vdots \\
H_{n1} - ES_{n1} & \cdots & H_{nn} - ES_{nn}
\end{vmatrix}
$$

  - – There exists a solution to the linear algebraic equations iff the secular determinant vanishes (equals 0).

- **Secular equation**: The equation obtained by expanding the secular determinant.

  - – The smaller root of a second-degree secular equation is an upper bound on the ground state energy.

  - – The larger root of a second-degree secular equation is an upper bound on the energy of the first excited state (albeit usually a crude one; we do not investigate methods of approximating energies other than that of the ground state here).

- Normalizing the trial wave function.

  - – Since the linear system is homogenous, all of the c_1 terms (for example) can be expressed as a linear combination of all of the other terms.

  - – From here, we can find the ratios $c_2/c_1, c_3/c_1, \ldots, c_N/c_1$.

  - – Thus, we simply integrate the modulus squared of our trial wave function with c_1 free and set the result equal to 1. Solving for c_1 normalizes the equation.

- Note that trial wave functions can be linear combinations of functions that also contain variational parameters, but minimization here must be done numerically as the system is no longer linear.

- We now discuss perturbation theory.

- Suppose we cannot solve the Schrödinger equation $\hat{H}\psi = E\psi$ but we can solve $\hat{H}^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$, which corresponds to a system that is in some sense similar to the unsolvable system. Then let $\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$.

- **Unperturbed Hamiltonian operator**: The Hamiltonian operator corresponding to the system we can solve exactly. *Denoted by* $\hat{\boldsymbol{H}}^{(0)}$.

- **Perturbation**: The difference between the Hamiltonian operator we cannot solve and the unperturbed Hamiltonian operator. *Denoted by* $\hat{\boldsymbol{H}}^{(1)}$.

- In perturbation theory, we let

$$
\psi = \psi^{(0)} + \psi^{(1)} + \psi^{(2)} + \cdots \qquad\qquad E = E^{(0)} + E^{(1)} + E^{(2)} + \cdots
$$

where $\psi^{(1)}, \psi^{(2)}, \ldots$ and $E^{(1)}, E^{(2)}, \ldots$ are successive corrections to $\psi^{(0)}$ and $E^{(0)}$, respectively.

- We can show (see Problem **??**) that

$$E^{(1)} = \int \psi^{(0)*} \hat{H}^{(1)} \psi^{(0)} \, \mathrm{d}\tau$$

  - Note that we can (although we will not here) derive explicit expressions for higher order corrections. These do get messy though.

- Uses perturbation theory to derive the energy of a particle in a one-dimensional slanted box, and separately the energy of a Helium electron.

Week 6

Multi-electron Atoms and Molecules

6.1 Many-electron Atoms and Molecules

- Picking up from last time, since $Z = 2$ for helium,

$$\left.\frac{\mathrm{d}E}{\mathrm{d}\lambda}\right|_{\lambda=0} = \frac{5}{8}Z = \frac{5}{4}$$

- Additionally,

$$E_{\mathrm{He}} = -Z^2 + \frac{5}{8}Z = -4 + \frac{5}{4} = -2.75\,\mathrm{a.u.}$$

  - The first equality is the ground state energy of two-electron atoms or ions.

- Summary:

  - Zeroeth-order Perturbation Theory approximation: $E_0 = -4\,\mathrm{a.u.}$
  - First-order approximation: $E_0 + E' = -2.75\,\mathrm{a.u.}$
  - Second-order: $E_0 + E' + \frac{1}{2}E'' = -2.9077\,\mathrm{a.u.}$
  - Thirteenth-order: $-2.903\,724\,33\,\mathrm{a.u.}$

- Variational calculation of Helium:

  - Simplest: $\psi_0(12) = 1\mathrm{s}(1)1\mathrm{s}(2)$. Gives $E = -2.75\,\mathrm{a.u.}$
  - Trial ψ with one parameter: $\psi_0(1,2) = \tilde{1\mathrm{s}}(1)\tilde{1\mathrm{s}}(2)$, where $\tilde{1\mathrm{s}}(1) = \sqrt{Z^3/\pi}\mathrm{e}^{-Zr_1}$. Energy: $E = -2.8477\,\mathrm{a.u.}$

- Ionization energy.

  - Simplest approximation:

$$\begin{aligned}
\mathrm{IE} &= E_{\mathrm{He}^+} - E_{\mathrm{He}} \\
&= -2 - (-2.75) \\
&= 0.75\,\mathrm{a.u.} \\
&= 1969\,\mathrm{kJ/mol}
\end{aligned}$$

  - Exact number:

$$\begin{aligned}
\mathrm{IE} &= E_{\mathrm{He}^+} - E_{\mathrm{He}} \\
&= -2 - (-2.903\,724) \\
&= 0.9033\,\mathrm{a.u.} \\
&= 2372\,\mathrm{kJ/mol}
\end{aligned}$$

- Optimal orbitals (Hartree-Fock): Optimizing the orbitals to lower the energy as much as possible.

  - $\psi(12) = \phi(r_1)\phi(r_2)$.
  - The orbital energies converge to
    $$E_{\mathrm{HF}} = -2.8617 \,\text{a.u.}$$

- Allow the $\psi(12)$ to move beyond a simple product of orbitals (Hylleras (1930)).

  - $\psi(r_1, r_2, r_{12}) = \mathrm{e}^{-Zr_1}\mathrm{e}^{-Zr_2}(1 + cr_{12})$.
  - Accounting for the electron-electron repulsion (the **electron correlation energy**) gives us an energy much better than the Hartree-Fock calculation:
    $$E = -2.8913 \,\text{a.u.}$$

  - Pekeris (1959): Did a variational calculation with 1078 parameters. Was working at IBM, who told him to do something with their newest computer that would be impressive to the world. Pekeris tackled this, and got
    $$E = -2.903\,724\,375 \,\text{a.u.}$$
    which is even more accurate than 13th order perturbation theory.

    - This value cannot be accurately measured to this precision in the laboratory. Additionally, relativistic quantum mechanics (using the Dirac equation of which the Schrödinger equation is only a part) predicts a value that diverges from this one around the fifth decimal point, and this is the experimentally verifiable value.
    - This is important because scientists want to figure out how accurately can we account for the electron cusp.

- To summarize, the improvement tiers are

  1. H orbitals.
  2. MO picture (Hartree-Fock).
  3. Solution of the Schrödinger equation (electron correlation).

- Recall that the electron has spin (from the Stern-Gerlach and Uhlenbeck-Goudsmit experiments).

  - This is analogous to orbital angular momentum:
    $$\hat{L}^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm} \qquad\qquad \hat{L}_z Y_{lm} = m\hbar Y_{lm}$$

  - These two operators give rise to
    $$\hat{S}^2 \sigma = s(s+1)\hbar^2 \sigma \qquad\qquad \hat{S}_z \sigma = m_s \hbar \sigma$$
    where σ is the spin eigenfunction, s is the total spin angular momentum quantum number, and m_s is the spin quantum number.
  - We have $\sigma = \alpha$ or $\sigma = \beta$ where α represents "up" and β represents "down."
  - $m_s = \pm 1/2$ where $s = 1/2$, so $m_s = -s, s$.
  - Spin eigenfunctions are orthonormal, i.e.,
    $$\int \alpha^* \alpha = \int \beta^* \beta = 1 \qquad\qquad \int \alpha^* \beta = \int \beta^* \alpha = 0$$

  - Hence, each electron has four degrees of freedom (three spatial and one spin).
  - This gives rise to a **spin orbital** $\psi(x, y, z, \sigma) = \phi(x, y, z)\sigma$, which is the product of the spin and spatial orbitals.

- In fact, our ability to calculate the energy of the helium atom was complete luck — we cannot calculate the energy of any other element on the periodic table without accounting for spin.

6.2 Many-electron Atoms and Molecules / Spin

11/3:
- **Spin orbital**: A spatial orbital augmented with a spin eigenfunction. *Given by*

$$\psi(x, y, z, \sigma) = \phi(x, y, z)\sigma$$

- Key idea: Electrons are indistinguishable, i.e., if $\psi(1, 2, \ldots, N)$ where each number represents the three spatial coordinates of an electron, the N electrons in ψ must be indistinguishable.

- There are two possible ways to achieve *mathematical* indistinguishability.

  1. We can require that
  $$\psi(1, 2, 3, \ldots, N) = \psi(2, 1, 3, \ldots, N)$$

     – Essentially, this is a symmetric permutation of all pairs of particles.

  2. We can alternatively require that
  $$\psi(1, 2, 3, \ldots, N) = -\psi(2, 1, 3, \ldots, N)$$

     – Because the probability is invariant to the sign (think about taking the modulus squared and how that eliminates sign considerations).
     – Essentially, this is an antisymmetric permutation of all pairs of particles.

- Experimental observation shows two types of particles in nature.

  1. Bozons (symmetric permutations).
  2. Fermions (antisymmetric permutations).

- Electrons are Fermions.

- Prob $= \psi^*(1, 2, \ldots, N)\psi(1, 2, \ldots, N)$ tells us the probability of finding the N electrons at the positions specified by 1 through N.

- Example (helium):

  – We had $\psi(1, 2) = 1s\alpha(1)1s\beta(2)$.
  – But since the electrons are distinguishable here, we have to make them indistinguishable by letting

  $$\psi(1, 2) = 1s\alpha(1)12\beta(2) - 1s\alpha(2)1s\beta(1)$$
  $$= 1s(1)1s(2)[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

     ■ Here, we've separated out the spatial and spin parts.

- How to represent antisymmetry.

  – Grassmann Wedge Product (1850s): Herman de Grassmann was studying linear algebra and would learn about higher dimensional spaces in his dreams.
  – de Grassman says

  $$\psi(1, 2) = 1s\alpha(1) \wedge 1s\beta(2)$$
  $$= \frac{1}{2!}(1s\alpha(1)1s\beta(2) - 1s\alpha(2)1s\beta(1))$$

  where $\wedge$ is the wedge product, a tensor product.
     ■ We can normalize the above by substituting $\sqrt{2!}$ for $2!$.
  – Slater determinant (1930): Took

  $$\psi(1, 2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix}$$

- We now consider lithium.

    - Let's put 3 electrons in a single orbital:

    $$\psi(1,2,3) = 1s\alpha(1) \wedge 1s\beta(2) \wedge 1s\beta(3)$$

        ■ $1s\beta(2) \wedge 1s\beta(3)$ will vanish as per Grassmann algebra since the electrons have the same spin state. In general, $\phi \wedge \phi = 0$.

