CHEM 3620 Lecture Notes

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TEXTBOOK ERRATA

Chapter 1

- p. 42 – In Brief illustration 1B.2 the v_{rms} is used where v_{mean} should be

- p. 46 – $Z = \dfrac{RT}{pV_m^\circ}$ in the paragraph between equations 1C.1 and 1C.2 is wrong. The expression for the molar volume of an ideal gas was erroneously substituted into the real gas molar volume

Chapter 2

- p.86 – Equations 2C.6 and 2C.7a both should have "...$= H(T_1)$..." instead of "...$= H(T_2)$..."

Chapter 5

- p.203 – Equation 5C.4 should be: $y_A = \dfrac{\chi_A p_A^\star}{p_B^\star + (p_A^\star - p_B^\star)\,\chi_A} = 1 - y_B$

Chapter 7

- p. 295 and 296 – The infinitesimals in the normalization integrals should be reversed to "$\mathrm{d}\phi\,\mathrm{d}\theta\,\mathrm{d}r$"

Chapter 8

- p. 388 – The bottom row of the table of j values should be $\frac{1}{2}$ for both electrons

Chapter 9

- p. 423 – The second secular equation (10D.5b) should have α_B, not α_A

INTRODUCTION TO QUANTUM THEORY

7A   The Origins of Quantum Mechanics

○ Classical theories relied on two particular ideas that were changed by quantum mechanics:

· The precise position, momentum, and other properties of a particle can be known

· Energetic modes can hold any amount of energy, large or small.

○ We will cover several experiments from the 19th to 20th century that lead to quantum mechanics

○ Black-body radiation and the ultraviolet catastrophe:

· Hot objects emit light of all wavelengths

· Physicists modeled this behavior as a network of oscillations, predicting radiation according to the Rayleigh-Jeans law: $\rho(\lambda, T) = \dfrac{8\pi k_B T}{\lambda^4}$

· This law predicted infinite light intensity as wavelengths approached 0

· Real black-body curves taper off at high frequencies (Blackbody figure)

· In 1990 Max Planck proposed that light can only be emitted in quantized amounts of energy, depending on the wavelength

· This is where we get $E = h\nu = \dfrac{hc}{\lambda}$

· In the first application of statistical mechanics, Planck used his idea of quantized energy to derive the Planck distribution: $\rho(\lambda, T) = \dfrac{8\pi hc}{\lambda^5 \left(e^{hc/\lambda k_B T} - 1\right)}$

· At long wavelengths, the exponential portion goes away and reproduces the Rayleigh-Jeans law. At short wavelengths the exponential portion causes ρ to approach 0

· Planck's distribution matched observations closely

○ Heat capacities:

· Heat capacities of solids were measured and found to follow a simple rule: $C_{V,m} = 3R$

· This matched well with a model of solid particles distributing energy equally into vibrations in three dimensions

· As measurements were made at lower and lower temperatures, the observed behavior deviated significantly from this model

· Again, Planck's idea of quantized energy and statistical mechanics were brought to bear. Einstein was cutting his teeth on this problem

- · The result was the Einstein formula:

$$C_{V,m} = 3R \left(\frac{\theta_E}{T}\right)^2 \left(\frac{e^{\theta_E/2T}}{e^{\theta_E/T} - 1}\right)^2 \qquad \theta_E = \frac{h\nu}{k_B} = \frac{hc}{\lambda k_B}$$

- · At high temperatures this equation again collapses to the classical result
- · At lower temperatures the heat capacity approaches 0
- · The Einstein formula was later improved by Debye, but it is correct in the essential observation that vibrational energy comes in discrete amounts rather than a continuum

○ Atomic spectra:

- · Atoms and molecules emit light when they are excited energetically, different from blackbody radiation
- · The light emitted always had a very narrow, precise wavelength
- · Bohr realized that atoms and molecules have discrete energy states, and light is emitted according to changes in energy states where $\Delta E = h\nu$

○ These experiments and their resolutions showed that energy is quantized – both in the matter energy states and in light emitted or absorbed

○ The photoelectric effect:

- · Certain metals will emit an electron when they are exposed to light
- · Even low intensities of very blue light will eject electrons with large kinetic energy
- · Even high intensities of very red light will not eject any electrons at all
- · If we follow Planck's $E = h\nu$, then the kinetic energy of the electron is: $E_k = h\nu - \phi$ for all wavelengths
- · ϕ is the work function, and represents the energy required to remove an electron from the metal
- · This experiment shows that light is always carried in discrete units of energy

○ Matter wave diffraction:

- · Waves of all kinds diffract - water waves, light waves, etc.
- · Diffraction of light stands in contrast to the photoelectric effect, together demonstrating wave/particle duality of light
- · In 1924 Luis de Broglie postulated that since light has momentum, perhaps moving things have a characteristic wavelength
- · He proposed his eponymous relation: $\lambda = \dfrac{h}{p} = \dfrac{h}{mv}$
- · de Broglie was not taken seriously at first, but in 1925 Davisson and Germer observed wavelike behavior in matter (specifically, electrons)
- · Davisson and Germer send a beam of electrons toward a crystal of Nickel metal and observed several orders of diffraction of the deflected electrons

- · Find the wavelength of an electron travelling at 1% of the speed of light, verses your own wavelength jogging at 8 miles per hour
  - · Atomic corral and standing electron waves
- ○ These two experiments show wave/particle duality in both particles and photons

7B Wavefunctions

- ○ The wavelike nature of matter was further explored in 1926 by Erwin Schrödinger
- ○ The Schrödinger equation is a complete description of any quantum mechanical system:
  - · This equation can be inferred by combining Maxwell's equations for electromagnetic radiation with de Broglie's relation for the wavelength of matter waves, but is not directly derived from them
  - · $-\dfrac{\hbar^2}{2m}\dfrac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x)\psi = E\psi$ (at least, in one-dimension)
  - · ψ is the wavefunction, and it is a complex time-dependent mathematical function
  - · $V(x)$ is the potential function, taking different forms depending on the fields affecting a quantum system
  - · Taken as a whole, this equation is a *differential* equation and has many solutions Table 7B.1 shows many forms of the Schrödinger equation (time-dependent, 3-dimensional, etc.)
- ○ The Schrödinger equation is just that – a mathematical equation. We trust its results (predicting position, energy levels, momenta, etc. of ensembles) because it works, just like everything else in science!
- ○ Nevertheless, we always try to interpret the laws of science in intuitive terms
- ○ The Born interpretation of the wavefunction states that the probability of a particle being found at particular location is: $p \propto |\psi|^2$
- ○ Figure 7B.3 shows a wavefunction and corresponding probability distribution function
- ○ Points where $|\psi|^2 = 0$ are called "nodes"
- ○ de Broglie espoused a different view, called pilot wave theory, which we will not be covering much but I will mention again when we dissect the interpretation of a phenomenon called superposition
- ○ Because $p \propto |\psi|^2$, and the probability of finding a particle in all of space must be 1, we know that
  $$N^2 \int \psi^*\psi \mathrm{d}\tau = 1$$
- ○ N is called a normalization constant, and scales the wavefunction so that its probabilities make physical sense
- ○ From now on, we will treat the normalization constant as an integral part of ψ

- When integrating over all space, we must consider the coordinate system:

  - For cartesian coordinates: $\displaystyle\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi^*\psi\mathrm{d}x\mathrm{d}y\mathrm{d}z = 1$

  - For spherical polar coordinates, θ is the angle with the z-axis and ϕ is the angle with the x-axis after projection on the x-y plane. This is opposite to how mathematicians define θ and ϕ

  - In spherical polar coordinates: $\displaystyle\int_{0}^{\infty}\int_{0}^{\pi}\int_{0}^{2\pi}\psi^*\psi r^2\sin\theta\mathrm{d}\phi\mathrm{d}\theta\mathrm{d}r = 1$

  - Note that the order of the infinitesimals is incorrect in the book

- A proper wavefunction must be single-valued, continuous in its first derivative, continuous itself, and finite over a finite region (Figure 7B.4)

- These constraints on the form of the wavefunctions are the mathematical reason for quantized energy states. This idea can give profound insight in predicting which systems might exhibit greater degrees of quantization

- To find the probability of finding a particle within a particular region, simply integrate $\psi^*\psi$ over that region.

- Practice Problem (P.I.B.):

  - Consider an un-normalized wavefunction $\psi(0,1) = \sin\pi x$ $\qquad \psi(-\infty, 0] \cup [1, \infty) = 0$

  - Normalize this function

  - Find the probability of finding the particle within $[0, 0.25]$

7C   Operators and Observables

- Quantum mechanics is practiced in the wold of linear algebra

- Operators are the linear algebra term for mathematical operations (such as multiplication, differentiation, integration, etc.)

