PHY294: Quantum and Thermal Review Notes

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I   The Three Dimensional Schrödinger's Equation

- From PHY293, we know that the time-independent, one-dimesional Schrödiger's Equation is:

$$\frac{d^2\psi}{dx^2} = \frac{2M}{\hbar^2}[U - E]\psi \tag{1}$$

  where U is the potential energy of the particle and M is the mass.

- In 3 dimensions, since we know that the wavefunction and the potential energy of the particle depend on the position of the particle:
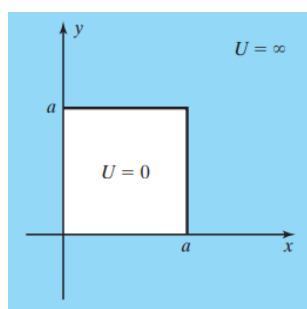
$$\psi(x, y, z) = \psi(\vec{r}), U(x, y, z) = U(\vec{r})$$

- As such, the 3-D SE is:

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = \frac{2M}{\hbar^2}[U - E]\psi(\vec{r}) \tag{2}$$

I.I   Two-Dimensional Square Well

- Consider a rigid, square box where the potential of the particle is 0 inside this box (U = 0):

$$U(\vec{r}) = \begin{cases} 0, & 0 \le x \le a \\ \infty, & \text{else} \end{cases} \tag{3}$$

- As such, energy E will be all kinetic and ranges from $0 \le E < \infty$.

- Now, we can write the 2-D SE as:

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} = -\frac{2ME}{\hbar^2}\psi(\vec{r})$$

- This equation can be solved by using separation of variables, taking the wavefunction to be a product of functions of x and y:

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

1

- Now, the equation can be rewritten as and solved by second-order ordinary differential equation strategies:

$$X"(x)Y(y) + X(x)Y"(y) = -\frac{2ME}{\hbar^2}X(x)Y(y) \tag{4}$$

$$\frac{X"(x)}{X(x)} + \frac{Y"(y)}{Y(y)} = -\frac{2ME}{\hbar^2} = -k^2 (\text{constant}) \tag{5}$$

- Using the boundary conditions found from the two-dimensional well, namely $X(0) = X(a) = Y(0) = Y(a) = 0$, we can solve the wavefunction to be:

$$\psi(x,y) = BC \sin\frac{n_x\pi x}{a} \sin\frac{n_y\pi y}{a}_1 \tag{6}$$

where n_x, n_y are positive integers.

I.I.1   Allowed Energies

$$\frac{X"(x)}{X(x)} + \frac{Y"(y)}{Y(y)} = -\frac{2ME}{\hbar^2}$$

$$\frac{n_x^2\pi^2}{a^2} + \frac{n_y^2\pi^2}{a^2} = -\frac{2ME}{\hbar^2}$$

$$E_{n_x,n_y} = \frac{\hbar^2\pi^2}{2Ma^2}(n_x^2 + n_y^2)$$

- This is the allowed energies given the two positive integers, n_x, n_y.

I.I.2   Degeneracy

- In a two-dimensional box, there can be different wavefunctions where the particle has the same energy, for example $\psi_{12}, \psi_{21} \longrightarrow E_{12} = E_{21} = 5E_0$.

- In general, if there are N independent wave functions with same energy E, we say that the energy level E is **degenerate** with **degeneracy** N.

I.II   Central Forces (2D Polar Schrödinger's Equation)

- Many physical systems are defined such as the potential energy of the particle is dependent on its distance to the center, r, rather than its direction. As such, we can rewrite it as:

$$\psi = \psi(r, \phi)$$

$$\frac{\partial^2\psi}{\partial r^2} + \frac{1}{r}\frac{\partial\psi}{\partial r} + \frac{\partial^2\psi}{\partial\phi^2} = \frac{2M}{\hbar^2}[U(r) - E]\psi(\vec{r}) \tag{7}$$

- Using the same strategy of separation of variables, we obtain that:

$$\frac{\Phi"(\phi)}{\Phi(\phi)} = -\frac{r^2R"(r) + rR'(r)}{R(r)} + \frac{2Mr^2}{\hbar^2}[U(r) - E]$$

$$\Phi"(\phi) = -m^2\Phi(\phi)$$

$$R" + \frac{R'}{r} - \left[\frac{m^2}{r^2} + \frac{2M}{\hbar^2}(U - E)\right]R = 0$$

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[1]Recall that in a 1D well, we have the property: $\psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$. Using this, we can solve for constants B, C.
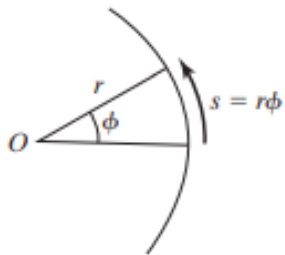
- The general solution for $\Phi(\phi)$ is a combination of $\sin m\phi$ and $\cos m\phi$, where m must be an integer:

$$\Phi(\phi) = \cos(m\phi) + i\sin(m\phi) = e^{im\phi}$$

I.II.1   Quantizing Angular Momentum

- So far, we can conclude that:

$$\psi(r, \phi) = R(r)e^{im\phi}$$

$$\psi(r, \phi) \propto e^{im\phi} = e^{i(m/r)s} \tag{8}$$

- Given a particle has momentum $\hbar k$, the angular momentum, L, of the particle is:

$$L = p_{tang}r = m\hbar$$

which shows that angular momentum is now quantized as multiples of $\hbar$.

I.II.2   Energy Levels

- Using the radial equation, we can note that for a different value of m, we get different allowed energies. In addition, since the m dependence is only found as $\frac{m^2}{r^2}$, meaning that we will have the same energies whether $\pm m$:

$$E_{n,m} = E_{n,-m}$$

- This also means that except when m = 0, the energy level $E_{n,m}$ is **twofold degenerate**.

I.III   Three-Dimensional Central-Force Problem

- Similar to two dimensions where we use polar coordinates, we now need an r to represent the distance to the central force, so we use **spherical coordinates**.

$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi \tag{9}$$
$$z = r cos\theta$$
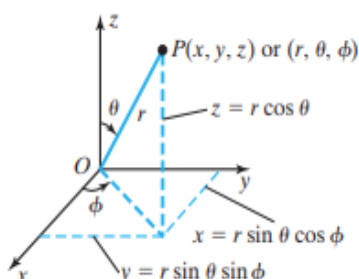
- The three-dimensional Schrödinger's Equation in spherical coordinates can be written as:

$$\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\psi}{\partial\theta}) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} = \frac{2M}{\hbar^2}[U(r) - E]\psi \tag{10}$$

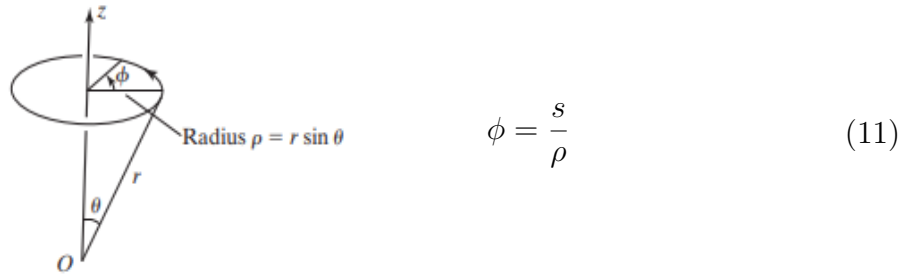- Once again, using the separation of variables technique ($\psi = R(r)\Phi(\phi)\Theta(\theta)$), we obtain:

$$\frac{\Phi"(\phi)}{\Phi(\phi)} = f(r,\theta)$$

$$\Phi"(\phi) = -m^2\Phi(\phi)$$

$$\Phi(\phi) = e^{im\phi}$$

and

$$\frac{1}{\sin\theta}\frac{d}{d\theta}(\sin\theta\frac{d\Theta}{d\theta}) + (k - \frac{m^2}{\sin^2\theta})\Theta = 0$$

$$\frac{2M}{\hbar^2}[U(r) + \frac{k\hbar^2}{2Mr^2} - E](rR) = \frac{d^2}{dr^2}(rR)$$

I.III.1   Quantizing Angular Momentum (again)

- Using the same idea as the 2D quantization of angular momentum:

$$\phi = \frac{s}{\rho} \tag{11}$$

$$\Phi(\phi) = e^{im\phi} = e^{i(m/\rho)s}$$

- Knowing that the tangential momentum $p_{tang} = \frac{\hbar m}{\rho}$, we can calculate p_{tang} by the radius:
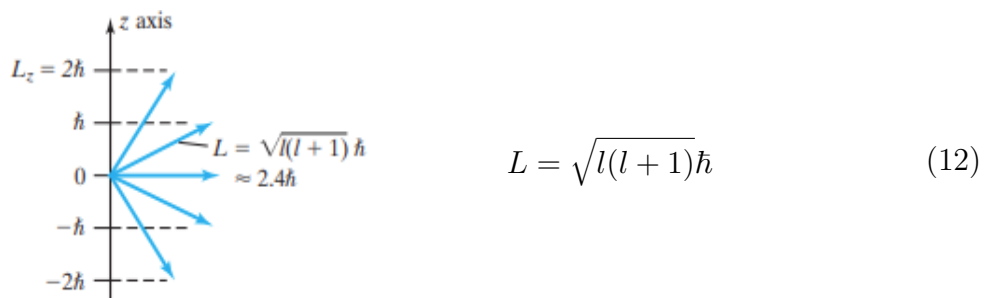
$$L_z = m\hbar$$

- Now, dealing with $\Theta(\theta)$, we observe that the only acceptable solution for k is:

$$k = l(l+1)$$

where l is a positive integer greater than or equal in magnitude to m ($l \geq |m|$).

- This way, we can define the magnitude of angular momentum and represent it using the vector model as:

$$L = \sqrt{l(l+1)}\hbar \tag{12}$$

- The Heisenberg uncertainty principle extends to angular momentum and implies that no two components of **L** can simultaneously have definite values.

I.IV   Energy Levels of The Hydrogen Atom

- Finally, we have to consider the radial equation, $R(r)$ since it is the only equation with E in it.

$$\frac{d^2}{dr^2}(rR) = \frac{2M}{\hbar^2}[U(r) + \frac{l(l+1)\hbar^2}{2Mr^2} - E](rR)$$

- The allowed values of E will depend on the angular momentum quantum number, l, and we can predict that in a central-force problem, a level with $L = \sqrt{l(l+1)}\hbar$ will be at least $(2l+1)$-fold degenerate.

- For the Hydrogen atom, we take an electron bound to a proton, where the potential energy function is:

$$U(r) = \frac{-e^2}{4\pi\varepsilon_0 r}$$

- After plugging $U(r)$ into the radial equation and solving for E, we obtain:

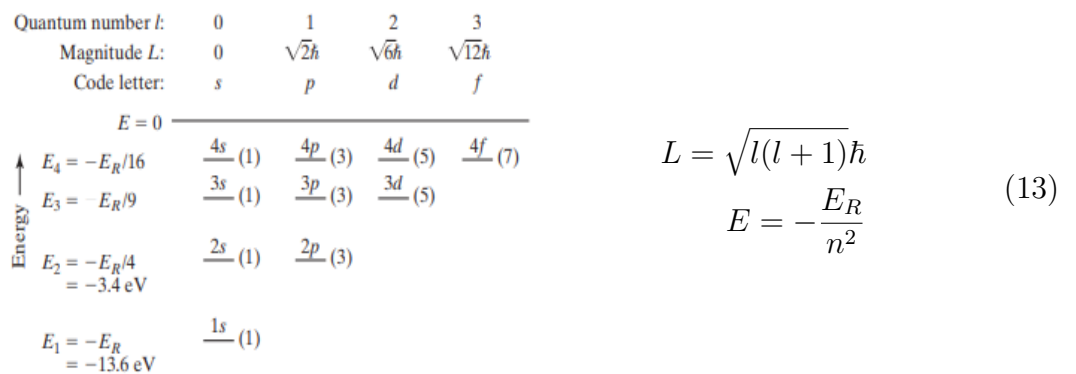$$E = -\frac{m_e(ke^2)^2}{2\hbar^2}\frac{1}{n^2}{}^2 = -\frac{E_R}{n^2}$$

Quantum number l:	0	1	2	3
Magnitude L:	0	$\sqrt{2}\hbar$	$\sqrt{6}\hbar$	$\sqrt{12}\hbar$
Code letter:	s	p	d	f

$$L = \sqrt{l(l+1)}\hbar$$

$$E = -\frac{E_R}{n^2} \tag{13}$$

Figure 1: Energy-level diagram of the hydrogen atom.

- The nth energy level has degeneracy n^2 because it has $l = 0, 1, ..., (n-1)$.