    - Thus, in general,

    $$\psi(1,2,3) = \sqrt{3!}(1s\alpha(1) \wedge 1s\beta(2) \wedge 2s\alpha(3))$$

    or, using the Slater determinant,

    $$\psi(1,2,3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) & 2s\alpha(1) \\ 1s\alpha(2) & 1s\beta(2) & 2s\alpha(2) \\ 1s\alpha(3) & 1s\beta(3) & 2s\alpha(3) \end{vmatrix}$$

- **Pauli exclusion principle**: Each electron must occupy a distinct spin orbital, that is, it must have a distinct set of 4 quantum numbers n, l, m, m_s.

    - Emerges naturally from the quantum mechanics as per the above.

- What if electrons were bozons?

    - Then

    $$\psi(1,2,3) = 1s\alpha(1) \vee 1s\beta(2) \vee 2s\alpha(3)$$

    where $\vee$ is the bozonic operator, i.e., the symmetric wedge product, which denotes the positive sum of all permutations.

    - We have

    $$\phi(1) \vee \phi(2) = \phi(1)\phi(2) + \phi(2)\phi(1)$$
    $$= 2\phi(1)\phi(2)$$

    - Thus, we could put an infinite number of electrons in the same orbital (all electrons could occupy the same orbital) if electrons were bozons, and our shell structure would disintegrate.

        ■ Everything would also merge; we could not form matter as we know it.

- Sodium atoms are bozons.

6.3   Chapter 8: Multielectron Atoms

From McQuarrie and Simon (1997).

11/7:
- **Atomic units**: A system of units widely adopted for atomic and molecular calculations to simplify the equations.

Property	Atomic unit	SI Equivalent
mass	mass of an electron, m_e	9.1094×10^{-31} kg
charge	charge on a proton, e	1.6022×10^{-19} C
angular momentum	reduced Planck constant, $\hbar$	1.0546×10^{-34} J s
distance	Bohr radius, $a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2$	5.2918×10^{-11} m
energy	$e^2/4\pi\epsilon_0 a_0 = E_\text{h}$	4.3597×10^{-18} J
permittivity	$4\pi\epsilon_0$	1.1127×10^{-10} C^2 J^{-1} m^{-1}

Table 6.1: Atomic units and their SI equivalents.

- **Hartree**: The atomic unit of energy. *Denoted by* E_{h}.

  - Note that in atomic units, the ground-state energy of a hydrogen atom (in the fixed nucleus approximation) is $-E_{\mathrm{h}}/2$.

- Another good reason to use atomic units is that we are still refining the values of m_e, e, $\hbar$, etc., so results computed in atomic units will hold even as these constants evolve.

- Both perturbation theory and the variational method can yield excellent results for helium.

- **Slater orbital**[1]: An orbital of the following form. *Denoted by* $S_{nlm}(r, \theta, \phi)$. *Given by*

$$S_{nlm}(r, \theta, \phi) = N_{nl} r^{n-1} \mathrm{e}^{-\zeta r} Y_l^m(\theta, \phi)^{[2]}$$

  where $N_{nl} = (2\zeta)^{n+1/2}/\sqrt{(2n)!}$ and the $Y_l^m(\theta, \phi)$ are the spherical harmonics.

  - The parameter ζ is arbitrary, i.e., not necessarily Z/n as in hydrogenlike orbitals.
  - The radial components of the Slater orbitals do not have nodes like the hydrogenlike orbitals.

- **Orbital**: A one-electron wave function.

- **Hartree-Fock limit**: The best value of the energy that can be obtained using a trial function of the form of a product of orbitals.

- As such, it is advantageous to generalize our trial wave functions past simple products of orbitals.

  - Better wave functions typically include the interelectronic distance.

- This realization led scientists to abandon the orbital concept altogether in favor of finding Hartree-Fock orbitals (because they are still a useful model) and correcting them using an approach such as perturbation theory.

- Self-consistent field method for finding the Hartree-Fock orbitals (of helium).

  - Write $\psi(\mathbf{r}_1, \mathbf{r}_2)$ as a product of orbitals $\phi(\mathbf{r}_1)\phi(\mathbf{r}_2)$.
  - It follows that the potential energy that electron 1 experiences at point $\mathbf{r}_1$ due to electron 2 is

$$V_1^{\mathrm{eff}}(\mathbf{r}_1) = \int \phi^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi(\mathbf{r}_2) \, \mathrm{d}\mathbf{r}_2$$

    where the superscript "eff" emphasizes that $V_1^{\mathrm{eff}}(\mathbf{r}_1)$ is an effective, or average, potential.
  - This allows us to define the effective one-electron Hamiltonian for electron 1 by

$$\hat{H}_1^{\mathrm{eff}}(\mathbf{r}_1) = -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} + V_1^{\mathrm{eff}}(\mathbf{r}_1)$$

  - Using this Hamiltonian and the corresponding Schrödinger equation, we can determine $\phi(\mathbf{r}_1)$, given an estimate for $\phi(\mathbf{r}_2)$. Since there is analogous Schrödinger equation for $\phi(\mathbf{r}_2)$, the self-consistent field method consists of starting with a guess for $\phi(\mathbf{r}_2)$, calculating from that $\phi(\mathbf{r}_1)$, calculating from that a better guess for $\phi(\mathbf{r}_2)$, and so on and so forth until the two wave equations are reasonably close, or **self-consistent**.
  - In practice, linear combinations of Slater orbitals are used for each $\phi(\diagdown)$.

- **Uncorrelated** (electrons): A set of electrons that are taken to be independent of each other, or at least to interact only through some average (or effective) potential.

  - Uncorrelated electrons occupy mathematically separable orbitals, as in $\psi(\mathbf{r}_1, \mathbf{r}_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)$.

---

[1]First introduced by American physicist John Slater in the 1930s.
[2]ζ is the Greek "zeta."

- **Correlation energy**: The difference between the exact energy and the Hartree-Fock approximation energy. *Denoted by* **CE**.

- **Spin quantum number**: The fourth quantum number, which represents the z-component of the electron spin angular momentum. *Denoted by m_s. Given by*

$$m_s = \pm \frac{1}{2} \text{ a.u.}$$

  - Uhlenbeck and Goudsmit first suggested in 1925 that electrons behave like spinning tops having z-components of spin angular momentum $\pm \hbar/2$ to explain the phenomena of sodium having a doublet in its atomic spectrum where quantum theory predicts it should have a singlet.

- We graft spin onto quantum theory in an ad hoc manner here. This will suit our purposes.

  - Note, however, that Dirac developed in the 1930s a relativistic extension of quantum mechanics in which spin arises in a perfectly natural way.

- As part of this grafting, we *define* the **spin operators** $\hat{S}^2$ and $\hat{S}_z$ in an analogous manner to how we defined the angular momentum operators $\hat{L}^2$ and $\hat{L}_z$, except that we introduce half-integral angular momentum for electron spin: Indeed, let

$$\hat{S}^2 \alpha = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2 \alpha \qquad\qquad \hat{S}^2 \beta = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2 \beta$$

and let

$$\hat{S}_z \alpha = m_s \alpha = \frac{1}{2}\hbar\alpha \qquad\qquad \hat{S}_z \beta = m_2 \beta = -\frac{1}{2}\hbar\beta$$

  - We can formally associate $\alpha = Y_{1/2}^{1/2}$ and $\beta = Y_{1/2}^{-1/2}$ in analogy with $\hat{L}^2$ and $\hat{L}_z$, but we do not have to.
  - To continue the analogy, we can actually say that the square of the *spin* angular momentum is $S^2 = \hbar^2 s(s+1)$, where $s = \pm 1/2$.
  - Since s cannot assume large values like l and thus cannot approach a classical limit, spin is strictly nonclassical.

- **Spin eigenfunctions**: The functions α and β.

- The spin operators are Hermitian, so α, β are orthonormal.

  - Formally,

$$\int \alpha^*(\sigma)\alpha(\sigma)\,\mathrm{d}\sigma = \int \beta^*(\sigma)\beta(\sigma)\,\mathrm{d}\sigma = 1$$
$$\int \alpha^*(\sigma)\beta(\sigma)\,\mathrm{d}\sigma = \int \beta^*(\sigma)\alpha(\sigma)\,\mathrm{d}\sigma = 0$$

    where σ is the **spin variable**, an object with no classical analog.

- We now include the spin function with the spatial wave function and postulate that the two are independent so that one of the following two cases holds.

$$\psi(x,y,z,\sigma) = \psi(x,y,z)\alpha(\sigma) \qquad\qquad \psi(x,y,z,\sigma) = \psi(x,y,z)\beta(\sigma)$$

- **Spin orbital**: The complete one-electron wave function ψ dependent on x, y, z, σ.

- For example, the first two spin orbitals of a hydrogenlike atom are

$$\psi_{100\frac{1}{2}} = \sqrt{\frac{Z^3}{\pi}}\mathrm{e}^{-Zr}\alpha \qquad\qquad \psi_{100-\frac{1}{2}} = \sqrt{\frac{Z^3}{\pi}}\mathrm{e}^{-Zr}\beta$$

– Note that these orbitals are orthonormal since

$$\int \psi^*_{100\frac{1}{2}}(\mathbf{r}, \sigma)\psi_{100\frac{1}{2}}(\mathbf{r}, \sigma)4\pi r^2\,\mathrm{d}r\,\mathrm{d}\sigma = \int_0^\infty \frac{Z^3}{\pi}\mathrm{e}^{-2Zr}4\pi r^2\,\mathrm{d}r\int \alpha^*\alpha\,\mathrm{d}\sigma = 1$$

and similarly for $\psi_{100-\frac{1}{2}}$, and since

$$\int \psi^*_{100\frac{1}{2}}(\mathbf{r}, \sigma)\psi_{100-\frac{1}{2}}(\mathbf{r}, \sigma)4\pi r^2\,\mathrm{d}r\,\mathrm{d}\sigma = \int_0^\infty \frac{Z^3}{\pi}\mathrm{e}^{-2Zr}4\pi r^2\,\mathrm{d}r\int \alpha^*\beta\,\mathrm{d}\sigma = 0$$

- **Pauli Exclusion Principle** (elementary): No two electrons in an atom can have the same values of all four quantum numbers.

- Consider the helium atom.

  – Let $\psi(1,2) = 1s\alpha(1)1s\beta(2)$ where $1s\alpha$ and $1s\beta$ represent $\psi_{100\frac{1}{2}}$ and $\psi_{100-\frac{1}{2}}$, respectively, and 1 and 2 represent all four coordinates (3 spatial plus 1 spin) of electrons 1 and 2, respectively.
  – Similarly, $\psi(2,1) = 1s\alpha(2)1s\beta(1)$.
  – Since no known experiment can distinguish one electron from another, $\psi(1,2) = \psi(2,1)$.
  – Formally, we must consider the two possible states

$$\psi_1 = \psi(1,2) + \psi(2,1) \qquad\qquad \psi_2 = \psi(1,2) - \psi(2,1)$$

  of two indistinguishable electrons.
  – Experimentally, ψ_2 describes the ground state of helium since $\psi_2(1,2) = -\psi_2(2,1)$, so ψ_2 is **antisymmetric**.
  – Note that the normalization constant of ψ_2 is $1/\sqrt{2}$.

