CHEM 20100 (Inorganic Chemistry I) Notes

Steven Labalme

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Topic 0

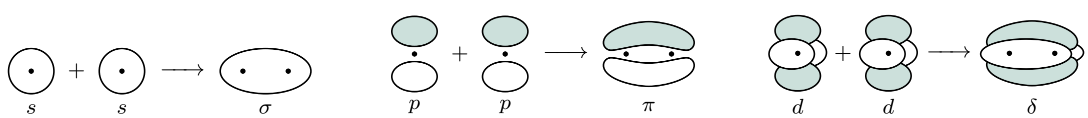
Course Prep

0.1 Chapter 1: Introduction to Inorganic Chemistry

From Miessler et al. (2014).

12/21:

- **Inorganic chemistry**: The chemistry of everything that is not organic chemistry, which is the chemistry of hydrocarbon compounds and their derivatives.
- **Organometallic chemistry**: The chemistry of compounds containing metal-carbon bonds and the catalysis of many organic reactions.
- There is also both **bioinorganic chemistry** and **environmental chemistry** (Miessler et al., 2014, p. 1), as well as **analytical chemistry**, **physical chemistry**, **petroleum chemistry**, and **polymer chemistry** (Miessler et al., 2014, p. 4).
  - Note, though, that there are no strict dividing lines between subfields of chemistry nowadays, and most professionals work in multiple fields.
- Single, double, and triple bonds (both metal-metal and metal-carbon bonds) are found in organic and inorganic chemistry.
- Quadruple bonds exist between metal atoms in some compounds.



(a) Sigma (σ) bond. (b) Pi (π) bond. (c) Delta (δ) bond.

Figure 0.1: Examples of bonding interactions.

  - No such bonds exist between carbon atoms because two carbon atoms max out at a triple bond.
  - Quadruple bonds possess one sigma bond, two pi bonds, and one delta (δ) bond.
  - The delta bond is only possible with metal atoms because these atoms possess energetically accessible d orbitals.
- Quintuple bonds between transition metals have been reported, but scientists have not yet reached a consensus on to what extent these exist.
- Hydrogen atoms and alkyl groups can act as bridges in inorganic chemistry, excessively disobeying the octet rule (see Figure 0.2).
- **Coordination number**: The number of other atoms, molecules, or ions to which an atom is bonded.

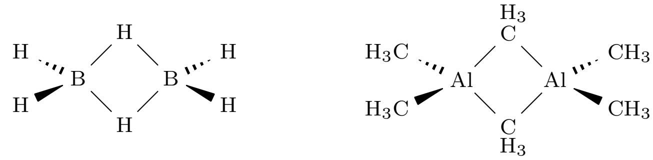


Figure 0.2: Inorganic compounds containing bridging hydrogens and alkyl groups.

- "Numerous inorganic compounds have central atoms with coordination numbers of five, six, seven, and higher" (Miessler et al., 2014, p. 2).
  - The most common coordination geometry for transition metals is octahedral.
- 4-coordinate carbon is almost always tetrahedral. 4-coordinate metals and nonmetals can be either tetrahedral or square planar.
- **Coordination complex**: A compound with a metal as the central atom or ion and some number of **ligands** bonded to it.
- **Ligand**: An anion or neutral molecule bonded to a central atom (frequently through N, O, or S).
- **Organometallic complex**: A coordination complex where carbon (potentially bonded to other things) is one of the ligands.

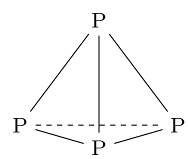


Figure 0.3: Tetrahedral geometry without a central atom.

- There are multiple kinds of tetrahedral structures. There is the standard arrangement seen in molecules such as methane, but there is also a form that lacks a central atom, as in elemental phosphorous P_4 (see Figure 0.3).
  - Other atoms such as boron and carbon also form units that surround a central cavity (e.g., icosahedral B_{12} and buckyballs C_{60}).
- Aromatic rings can bond to metals using all of their pi orbitals. This results in a metal suspended above the ring's center.
- **Cluster compound**: A compound where "a carbon atom is at the center of a polyhedron of metal atoms" (Miessler et al., 2014, p. 3).
  - There exist examples of carbon surrounded by five, six, or more metal atoms[1].
- Many new forms of elemental carbon have been discovered since the mid-1980s, notably including fullerenes (such as buckminsterfullerene, or buckyballs), carbon nanotubes, graphene, and polyyne wires.
- Miessler et al. (2014) give a brief history of inorganic chemistry for context.
  - Be aware of **crystal field theory** and **ligand field theory**.

[1]This provides a challenge to theoretical inorganic chemists.

0.2 Chapter 2: Atomic Structure

From Miessler et al. (2014).

12/22: - **Coinage metals**: Copper, silver, and gold, i.e., the transition metals in IUPAC Group 11.
- **Chalcogens**: Oxygen, sulfur, selenium, tellurium, and polonium, i.e., the nonmetals in Group 16.
- The energies of visible light emitted by the hydrogen atom are given by[2]

$$E = R_H \left(\frac{1}{2^2} - \frac{1}{n_h^2}\right)$$

  where n_h is an integer greater than 2 and R_H is the Rydberg constant for hydrogen (H).
  - Note that $R_H = 1.097 \times 10^7\,\mathrm{m^{-1}} = 2.179 \times 10^{-18}\,\mathrm{J} = 13.61\,\mathrm{eV}$.
  - This equation was first discovered by Johann Balmer in 1885.
  - Infrared and ultraviolet emissions can be described by replacing 2^2 with integers n_l^2 in the above equation on the condition that $n_l < n_h$[3].
- The energy of the light emitted is related to its wavelength, frequency, and wavenumber by the equations

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

  where h is Planck's constant ($6.626 \times 10^{-34}\,\mathrm{J\,s}$), c is the speed of light ($2.998 \times 10^8\,\mathrm{m\,s^{-1}}$), ν is the frequency of the light, λ is the wavelength of the light, and $\bar{\nu}$ is the **wavenumber** of the light.
- **Wavenumber**: The number of waves that exist between two points along the light's path a given distance apart. *Measured in* waves per centimeter (SI: $\mathrm{cm^{-1}}$).
  - Wavenumber is proportional to energy. This is why $\mathrm{m^{-1}}$ or $\mathrm{cm^{-1}}$ can be used as an energy unit.
- **Principal quantum number**: One of the quantities n in Balmer's equation.
- Bohr's atomic theory first explained the phenomenon of Balmer's equation, positing that "electrons may absorb light of certain specific energies and be excited to orbits of higher energy; they may also emit light of specific energies and fall to orbits of lower energy" (Miessler et al., 2014, pp. 11–12).
  - Bohr rewrote the Rydberg constant in terms of other quantities:

$$R = \frac{2\pi^2 \mu Z^2 e^4}{(4\pi\varepsilon_0)^2 h^2}$$

    where...
    - μ is the reduced mass of the electron/nucleus combination $\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_{\text{nucleus}}}$, where $m_e = 9.11 \times 10^{-31}\,\mathrm{kg}$ is the mass of the electron and m_{nucleus} is the mass of the nucleus.
    - Z is the nuclear charge.
    - $e = 1.602 \times 10^{-19}\,\mathrm{C}$ is the charge of the electron.
    - h is Planck's constant.
    - $4\pi\varepsilon_0$ is the permittivity of a vacuum.
  - Importantly, note that the Rydberg constant for hydrogen R_H is not universal, and changes for the atom at hand based on factors like the mass of the nucleus.
  - Also note that some of the terms cancel or can be written in terms of others, making the above equation equivalent to the one given in Chapter 7 of Labalme (2020a).

[2]Refer to Labalme (2020a), specifically Figure 7.6 and the accompanying discussion.
[3]n_l denotes the lower final energy level while n_h denotes the higher initial energy level.

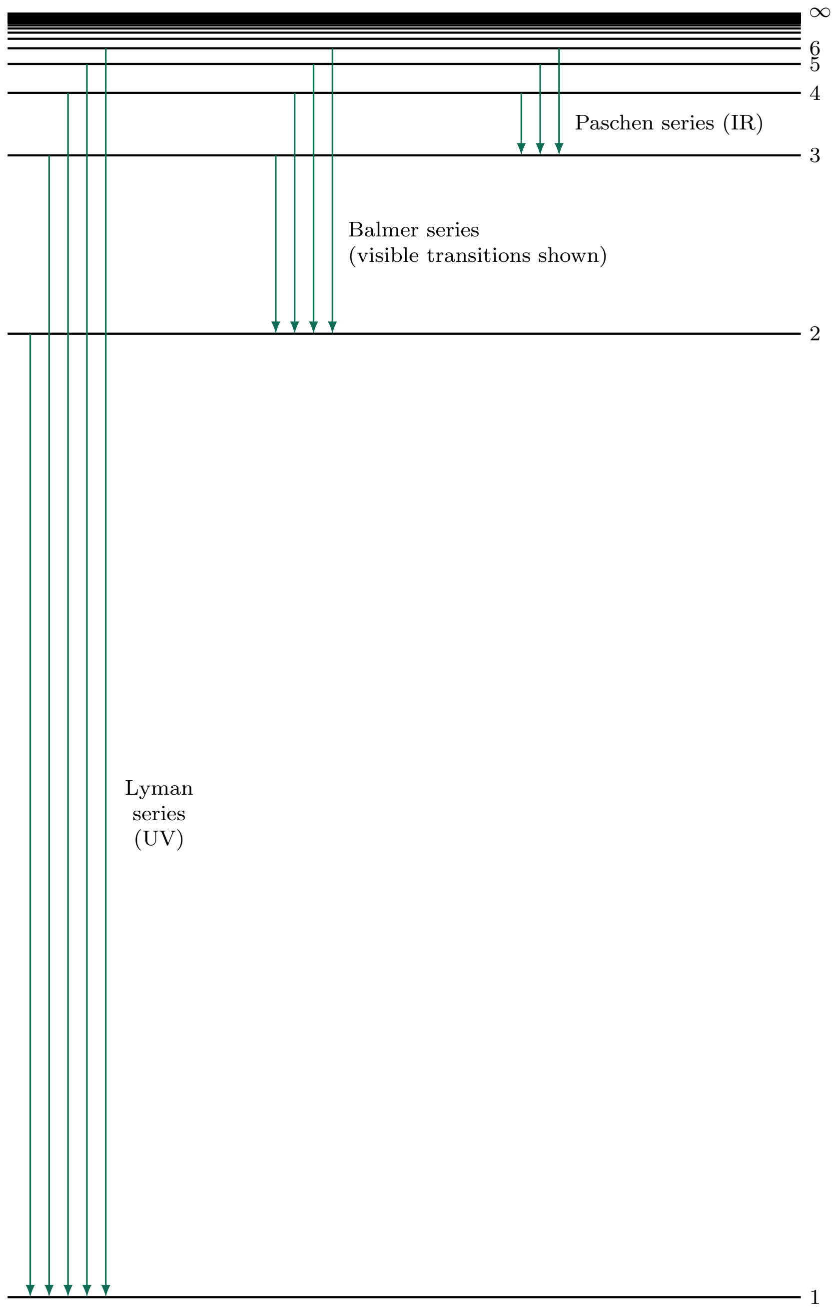


Figure 0.4: Hydrogen atom energy levels.

- **Balmer series**: The four main electron transitions in hydrogen that release electromagnetic radiation in the visible spectrum.
- **Lyman series**: The five main electron transitions in hydrogen that release electromagnetic radiation in the ultraviolet spectrum.
- **Paschen series**: The three main electron transitions in hydrogen that release electromagnetic radiation in the infrared spectrum.
- "The inverse square dependence of energy on n results in energy levels that are far apart in energy at small n and become much closer in energy at larger n" (Miessler et al., 2014, p. 12)

  - Individual electrons can have more energy than they would possess in the infinite energy level, but at and above this point, the nucleus and electron are considered to be separate entities.

- **Heisenberg's uncertainty principle**: "There is a relationship between the inherent uncertainties in the location and momentum of an electron" (Miessler et al., 2014, p. 14).

$$\Delta x \, \Delta p_x \geq \frac{h}{4\pi}$$

  - The above equation describes the x-component of the uncertainty, where Δx is the uncertainty in the position of the electron and Δp_x is the uncertainty in the momentum of the electron in the x-direction.

- Because of the uncertainty principle, we cannot treat electrons as particles with precisely described motion; instead, we must describe them in **orbitals**.
- **Orbital**: A region that describes the probable locations of an electron.
- **Electron density**: "The probability of finding the electron at a particular point in space" (Miessler et al., 2014, p. 14).
  - This can be calculated in principle.
- Schrödinger and Heisenberg published (in 1926 and 1927, respectively) papers on atomic wave mechanics. Although they used very different mathematical techniques, their theories can be shown to be equivalent. However, we will introduce Schrödinger's more commonly used differential equations.
- "The Schrödinger equation describes the wave properties of an electron in terms of its position, mass, total energy, and potential energy" (Miessler et al., 2014, p. 14).

$$H\Psi = E\Psi$$

  - In its simplest form, it is given by the above, where H is the **Hamiltonian operator**, E is the energy of the electron, and Ψ is the **wave function**.

- **Wave function**: A function that describes an electron wave in space, i.e., an atomic orbital.
- Energy values are another way of describing the quantization introduced with the Bohr model; different orbitals, characterized by different wave functions, each have characteristic energies.
- **Operator**: "An instruction or set of instructions that states what to do with the function that follows it" (Miessler et al., 2014, p. 14).
- **Hamiltonian operator**: An operator including derivatives that transforms the wave function into a constant (the energy) times Ψ. *Also known as* $\boldsymbol{\hat{H}}$.

$$H = \frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{Ze^2}{4\pi\varepsilon_0\sqrt{x^2+y^2+z^2}}$$

  - In the form used for calculating the energy levels of one-electron systems, it is given by the above, where...
    - h is Planck's constant.
    - m is the mass of the electron.
    - e is the charge of the electron.
    - $\sqrt{x^2+y^2+z^2} = r$ is the distance from the nucleus.
    - Z is the charge of the nucleus.
    - $4\pi\varepsilon_0$ is the permittivity of a vacuum.
  - The first part describes the kinetic energy of the electron, its energy of motion.

  - The second part describes the potential energy of the electron, the result of the electrostatic attraction between it and the nucleus. It is commonly designated as $V(x, y, z)$.

- "Because n varies from 1 to ∞, and every atomic orbital is described by a unique Ψ, there is no limit to the number of solutions of the Schrödinger equation for an atom. Each Ψ describes the wave properties of a given electron in a particular orbital" (Miessler et al., 2014, p. 15).
- Electron density is proportional to Ψ^2.
- Necessary conditions for a physically realistic solution for Ψ:
  1. Ψ must be single-valued: There cannot be two probabilities for an electron at any position in space.
  2. Ψ and its first derivatives must be continuous: The probability must be defined at all positions in space and cannot change abruptly from one point to the next.
  3. Ψ must approach zero as $r \to \infty$: For large distances from the nucleus, the probability must grow smaller and smaller (the atom must be finite).
  4. The integral
  $$\int_{\text{all space}} \Psi_A {\Psi_A}^* \, \mathrm{d}\tau = 1$$
  The total probability of an electron being somewhere in space must be 1. Applying this stipulation is called **normalizing** the wave function[4].
  5. The integral
  $$\int_{\text{all space}} \Psi_A {\Psi_B}^* \, \mathrm{d}\tau = 0$$
  Ψ_A and Ψ_B are different orbitals within the same atom, and this stipulation reflects the fact that all orbitals in the same atom must be **orthogonal** to each other.

12/23:

- The Particle in a Box.
  - Imagine a one-dimensional "box" between $x = 0$ and $x = a$ with potential energy everywhere zero inside the "box" and everywhere infinite outside the box.
    - These energy constraints mean that the particle is completely trapped within the box (it would take an infinite amount of energy to leave), but also that no forces act on it within the box.
  - It follows that the wave equation for locations within the box is
  $$\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2 \Psi(x)}{\partial x^2}\right) = E\Psi(x)$$
  - Since sine and cosine functions have properties associated with waves, we propose that a general solution describing possible waves in the box is
  $$\Psi(x) = A \sin rx + B \cos sx$$
  where A, B, r, s are constants.
  - As seen in Problem 2.8a, substituting the above general solution into the wave equation allows us to solve for
  $$r = s = \sqrt{2mE}\,\frac{2\pi}{h}$$

[4] ${\Psi_A}^*$ denotes the complex conjugate of Ψ_A. This is necessary because wave functions may have imaginary values. However, in many cases, the wave functions are real and the integrand reduces to Ψ_A^2.

- Because Ψ must be continuous and equal 0 for $x < 0$ and $x > a$, Ψ must approach 0 as $x \to 0$ and $x \to a$. Since $\cos(s \cdot 0) = 1$, $\Psi(0)$ can only equal 0 if $B = 0$. Therefore, the wave function reduces to

$$\Psi(x) = A \sin rx$$

- We must also have $\Psi(a) = 0$, which is only possible if rx is an integer multiple of π. This means that

$$ra = \pm n\pi$$
$$r = \frac{\pm n\pi}{a}$$

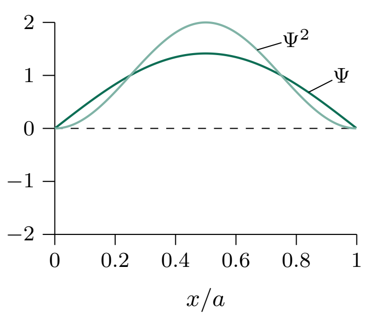
- Combining the two expressions for r, we can solve for E:

$$E = \frac{n^2h^2}{8ma^2}$$

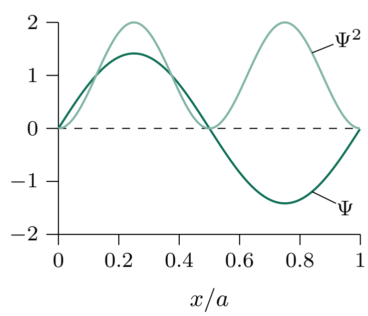
  - "These are the energy levels predicted by the particle-in-a-box model for any particle in a one dimensional box of length a. The energy levels are quantized according to quantum numbers $n = 1, 2, 3, \dots$" (Miessler et al., 2014, p. 17).

- As seen in Problem 2.8d, substituting $r = n\pi/a$ into $\Psi(x)$ and applying the normalizing requirement allows us to solve for the total solution

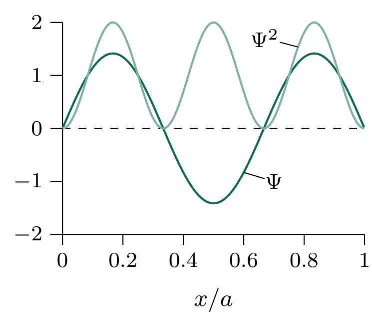
$$\Psi(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$



(a) $n = 1$.



(b) $n = 2$.



(c) $n = 3$.

Figure 0.5: Particle in a box: Wave functions and their squares at different energy levels.

- The predicted probability densities for an electron at different energy levels (see Figure 0.5) showcase a difference between classical mechanics' and quantum mechanics' predictions about the behavior of this particle: Classical predicts an equal probability at any point in the box, but the (quantum) wave nature of the particle predicts varied probabilities in different locations.
  - "The greater the square of the electron amplitude, the greater the probability of the electron being located at the specified coordinate when at the quantized energy defined by Ψ" (Miessler et al., 2014, p. 17).

- Atomic orbitals, mathematically, are discrete solutions of the three-dimensional Schrödinger equations.
  - These orbital equations include four quantum numbers (see Table 0.1).
  - Orbitals with l values $0, 1, 2, 3, 4, \dots$ are known by the labels $s, p, d, f, g, \dots$ (continuing alphabetically), respectively, derived from early terms for different families of spectroscopic lines.

Symbol	Name	Values	Role
n	Principal	$1, 2, 3, \ldots$	Determines the major part of the energy.
l	Angular momentum[5]	$0, 1, 2, \ldots, n-1$	Describes angular dependence and contributes to the energy.
m_l	Magnetic	$0, \pm 1, \pm 2, \ldots, \pm l$	Describes orientation in space (angular momentum in the z-direction).
m_s	Spin	$\pm\frac{1}{2}$	Describes orientation of the electron spin (magnetic moment) in space.

Table 0.1: Quantum numbers and their properties.

- n is the primary quantum number affecting the overall energy.
- l determines the type of shape. See Table 0.2.
- m_l determines the "orientation of the angular momentum vector in a magnetic field, or the position of the orbital in space" (Miessler et al., 2014, p. 18). See Table 0.2.
- m_s determines the electron spin[6] in the orbital, or "the orientation of the electron's magnetic moment in a magnetic field, either in the direction of the field ($+\frac{1}{2}$) or opposed to it ($-\frac{1}{2}$)" (Miessler et al., 2014, p. 18).
- n, l, and m_l specify an orbital; m_s specifies one of the two electrons in the orbital.

- A note on $i = \sqrt{-1}$ in Table 0.2:
  - Any linear combination of solutions to the wave equation is another solution.
  - Because it is more convenient to work with real functions as opposed to complex functions, we make use of the above fact to decomplexify the solutions, as in the following examples.

$$
\begin{aligned}
\Psi_{2p_x} &= \frac{1}{\sqrt{2}}(\Psi_{+1} + \Psi_{-1}) \\
&= \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2\pi}}\mathrm{e}^{i\phi} \cdot \frac{\sqrt{3}}{2}\sin\theta \cdot [R(r)] + \frac{1}{\sqrt{2\pi}}\mathrm{e}^{-i\phi} \cdot \frac{\sqrt{3}}{2}\sin\theta \cdot [R(r)]\right) \\
&= \left(\frac{1}{\sqrt{\pi}}\frac{\sqrt{3}}{2}[R(r)]\sin\theta\right)\frac{\mathrm{e}^{i\phi} + \mathrm{e}^{-i\phi}}{2} \\
&= \frac{1}{2}\sqrt{\frac{3}{\pi}}[R(r)]\sin\theta\cos\phi
\end{aligned}
$$

$$
\begin{aligned}
\Psi_{2p_y} &= \frac{-i}{\sqrt{2}}(\Psi_{+1} - \Psi_{-1})^{[7]} \\
&= \left(\frac{1}{\sqrt{\pi}}\frac{\sqrt{3}}{2}[R(r)]\sin\theta\right)\frac{\mathrm{e}^{i\phi} - \mathrm{e}^{-i\phi}}{2i} \\
&= \frac{1}{2}\sqrt{\frac{3}{\pi}}[R(r)]\sin\theta\sin\phi
\end{aligned}
$$

[5] *Also known as* **azimuthal** (quantum number).
[6] Note that the spin of an electron is purely quantum mechanical, and should not be related back to classical mechanics.
[7] Errata: Miessler et al. (2014) incorrectly normalizes this expression with $i/\sqrt{2}$.

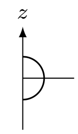
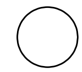
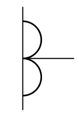
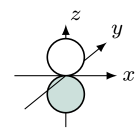
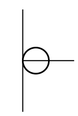
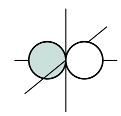
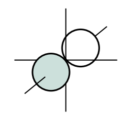
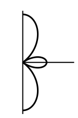
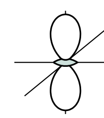
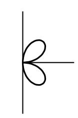
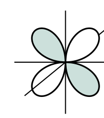
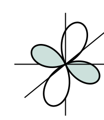
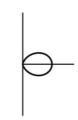
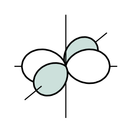
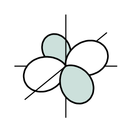
Angular factors					**Real Wave Functions**			
Related to Angular Momentum				**Functions of θ**	**In Polar Coordinates**	**In Cartesian Coordinates**	**Shapes**	**Label**
l	m_l	Φ	Θ		$\Theta\Phi(\theta,\phi)$	$\Theta\Phi(x,y,z)$		
$0(s)$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$		$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{2\sqrt{\pi}}$		s
$1(p)$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{z}{r}$		p_z
	$+1$	$\frac{1}{\sqrt{2\pi}}e^{i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\sin\theta\cos\phi$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{x}{r}$		p_x
	-1	$\frac{1}{\sqrt{2\pi}}e^{-i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\sin\theta\sin\phi$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{y}{r}$		p_y
$2(d)$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{2}\sqrt{\frac{5}{2}}(3\cos^2\theta-1)$		$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta-1)$	$\frac{1}{4}\sqrt{\frac{5}{\pi}}\frac{2z^2-x^2-y^2}{r^2}$		d_{z^2}
	$+1$	$\frac{1}{\sqrt{2\pi}}e^{i\phi}$	$\frac{\sqrt{15}}{2}\cos\theta\sin\theta$		$\frac{1}{2}\sqrt{\frac{15}{\pi}}\cos\theta\sin\theta\cos\phi$	$\frac{1}{2}\sqrt{\frac{15}{\pi}}\frac{xz}{r^2}$		d_{xz}
	-1	$\frac{1}{\sqrt{2\pi}}e^{-i\phi}$	$\frac{\sqrt{15}}{2}\cos\theta\sin\theta$		$\frac{1}{2}\sqrt{\frac{15}{\pi}}\cos\theta\sin\theta\sin\phi$	$\frac{1}{2}\sqrt{\frac{15}{\pi}}\frac{yz}{r^2}$		d_{yz}
	$+2$	$\frac{1}{\sqrt{2\pi}}e^{2i\phi}$	$\frac{\sqrt{15}}{4}\sin^2\theta$		$\frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\cos 2\phi$	$\frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{x^2-y^2}{r^2}$		$d_{x^2-y^2}$
	-2	$\frac{1}{\sqrt{2\pi}}e^{-2i\phi}$	$\frac{\sqrt{15}}{4}\sin^2\theta$		$\frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\sin 2\phi$	$\frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{xy}{r^2}$		d_{xy}

Table 0.2: Hydrogen atom wave functions: Angular functions.

- Note that d_{z^2} actually uses the function $2z^2-x^2-y^2$, so we should write $d_{2z^2-x^2-y^2}$ but we shorthand for convenience.
- Since the functions in the polar and Cartesian coordinates columns of Table 0.2 are real, $\Psi=\Psi^*$ and $\Psi\Psi^*=\Psi^2$.

12/25: - Ψ may be expressed in terms of Cartesian coordinates (x,y,z) or in terms of spherical coordinates (r,θ,ϕ).
    - Using spherical coordinates comes with the advantage that r is the distance from the nucleus (see Figure 0.6).

12/23:

Radial Functions $R(r)$, with $\sigma = Zr/a_0$			
Orbital	n	l	$R(r)$
$1s$	1	0	$R_{1s} = 2\left[\frac{Z}{a_0}\right]^{3/2} \mathrm{e}^{-\sigma}$
$2s$	2	0	$R_{2s} = \left[\frac{Z}{2a_0}\right]^{3/2} (2-\sigma)\mathrm{e}^{-\sigma/2}$[8]
$2p$		1	$R_{2p} = \frac{1}{\sqrt{3}}\left[\frac{Z}{2a_0}\right]^{3/2} \sigma\mathrm{e}^{-\sigma/2}$
$3s$	3	0	$R_{3s} = \frac{2}{27}\left[\frac{Z}{3a_0}\right]^{3/2} (27-18\sigma+2\sigma^2)\mathrm{e}^{-\sigma/3}$
$3p$		1	$R_{3p} = \frac{1}{81\sqrt{3}}\left[\frac{2Z}{a_0}\right]^{3/2} (6-\sigma)\sigma\mathrm{e}^{-\sigma/3}$
$3d$		2	$R_{3d} = \frac{1}{81\sqrt{15}}\left[\frac{2Z}{a_0}\right]^{3/2} \sigma^2\mathrm{e}^{-\sigma/3}$

Table 0.3: Hydrogen atom wave functions: Radial functions.

12/25:

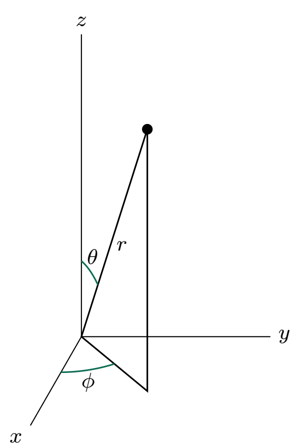


Figure 0.6: Spherical coordinates.

- Know the following volume element conversions[9].

$$\mathrm{d}V = \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z = r^2 \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\,\mathrm{d}r$$

- The volume of the thin shell between r and $r + \mathrm{d}r$ is as follows[10], and is useful for describing the electron density as a function of distance from the nucleus.

$$\begin{aligned}\int_0^{2\pi}\int_0^{\pi} 1\,r^2 \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\,\mathrm{d}r &= \int_0^{2\pi} 2r^2\,\mathrm{d}\phi\,\mathrm{d}r\\ &= 4\pi r^2\,\mathrm{d}r\end{aligned}$$

[8]Errata: This differs from the corresponding equation in Miessler et al. (2014) because the textbook is wrong.
[9]Refer to Labalme (2020b), specifically Figure 16.9 and the accompanying discussion.
[10]Errata: Miessler et al. (2014) flips the bounds over which θ and ϕ should be evaluated, but I use the right ones.

– Ψ can be factored into a **radial component** R and two **angular components** Θ and Φ, which are sometimes combined into a single component Y:

$$\Psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) = R(r)Y(\theta, \phi)$$

- Refer to Table 0.2 for examples of Θ and Φ, and Table 0.3 for examples of R.
- Note that in Table 0.2, the shaded orbital lobes correspond to where the wave function is negative. Distinguishing regions of opposite signs is useful for bonding purposes.

– The radial component can also be manipulated to give the **radial probability function** $4\pi r^2 R^2$.

- R is the radial function, so R^2 is the probability function (think $\Psi = RY$, so $\Psi^2 = R^2Y^2$).

