

# CHEM 20100 (Inorganic Chemistry I) Notes

Steven Labalme

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# Topics

<b>0</b>	<b>Course Prep</b>	<b>1</b>
0.1	Chapter 1: Introduction to Inorganic Chemistry . . . . .	1
0.1.1	Notes . . . . .	1
0.2	Chapter 2: Atomic Structure . . . . .	3
0.2.1	Notes . . . . .	3
0.2.2	Problems . . . . .	19
<b>I</b>	<b>Review of VSEPR Theory</b>	<b>22</b>
I.1	Module 1: Course Logistics and History . . . . .	22
I.2	Module 2: Molecular Geometries and VSEPR . . . . .	23
I.3	Chapter 3: Simple Bonding Theory . . . . .	24
I.3.1	Notes . . . . .	24
<b>II</b>	<b>Symmetry and Group Theory in Chemistry</b>	<b>27</b>
II.1	Module 3: Symmetry Elements and Operations . . . . .	27
II.2	Module 4: Symmetry Point Groups . . . . .	29
II.3	Module 5: Group Theory 101 . . . . .	30
II.4	Module 6: Representations . . . . .	32
II.5	Module 7: Characters and Character Tables . . . . .	34
II.6	Module 8: Using Character Tables . . . . .	38
II.7	Chapter 4: Symmetry and Group Theory . . . . .	40
II.7.1	Notes . . . . .	40
	<b>References</b>	<b>42</b>

# List of Figures

1	Examples of bonding interactions. . . . .	1
2	Inorganic compounds containing bridging hydrogens and alkyl groups. . . . .	2
3	Tetrahedral geometry without a central atom. . . . .	2
4	Hydrogen atom energy levels. . . . .	4
5	Particle in a box: Wave functions and their squares at different energy levels. . . . .	7
6	Spherical coordinates. . . . .	10
7	Radial wave functions. . . . .	11
8	Radial probability functions. . . . .	12
9	Coulombic energy of repulsion and exchange energy. . . . .	15
10	Schematic energy levels for transition elements. . . . .	17
11	First and second ionization energies and electron affinities. . . . .	19
I.1	VSEPR structure of $\text{BrF}_3$ . . . . .	23
I.2	Lewis structure of $\text{PF}_2\text{Cl}_3$ . . . . .	24
II.1	Methane's $S_4$ symmetry. . . . .	28
II.2	Low symmetry point groups. . . . .	29
II.3	Symmetry elements for $\text{H}_2\text{O}$ . . . . .	31
II.4	A character table. . . . .	35
II.5	$\text{XeOF}_4$ . . . . .	39
II.6	Rotations of a snowflake design. . . . .	40

# List of Tables

1	Quantum numbers and their properties. . . . .	8
2	Hydrogen atom wave functions: Angular functions. . . . .	9
3	Hydrogen atom wave functions: Radial functions. . . . .	10
4	Hund's rule and multiplicity. . . . .	15
I.1	VSEPR predictions. . . . .	25
I.2	Electronegativity and bond angles. . . . .	26
II.1	Group multiplication table for the $C_{2h}$ point group. . . . .	32
II.2	Group multiplication table for the $C_{3v}$ point group. . . . .	32
II.3	Character table for the $D_3$ point group. . . . .	36
II.4	Changes in the fluorine atoms of $\text{XeOF}_4$ under the $C_{4v}$ symmetry operations. . . . .	40

# Topic 0

## Course Prep

### 0.1 Chapter 1: Introduction to Inorganic Chemistry

*From Miessler et al. (2014).*

#### 0.1.1 Notes

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.

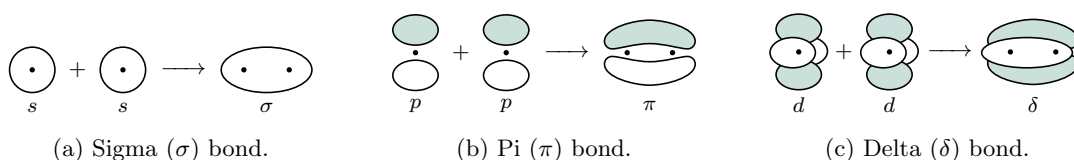


Figure 1: Examples of bonding interactions.

- 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 ( $\delta$ ) 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.

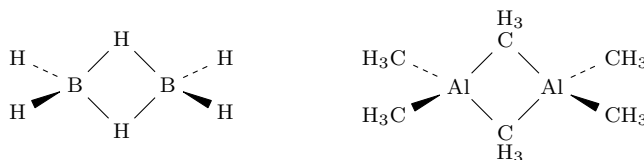


Figure 2: Inorganic compounds containing bridging hydrogens and alkyl groups.

- Hydrogen atoms and alkyl groups can act as bridges in inorganic chemistry, excessively disobeying the octet rule (see Figure 2).
- **Coordination number:** The number of other atoms, molecules, or ions to which an atom is bonded.
- “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.

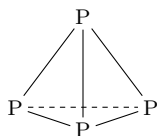


Figure 3: Tetrahedral geometry without a central atom.

- 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 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<sup>[1]</sup>.
- 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**.

<sup>1</sup>This provides a challenge to theoretical inorganic chemists.

## 0.2 Chapter 2: Atomic Structure

From Miessler et al. (2014).

### 0.2.1 Notes

- 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<sup>[2]</sup>

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

where  $n_h$  is an integer greater than 2 and  $R_H$  is the Rydberg constant for hydrogen (H).

- Note that  $R_H = 1.097 \times 10^7 \text{ m}^{-1} = 2.179 \times 10^{-18} \text{ J} = 13.61 \text{ eV}$ .
- 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  $n_l < n_h$ <sup>[3]</sup>.
- 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 ( $6.626 \times 10^{-34} \text{ J s}$ ),  $c$  is the speed of light ( $2.998 \times 10^8 \text{ m s}^{-1}$ ), and  $\nu$ ,  $\lambda$ , and  $\bar{\nu}$  are the frequency, wavelength, and **wavenumber**, respectively, 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:  $\text{cm}^{-1}$ ).*
  - Wavenumber is proportional to energy. This is why  $\text{m}^{-1}$  or  $\text{cm}^{-1}$  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:

$$R = \frac{2\pi^2 \mu Z^2 e^4}{(4\pi\epsilon_0)^2 h^2}$$

where...

- $\mu$  is the reduced mass of the electron/nucleus combination  $\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_{\text{nucleus}}}$ , where  $m_e = 9.11 \times 10^{-31} \text{ kg}$  is the mass of the electron and  $m_{\text{nucleus}}$  is the mass of the nucleus.
- $Z$  is the nuclear charge.
- $e = 1.602 \times 10^{-19} \text{ C}$  is the charge of the electron.
- $h$  is Planck's constant.
- $4\pi\epsilon_0$  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.

<sup>2</sup>Refer to Labalme (2020a), specifically Figure 7.6 and the accompanying discussion.

<sup>3</sup> $n_l$  denotes the lower final energy level while  $n_h$  denotes the higher initial energy level.