- **Antisymmetric wave function**: A wave function that changes sign when two electrons are interchanged.

- The importance of antisymmetry is captured by the following more fundamental statement of the Pauli Exclusion Principle.

  Postulate 6. *All electronic wave functions must be antisymmetric under the interchange of any two electrons.*

- We were able to ignore spin in previous treatments of helium since ψ_2 can be factored into a spatial and a spin part, and any contributions from spin cancel under a Hamiltonian that does not contain any spin operators.

  – Note that factorization of $\psi^*\hat{H}\psi$ and $\psi^*\psi$ does not occur in general, but does occur for two-electron systems.

- **Determinantal wave function**: A wave function given by the determinant of a matrix whose entries are individual spin orbitals.

  – Since the determinant representation changes signs when two rows are interchanged (representing interchanging two electrons) and is equal to zero under repeated rows/columns (representing multiple electrons in the same spin orbital), the determinant representation is antisymmetric and satisfies the Pauli Exclusion Principle, respectively.

- **Normalized N-electron determinantal wave function**: The normalized determinantal wave function

$$\psi(1,\ldots,N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} u_1(1) & \cdots & u_N(1) \\ \vdots & \ddots & \vdots \\ u_1(N) & \cdots & u_N(N) \end{vmatrix}$$

where the u's are orthonormal spin orbitals.

- **Fock operator**: The more general effective Hamiltonian operator used for self-consistent field solutions to systems more complex than helium. *Denoted by* $\hat{F}_i$.

- **Hartree-Fock orbital**: An eigenfunction of the Fock operator. *Denoted by* ϕ_i.

- **Orbital energy**: An eigenvalue of the Fock operator. *Denoted by* ϵ_i.

  - Alternatively, the energy of a Hartree-Fock orbital.
  - ϵ_i approximates the ionization energy of an electron from the ith orbital.

11/13:
- **Russell-Saunders coupling**: The result of determining the total angular momentum $\mathbf{L}$ and the total spin angular momentum $\mathbf{S}$ and then adding $\mathbf{L}$ and $\mathbf{S}$ together vectorially to obtain the total angular momentum $\mathbf{J}$.

- **Atomic term symbol**: A scheme denoting an electronic configuration of a specific energy, as determined by Russell-Saunders coupling. *Also known as* **spectroscopic term symbol**. *Denoted by* $^{2S+1}L_J$.

- **L**: The total orbital angular momentum quantum number. *Given by*

$$\mathbf{L} = \sum_i \mathbf{l}_i$$

  - Each $\mathbf{l}$ is the angular momentum of a single electron in the atom at hand.

- **S**: The total spin quantum number.

  - Each $\mathbf{s}$ is the spin of a single electron in the atom at hand.

- **J**: The total angular momentum quantum number.

- **Spin multiplicity**: The quantity $2S + 1$.

- "Just as the z-component of $\mathbf{l}$ can assume the $2l+1$ values $m_l = l, l-1, \ldots, 0, \ldots, -l$, the z-component of $\mathbf{L}$ can assume the $2L+1$ value $M_L = L, L-1, \ldots, 0, \ldots, -L$" (McQuarrie & Simon, 1997, p. 293).

- "M_S can take on the $2S+1$ values $S, S-1, \ldots, -S+1, -S$. Thus, the spin multiplicity is simply the $2S+1$ projections that the z-component of $\mathbf{S}$ can assume" (McQuarrie & Simon, 1997, p. 294).

- Example (ns^2 electron configuration):

  - The only possible set of quantum numbers is

$$m_{l_1} = 0 \qquad m_{s_1} = +\frac{1}{2} \qquad m_{l_2} = 0 \qquad m_{s_2} = -\frac{1}{2}$$

$$M_L = 0 \qquad\qquad M_S = 0$$

  - Since $M_L = 0$, $L = 0$. Similarly, $S = 0$.
  - Thus, $J = 0$.
  - Therefore, our term symbol is $^1S_0$ ("singlet S zero").

- Every filled subshell is in the $^1S_0$ state because each all spin and orbital angular momentum cancels, as in the above example.

  - This allows us to completely ignore the contributions of all filled orbitals in any electron configuration, for example, the $1s^2 2s^2$ in $1s^2 2s^2 2p^2$ wrt. the carbon atom.

- Covers microstates and microstate tables from Labalme (2021) (see Module 41).

- Shows that the electron configuration $1s^1 2s^1$ of a helium atom has two term symbols (the triplet S and the singlet S states).

- Derives the term symbols for a carbon atom in a generalizable procedure also done in Labalme (2021).

- Each state designated by a term symbol corresponds to a determinantal wave function that is an eigenfunction of $\hat{L}^2$ and $\hat{S}^2$, and each state corresponds to a certain energy. These energies *could* be calculated from the quantum mechanics, but instead we'll use **Hund's rules**.

- **Hund's rules**: Three empirical rules formulated by German spectroscopist Friedrich Hund. *Given by*

    1. The state with the largest value of S is the most stable (has the lowest energy) and stability decreases with decreasing S.
    2. For states with the same value of S, the state with the largest value of L is the most stable.
    3. If the states have the same value of L and S, then for a subshell that is less than half filled, the state with the smallest value of J is the most stable, and vice versa for a subshell that is more than half filled.

- The Schrödinger equation implies that the electronic energy of the hydrogen atom depends only upon the principal quantum number.

    - However, **spin-orbit coupling** implies that the various n levels are split into sets of closely lying energy levels.

- **Spin-orbit interaction**: The interaction of the magnetic moment associated with the spin of an electron with the magnetic field generated by the electric current produced by the electron's own orbital motion.

    - There also exist **spin-spin interaction** and **orbit-orbit interaction**.

- A quantum mechanical treatment of spin-orbit coupling.

    - Essentially, consider the Hamiltonian operator for a multielectron atom

    $$\hat{H} = -\frac{1}{2} \sum_j \delta_j^2 - \sum_j \frac{Z}{r_j} + \sum_{i<j} \frac{1}{r_{ij}} + \sum_j \xi(r_j) \mathbf{l}_j \cdot \mathbf{s}_j$$

    where $\xi(r_j)$ is a scalar function of r.

    - We've treated the first three terms previously, and for light elements, we can treat the fourth term as a sufficiently small perturbation. Applying perturbation theory then predicts the observed orbital splitting.

- **Fine structure**: The increased spectral complexity caused by spin-orbit coupling.

Week 7

Molecular Spectroscopy and Group Theory

7.1 Hydrogen Molecule

- Reviews what would happen if electrons were bozons.

    - The wave function ψ of the lithium atom would be

    $$\psi(123) = 1s\alpha(1) \vee 1s\alpha(2) \vee 1s\alpha(3)$$

    - Reviews wedge products.
    - Conclusion: All electrons could occupy the same orbital.

- A sodium atom (the nucleus and the electrons jointly) acts like a bozon.

    - At temperatures on the order of microkelvin, 10^{11} atoms have been placed in the same ground-state orbital.
    - These substances are known as **Bose-Einstein condensates**.
    - We use a magnetic field to confine the atoms to a harmonic potential. Since the atoms form a Gaussian curve at the bottom of said potential, they are all in the ground state (see Figure 3.3).
    - Evaporative cooling and laser cooling allow you to reach such temperatures.
    - Fermionic atoms cannot condense in such a way (because of the Pauli Exclusion Principle).
    - Superconductivity is a condensation phenomena.
    - Bose-Einstein condensates were predicted by Einstein in the 1930s but not experimentally verified until the 1990s.
    - A very dilute gas was used here. In such a condition, the atoms feel the statistics force of the wedge product which forces them into such a state.

- Consider the Boron atom:
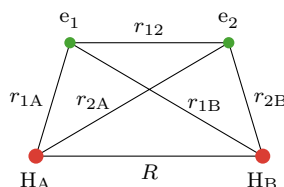
    - It has 5 electrons.
    - It's electron configuration is $1s^2 2s^2 sp^1$.
    - It's wave function is

    $$\psi(12345) = 1s\alpha(1) \wedge 1s\beta(2) \wedge 2s\alpha(3) \wedge 2s\beta(4) \wedge 2p\alpha(5)$$

        ■ Recall that this is not the exact wave function; this is still a product of hydrogenlike orbitals at the Hartree-Fock level.

■ More general wave functions can be used to obtain more accurate results.

- Consider the diatomic molecule H_2.

Figure 7.1: H_2 distances.

  – We have hydrogen atoms H_A and H_B, separated by a distance R.
  – We have electrons e_1 and e_2.
  – The distance from object i to j where $i, j = A, B, 1, 2$ and $i \neq j$ is r_{ij}.
  – Hamiltonian:
$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R}$$

- This is pretty complicated.

- Thus, let's start with the hydrogen molecular ion $(H_2{}^+)$.
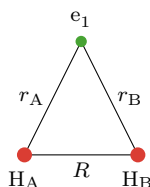
Figure 7.2: $H_2{}^+$ distances.

  – Hamiltonian:
$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

  – This *can* be solved exactly in cylindrical coordinates, but it's nasty.
  – Thus, let's approximate with the following variational wave function (originally by Heitler and London in the 1960s).
$$\psi(1) = c_1 1s_A + c_2 1s_B$$

    ■ Albeit simple, this wave function gives pretty good results.
  – By the variational principle, $\mathbb{H}\vec{c} = E\mathbb{S}\vec{c}$, or

$$\begin{vmatrix} H_{AA} - ES_{AA} & H_{AB} - ES_{AB} \\ H_{BA} - ES_{BA} & H_{BB} - ES_{BB} \end{vmatrix} = 0$$

solves for E.