I.V   Wavefunctions of Hydrogen

I.V.1   1s (Ground) State

- Recall, the ground state has quantum numbers, n = 1, l = 0, m = 0. It is also spherically symmetric, which means that the wavefunction is only dependent on the radius.

$$\psi_{1s} = R_{1s}(r)$$

- We can rewrite the radial equation as:

$$\frac{d^2}{dr^2}(rR) = \frac{2M}{\hbar^2}[-\frac{ke^2}{r} + \frac{E_R}{n^2}](rR)$$

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[2]This first term is the Rydberg energy, equivalent to 13.6 eV.

which can be further simplified as [3]:

$$\frac{d^2}{dr^2}(rR) = \left(\frac{1}{n^2 a_B^2} - \frac{2}{a_B r}\right)(rR)$$

$$R_{1s}(r) = A e^{-r/a_B} \qquad (14)$$
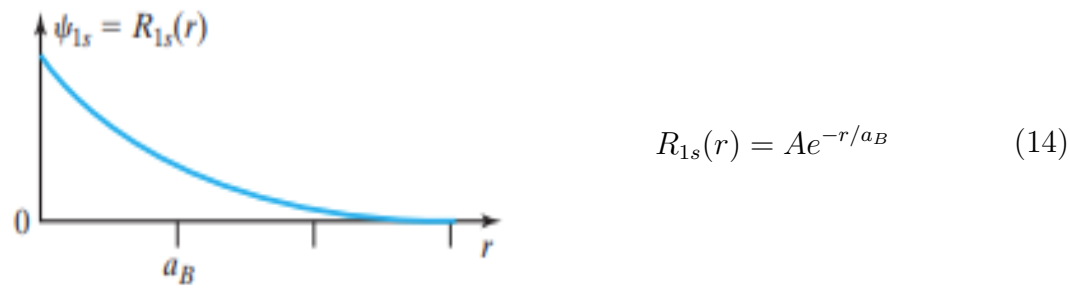
Figure 2: Wavefunction of 1s state of hydrogen.

- The probability of finding an electron in a small spherical volume, namely between r and r + dr, is:

$$\mathbb{P}(r \le \rho \le r + dr) = |\psi|^2 dV = |R(r)|^2 4\pi r^2 dr$$

- The radial probability density (radial distribution) is:

$$P(r) = 4\pi r^2 |R(r)|^2$$
$$P_{1s}(r) = 4\pi A^2 r^2 e^{-2r/a_B}$$

- To solve for constant A, we can use the property of a probability density function [4] to obtain $A = \frac{1}{\sqrt{\pi a_B^3}}$.

I.V.2   The $2p_x$, $2p_y$, $2p_z$ Wavefunctions

- In the $l = 1$ state, there are 3 2p wave functions, which corresponds to the three orientations (x, y, z). Now we cannot omit the $\Theta(\theta)$ component since $l \ne 0$, and as such, $\Theta(\theta) = \cos\theta$:

$$\psi = R_{2p}(r)\cos\theta \longrightarrow R_{2p}(r) = A r e^{-r/2a_B}$$

- Now for the x, y and z orientations respectively, the wavefunctions are $Axe^{-r/2a_B}$, $Aye^{-r/2a_B}$, $Aze^{-r/2a_B}$.

TABLE 8.2

The first few radial functions $R_{lm}(r)$ for the hydrogen atom. The variable ρ is an abbreviation for $\rho = r/a_B$ and a stands for a_B.

	$n = 1$	$n = 2$	$n = 3$
$l = 0$	$\frac{1}{2\sqrt{a^3}}e^{-\rho}$	$\frac{1}{\sqrt{2a^3}}\left(1 - \frac{1}{2}\rho\right)e^{-\rho/2}$	$\frac{2}{\sqrt{27a^3}}\left(1 - \frac{2}{3}\rho + \frac{2}{27}\rho^2\right)e^{-\rho/3}$
$l = 1$		$\frac{1}{\sqrt{24a^3}}\rho e^{-\rho/2}$	$\frac{8}{27\sqrt{6a^3}}\left(1 - \frac{1}{6}\rho\right)\rho e^{-\rho/3}$
$l = 2$			$\frac{4}{81\sqrt{30a^3}}\rho^2 e^{-\rho/3}$

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[3]Recall that Bohr radius, $a_B = \frac{\hbar^2}{m_e k e^2}$, and Rydberg energy, $E_R = \frac{ke^2}{2a_B}$

[4]For density function $f(x)$, $\int_{-\infty}^{\infty} f(x) = 1$.
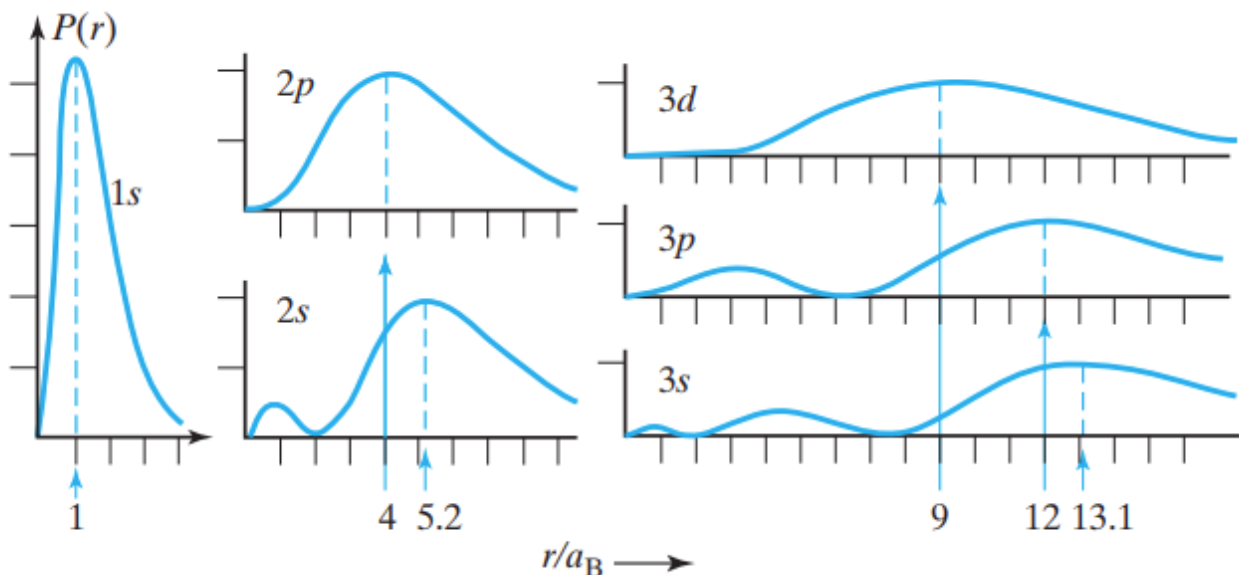
I.VI Shells

Figure 3: Just remember how to draw these by heart.

I.VII Hydrogen-Like Atoms

- Similar to how the potential energy, $U(r)$, of a hydrogen atom is $\frac{-ke^2}{r}$, the potential energy of a hydrogen-like atom is $U(r) = -\frac{Zke^2}{r}$, where Z is the number of protons in the nucleus. As such, the allowed energy of the particle is:

$$E = -Z^2 \frac{E_R}{n^2}$$

II Electron Spin

II.I Spin Angular Momentum (S)

- The total angular momentum, $\mathbf{J}$, is the sum of the orbital angular momentum, $\mathbf{L}$, and the spin angular momentum, $\mathbf{S}$.

- Similar to the way $\mathbf{L}$ is quantized, the magnitude of $\mathbf{S}$ can also be quantized:

$$S = \sqrt{s(s+1)}\hbar$$

where s is fixed at a value of $s = \frac{1}{2}$, meaning S is fixed at a magnitude of $S = \frac{\sqrt{3}}{2}\hbar$.

- Similar to orbital angular momentum, the magnitude of spin angular momentum can be represented as:

$$S_z = m_s \hbar$$

where $m_s \in -s, s$. This leaves us with $m_s = \pm\frac{1}{2}$.

- Contrary to what was said in section I.IV, the degeneracy of the nth energy level is actually $2n^2$ because the energy of the hydrogen atom is **independent of the spin orientation**.

II.II   Magnetic Moments

- An orbiting charge acts like a small current loop, i, producing a magnetic field, $\mathbf{B}$ and a torque $\boldsymbol{\Gamma}$.

$$\boldsymbol{\Gamma} = i\mathbf{A} \times \mathbf{B}$$
$$\boldsymbol{\Gamma} = \boldsymbol{\mu} \times \mathbf{B} \tag{15}$$
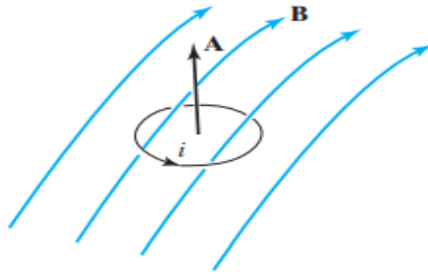
where μ is the magnetic moment of the loop.

- The torque done on the current loop will produce a work which varies with the orientation of the loop:
$$W = -\int \Gamma d\theta = -\mu B \int \sin\theta d\theta = \mu B \cos\theta + C$$

- Potential energy U is the negative of work:

$$U = -\mu B \cos\theta = -\boldsymbol{\mu} \cdot \mathbf{B} \tag{16}$$

where it is at its minimum when $\theta = 0$ (or μ is parallel to $\mathbf{B}$).

- The magnitude of the current loop can be defined by the charge of the electron e and its speed v ($v = \frac{2\pi r}{T}$):
$$i = \frac{e}{T} = e\frac{v}{2\pi r}$$

- From this we can find the gyromagnetic ratio ($\frac{\mu}{L}$):

$$\frac{\mu}{L} = \frac{evr}{2m_e vr} = \frac{e}{2m_e}$$

- The current is travelling in a direction opposite of the electron's velocity so μ and $\mathbf{L}$ are actually antiparallel (opposite-facing).
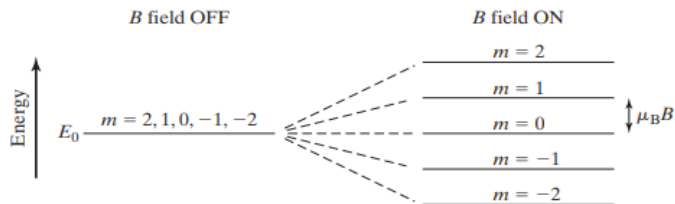
$$\mu = -\frac{e}{2m_e}\mathbf{L}$$

II.III   The Zeeman Effect

- **Zeeman effect:** putting an atom in a magnetic field to change its spectrum.

- Consider an atom where the magnetic moments due to the electrons' spins cancel out. In a state where there is zero total spin, it is called a **singlet state**.

- Let helium have an energy E_0, where its angular momentum $\mathbf{L}$ has 2l+1 possible different orientations. Without a magnetic field, the energy is the same for all states, meaning E_0 is $(2l + 1)$-fold degenerate.

- Now when we apply magnetic field $\mathbf{B}$, the energy will change by $-\boldsymbol{\mu} \cdot \mathbf{B}$, depending on the orientation of μ. We can conclude that we remove the degeneracy of the energy level but

add $2l+1$ orientations of the magnetic moment. We can denote this change in energy to be:

$$\Delta E = -\mu \cdot \mathbf{B} = (\frac{e}{2m_e})\mathbf{L} \cdot \mathbf{B}$$

$$\Delta E = m\mu_B B$$

$$(17)$$

II.IV Spin Magnetic Moments

$$\vec{\mu}_{orb} = -\frac{e}{2m_e}\mathbf{L}$$

- Similarly, the spin magnetic moment is proportional to the spin angular momentum $\mathbf{S}$:

$$\vec{\mu}_{spin} \propto \mathbf{S} = -\gamma\mathbf{S}$$

where γ is the spin gyromagnetic ratio.

- The total magnetic moment of any electron is just the sum of its orbital and spin moments:
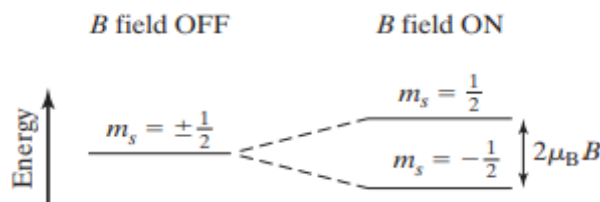
$$\vec{\mu}_{tot} = \vec{\mu}_{orb} + \vec{\mu}_{spin} = -\frac{e}{2m_e}(\mathbf{L} + 2\mathbf{S})$$

II.V The Anomalous Zeeman Effect

- The difference between the anomalous and the normal Zeeman effect is that the spin will contribute to the splitting of the magnetic moment.

- We can now denote the change in energy as:

$$\Delta E = -\vec{\mu} \cdot \mathbf{B} = \frac{e}{m_e}S_z B = \pm\mu_B B$$

meaning the separation of levels is $2\mu_B B$.

III Multielectron Atoms

III.I The Independent-Particle Approximation

- The force on the electron in a multielectron atom is the sum of the force of nucleus and the repulsion by the other electrons.

- We want to treat each electron individually, so we call its potential energy $U(\vec{r})$. This is the Independent-Particle Approximation, or the IPA potential energy function.

- We can use this to solve wavefunctions of multielectron atoms (find a set of wavefunctions).

- **Gauss's Law:** if the electron is outside spherical charge Q, the electron experiences the same electric force, F_e, if the entire charge Q were a point charge at r = 0:

$$F = k\frac{Qe}{r^2}$$

- If the electron is inside the spherical charge, it experiences **no force** from the shell.