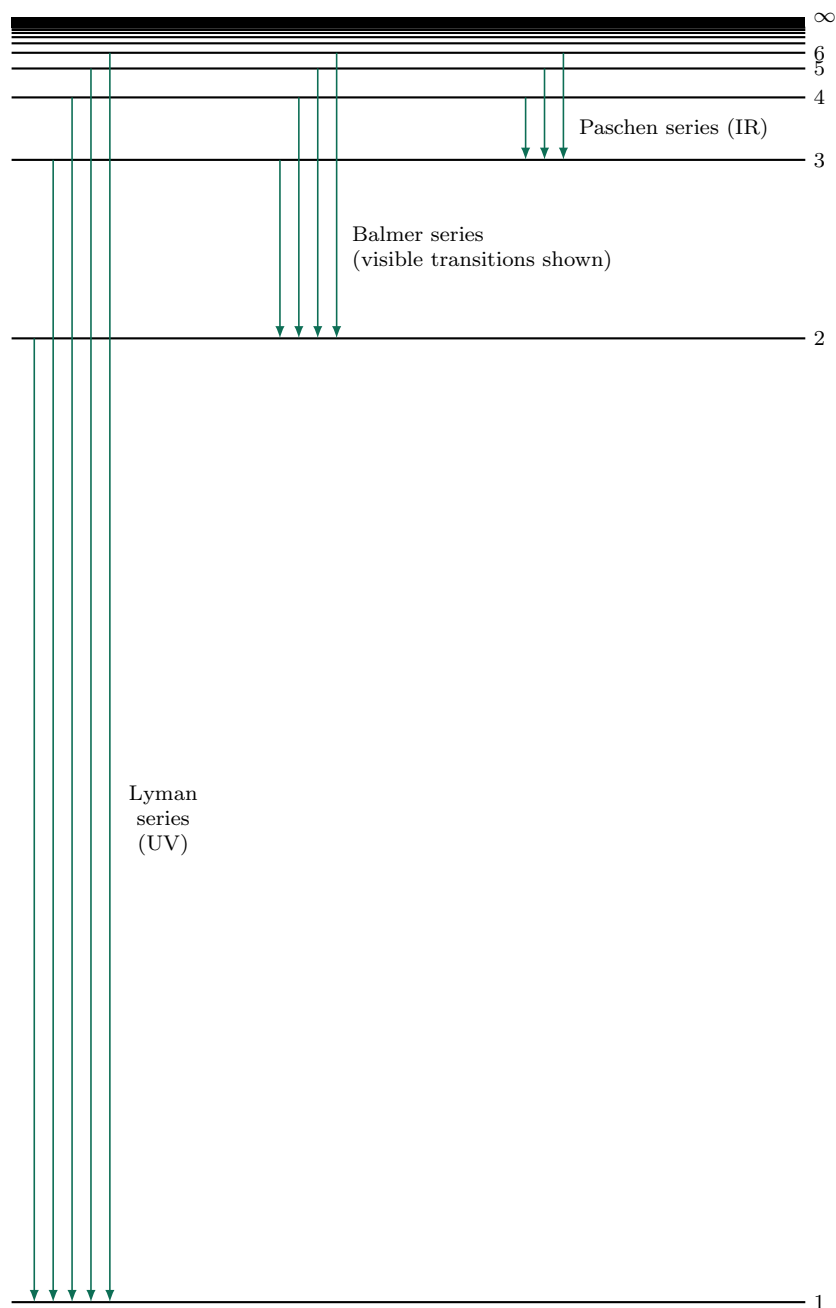


Figure 4: Hydrogen atom energy levels.

- **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  $\Delta x$  is the uncertainty in the position of the electron and  $\Delta p_x$  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  $\Psi$  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  $\Psi$ . *Also known as  $\hat{H}$ .*

$$H = \frac{-h^2}{8\pi^2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{Ze^2}{4\pi\epsilon_0\sqrt{x^2 + y^2 + z^2}}$$

- 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.
- $4\pi\epsilon_0$  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  $\infty$ , and every atomic orbital is described by a unique  $\Psi$ , there is no limit to the number of solutions of the Schrödinger equation for an atom. Each  $\Psi$  describes the wave properties of a given electron in a particular orbital” (Miessler et al., 2014, p. 15).
- Electron density is proportional to  $\Psi^2$ .
- Necessary conditions for a physically realistic solution for  $\Psi$ :
  1.  $\Psi$  must be single-valued: There cannot be two probabilities for an electron at any position in space.
  2.  $\Psi$  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.  $\Psi$  must approach zero as  $r \rightarrow \infty$ : For large distances from the nucleus, the probability must grow smaller and smaller (the atom must be finite).
  4. The integral

$$\int_{\text{all space}} \Psi_A \Psi_A^* d\tau = 1$$

The total probability of an electron being somewhere in space must be 1. Applying this stipulation is called **normalizing** the wave function<sup>[4]</sup>.

5. The integral

$$\int_{\text{all space}} \Psi_A \Psi_B^* d\tau = 0$$

$\Psi_A$  and  $\Psi_B$  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

$$\frac{-h^2}{8\pi^2m} \left( \frac{\partial^2 \Psi(x)}{\partial x^2} \right) = E\Psi(x)$$

- 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

$$r = s = \sqrt{2mE} \frac{2\pi}{h}$$

---

<sup>4</sup> $\Psi_A^*$  denotes the complex conjugate of  $\Psi_A$ . This is necessary because wave functions may have imaginary values. However, in many cases, the wave functions are real and the integrand reduces to  $\Psi_A^2$ .

- Because  $\Psi$  must be continuous and equal 0 for  $x < 0$  and  $x > a$ ,  $\Psi$  must approach 0 as  $x \rightarrow 0$  and  $x \rightarrow a$ . 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  $\pi$ . This means that

$$ra = \pm n\pi$$

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

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

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

- “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

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

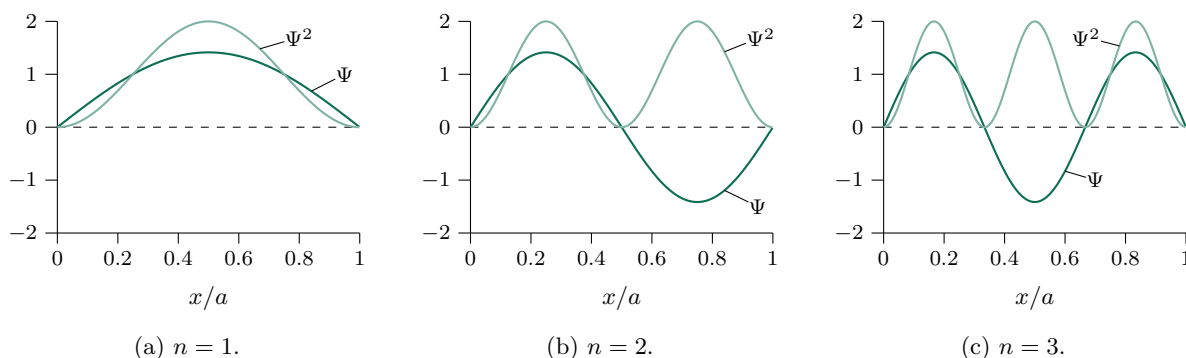


Figure 5: Particle in a box: Wave functions and their squares at different energy levels.