- The Hamiltonian operator gives the energy of a wavefunction, as it includes the kinetic and potential energy of a system. In one dimension: $\hat{H} = -\dfrac{\hbar^2}{2m}\dfrac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)$

- Now we can write the Schrödinger equation as: $\hat{H}\psi = E\psi$

- The Schrödinger equation is an example of an *eigenvalue equation*

  - $\hat{A}f = Cf$ is the general form for eigenvalue equations
  - ψ is called an *eigenfunction*
  - E is the corresponding *eigenfunction*

○ Other observable quantities also have operators like the hamiltonian

  · $\hat{x} = x$

  · $\hat{p}_x = \dfrac{\hbar}{i}\dfrac{\mathrm{d}}{\mathrm{d}x}$

  · Many more – one for each observable quantity

  · The eigenvalue *is* the measurable value for the property represented by the operator

○ The potential function will take a form to match the system being modeled

○ All of the operators for observables are *Hermitian*, meaning that:

  · $\int \psi_i^* \hat{\Omega} \psi_j \mathrm{d}\tau = \left[\int \psi_j^* \hat{\Omega} \psi_i \mathrm{d}\tau\right]^*$

  · The eigenvalues are real (not complex-valued)

  · The eigenfunctions are an orthogonal set

○ Orthogonality takes a broader definition in the context of linear algebra

○ Two functions are orthogonal if $\int f^* g \mathrm{d}\tau = 0$

○ So, for eigenfunctions of an Hermitian operator: $\int \psi_i^* \psi_j \mathrm{d}\tau = 0 \quad \text{for} \quad i \neq j$

○ Orthogonality can sometimes be confirmed by inspection through symmetry arguments

○ After normalization, a set of Hermitian eigenfunctions are *orthonormal*

○ Superpositions:

  · Not every proper QM wavefunction is an eigenfunction of all QM operators

  · Eigenfunctions are often mixed in linear combinations: $\Psi = \sum c_i \psi_i$

  · Such a quantum mechanical state is called a "Superposition"

  · This is the infamous Schrödinger's cat state

  · More later on how and why a particle might be in an eigenstate vs a superposition

  · Suppose a particle is in a superposition of two linear momentum eigenstates:

    * Any single measurement will yield the momentum which corresponds to one of the eigenstates

    * The probability of observing a particular momentum is proportional to the value $|c_k|^2$

    * Many repeat measurements (measurements on identical systems) will yield an average value equal to the *expectation value*: $\langle \hat{p} \rangle = \int \psi^* \hat{p} \psi \mathrm{d}\tau$

    * This is as good a time as any to introduce bra-ket notation

○ The Uncertainty Principle:

- It is clear by inspection that a wavefunction cannot give a QM particle a well-defined position
- Closer analysis shows that systems with more well-defined positions will always have less-defined momenta
- My Wavepacket visualization shows this relationship
- This is the Heissenberg Uncertainty Principle – That you cannot know both the momentum and position of a QM particle
- The principle can be expressed mathematically as: $\Delta p_x \Delta x \geq \frac{1}{2}\hbar$
- Δp_x can be interpreted as the uncertainty in momentum along x
- We can quantify the uncertainty with: $\Delta p_x = \left[\langle p_x^2 \rangle - \langle p_x \rangle^2\right]^{1/2}$
- Actually, the uncertainty principle can be extended to other complementary pairs of observables as well
- Observables are complementary if $\hat{\Omega}_1 \hat{\Omega}_2 \psi \neq \hat{\Omega}_2 \hat{\Omega}_1 \psi$ (the operators don't commute)
- We can create a new operator, called the commutator: $\left[\hat{\Omega}_1, \hat{\Omega}_2\right] = \hat{\Omega}_1 \hat{\Omega}_2 - \hat{\Omega}_2 \hat{\Omega}_1$
- The generalized uncertainty principle is: $\Delta\Omega_1 \Delta\Omega_2 \geq \frac{1}{2}\left|\left\langle\left[\hat{\Omega}_1, \hat{\Omega}_2\right]\right\rangle\right|$

○ The Postulates of QM:

- We have already been talking about the fundamental postulates of quantum mechanics, which give the mathematical foundation for all of QM
- All dynamical information for a system is contained in the wavefunction ψ
- The probability of finding a particle at a particular point is proportional to $|\psi|^2$
- Wavefunctions must be continuous, finite, single-valued, and continuous in their 1st derivative
- Observable values are found from corresponding operators (either eigenvalues or expectation values)
- Complementary observables are constrained by an uncertainty relationship

Experiments and Interpretations in QM

○ Single photon diffraction – wave-particle duality

○ Silver atom spin – Superposition created by changing field direction

○ Light polarization – With demo! and minutephysics Bell's theorem video

○ Delayed Choice Quantum Eraser – "Entanglement"

○ Bell's Inequality – No hidden variables, with Veritasium video

○ My Quantum Mechanics Strangeness Soap Box regarding coherence and scientism

○ Pilot Wave Theory – With Veritasium video "Is this what quantum mechanics looks like?"

7D   Translational Motion

○ Free motion in one dimension:

- The appropriate form of the Schrödinger equation is: $-\dfrac{\hbar^2}{2m}\dfrac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} = E\psi(x)$

- The solutions are: $\psi_k(x) = Ae^{ikx} + Be^{-ikx}$ with $E_k = \dfrac{k^2\hbar^2}{2m}$

- For the free particle, all values of k are acceptable, and there is no energy quantization

- B and A are parameters that define what ratio of the wave is traveling left vs right

○ Confined motion in one dimension (Particle in a box):

- For confined motion, we set the potential to be infinite everywhere except a small range ($x \in (0, L)$)

- To find the solution over this range, we first rearrange the free-particle solution as: $\psi_k\,(x \in [0, l]) = C \sin kx + D \cos kx$

- Because of the infinite potential walls, the wavefunction must go to zero at $x = 0$ and $x = L$

- This requirement further constrains the acceptable solutions and after normalization we are left with:
$\psi_n(x) = \sqrt{\dfrac{2}{L}} \sin\left(\dfrac{n\pi x}{L}\right)$ and $E_n = \dfrac{n^2 h^2}{8mL^2}$ with $n = 1, 2, \cdots$

- Because n must be an integer, only certain states and energies are allowed

- With increasing n, there is increasing energy and and increasing number of nodes

- Find a general solution for transition energies $n + 1 \leftarrow n$

- There is a zero-point energy of $\dfrac{h^2}{8mL^2}$

- This model can be extended to multiple dimensions with:
$\psi_{n_x,n_y}(x, y) = \dfrac{2}{\sqrt{L_x L_y}} \sin\left(\dfrac{n_x \pi x}{L_x}\right) \sin\left(\dfrac{n_y \pi y}{L_y}\right)$ with $E_{n_x,n_y} = \dfrac{h^2}{8m}\left(\dfrac{n_x^2}{L_x^2} + \dfrac{n_y^2}{L_y^2}\right)$
$\psi_{n_x,n_y,n_z}(x, y, z) = \sqrt{\dfrac{8}{L_x L_y L_z}} \sin\left(\dfrac{n_x \pi x}{L_x}\right) \sin\left(\dfrac{n_y \pi y}{L_y}\right) \sin\left(\dfrac{n_z \pi z}{L_z}\right)$
with $E_{n_x,n_y,n_z} = \dfrac{h^2}{8m}\left(\dfrac{n_x^2}{L_x^2} + \dfrac{n_y^2}{L_y^2} + \dfrac{n_z^2}{L_z^2}\right)$

- The wavefunctions for 2 and 3 dimensions are 2 and 3 dimensional sin functions

- Note that for 2 and 3 dimensions, the energy spacings are more complex and include some degenerate energy levels

○ PIB in the real world – "Tunneling"

- In reality, no potentials rise to infinity so particles are not *completely* confined in space

- A potential that is lower than the kinetic energy can be easily overcome, but for quantum objects a particle can also transmit through a barrier greater than the kinetic energy
- Such a barrier is called a "classically forbidden region," and within them the wavefunction decays exponentially $\psi \propto e^{-\kappa x}$
- The decay constant is: $\kappa = \dfrac{\sqrt{2m(V-E)}}{\hbar}$, so more massive particles tunnel with less efficiency
- Figure 8A.9 illustrates the wavefunction decay and transmission through a classically forbidden region
- The transmission probability is: $T = \left[1 + \dfrac{\left(e^{\kappa L} - e^{-\kappa L}\right)^2}{16\varepsilon(1-\varepsilon)}\right]^{-1}$
- Here, L is the barrier width, and $\varepsilon = \dfrac{E}{V}$
- Note that even when $E > V$, there is still a probability of scattering backward

7E Vibrational Motion

○ The Harmonic Oscillator:

- For an harmonic oscillator, the restorative force is: $F = -k_f x$
- And the potential is the integral of that force: $V(x) = \frac{1}{2}k_f x^2$
- This gives a Schrödinger equation of: $-\dfrac{\hbar^2}{2m}\dfrac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + \frac{1}{2}k_f x^2 \psi(x) = E\psi(x)$
- And energy levels of: $E_v = \left(v + \frac{1}{2}\right)\hbar\omega$
- ω is the fundamental frequency, and has the value $\omega = \sqrt{\dfrac{k_f}{\mu}}$
- μ is the reduced mass, which for a diatomic molecule is: $\mu = \dfrac{m_A m_B}{m_a + m_B}$
- For the harmonic oscillator, energy states are always separated by $\hbar\omega$
- The zero-point energy is $E_0 = \frac{1}{2}\hbar\omega$
- The solutions to the Schrödinger equation are much more complex in this case:

$\psi_v(x) = N_v H_v\left(\dfrac{x}{\alpha}\right) e^{-\dfrac{x^2}{2\alpha^2}}$ where $\alpha = \left(\dfrac{\hbar^2}{\mu k_f}\right)^{1/4}$

- N_v is just a normalization constant, which cannot be represented by a simple formula
- $H_v(y)$ are the Hermite Polynomials, given in table 8B.1. Thank mathematicians for them
- Note that the wavefunctions all decay at either end, according to a gaussian function, and contain oscillatory behavior like the PIB solutions
- At higher levels of excitation, the probability density is concentrated into the wings (Figure 8B.7)

○ The Properties of Oscillators:

- We can find some interesting mean values by calculating expectation values
- $\langle x \rangle = 0$
- $\langle x^2 \rangle = \left(v + \frac{1}{2}\right) \dfrac{\hbar}{\sqrt{\mu k_f}}$
- $\langle V \rangle = \frac{1}{2}\left(v + \frac{1}{2}\right)\hbar\omega = \frac{1}{2}E_v$
- $\langle E_k \rangle = \frac{1}{2}E_v$
- Tunneling can occur both at the extended and compressed end of an harmonic oscillator

○ Real vibrational potentials are not harmonic, with significant consequences which we will cover in chapter 12

7F   Rotational Motion

○ Rotation in two dimensions (particle on a ring):

- Classically, a rotating object has: $E = \dfrac{J_z^2}{2I}$ where $I = mr^2$
- We know that $J_z = \pm pr$ and $p = \dfrac{h}{\lambda}$, so $J_z = \pm\dfrac{hr}{\lambda}$
- Since the ring forms a closed loop, and ψ must be single-valued, λ is constrained to be simple fractions of the circumference (Figure 8C.2)
- The solutions to the Schrödinger equation are: $\psi_{m_l}(\phi) = \dfrac{e^{im_l\phi}}{\sqrt{2\pi}}$ where $m_l = 0, \pm 1, \pm 2, \ldots$
- The energies are: $E_{m_l} = \dfrac{m_l^2\hbar^2}{2I}$
- The angular momentum is also quantized: $J_z = m_l\hbar$ with $m_l = 0, \pm 1, \pm 2, \ldots$