- If the electron is close enough to the nucleus, it will experience the force of the nuclear charge, Ze, where Z is the number of protons. As the electron moves away from the nucleus $(r \to \infty)$, it will move past the $Z - 1$ electrons, reducing the electric force of the nucleus by $(Z - 1)e$:
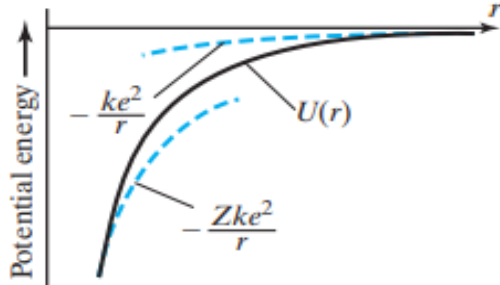
Figure 4: As $r \to 0$, the electron will experience nearly the entire force of the nucleus.

$$F_{out} = \frac{[Z - (Z - 1)]ke^2}{r^2} = \frac{ke^2}{r^2}$$

$$U(\vec{r}) = \int F_{out}dr = -\frac{ke^2}{r}(r \to \infty) \quad (18)$$

$$U(\vec{r}) = \int F_{in}dr = -\frac{Zke^2}{r}(r \to 0)$$

- The general case can be expressed as $Z \approx Z_{eff}$, where it is the effective charge felt by the electron with the same properties as the force experienced by the electron.

$$Z_{eff} \approx Z \quad (r \to 0), Z_{eff} \approx 1 \quad (r \to \infty)$$

III.II   The IPA Energy Levels

- Potential $U(\vec{r})$ is sufficiently like the potential energy of the hydrogen atom. The two angular equations are the same as the hydrogen atom, meaning they have the same m and l quantum numbers: $(2l + 1)$ orientations of $m = -l, ..., l$.

- As seen previously, $U(\vec{r})$ is not affected by spin, meaning each energy level has a degeneracy of at least $2(2l + 1)$.
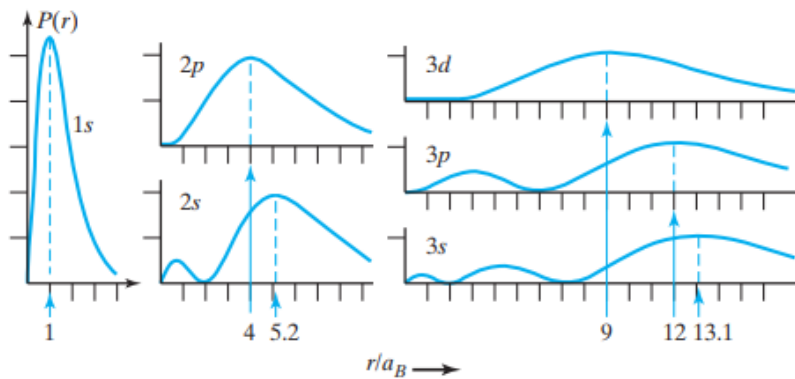
Figure 5: Radial probability distributions for hydrogen.

- For the 1s state (ground state), the wavefunction is very closely concentrated to the nucleus (probability density is very favored to $r = 0$), so we can use $Z_{eff} \approx Z$.

$$E_{1s} \approx -Z^2 E_R$$

- Now for the 2s and 2p states, in a hydrogen item, their states are degenerate, whereas in a multielectron atoms, the 2s states **are lower in energy**. This is because the 2s and 2p wavefunctions are concentrated in a region where the nuclear charge is screened by electrons in the 1s state. Thus, $Z_{eff} << Z$.

  - Note that in Figure 5 in the 1s distribution, the electron is most likely found at $\frac{r}{a_B}$ (highest density).

    - 2s and 2p states peak at $\frac{4r}{a_B}$ and $\frac{5.2r}{a_B}$, so they are being screened by the 1s electrons at $r = \frac{r}{a_B}$.

- However, the 2s state has a secondary peak at $r << \frac{5.2r}{a_B} \approx 0$, meaning a small density of the 2s electrons have $Z_{eff} \approx Z$. Since on average the 2s electron is more greatly affected by the nuclear force than the 2p electron, it will have lower energy *(lower energy to break attractive nuclear force)*.

- In general, for principal quantum number n, **states with smaller l penetrate closer to the nucleus on average and are lower in energy.**
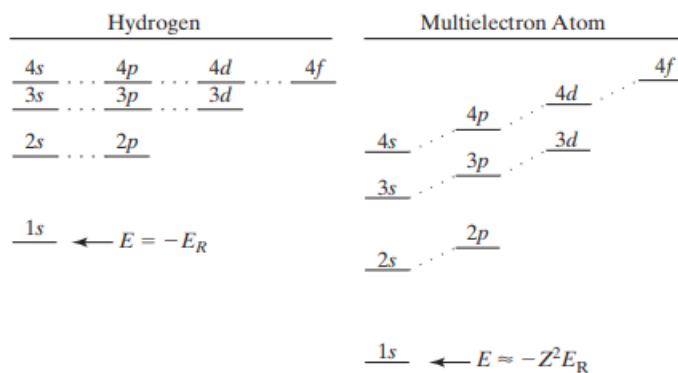

Figure 6: Hydrogen energy levels versus multielectron energy levels.

- The most probable radius (of finding an electron) can be approximated as:

$$r_{mp} \approx \frac{n^2 a_B}{Z_{\text{eff}}}$$

III.III The Pauli Exclusion Principle

- The ground state of the atom is not necessarily found by placing all Z electrons in the 1s state.

- **Pauli Exclusion Principle:** no two electrons in a quantum system can occupy the same quantum state. The easiest example of this is electron configuration of helium.
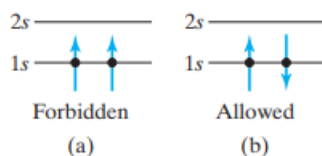
Figure 7: The two electrons cannot both have quantum numbers $m_s = \frac{1}{2}$. In the right figure, the magnetic moment, μ, is always 0.

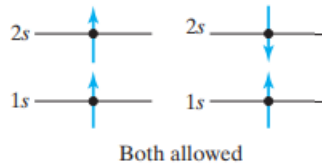- Instead, the electrons can be arranged in a fashion where they are placed in the 2s shell.

Figure 8: No spin orientation restriction for this case.

III.IV   Fermions and Bosons

- To begin, we distinguish **fermions** and **bosons** by their obedience to the Pauli Exclusion Principle: fermions follow the PEP, while bosons do not.

- Now, we can establish that two particles are identical if they have the same intrinsic properties, such as mass, charge, and spin.

- In quantum mechanics (what we are concerned about), two identical particles are indistinguishable. We can now state that for two spinless particles:

$$\left|\psi(x_1, x_2)\right|^2 dx_1 dx_2 = \begin{cases} \text{probability of finding two particles} \\ \text{between } x_{1,2} \text{ and } x_{1,2} + dx_{1,2}, \text{ respectively.} \end{cases}$$

- However, if they have spin:

$$\left|\psi(x_1, m_1, x_2, m_2)\right|^2 dx_1 dx_2 = \begin{cases} \text{probability of finding a particle between} \\ x_1 \text{ and } x_1 + dx_1 \text{with } S_z = m_1 \hbar \text{ and another} \\ \text{between } x_2 \text{ and } x_2 + dx_2 \text{ with } S_z = m_2 \hbar. \end{cases}$$

- To determine the property of the particle (fermion or boson), we use this property:

  - ◼ $\psi(2,1) = +\psi(1,2) \longrightarrow$ wavefunctions satisfying this property are **bosons**, which are symmetric, such as a photon (s = 1) or pion (s = 0).

  - ◼ $\psi(2,1) = -\psi(1,2) \longrightarrow$ wavefunctions satisfying this antisymmetric property are **fermions**, such as an electron, proton, or neutron.

- Two identical bosons can occupy the same one-particle state.

- Let's consider a two-particle wave functions with two non-identcal particles, such as one proton, one electron.

$$\psi(1,2) = \phi(1)\chi(2)$$

  where ϕ is the state of the proton and χ is the state of the electron.

- Now consider two identical fermions with combined wavefunction:

$$\psi(1,2) = \phi(1)\chi(2) - \phi(2)\chi(1)$$

  - ◼ This equation satisfies $\psi(2,1) = -\psi(1,2)$; also note that if $\phi = \chi$, then $\psi = 0$, meaning there are **no wavefunctions where** ϕ and χ can occupy the same state. This is the whole basis of the Pauli's Exclusion Principle.

- Now consider two identical bosons with combined wavefunction:

$$\psi(1,2) = \phi(1)\chi(2) + \phi(2)\chi(1)$$

  - ◼ This equation satisfies $\psi(2,1) = +\psi(1,2)$; also note that if $\phi = \chi$, then $\psi \neq 0$, meaning two particles can occupy the same state, which violates Pauli's Exclusion Principle.

III.V   Ground States of the First Few Elements

- The ground state of the hydrogen electron (1s state) is $E = -E_R = -13.6eV$.

  - ■ The **ionization energy** is the energy required to remove electron — $13.6eV$.

- The energy of electron in the 1s state of helium is $E = -Z_{\text{eff}}^2 E_R$.

  - ■ The first ionization energy of helium is $24.6eV$, where $Z_{\text{eff}} \approx \sqrt{2}$.

  - ■ $E_{\text{ion}} \propto Z_{\text{eff}}^2$.

- The **first excitation energy** is the energy needed to lift an electron to its first excited state $(n = 1 \rightarrow 2)$.

  - ■ $E_{\text{excite}} \approx Z_{\text{eff}}^2 \rightarrow$ for helium $(Z = 2)$, $E_{\text{excite}} = 19.8eV$, whereas for hydrogen $(Z = 1)$, $E_{\text{excite}} = 10.2eV$.

- Higher ionization and excitation energy indicates a high atomic stability and low chemical activity. Helium has the highest ionization and excitation energy of any atom.

- In terms of size, the radius of helium is about $\frac{1}{Z_{\text{eff}}}$ times that of hydrogen.

- For lithium $(Z = 3)$, $Z_{\text{eff}} \approx 1$, which is the same as the electron in the 1s state of hydrogen. As such, its ionization energy is:

$$E_{\text{ion}} \approx E_{2s,H} = \frac{E_R}{n^2} \approx 3.4eV$$

  Its true value is actually around $5.4eV$ but that is because Z_{eff} is not exactly 1.

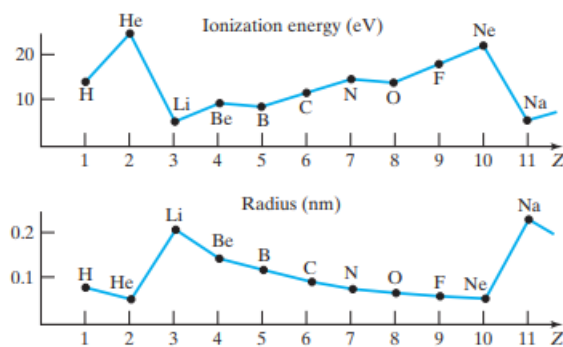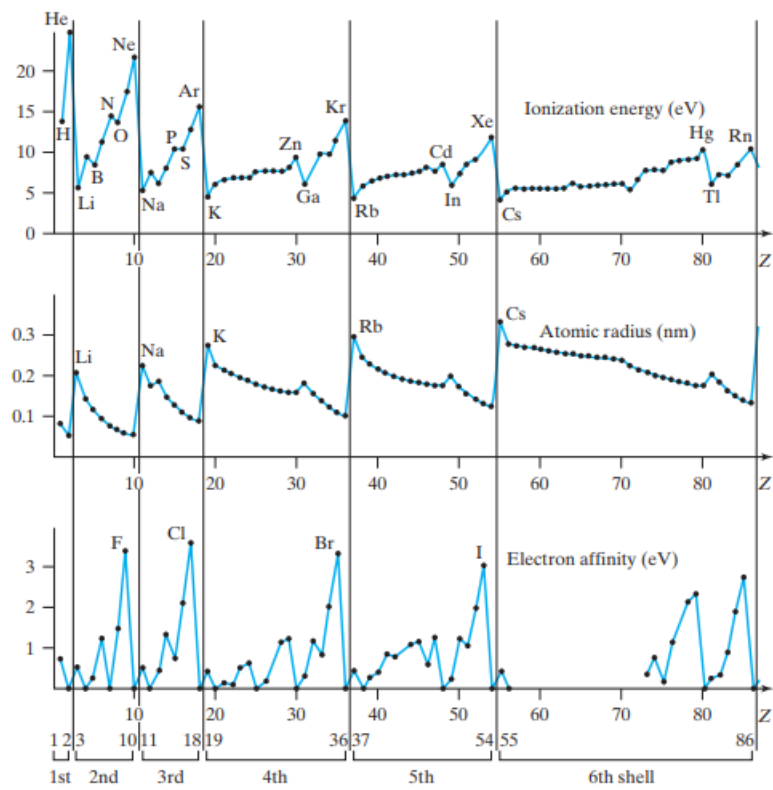- By increasing Z, the radius of the atom shrinks, thereby **increasing ionization energy**.

Figure 9: This trend shows that $E_{\text{ion}} \propto \frac{1}{r}$.

- **Electron affinity** is the tendency of an atom to bind an extra electron and can be measured by the energy released when an atom captures an electron.

III.VI   The Remaining Elements

- The total spin ($\sum \mathbf{S}$) and orbital momentum ($\sum \mathbf{L}$) of a **filled valence shell** is always zero.

IV   Molecules

IV.I   Molecular Properties

- Ordinary matter is electrically neutral: increasing electrostatic interaction increases strength in solids.

Noble Gases:

- These are Column 18 elements, where the full valence shell is filled.

- They have **no stable molecules** because of its reluctance to mingle; the electron affinity is approximately 0. As such, the electron distribution cannot easily be changed because excited states are very high in energy.

- When a noble atom is close to another noble atom, there is no force between the two because they are spherically symmetric. As such, no external electric field will be produced and no net force will be experienced when placed in an applied field.

Ionic Bonding:

- The strongest electrostatic attraction is between two oppositely charged stable spheres, this being lithium and fluorine.