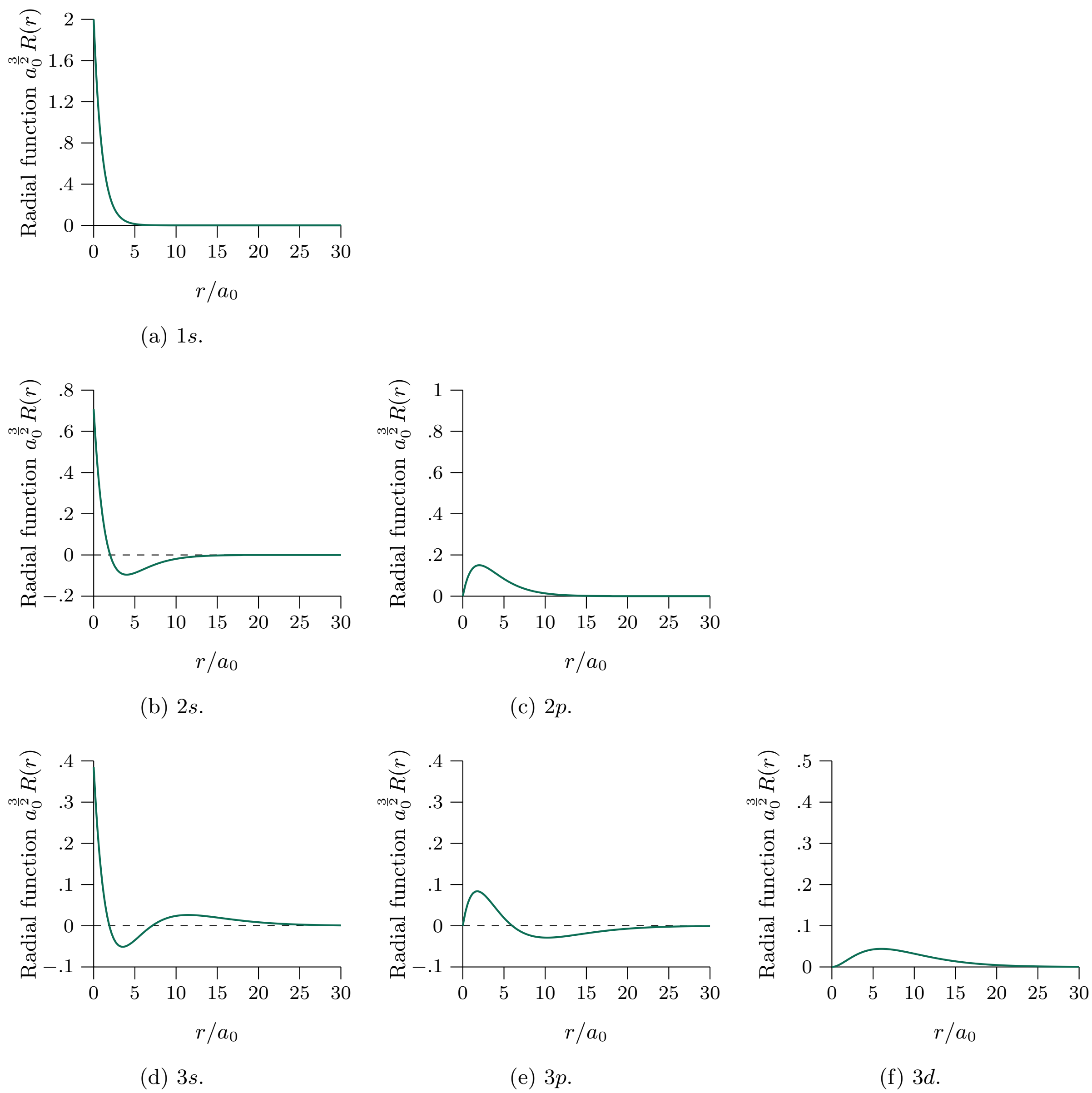


Figure 0.7: Radial wave functions.

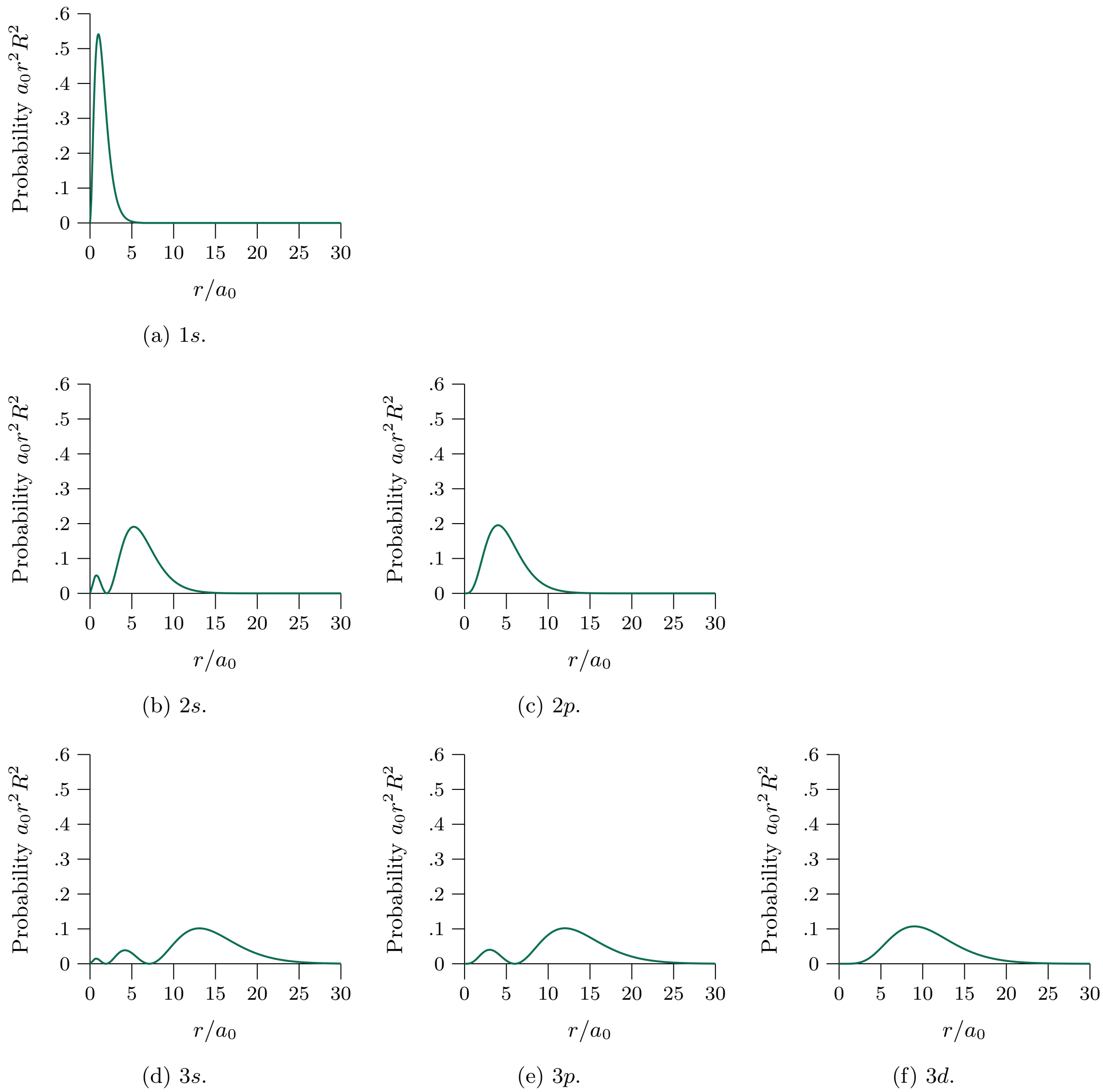


Figure 0.8: Radial probability functions.

- **Radial component**: The part of Ψ that describes "electron density at different distances from the nucleus" (Miessler et al., 2014, p. 20).
  - Determined by quantum numbers n and l.
  - Plotted for the $n = 1, 2, 3$ orbitals in Figure 0.7.
- **Angular components**: The parts of Ψ that describe "the shape of the orbital and its orientation in space" (Miessler et al., 2014, p. 20).
  - Determined by quantum number l and m_l.
- **Radial probability function**: The function describing "the probability of finding the electron at a given distance from the nucleus, summed over all angles, with the $4\pi r^2$ factor the result of integrating over all angles" (Miessler et al., 2014, p. 21).

- Plotted for the $n = 1, 2, 3$ orbitals in Figure 0.8.

- **Bohr radius**: "The value of r at the maximum of Ψ^2 for a hydrogen $1s$ orbital (the most probable distance from the hydrogen nucleus for the $1s$ electron), and it is also the radius of the $n = 1$ orbit according to the Bohr model" (Miessler et al., 2014, p. 23).
  - See Figure 0.8a.
  - Its value is $a_0 = 52.9\,\text{pm}$.
  - It is a common unit in quantum mechanics.
  - It is used to scale the functions in Figures 0.7 and 0.8 to give reasonable axis units[11].
- Figure 0.8 shows that the electron density falls off rapidly after the absolute maximum in every case.
  - However, it falls off more quickly for lower energy levels.
- The electron density at the nucleus is always zero.
  - Mathematically, this is because $4\pi r^2 R^2$ naturally equals zero when $r = 0$.
- "Because chemical reactions depend on the shape and extent of orbitals at large distances from the nucleus, the radial probability functions help show which orbitals are most likely to be involved in reactions" (Miessler et al., 2014, p. 23).

12/26:

- **Nodal surface**: A surface within an orbital having zero electron density.
  - The wave function is zero at these because it is changing sign.
    - Knowing where the wave function is positive and negative can be useful when working with molecular orbitals.
- To find nodal surfaces, we must find places where
$$0 = \Psi^2 = \Psi = R(r)Y(\theta, \phi)$$
or where
$$0 = R(r) \qquad\qquad 0 = Y(\theta, \phi)$$
- "The total number of nodes in any orbital is $n - 1$ if the conical nodes of some d and f orbitals count as two nodes" (Miessler et al., 2014, p. 23).
  - The conical node of the d_{z^2} orbital (see Table 0.2) is mathematically one surface, but we must count it as two (perhaps think of it as a top and bottom section) to fit the pattern.
- **Angular node**: A node that results when $Y = 0$.
  - There are l angular nodes in any orbital.
- **Radial node**: A node that results when $R = 0$. *Also known as* **spherical nodes**.
  - There are $n - l - 1$ radial nodes in any orbital.
- Note that on the basis of relativity, electron density at nodes may not be zero but may in fact be a very small finite value.
  - Alternatively, if we think of an electron wave like a wave in a violin string, which also has places of zero vibration where the string still exists, nodes may just be places where electron waves have zero amplitude, not places where they don't exist.

[11]Errata?: Should the y-axis in Figure 0.8 be $a_0^3 r^2 R^2$?

- A further possible explanation is that electrons can 'teleport' between two places without ever passing in between.

- We now look at a few examples of finding nodes in orbitals.
- Nodal structure of p_z:
  - From Table 0.2, the angular factor of this orbital in Cartesian coordinates is
$$Y = \frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{z}{r}$$
  - When we set this equal to zero, we find that the above is only equal to zero when $z = 0$.
  - Indeed, $z = 0$, i.e., the xy-plane, is an angular node in the p_z orbital, as we can see in Table 0.2.
  - Additionally, we can tell from the above equation that the wave function is positive when $z > 0$ and negative when $z < 0$; this is also reflected in Table 0.2.
- Nodal structure of $d_{x^2-y^2}$:
  - The angular factor:
$$Y = \frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{x^2 - y^2}{r^2}$$
  - This is only equal to zero when
$$\begin{aligned} 0 &= x^2 - y^2 \\ y^2 &= x^2 \\ y &= \pm x \end{aligned}$$
  - This translates to Table 0.2, where we can see that the planes $x = y$ and $x = -y$, i.e., those that contain the z-axis and make 45° angles with the x- and y-axes, are nodes.
  - Additionally, the function is positive where $|x| > |y|$ and negative where $|x| < |y|$[12], and we can see this in Table 0.2.
- Be aware of lines/surfaces of constant electron density.
- When filling orbitals in polyelectronic atoms, "we start with the lowest n, l, and m_l values (1, 0, and 0, respectively) and either of the m_s values (we will arbitrarily use $+\frac{1}{2}$ first)" (Miessler et al., 2014, p. 26). We then utilize the three following rules.
  - See them used to fill a p orbital in Table 0.4.
- **Aufbau principle**: The buildup of electrons in atoms results from continually increasing the quantum numbers. *Etymology* **aufbau** from German "building up."
  - "Electrons are placed in orbitals to give the lowest total electronic energy to the atom. This means that the lowest values of n and l are filled first. Because the orbitals within each subshell (p, d, etc.) have the same energy, the orders for values of m_l and m_s are indeterminate" (Miessler et al., 2014, p. 26).
- **Pauli exclusion principle**: Each electron in an atom must have a unique set of quantum numbers.
  - Note that this is experimentally derived, and does not follow from the Schrödinger equation.
- **Hund's rule** (of maximum multiplicity): Electrons must be placed in orbitals to give the maximum total spin (the maximum number of parallel spins).
  - This is a consequence of the Aufbau principle, as two electrons in the same orbital have higher energy than two in different orbitals due to electrostatic repulsions.

[12]Errata: Miessler et al. (2014) incorrectly use $x > y$ and $x < y$.

Number of electrons	Arrangement	Unpaired e^-	Multiplicity
1	$\underline{\uparrow\ }\ \underline{\quad}\ \underline{\quad}$	1	2
2	$\underline{\uparrow\ }\ \underline{\uparrow\ }\ \underline{\quad}$	2	3
3	$\underline{\uparrow\ }\ \underline{\uparrow\ }\ \underline{\uparrow\ }$	3	4
4	$\underline{\uparrow\downarrow}\ \underline{\uparrow\ }\ \underline{\uparrow\ }$	2	3
5	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\ }$	1	2
6	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}$	0	1

Table 0.4: Hund's rule and multiplicity.

- **Spin multiplicity**: The number of unpaired electrons plus 1.

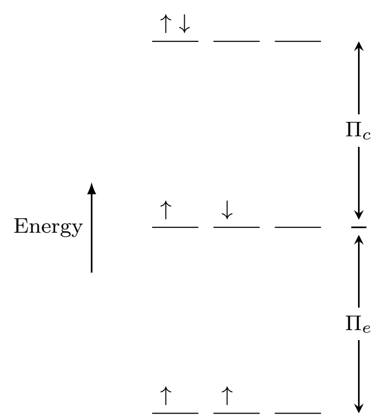


Figure 0.9: Coulombic energy of repulsion and exchange energy.

- **Coulombic energy of repulsion**: The potential energy of two negatively charged electrons that occupy the same orbital (as opposed to separate orbitals). *Denoted by* $\mathbf{\Pi_c}$.
  - Note that all polyelectronic species are subject to *some* Coulombic repulsions, but the contribution is significantly higher for paired electrons.
- **Exchange energy**: The potential energy of two electrons that have opposite spins (as opposed to the same spin). *Denoted by* $\mathbf{\Pi_e}$.
  - This arises from purely quantum mechanical considerations.
  - Basically, there are three possible ways to arrange two electrons in degenerate orbitals (see Figure 0.9). The exchange energy between two of the states reflects the fact that electrons with opposite spins are distinguishable, but electrons with identical spins can be exchanged (can switch places) and no observer would be the wiser. This event, when it happens, is called **one exchange of parallel electrons**; the fact that it can happen lowers the energy of the system with electrons of identical spin simply by virtue of creating more possible states that each electron can occupy.

12/27:
- Energies with oxygen:
  - Three possible configurations: $\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\quad}$, $\underline{\uparrow\downarrow}\ \underline{\uparrow\ }\ \underline{\ \downarrow}$, and $\underline{\uparrow\downarrow}\ \underline{\uparrow\ }\ \underline{\uparrow\ }$.
  - In the first one, we have two pairs of electrons (so $2\Pi_c$) and two possible exchanges (one for each pair of electrons with like spin, so $2\Pi_e$).

- In the second one, we have one pair of electrons (so $1\Pi_c$) and two possible exchanges (one for each pair of electrons with like spin, so $2\Pi_e$).
- In the third one, we have one pair of electrons (so $1\Pi_c$) and three possible exchanges (1-2, 1-3, and 2-3, so $3\Pi_e$).
- Thus, the energies from greatest to least are 1, 2, 3, and indeed the three rules suggest that the third one is how we should put four electrons into a p orbital.

- **Degenerate** (orbitals): Orbitals with the same energy.
- Energy minimization is the driving force determining the ground state, and this usually means that lower subshells are filled before higher ones.
  - However, in some transition elements, subshells are so close in energy ($4s$ and $3d$, for example) that the sum of the Coulombic and exchange terms can exceed the energy difference between subshells.
- **Klechkowsky's rule**: "The order of filling of the orbitals proceeds from the lowest available value for the sum $n + l$. When two combinations have the same value, the one with the smaller value of n is filled first" (Miessler et al., 2014, p. 29).
- The periodic table can also be used to predict orbital filling.
  - Both Klechkowsky's rule and the periodic table method are imperfect, but they work for the majority of atoms and provide starting points for the others.
- Miessler et al. (2014) includes a table listing ground state electron configurations for every atom, including variant ones.
- **Shielding**: "Each electron acts as a shield for electrons farther from the nucleus, reducing the attraction between the nucleus and the more distant electrons" (Miessler et al., 2014, p. 30).
- As Z increases, orbital energies decrease (electrons are pulled closer to the nucleus).
- When ranking higher energy orbitals, l must be considered in addition to n (e.g., to know that $4s$ fills before $3d$)[13].
- **Slater's rules**: Four rules that approximately determine the magnitude of the effective nuclear charge $Z^* = Z - S$, where Z is the nuclear charge and S is the shielding constant.
  1. Write the atom's electronic structure in order of increasing quantum numbers n and l, grouped as follows:
  $$(1s)\ (2s,2p)\ (3s,3p)\ (3d)\ (4s,4p)\ (4d)\ (4f)\ (5s,5p)\ (5d)\ \text{(and so on)}$$
  2. Electrons in groups to the right in this list do not shield electrons to their left.
  3. We may now determine S. For ns and np valence electrons:
     a. Each electron in the same group contributes 0.35 to the value of S for each other electron in the group, with one exception: A $1s$ electron contributes 0.30 to S for another $1s$ electron.
     b. Each electron in $n-1$ groups contributes 0.85 to S.
     c. Each electron in $n-2$ or lower groups contributes 1.00 to S.
  4. For nd and nf valence electrons:
     a. Each electron in the same group contributes 0.35 to the value of S for each other electron in the group[14].
     b. Each electron in groups to the left contributes 1.00 to S.

[13] See Labalme (2020a), specifically Figure 7.12.
[14] This is the same as Rule 3a.

- Slater's rules for nickel:
  - Rule 1: The electron configuration is written $(1s^2)(2s^2,2p^6)(3s^2,3p^6)(3d^8)(4s^2)$.
  - For a $3d$ electron:
    - Rule 4a: Each other electron in the $(3d^8)$ group contributes 0.35 to S, so the total contribution is $7 \times 0.35 = 2.45$.
    - Rule 4b: Each electron in groups to the left of $(3d^8)$ contributes 1.00 to S, so the total contribution is $18 \times 1.00 = 18.00$.
    - Thus, $S = 2.45 + 18.00 = 20.45$, so $Z^* = 28 - 20.45 = 7.55$.
  - For a $4s$ electron:
    - Rule 3a: The other electron in the $(4s^2)$ group contributes 0.35 to S.
    - Rule 3b: Each electron in the $n-1$ groups $(3s^2,3p^6)(3d^8)$ contributes 0.85 to S, so the total contribution is $16 \times 0.85 = 13.60$.
    - Rule 3c: Each other electron to the left contributes 1.00 to S, so the total contribution is $10 \times 1.00 = 10.00$.
    - Thus, $S = 0.35 + 13.60 + 10.00 = 23.95$, so $Z^* = 28 - 23.95 = 4.05$.
  - Note that the fact that the $4s$ electrons are held less tightly than the $3d$ electrons is reflected in the fact that when $\text{Ni} \longrightarrow \text{Ni}^{2+} + 2\,\text{e}^-$, the two electrons removed are the $4s$ electrons.
- Slater's rules are justified by electron probability curves (see Figure 0.8) and experimental data.
- Rich provided another explanation of orbital filling (refer to Figure 0.10 throughout the following discussion).

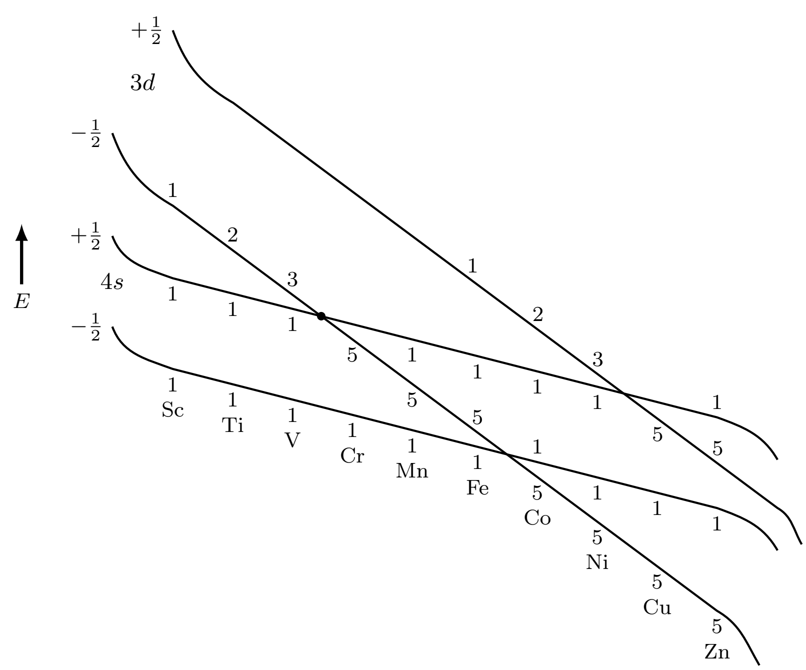


Figure 0.10: Schematic energy levels for transition elements.

  - Each orbital can be conceived as two half-orbitals, separated energetically by a variable electron pairing energy of the form $a\Pi_c + b\Pi_e$ where $a,b \in \mathbb{Z}^+$.
    - Take Fe, for example. If one of the $3d$ electrons with $m_s = -\frac{1}{2}$ were changed to have $m_s = +\frac{1}{2}$ (i.e., paired with another electron), we would expect the energy of the system to increase by $\Pi_c + 4\Pi_e$.

- Each of these half orbitals naturally decreases in energy (is pulled closer to the nucleus) as Z increases.
- Since orbitals in lower energy levels have shorter most probable distances to the nucleus, they are stabilized more as Z increases (this is why the slope of the $3d$ half orbitals is steeper).
- Electrons are placed into the lowest energy positions possible.
  - Thus, the $4s$ orbital usually fills up first, but there are exceptions since, for example, the $3d$ half orbital with $m_s = -\frac{1}{2}$ crosses over the $4s$ half orbital with $m_s = +\frac{1}{2}$ between V and Cr (at the dot) as opposed to somewhere after Cr.
- Note that as electrons are sequentially added, Figure 0.10 shows them generally having the same spin, in accordance with Hund's rule.
- For ions, the crossover points shift left.
  - This is because the removal of the electron causes Z^* to increase dramatically for all electrons, but more for $(n-1)d$ orbitals than ns orbitals.
- "This approach to electron configurations of transition metals does not depend on the stability of half-filled shells or other additional factors" (Miessler et al., 2014, p. 36).
- Introductory chem: Electrons in the highest energy level are always removed first when ionizing transition metals. This chem: "Regardless of which electron is lost to form a transition metal ion, the lowest energy electron configuration of the resulting ion will always exhibit the vacancy in the ns orbital" (Miessler et al., 2014, p. 36).
- Similar but more complex diagrams can treat other situations in higher energy levels and subshells.

- Since the periodic table arranges[15] atoms on the basis of similar electronic configurations, a given atom's position provides information about its properties.

- **Ionization energy**: The energy required to remove an electron from a gaseous atom or ion. *Also known as* **ionization potential**.

$$\mathrm{A^{n+}}_{(g)} + \Delta\mathrm{U} \longrightarrow \mathrm{A^{(n+1)+}}_{(g)} + \mathrm{e^-}$$

  - When $n = 0$, ΔU is the first ionization energy IE_1. When $n = 1$, ΔU is the second ionization energy IE_2. The pattern continues.
  - Ionization energy trends[16]:
    - Increases across a period (the major change).
    - Decreases down a group (a minor change; occurs because an increase in quantum number is associated with a much higher energy, and electrons with more energy need less to make it to the infinite energy level).
    - The trend breaks at boron and oxygen due to core shielding and Π_c, respectively.
    - Such trends are most pronounced in the main group elements; in the transition metals, the lanthanides, and the actinides, "the effects of shielding and increasing nuclear charge [are] more nearly in balance" (Miessler et al., 2014, p. 37).

- **Electron affinity**: The energy required to remove an electron from a negative ion. *Also known as* **zeroth ionization energy**.

$$\mathrm{A^-_{(g)}} + \Delta\mathrm{U} \longrightarrow \mathrm{A_{(g)}} + \mathrm{e^-}$$

  - Electron affinity is often thought of as the energy released by adding an electron to a neutral atom, but taking this perspective facilitates comparisons with ionization energy.
  - This reaction is endothermic, except for the noble gases and the alkaline earth elements.
  - Trends are similar to those for ionization energy, but "for one larger Z value (one more electron for each species[17]) and with much smaller absolute numbers" (Miessler et al., 2014, p. 37).
    - The magnitude decreases because outer electrons in anions are better shielded.

[15] Errata: Miessler et al. (2014) misspells arrangement as "arrangment" (p. 36).
[16] Refer to Labalme (2020a), specifically Figure 7.19 as well as Exercise on Z_{eff}.
[17] Think isoelectricity (see Figure 0.11).

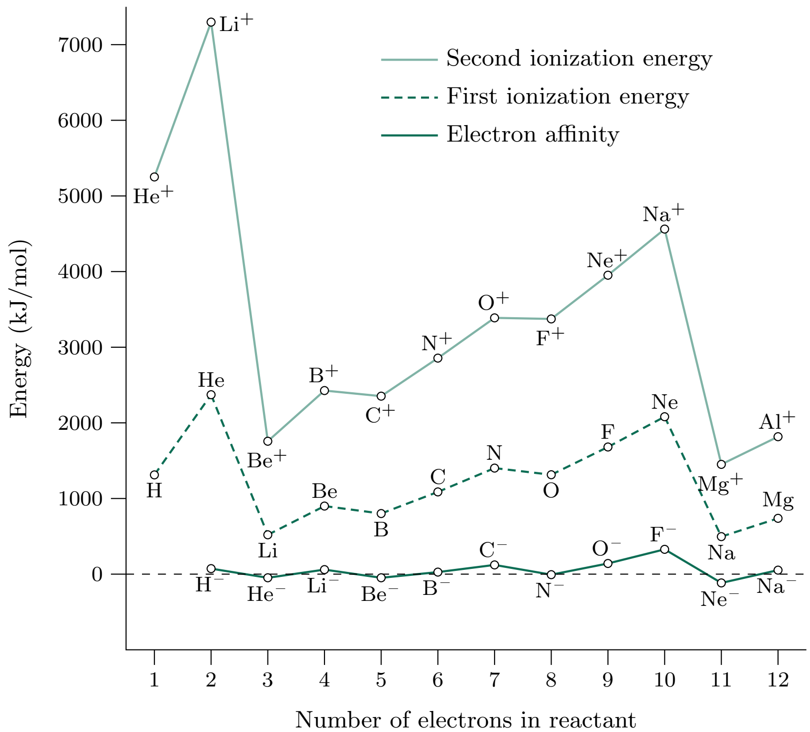


Figure 0.11: First and second ionization energies and electron affinities.

- Atomic radius decreases across periods and increases down groups.
- **Nonpolar covalent radius**: The radius of an atom as determined from bond lengths in nonpolar molecules.
- **Van der Waals radius**: The radius of an atom as determined from collisions with other atoms.
  - Because compounds vary so much, it is hard to use either of these or any method to definitively determine atomic radius.
- **Pauling's approach**: A method for determining ionic radii based on the assumption that the ratio of the radii of isoelectronic atoms equals the ratio of their effective nuclear charges.
  - This is not entirely accurate. Modern cation **crystal radii** differ by $+14$ pm, and such anion radii differ by -14 pm.
- Factors that influence ionic size: "the coordination number of the ion, the covalent character of the bonding, distortions of regular crystal geometries, and delocalization of electrons (metallic or semiconducting character...)" (Miessler et al., 2014, p. 40).

Topic I

Review of VSEPR Theory

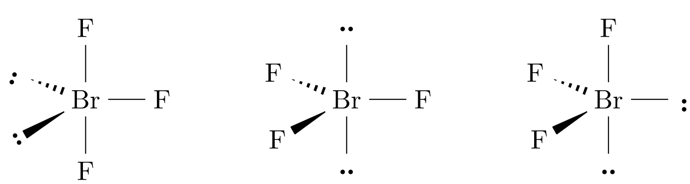
I.1 Module 1: Course Logistics and History

1/11:

- Homework questions will be similar to exam questions, so although you probably *can* find answers online, you shouldn't.
- Submit Psets to chem201hw@gmail.com.
- Watch modules before office hours and bring questions.
- If you have a question outside of office hours, post it on Slack.
- It's a difficult class, but he is open to and welcomes our feedback (via Slack, again).
- You do need to read from Miessler et al. (2014), too; his class is not a replacement for this textbook.
  - He is a big fan of Cotton (1990).
  - There is an extra, new textbook to look for!
- Convince yourself not to be afraid of time-independent quantum mechanics (we won't go too deep, but know wave functions and the like).
- Exams will probably be open book/open note.
- Inorganic chemistry contains too much information to rationalize empirically, so we need a system (the development of this system will be the focus of this course).
- Reviews history of chemistry from Miessler et al. (2014) Chapter 1.
- What is Nickel's electron configuration?
  - When Nickel is a free atom, the $[\text{Ar}]4s^2 3d^8$ electron configuration is the lowest energy.
  - When Nickel is chemically bound, the $[\text{Ar}]3d^{10}$ electron configuration is the lowest energy because it is energetically unfavorable to have a large 4s orbital pushing the bounds of the atom.
  - What is a **term symbol**?
- Homework: Refresh Chapter 2 in Miessler et al. (2014).
- **Covalent bond**: The sharing of pairs of electrons...?
- G. N. Lewis predicts in 1916 (before Rutherford) that the atom has a positive **kernel** surrounded by a shell containing up to 8 electrons.
  - Also orbital penetration.
  - He recommends that we read the full paper: Lewis (1916).

I.2 Module 2: Molecular Geometries and VSEPR

- The easiest way to approach a new Lewis structure:
  1. Draw a valid Lewis structure for a molecule.
  2. Place electron pairs in the valence shell as far away from each other as possible. Use the σ-bond framework first.
  3. Add π-bonds to complete the molecule.
- Through the VSEPR approach, think of a molecule as arranged around a central atom A by m atoms or groups of atoms X and n lone electron pairs E.
- **Steric number**: The sum $n + m$ of groups and electron pairs around the central atom.
- Steric numbers correspond to geometries.
- VSEPR is ok but it doesn't capture reality too well.
- Consider trimethyl boron (BMe_3).
  - Trigonal planar (D_{3h}).
- Octahedral: O_h.
- Bent: C_{2v}.
- **Order of the repulsive forces**: lone pair - lone pair > lone pair - bonding pair > bonding pair - bonding pair.
- In SF_4 (see-saw), will the lone pair be axial or equatorial?
  - Equatorial — $2 \times 120°$ and $2 \times 90°$ vs. $3 \times 90°$.
- In BrF_3...



(a) $4 \times 90°$. (b) $6 \times 90°$. (c) Cis lone pairs.

Figure I.1: VSEPR structure of BrF_3.

  - T-shaped → Distorted T — $4 \times 90°$ vs. $6 \times 90°$ or lone pairs in cis-position.
- In ions such as ICl_4^-, we get square planar (D_{4h}).
- With mixed substituents (such as PF_2Cl_3)...

