

# CHEM 20100 (Inorganic Chemistry I) Notes

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# Topics

<b>0 Course Prep</b>	<b>1</b>
0.1 Chapter 1: Introduction to Inorganic Chemistry . . . . .	1
0.2 Chapter 2: Atomic Structure . . . . .	3
<b>I Review of VSEPR Theory</b>	<b>20</b>
I.1 Module 1: Course Logistics and History . . . . .	20
I.2 Module 2: Molecular Geometries and VSEPR . . . . .	21
I.3 Chapter 3: Simple Bonding Theory . . . . .	22
<b>II Symmetry and Group Theory in Chemistry</b>	<b>25</b>
II.1 Module 3: Symmetry Elements and Operations . . . . .	25
II.2 Module 4: Symmetry Point Groups . . . . .	27
II.3 Module 5: Group Theory 101 . . . . .	28
II.4 Module 6: Representations . . . . .	30
II.5 Module 7: Characters and Character Tables . . . . .	32
II.6 Module 8: Using Character Tables . . . . .	36
II.7 Nocera Lecture 3 . . . . .	38
II.8 TA Review Session 1 . . . . .	38
II.9 Module 9: Molecular Vibrations . . . . .	39
II.10 Module 10: IR and Raman Active Vibrations (part 1) . . . . .	41
II.11 Chapter 4: Symmetry and Group Theory . . . . .	42
<b>III Introduction to Structure and Bonding</b>	<b>45</b>
III.1 Module 11: Quantum Chemistry 101 . . . . .	45
III.2 Module 12: IR and Raman Active Vibrations (part 2) . . . . .	48
III.3 Nocera Lecture 6 . . . . .	49
III.4 Nocera Lecture 7 . . . . .	52
III.5 Module 13: Why Molecular Orbitals? . . . . .	54
III.6 Module 14: Constructing Molecular Orbitals (Part 1) . . . . .	56
III.7 Office Hours (Wang) . . . . .	59
III.8 Office Hours (Talapin) . . . . .	59
III.9 Module 15: Constructing Molecular Orbitals (Part 2, HF Molecule) . . . . .	60
III.10 Module 16: Constructing Molecular Orbitals (Part 3, H <sub>2</sub> O Molecule) . . . . .	61
III.11 Module 17: Constructing Molecular Orbitals (Part 4, NH <sub>3</sub> Molecule) . . . . .	65
III.12 Module 18: Constructing Molecular Orbitals (Part 5, H <sub>2</sub> C=CH <sub>2</sub> Molecule) . . . . .	66
III.13 Module 19: Isolobal Principle . . . . .	67
III.14 Module 20: Orbital Hybridization . . . . .	67
III.15 Chapter 5: Molecular Orbitals . . . . .	67
<b>IV Hard-Soft Acid-Base and Donor-Acceptor Concepts of Transition Metals</b>	<b>78</b>
IV.1 Module 24: Acid-Base Chemistry . . . . .	78
IV.2 Module 25: Acid-Base Chemistry: Lewis Acids and Bases . . . . .	79
IV.3 Module 26: Hard and Soft Acids and Bases (HSAB) Principle . . . . .	80
IV.4 Module 27: Steric Effects in Inorganic Chemistry . . . . .	83

IV.5	Chapter 6: Acid-Base and Donor-Acceptor Chemistry . . . . .	84
<b>V</b>	<b>Coordination Chemistry: Structures and Isomers of Metal Complexes</b>	<b>90</b>
V.1	Module 28: Introduction to Coordination Compounds . . . . .	90
V.2	Module 29: Types and Classes of Ligands . . . . .	91
V.3	Module 30: Nomenclature and Isomers of Metal Complexes . . . . .	93
V.4	Module 31: Crystal Field Theory . . . . .	96
<b>VII</b>	<b>Band Theory in Solids</b>	<b>99</b>
VII.1	Module 21: Electronic Structure of Solids (1D Solids) . . . . .	99
VII.2	Module 22: Electronic Structure of Solids (2D and 3D solids) . . . . .	102
VII.3	Module 23: Filling Bands With Electrons . . . . .	104
<b>References</b>		<b>106</b>

# List of Figures

0.1	Examples of bonding interactions.	1
0.2	Inorganic compounds containing bridging hydrogens and alkyl groups.	2
0.3	Tetrahedral geometry without a central atom.	2
0.4	Hydrogen atom energy levels.	4
0.5	Particle in a box: Wave functions and their squares at different energy levels.	7
0.6	Spherical coordinates.	10
0.7	Radial wave functions.	11
0.8	Radial probability functions.	12
0.9	Coulombic energy of repulsion and exchange energy.	15
0.10	Schematic energy levels for transition elements.	17
0.11	First and second ionization energies and electron affinities.	19
I.1	VSEPR structure of $\text{BrF}_3$ .	21
I.2	Lewis structure of $\text{PF}_2\text{Cl}_3$ .	21
II.1	Methane's $S_4$ symmetry.	26
II.2	Low symmetry point groups.	27
II.3	Symmetry elements for $\text{H}_2\text{O}$ .	29
II.4	A character table.	33
II.5	$\text{XeOF}_4$ .	37
II.6	Rotations of a snowflake design.	43
III.1	Molecular orbitals of benzene.	51
III.2	Energy level diagram of benzene.	52
III.3	Energy level diagram of ethene.	53
III.4	Photoelectron spectroscopy at an atomic level.	55
III.5	Correspondence between MO predictions and scanning tunnelling microscopy.	55
III.6	Combining orbitals of varying energies.	56
III.7	Orbital potential energies.	57
III.8	Constructing $s$ , $p$ , and $d$ molecular orbitals.	58
III.9	Tetrahedral point groups.	59
III.10	HF orbital diagram.	61
III.11	$\text{H}_2\text{O}$ orbital diagram.	62
III.12	Photoelectron spectrum for $\text{H}_2\text{O}$ .	63
III.13	Coordinate system for $\text{NH}_3$ .	63
III.14	$\text{NH}_3$ orbital diagram.	65
III.15	$\text{H}_2\text{C}=\text{CH}_2$ orbital diagram.	66
III.16	Choice of $z$ -axis direction.	68
III.17	Molecular orbitals for the first 10 elements.	70
III.18	Interaction of fluorine group orbitals with the hydrogen 1s orbital.	72
III.19	Molecular orbitals for $\text{CO}_2$ .	74
III.20	Group orbitals for $\text{BF}_3$ .	76
IV.1	Hard vs. soft metal ions.	81
IV.2	Four Lewis bases.	87

IV.3	FLP phosphino-borane compound.	87
V.1	An example of a bidentate chelating ligand.	91
V.2	A coordination compound with bridging ligands.	94
V.3	Facial and meridional geometric isomers.	95
V.4	Methods of sketching octahedral complexes.	95
V.5	Chirality of octahedral complexes with two bidentate ligands.	95
V.6	CFSE as a function of the number of <i>d</i> -electrons.	97
VII.1	<i>s</i> orbital bonding states.	100
VII.2	<i>p</i> orbital bonding states.	101
VII.3	Density of states.	101
VII.4	2D Brillouin zone.	102
VII.5	Special <i>k</i> points.	102
VII.6	Schematic band structure (2D).	103
VII.7	Electronic band structure of Si.	104

# List of Tables

0.1	Quantum numbers and their properties. . . . .	8
0.2	Hydrogen atom wave functions: Angular functions. . . . .	9
0.3	Hydrogen atom wave functions: Radial functions. . . . .	10
0.4	Hund's rule and multiplicity. . . . .	15
I.1	VSEPR predictions. . . . .	23
I.2	Electronegativity and bond angles. . . . .	24
II.1	Group multiplication table for the $C_{2h}$ point group. . . . .	30
II.2	Group multiplication table for the $C_{3v}$ point group. . . . .	30
II.3	Character table for the $D_3$ point group. . . . .	34
II.4	Changes in the fluorine atoms of $\text{XeOF}_4$ under the $C_{4v}$ symmetry operations. . . . .	38
II.5	Character table for the $D_{3h}$ point group. . . . .	41
III.1	Character table for the $C_{3v}$ . . . . .	64
III.2	Molecular orbital equations for $\text{H}_2\text{O}$ . . . . .	75
IV.1	Hard and soft formation constants. . . . .	82
V.1	Irregular and unfamiliar monodentate ligands. . . . .	94

# Topic 0

## Course Prep

### 0.1 Chapter 1: Introduction to Inorganic Chemistry

From Miessler et al. (2014).

12/21:

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



Figure 0.1: Examples of bonding interactions.

- No such bonds exist between carbon atoms because two carbon atoms max out at a triple bond.
- Quadruple bonds possess one sigma bond, two pi bonds, and one delta ( $\delta$ ) 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.
- Hydrogen atoms and alkyl groups can act as bridges in inorganic chemistry, excessively disobeying the octet rule (see Figure 0.2).
- **Coordination number:** The number of other atoms, molecules, or ions to which an atom is bonded.

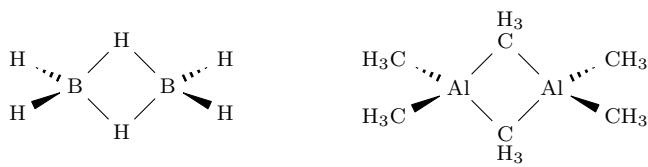


Figure 0.2: Inorganic compounds containing bridging hydrogens and alkyl groups.

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



Figure 0.3: Tetrahedral geometry without a central atom.

- There are multiple kinds of tetrahedral structures. There is the standard arrangement seen in molecules such as methane, but there is also a form that lacks a central atom, as in elemental phosphorous  $P_4$  (see Figure 0.3).
  - Other atoms such as boron and carbon also form units that surround a central cavity (e.g., icosahedral  $B_{12}$  and buckyballs  $C_{60}$ ).
- Aromatic rings can bond to metals using all of their pi orbitals. This results in a metal suspended above the ring’s center.
- **Cluster compound:** A compound where “a carbon atom is at the center of a polyhedron of metal atoms” (Miessler et al., 2014, p. 3).
  - There exist examples of carbon surrounded by five, six, or more metal atoms<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).*

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 ( $6.626 \times 10^{-34} \text{ Js}$ ),  $c$  is the speed of light ( $2.998 \times 10^8 \text{ m s}^{-1}$ ),  $\nu$  is the frequency of the light,  $\lambda$  is the wavelength of the light, and  $\bar{\nu}$  is the **wavenumber** of the light.

- **Wavenumber:** The number of waves that exist between two points along the light's path a given distance apart. *Measured in waves per centimeter (SI: cm<sup>-1</sup>)*.
  - Wavenumber is proportional to energy. This is why m<sup>-1</sup> or cm<sup>-1</sup> 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:

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

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.
- $4\pi\varepsilon_0$  is the permittivity of a vacuum.
- Importantly, note that the Rydberg constant for hydrogen  $R_H$  is not universal, and changes for the atom at hand based on factors like the mass of the nucleus.
- Also note that some of the terms cancel or can be written in terms of others, making the above equation equivalent to the one given in Chapter 7 of Labalme (2020a).

<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 0.4: Hydrogen atom energy levels.

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

- Individual electrons can have more energy than they would possess in the infinite energy level, but at and above this point, the nucleus and electron are considered to be separate entities.
- **Heisenberg's uncertainty principle:** “There is a relationship between the inherent uncertainties in the location and momentum of an electron” (Miessler et al., 2014, p. 14).

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

- The above equation describes the  $x$ -component of the uncertainty, where  $\Delta x$  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  $\hat{H}$ .*

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

- 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

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

- Since sine and cosine functions have properties associated with waves, we propose that a general solution describing possible waves in the box is

$$\Psi(x) = A \sin rx + B \cos sx$$

where  $A, B, r, s$  are constants.

- As seen in Problem 2.8a, substituting the above general solution into the wave equation allows us to solve for

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

---

<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

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

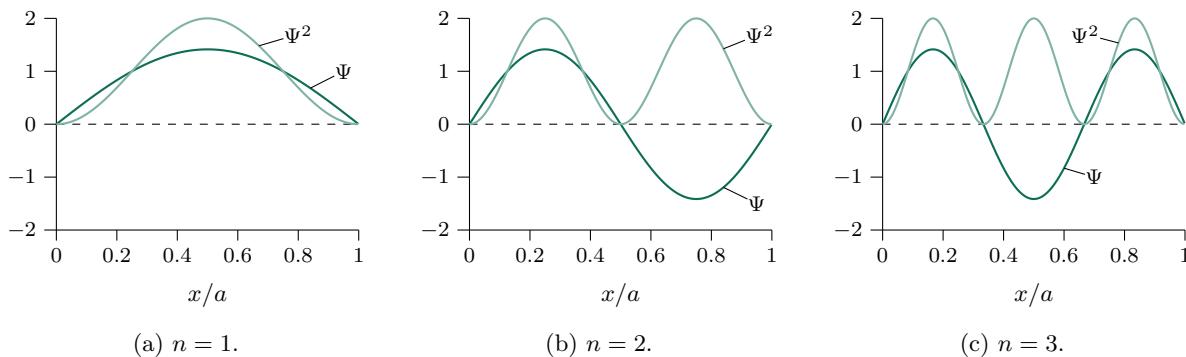


Figure 0.5: Particle in a box: Wave functions and their squares at different energy levels.

- The predicted probability densities for an electron at different energy levels (see Figure 0.5) showcase a difference between classical mechanics’ and quantum mechanics’ predictions about the behavior of this particle: Classical predicts an equal probability at any point in the box, but the (quantum) wave nature of the particle predicts varied probabilities in different locations.
- “The greater the square of the electron amplitude, the greater the probability of the electron being located at the specified coordinate when at the quantized energy defined by  $\Psi$ ” (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 0.1).
  - Orbitals with  $l$  values  $0, 1, 2, 3, 4, \dots$  are known by the labels  $s, p, d, f, g, \dots$  (continuing alphabetically), respectively, derived from early terms for different families of spectroscopic lines.

Symbol	Name	Values	Role
$n$	Principal	1, 2, 3, ...	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	$0, \pm 1, \pm 2, \dots, \pm l$	Describes orientation in space (angular momentum in the $z$ -direction).
$m_s$	Spin	$\pm \frac{1}{2}$	Describes orientation of the electron spin (magnetic moment) in space.

Table 0.1: Quantum numbers and their properties.

- $n$  is the primary quantum number affecting the overall energy.
- $l$  determines the type of shape. See Table 0.2.
- $m_l$  determines the “orientation of the angular momentum vector in a magnetic field, or the position of the orbital in space” (Miessler et al., 2014, p. 18). See Table 0.2.
- $m_s$  determines the electron spin<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 0.2:
  - Any linear combination of solutions to the wave equation is another solution.
  - Because it is more convenient to work with real functions as opposed to complex functions, we make use of the above fact to decomplexify the solutions, as in the following examples.

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

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

<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  $i/\sqrt{2}$ .

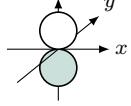
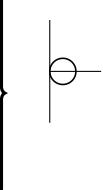
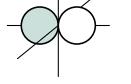
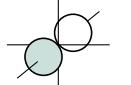
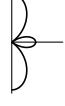
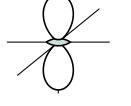
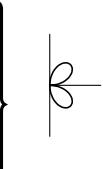
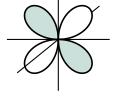
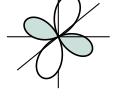
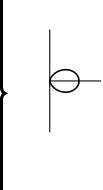
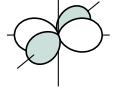
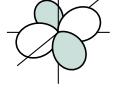
Angular factors			Real Wave Functions					
Related to Angular Momentum			Functions of $\theta$	In Polar Coordinates	In Cartesian Coordinates	Shapes	Label	
$l$	$m_l$	$\Phi$	$\Theta$	$\Theta\Phi(\theta, \phi)$	$\Theta\Phi(x, y, z)$			
0(s)	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$		$\frac{1}{2\sqrt{\pi}}$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

Table 0.2: Hydrogen atom wave functions: Angular functions.

- Note that  $d_{z^2}$  actually uses the function  $2z^2 - x^2 - y^2$ , so we should write  $d_{2z^2 - x^2 - y^2}$  but we shorthand for convenience.
- Since the functions in the polar and Cartesian coordinates columns of Table 0.2 are real,  $\Psi = \Psi^*$  and  $\Psi\Psi^* = \Psi^2$ .
- 12/25: •  $\Psi$  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 0.6).

12/23:

Orbital	$n$	$l$	Radial Functions $R(r)$ , with $\sigma = Zr/a_0$
$1s$	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 0.3: Hydrogen atom wave functions: Radial functions.

12/25:



Figure 0.6: 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  $Y$ :

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

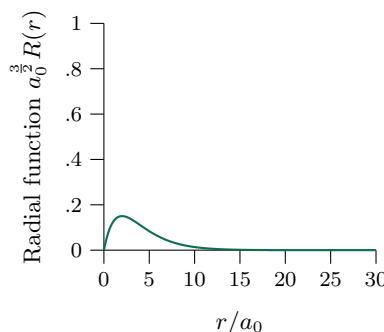
- Refer to Table 0.2 for examples of  $\Theta$  and  $\Phi$ , and Table 0.3 for examples of  $R$ .
- Note that in Table 0.2, the shaded orbital lobes correspond to where the wave function is negative. Distinguishing regions of opposite signs is useful for bonding purposes.
- The radial component can also be manipulated to give the **radial probability function**  $4\pi r^2 R^2$ .
- $R$  is the radial function, so  $R^2$  is the probability function (think  $\Psi = RY$ , so  $\Psi^2 = R^2 Y^2$ ).



(a) 1s.



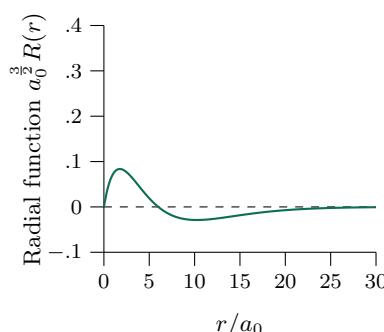
(b) 2s.



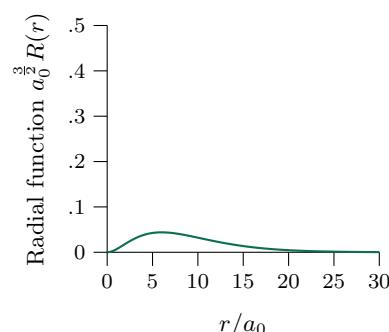
(c) 2p.



(d) 3s.



(e) 3p.



(f) 3d.

Figure 0.7: Radial wave functions.



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

12/26:

- **Nodal surface:** A surface within an orbital having zero electron density.
  - The wave function is zero at these because it is changing sign.
    - Knowing where the wave function is positive and negative can be useful when working with molecular orbitals.
  - To find nodal surfaces, we must find places where

$$0 = \Psi^2 = \Psi = R(r)Y(\theta, \phi)$$

or where

$$0 = R(r) \quad 0 = Y(\theta, \phi)$$

- “The total number of nodes in any orbital is  $n - 1$  if the conical nodes of some  $d$  and  $f$  orbitals count as two nodes” (Miessler et al., 2014, p. 23).
  - The conical node of the  $d_{z^2}$  orbital (see Table 0.2) is mathematically one surface, but we must count it as two (perhaps think of it as a top and bottom section) to fit the pattern.
- **Angular node:** A node that results when  $Y = 0$ .
  - There are  $l$  angular nodes in any orbital.
- **Radial node:** A node that results when  $R = 0$ . *Also known as spherical nodes.*
  - There are  $n - l - 1$  radial nodes in any orbital.
- Note that on the basis of relativity, electron density at nodes may not be zero but may in fact be a very small finite value.
  - Alternatively, if we think of an electron wave like a wave in a violin string, which also has places of zero vibration where the string still exists, nodes may just be places where electron waves have zero amplitude, not places where they don’t exist.

<sup>11</sup>Errata?: Should the  $y$ -axis in Figure 0.8 be  $a_0^3 r^2 R^2$ ?

- A further possible explanation is that electrons can ‘teleport’ between two places without ever passing in between.
- We now look at a few examples of finding nodes in orbitals.
- Nodal structure of  $p_z$ :
  - From Table 0.2, the angular factor of this orbital in Cartesian coordinates is
$$Y = \frac{1}{2} \sqrt{\frac{3}{\pi}} \frac{z}{r}$$
  - When we set this equal to zero, we find that the above is only equal to zero when  $z = 0$ .
  - Indeed,  $z = 0$ , i.e., the  $xy$ -plane, is an angular node in the  $p_z$  orbital, as we can see in Table 0.2.
  - Additionally, we can tell from the above equation that the wave function is positive when  $z > 0$  and negative when  $z < 0$ ; this is also reflected in Table 0.2.
- Nodal structure of  $d_{x^2-y^2}$ :
  - The angular factor:
$$Y = \frac{1}{4} \sqrt{\frac{15}{\pi}} \frac{x^2 - y^2}{r^2}$$
  - This is only equal to zero when
$$\begin{aligned} 0 &= x^2 - y^2 \\ y^2 &= x^2 \\ y &= \pm x \end{aligned}$$
  - This translates to Table 0.2, where we can see that the planes  $x = y$  and  $x = -y$ , i.e., those that contain the  $z$ -axis and make  $45^\circ$  angles with the  $x$ - and  $y$ -axes, are nodes.
  - Additionally, the function is positive where  $|x| > |y|$  and negative where  $|x| < |y|^{[12]}$ , and we can see this in Table 0.2.
- Be aware of lines/surfaces of constant electron density.
- When filling orbitals in polyelectronic atoms, “we start with the lowest  $n$ ,  $l$ , and  $m_l$  values (1, 0, and 0, respectively) and either of the  $m_s$  values (we will arbitrarily use  $+\frac{1}{2}$  first)” (Miessler et al., 2014, p. 26). We then utilize the three following rules.
  - See them used to fill a  $p$  orbital in Table 0.4.
- **Aufbau principle:** The buildup of electrons in atoms results from continually increasing the quantum numbers. *Etymology aufbau* from German “building up.”
  - “Electrons are placed in orbitals to give the lowest total electronic energy to the atom. This means that the lowest values of  $n$  and  $l$  are filled first. Because the orbitals within each subshell ( $p$ ,  $d$ , etc.) have the same energy, the orders for values of  $m_l$  and  $m_s$  are indeterminate” (Miessler et al., 2014, p. 26).
- **Pauli exclusion principle:** Each electron in an atom must have a unique set of quantum numbers.
  - Note that this is experimentally derived, and does not follow from the Schrödinger equation.
- **Hund’s rule** (of maximum multiplicity): Electrons must be placed in orbitals to give the maximum total spin (the maximum number of parallel spins).
  - This is a consequence of the Aufbau principle, as two electrons in the same orbital have higher energy than two in different orbitals due to electrostatic repulsions.