- Since the ions are both spherically symmetric, they can be treated like point charges, forming an **electric dipole**. The **dipole moment** of equal but opposite charges is defined to be:

$$p = qd$$

Covalent Bonding:

- Some diatomic molecules have dipole moments much smaller than ionic bonds. In this case, their valence electrons are shared.
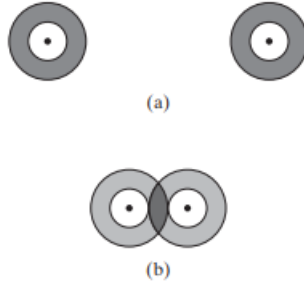

(a)

(b)

Figure 10: The shaded region is where the wavefunctions between the two atoms interfere constructively. There is a concentration of charge in the region between the two nuclei.

Estimating Bond Strength:

- For an ionic molecule, we can make the assumption that the electron is fully transferred from one molecule to the next, and the potential energy between the two ions at separation R is:
$$U(r) = -\frac{ke^2}{R}$$

- Since we know that potential energy is the majority of the molecule's total energy, we can estimate that $E \approx U(r)$, meaning the binding energy $B = -E \approx -U$.

- This is similar for a covalent molecule by making similar assumptions regarding the distribution of charge in the molecule.
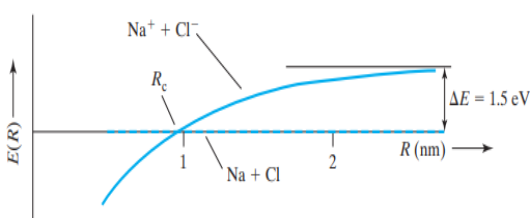
IV.II   The Ionic Bond

- An **ionic bond** is formed when one electron is transferred from one atom to another, producing a pair of oppositely charged ions with strong attraction between them.

  - ∎ This occurs when the first atom has a low E_{ion} and the other atom has a high electron affinity.

Example: NaCl

- If we were to determine the energy needed to transfer an electron from the Na to the Cl if the atoms were far apart, it would cost energy. This is to say $E(R) = \Delta E$

- However as they come closer, potential energy comes into play. This is to say $E(R) \neq \Delta E$.

Figure 11: As $R \to \infty$, $E(R) = \Delta E$. However beyond R_c, the critical radius, the energy will be less than $E(R)$ due to the potential energy.

$$E(R) = \Delta E = E_{ion}(Na) - EA(Cl) = 1.5eV$$

$$E(R) = \Delta E - U(R) = \Delta E - \frac{ke^2}{R}$$

$$(R > R_c): \quad E_{[Na^{+}+Cl^{-}]} > E_{[Na+Cl]}$$

$$(19)$$

- As seen above, once $R < R_c$, the ions have less energy than the neutral atoms since the potential energy, $U(R)$ offsets the costs ΔE of transferring the electron.

- Interestingly, the energy does not continue to decrease as $R \to 0$ since once the ions overlap, they begin to **repel each other**, causing the energy to rise once more.
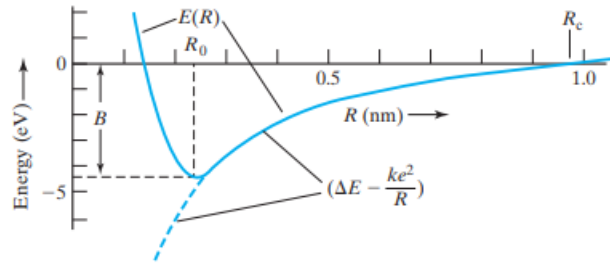

Figure 12: At $R < R_0$, repulsive forces dominate and $E(R)$ rises quickly. $E(R_0) = -B$, the binding energy (minimum).

- We can safely predict the values of R_0 (center-to-center distance of the two atoms in the lowest state of the stable molecule) and B:

$$B = -E(R_0) \approx \frac{ke^2}{R_0} - \Delta E$$

IV.III   The Covalent Bond

- A **covalent bond** involves the concentration of one or more electrons from each atom in the region between the two nuclei; sharing of electrons.

IV.III.1 H_2^+ Molecular Ion

- In H_2^+, the single present electron moves in the field of the two protons, but we can treat the protons as stationary since $m_{p^+} >> m_{e^-}$.

- Solving Schrödinger's Equation, we can obtain its lowest allowed energy E, which is, as established previously, dependent on R. Similar to ionic bonds, if $E(R)$ has a minimum at some separation R_0, a stable molecule will exist with bond length R_0 and energy $E(R_0)$.

- We can use the following diagram to denote the electron's position relative to the two protons, denoted $\vec{r}$. This is used to find the wavefunction of the electron that gives us minimum energy with separation R.

$$\psi_1(\vec{r}) = Ae^{-r_1/a_B} \text{ (e- close to p1)}$$
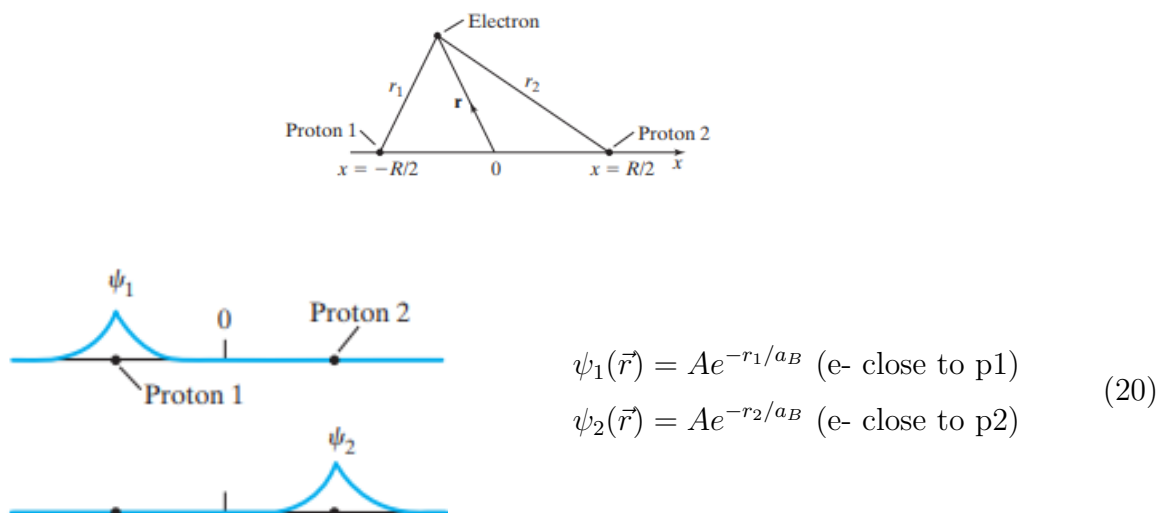$$\psi_2(\vec{r}) = Ae^{-r_2/a_B} \text{ (e- close to p2)}$$

(20)

Figure 13: We are assuming that the protons are far apart, or $R >> a_B$.

- Now since we know that the equations above solve for the wavefunction yielding the same energy, any linear combination (ψ, generalized) will also be degenerate:

$$\psi = B\psi_1 + C\psi_2$$

- We have to consider 2 states (symmetric and antisymmetric) of the wavefunction since they are both valid solutions to Schrödinger's Equation:
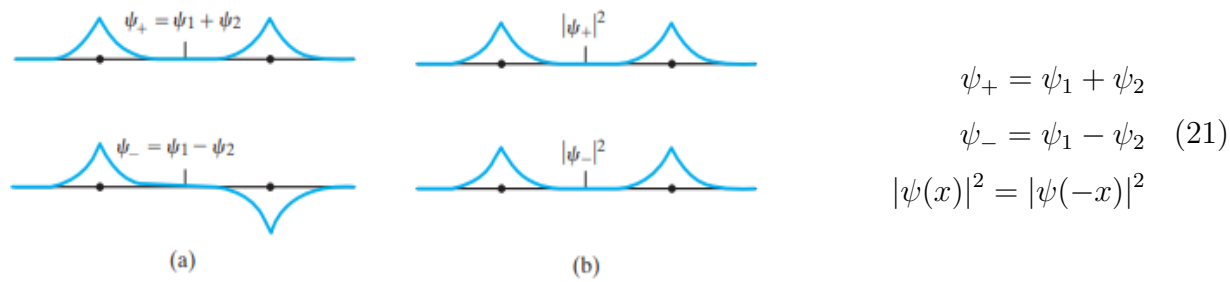

$$\psi_+ = \psi_1 + \psi_2$$
$$\psi_- = \psi_1 - \psi_2 \quad (21)$$
$$|\psi(x)|^2 = |\psi(-x)|^2$$

Figure 14: The right-hand plot shows how the probability density of the electron, $|\psi_\pm|^2$, is identical regardless of the state.

- The individual wavefunctions are known as **atomic orbitals**, while the combinations of ψ_+ and ψ_- are called **molecular orbitals** — describe states where the electron is associate with both nuclei.

- When the two protons approach each other, the two wavefunctions will overlap, causing the electron to be influenced by both protons simultaneously. However, $\psi_\pm = \psi_1 \pm \psi_2$ still holds under reasonable assumptions due to symmetry properties.
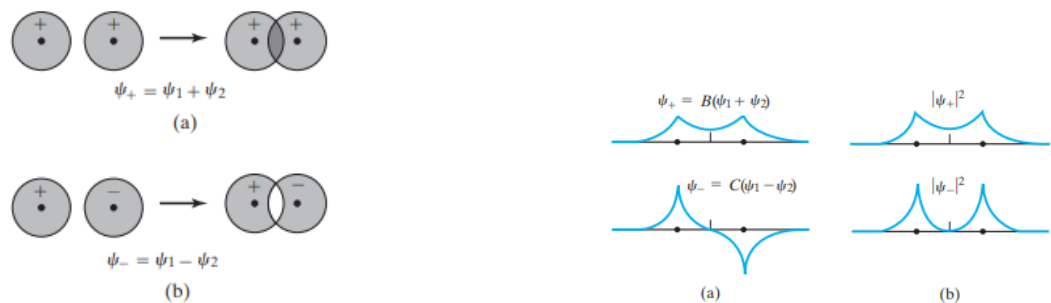
(a) Symmetric state results in **constructive interference** and increased electron density between the nuclei. Antisymmetric state results in **destructive interference** and decreased electron density.

(b) This figure explains the effect of Figure 26a, showing that the density of electrons at the origin (maximum overlap) is zero for an antisymmetric state (bottom), whereas it is enhanced in the symmetric state (top).

- Using all of the information from Figures 26a and 26b, we can determine the trend of the energy given a symmetric or antisymmetric state.

  - For the symmetric state, known now as the **bonding orbital** (ψ_+), the energy decreases as the protons get closer until it reaches a minimum at $R = R_0$. Once $R < R_0$, the dominant force is the repulsive force of the two protons.

  - For the antisymmetric state, known now as the **antibonding orbital** (ψ_-), the energy increases steadily as R decreases and has no minimum, meaning that there is no stable bound state for this state.
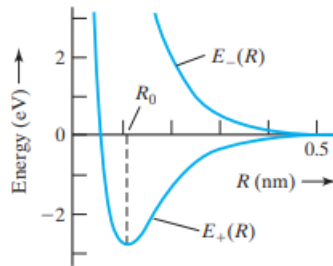
Figure 16: The curve E_+ represents the bonding orbital while the curve E_- represents the anti-bonding orbital.

IV.III.2   Covalent Bonding of Multielectron Atoms

- The formation of molecules is pretty simple; only the valence electrons will overlap enough to have an important role in the molecular bond. Now all we have to recall is that the $2p$ orbital has 3 independent wavefunctions.

  ■ **Example (Fluorine):** Fluorine has 5 valence electrons with electron configuration:

  $$F : 1s^2 2s^2 2p^5$$

  · This can be rewritten, taking into account the orientations of the orbitals:

  $$F : 1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$$

  · It does not matter which orbital is filled ($2p_x$, $2p_y$, or $2p_z$), the point is the two that are filled will have antiparallel spins and cannot participate in a covalent bond. This leaves only 1 electron available to form a covalent bond.

IV.IV   Constructing Molecular Bonds

- For the molecular orbital energy level diagram, it is directly related to the bonding and antibonding orbitals.

- For the 1s level ($\mathbf{n = 1}$), the antibonding orbitals ($\sigma(1s)^*$) are placed on top, while the bonding orbitals ($\sigma(1s)$) are placed on the bottom.
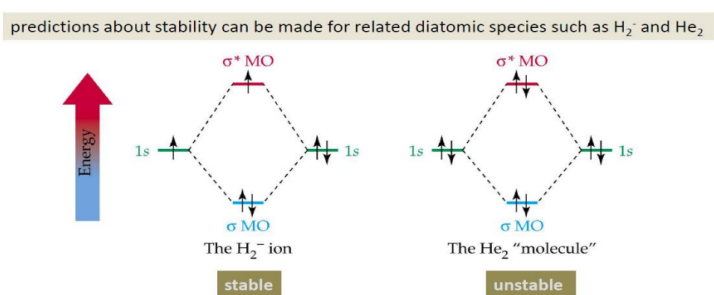
$$BO = \frac{\# \text{ of BO} - \# \text{ of AO}}{2}$$

$$(22)$$

- For ($\mathbf{n = 2}$), the LCAO-MO (linear combination of atomic orbital-molecular orbital) overlap to forms to MO's. σ bonds are formed by the overlap between $2s$ and $2p_z$ atomic orbitals, while π bonds are formed by the overlap of two $2p$ bonds.