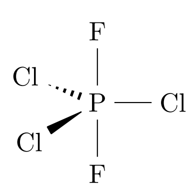


Figure I.2: Lewis structure of PF_2Cl_3.

- We need **Bent's rule**, which tells us that atoms share electrons from p- or d-orbitals to a greater extent than they do from s-orbitals.
- Thus, when phosphorous excites $3s^2 3p^3$ to $3s^1 3p_x^1 3p_y^1 3p_z^1 3d_{z^2}^1$ and then rehybridizes to create three sp^2 orbitals (each composed of $s + p_x + p_y$) and two "*pd*" hybrid orbitals (each composed of $p_z + d_{z^2}$), the equatorial sp^2 orbitals bond to the more **electropositive** chlorines and the axial "*pd*" hybrid orbitals bond to the remaining more electronegative fluorines.
- There is also sometimes a tendency for symmetry.

- **Bent's rule**: Atomic s-character concentrates in orbitals directed toward electropositive substituents.
- **Electropositive** (species): A species that has relatively lower electronegativity than another.
- For molecules with multiple bonds, ignore π-bonds.
- Problems with VSEPR:
  - XeF_6 with 14 bonding electrons (7 pairs) is supposed to be pentagonal bipyramidal, but is actually octahedral (a known problem for $14\,e^-$ systems).
  - Heavy main group elements with no hybridization.
    - $H{-}C{\equiv}C{-}H$ is linear, but $H{-}Si{\equiv}Si{-}H$ is not.
    - No σ-bond exists in the latter species — it's all π-bonding interactions.
- You maybe don't have to watch the modules and textbook *and* attend class.

I.3 Chapter 3: Simple Bonding Theory

From Miessler et al. (2014).

1/14:
- **Hypervalent** (central atom): A central atom that has an electron count greater than the atom's usual requirement.
- There are rarely more than 18 electrons around a central atom (2 for s, 6 for p, 10 for d). Even heavier atoms with energetically accessible f orbitals usually don't have more surrounding electrons because of crowding.
- With BeF_2, instead of getting the predicted double-bonded Lewis structure, it forms a complex network with Be having coordination number 4.
  - $BeCl_2$ dimerizes to a 3-coordinate structure in the vapor phase.
- Boron trihalides exhibit partial double bond character.
  - It is also possible that the high polarity of $B{-}X$ bonds and the **ligand-close packing** (LCP) model account for the observed shorter bond length.
  - Boron trihalides also act as Lewis acids.

1/17:
- The variety of structures means that one unified VSEPR theory will not likely[1] work.
- **Not stereochemically active** (lone pair): "A lone pair that appears in the Lewis-dot structure but has no apparent effect on the molecular geometry" (Miessler et al., 2014, p. 54).
- Double and triple bonds have slightly greater repulsive effects than single bonds in the VSEPR model.
- Multiple bonds tend to occupy the same positions as lone pairs.
- Electronegativity varies for a given atom based on the neighboring atom to which it is bonded.

[1] Errata: "unlikely."

1/14:

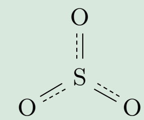
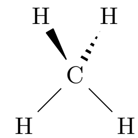
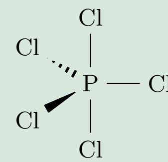
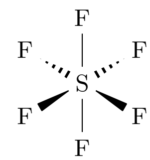
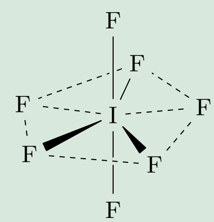
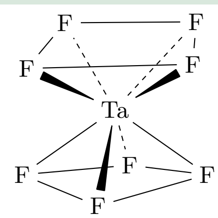
Steric Number	Geometry	Examples	Calculated Bond Angles	
2	Linear	CO_2	180°	O = C = O
3	Trigonal (triangular)	SO_3	120°	
4	Tetrahedral	CH_4	109.5°	
5	Trigonal bipyrimidal	PCl_5	120°, 90°	
6	Octahedral	SF_6	90°	
7	Pentagonal bipyrimidal	IF_7	72°, 90°	
8	Square antiprismatic	$[TaF_8]^{3-}$	70.5°, 9.6°, 109.5°	

Table I.1: VSEPR predictions.

1/17:

- "With the exception of helium and neon, which have large calculated electronegativities and no known stable compounds, fluorine has the largest value" (Miessler et al., 2014, p. 59).
- Although usually classified with Group 1, hydrogen's chemistry is distinct from that of the alkali metals and actually all of the groups.
- Some bond angle trends can be explained by electronegativity (see Table I.2).
  - For instance, electronegative outer atoms pull electrons away from the central atom, allowing lone pairs to further push together such atoms.
  - Electronegative central atoms pull electrons toward the central atom, pushing bonding pairs farther apart.
- Atomic size can also have effects on VSEPR predictions.

Molecule	X−P−X Angle (°)	Molecule	Bond Angle (°)
PF_3	97.8	H_2O	104.5
PCl_3	100.3	H_2S	92.1
PBr_3	101.0	H_2Se	90.6

Table I.2: Electronegativity and bond angles.

  - For example, the C−N−C angle in $N(CF_3)_3$ is larger than that of $N(CH_3)_3$ despite the prediction we'd make based on electronegativity alone. This is because F atoms are significantly larger than H atoms so we get some steric hindrance.

- In molecules with steric number 5, axial bond length is greater than equatorial.
- Symmetric structures are often preferred.
- Groups (such as CH_3 and CF_3) have the ability to attract electrons, too — thus, they are also assigned electronegativities.
- **Ligand close-packing**: A model that uses the distances between outer atoms in molecules as a guide to molecular shapes. *Also known as* **LCP**.
  - Works off of the observation that the nonbonded distances between outer atoms are consistent across molecules with the same central atom, but the bond angles and lengths change.
  - This contrasts with VSEPR theory's concern with the central atom, as opposed to the ligands.
- **Dielectric constant**: "The ratio of the capacitance of a cell filled with the substance to be measured to the capacitance of the same cell with a vacuum between the electrodes" (Miessler et al., 2014, p. 66).
  - This is measured to experimentally determine the polarity of molecules.
- **Dipole moment**: The product Qr of the distance r between two charges' centers and the difference Q between the charges. *Also known as* $\boldsymbol{\mu}$.
  - This is calculated by measuring the dielectric constant at different temperatures.
  - SI unit: Coulomb meter; C m. Common unit: Debye; $1\,\mathrm{D} = 3.335\,64 \times 10^{-30}\,\mathrm{C\,m}$.

Topic II

Symmetry and Group Theory in Chemistry

II.1 Module 3: Symmetry Elements and Operations

1/13:
- He will upload lecture slides in advance in the future.
- An object is symmetric if one part is the same as other parts.
- The symmetry of discrete objects is described using **point symmetry**.
- **Point groups** (~ 32 for molecules) provide us with a way to indicate the symmetry unambiguously.
  - These have symmetry about a single point at the center of mass of the system.
- Extended objects (e.g., crystals) have **translational symmetry** described by **Space groups**[1] (230 total).
- Readings: Miessler et al. (2014) Chapter 4 and https://en.wikipedia.org/wiki/Molecular_symmetry.
- **Symmetry elements**: Geometric entities about which a **symmetry operation** can be performed. In a point group, all symmetry elements must pass through the center of mass (the point).
- **Symmetry operation**: The action that produces an object identical to the initial object.

Element	Operation
Identity, E	nothing
Rotation axis, C_n	n-fold rotation
Improper rotation axis, S_n	n-fold improper rotation
Plane of symmetry, σ	Reflection
Center of symmetry, i	Inversion

- **Identity**: Does nothing to the object, but is necessary for mathematical completeness.
- ***n*-fold rotation**: A rotation of $360^\circ/n$ about the C_n axis ($n \in [1, \infty)$).
  - In H_2O, there is a C_2 axis, so we can perform a 2-fold (180°) rotation to get the same molecule.
    - Remember, because of quantum mechanical properties, the hydrogens are indistinguishable so when we rotate it 180°, we cannot tell it apart from the unrotated molecule.
  - Rotations are considered positive in the counterclockwise direction.

[1] Not covered in this course.

  - Each possible rotation operation is assigned using a superscript integer m of the form ${C_n}^m$. m is the number of sequential applications.
  - The rotation ${C_n}^n \equiv E$ is equivalent to the identity operation (nothing is moved).
  - Linear molecules have an infinite number of rotational options C_∞ because any rotation on the molecular axis will give the same arrangement.
- **Principal axis**: The highest order rotation axis.
  - By convention, the principal axis is assigned to the z-axis if we are using Cartesian coordinates.
- **Reflection**: Exchanges one half of the object with the reflection of the other half.
- **Vertical mirror plane**: A mirror plane that contains the principal axis. *Also known as* $\boldsymbol{\sigma_v}$.
- **Horizontal mirror plane**: A mirror plane that is perpendicular to the principal axis. *Also known as* $\boldsymbol{\sigma_h}$.
- **Dihedral mirror planes**: A special type of σ_v that is between sides or planes. *Also known as* $\boldsymbol{\sigma_d}$.
  - For example, we might have vertical mirror planes in the xz- or yz-planes. In this case, the dihedral planes would contain the lines $y = \pm x$.
- Two successive reflections are equivalent to the identity operation.
- **Inversion**: Every part of the object is reflected through the inversion center, which must be at the center of mass of the object.
  - $(x, y, z) \xrightarrow{i} (-x, -y, -z)$.
- $\boldsymbol{n}$**-fold improper rotation**: This operation involves a rotation of $360°/n$ followed by a reflection perpendicular to the axis. It is a single operation and is labeled in the same manner as "proper" rotations. *Also known as* $\boldsymbol{{S_n}^m}$, **rotation-reflection operation**.

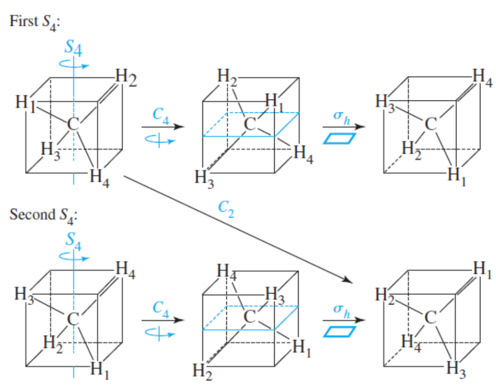
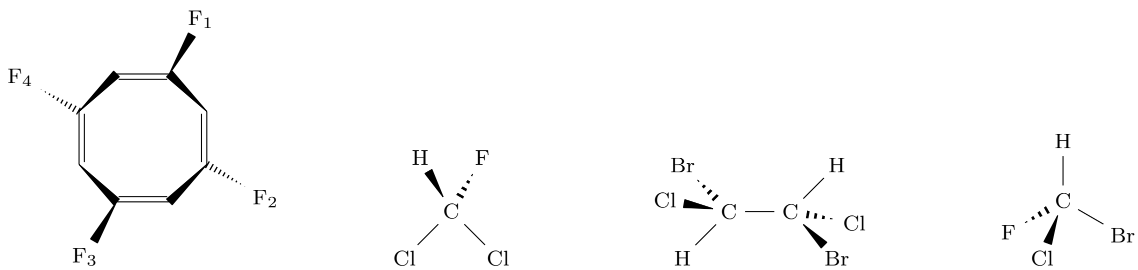


Figure II.1: Methane's S_4 symmetry.

  - Methane has S_4 symmetry.
  - Note that $S_1 \equiv \sigma_h$, $S_2 \equiv i$, and sometimes $S_{2n} \equiv C_n$. In methane, for example, ${S_4}^2 \equiv C_2$.
  - Applied to a triangular prism, is a good example.
  - If n is even, we have n unique operations. There should be $C_{n/2}$.
  - If n is odd, we have $2n$ unique operations. There should be C_n and σ_h.
- The absence of an S_n axis is the defining symmetry property of **chiral** molecules.
  - Formerly, we learned that chiral molecules should not have mirror planes and inversion centers.
  - Rigorously, chiral molecules must not have any improper rotation axes.

II.2 Module 4: Symmetry Point Groups

- Identifying the point groups:
  1. Determine if the symmetry is special (e.g., octahedral).
  2. Determine if there is a principal rotation axis.
  3. Determine if there are rotation axes perpendicular to the principal axis.
  4. Determine if there are mirror planes.
  5. Assign point groups.
- High symmetry and low symmetry groups are the most difficult to identify.
- High symmetry:
  - Perfect tetrahedral (T_d), e.g., P_4 and CH_4.
  - Perfect octahedral (O_h), e.g., SF_6.
  - Perfect icosahedral (I_h), e.g., C_{60} and ${B_{12}H_{12}}^{2-}$.
- Low symmetry:



(a) S_4. (b) C_s (c) C_i (d) C_1

Figure II.2: Low symmetry point groups.

  - Only an improper axis: S_n.
  - Only a mirror plane: C_s.
  - Only an inversion center: C_i.
  - No symmetry: C_1.
- C_n groups:
  - Only a C_n axis. Note that conformation is important.
- C_{nh} groups have a C_n axis and a σ_h reflection plane (such as $B(OH)_3$).
  - H_2O_2 has C_{2h} symmetry.
- All symmetry elements are listed in the top row of the corresponding characters table (Appendix C in Miessler et al. (2014)).
- C_{nv} groups have a C_n axis and a σ_v reflection plane.
  - NH_3 has C_{3v} symmetry.
  - CO has $C_{\infty v}$ symmetry since there are an infinite number of both C_n axes and σ_v mirror planes.
- D_{nh} groups: A C_n axis, n perpendicular C_2 axes, and a σ_h reflection plane.

  - BH_3 has D_{3h} symmetry.
  - A square prism has D_{4h} symmetry.
  - CO_2 has $D_{\infty h}$ symmetry.
- D_n groups: A C_n axis, n perpendicular C_2 axes, and no mirror planes.
  - A 3-bladed propeller has D_3 symmetry.
- D_{nd} groups: A C_n axis, n perpendicular C_2 axes, and a σ_d.
  - Ethane in the staggered conformation has D_{3d} symmetry.
- Local symmetry:
  - Sometimes, rigorous math analysis needs to be adjusted to physical reality.
  - If a cyclopentane ring is bonded through the center to $Mn(CO)_3$, this molecule has only C_s symmetry.
  - However, spectroscopically, there is fast rotation about the Mn−Cp bond. This means that the $Mn(CO)_3$ fragment exhibits pseudo-C_{3v} symmetry while the C_5H_5 ligand exhibits pseudo-C_{5v} symmetry.
  - Often, the absolute symmetry of a molecule is very low, but the interactions are far away from the centers of interest, and do not perturb them significantly.
  - If we have platinum as a central atom bonded to two chlorines and two $P(Et)_3$ groups, this molecule technically has C_1 symmetry due to the orientations of atoms within R groups (staggered), but IR spectroscopy is characteristic of highly symmetric species (D_{2h}).

II.3 Module 5: Group Theory 101

1/15:
- **Group**: A set of elements together with an operation that combines any two of its elements to form a third element satisfying four conditions called the group axioms.
- **Closure**: All binary products must be members of the group.
- **Associativity**: Associative law of multiplication must hold.
- **Identity**: A group must contain the identity operator.
- **Inverse**: Every operator must have an inverse.
- The integers with the addition operation form a group, for example.
- History:
  - Early group theory was driven by the quest for solutions of polynomial equations of degree 5 and above.
  - Early 1800s: Évariste Galois realized that the algebraic solution to a polynomial equation is related to the structure of a group of permutations associated with the roots off the polynomial, the Galois group of the polynomial.
    - Link to Galois video here.
  - 1920s: Group theory was applied to physics and chemistry.
  - 1931: It is often hard or even impossible to obtain a solution of the Schrödinger equation — however, a large part of qualitative results can be obtained by group theory. Almost all the rules of spectroscopy follow from the symmetry of a problem.
- We will use group theory for describing symmetry of molecules. We will use group theory to understand the bonding and spectroscopic features of molecules.

- For us, a group consists of a set of symmetry elements (and associated symmetry operations) that completely describes the symmetry of a molecule.
- **Order** (of a group): The total number of elements (i.e., symmetry operations) in the group. *Also known as* $\boldsymbol{h}$.
- Rule 1: Closure.

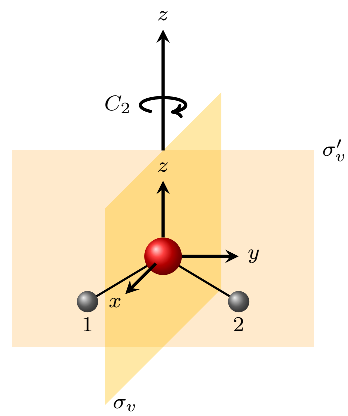


Figure II.3: Symmetry elements for H_2O.

  - H_2O is of the C_{2v} point group (refer to Figure II.3).
    - Symmetry operations: E, C_2, $\sigma_{v(xz)}$, and $\sigma'_{v(yz)}$.
    - $\sigma_v \cdot C_2 = \sigma_v' = C_2 \cdot \sigma_v$.
    - The above property (order *does not* matter) shows that C_{2v} is an **Abelian group**.
  - NH_3 is of the C_{3v} point group.
    - Symmetry operations: E, ${C_3}^+$, ${C_3}^-$, σ_v, σ_v', and σ_v''.
    - $\sigma_v'' \cdot C_3 = \sigma_v$, but $C_3 \cdot \sigma_v'' = {C_3}^- = {C_3}^2$.
    - The above property (order *does* matter) shows that C_{3v} is a **non-Abelian group**.
- Rule 2: Associativity.
  - H_2O is of the C_{2v} point group (refer to Figure II.3).

$$\begin{aligned}\sigma_v' C_2 \sigma_v(1,2) &= \sigma_v' C_2(2,1) \\ &= \sigma_v'(1,2) \\ &= (1,2)\end{aligned} \qquad \begin{aligned}\sigma_v'(C_2\sigma_v)(1,2) &= \sigma_v' E(1,2) \\ &= \sigma_v'(1,2) \\ &= (1,2)\end{aligned} \qquad \begin{aligned}(\sigma_v' C_2)\sigma_v(1,2) &= \sigma_v\sigma_v(1,2) \\ &= \sigma_v(2,1) \\ &= (1,2)\end{aligned}$$

- Rule 3: Identity.
- Rule 4: Inverse.
  - For a C_{2v} point group:

$$E \cdot E = E \qquad C_2 \cdot C_2 = E \qquad \sigma_v \cdot \sigma_v = E \qquad \sigma_v' \cdot \sigma_v' = E$$

- Group multiplication tables.

C_{2h}	$\boldsymbol{E}$	$\boldsymbol{C_2}$	$\boldsymbol{\sigma_h}$	$\boldsymbol{i}$
$\boldsymbol{E}$	E	C_2	σ_h	i
$\boldsymbol{C_2}$	C_2	E	i	σ_h
$\boldsymbol{\sigma_h}$	σ_h	i	E	C_2
$\boldsymbol{i}$	i	σ_h	C_2	E

Table II.1: Group multiplication table for the C_{2h} point group.

- Table II.1 corresponds to the C_{2h} point group, which has E, C_2, σ_h, and i operations.
- Note that the operation in the top row is the one that's applied first, while the one in the left column will be applied second.

- **Subgroup**: Fractional parts of groups that are groups, too.

C_{3v}	$\boldsymbol{E}$	$\boldsymbol{C_3}$	$\boldsymbol{C_3^2}$	$\boldsymbol{\sigma_v}$	$\boldsymbol{\sigma_v'}$	$\boldsymbol{\sigma_v''}$
$\boldsymbol{E}$	E	C_3	${C_3}^2$	σ_v	σ_v'	σ_v''
$\boldsymbol{C_3}$	C_3	${C_3}^2$	E	σ_v''	σ_v	σ_v'
$\boldsymbol{C_3^2}$	${C_3}^2$	E	C_3	σ_v'	σ_v''	σ_v
$\boldsymbol{\sigma_v}$	σ_v	σ_v'	σ_v''	E	C_3	${C_3}^2$
$\boldsymbol{\sigma_v'}$	σ_v''	σ_v	σ_v'	C_3	${C_3}^2$	E
$\boldsymbol{\sigma_v''}$	σ_v'	σ_v''	σ_v	${C_3}^2$	E	C_3

Table II.2: Group multiplication table for the C_{3v} point group.

- If $h = 6$ (as in the C_{3v} group), subgroup order can be $h = 3, 2, 1$. Why only these?
- The order 1 and 3 charts are subgroups.
- The order 2 chart is not a subgroup because ${C_3}^2$ is not an operation in the group (therefore, the "subgroup" is not closed).

- We use subgroups because they can make complex problems simpler.
  - For example, calculating the vibrational modes of CO_2.
  - As another example, D_{2h} is a subgroup of $D_{\infty h}$.

II.4 Module 6: Representations

- Items of the same point group have the same vibration modes.
- **Representation** (of a group): Any collection of quantities (or symbols) which obey the multiplication table of a group. *Also known as* Γ.
- For our purposes, these quantities are the matrices that show how certain characteristic of a molecule behave under the symmetry operations of the group.
- Operations (on a point (x, y, z) in Cartesian coordinates):
  - $E(x, y, z) = (x, y, z)$.
  - $\sigma_{xz}(x, y, z) = (x, -y, z)$.
  - $i(x, y, z) = (-x, -y, -z)$.
  - C_n: Convention is a counterclockwise rotation of the point by $\theta = \frac{2\pi}{n}$ radians.
  - S_n: Convention is a clockwise rotation of the point C_n followed by a σ through a plane perpendicular to C.

- Matrix forms of operations:
  - Identity: $E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$.
  - One example of a reflection (there are two more): $\sigma_{xy} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$.
  - Inversion: $i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$.
  - Rotation: Counterclockwise is $C_n(\theta) = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$ and clockwise is $C_n(\theta) = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$.
    - A derivation of this matrix can be found in the slides.
  - Improper rotation: $S_n(\theta) = \sigma_h C_n(\theta)$.
- **Reducible representations** (Γ):
  - A representation of a symmetry operation of a group.
  - Can be expressed in terms of a representation of lower dimension.
  - Can be broken down into a simpler form.
  - Characters can be further diagonalized.
  - Are composed of the direct sum of irreducible representations.
  - Infinite possibilities.
- **Irreducible representations** (Γ_i):
  - A fundamental representation of a symmetry operation of a group.
  - Cannot be expressed in terms of a representation of lower dimension.
  - Cannot be broken down into a simpler form.
  - Characters cannot be further diagonalized.
  - Small finite number dictated by point group.
- Good example of reducible/irreducible representations?
- A representation shows how certain characteristics of an object (a basis) behave under the symmetry operation of the group.
- **Conjugate elements**: Two elements X and Y for which there exists an element Z in the group such that
$$Z^{-1} \cdot X \cdot Z = Y$$
  - Every element is conjugated with itself (let $Z = E$).
  - If X is conjugated with Y, then Y is conjugated with X.
  - If X is conjugated with Y and W, then Y and W are also conjugate.
- **Class**: A complete set of elements of a group that are conjugate to one another.
  - Geometric meaning: operations in the same class can be converted into one another by changing the axis system through application of some symmetry operation of the group.
- Find the conjugates to C_3 in the C_{3v} point group (refer to Table II.2 throughout the following discussion).

- Let $X = C_3$, let Z iterate through the six symmetry elements $(E, C_3, {C_3}^2, \sigma_v, \sigma_v', \sigma_v'')$, and let Z^{-1} iterate through the corresponding inverses $(E, {C_3}^2, C_3, \sigma_v, \sigma_v', \sigma_v'')$.
- Thus, we have

$$
\begin{aligned}
E \cdot C_3 \cdot E &= C_3 \\
{C_3}^2 \cdot C_3 \cdot C_3 &= C_3 \\
C_3 \cdot C_3 \cdot {C_3}^2 &= C_3 \\
\sigma_v \cdot C_3 \cdot \sigma_v &= {C_3}^2 \\
\sigma_v' \cdot C_3 \cdot \sigma_v' &= {C_3}^2 \\
\sigma_v'' \cdot C_3 \cdot \sigma_v'' &= {C_3}^2
\end{aligned}
$$

- It follows from the above that C_3 and C_3 are conjugates, and C_3 and ${C_3}^2$ are conjugates.
- Thus, C_3 and ${C_3}^2$ are in the same class.
- We can use a similar method to prove that σ_v, σ_v', and σ_v'' are all in the same class within the C_{3v} point group.
- Likewise E is in a class by itself.
- Thus, for the C_{3v} point group, E forms a class of order 1, $C_3, {C_3}^2$ form a class of order 2, and $\sigma_v, \sigma_v', \sigma_v''$ form a class of order 3.

- **Similarity transformation**: The transformation

$$v^{-1} \cdot A \cdot v = A'$$

  - A is a representation for some type of symmetry operation.
  - v is a similarity transform operator.
  - v^{-1} is the inverse of the similarity transform operator.
  - A' is the product.
  - A and A' are conjugates, and we say that A' is the similarity transform of A by v.

- **Block-diagonal** (matrix): A matrix with nonzero values only in square blocks along the diagonal from the top left to the bottom right.

$$
\begin{bmatrix}
2 & 3 & 0 & 0 & 0 \\
1 & 2 & 0 & 0 & 0 \\
0 & 0 & 1 & 1 & 0 \\
0 & 0 & 1 & 1 & 0 \\
0 & 0 & 0 & 0 & 2
\end{bmatrix}
$$

  - The above matrix is an example of a block-diagonal matrix.

- Irreducible representations are the corresponding blocks within a set of block-diagonalized matrices representing each operation in a group.

II.5 Module 7: Characters and Character Tables

1/19:

- Nocera Lecture 3 notes (on Canvas) explain how reducible and irreducible transformations are related to each other through the similarity transformations.
- For H_2O, each atom has 3 Cartesian coordinates, so our transformation matrix[2] is 9-square.

[2] Some values in it are negative because of the cosine/sine definition of a rotation matrix for $\theta = 180°$.

  - However, we can also apply a smaller matrix to the molecule as a whole and invoke symmetry to find the position of the individual atoms.

- **Characters** (of a representation): The traces (i.e., sums of the diagonal matrix elements) of the representation matrices for each operation. *Also known as* $\boldsymbol{\chi}$.
  - The character is an invariant for each type of symmetry operation (e.g., regardless of the axis about which a C_n operation is performed, the trace of the corresponding matrix will be the same).
- Common characters:
  - C_n character: $\chi = 2\cos\theta + 1$.
  - σ_v, σ_d character: $\chi = 1$.
  - $S_2 \equiv i$ character: $\chi = -3$.
  - S_n character: $\chi = 2\cos\theta - 1$.
  - $\perp C_2$ axes character: $\chi = -1$.
- **Character table**: The collection of characters for a given irreducible representation, under the operations of a group. *Also known as* $\boldsymbol{\chi}$ **table**.

Group Symbol; Symmetry Elements

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

Irreducible Represen-tations; Characters; Basis Functions

Figure II.4: A character table.

  - Character tables for all point groups are listed in Appendix C of Miessler et al. (2014).
- **Mulliken symbols** are used to classify irreducible representations based on degeneracy and symmetry.
  - A or B: singly degenerate (the maximum block size in the block-diagonalized irreducible transformation matrix is 1×1).
  - E: Doubly degenerate (the maximum block size in the block-diagonalized irreducible transformation matrix is 2×2).
  - T: Triply degenerate (the maximum block size in the block-diagonalized irreducible transformation matrix is 3×3).
  - A: symmetric (+) with respect to C_n.
  - B: anti-symmetric (−) with respect to C_n.
  - Subscript g: symmetric (+) with respect to i. *Etymology* short for gerade (German for symmetric).
  - Subscript u: anti-symmetric (−) with respect to i. *Etymology* short for ungerade (German for unsymmetric).
    - If the molecule has a center of inversion, we label irreducible representations with g or u.
  - Subscript 1: symmetric (+) with respect to $\perp C_2$ or σ_v.
  - Subscript 2: anti-symmetric (−) with respect to $\perp C_2$ or σ_v.
  - Superscript $'$: symmetric (+) under σ_h (if no i).
  - Superscript $''$: anti-symmetric (−) under σ_h (if no i).

- Don't mistake the operation E for the Mulliken symbol E.
- To assign Mulliken symbols, use the character table.
  - Assigning the main letter:
    - If E-character $= 1$ and C_n-character $= 1$: A.
    - If E-character $= 1$ and C_n-character $= -1$: B.
    - If E-character $= 2$: E.
    - If E-character $= 3$: T.
  - Assigning a subscript g or u:
    - If i-character $= 1$: g.
    - If i-character $= -1$: u.
    - This subscript can be assigned to A, B, E, T representations.
  - Assigning a superscript $'$ or $''$:
    - If σ_h-character $= 1$: $'$.
    - If σ_h-character $= -1$: $''$.
    - This subscript can be assigned to A, B representations.
  - Assigning a subscript 1 or 2:
    - If $\perp C_2$ or σ_v-character $= 1$: 1.
    - If $\perp C_2$ or σ_v-character $= -1$: 2.
    - This subscript can be assigned to A, B representations.
- σ, π, and δ bonds come from the Mulliken symbols!
  - Infinity tables use Greek rather than Latin letters.

D_3	E	$2C_3(z)$	$3C_2'$	linear	quadratic
A_1	1	1	1		x^2+y^2, z^2
A_2	1	1	-1	z, R_z	
E	2	-1	0	$(x,y)(R_x,R_y)$	$(x^2-y^2, xy)(xz, yz)$.

Table II.3: Character table for the D_3 point group.

- In character tables, we need to multiply each symmetry operation by the number of types there are (see Table II.3).
- Basis functions show us how different functions transform under different symmetry operations.
- In the C_{2v} point group:
  - The p_x orbital has B_1 symmetry.
  - p_x transforms as B_1.
  - p_x has the same symmetry as B_1.
  - p_x forms a basis for the B_1 irreducible representation.
  - p_x is B_1 because (see Table 0.2 and Figure II.4) it does not change under E, it inverts under C_2, it does not change under $\sigma_v(xz)$, and it inverts under $\sigma_v'(yz)$ (note that the C_2 axis is the z-axis, not the x-axis).
- We can apply the same procedure to other more complex functions.
  - For example, in the C_{2v} point group, we know that (with respect to orbitals):

- p_y is B_2.
- p_z is A_1.
- d_{z^2} is A_1.
- $d_{x^2-y^2}$ is A_1.
- d_{yz} is B_2.
- d_{xy} is A_2.
- d_{xz} is B_1.
- We can even go into the cubic functions describing the f orbitals and assign them Mulliken symbols.