<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	$\begin{array}{c} \uparrow \\ \hline \end{array}$ ____	1	2
2	$\begin{array}{cc} \uparrow & \uparrow \\ \hline & \hline \end{array}$ ____	2	3
3	$\begin{array}{ccc} \uparrow & \uparrow & \uparrow \\ \hline & \hline & \hline \end{array}$	3	4
4	$\begin{array}{ccc} \uparrow \downarrow & \uparrow & \uparrow \\ \hline & \hline & \hline \end{array}$	2	3
5	$\begin{array}{ccc} \uparrow \downarrow & \uparrow \downarrow & \uparrow \\ \hline & \hline & \hline \end{array}$	1	2
6	$\begin{array}{ccc} \uparrow \downarrow & \uparrow \downarrow & \uparrow \downarrow \\ \hline & \hline & \hline \end{array}$	0	1

Table 0.4: Hund's rule and multiplicity.

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



Figure 0.9: Coulombic energy of repulsion and exchange energy.

- **Coulombic energy of repulsion:** The potential energy of two negatively charged electrons that occupy the same orbital (as opposed to separate orbitals). *Denoted by  $\Pi_c$ .*
  - 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 0.9). The exchange energy between two of the states reflects the fact that electrons with opposite spins are distinguishable, but electrons with identical spins can be exchanged (can switch places) and no observer would be the wiser. This event, when it happens, is called **one exchange of parallel electrons**; the fact that it can happen lowers the energy of the system with electrons of identical spin simply by virtue of creating more possible states that each electron can occupy.

12/27:

- Energies with oxygen:

- Three possible configurations:  $\begin{array}{cccc} \uparrow \downarrow & \uparrow \downarrow & \_ & \_ \end{array}$ ,  $\begin{array}{cccc} \uparrow \downarrow & \uparrow & \_ & \downarrow \end{array}$ , and  $\begin{array}{cccc} \uparrow \downarrow & \uparrow & \_ & \uparrow \end{array}$ .
- 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) (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  $\text{Ni} \longrightarrow \text{Ni}^{2+} + 2e^-$ , the two electrons removed are the  $4s$  electrons.
- Slater's rules are justified by electron probability curves (see Figure 0.8) and experimental data.
- Rich provided another explanation of orbital filling (refer to Figure 0.10 throughout the following discussion).



Figure 0.10: Schematic energy levels for transition elements.

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

- Each of these half orbitals naturally decreases in energy (is pulled closer to the nucleus) as  $Z$  increases.
  - Since orbitals in lower energy levels have shorter most probable distances to the nucleus, they are stabilized more as  $Z$  increases (this is why the slope of the  $3d$  half orbitals is steeper).
  - Electrons are placed into the lowest energy positions possible.
    - Thus, the  $4s$  orbital usually fills up first, but there are exceptions since, for example, the  $3d$  half orbital with  $m_s = -\frac{1}{2}$  crosses over the  $4s$  half orbital with  $m_s = +\frac{1}{2}$  between V and Cr (at the dot) as opposed to somewhere after Cr.
  - Note that as electrons are sequentially added, Figure 0.10 shows them generally having the same spin, in accordance with Hund's rule.
  - For ions, the crossover points shift left.
    - This is because the removal of the electron causes  $Z^*$  to increase dramatically for all electrons, but more for  $(n-1)d$  orbitals than  $ns$  orbitals.
  - “This approach to electron configurations of transition metals does not depend on the stability of half-filled shells or other additional factors” (Miessler et al., 2014, p. 36).
  - Introductory chem: Electrons in the highest energy level are always removed first when ionizing transition metals. This chem: “Regardless of which electron is lost to form a transition metal ion, the lowest energy electron configuration of the resulting ion will always exhibit the vacancy in the  $ns$  orbital” (Miessler et al., 2014, p. 36).
  - Similar but more complex diagrams can treat other situations in higher energy levels and subshells.
- Since the periodic table arranges<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  $IE_1$ . When  $n = 1$ ,  $\Delta U$  is the second ionization energy  $IE_2$ . 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  $Z_{eff}$ .

<sup>17</sup>Think isoelectricity (see Figure 0.11).



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

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

# Topic I

## Review of VSEPR Theory

### I.1 Module 1: Course Logistics and History

1/11:

- Homework questions will be similar to exam questions, so although you probably *can* find answers online, you shouldn't.
- Submit Psets to chem201hw@gmail.com.
- Watch modules before office hours and bring questions.
- If you have a question outside of office hours, post it on Slack.
- It's a difficult class, but he is open to and welcomes our feedback (via Slack, again).
- You do need to read from Miessler et al. (2014), too; his class is not a replacement for this textbook.
  - He is a big fan of Cotton (1990).
  - There is an extra, new textbook to look for!
- Convince yourself not to be afraid of time-independent quantum mechanics (we won't go too deep, but know wave functions and the like).
- Exams will probably be open book/open note.
- Inorganic chemistry contains too much information to rationalize empirically, so we need a system (the development of this system will be the focus of this course).
- Reviews history of chemistry from Miessler et al. (2014) Chapter 1.
- What is Nickel's electron configuration?
  - When Nickel is a free atom, the  $[Ar]4s^23d^8$  electron configuration is the lowest energy.
  - When Nickel is chemically bound, the  $[Ar]3d^{10}$  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:
  - Draw a valid Lewis structure for a molecule.
  - Place electron pairs in the valence shell as far away from each other as possible. Use the  $\sigma$ -bond framework first.
  - 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 ( $BMe_3$ ).
  - Trigonal planar ( $D_{3h}$ ).
- Octahedral:  $O_h$ .
- Bent:  $C_{2v}$ .
- Order of the repulsive forces:** lone pair - lone pair > lone pair - bonding pair > bonding pair - bonding pair.
- In  $SF_4$  (see-saw), will the lone pair be axial or equatorial?
  - Equatorial —  $2 \times 120^\circ$  and  $2 \times 90^\circ$  vs.  $3 \times 90^\circ$ .
- In  $BrF_3$ ...

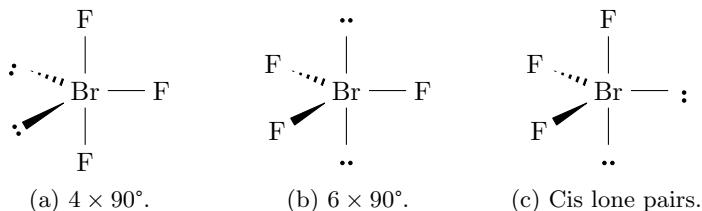


Figure I.1: VSEPR structure of  $BrF_3$ .

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

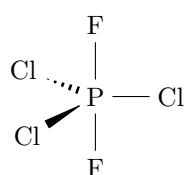


Figure I.2: Lewis structure of  $PF_2Cl_3$ .

- We need **Bent's rule**, which tells us that atoms share electrons from *p*- or *d*-orbitals to a greater extent than they do from *s*-orbitals.
- Thus, when phosphorous excites  $3s^23p^3$  to  $3s^13p_x^13p_y^13p_z^13d_{z^2}^1$  and then rehybridizes to create three  $sp^2$  orbitals (each composed of  $s + p_x + p_y$ ) and two “*pd*” hybrid orbitals (each composed of  $p_z + d_{z^2}$ ), the equatorial  $sp^2$  orbitals bond to the more **electropositive** chlorines and the axial “*pd*” hybrid orbitals bond to the remaining more electronegative fluorines.
- There is also sometimes a tendency for symmetry.
- **Bent's rule:** Atomic *s*-character concentrates in orbitals directed toward electropositive substituents.
- **Electropositive** (species): A species that has relatively lower electronegativity than another.
- For molecules with multiple bonds, ignore  $\pi$ -bonds.
- Problems with VSEPR:
  - $XeF_6$  with 14 bonding electrons (7 pairs) is supposed to be pentagonal bipyramidal, but is actually octahedral (a known problem for  $14 e^-$  systems).
  - Heavy main group elements with no hybridization.
    - $H-C\equiv C-H$  is linear, but  $H-Si\equiv Si-H$  is not.
    - No  $\sigma$ -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).*

1/14:

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

1/17:

- The variety of structures means that one unified VSEPR theory will not likely<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).
- 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.

<sup>[1]</sup>Errata: “unlikely.”

1/14:

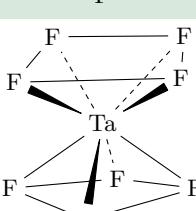
	Steric Number	Geometry	Examples	Calculated Bond Angles	
2	Linear	$\text{CO}_2$	180°	$\text{O} = \text{C} = \text{O}$	
3	Trigonal (triangular)	$\text{SO}_3$	120°		
4	Tetrahedral	$\text{CH}_4$	109.5°		
5	Trigonal bipyramidal	$\text{PCl}_5$	120°, 90°		
6	Octahedral	$\text{SF}_6$	90°		
7	Pentagonal bipyramidal	$\text{IF}_7$	72°, 90°		
8	Square antiprismatic	$[\text{TaF}_8]^{3-}$	70.5°, 9.6°, 109.5°		

Table I.1: VSEPR predictions.

1/17:

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

Molecule	X–P–X Angle (°)	Molecule	Bond Angle (°)
PF <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.

- 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 so we get some steric hindrance.
- In molecules with steric number 5, axial bond length is greater than equatorial.
- Symmetric structures are often preferred.
- Groups (such as CH<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 contrasts with VSEPR theory's concern with the central atom, as opposed to the ligands.
- **Dielectric constant:** “The ratio of the capacitance of a cell filled with the substance to be measured to the capacitance of the same cell with a vacuum between the electrodes” (Miessler et al., 2014, p. 66).
  - This is measured to experimentally determine the polarity of molecules.
- **Dipole moment:** The product  $Qr$  of the distance  $r$  between two charges' centers and the difference  $Q$  between the charges. *Also known as  $\mu$ .*
  - This is calculated by measuring the dielectric constant at different temperatures.
  - SI unit: Coulomb meter; C m. Common unit: Debye; 1 D =  $3.335\,64 \times 10^{-30}$  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.
  - These have symmetry about a single point at the center of mass of the system.
- Extended objects (e.g., crystals) have **translational symmetry** described by **Space groups<sup>[1]</sup>** (230 total).
- Readings: 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.

<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.*

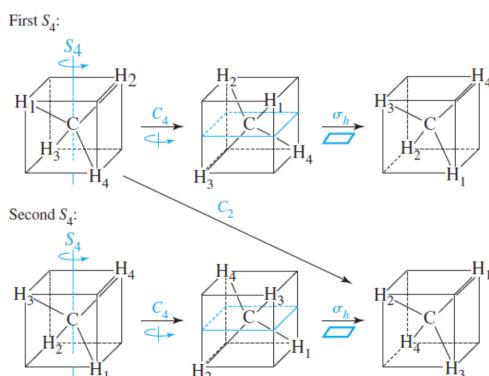


Figure II.1: Methane’s  $S_4$  symmetry.

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

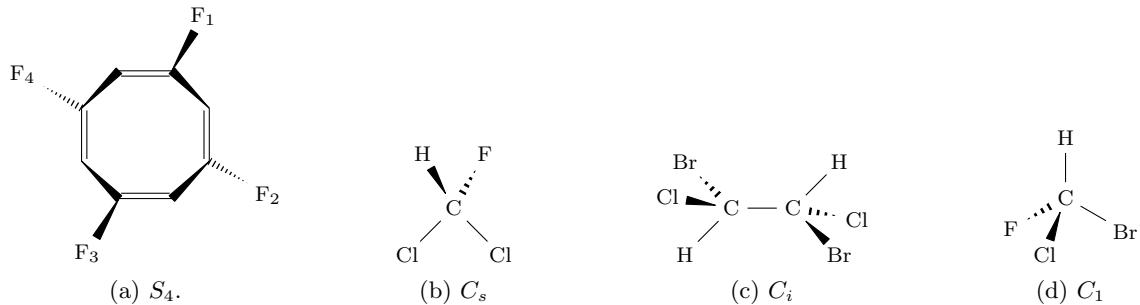


Figure II.2: Low symmetry point groups.

- 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.

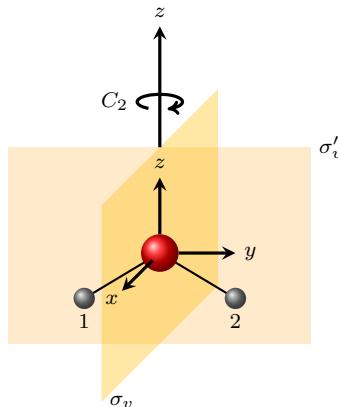
- $\text{BH}_3$  has  $D_{3h}$  symmetry.
- A square prism has  $D_{4h}$  symmetry.
- $\text{CO}_2$  has  $D_{\infty h}$  symmetry.
- $D_n$  groups: A  $C_n$  axis,  $n$  perpendicular  $C_2$  axes, and no mirror planes.
  - A 3-bladed propeller has  $D_3$  symmetry.
- $D_{nd}$  groups: A  $C_n$  axis,  $n$  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  $\text{Mn}-\text{Cp}$  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 off the polynomial, the Galois group of the polynomial.
    - Link to Galois video here.
  - 1920s: Group theory was applied to physics and chemistry.
  - 1931: It is often hard or even impossible to obtain a solution of the Schrödinger equation — however, a large part of qualitative results can be obtained by group theory. Almost all the rules of spectroscopy follow from the symmetry of a problem.
- We will use group theory for describing symmetry of molecules. We will use group theory to understand the bonding and spectroscopic features of molecules.

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

Figure II.3: Symmetry elements for  $\text{H}_2\text{O}$ .

- $\text{H}_2\text{O}$  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**.
- $\text{NH}_3$  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.

- $\text{H}_2\text{O}$  is of the  $C_{2v}$  point group (refer to Figure II.3).

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

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

$$E \cdot E = E \quad C_2 \cdot C_2 = E \quad \sigma_v \cdot \sigma_v = E \quad \sigma'_v \cdot \sigma'_v = E$$

- 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  $h = \textcolor{purple}{3}, \textcolor{blue}{2}, \textcolor{red}{1}$ . Why only these?
- The order  $\textcolor{red}{1}$  and  $\textcolor{purple}{3}$  charts are subgroups.
- The order  $\textcolor{blue}{2}$  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  $C_3$  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 corresponding blocks within a set of block-diagonalized matrices representing each operation in a group.

## II.5 Module 7: Characters and Character Tables

1/19:

- Nocera Lecture 3 notes (on Canvas) explain how reducible and irreducible transformations are related to each other through the similarity transformations.
- For  $\text{H}_2\text{O}$ , each atom has 3 Cartesian coordinates, so our transformation matrix<sup>[2]</sup> is 9-square.

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<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. *Also known as  $\chi$  table.*

	Group Symbol	Symmetry Elements				linear	quadratic
		$E$	$C_2$	$\sigma_v(xz)$	$\sigma'_v(yz)$		
Irreducible Representations	$A_1$	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 0.2 and Figure II.4) it does not change under  $E$ , it inverts under  $C_2$ , it does not change under  $\sigma_v(xz)$ , and it inverts under  $\sigma'_v(yz)$  (note that the  $C_2$  axis is the  $z$ -axis, not the  $x$ -axis).
- We can apply the same procedure to other more complex functions.
  - For example, in the  $C_{2v}$  point group, we know that (with respect to orbitals):

- $p_y$  is  $B_2$ .
- $p_z$  is  $A_1$ .
- $d_{z^2}$  is  $A_1$ .
- $d_{x^2-y^2}$  is  $A_1$ .
- $d_{yz}$  is  $B_2$ .
- $d_{xy}$  is  $A_2$ .
- $d_{xz}$  is  $B_1$ .
- We can even go into the cubic functions describing the  $f$  orbitals and assign them Mulliken symbols.
- Essentially, the right hand side of a character table tells you how atomic orbitals will transform under certain symmetry operations.
- Properties of a character table:
  1. The characters of all matrices belonging to the operations in the same class are identical in a given irreducible representation.
    - We most commonly form a **rotational class** and a **reflection class**.
  2. The number of irreducible representations in a group is equal to the number of classes of that group.
  3. There is always a totally symmetric representation for any group.
    - I.e., a representation where every character is 1.
  4. The sum of the squares of the **dimensionality** of all the irreducible representations is equal to the order of the group. Mathematically,
$$h = \sum_i [\chi_i(E)]^2$$
  - For example, the dimensionalities of the  $D_3$  point group (see Table II.3) are 1, 1, and 2, and the order is, indeed,  $6 = 1^2 + 1^2 + 2^2$ .
  5. The sum of the squares of the characters multiplied by the number of operations in the class equals the order of the group. Mathematically,
$$h = \sum_{R_c} g_c [\chi_i(R_c)]^2$$
  - For example, with respect to the  $D_3$  point group (see Table II.3),
 
$$\begin{aligned} 6 &= (1)(1)^2 + (2)(1)^2 + (3)(1)^2 \\ &= (1)(1)^2 + (2)(1)^2 + (3)(-1)^2 \\ &= (1)(2)^2 + (2)(-1)^2 + (3)(0)^2 \end{aligned}$$
  - 6. The sum of the products of the corresponding characters of any two different irreducible representations of the same group is zero. Mathematically,
 
$$\sum_{R_c} g_c \chi_i(R_c) \chi_f(R_c) = 0$$
    - Basically, this means that if we treat irreducible representations as vectors in  $h$ -space, they are orthogonal.
    - For example, with respect to the  $D_3$  point group (see Table II.3),
 
$$\begin{aligned} 0 &= 1(1)(1) + 2(1)(1) + 3(1)(-1) \\ &= 1(1)(2) + 2(1)(-1) + 3(1)(0) \\ &= 1(1)(2) + 2(1)(-1) + 3(-1)(0) \end{aligned}$$
- **Dimensionality:** The character of the identity operation  $E$ . Also known as **dimension**.

## II.6 Module 8: Using Character Tables

- A reducible representation of a group is any representation  $\Gamma$  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 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  $\Gamma$ .
- $h$  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 → reducible representation → 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,  $\chi(C_2) = -1$ .

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

- 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,  $\chi(\sigma_v(xz)) = 1$ <sup>3</sup>.

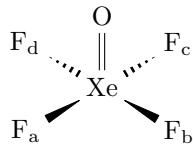
$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

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

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

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

Table II.4: Changes in the fluorine atoms of  $\text{XeOF}_4$  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 Nocera Lecture 3

*From Nocera (2008).*

- 1/25:
- Corresponding blocks within block-diagonalized matrices obey the same multiplication properties as the block-diagonalized matrices, themselves.
  - One basis may not uncover all irreducible representations.
    - For example, we can use a Cartesian basis to uncover the  $A_1$  and  $E$  irreducible representations of the  $D_3$  point group (see Table II.3) and the basis function  $R_z$  ( $E : R_z \rightarrow R_z$ ,  $C_3 : R_z \rightarrow R_z$ ,  $\sigma_v : R_z \rightarrow R_z$ ) to uncover the  $A_2$  irreducible representation.
  - We can also construct a character table algebraically. Continuing with the  $D_3$  example...
    - There is one totally symmetric representation  $\Gamma_i = (1, 1, 1)$ .
    - $h = 6 = \sum_i [\chi_i(E)]^2$ . Since each  $\chi_i(E)$  can only be 1, 2, or 3, we know that  $\chi_1(E) = \chi_2(E) = 1$  and  $\chi_3(E) = 2$ .
    - This combines with orthogonality to reveal that

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

i.e.,  $\Gamma_i = (1, 1, -1)$ .

- To determine the last representation, we can use two rules and solve as a system of equations.

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

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

## II.8 TA Review Session 1

- 1/22:
- We also don't need to show the equatorial electron pair in the shape picture.
  - For  $\text{SeCl}_4$ , we need to show that the axial bonds are longer and are not straight up and down.
  - For  $\text{I}_3^-$ , it's trigonal bipyramidal EPA and linear molecular geometry — there's an extra electron pair around the central iodine atom. This makes it  $D_{\infty h}$  point group.

- For  $\text{SeOCl}_4$ , we should also make the axial longer and bent away from the oxygen atom.
  - This molecule is  $sp^3d$  hybridized, not  $sp^2d^2$ , as it would be if the oxygen were axial.
- For  $\text{IO}(\text{OH})_5$ , we should show the equatorial OH's pushed away from the oxygen atom. The oxygen bond should also be a bit shorter.
- In the exam, they will specify whether we need to consider the hydrogens or not when calculating symmetry.
- For  $\text{ClOF}_4^-$ , one or the other of the lone pair/oxygen will push the equatorial fluorines a bit. You don't have to know which, just show bent.
- For  $\text{XeO}_2\text{F}_2$ , show the lone pair pushing the axial fluorines away.
- For  $\text{IF}_3^{2-}$ , show that this is a *distorted T*.
- A tennis ball belongs to the  $D_{2d}$  point group since you have perpendicular  $C_2$  axes punching through the seam and mirror planes at  $45^\circ$  angles to the  $C_2$  axes (i.e., dihedral).
- $\text{FeF}_6^{3-}$  also loses 4  $C_2$  axes.
- There are three possible isomers of  $\text{IF}_3\text{O}_2$  (see Figure I.1), but the one with equatorial oxygens is the most stable.
  - The structure analogous to Figure I.1a has  $C_{2v}$  symmetry.
  - The structure analogous to Figure I.1b has  $D_{3h}$  symmetry.
  - The structure analogous to Figure I.1c has  $C_s$  symmetry.
- Determine the point group of  $\text{NO}_3^{2-}$ ,  $\text{HFC}=\text{C}=\text{CHF}$ ,  $\text{H}_2\text{C}=\text{CF}_2$ , and  $\text{C}_2\text{H}_6$  (consider three possible conformers).
  - $\text{NO}_3^{2-}$  is of the  $D_{3h}$  point group.
  - $\text{HFC}=\text{C}=\text{CHF}$  is of the  $C_2$  point group.
  - $\text{H}_2\text{C}=\text{CF}_2$  is of the  $C_{2v}$  point group.
  - $\text{C}_2\text{H}_6$  eclipsed has  $D_{3h}$  symmetry, staggered has  $D_{3d}$  symmetry, and others have  $D_3$  symmetry.

## II.9 Module 9: Molecular Vibrations

1/25:

- If you have a nonlinear triatomic molecule (like  $\text{H}_2\text{O}$ ), we have 3 atoms  $\times$  3 DOF = 9 DOF.
  - This accounts for any possible perturbations of our molecules.
- We can break this down into three types of motion:
  - Translational motion along the  $x$ -,  $y$ -, and  $z$ -axes (3 DOFs).
  - Rotational motion about the  $x$ -,  $y$ -, and  $z$ -axes (3 more DOFs).
  - The remaining degrees of freedom are vibrational.
- Every *nonlinear* molecule has 3 translational and 3 rotational DOFs.
  - The number of vibrations is  $3N - 6$ , where  $N$  is the number of atoms.
- Every *linear* molecule has 3 translational and 2 rotational DOFs.
  - The number of vibrations is  $3N - 5$ , where  $N$  is the number of atoms.
- **Vibrational mode:** A perturbation of molecular structure that keeps the center of mass of the molecule in one place.