- For **homonuclear atoms** (such as N_2), contribution from both atoms are same. For **heteronuclear atoms** (such as NO), more contribution from one atomic orbital than another: more ionic and less covalent. **More electronegative means less energy**.
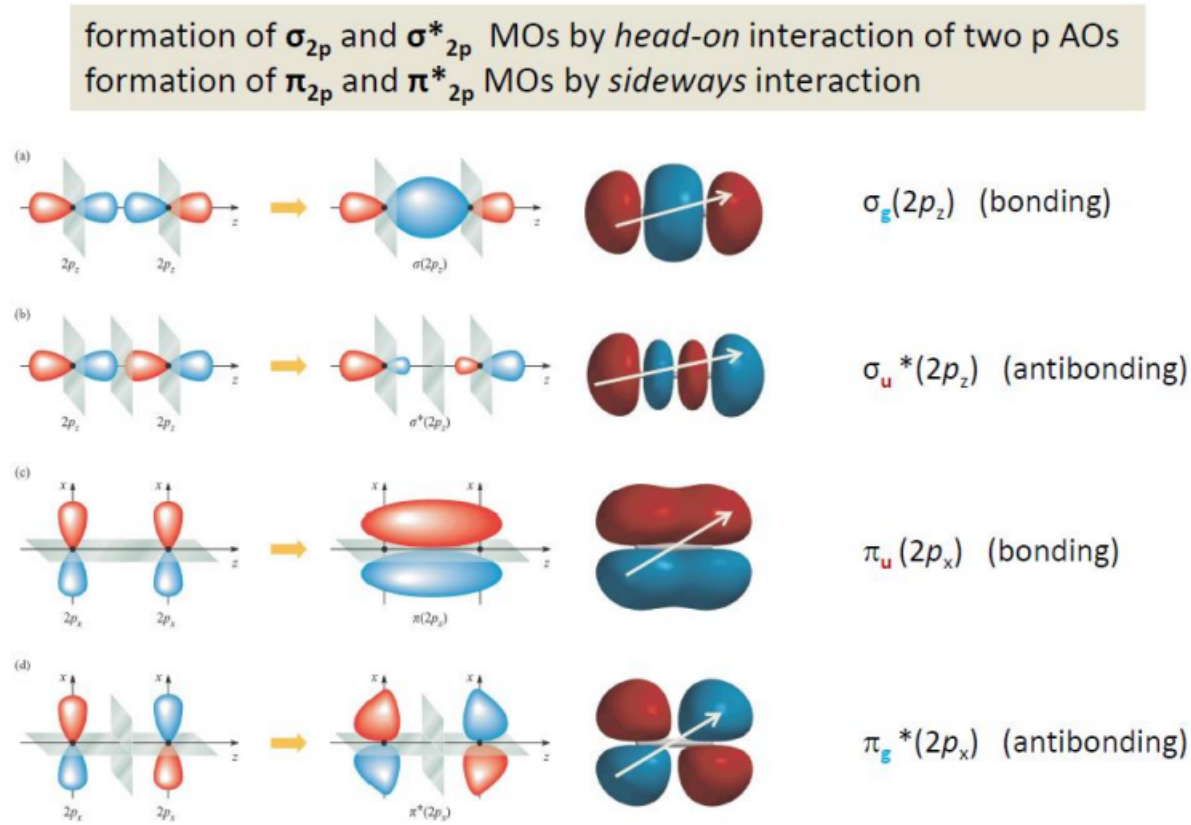
Figure 17: Only same orientation $2p$ orbitals will affect the electron density at the overlap. Orthogonal p orbitals cannot mix to increase electron density, such as $p_x + p_y$.
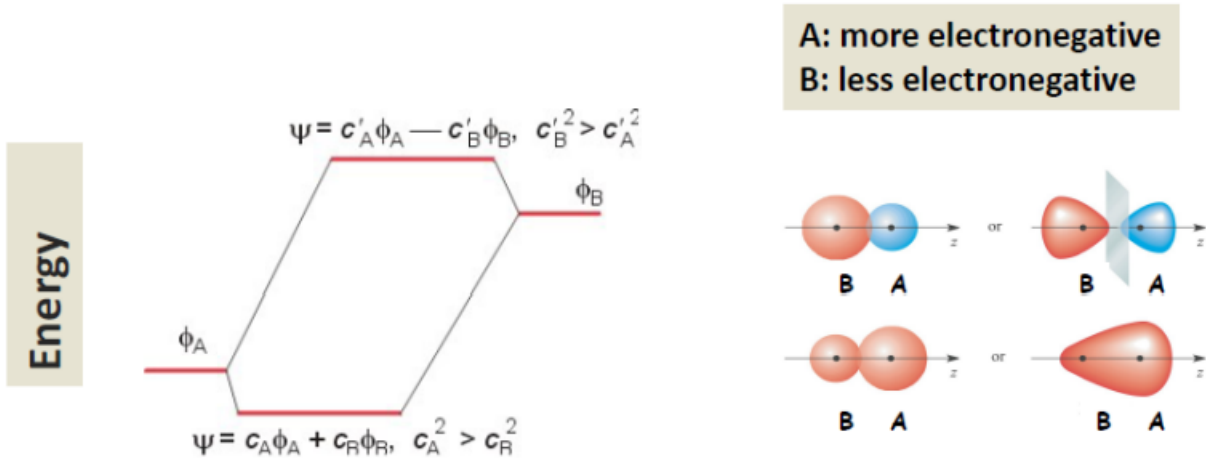
Figure 18: The lower energy atom in bonding pair will contribute the most amplitude in electron probability distribution.

IV.IV.1   Example: NO

- For nitric oxide, the ground state configuration can be simplified to:

$$NO : \sigma(2s)^2 \sigma^*(2s) 2\pi(2p_x, p_y)^4 \sigma(p_z)^2 2\pi(2p_x, p_y)^{*1}$$
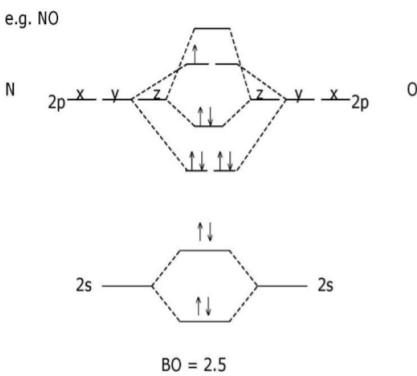
IV.V   VESPR

- This is a theory used to predict the geometry of individual molecules from the number of electron pairs surrounding the central atoms.


IV.V.1   sp³ Hybridization

- Formation of sp^3 hybrid orbitals by combination of an s orbital and three p orbitals, creating a formation of four lobes with an angle of **109.5°**.

- Either 4 bonds (CH_4), 3 bonds + 1 lone pair (NH_3) or 2 bonds + 2 lone pairs (H_2O).
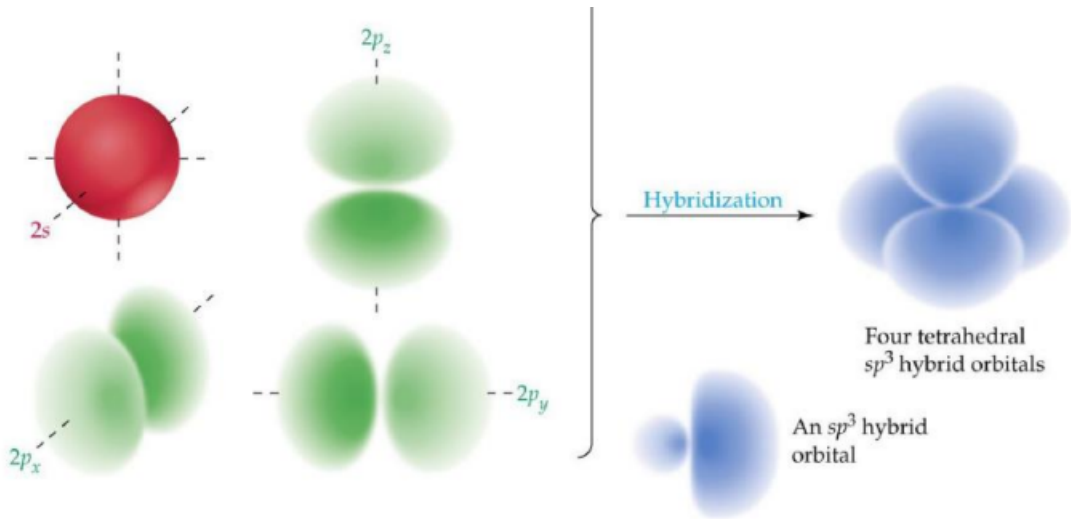
- Filling out electron configuration in sp^3 hybrid is different than normal:
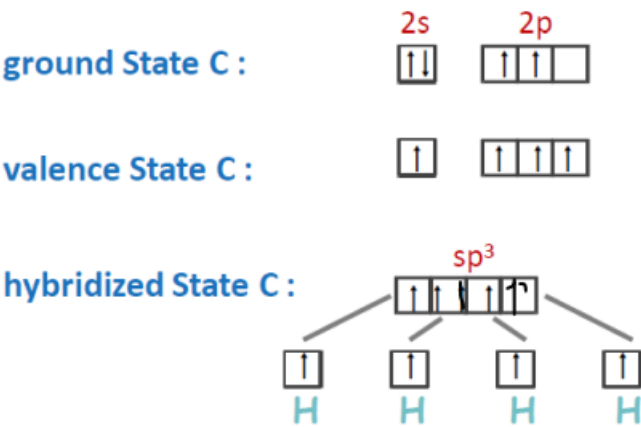
Figure 19: CH_4

IV.V.2   sp² Hybridization

- Combination of one s orbital and 2 p orbitals, results in 3 sp^2 orbitals with bond angle of **120°**.

- sp^2 bonds can form both σ and π bonds depending on the linear combination with the unhybridized p orbital.
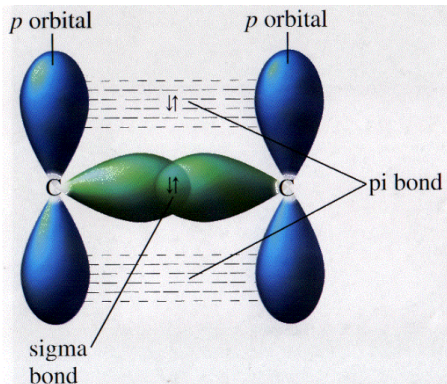
(a) Sideways overlap forms a π bond, head-on overlap forms σ bond.
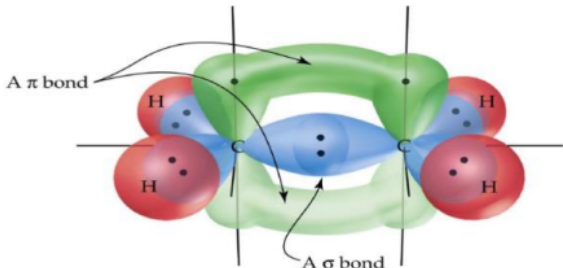
(b) Example of ethylene ($H_2C = CH_2$) with a combination of σ and π bonds.

IV.V.3   sp Hybridization

- Combination of one s and one p orbital gives two sp hybrid orbitals with bond angle of **180°**. The two unhybridized orbitals remain and are oriented at 90° angles to the hybrids.

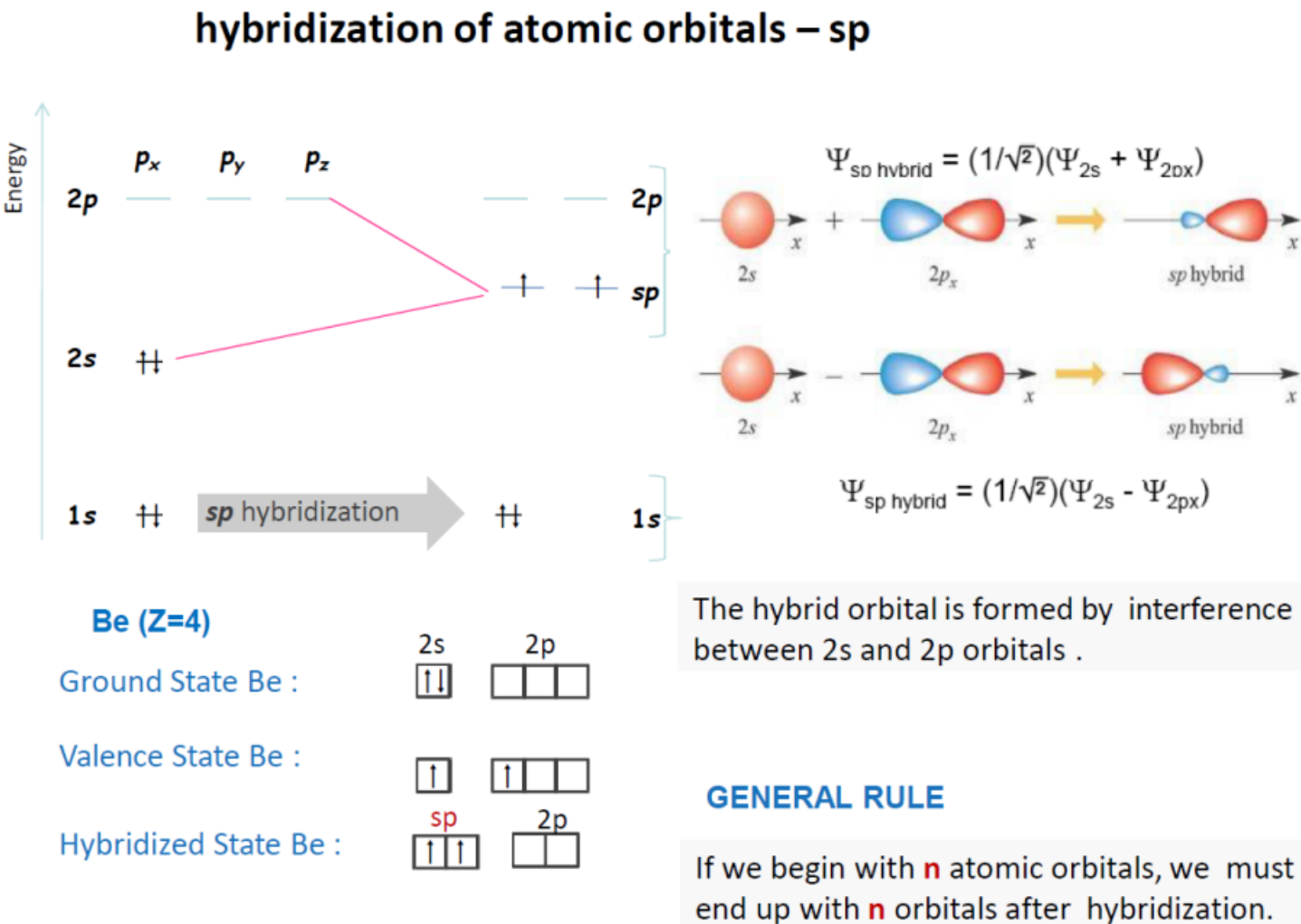- This hybridization results in minimum electron repulsion.