- Essentially, the right hand side of a character table tells you how atomic orbitals will transform under certain symmetry operations.
- Properties of a character table:
  1. The characters of all matrices belonging to the operations in the same class are identical in a given irreducible representation.
     - We most commonly form a **rotational class** and a **reflection class**.
  2. The number of irreducible representations in a group is equal to the number of classes of that group.
  3. There is always a totally symmetric representation for any group.
     - I.e., a representation where every character is 1.
  4. The sum of the squares of the **dimensionality** of all the irreducible representations is equal to the order of the group. Mathematically,

$$h = \sum_i [\chi_i(E)]^2$$

     - For example, the dimensionalities of the D_3 point group (see Table II.3) are 1, 1, and 2, and the order is, indeed, $6 = 1^2 + 1^2 + 2^2$.
  5. The sum of the squares of the characters multiplied by the number of operations in the class equals the order of the group. Mathematically,

$$h = \sum_{R_c} g_c[\chi_i(R_c)]^2$$

     - For example, with respect to the D_3 point group (see Table II.3),

$$\begin{aligned} 6 &= (1)(1)^2 + (2)(1)^2 + (3)(1)^2 \\ &= (1)(1)^2 + (2)(1)^2 + (3)(-1)^2 \\ &= (1)(2)^2 + (2)(-1)^2 + (3)(0)^2 \end{aligned}$$

  6. The sum of the products of the corresponding characters of any two different irreducible representations of the same group is zero. Mathematically,

$$\sum_{R_c} g_c \chi_i(R_c) \chi_f(R_c) = 0$$

     - Basically, this means that if we treat irreducible representations as vectors in h-space, they are orthogonal.
     - For example, with respect to the D_3 point group (see Table II.3),

$$\begin{aligned} 0 &= 1(1)(1) + 2(1)(1) + 3(1)(-1) \\ &= 1(1)(2) + 2(1)(-1) + 3(1)(0) \\ &= 1(1)(2) + 2(1)(-1) + 3(-1)(0) \end{aligned}$$

- **Dimensionality**: The character of the identity operation E. *Also known as* **dimension**.

II.6 Module 8: Using Character Tables

- A reducible representation of a group is any representation Γ of the form

$$\Gamma = \sum_i a_i \Gamma_i$$

where each Γ_i is an irreducible representation of the group and a_i is a real scalar.

  - Basically, a reducible representation is any linear combination of irreducible representations.
  - For example, with respect to the C_{2v} point group (see Figure II.4), $\Gamma = (7, 1, 5, 3) = 4A_1 + 2B_1 + B_2$ is a reducible representation.

- We may "factor" reducible representations by inspection, or by the...
- Decomposition/reduction formula for a reducible representation:

$$a_i = \frac{1}{h} \sum_Q N \cdot \chi(R)_Q \cdot \chi_i(R)_Q$$

  - a_i is the number of times the irreducible representation appears in Γ_1.
  - h is the order of the group.
  - N is the number of operations in class Q.
  - $\chi(R)_Q$ is the character of the reducible representation.
  - $\chi_i(R)_Q$ is the character of the irreducible representation.
  - This formula cannot be applied to $D_{\infty h}$ and $C_{\infty v}$.

- Let's look at decomposing $\Gamma = (7, 1, 5, 3)$ into its component irreducible point groups using the above formula.

$$\begin{aligned}
a_{A_1} &= \frac{1}{4}(1 \cdot 7 \cdot 1 + 1 \cdot 1 \cdot 1 + 1 \cdot 5 \cdot 1 + 1 \cdot 3 \cdot 1) = 4 \\
a_{A_2} &= \frac{1}{4}(1 \cdot 7 \cdot 1 + 1 \cdot 1 \cdot 1 + 1 \cdot 5 \cdot -1 + 1 \cdot 3 \cdot -1) = 0 \\
a_{B_1} &= \frac{1}{4}(1 \cdot 7 \cdot 1 + 1 \cdot 1 \cdot -1 + 1 \cdot 5 \cdot 1 + 1 \cdot 3 \cdot -1) = 2 \\
a_{B_2} &= \frac{1}{4}(1 \cdot 7 \cdot 1 + 1 \cdot 1 \cdot -1 + 1 \cdot 5 \cdot -1 + 1 \cdot 3 \cdot 1) = 1
\end{aligned}$$

- You can also find websites that will apply the formula for you.
- Basis $\to$ reducible representation $\to$ irreducible representations workflow:
  1. Assign a point group.
  2. Choose a basis function (bond, vibration, orbital, angle, etc.).
  3. Apply operations.
     - The following shortcuts allow us to skip matrix math in certain situations.
       - If the basis stays the same: $+1$.
       - If the basis is reversed: -1.
       - If it is a more complicated change: 0.
  4. Generate a reducible representation.
  5. Reduce to irreducible representation.
- We now look at an example of applying the above method to H_2O.

- H_2O is of the C_{2v} point group.
- The 9×9 identity matrix represents the identity operation on the 3 atoms in H_2O, each described by 3 Cartesian coordinates. Thus, $\chi(E) = 9$.
- The following matrix represents the C_2 symmetry operation. Thus, $\chi(C_2) = -1$.

$$\begin{array}{r} \mathrm{O}\left\{\begin{matrix}x'\\y'\\z'\end{matrix}\right.\\ \mathrm{H}_a\left\{\begin{matrix}x'\\y'\\z'\end{matrix}\right.\\ \mathrm{H}_b\left\{\begin{matrix}x'\\y'\\z'\end{matrix}\right.\end{array} = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix} \begin{array}{l}\left.\begin{matrix}x\\y\\z\end{matrix}\right\}\mathrm{O}\\ \left.\begin{matrix}x\\y\\z\end{matrix}\right\}\mathrm{H}_a\\ \left.\begin{matrix}x\\y\\z\end{matrix}\right\}\mathrm{H}_b\end{array}$$

  - ■ Note that atoms moved during the transformation do not contribute to the character of the transformation matrix.
- Since under $\sigma_v(xz)$ only O is unshifted, we need only consider its part of the transformation matrix (as follows) when looking for the character. Thus, $\chi(\sigma_v(xz)) = 1$[3].

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

- Since under $\sigma_v(yz)$ no atom is shifted, we need to consider each (identical) part of the transformation matrix (as follows) when looking for the character. Thus, $\chi(\sigma_v(yz)) = 3$.

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

- Thus, the characters of our final reducible representation is $\Gamma_{3N} = (9, -1, 1, 3)$.
  - ■ This representation represents fully unrestricted motion of all 3 ambiguities of freedom.

• Another example: $XeOF_4$.

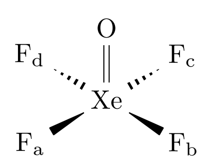


Figure II.5: $XeOF_4$.

- Point group: C_{4v}.
- Basis function: F atoms.
- Let's see what happens to the fluorine atoms under the C_{4v} operations (remember that if a basis element (a fluroine atom) stays the same, it contributes +1 to the character of an operation, and if it moves, it contributes 0 to the character).

[3]Note also that $a_{11} = 1$ since the x-vector (a basis) is unchanged under $\sigma_v(xz)$, $a_{22} = -1$ since the y-vector is reversed under $\sigma_v(xz)$, and $a_{33} = 1$ since the z vector is unchanged under $\sigma_v(xz)$.

E	all unchanged	4
C_4	all move	0
C_2	all move	0
$2\sigma_v$	2 move, 2 unchanged	2
$2\sigma_d$	all move	0

Table II.4: Changes in the fluorine atoms of $XeOF_4$ under the C_{4v} symmetry operations.

- Thus, $\Gamma = (4, 0, 0, 2, 0)$.
- With the C_{4v} character table and the decomposition formula, we can discover that $\Gamma = A_1+B_1+E$.

II.7 Nocera Lecture 3

From Nocera (2008).

1/25:

- Corresponding blocks within block-diagonalized matrices obey the same multiplication properties as the block-diagonalized matrices, themselves.
- One basis may not uncover all irreducible representations.
  - For example, we can use a Cartesian basis to uncover the A_1 and E irreducible representations of the D_3 point group (see Table II.3) and the basis function R_z ($E : R_z \to R_z$, $C_3 : R_z \to R_z$, $\sigma_v : R_z \to \bar{R}_z$) to uncover the A_2 irreducible representation.
- We can also construct a character table algebraically. Continuing with the D_3 example...
  - There is one totally symmetric representation $\Gamma_i = (1, 1, 1)$.
  - $h = 6 = \sum_i [\chi_i(E)]^2$. Since each $\chi_i(E)$ can only be 1, 2, or 3, we know that $\chi_1(E) = \chi_2(E) = 1$ and $\chi_3(E) = 2$.
  - This combines with orthogonality to reveal that

$$\begin{aligned} 0 &= \sum_{R_c} g_c \chi_1(R_c)\chi_2(R_c) \\ &= 1 \cdot 1 \cdot 1 + 2 \cdot 1 \cdot \chi_2(C_3) + 3 \cdot 1 \cdot \chi_2(\sigma_v) \\ &= 1 + 2\chi_2(C_3) + 3\chi_2(\sigma_v) \end{aligned}$$

    i.e., $\Gamma_i = (1, 1, -1)$.
  - To determine the last representation, we can use two rules and solve as a system of equations.

$$\begin{aligned} 0 &= \sum_{R_c} g_c \chi_1(R_c)\chi_3(R_c) & 6 &= \sum_{R_c} g_c [\chi_3(R_c)]^2 \\ &= 2 + 2\chi_3(C_3) + 3\chi_3(\sigma_v) & &= 4 + 2[\chi_3(C_3)]^2 + 3[\chi_3(\sigma_v)]^2 \end{aligned}$$

    From this, we can determine that $\chi_3(C_3) = -1$ and $\chi_3(\sigma_v) = 0$. Therefore, $\Gamma_i = (2, -1, 0)$.

II.8 TA Review Session 1

1/22:

- We also don't need to show the equatorial electron pair in the shape picture.
- For $SeCl_4$, we need to show that the axial bonds are longer and are not straight up and down.
- For $I_3{}^-$, it's trigonal bipyrimidal EPA and linear molecular geometry — there's an extra electron pair around the central iodine atom. This makes it $D_{\infty h}$ point group.

- For $SeOCl_4$, we should also make the axials longer and bent away from the oxygen atom.
  - This molecule is sp^3d hybridized, not sp^2d^2, as it would be if the oxygen were axial.
- For $IO(OH)_5$, we should show the equatorial OH's pushed away from the oxygen atom. The oxygen bond should also be a bit shorter.
- In the exam, they will specify whether we need to consider the hydrogens or not when calculating symmetry.
- For ${ClOF_4}^-$, one or the other of the lone pair/oxygen will push the equatorial fluorines a bit. You don't have to know witch, just show bent.
- For XeO_2F_2, show the lone pair pushing the axial fluorines away.
- For ${IF_3}^{2-}$, show that this is a *distorted* T.
- A tennis ball belongs to the D_{2d} point group since you have perpendicular C_2 axes punching through the seam and mirror planes at 45° angles to the C_2 axes (i.e., dihedral).
- ${FeF_6}^{3-}$ also loses 4 C_2 axes.
- There are three possible isomers of IF_3O_2 (see Figure I.1), but the one with equatorial oxygens is the most stable.
  - The structure analogous to Figure I.1a has C_{2v} symmetry.
  - The structure analogous to Figure I.1b has D_{3h} symmetry.
  - The structure analogous to Figure I.1c has C_s symmetry.
- Determine the point group of ${NO_3}^{2-}$, HFC=C=CHF, $H_2C{=}CF_2$, and C_2H_6 (consider three possible conformers).
  - ${NO_3}^{2-}$ is of the D_{3h} point group.
  - HFC=C=CHF is of the C_2 point group.
  - $H_2C{=}CF_2$ is of the C_{2v} point group.
  - C_2H_6 eclipsed has D_{3h} symmetry, staggered has D_{3d} symmetry, and others have D_3 symmetry.

II.9 Module 9: Molecular Vibrations

1/25:

- If you have a nonlinear triatomic molecule (like H_2O), we have 3 atoms $\times$ 3 DOF = 9 DOF.
  - This accounts for any possible perturbations of our molecules.
- We can break this down into three types of motion:
  - Translational motion along the x-, y-, and z-axes (3 DOFs).
  - Rotational motion about the x-, y-, and z-axes (3 more DOFs).
  - The remaining degrees of freedom are vibrational.
- Every *nonlinear* molecule has 3 translational and 3 rotational DOFs.
  - The number of vibrations is $3N - 6$, where N is the number of atoms.
- Every *linear* molecule has 3 translational and 2 rotational DOFs.
  - The number of vibrations is $3N - 5$, where N is the number of atoms.
- **Vibrational mode**: A perturbation of molecular structure that keeps the center of mass of the molecule in one place.

- For H_2O, there are three vibrational modes: antisymmetric stretch (one H moves away from the O as the other moves in, and then the process reverses), symmetric stretch (both H's move away from the O and then move back in), and scissoring bend (the bond angle changes).
- For molecules in general, there are these three and an additional three: wagging (in H_2O, the H's rotate out of the plane of the molecule and then back), twisting (in H_2O, both H's rotate out of the plane of the molecule, but one in one direction and one in the other), and rocking (in H_2O, both H's rotate about the O within the plane of the molecule preserving the bond angle, and then go back).
- What vibrational modes a molecule can and cannot have is governed by its point group and group theory.
- Each normal mode of vibration forms a basis for an irreducible representation of the point group of the molecule.
- Workflow to identify the vibrational properties of a molecule:
  1. Find number/symmetry of vibrational modes.
  2. Assign the symmetry of known vibrations.
  3. What does the vibration look like?
  4. Find if a vibrational mode is IR or Raman Active.
- To find vibrational modes, follow the 5-step Basis $\rightarrow$ reducible representation $\rightarrow$ irreducible representation workflow and then subtract translational and rotational motion.
  - For example, with H_2O, as before, we have C_{2v} point group, $3N$ basis, $\Gamma_{3N} = (9, -1, 1, 3)$, and $\Gamma_{3N} = 3A_1 + A_2 + 2B_1 + 3B_2$.
  - We now need to use the basis functions in the C_{2v} character table to determine the translational and rotational degrees of freedom. From Figure II.4, the x, y, z-translational modes come from the B_1, B_2, and A_1 Γ_i's, respectively. Thus, the total translational mode, sufficient to describe all possible translations in 3 DOFs, is trans $= A_1 + B_1 + B_2$. Similarly, we can determine that the total rotational mode is rot $= A_2 + B_1 + B_2$.
  - Thus, we can determine that the total vibrational mode is $\Gamma_{3N} - \text{trans} - \text{rot} = 2A_1 + B_2$.
  - When H_2O scissors or symmetrically stretches, it maintains its C_{2v} symmetry. Thus, both of these vibrations are represented by the totally symmetric irreducible representation A_1 (hence the $2A_1$ component).
  - As to asymmetric stretch, there exist points in time where H_2O lowers its symmetry from C_{2v} to C_s, losing its C_2 and $\sigma_v(xz)$ symmetry elements but maintaining E and $\sigma_v(yz)$. This shift is encapsulated by the B_2 irreducible representation.
  - We can see all of these modes in H_2O's infrared absorption spectrum.
    - Note that this spectrum does not tell us the energy of vibrations (we can model this with quantum mechanics), or if it is IR or Raman active (which modes will appear in the respective spectrum).
- Determine the number and symmetry types for the translations, vibrations, and rotations of PF_5.
  - Point group: D_{3h}.
  - We could write out all 18 x, y, z-vectors, or we can use a shortcut: To construct Γ_{3N}, we can, for each symmetry element, multiply the number of atoms atoms unmoved under the operation by the corresponding character the representation that accounts for x, y, z-movements.

$$\Gamma_{3N} = (\Gamma_{x,y,z}) \cdot (\#\text{ unmoved atoms})$$

  Applying this shortcut, we have $\Gamma_{x,y,z} = E' + A_2'' = (3, 0, -1, 1, -2, 1)$. We also have # unmoved atoms $= (6, 3, 2, 4, 1, 4)$. Thus, $\Gamma_{3N} = (18, 0, -2, 4, -2, 4)$.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_c$	$3\sigma_v$	linear	quadratic
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x,y)	(x^2-y^2, xy)
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

Table II.5: Character table for the D_{3h} point group.

- We can now reduce it into $\Gamma_{3N} = 2A_1' + A_2' + 4E' + 3A_2'' + 2E''$.
  - Note that we still have our 18 degrees of freedom because each E is double degenerate, meaning that $4E'$ counts for 8 degrees of freedom and $2E''$ counts for 4 degrees of freedom.
- This combined with the fact that $\Gamma_{\text{trans}} = \Gamma_{x,y,z} = E' + A_2''$ and $\Gamma_{\text{rot}} = A_2' + E''$ implies that $\Gamma_{\text{vibs}} = 2A_1' + 3E' + 2A_2'' + E''$.
  - For a similar reason to the note above, we can count $12 = 3N - 6$ degrees of freedom (vibrational modes) in Γ_{vibs}.
- Although degenerate modes count for multiple DOFs, the multiple modes they count for are of the same type.
  - In an ideal world, those modes corresponding to E would be twice as intense as the others.
  - From the definition of Γ_{vibs} and the above discussion, we know that PF_5 has $2+3+2+1=8$ distinct vibrational modes.

- There are (broadly) two types of vibrations: **stretches** (ν) and **bends** (δ).
  - These two types appear in different energies in IR and Raman spectra.
- To differentiate between stretching and bending modes: Look at how the stretching modes transform. Each stretch happens along a single vector from central atom to ligand. Thus, if we let these vectors be our basis and look at how many vectors stay the same (+1) or change (−1) under each operation, we will have a reducible representation that can be decomposed. Its components will be the stretching modes and $\Gamma_{\text{vibs}} - \Gamma_\nu$ will equal Γ_δ.
  - Applied to PF_5, we have $\Gamma_\nu = (5,2,1,3,0,3) = 2A_1' + E' + A_2''$.
  - Thus, both A_1' representations, one E' representation, and one A_2'' representation correspond to stretching modes (or [spectroscopic] bands; note that the E' band will be twice as large). Consequently, the other two E' representations, the other A_2'' representation, and the E'' representation correspond to bending modes.

II.10 Module 10: IR and Raman Active Vibrations (part 1)

- Today, we will learn what we need to know for PSet 2. Wednesday, we will introduce a more rigorous, quantum mechanical foundation.
- Molecular vibrations can be experimentally observed by **infrared spectroscopy** or **Raman spectroscopy**.
- **Infrared spectroscopy**: A method of measuring the change in dipole moment during a vibration[4]. *Also known as* **IR spectroscopy**.

[4]Refer to Labalme (2020a), specifically the discussion of spectroscopy in Chapter 13.

- **Raman spectroscopy**: A method of measuring the change in the polarizability during a vibration. We impinge upon a sample of a substance with an incident light (a powerful laser). Most of the light that scatters will be a **Raleigh scatter**, but some will be a **Raman scatter** (a new wavelength).
- **Raleigh scatter**: The same wavelength is emitted as was impinged by the incident light because the laser was elastically scattered. The electrons fell the same number of energy levels that they rose after absorbing the light.
- **Raman scatter**: A new wavelength is emitted, different than the one impinged by the incident light. The electrons fell fewer (**Stokes Raman scattering**) or more (**Anti-Stokes Raman scattering**) energy levels than they rose after absorbing the light.
- **IR active** (vibration): A vibration that transforms with the same symmetry as the $\vec{x}$, $\vec{y}$, and $\vec{z}$ vectors (see the χ tables).
- **Raman active** (vibration): A vibration having the same symmetry as the quadratic x, y, z terms, i.e., x^2, z^2, yz, etc.
- For molecules possessing inversion centers, IR and Raman activity will be mutually exclusive.
- Activity data comes from character tables.
  - All vibration representations that have a linear term are IR active, while those that have a quadratic term are Raman active.
- Continuing with the PF_5 example...
  - Table II.5 tells us that E' and A_2'' vibrations are IR active, and A_1', E', and E'' are Raman active.
  - Thus, since $\Gamma_{\text{vibs}} = 2A_1' + 3E' + 2A_2'' + E''$, there are $3 + 2 = 5$ IR active bonds (corresponding to $3 \cdot 2 + 2 = 8$ vibrations) and $2 + 3 + 1 = 6$ Raman active bonds (corresponding to $2 + 3 \cdot 2 + 1 \cdot 2 = 10$ vibrations).

II.11 Chapter 4: Symmetry and Group Theory

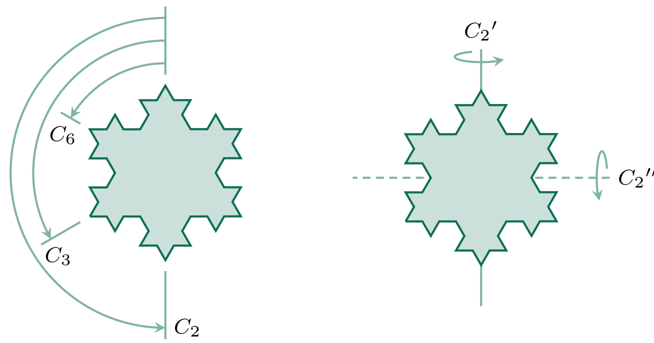
From Miessler et al. (2014).

1/18:

- **Coincident** (axes): Two identical axes.
  - For example, the C_3 rotation axis of $CHCl_3$ is **coincident** with the C−H bond axis.
- Snowflakes, which are often planar and have hexagonal symmetry, have a twofold (C_2), threefold (C_3), and sixfold (C_6) axis through their center and perpendicular to their plane (see Figure II.6).
  - Rotations ${C_3}^2$ and ${C_6}^5$ are also symmetry operations.
- "When necessary, the C_2 axes perpendicular to the principal axis are designated with primes; a single prime (${C_2}'$) indicates that the axis passes through several atoms of the molecule, whereas a double prime (${C_2}''$) indicates that it passes between the outer atoms" (Miessler et al., 2014, p. 77).

1/19:

- Even though $S_2 \equiv i$ and $S_1 \equiv \sigma$, the i and σ notations are preferred because of the group theory requirement of maximizing the number of unique classes of symmetry operations associated with a molecule.
- **Point group**: A set of symmetry operations that describes a molecule's overall symmetry.
- Alternative steps for assigning point groups:
  1. Determine whether the molecule exhibits very low symmetry (C_1, C_s, C_i) or high symmetry (T_d, O_h, $C_{\infty v}$, $D_{\infty h}$, I_h).



(a) About the principal axis. (b) About perpendicular axes.

Figure II.6: Rotations of a snowflake design.

2. If not, find the highest order C_n axis for the molecule.
3. Does the molecule have any C_2 axes perpendicular to the principal C_n axis? If it does, there will be n of such C_2 axes, and the molecule is in the D set of groups. If not, it is in the C or S set.
4. Does the molecule have a mirror plane (σ_h) perpendicular to the principal C_n axis? If so, it is classified as C_{nh} or D_{nh}. If not, continue with Step 5.
5. Does the molecule have any mirror planes that contain the principal C_n axis (σ_v or σ_d)? If so, it is classified as C_{nv} or D_{nd}. If not, but it is in the D set, it is classified as D_n. If the molecule is in the C or S set, continue with Step 6.
6. Is there an S_{2n} axis collinear with the principal C_n axis? If so, it is classified as S_{2n}. If not, the molecule is classified as C_n.

- Groups of high symmetry:
  - $C_{\infty v}$ (linear): These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They do not have a center of inversion.
  - $D_{\infty h}$ (linear): These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They also have perpendicular C_2 axes, a perpendicular reflection plane, and an inversion center.
  - T_d (tetrahedral): Most (but not all) molecules in this point group have the familiar tetrahedral geometry. They have four C_3 axes, three C_2 axes, three S_4 axes, and six σ_d planes. They have no C_4 axes.
    - Look for C_3 and C_2 axes.
  - O_h (octahedral): These molecules include those of octahedral structure, although some other geometrical forms, such as the cube, share the same set of symmetry operations. Among their 48 symmetry operations are four C_3 rotations, three C_4 rotations, and an inversion.
    - Look for C_4, C_3, and C_2 axes.
  - I_h (icosahedral): Icosahedral structures are best recognized by their six C_5 axes, as well as many other symmetry operations — 120 in all.
    - Look for C_5, C_3, and C_2 axes.
  - T_h: Adds i to T_d. Example: $W[N(CH_3)_2]_6$.

1/24:

- When we have a block-diagonalized reducible representation, the irreducible representations can be obtained from the individual blocks.
  - This is because we will find that an analogous set of blocks satisfies the multiplication table for the group.

- For the C_{2v} point group, we have the following reducible representation that can be applied to each coordinate.

$$E:\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}\qquad C_2:\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix}\qquad \sigma_v(xz):\begin{bmatrix}1&0&\\0&-1&0\\0&0&1\end{bmatrix}\qquad \sigma_v(yz):\begin{bmatrix}-1&0&0\\0&1&0\\0&0&1\end{bmatrix}$$

  - The above matrices are block diagonalized. Thus, the sets of a_{11}, a_{22} and a_{33} form three irreducible representations (and we can confirm that these obey the C_{2v} group multiplication table).

$$\begin{array}{llll} E:\begin{bmatrix}1\end{bmatrix} & C_2:\begin{bmatrix}-1\end{bmatrix} & \sigma_v(xz):\begin{bmatrix}1\end{bmatrix} & \sigma_v(yz):\begin{bmatrix}-1\end{bmatrix}\\ E:\begin{bmatrix}1\end{bmatrix} & C_2:\begin{bmatrix}-1\end{bmatrix} & \sigma_v(xz):\begin{bmatrix}-1\end{bmatrix} & \sigma_v(yz):\begin{bmatrix}1\end{bmatrix}\\ E:\begin{bmatrix}1\end{bmatrix} & C_2:\begin{bmatrix}1\end{bmatrix} & \sigma_v(xz):\begin{bmatrix}1\end{bmatrix} & \sigma_v(yz):\begin{bmatrix}1\end{bmatrix} \end{array}$$

  - Three of the C_{2v} irreducible representations can be found in this way. The fourth can be found w/ linear algebra and the character table properties (or by inspection).
- If one matrix in the reducible representation cannot be blocked past having a 2×2 chunk, per se, then the others must also have that 2×2 chunk (so that we have an irreducible 2×2 representation).
- "Matching the symmetry operations of a molecule with those listed in the top row of the character table will confirm any point group assignment" (Miessler et al., 2014, p. 99).
- **Symmetric**: Character of 1.
- **Antisymmetric**: Character of -1.
- Mulliken symbol rules:
  1. "Letters are assigned according to the dimension of the irreducible representation" (Miessler et al., 2014, p. 99).
     - Assign A if the dimension is 1 and the representation is symmetric to the principal rotation operation ($\chi(C_n)=1$).
     - Assign B if the dimension is 1 and the representation is antisymmetric to the principal rotation operation ($\chi(C_n)=-1$), or if $\chi(S_{2n})=-1$ even if $\chi(C_n)=1$.
     - Assign E if the dimension is 2.
     - Assign T if the dimension is 3.
  2. "Subscript 1 designates a representation symmetric to a C_2 rotation perpendicular to the principal axis, and subscript 2 designates a representation antisymmetric to the C_2. If there are no perpendicular C_2 axes, 1 designates a representation symmetric to a vertical plane, and 2 designates a representation antisymmetric to a vertical plane" (Miessler et al., 2014, p. 100).
  3. "Subscript g designates representations symmetric to inversion, and subscript u designates representations antisymmetric to inversion" (Miessler et al., 2014, p. 100).
  4. "Single primes are symmetric to σ_h and double primes are antisymmetric to σ_h when a distinction between representations is needed (C_{3h}, C_{5h}, D_{3h}, D_{5h})" (Miessler et al., 2014, p. 100).

1/26:

- **Chiral** (molecule): A molecule that is not superimposable on its mirror image. *Also known as* **dissymmetric**.
  - "In general, a molecule or object is chiral if it has no symmetry operations (other than E), or if it has only proper rotation axes" (Miessler et al., 2014, p. 100).
- Raman spectroscopy makes use of higher energy radiation than IR, exciting molecules to higher electronic states that are envisioned as short-lived "virtual" states.

Topic III

Introduction to Structure and Bonding

III.1 Module 11: Quantum Chemistry 101

1/27:
- We will have a normal class on Friday and hold review sessions at different times where we can ask questions.
- Suggested readings: Nocera Lecture 6, Nocera Lecture 7, MIT OCW quantum mechanics[1].
- In chemistry, most problems are solved with the time-independent Schrödinger equation $\hat{H}\Psi = E\Psi$.
  - Ψ is the wavefunction; it contains information on movement of the electron and its position.
  - $|\Psi(x,y,z)|^2 \propto P(x,y,z)$.
  - E is an eigenvalue of $\hat{H}$.
- If we are working with the time-dependent Schrödinger equation, we have another variable besides x, y, z, namely t. This allows us to calculate the probability that an electron is in a certain position at a given time.
- The Hamiltonian operator $\hat{H} = \hat{T} + \hat{V}$ describes the total energy.
  - $\hat{T}$ is the kinetic energy operator. $\hat{T} = \frac{\hat{p}^2}{2m}$, where $\hat{p}_x = -i\hbar\frac{\mathrm{d}}{\mathrm{d}x}$ is the momentum operator.
  - $\hat{V}$ is the potential energy operator. It typically describes the Coulombic attraction between the nucleus and the electron, which is approximately $\frac{1}{r}$ where r is the distance from the nucleus to the electron.
- For a free electron in one dimension, the Schrödinger equation reduces to

$$
\begin{aligned}
-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} &= E\Psi \\
\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} &= -\frac{2mE}{\hbar^2}\Psi
\end{aligned}
$$

- Dirac's bra-ket notation $\langle\Psi|A|\Psi\rangle \equiv \int_V \Psi^*\hat{H}\Psi\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$.
  - The **bra vector** (the first term inside the brackets) and **ket vector** (the last term inside the brackets) correspond to complex conjugates of the wave function.

[1] Many chemistry courses go too deep into the math and physics of quantum mechanics, which obfuscates the chemistry and confuses us in Dr. Talapin's opinion.

- **LCAO method**: A way of finding the wavefunction of a molecule; of solving the Schrödinger equation after applying simplifications. Short for linear combination of atomic wavefunctions, i.e., the atomic orbitals ϕ.

$$\Psi = \sum_i c_i \phi_i$$

  - Each c_i is a coefficient, and the atomic orbitals form the basis set.
  - Basically, we think of the wave function of a molecule as a linear combination of its atomic orbitals.
  - ϕ is normalized, thus $\int \phi_i^2 \, \mathrm{d}\tau = 1$ where $\mathrm{d}\tau = \partial x \, \partial y \, \partial z$.
  - Continuing, we can calculate the expected value of $\hat{H}$:

$$E = \frac{\int \Psi \hat{H} \Psi \, \mathrm{d}\tau}{\int \Psi^2 \, \mathrm{d}\tau}$$

  - Shortcomings: Does not count for electron correlation and a few other things.