- The predicted probability densities for an electron at different energy levels (see Figure 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 wave nature of the particle (as described by quantum) 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  $\Psi$ ” (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 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, ...	Determines the major part of the energy.
$l$	Angular momentum <sup>[5]</sup>	0, 1, 2, ..., $n - 1$	Describes angular dependence and contributes to the energy.
$m_l$	Magnetic	0, $\pm 1$ , $\pm 2$ , ..., $\pm l$	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 1: Quantum numbers and their properties.

- $n$  is the primary quantum number affecting the overall energy.
- $l$  determines the type of shape. See Table 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 2.
- $m_s$  determines the electron spin<sup>[6]</sup> 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 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.

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

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

<sup>5</sup>Also known as **azimuthal** (quantum number).

<sup>6</sup>Note that the spin of an electron is purely quantum mechanical, and should not be related back to classical mechanics.

<sup>7</sup>Errata: Miessler et al. (2014) incorrectly normalizes this expression with  $i/\sqrt{2}$ .

Angular factors				Real Wave Functions				
Related to Angular Momentum				Functions of $\theta$	In Polar Coordinates	In Cartesian Coordinates	Shapes	Label
$l$	$m_l$	$\Phi$	$\Theta$		$\Theta\Phi(\theta, \phi)$	$\Theta\Phi(x, y, z)$		
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 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 2 are real,  $\Psi = \Psi^*$  and  $\Psi\Psi^* = \Psi^2$ .
- $\Psi$  may be expressed in terms of Cartesian coordinates  $(x, y, z)$  or in terms of spherical coordinates  $(r, \theta, \phi)$ .

– Using spherical coordinates comes with the advantage that  $r$  is the distance from the nucleus (see Figure 6).

12/23:

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

Table 3: Hydrogen atom wave functions: Radial functions.

12/25:

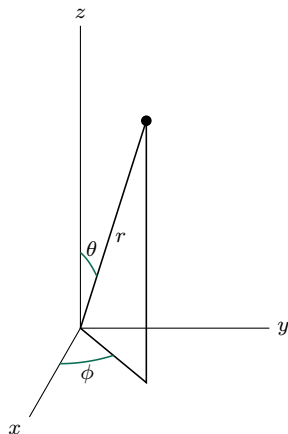


Figure 6: Spherical coordinates.

- Know the following volume element conversions<sup>[9]</sup>.

$$dV = dx dy dz = r^2 \sin \theta d\theta d\phi dr$$

- The volume of the thin shell between  $r$  and  $r + dr$  is as follows<sup>[10]</sup>, and is useful for describing the electron density as a function of distance from the nucleus.

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

<sup>8</sup>Errata: This differs from the corresponding equation in Miessler et al. (2014) because the textbook is wrong.

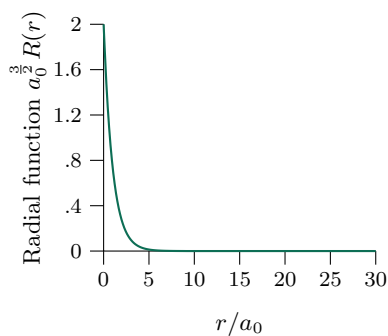
<sup>9</sup>Refer to Labalme (2020b), specifically Figure 16.9 and the accompanying discussion.

<sup>10</sup>Errata: Miessler et al. (2014) flips the bounds over which  $\theta$  and  $\phi$  should be evaluated, but I use the right ones.

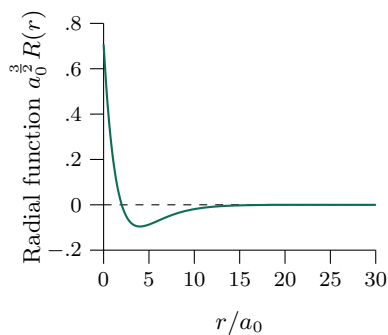
- $\Psi$  can be factored into a **radial component**  $R$  and two **angular components**  $\Theta$  and  $\Phi$ , which are sometimes combined into a single component  $Y$ :

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

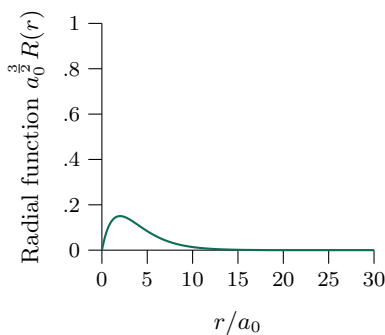
- Refer to Table 2 for examples of  $\Theta$  and  $\Phi$ , and Table 3 for examples of  $R$ .
- Note that in Table 2, the shaded orbital lobes correspond to where the wave function is negative. Distinguishing regions of opposite signs is useful for bonding purposes.
- The radial component can also be 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  $\Psi^2 = R^2 Y^2$ ).



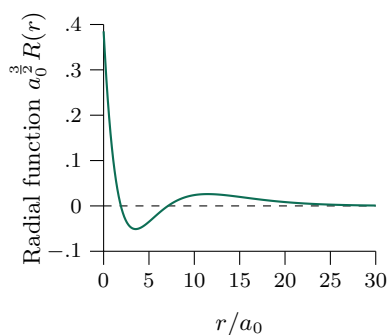
(a) 1s.



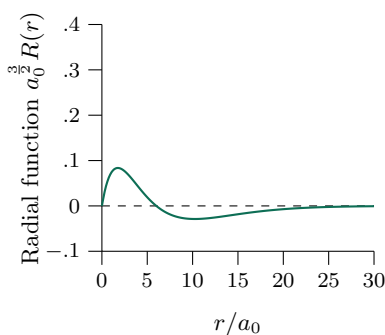
(b) 2s.



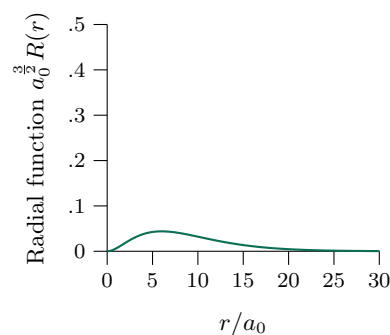
(c) 2p.



(d) 3s.



(e) 3p.



(f) 3d.

Figure 7: Radial wave functions.