- For  $\text{H}_2\text{O}$ , there are three vibrational modes: antisymmetric stretch (one H moves away from the O as the other moves in, and then the process reverses), symmetric stretch (both H's move away from the O and then move back in), and scissoring bend (the bond angle changes).
- For molecules in general, there are these three and an additional three: wagging (in  $\text{H}_2\text{O}$ , the H's rotate out of the plane of the molecule and then back), twisting (in  $\text{H}_2\text{O}$ , both H's rotate out of the plane of the molecule, but one in one direction and one in the other), and rocking (in  $\text{H}_2\text{O}$ , both H's rotate about the O within the plane of the molecule preserving the bond angle, and then go back).
- What vibrational modes a molecule can and cannot have is governed by its point group and group theory.
- Each normal mode of vibration forms a basis for an irreducible representation of the point group of the molecule.
- Workflow to identify the vibrational properties of a molecule:
  1. Find number/symmetry of vibrational modes.
  2. Assign the symmetry of known vibrations.
  3. What does the vibration look like?
  4. Find if a vibrational mode is IR or Raman Active.
- To find vibrational modes, follow the 5-step Basis  $\rightarrow$  reducible representation  $\rightarrow$  irreducible representation workflow and then subtract translational and rotational motion.
  - For example, with  $\text{H}_2\text{O}$ , as before, we have  $C_{2v}$  point group,  $3N$  basis,  $\Gamma_{3N} = (9, -1, 1, 3)$ , and  $\Gamma_{3N} = 3A_1 + A_2 + 2B_1 + 3B_2$ .
  - We now need to use the basis functions in the  $C_{2v}$  character table to determine the translational and rotational degrees of freedom. From Figure II.4, the  $x, y, z$ -translational modes come from the  $B_1, B_2$ , and  $A_1$   $\Gamma_i$ 's, respectively. Thus, the total translational mode, sufficient to describe all possible translations in 3 DOFs, is  $\text{trans} = A_1 + B_1 + B_2$ . Similarly, we can determine that the total rotational mode is  $\text{rot} = A_2 + B_1 + B_2$ .
  - Thus, we can determine that the total vibrational mode is  $\Gamma_{3N} - \text{trans} - \text{rot} = 2A_1 + B_2$ .
  - When  $\text{H}_2\text{O}$  scissors or symmetrically stretches, it maintains its  $C_{2v}$  symmetry. Thus, both of these vibrations are represented by the totally symmetric irreducible representation  $A_1$  (hence the  $2A_1$  component).
  - As to asymmetric stretch, there exist points in time where  $\text{H}_2\text{O}$  lowers its symmetry from  $C_{2v}$  to  $C_s$ , losing its  $C_2$  and  $\sigma_v(xz)$  symmetry elements but maintaining  $E$  and  $\sigma_v(yz)$ . This shift is encapsulated by the  $B_2$  irreducible representation.
  - We can see all of these modes in  $\text{H}_2\text{O}$ 's infrared absorption spectrum.
    - Note that this spectrum does not tell us the energy of vibrations (we can model this with quantum mechanics), or if it is IR or Raman active (which modes will appear in the respective spectrum).
- Determine the number and symmetry types for the translations, vibrations, and rotations of  $\text{PF}_5$ .
  - Point group:  $D_{3h}$ .
  - We could write out all 18  $x, y, z$ -vectors, or we can use a shortcut: To construct  $\Gamma_{3N}$ , we can, for each symmetry element, multiply the number of atoms atoms unmoved under the operation by the corresponding character the representation that accounts for  $x, y, z$ -movements.

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

Applying this shortcut, we have  $\Gamma_{x,y,z} = E' + A''_2 = (3, 0, -1, 1, -2, 1)$ . We also have # unmoved atoms = (6, 3, 2, 4, 1, 4). Thus,  $\Gamma_{3N} = (18, 0, -2, 4, -2, 4)$ .

$D_{3h}$	$E$	$2C_3$	$3C_2$	$\sigma_h$	$2S_c$	$3\sigma_v$	linear	quadratic
$A'_1$	1	1	1	1	1	1		$x^2 + y^2, z^2$
$A'_2$	1	1	-1	1	1	-1	$R_z$	
$E'$	2	-1	0	2	-1	0	$(x, y)$	$(x^2 - y^2, xy)$
$A''_1$	1	1	1	-1	-1	-1		
$A''_2$	1	1	-1	-1	-1	1	$z$	
$E''$	2	-1	0	-2	1	0	$(R_x, R_y)$	$(xz, yz)$

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

- We can now reduce it into  $\Gamma_{3N} = 2A'_1 + A'_2 + 4E' + 3A''_2 + 2E''$ .
  - Note that we still have our 18 degrees of freedom because each  $E$  is double degenerate, meaning that  $4E'$  counts for 8 degrees of freedom and  $2E''$  counts for 4 degrees of freedom.
- This combined with the fact that  $\Gamma_{\text{trans}} = \Gamma_{x,y,z} = E' + A''_2$  and  $\Gamma_{\text{rot}} = A'_2 + E''$  implies that  $\Gamma_{\text{vibs}} = 2A'_1 + 3E' + 2A''_2 + E''$ .
  - For a similar reason to the note above, we can count  $12 = 3N - 6$  degrees of freedom (vibrational modes) in  $\Gamma_{\text{vibs}}$ .
  - Although degenerate modes count for multiple DOFs, the multiple modes they count for are of the same type.
    - In an ideal world, those modes corresponding to  $E$  would be twice as intense as the others.
    - From the definition of  $\Gamma_{\text{vibs}}$  and the above discussion, we know that  $\text{PF}_5$  has  $2+3+2+1=8$  distinct vibrational modes.
- There are (broadly) two types of vibrations: **stretches ( $\nu$ )** and **bends ( $\delta$ )**.
  - These two types appear in different energies in IR and Raman spectra.
  - To differentiate between stretching and bending modes: Look at how the stretching modes transform. Each stretch happens along a single vector from central atom to ligand. Thus, if we let these vectors be our basis and look at how many vectors stay the same (+1) or change (-1) under each operation, we will have a reducible representation that can be decomposed. Its components will be the stretching modes and  $\Gamma_{\text{vibs}} - \Gamma_{\nu}$  will equal  $\Gamma_{\delta}$ .
    - Applied to  $\text{PF}_5$ , we have  $\Gamma_{\nu} = (5, 2, 1, 3, 0, 3) = 2A'_1 + E' + A''_2$ .
    - Thus, both  $A'_1$  representations, one  $E'$  representation, and one  $A''_2$  representation correspond to stretching modes (or [spectroscopic] bands; note that the  $E'$  band will be twice as large). Consequently, the other two  $E'$  representations, the other  $A''_2$  representation, and the  $E''$  representation correspond to bending modes.

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

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

<sup>4</sup>Refer to Labalme (2020a), specifically the discussion of spectroscopy in Chapter 13.

- **Raman spectroscopy:** A method of measuring the change in the polarizability during a vibration. We impinge upon a sample of a substance with an incident light (a powerful laser). Most of the light that scatters will be a **Raleigh scatter**, but some will be a **Raman scatter** (a new wavelength).
- **Raleigh scatter:** The same wavelength is emitted as was impinged by the incident light because the laser was elastically scattered. The electrons fell the same number of energy levels that they rose after absorbing the light.
- **Raman scatter:** A new wavelength is emitted, different than the one impinged by the incident light. The electrons fell fewer (**Stokes Raman scattering**) or more (**Anti-Stokes Raman scattering**) energy levels than they rose after absorbing the light.
- **IR active** (vibration): A vibration that transforms with the same symmetry as the  $\vec{x}$ ,  $\vec{y}$ , and  $\vec{z}$  vectors (see the  $\chi$  tables).
- **Raman active** (vibration): A vibration having the same symmetry as the quadratic  $x, y, z$  terms, i.e.,  $x^2, z^2, yz$ , etc.
- For molecules possessing inversion centers, IR and Raman activity will be mutually exclusive.
- Activity data comes from character tables.
  - All vibration representations that have a linear term are IR active, while those that have a quadratic term are Raman active.
- Continuing with the  $\text{PF}_5$  example...
  - Table II.5 tells us that  $E'$  and  $A_2''$  vibrations are IR active, and  $A'_1$ ,  $E'$ , and  $E''$  are Raman active.
  - Thus, since  $\Gamma_{\text{vibs}} = 2A'_1 + 3E' + 2A_2'' + E''$ , there are  $3 + 2 = 5$  IR active bonds (corresponding to  $3 \cdot 2 + 2 = 8$  vibrations) and  $2 + 3 + 1 = 6$  Raman active bonds (corresponding to  $2 + 3 \cdot 2 + 1 \cdot 2 = 10$  vibrations).

## II.11 Chapter 4: Symmetry and Group Theory

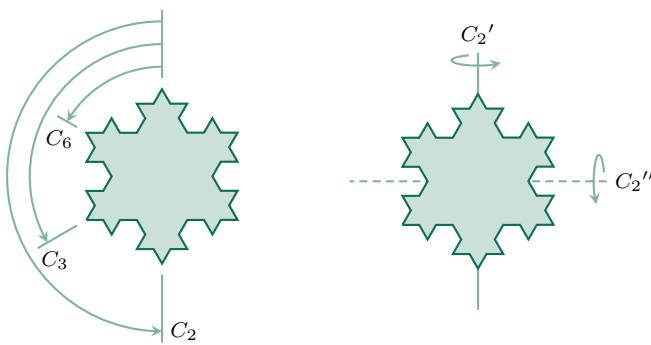
*From Miessler et al. (2014).*

1/18:

- **Coincident** (axes): Two identical axes.
  - For example, the  $C_3$  rotation axis of  $\text{CHCl}_3$  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 (see Figure II.6).
  - Rotations  $C_3^2$  and  $C_6^5$  are also symmetry operations.
- “When necessary, the  $C_2$  axes perpendicular to the principal axis are designated with primes; a single prime ( $C_2'$ ) indicates that the axis passes through several atoms of the molecule, whereas a double prime ( $C_2''$ ) indicates that it passes between the outer atoms” (Miessler et al., 2014, p. 77).

1/19:

- Even though  $S_2 \equiv i$  and  $S_1 \equiv \sigma$ , the  $i$  and  $\sigma$  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 ( $T_d, O_h, C_{\infty v}, D_{\infty h}, I_h$ ).



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

Figure II.6: Rotations of a snowflake design.

2. If not, find the highest order  $C_n$  axis for the molecule.
  3. Does the molecule have any  $C_2$  axes perpendicular to the principal  $C_n$  axis? If it does, there will be  $n$  of such  $C_2$  axes, and the molecule is in the  $D$  set of groups. If not, it is in the  $C$  or  $S$  set.
  4. Does the molecule have a mirror plane ( $\sigma_h$ ) 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:  $\text{W}[\text{N}(\text{CH}_3)_2]_6$ .

1/24:

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

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

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

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

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

- Three of the  $C_{2v}$  irreducible representations can be found in this way. The fourth can be found w/ linear algebra and the character table properties (or by inspection).

- If one matrix in the reducible representation cannot be blocked past having a  $2 \times 2$  chunk, per se, then the others must also have that  $2 \times 2$  chunk (so that we have an irreducible  $2 \times 2$  representation).

- “Matching the symmetry operations of a molecule with those listed in the top row of the character table will confirm any point group assignment” (Miessler et al., 2014, p. 99).

- Symmetric:** Character of 1.

- Antisymmetric:** Character of -1.

- Mulliken symbol rules:

- Letters are assigned according to the dimension of the irreducible representation” (Miessler et al., 2014, p. 99).

- Assign *A* if the dimension is 1 and the representation is symmetric to the principal rotation operation ( $\chi(C_n) = 1$ ).
- Assign *B* if the dimension is 1 and the representation is antisymmetric to the principal rotation operation ( $\chi(C_n) = -1$ ), or if  $\chi(S_{2n}) = -1$  even if  $\chi(C_n) = 1$ .
- Assign *E* if the dimension is 2.
- Assign *T* if the dimension is 3.

- “Subscript 1 designates a representation symmetric to a  $C_2$  rotation perpendicular to the principal axis, and subscript 2 designates a representation antisymmetric to the  $C_2$ . If there are no perpendicular  $C_2$  axes, 1 designates a representation symmetric to a vertical plane, and 2 designates a representation antisymmetric to a vertical plane” (Miessler et al., 2014, p. 100).

- “Subscript *g* designates representations symmetric to inversion, and subscript *u* designates representations antisymmetric to inversion” (Miessler et al., 2014, p. 100).

- “Single primes are symmetric to  $\sigma_h$  and double primes are antisymmetric to  $\sigma_h$  when a distinction between representations is needed ( $C_{3h}$ ,  $C_{5h}$ ,  $D_{3h}$ ,  $D_{5h}$ )” (Miessler et al., 2014, p. 100).

1/26:

- Chiral** (molecule): A molecule that is not superimposable on its mirror image. *Also known as disymmetric.*

- “In general, a molecule or object is chiral if it has no symmetry operations (other than *E*), or if it has only proper rotation axes” (Miessler et al., 2014, p. 100).

- Raman spectroscopy makes use of higher energy radiation than IR, exciting molecules to higher electronic states that are envisioned as short-lived “virtual” states.

## Topic III

# Introduction to Structure and Bonding

### III.1 Module 11: Quantum Chemistry 101

1/27:

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

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

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

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

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

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

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

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

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

- Electronic structure of  $H_2$  molecule.

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

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

- The first orbital is  $\sigma_g$  bonding.
- The second orbital is  $\sigma_u^*$  antibonding.
- Introducing the normalizing requirement gives us the above coefficients.
- In the Hückel theory:

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

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

- Expectation values for energy are

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

so

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

- Note that  $\beta < 0$  for atomic  $s$ -orbitals and  $\beta > 0$  for  $p$ -orbitals in  $\sigma$ -bonds.
- Also, in the Hückel one-electron model, the integrals  $\alpha$  and  $\beta$  remain unsolved.
- Note: As always, the bonding orbitals are less stabilized than the antibonding orbitals are destabilized.
  - This is a consequence of overlap, e.g., for a dimer, the  $1 \pm S$  term in  $E_{+/-} = \frac{\alpha \pm \beta}{1 \pm S}$ .
  - This is why  $\text{He}_2$  does not exist.

- **Overlap integral:** An integral proportional to the degree of spatial overlap between two orbitals. It is the product of wave functions centered on different lattice sites. Varies from 0 (no overlap) to 1 (perfect overlap). *Also known as  $S$ .*
- **Coulomb integral:** An integral giving the kinetic and potential energy of an electron in an atomic orbital experiencing interactions with all the other electrons and all the positive nuclei. *Also known as  $\alpha$ .*
- **Interaction integral** (on two orbitals 1,2): An integral giving the energy of an electron in the region of space where orbitals 1 and 2 overlap. The value is finite for orbitals on adjacent atoms, and assumed to be zero otherwise. *Also known as  $\beta_{12}$ , resonance integral, exchange integral.*
- Symmetry and quantum mechanics:

- Say we have  $\hat{H}\Psi = E\Psi$  where  $\hat{H}$  is the Hamiltonian and  $R$  is a symmetry operator (e.g.,  $C_2$  or  $\sigma_v$ ).
- Note that the Hamiltonian commutes with the symmetry operator:  $R\hat{H} = \hat{H}R$ .
- Since a symmetry operation does not change the energy of a molecule (it just moves it),  $\hat{H}R\Psi_i = E_i R\Psi_i$ .
- It follows that  $R$  does not change the form of the wave function, i.e.,  $R\Psi_i = \pm 1\Psi_i$ . This reflects the fact that  $R$  cannot change the probability  $P[e(x, y, z)] = |\Psi(x, y, z)|^2$  of finding an electron somewhere.
- Thus, the eigenfunctions of the Schrödinger equation generate a representation of the group.
- Non-degenerate wave functions are  $A$  or  $B$  type.
- Double-degenerate wave functions are  $E$  type.
- Triple-degenerate wave functions are  $T$  type.

- Back to the LCAO method:

$$E_i = \frac{\int \Psi_i^* H \Psi_i \, dV}{\int \Psi_i^* \Psi_i \, dV} \quad \Psi_i = \sum_i c_i \phi_i$$

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

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

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

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

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

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

- $\delta(E_f - E_i - h\nu)$  is the resonance condition (energy conservation).
- In the dipole approximation,  $H' = -e\vec{r} \cdot \vec{E}$ .
- This is derived with time-dependent perturbation theory.
  - The matrix element  $M = \langle f | H' | i \rangle = \int \Psi_f^*(\vec{r}) H' \Psi_i(\vec{r}) d^3\vec{r}$ .
  - Perturbation:  $H' = -\vec{p}_e \cdot \vec{E}_{\text{photon}}$ . Dipole moment:  $\vec{p}_e = -e\vec{r}$ . Light wave:  $\vec{E}_{\text{photon}}(r) = \vec{E}_0 e^{\pm i\vec{k} \cdot \vec{r}}$ ,  $H'(\vec{r}) = e\vec{E}_0 \cdot \vec{r} e^{\pm i\vec{k} \cdot \vec{r}}$ .
  - This implies that in one dimension,  $|M| \propto \int \Psi_f^*(\vec{r}) x \Psi_i(\vec{r}) d^3\vec{r}$ .
  - We include other variables in higher dimensions.
- For IR absorption, the intensity  $I$  satisfies  $I \propto \int \Psi_{\text{e.s.}} \hat{\mu}_e \Psi_{\text{g.s.}} d\tau$ .
  - $\Psi_{\text{e.s.}}$  is the excited state wavefunction,  $\Psi_{\text{g.s.}}$  is the ground state wavefunction, and  $\hat{\mu}_e$  is the dipole operator.
  - We now apply the three theorems:
  - It is always true in vibration spectroscopy that  $\Gamma_{\text{g.s.}} = A_1$ . This is because in the ground state, the molecule is completely relaxed (nothing is perturbed).
  - Thus, we can already reduce to  $\Gamma_{\text{e.s.}} \cdot \Gamma_\mu \cdot \Gamma_{\text{g.s.}} = \Gamma_{\text{e.s.}} \cdot \Gamma_\mu \cdot 1$ .
  - Now  $\Gamma_\mu$  transforms as  $x, y, z$  unit vectors. In  $D_{3h}$ , this implies that  $\Gamma_\mu = E' + A''_2$ .
  - Therefore,  $I \propto \Gamma_{\text{vibs}} \cdot (E' + A''_2)$ .
  - For  $\text{PF}_5$ , since  $\Gamma_{\text{vibs}} = 2A'_1 + 3E' + 2A''_2 + E''$  has  $E'$  and  $A''_2$  in common with  $\Gamma_\mu$ , only  $3E'$  and  $2A''_2$  are IR active.
  - Additionally, with elements in common,  $\Gamma_{\text{vibs}} \cdot \Gamma_\mu$  will contain  $A_1$  by Theorem 2, and thus, the integrals  $\int \Psi_{\text{e.s.}} x \Psi_{\text{g.s.}} d\tau$ ,  $\int \Psi_{\text{e.s.}} y \Psi_{\text{g.s.}} d\tau$ , and  $\int \Psi_{\text{e.s.}} z \Psi_{\text{g.s.}} d\tau$  are all nonzero. Some linear combination of them will be proportional to  $I$ .
- The exam will include material from today's class, but not Friday's class.
- PSets 1 and 2 will cover all material on the exam?

### III.3 Nocera Lecture 6

*From Nocera (2008).*

1/29: • Solving the Schrödinger equation with the LCAO method for the  $k$ th molecular orbital  $\Psi_k$ :

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

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

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

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

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

where  $H_{ij} = \int \phi_i \hat{H} \phi_j d\tau$  and  $S_{ij} = \int \phi_i \phi_j d\tau$ .

- To evaluate these integrals, see the notes in Module 11 concerning the Hückel approximation.

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

- A **semi-empirical** method.
- **Semi-empirical** (method): A method that relies on experimental data for the quantification of parameters.
- Other semi-empirical methods include CNDO, MINDO, and INDO.
- Hückel's method and LCAO example: Examine the frontier orbitals and their associated energies (i.e., determine eigenfunctions and eigenvalues, respectively) of benzene.

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

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

- $\ell_i$  is the dimension of  $\Gamma_i$ .
- $h$  is the order.
- $\chi^{(i)}(R)$  is the character of  $\Gamma_i$  under operation  $R$ .
- $R$  is the corresponding operator.

- To actually apply the above projection operator, we will drop to the  $C_6$  subgroup of  $D_{6h}$  to simplify calculations. The full extent of mixing among  $\phi_1$ - $\phi_6$  is maintained within this subgroup, but the inversion centers are lost, meaning that in the final analysis, the  $\Gamma_i$ s in  $C_6$  will have to be correlated to those in  $D_{6h}$ .
- In  $C_6$ , we have  $\Gamma_{p\pi} = (6, 0, 0, 0, 0, 0) = A + B + E_1 + E_2$ .
- The projection of the Symmetry Adapted Linear Combination (SALC) that from  $\phi_1$  transforms as  $A$  is

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

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

- With a similar process, we can find that

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

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

$$\begin{aligned} \Psi_3(E_1) &= \Psi'_3(E_{1a}) + \Psi'_4(E_{1b}) = 2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6 \\ \Psi_4(E_1) &= \Psi'_3(E_{1a}) - \Psi'_4(E_{1b}) = \phi_2 + \phi_3 - \phi_5 - \phi_6 \\ \Psi_5(E_2) &= \Psi'_5(E_{2a}) + \Psi'_6(E_{2b}) = 2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 + \phi_6 \\ \Psi_6(E_2) &= \Psi'_5(E_{2a}) - \Psi'_6(E_{2b}) = \phi_2 - \phi_3 + \phi_5 - \phi_6 \end{aligned}$$

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

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

meaning that

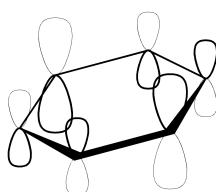
$$\begin{array}{ll} \Psi_1(A) = \frac{1}{\sqrt{6}} (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) & \Psi_2(B) = \frac{1}{\sqrt{6}} (\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6) \\ \Psi_3(E_1) = \frac{1}{\sqrt{12}} (2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6) & \Psi_4(E_1) =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



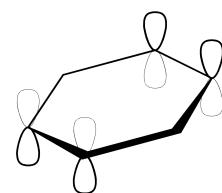
(a)  $\Psi_1(A) \sim \Psi(A_{2u})$ .



(b)  $\Psi_2(B) \sim \Psi(B_{2g})$ .



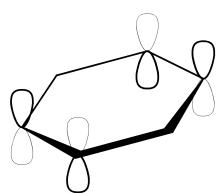
(c)  $\Psi_3(E_1) \sim \Psi(E_{1g}^a)$ .



(d)  $\Psi_4(E_1) \sim \Psi(E_{1g}^b)$ .



(e)  $\Psi_5(E_2) \sim \Psi(E_{2u}^a)$ .



(f)  $\Psi_6(E_2) \sim \Psi(E_{2u}^b)$ .

Figure III.1: Molecular orbitals of benzene.

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

### III.4 Nocera Lecture 7

*From Nocera (2008).*

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

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

- Similarly, we can determine that

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

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

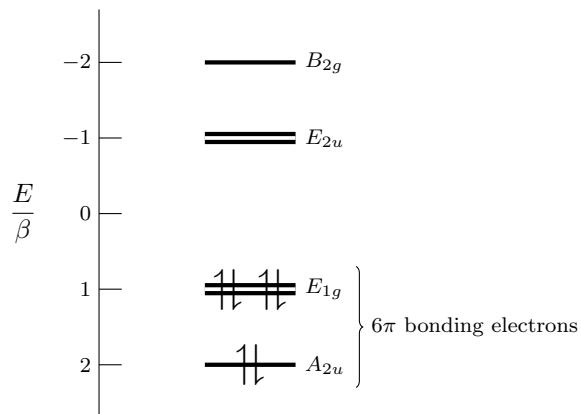


Figure III.2: Energy level diagram of benzene.