- Electronic structure of H_2 molecule.
  - H_2's structure is H−H.
  - $\Psi = a\phi_1 + b\phi_2$, where $\phi_{1,2}$ are two atomic hydrogen $1s$ orbitals.
  - The electron density function is: $\phi^2 = a^2\phi_1^2 + b^2\phi_2^2 + 2ab\phi_1\phi_2$.
  - By symmetry of H−H molecule, $a = \pm b$.
    - Symmetry of the coefficients should reflect symmetry of the atoms.
    - Hydrogen atoms are indistinguishable, so since the electron can't identify which atom it corresponds to, the math shouldn't either.
  - If $S = \int_\tau \phi_1\phi_2 \, \mathrm{d}\tau$ or $\langle \phi_1 | \phi_2 \rangle$ is the overlap integral between two hydrogen $1s$ orbitals, we have bonding and antibonding orbitals:

$$\Psi_b = \frac{1}{\sqrt{2(1+s)}}(\phi_1 + \phi_2) \qquad \Psi_a = \frac{1}{\sqrt{2(1-s)}}(\phi_1 - \phi_2)$$

    - The first orbital is σ_g bonding.
    - The second orbital is σ_u^* antibonding.
    - Introducing the normalizing requirement gives us the above coefficients.
  - In the Hückel theory:

$$\alpha = \langle \phi_1 | \hat{H}_{\text{eff}} | \phi_1 \rangle = \langle \phi_2 | \hat{H}_{\text{eff}} | \phi_2 \rangle \qquad \beta = \langle \phi_1 | \hat{H}_{\text{eff}} | \phi_2 \rangle$$

    - If we calculate the expectation integrals, we will arrive at the above.
    - $\hat{H}_{\text{eff}}$ is some effective Hamiltonian.
    - The α integral is the **Coulomb integral**.
    - The β integral is the **interaction integral**.
  - In the **Hückel approximation** (the simplest approximation of quantum mechanics), we define integrals as parameters that we can extract from empirical data:
    - $H_{ii} = \alpha$.
    - $H_{ij} = 0$ for ϕ_i not adjacent to ϕ_j.
    - $H_{ij} = \beta$ for ϕ_i adjacent to ϕ_j.
    - $S_{ii} = 1$.
    - $S_{ij} = 0$.

- Expectation values for energy are

$$E_{a,b} = \frac{\langle \Psi_{a,b} | \hat{H}_{\text{eff}} | \Psi_{a,b} \rangle}{\langle \Psi_{a,b} | \Psi_{a,b} \rangle}$$

so

$$E_a = \frac{\alpha - \beta}{1 - s} \qquad E_b = \frac{\alpha + \beta}{1 + s}$$

  - Note that $\beta < 0$ for atomic s-orbitals and $\beta > 0$ for p-orbitals in σ-bonds.
  - Also, in the Hückel one-electron model, the integrals α and β remain unsolved.
- Note: As always, the bonding orbitals are less stabilized than the antibonding orbitals are destabilized.
  - This is a consequence of overlap, e.g., for a dimer, the $1 \pm S$ term in $E_{+/-} = \frac{\alpha \pm \beta}{1 \pm S}$.
  - This is why He_2 does not exist.

- **Overlap integral**: An integral proportional to the degree of spatial overlap between two orbitals. It is the product of wave functions centered on different lattice sites. Varies from 0 (no overlap) to 1 (perfect overlap). *Also known as* $\boldsymbol{S}$.
- **Coulomb integral**: An integral giving the kinetic and potential energy of an electron in an atomic orbital experiencing interactions with all the other electrons and all the positive nuclei. *Also known as* $\boldsymbol{\alpha}$.
- **Interaction integral** (on two orbitals 1,2): An integral giving the energy of an electron in the region of space where orbitals 1 and 2 overlap. The value is finite for orbitals on adjacent atoms, and assumed to be zero otherwise. *Also known as* $\boldsymbol{\beta_{12}}$, **resonance integral**, **exchange integral**.
- Symmetry and quantum mechanics:
  - Say we have $\hat{H}\Psi = E\Psi$ where $\hat{H}$ is the Hamiltonian and R is a symmetry operator (e.g., C_2 or σ_v).
  - Note that the Hamiltonian commutes with the symmetry operator: $R\hat{H} = \hat{H}R$.
  - Since a symmetry operation does not change the energy of a molecule (it just moves it), $\hat{H}R\Psi_i = E_iR\Psi_i$.
  - It follows that R does not change the form of the wave function, i.e., $R\Psi_i = \pm 1\Psi_i$. This reflects the fact that R cannot change the probability $P[e(x,y,z)] = |\Psi(x,y,z)|^2$ of finding an electron somewhere.
  - Thus, the eigenfunctions of the Schrödinger equation generate a representation of the group.
  - Non-degenerate wave functions are A or B type.
  - Double-degenerate wave functions are E type.
  - Triple-degenerate wave functions are T type.
- Back to the LCAO method:

$$E_i = \frac{\int \Psi_i^* H \Psi_i \, \mathrm{d}V}{\int \Psi_i^* \Psi_i \, \mathrm{d}V} \qquad \Psi_i = \sum_i c_i \phi_i$$

  - If we have a sizeable molecule with a couple dozen atoms, every molecular orbital (wave function) will be the sum of a couple dozen atomic orbitals.
  - This generates a set of i linear homogenous equations, numbering in the hundreds or thousands that need to be solved.
  - This is clearly too computationally expensive, so we need a trick.

- An example where symmetry arguments help a lot:
  - If f is odd ($f(x) = -f(-x)$), then we know that $\int_{-\infty}^{\infty} f(x)\,\mathrm{d}x = 0$.
- Group theory allows us to generalize this method to broader symmetry operations.
- Three important theorems:
  1. The characters of the representation of a direct product are equal to the products of the characters of the representations based on the individual sets of functions.
     - For example, in the T_d point group, $T_1 = (3, 0, -1, 1, -1)$, and $T_2 = (3, 0, -1, -1, 1)$. By the theorem, $T_1 \times T_2 = (9, 0, 1, -1, -1)$.
  2. A representation of a direct product, $\Gamma_c = \Gamma_a \times \Gamma_b$, will contain the totally symmetric representation only if the irreducible representations of a and b contain at least one common irreducible representation.
     - Continuing with the above example, $T_1 \times T_2$ can be decomposed into $A_2 + E + T_1 + T_2$. Thus, by this theorem, if we take the product $\Gamma_c = E \times T_1 \times T_2$, the representation will contain the totally symmetric representation A_1 (since $\Gamma_b = E$ and $\Gamma_a = T_1 \times T_2$ contains E). Indeed, $E \times T_1 \times T_2 = (18, 0, 2, 0, 0)$.
  3. The value of any integral relating to a molecule $\int_V \Psi\,\mathrm{d}\tau$ will be zero unless the integrand is invariant under all operations of the symmetry point group to which the molecule belongs. That is Γ_Ψ must contain the totally symmetric irreducible representation.
     - This example will concern the D_{4d} point group. We want to evaluate the integral $\int_V \Psi_a \mu_z \Psi_b\,\mathrm{d}\tau$ where $\Gamma_{\Psi_a} = A_1$, $\Gamma_{\mu_z} = B_2$, and $\Gamma_{\Psi_b} = E_1$.
     - By Theorem 1, we can easily determine the representation $\Psi_a \times \mu_z$. We can then decompose it.
     - Noting that it does not contain the E_1 irreducible representation (the only representation in Ψ_b), we can learn from Theorem 2 that $\Psi_a \mu_z \Psi_b$ does not contain the A_1 irreducible representation.
     - Therefore, by Theorem 3, $\int_V \Psi\,\mathrm{d}\tau = \int_V \Psi_a \mu_z \Psi_b\,\mathrm{d}\tau = 0$.
- We use these three theorems to tell us what integrals will be zero in a much less computationally intensive fashion. We can then evaluate the remaining nonzero integrals.
- We can take direct products by hand, but there are also tables of direct products of irreducible representations.

III.2 Module 12: IR and Raman Active Vibrations (part 2)

- **Fermi's golden rule**: The rate of an optical transition from a single initial state to a final state is given by the transition rate for a single state.

$$\Gamma_{i \to f} = \frac{2\pi}{\hbar} E_0^2 |\langle f|H'|i\rangle|^2 \delta(E_f - E_i - h\nu)$$

  - By state, we typically mean energy level.
  - The transition rate is the probability of a transition happening.
  - If it's an optical transition, conservation of energy implies that the energy difference between the initial and final state will equal the energy of the photon that the molecule absorbs or emits.
  - E_0^2 is the light intensity.
  - $h\nu$ is the photon energy.
  - $\langle f|H'|i\rangle = \int \Psi_f^* H' \Psi_i\,\mathrm{d}\tau$ is the square of the matrix element (the strength of the coupling between the states).

  - $\delta(E_f - E_i - h\nu)$ is the resonance condition (energy conservation).
  - In the dipole approximation, $H' = -e\vec{r} \cdot \vec{E}$.
  - This is derived with time-dependent perturbation theory.
    - The matrix element $M = \langle f|H'|i\rangle = \int \Psi_f^*(\vec{r})H'\Psi_i(\vec{r})\,\mathrm{d}^3\vec{r}$.
    - Perturbation: $H' = -\vec{p}_e \cdot \vec{E}_{\text{photon}}$. Dipole moment: $\vec{p}_e = -e\vec{r}$. Light wave: $\vec{E}_{\text{photon}}(r) = \vec{E}_0 \mathrm{e}^{\pm i\vec{k}\cdot\vec{r}}$, $H'(\vec{r}) = e\vec{E}_0 \cdot \vec{r}\mathrm{e}^{\pm i\vec{k}\cdot\vec{r}}$.
    - This implies that in one dimension, $|M| \propto \int \Psi_f^*(\vec{r})x\Psi_i(\vec{r})\,\mathrm{d}^3\vec{r}$.
    - We include other variables in higher dimensions.

- For IR absorption, the intensity I satisfies $I \propto \int \Psi_{\text{e.s.}}\hat{\mu}_e\Psi_{\text{g.s.}}\,\mathrm{d}\tau$.
  - $\Psi_{\text{e.s.}}$ is the excited state wavefunction, $\Psi_{\text{g.s.}}$ is the ground state wavefunction, and $\hat{\mu}_e$ is the dipole operator.
  - We now apply the three theorems:
  - It is always true in vibration spectroscopy that $\Gamma_{\text{g.s.}} = A_1$. This is because in the ground state, the molecule is completely relaxed (nothing is perturbed).
  - Thus, we can already reduce to $\Gamma_{\text{e.s.}} \cdot \Gamma_\mu \cdot \Gamma_{\text{g.s.}} = \Gamma_{\text{e.s.}} \cdot \Gamma_\mu \cdot 1$.
  - Now Γ_μ transforms as x, y, z unit vectors. In D_{3h}, this implies that $\Gamma_\mu = E' + A_2''$.
  - Therefore, $I \propto \Gamma_{\text{vibs}} \cdot (E' + A_2'')$.
  - For PF_5, since $\Gamma_{\text{vibs}} = 2A_1' + 3E' + 2A_2'' + E''$ has E' and A_2'' in common with Γ_μ, only $3E'$ and $2A_2''$ are IR active.
    - Additionally, with elements in common, $\Gamma_{\text{vibs}} \cdot \Gamma_\mu$ will contain A_1 by Theorem 2, and thus, the integrals $\int \Psi_{\text{e.s.}}x\Psi_{\text{g.s.}}\,\mathrm{d}\tau$, $\int \Psi_{\text{e.s.}}y\Psi_{\text{g.s.}}\,\mathrm{d}\tau$, and $\int \Psi_{\text{e.s.}}z\Psi_{\text{g.s.}}\,\mathrm{d}\tau$ are all nonzero. Some linear combination of them will be proportional to I.

- The exam will include material from today's class, but not Friday's class.
- PSets 1 and 2 will cover all material on the exam?

III.3 Nocera Lecture 6

From Nocera (2008).

1/29:
- Solving the Schrödinger equation with the LCAO method for the kth molecular orbital Ψ_k:

$$\begin{aligned}
\hat{H}\Psi_k &= E\Psi_k \\
|\,\hat{H} - E\,|\,\Psi_k\rangle &= 0 \\
|\,\hat{H} - E\,|\,c_a\phi_a + c_b\phi_b + \cdots + c_i\phi_i\rangle &= 0
\end{aligned}$$

  - Left-multiplying the above by each ϕ_i yields a set of i linear homogenous equations.

$$\begin{aligned}
c_a\langle\phi_a|\hat{H} - E|\phi_a\rangle + c_b\langle\phi_a|\hat{H} - E|\phi_b\rangle + \cdots + c_i\langle\phi_a|\hat{H} - E|\phi_i\rangle &= 0 \\
c_a\langle\phi_b|\hat{H} - E|\phi_a\rangle + c_b\langle\phi_b|\hat{H} - E|\phi_b\rangle + \cdots + c_i\langle\phi_b|\hat{H} - E|\phi_i\rangle &= 0 \\
&\vdots \\
c_a\langle\phi_i|\hat{H} - E|\phi_a\rangle + c_b\langle\phi_i|\hat{H} - E|\phi_b\rangle + \cdots + c_i\langle\phi_i|\hat{H} - E|\phi_i\rangle &= 0
\end{aligned}$$

- We can then solve the **secular determinant**,

$$\begin{vmatrix} H_{aa}-ES_{aa} & H_{ab}-ES_{ab} & \cdots & H_{ai}-ES_{ai} \\ H_{ba}-ES_{ba} & H_{bb}-ES_{bb} & \cdots & H_{bi}-ES_{bi} \\ \vdots & \vdots & \ddots & \vdots \\ H_{ia}-ES_{ia} & H_{ib}-ES_{ib} & \cdots & H_{ii}-ES_{ii} \end{vmatrix} = 0$$

  where $H_{ij} = \int \phi_i \hat{H} \phi_j \, \mathrm{d}\tau$ and $S_{ij} = \int \phi_i \phi_j \, \mathrm{d}\tau$.
- To evaluate these integrals, see the notes in Module 11 concerning the Hückel approximation.

- **Extended Hückel theory**: An alternate integral approximation method that includes all valence orbitals in the basis (as opposed to just the highest energy atomic orbitals), calculates all S_{ij}s, estimates the H_{ii}s from spectroscopic data (as opposed to a constant α), and estimates H_{ij}s from a simple function of S_{ii}, H_{ii}, and H_{ij}. This is a zero differential overlap approximation. *Also known as* **EHT**.
  - A **semi-empirical** method.

- **Semi-empirical** (method): A method that relies on experimental data for the quantification of parameters.

- Other semi-empirical methods include CNDO, MINDO, and INDO.

- Hückel's method and LCAO example: Examine the frontier orbitals and their associated energies (i.e., determine eigenfunctions and eigenvalues, respectively) of benzene.
  - We assume that the frontier MO's will be composed of LCAO of the $2p\pi$ orbitals.
  - Using orbitals as our basis and noting that benzene is of the D_{6h} point group, we can determine that $\Gamma_{p\pi} = (6,0,0,0,-2,0,0,0,0,-6,2,0)$.
  - Using the decomposition formula, we can reduce $\Gamma_{p\pi}$ into $\Gamma_{p\pi} = A_{2u} + B_{2g} + E_{1g} + E_{2u}$. These are the symmetries of the MO's formed by the LCAO of $p\pi$ orbitals in benzene.
  - With symmetries established, LCAOs may be constructed by "projecting out" the appropriate linear combination with the following projection operator, which determines the linear combination of the ith irreducible representation.

$$P^{(i)} = \frac{\ell_i}{h} \sum_R [\chi^{(i)}(R)] \cdot R$$

    - ℓ_i is the dimension of Γ_i.
    - h is the order.
    - $\chi^{(i)}(R)$ is the character of Γ_i under operation R.
    - R is the corresponding operator.
  - To actually apply the above projection operator, we will drop to the C_6 subgroup of D_{6h} to simplify calculations. The full extent of mixing among ϕ_1-ϕ_6 is maintained within this subgroup, but the inversion centers are lost, meaning that in the final analysis, the Γ_is in C_6 will have to be correlated to those in D_{6h}.
  - In C_6, we have $\Gamma_{p\pi} = (6,0,0,0,0,0) = A + B + E_1 + E_2$.
  - The projection of the Symmetry Adapted Linear Combination (SALC) that from ϕ_1 transforms as A is

$$\begin{aligned} P^{(A)}\phi_1 &= \frac{1}{6}[1E + 1C_6 + 1{C_6}^2 + 1{C_6}^3 + 1{C_6}^4 + 1{C_6}^5]\phi_1 \\ &= \frac{1}{6}[E\phi_1 + C_6\phi_1 + {C_6}^2\phi_1 + {C_6}^3\phi_1 + {C_6}^4\phi_1 + {C_6}^5\phi_1] \\ &= \frac{1}{6}[\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6] \\ &\cong \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6 \end{aligned}$$

where we make the last congruency (dropping the constant) because the LCAO will be normalized, which will change the constant, regardless.

– With a similar process, we can find that

$$\begin{aligned}
P^{(B)}\phi_1 &= \phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6 \\
P^{(E_{1a})}\phi_1 &= \phi_1 + \varepsilon\phi_2 - \varepsilon^*\phi_3 - \phi_4 - \varepsilon\phi_5 + \varepsilon^*\phi_6 \\
P^{(E_{1b})}\phi_1 &= \phi_1 + \varepsilon^*\phi_2 - \varepsilon\phi_3 - \phi_4 - \varepsilon^*\phi_5 + \varepsilon\phi_6 \\
P^{(E_{2a})}\phi_1 &= \phi_1 - \varepsilon^*\phi_2 - \varepsilon\phi_3 + \phi_4 - \varepsilon^*\phi_5 + \varepsilon\phi_6 \\
P^{(E_{2b})}\phi_1 &= \phi_1 - \varepsilon^*\phi_2 - \varepsilon^*\phi_3 + \phi_4 - \varepsilon\phi_5 - \varepsilon^*\phi_6
\end{aligned}$$

– Since some of the projections contain imaginary components, we can obtain real components by taking $\pm$ linear combinations and noting that $\varepsilon = \mathrm{e}^{2\pi i/6}$ in the C_6 point group.

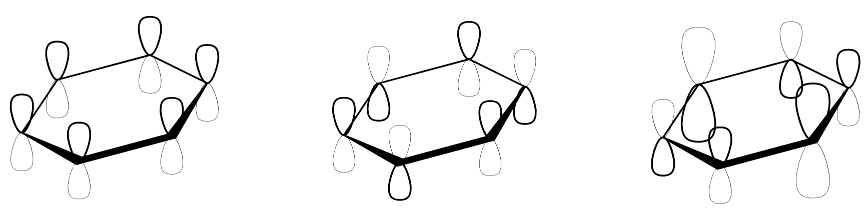
$$\begin{aligned}
\Psi_3(E_1) &= \Psi_3'(E_{1a}) + \Psi_4'(E_{1b}) = 2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6 \\
\Psi_4(E_1) &= \Psi_3'(E_{1a}) - \Psi_4'(E_{1b}) = \phi_2 + \phi_3 - \phi_5 - \phi_6 \\
\Psi_5(E_2) &= \Psi_5'(E_{2a}) + \Psi_6'(E_{2b}) = 2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 + \phi_6 \\
\Psi_6(E_2) &= \Psi_5'(E_{2a}) - \Psi_6'(E_{2b}) = \phi_2 - \phi_3 + \phi_5 - \phi_6
\end{aligned}$$

– We can now normalize: If $\Psi_i = \sum_j c_j\phi_j$ where $\gcd(c_1, \dots, c_n) = 1$, the normalizing constant is

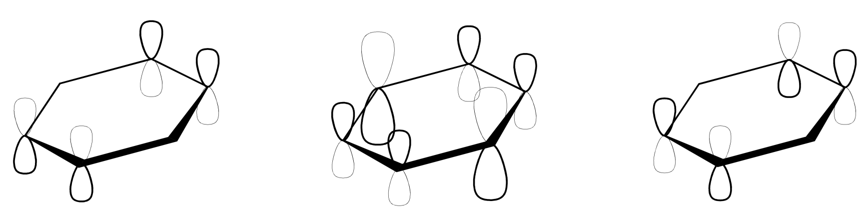
$$N = \frac{1}{\sqrt{\sum_j c_j^2}}$$

meaning that

$$\begin{aligned}
\Psi_1(A) &= \frac{1}{\sqrt{6}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) & \Psi_2(B) &= \frac{1}{\sqrt{6}}(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6) \\
\Psi_3(E_1) &= \frac{1}{\sqrt{12}}(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6) & \Psi_4(E_1) &= \frac{1}{2}(\phi_2 + \phi_3 - \phi_5 - \phi_6) \\
\Psi_5(E_2) &= \frac{1}{\sqrt{12}}(2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 + \phi_6) & \Psi_6(E_2) &= \frac{1}{2}(\phi_2 - \phi_3 + \phi_5 - \phi_6)
\end{aligned}$$



(a) $\Psi_1(A) \sim \Psi(A_{2u})$. (b) $\Psi_2(B) \sim \Psi(B_{2g})$. (c) $\Psi_3(E_1) \sim \Psi({E_{1g}}^a)$.



(d) $\Psi_4(E_1) \sim \Psi({E_{1g}}^b)$. (e) $\Psi_5(E_2) \sim \Psi({E_{2u}}^a)$. (f) $\Psi_6(E_2) \sim \Psi({E_{2u}}^b)$.

Figure III.1: Molecular orbitals of benzene.

– Figure III.1 shows pictorial representations of the SALCs.

III.4 Nocera Lecture 7

From Nocera (2008).

- This lecture continues with the benzene example from Nocera Lecture 6.
- Finding the total energy of benzene:
  - The energies (eigenvalues of the individual wavefunctions) may be determined using the Hückel approximation as follows.

$$\begin{aligned}
E(\Psi_{A_{1g}}) &= \int \Psi_{A_{1g}} \hat{H} \Psi_{A_{1g}} \,\mathrm{d}\tau \\
&= \left\langle \Psi_{A_{1g}} \middle| \hat{H} \middle| \Psi_{A_{1g}} \right\rangle \\
&= \left\langle \frac{1}{\sqrt{6}} (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) \middle| \hat{H} \middle| \frac{1}{\sqrt{6}} (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) \right\rangle \\
&= \frac{1}{6} \left((H_{11} + H_{12} + H_{13} + H_{14} + H_{15} + H_{16}) + (H_{21} + H_{22} + H_{23} + H_{24} + H_{25} + H_{26}) + \sum_{i=3}^{6} \sum_{j=1}^{6} H_{ij} \right) \\
&= \frac{1}{6} \left((\alpha + \beta + 0 + 0 + 0 + \beta) + (\beta + \alpha + \beta + 0 + 0 + 0) + \sum_{i=3}^{6} (\alpha + 2\beta) \right) \\
&= \frac{1}{6}(6)(\alpha + 2\beta) \\
&= \alpha + 2\beta
\end{aligned}$$

  - Similarly, we can determine that

$$\begin{aligned}
E(\Psi_{B_{2g}}) &= \alpha - 2\beta \\
E(\Psi_{E_{1g}{}^a}) = E(\Psi_{E_{1g}{}^b}) &= \alpha + \beta \\
E(\Psi_{E_{2u}{}^a}) = E(\Psi_{E_{2u}{}^b}) &= \alpha - \beta
\end{aligned}$$

  - We can now construct an energy level diagram (Figure III.2). We set $\alpha = 0$ and let β be the energy parameter (a negative quantity; thus, a MO whose energy is positive in units of β has an absolute energy that is negative).

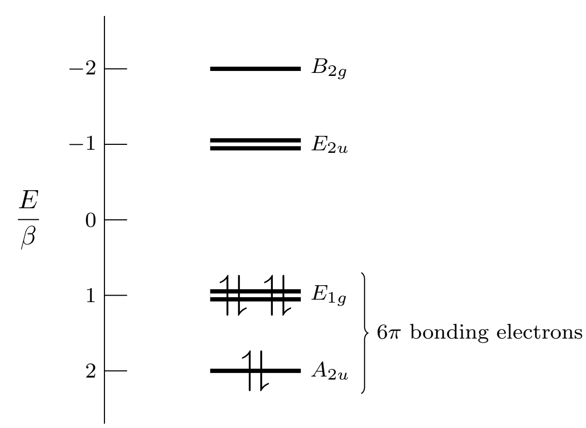


Figure III.2: Energy level diagram of benzene.

  - From Figure III.2, we can determine that the energy of benzene based on the Hückel approximation is

$$E_{\text{total}} = 2(2\beta) + 4(\beta) = 8\beta$$

- **Delocalization energy**: The difference in energy between a molecule that delocalizes electron density in a delocalized state versus a localized state. *Also known as* **resonance energy**.
- Finding the delocalization energy of benzene:
  - Consider cyclohexatriene, a molecule equivalent to benzene except that it has 3 *localized* π bonds. Cyclohexatriene is the product of three condensed ethene molecules.
  - Ethene has 2 π bonds ϕ_1 and ϕ_2.
  - Following the procedure of Nocera Lecture 6, we can determine that

$$\Psi_1(A) = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \qquad\qquad \Psi_2(B) = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$$

  - Thus,

$$\begin{aligned} E(\Psi_1) &= \left\langle \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \middle| \hat{H} \middle| \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \right\rangle = \frac{1}{2}(2\alpha + 2\beta) = \beta \\ E(\Psi_2) &= \left\langle \frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \middle| \hat{H} \middle| \frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \right\rangle = \frac{1}{2}(2\alpha - 2\beta) = -\beta \end{aligned}$$

  - Correlating the above calculations (performed within $C_2 \subset D_{2h}$) to the D_{2h} point group gives $A \to B_{1u}$ and $B \to B_{2g}$.
  - We can now construct an energy level diagram.

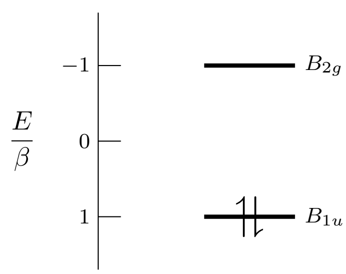


Figure III.3: Energy level diagram of ethene.

  - Figure III.3 tells us that $E_{\text{total}} = 2(\beta) = 2\beta$. Consequently, the total energy of cyclohexatriene is $3(2\beta) = 6\beta$.
  - Therefore, the resonance energy of benzene based on the Hückel approximation is

$$E_{\text{res}} = 8\beta - 6\beta = 2\beta$$

- **Bond order**: A quantity defined for a given bond as

$$\text{B.O.} = \sum_{i,j} n_e c_i c_j$$

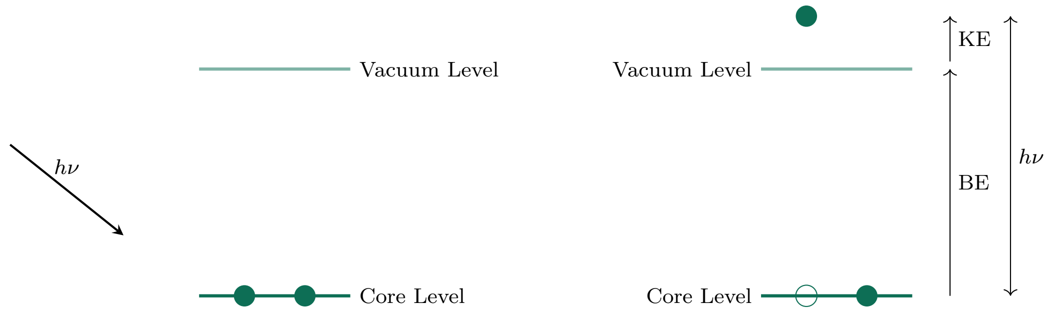
  where n_e is the orbital e$^-$ occupancy and $c_{i,j}$ are the coefficients of the electrons i, j in a given bond.
- Finding the bond order of benzene between carbons 1 and 2:
  - Just apply the formula:

$$\begin{aligned} \text{B.O.} &= [\Psi_1(A_2)] + [\Psi_3({E_{1g}}^a)] + [\Psi_4({E_{1g}}^b)] \\ &= (2)\left(\frac{1}{\sqrt{6}}\right)\left(\frac{1}{\sqrt{6}}\right) + (2)\left(\frac{2}{\sqrt{12}}\right)\left(\frac{1}{\sqrt{12}}\right) + (2)(0)\left(\frac{1}{2}\right) \\ &= \frac{1}{3} + \frac{1}{3} + 0 \\ &= \frac{2}{3} \end{aligned}$$

III.5 Module 13: Why Molecular Orbitals?

- Note that in the point group flow chart, there is no D_{nv}; only D_{nd}.
- We will not need LCAO for the exam tomorrow.
- The exam covers Modules 1-12.
- Lewis (1916) first proposed that bonds came form interpenetrability of electron density.
- The next step came from Linus Pauling, who proposed valence bond theory.
  - In order to account for polarity of the bond, he created a term that described the probability that both electrons bond to one atom.
- A new approach then emerged from Robert Mulliken, Friedrich Hund, and Clemens C.J. Roothaan. All three men worked at UChicago!
  - Mulliken is mainly credited for the development of MO theory.
  - Roothaan retired, found retirement boring, moved to Palo Alto and was key in the development of computer processors.
- Molecular orbital theory:
  - Atomic orbitals of different atoms combine to create molecular orbitals.
  - The number of atomic orbitals equals the number of molecular orbitals.
  - Electrons in these molecular orbitals are shared by the molecule as a whole.
  - Molecular orbitals can be constructed from LCAO.
    - For diatomic molecules: $\Psi = c_a\Psi_a + c_b\Psi_b$.
- There is no such think as a chemical bond (this model is only intuitively helpful), only molecular orbitals!
- **Bonding** (orbital): An orbital that has most of the electron density between the two nuclei.
- **Anti-bonding** (orbital): An orbital that has a node between the two nuclei.
- **Nonbonding** (orbital): An orbital that is essentially the same as if it was only one nuclei.
- We find the energy of electronic states using theoretical calculations that we test with photoelectron spectroscopy[2].
- **Photoelectron spectroscopy**: A photo-ionization and energy-dispersive analysis of the emitted photoelectrons to study the composition and electronic state of a sample. *Also known as* **PES**.
  - A sample (solid, liquid, or gas) is impinged upon by to a focused beam of X-rays (say of 1.5 kV).
  - When the sample is exposed to the X-rays, electrons fly out of the sample. The KE of these electrons can be measured.
  - Essentially, $h\nu$ takes an electron from the core level to above the vacuum level. We know $h\nu$ and we measure KE_{electron}, allowing us to calculate the bonding energy of the electron: $h\nu = I_{\text{BE}} + E_{\text{kinetic}}$ (see Figure III.4).
- **X-ray photoelectron spectroscopy**: Using soft (200-2000 eV) x-ray excitation (photons in the x-ray energy range) to examine core levels. *Also known as* **XPS**.
- **Ultraviolet photoelectron spectroscopy**: Using vacuum UV (10-45 eV) radiation (photons is in UV energy range) from discharge lamps to examine valence levels. *Also known as* **UPS**.

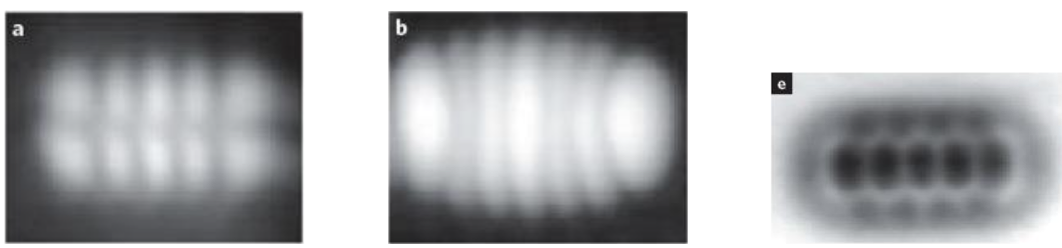
[2] Refer to Labalme (2020a), specifically Figure 7.20 and the accompanying discussion.