– We have that

$$H_{AA} = H_{BB} = \int d\vec{r}\, 1s_A^* \hat{H} 1s_A = \int d\vec{r}\, 1s_B^* \hat{H} 1s_B$$

$$H_{AB} = H_{BA} = \int d\vec{r}\, 1s_A^* \hat{H} 1s_B = \int d\vec{r}\, 1s_B^* \hat{H} 1s_A$$

$$S_{AA} = S_{BB} = \int d\vec{r}\, 1s_A^* 1s_A = \int d\vec{r}\, 1s_B^* 1s_B$$

$$S_{AB} = S_{BA} = \int d\vec{r}\, 1s_A^* 1s_B = \int d\vec{r}\, 1s_B^* 1s_A$$

– We can show that

$$H_{AA} = H_{BB} = E_{1s} + J$$
$$H_{AB} = H_{BA} = E_{1s}\mathbb{S} + K$$

where E_{1s} is the energy of the $1s$ orbital of the hydrogen atom, J is the **Coulomb integral**

$$J = \int d\vec{r}\, 1s_A^* \left(-\frac{1}{r_B} + \frac{1}{R} \right) 1s_A$$

and K is the **exchange integral**

$$K = \int d\vec{r}\, 1s_B^* \left(-\frac{1}{r_B} + \frac{1}{R} \right) 1s_A$$

7.2 The Hydrogen Molecular Ion

11/10:

- Continuing from last time, the determinant for the equation $\mathbb{H}\vec{c}_n = E_n \mathbb{S}\vec{c}_n$ is

$$\begin{vmatrix} E_{1s} + J - E & E_{1s}S + K \\ E_{1s}S + K & E_{1s} + J - E \end{vmatrix}$$

- Therefore, the characteristic polynomial is a quadratic equation in E.

- Solving said quadratic gives us

$$E_\pm = E_{1s} + \frac{J \pm K}{1 \pm S}$$

where

$$J(R) = e^{-2R}\left(1 + \frac{1}{R}\right) \qquad S(R) = e^{-R}\left(1 + R + \frac{R^2}{3}\right) \qquad K(R) = \frac{S(R)}{R} - e^{-R}(1 + R)$$

- We then determine $\vec{c}_n$ in the two different cases. But this yields

$$|c_1| = |c_2| = k$$

- Therefore,
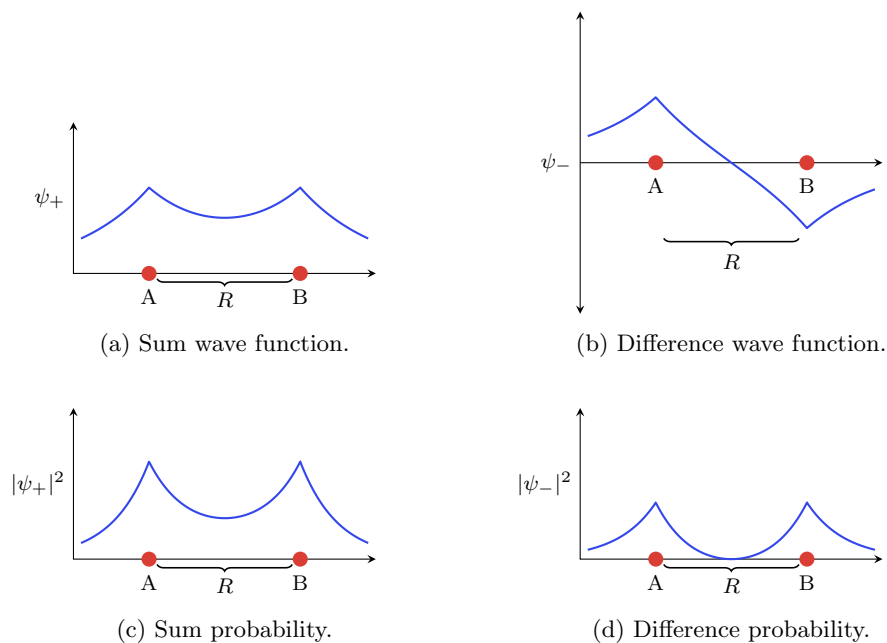
$$\psi_\pm = k(1s_A \pm 1s_B)$$

(a) Sum wave function.

(b) Difference wave function.

(c) Sum probability.

(d) Difference probability.

Figure 7.3: Hydrogen ion bonding.

- Note that in ψ_-, a node arises naturally from the quantum mechanics.
- Thus, ψ_+ is a bonding orbital and ψ_- is an antibonding orbital.

• We now consider the **potential energy surface** or **PES** of the molecule.
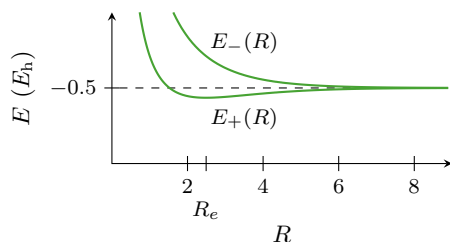

Figure 7.4: Potential energy surface of the hydrogen molecular ion.

- The x, y-axis units are Bohrs and Hartrees, respectively.
- The bound state only occurs in the bonding orbital; if the electron is excited to the antibonding orbital, the atoms will drift apart to ∞ to minimize energy.

• **Born-Oppenheimer approximation**.

- Throughout this derivation, we neglected the kinetic energy of the nuclei.
- Thus, technically the total Hamiltonian is

$$\hat{H}_{\text{tot}} = -\frac{\hbar^2}{2M}(\hat{\nabla}_{\text{A}}^2 + \hat{\nabla}_{\text{B}}^2) + \hat{H}_{\text{electr}}$$

where $\hat{H}_{\text{electr}}$ is the Hamiltonian associated with Figure 7.2.

- We have assumed that the nuclei are fixed relative to the motion of the electrons. We can do this because $m_e/M \approx 10^{-3}$, i.e., the electrons travel much faster than the nuclei. Therefore, the kinetic energy of the electrons is more important.

– The wave functions of the nuclei (which do exist) are very sharp peaks, so the nuclei don't move much, so we may regard them as fixed.

- **Molecular orbital**: A linear combination of atomic orbitals. *Also known as* **MO**.

- Example (H_2):

    – $\psi_\pm = 1s_A \pm 1s_B$ (bonding and antibonding).
    – $\phi_{MO} = \phi_{1s_A} + \phi_{1s_B}$.
    – $\phi(12) = \phi_{MO}\alpha(1) \wedge \phi_{MO}\beta(2)$; thus, the MO diagram is connected back to the rigorous mathematics of Schrödinger.

- Filling rules: Fill the MOs that are lower in energy first.

- Example (C_2):

    – The MO diagram is identical to Figure III.17 from Labalme (2021) except that the σ_g corresponding to the $2p$ orbitals has higher energy than the π_u's due to mixing.

7.3 Huckel Theory

11/12:
- Reviews that diatomics with more electrons will have less mixing.

- **Bond order**: A measure of stability. *Given by*

$$BO = \frac{1}{2}[(\# \text{ of electrons in } BO_1) - (\# \text{ of electrons in } ABO_1)]$$

    – For example, for C_2, we will have $BO = \frac{1}{2}(8 - 4) = 2$.

- Huckel was a physicist/chemist from the 1930s who worked out the MO theory for conjugated molecules.

- Huckel's strategy.

    1. $\mathbb{H}\vec{c} = E\mathbb{S}\vec{c}$ becomes $\mathbb{H}\vec{c} = E\vec{c}$, where the only orbitals considered are the p_z orbitals.
    2. We let $\mathbb{S} = \mathbb{I}$, i.e., we assume all orbitals are orthonormal. $S_{ij} = \delta_{ij}$.
    3. $H_{ii} = \alpha$ (the energy of the electrons in p_z).
        – $H_{i,i+1} = H_{i+1,i} = \beta$ (interaction between adjacent p_z orbitals).
        – Everything else is zero!
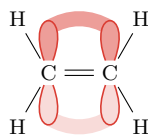
- Example: Ethene.

Figure 7.5: Ethene orbital diagram.

    – The Hamiltonian matrix is

$$\mathbb{H} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}$$

- If we let $(\alpha - E)/\beta = x$, then

$$
\begin{aligned}
0 &= \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} \\
&= \frac{1}{\beta^2} \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} \\
&= \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix}
\end{aligned}
$$

- Thus, our characteristic polynomial is

$$
\begin{aligned}
0 &= x^2 - 1 \\
&= (x+1)(x-1)
\end{aligned}
$$

so $x = \pm 1$.

- It follows from returning the substitution that $\alpha \pm \beta = E_{\mp}$.
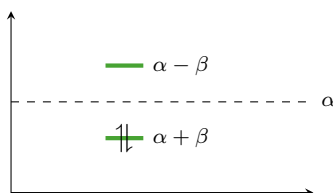- This yields the following energy diagram.

Figure 7.6: Ethene energy diagram.

- Note that the ground state MO is more stable than the 1-electron in each p_z orbital scenario; thus bonding occurs.
- It follows that

$$
\psi_{\alpha+\beta} = 2p_{z_{\mathrm{A}}} + 2p_{z_{\mathrm{B}}} \qquad\qquad \psi_{\alpha-\beta} = 2p_{z_{\mathrm{A}}} - 2p_{z_{\mathrm{B}}}
$$

■ Thus, $\psi_{\alpha+\beta}$ has π_u symmetry and $\psi_{\alpha-\beta}$ has π_g symmetry.

- Example: 1,3-butadiene.

   - Our determinant here will be

$$
\begin{aligned}
0 &= \begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} \\
&= \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} \\
&= x^4 - 3x^2 + 1 \\
&= y^2 - 3y + 1 \\
y &= \frac{3 \pm \sqrt{5}}{2} \\
x &= \pm 1.618, \pm 0.618
\end{aligned}
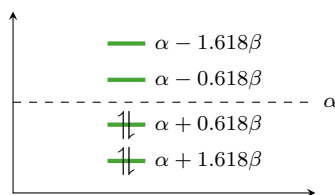$$

- Thus, our energy diagram will be

$$\text{——} \quad \alpha - 1.618\beta$$
$$\text{——} \quad \alpha - 0.618\beta$$
$$\text{- - - - - - - - - - - -} \quad \alpha$$
$$\text{⥮} \quad \alpha + 0.618\beta$$
$$\text{⥮} \quad \alpha + 1.618\beta$$

Figure 7.7: 1,3-butadiene energy diagram.

– This yields the bond order $BO = \frac{1}{2}(4 - 0) = 2$.

– Solving for the possible $\vec{c}$'s yields four wave function LCAOs analogous to the particle in a box wave functions (even function, odd function with one node, even function with two nodes, odd function with three nodes).

■ Thus, the Huckel approximation agrees with the approximation of four particles in a box.

• Example 3: 1,3,5-hexatriene.

– Working out the determinant yields

$$0 = x^6 - 5x^4 + 6x^2 - 1$$
$$= y^3 - 5y^2 + 6y - 1$$

– Our energy diagram is as one might expect with 3 bonding orbitals and 3 antibonding orbitals.

7.4　Office Hours (Mazziotti)

• How does the asymptotic analysis guarantee us the $n = 1$ solution, from Problem Set 5.1e?

– $n = 1$ dominates in the asymptotic analysis, especially among the ground states.

• Math that we're using?

– We're doing a lot of linear algebra, ordinary differential equations, and partial differential equations (boundary condition differential equations). Typically eliptic boundary conditions.

– Eigenvalue equations, determinants, etc.

– We're in a Hilbert space. Hilbert spaces are subsets of the Banach spaces, so all of that linear algebra applies.