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

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

- **Delocalization energy:** The difference in energy between a molecule that delocalizes electron density in a delocalized state versus a localized state. *Also known as resonance energy.*

- Finding the delocalization energy of benzene:

- Consider cyclohexatriene, a molecule equivalent to benzene except that it has 3 *localized*  $\pi$  bonds. Cyclohexatriene is the product of three condensed ethene molecules.

- Ethene has 2  $\pi$  bonds  $\phi_1$  and  $\phi_2$ .

- Following the procedure of Nocera Lecture 6, we can determine that

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

- Thus,

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

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

- Correlating the above calculations (performed within  $C_2 \subset D_{2h}$ ) to the  $D_{2h}$  point group gives  $A \rightarrow B_{1u}$  and  $B \rightarrow B_{2g}$ .

- We can now construct an energy level diagram.

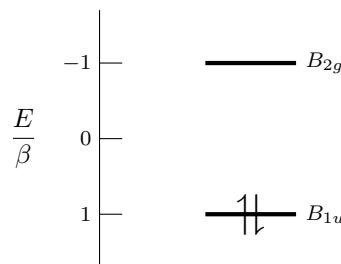


Figure III.3: Energy level diagram of ethene.

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

- Therefore, the resonance energy of benzene based on the Hückel approximation is

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

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

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

where  $n_e$  is the orbital  $e^-$  occupancy and  $c_{i,j}$  are the coefficients of the electrons  $i, j$  in a given bond.

- Finding the bond order of benzene between carbons 1 and 2:

- Just apply the formula:

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

### III.5 Module 13: Why Molecular Orbitals?

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

<sup>2</sup>Refer to Labalme (2020a), specifically Figure 7.20 and the accompanying discussion.



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

- If we apply PES to O<sub>2</sub>, we get counts that correspond to molecular orbitals  $\pi_g^*$ ,  $\pi_u$ ,  $\sigma_g$ , and  $\sigma_u^*$ .
- Photoelectron spectrum of H<sub>2</sub>O:
  - Pauling's theory suggest that the lone pairs should have equal energy greater than the equal energy of the bonds.
  - However, PES reveals that the lone pairs have two different energies. This is a nail in the coffin of Pauling's valence bond theory.
- PES of CH<sub>4</sub>:
  - There are two states; one with degeneracy 3 and one with degeneracy 1.
  - We have 3 bonds of one energy and 1 with another.
  - Another nail in the coffin.



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

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

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

- Bonding:  $\Psi_\sigma = \Psi_+ = \frac{1}{\sqrt{2}}(\psi_{1s_a} + \psi_{1s_b})$ .
- Anti-bonding:  $\Psi_{\sigma^*} = \Psi_- = \frac{1}{\sqrt{2}}(\psi_{1s_a} - \psi_{1s_b})$ .
  - Addition doesn't necessarily correlate to bonding and subtraction to anti-bonding.
- With simple orbitals, we can combine orbitals by inspection.
  - However, we will learn to build molecular orbitals for much more complicated molecular orbitals, such as those of ferrocene ( $\text{Fe}(\text{C}_5\text{H}_5)_2$ ).
- Degree of orbital overlap/mixing depends on:
  1. Energy of the orbitals (the closer the energy, the more mixing; when the energies differ greatly, the reduction energy due to bonding is insignificant).
  2. Spatial proximity (the atoms must be close enough that there is *reasonable* orbital overlap, but not so close that repulsive forces interfere).
  3. Symmetry (atomic orbitals mix if they have similar symmetries; regions with the same sign of  $\Psi$  overlap).
- The strength of the bond depends upon the degree of orbital overlap.
- For heteronuclear molecules:



Figure III.6: Combining orbitals of varying energies.

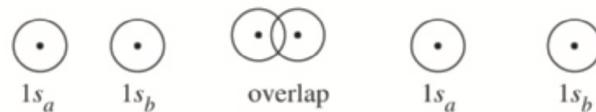
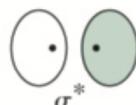
- The bonding orbital(s) will reside predominantly on the atom of lower orbital energy (the more electronegative atom).
- The anti-bonding orbital(s) will reside predominantly on the atom with greater orbital energy (the less electronegative atom).
- The energies of atomic orbitals (measured by PES)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



Figure III.7: Orbital potential energies.

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

$$\sigma^* = \frac{1}{\sqrt{2}}[\psi(1s_a) - \psi(1s_b)]$$



$$\sigma = \frac{1}{\sqrt{2}}[\psi(1s_a) + \psi(1s_b)]$$

(a)  $\sigma_s$ .

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

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

### III.7 Office Hours (Wang)

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

$$A_1 \times (A_1 + B_1 + B_1) = A_1 \times A_1 + A_1 \times B_1 + A_1 \times B_2$$
    - Since  $A_1 \times A_1 = A_1$ , we already know after taking only this product that  $A_1$  is IR active.
    - Things aren't IR active because they're linear. Things are IR active because their direct product with the sum of the linear groups contains the totally symmetric representation.
- You can only take the direct product of irreducible representations?

### III.8 Office Hours (Talapin)

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

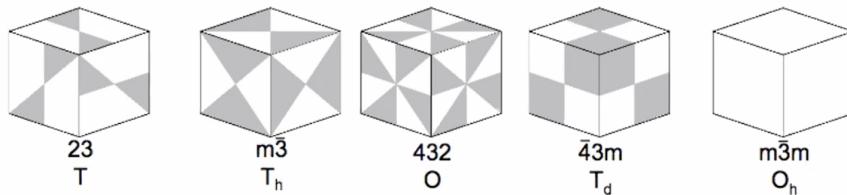


Figure III.9: Tetrahedral point groups.

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

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

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

2/1:

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

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

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

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

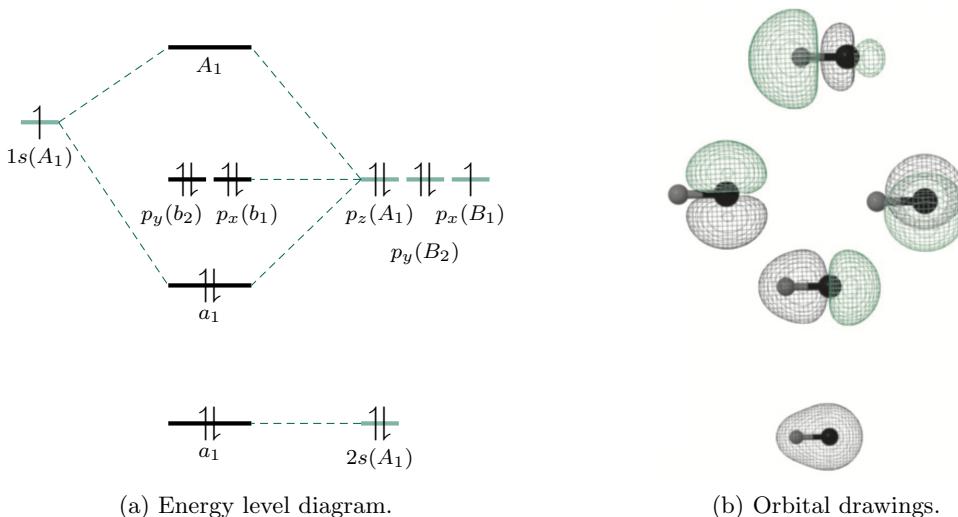


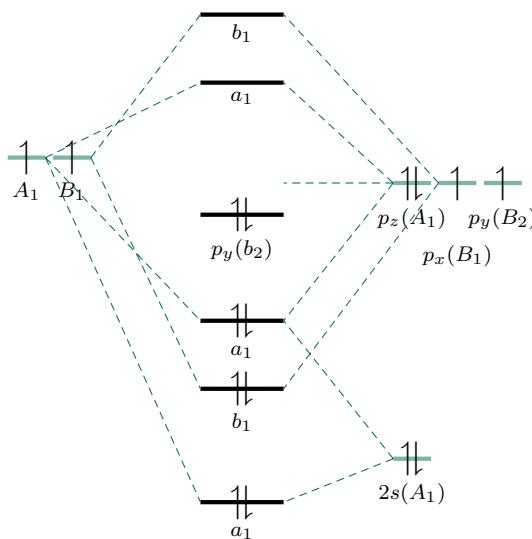
Figure III.10: HF orbital diagram.

- We can now fill the MOs with the atomic electrons using the Aufbau principle, the Pauli exclusion principle, and Hund's rule. We can also draw these orbitals.
- Orbital energies can be found in Table 5.2 of Miessler et al. (2014).
- If the energy difference between orbitals is more than 10 eV, then we can *probably* (not always) ignore mixing.
  - The approximate scaling is that the stabilization energy (or energy gain) is inversely proportional to the energy gap.
  - The magnitude of the interaction integral will be approximately inversely proportional to the energy gap between the atomic orbitals participating.
- Organic chemists can go a long way with a hybridization approach even though it is not reflected in inorganic chemistry.

### III.10 Module 16: Constructing Molecular Orbitals (Part 3, $\text{H}_2\text{O}$ Molecule)

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

- Once  $z$  is defined, the  $y$ -axis is defined as the axis of the remaining two axes which has the largest number of atoms unmoved by the  $\sigma$  symmetry operation.
- The  $x$ -axis is the remaining axis.
- The overall result is that the symmetry axes in ethylene are defined as:  $z$  - along the C=C bond;  $y$  - in the molecular plane, perpendicular to the C=C bond; and  $x$  - out of the plane.
- Similar approaches apply to the  $C_{2v}$  point group.
- We will need SALCs here.
  - Since the hydrogen atoms do not lie on the principal rotation axis, they will not individually obey the symmetry operations.
  - Thus, we need **Symmetry Adapted Linear Combinations**.
- **Symmetry Adapted Linear Combination** (of atomic orbitals): The linear combination of multiple atomic orbitals corresponding to peripheral atoms (atoms that do not lie on the principal axis). This linear combination will obey the symmetry modes. *Also known as SALC.*
- To generate SALCs, the steps are:
  - Group the atomic orbitals in the molecule into sets which are equivalent by symmetry.
  - Generate and reduce the reducible representation for each set.
  - Use the projection operator for one basis.
- $\text{H}_2\text{O}$  example:
  - Point group:  $C_{2v}$ .
  - Choose basis functions (both  $\text{H}_{1s}$  orbitals, O the same as F in the last example).
  - Applying operations, we get
 
$$\Gamma_{\text{H}} = (2, 0, 2, 0) = A_1 + B_1$$
    - For the hydrogens, it makes sense that we need two irreducible representations to describe two atoms. More formally, the number of basis functions should match the number of irreducible representations to account for possible degeneracy of irreducible representations.
    - The O orbitals are the same as the F orbitals in the last example.
  - Combining orbitals by their symmetry and energy again, we get the following MOs.

Figure III.11:  $\text{H}_2\text{O}$  orbital diagram.

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



Figure III.12: Photoelectron spectrum for  $\text{H}_2\text{O}$ .

- We see four different states, which matches the prediction of Figure III.11.
- The lowest state is called  $2a_1$  because it is the second state that transforms as  $A_1$  going out from the core (the first is  $1a_1$  corresponding to oxygen's  $1s$  electrons [this state is not shown in Figure III.11 because it is so core as to not be significantly relevant to the chemistry of  $\text{H}_2\text{O}$ ]).
- Then  $1b_1$  is the first  $A_1$  state going out from the core,  $3a_1$  is the third  $A_1$  state, and  $1b_2$  is the first  $B_2$  state.
- There are no  $4a_1$  and  $2b_1$  electrons (see Figure III.11); hence, there are no such PES peaks (see Figure III.12).
- Note that the numbers along the bottom axis correspond to the orbital potential energies of the corresponding molecular orbitals.
- For  $\text{H}_2\text{O}$ , hybridization is qualitatively wrong.
- To generate SALCs:
  - Use the projection operator. See Nocera Lecture 6 for how to mathematically apply it.
  - Projection operators constitute a method of generating the symmetry allowed combinations.
  - Taking one AO and projecting it out using symmetry.
- Using the projection operator method to reconstruct SALC orbitals ( $\text{NH}_3$  example):

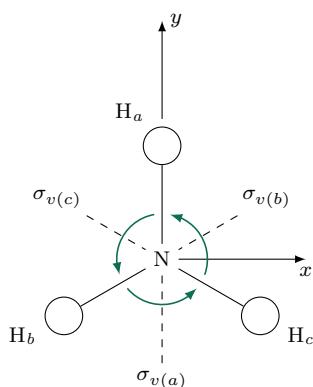


Figure III.13: Coordinate system for  $\text{NH}_3$ .

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

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

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

$$\begin{aligned} A_1 &= H_a + H_b + H_c + H_a + H_c + H_b = 2H_a + 2H_b + 2H_c \\ A_2 &= H_a + H_b + H_c - H_a - H_c - H_b = 0 \\ E &= 2H_a - H_b - H_c + 0 + 0 + 0 = 2H_a - H_b - H_c \end{aligned}$$

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

- Continuing with the  $\text{H}_2\text{O}$  example:

- Using the projection operator, we get

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

- $P^{A_1}$  is a sum of the two hydrogen 1s orbitals.
- $P^{B_1}$  is a difference of the two hydrogen 1s orbitals.
- This step allows us to construct electron density maps for the SALCs of the hydrogen's atomic orbitals.
- We can now see if the symmetry of various orbitals matches up or doesn't match up and use this information to sketch molecular orbitals.
- Oxygen atomic orbital coefficients can only be analytically derived with quantum mechanical calculations.
- How can we predict the shape of molecules from MO theory (i.e., without VSEPR theory)?
- **Walsh diagrams** help understand the molecular shapes (bond angles).
  - If  $\text{H}_2\text{O}$  is linear, it is part of the  $D_{\infty h}$  point group (which can be reduced to  $D_{2h}$  for further mysterious reasons).
  - $1\sigma_g^+$ : If we slowly decrease the bond angle, the hydrogen orbital overlap will increase, meaning that  $1\sigma_g^+$  energy decreases.
  - $1\sigma_u^+$ : If we slowly decrease the bond angle, the  $s$  and  $p$  orbitals will become less aligned, meaning that  $1\sigma_u^+$  energy increases.
  - $\pi_u, 2a_1$ : Energy decreases as hydrogen orbitals get closer to the appropriately signed region of the  $\text{O}_p$  orbital.
  - $\pi_u, b_2$ : Energy is constant.
  - Now all orbitals with electrons have been accounted for. Since 2 energies go down, 1 goes up, and 1 stays the same as bond angle decreases, we know that bond angle will decrease to an equilibrium.

### III.11 Module 17: Constructing Molecular Orbitals (Part 4, NH<sub>3</sub> Molecule)

2/3: • NH<sub>3</sub> example:

- Point group:  $C_{3v}$ .
- Basis functions: H<sub>1s</sub>, N<sub>2s</sub>, N<sub>2p<sub>x</sub></sub>, N<sub>2p<sub>y</sub></sub>, and N<sub>2p<sub>z</sub></sub>.
- Apply operations (pick any one operation from each class)/construct reducible representations:

$$\Gamma_H = (3, 0, 1) = A_1 + E$$

$$\Gamma_{N_{2s}} = A_1$$

$$\Gamma_{N_{2p_x}} = E$$

$$\Gamma_{N_{2p_y}} = E$$

$$\Gamma_{N_{2p_z}} = A_1$$

- N<sub>2p<sub>x</sub></sub> and N<sub>2p<sub>y</sub></sub> are doubly degenerate — their transformation cannot be decoupled and they transform together.
- Look at the relevant energies and plot them against each other.
- 3  $A_1$  type atomic orbitals form 3  $a_1$  type MOs.



Figure III.14: NH<sub>3</sub> orbital diagram.

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

- For the last  $E$  SALC, we apply the projection to each hydrogen atom (we can choose any basis function) giving us, in addition to the other projections,  $P^E \approx 2\phi_2 - \phi_3 - \phi_1$  and  $P^E \approx 2\phi_3 - \phi_1 - \phi_2$ . By subtracting these two, we get  $\Psi_E = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3)$ . Do we choose this linear combination because it's orthogonal to the other two? Because its structure is different and simple (you *can* do it with any linear combination, but it will make the analysis much more complicated if you do it with a trickier linear combination).
- We need to renormalize our SALCs so that the integral of their square over all space is 1. To normalize, we must guarantee that the sum of the squares of the coefficients is 1. For  $P^{A_1}$  for example,  $1^2 + 1^2 + 1^2 = 3$ , so we must scale the whole thing by  $\frac{1}{\sqrt{3}}$ .
- In the PES spectrum, we see three peaks, one being approximately twice as wide as the others (corresponding to the double degenerate state).
- Walsh diagrams (rely on the pictures that we draw of orbitals):
  - $1a'_1$  energy decreases,  $1e'$  energy increases,  $a''_2$  energy decreases rather dramatically.
  - If we promote electrons to the excited state, the relevant Walsh diagrams will change, and this will cause the molecule to change shape.
- Also try to sketch the MOs in the homework.

### III.12 Module 18: Constructing Molecular Orbitals (Part 5, $\text{H}_2\text{C}=\text{CH}_2$ Molecule)

- $\text{H}_2\text{C}=\text{CH}_2$  example:

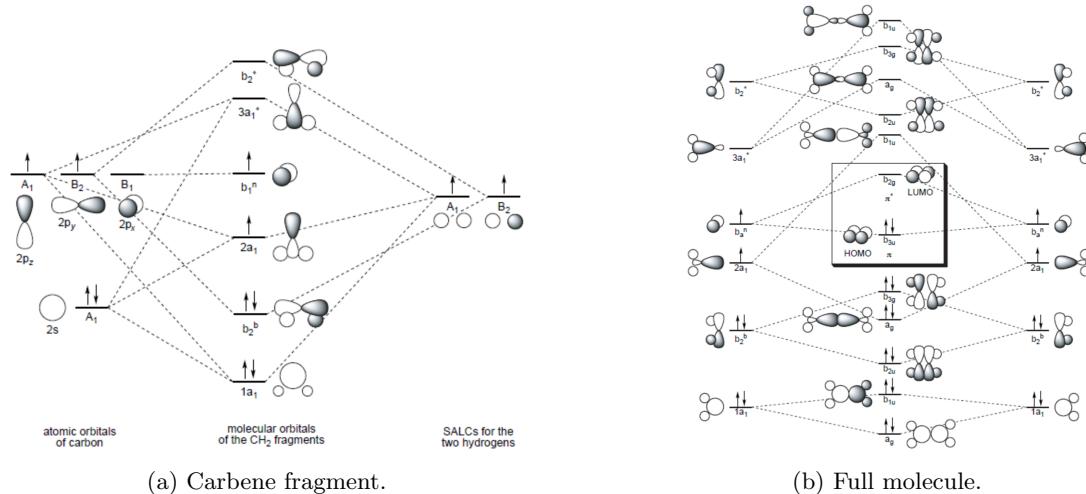


Figure III.15:  $\text{H}_2\text{C}=\text{CH}_2$  orbital diagram.

- Two different approaches ( $D_{2h}$ ):  $\text{C}_1 + \text{C}_2$  then  $\text{H}_{1-4}$ , or two carbene fragments ( $\text{CH}_2$ ).
  - We can read about the first approach in the linked JCE article (*cite*).
- $C_{2v}$  for the  $\text{CH}_2$  fragment.
- When we make the MO diagram, we have two unpaired electrons, one in each of the upper two orbitals. These will be used for bonding to the other carbene fragment.
- We will then combine the MO diagrams and will need to reassign orbital names because ethene isn't  $C_{2v}$ ; it's  $D_{2h}$ .

### III.13 Module 19: Isolobal Principle

- **Isolobal** (fragment): A fragment with similar (not identical) numbers, symmetry properties, approximate energies, and shapes of the frontier orbitals and the number of electrons in them.
- This allows us to show, for example, that a carbene fragment and a  $d^7$  metal complex have similar properties.
- Two  $\text{CH}_3$  fragments will tend to couple into ethane. But so will two isolobal  $\text{Mn}(\text{CO})_5$  fragments!

### III.14 Module 20: Orbital Hybridization

- **Hybridization:** The concept of mixing atomic orbitals into new hybrid orbitals (with different energies, shapes, etc. than the component atomic orbitals) suitable for the pairing of electrons to form chemical bonds.
- Hybridization accomplishes the work of MO theory in steps: Creating new orbitals and then bonding atoms with them, as opposed to defining new orbitals and filling them.
- This was the dominant approach in chemistry before MO theory, and is still widely used in organic chemistry.
- For light elements, the energy gaps between orbitals aren't very large and this method is legitimate to some degree.
  - For carbon, it's acceptable.
  - For silicon and lead (in the same group), this is not a good approach; it will give you incorrect predictions (e.g., around bond angles and lengths).
- Steps to determine the hybridization of a bond:
  1. Assign a point group.
  2. Choose basis function ( $\sigma$  bonds).
  3. Apply operations.
  4. Reduce to irreducible representations.
  5. Compare symmetry of irreducible representations to central atom MOs.
- $\text{BF}_3$  example:
  - Point group:  $D_{3h}$ .
  - $\Gamma_\sigma = (3, 0, 1, 3, 0, 1)$ .
  - $\Gamma_\sigma = A'_1 + E'$ .
  - For boron,  $\text{B}(s) = A'_1$ ,  $\text{B}(p_x) = E'$ ,  $\text{B}(p_y) = E'$ , and  $\text{B}(p_z) = A''_2$ . Thus, since one orbital matches up on  $s$  and two match up on  $p$  (specifically,  $p_x, p_y$ ), the hybrid orbitals will be  $sp^2$  (hybrid of  $s, p_x, p_y$ ).
- It is not generally justifiable to say that atomic orbitals in *individual* atoms mix before bonding.

### III.15 Chapter 5: Molecular Orbitals

From Miessler et al. (2014).

- 1/29:
  - MO theory uses group theory to describe molecular bonding, complementing and extending Chapter 3.