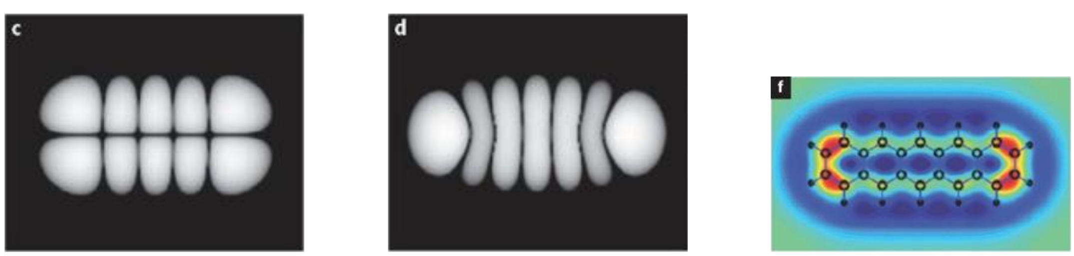
(a) Initial state. (b) Final state.

Figure III.4: Photoelectron spectroscopy at an atomic level.

- If we apply PES to O_2, we get counts that correspond to molecular orbitals π_g^*, π_u, σ_g, and σ_u^*.
- Photoelectron spectrum of H_2O:
  - Pauling's theory suggest that the lone pairs should have equal energy greater than the equal energy of the bonds.
  - However, PES reveals that the lone pairs have two different energies. This is a nail in the coffin of Pauling's valence bond theory.
- PES of CH_4:
  - There are two states; one with degeneracy 3 and one with degeneracy 1.
  - We have 3 bonds of one energy and 1 with another.
  - Another nail in the coffin.



(a) HOMO actual. (b) LUMO actual. (c) Atomic structure actual.



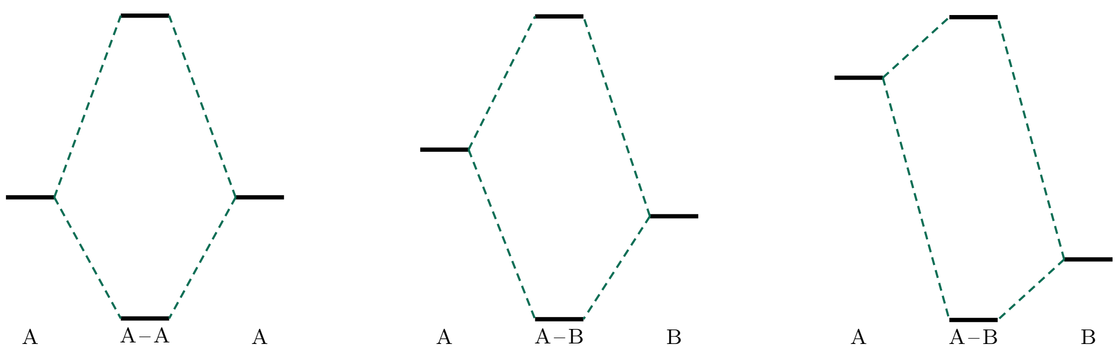
(d) HOMO prediction. (e) LUMO prediction. (f) Atomic structure prediction.

Figure III.5: Correspondence between MO predictions and scanning tunnelling microscopy.

- Can one "see" molecular orbitals? With a scanning tunneling microscope, we can "see" pentatene (5 linearly fused benzene rings). The correspondence between the pictures and MO theory's predictions is impressive (see Figure III.5).

III.6 Module 14: Constructing Molecular Orbitals (Part 1)

- Bonding: $\Psi_\sigma = \Psi_+ = \frac{1}{\sqrt{2}}(\psi_{1s_a} + \psi_{1s_b})$.
- Anti-bonding: $\Psi_{\sigma^*} = \Psi_- = \frac{1}{\sqrt{2}}(\psi_{1s_a} - \psi_{1s_b})$.
  - Addition doesn't necessarily correlate to bonding and subtraction to anti-bonding.
- With simple orbitals, we can combine orbitals by inspection.
  - However, we will learn to build molecular orbitals for much more complicated molecular orbitals, such as those of ferrocene ($Fe(C_5H_5)_2$).
- Degree of orbital overlap/mixing depends on:
  1. Energy of the orbitals (the closer the energy, the more mixing; when the energies differ greatly, the reduction energy due to bonding is insignificant).
  2. Spatial proximity (the atoms must be close enough that there is *reasonable* orbital overlap, but not so close that repulsive forces interfere).
  3. Symmetry (atomic orbitals mix if they have similar symmetries; regions with the same sign of Ψ overlap).
- The strength of the bond depends upon the degree of orbital overlap.
- For heteronuclear molecules:



(a) Equal energies. (b) Unequal energies. (c) Very unequal energies.

Figure III.6: Combining orbitals of varying energies.

  - The bonding orbital(s) will reside predominantly on the atom of lower orbital energy (the more electronegative atom).
  - The anti-bonding orbital(s) will reside predominantly on the atom with greater orbital energy (the less electronegative atom).
- The energies of atomic orbitals (measured by PES) have been tabulated (see Figure III.7).
- If you want to measure orbital energies in the range of -10 eV (i.e., upper valence orbitals; see Table 5.2 in Miessler et al. (2014)), use UPS. If you want to look at energy states that are very deep, very core (i.e., 1s in Fe), use XPS.
- Symmetry and orbital diagrams (suggested reading Cass and Hollingsworth (2004)):
  - **State conservation principle**: The number of molecular orbitals is equal to the number of incipient (atomic) orbitals.

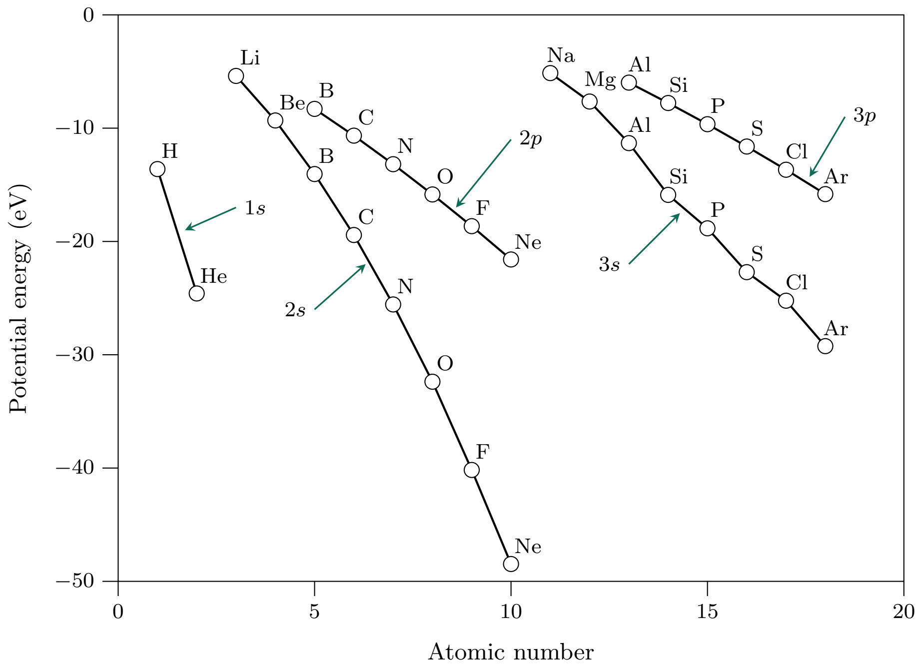
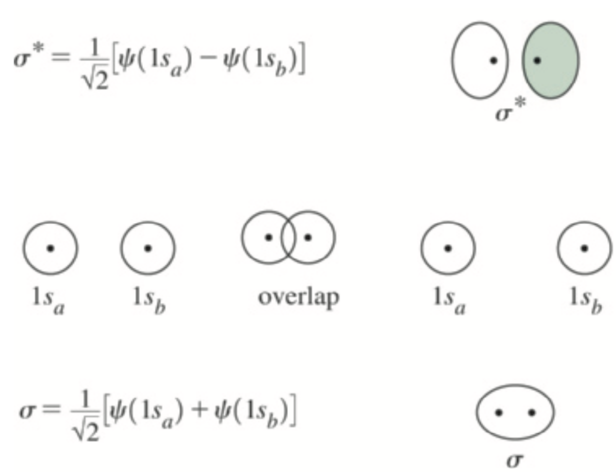
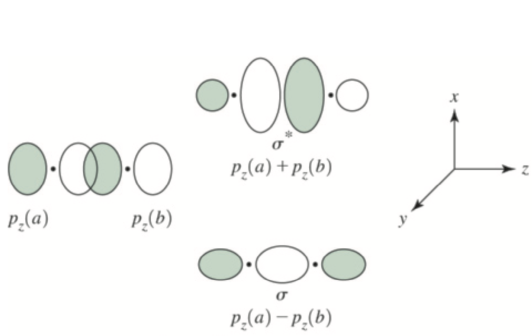


Figure III.7: Orbital potential energies.

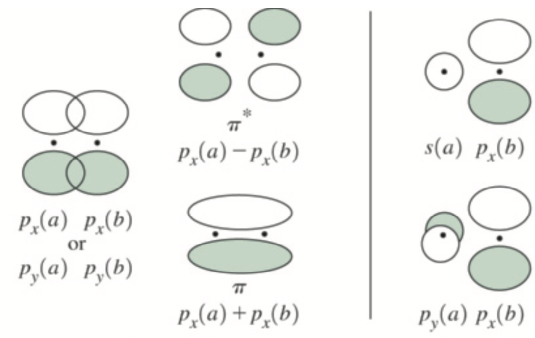
- Orbitals of the same symmetry mix.
- Orbital interactions can be bonding, nonbonding, or antibonding.
- There are three basic types of orbital overlap: σ (end-on interaction), π (side-by-side approach) and δ (off-axis approach).
  - σ orbitals are symmetric to rotation about the line connecting nuclei.
  - π orbitals change sign of the wave function with C_2 rotation about the bond axis.
  - Orbitals also denoted g are symmetric to inversion.
  - Orbitals also denoted u are antisymmetric to inversion.
- Orbitals with the correct symmetry and most similar energy mix to the greatest extent.



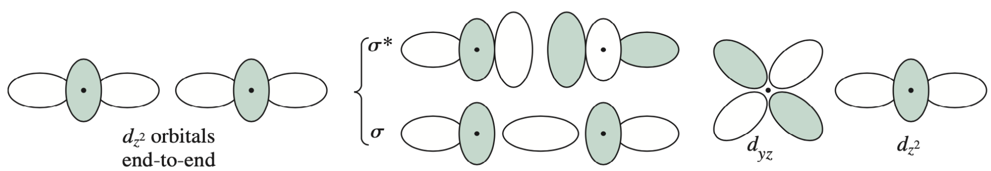
(a) σ_s.



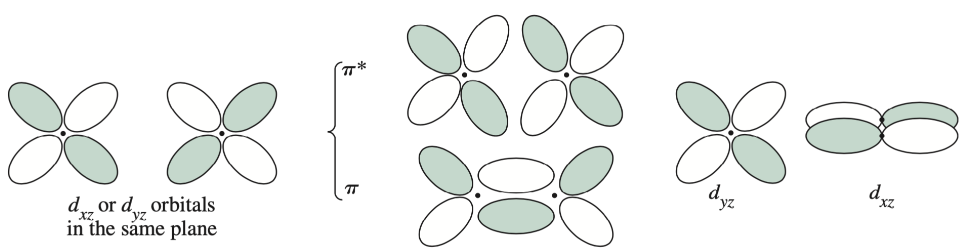
(b) π_s.



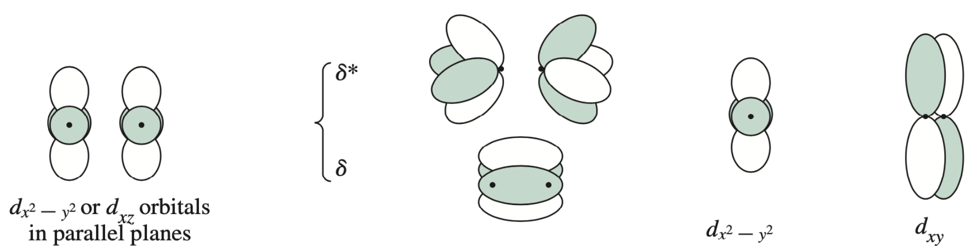
(c) π_p.



(d) δ_s.



(e) δ_p.



(f) δ_d.

Figure III.8: Constructing s, p, and d molecular orbitals.

- There are six MO constructions to be aware of: s-s, p-p (σ and π), and d-d (σ, π, and δ). See Figure III.8.
  - There are similar orbitals in simple diatomic molecules.
- As the mixing of σ_g orbitals gets stronger, the $2p$ state drops in energy faster than the $2s$ state, causing the $2p$ state to have lower energy than the $2s$ state after a while.

III.7 Office Hours (Wang)

- Quantum mechanics will not be included on tomorrow's exam.
- Hybridization was developed (1931 by Pauling) earlier than VSEPR theory (1940 by Sidgwick and Powell).
- What *is* a direct product of representations?
  - The direct product generates an $n \times m$ matrix?
  - Di has no idea what's going on, but he's gonna give me a link to his Advanced Inorganic Chemistry textbook.
- Can you go over how to do problems IV and VI with direct product analysis?
  - The IR absorption way from Module 12?
  - $\Gamma_{\text{g.s.}} = A_1$ always.
  - Γ_μ is the sum of the x, y, z linear irreducible representations.
  - $\Gamma_{\text{e.s.}} = \Gamma_{\text{vibs}}$.
  - We need to calculate the direct product of every representation in Γ_{vibs} with every term in Γ_μ. Products that contain A_1 are IR active?
  - Example:
    $$A_1 \times (A_1 + B_1 + B_1) = A_1 \times A_1 + A_1 \times B_1 + A_1 \times B_2$$
    - Since $A_1 \times A_1 = A_1$, we already know after taking only this product that A_1 is IR active.
  - Things aren't IR active because they're linear. Things are IR active because their direct product with the sum of the linear groups contains the totally symmetric representation.
- You can only take the direct product of irreducible representations?

III.8 Office Hours (Talapin)

- To what extent do we need to know term symbols (they appeared briefly in Module 1)?
- How do we identify the T_h point group?

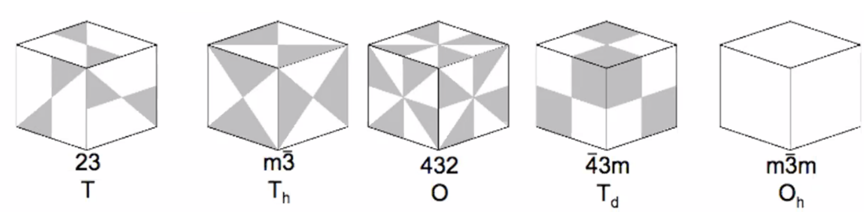


Figure III.9: Tetrahedral point groups.

  - It's a very rare point group. It has no dihedral planes.
- What is the point of conjugate elements?
  - Conjugate elements allow us to group symmetry elements into classes — conjugate elements are in the same class!
- Will we need to be able to work with infinite character tables?
- What was that whole thing you did with a symmetry operation R and the Schrödinger equation?

- What level of familiarity do we need with Dirac's bra-ket notation?
  - Just know that it represents an integral.
- Do we need to evaluate/what do we need to know about those integrals from Wednesday's class?
  - It will be sufficient to write down representations.
- Why does Γ_μ, the representation of the dipole moment, transform with x, y, z?
  - n-degree perturbation theory.
- The problems will be similar to homework problems.

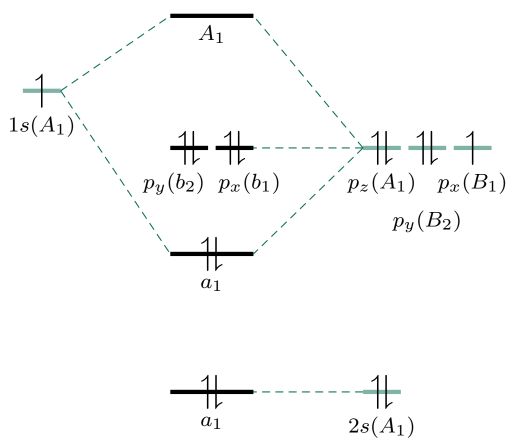
III.9 Module 15: Constructing Molecular Orbitals (Part 2, HF Molecule)

2/1: - MO Diagrams from Group Theory:
  1. Assign a point group.
  2. Choose basis functions (orbitals).
  3. Apply operations.
  4. Generate a reducible representations and SALCs (the latter if applicable).
  5. Reduce to irreducible representations.
  6. Combine central and peripheral orbitals by their symmetry.
  7. Fill MOs with e^-'s. Draw orbitals.
  8. Generate SALCs of peripheral atoms (if applicable).
  9. Draw peripheral atom SALC with central atom orbital to generate bonding/antibonding MOs (if applicable).
- We will not need SALCs here.
- H−F example:
  - Point group: $C_{\infty v}$. However, we will work within the C_{2v} subgroup (knowing why to choose this *specific* subgroup will come later; just accept it for now).
  - Choose basis functions (H_{1s}, F_{1s}, F_{2p_x}, F_{2p_y}, and F_{2p_z}).
  - Applying operations, we get

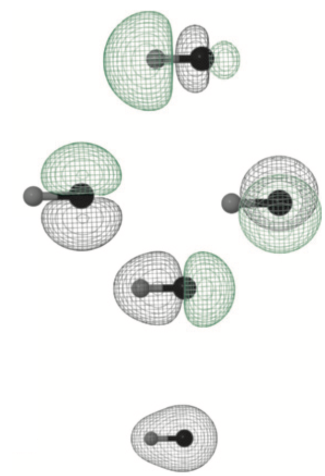
$$
\begin{aligned}
\Gamma_{H_{1s}} &= (1, 1, 1, 1) = A_1 \\
\Gamma_{F_{1s}} &= (1, 1, 1, 1) = A_1 \\
\Gamma_{F_{2\mathrm{p_z}}} &= (1, 1, 1, 1) = A_1 \\
\Gamma_{F_{2\mathrm{p_x}}} &= (1, -1, 1, -1) = B_1 \\
\Gamma_{F_{2\mathrm{p_y}}} &= (1, -1, -1, 1) = B_2
\end{aligned}
$$

    - Therefore, the H_{1s}, F_{1s}, F_{2p_x}, F_{2p_y}, and F_{2p_z} orbitals transform with the A_1, A_1, A_1, B_1, and B_2 irreducible representations, respectively.
    - Note that we can also extract p-orbital information from the corresponding linear functions in the character table.
    - Also note that one orbital $\Rightarrow$ one degree of freedom. We do not have x, y, z-DOFs as before.

- When we bring the atoms together, those orbitals with similar symmetry (in this case, all the A_1 orbitals) will start mixing. However, from Figure III.7, the F_{1s} orbital has a very different energy (much lower) than the H_{1s} orbital, meaning that it has negligible mixing with H_{1s}. On the other hand, H_{1s} along with the 2p-orbitals in fluorine have comparable energies, so they will have significant mixing.
- We will get a low energy MO from F_{1s}, a higher bonding MO from H_{1s} and F_{2p_z}, two higher nonbonding MOs from F_{2p_x} and F_{2p_y}, and a higher anti-bonding MO from H_{1s} and F_{2p_z}.



(a) Energy level diagram.



(b) Orbital drawings.

Figure III.10: HF orbital diagram.

- We can now fill the MOs with the atomic electrons using the Aufbau principle, the Pauli exclusion principle, and Hund's rule. We can also draw these orbitals.

- Orbital energies can be found in Table 5.2 of Miessler et al. (2014).
- If the energy difference between orbitals is more than 10 eV, then we can *probably* (not always) ignore mixing.
  - The approximate scaling is that the stabilization energy (or energy gain) is inversely proportional to the energy gap.
  - The magnitude of the interaction integral will be approximately inversely proportional to the energy gap between the atomic orbitals participating.
- Organic chemists can go a long way with a hybridization approach even though it is not reflected in inorganic chemistry.

III.10 Module 16: Constructing Molecular Orbitals (Part 3, H_2O Molecule)

- Beware: Orientation of the point groups C_{2v} and D_{2h}.
  - Unlike all other groups, C_{2v} and D_{2h} present problems in assigning the irreducible representations. For most groups, the symmetry axis is obvious, or if their are several axes, the principal axis is obvious. For C_{2v} and D_{2h}, an ambiguity exists. The commonly (but not unanimously) used convention is the following:
  - If there are three C_2 axes, the one with the largest number of atoms unmoved by a C_2 operation is z. If there is only one C_2 axis, that is z.

  - Once z is defined, the y-axis is defined as the axis of the remaining two axes which has the largest number of atoms unmoved by the σ symmetry operation.
  - The x-axis is the remaining axis.
  - The overall result is that the symmetry axes in ethylene are defined as: z - along the C=C bond; y - in the molecular plane, perpendicular to the C=C bond; and x - out of the plane.
  - Similar approaches apply to the C_{2v} point group.
- We will need SALCs here.
  - Since the hydrogen atoms do not lie on the principal rotation axis, they will not individually obey the symmetry operations.
  - Thus, we need **Symmetry Adapted Linear Combinations**.
- **Symmetry Adapted Linear Combination** (of atomic orbitals): The linear combination of multiple atomic orbitals corresponding to peripheral atoms (atoms that do not lie on the principal axis). This linear combination will obey the symmetry modes. *Also known as* **SALC**.
- To generate SALCs, the steps are:
  - Group the atomic orbitals in the molecule into sets which are equivalent by symmetry.
  - Generate and reduce the reducible representation for each set.
  - Use the projection operator for one basis.
- H_2O example:
  - Point group: C_{2v}.
  - Choose basis functions (both H_{1s} orbitals, O the same as F in the last example).
  - Applying operations, we get
$$\Gamma_{\text{H}} = (2, 0, 2, 0) = A_1 + B_1$$
    - For the hydrogens, it makes sense that we need two irreducible representations to describe two atoms. More formally, the number of basis functions should match the number of irreducible representations to account for possible degeneracy of irreducible representations.
    - The O orbitals are the same as the F orbitals in the last example.
  - Combining orbitals by their symmetry and energy again, we get the following MOs.

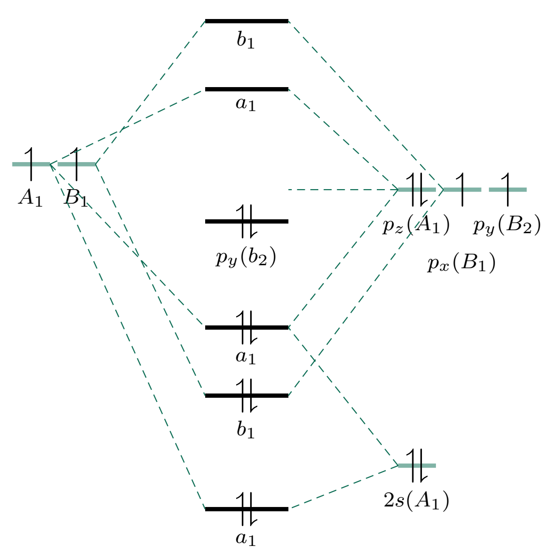


Figure III.11: H_2O orbital diagram.

- We can now compare this with the results from photoelectron spectroscopy and see that our predictions are correct.

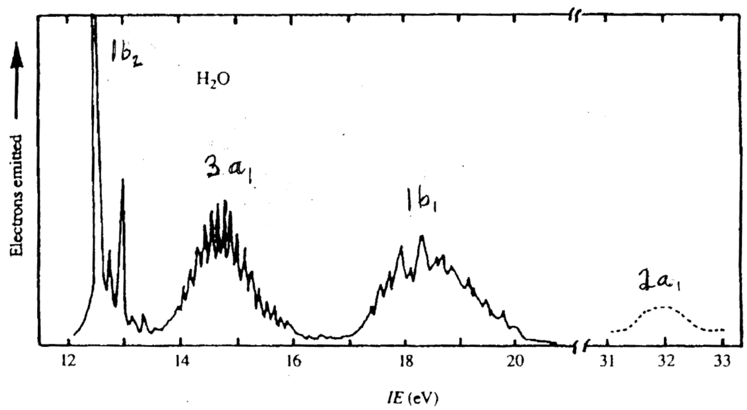


Figure III.12: Photoelectron spectrum for H_2O.

  - We see four different states, which matches the prediction of Figure III.11.
  - The lowest state is called $2a_1$ because it is the second state that transforms as A_1 going out from the core (the first is $1a_1$ corresponding to oxygen's $1s$ electrons [this state is not shown in Figure III.11 because it is so core as to not be significantly relevant to the chemistry of H_2O]).
  - Then $1b_1$ is the first A_1 state going out from the core, $3a_1$ is the third A_1 state, and $1b_2$ is the first B_2 state.
  - There are no $4a_1$ and $2b_1$ electrons (see Figure III.11); hence, there are no such PES peaks (see Figure III.12).
  - Note that the numbers along the bottom axis correspond to the orbital potential energies of the corresponding molecular orbitals.
- For H_2O, hybridization is qualitatively wrong.

- To generate SALCs:
  - Use the projection operator. See Nocera Lecture 6 for how to mathematically apply it.
  - Projection operators constitute a method of generating the symmetry allowed combinations.
  - Taking one AO and projecting it out using symmetry.
- Using the projection operator method to reconstruct SALC orbitals (NH_3 example):

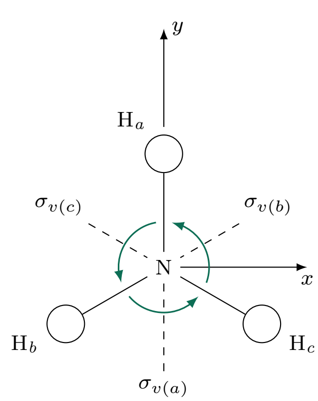


Figure III.13: Coordinate system for NH_3.

C_{3v}	E	$2C_3$	$3\sigma_v$	linear	quadratic
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(x,y),(R_x,R_y)$	$(x^2-y^2,xy),(xz,yz)$

Table III.1: Character table for the C_{3v}

- Ungroup the operations in the classes in Table III.1. Choose H$_a$ and see into which H it projects under each operation. If we order the operations $E, C_3, {C_3}^2, \sigma_{v(a)}, \sigma_{v(b)}, \sigma_{v(c)}$, then H$_a$ becomes H$_a$, H$_b$, H$_c$, H$_a$, H$_c$, H$_b$, respectively.
- Multiply each projected atom by the corresponding character and sum. Thus, for the three representations, we have

$$\begin{aligned} A_1 &= \mathrm{H}_a+\mathrm{H}_b+\mathrm{H}_c+\mathrm{H}_a+\mathrm{H}_c+\mathrm{H}_b = 2\mathrm{H}_a+2\mathrm{H}_b+2\mathrm{H}_c \\ A_2 &= \mathrm{H}_a+\mathrm{H}_b+\mathrm{H}_c-\mathrm{H}_a-\mathrm{H}_c-\mathrm{H}_b = 0 \\ E &= 2\mathrm{H}_a-\mathrm{H}_b-\mathrm{H}_c+0+0+0 = 2\mathrm{H}_a-\mathrm{H}_b-\mathrm{H}_c \end{aligned}$$

  - We have essentially just done what the projection operator would enable us to do.

- Continuing with the H_2O example:
  - Using the projection operator, we get

$$\begin{aligned} P^{A_1} &= \frac{1}{4}[1E\phi_1 + 1C_2\phi_1 + 1\sigma_{xz}\phi_1 + 1\sigma_{yz}\phi_1] = \frac{1}{2}(\phi_1+\phi_2) \\ P^{B_1} &= \frac{1}{4}[1E\phi_1 - 1C_2\phi_1 + 1\sigma_{xz}\phi_1 - 1\sigma_{yz}\phi_1] = \frac{1}{2}(\phi_1-\phi_2) \end{aligned}$$

    - P^{A_1} is a sum of the two hydrogen 1s orbitals.
    - P^{B_1} is a difference of the two hydrogen 1s orbitals.
    - This step allows us to construct electron density maps for the SALCs of the hydrogen's atomic orbitals.
  - We can now see if the symmetry of various orbitals matches up or doesn't match up and use this information to sketch molecular orbitals.
  - Oxygen atomic orbital coefficients can only be analytically derived with quantum mechanical calculations.
- How can we predict the shape of molecules from MO theory (i.e., without VSEPR theory)?
- **Walsh diagrams** help understand the molecular shapes (bond angles).
  - If H_2O is linear, it is part of the $D_{\infty h}$ point group (which can be reduced to D_{2h} for further mysterious reasons).
  - $1\sigma_g^+$: If we slowly decrease the bond angle, the hydrogen orbital overlap will increase, meaning that $1\sigma_g^+$ energy decreases.
  - $1\sigma_u^+$: If we slowly decrease the bond angle, the s and p orbitals will become less aligned, meaning that $1\sigma_u^+$ energy increases.
  - π_u, $2a_1$: Energy decreases as hydrogen orbitals get closer to the appropriately signed region of the O$_p$ orbital.
  - π_u, b_2: Energy is constant.
  - Now all orbitals with electrons have been accounted for. Since 2 energies go down, 1 goes up, and 1 stays the same as bond angle decreases, we know that bond angle will decrease to an equilibrium.

III.11 Module 17: Constructing Molecular Orbitals (Part 4, NH_3 Molecule)

2/3: • NH_3 example:

- Point group: C_{3v}.
- Basis functions: H_{1s}, N_{2s}, N_{2p_x}, N_{2p_y}, and N_{2p_z}.
- Apply operations (pick any one operation from each class)/construct reducible representations:

$$\begin{aligned}\Gamma_{\mathrm{H}} &= (3,0,1) = A_1 + E\\ \Gamma_{\mathrm{N}_{2s}} &= A_1\\ \Gamma_{\mathrm{N}_{2p_x}} &= E\\ \Gamma_{\mathrm{N}_{2p_y}} &= E\\ \Gamma_{\mathrm{N}_{2p_z}} &= A_1\end{aligned}$$

  - N_{2p_x} and N_{2p_y} are doubly degenerate — their transformation cannot be decoupled and they transform together.
- Look at the relevant energies and plot them against each other.
- 3 A_1 type atomic orbitals form 3 a_1 type MOs.