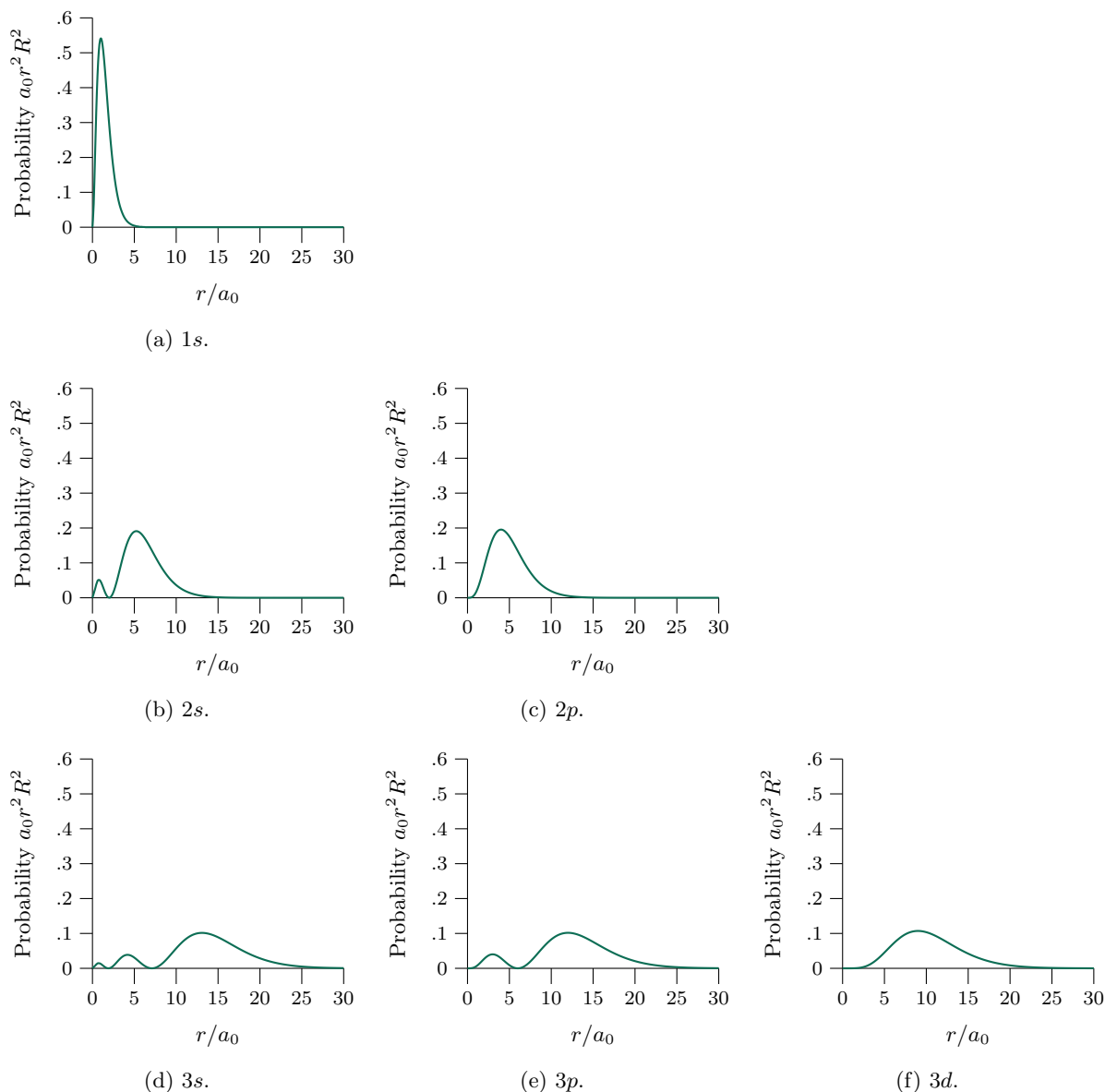


Figure 8: Radial probability functions.

- **Radial component:** The part of  $\Psi$  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 7.
- **Angular components:** The parts of  $\Psi$  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 8.
- **Bohr radius:** “The value of  $r$  at the maximum of  $\Psi^2$  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 8a.
  - Its value is  $a_0 = 52.9$  pm.
  - It is a common unit in quantum mechanics.
  - It is used to scale the functions in Figures 7 and 8 to give reasonable axis units<sup>[11]</sup>.
- Figure 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

$$0 = R(r)$$

$$0 = Y(\theta, \phi)$$

- “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 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.

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<sup>11</sup>Errata?: Should the  $y$ -axis in Figure 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 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 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 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
 
$$0 = x^2 - y^2$$

$$y^2 = x^2$$

$$y = \pm x$$
- This translates to Table 2, where we can see that the planes  $x = y$  and  $x = -y$ , i.e., those that contain the  $z$ -axis and make  $45^\circ$  angles with the  $x$ - and  $y$ -axes, are nodes.
- Additionally, the function is positive where  $|x| > |y|$  and negative where  $|x| < |y|$ <sup>[12]</sup>, and we can see this in Table 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 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.

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

Number of electrons	Arrangement	Unpaired e <sup>-</sup>	Multiplicity
1	$\uparrow$ $\underline{\hspace{0.5cm}}$ $\underline{\hspace{0.5cm}}$	1	2
2	$\uparrow$ $\uparrow$ $\underline{\hspace{0.5cm}}$	2	3
3	$\uparrow$ $\uparrow$ $\uparrow$	3	4
4	$\uparrow\downarrow$ $\uparrow$ $\uparrow$	2	3
5	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$	1	2
6	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	0	1

Table 4: Hund's rule and multiplicity.

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

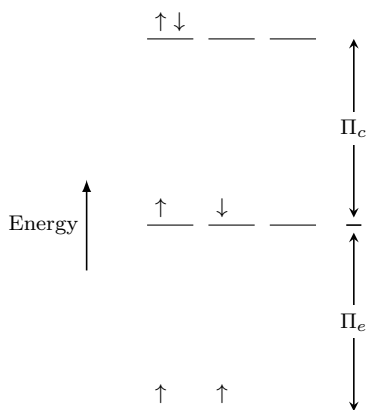


Figure 9: Coulombic energy of repulsion and exchange energy.

- **Coulombic energy of repulsion:** The potential energy of two negatively charged electrons that occupy the same orbital (as opposed to separate orbitals). *Denoted by  $\Pi_c$ .*
  - 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  $\Pi_e$ .*
  - This arises from purely quantum mechanical considerations.
  - Basically, there are three possible ways to arrange two electrons in degenerate orbitals (see Figure 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:  $\uparrow\downarrow$   $\uparrow\downarrow$   $\underline{\hspace{0.5cm}}$  ,  $\uparrow\downarrow$   $\uparrow$   $\downarrow$  , and  $\uparrow\downarrow$   $\uparrow$   $\uparrow$  .
- 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  $3d$ )<sup>[13]</sup>.
  - **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<sup>[14]</sup>.
      - b. Each electron in groups to the left contributes 1.00 to  $S$ .

<sup>13</sup>See Labalme (2020a), specifically Figure 7.12.

<sup>14</sup>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  $\text{Ni} \rightarrow \text{Ni}^{2+} + 2e^-$ , the two electrons removed are the  $4s$  electrons.
- Slater's rules are justified by electron probability curves (see Figure 8) and experimental data.
- Rich provided another explanation of orbital filling (refer to Figure 10 throughout the following discussion).