- “In molecular orbital theory the symmetry properties and relative energies of atomic orbitals determine how these orbitals interact to form molecular orbitals” (Miessler et al., 2014, p. 117).
  - The molecular orbitals are filled according to the same rules discussed in Chapter 2.
  - If the total energy of the electrons in the molecular orbitals is less than that of them in the atomic orbitals, the molecule is stable relative to the separate atoms (and forms). If the total energy of the electrons in the molecular orbitals exceeds that of them in the atomic orbitals, the molecule is unstable (and does not form).
  - Homonuclear** (molecule): A molecule in which all constituent atoms have the same atomic number.
  - Heteronuclear** (molecule): A molecule that is not homonuclear, i.e., one in which at least two atoms differ in atomic number.
  - A less rigorous pictorial approach can describe bonding in many small molecules and help us to build a more rigorous one, based on symmetry and employing group theory, that will be needed to understand orbital interactions in more complex molecular structures.
  - Schrödinger equations can be written for electrons in molecules as they can for electrons in atoms. Approximate solutions can be constructed from the LCAO method.
    - In diatomic molecules for example,  $\Psi = c_a\psi_a + c_b\psi_b$  where  $\Psi$  is the molecular wave function,  $\psi_{a,b}$  are the atomic wave functions for atoms  $a$  and  $b$ , and  $c_{a,b}$  are adjustable coefficients that quantify the contribution of each atomic orbital to the molecular orbital.
  - “As the distance between two atoms is decreased, their orbitals overlap, with significant probability for electrons from both atoms being found in the region of overlap” (Miessler et al., 2014, p. 117).
  - Electrostatic forces between nuclei and electrons in bonding molecular orbitals hold atoms together.
- 2/5:
- Precise calculations show that the coefficient of the  $\sigma^*$  hydrogen antibonding orbital is slightly larger than that of the  $\sigma$  orbital, but we typically neglect this distinction.
    - This technically implies that  $\Delta E_{\sigma^*} > \Delta E_\sigma$ , i.e., that the increase in energy from electrons in atomic orbitals moving into the  $\sigma^*$  antibonding molecular orbital is greater in magnitude than the decrease in energy from electrons in atomic orbitals moving into the  $\sigma$  bonding molecular orbital.
  - $\sigma$  orbital:** A molecular orbital that is symmetric to rotation about the line connecting the nuclei.
  - Orbital asterisk:** Denotes antibonding orbitals for those molecules where bonding and antibonding orbital descriptions are unambiguous (i.e., smaller molecules).
  - When two regions of like sign overlap, the sum of the orbitals exhibits increased electron probability in the overlap region, and vice versa for regions of opposite sign.
  - When the  $z$ -axes are drawn pointing in the same direction, their difference is  $\sigma$  and their sum is  $\sigma^*$ .

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

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

- However, in Figure III.16a, with a more standard coordinate system, we have to flip the signs of one of the orbitals before merging them (multiply it by  $-1$  and add it to the other orbital/subtract it from the other orbital) to create a bonding orbital. If we add them as they are, we will get an antibonding orbital.
- **$\pi$  orbital:** A molecular orbital with a change in sign of the wave function under  $C_2$  rotation about the  $z$ -axis (the bond axis).
  - $\pi$  and  $\pi^*$  orbitals arise from the interactions between  $p_x$  and  $p_y$  atomic orbitals.
- MOs that form from  $p_z$  orbitals are  $\sigma$  and  $\sigma^*$  orbitals.
- “When orbitals overlap equally with both the same and opposite signs... the bonding and antibonding effects cancel, and no molecular orbital results” (Miessler et al., 2014, p. 121).
- $d$  orbitals can also be involved in bonding in heavier elements such as the transition metals.
  - Two  $d_{z^2}$  orbitals participate in  $\sigma$  bonding.
  - Two  $d_{xz}$  or  $d_{yz}$  orbitals participate in  $\pi$  bonding.
  - Two  $d_{x^2-y^2}$  or  $d_{xz}$  orbitals participate in  **$\delta$  bonding**.
- **$\delta$  orbital:** A molecular orbital with a change in sign of the wave function under  $C_4$  rotation about that  $z$ -axis.
  - $\delta$  and  $\delta^*$  orbitals arise from the interactions of atomic orbitals meeting in parallel planes and combining side to side.
- “Sigma orbitals have no nodes that include the line connecting the nuclei, pi orbitals have one node that includes the line connecting the nuclei, and delta orbitals have two nodes that include the line connecting the nuclei” (Miessler et al., 2014, p. 121).
- Note that  $p_x$  and  $d_{xz}$  orbitals (for example) could, in theory, interact.
- Additional thoughts on Figure III.6:
  - Similarity in energy is correlated with similarity in structure.
  - When orbital energies are similar (Figure III.6a), there is a large difference between the atomic orbitals and the molecular orbitals, resulting in a great potential for stabilization through bonding.
- Molecular orbitals help us understand the structure of  $\text{Li}_2$ ,  $\text{Be}_2$ , and other diatomic molecules that violate the octet rule.
  - They also explain experimental phenomena that clash with VSEPR theory — for example, the Lewis structure of  $\text{O}_2$  predicts a diamagnetic molecule, but in reality,  $\text{O}_2$  is paramagnetic with two unpaired electrons.
- See Figure III.17 for the molecular orbitals in the homonuclear diatomic molecules formed by the first 10 elements, neglecting interactions between atomic orbitals of differing energy levels.
- Bond order:
$$\text{B.O.} = \frac{1}{2}(\text{number of electrons in bonding orbitals} - \text{number of electrons in antibonding orbitals})$$
  - Generally, we need only consider valence electrons to calculate the bond order: For example,  $\text{O}_2$  has  $\text{B.O.} = 2$  whether or not you factor valence electrons into the calculation.
- Core electrons are generally assumed to reside mostly on the original atom and negligibly participate in bonding and antibonding interactions.



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

- This is reflected by how much lower the 1s MOs are in Figure III.17 than the others, and by how slight the difference is between bonding and antibonding.
- “When two molecular orbitals of the same symmetry have similar energies, they interact to lower the energy of the lower orbital and raise the energy of the higher orbital” (Miessler et al., 2014, p. 124).
- **$\sigma_g$  symmetry:** Symmetry to infinite rotation and inversion.
  - Possessed by the  $\sigma_g(2s)$  and  $\sigma_g(2p)$  orbitals in Figure III.17, for example.
- Molecular orbitals with the same symmetry and similar energies can **mix**, lowering the energy of the lower orbital and raising the energy of the higher orbital.
  - For example, the  $\sigma_g(2s)$  and  $\sigma_g(2p)$  orbitals in Figure III.17 can mix, lowering the energy of the 2s one and raising the energy of the 2p one.
- 2/6:     • Atomic orbital energies decrease across a row in the periodic table.
- Characterization of selected homonuclear diatomic molecules:

- He<sub>2</sub>’s bond order is 0, with two bonding and two antibonding electrons. Thus, it has no significant tendency to form (it’s bone energy is 0.01 J/mol, compared to H<sub>2</sub>’s 436 kJ/mol).
- B<sub>2</sub> is paramagnetic (because of its two unpaired  $\pi_u$  electrons). The 2p valence electrons do not occupy the  $\sigma_g$  MO because of orbital mixing and because the energy difference between  $\sigma_g(2p)$  and  $\pi_u(2p)$  is greater than  $\Pi_c$  (even if there were no mixing, the electrons would still occupy the  $\pi_u$  orbitals if it was more energetically favorable to do this than to occupy the same orbital).
- C<sub>2</sub> is a rarely encountered allotrope of carbon, but it has two  $\pi$  bonds and no  $\sigma$  bonds.
- In N<sub>2</sub>, some larger trends become apparent:
  - Since electrons in different orbitals vary in their shielding abilities and electron-electron interactions, the difference between the 2s and 2p energies increase as  $Z$  increases.
  - More specifically, 2s electrons have higher probabilities close to the nucleus than 2p electrons (Figure 0.8), so they are more affected by increasing nuclear charge (inverse square law).
  - As a result of this separation, the  $\sigma_g(2s)$  and  $\sigma_g(2p)$  orbitals mix less in N<sub>2</sub> than in C<sub>2</sub> or B<sub>2</sub>.
- The ions of O<sub>2</sub> (which include dioxygenyl O<sub>2</sub><sup>+</sup>, superoxide O<sub>2</sub><sup>-</sup>, and peroxide O<sub>2</sub><sup>2-</sup>) reveal that bond order and bond distance are inversely proportional. Here, mixing finally becomes small enough that the normal filling order (as in Figure III.17) returns.
- Notice how atomic radius consistently decreases across the second period, but bond length decreases until N<sub>2</sub> and then increases (because of the addition of antibonding electrons).
- At this point, we’ll assume (for PES purposes) the energy levels in the uncharged molecule to be essentially the same as those in the charged ions generated when we seek to examine core energy levels<sup>[3]</sup>.
- Comparing the PES spectrums for N<sub>2</sub> and O<sub>2</sub>, it can be seen that the N<sub>2</sub> energy levels are closer together than the O<sub>2</sub> ones.
- PES also provides evidence for the existence of **vibrational energy levels**, energy levels that are much more closely spaced than electronic levels that cause the multiple peaks within one “peak.”
- Orbitals that are strongly involved in bonding have **vibrational fine structure** (multiple peaks), and vice versa for less involved orbitals.
  - Thus, the 10  $\pi_u$  vs. the 6  $\sigma_g$  vibrational peaks in O<sub>2</sub> indicate that the  $\pi_u$  orbitals are more strongly involved in bonding than the  $\sigma_g$  orbital.
- “The atomic orbitals of atoms that form homonuclear diatomic molecules have identical energies, and both atoms contribute equally to a given MO. Therefore, in the molecular orbital equations, the coefficients associated with the same atomic orbitals of each atom...are identical. In heteronuclear diatomic molecules...the atomic orbitals have different energies, and a given MO receives unequal contributions from these atomic orbitals; the MO equation has a different coefficient for each of the atomic orbitals that contribute to it” (Miessler et al., 2014, pp. 134, 136).
- Atomic orbitals closer in energy to an MO contribute more to that MO, and thus have larger coefficients in the wave equation.
- CO example:
  - The 1 $\pi$  orbitals are lower than the 3 $\sigma$  orbitals because of the strong mixing between the 2p<sub>z</sub> orbital of oxygen and the 2s and 2p<sub>z</sub> orbitals of carbon.
  - The 3 $\sigma$  orbital has a large lobe on the carbon end because two carbon orbitals (2s and 2p<sub>z</sub>) mix with one oxygen orbital (2p<sub>z</sub>).

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

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



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

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

<sup>4</sup>See Labalme (2020a), specifically Figure 8.2 and the associated discussion

- Since the H(2s) orbitals match better energetically with the F(2p<sub>z</sub>) orbitals than the F(2s) orbitals, the 2p<sub>z</sub> interactions will be stronger.
  - Notice that the lone pairs are delocalized over both fluorine atoms, not confined to one as the Lewis dot model predicts.
  - Additionally, the Lewis approach predicts two, 2-electron bonds, resulting in 4 electrons around the central H atom. However, the MO model suggests 2 electrons (in a  $\sigma$  bond [ $a_g$ ]) decentralized over all three atoms.
- A stepwise approach to building MOs for more complex molecules (Miessler et al., 2014, p. 143):
    1. Determine the point group of the molecule. If it is linear, substituting a simpler point group that retains the symmetry of the orbitals (ignoring the wave function signs) makes the process easier. It is useful to substitute  $D_{2h}$  for  $D_{\infty h}$  and  $C_{2v}$  for  $C_{\infty v}$ . This substitution (known as a **Descent in Symmetry**) retains the symmetry of the orbitals without the need to use infinite-fold rotation axes.
    2. Assign  $x, y, z$  coordinates to the atoms, chosen for convenience. Experience is the best guide here. A general rule is that the highest order rotation axis of the molecule is assigned as the  $z$ -axis of the central atom. In nonlinear molecules, the  $y$ -axes of the outer atoms are chosen to point toward the central atom.
    3. Construct a (reducible) representation for the combination of the valence  $s$  orbitals on the outer atoms. If the outer atom is not hydrogen, repeat the process, finding the representations for each of the other sets of outer atom orbitals (for example,  $p_x$ ,  $p_y$ , and  $p_z$ ). As in the case of the vectors described in Chapter 4, any orbital that changes position during a symmetry operation contributes 0 to the character of the resulting representation; any orbital that remains in its original position — such as a  $p$  orbital that maintains its position and direction (signs of its orbital lobes) — contributes 1; and any orbital that remains in the original position, with the signs of its lobes reversed, contributes -1.
    4. Reduce each representation from Step 3 to the sum of its irreducible representations. This is equivalent to finding the symmetry of the group orbitals or the **symmetry-adapted linear combinations** (SALCs) of the orbitals. The group orbitals are then the combinations of atomic orbitals that match the symmetry of the irreducible representations.
    5. Identify the atomic orbitals of the central atom with the same symmetries (irreducible representations) as those found in Step 4.
    6. Combine the atomic orbitals of the central atom and those of the group orbitals with matching symmetry and similar energy to form molecular orbitals. The total number of molecular orbitals formed must equal the number of atomic orbitals used from all the atoms. Note that the MOs are assigned lowercase Mulliken symbols (e.g.,  $a_1$ ), whereas atomic orbitals and representations in general are assigned uppercase Mulliken symbols (e.g.,  $A_1$ ).
  - CO<sub>2</sub> example:
    - We find the same group orbitals as in FHF<sup>-</sup> but by using the stepwise procedure.
      - Note that saying  $\Gamma_{2s} = A_g + B_{1u}$ , for example, expresses the fact that there are two 2s orbitals (the sum and difference of the O(2s) orbitals) and that one has  $A_g$  symmetry while the other has  $B_{1u}$  symmetry.
      - The orbitals on the central atom are 2s, 2p<sub>z</sub>, 2p<sub>x</sub>, 2p<sub>y</sub>.
      - The  $A_g$  O(2s) orbital can be added to and subtracted from the C(2s) orbital, and the  $B_{1u}$  O(2s) orbital can be added to and subtracted from the C(2p<sub>z</sub>) orbital.
        - However, due to the large energy difference between the O and C orbitals, these do not generally form and are not included in Figure III.19.
        - Instead, the two O(2s) orbitals are included as  $\sigma$  2a<sub>g</sub> and 2b<sub>1u</sub>, respectively, nonbonding orbitals.

Figure III.19: Molecular orbitals for  $\text{CO}_2$ .

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

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

Symmetry	Molecular Orbitals	=	Oxygen Atomic Orbitals	Group Orbitals from Hydrogen Atoms	Description
$B_1$	$\Psi_6$	=	$c_9\psi(p_x)$	$+ c_{10}[\psi(H_a) - \psi(H_b)]$	Antibonding ( $c_{10}$ is negative)
$A_1$	$\Psi_5$	=	$c_7\psi(s)$	$+ c_8[\psi(H_a) + \psi(H_b)]$	Antibonding ( $c_8$ is negative)
$B_2$	$\Psi_4$	=	$\psi(p_y)$		Nonbonding
$A_1$	$\Psi_3$	=	$c_5\psi(p_z)$	$+ c_6[\psi(H_a) + \psi(H_b)]$	Slightly bonding ( $c_6$ is small)
$B_1$	$\Psi_2$	=	$c_3\psi(p_x)$	$+ c_4[\psi(H_a) - \psi(H_b)]$	Bonding ( $c_4$ is positive)
$A_1$	$\Psi_1$	=	$c_1\psi(s)$	$+ c_2[\psi(H_a) + \psi(H_b)]$	Bonding ( $c_2$ is positive)

Table III.2: Molecular orbital equations for H<sub>2</sub>O.

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

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

- In the projection operator method, orbitals can become the inverses of other orbitals.
- $\text{BF}_3$  example:

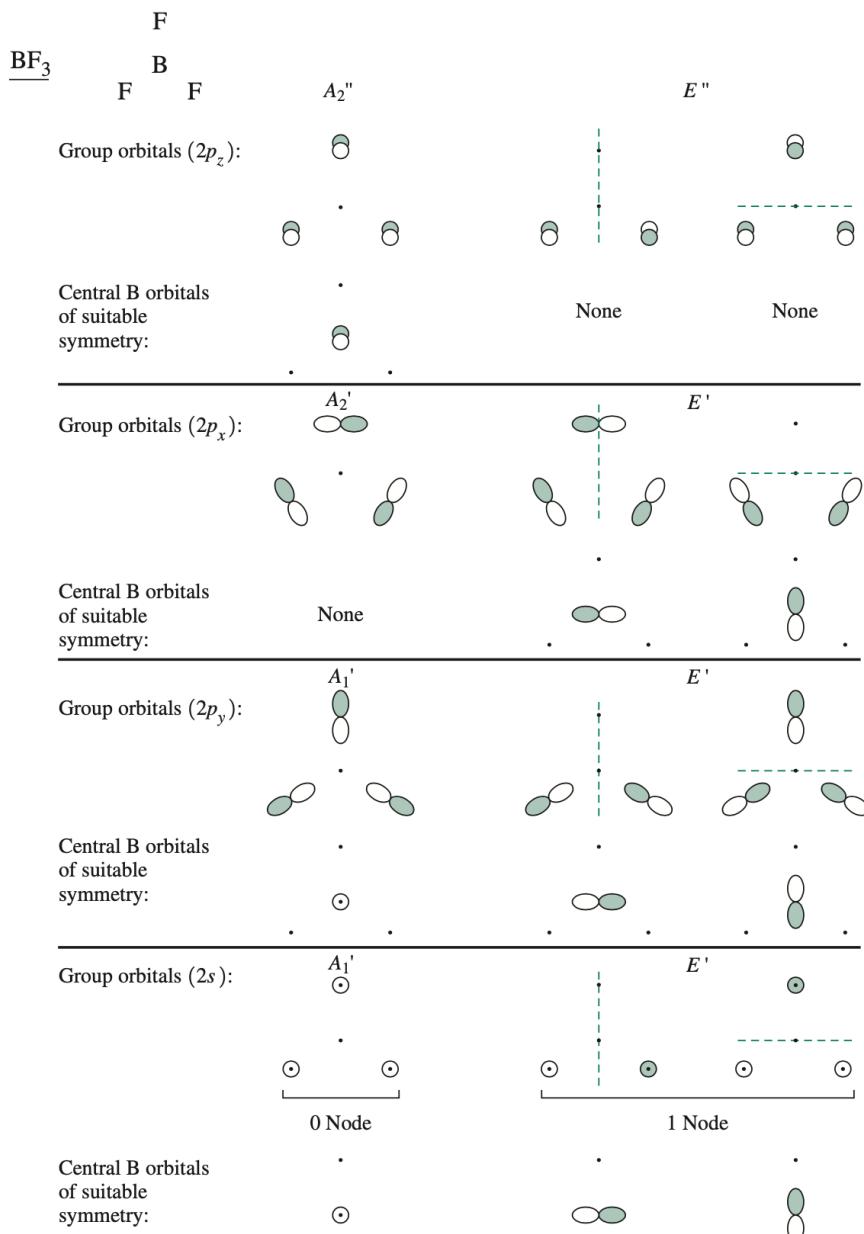


Figure III.20: Group orbitals for  $\text{BF}_3$ .

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

- The partial double bonding character of the B–F bonds discussed in Chapter 3 can now be explained.
- The LUMO of  $\text{BF}_3$  is an empty antibonding  $\pi$  orbital with large lobes on boron that can act as electron pair acceptors; this is why  $\text{BF}_3$  is a Lewis acid.
- This approach is also applicable to other isoelectronic trigonal planar species such as  $\text{SO}_3$ ,  $\text{NO}_3^-$ , and  $\text{CO}_3^{2-}$ .
- “Because the extent of orbital overlap in  $\pi$  interactions is generally less than that in most  $\sigma$  interactions, a double bond composed of one filled  $\sigma$  orbital and one filled  $\pi$  orbital is not twice as strong as a single bond” (Miessler et al., 2014, p. 161).
- Note that single bond energies between the same atoms can vary widely based on steric crowding and adjacent bonding.
- A qualitative group orbital approach (what we’re doing) does not allow for the determination of the precise MO energies, but it generally allows for the placement of the MOs in the approximate order based on their shapes and expected orbital overlaps.
- “In the hybrid concept, the orbitals of the central atom are combined into sets of equivalent hybrids. These hybrid orbitals form bonds with orbitals of other atoms” (Miessler et al., 2014, p. 161).
- Hybrid orbitals correctly describe methane’s PES spectrum.
- “Like all bonding models, hybrids are useful so long as their limits are recognized” (Miessler et al., 2014, p. 161).
- $\text{CH}_4$  example:
  - Point group:  $T_d$ .
  - Basis functions:  $\sigma$  bond vectors.
  - $\Gamma = (4, 1, 0, 0, 2)$ .
  - $\Gamma = A_1 + T_2$ .
  - “The atomic orbitals of carbon used in the hybrids must have symmetry matching  $A_1 + T_2$ ; more specifically, one orbital must match  $A_1$ , and a set of three (degenerate) orbitals must match  $T_2$ ” (Miessler et al., 2014, p. 162).
  - For  $A_1$ , we choose the  $2s$  orbital. For  $T_2$ , we could choose  $d_{xy}, d_{xz}, d_{yz}$ , but since they’re much higher energy (and thus won’t mix well with the  $\text{H}(1s)$  orbitals), we’ll go for  $p_x, p_y, p_z$ .
  - Therefore, the hybridization is  $sp^3$ , combining four atomic orbitals into four equivalent hybrid orbitals, one directed toward each hydrogen atom.
- In addition to the  $sp^3$  explanation of  $\text{H}_2\text{O}$ , it is sometimes explained through a slightly more MO theory lens as  $sp^2$  since the oxygen orbitals used in MO bonding are  $2s, 2p_x, 2p_z$  where the  $\text{H}_2\text{O}$  molecule lies in the  $xz$ -plane.
- Only  $\sigma$  bonding is considered when determining the orbitals used in hybridization.

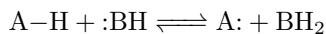
## Topic IV

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

### IV.1 Module 24: Acid-Base Chemistry

2/8:

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



- Protons do not exist free in solution but must be attached to an electron pair.
- Water is amphoteric.
- In the Brønsted-Lowry paradigm, we cannot separate the acids/bases from the solvent (no protons; only *solvated* protons). In a non-aqueous medium such as DMSO, however, we have much broader scope of acids and bases.
- **Carbon acid:** Any molecule containing a C–H bond can lose a proton forming the carbanion.
- Carborane ( $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$ ) is a superacid one million times stronger than sulfuric acid since it’s conjugate basis is incredibly stable (super easy to delocalize the charge).
- The base dissociation constant or  $K_b$  is a measure of basicity.  $\text{p}K_b$  is the negative log of  $K_b$  and related to the  $\text{p}K_a$  by the simple relationship  $\text{p}K_a + \text{p}K_b = 14$ . The larger the  $\text{p}K_b$ , the more basic the compound.
- **Superacid:** An acid with acidity greater than that of 100% pure sulfuric acid.
  - In water, the strongest acid you can have is  $\text{H}_3\text{O}^+$ .
  - The strongest superacids are prepared by the combination of two components, a strong Lewis acid and a strong Brønsted-Lowry acid.
  - Fluoroantimonic acid  $\text{HF-SbF}_5$  is  $2 \times 10^{19}$  stronger than 100% sulfuric acid.

- Olah's magic acid ( $\text{FSO}_3\text{H}-\text{SbF}_5$ ) can dissolve paraffin (candle wax; extremely inert), converting methane into the t-butyl carbocation.

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

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

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

- **Superbase:** A compound that has a high affinity for protons.

- Again, these do not exist in water.
- Often destroyed by water,  $\text{CO}_2$ , and  $\text{O}_2$ .
- A superbase has been defined as an organic compound whose basicity is greater than that of proton sponge, which has conjugate  $\text{p}K_a$  of 12.1.
- These are valuable in organic chemistry, which abounds in very weak acids.
- A common superbase is lithium diisopropylamide.