Figure 21: Can make 2 π bonds from the unhybridized orbitals.

V Intermolecular Forces

- [5]Quantum mechanics effects everything. Even rotational motions of molecules show quantization effects due to underlying wave properties and continuous force relationships. However, rotational motion travels at the lowest frequency and so the energy levels become so closely spaced that we can treat them classically, known as the **Correspondence Principle**.

- Any variable affecting the energy of the system can be extrapolated to the classical limit, $\Delta E << kT$.

Table 12.2 Comparison of Bonding and Nonbonding (Intermolecular) Forces

Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Bonding				
Ionic		Cation−anion	400−4000	NaCl
Covalent		Nuclei−shared e^- pair	150−1100	H—H
Metallic		Cations−delocalized electrons	75−1000	Fe
Nonbonding (Intermolecular)				
Ion-dipole		Ion charge−dipole charge	40−600	Na$^+$·····O
H bond	—A—H·······:B—	Polar bond to H−dipole charge (high EN of N, O, F)	10−40	:Ö—H····:Ö—H
Dipole-dipole		Dipole charges	5−25	I—Cl····I—Cl
Ion−induced dipole		Ion charge−polarizable e$^-$ cloud	3−15	Fe^{2+}·····O$_2$
Dipole−induced dipole		Dipole charge−polarizable e$^-$ cloud	2−10	H—Cl···Cl—Cl
Dispersion (London)		Polarizable e$^-$ clouds	0.05−40	F—F····F—F

Figure 22: Intra. (bonding) versus Inter. (non-bonding) forces. Bonding forces are typically long range and require more energy, while nonbonding are short range less energy.

- For intermolecular forces, the potential energy curves all look very similar, all similar to Figure 12. Nothing breaks in compression, not even molecules. Shear force is the main contributor. As we already know, force is **always** the gradient of the operating potential.

$$F = -\nabla U(r)$$

V.I Metallic Bonding

- **Metallic bonds** describe covalent bonding with different degrees of ionic character, typically involving $n > 3$ periods.

V.II Ion-Dipole Interaction

- This force involves a fully unscreened ion (anion or cation with specific charges $\pm 1, \pm 2, \pm 3$ etc. possible depending on ion) coupled through Coulombic interaction to a polar molecule with a permanent dipole moment.

[5]RJDM Chapter 4.1, pg.93

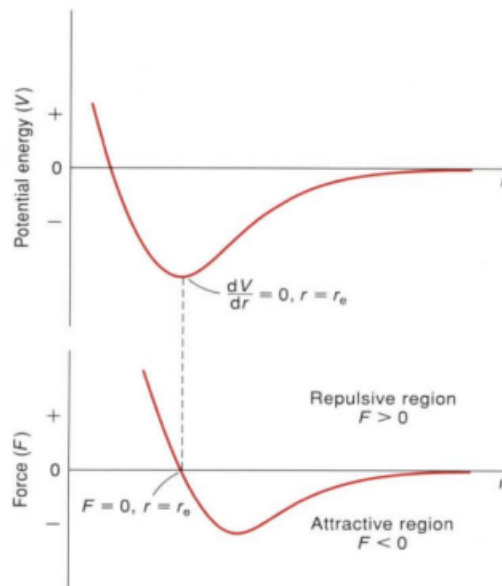Figure 23: The repulsive potential is due to n-n and e-e repulsion overcoming the attractive potential, scaling with a factor of $\frac{1}{r^n}, n \in [9, 12]$.

- This interaction requires a large difference in electronegativities between bonded atoms.

- The potential of this intermolecular force is on the order of $U(r) \propto \frac{1}{r^6}$.

V.III Hydrogen Bonding

- This force arises only when hydrogen is bonded with oxygen, fluorine, or nitrogen. Its specificity is the reason for the directional natures of biological molecules.

- This potential also scales on the order of $U(r) \propto \frac{1}{r^6}$.

V.IV Dipole-Dipole Interaction

- This force occurs between two polar molecules, where the molecules will arrange itself such that the positive end of a polar molecule will be attracted to the negative end of a molecule. This will lead to solid state structures, often repeating to create the crystal lattice structure.

V.V Ion-Induced Dipole Interaction

- This force occurs when an ion approaches a molecule/atom with uniform charge distribution, causing the electrons within the molecule/atom to be either attracted to or repelled by depending on the charge of the ion. This induces a dipole in the atom.

- The potential energy of this force scales on the order of $U(r) = \frac{1}{r^4}$.

V.VI Dipole-Induced Dipole Interaction

- Same idea as ion-induced dipole, but with a dipole in place of an ion. It will polarize the adjacent atom, depending on its orientation.

V.VII Van der Waals Force

- The weakest, shortest force and it occurs between molecules with uniform charge distributions.

- At a standstill snapshot, the electrons will arrange themselves such that they are not evenly distributed throughout the molecule despite it being electrically neutral. So when two molecules get close to each other, dipoles will temporarily be induced between the molecules.

V.VIII   The Hydrogen Bond

- Hydrogen bonds arise due to the induction of electron density and the creation of a δ^+ charge on the hydrogen atom. The hydrogen atom will lose a "tug-of-war" battle for electrons to more electronegative atoms (N, O, F).

- Hydrogen bonding explains the high boiling/melting point in water compared to other liquid substances. Hydrogen bonds require more energy to overcome in comparison other intermolecular forces.

VI   Spectroscopy

VI.I   Photon and the Quantization of Light

- The energy of the photon $(E = h\nu)$ absorbed or emitted must match the change in internal energy of the molecules or material involved. Since we have exact solutions to the hydrogen atom, we can use it to draw conclusions on the interaction of light with matter.

- Both absorption and emission indicate the energy difference between two quantized energy levels:

$$\Delta E = E_m - E_n = h\nu$$
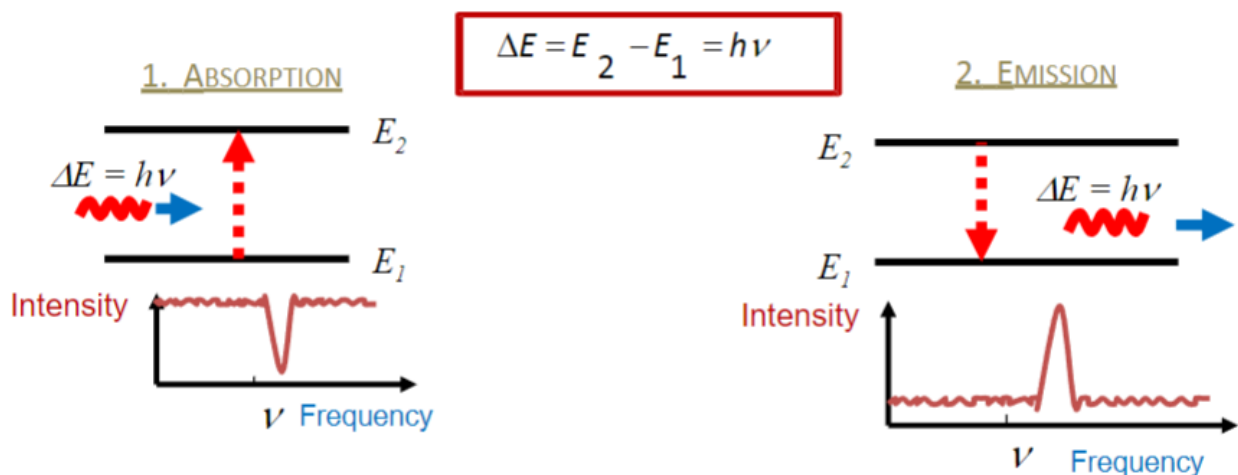
- Light is the propagation of an electromagnetic field. It is the electric field component to light that can interact with the electrons and change their distribution.

- It is possible to promote an electron in an atom or molecule to a higher energy level by sending light to it, if the energy from the light is sufficient.

- Now recall the Hamiltonian operator. We have to make modifications to potential $U(r)$ because there is potential when an electric field interacts with a dipole:

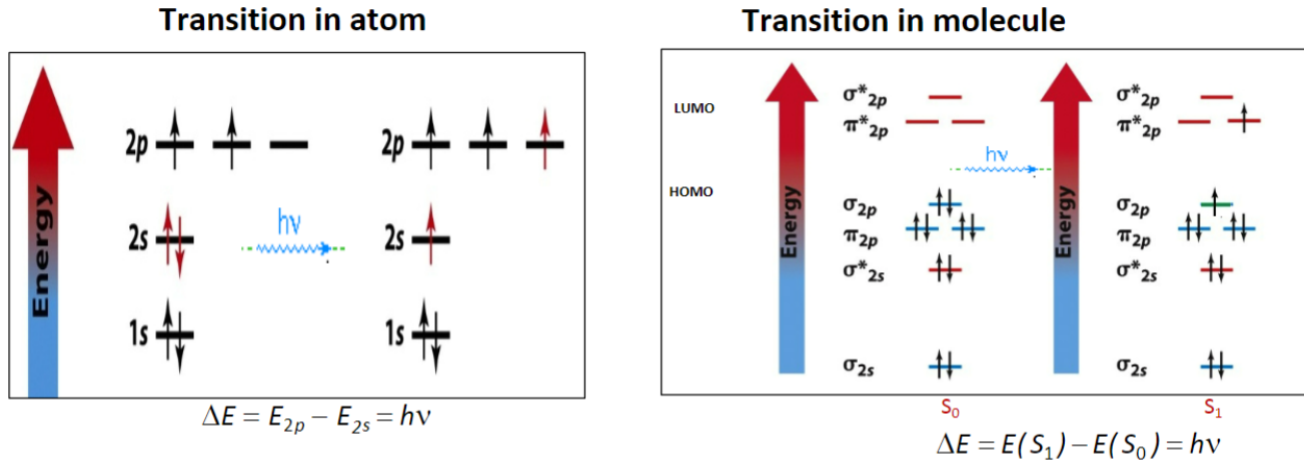$$U(r) = -\frac{ke^2}{r} + \mu \mathbf{E(t)}$$

Figure 24: Sending an electron from a bonding orbital to an antibonding orbital will weaken the chemical bond.

- The probability of transitioning energy states, defined by μ_{mn} meaning $\mathbb{P}(n \to m)$ is:

$$\mu_{mn} = \int_{-\infty}^{\infty} \psi_m \vec{\mu} \psi_n d\tau \tag{23}$$

  where τ is defined as all of space.

- All transitions must involve a change in symmetry, leading to the understanding that $\boldsymbol{\Delta l} = \pm 1$. This means an atom cannot transition from a 1s state to its 2s state, must transition from 1s to 2p otherwise it will not induce a dipole moment.

VI.I.1   Selection Rules for Transitions

1. **Spin selection rule:** changes in spin multiplicity are forbidden.

$$\Delta S = 0$$

   This means the allowed transitions are:

   - singlet (S = 0) $\to$ singlet
   - triplet (S = 1) $\to$ triplet

2. **Laporte selection rule:** there must be a change in symmetry.

3. **Angular momentum selection rule:** $\Delta l = \pm 1$

VI.I.2   Absorption and Emission (Beer-Lambert Law)

- Absorbance can be quantified if we know the incident light intensity, I_0 using the Beer-Lambert law:

$$A = -\log T = -\log(\frac{I}{I_0}) = \varepsilon bC \tag{24}$$

  where b is the thickness of the medium, T is the transmittance.