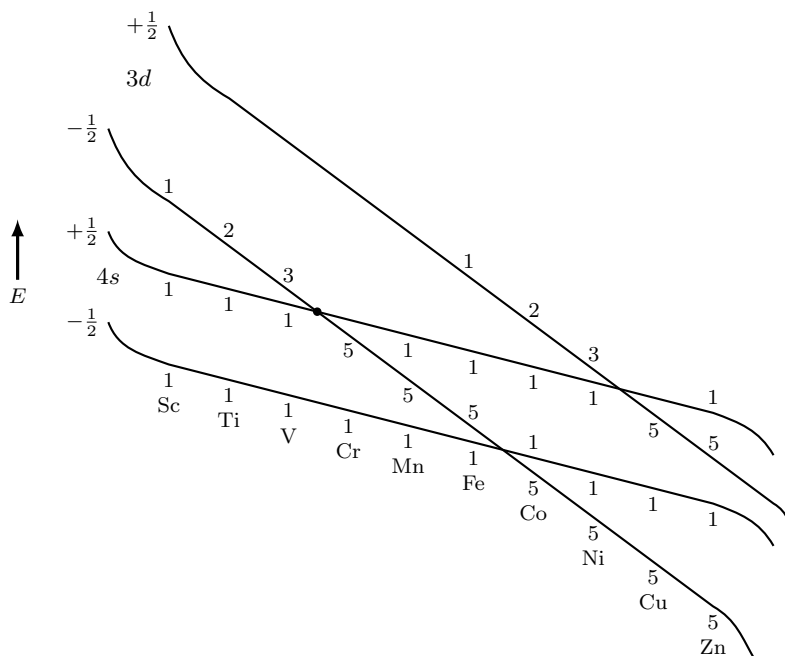
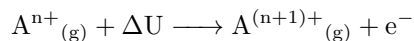


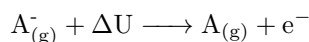
Figure 10: Schematic energy levels for transition elements.

- 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 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<sup>[15]</sup> 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.*



- When  $n = 0$ ,  $\Delta U$  is the first ionization energy  $\text{IE}_1$ . When  $n = 1$ ,  $\Delta U$  is the second ionization energy  $\text{IE}_2$ . The pattern continues.
- Ionization energy trends<sup>[16]</sup>:
  - 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  $\Pi_c$ , 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.*



- 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<sup>[17]</sup>) and with much smaller absolute numbers” (Miessler et al., 2014, p. 37).
  - The magnitude decreases because outer electrons in anions are better shielded.

<sup>15</sup>Errata: Miessler et al. (2014) misspells arrangement as “arrangment” (p. 36).

<sup>16</sup>Refer to Labalme (2020a), specifically Figure 7.19 as well as Exercise on  $Z_{\text{eff}}$ .

<sup>17</sup>Think isoelectricity (see Figure 11).

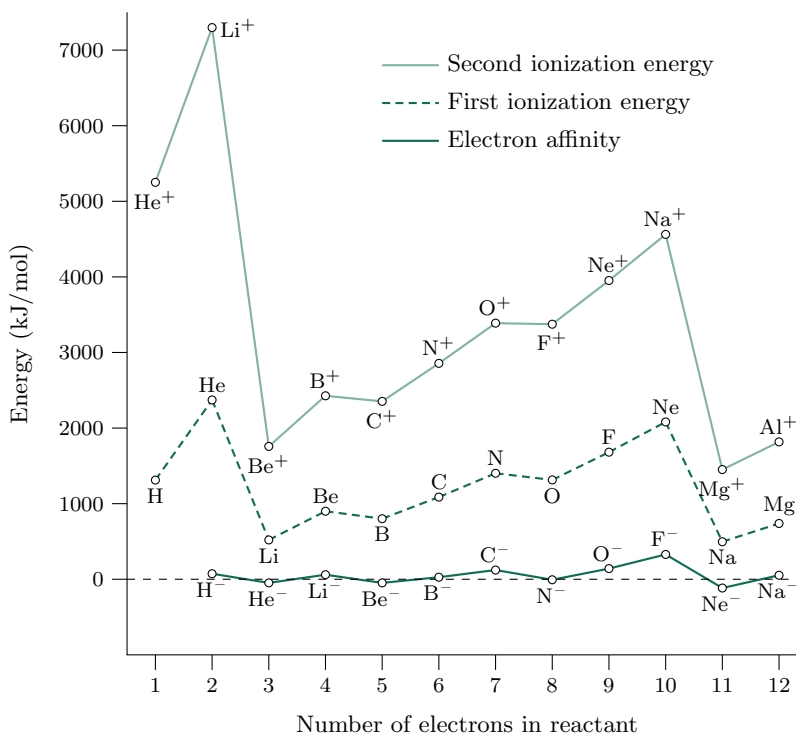


Figure 11: First and second ionization energies and electron affinities.

- 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).

## 0.2.2 Problems

9/13: **2.8** The details of several steps in the particle-in-a-box model in this chapter have been omitted. Work out the details of the following steps:

- Show that if  $\Psi = A \sin rx + B \cos sx$  ( $A$ ,  $B$ ,  $r$ , and  $s$  are constants) is a solution to the wave equation for the one-dimensional box, then

$$r = s = \sqrt{2mE} \left( \frac{2\pi}{h} \right)$$

*Solution.*

$$\begin{aligned}
 \frac{-h^2}{8\pi^2 m} \cdot \frac{\partial^2 \Psi(x)}{\partial x^2} &= E\Psi(x) \\
 \frac{-h^2}{8\pi^2 m} \cdot \frac{\partial^2}{\partial x^2} (A \sin rx + B \cos sx) &= E(A \sin rx + B \cos sx) \\
 \frac{-h^2}{8\pi^2 m} \cdot \frac{\partial}{\partial x} (Ar \cos rx - Bs \sin sx) &= E(A \sin rx + B \cos sx) \\
 \frac{-h^2}{8\pi^2 m} \cdot (-Ar^2 \sin rx - Bs^2 \cos sx) &= E(A \sin rx + B \cos sx) \\
 \frac{Ar^2 h^2}{8\pi^2 m} \sin rx + \frac{Bs^2 h^2}{8\pi^2 m} \cos sx &= AE \sin rx + BE \cos sx \\
 0 &= \left( \frac{Ar^2 h^2}{8\pi^2 m} - AE \right) \sin rx + \left( \frac{Bs^2 h^2}{8\pi^2 m} - BE \right) \cos sx
 \end{aligned}$$

Choose  $x = 0$ .

$$\begin{aligned}
 &= \frac{Bs^2 h^2}{8\pi^2 m} - BE \\
 E &= \frac{s^2 h^2}{8\pi^2 m} \\
 \frac{8\pi^2 m E}{h^2} &= s^2 \\
 s &= \sqrt{\frac{8\pi^2 m E}{h^2}} \\
 \boxed{s = \sqrt{2mE} \frac{2\pi}{h}}
 \end{aligned}$$

With this result ...

$$\begin{aligned}
 0 &= \left( \frac{Ar^2 h^2}{8\pi^2 m} - AE \right) \sin rx + \left( \frac{Bs^2 h^2}{8\pi^2 m} - BE \right) \cos sx \\
 &= \left( \frac{Ar^2 h^2}{8\pi^2 m} - AE \right) \sin rx + \left( B \left( \frac{s^2 h^2}{8\pi^2 m} \right) - BE \right) \cos sx \\
 &= \left( \frac{Ar^2 h^2}{8\pi^2 m} - AE \right) \sin rx + (BE - BE) \cos sx \\
 &= \left( \frac{Ar^2 h^2}{8\pi^2 m} - AE \right) \sin rx
 \end{aligned}$$

Choose  $x = \frac{\pi}{2r}$ .

$$\begin{aligned}
 &= \frac{Ar^2 h^2}{8\pi^2 m} - AE \\
 \boxed{r = \sqrt{2mE} \frac{2\pi}{h}}
 \end{aligned}$$

□

- d. Show that substituting the value of  $r$  given in part c into  $\Psi = A \sin rx$  and applying the normalizing requirement gives  $A = \sqrt{2/a}$ .