## IV.2 Module 25: Acid-Base Chemistry: Lewis Acids and Bases

2/10:

- The second midterm will be Saturday, February 20.
- Talapin will hold office hours this Friday from 3:00-4:00 PM.
- **Lewis acid:** Any species with a vacant orbital.
  - An atomic or molecular species that has an empty atomic or molecular orbital of low energy (LUMO) that can accommodate a pair of electrons.
- **Lewis base:** A compound with an available pair of electrons, either unshared or in a  $\pi$  orbital.
  - An atomic or molecular species that has a lone pair of electrons in the HOMO.
- Examples of Lewis acids:
  - The proton, onium ions (e.g.,  $\text{NH}_4^+$ ,  $\text{H}_3\text{O}^+$ ), metal cations (e.g.,  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ), trigonal planar species (e.g.,  $\text{BF}_3$ ,  $\text{CH}_3^+$ ), and electron-poor  $\pi$ -systems (e.g., enones, tetracyanoethylene [TCNE]).
- **Lewis base adduct:** The product of a Lewis acid reaction.
  - Simple Lewis acids:
    - Examples include  $\text{BF}_4^-$  in  $\text{BF}_3 + \text{F}^- \longrightarrow \text{BF}_4^-$  and  $\text{BF}_3\text{OMe}_2$  in  $\text{BF}_3 + \text{OMe}_2 \longrightarrow \text{BF}_3\text{OMe}_2$ , which are Lewis base adducts of  $\text{BF}_3$ .
    - In many cases, Lewis base adducts violate the octet rule.
    - In some cases, Lewis acids can bind to two Lewis bases (e.g.,  $\text{SiF}_4 + 2\text{F}^- \longrightarrow \text{SiF}_6^{2-}$ ).
  - Complex Lewis acids:
    - Most compounds considered to be Lewis acids require an activation step prior to the formation of the adduct.
    - For example, the reaction  $\text{B}_2\text{H}_6 + 2\text{H}^- \longrightarrow 2\text{BH}_4^-$  goes through the intermediate  $\text{B}_2\text{H}_7^-$ .
- The proton ( $\text{H}^+$ ) is one of the strongest but is also one of the most complicated Lewis acids. It is convention to ignore the fact that a proton is heavily solvated (bound to solvent). With this simplification in mind, acid-base reactions can be viewed as the formation of adducts.

- For example,  $\text{H}^+ + \text{NH}_3 \longrightarrow \text{NH}_4^+$  and  $\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O}$ .
- In the first reaction, essentially what happens is the frontier orbitals of  $\text{H}^+$  and  $\text{NH}_3$  are very similar in energy, and thus strongly combine when they form bonding and antibonding orbitals. Two electrons previously in the HOMO of  $\text{NH}_3$  drop the bonding energy into the new lower MO of  $\text{NH}_4^+$ . More rigorously, we have to account for the change in symmetry group from  $C_{3v}$  to  $T_d$ , but the above description basically encapsulates what happens.
- Examples of Lewis bases:
  - $\text{NH}_{3-x}\text{R}_x$  where R = alkyl or aryl.
  - $\text{PR}_{3-x}\text{A}_x$  where R = alkyl and A = aryl.
  - Compounds of O, S, Se, and Te in oxidation state 2, including water, ethers, and ketones.
  - Simple anions (e.g.,  $\text{H}^-$ ,  $\text{F}^-$ ), other lone pair-containing species (e.g.,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{OH}^-$ ,  $\text{CH}_3^-$ ), complex anions (e.g., sulfate), and electron-rich  $\pi$ -systems (e.g., ethyne, ethene, benzene).
- To quantify the strength of Lewis acids and bases, compare the standard enthalpies of complexation in kJ/mol.
  - For example, heats of binding of Lewis bases to  $\text{BF}_3$ .
  - We do this because we cannot use  $\text{p}K_b$  in the same way as we can in the Brønsted-Lowry description.
- **Electrides:** Compounds where the anions are electrons.
  - Put an alkali metal in liquid ammonia; the deep blue color comes from solvated electrons floating freely in solution surrounded by ammonia molecules.
  - If you add a very strong complexing agent for alkali metal ions to the solution, then the electrons will not be able to react back with the alkali metal and we will have crystallized an electride.
  - Electrides are dielectrics.
- The power of the Lewis approach is that it allows us to classify many reactions as acid-base reactions.
  - For example, Wilkinson's catalyst ( $\text{Rh}(\text{PPh}_3)\text{Cl}$  where Ph is a phenyl group) is probably the first hydrogenation catalyst to be explained.
  - The Lewis approach allows us to view every step in the mechanism<sup>[1]</sup> as an acid-base reaction.

### IV.3 Module 26: Hard and Soft Acids and Bases (HSAB) Principle

- HSAB principle can't be derived, but it's been proven to be a very powerful tool for chemists.
- The affinity of hard acids and hard bases for each other is mainly ionic in nature, whereas the affinity of soft acids and bases for each other is mainly covalent in nature.
- Hard acids and hard bases tend to have:
  - Small atomic/ionic radius.
  - High oxidation state.
  - Low polarizability.
  - High electronegativity.
  - Energy low-lying HOMO (bases) or energy high-lying LUMO (acids).

<sup>1</sup>We will study this mechanism in depth in CHEM 20200.

- Examples:  $\text{H}^+$ , alkali ions,  $\text{OH}^-$ ,  $\text{F}^-$ .
- Small stabilization energy when bonding, so attraction is mostly electrostatic.
- Soft acids and soft bases tend to have:
  - Large atomic/ionic radius.
  - Low or zero oxidation state.
  - High polarizability.
  - Low electronegativity.
  - Energy high-lying HOMO (bases) or energy low-lying LUMO (acids).
  - Examples:  $\text{CCH}_3\text{Hg}^+$ ,  $\text{Pt}^{2+}$ ,  $\text{H}^-$ ,  $\text{R}_3\text{P}$ ,  $\text{I}^-$ .
  - Large stabilization energy when bonding, so attraction is mostly covalent.
- Hard acids don't readily react with soft bases and vice versa.
- You should be able to intuitively classify acids/bases as hard or soft.

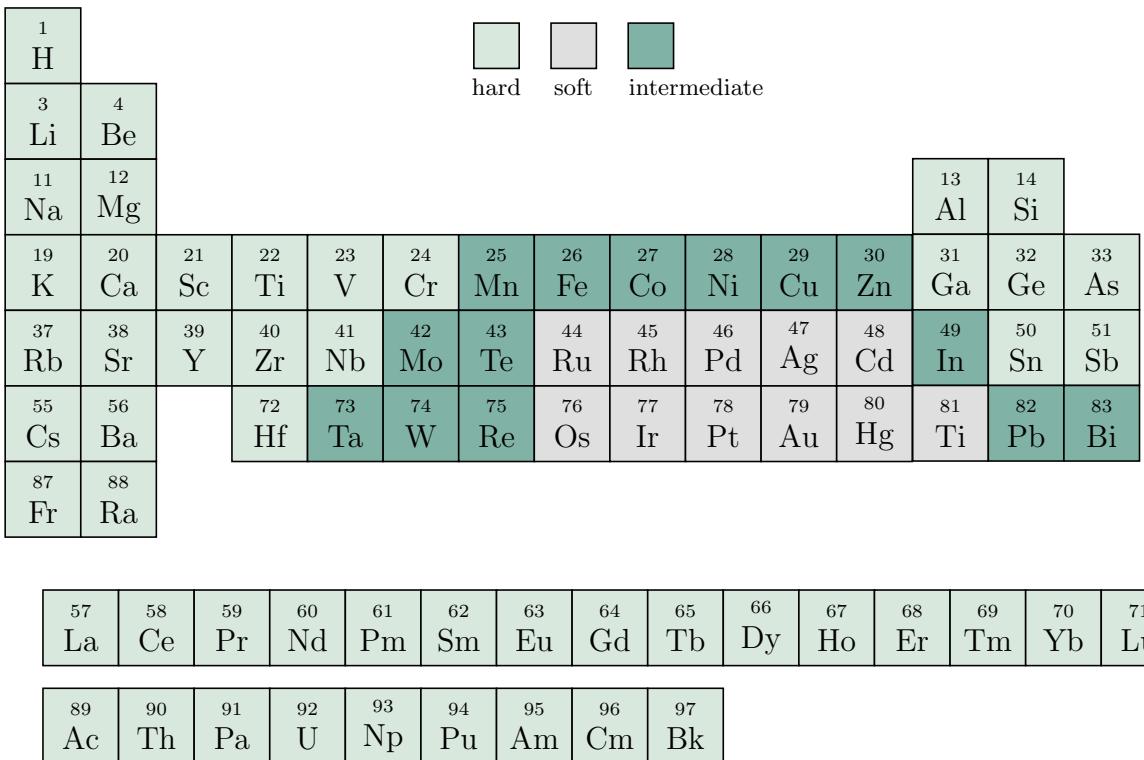


Figure IV.1: Hard vs. soft metal ions.

- The affinity that metal ions have for ligands is controlled by size, charge, and electronegativity.
- This can be refined further by noting that for some metal ions, their chemistry is dominated by size and charge, while for others it is dominated by their electronegativity. These two categories of metal ions have been termed by Pearson as **hard** (metal ions) and **soft** (metal ions).
- Soft Lewis acids are transition metals with unusually high electronegativities (these go against typical periodic trends).
  - Note that QMech can't explain this island of high electronegativities in the transition metals; we need relativistic corrections and Dirac equations.

- The higher electronegativity stabilizes the LUMO of the acid.
- These ions are a treasure trove for catalytic chemistry.
- **Chemical hardness:** One half the difference between the ionization potential  $I$  and the electron affinity  $A$ .

$$\eta = \frac{I - A}{2}$$

- Note that the above equation cannot be applied to anions because electron affinity cannot be measured for them; the assumption is made that  $\eta$  for an anion  $X^-$  is same as that for the radical  $X\cdot$ .
- Related to the **Mulliken electronegativity**:

$$\chi = \frac{I + A}{2}$$

- **HSAB principle:**

- (i) Hard acids prefer to bond to hard bases, and soft acids prefer to bond to soft bases.
  - Note that this rule has nothing to do with acid or base strength but merely says that the product  $A-B$  will have extra stability if  $A$  and  $B$  are both hard or both soft.
- (ii) A soft Lewis acid and a soft Lewis base tend to form a covalent bond, while a hard acid and a hard base tend to form ionic bonds.
- Solubility: Hard solvents (e.g., HF,  $H_2O$ , and the protic solvents) tend to solvate strong solute bases (e.g.,  $F^-$  and the oxygen anions). Dipolar aprotic solvents (e.g.,  $Me_2SO$  and  $CH_3COCH_3$ ) are soft solvents with a preference for solvating large anions and soft bases.
  - For example,  $LiI + AgF \longrightarrow LiF + AgI$ . In this reaction, two mixed reactants recombine exothermically to form a hard-hard product and a soft-soft precipitate. Because of the Lewis definition, we can treat this as an acid-base reaction.

Classification		Hard	Intermediate	Soft	
		$F^-$	$Cl^-$	$Br^-$	$I^-$
Soft	$Ag^+$	0.4	3.3	4.7	6.6
Intermediate	$Pb^{2+}$	1.3	0.9	1.1	1.3
Hard	$Fe^{3+}$	6.0	1.4	0.5	-

Table IV.1: Hard and soft formation constants.

- As another example, we can see in Table IV.1 that soft-soft and hard-hard ions have higher formation constants ( $\log K_1$ ) than any other combination, and hard-soft ions have lower formation constants than any other combination.
- Coordination chemistry: Numerous experiments have been done to determine the relative ordering of ligands and transition metal ions in terms of their hardness and softness.
- Au (I) is the softest metal ion.
  - Soft to the extent that compounds such as  $AuF$  and  $Au_2O$  are unknown.
  - Nevertheless, it forms stable compounds with soft ligands such as cyanide.
- Al (III) is a very hard metal ion.
  - It has very high formation constants with both  $F^-$  and  $OH^-$ ; additionally, it has virtually no affinity in solution for heavier halides such as  $Cl^-$ .

- Its solution chemistry is dominated by its affinity for  $\text{F}^-$  and for ligands with negative O-donors.
- **Symbiosis effect:** Taking a borderline element and reacting it with a soft Lewis base to soften it, or a hard Lewis base to harden it.
  - For example,  $\text{B}^{3+}$  can be reacted with  $3\text{H}^-$ , we make the soft compound  $\text{BH}_3$ . If we react it with  $3\text{F}^-$ , we make the hard compound  $3\text{F}^-$ .
  - Now  $\text{BH}_3$  and  $\text{F}^-$  do not react, but we can further soften it in the reaction  $\text{BH}_3 + \text{H}^- \longrightarrow \text{BH}_4^-$ .
  - Similarly,  $\text{BF}_3$  and  $\text{H}^-$  don't react, but we can further harden  $\text{BF}_3$  by reacting it with  $\text{F}^-$  to form  $\text{BF}_4^-$ .
- There is a preference against combining hard and soft ligands in the first coordination sphere. Examples:
  - $\text{CH}_3\text{F} + \text{CF}_3\text{I} \rightleftharpoons \text{CH}_3\text{I} + \text{CF}_4$  since  $\text{CH}_3^+$  and  $\text{I}^-$  are soft while  $\text{CF}_3^+$  and  $\text{F}^-$  are hard.
  - $\text{Co}(\text{NH}_3)_5\text{F}$  is stable since it has all hard ligands, but  $\text{Co}(\text{NH}_3)_5\text{I}$  will react with  $\text{H}_2\text{O}$  to produce  $\text{Co}(\text{NH}_3)_5\text{OH}$  since the former combines hard and soft and the latter does not.
  - Thiocyanate is **ambidentate**. Thus, we have  $\text{Fe}-\text{N}$  bonds in  $\text{Fe}(\text{NCS})_6^{3+}$  (with the hard Fe (III) ion) and  $\text{Au}-\text{S}$  bonds in  $\text{Au}(\text{SCN})_2^-$  (with the soft Au (I) ion).
    - Note that intermediate metal ions tend to bond to thiocyanate through nitrogen; indeed, intermediate Cu (II) forms  $\text{Cu}(\text{NCS})_4^{2-}$ .
- **Ambidentate (ligand):** A polyatomic ligand that can bind through more than one of its constituent atoms.

## IV.4 Module 27: Steric Effects in Inorganic Chemistry

2/12:

- Chemistry is a game of two players: Electronic and steric effects.
- Gallanes, gallenes, cyclogallenes, and gallynes:
  - Various compounds with gallium.
  - React gallium (III) chloride with a Grignard reagent containing mesityl (2,4,6-trimethylphenyl; Mes;  $\text{Me}_3\text{C}_6\text{H}_2$ ):  $3(\text{Me}_3\text{C}_6\text{H}_2)\text{MgBr} + \text{GaCl}_3 \xrightarrow{-3\text{MgBrCl}} \text{Ga}(\text{Me}_3\text{C}_6\text{H}_2)_3$ .
  - A molecule with even more steric hindrance: a three gallium ring with a 2,6-dimesitylphenyl groups attached to each gallium.
  - The triphenylcyclopropenium cation is aromatic but the cyclogallene dianion is metalloaromatic.
  - In another compound, a  $\text{Ga}\equiv\text{Ga}$  triple bond holds two massive groups together.
    - The debate over this is a good example of chemistry not being black and white.
  - Acetylene and gallyne both show band structure.
    - Additionally, the former is linear while the latter is trans-bent with a donor-acceptor bond lacking a sigma bond.
    - To learn more about such bonding, read Power (2010).
- Steric effects are much more common in Lewis acid-base reactions in which larger acids are used.
  - With a small acid, increasing size in the base (i.e., replacing hydrogens with methyl groups) correlates with increasing strength.
  - With a large acid, decreasing size in the base correlates with increasing strength.
- Frustrated Lewis pairs:
  - Excessive steric bulk can prevent acids and bases from reacting to form an adduct.

- However, you can also have alternate reactions that yield compounds with Lewis acidic *and* Lewis basic regions.
- Frustrated Lewis pairs can activate (cleave) H<sub>2</sub>.
  - They can also activate CO<sub>2</sub>; this has applications in the realm of CO<sub>2</sub> sequestration.

## IV.5 Chapter 6: Acid-Base and Donor-Acceptor Chemistry

*From Miessler et al. (2014).*

- IUPAC calls hydronium “oxonium” and uses “hydrogen ion” instead of “proton.”
- In the Brønsted-Lowry paradigm, “the equilibrium always favors the formation of *weaker* acids and bases” (Miessler et al., 2014, p. 171).
- Common amphoteric solvents: sulfuric acid, hydrofluoric acid, water, acetic acid, methanol, ammonia, and acetonitrile.
- H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> are the strongest acid and base, respectively, that<sup>[2]</sup> can exist in H<sub>2</sub>O.
- **Leveling effect:** Acids stronger than H<sub>3</sub>O<sup>+</sup> cannot be differentiated by their aqueous ionization.
- Because of leveling, the strength of the strong acids cannot be differentiated in aqueous solution.
  - Thus, we use more strongly acidic solvents, such as **glacial** acetic acid.
  - The use of this solvent allows us to determine that HClO<sub>4</sub> > HCl > H<sub>2</sub>SO<sub>4</sub> > HNO<sub>3</sub>.
  - Note that basic solvents similarly permit the differentiation of strong bases.
- **Glacial** (substance): A 100% pure, concentrated sample of a substance.
- “Nonamphoteric solvents... do not limit solute acidity or basicity because the solute does not react with the solvent. In these solvents, the inherent solute acid or base strength determines the reactivity, without a leveling effect” (Miessler et al., 2014, p. 173).
- **Superelectrophilic activation:** The result of generating small organic ions bearing a large amount of positive charge.
- Introduces the Hammett acidity function<sup>[3]</sup>.
- Protonating CH<sub>4</sub> is of particular interest since the natural abundance of methane (from natural gas) makes it attractive as a starting point for synthesis of more complex molecules.
  - CH<sub>5</sub><sup>+</sup> has been isolated; CH<sub>6</sub><sup>2+</sup> and CH<sub>7</sub><sup>3+</sup> have been proposed.
- Dissolving SO<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub> results in **fuming sulfuric acid**, which contains higher polysulfuric acids such as H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>, all of which are stronger than H<sub>2</sub>SO<sub>4</sub>.
- Water is a strong base in superacid media: Adding H<sub>2</sub>O to superacids produces hydronium salts.
  - As a consequence, we can form [H<sub>3</sub>O][Ln][AsF<sub>6</sub>]<sub>3</sub> where Ln is a lanthanide element as AsF<sub>6</sub> is part of a superacid.
- Thermodynamic measurements:
  - Hess’s law is often used to express the enthalpy of weak acid reactions in terms of reactions that do go to completion; this is not perfect, but it’s an ok starting point.

<sup>2</sup>Errata: Miessler et al. (2014, p. 173) has a typo: “than” instead of “that.”

<sup>3</sup>Errata: The – sign should be a + sign.

- One can also measure  $K_a$  via titration curves at different temperatures and use the van't Hoff equation

$$\ln K_a = \frac{-\Delta H}{R} \frac{1}{T} + \frac{\Delta S}{R}$$

- According to the above equation the plot of  $\ln K_a$  vs.  $\frac{1}{T}$  will be linear with a slope that allows us to determine  $\Delta H$  and a  $y$ -intercept that allows us to determine  $\Delta S$ .
- Brønsted basicity scale: Enthalpy changes associated with protonation by the superacid fluorosulfonic acid ( $\text{HSO}_3\text{F}$ ).

- The best measure of acid/base strength is gas-phase acidity/basicity, since there are no solvent effects.
  - Wrt.  $\text{HA(g)} \longrightarrow \text{A}^-(g) + \text{H}^+(g)$ ,  $\Delta G = \text{Gas-Phase Acidity (GA)}$  and  $\Delta H = \text{Proton Affinity (PA)}$ .
  - There exist analogous definitions for bases.
  - Modern measurement techniques can measure these values very accurately for a select few molecules; from these molecules and Hess's law, we can build pretty good approximations of other reactions.
- **Superbase:** A base with a gas-phase proton affinity greater than  $1000 \text{ kJ mol}^{-1}$ .
  - Examples such as Grignard and organolithium reagents are ubiquitous in organic synthesis.
- Considers inductive effects.
  - “Solvation [of amines] is dependent on the number of hydrogen atoms available to form  $\text{O} \cdots \text{H}-\text{N}$  hydrogen bonds with water” (Miessler et al., 2014, p. 181).
  - Steric effects are less obvious — for example, 2,6-dimethylpyridine is more basic than 4-methylpyridine, but the latter is more basic than 2-*t*-butylpyridine.
- Binary hydrogen compounds:
  - Acidity increases left-to-right across a period and down a group (wrt. the non-hydrogen atom).
  - The three heaviest hydrohalic acids are all equally acidic in water due to leveling.
- Considers relative strengths of various chlorine-based oxyacids (e.g.,  $\text{HClO}_4$  vs.  $\text{HClO}_3$ ).
  - As the number of oxygens increases, the electronegativity of the terminal oxygen increases. Less and less electron density binds the hydrogen, making the bond increasingly weak and susceptible to heterolytic cleavage.
- In polyprotic acids, the  $pK_a$  increases about 5 units with each successive proton removal.
- Aqueous cations get surrounded by  $\text{H}_2\text{O}$ .
  - Then these complexes react in acid-base reactions.
  - When the concentration is sufficiently high, they can two complexes can combine via hydroxide or oxide bridges between the metal atoms.
  - Metal ions with charges of 4+ or higher are the really acidic ones. They're acidic to the extent that they do not exist by themselves in solution, but are present in oxygenated forms such as permanganate ( $\text{MnO}_4^-$ ).
- **Coordinate covalent** (bond): A bond that links a Lewis acid and base into their adduct. *Also known as dative* (bond).
- **Coordination compound:** A Lewis acid-base adduct involving one or more metal ions.
- “In most Lewis acid-base reactions, the HOMO-LUMO combination forms new HOMO and LUMO orbitals of the product” (Miessler et al., 2014, p. 186).

- When the symmetries match and the energies are close, a stable adduct forms.
  - Since every molecule has a HOMO and LUMO, technically any molecule can act as acid, base, oxidizing agent, or reducing agent when combined with the right reactants.
    - For example,  $\text{H}_2\text{O}$  can oxidize Ca metal, forming  $\text{Ca}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$ .  $\text{H}_2\text{O}^-$  is not formed because the addition of electrons to antibonding orbitals in  $\text{H}_2\text{O}$  weakens one O–H bond.
- 2/14:
- Section on spectroscopic support for frontier orbital interactions.
    - Very confusing; electron transitions' colors in  $\text{I}_2$  when it acts as a Lewis acid.
  - **Lewis basicity:** The thermodynamic tendency of a substance to act as a Lewis base.
    - It would be ideal to measure in the gas phase, but this is hard to do.
    - Determining a good reference acid is difficult.
    - When in solution, we want to make sure that we choose a solvent that will not react significantly as a Lewis acid with the solutes.
      - In other words, we need a solvent that primarily solvates the solutes through dispersion forces (i.e., nonpolar solvents).
    - Once we have a solvent, we quantify the Lewis basicity of a substance by finding the  $K_b$  and  $\log K_b$  values for its complexation with a reference acid (such as  $\text{I}_2$ ). The absolute basicity will vary based on the solvent, but the Lewis basicity ranking will be the same overall.
  - The standard scale for Lewis basicity is its  $\text{BF}_3$  affinity, or  $-\Delta H^\circ$  in the following reaction, corrected for the enthalpy of  $\text{BF}_3$  dissolving in the solvent.