○ Rotation in three dimensions (rigid rotor):

- With rotation in three dimensions, the wavefunction must be continuous across the entire surface of a sphere
- In spherical polar coordinates, the solutions to the Schrödinger equation are separable (i.e. $\psi(\theta, \phi) = \Theta(\theta)\Phi(\phi)$)
- The solutions are a family of functions called *spherical harmonics*, which have two quantum numbers l and m_l
- l takes values of $0, 1, 2, \ldots$ and m_l takes values of $-l, -l + 1, \ldots, l - 1, l$
- Table 8C.1 gives the functions, and Figure 8C.8 shows how some spherical harmonics look
- The energies of a rigid rotor are: $E_{l,m_l} = l(l+1)\dfrac{\hbar^2}{2I}$
- For rotors, there is no zero point energy

- The energy level degeneracy is $(2l+1)$ because of all the degenerate values of m_l
- Total angular momentum can be found by: $\hat{l}^2\psi = l(l+1)\hbar^2$
- The z-projection of angular momentum is: $\hat{l}_z\psi = m_l\psi$
- Since the z-component of the angular momentum is quantized, that means that the physical orientation of the rotating molecule is quantized. Molecules can literally only rotate at certain angles! (Figure 8C.9)
- Note that $\left[\hat{l}^2, \hat{l}_q\right] = 0$ where $q = x, y, or z$
- However, $\left[\hat{l}_x, \hat{l}_y\right] = i\hbar\hat{l}_z$, $\left[\hat{l}_y, \hat{l}_z\right] = i\hbar\hat{l}_x$, and $\left[\hat{l}_z, \hat{l}_x\right] = i\hbar\hat{l}_y$
- These commutators mean that if the z momentum is known, then the x and y momenta are unknown
- The normal vector of the rotation forms a cone, as shown in Figure 8C.11

ATOMIC STRUCTURE AND SPECTRA

8A   Hydrogenic Atoms

○ Hydrogen atoms have only a single electron, so it makes a very simple system for electronic energy levels

○ The atomic emission lines of H have been analyzed for hundreds of years

○ Johannes Rydberg found a pattern to the lines: $\tilde{\nu} = \tilde{R}_H \left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2} \right)$

○ $\tilde{\nu}$ is the *wavenumber* (cm^{-1}), which is proportional to the energy. $\tilde{\nu} = \dfrac{1}{\lambda} = \dfrac{\nu}{c}$

○ $\tilde{R}_H = 109677 \; cm^{-1}$

○ The Schrödinger equation and solutions:

  · The only energy levels in a hydrogen atom are electronic energy levels

  · The potential for an electron comes from the Coulombic attraction to the nucleus: $V(r) = -\dfrac{Ze^2}{4\pi\epsilon_0 r}$

  · r is the radius, Z is the nuclear charge, e is the elemental charge, and ϵ_0 is the vacuum permittivity

  · There are also two components to the kinetic energy: $E_{k,electron}$ and $E_{k,nucleus}$

  · Thea final Hamiltonian is: $\hat{H} = -\dfrac{\hbar^2}{2m_e}\nabla_e^2 - \dfrac{\hbar^2}{2m_N}\nabla_N^2 - \dfrac{Ze^2}{4\pi\epsilon_0 r}$

  · First, the Born/Oppenheimer approximation lets us separate out all of the nuclear position variables

  · All of the nuclear motion is what we covered before: translation, vibration, and rotation

  · What's left is the electronic energy with variables r, θ, and ϕ centered about the nucleus

  · Thankfully, the potential is centrosymmetric, so the angular components can separate out: $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$

  · We already know the angular solutions - the spherical harmonics!

  · The angular momentum operators and eigenvalues are precisely the same for a hydrogen atom as for a 3-D rigid rotor

  · The radial function is also thankfully solved by the mathematicians of centuries gone by

  · $R_{n,l}(r) = N_{n,l}\rho^l L_{n-l-1}^{2l+1}(\rho)e^{-\rho/2}$

- $L_{n-l-1}^{2l+1}(\rho)$ are the *associated Laguerre polynomials*, which are defined through a complex recursive algorithm
- Note that although $R(r)$ has no angular dependence, the function is parameterized by l
- Table 9A.1 gives the radial wavefunction for a number of electronic states

○ In the end, this gives us three quantum numbers to define the electron wavefunction:

- n – The principle quantum number, which determines energy
- l – The angular momentum number, which determines the total angular momentum
- m_l – The orbital quantum number, which determines the orientation in space

○ The energy levels (in J) are similar to the Rydberg Equation: $E_n = -\dfrac{hcZ^2\tilde{R}_N}{n^2}$

○ $\tilde{R}_N = \dfrac{\mu e^4}{32\pi^2\epsilon_0^2\hbar^2} \approx 109700 cm^{-1}$ (slightly lower for H and slightly more for heavier atoms)

○ The wavefunction for an electron is called an *orbital*:

- The orbitals are categorized according to their quantum numbers in shells and subshells
- "s" orbitals are spherically symmetric with highest intensity near the center
- The radial probability of an orbital is: $P(r) = r^2 |R(r)|^2$
- "p" orbitals are dumbell shaped
- p orbitals are complex functions, but combinations can produce real-valued orbitals oriented along the x and y axes
- "d" orbitals are clover-leaf shaped

8B Many-Electron Atoms

○ In many-electron atoms, the Hamiltonian must include the mutual repulsions between all pairings of electrons

○ These electron-electron repulsion terms make the Schrödinger equation unsolvable with current methods

○ The orbital approximation is a simple approximation to the true, unknown solutions

- We can assume that each electron has its own wavefunction
- The unknown energy terms can be estimated using methods we will discuss later
- The shapes will deviate only slightly from the hydrogen atom orbitals, so we use them as models and use the same names and categories to describe each electron's wavefunction
- We call the collection of wavefunctions for each electron a *configuration*

○ Electron Spin:

- Magentic spin is an intrinsic, quantum mechanical property of electrons (and other particles)
- The s quantum number for electrons is always $s = \frac{1}{2}$
- There is also a new quantum number, $m_s = \pm\frac{1}{2}$ (for electrons)
- The spin angular momentum has the same operators as other angular momentum
    * $\hat{s}^2\psi = s(s+1)\hbar^2\psi$
    * $\hat{s}_z\psi = m_s\psi$
- The spin is represented by α for up-spin and β for down-spin

○ The Pauli Principle:

- You are familiar with the Pauli Exclusion Principle: An orbital can hold at most two electrons, and their spins must be opposite
- This is merely a special case of the more complete *Pauli Principle*:

    When the labels of any two identical fermions are exchanged, the total wavefunction changes sign; when the labels of any two identical bosons are exchanged, the sign of the total wavefunction remains the same.

- i.e. Fermions must be antisymmetric with respect to exchange, and bosons must be symmetric
- How can we construct a total wavefunction which conforms to this principle?
    * Consider the ground state of He: $1s^2$
    * We call the wavefunction for an upspin electron α, and a downspin electron β
    * For He, we might say $\psi = \alpha(1)\beta(2)$, or $\psi = \alpha(2)\beta(1)$, but neither of those obey the Pauli principle
    * A combination, specifically $\psi = \dfrac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]$ does!
    * This expression can be found as the determinant of the matrix: $\dfrac{1}{\sqrt{2}}\begin{bmatrix}\alpha(1) & \alpha(2) \\ \beta(1) & \beta(2)\end{bmatrix}$
    * What about for Li? take the determinant of the following matrix:

    $$\frac{1}{\sqrt{N!}}\begin{bmatrix}1s\alpha(1) & 1s\alpha(2) & 1s\alpha(3) \\ 1s\beta(1) & 1s\beta(2) & 1s\beta(3) \\ 2s\alpha(1) & 2s\alpha(2) & 2s\alpha(3)\end{bmatrix}$$

    * Such determinants will always obey the Pauli principle, and are called Slater Determinants

○ The 2s orbital is lower in energy than the 2p orbitals because they are less effectively shielded

○ The radial probability distribution functions (Figure 9B.4) show how s orbitals penetrate closer to the nucleus than p orbitals

○ Table 9B.1 shows the effective nuclear charge ($Z_{eff} - Z - \sigma$) for different orbitals

○ Hund's rule comes because electrons want to spread out spatially, and because electrons of the same spin exhibit more favorable spin correlation than electrons of different spins

○ Self-Consistent Field Orbitals (Hartree-Fock methods):

    · The true orbitals are still different from the hydrogenic atomic orbitals

    · One attempt to find the correct energies is called self-consistent field theory

    · $\hat{H}_{total} = \sum\limits_{electrons} \hat{H}_{Hydrogenic} + V_{Electron\ Repulsions} - V_{Exchange\ Correlation}$

    · Begin with the hydrogenic orbitals

    · Pick one electron, and calculate the potential based on the total probability distribution functions of the other electrons

    · Use this new potential term to find a new wavefunction for that single electron

    · Do the same for all other electrons in turn

    · Repeat the entire process until the wavefunctions converge to within your tolerances

    · The exchange correlation tries to account for the fact that in real-time, electron positions are correlated

    · There are many different, complex ways of calculating this term, and it is a rich field for computational chemistry research

8C   Atomic Spectra

○ Atomic spectra arise from transitions between different electronic energy levels

○ Note that this is not quite equivalent to the idea of different electronic configurations

○ Hydrogenic atoms

    · We already know the transition energies

    · We need to introduce some *selection rules*

    · $\Delta l = \pm 1$, $\Delta m_l = 0, \pm 1$, and $\Delta m_s = 0$

    · A Grotrian Diagram (Figure 9C.1) shows all of the allowed transitions

○ Complex Atoms

    · With multi-electron atoms, we must deal with the S and m_S quantum numbers more directly (the capital letters denote total electron spin, rather than the spin of a single electron)

    · Consider the excited He configuration $1s^1 2s^1$

    · If all electrons are paired, this is called a singlet state

    · In a singlet state $S = 0$ and there is only one wavefunction: $\dfrac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$

- · If there are two unpaired electrons, then this is called a triplet state
- · Im a triplet state, $S = 1$ and $m_S = 0, \pm 1$, and there are three wavefunctions:

$$\alpha(1)\alpha(2), \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \alpha(2)\beta(1)\right], \text{ and } \beta(1)\beta(2)$$