– Differential equations in a subspace can be rewritten as eigenvalue equations?

– Ties into real analysis and complex analysis with $e^{i\phi}$.

– The Grassmann algebra is a piece of classical mathematics that plays in.

– Point groups and spin groups fall under abstract algebra; more specifically, Lie algebra.

7.5　Chapter 9: The Chemical Bond — Diatomic Molecules

From McQuarrie and Simon (1997).

11/8:　• Quantum mechanics was the first theory to explain why atoms combined to form a stable bond.

• Since H_2^+ has the simplest chemical bond, we will discuss it in detail.

– The ideas developed will be applicable to more complex molecules, motivating molecular orbitals.

• Describes the Hamiltonian for H_2, as in the discussion associated with Figure 7.1.

- **Born-Oppenheimer approximation**: The approximation of neglecting the nuclear motion, allowing us to ignore $\nabla_{A,B}$ terms.

  - We can correct for the BO approximation using perturbation theory, but realistically we don't really need to (corrections are on the order of the mass ratio 10^{-3}).

- **Molecular-orbital theory**: The method we will use to describe the bonding properties of molecules.

- **Molecular orbital**: A single-electron wave function corresponding to a molecule.

- Like we constructed atomic wave functions in terms of determinants involving atomic orbitals, we will construct molecular wave functions in terms of determinants involving molecular orbitals.

- Note that H_2^+ is a stable, well-studied species in real life.

- Although the Schrödinger equation for H_2^+ can be solved exactly within the BO approximation, the solutions are not easy to use and their mathematical form gives little physical insight into how and why bonding occurs.

  - Thus, we use approximate solutions that provide good physical insight and are in good agreement with experimental observations.

- As a first trial wave function $\psi(r_A, r_B; R)$, use

$$\psi_\pm = c_1 1s_A \pm c_2 1s_B$$

  where $1s_{A,B}$ are the hydrogen atomic orbitals centered on nuclei A and B, respectively.

  - By symmetry, $c_1 = c_2$ for H_2^+.

- **LCAO molecular orbital**: A molecular orbital that is a linear combination of atomic orbitals.

- We seek to find $E_\pm$ by taking the quotient the integrals $\int d\mathbf{r} \, \psi_\pm^* \hat{H} \psi_\pm$ and $\int d\mathbf{r} \, \psi_\pm^* \psi_\pm$.

- Considering $\int d\mathbf{r} \, \psi_\pm^* \psi_\pm$ first, we are lead to define the **overlap integral**.

- **Overlap integral**: The following integral, which is only significant where there is a large overlap between the two hydrogenlike atomic orbitals. *Denoted by* $\boldsymbol{S}$. *Given by*

$$S = \int d\mathbf{r} \, nl_A^* nl_B = \int d\mathbf{r} \, nl_B^* nl_A = \int d\mathbf{r} \, nl_A nl_B$$

(a) Small overlap. (b) Large overlap.
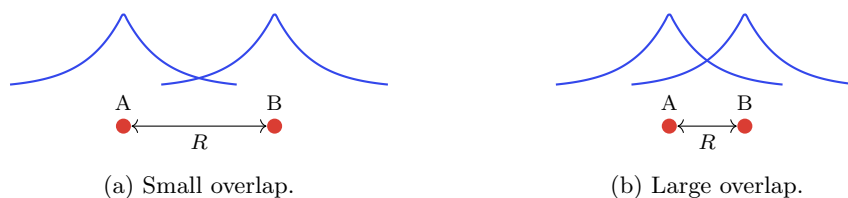
Figure 7.8: Overlap integral vs. internuclear distance.

  - As $R \to 0$, $S \to 1$. As $R \to \infty$, $S \to 0$.

- The overlap integral when $nl = 1s$ can be evaluated analytically, giving

$$S(R) = e^{-R}\left(1 + R + \frac{R^2}{3}\right)$$

- The overlap integral allows us to express $\int d\mathbf{r}\, \psi_{\pm}^{*}\psi_{\pm}$ in the following convenient form.

$$\int d\mathbf{r}\, \psi_{+}^{*}\psi_{+} = \int d\mathbf{r}\, (1s_{A}^{*} + 1s_{B}^{*})(1s_{A} + 1s_{B})$$

$$= \int d\mathbf{r}\, 1s_{A}^{*}1s_{A} + \int d\mathbf{r}\, 1s_{A}^{*}1s_{B} + \int d\mathbf{r}\, 1s_{B}^{*}1s_{A} + \int d\mathbf{r}\, 1s_{B}^{*}1s_{B}$$

$$= 1 + S + S + 1$$

$$= 2(1 + S)$$

- It follows that the normalized $\psi_{\pm}$ are

$$\psi_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}}(1s_{A} \pm 1s_{B})$$

11/14:
- We now look to evaluate the integral $\int d\mathbf{r}\, \psi_{+}^{*}\hat{H}\psi_{+}$.

- To begin, we have that

$$\int d\mathbf{r}\, \psi_{+}^{*}\hat{H}\psi_{+} = \int d\mathbf{r}\, (1s_{A}^{*} + 1s_{B}^{*})\left(-\frac{1}{2}\nabla^{2} - \frac{1}{r_{A}} - \frac{1}{r_{B}} + \frac{1}{R}\right)(1s_{A} + 1s_{B})$$

$$= \int d\mathbf{r}\, (1s_{A}^{*} + 1s_{B}^{*})\left(-\frac{1}{2}\nabla^{2} - \frac{1}{r_{A}} - \frac{1}{r_{B}} + \frac{1}{R}\right)1s_{A}$$

$$+ \int d\mathbf{r}\, (1s_{A}^{*} + 1s_{B}^{*})\left(-\frac{1}{2}\nabla^{2} - \frac{1}{r_{A}} - \frac{1}{r_{B}} + \frac{1}{R}\right)1s_{B}$$

$$= \int d\mathbf{r}\, (1s_{A}^{*} + 1s_{B}^{*})\left(E_{1s} - \frac{1}{r_{B}} + \frac{1}{R}\right)1s_{A}$$

$$+ \int d\mathbf{r}\, (1s_{A}^{*} + 1s_{B}^{*})\left(E_{1s} - \frac{1}{r_{A}} + \frac{1}{R}\right)1s_{B}$$

$$= \int d\mathbf{r}\, \left(E_{1s} - \frac{1}{r_{B}} + \frac{1}{R}\right)1s_{A}^{*}1s_{A} + \int d\mathbf{r}\, \left(E_{1s} - \frac{1}{r_{B}} + \frac{1}{R}\right)1s_{B}^{*}1s_{A}$$

$$+ \int d\mathbf{r}\, \left(E_{1s} - \frac{1}{r_{B}} + \frac{1}{R}\right)1s_{A}^{*}1s_{B} + \int d\mathbf{r}\, \left(E_{1s} - \frac{1}{r_{B}} + \frac{1}{R}\right)1s_{B}^{*}1s_{B}$$

$$= E_{1s} \cdot 1 + \int d\mathbf{r}\, \left(-\frac{1}{r_{B}} + \frac{1}{R}\right)1s_{A}^{*}1s_{A} + E_{1s} \cdot S + \int d\mathbf{r}\, \left(-\frac{1}{r_{B}} + \frac{1}{R}\right)1s_{B}^{*}1s_{A}$$

$$+ E_{1s} \cdot 1 + \int d\mathbf{r}\, \left(-\frac{1}{r_{B}} + \frac{1}{R}\right)1s_{A}^{*}1s_{B} + E_{1s} \cdot S + \int d\mathbf{r}\, \left(-\frac{1}{r_{B}} + \frac{1}{R}\right)1s_{B}^{*}1s_{B}$$

$$= 2E_{1s}(1 + S)$$

$$+ \int d\mathbf{r}\, \left(-\frac{1}{r_{B}} + \frac{1}{R}\right)1s_{A}^{*}1s_{A} + \int d\mathbf{r}\, \left(-\frac{1}{r_{B}} + \frac{1}{R}\right)1s_{B}^{*}1s_{A}$$

$$+ \int d\mathbf{r}\, \left(-\frac{1}{r_{B}} + \frac{1}{R}\right)1s_{A}^{*}1s_{B} + \int d\mathbf{r}\, \left(-\frac{1}{r_{B}} + \frac{1}{R}\right)1s_{B}^{*}1s_{B}$$

where $E_{1s} = -E_{h}/2$ is the ground-state energy of the hydrogen atom (the energy corresponding to the $1s_{A}$ wave function).

- **Coulomb integral**: The following integral, which reflects both the charge density of the electron about nucleus A interacting with nucleus B via the Coulumb potential and the internuclear repulsion. *Denoted by J. Given by*

$$J = \int d\mathbf{r}\, 1s_{A}^{*}\left(-\frac{1}{r_{B}} + \frac{1}{R}\right)1s_{A}$$

- **Exchange integral**: The following integral. *Also known as* **resonance integral**. *Denoted by* $\boldsymbol{K}$. *Given by*

$$K = \int d\mathbf{r}\, 1s_{\mathrm{B}}^* \left(-\frac{1}{r_{\mathrm{B}}} + \frac{1}{R} \right) 1s_{\mathrm{A}}$$

  - The exchange integral describes a purely quantum-mechanical effect; it has no analogy in classical mechanics.

- Using the definitions of the Coluomb and exchange integrals, we have that

$$\int d\mathbf{r}\, \psi_+^* \hat{H} \psi_+ = 2E_{1s}(1 + S) + 2J + 2K$$

- We can now determine a final expression for the energy E_+ corresponding to ψ_+.

$$\begin{aligned}
E_+ &= \frac{\int d\mathbf{r}\, \psi_+^* \hat{H} \psi_+}{\int d\mathbf{r}\, \psi_+^* \psi_+} \\
&= \frac{2E_{1s}(1 + S) + 2J + 2K}{2(1 + S)} \\
&= E_{1s} + \frac{J + K}{1 + S}
\end{aligned}$$

- The Coulomb and exchange integrals can be evaluated analytically, giving

$$J = e^{-2R}\left(1 + \frac{1}{R} \right) \qquad\qquad K = \frac{S}{R} - e^{-R}(1 + R)$$

  - Note that since the Coulomb integral is always positive, the exchange integral is entirely responsible for the existence of the chemical bond in H_2^+.
  - This highlights the importance of the quantum-mechanical nature of the chemical bond.

- **Bonding orbital**: A state that exhibits a stable chemical bond.

  - Example: ψ_+.

- **Antibonding orbital**: A state that leads to a repulsive interaction between the two nuclei for all internuclear distances.

  - Example: ψ_-.

- The bonding orbital $\psi_{\mathrm{b}} = \psi_+$ describes the ground state of H_2^+, while the antibonding orbital $\psi_{\mathrm{a}} = \psi_-$ describes an excited state.