- **Halogen (bond):** A coordinate covalent bond formed by a halogen  $\text{X}_2$  (e.g.,  $\text{I}_2$ ) or interhalogen XY (e.g.,  $\text{ICl}$ ) to a Lewis base.
  - Exhibit approximately  $180^\circ$  angles about the halogen donor atom, supporting use of  $\sigma^*$  LUMO.
  - $\text{I}_2$  affinity values are commonly determined in heptane, and while there is interest in creating an  $\text{I}_2$  affinity scale analogous to the  $\text{BF}_3$  one, as of yet, various experimental designs have not been reconciled.
  - Since the formation of a halogen bond involves donation into the halogen  $\sigma^*$  LUMO, the X–Y bond weakens and lengthens. This also decreases the stretching frequency. Measuring changes in stretching frequency induced in  $\text{I}_2$ ,  $\text{ICN}$ , and  $\text{ICl}$  via Raman spectroscopy has correlated reasonably well to basicity, but not perfectly since these stretching bands are affected by the presence of the Lewis base, too.
  - Inductive effects:
    - Adding more electronegative substituents decreases Lewis basicity (in  $C_{3v}$  Lewis bases).
    - Adding more alkyl substituents increases Lewis basicity (in  $C_{3v}$  Lewis bases).
    - Adding more electronegative substituents increases Lewis basicity (in  $D_{3h}$  Lewis bases) since the increase in bond lengths draws  $\pi$ -bonding electrons farther from the central boron.
  - Steric effects on Lewis acidity and basicity: **front strain**, **back strain**, and **internal strain**.
  - **Front strain:** Bulky groups interfering directly with the approach of an acid and a base to each other. *Also known as F strain.*
  - **Back strain:** Bulky groups interfering with each other when VSEPR effects force them to bend away from the other molecule forming the adduct. *Also known as B strain.*

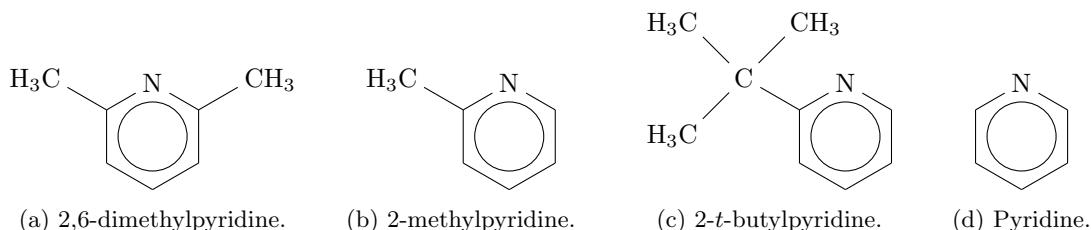


Figure IV.2: Four Lewis bases.

- **Internal strain:** Effects from electronic differences within similar molecules. *Also known as I strain.*
- An example of differences caused by F strain:
  - When reacting with  $\text{H}^+$ , 2,6-dimethylpyridine > 2-methylpyridine > 2-*t*-butylpyridine > pyridine.
  - When reacting with  $\text{BF}_3$  or  $\text{BMe}_3$ , pyridine > 2-methylpyridine > 2,6-dimethylpyridine > 2-*t*-butylpyridine.
- An example of B strain: The fact that tri(*t*-butyl)boron vs.  $\text{H}^+$  elicit a reversed order of the basicity of  $\text{NH}_3$ ,  $\text{MeNH}_2$ ,  $\text{Me}_2\text{NH}$ , and  $\text{Me}_3\text{N}$ .
- **Frustrated Lewis pair:** A lone pair on a Lewis base that does not form a traditional adduct with a Lewis acid because both molecules are hindered by excessive steric bulk. *Also known as FLP.*
- Example (refer to Figure IV.3 throughout the following discussion):

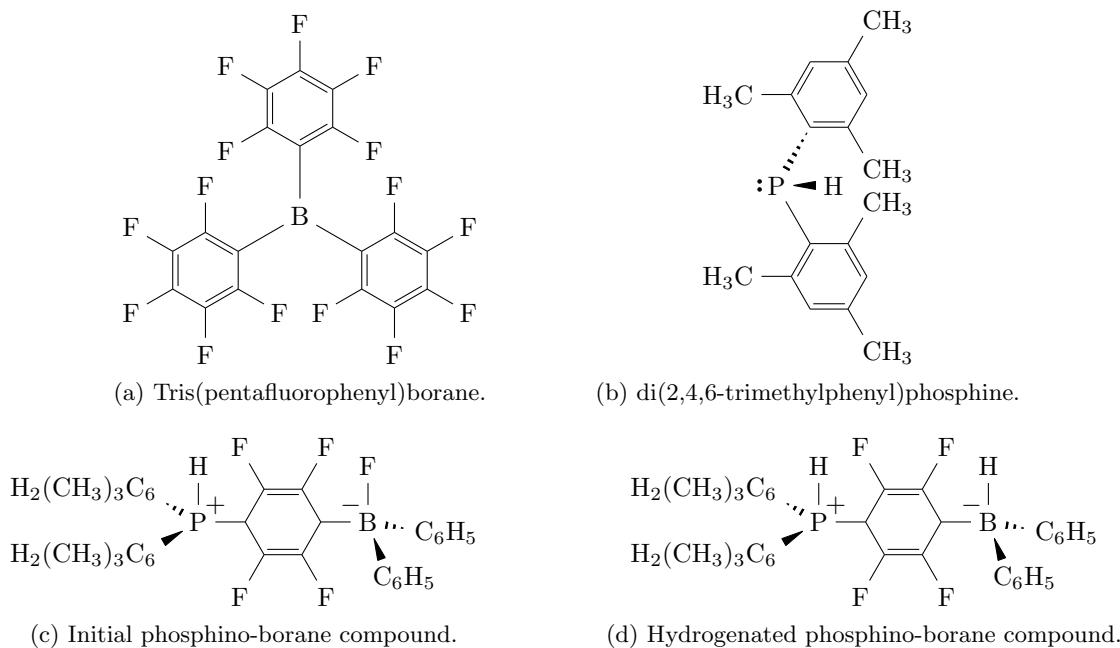


Figure IV.3: FLP phosphino-borane compound.

- Although the FLP in di(2,4,6-trimethylphenyl)phosphine does not attack the boron in tris(pentafluorophenyl)borane, it reacts with a para carbon of the borane to create a **zwitterionic** species after fluoride migration.
- This fluoride can be substituted for a hydrogen, creating a species that releases hydrogen gas upon heating and reacts with hydrogen gas at ambient temperature to reform the zwitterion.

- The phosphino-borane is the first non-transition metal species that can reversibly activate the H–H bond in H<sub>2</sub>.
- **Zwitterion:** A species that contains at least one formal positive and negative charge.
- More small molecules have been activated with FLPs, including CO<sub>2</sub> and N<sub>2</sub>O.
- **Hydrogen (bond):** An X–H…B bond formed from an attraction between an X–H unit (where the electronegativity of X is greater than that of H) and a donor atom B.
  - The components may be incorporated into larger molecular fragments.
  - Hydrogen bonds can be either intermolecular or intramolecular.
- Hydrogen bonds can be described on the basis of the varying relative contributions from three components:
  - Electrostatic contribution: The polarity of X–H.
  - Partial covalent character and charge transfer: The donor-acceptor nature of the interaction.
  - Dispersion forces.
- Experimental stipulations that must be satisfied for an interaction to be declared a hydrogen bond.
  - Bond angle close to 180°.
  - Red-shifted IR stretching frequency for the X–H bond (indicative of the bond weakening and, thus, donation into antibonding orbitals).
  - High deshielding of NMR chemical shift (extremely sensitive probe for hydrogen bonding).
  - Magnitude of  $\Delta G$  for bond formation must exceed the thermal energy of the system.
- **H-bond puzzle:** Predicting the strength of hydrogen bonds solely on the basis of the structures of the participating molecules.
  - Based in the fact that structurally very similar hydrogen bonds can exhibit massive differences in strength.
  - For example, the O–H…O bond between hydronium and water is roughly six times stronger than the comparable bond between two water molecules.
- **pK<sub>a</sub> equalization (paradigm):** An approach to predicting the strength of hydrogen bonds in aqueous solution by envisioning H-bond strength as associated with the 3-way proton transfer equilibrium between X and B.
  - The better matched the pK<sub>a</sub> values, the stronger the predicted H-bond.
  - In effect, a strong H-bond minimizes  $\Delta pK_a(X-H \cdots B) = pK_a(HX) - pK_a(BH^+)$ .
- **Receptor-guest interaction:** An interaction between molecules with extended pi systems where their pi systems interact with each other to hold the molecules or portions of the molecules together. *Also known as receptor-substrate interaction, host-guest interaction.*
  - One example is a double-concave hydrocarbon buckycatcher that forms a ball-and-socket structure with C<sub>60</sub>. This is an example of an **inclusion complex**.
  - The hard vs. soft distinction is largely a result of polarizability, with soft acids having high polarizability and hard acids having low polarizability.
  - Soft transition metals have *d* electrons available for  $\pi$ -bonding.
  - **Exchange reaction:** A reaction involving the exchange of a water and a base B.

- Is  $\text{OH}^-$  or  $\text{S}^{2-}$  more likely to form insoluble salts with 3+ transition-metal ions? Which is more likely to form insoluble salts with 2+ transition-metal ions?
  - $\text{OH}^-$  and 3+ are hard, and thus will form insoluble salts.
  - $\text{S}^{2-}$  and 2+ are soft, and thus will form insoluble salts.
- Both hardness/softness and strength must be considered to determine reactivity.
- MO diagrams for hard-hard and soft-soft interactions reveal that there is a lower covalent contribution in hard-hard interactions, but this is compensated for by a strong ionic contribution, so don't think that hard-hard interactions are weaker.
- Wrt. chemical hardness  $\eta$  (Greek “eta”), ionization energy is assumed to measure the energy of the HOMO ( $E_{\text{HOMO}} = -I$ ) and electron affinity the energy of the LUMO ( $E_{\text{LUMO}} = -A$ ); thus, a hard species is one with a high difference in energy between its HOMO and LUMO.
- **Chemical softness:** The inverse  $\sigma = \frac{1}{\eta}$  of hardness.
- Reviews a quantitative system of acid-base parameters to account for reactivity by explicitly including electrostatic and covalent factors.

## Topic V

# Coordination Chemistry: Structures and Isomers of Metal Complexes

### V.1 Module 28: Introduction to Coordination Compounds

2/12:

- Modern inorganic chemistry is heavily concerned with the transition metals, i.e., the *d*-block elements.
  - Most industrial catalysts utilize transition metal compounds.
- Transition metals vs. main-group elements:

Transition-Metal Compounds	Main-Group Elements
Multiple oxidation states (e.g., the 11 oxidation states of Mn from $-3$ to $+7$ )	Single oxidation state
Brightly colored (thus a gap between HOMO and LUMO of a few electron volts)	Usually colorless
Usually have partially occupied valence <i>d</i> -orbitals that are often relatively close in energy	The valence <i>s</i> - or <i>p</i> -orbitals are either fully occupied or empty and are far apart energetically
Often paramagnetic	Usually diamagnetic
Often interact with small molecules such as CO, C <sub>2</sub> H <sub>4</sub> , and H <sub>2</sub>	Generally do not interact strongly with CO, C <sub>2</sub> H <sub>4</sub> , or H <sub>2</sub>

- The orbital energy gap matches the bond energies of small molecules pretty well.
  - This is exactly what is needed for activating those chemical bonds, i.e., making catalytic cycles!
- History:
  - Prussian blue ink is the first synthetic blue dye, and one of the first coordination compounds created (used in famous paintings such as *Starry Night*).
  - The structure of coordination complexes was not understood until 1907, however.
  - Blomstrand and Jorgenson tried to determine the structure of Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>3</sub>, but their guess didn't explain isomers.
  - Alfred Werner (late 1800s) was the father of coordination chemistry.
    - He noticed that excess AgNO<sub>3</sub> could only liberate and precipitate as AgCl one chlorine from both the green and violet isomers of CoCl<sub>3</sub> · (NH<sub>3</sub>)<sub>4</sub>.
    - However, it could precipitate two chlorines from CoCl<sub>3</sub> · (NH<sub>3</sub>)<sub>5</sub> and three from CoCl<sub>3</sub> · (NH<sub>3</sub>)<sub>6</sub>.
    - This observation plus a number of controls led him to **Werner's Conclusions**.

- **Werner's Conclusions:**

1. In this series of compounds, cobalt has a constant **coordination number** of 6.
2. As the  $\text{NH}_3$  molecules are removed, they are replaced by  $\text{Cl}^-$ , which acts as if it is covalently bonded to cobalt.
3. Chloride and ammonia are now called ligands.
4. Ligands are a Lewis base/electron pair donors that can bind to a metal ion.
5. A metal complex is a metal ion combined with ligands.
6. Coordination complexes are neutral and counter ions are not bonded to the central metal ion but balance the charge.

– For example, in  $[\text{Co}(\text{NH}_3)_6]^{+3}\text{Cl}_3^{-3}$ , the three chloride ions are the counter ions.

- **Coordination number:** The number of groups that can bond directly to the metal.

- Werner also hypothesized an octahedral geometry for all cobalt complexes.
  - If it were hexagonal planar or trigonal antiprismatic, there would be three isomers of the coordination sphere for the compound with two chlorines (think ortho, meta, para isomers for the hexagonal planar example).
  - However, if it is octahedral, the compound with two chlorines will have two isomers (the chlorines can either be  $180^\circ$  to each other or  $90^\circ$  to each other).
  - Octahedral also reduces steric crowding.

- **Coordination compound:** A compound with a metal center, a coordination sphere, and counter ions. *Also known as coordination complex.*

- Werner also resolved hexol into optically active isomers. This was the first optically active chiral *inorganic* compound.

## V.2 Module 29: Types and Classes of Ligands

- **Monodentate ligand:** A ligand that binds to a metal ion through a single donor site. *Etymology* one-toothed.
  - For example,  $\text{NH}_3$  is a monodentate ligand.
- **Bridging ligand:** A ligand that binds to two or more metal ions simultaneously.
  - For example,  $\text{O}^{2-}$  is a bridging ligand.
- **Ambidentate ligand:** A ligand with two kinds of binding sites that can bind through one or the other but not both simultaneously.
  - For example, thiocyanide can bond through S or N but not both simultaneously.
- **Multidentate chelating ligand:** A ligand bound to a metal through several donor sites. *Etymology* multitooth crab claw (crabs grab their food with two claws in the same way a metal can be attracted to two lone pairs from different groups on the same ligand). *Also known as polydentate chelating ligand.*

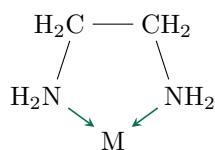


Figure V.1: An example of a bidentate chelating ligand.

- For example, ethylenediamine ( $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ; see Figure V.1) can bond to the same metal with both of its nitrogens' lone pairs at the same time.
  - Thus, ethylenediamine is bidentate, and it forms a 5-membered chelate ring.
- The chelate effect: For a given metal ion, the thermodynamic stability of a chelated complex involving bidentate or polydentate ligands is greater than that of a complex containing a corresponding number of comparable monodentate ligands.
  - Note that 5-membered rings are more stable than 6, and 4-membered rings (or smaller) are not stable due to angle strain.
  - For example, ethylenediaminetetraacetate (EDTA) is a hexadentate ligand has two nitrogens and four oxygens that wrap entirely around a metal atom and bond very strongly.
  - $\beta$ -diketones and acetylacetone are also polydentate ligands.
  - Multidentate bonding is incredibly strong.
  - As one last example, hemoglobin and chlorophyll have extra stability because the iron/magnesium ion is attached to four nitrogens.
- Explanations of the chelate effect:
  - Effective concentration: If one bond breaks, the bridge between the two bonding sites in the ligands still holds the other site in close proximity to the metal, making it more likely that the bond will reform than if the metal and ligand were floating entirely independently.
  - Entropy considerations:
    - Imagine you have a coordination complex. If you substitute two monodentate ligands for two other monodentate ligands, you do not change the number of particles.
    - However, if you substitute one polydentate chelating ligand for two monodentate ligands, you increase the number of particles by 1, increasing disorder in the universe and favoring the forward reaction.
  - Looking at the temperature-dependence of equilibrium, we can calculate  $\Delta G^\circ$ . We can then use this to calculate  $\Delta H$  and  $\Delta S$ , and we find that the contributions are very similar. Thus, both explanations of the chelate effect contribute about equally.
- Covalent bond classification (CBC) method:
- **X-type** (ligand): A ligand that donates one electron to the metal and accepts one electron from the metal when using the neutral ligand method of electron counting, or donates two electrons to the metal when using the donor pair method of electron counting.
  - Examples: hydrogen, the halogens, hydroxide, cyanide, carbocation, and nitric oxide.
- **L-type** (ligand): A neutral ligand that donates two electrons to the metal center regardless of the electron counting method being used.
  - Examples: carbon monoxide,  $\text{PR}_3$ , ammonia, water, carbenes ( $=\text{CRR}'$ ), and alkenes.
- **Z-type** (ligand): A ligand that accepts two electrons from the metal center as opposed to the donation occurring with the other two types of ligands.
  - Examples: Lewis acids, such as  $\text{BR}_3$ .
- LXZ notation:
  - Take the traditional formula and replace the central metal atom with M, each X-type ligand with X, each L-type ligand with L, and each Z-type ligand with Z. Then, if necessary, combine ligands of the same type using subscript arabic numerals, as per usual. Conserve the braces and charge.
  - For example,  $[\text{Ir}(\text{CO})(\text{PPh}_3)_2(\text{Cl})(\text{NO})]^{2+}$  becomes  $[\text{ML}_3\text{X}_2]^{2+}$ .

### V.3 Module 30: Nomenclature and Isomers of Metal Complexes

2/15:

- Midterm 1:
  - Average: 67.0.
  - Standard deviation: 14.8.
  - Max: 93.
  - 80+ scores: 10.
- Midterm 2 will cover modules 13-31 (with concepts from modules 1-12).
- Suggested reading: Miessler et al. (2014) Section 9.2.
- Naming metal complexes:
  1. For complex ions, write the cation first and anion last.
    - For example,  $K_2[PtCl_4]$  is potassium tetrachloroplatinate.
    - Note that you do not use the prefix mono, di, tri, etc. here to indicate the number of cations.
  2. Name the ligands first in alphabetical order, the metals last.
  3. Prefixes to indicate numbers (di, tri, tetra, ...) for all monoatomic ligands, polyatomic ligands with short names and neutral ligands with special names.
  4. Prefixes bis-, tris-, tetrakis-, pentakis-, hexakis- for ligands whose names contain a prefix of the first type, neutral ligands without special names, and ionic ligands with particularly long names.
  5. If the anion is complex, add the suffix -ate to the name of the metal. If the symbol comes from Latin/Greek, then we go back to the Latin/Greek for the name of the anion.
  6. Put the oxidation state in Roman numerals in parentheses after the name of the central metal ion of the ligand.
- Examples:
  - $[CoCl_4]^{2-}$  is the tetrachlorocobaltate (II) ion.
  - $[Fe(CN)_6]^{4-}$  is the hexacyanoferrate (II) ion.
    - Notice the use of “ferr” for iron (this is going back to the Latin/Greek name of the central metal ion as in Step 5).
  - $[Cr(H_2O)_4Cl_2]^+$  is the tetraaquadicchlorochromium (III) ion.
    - No use of -ate because this is a cation (not an anion).
  - $[Cr(NH_2CH_2CH_2NH_2)_3]^{3+}$  is the tris(ethylenediammine)chromium (III) ion.
    - Note that ammine with two m's is correct — an **amine** is a functional group from ammonia, while an **ammine** is a group of coordination compounds where ammonia is a ligand.
- Neutral ligands have the same name as the molecule with 4 exceptions:
  - $NH_3$  is ammine.
  - $H_2O$  is aquo.
    - Aquo or aqua?
  - CO is carbonyl.
  - NO is nitrosyl.
- Anionic ligands require replacing -ide in the ionic name (if present) with -o. For example:
  - $Cl^-$  becomes chloro.
  - $OH^-$  becomes hydroxo.

- $\text{SO}_4^{2-}$  is still sulfate.

- Bridging ligands:

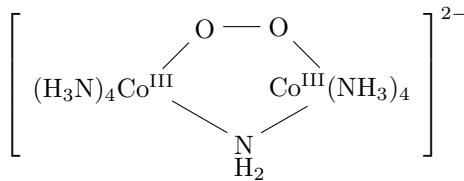


Figure V.2: A coordination compound with bridging ligands.

- Use  $\mu$  to indicate a bridge.
- If there are more than one of a given bridging ligand, the prefix indicating the number of ligands is placed after the  $\mu$ .
- If there are more than one different bridging ligands, they are given in alphabetical order.
- For example, the compound in Figure V.2 is the tetraaminecobaltate(III)- $\mu$ -amido- $\mu$ -peroxo-tetraaminecobaltate(III) ion.

Common Name	IUPAC Name	Formula
nitrido	nitrido	$\text{N}^{3-}$
azido	azido	$\text{N}_3^-$
oxo	oxido	$\text{O}^{2-}$
thiocyanato	thiocyanato-S	$\text{SCN}^-$
isothiocyanato	thiocyanato-N	$\text{NCS}^-$
thiocarbonyl	thiocarbonyl	$\text{CS}$
nitro	nitrito-N	$\text{NO}_2^-$
nitrito	nitrito-O	$\text{ONO}^-$
phosphine	phosphane	$\text{PR}_3$
pyridine	pyridine (abbrev. py)	$\text{C}_5\text{H}_5\text{N}$
amido	azanido	$\text{NH}_2^-$
imido	azanediido	$\text{NH}^{2-}$

Table V.1: Irregular and unfamiliar monodentate ligands.

- Table V.1 lists some more common but irregular or unfamiliar ligands.
  - Note that when listed in Table V.1, ambidentate ligands bind through the atom listed most to the left in the formula.
  - Note also that the slides list a number of common bidentate and polydentate ligands.
- Suggested reading: Miessler et al. (2014) Section 9.3.
- Coordination complex isomers are divided into:
  - Structural isomers (different bonds).
    - Coordination isomerism.
    - Linkage isomerism.
  - Stereoisomers (same bonds, different spatial arrangements).

- Geometric isomerism (*cis-trans*).
  - Optical isomerism.
  - **Ionization isomers:** Ligands inside the coordination sphere exchange places with ligands outside the coordination sphere.
    - So named because these give different ions when dissolved in water.
    - Werner's four isomers of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  are ionization isomers.
  - **Linkage isomers:** Variations in at which site an ambidentate ligand bonds.
  - **Geometric isomers:** Found in square planar and octahedral complexes — *cis*- vs. *trans*-isomers.
- octahedral
- (a) fac-triamminetrichlorocobalt(III).