- · Vector diagrams of these wavefunctions are shown in Figure 9C.2
- · Spin-orbit coupling is an effect that arises from the fact that an electron in an orbital with $l \geq 1$ has magnetic moments associated with both its orbital and its spin
- · The spin-orbit interaction gives rise to new total angular momentum quantum numbers for each electron: j and m_j
- · j can range in whole steps from $j = l + \frac{1}{2}$ to $j = l - \frac{1}{2}$, but $j \geq 0$
- · The magnitude of the spin-orbit interaction increases with greater nuclear charge
- · Splitting from the spin-orbit interaction produces *fine structure* to atomic spectra, like the doublet seen in sodium vapor lamps
- · External magnetic fields can also increase the strength of the spin-orbit interaction

○ Term Symbols

- · The total angular momenta of all electrons combined (L, S, and J) can be conveyed in a *term symbol*
- · L is represented by a capital Roman letter
- · S is represented by the multiplicity as a left-superscript
- · J (when relevant), is represented by a right-supscript number
- · The simple configuration p^2 gives rise to many terms: ^1D, $^3P_2$, $^3P_1$, $^3P_0$, ^1P, and ^1S
- · Hund's rule: Highest multiplicity is lowest in energy. For terms with similar multiplicity highest L is lowest in energy
- · Hund's rule makes it easy to find the ground state term for a given configuration
    - ∗ draw the electron configuration like in 1210, with electrons favoring higher m_l orbitals first
    - ∗ $L = \sum m_l$ and $S = \sum m_s$
- · For all the terms, there is a more tedious process which we will not learn here but which is totally awesome!
- · Russell-Saunders coupling has been presented here, where L and S (total momenta) interact. "j-j" coupling, where all momenta interact on the single-electron level, only applies for heavy atoms
- · Error on p. 388 – The bottom row of the table of j values should be $\frac{1}{2}$ for both electrons

○ Selection rules for complex atoms are: $\Delta S = 0$, $\Delta L = 0, \pm 1$, $\Delta l = \pm 1$, and $\Delta J = 0, \pm 1$ (but $J = 0$ cannot transition to $J = 0$)

○ The ΔS selection rule is relaxed in heavy atoms

○ Selection Rules come from the transition dipole integral: $\mu_{jk} = \int \psi_j^* \hat{\mu} \psi_k \mathrm{d}\tau$

MOLECULAR STRUCTURE

9A Valence-Bond Theory

○ The Born-Oppenheimer approximation means that we can find the energy for any given internuclear distance

○ Figure 10A.1 shows a molecular potential energy curve

○ The lowest point in the energy curve gives the equilibrium bond length and the bond dissociation energy

○ For polyatomic molecules, there is a multi-dimensional surface but all bond lengths are shifted to minimize the total potential energy

○ The basic shape can be explained by a number of energetic terms

  · At very close distances, nuclear and electronic repulsions give very high energies

  · At very large distances, the energy approaches zero because there are no interactions

  · At intermediate distances, the bonding electrons are able to spread out, spanning the two atoms. This lowers the energy by confining the electrons less, and enhances the electron density which is attracted to both nuclei

○ Bonds are often described as orbital overlap:

  · Draw the model for H_2

  · $\Psi(1, 2) = A(1)B(2) + A(2)B(1)$

  · This arrangement enhances the electron density between the two nuclei

  · Figure 10A.3 and 10A.4 show some atomic orbital arrangements which can lead to σ and π bonds

○ For some diatomics, it becomes helpful to express the bond as partially ionic and partially covalent: $\Psi = \psi_{covalent} + \lambda\psi_{ionic}$

○ We can vary the value of λ to find the ratio with minimum energy

○ Because of the *variational* principle, we know that the energy of this trial function is equal-to or greater-than the true energy

○ We can also find the energy of a system with resonance: $\Psi = \sum \lambda_1 \psi_i$

○ Using atomic orbitals as-is will not give the right angles, or the right number of bonds

○ Hybridization combines the atomic orbitals to create new orbitals with the right energies and right angles to match experiment

○ sp, sp^2, sp^3, sp^3d, and sp^3d^2 hybridizations give rise to the different electron domain geometries

○ σ bonds are made from overlap of hybridized orbitals, while π bonds are made from overlap of unhybridized p orbitals

9B   Molecular Orbital Theory: The Hydrogen Molecule-Ion

○ While valence bond theory can explain several trends and properties, but it really has no connection to the Schrödinger equation

○ Sketch the H_2^+ system

○ Actual solutions to the Schrödinger equation are orbitals which aren't centered around any single atom. They are called *molecular orbitals*

○ These orbitals can be *approximated* by linear combinations of atomic orbitals (LCAO-MOs)

○ The two lowest MOs for H_2^+ are $\psi = N\left(1s_A \pm 1s_B\right)$

○ The addition of the two orbitals gives rise to a *bonding* orbital, where the density of electrons between the nuclei is enhanced through constructive interference

○ This shift of density to the bonding region *is* the bond. Why it gives rise to the molecular potential energy curve is a complex issue

　　· The electron is now attracted to two nuclei instead of one, but it is farther away from them both

　　· The kinetic energy is decreased. This can be discussed in terms of ψ curvature, and reduced confinement (Think two shadows or two water droplets which merge)

　　· The potential energy is also lowered by tightening around the nuclei around the edges

　　· Apparently there is still some controversy over the best way to explain chemical bonds

○ Figures 10B.7 and 10B.8 show the two combinations of H1s orbitals

○ The difference of the two orbitals gives rise to an *antibonding* orbital, where the density of electrons between the nuclei is suppressed through destructive interference

○ Both of these MOs are σ-type orbitals: σ and σ^*

○ MOs can also be notated by their symmetry: σ_g and σ_u^*

9C   Molecular Orbital Theory: Homonuclear Diatomic Molecules

- As we add electrons, the energies and shapes become more complex but they follow the same basic principles

- That is, orbitals can be approximated as LCAO-MOs, forming bonding and antibonding orbitals with different symmetries

- For diatomics, MOs are created by combining one atomic orbital from each atom

- We common draw MO energy level diagrams like that seen in Figure 10C.1

- In addition to the s orbitals, p orbitals also combine (Figure 10C.4 and 10C.5)

- The p orbitals create both σ and π MOs

- The overlap integral is an important quantity: $S = \int \chi_A^* \chi_B \mathrm{d}\tau$

- $S(1sA, 1sB) = \left[1 + \dfrac{ZR}{a_0} + \dfrac{1}{3} \left(\dfrac{ZR}{a_0} \right)^2 \right] e^{-ZR/a_0}$

- Symmetry arguments can be used to show many overlap integrals are 0 (i.e. s-p and p_i-p_j), which limits which AOs are even able to combine at all

- Figures 10C.10 and 10C.12 show two different orderings in the diatomic MOs

- The difference can be explained in two ways

    - As internuclear distance increases, the relative value of the overlap integrals for p_z-p_z and $p_{x,y}$-$p_{x,y}$ orbitals switches places. For smaller atoms, the p_z overlap is greatest
    - s-p mixing is greater for Li, etc. than for F. This means that for Li the AOs used are slightly hybridized, shifting the energies of the orbitals involved. For N_2, the $2p\sigma_g$ MO is actually 27% s character, while for O_2 it is only 13% s character

- Figure 10C.11 shows how these MO energies shift across the periodic table

- Overall bond order is $b = \frac{1}{2} \left(N - N^* \right)$

- Photoelectron spectroscopy (Figure 10C.14) shows observed ionization energies are similar to calculated MO energies

9D   Molecular Orbital Theory: Heteronuclear Diatomic Molecules

- For heteronuclear diatomics, the atoms contribute asymmetrically to molecular orbitals

- $\psi = c_A \chi_A + c_B \chi_B$

- This leads to a *polar* bond, where electron density is concentrated around one atom

- ○ The uneven sharing is governed by the abstract property *electronegativity* (χ)
  - · Mulliken electronegativity is defined as: $\chi = \frac{1}{2}(I + E_{ea})$
  - · Pauling electronegativity is defined through the equation:
  $|\chi_A - \chi_B| = \left[D_0(AB) - \frac{1}{2}(D_0(AA) + D_0(BB))\right]^{1/2}$
  - · Here, D_0 are the bond dissociation energies for bonds between A and B

- ○ The coefficients can be found using the variation principle:

  - · Like before, we find the energy of a trial function by: $E = \int \psi_{trial}^* \hat{H} \psi_{trial} \mathrm{d}\tau$
  - · Solving that integral generally and finding the minimum energy with respect to c_A and c_B yields the following two *secular equations*:
  $(\alpha_A - E)\,c_A + (\beta - ES)\,c_B = 0$
  $(\beta - ES)\,c_A + (\alpha_B - E)\,c_B = 0$ (Note that this is incorrect in the book)
    - * α_A and α_B are the hydrogenic orbital energies (H_{11} and H_{22}), called the *Coulomb integral*
    - * S is the overlap integral
    - * E is the MO energy we are solving for
    - * β is the *resonance integral* (H_{12}), and vanishes as S goes to 0
  - · Solving the system of secular equations is a matter of finding the determinant of the matrix:

  $$\begin{vmatrix} \alpha_A - E & \beta - SE \\ \beta - SE & \alpha_B - E \end{vmatrix} = 0$$

  - · This results in a quadratic equation, whose solutions are the two MO energies
  - · For homonuclear diatomics, $\alpha_A = \alpha_B$ and $E_{\pm} = \dfrac{\alpha \pm \beta}{1 \pm S}$
  - · For heteronuclear diatomics, we must simplify the expression by assuming that $S = 0$:

  $$E_{\pm} = \frac{1}{2}(\alpha_A + \alpha_B) \pm \frac{1}{2}(\alpha_A - \alpha_B)\left[1 + \left(\frac{2\beta}{\alpha_A - \alpha_B}\right)^2\right]^{1/2}$$