- Note that we have only found two molecular orbitals (as opposed to the infinitely many hydrogenlike atomic orbitals) because we used a trial wave function that was the linear combination of only two atomic orbitals. We could use longer linear combinations to find more molecular orbitals, but for pedagogical reasons, we will limit ourselves to two for now.

- "Because ψ_{b} is the molecular orbital corresponding to the ground-state energy of H_2^+, we can describe the ground state of H_2 by placing two electrons with opposite spins in ψ_{b}, just as we placed two electrons in a $1s$ atomic orbital to describe the helium atom" (McQuarrie & Simon, 1997, p. 336).

- This leads to the Slater determinantal wave function

$$\psi = \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_{\mathrm{b}}\alpha(1) & \psi_{\mathrm{b}}\beta(1) \\ \psi_{\mathrm{b}}\alpha(2) & \psi_{\mathrm{b}}\beta(2) \end{vmatrix}$$

for H_2.

      – As before, the spatial and spin parts of this two-electron wave function separate.

- It follows that the spatial molecular wave function is

$$\psi_{\text{MO}} = \psi_{\text{b}}(1)\psi_{\text{b}}(2)$$
$$= \frac{1}{2(1+S)}[1s_{\text{A}}(1) + 1s_{\text{B}}(1)][1s_{\text{A}}(2) + 1s_{\text{B}}(2)]$$

- **Linear combination of atomic orbitals-molecular orbitals method**: The method of construct-
  ing molecular wave functions by taking the product of molecular orbitals, which are in turn linear
  combinations of atomic orbitals. *Also known as* **LCAO-MO method**.

  – This is how we constructed ψ_{MO}, above.

- Knowing that ψ_{MO} is normalized, we have that

$$E_{\text{MO}} = \int d\mathbf{r}_1 \, d\mathbf{r}_2 \, \psi_{\text{MO}}^*(1,2)\hat{H}\psi_{\text{MO}}(1,2)$$

- **σ orbital**: An orbital that is symmetric about the internuclear axis.

  – Both $\psi_{\pm}$ are σ orbitals.

  – Molecular orbitals constructed from $1s$ orbitals are denoted by $\sigma 1s$.

- Distinguishing between $\sigma 1s$ bonding and antibonding orbitals.

  – We may let $\sigma 1s$ refer to ψ_+ and $\sigma^* 1s$ refer to ψ_-.

  – We may let $\sigma_g 1s$ refer to ψ_+ (g being short for "gerade" [the German word for even] since ψ_+
    does not change sign under inversion) and $\sigma_u 1s$ refer to ψ_- (u being short for "ungerade" [the
    German word for odd] since ψ_- does change sign under inversion).

  – McQuarrie and Simon (1997) will favor the latter notation.

- $\sigma 2s$ molecular orbitals.

  – Of the form $2s_{\text{A}} \pm 2s_{\text{B}}$.

  – Have radial nodes about each nuclei (owing to the structure of the $2s$ hydrogenlike atomic orbital)
    in addition to the possible planar node in the middle of the molecule.

  – Have higher energies than $\sigma 1s$ MOs since they're associated with higher energy atomic orbitals.
    This can be demonstrated rigorously the same way we calculated the energies for the $\sigma 1s$ MOs.

  – In terms of energy, $\sigma_g 1s < \sigma_u 1s < \sigma_g 2s < \sigma_u 2s$.

- $2p$ molecular orbitals.

  – Choose the internuclear axis to be the z-axis.

  – $2p_{z_{\text{A}}} \pm 2p_{z_{\text{B}}}$ are cylindrically symmetric about the internuclear axis and are therefore $\sigma_u 2p_z$ and
    $\sigma_g 2p_z$ orbitals, respectively.

  – $2p_{x,y_{\text{A}}} \pm 2p_{x,y_{\text{B}}}$ are **π orbitals**, denoted $\pi_u 2p_{x,y}$ and $\pi_g 2p_{x,y}$, respectively.

  – $\pi_u 2p_x, \pi_u 2p_y$ and $\pi_g 2p_x, \pi_g 2p_y$ are degenerate pairs of orbitals since they are identical except for
    their spatial orientation.

- **π orbital**: A molecular orbital with one nodal plane that contains the internuclear axis.

- From Li_2 through N_2, the energy order is

$$\sigma_g 2s < \sigma_u 2s < \pi_u 2p_{x,y} < \sigma_g 2p_z < \pi_g 2p_{x,y} < \sigma_u 2p_z$$

– From O_2 through F_2, the energy order is

$$\sigma_g 2s < \sigma_u 2s < \sigma_g 2p_z < \pi_u 2p_{x,y} < \pi_g 2p_{x,y} < \sigma_u 2p_z$$

- Diatomic helium does not exist since the bonding and antibonding electrons cancel each other out, leaving only repulsive nuclei.

  – Bond order formalizes this notion.
  – Note that in 1993, Gentry and co. reported spectroscopic observations of He_2 in a gas-phase sample of helium of temperature $0.001\,K$, possessing by far the weakest chemical bond known.

- Note that since there is little difference between the electron densities of core electron-derived molecular orbitals, we need only consider electrons in the valence shell when discussing chemical bonding.

- We denote the filled $n = 1$ shell by K, e.g., the ground state electron configuration of Li_2 is $KK(\sigma_g 2s)^2$.

- MO theory accurately predicts that O_2 is paramagnetic.

  – MO theory also predicts bond orders of $2.5, 2, 1.5, 1$ for O_2^+, O_2, O_2^-, O_2^{2-}, respectively. This would suggest that bond length increases and bond energy decreases down this list, as we do indeed observe experimentally.

- McQuarrie and Simon (1997) provides data on the ground-state electron configuration, bond order, bond length, and bond energy for the homonuclear diatomics of lithium through neon.

- **Ionization energy**: The energy required to eject an electron from a molecule.

- **Photoelectron spectroscopy**: The measurement of the energies of the electrons ejected by radiation incident on gaseous molecules.

  – Goes through how PES supports MO theory, as on Labalme (2021, p. 56).

- **Heteronuclear diatomic molecule**: A diatomic molecule in which the two nuclei are different.

- For heteronuclear diatomics whose constituent atoms' atomic numbers differ by 1 or 2, the scheme we used for homonuclear diatomics is good enough.

- For heteronuclear diatomics whose constituent atoms' atomic numbers differ greatly (e.g., HF), we need a new scheme.

  – Noting that the energy of the $1s$ atomic orbital of H is similar to the energy of the $2p$ atomic orbitals of F, we look for constructive and destructive interference and find that $1s_H$ and $2p_{z_F}$ interact nicely.
  – Thus, a first approximation the molecular orbital would be $\psi = c_1 1s_H + c_2 2p_{z_F}$.
  – Note that both MOs have σ symmetry.

- The scheme presented thus far is the simplest possible.

- More generally, we may create trial wave functions that include more and orbitals, minimizing the coefficients with the variational method along the way, until we reach the Hartree-Fock limit.

- **SCF-LCAO-MO wave function**: A wave function obtained from molecular orbitals that are linear combinations of atomic orbitals whose coefficients are determined by a self-consistent field method.

  – Such orbitals, obtained from many atomic orbitals, cannot be meaningfully classified as $\sigma 2s$ or $\pi 2p$, for example, so we classify them as the first σ_g orbital $(1\sigma_g)$, the first σ_u orbital $(1\sigma_u)$, and so on and so forth.
  – An SCF-LCAO-MO is only the same as a Hartree-Fock orbital if the SCF-LCAO-MO contains enough terms to reach the Hartree-Fock limit.

- **Hartree-Fock-Roothaan method**: The method for determining a SCF-LCAO-MO wave function.

- McQuarrie and Simon (1997) lists data on the Hartree-Fock limit vs. experimental calculations.

- Molecular term symbols.

- Excited states of molecules.

  – Consider H_2 with one electron in the $\sigma_g 1s$ orbital and one electron in the $\sigma_g 2s$ orbital. This species has a slightly longer bond length than ground state H_2.

7.6 Chapter 10: Bonding in Polyatomic Molecules

From McQuarrie and Simon (1997).

11/15:
- **π-electron approximation**: The approximation of the delocalized π electrons of a conjugated polyene or benzene as moving in some fixed, effective, electrostatic potential due to the electrons in the σ framework.

  – Note that this can be rigorously developed from the Schrödinger equation.

  – We may write the wave function of the π orbital of ethene as

  $$\psi_\pi = c_1 2p_{z_A} + c_2 2p_{z_B}$$

  – The diagonal entries in the corresponding secular determinant are **Coulomb integrals** and the off-diagonal entries are **resonance integrals**.

  – To evaluate the determinant, we either need to specify the Hamiltonian or come up with another approximation for the integrals.

- **Hückel molecular-orbital theory**: An approximation composed of the following three assertions.

  1. The overlap integrals $S_{ij} = \delta_{ij}$.

  2. All of the Coulomb integrals are assumed to be the same for all carbon atoms and are commonly denoted by α.

  3. The resonance integrals involving nearest-neighbor carbon atoms are assumed to be the same and are denoted by β.

- Once we calculate E from the reworked secular determinant, we plug in experimental values for α and β and go from there (no effective Hamiltonian needed).

- McQuarrie and Simon (1997) covers the same butadiene derivation from class.

  – Addendum: The total π-electronic energy of butadiene is

  $$E_\pi = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta)$$
  $$= 4\alpha + 4.472\beta$$

  – Comparing this energy to the energy of two ethene molecules gives us the **delocalization energy**.

  – The molecular orbitals are given and their schematic diagrams drawn.

- McQuarrie and Simon (1997) treats benzene the same way. See Nocera Lectures 6-7 from Labalme (2021).

Week 8

Electronic Structure of Atoms and Molecules

8.1 Hybridization and Time-Dependent Quantum Mechanics

11/15:
- Consider BeH_2.
  - Then we can form the sp molecular orbital
  $$\psi_{sp} = \frac{1}{\sqrt{2}}(2s \pm 2p_z)$$
  - Draws an orbital diagram of BeH_2.
- BH_3.
  - Lists sp^2 hybrid orbital wave functions.
- CH_4.
  - Lists sp^3 hybrid orbital wave functions.
- The probability of finding a ψ_1 electron in the $2p_z$ orbital.
  - The absolute value of the coefficient of $2p_z$ in the wave function, squared.
  - Alternatively,
  $$\text{Prob} = \left| \int 2p_z^* \psi_1 \, \mathrm{d}\tau \right|^2$$
- Time-dependent Schrödinger equation:
  $$\hat{H}\psi = i\hbar \frac{\mathrm{d}\psi}{\mathrm{d}t}$$
  - Let $\psi_n(r,t) = \phi_n(r)\mathrm{e}^{-iE_n t/\hbar}$. Plugging this into the time-dependent Schrödinger equation yields
  $$\begin{aligned} \hat{H}\psi &= i\hbar \frac{\mathrm{d}}{\mathrm{d}t}\left(\phi_n(r)\mathrm{e}^{-iE_n t/\hbar} \right) \\ &= i\hbar \cdot -\frac{iE_n}{\hbar} \cdot \phi_n(r)\mathrm{e}^{-iE_n t/\hbar} \\ &= E_n \psi_n \end{aligned}$$
  - Thus, to this point, we've been solving the spatial part of the time-dependent Schrödinger equation.