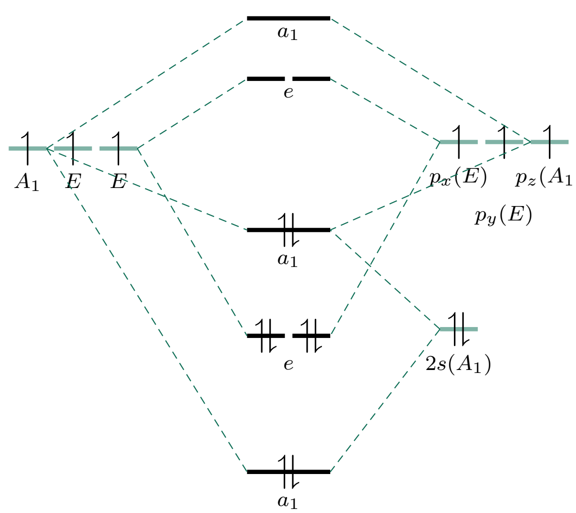


Figure III.14: NH_3 orbital diagram.

  - Since $2s(A_1)$ and $1s(A_1)$ are so far away energetically, their combination will have very low energy.
  - On the other hand, since the $1s(A_1)$ and $p_z(A_1)$ are close in energy, they have a lot of overlap.
  - We can't analytically calculate orbital energies at this level. Take an educated guess on the homework and explain your reasoning. Note that here, e orbitals are more stabilizing because they are bigger and have larger overlap. Also, σ bonds are stronger than π bonds because there is a higher degree of overlap.
- To see what these orbitals look like, we need to apply the projection operator.
  - We need to construct one A_1 orbital and two E orbitals.
  - Modifying from the example from last time, we have $P^{A_1} \approx \phi_1 + \phi_2 + \phi_3$ and $P^E \approx 2\phi_1 - \phi_2 - \phi_3$.

- For the last E SALC, we apply the projection to each hydrogen atom (we can choose any basis function) giving us, in addition to the other projections, $P^E \approx 2\phi_2 - \phi_3 - \phi_1$ and $P^E \approx 2\phi_3 - \phi_1 - \phi_2$. By subtracting these two, we get $\Psi_E = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3)$. Do we choose this linear combination because it's orthogonal to the other two? Because it's structure is different and simple (you *can* do it with any linear combination, but it will make the analysis much more complicated if you do it with a trickier linear combination).

– We need to renormalize our SALCs so that the integral of their square over all space is 1. To normalize, we must guarantee that the sum of the squares of the coefficients is 1. For P^{A_1} for example, $1^2 + 1^2 + 1^2 = 3$, so we must scale the whole thing by $\frac{1}{\sqrt{3}}$.

– In the PES spectrum, we see three peaks, one being approximately twice as wide as the others (corresponding to the double degenerate state).

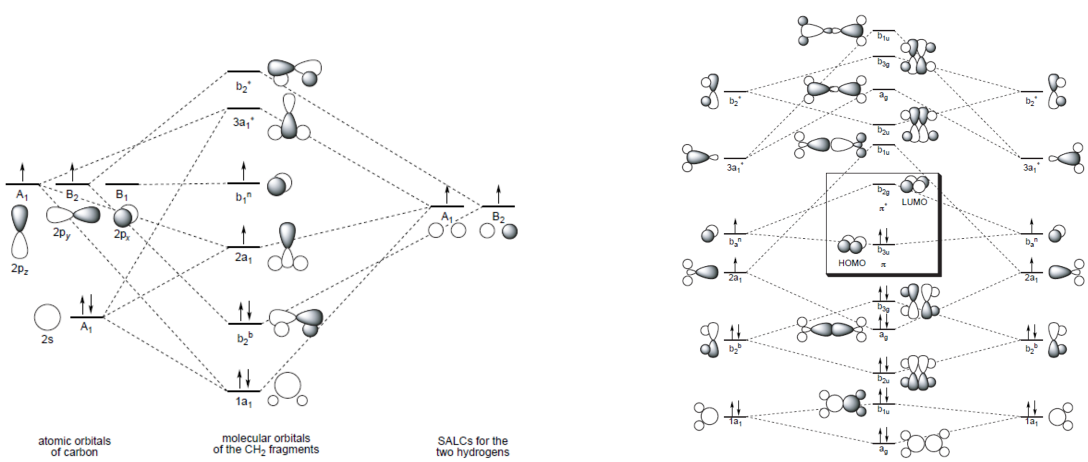
– Walsh diagrams (rely on the pictures that we draw of orbitals):

- $1a_1'$ energy decreases, $1e'$ energy increases, a_2'' energy decreases rather dramatically.
- If we promote electrons to the excited state, the relevant Walsh diagrams will change, and this will cause the molecule to change shape.

• Also try to sketch the MOs in the homework.

III.12 Module 18: Constructing Molecular Orbitals (Part 5, $H_2C{=}CH_2$ Molecule)

• $H_2C{=}CH_2$ example:



(a) Carbene fragment. (b) Full molecule.

Figure III.15: $H_2C{=}CH_2$ orbital diagram.

– Two different approaches (D_{2h}): $C_1 + C_2$ then H_{1-4}, or two carbene fragments (CH_2).

- We can read about the first approach in the linked JCE article (*cite*).

– C_{2v} for the CH_2 fragment.

– When we make the MO diagram, we have two unpaired electrons, one in each of the upper two orbitals. These will be used for bonding to the other carbene fragment.

– We will then combine the MO diagrams and will need to reassign orbital names because ethene isn't C_{2v}; it's D_{2h}.

III.13 Module 19: Isolobal Principle

- **Isolobal** (fragment): A fragment with similar (not identical) numbers, symmmetry properties, approximate energies, and shapes of the frontier orbitals and the number of electrons in them.
- This allows us to show, for example, that a carbene fragment and a d^7 metal complex have similar properties.
- Two CH_3 fragments will tend to couple into ethane. But so will two isolobal $Mn(CO)_5$ fragments!

III.14 Module 20: Orbital Hybridization

- **Hybridization**: The concept of mixing atomic orbitals into new hybrid orbitals (with different energies, shapes, etc. than the component atomic orbitals) suitable for the pairing of electrons to form chemical bonds.
- Hybridization accomplishes the work of MO theory in steps: Creating new orbitals and then bonding atoms with them, as opposed to defining new orbitals and filling them.
- This was the dominant approach in chemistry before MO theory, and is still widely used in organic chemistry.
- For light elements, the energy gaps between orbitals aren't very large and this method is legitimate to some degree.
  - For carbon, it's acceptable.
  - For silicon and lead (in the same group), this is not a good approach; it will give you incorrect predictions (e.g., around bond angles and lengths).
- Steps to determine the hybridization of a bond:
  1. Assign a point group.
  2. Choose basis function (σ bonds).
  3. Apply operations.
  4. Reduce to irreducible representations.
  5. Compare symmetry of irreducible representations to central atom MOs.
- BF_3 example:
  - Point group: D_{3h}.
  - $\Gamma_\sigma = (3,0,1,3,0,1)$.
  - $\Gamma_\sigma = A_1' + E'$.
  - For boron, $\text{B}(s) = A_1'$, $\text{B}(p_x) = E'$, $\text{B}(p_y) = E'$, and $\text{B}(p_z) = A_2''$. Thus, since one orbital matches up on s and two match up on p (specifically, p_x, p_y), the hybrid orbitals will be sp^2 (hybrid of s, p_x, p_y).
- It is not generally justifiable to say that atomic orbitals in *individual* atoms mix before bonding.

III.15 Chapter 5: Molecular Orbitals

From Miessler et al. (2014).

1/29:

- MO theory uses group theory to describe molecular bonding, complementing and extending Chapter 3.

- "In molecular orbital theory the symmetry properties and relative energies of atomic orbitals determine how these orbitals interact to form molecular orbitals" (Miessler et al., 2014, p. 117).
- The molecular orbitals are filled according to the same rules discussed in Chapter 2.
- If the total energy of the electrons in the molecular orbitals is less than that of them in the atomic orbitals, the molecule is stable relative to the separate atoms (and forms). If the total energy of the electrons in the molecular orbitals exceeds that of them in the atomic orbitals, the molecule is unstable (and does not form).
- **Homonuclear** (molecule): A molecule in which all constituent atoms have the same atomic number.
- **Heteronuclear** (molecule): A molecule that is not homonuclear, i.e., one in which at least two atoms differ in atomic number.
- A less rigorous pictorial approach can describe bonding in many small molecules and help us to build a more rigorous one, based on symmetry and employing group theory, that will be needed to understand orbital interactions in more complex molecular structures.
- Schrödinger equations can be written for electrons in molecules as they can for electrons in atoms. Approximate solutions can be constructed from the LCAO method.
  - In diatomic molecules for example, $\Psi = c_a\psi_a + c_b\psi_b$ where Ψ is the molecular wave function, $\psi_{a,b}$ are the atomic wave functions for atoms a and b, and $c_{a,b}$ are adjustable coefficients that quantify the contribution of each atomic orbital to the molecular orbital.
- "As the distance between two atoms is decreased, their orbitals overlap, with significant probability for electrons from both atoms being found in the region of overlap" (Miessler et al., 2014, p. 117).
- Electrostatic forces between nuclei and electrons in bonding molecular orbitals hold atoms together.

2/5:

- Precise calculations show that the coefficient of the σ^* hydrogen antibonding orbital is slightly larger than that of the σ orbital, but we typically neglect this distinction.
  - This technically implies that $\Delta E_{\sigma^*} > \Delta E_{\sigma}$, i.e., that the increase in energy from electrons in atomic orbitals moving into the σ^* antibonding molecular orbital is greater in magnitude than the decrease in energy from electrons in atomic orbitals moving into the σ bonding molecular orbital.
- $\boldsymbol{\sigma}$ **orbital**: A molecular orbital that is symmetric to rotation about the line connecting the nuclei.
- **Orbital asterisk**: Denotes antibonding orbitals for those molecules where bonding and antibonding orbital descriptions are unambiguous (i.e., smaller molecules).
- When two regions of like sign overlap, the sum of the orbitals exhibits increased electron probability in the overlap region, and vice versa for regions of opposite sign.
- When the z-axes are drawn pointing in the same direction, their difference is σ and their sum is σ^*.

(a) Same direction. (b) Opposite directions.

Figure III.16: Choice of z-axis direction.

  - Notice how in Figure III.16b, we can simply push the orbitals together (add them) to have regions of like sign overlap and form a bonding orbital.

- However, in Figure III.16a, with a more standard coordinate system, we have to flip the signs of one of the orbitals before merging them (multiply it by -1 and add it to the other orbital/subtract it from the other orbital) to create a bonding orbital. If we add them as they are, we will get an antibonding orbital.

- **π orbital**: A molecular orbital with a change in sign of the wave function under C_2 rotation about the z-axis (the bond axis).
  - π and π^* orbitals arise from the interactions between p_x and p_y atomic orbitals.
- MOs that form from p_z orbitals are σ and σ^* orbitals.
- "When orbitals overlap equally with both the same and opposite signs... the bonding and antibonding effects cancel, and no molecular orbital results" (Miessler et al., 2014, p. 121).
- d orbitals can also be involved in bonding in heavier elements such as the transition metals.
  - Two d_{z^2} orbitals participate in σ bonding.
  - Two d_{xz} or d_{yz} orbitals participate in π bonding.
  - Two $d_{x^2-y^2}$ or d_{xz} orbitals participate in **δ bonding**.
- **δ orbital**: A molecular orbital with a change in sign of the wave function under C_4 rotation about that z-axis.
  - δ and δ^* orbitals arise from the interactions of atomic orbitals meeting in parallel planes and combining side to side.
- "Sigma orbitals have no nodes that include teh line connecting the nuclei, pi orbitals have one node that includes the line connecting the nuclei, and delta orbitals have two nodes that include the line connecting the nuclei" (Miessler et al., 2014, p. 121).
- Note that p_x and d_{xz} orbitals (for example) could, in theory, interact.
- Additional thoughts on Figure III.6:
  - Similarity in energy is correlated with similarity in structure.
  - When orbital energies are similar (Figure III.6a), there is a large difference between the atomic orbitals and the molecular orbitals, resulting in a great potential for stabilization through bonding.
- Molecular orbitals help us understand the structure of Li_2, Be_2, and other diatomic molecules that violate the octet rule.
  - They also explain experimental phenomena that clash with VSEPR theory — for example, the Lewis structure of O_2 predicts a diamagnetic molecule, but in reality, O_2 is paramagnetic with two unpaired electrons.
- See Figure III.17 for the molecular orbitals in the homonuclear diatomic molecules formed by the first 10 elements, neglecting interactions between atomic orbitals of differing energy levels.
- Bond order:

$$\text{B.O.} = \frac{1}{2}(\text{number of electrons in bonding orbitals} - \text{number of electrons in antibonding orbitals})$$

  - Generally, we need only consider valence electrons to calculate the bond order: For example, O_2 has B.O. = 2 whether or not you factor valence electrons into the calculation.
- Core electrons are generally assumed to reside mostly on the original atom and negligibly participate in bonding and antibonding interactions.

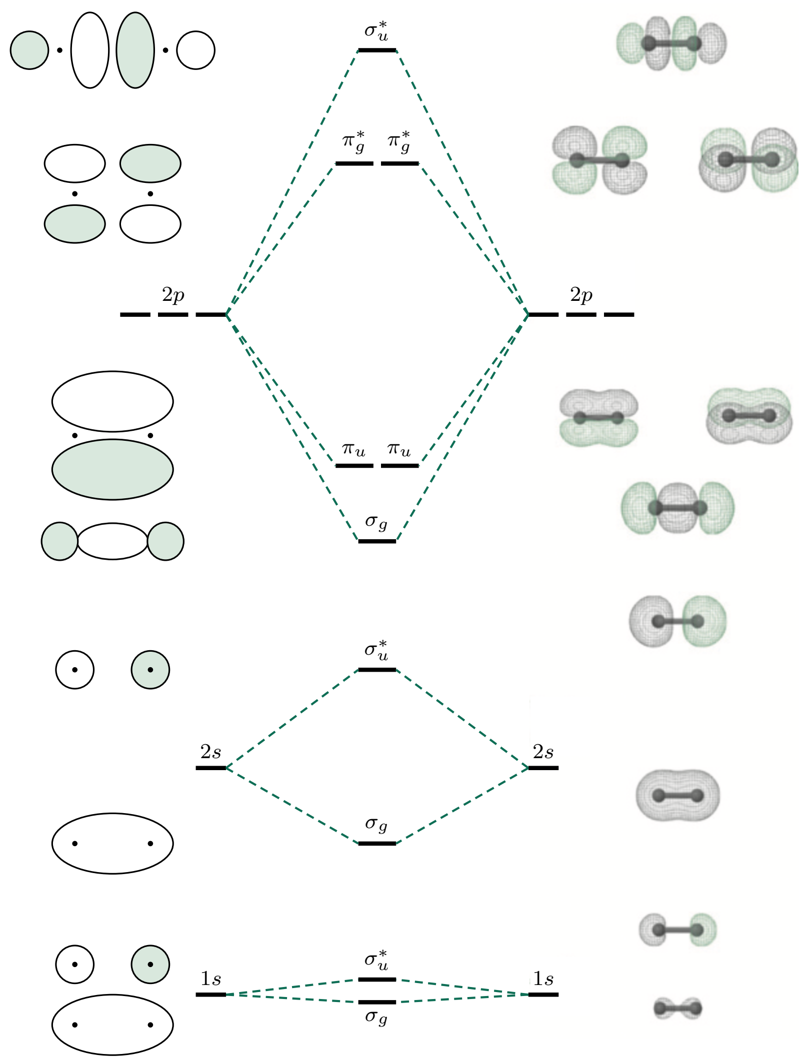


Figure III.17: Molecular orbitals for the first 10 elements.

  - This is reflected by how much lower the $1s$ MOs are in Figure III.17 than the others, and by how slight the difference is between bonding and antibonding.

- "When two molecular orbitals of the same symmetry have similar energies, they interact to lower the energy of the lower orbital and raise the energy of the higher orbital" (Miessler et al., 2014, p. 124).
- $\boldsymbol{\sigma_g}$ **symmetry**: Symmetry to infinite rotation and inversion.
  - Possessed by the $\sigma_g(2s)$ and $\sigma_g(2p)$ orbitals in Figure III.17, for example.
- Molecular orbitals with the same symmetry and similar energies can **mix**, lowering the energy of the lower orbital and raising the energy of the higher orbital.
  - For example, the $\sigma_g(2s)$ and $\sigma_g(2p)$ orbitals in Figure III.17 can mix, lowering the energy of the $2s$ one and raising the energy of the $2p$ one.

2/6:
- Atomic orbital energies decrease across a row in the periodic table.
- Characterization of selected homonuclear diatomic molecules:

- He_2's bond order is 0, with two bonding and two antibonding electrons. Thus, it has no significant tendency to form (it's bone energy is 0.01 J/mol, compared to H_2's 436 kJ/mol).
- B_2 is paramagnetic (because of its two unpaired π_u electrons). The $2p$ valence electrons do not occupy the σ_g MO because of orbital mixing and because the energy difference between $\sigma_g(2p)$ and $\pi_u(2p)$ is greater than Π_c (even if there were no mixing, the electrons would still occupy the π_u orbitals if it was more energetically favorable to do this than to occupy the same orbital).
- C_2 is a rarely encountered allotrope of carbon, but it has two π bonds and no σ bonds.
- In N_2, some larger trends become apparent:
  - Since electrons in different orbitals vary in their shielding abilities and electron-electron interactions, the difference between the $2s$ and $2p$ energies increase as Z increases.
  - More specifically, $2s$ electrons have higher probabilities close to the nucleus than $2p$ electrons (Figure 0.8), so they are more affected by increasing nuclear charge (inverse square law).
  - As a result of this separation, the $\sigma_g(2s)$ and $\sigma_g(2p)$ orbitals mix less in N_2 than in C_2 or B_2.
- The ions of O_2 (which include dioxygenyl ${O_2}^+$, superoxide ${O_2}^-$, and peroxide ${O_2}^{2-}$) reveal that bond order and bond distance are inversely proportional. Here, mixing finally becomes small enough that the normal filling order (as in Figure III.17) returns.

- Notice how atomic radius consistently decreases across the second period, but bond length decreases until N_2 and then increases (because of the addition of antibonding electrons).
- At this point, we'll assume (for PES purposes) the energy levels in the uncharged molecule to be essentially the same as those in the charged ions generated when we seek to examine core energy levels[3].
- Comparing the PES spectrums for N_2 and O_2, it can be seen that the N_2 energy levels are closer together than the O_2 ones.
- PES also provides evidence for the existence of **vibrational energy levels**, energy levels that are much more closely spaced than electronic levels that cause the multiple peaks within one "peak."
- Orbitals that are strongly involved in bonding have **vibrational fine structure** (multiple peaks), and vice versa for less involved orbitals.
  - Thus, the 10 π_u vs. the 6 σ_g vibrational peaks in O_2 indicate that the π_u orbitals are more strongly involved in bonding than the σ_g orbital.
- "The atomic orbitals of atoms that form homonuclear diatomic molecules have identical energies, and both atoms contribute equally to a given MO. Therefore, in the molecular orbital equations, the coefficients associated with the same atomic orbitals of each atom... are identical. In heteronuclear diatomic molecules... the atomic orbitals have different energies, and a given MO receives unequal contribbutions from these atomic orbitals; the MO equation has a different coefficient for each of the atomic orbitals that contribute to it" (Miessler et al., 2014, pp. 134, 136).
- Atomic orbitals closer in energy to an MO contribute more to that MO, and thus have larger coefficients in the wave equation.
- CO example:
  - The 1π orbitals are lower than the 3σ orbitals because of the strong mixing between the $2p_z$ orbital of oxygen and the $2s$ and $2p_z$ orbitals of carbon.
  - The 3σ orbital has a large lobe on the carbon end because two carbon orbitals ($2s$ and $2p_z$) mix with one oxygen orbital ($2p_z$).

[3] However, we should note that this is an oversimplification; a rigorous treatment of PES considers how the energy levels and orbital shapes vary between the neutral and ionized species.

  - The π orbital has electron density concentrated on oxygen because of the better energy match between the MO and the $2p_{x,y}$ orbitals of oxygen; the π^* orbital has electron density concentrated on carbon because of the better energy match between the MO and the $2p_{x,y}$ orbitals of carbon.
- Atomic orbitals with energy differences greater than 10-14 eV usually do not interact significantly.
- MOs in HF predict a polar bond since electron density is concentrated on F to such a greater extent in every occupied orbital.
- **Frontier orbitals**: The HOMO and LUMO, so-nambed because they lie at thee occupied-unocupied frontier.
- Frontier orbitals help explain reaction chemistry with transition metals.
  - In CO for example, we'd predict based on electronegativity that the O would be more reactive, and hence we'd get a preponderance of M−O−C structures.
  - However, carbonyl complexes are typically of the form M−C−O because the frontier orbitals both lie more on C. Indeed, the HOMO contains the least stabilized (most reactive) electrons in the molecule, and the LUMO is ready to accept whatever electrons are donated first.
- Ionic compounds can still be treated, MO theory-wise, like covalent compounds; we just get MOs that are almost identical to the more favored constitutent atomic orbitals.
- Crystalline lattice salts are much more stable than diatomic ones.
  - Such crystal lattices are held together by a combination of electrostatics (ionic) attraction and covalent bonding.
  - Salts do not exhibit directional bonds; instead, the orbitals form energy bands (see Chapter 7).
- Considers lattice enthalpies and Born-Haber cycles[4].
- **Group orbitals**: Collections of matching orbitals on outer atoms.
  - Sets of orbitals that potentially could interact with the central atom orbitals.
  - The same combinations that formed bonding and antibonding orbitals in diatomics.
- FHF^- example:
  - The group orbitals are formed by adding and subtracting the F orbitals as we would in F_2.

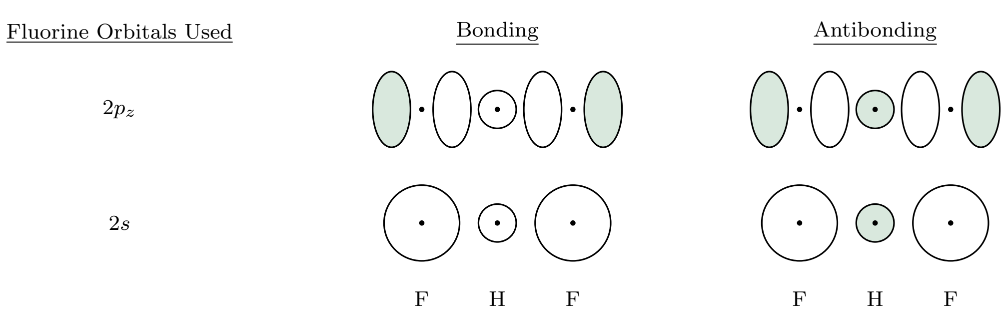


Figure III.18: Interaction of fluorine group orbitals with the hydrogen $1s$ orbital.

  - The only two group orbitals eligible for bonding with the H($1s$) orbital based on symmetry are $2s + 2s$ and $2p_{z_a} - 2p_{z_b}$. Having the H orbital with the same sign as the surrounding lobes gives bonding orbitals, and the opposite sign generates antibonding orbitals.

[4]See Labalme (2020a), specifically Figure 8.2 and the associated discussion

  - Since the H($2s$) orbitals match better energetically with the F($2p_z$) orbitals than the F($2s$) orbitals, the $2p_z$ interactions will be stronger.
  - Notice that the lone pairs are delocalized over both fluorine atoms, not confined to one as the Lewis dot model predicts.
  - Additionally, the Lewis approach predicts two, 2-electron bonds, resulting in 4 electrons arount the central H atom. However, the MO model suggests 2 electrons (in a σ bond [a_g]) decentralized over all three atoms.

- A stepwise approach to building MOs for more complex molecules (Miessler et al., 2014, p. 143):
  1. Determine the point group of the molecule. If it is linear, substituting a simpler point group that retains the symmetry of the orbitals (ignoring the wave function signs) makes the process easier. It is useful to substitute D_{2h} for $D_{\infty h}$ and C_{2v} for $C_{\infty v}$. This substitution (known as a **Descent in Symmetry**) retains the symmetry of the orbitals without the need to use infinite-fold rotation axes.
  2. Assign x, y, z coordinates to the atoms, chosen for convenience. Experience is the best guide here. A general rule is that the highest order rotation axis of the molecule is assigned as the z-axis of the central atom. In nonlinear molecules, the y-axes of the outer atoms are chosen to point toward the central atom.
  3. Construct a (reducible) representation for the combination of the valence s orbitals on the outer atoms. If the outer atom is not hydrogen, repeat the process, finding the representations for each of the other sets of outer atom orbbitals (for example, p_x, p_y, and p_z). As in the case of the vectors described in Chapter 4, any orbital that changes position during a symmetry operation contributes 0 to the character of the resulting representation; any orbital that remains in its original position — such as a p orbital that maintains its position and direction (signs of its orbital lobes) — contributes 1; and any orbital that remains in the original position, with the signs of its lobes reversed, contributes -1.
  4. Reduce each representation from Step 3 to the sum of its irreducible representations. This is equivalent to finding the symmetry of the group orbitals or the **symmetry-adapted linear combinations** (SALCs) of the orbitals. The group orbitals are then the combinations of atomic orbitals that match the symmetry of the irreducible representations.
  5. Identify the atomic orbitals of the central atom with the same symmetries (irreducible representations) as those found in Step 4.
  6. Combine the atomic orbitals of the central atom and those of th group orbitals with matching symmetry and similar energy to form molecular orbitals. The total number of molecular orbitals formed must equal the number of atomic orbitals used from all the atoms. Note that the MOs are assigned lowercase Mulliken symbols (e.g., a_1), whereas atomic orbitals and representations in general are assigned uppercase Mulliken symbols (e.g., A_1).

- CO_2 example:
  - We find the same group orbitals as in FHF^- but by using the stepwise procedure.
    - Note that saying $\Gamma_{2s} = A_g + B_{1u}$, for example, expresses the fact that there are two $2s$ orbitals (the sum and difference of the O($2s$) orbitals) and that one has A_g symmetry while the other has B_{1u} symmetry.
  - The orbitals on the central atom are $2s, 2p_z, 2p_x, 2p_y$.
  - The A_g O($2s$) orbital can be added to and subtracted from the C($2s$) orbital, and the B_{1u} O($2s$) orbital can be added to and subtracted from the C($2p_z$) orbital.
    - However, due to the large energy difference between the O and C orbitals, these do not generally form and are not included in Figure III.19.
    - Instead, the two O($2s$) orbitals are included as σ $2a_g$ and $2b_{1u}$, respectively, nonbonding orbitals.

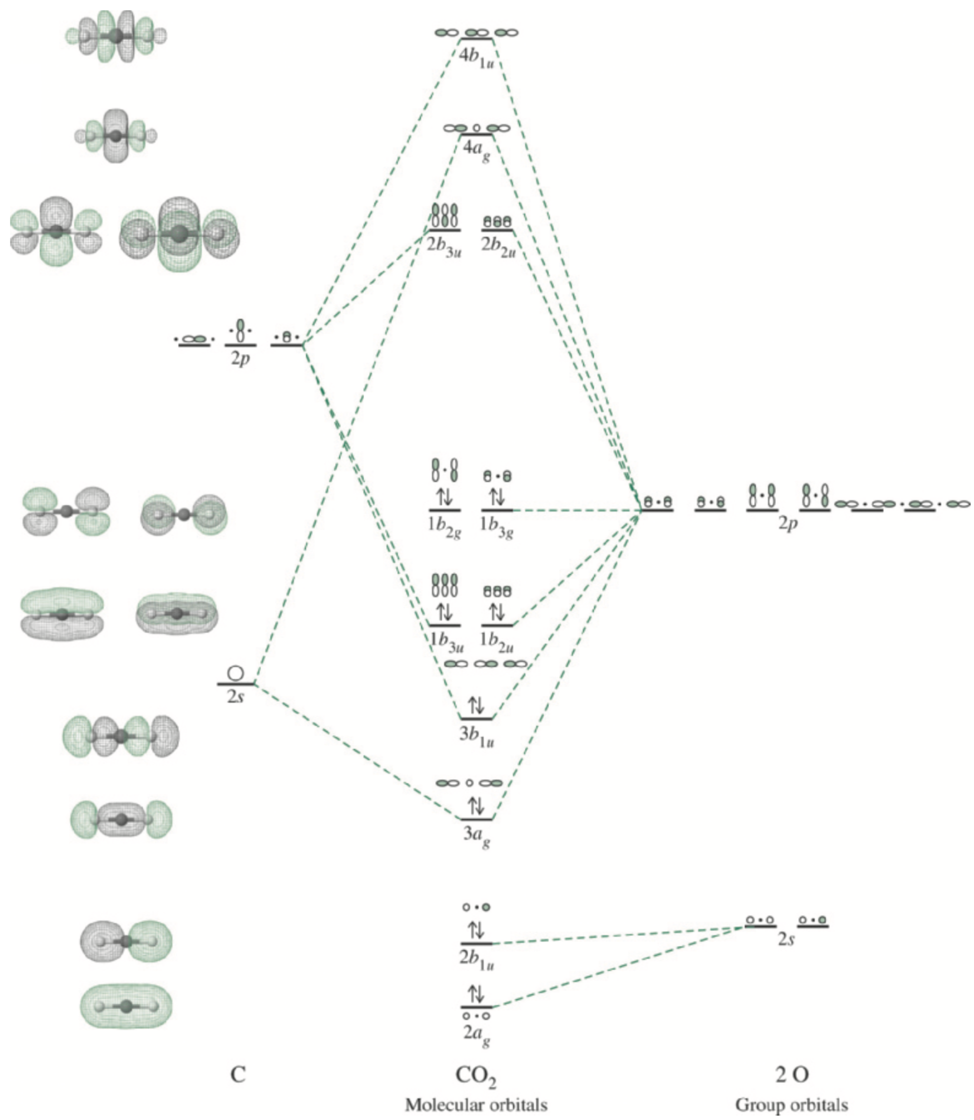


Figure III.19: Molecular orbitals for CO_2.

- The A_g O($2p_z$) orbital can be added to and subtracted from the C($2s$) orbital, and the B_{1u} O($2p_z$) orbital can be added to and subtracted from the C($2p_z$) orbital.
  - From the first interaction: The σ $3a_g$ bonding orbital formed is the most stable, with only two nodes and an uninterrupted probability region between the three nuclei. The σ^* $4a_g$ antibonding orbital is the second least stable with four nodes.
  - From the second interaction: The σ $3b_{1u}$ bonding orbital formed is the second most stable, with only three nodes. The σ^* $4b_{1u}$ antibonding orbital is the least stable with a whopping five nodes.
- The B_{2u} O($2p_y$) orbital can be added to and subtracted from the C($2p_y$) orbital, yet the B_{3g} O($2p_y$) orbital does not have matching symmetry with any C orbital.
  - From the first interaction: The π $1b_{2u}$ bonding orbital formed is less stable than the σ $3b_{1u}$ orbital since it lacks such direct probability between the nuclei but also has few nodes. The π^* $2b_{2u}$ antibonding orbital is more stable than the σ^* $4a_g$ antibonding orbital since it has fewer nodes.