  - · Figure 10D.4 shows the MO energies for different AO energy ratios. Note that with any degree of mixing, the energies are always split by a minimum value
  - · AOs with dissimilar energies will lead to MOs dominated by one AO and to weaker bonding and antibonding effects
  - · We can go back and solve for the coefficients
  - · For homonuclear diatomics: $c_A = \dfrac{1}{\sqrt{2(1 \pm S)}}$ and $c_B = \pm c_A$
  - · For heteronuclear diatomics, we again simplify by assuming $S = 0$. For the ground state:

  $$c_A = \left[1 + \left(\frac{\alpha_A - E}{\beta}\right)^2\right]^{-1/2} \quad \text{and} \quad c_B = \left[1 + \left(\frac{\beta}{\alpha_A - E}\right)^2\right]^{-1/2}$$

9E   Molecular Orbital Theory: Polyatomic Molecules

○ The same approach of using LCAOs to form MOs can be extended to polyatomic molecules

○ Hückel theory uses secular determinants to estimate the energies of conjugated π systems

  · Here, the AOs which overlap are all the involved p-bonds

  · Of course, for rigorous computations full integrals are calculated

  · For work done by hand, we make several approximations:

    * All overlap integrals are set to o ($S = 0$)

    * All resonance integrals for non-adjacent orbitals are set to o ($\beta_{non-adjacent} = 0$)

    * All resonance integrals for adjacent orbitals are set equal to each other, and all Coulomb integrals are set equal to each other

  · These approximations simplify the secular determinant to (for the case of butadiene):

$$
\begin{vmatrix}
\alpha - E & \beta & 0 & 0 \\
\beta & \alpha - E & \beta & 0 \\
0 & \beta & \alpha - E & \beta \\
0 & 0 & \beta & \alpha - E
\end{vmatrix} = 0
$$

or

$$
\mathbf{H} = \alpha\mathbf{1} + \beta \begin{vmatrix}
0 & 1 & 0 & 0 \\
1 & 0 & 1 & 0 \\
0 & 1 & 0 & 1 \\
0 & 0 & 1 & 0
\end{vmatrix}
$$

which diagonalizes to give the energies as:

$$
\begin{vmatrix}
-\dfrac{1}{2} - \dfrac{\sqrt{5}}{2} & 0 & 0 & 0 \\
0 & \dfrac{1}{2} - \dfrac{\sqrt{5}}{2} & 0 & 0 \\
0 & 0 & -\dfrac{1}{2} + \dfrac{\sqrt{5}}{2} & 0 \\
0 & 0 & 0 & \dfrac{1}{2} + \dfrac{\sqrt{5}}{2}
\end{vmatrix}
$$

  · Such the matrix is sparse (populated by many os) is isn't quite as tedious to solve as it might be

- For butadiene, this solves to: $E = \alpha \pm 1.62\beta$ and $E = \alpha \pm 0.62\beta$ (Figure 10E.2)
- With 4 electrons in the π system, this gives total energy of $4\alpha + 4.48\beta$
- The HOMO-LUMO gap is -1.24β
- α is the energy of the atomic orbitals, so the deviation from alpha can be considered the bond (or anti-bond) strength (4.48β for butadiene)
- $\beta \approx -110\ ^{kJ}/_{mol}$, and 2β is the bonding energy of a single π bond without any delocalization or resonance stabilization
- For butadiene, resonance stabilization contributes 0.48β beyond the binding energy of two isolated π bonds
- For cyclic molecules, like benzene, remember to put the β term linking C_1 to C_6 as neighbors

○ Computational Chemistry is covered more thoroughly in our labs on the subject

- Semi-empirical methods will simplify the problem by selectively ignoring as many integrals as reasonable. Hückel theory is one example of a semi-empirical approach
- Ab-initio methods simplify the problem by representing orbitals as gaussian functions, which are easier to integrate, differentiate, and multiply
- Density Functional Theory (DFT) simplifies the problem by finding only the electron density, rather than the actual wavefunction
- Solutions can be visually represented as isosurfaces or solvent-accessible surfaces, painted with a colorscale representing electrostatic potential

MOLECULAR SYMMETRY

10A   Shape and Symmetry

○ Some objects have more symmetry than other objects

○ We can robustly characterize symmetry by the operations (rotations, reflections, etc.) which produce identical configurations

○ Symmetry elements are the points, lines, or planes symmetry operations are built around:

· Rotational axes are labeled C_n with rotations of $\dfrac{360°}{n}$

· Planes of reflection are labeled σ_v, σ_h, σ_v', etc.

· Inversion symmetry is labeled as i

· Axes of improper rotation are labeled S_n, combining a reflection with a a rotation C_n

· The identity element E makes no changes at all

○ Objects with the same symmetry elements are classified as belonging to s certain symmetry point group

· Figure 11A.7 shows a flow chart for finding the symmetry point group for a given molecule

· Figure 11A.8 shows graphical representations for many of the most common point groups

○ The most immediate result of symmetry is the presence or absence of a dipole

○ Chirality is an interesting counterpoint to symmetry

· Chiral molecules are not superimposable on their reflection

· A common sort of chiral center will have four different groups bound in tetrahedral geometry

· Chiral molecules are *optically active*, meaning that they will rotate the plane of polarized light

· Many biological molecules are chiral, and pharmacological molecules may need to be manufactured enantiometrically pure (levomethamphetamine, for example)

10B Group Theory

○ Group theory is the branch of mathematics which is relevant to molecular symmetry

○ Symmetry operations can be represented by matrices ($\mathbf{D}$):

· The form of the matrix $\mathbf{D}$ depends on the basis it is operating on. Your book uses atomic orbital basis sets, but I think it is easier to use unit vectors $\vec{x}$, $\vec{y}$, and $\vec{z}$

· $\mathbf{D}(\sigma_v) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ so $\mathbf{D}(\sigma_v) \begin{bmatrix} \vec{x} & \vec{y} & \vec{z} \end{bmatrix} = \begin{bmatrix} \vec{x} & -\vec{y} & \vec{z} \end{bmatrix}$

$\mathbf{D}(\sigma_v') = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ $\qquad \mathbf{D}(\sigma_h) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$ $\qquad \mathbf{D}(i) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$

$\mathbf{D}(C_n) = \begin{bmatrix} \cos\left(\dfrac{2\pi}{n}\right) & \sin\left(\dfrac{2\pi}{n}\right) & 0 \\ -\sin\left(\dfrac{2\pi}{n}\right) & \cos\left(\dfrac{2\pi}{n}\right) & 0 \\ 0 & 0 & 1 \end{bmatrix}$ $\qquad \mathbf{D}(S_n) = \begin{bmatrix} \cos\left(\dfrac{2\pi}{n}\right) & \sin\left(\dfrac{2\pi}{n}\right) & 0 \\ -\sin\left(\dfrac{2\pi}{n}\right) & \cos\left(\dfrac{2\pi}{n}\right) & 0 \\ 0 & 0 & -1 \end{bmatrix}$

○ All symmetric features of a molecule (such as a subset of the atomic orbitals) can be represented by an *irreducible representation* of the point group

· Consider the example of water: C_{2v} point group (note that the molecules lies in the yz plane)

· The Op_z orbital or the sum of H1s orbitals will respond similarly under all symmetry operations, and are represented by the irreducible representation A_1

· The character (χ) of an operation on a representation is indicative of whether that representation is symmetric or antisymmetric under the operation

· The character table outlines the effect of all operations on the irreducible representations

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	linear	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

· What is the proper representation for the difference of H1s orbitals? For Op_y and Op_x? For the difference of Hp_x orbitals?

- There are also irreducible representations, like E or T, which can only be represented in multiple dimensions
- They may have characters that are not 1 or -1
- E represents doubly degenerate entities, and T represents triply degenerate entities
- Atomic orbitals from the same representation are combined to form molecular orbitals, called symmetry-adapted LCAO-MOs
- First, group AOs into similar representations, making sums and differences of some orbitals to create symmetric and antisymmetric sets
- To get the actual MO energies, solve the full secular determinant for each set
- Consider the set of molecular orbitals for water (figures easily found on Google)

10C Applications of Symmetry

○ Symmetry and group theory can help with solving many integrals

- Any symmetric or antisymmetric function can be assigned to an irreducible symmetry representation
- For each symmetry element, multiply the characters of the representations for each function involved in a product
- The direct product can then be decomposed into the irreducible representations which it spans by finding which representations can add their characters to match the direct product
- If the decomposition does not include A_1, then the integral *must* go to 0

○ Decomposition of large direct products can be difficult, but there is a reliable method to do it

- $n(\Gamma) = \frac{1}{h} \sum \chi^{(\Gamma)}(R)\chi(R)$
- h is the order of the group, or how many symmetry elements it contains
- $\chi^{(\Gamma)}(R)$ is the character of representation Γ for symmetry element R
- $\chi(R)$ is the character of the direct product for symmetry element R
- Decompose the direct product $9 -1\ 1\ 3$ in the C_{2v} point group (water motions)

○ Symmetry can also be used to predict transition dipoles

- Identify the representations of the initial and final states
- Identify the direct products $\psi_f^\star \vec{x} \psi_i$, $\psi_f^\star \vec{y} \psi_i$, and $\psi_f^\star \vec{z} \psi_i$
- If none of them contain A_1, then the transition dipole *must* be 0

MOLECULAR SPECTROSCOPY

11A   General Features of Molecular Spectroscopy

○ Einstein A and B coefficients can give the absorption and emission rates:

- Stimulated absorption transition rate constant: $w_{f \leftarrow i} = B_{fi}\rho$

- ρ is essentially the intensity of light at the resonant frequency

- Total absorption rate: $W_{f \leftarrow i} = N_i w_{f \leftarrow i} = N_i B_{fi}\rho$

- Stimulated emission transition rate constant: $w_{f \rightarrow i} = B_{fi}\rho$

- With these constants, even dim light would eventually equalize the excited and ground state populations

- Adding the spontaneous emission rate constant (A), gives the total emission rate constant $w_{f \rightarrow i} = A + B_{fi}\rho$

- At equilibrium, $N_i B_{fi}\rho = N_f (A + B_{fi}\rho)$

- We can relate the A and B coefficients: $A = \left(\dfrac{8\pi h \nu^3}{c^3} \right) B$

- This gives an estimate of the intensity of vacuum photons, and shows how large energy transitions will tend to spontaneously decay more rapidly than low energy transition