– The probability density of the time-dependent solution is equal to the probability density of the time-independent solution.

$$
\begin{aligned}
|\psi(r,t)|^2 &= \left|\phi(r)\mathrm{e}^{-iEt/\hbar}\right|^2 \\
&= \psi^*(r)\psi(r)\mathrm{e}^{iEt/\hbar}\mathrm{e}^{-iEt/\hbar} \\
&= \psi^*(r)\psi(r) \\
&= |\psi(r)|^2
\end{aligned}
$$

- The time-dependent Schrödinger equation allows us to make predictions for how long it takes an electron to relax back to a lower energy state after excitation, for instance.

- Using the time-dependent Schrödinger equation to describe the interaction of the system with electromagnetic radiation.

  1. Solution: $\vec{E} = \vec{E}_0 \cos(\omega t)$[1].

  2. Dipole moment of the molecule (μ).

  – We let $\hat{V} = -\vec{\mu} \cdot \vec{E}$. This is how radiation interacts with matter.

  – This leads to the overall Hamiltonian for the molecule interacting with the electric field as $\hat{H} = \hat{H}_0 + \hat{V}$, where $\hat{H}_0$ is the Hamiltonian of the molecule and $\hat{V}$ is the dipole-electric field perturbation defined above.

  – If the electron is transitioning from the ground to the first-excited state, we let

$$
\psi(t) = a_1(t)\phi_1 \mathrm{e}^{-iE_1 t/\hbar} + a_2(t)\phi_2 \mathrm{e}^{-iE_2 t/\hbar}
$$

  where the first part refers to the ground state, the second part refers to the excited state, and a_1, a_2 are time-dependent expansion coefficients that we are solving for.

  – Substitution into the time-dependent Schrödinger equation yields

$$
i\hbar\left(\psi_1 \frac{\mathrm{d}a_1}{\mathrm{d}t} + \psi_2 \frac{\mathrm{d}a_2}{\mathrm{d}t}\right) = a_1(t)\hat{V}\psi_1 + a_2(t)\hat{V}\psi_2
$$

$$
i\hbar\mathrm{e}^{-iE_2 t/\hbar}\frac{\mathrm{d}a_2}{\mathrm{d}t} = a_1(t)\int \phi_2^* \hat{V}\psi_1 \,\mathrm{d}\vec{r} + a_2(t)\int \phi_2^* \hat{V}\psi_2 \,\mathrm{d}\vec{r}
$$

8.2 Time-Dependent Schrödinger Equation

11/17:
- The TD SE is an **initial value differential equation** since we know ψ_0 and can propagate that over time.

- We will approximate the solutions to this with both an expansion (variational method) and perturbation theory.

- Now we continue from before (finding the time-dependence of the interaction of a EM radiation with a molecule).

  – Let

$$
\hat{H} = \hat{H}_0 + \hat{V}
$$

  where $\hat{H}_0$ is the Hamiltonian of the molecule and $\hat{V}$ describes the interaction of the photon and the molecule.

---

[1]This is the definition of a classical electric radiation field. In Advanced Quantum Mechanics, we can turn this into a photon field for quantum electrodynamics.

- Let

$$\psi(t) = a_1(t) \underbrace{\phi_1 \mathrm{e}^{-iE_1 t/\hbar}}_{\psi_1} + a_2(t) \underbrace{\phi_2 \mathrm{e}^{-iE_2 t/\hbar}}_{\psi_2}$$

- Substituting into the TD SE, multiplying through by ϕ_2^*, and integrating and simplifying yields (continuing from before)

$$i\hbar \frac{\mathrm{d}a_2}{\mathrm{d}t} = a_1(t) \mathrm{e}^{-i(E_1 - E_2)t/\hbar} \int \phi_2^* \hat{V} \phi_1 \, \mathrm{d}\vec{r} + a_2(t) \int \phi_2^* \vec{V} \phi_2 \, \mathrm{d}\vec{r}$$

- Computing $a_2(t)$ as a function of time.
- Initial values:

$$a_1(0) = 1 \qquad\qquad a_2(0) = 0$$

  i.e., all of the electron density is in the ground state, and none is in the excited state.
- Assume a small perturbation and use the initial conditions on the right hand side of the above equation.
- This yields

$$i\hbar \frac{\mathrm{d}a_2}{\mathrm{d}t} = \mathrm{e}^{-i(E_1 - E_2)t/\hbar} \int \phi_2^* \hat{V} \phi_1 \, \mathrm{d}\vec{r}$$

- But since

$$\hat{V} = -\frac{\mu_z}{2} E_{0_z} (\mathrm{e}^{i2\pi\nu t} + \mathrm{e}^{-i2\pi\nu t})$$

  where we focus on the component of the electric field along the internuclear axis, we get

$$\frac{\mathrm{d}a_2}{\mathrm{d}t} \propto \underbrace{\left(\int \phi_2 \mu_z \phi_1 \, \mathrm{d}\vec{r} \right)}_{(\mu_z)_{12}} E_{0_z} \left(\mathrm{e}^{i(E_2 - E_2 + h\nu)t/\hbar} + \mathrm{e}^{i(E_2 - E_1 - h\nu)t/\hbar} \right)$$

  where $(\mu_z)_{12}$ is the **transition dipole moment** between states 1 and 2.

  ∎ $(\mu_z)_{12}$ must be nonzero to get a transition.
- Integrating from 0 to τ gives

$$a_1(t) = (\mu_z)_{12} E_{0_z} \left(\frac{1 - \mathrm{e}^{i(E_2 - E_1 + h\nu)t/\hbar}}{E_2 - E_1 + h\nu} + \frac{1 - \mathrm{e}^{i(E_2 - E_1 - h\nu)t/\hbar}}{E_2 - E_1 - h\nu} \right)$$

- The second term becomes large as $E_2 - E_1 - h\nu \to 0$.
- Thus, the probability in state 2 at τ is

$$a_2^*(\tau) a_2(\tau) \propto \frac{\sin^2[(E_2 - E_1 - \hbar\omega)t/2\hbar]}{(E_2 - E_1 - \hbar\omega)^2}$$

- The right term above is a function of the form $\sin^2(xt/2\hbar)/x^2$, which has a peak right at the resonance frequency.
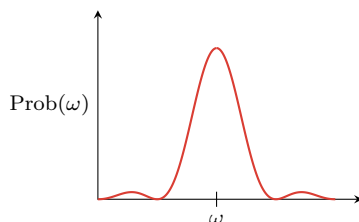

Figure 8.1: The sinc function.

> ■ This is the **sinc function**.

- Test 3:

  - Problem sets 6-7.
  - Helium from a perturbation theory/variational principle perspective.
  - Chemical bonding (MOs for H_2^+, bonding and antibonding orbitals).
  - MO diagrams for diatomics (N_2, O_2, etc.)
  - Grassmann wedge notation.
  - Huckel theory (the MOs for conjugated molecules). There WILL be one of these on the test.
  - Hybridization.
  - Time-dependent perturbation theory and the TD SE (probably not a question on this, but if you have expansion coefficients evolving with time, how do you find the probability [modulus squared]).
  - 5 parts, formula page, calculator allowed.

8.3 Chapter 10: Bonding in Polyatomic Molecules

From McQuarrie and Simon (1997).

11/15:
- Consider BeH_2.

  - The two $Be-H$ bonds are equivalent with an angle of $180°$ between them
  - MOs are formed from orbitals that are similar in energy, so in addition to the $H(1s)$ and $Be(2s)$, throw in the energetically close $Be(2p)$.
  - We also add in a $2p$ orbital because we need the resultant molecular orbitals to point in opposite directions so as to explain the linear structure of the molecule, and directionality is not something the spherically symmetric $2s$ orbital can provide.
  - Thus, choose

  $$\psi_{Be-H} = c_1 \psi_{Be(2s)} + c_2 \psi_{Be(2p)} + c_3 \psi_{H(1s)}$$

  - The first two terms in the above linear combination can be thought of as representing a new **hybrid** "orbital" on beryllium.
  - The normalized sp hybrid orbitals are given by

  $$\psi_{sp} = \frac{1}{\sqrt{2}}(2s \pm 2p_z)$$

  where the z-axis is defined to be the internuclear $H-Be-H$ axis.

    - ■ Note that sp hybrid orbitals concentrate electron density in one specific direction since the sign of the $2p$ wave function is different in the two direction ($\pm z$) but the sign of the $2s$ wave function is everywhere positive.

- **Hybrid orbital**: A linear combination of atomic orbitals on the same atom.

- The normalized sp^2 hybrid orbitals are

$$\psi_1 = \frac{1}{\sqrt{3}}2s + \sqrt{\frac{2}{3}}2p_z \qquad\qquad \psi_2 = \frac{1}{\sqrt{3}}2s - \frac{1}{\sqrt{6}}2p_z + \frac{1}{\sqrt{2}}2p_x$$

$$\psi_3 = \frac{1}{\sqrt{3}}2s - \frac{1}{\sqrt{6}}2p_z - \frac{1}{\sqrt{2}}2p_x$$

- The normalized sp^3 hybrid orbitals are

$$\psi_1 = \frac{1}{2}(2s + 2p_x + 2p_y + 2p_z) \qquad\qquad \psi_2 = \frac{1}{2}(2s - 2p_x - 2p_y + 2p_z)$$

$$\psi_3 = \frac{1}{2}(2s + 2p_x - 2p_y - 2p_z) \qquad\qquad \psi_4 = \frac{1}{2}(2s - 2p_x + 2p_y - 2p_z)$$

- Bonding vs. lone pair electrons: H_2O.