    - From the second interaction: The π $1b_{3g}$ nonbonding orbital formed resides in the middle of the energy diagram.
  - The B_{3u} $O(2p_x)$ orbital can be added to and subtracted from the $C(2p_x)$ orbital, yet the B_{2g} $O(2p_x)$ orbital does not have matching symmetry with any C orbital.
    - The cases are symmetric to the previous two.
- This process may be used to obtain numerical values for the coefficients of the atomic orbitals, but the computational methods are beyond the scope of Miessler et al. (2014).
- H_2O example:
  - We canonically select that xz-plane as the plane of the molecule when we have a choice.
  - Because the $H(1s)$ orbitals have no directionality, it is not necessary to assign coordinate axes to the hydrogen atoms.

Symmetry	Molecular Orbitals		Oxygen Atomic Orbitals		Group Orbitals from Hydrogen Atoms	Description
B_1	Ψ_6	$=$	$c_9\psi(p_x)$	$+$	$c_{10}[\psi(\mathrm{H}_a) - \psi(\mathrm{H}_b)]$	Antibonding (c_{10} is negative)
A_1	Ψ_5	$=$	$c_7\psi(s)$	$+$	$c_8[\psi(\mathrm{H}_a) + \psi(\mathrm{H}_b)]$	Antibonding (c_8 is negative)
B_2	Ψ_4	$=$	$\psi(p_y)$			Nonbonding
A_1	Ψ_3	$=$	$c_5\psi(p_z)$	$+$	$c_6[\psi(\mathrm{H}_a) + \psi(\mathrm{H}_b)]$	Slightly bonding (c_6 is small)
B_1	Ψ_2	$=$	$c_3\psi(p_x)$	$+$	$c_4[\psi(\mathrm{H}_a) - \psi(\mathrm{H}_b)]$	Bonding (c_4 is positive)
A_1	Ψ_1	$=$	$c_1\psi(s)$	$+$	$c_2[\psi(\mathrm{H}_a) + \psi(\mathrm{H}_b)]$	Bonding (c_2 is positive)

Table III.2: Molecular orbital equations for H_2O.

  - Note that the nonbonding pairs afforded by the MO model are not equivalent as in the Lewis model.
- NH_3 example:
  - Is it not a bit circular to assign the point group C_{3v} and then later use Walsh diagrams to determine that it has a C_{3v} structure?
  - Here, we can no longer just add and subtract atomic orbitals. Instead, we must apply "the projection operator method, a systematic approach for deduction of group orbitals" (Miessler et al., 2014, p. 152).
  - This method illustrates how atomic orbitals should be combined to afford the SALCs that define the group orbitals.
  - First, determine the impact of each point group symmetry operation (individually, not within classes) on one atomic orbital.
  - Linear combinations of these atomic orbitals that match the symmetries of the group's irreducible representations can be obtained via (1) multiplication of each outcome by the characters associated with each operation for these irreducible representations, followed by (2) addition of the results.
  - Finding $\mathrm{SALC}(A_1) = \frac{1}{\sqrt{3}}[\Psi(\mathrm{H}_a) + \Psi(\mathrm{H}_b) + \Psi(\mathrm{H}_c)]$ and $\mathrm{SALC}(E) = \frac{1}{\sqrt{6}}[2\Psi(\mathrm{H}_a) - \Psi(\mathrm{H}_b) - \Psi(\mathrm{H}_c)]$ is easy.
  - Now SALC(E) has y symmetry (note that this means that choosing the H_a that we did in Figure III.13 [i.e., the one lying along a coordinate axis] has simplified calculations). Thus, the other SALC should have x symmetry.

- H_a should not contribute to the new SALC because of the orthogonal node defined by the yz-plane (if it contributed, there would be no yz node). Thus, only H_b and H_c can contribute, and we can deduce that their coefficients are $\frac{1}{\sqrt{2}}$ and $-\frac{1}{\sqrt{2}}$, respectively, to satisfy the normalization requirement whiile also leading to identical total contributions from all three $1s$ wave functions across the three group orbitals.

- In the projection operator method, orbitals can become the inverses of other orbitals.
- BF_3 example:

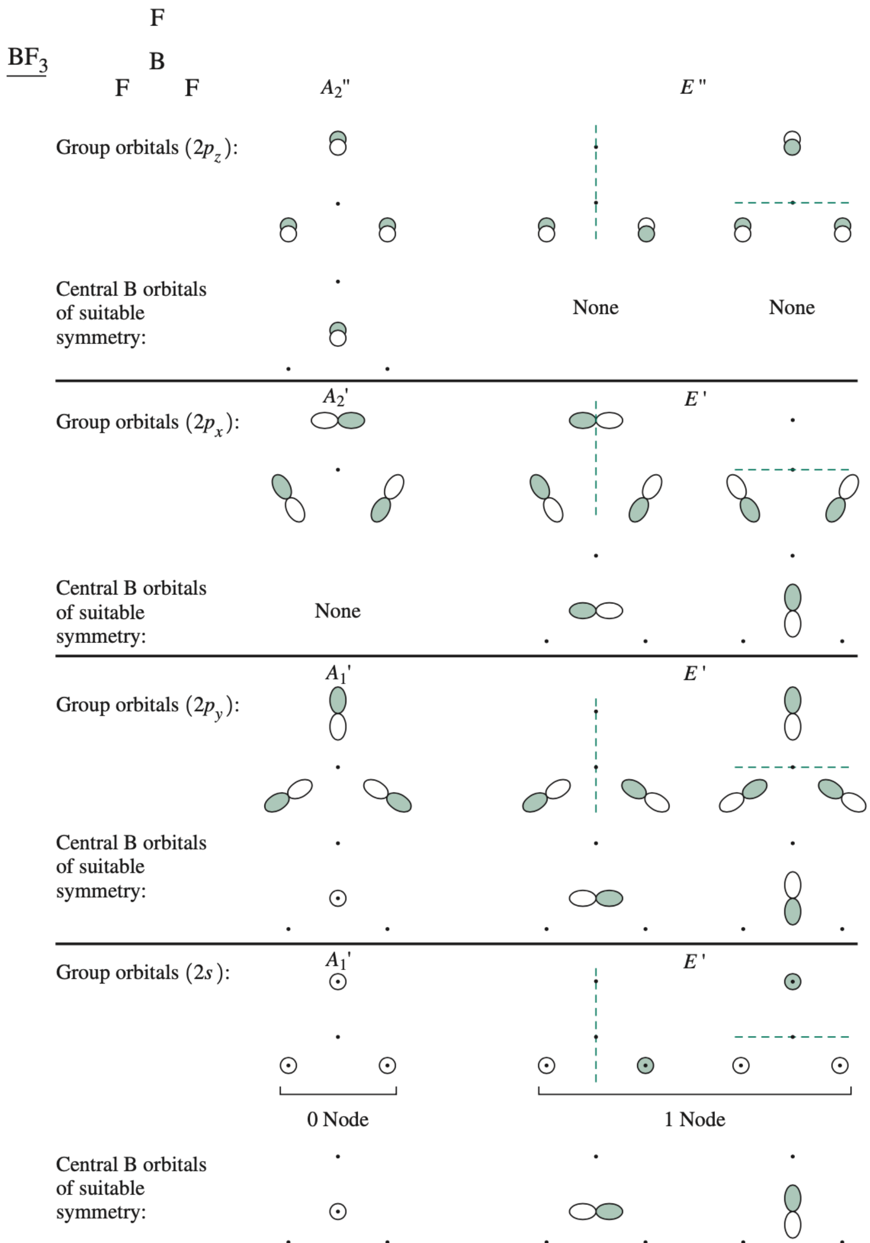


Figure III.20: Group orbitals for BF_3.

- The fluorine ligands have $2p$ electrons, too, now. As such, let the C_3 axis be the z-axis, the p_y axes point towards the central boron atom, and the p_x axes lie in the molecular plane.

- The partial double bonding character of the B−F bonds discussed in Chapter 3 can now be explained.
- The LUMO of BF_3 is an empty antibonding π orbital with large lobes on boron that can act as electron pair acceptors; this is why BF_3 is a Lewis acid.
- This approach is also applicable to other isoelectronic trigonal planar species such as SO_3, ${NO_3}^-$, and ${CO_3}^{2-}$.

- "Because the extent of orbital overlap in π interactions is generally less than that in most σ interactions, a double bond composed of one filled σ orbital and one filled π orbital is not twice as strong as a single bond" (Miessler et al., 2014, p. 161).
- Note that single bond energies between the same atoms can vary widely based on steric crowding and adjacent bonding.
- A qualitative group orbital approach (what we're doing) does not allow for the determination of the precise MO energies, but it generally allows for the placement of the MOs in the approximate order based on their shapes and expected orbital overlaps.
- "In the hybrid concept, the orbitals of the central atom are combined into sets of equivalent hybrids. These hybrid orbitals form bonds with orbitals of other atoms" (Miessler et al., 2014, p. 161).
- Hybrid orbitals correctly describe methane's PES spectrum.
- "Like all bonding models, hybrids are useful so long as their limits are recognized" (Miessler et al., 2014, p. 161).
- CH_4 example:
  - Point group: T_d.
  - Basis functions: σ bond vectors.
  - $\Gamma = (4, 1, 0, 0, 2)$.
  - $\Gamma = A_1 + T_2$.
  - "The atomic orbitals of carbon used in the hybrids must have symmetry matching $A_1 + T_2$; more specifically, one orbital must match A_1, and a set of three (degenerate) orbitals must match T_2" (Miessler et al., 2014, p. 162).
  - For A_1, we choose the $2s$ orbital. For T_2, we could choose d_{xy}, d_{xz}, d_{yz}, but since they're much higher energy (and thus won't mix well with the $H(1s)$ orbitals), we'll go for p_x, p_y, p_z.
  - Therefore, the hybridization is sp^3, combining four atomic orbitals into four equivalent hybrid orbitals, one directed toward each hydrogen atom.
- In addition to the sp^3 explanation of H_2O, it is sometimes explained through a slightly more MO theory lens as sp^2 since the oxygen orbitals used in MO bonding are $2s, 2p_x, 2p_z$ where the H_2O molecule lies in the xz-plane.
- Only σ bonding is considered when determining the orbitals used in hybridization.

Topic IV

Hard-Soft Acid-Base and Donor-Acceptor Concepts of Transition Metals

IV.1 Module 24: Acid-Base Chemistry

2/8: • Brønsted-Lowry Acid-Base Theory of Acids and Bases (1923).
  - Acid: Any chemical species (molecule or ion) that is able to lose, or "donate," a hydrogen ion (proton).
  - Base: Any chemical species that is able to gain, or "accept", a proton.
    - A base must have a pair of electrons available to share with the proton; this is usually present as an unshared pair, but sometimes is in a π orbital.
  - Acid-base reactions: The transfer of a proton from an acid to a base.

$$\mathrm{A{-}H + {:}BH \rightleftharpoons A{:} + BH_2}$$

    - Protons do not exist free in solution but must be attached to an electron pair.
  - Water is amphoteric.

- In the Brønsted-Lowry paradigm, we cannot separate the acids/bases from the solvent (no protons; only *solvated* protons). In a non-aqueous medium such as DMSO, however, we have much broader scope of acids and bases.
- **Carbon acid**: Any molecule containing a C−H bond can lose a proton forming the carbanion.
- Carborane ($H(CHB_{11}Cl_{11})$) is a superacid one million times stronger than sulfuric acid since it's conjugate basis is incredibly stable (super easy to delocalize the charge).
- The base dissociation constant or K_b is a measure of basicity. pK_b is the negative log of K_b and related to the pK_a by the simple relationship $\mathrm{p}K_a + \mathrm{p}K_b = 14$. The larger the p$K_b$, the more basic the compound.
- **Superacid**: An acid with acidity greater than that of 100% pure sulfuric acid.
  - In water, the strongest acid you can have is H_3O^+.
  - The strongest superacids are prepared by the combination of two components, a strong Lewis acid and a strong Brønsted-Lowry acid.
  - Fluoroantimonic acid $HF{-}SbF_5$ is 2×10^{19} stronger than 100% sulfuric acid.

- Olah's magic acid (FSO_3H-SbF_5) can dissolve paraffin (candle wax; extremely inert), converting methane into the t-butyl carbocation.

- **Hammett acidity function**: Can replace the pH in concentrated solutions. *Also known as* $\boldsymbol{H_0}$.

$$H_0 = \text{p}K_{\text{BH}^+} + \log \frac{[\text{B}]}{[\text{BH}^+]}$$

  - Let BH^+ be the conjugate acid of a very weak base B, with a very negative pK_{BH^+}. In this way, it is rather as if the pH scale has been extended to very negative values.
  - Hammett originally used a series of anilines with EWGs for the bases.

- **Superbase**: A compound that has a high affinity for protons.
  - Again, these do not exist in water.
  - Often destroyed by water, CO_2, and O_2.
  - A superbase has been defined as an organic compound whose basicity is greater than that of proton sponge, which has conjugate pK_a of 12.1.
  - These are valuable in organic chemistry, which abounds in very weak acids.
  - A common superbase is lithium diisopropylamide.

Topic VII

Band Theory in Solids

VII.1 Module 21: Electronic Structure of Solids (1D Solids)

2/5:

- Solid silicon's symmetry space group would be $Fd\bar{3}m$.
- Suggested reading: Hoffmann (1987).
- To consider solids, let's first consider an infinite chain of hydrogen atoms.
  - This should separate into H_2 molecules (**Peierl's instability**).
  - However, other substances can have chains of p_z orbitals, such as platinum atoms.
- An imaginary zoo of hydrogen molecules (we use the limit of a cycle of hydrogen atoms to approximate an infinitely long chain):
  - H_2 has a bonding and antibonding MO.
  - Cyclic ${H_3}^+$ is the most abundant ion in the universe (recently discovered by UChicago). One bonding and two antibonding orbitals.
  - We can keep adding hydrogen atoms to our rings.
  - For an infinitely long cycle of hydrogen atoms, we will have an infinite number of states close together that resembles a band in solids.
- Back to the chain of H atoms:
  - The basis function on each lattice point is a H_{1s} orbital.
  - The appropriate SALC ψ is
$$\psi_k = \sum_n \mathrm{e}^{ikna}\phi_n$$
  - In this formalism, k is an index labeling irreducible representations of the translation group. ψ transforms just like a, e_1, and e_2 (e.g., in the C_5 point symmetry group).
  - This process of symmetry adaptation is called "forming Bloch functions."
- Elementary band theory for extended solids:
  - Energy bands in solids arise from overlapping atomic orbitals, which become the **crystal orbitals** that make up the bands.
  - Recipe: Use LCAO (tight binding) approach.
  - A crystal is a regular periodic array with translational symmetry.
  - Periodic boundary conditions require $\psi(x+Na) = \psi(x)$, i.e., each wavefunction must be symmetry equivalent to the one in the neighboring cells.

  - For a 1D solid with lattice constant a and atom index n, **Bloch's theorem** tells us that the above SALC ψ_k is a solution to the Schrödinger equation.

- If we calculate ψ_0 and $\psi_{\pi/a}$, we get the most and least bonding states possible, respectively (the least bonding state is the most antibonding state and has the highest energy).

(a) $k = 0$. (b) $k = \frac{\pi}{a}$.

Figure VII.1: s orbital bonding states.

$$\psi_0 = \phi_0 + \phi_1 + \phi_2 + \phi_3 + \cdots$$
$$\psi_{\pi/a} = \phi_0 - \phi_1 + \phi_2 - \phi_3 + \cdots$$

- At this point, we can construct a band between these two states. *picture*
  - The band is *almost* infinite; it's on the order of Avogadro's number.
  - We have as many k values as translations in the crystal or as many unit cells in a crystal.

...

- **First Brillouin zone**: The region that covers all possible energy states that the crystal can have.
  - It is $-\frac{\pi}{a} < k < \frac{\pi}{a}$; which is the range of all possible values that the sine function will give.
- There is one energy level for each value of k, but $E(k) = E(-k)$.
- The energy is proportional to the electron momentum.
- Calculation of 1D band structure:
  - We have N atoms such that $\psi_k = \sum_{n=0}^{N} \mathrm{e}^{inka}\phi_n$.
  - The crystal Schrödinger equation is $\hat{H}\Psi(k) = E(k)\Psi(k)$.
  - Thus, the electron energies are given by

$$E(k) = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}$$

  - Recall that in Dirac's bra-ket notation, $\langle\psi|\hat{H}|\psi\rangle \equiv \int \psi^*\hat{H}\psi\,\mathrm{d}\tau$; for normalized atomic orbitals and ignoring overlap integrals:

$$\langle\phi_m|\phi_n\rangle = \begin{cases} 1 & m = n \\ 0 & m \neq n \end{cases}$$

  - Also recall that

$$\langle\psi|\psi\rangle = \sum_{m,n} \mathrm{e}^{i(n-m)ka}\,\langle\phi_m|\phi_n\rangle = N$$

  - Thus, we can calculate for on-site ($m = n$):

$$\langle\psi(k)|\hat{H}|\psi(k)\rangle = \sum_n \,\langle\phi_n|\hat{H}|\phi_n\rangle = N\alpha$$

  And for resonance ($m \neq n$), where we need only consider the two nearest neighbors:

$$\left\langle \mathrm{e}^{-inka}\phi_n \middle| \hat{H} \middle| \mathrm{e}^{i(n\pm1)ka}\phi_{n\pm1} \right\rangle = \beta\mathrm{e}^{\pm ika}$$

- Putting everything together, we have

$$E(k) = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{N\alpha + N\beta(\mathrm{e}^{ika} + \mathrm{e}^{-ika})}{N} = \alpha + 2\beta\cos(ka)$$

- **Zone center**: The ? where all atomic orbitals are in phase (all bonding σ). *Also known as* $\mathbf{\Gamma}$.
- **Zone border**: The ? where all atomic orbitals are out of phase (all antibonding σ^*). *Also known as* $\boldsymbol{X}$.
- Large numbers of MOs form bands of states.
- **Band structure**: The plot of E as a function of k.
  - The one we've derived so far is an s-shape curve.
- The p-orbitals are opposite — they form a bonding state with inverted phases.

(a) $k = 0$. (b) $k = \frac{\pi}{a}$.

Figure VII.2: p orbital bonding states.

- The analysis of Figures VII.1 and VII.2 can be done for many more types of orbitals, including p_z, d_{z^2}, and d_{xz}.
- Bonding orbital bands run uphill (concave upwards $E(k)$) at $k = 0$ and antibonding orbital bands run downhill (concave downwards $E(k)$) at $k = 0$.
- Energy bands run from $\alpha + 2\beta$ to $\alpha - 2\beta$ since β is negative for s orbitals.
- **Density of states**: The number of energy levels in the energy interval ΔE. *Also known as* **DOS**.

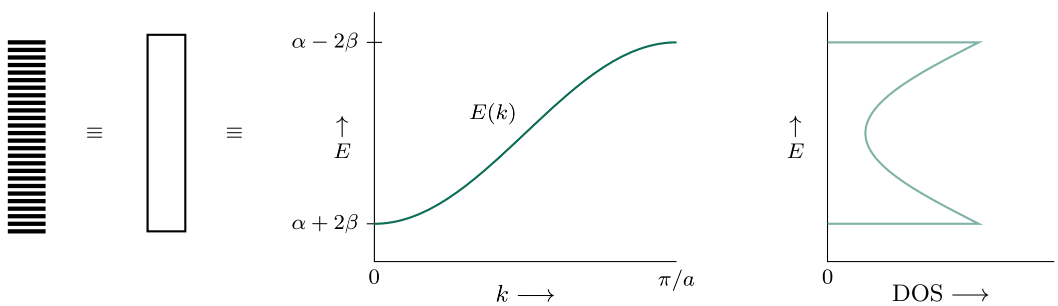


Figure VII.3: Density of states.

  - Proportional to the inverse slope of the band; steep bands with large overlap yield a small DOS, and vice versa for flat bands.
  - Reality check: PES for a long-chain alkane ($C_{36}H_{74}$) shows this inverse DOS relationship for a little while.

VII.2 Module 22: Electronic Structure of Solids (2D and 3D solids)

- 2D band structure:
  - Simple Hückel: A two-dimensional square net (s orbitals only (or p_z)).

$$\psi(k) = \sum_{m,n} \mathrm{e}^{ik_x ma + ik_y na} \cdot \phi_{m,n}$$

  - Consider the **crystal orbitals** at special k points (high symmetry).
  - The **Brillouin zone** is 2D here (we have a **wave vector**).

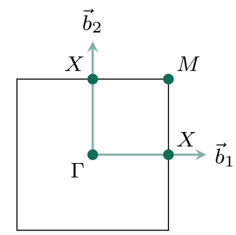
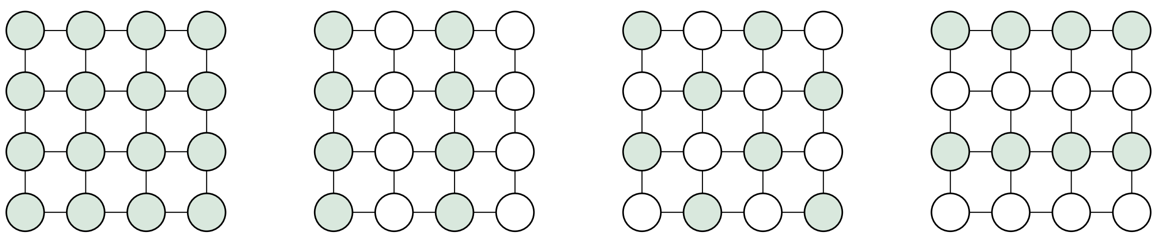


Figure VII.4: 2D Brillouin zone.



(a) Γ: $k_x, k_y = 0$. (b) X: $k_x = \pi/a, k_y = 0$. (c) M: $k_x, k_y = \pi/a$. (d) X: $k_x = 0, k_y = \pi/a$.

Figure VII.5: Special k points.

- ■ The center is the Γ point ($k_x = k_y = 0$). The midpoint of the lines are called X points ($k_x = \frac{\pi}{a}, k_y = 0$, and vice versa). The maximum point is the M point ($k_x = k_y = \frac{\pi}{a}$).

  - Calculating $E(k)$ in two dimensions.

$$E(k) = \alpha + 2\beta(\cos(k_x a) + \cos(k_y a))$$

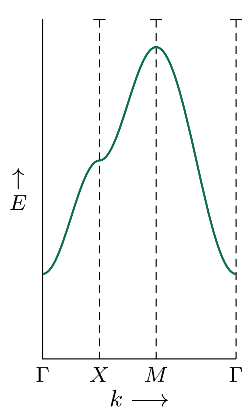


Figure VII.6: Schematic band structure (2D).

- Our schematic band structure (Figure VII.6) traces a 2D path $\Gamma \to X \to M \to \Gamma$.

2/8: • The bandwidth $4|\beta|$ is proportional to the degree of interaction between neighboring orbitals.
  - Since β is the interaction integral and $E(k)$ varies from $\alpha - 2\beta$ to $\alpha + 2\beta$.
- For p_σ orbitals, $\beta > 0$.
- Deriving the density of states formula:
  - We often simplify $E(k)$ with the first term of the Taylor series expansion; this gives us

$$E = \frac{\hbar}{2m}k^2$$

  - This implies that $E \propto k^2$ and, hence, $k \propto \sqrt{E}$.
  - Thus, the one-dimensional density $D_{1d}(k)$ of states as a function of k is $\mathrm{d}N(k)/\mathrm{d}k = 1$ since the number of states is evenly distributed along the k axis (i.e., in Figure VII.3).
  - It follows that the one-dimensional density $D_{1d}(E)$ of states as a function of E is

$$D_{1d}(E) = \frac{\mathrm{d}N(E)}{\mathrm{d}E} = \frac{\mathrm{d}N(k)}{\mathrm{d}k}\frac{\mathrm{d}k}{\mathrm{d}E} \propto 1 \cdot \frac{1}{\sqrt{E}} = \frac{1}{\sqrt{E}}$$

- For each orbital, there is a unique path akin to Figure VII.6. The combination of all of these **bands** in one graph characterizes a material.
- **Wigner-Seitz cell** (of the reciprocal lattice): The first Brillouin zone, or FBZ.
  - A primitive cell with a lattice point at its center.
  - A 3D discrete Fourier transform of the lattice.
  - Has $k_{x,y,z}$.
  - What is "d.I." and "r.I."?
  - We once again can find high symmetry points and directions akin to those in Figure VII.4.

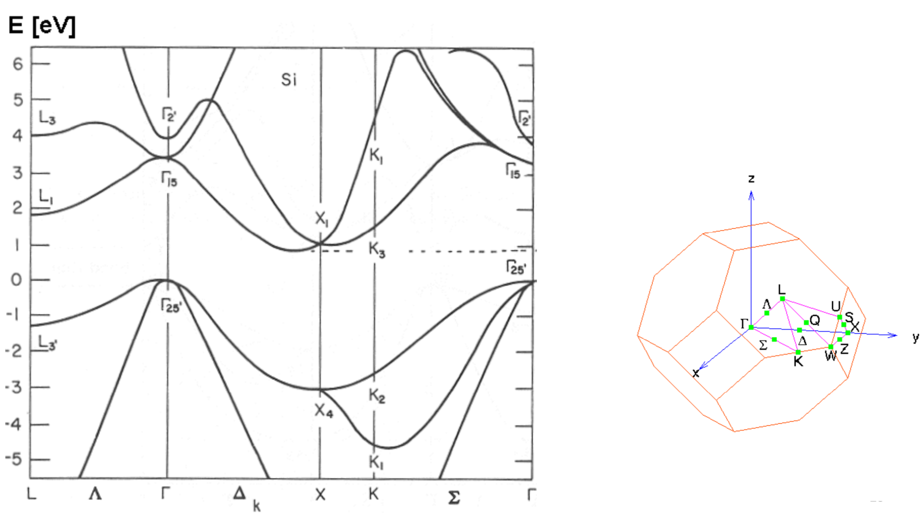


Figure VII.7: Electronic band structure of Si.

- Electronic band structure is calculated within the first Brillouin zone to give us the electronic band structure of a solid.

- **Angle-resolved photoemission spectroscopy**[1]: If the incoming photon's energy is greater than the electron's ginding energy, the electron will eventually be emitted with a characteristic kinetic energy and angle relative to the surface normal. This angle is related to the electron's crystal momentum. The Bloch wave vector is linked to the measured electron's momentum. *Also known as* **ARPES**.
  - Indeed, ARPES can be used to reconstruct the band structure of a solid. The bands are real!

VII.3 Module 23: Filling Bands With Electrons

- The Fermi-Dirac statistics and Fermi Energy:
  - At $T = 0$, we expect all of the atoms in a solid to be in the ground state. The distribution of electrons (fermions) at the various energy levels is governed by the Fermi-Dirac distribution:

$$F(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}$$

    where E_F is the Fermi energy.
    - $F(E)$ is the probability to fill the states with a given energy E.
  - When $T = 0\,\mathrm{K}$, the Fermi energy is the energy of the last occupied state. Moreover,
  - The Fermi energy is the energy of the last occupied state at $T = 0\,\mathrm{K}$; it is proportional to the square of the Fermi state k_F, i.e., $E_F \propto k_F^2$.
- If $T > 0$, then:
  - We fill the states from bottom to top.
  - Instead of having a sharp shift from occupied to unoccupied states, we have a sort-of washed-out step function.
  - Far below E_F, $F(E) = 1$; far above E_F, $F(E) = 0$. In the small **Fermi window** (aka. **Fermi level**) at the border (where the washed-out step function is), $0 < F(E) < 1$.
    - The Fermi window is $4kbt$.
  - It is in the Fermi level that all of the important stuff happens (i.e., electrons flowing in metals).
- If the gap (range where $\mathrm{DOS}(E) = 0$) in the density of states at the Fermi level is smaller than $3\,\mathrm{eV}$, then we have a semiconductor. If larger, we have an insulator. If 0, we have a conductor. Magnitude of DOS at Fermi level correlates with conductivity (e.g., Al has a higher DOS at the Fermi level than Ag, and we observe that Al is more conductive than Ag).
  - In metals and insulators, the Fermi level is within bands.
  - In semiconductors, it is between bands.
  - In physics, everything is a metal or insulator; semiconductors are a constructed perspective.
- Fermi sphere:
  - The surface of the Fermi sphere separates occupied and unoccupied states in k-space.
  - Bounded by Fermi surface.
  - Radius is Fermi wave vector $k_F = \sqrt[3]{3\pi^2 n}$ where n is a parameter related to the density of electrons.
  - Fermi energy: $E_F = \hbar^2 k_F^2 / 2m$.
  - Fermi momentum: $p_F = \hbar k_F$.
  - Fermi velocity: $v_F = \hbar k_F / m$.

[1] Figure 7.20 in Labalme (2020a) actually refers to this kind of photoelectron spectroscopy!

  - Fermi temperature: $T_F = E_F/k_B$.

- Electrons at $T = 0\,\mathrm{K}$ still move very quickly (approximately 0.06 the speed of light) since they're quantum particles (not classical ones).
- 3D density of states:
  - The density of states $g(E)$ is the number of one-electron states (including spin multiplicity) per unit energy and volume:
$$g(E)_{3D} \equiv \frac{1}{V}\frac{\mathrm{d}N}{\mathrm{d}E}$$
    - N is twice the product of the Fermi sphere volume and the number of levels per unit volume.
  - Thus,
$$N = 2 \times \frac{4}{3}\pi k^3 \times \frac{V}{8\pi^3} = \frac{V}{3\pi^2\hbar^3}(2m^*E)^{3/2}$$
so
$$g(E)_{3D} = \frac{1}{V}\frac{\mathrm{d}N}{\mathrm{d}E} = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\sqrt{E}$$
  - Take CHEM 39000 Solids, Materials, and Surfaces to learn more.

References

Cass, M. E., & Hollingsworth, W. E. (2004). Moving beyond the single center: Ways to reinforce molecular orbital theory in an inorganic course. *Journal of Chemical Education*, *81*(7), 997–1005. https://doi.org/10.1021/ed081p997

Cotton, F. A. (1990). *Chemical applications of group theory* (third). John Wiley & Sons.

Hoffmann, R. (1987). How chemistry and physics meet in the solid state. *Angewandte Chemie*, *26*(9), 846–878. https://doi.org/10.1002/anie.198708461

Labalme, S. (2020a). *AP chemistry notes* (Accessed 22 December 2020.). https://github.com/shadypuck/APChemNotes/blob/master/main.pdf

Labalme, S. (2020b). *CAAG Thomas notes* (Accessed 25 December 2020.). https://github.com/shadypuck/CAAGThomasNotes/blob/master/main.pdf

Lewis, G. N. (1916). The atom and the molecule. *Journal of the American Chemical Society*, *38*(4), 762–785. https://doi.org/10.1021/ja02261a002

Miessler, G. L., Fischer, P. J., & Tarr, D. A. (2014). *Inorganic chemistry* (fifth). Pearson Education.

Nocera, D. (2008). *Principles of inorganic chemistry ii: 5.04*. Massachusetts Institute of Technology: MIT OpenCourseWare. https://ocw.mit.edu License: Creative Commons BY-NC-SA