*Solution.*

$$\begin{aligned}
 1 &= \int_{\text{all space}} \Psi \Psi^* \, d\tau \\
 &= \int_0^a \left( A \sin \frac{n\pi x}{a} \right) \left( A \sin \frac{n\pi x}{a} \right) dx \\
 &= \int_0^a A^2 \sin^2 \frac{n\pi x}{a} \, dx
 \end{aligned}$$

Use  $\sin^2 u = \frac{1 - \cos 2u}{2}$ .

$$\begin{aligned}
 &= A^2 \int_0^a \frac{1 - \cos \frac{2n\pi x}{a}}{2} \, dx \\
 &= \frac{A^2}{2} \left( \int_0^a dx - \int_0^a \cos \frac{2n\pi x}{a} \, dx \right) \\
 &= \frac{A^2}{2} \left( [x]_0^a - \left[ \frac{a}{2n\pi} \sin \frac{2n\pi x}{a} \right]_0^a \right) \\
 &= \frac{A^2}{2} \left( (a - 0) - \left( \frac{a}{2n\pi} \sin 2n\pi - \frac{a}{2n\pi} \sin 0 \right) \right) \\
 &= \frac{A^2}{2} \left( a - \left( \frac{a}{2n\pi} \sin 2n\pi \right) \right)
 \end{aligned}$$

Since  $n$  is an integer,  $\sin 2n\pi = 0$ .

$$\begin{aligned}
 &= \frac{aA^2}{2} \\
 \frac{2}{a} &= A^2 \\
 \boxed{A} &= \sqrt{\frac{2}{a}}
 \end{aligned}$$

□

# 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  $[\text{Ar}]4s^23d^8$  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  $\sigma$ -bond framework first.
  3. Add  $\pi$ -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 ( $\text{BMe}_3$ ).
  - 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  $\text{SF}_4$  (see-saw), will the lone pair be axial or equatorial?
  - Equatorial —  $2 \times 120^\circ$  and  $2 \times 90^\circ$  vs.  $3 \times 90^\circ$ .
- In  $\text{BrF}_3 \dots$

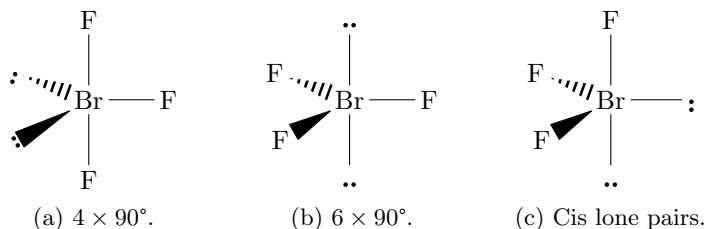
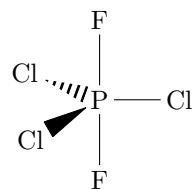


Figure I.1: VSEPR structure of  $\text{BrF}_3$ .

- T-shaped  $\rightarrow$  Distorted T —  $4 \times 90^\circ$  vs.  $6 \times 90^\circ$  or lone pairs in cis-position.
- In ions such as  $\text{ICl}_4^-$ , we get square planar ( $D_{4h}$ ).
- With mixed substituents (such as  $\text{PF}_2\text{Cl}_3$ )...
  - 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  $3s^1 3p_x^1 3p_y^1 3p_z^1 3d_{z^2}^2$  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.

Figure I.2: Lewis structure of  $\text{PF}_2\text{Cl}_3$ .

- **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  $\pi$ -bonds.
- Linear:  $D_{\infty h}$ .
- Problems with VSEPR:
  - $\text{XeF}_6$  with 14 bonding electrons (7 pairs) is supposed to be pentagonal bipyramidal, but is actually octahedral (a known problem for  $14e^-$  systems).
  - Heavy main group elements with no hybridization.
    - $\text{H}-\text{C}\equiv\text{C}-\text{H}$  is linear, but  $\text{H}-\text{Si}\equiv\text{Si}-\text{H}$  is not.
    - No  $\sigma$ -bond exists in the latter species — it's all  $\pi$ -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).

### I.3.1 Notes

- 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  $\text{BeF}_2$ , instead of getting the predicted double-bonded lewis structure, it forms a complex network with Be having coordination number 4.
    - $\text{BeCl}_2$  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  $\text{B}-\text{X}$  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<sup>[1]</sup> 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).

<sup>1</sup>Eratta: "unlikely."

1/14:

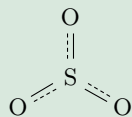
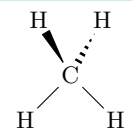
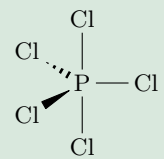
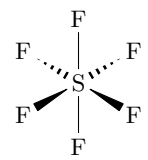
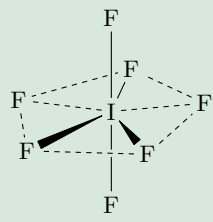
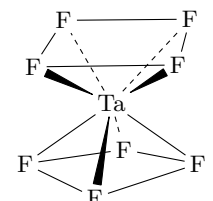
Steric Number	Geometry	Examples	Calculated Bond Angles	
2	Linear	CO <sub>2</sub>	180°	O=C=O
3	Trigonal (triangular)	SO <sub>3</sub>	120°	
4	Tetrahedral	CH <sub>4</sub>	109.5°	
5	Trigonal bipyramidal	PCl <sub>5</sub>	120°, 90°	
6	Octahedral	SF <sub>6</sub>	90°	
7	Pentagonal bipyramidal	IF <sub>7</sub>	72°, 90°	
8	Square antiprismatic	[TaF <sub>8</sub> ] <sup>3-</sup>	70.5°, 9.6°, 109.5°	

Table I.1: VSEPR predictions.

1/17:

- 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.
- “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.
  - For instance, electronegative outer atoms pull electrons away from the central atom, allowing lone pairs to further push together such atoms.