○ The Beer-Lambert law shows how much light is absorbed as it passes through an absorbing species

- $I = I_0 10^{-\epsilon C l}$

  ϵ is the molar absorption coefficient, C is the concentration, and l is the pathlength

- The Beer-Lambert law can be derived through calculus, considering the absorption through infinitesimally thin slices along the pathlength, but we will do bother with the derivation here

- Intensity can be converted to transmittance: $T = \dfrac{I}{I_0}$ or absorbance: $A = \log \dfrac{I_0}{I}$

- Absorbance is particularly useful because it is proportional to concentration: $A = \epsilon C l$

○ Real transitions have finite linewidths due to at least a few factors

- Doppler broadening involves the apparent shift in light frequency that arises from translational motion toward or away from the source of light

- $\nu_{receding} = \left(\dfrac{1 - \frac{s}{c}}{1 + \frac{s}{c}} \right)^{1/2} \nu$ and $\nu_{approaching} = \left(\dfrac{1 + \frac{s}{c}}{1 - \frac{s}{c}} \right)^{1/2} \nu$

- For non-relativistic speeds, these simplify to: $\nu_{receding} \approx \dfrac{\nu}{1 + \frac{s}{c}}$ and $\nu_{approaching} \approx \dfrac{\nu}{1 - \frac{s}{c}}$

- In the lab, gas phase molecules will travel in all directions at a distribution of speeds according to the Maxwell-Boltzmann law

- This distribution of speeds leads to Doppler broadening of:

$$\delta\nu_{obs} = \frac{2\nu}{c}\left(\frac{2k_BT\ln 2}{m}\right)^{1/2} \text{ and } \delta\lambda_{obs} = \frac{2\lambda}{c}\left(\frac{2k_BT\ln 2}{m}\right)^{1/2}$$

- Lifetime broadening is an essential feature of the Heissenberg uncertainty principle. See the recent 3blue1brown video on that principle

- Lifetime broadening is: $\delta\tilde{\nu} \approx \dfrac{5.3\ cm^{-1}}{\tau/ps}$

○ Experimental Techniques

- Sources of light include lamps, lasers, and synchrotrons
- Spectral analysis is done either in the frequency or the time domain
- Frequency domain techniques use a polychromator or monochromator
- Time domain techniques include fourier transform and heterodyne/homodyne techniques
- Detectors can be photovoltaic, pyroelectric, photomultipliers, photodiodes, CCDs, etc.

11B Rotational Spectroscopy

○ Molecular rotation energies are calculated based on the rigid rotor model

○ Table 12B.1 shows the ways to calculate the moment of inertia for various common molecular geometries

○ Rotors are classified as spherical, symmetric, linear, or asymmetric

○ Spherical and Linear Rotors:

- $E_J = J(J+1)\dfrac{\hbar^2}{2I}$ and $\tilde{E}_J = \tilde{B}J(J+1)$

- The rotational constant is defined as: $\tilde{B} = \dfrac{\hbar}{4\pi cI}$

- States are $2J + 1$-fold degenerate, with M_J values ranging from J to $-J$

○ Symmetric Rotors:

- Symmetric rotors are oblate if the unique axis has a higher moment of inertia (like a pancake)

- Symmetric rotors are prolate if the unique axis has a smaller moment of inertia (like a pencil)

- $E_{J_a,J_b,J_c} = \dfrac{J_b^2 + J_c^2}{2I_\perp} + \dfrac{J_a^2}{2I_\parallel}$

- These energies can be reframed in terms of total angular momentum and the projection onto the principal axis

- $\tilde{E}_{J,K} = \tilde{B}J(J+1) + \left(\tilde{A} - \tilde{B}\right)K^2$ with $J = 0, 1, 2, \ldots$ and $K = 0, \pm 1, \ldots, \pm J$

- $\tilde{A} = \dfrac{\hbar}{4\pi c I_{\parallel}}$ and $\tilde{B} = \dfrac{\hbar}{4\pi c I_{\perp}}$

- When $K = \pm J$ rotation is primarily about the unique axis, when $K = 0$ rotation is entirely about the other axes

- K is not the same as M_J. M_J does not affect the energy of a state while K does

- States are $2J+1$-fold degenerate for states with $K = 0$, and $2(2J+1)$-fold degenerate for states with $K \neq 0$

○ Centrifugal distortion is a correction which accounts for the fact that bonds stretch with higher rotational excitations

○ $\tilde{E}_J = \tilde{B}J(J+1) - \tilde{D}_J J^2 (J+1)^2$

○ $\tilde{D}_J = \dfrac{4\tilde{B}^3}{\tilde{\nu}^2}$ where $\tilde{\nu}$ is the vibrational wavenumber

○ Pure rotational spectra are in the microwave region

- Microwave spectra require a permanent dipole (H_2, for example, has no microwave spectrum)

- Rotational transitions occur only between adjacent levels due to the conservation of angular momentum

- The selection rules are: $\Delta J = \pm 1$, $\Delta M_J = 0, \pm 1$, and $\Delta K = 0$

- These selection rules make the transition energies (for all rotor types):
  $E_{J+1} - E_J = 2\tilde{B}(J+1) - 4\tilde{D}_J(J+1)^3$

- Recall that the degeneracy of rotational states is: $g_J = 2J+1$

- States will be populated according to the Boltzmann formula: $N_J \propto g_J e^{E_J/k_B T}$

- We can find the maximum of this function to give the most populated state: $J_{max} = \left(\dfrac{k_B T}{2hc\tilde{B}}\right)^{1/2} - \dfrac{1}{2}$

- Analyze the pure rotational spectrum of CO

  * Find $\tilde{B}$ and the bond length
  * Try to find $\tilde{D}_J$ and $\tilde{\nu}$
  * Find the rotational temperature by modeling the spectrum

11C Vibrational Spectroscopy of Diatomic Molecules

○ Recall that for an harmonic oscillator: $E_v = \left(v + \frac{1}{2}\right)\hbar\omega$ with $\omega = \left(\dfrac{k_f}{m_{eff}}\right)^{1/2}$

○ And in wavenumbers: $\tilde{E}_v = \left(v + \frac{1}{2}\right)\tilde{\nu}$ with $\tilde{\nu} = \dfrac{1}{2\pi c}\left(\dfrac{k_f}{m_{eff}}\right)^{1/2}$

○ Infrared vibrational spectra

  · The vibrational selection rule is that $\Delta v = \pm 1$
  · This gives transition energies of:
    $E_{v+1} - E_v = \hbar\omega$ or (in wavenumbers) $\tilde{E}_{v+1} - \tilde{E}_v = \tilde{\nu}$
  · This would place all transitions at the same energy!
  · Real molecules are not *harmonic* oscillators, which leads to vibrational levels which get closer together at v increases
  · A common approximation for a real potential well is called a Morse oscillator
  · The deviation from harmonicity can be characterized by the anharmonicity constant
    $x_e = \dfrac{\tilde{\nu}}{4\tilde{D}_e}$ where $\tilde{D}_e$ is the equlibrium bond dissociation energy (See figure 12D.5)
  · The vibrational energies are now: $\tilde{E}_v = \left(v + \frac{1}{2}\right)\tilde{\nu} - \left(v + \frac{1}{2}\right)^2 x_e\tilde{\nu}$
  · And the transition energies are: $\tilde{E}_{v+1} - \tilde{E}_v = \tilde{\nu} - 2\left(v + 1\right)x_e\tilde{\nu}$
  · A Birge-Sponer plot approximates the equilibrium bond dissociation energy by taking the integral of a curve of transition energies vs $\left(v + \frac{1}{2}\right)$ (See figure 12D.8)

○ Ro-vibrational spectra

  · We have been talking only about the fundamental transition energies, but all vibrational spectroscopy also includes rotational states
  · The rotational selection rules are: $\Delta J = \pm 1, \Delta M_J = 0, \pm 1$, and $\Delta K = 0$
  · The three brances are labeled as $P\left(\Delta J = 1\right), Q\left(\Delta J = 0\right)$, and $R\left(\Delta J = -1\right)$
  · A Q branch is only present for molecules with a degenerate vibration which carries angular momentum (such as CO_2)

○ Raman spectroscopy

  · Raman doesn't require a permanent dipole, but it does require anisotropically polarizable molecules (that is any non-spherical rotors)
  · For Raman spectroscopy, two photons are ultimately involved, giving new selection rules
  · $\Delta J = 0, \pm 2$ for linear rotors, and $\Delta J = 0, \pm 1, \pm 2$ with $\Delta K = 0$ for symmetric rotors
  · The three brances are labeled as $O\left(\Delta J = -2\right), Q\left(\Delta J = 0\right)$, and $S\left(\Delta J = +2\right)$
  · We can also call the O branch "Stokes lines" and the S branch "Anti-Stokes lines"
  · See figure 12D.14 for the Raman spectrum of CO

11D   Vibrational Spectroscopy of Polyatomic Molecules

○ Polyatomic molecules don't vibrate at a single bond, but rather the whole molecule vibrates in what is called a normal mode

○ The number of normal modes is: $3N - 5$ for linear molecules and $3N - 6$ for nonlinear molecules

○ Modes can involve stretches, bends, and twists

○ Some modes are distributed throughout the molecule, while others are largely localized

○ Table 12E.1 (resource section) gives typical vibrational energies for localized vibrations

○ In addition to identifying functional groups, and IR spectrum can be compared to a database for compound identification

○ In condensed phases (liquid, aqueous), rotations cannot be resolved and vibrational transitions are relatively broad

○ Raman vibrational spectroscopy – A coherent technique

   · Because Raman is a coherent technique, there are many ways to get further information from the spectrum

   · Depolarization: Raman scatter from symmetric modes will preserve the incident polarity. All others will scatter depolarized light

   · Resonance Raman: By tuning the visible light near to a resonant electronic transition, the scattering intensity can be enhanced. This is useful for getting signal selectively from one component of a mixture

   · Coherent anti-Stokes Raman Spectroscopy (CARS): CARS can give a spatially coherent output beam, making it easier to separate from fluorescence or incandescence in the sample

○ Remember, modes which belong to the same irreducible representation as linear terms are IR active, while those which belong to the same irreducible representations as quadratic terms are Raman active