    - We could form bond orbitals out of the singly occupied $p_{y,z}$ orbitals of O, but this would predict a bond angle of $90°$. Thus, we need hybrid orbitals.
    - The bond angle in water is between that predicted using sp^2 hybrid orbitals and $2p$ orbitals.
    - Since oxygen has two bonding and four lone pair electrons, we let

$$\psi = c_1 2s + c_2 2p_y + c_3 2p_z$$

    - Determining the coefficients such that two orthogonal orbitals directed at an angle of $104.5°$ are generated yields

$$\psi_1 = 0.45 \cdot 2s + 0.71 \cdot 2p_y + 0.55 \cdot 2p_z \qquad \psi_2 = 0.45 \cdot 2s - 0.71 \cdot 2p_y + 0.55 \cdot 2p_z$$

    - Physical interpretation of the normalization constants: c_i^2 is the fractional character of the ith orbital[2].
    - ψ_1, ψ_2 accommodate the bonding electrons. Our unused hybrid orbital and unused $2p_x$ orbital accommodate the lone pair electrons as a linear combination (since symmetry necessitates that the two lone pair orbitals be equivalent).

- Why BeH_2 is linear but H_2O is bent.

    - Using a more general LCAO-MO with all relevant orbitals and solving yields a set of molecular orbitals.
    - Upon bending, the degeneracy of the π orbitals is lifted as the hydrogen orbitals move to intersect more with one specific side of the molecule.
    - Such changes are summarized by a **Walsh correlation diagram** (see Labalme (2021, p. 65)).
    - We want the minimal energy for however many electrons we have, and with the additional electrons of H_2O, it is more energetically favorable to bend then to remain linear.

- **Walsh correlation diagram**: A plot of the energy of a molecular orbital as a function of a systematic change in molecular geometry.

- **σ-bond framework**: The collection of all σ bonds in a molecule.

8.4 Chapter 12: Group Theory — The Exploitation of Symmetry

From McQuarrie and Simon (1997).

11/30:
- **Dihedral** (plane of symmetry): A plane of symmetry that bisects the angle between two-fold axes that are perpendicular to the principal axis.

- Deriving the two-dimensional irreducible representation E corresponding to the $\mathbf{C}_{3v}$ point group.

    - Consider an arbitrary vector $\mathbf{u}_1 = u_{1x}\mathbf{i} + u_{1y}\mathbf{j} = (\cos\alpha)\mathbf{i} + (\sin\alpha)\mathbf{j}$.

---

[2]Think s-character, p-character.

– Applying $\hat{C}_3$ to $\mathbf{u}_1$ yields

$$
\begin{aligned}
\mathbf{u}_2 &= \hat{C}_3 \mathbf{u}_1 \\
&= \cos(120° + \alpha)\mathbf{i} + \sin(120° + \alpha)\mathbf{j} \\
&= \left(-\frac{1}{2}\cos\alpha - \frac{\sqrt{3}}{2}\sin\alpha \right)\mathbf{i} + \left(\frac{\sqrt{3}}{2}\cos\alpha - \frac{1}{2}\sin\alpha \right)\mathbf{j} \\
&= \left(-\frac{1}{2}u_{1x} - \frac{\sqrt{3}}{2}u_{1y} \right)\mathbf{i} + \left(\frac{\sqrt{3}}{2}u_{1x} - \frac{1}{2}u_{1y} \right)\mathbf{j} \\
&= \underbrace{\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}}_{\hat{C}^3} \underbrace{\begin{pmatrix} u_{1x} \\ u_{1y} \end{pmatrix}}_{\mathbf{u}_1}
\end{aligned}
$$

– The other matrices can be derived similarly.
– This derivation also illustrates why (x, y) are coupled in this point group.

- **Basis** (of a representation): The components of the vectors used to generate the representation.

  – For example, u_x, u_y form a basis of E. Alternatively, we can say that they **belong** to E.
  – As another example, the basis vectors for R_z corresponding to the $\mathbf{C}_{3v}$. are depicted in the following figure.
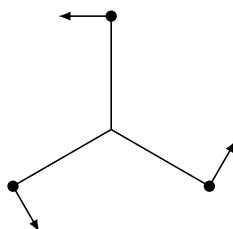

Figure 8.2: Rotational basis vectors.

8.5 Chapter 13: Molecular Spectroscopy

From McQuarrie and Simon (1997).

11/30:
- **Spectroscopy**: The study of the interaction of electromagnetic radiation with atoms and molecules.

- "Electromagnetic radiation is customarily divided into different energy regions reflecting the different types of molecular processes that can be caused by such radiation" (McQuarrie & Simon, 1997, pp. 495–96).

- Vibrational selection rule: Transitions among vibrational levels resulting from the absorption of radiation have $\Delta v = \pm 1$ and have a dipole moment that varies during the vibration.

  – For a harmonic oscillator, the spectrum consists of one line in the infrared region at the frequency $\nu_{\text{obs}} = \sqrt{k/\mu}/2\pi$.

- **Vibrational term**: The vibrational energy of a molecule. *Denoted by* $\boldsymbol{G(v)}$. *Units* cm^{-1}. *Given by*

$$
G(v) = \frac{E_v}{hc}
$$

  where $E_v = (v + 1/2)h\nu$ and $\nu = \sqrt{k/\mu}/2\pi$.

- Each energy $E_J = \hbar^2/(2I) \cdot J(J + 1)$ of the rigid rotator is associated with degeneracy $g_J = 2J + 1$.

Week 9

Quantum Dynamics and Control

9.1 Time-Dependent Schrödinger Equation and Spectroscopy

11/29:
- From last time:
  - The probability of a two-level system being in state 2 at time τ is

  $$|a_2(\tau)|^2 \equiv a_2^*(\tau)a_2(\tau) \propto \frac{\sin^2[(E_2 - E_1 - \hbar\omega)t/2\hbar]}{(E_2 - E_1 - \hbar\omega)^2}$$

  - When $\hbar\omega = E_2 - E_1$, you'll have the maximum resonance/strongest absorption and the peak in the graph of the sinc function.
  - Leads to selection rules: Only certain states directly couple with a weak perturbation.

- Now consider the transition dipole moment:

  $$(\mu_z)_{12} = \int \phi_2^* \mu_z \phi_1 \, \mathrm{d}x$$

- The integral will vanish in the rigid rotor approximation.

  - Up to the approximation of the rigid rotor, l can only change by ± 1 and m stays the same.

- Taking the harmonic oscillator as the paradigm for vibrational motion, we find that the quantum number must be $\Delta n = \pm 1$.

  - The harmonic oscillator wave functions are of the form

  $$\psi_n(x) = N_n H_n(\sqrt{\alpha}x)\mathrm{e}^{-\alpha x^2/2}$$

  where $\alpha = \sqrt{k\mu}/\hbar$.
  - Assume $\alpha = 1$. Then $\psi_n = N_n H_n(x)\mathrm{e}^{-x^2/2}$.
  - We want to evaluate

  $$(\mu_z)_{12} = \int \psi_{n'}(q)\mu_z(q)\psi_n(q) \, \mathrm{d}q$$

  where

  $$\mu_z(q) = \mu_0 + \left(\frac{\mathrm{d}\mu}{\mathrm{d}q}\right)_{q=0} q + \cdots$$

    - This means that the transition dipole moment changes as a function of the bond length.
    - When $q = 0$ (at equilibrium), the transition dipole moment is the equilibrium one (μ_0).
    - Then we Taylor series expand to correct the transition dipole moment away from equilibrium.

– Therefore,

$$(\mu_z)_{nn'} \equiv \mu_0 \int_{-\infty}^{\infty} H_{n'}(q) H_n(q) \mathrm{e}^{-q^2} \, \mathrm{d}q + \left(\frac{\mathrm{d}\mu}{\mathrm{d}q}\right)_{q=0} \int_{-\infty}^{\infty} H_{n'}(q) q H_n(q) \mathrm{e}^{-q^2} \, \mathrm{d}q + \cdots$$

■ The first term goes to zero as long as $n \neq n'$ because the Hermite polynomials are orthonormal.

– Recall that we used a recurrence relation to define the Hermite polynomials.

– In addition to the one we used previously, we have the recurrence relation

$$q H_n(q) = n H_{n-1}(q) + \frac{1}{2} H_{n+1}(q)$$

for all n.

– Thus,

$$\int_{-\infty}^{\infty} H_{n'}(q) q H_n(q) \mathrm{e}^{-q^2} \, \mathrm{d}q = \int_{-\infty}^{\infty} H_{n'}(q) \left[n H_{n-1}(q) + \frac{1}{2} H_{n+1}(q) \right] \mathrm{e}^{-q^2} \, \mathrm{d}q$$

– Thus, unless $n' = n \pm 1$, the integral vanishes.

– This is the selection rule!

• Note that we're just tickling the molecule with a bit of radiation to get this to happen — if we hit it with too hard of a hammer, the selection rule will no longer hold.

• Spectroscopy.

– $\Delta E = E_n - E_l = h\nu$.

– Regions of EM:

Region	Microwave	Far IR	IR	Vis/UV
Wavenumber ($\mathbf{cm^{-1}}$)	$0.033 - 3.3$	$3.3 - 330$	$330 - 14\,500$	$14\,500 - 500\,000$
Molecular property	Rotation of polyatomics	Rotation of small molecules	Vibration	Electron transitions

Table 9.1: Spectroscopy in various regions of the electromagnetic spectrum.

• The Schrödinger equation within the Born-Oppenheimer approximation:

$$\left[\sum_A \left(-\frac{\nabla_A^2}{2} \right) + \hat{H}_{\mathrm{elec}} \right] \psi_{\mathrm{elec}} \psi_{\mathrm{nucl}} = (E_{\mathrm{elec}} + E_{\mathrm{nucl}}) \psi_{\mathrm{elec}} \psi_{\mathrm{nucl}}$$

– We invoke the Born-Oppenheimer approximation to split the wavefunction into electronic and nuclear components.

• We then split this equation into two parts. The first of which is the electronic Schrödinger equation

$$\hat{H}_{\mathrm{elec}} \psi_{\mathrm{elec}} = E_{\mathrm{elec}} \psi_{\mathrm{elec}}$$

– The BO approximation is what allows us to split the original Schrödinger equation in two.

• We now multiply by ψ_{elec} and integrate over all of the electrons.

$$\left[\sum_A \left(-\frac{\nabla_A^2}{2} \right) + V(R) \right] \psi_{\mathrm{nucl}} = (E_{\mathrm{elec}} + E_{\mathrm{nucl}}) \psi_{\mathrm{nucl}}$$

– $V(R) = E_{\mathrm{elec}}(R) = \int \psi_{\mathrm{elec}}^* \hat{H}_{\mathrm{elec}} \psi_{\mathrm{elec}} \, \mathrm{d}x$ is the potential energy surface (PES).

References

Dudik, R. (2004). The quantum harmonic oscillator. Retrieved November 17, 2021, from http://physics.gmu.edu/~dmaria/590%20Web%20Page/public_html/qm_topics/harmonic/

Labalme, S. (2021). CHEM 20100 (Inorganic Chemistry I) notes. Retrieved October 20, 2021, from https://github.com/shadypuck/CHEM20100Notes/blob/master/Notes/notes.pdf

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