Molecule	X–P–X Angle (°)	Molecule	Bond Angle (°)
PF <sub>3</sub>	97.8	H <sub>2</sub> O	104.5
PCl <sub>3</sub>	100.3	H <sub>2</sub> S	92.1
PBr <sub>3</sub>	101.0	H <sub>2</sub> Se	90.6

Table I.2: Electronegativity and bond angles.

- Electronegative central atoms pull electrons toward the central atom, pushing bonding pairs farther apart.
- Atomic size can also have effects on VSEPR predictions.
  - For example, the C–N–C angle in N(CF<sub>3</sub>)<sub>3</sub> is larger than that of N(CH<sub>3</sub>)<sub>3</sub> despite the prediction we'd make based on electronegativity alone. This is because F atoms are significantly larger than H atoms and 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<sub>3</sub> and CF<sub>3</sub>) 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 stands in contrast to 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  $\mu$ .*
  - This is calculated by measuring the dielectric constant at different temperatures.
  - SI unit: Coulomb meter; C m. Common unit: Debye;  $1\text{ D} = 3.335\,64 \times 10^{-30}\text{ C m}$ .

## 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** ( $\sim 32$  for molecules) provide us with a way to indicate the symmetry unambiguously.
  - Point groups 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**<sup>[1]</sup> (230 total).
  - Reading: Miessler et al. (2014) Chapter 4 and [https://en.wikipedia.org/wiki/Molecular\\_symmetry](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.

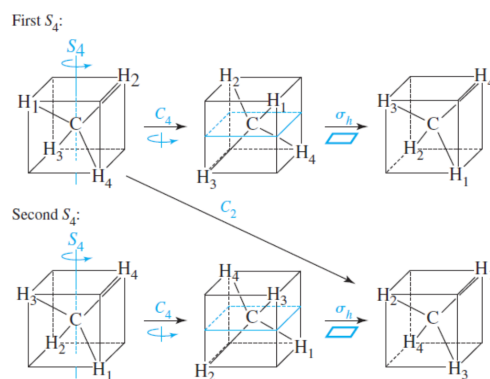
Element	Operation
Identity, $E$	nothing
Rotation axis, $C_n$	$n$ -fold rotation
Improper rotation axis, $S_n$	$n$ -fold improper rotation
Plane of symmetry, $\sigma$	Reflection
Center of symmetry, $i$	Inversion

- **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  $\text{H}_2\text{O}$ , there is a  $C_2$  axis, so we can perform a 2-fold ( $180^\circ$ ) rotation to get the same molecule.
    - Remember, because of quantum mechanical properties, the hydrogens are indistinguishable so when we rotate it  $180^\circ$ , we cannot tell it apart from the unrotated molecule.
  - Rotations are considered positive in the counterclockwise direction.

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<sup>1</sup>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  $C_\infty$  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  $\sigma_v$ .*
- **Horizontal mirror plane:** A mirror plane that is perpendicular to the principal axis. *Also known as  $\sigma_h$ .*
- **Dihedral mirror planes:** A special type of  $\sigma_v$  that is between sides or planes. *Also known as  $\sigma_d$ .*
  - 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.
  - $(x, y, z) \xrightarrow{i} (-x, -y, -z)$ .
- **$n$ -fold improper rotation:** This operation involves a rotation of  $360^\circ/n$  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  $S_n^m$ , 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  $\sigma_h$ .
- 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:
  - Determine if the symmetry is special (e.g., octahedral).
  - Determine if there is a principal rotation axis.
  - Determine if there are rotation axes perpendicular to the principal axis.
  - Determine if there are mirror planes.
  - 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:

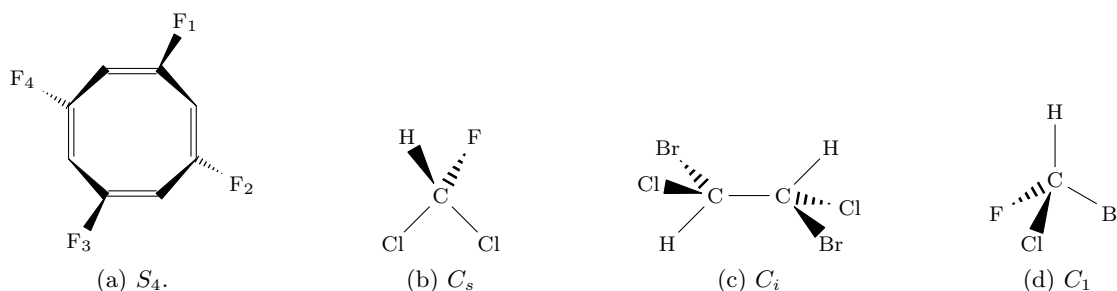


Figure II.2: Low symmetry point groups.

- 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  $\sigma_h$  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  $\sigma_v$  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  $\sigma_v$  mirror planes.
- $D_{nh}$  groups: A  $C_n$  axis,  $n$  perpendicular  $C_2$  axes, and a  $\sigma_h$  reflection plane.
  - $BH_3$  has  $D_{3h}$  symmetry.

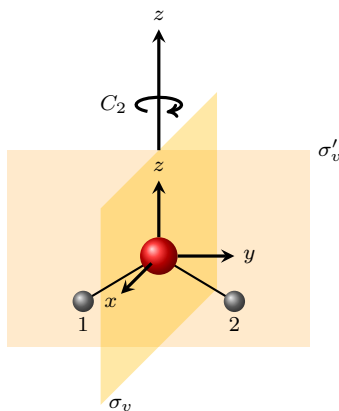
- A square prism has  $D_{4h}$  symmetry.
- $\text{CO}_2$  has  $D_{\infty h}$  symmetry.
- $D_n$  groups: A  $C_n$  axis,  $n$  perpendicular  $C_2$  axes, and no mirror planes.
  - A 3-bladed propeller has  $D_3$  symmetry.
- $D_{nd}$  groups: A  $C_n$  axis,  $n$  perpendicular  $C_2$  axes, and a  $\sigma_d$ .
  - 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  $\text{Mn}(\text{CO})_3$ , this molecule has only  $C_s$  symmetry.
  - However, spectroscopically, there is fast rotation about the Mn–Cp bond. This means that the  $\text{Mn}(\text{CO})_3$  fragment exhibits pseudo- $C_{3v}$  symmetry while the  $\text{C}_5\text{H}_5$  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  $\text{P}(\text{Et})_3$  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 of 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  $h$ .*
- Rule 1: Closure.

Figure II.3: Symmetry elements for H<sub>2</sub>O.

- H<sub>2</sub>O 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<sub>3</sub> is of the  $C_{3v}$  point group.
  - Symmetry operations:  $E$ ,  $C_3^+$ ,  $C_3^-$ ,  $\sigma_v$ ,  $\sigma'_v$ , and  $\sigma''_v$ .
  - $\sigma''_v \cdot C_3 = \sigma_v$ , 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<sub>2</sub>O is of the  $C_{2v}$  point group (refer to Figure II.3).
 