- As such, it can be noted that absorbance and transmittance have an inversely, logarithmic relationship:

$$A = -\log T \to T = 10^{-A} \tag{25}$$

VI.II   Quantum Mechanic Harmonic Oscillators

- A vibrating molecule behaves like 2 masses joined by a spring — a spring system. As such, we can use Hooke's law to find the potential of the system.
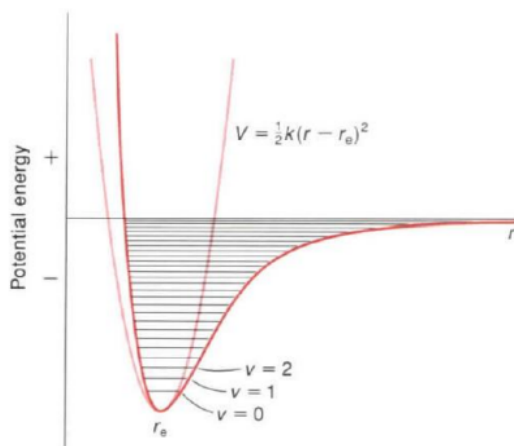
$$F = -kx$$

$$U = -\frac{dF}{dx} = \frac{1}{2}kx^2$$

- For two masses joined together by a spring, their effective mass μ vibrates with a frequency ν, defined as:

$$\mu = \frac{m_a m_b}{m_a + m_b}; \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

- The potential energy of a molecule behaving like a harmonic oscillator is

$$V = \frac{1}{2}k(r - r_e)^2$$
$$E_{vib} = (n + \frac{1}{2})h\nu, \quad n = 0, 1, ... \tag{26}$$

- In comparison to real molecular potential, it is missing a factor due to anharmonic character:

$$E_{vib} = (n + \frac{1}{2})h\nu - x(n + \frac{1}{2})^2 h\nu \tag{27}$$

with a selection rule of $n = \pm 1$

VI.II.1   Infrared Active Molecules (IR Active)

- The condition to be **IR Active** is if the electric dipole changes with bond length during a vibration.

$$\frac{d\mu}{dr} > 0$$

- This means if a molecule is symmetric, such as a diatomic molecule (N_2), it can only vibrate in one mode, meaning it is not IR Active.

VI.III   Franck-Condon Principle

- The Franck-Condon principle states that in a molecule, an electronic transition occurs much faster than nuclear motion. This means that during an electronic transition, the nuclei do not move significantly from their original positions. Therefore, the probability of a molecule undergoing an electronic transition depends on the overlap between the vibrational wavefunctions of the initial and final electronic states.

- When a molecule absorbs or emits a photon, it will undergo a transition. It is most likely to occur when the wavefunctions of the initial and final state maximally overlap.
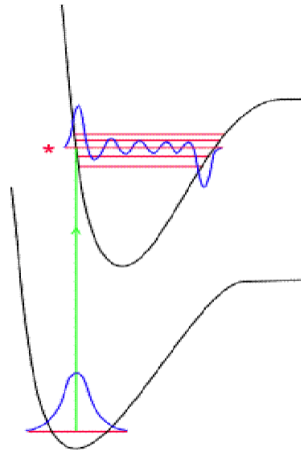
Figure 25: Vertical transition.

VI.III.1   Possible Transitions for Excited Molecules

- **Radiative Transition:** photon is absorbed or emitted (solid line).

- **Non-Radiative Transition:** energy is transferred between different degrees of freedom of a molecule or to the surroundings.

- **Intersystem Crossing:** transition between singlet and triplet state, which is otherwise forbidden.
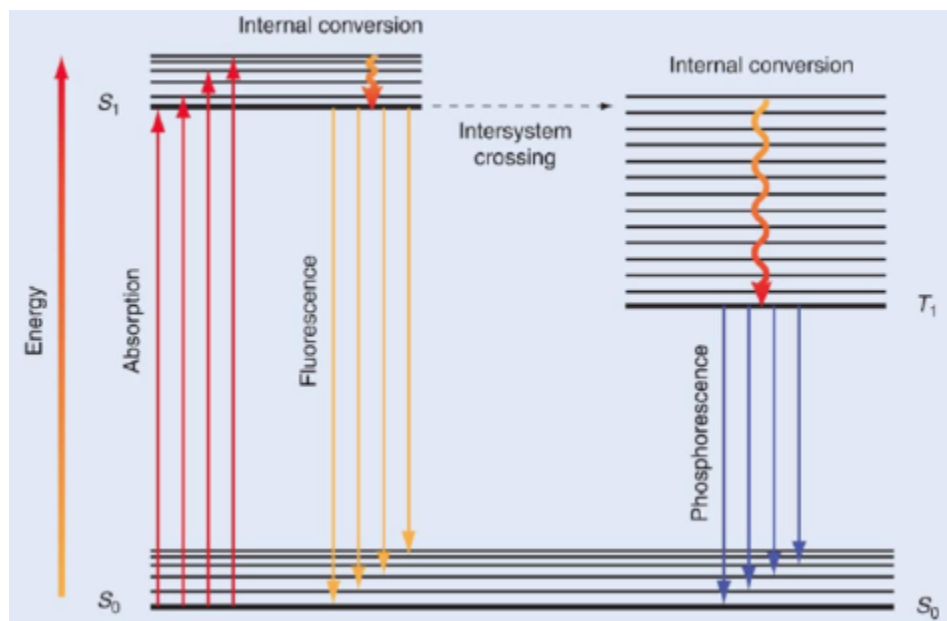
VII   Thermal Physics

- System implies thermodynamic system, which just means there is a lot of particles. To get an idea about general properties, we use the ideal gas, which has order of $\approx 10^{23}$ molecules.

- Thermodynamic equilibrium is achieved when pressure, temperature, and density are all **uniform** and **constant**.

- **Ideal Gas Law:**

$$pV = NkT \tag{28}$$

  - at a fixed V, if T increases, so does P and vice versa.

  - at a fixed T, if V increases, P decreases and vice versa.

- We also know that $pV = Nm\bar{v}^2$, when we consider particles bouncing inside a box, where $\bar{v}^2$ is the square of the average velocity. We also concluded that the square of the average is equivalent to the average of the squared directional velocities ($\bar{v}^2 = \overline{v_{x,y,z}^2}$), meaning:

$$kT = m\bar{v}_x^2 = \frac{1}{3}m\bar{v}^2 = \frac{2}{3}\frac{m\bar{v}^2}{2}$$

- Thus in thermodynamic equilibrium, the average kinetic energy per particle in an ideal gas is $\frac{3}{2}kT$, known as the **equipartition theorem**. This energy can be broken down into three contributors, or degrees of freedom:

  1. a translational DOF: $\frac{kT}{2}$

  2. a rotational DOF: $\frac{kT}{2}$

  3. a vibrational DOF: kT

- For a **linear**, n-atomic molecule, it has 3 translational, 2 rotational, and $3n - 5$ vibrational ($\sum DOF = 3n$) degrees of freedom.

- For a **non-linear**, n-atomic molecule, it has 3 translational, 2 rotational, and $3n - 6$ vibrational ($\sum DOF = 3n$) degrees of freedom.

- N n-atomic molecules (at T) has average energy U ($n \geq 3$):

$$U = N(\frac{3}{2}kT + \frac{3}{2}kT + (3n - 5/6)kT) \tag{29}$$

depending if the molecule is linear or non-linear.

VII..1 Moving a piston

- This example is to demonstrate the **First Law of Thermodynamics**, and doing work:

$$\Delta U = Q - W \tag{30}$$

where ΔU is the change in energy of the system and Q is the heat transferred to or from the system. If W is positive, it is work done by the system; if it is negative, it is work done on the system. It is also important to note that given a P-V diagram, the work done is its integral:

$$W = \int_{V_i}^{V_f} P dV \tag{31}$$

- If pressure is dependent on volume, we have a slightly different relationship:

$$W = -\int_{V_i}^{V_f} P(V)dV = -NkT \int_{V_i}^{V_f} \frac{dV}{V} = -NkT \log \frac{V_f}{V_i}$$

This is the work done on an ideal gas during **isothermal expansion/compression**.

- If the gas is ideal, its energy will not change during an isothermal compression.

- We also know at every instance, the energy is defined as:

$$U = \frac{f}{2}NkT$$

where $f = 3$ for a monatomic molecule, $f = 7$ for a diatomic molecule.

- **Heat capacity** is the measure of how much heat is needed to raise the T of an object by 1 K, defined colloquially as $C = \frac{Q}{\Delta T}$. However if V is fixed, we have:

$$c_V \equiv \left(\frac{Q}{\Delta T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{32}$$

VII.I   Main Postulate of Statistical Mechanics

In a closed (isolated: fixed-energy) system, all accessible microstates are **equally likely** in thermodynamic equilibrium.

- A **microstate** is one arrangement of the molecular position and kinetic energy of the system. Collisions change the microstate continuously, allowing the system to be in different microstates at different times.

For isolated systems: all microstates are equally likely, meaning:

$$\mathbb{P}(\text{microstate}) = \frac{1}{\Omega(N, U)} \tag{33}$$

VII.I.1   Physical Picture: The Paramagnet

- Picture in a crystal, every atom has a magnetic moment, $\vec{\mu}$, and this magnetic moment has a spin either up or down (like in quantum mechanics), $\vec{S} = \pm 1$.

- One atom's internal energy will be defined as $u = -\vec{\mu} \cdot \vec{B}$, which is minimized when the RHS is maximized, or when μ is parallel to B.

- The total energy of the system, $U = -\mu_0 B \sum_{i=0}^{N} S_i$ with N spins. One combination of the total energy is defined as the microstate of this system.

- If we define the total spin by the number of up-spins, N_{up}, as the macrostates, there are N macrostates:
$$S = 2N_{up} - N, \quad N_{up} = 0, 1, ..., N$$

The total number of microstates with N_{up} is defined as the number of ways to choose N_{up} from N, namely the **multiplicity function**, or the number of microstates accessible to macrostate $N_{up}(S)$:
$$\Omega(N_{up}, N) = \binom{N}{N_{up}} = \frac{N!}{N_{up}!(N - N_{up})!} \tag{34}$$

VII.I.2   Simple Harmonic Oscillator: The Einstein Solid

- An **Einstein solid** is a collection of N quantum SHO's. The microstate for this example is defined as n_i, which is the energy of one quantum SHO. The macrostate is defined as q, or the total energy of the system:
$$q = \sum_{i=0}^{N} n_i$$

- As defined in QM, the vibrational energy of a SHO is $E_{vib} \approx \hbar\omega n$, meaning the total energy of the system is $E_{tot} = \hbar\omega q$.

The multiplicity function of an Einstein solid can be pictured as finding the total combinations of placing q balls in N boxes.

$$\Omega(N, q) = \binom{N - 1 + q}{q} = \frac{(N - 1 + q)!}{(N - 1)!q!} \tag{35}$$

- This is helpful when considering combining two isolated systems together, with numbers ($N >> 1$) and energies, q_A and q_B, with $q = q_A + q_B$.

- Some equations for this:

$$\mathbb{P}(\text{any microstate of A+B}) = \frac{1}{\text{total no. of microstates of A+B with q}}$$

$$\mathbb{P}(q'_A) = \frac{\Omega_A(q'_A)\Omega_B(q - q'_A)}{\text{total no. of microstates of A+B with q}}$$

Microscopic definition of entropy:

$$S(E, N, V) = k \ln \Omega(E, N, V) \tag{36}$$

$$\frac{1}{T} = \left(\frac{\partial S(E, N, V)}{\partial E}\right)_{N,V} \tag{37}$$

- To find entropy of the Einstein solid, we must use Stirling's approximation for factorials:

$$\ln n!|_{n \to \infty} \approx \ln\left(\left(\frac{n}{e}\right)^n \sqrt{2\pi n}\right) = n(\ln n - 1) + \frac{1}{2}\ln(2\pi n)$$

- We can safely make the assumption that $N >> 1, q >> N$, which gives $\frac{q}{N} >> 1$. This assumption essentially means that on average there is large number of quanta per oscillator. After some calculation, we obtain that the multiplicity function simplifies to:

$$\Omega(N, q)|_{N>>1, q>>N} \approx \left(\frac{qe}{N}\right)^N$$

- Knowing that $S = k \ln \Omega$ and $E = \hbar \omega q$, we can manipulate these 3 equations to obtain the relationship:

$$kT \approx \frac{\hbar \omega q}{N} \longrightarrow kT >> \hbar \omega$$

- This is known as the high-T limit of the Einstein solid and equipartition only holds in this limit. This can be physically described as the internal energy of the system (kT) being much larger than the energy of a singular SHO ($\hbar\omega$).

VII.I.3   Returning to The Paramagnet

- Recall $U = -\mu_0 BS = -\mu_0 B(2N_{up} - N)$. How do we relate the total up-spin of the system with the entropy of the system? We note that $N_{up} = 0$ is U_{max}, $N_{up} = N$ is U_{min}, so we determine that for maximum multiplicity, $N_{up} = \frac{N}{2}$ (total spin = 0).
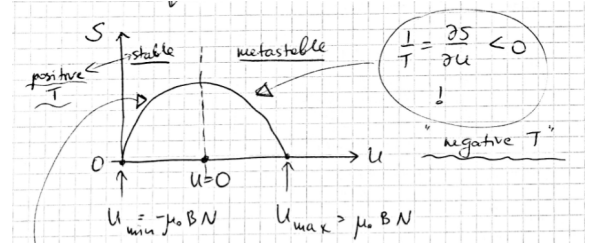
VII.I.4   The Ideal Gas

- Recall the classical kinetic energy of an ideal gas:

$$U = \sum_{i=1}^{N} \frac{\vec{p_i}^2}{2m}$$
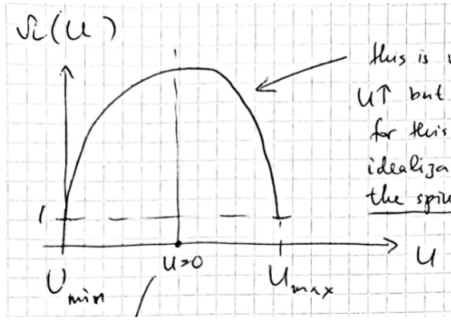
(a) Odd that U increases when multiplicity decreases.