(b) mer-triamminetrichlorocobalt(III).
- Figure V.3: Facial and meridional geometric isomers.
- Be aware of **facial** (fac) vs. **meridional** (mer) geometric isomers.
  - In Figure V.3a, all three  $\text{Cl}-\text{Co}-\text{Cl}$  bond angles are  $90^\circ$ .
  - In Figure V.3b, two  $\text{Cl}-\text{Co}-\text{Cl}$  bond angles are  $90^\circ$ , and the other is  $180^\circ$ .
  - Note that there are several different ways to represent an octahedrally coordinated metal ion.

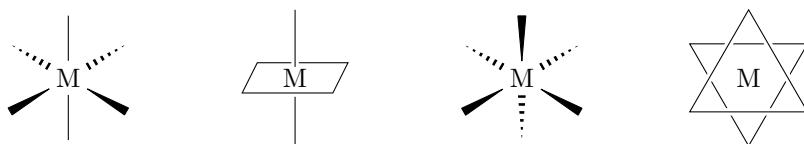


Figure V.4: Methods of sketching octahedral complexes.

- Which way you choose depends on what you are trying to show.
- **Optical isomers:** Two compounds with non-superimposable mirror images (two chiral molecules).
  - $C_1$ ,  $C_n$ ,  $D_n$ ,  $T$ ,  $O$ , and  $I$  point groups are chiral.
  - Usually associated with tetrahedral/octahedral geometries.
- Octahedral complexes have special chirality.

– Octahedral complexes with two bidentate ligands:

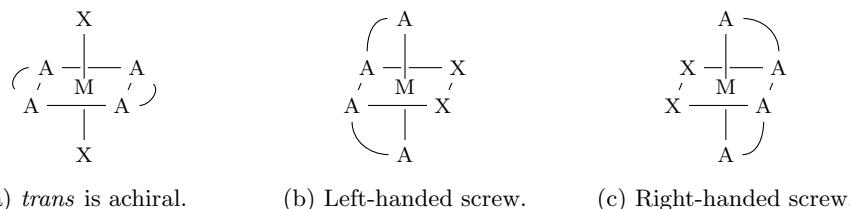


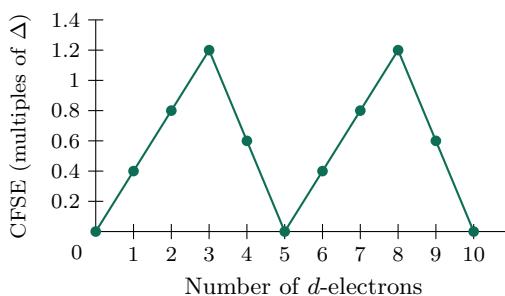
Figure V.5: Chirality of octahedral complexes with two bidentate ligands.

- As we can see in Figure V.5, *trans*-M(A–A)<sub>2</sub>X<sub>2</sub> is not chiral, but *cis*-M(A–A)<sub>2</sub>X<sub>2</sub> is chiral with two specially named forms.
- Octahedral complexes with three bidentate ligands:
  - *Also known as propellor chirality.*
  - Left-handed helices are  $\Lambda$  form, while right-handed helices are  $\Delta$  form.

## V.4 Module 31: Crystal Field Theory

- The first attempt to understand and rationalize the electronic structure of transition metal complexes.
  - Originally introduced to analyze crystals' electronic structure.
  - Since the coordination of a central atom in a crystalline closely mimics that of it in a coordination complex, the concepts of crystal field theory can easily be transferred to chemistry.
- Suggested reading: Miessler et al. (2014) Section 10.2.
- Refresher on *d*-orbitals.
  - There are four *d*-orbitals with four lobes and one strange  $d_{z^2}$  orbital.
  - Higher energy level ones have lobes corresponding to the change in sign of the radial component..
  - The  $d_{z^2}$  orbital is a linear combination of two four-lobed orbitals; it is created to reconcile mathematical theory with physical reality (the Pauli exclusion principle).
- Crystal field theory describes an electrostatic (ionic) approach to bonding — it is so named because it was first applied to crystalline substances.
  - Interactions between filled *d*-orbitals and ligands with excessive electrons are repulsive.
- Assumptions:
  1. Metal ion at the center.
  2. Ligands are treated as point charges.
  3. Bonding occurs through M<sup>+</sup> and L<sup>−</sup> electrostatic attraction.
  4. Bonding is purely ionic.
  5. M and L electrons repel each other.
  6. *d*-orbital degeneracy is broken as ligands approach.
- Consider *d*-orbitals bonding to six ligands.
  - Keep Coulomb's Law ( $E \propto \frac{q_1 q_2}{r}$ ) in mind: *d*-orbitals that overlap more with the ligands (smaller *r*) will be more destabilized (higher *E*).
  - $d_{z^2}$  overlaps with the two axial ligands, and  $d_{x^2-y^2}$  overlaps with the four equatorial ligands.
  - None of  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  overlap significantly with any ligands.
  - Therefore, the five degenerate *d*-orbitals split into the  **$t_{2g}$  set** and the  **$e_g$  set**.
  - When the orbitals split, they maintain an energetic “center of mass,” i.e., their combined energy as molecular orbitals must still be equal to their combined energy as degenerate, atomic orbitals. Thus, the stabilization energy of the three orbitals in the  $t_{2g}$  set is  $-\frac{2}{5}\Delta$  while the destabilization energy of the two orbitals in the  $e_g$  set is  $\frac{3}{5}\Delta$ , where  $\Delta$  is the **crystal field splitting parameter**.
- **$t_{2g}$  set:** The three orbitals that lie between the ligand donor atoms.
- **$e_g$  set:** The two orbitals that lie along the Cartesian coordinates, and so are adjacent to the donor atoms of the ligands, raising the set in energy.

- **Crystal field splitting parameter:** Different ligands produce different extents of splitting between the  $e_g$  and the  $t_{2g}$  levels. This energy difference is the crystal field splitting parameter. *Units*  $\text{cm}^{-1}$ . *Also known as*  $\Delta$ ,  $10Dq$ .
- Experimental verification of orbital splitting.
  - Consider a coordination complex with just one  $d$ -electron, i.e., electron configuration  $d^1$ .
    - An example is  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ .
  - In such a complex, the electron will occupy the lowest energy orbital available, i.e., one of the three degenerate  $t_{2g}$  orbitals.
  - Shining light on the complex can promote the  $t_{2g}$  electron into the  $e_g$  energy level.
  - The UV-Vis absorption spectrum reveals that this transition occurs with a maximum at  $20\,300 \text{ cm}^{-1}$ , or  $\Delta = 243 \text{ kJ/mol} \neq 0$ .
- Note that  $1000 \text{ cm}^{-1} = 11.96 \text{ kJ/mol} = 2.86 \text{ kcal/mol} = 0.124 \text{ eV}$ .
- **Crystal field stabilization energy:** The overall change in energy when the  $d$ -subshell splits, which is given by  $(0.4n(t_{2g}) - 0.6n(e_g))\Delta$  where  $n(t_{2g})$  and  $n(e_g)$  are the numbers of electrons in the  $t_{2g}$  and  $e_g$  levels respectively. *Also known as* CFSE.
  - When splitting of the  $d$ -subshell occurs, the occupation of the lower energy  $t_{2g}$  level by electrons causes a stabilization of the complex, whereas occupation of the  $e_g$  level causes a rise in energy. The  $t_{2g}$  level drops by  $0.4\Delta$ , whereas the  $e_g$  level is raised by  $0.6\Delta$ .
- High and low-spin complexes:
  - Whether a complex is **high-spin** or **low-spin** depends on  $\Delta$ .
  - If  $\Delta > P$  where  $P$  is the **spin-pairing energy**, then the complex is low-spin, and vice versa if  $\Delta < P$ .
- **High-spin** (complex): A complex with  $d^4$  to  $d^8$  electron configuration, where the electrons spread out and occupy the whole  $d$ -subshell.
  - High-spin complexes are often paramagnetic.
  - Electrons fill the whole  $d$ -subshell according to Hund's rule.
- **Low-spin** (complex): A complex with  $d^4$  to  $d^8$  electron configurations, where the  $t_{2g}$  energy level is filled first.
  - Low-spin complexes are often diamagnetic.
- **Spin-pairing energy:** The energy required to take pairs of electrons with the same spin orientation, and pair them up with the opposite spin. *Also known as*  $P$ .
- Calculating CFSE of  $d^0$  to  $d^{10}$  high-spin M (II) ions.

Figure V.6: CFSE as a function of the number of  $d$ -electrons.

- Most first row and many second and third row transition elements will be prone to forming high-spin complexes.
  - The variation shown in Figure V.6 reveals that complexes of metal ions with high CFSE (such as Ni (II)) will undergo greater stabilization, and vice versa for metal ions with low CFSE (such as Ca (II)).
  - The predicted variation matches relatively well with formation constant values ( $\log K_1$ ) obtained experimentally for these compounds.
- We can also look at orbital splitting in coordination compounds of other geometries.
    - In  $T_d$  compounds, for example, the splitting is flipped with the  $d_{xy,xz,yz}$  orbitals destabilized and the  $d_{x^2-y^2,z^2}$  orbitals stabilized.
    - We can also look analyze linear and square planar geometries.
  - Merits of crystal field theory:
    - Can be used to predict the most favorable geometry for the complex.
    - Can account for why some complexes are tetrahedral and others are square planar.
    - Useful in interpreting magnetic properties.
    - The colors of many transition metal complexes can be rationalized.
  - Limitations of crystal field theory:
    - Becomes less accurate as delocalization (covalent character) increases.
    - Point charge does not accurately represent complexes.
    - Does not account for  $\pi$  bonding interactions.
    - Does not account for the relative strengths of the ligands.

# Topic VII

## Band Theory in Solids

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

2/5:

- Solid silicon's symmetry space group would be  $Fd\bar{3}m$ .
- Suggested reading: Hoffmann (1987).
  - A rare less mathematical article on band theory that has taught generations of chemists; comes at it from a physics perspective.
- To consider solids, let's first consider an infinite chain of hydrogen atoms.
  - This should separate into  $H_2$  molecules (**Peierls's instability**); considering it to exist is a consequence of looking at chemistry through a physics perspective, where this is a simple model.
  - However, other substances can have chains of  $p_z$  orbitals, such as platinum atoms.
- An imaginary zoo of hydrogen molecules (we use the limit of a cycle of hydrogen atoms to approximate an infinitely long chain):
  - $H_2$  has a bonding and antibonding MO.
  - Cyclic  $H_3^+$  is the most abundant ion in the universe (recently discovered by UChicago). One bonding and two antibonding orbitals.
  - We can keep adding hydrogen atoms to our rings.
  - For an infinitely long cycle of hydrogen atoms, we will have an infinite number of states close together that resembles a band in solids.
- Back to the chain of H atoms:
  - The basis function on each lattice point is a  $H_{1s}$  orbital; there are countably many.
  - The appropriate SALCs  $\psi_k$  are based in translating every orbital by a finite number of units:

$$\psi_k = \sum_n e^{ikna} \phi_n$$

- $a$  is the distance between neighboring hydrogen atoms.
- Since there are infinitely many translations, there should be infinitely many translational symmetry elements, so infinitely many irreducible representations, too.
- The coefficients  $e^{ikna}$  come from **Bloch's theorem**.
  - In this formalism,  $k$  is an index labeling irreducible representations of the translation group.  $\psi$  transforms just like  $a$ ,  $e_1$ , and  $e_2$  (e.g., in the  $C_5$  point symmetry group).
  - This process of symmetry adaptation is called “forming Bloch functions.”

- Elementary band theory for extended solids:
  - Energy bands in solids arise from overlapping atomic orbitals, which become the **crystal orbitals** that make up the bands.
  - Recipe: Use LCAO (tight binding) approach.
  - A crystal is a regular periodic array with translational symmetry.
  - Periodic boundary conditions require  $\psi(x+Na) = \psi(x)$ , i.e., each wavefunction must be symmetry equivalent to the one in the neighboring cells.
  - For a 1D solid with lattice constant  $a$  and atom index  $n$ , Bloch's theorem tells us that the above SALC  $\psi_k$  is a solution to the Schrödinger equation.
- If we calculate  $\psi_0$  and  $\psi_{\pi/a}$ , we get the most and least bonding states possible, respectively (the least bonding state is the most antibonding state and has the highest energy).

Figure VII.1:  $s$  orbital bonding states.

$$\begin{aligned}\psi_0 &= \phi_0 + \phi_1 + \phi_2 + \phi_3 + \dots \\ \psi_{\pi/a} &= \phi_0 - \phi_1 + \phi_2 - \phi_3 + \dots\end{aligned}$$

- At this point, we can construct a band between these two states.
  - The band is *almost* infinite; it's on the order of Avogadro's number.
  - We have as many  $k$  values as translations in the crystal or as many unit cells in a crystal.
- **First Brillouin zone:** The region that covers all possible energy states that the crystal can have.
  - It is  $-\frac{\pi}{a} < k < \frac{\pi}{a}$ ; which is the range of all possible values that the sine function will give.
- There is one energy level for each value of  $k$ , but  $E(k) = E(-k)$ .
- $k$  is proportional to the electron momentum, or electron velocity.
- Calculation of 1D band structure:
  - We have  $N$  atoms such that  $\psi_k = \sum_{n=0}^N e^{inka} \phi_n$ .
  - The crystal Schrödinger equation is  $\hat{H}\Psi(k) = E(k)\Psi(k)$ .
  - Thus, the electron energies are given by
$$E(k) = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}$$
  - Recall that in Dirac's bra-ket notation,  $\langle \psi | \hat{H} | \psi \rangle \equiv \int \psi^* \hat{H} \psi d\tau$ ; for normalized atomic orbitals and ignoring overlap integrals:
$$\langle \phi_m | \phi_n \rangle = \begin{cases} 1 & m = n \\ 0 & m \neq n \end{cases}$$
  - Also recall that
$$\langle \psi | \psi \rangle = \sum_{m,n} e^{i(n-m)ka} \langle \phi_m | \phi_n \rangle = N$$

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

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

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

$$\left\langle e^{-inka} \phi_n | \hat{H} | e^{i(n\pm 1)ka} \phi_{n\pm 1} \right\rangle = \beta e^{\pm ika}$$

- Putting everything together, we have

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

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



Figure VII.2:  $p$  orbital bonding states.

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

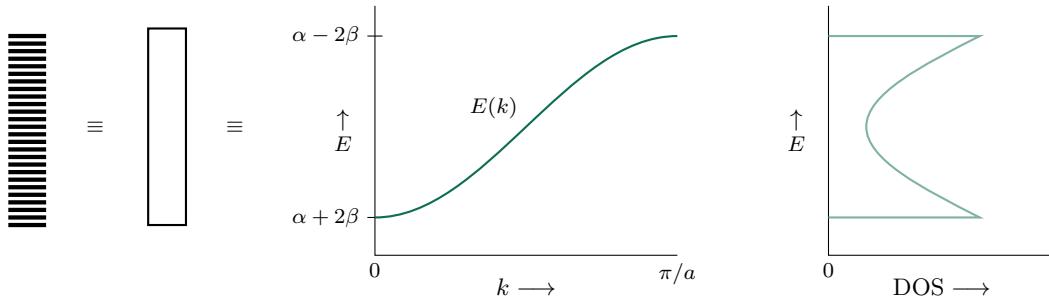


Figure VII.3: Density of states.

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

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

- 2D band structure:

- Simple Hückel: A two-dimensional square net ( $s$  orbitals only (or  $p_z$ )).

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

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

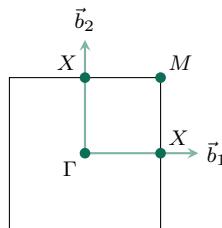


Figure VII.4: 2D Brillouin zone.

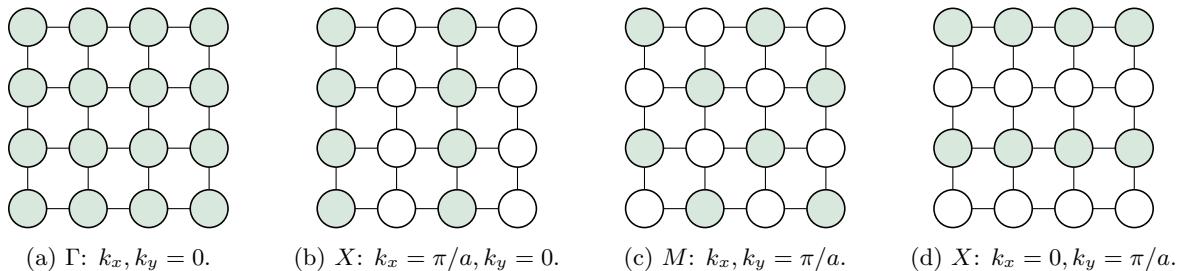


Figure VII.5: Special  $k$  points.

- The center is the  $\Gamma$  point ( $k_x = k_y = 0$ ; every orbital is surrounded by 4 orbitals of matching phase). The midpoint of the lines are called  $X$  points ( $k_x = \frac{\pi}{a}, k_y = 0$ , and vice versa; every orbital is surrounded by 2 orbitals of matching phase and 2 orbitals of unlike phase). The maximum point is the  $M$  point ( $k_x = k_y = \frac{\pi}{a}$ ; every orbital is surrounded by 4 orbitals of unlike phase).
- Calculating  $E(k)$  in two dimensions.

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

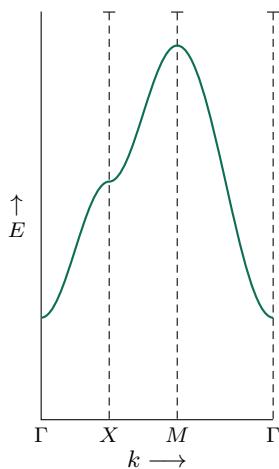


Figure VII.6: Schematic band structure (2D).

- Our schematic band structure (Figure VII.6) traces values along a 1D path in two-space from  $\Gamma \rightarrow X \rightarrow M \rightarrow \Gamma$ .

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

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

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

$$D_{1d}(E) = \frac{dN(E)}{dE} = \frac{dN(k)}{dk} \frac{dk}{dE} \propto 1 \cdot \frac{1}{\sqrt{E}} = \frac{1}{\sqrt{E}}$$

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

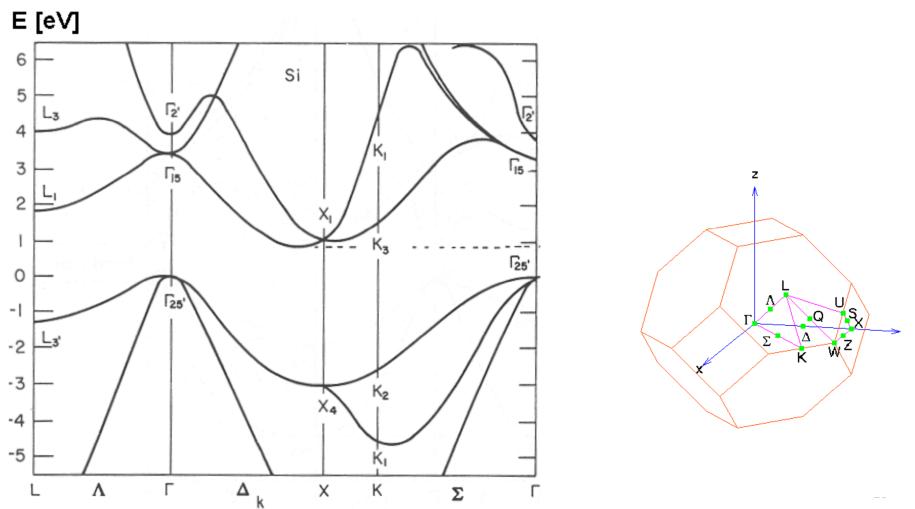


Figure VII.7: Electronic band structure of Si.

- **Angle-resolved photoemission spectroscopy<sup>[1]</sup>:** If the incoming photon's energy is greater than the electron's binding energy, the electron will eventually be emitted with a characteristic kinetic energy and angle relative to the surface normal. This angle is related to the electron's crystal momentum. The Bloch wave vector is linked to the measured electron's momentum. *Also known as ARPES.*

– Indeed, ARPES can be used to reconstruct the band structure of a solid. The bands are real!

### VII.3 Module 23: Filling Bands With Electrons

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

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

where  $E_F$  is the Fermi energy.

- $F(E)$  is the probability to fill the states with a given energy  $E$ .
- When  $T = 0$  K, the Fermi energy is the energy of the last occupied state. Moreover,
- The Fermi energy is the energy of the last occupied state at  $T = 0$  K; it is proportional to the square of the Fermi state  $k_F$ , i.e.,  $E_F \propto k_F^2$ .
- If  $T > 0$ , then:
  - We fill the states from bottom to top.
  - Instead of having a sharp shift from occupied to unoccupied states, we have a sort-of washed-out step function.
  - Far below  $E_F$ ,  $F(E) = 1$ ; far above  $E_F$ ,  $F(E) = 0$ . In the small **Fermi window** (aka. **Fermi level**) at the border (where the washed-out step function is),  $0 < F(E) < 1$ .
    - The Fermi window is  $4kbt$ .
    - It is in the Fermi level that all of the important stuff happens (i.e., electrons flowing in metals).

<sup>1</sup>Figure 7.20 in Labalme (2020a) actually refers to this kind of photoelectron spectroscopy!

- If the gap (range where  $\text{DOS}(E) = 0$ ) in the density of states at the Fermi level is smaller than 3 eV, then we have a semiconductor. If larger, we have an insulator. If 0, we have a conductor. Magnitude of DOS at Fermi level correlates with conductivity (e.g., Al has a higher DOS at the Fermi level than Ag, and we observe that Al is more conductive than Ag).
  - In metals and insulators, the Fermi level is within bands.
  - In semiconductors, it is between bands.
  - In physics, everything is a metal or insulator; semiconductors are a constructed perspective.
- Fermi sphere:
  - The surface of the Fermi sphere separates occupied and unoccupied states in  $k$ -space.
  - Bounded by Fermi surface.
  - Radius is Fermi wave vector  $k_F = \sqrt[3]{3\pi^2 n}$  where  $n$  is a parameter related to the density of electrons.
  - Fermi energy:  $E_F = \hbar^2 k_F^2 / 2m$ .
  - Fermi momentum:  $p_F = \hbar k_F$ .
  - Fermi velocity:  $v_F = \hbar k_F / m$ .
  - Fermi temperature:  $T_F = E_F / k_B$ .
- Electrons at  $T = 0$  K still move very quickly (approximately 0.06 the speed of light) since they're quantum particles (not classical ones).
- 3D density of states:
  - The density of states  $g(E)$  is the number of one-electron states (including spin multiplicity) per unit energy and volume:
 
$$g(E)_{3D} \equiv \frac{1}{V} \frac{dN}{dE}$$
    - $N$  is twice the product of the Fermi sphere volume and the number of levels per unit volume.
    - Thus,
$$N = 2 \times \frac{4}{3}\pi k^3 \times \frac{V}{8\pi^3} = \frac{V}{3\pi^2 \hbar^3} (2m^* E)^{3/2}$$

so

$$g(E)_{3D} = \frac{1}{V} \frac{dN}{dE} = \frac{1}{2\pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{3/2} \sqrt{E}$$
  - Take CHEM 39000 Solids, Materials, and Surfaces to learn more.

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