$\sigma'_v C_2 \sigma_v(1, 2) = \sigma'_v C_2(2, 1)$	$\sigma'_v (C_2 \sigma_v)(1, 2) = \sigma'_v E(1, 2)$	$(\sigma'_v C_2) \sigma_v(1, 2) = \sigma_v \sigma_v(1, 2)$
$= \sigma'_v(1, 2)$	$= \sigma'_v(1, 2)$	$= \sigma_v(2, 1)$
$= (1, 2)$	$= (1, 2)$	$= (1, 2)$
- Rule 3: Identity.
- Rule 4: Inverse.
  - For a  $C_{2v}$  point group:
 

$E \cdot E = E$	$C_2 \cdot C_2 = E$	$\sigma_v \cdot \sigma_v = E$	$\sigma'_v \cdot \sigma'_v = E$
-----------------	---------------------	-------------------------------	---------------------------------
- Group multiplication tables.

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

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

- Table II.1 corresponds to the  $C_{2h}$  point group, which has  $E$ ,  $C_2$ ,  $\sigma_h$ , 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.

$C_{3v}$	$E$	$C_3$	$C_3^2$	$\sigma_v$	$\sigma'_v$	$\sigma''_v$
$E$	$E$	$C_3$	$C_3^2$	$\sigma_v$	$\sigma'_v$	$\sigma''_v$
$C_3$	$C_3$	$C_3^2$	$E$	$\sigma''_v$	$\sigma_v$	$\sigma'_v$
$C_3^2$	$C_3^2$	$E$	$C_3$	$\sigma'_v$	$\sigma''_v$	$\sigma_v$
$\sigma_v$	$\sigma_v$	$\sigma'_v$	$\sigma''_v$	$E$	$C_3$	$C_3^2$
$\sigma'_v$	$\sigma''_v$	$\sigma_v$	$\sigma'_v$	$C_3$	$C_3^2$	$E$
$\sigma''_v$	$\sigma'_v$	$\sigma''_v$	$\sigma_v$	$C_3^2$	$E$	$C_3$

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  $\text{CO}_2$ .
  - 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*  $\Gamma$ .
- 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  $\sigma$  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** ( $\Gamma$ ):

- 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** ( $\Gamma_i$ ):

- 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  $C_3^2$  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  $\sigma_v, \sigma'_v$ , and  $\sigma''_v$  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 ones where the matrices have the most block-diagonalized form that they can.

## 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<sup>[2]</sup> is 9-square.

<sup>2</sup>Some values in it are negative because of the cosine/sine definition of a rotation matrix for  $\theta = 180^\circ$ .

- 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  $\chi$ .*
  - 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:  $\chi = 2 \cos \theta + 1$ .
  - $\sigma_v, \sigma_d$  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.

	Group Symbol	Symmetry Elements				linear	quadratic
		$E$	$C_2$	$\sigma_v(xz)$	$\sigma'_v(yz)$		
Irreducible Representations	$C_{2v}$						
	$A_1$	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	$y, R_x$	$yz$
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  $1 \times 1$ ).
  - E: Doubly degenerate (the maximum block size in the block-diagonalized irreducible transformation matrix is  $2 \times 2$ ).
  - T: Triply degenerate (the maximum block size in the block-diagonalized irreducible transformation matrix is  $3 \times 3$ ).
  - 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  $\sigma_v$ .
  - Subscript 2: anti-symmetric (–) with respect to  $\perp C_2$  or  $\sigma_v$ .
  - Superscript ': symmetric (+) under  $\sigma_h$  (if no  $i$ ).
  - Superscript ": anti-symmetric (–) under  $\sigma_h$  (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  $\sigma_h$ -character = 1:  $'$ .
    - If  $\sigma_h$ -character =  $-1$ :  $''$ .
    - This subscript can be assigned to  $A, B$  representations.
  - Assigning a subscript 1 or 2:
    - If  $\perp C_2$  or  $\sigma_v$ -character = 1: 1.
    - If  $\perp C_2$  or  $\sigma_v$ -character =  $-1$ : 2.
    - This subscript can be assigned to  $A, B$  representations.
- $\sigma$ ,  $\pi$ , and  $\delta$  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 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  $\sigma_v'(yz)$ .
- 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.
      - As such, we form **classes** of operations.
      - 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 (characters under  $E$ ) 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),

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

## II.6 Module 8: Using Character Tables

- A reducible representation of a group is any representation  $\Gamma$  of the form

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

where each  $\Gamma_i$  is an irreducible representation of the group and  $a_i$  is a real scalar.

- Basically, a reducible representation is any nontrivial 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  $\Gamma_1$ .
- $h$  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  $\rightarrow$  reducible representation  $\rightarrow$  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  $\text{H}_2\text{O}$ .
  - $\text{H}_2\text{O}$  is of the  $C_{2v}$  point group.
  - The  $9 \times 9$  identity matrix represents the identity operation on the 3 atoms in  $\text{H}_2\text{O}$ , each described by 3 Cartesian coordinates. Thus,  $\chi(E) = 9$ .
  - The following matrix represents the  $C_2$  symmetry operation. Thus,  $\chi(C_2) = -1$ .

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

- 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,  $\chi(\sigma_v(xz)) = 1$ .

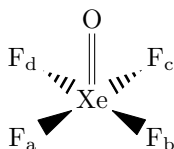
$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

- 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:  $\text{XeOF}_4$ .

Figure II.5:  $\text{XeOF}_4$ .

- 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 fluorine atom) stays the same, it contributes +1 to the character of an operation, and if it moves, it contributes 0 to the character).

$E$	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  $\text{XeOF}_4$  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 Chapter 4: Symmetry and Group Theory

From Miessler et al. (2014).

### II.7.1 Notes

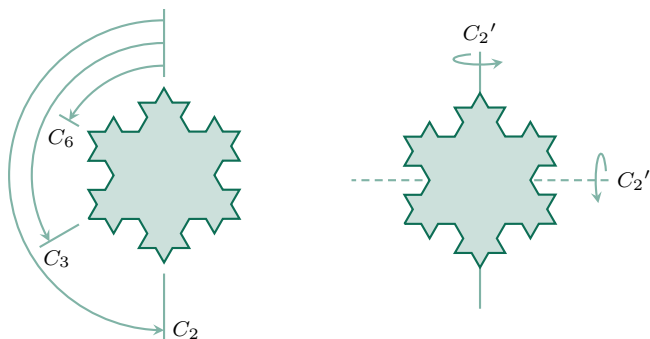
1/18: • **Coincident** (axes): Two identical axes.

- For example, the  $C_3$  rotation axis of  $\text{CHCl}_3$  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.

- Rotations  $C_3^2$  and  $C_6^5$  are also symmetry operations.

1/19:



(a) About the principal axis.

(b) About perpendicular axes.

Figure II.6: Rotations of a snowflake design.

1/18: • “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  $\sigma$  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 ( $T_d$ ,  $O_h$ ,  $C_{\infty v}$ ,  $D_{\infty h}$ ,  $I_h$ ).

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 ( $\sigma_h$ ) 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 ( $\sigma_v$  or  $\sigma_d$ )? 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  $\sigma_d$  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:  $\text{W}[\text{N}(\text{CH}_3)_2]_6$ .

# References

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