(b) For $U > 0$, $\frac{\partial S}{\partial U} = \frac{1}{T<0}$, meaning negative T, and vice versa.

- We want to find how many ways we can choose the 3N numbers such that $\sum_{i=1}^{N} \vec{p_i}^2 = 2mU$ since the energy of the gas is dependent on the momenta of the atoms. This is essentially finding the multiplicity of the ideal gas. Intuitively, the energy increases as the number of choices increases.

- The multiplicity can be "dumbed down" to the area of a 3N-dimension sphere of radius-squared = 2mU. With the example of N = 1 (circle, 2D), we obtain that the area is:

$$A_{3N-1}(R) = \frac{2\pi^{3N/2}}{(\frac{3N}{2} - 1)!} R^{3N-1}$$

As such we expect the multiplicity function to be proportional to the above with $R = \sqrt{2mU}$, which does not yield a dimensionless number so we are not satisfied. After some factors the multiplicity function becomes:

$$\Omega(N, U) = \frac{1}{N!} \frac{1}{2^{3N}} \frac{2\pi^{3N/2}}{(\frac{3N}{2} - 1)!} \left(\frac{\sqrt{2mU}L}{\pi\hbar}\right)^{3N-1} \tag{38}$$

- This means that the momenta are quantized in units $\frac{\pi\hbar}{L}$..

- The entropy of this system (single-atomic ideal gas) is defined as:

$$S(N, U, V) = k \ln \Omega(N, U, V) = Nk[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{\frac{3}{2}}\right) + \frac{5}{2}]$$

- Using $c_V = \frac{\partial U}{\partial T}$ and $U = \frac{3}{2}NkT$, we can get $c_V = \frac{3}{2}Nk$.

- The condition that the total entropy was **extremized** yielded the thermodynamic equilibrium condition that:

$$\frac{1}{T_1} = \left(\frac{\partial S_1}{\partial U_1}\right)_{N_1, V_1} = \frac{1}{T_2} = \left(\frac{\partial S_2}{\partial U_2}\right)_{N_2, V_2}$$

- Now, we want to determine the mechanical equilibrium from the postulate of statistical mechanics. For a system with S_1 and S_2, S_{1+2} should be extremized with respect to both U_2' and V_2'. The total entropy of the system can be represented as:

$$S_{1+2} = S_1(U - U_2', N_1, V - V_2') + S_2(U_2', N_2, V_2')$$

- Extremizing the entropy would mean that we want $\nabla S|_N = 0$.

Extremizing entropy is defined as finding the gradient of S with respect to U_2' and V_2'

$$\nabla S = \frac{\partial S_{1+2}}{\partial U_2'} = 0 \to T_1 = T_2 \tag{39}$$

$$\nabla S = \frac{\partial S_{1+2}}{\partial V_2'} = 0 \to (\frac{\partial S_1}{\partial V_1'}) = (\frac{\partial S_2}{\partial V_2'}) \tag{40}$$

These are the two conditions to achieve mechanical equilibrium.

- We can now statistically define pressure as:

$$\frac{p_1}{T_1} = (\frac{\partial S_1}{\partial V_1})_{N_1, U_1} \tag{41}$$

$$p = T(\frac{\partial S}{\partial V})_{N,U} \tag{42}$$

- Rearrange this equation and compute and note that you will return to the ideal gas law with $\frac{p}{T} = \frac{Nk}{V}$.

- This helps us come to the formal definition of entropy with:

$$(\frac{\Delta S}{\Delta U}) = \frac{1}{T}$$

$$\Delta S = \frac{\Delta U}{T} \approx \frac{Q}{T}$$

from the First Law of thermodynamics

- The **Second Law of thermodynamics** states that the change in entropy is always positive (entropy is always increasing: $\Delta S \geq 0$).

- Consider two systems with T_1 and T_2, respectively. If the first system gives away heat Q, the total change in entropy can be calculated as:

$$\Delta S = \Delta(S_1 + S_2) = Q(-\frac{1}{T_1} + \frac{1}{T_2}) \geq 0$$

- We also know that by definition $c_V = \frac{\partial U}{\partial T}$, meaning that when we rearrange it $\Delta U = c_V \Delta T$. This way we can express change in entropy in another way.

$$\Delta S = c_V \frac{\Delta T}{T} = \int_{T_i}^{T_f} c_V \frac{dT}{T}$$

VII.II Boltzmann Statistics

- Everything we have studied so far is known as the microcanonical distribution which refers to an isolated system with variables that were fixed. Thanks to Boltzmann, we have the canonical distribution, or the **Boltzmann distribution**, referring to a system where the temperature T is fixed rather than the energy E. Imagine a system being attached to a large reservoir system with a thermostat with energy U_R. The total energy U is equal to $U = U_R + E$, which is fixed because the thermostat system is isolated (fixed N, V). We can now apply the fundamental postulate of statistical mechanics stating that:

$$\mathbb{P}(\text{any accessible microstate of system+R}) = \frac{1}{\Omega_{\text{system+R}}(U)}$$

- Since we know that $U_R = U - E$, we say $\Omega_{\text{system+R}}(U) = \sum_E \Omega(E)\Omega_R(U - E)$, where E is every allowed eigenvalue of the Hamiltonian of the system (any allowed energy state when solving Schrödinger's Equation).

- Let us denote the energy of some particular state as E_S. The probability of the system being in such a microstate is equivalent to the probability that the reservoir can be in a microstate with energy $U - E_S$, having exactly $\Omega_R(U - E_S)$ combinations. Mathematically:

$$\mathbb{P}(\text{system w/ } E_S) = \mathbb{P}(\text{system+R in any microstate}) \times \Omega_R(U - E_S)$$

$$\mathbb{P}(E_S) = \frac{\Omega_R(U - E_S)}{\sum_E \Omega(E)\Omega_R(U - E)}$$

- Now consider the probability of two allowed energies (E_{S1}, E_{S2}):

$$\frac{\mathbb{P}(E_{S1})}{\mathbb{P}(E_{S2})} = \frac{\sigma_R(U - E_{S1})}{\sigma_R(U - E_{S2})} = \frac{\exp\left(\frac{S_R(U - E_{S1})}{k}\right)}{\exp\left(\frac{S_R(U - E_{S2})}{k}\right)} = e^{\frac{1}{k}(S_R(U - E_{S1}) - S_R(U - E_{S2}))}$$

- Since the reservoir is so much larger than the system, we are able to expand the expressions for the entropy:

$$S_R(U - E_S) \approx S_R(U) - E_S \frac{\partial S_R(U)}{\partial U_R}$$

- Now we can further expand the ratio of probabilities to:

$$\frac{\mathbb{P}(E_{S1})}{\mathbb{P}(E_{S2})} = e^{\frac{1}{k}(E_{S1} - E_{S2})\frac{\partial S_R(U)}{\partial U_R}} = e^{-\frac{E_{S1} - E_{S2}}{kT}}$$

- $\frac{\mathbb{P}(E_{S1})}{e^{-\frac{E_{S1}}{kT}}}$ can not depend on the energy of the microstate and be constant which is the same for all E_S:

$$\mathbb{P}(E_S) = \frac{e^{-\frac{E_S}{kT}}}{Z}$$

- What is Z? Recall that the microstate of the system is determined by quantum numbers and energy:

$$E = \left(\frac{\pi\hbar}{L}\right)^2 \frac{1}{2m} \sum_{i=1}^{N} \vec{n_i}^2$$

- We also know that summing the probability of all energies will be 1.

$$\sum_E \mathbb{P}(E)\Omega(E) = \frac{1}{Z} \sum_E \Omega(E) e^{\frac{-E}{kT}}$$

- We can rearrange for Z:

$$Z = \sum_E \Omega(E) e^{\frac{-E}{kT}} \text{ or } \sum_n e^{\frac{-E(n)}{kT}}$$

- The probability at a given T that a system has energy E can use Gibbs' Free Energy, $F(E) = E - TS(E)$:

$$\mathbb{P}(\text{at T that a system has E}) = \frac{1}{Z}\sum_E \Omega(E) e^{\frac{-E}{kT}} = \frac{1}{Z} e^{\frac{S(E)}{k} - \frac{E}{kT}} = \frac{1}{Z} e^{-\frac{E - TS(E)}{kT}} = \frac{1}{Z} e^{-\frac{F(E)}{kT}}$$

The most likely value of E is where F(E) is at its minimum.

VII.II.1 Free Energy

- What does $F(T, V, N)$ determine?

$$\Delta F = \Delta E - \Delta T S - T \Delta S = \Delta E - \Delta T S - T \left(\frac{\partial S}{\partial E} \Delta E + \frac{\partial S}{\partial V} \Delta V + \frac{\partial S}{\partial N} \Delta N \right) = -S \Delta T - p \Delta V + \mu \Delta N$$

- As such, we have that for a (T, V, N) system, F is the **thermodynamic potential** meaning its partial derivatives determine S, p, μ in thermodynamic equilibrium.

$$S = -\frac{\partial F}{\partial T}; p = -\frac{partial F}{\partial V}; \mu = \frac{\partial F}{\partial N}$$

- We also know that for a process with fixed T, $\Delta F = \Delta E - T \Delta S = Q + W - T \Delta S$. Now if the process is quasistatic, $Q = T \Delta S$, and as such $\Delta F = W$. It is generally more useful to know that **minimizing F determines thermodynamic equilibrium state**.

- Relationship between F and constant Z is important since for a T, V, N system, $Z(T, V, N)$ determines all:

$$F = -kT \ln Z(T, V, N) \tag{43}$$

- We use F in more real applications because not all systems will be isolated. Open systems use F because S (entropy) cannot always be maxed, but instead, we can minimize F to achieve order.

VII.II.2 Einstein Solid (Z now)

- Interestingly, Z is easier to calculate than Ω. The energy of a microstate in an Einstein solid is $E(q_1 + ... q_N) = \hbar \omega (q_1 + ... q_N)$. Now the Z value of the Einstein solid can be defined as:

$$Z = \sum_{s: \text{ microstates}} e^{\frac{-E_s}{kT}} = \sum_{q_1=0}^{\infty} ... \sum_{q_N=0}^{\infty} e^{-\frac{\hbar \omega (q_1 + ... q_N)}{kT}} = \left(\sum_{q_1=0}^{\infty} e^{-\frac{\hbar \omega}{kT} q_1} \right) ... \left(\sum_{q_N=0}^{\infty} e^{-\frac{\hbar \omega}{kT} q_N} \right)$$

Each individual sum represents the Z of a single harmonic oscillator. This means that for an Einstein solid of N oscillators, we have:

$$Z_N = (Z_1)^N, Z_1 = \sum_{q=0}^{\infty} e^{-\frac{\hbar \omega}{kT} q} = \frac{1}{1 - e^{-\frac{\hbar \omega}{kT}}}$$

- General guideline, if a system has $E = E_1 + E_2$, then $Z = Z_1 Z_2$. Another way to express Z_1 is:

$$Z_1 = 1 + e^{-\frac{\hbar \omega}{kT}} + ... e^{-N \frac{\hbar \omega}{kT}} = e^{-\frac{E_0}{kT}} + ... e^{-\frac{E_N}{kT}}$$

- This shows us that states with $E >> kT$ will not contribute to thermodynamic equilibrium, whereas $E << kT$ will. At T = 0, we have energy E_0 and all states with $E > E_0$ have suppressed contributions due to the $e^{-\text{constant}}$ factor, meaning

$$Z \approx e^{-\frac{E_0}{kT}}, T \to 0$$

- At absolute zero (T = 0K), energy $E_0 = 0$, meaning $Z \to 1$ as $T \to 0$. However as $T \to \infty$, Z is the total number of microstates. As such, we can interpolate that Z is an approximation of **how many systems contribute to the thermodynamic equilibrium** physics.

- Back to the Einstein solid, we now have $Z = (\frac{1}{1-e^{-\frac{\hbar\omega}{kT}}})^N$ and $\mathbb{P}(E_S) = \frac{1}{Z}e^{-\frac{E_S}{kT}}$. The expectation value (average) of the energy:

$$< E >= \sum_S E_S \mathbb{P}(E_S) = \frac{1}{Z}\frac{\partial}{\partial(-\frac{1}{kT})}\sum_S e^{-\frac{E_S}{kT}} = \frac{\partial}{\partial(-\frac{1}{kT})}\ln Z = kT^2\frac{\partial}{\partial T}\ln Z$$

i have no idea why $Z = \ln Z$, but let's now consider $\frac{1}{kT} \equiv \beta$, meaning $Z = \sum_S e^{-\beta E_S}$ and $< E >= -\frac{\partial}{\partial \beta}\ln Z$. With $Z = (1 - e^{-\frac{\hbar\omega}{kT}})^{-N}$, we can rearrange the average energy formula to be:

$$< E >= \frac{N\hbar\omega}{e^{\frac{\hbar\omega}{kT}} - 1} \tag{44}$$

- If $kT << \hbar\omega$, we have $\frac{<E>}{N} \approx \hbar\omega e^{-\frac{\hbar\omega}{kT}}$. If $kT >> \hbar\omega$, $\frac{<E>}{N} \approx kT$. This are the expressions for the average energy per oscillator with the high and low temperature limits.

- The standard deviation of the energy σ_E is $\sigma_E = kT\sqrt{\frac{c_V}{k}}\ \sqrt{N}$, meaning $\frac{\sigma_E}{<E>}\ \frac{1}{\sqrt{N}}$. From this we see that as $N \to \infty$, the fluctuations of the energy around the mean are vanishingly small.