11E   Symmetry Analysis of Vibrational Spectra

11F   Electronic Spectra

○ Electronic transitions in gas phase can resolve vibrational structure, but condensed phases have broad bands instead

○ Recall that atoms have electronic states characterized by term symbols, such as ^3P

○ Molecules also have electronic states characterized by term symbols

   · Molecular terms use Greek letters

- Λ is the orbital angular momentum about the bond axis and Σ is the total spin (note that this will be different from the term Σ)
- Σ is for $\Lambda = 0$, Π is for $\Lambda = \pm 1$, Δ is for $\Lambda = \pm 2$, etc.
- Electronic configurations build up to molecular term symbols in much the same way that atomic configurations do
- Consider the terms that arise from the following configurations: σ_g^1 ($^2\Sigma$), π_u^1 ($^2\Pi$), or π_u^2 ($^3\Sigma$ and $^1\Delta$)
- Terms for molecules with inversion symmetry are also labeled with g and u symmetry, calculated as a product of the symmetries of each electron
- Symmetry across a reflecting plane which includes the bond axis gives labels $^+$ and $^-$
- When spin-orbit coupling is strong, Ω is calculated just like J (i.e. $\Omega = \Lambda + \Sigma$)

○ Electronic transitions for molecules follow selection rules:

- $\Delta\Lambda = 0, \pm 1$
- $\Delta S = 0$
- $\Delta\Sigma = 0$
- $\Delta\Omega = 0, \pm 1$
- For Σ terms, only $\Sigma^+ \leftrightarrow \Sigma^+$ or $\Sigma^- \leftrightarrow \Sigma^-$ are allowed
- For centrosymmetric molecules, only $u \leftrightarrow g$ transitions are allowed (Laporte rule)
- Forbidden $g \leftrightarrow g$ and $u \leftrightarrow u$ transitions can become allowed if they simultaneously excite an asymmetric vibration (thus destroying i symmetry). This is called a vibronic transition

○ Electronic spectra of gas phase molecules includes vibrational structure

- Franck-Condon Principle: Electronic transitions take place much faster then nuclear motions can respond
- That is, if an excited electronic state has a different bond length, the bond length will respond only after the electrons assume their new configuration
- Electronic transitions are said to be *vertical,* meaning nuclei do not initially move
- The wavefunctions of the initial and final states must overlap for a transition to be efficient (Figure 13A.7)
- This requirement leads to Franck-Condon factors: $|S(v_f, v_i)|^2 = \left(\int \psi_{v_f}^* \psi_{v_i} \mathrm{d}\tau \right)^2$

○ Rotational structure

- In the gas phase, with an instrument of sufficiently high resolution, rotational structure can be resolved as well!
- Since the transition involves vibrational states from two different potential wells, there is a good deal more complexity in the branch structure

- P-branch ($\Delta J = -1$): $\tilde{\nu}_P(J) = \tilde{\nu} - \left(\tilde{B}' + \tilde{B} \right) J + \left(\tilde{B}' - \tilde{B} \right) J^2$

- Q-branch ($\Delta J = 0$): $\tilde{\nu}_Q(J) = \tilde{\nu} + \left(\tilde{B}' - \tilde{B} \right) J(J+1)$

- R-branch ($\Delta J = 1$): $\tilde{\nu}_R(J) = \tilde{\nu} - \left(\tilde{B}' + \tilde{B} \right) (J+1) + \left(\tilde{B}' - \tilde{B} \right) (J+1)^2$

- Often, the P branch (where $\tilde{B}' > \tilde{B}$) or R branch (where $\tilde{B}' < \tilde{B}$) will curve around on itself, forming a branch head (Figure 13A.10)

○ For polyatomic molecules, many molecular orbitals are spread out over the whole molecule, but others are highly localized around significant moieties, such as a carbonyll

○ These moieties give rise to characteristic absorption peaks just like local vibrational modes do (Table 13A.2)

○ Ligand Field Theory:

- d-Metal complexes will have the central metals d-orbitals split by the electronic environment of the ligands

- Octahedral geometry places the t_{2g} triplet of states below the e_g pair

- Tetrahedral geometry places the e pair of states below the t_2 triplet

- The ligand-field splitting parameter (Δ_O for octahedral geometry, and Δ_T for tetrahedral geometry) is the $d \to d$ transition energy, and usually in the visible range

- Though these transitions are formally forbidden by several rules, they become possible as vibronic transitions

- metal complexes also have visible light transitions in the form of ligand-to-metal charge transfer (LMCT) and metal-to-ligand charge transfer (MLCT)

- A LMCT transition is responsible for permanganate's vivid color

11G   Decay of Excited States

○ Fluorescence and phosphorescence are both spontaneous emission processes, but phosphorescence occurs over much longer time scales

○ Radiationless decay to the ground vibrational state makes fluorescence red-shifted from absorption

○ For well-resolved vibrational structure (i.e. gas phase), the absorption spectrum gives the vibrational structure of the excited electronic state, and the fluorescence spectrum gives the vibrational structure of the ground electronic state (Figures 13B.2 and 13B.3)

○ For condensed phases, there might be an even greater red shift due to solvent/neighbor reorganization (Figure 13B.4)

○ Phosphorescence is caused by an inter-system crossing (Figure 13B.5)

- A Jablonski diagram (Figure 13B.6) shows all the various transitions possible within and between spin systems

- Electronic transitions will lose vibrational structure and transition into a continuum when the excited state exceeds the bond dissociation energy (Figure 13B.7)

- If an unbound state crosses the excited state, then predissociation can be observed near the crossing point (Figure 13B.8)

Lasers

- Lasers have many useful properties, as summarized in Table 13C.1

- Lasers rely on a population inversion, which makes a resonant photon more likely to stimulate emission than to be absorbed (Figure 13C.5)

- Population inversion is only possible for systems with at least a third, metastable state (Figures 13C.1 and 13C.2)

- For a laser cavity, standing waves are built up within the cavity. Those standing waves must match the cavity length like vibrations on a guitar string: $n\frac{1}{2}\lambda = L$

- Any practical laser will have many longitudinal cavity modes

- There are also transverse laser modes, though many lasers seek to emit only in a single mode

- Laser light is also *coherent* both spatially and temporally

- Spatial coherence is characterized by the coherence length: $l_C = \dfrac{\lambda^2}{2\Delta\lambda}$

- Very spectrally sharp lasers will spread more slowly than broadband lasers

- Materials with very high gains are "superluminous," and may operate without a cavity at all

- Pulsed Lasers:

  · It is useful sometimes to produce laser pulses rather than a continuous laser beam

  · Q-switching:

    * Q-switching is a way to achieve a very high power short (nanosecond) pulses
    * A laser will begin to lase at a certain threshold level of population inversion, and remain at that threshold
    * "Spoiling" the cavity will require a higher threshold before lasing, and so a higher population inversion can be achieved with a poor cavity
    * Suddenly switching the cavity to a good one will immediately dump out all of that excess energy in one big pulse
    * Switching is achieved by AOMs, Pockel's Cells, and perhaps other means

- Mode-locking:
  * Mode-locking gives the very shortest pulses on the Earth (43 attoseconds!)
  * A lasing medium with a broad bandwidth will produce many, many closely spaced longitudinal modes
  * Generally, each mode will have its own phase
  * If all of the phases could be lined up, then a single sharp pulse would be produced (See spreadsheet)
  * In practice, mode-locking can be achieved by an AOM, end-mirror fibrillation, a Kerr Medium, a saturable absorber, or other means
- Figure 13C.10 shows a time-resolved (pump-probe) spectrum

○ Practical lasers:

- HeNe lasers (Figure 13C.12) pump the He through electric discharge, which transfers energy to Ne though collisions. Ne lases at many frequencies, but 633 nm is prominent
- Argon Ion lasers (Figure 13C.13, and in our research lab) ionize Ar gas through electric discharge, which then relaxes to new electronic states and emits red and UV light
- CO_2 lasers (Figure 13C.14) excite N_2 through electric discharge, and transfer that energy to CO_2 through collisions. The CO_2 lases in the infrared as the antisymmetric stretch decays into the symmetric stretch. Collisions with He depletes the symmetric stretch to maintain a population inversion
- Exciplex lasers (Figure 13C.15) have a dissociative ground electronic state, but a bound excited electronic state. After electric discharge bound complexes form. Once they emit, they immediately fall apart, thus maintaining the population inversion
- Dye lasers use a fluorophore in solution with a broad fluorescence spectrum. By introducing a grating into the cavity, a tunable narrowband laser can be produced. Fluorophores can also be swapped out to give a very wide range of possible colors from a single laser apparatus
- Ti:sapphire lasers (vibronic lasers) are very broadband lasers due to vibronic transitions in the crystal lattice (Figure 13C.17). These lasers are well suited for mode-locking

MAGNETIC RESONANCE

For this chapter, I lectured without following the book sections very closely, as they get very technical and lost in obscure formulas, etc.

12A   General Principles (my version)

○ Nuclei have quantum mechanical spin just like electrons do.

○ The spin states are normally equal in energy, but a strong magnetic field can split them, Fig. 12A.1 (Zeeman effect)

○ NMR and EPR spectroscopy probe transitions between nuclear and electric spin states

○ Tables 12A.1 and 12A.2 give some information about nuclear spins for a few elements

○ Figures 12A.3 and 12A.5 show the anatomy of NMR and EPR instruments

12B   Features of NMR Spectra

○ All nuclei of the same type have transition in the same neighborhood, but we have very fine resolution with NMR so we can see very slight shifts in transition frequency

○ Shielding and chemical shift

    · The local electronic environment can shift the transition energy

    · Solvent arrangement, conformational changes, etc. will tend to smear out all transitions a bit with *homogeneous* broadening

    · Permanent differences, like the presence of electron-withdrawing moieties on a molecule, will produce peaks at clearly resolvable different frequencies

    · Groups of atoms in the same environment will have transitions at the same frequency (consider the two groups of Hs in methanol) Figure 12B.1 shows regions of chemical shift for H and C in common environments, and Figure 12B.2 shows a simple spectrum

○ Spin coupling between groups is a source of fine structure in NMR spectra

    · Nearby groups (such as Hs on adjacent Cs) can have their spins correlated or anti-correlated to produce a multiplet of transitions

    · Figure 12B.10 shows an energy level diagram for AX-coupling, and figure 12B.11 shows the resulting spectrum

- With more nuclei involved in the coupling, the multiplets become more complex (Figures 12B.13 and 12B.14)
- The peak heights can be predicted by Pascal's triangle
- The multiplet splitting spacing shows the strength of coupling between groups, and so corresponding multiplets should have equal spacings
- Figures 12B.8 and 12B.22 shows a simple spectrum with fine structure
- With neighbors on both sides, we can see doublets of triplets, etc.
- A multiplet can be collapsed into a single peak at its center by decoupling pulse sequences (covered in the next section)

12C   Pulse Techniques in NMR

- Modern NMR is almost always done using a "time-domain" or Fourier transform method
- Classical view and precession (Fig. 12A.2, and gyroscope demo)
- The precession produces a literal radio wave, which we can collect and analyze with a receiver antenna
- FID signal
  - First, a sample is excited by a broadband radio pulse
  - The free-induction decay signal is captured. Figure 12C.6
  - The frequency of the FID signal is the transition frequency (Larmor frequency), so the FID signal can be transformed into a spectrum (Figure 12C.8)
- Spin relaxation (How long the FID signal lasts)
  - Resolution is limited by how long the FID signal persists
  - This can be literally seconds for H spectra, which is kind of incredible!
  - The FID signal drops due to 2 factors: Population relaxation, and decoherence
  - Population relaxation is ...inevitable
  - Decoherence is caused by homogeneous and inhomogeneous effects
  - These effects lead to peak broadening, as the shorter FID signal limits resolution
  - inhomogeneous decoherence (broadening) can be undone by *refocusing* pulse sequences (spin echos)
- Complex pulse sequences and 2-d spectra can achieve very finely-tuned effects
  - Polarization transfer is the foundation of many of these pulse sequences
  - HetCor (Heteronuclear correlation) can show explicitly which C signals are couples with which H signals

- Nuclear Overhauser Effect (NOE) can enhance weak C signals by transferring signal from H to C

- Couplings and splittings can be probed or collapsed at will

- Some pulse sequences probe through-space distances instead of through-bond distances

- Some pulse sequences can have dozens of pulses, and reveal obscure things like "which H signals arise from H groups which are exactly 8 bonds removed from the N atom"

12D Electron Paramagnetic Resonance

CHAPTER 13

STATISTICAL THERMODYNAMICS

13A The Boltzmann Distribution

○ Energy can be distributed between molecules and energetic degrees of freedom in many different ways

○ We assume that energy and temperature are the only important factors

○ A particular division of energy between different levels is called a configuration

○ The weight of a configuration is the number of ways a particular configuration can be achieved (considering the indistinguishability of molecules):

$$\mathcal{W} = \frac{N!}{N_0! N_1! N_2! \dots}$$

○ Try with the configurations {0,2,0,0} and {1,0,1,0}, which have equal energy ()

○ Figure 15A.2 gives another example

○ It will be convenient to find the natural log of $\mathcal{W}$, which is:

$$\ln \mathcal{W} = \ln N! - \sum \ln N_i!$$

○ Here, Sterling's approximation is useful: $\ln x! \approx x \ln x - x$

○ For a fixed energy E and a fixed total number of particles N, there may be many different configurations

○ The configuration with the greatest weight is the most probably configuration

○ The distribution in this most probable configuration (greatest $\mathcal{W}$) is the Boltzmann distribution:

$$\frac{N_i}{N} = \frac{e^{-\beta \epsilon_i}}{\sum_j e^{-\beta \epsilon_j}} \qquad \beta = (kT)^{-1}$$

○ The denominator is also called the partition function: $q = \sum_j e^{-\beta \epsilon_j}$

○ If we want to consider energy levels with degenerate states, then we add the degeneracy to both the Boltzmann distribution and the partition function:

$$\frac{N_i}{N} = \frac{g_i e^{-\beta \epsilon_i}}{\sum_j g_j e^{-\beta \epsilon_j}} \qquad q = \sum_j g_j e^{-\beta \epsilon_j}$$

13B   Molecular Partition Functions

- For a single molecule, the partition function should include all energetic degrees of freedom

- $q = q^T q^R q^V q^E$

- For translations, we can define a thermal wavelength: $\Lambda = \dfrac{h}{\sqrt{2\pi m k_B T}}$

- q^T can be calculated two ways: $q^T = \left(\dfrac{2\pi m}{h^2 \beta}\right)^{3/2} L_x L_y L_z = \dfrac{V}{\Lambda^3}$

13C   Molecular Energies

13D   The Canonical Ensemble

13E   The Internal Energy and the Entropy

13F   Derived Functions

MOLECULAR INTERACTIONS

14A   The Electric Properties of Molecules

○ A point electric dipole is an electric dipole where the distance between charges is small compared to the distance to the observer

$\mu = QR$

○ The SI unit is clumsy, so we use the Debye instead: $1\ D = 3.335 \times 10^{-30}\ Cm$

○ Table 16A.1 shows the dipole magnitutde for some common molecules

○ Figure 16A.1 shows how polar bonds can add up to make an overall molecular dipole

○ A non-polar molecule may nevertheless contain a quadrupole or octupole

○ Figure 16A.2 shows different configurations which lead to multipoles

○ Polarizability measures the electronic response to an electric field

  · Think of it as the squishiness of an electron cloud (beach ball vs. basketball)

  · $\mu^* = \alpha \mathcal{E}$

  · In reality, the induced dipole is a Taylor series: $\mu^* = \alpha \mathcal{E} + \frac{1}{2}\beta \mathcal{E}^2 + \cdots$

  · Here, α is called the polarizabilty and β is called the hyperpolarizability

  · Polarizability has strange units $\left(\dfrac{C^2 m^2}{J} \right)$, so instead we sometimes use the polarizability volume
  $\alpha' = \dfrac{\alpha}{4\pi\epsilon_0}$

  · α' is on the scale of actual molecular volumes

○ Polarization is the dipole moment density for an ensemble in an electric field

  · $P = \langle \mu \rangle \, \mathcal{N}$

  · Now $\langle \mu \rangle$ is not actually the same as μ because thermal fluctuations prevent all molecules from lining up perfectly with the electric field

  · $\langle \mu_z \rangle = \dfrac{\mu^2 \mathcal{E}}{3k_B T}$

  · This equation is only valid for a constant electric field, and note the temperature dependence

- · Changing electric fields (like light waves) will induce smaller and smaller polarizations as the frequency increases
- · Orientation polarization is caused by the physical orientation of a molecule's permanent dipole. The orientation polarization is lost in the microwave region of the spectrum, as molecules are able to tumble faster than the period of the electric field itself
- · Distortion polarization is from changes in the shape of the molecules. This polarization is lost in the infrared region of the spectrum, as the molecules vibrations dominate any distortions on that time scale

14B   Interactions Between Molecules

- ○ The attraction between two charges is the Coulomb potential: $V = \dfrac{Q_1 Q_2}{4\pi\epsilon r}$

- ○ A charge-dipole interaction is different because the dipole has both positive and negative charge

- ○ $V = -\dfrac{\mu_1 Q_2}{4\pi\epsilon_0 r^2}$

- ○ Two dipoles aligned together have the potential: $V = -\dfrac{\mu_1 \mu_2}{2\pi\epsilon_0 r^3}$

- ○ And two dipoles which rotate freely have the potential: $\langle V \rangle = -\dfrac{C}{r^6}$ where $C = \dfrac{2\mu_1^2 \mu_2^2}{3\left(4\pi\epsilon_0\right)^2 k_B T}$

- ○ For multipoles, $V \propto \dfrac{1}{r^{n+m-1}}$ where n and m are the orders of the multipoles

- ○ For dipole-induced dipole interactions: $V = -\dfrac{C}{r^6}$ where $C = \dfrac{\mu_1^2 \alpha_2'}{4\pi\epsilon_0}$

- ○ Finally, the London forces have $V = -\dfrac{C}{r^6}$ where $C = \frac{3}{2}\alpha_1' \alpha_2' \dfrac{I_1 I_2}{I_1 + I_2}$ and I are the ionization energies

- ○ Table 16B.1 summarizes and compares these intermolecular interactions

14C   Liquids

- ○ We are almost out of time for this semester, so I only want to cover a few basics

- ○ Figure 16C.1 shows the radial distribution function of oxygen atoms in liquid water

- ○ Surface Tension:

  - · Changing the surface area of a liquid can do work just like PV work: $\mathrm{d}w = \gamma \mathrm{d}\sigma$
  - · Because liquids are incompressible, the volume is constant and this can also be taken as a Helholtz energy: $\mathrm{d}A = \gamma \mathrm{d}\sigma$

- · Energy is minimized and work is done by a liquid contracting into a curved droplet to minimize its surface area
- · The laplace equation relates the pressures on either side of the interface in a bubble, droplet, or cavity

$$p_{in} = p_{out} + \frac{2\gamma}{r}$$

- · A capillary will draw a liquid up to a height of: $h = \dfrac{2\gamma}{\rho g r}$ where r is the radius of the capillary
- · Surface tension can be measured by the contact angle of a droplet on a surface:

$$w_{ad} = \gamma_{sg} + \gamma_{lg} - \gamma_{sl} \ \ \text{and} \ \ \cos\theta_c = \frac{w_{ad}}{\gamma_{lg}} - 1 = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}}$$

- · S will concentrate at the surface giving a surface excess of:

$$\Gamma_J = \frac{n_J(\sigma)}{\sigma} \ \ \text{where} \ \ n_J(\sigma) = n_J - (n_J(\alpha) + n_J(\beta))$$

- · And the surface tension changes by concentration according to: $\left(\dfrac{\partial\gamma}{\partial c}\right)_T = -\dfrac{RT\Gamma_S}{c}$

○ Finally, we have the Kelvin equation which gives vapor pressures for curved surfaces (which are greater than the pressure for a flat, pure substance)

$$p = p^\star e^{2\gamma Vm/rRT}$$

○ The Kelvin equation predicts that any droplet below a certain size will vaporize away, even if the relative humidity is $> 100\%$

14D   Macromolecules

14E   Self-Assembly

CHAPTER 15

SOLIDS

My Take on Semiconductors