

# CHEM 121: Summary of Important Concepts

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## Chapter 2 - Chemical Bonding and Lewis Structures

Equation or Concept	Info About Equation/Concept
Ions	These are charged species. Individual ions may be atomic (simple ions) or molecular (complex or polyatomic ions). Positive ions are called <b>cations</b> while negative ions are called <b>anions</b> .
Ionic bonds	Ionic bonds occur between oppositely charged ions. Pure ionic bonds do not involve the sharing of electrons, and as a result are not constrained to the geometries seen in covalent bonds. Many “ionic bonds” seen in nature are actually highly polar covalent bonds.
Covalent bonds	Covalent bonds are bonds created by the mutual attraction of a pair of electrons between adjacent atoms. Covalent bonding is an inherently quantum mechanical phenomenon. Electrons are shared in covalent bonds. Perfectly covalent bonds share the electrons equally between the bonded atoms, while polar covalent bonds contain an asymmetric distribution of electron density. In covalent bonds — unlike ionic bonds — the bonding electrons are subject to repulsive interactions with nearby covalent bonds and lone pairs which may constrain the bond geometries.
Metallic bonds	Metallic bonds occur in the bulk phase of metals and are responsible for many metallic properties. They can be thought of as a network of conjugated (delocalized) covalent bonds that generate a “sea of electrons”. Such bonding electrons are free to flow between metal nuclei.
Electronegativity	The tendency of an atom in a molecule to attract electrons to itself. More electronegative atoms attract electrons more readily and tend to form polar covalent or ionic bonds with less electronegative atoms. In polar covalent bonds, the electron density of the bond is concentrated more towards the more electronegative species.
Ionic compounds	These are compounds consisting of ions held together by ionic bonds. Ionic compounds are also called salts. They have very high melting and boiling points. Liquid ionic compounds conduct electricity because charged ions can move freely past one another across a voltage, generating a current.
Redox reaction	A reaction that involves the transfer of electrons. In a redox reaction, one reactant is reduced. The reduced reactant gains electrons (i.e. its charge is reduced). The other reactant is oxidized. The oxidized reactant loses electrons (i.e. its charge is increased). Oxidizing agents cause other compounds to be oxidized, and are themselves reduced. Reducing agents cause other compounds to be reduced, and are themselves oxidized.
Lone pair	A pair of valence electrons that does not contribute to bonding.
Valence electrons	Electrons in the outermost shell of an atom or molecule.
Closed shell	When the number of valence electrons is exactly enough to completely fill the valence shell. Closed shell atoms and ions have the same electronic structure as noble gases. For p-block elements in the second row, a closed shell consists of eight electrons, forming an octet.
Bond order	Bond order is the number of bond pairs of electrons found between two atoms. Bond order = (# of bonding electrons) ÷ 2. Bond length reduces with increasing bond order. Bond dissociation energy increases with bond order.
Bond dissociation energy	The experimentally measured value describing how much energy needs to be added to fully break a particular bond.
Polar covalent bond	A covalent bond where electron density is not shared equally between the bonding atoms. Polar covalent bonds occur between atoms with differing electronegativities and result in a non-zero bond dipole.
Bond dipole	A bond dipole is created by a separation of charge across a bond. The molecule may be neutrally charged overall. A bond dipole has a non-zero <b>dipole moment</b> , which is a vector quantity (i.e. it has a direction and magnitude) defined in the idealized point-particle case as $\vec{d} = q\vec{d}$ , where $q$ is the magnitude of the separated charge and $\vec{d}$ is the vector that points from negative charge $-q$ to positive charge $q$ .
Percent ionic character	Percent ionic character of a bond = $\frac{\text{measured dipole moment of X-Y}}{\text{calculated dipole moment of X}^+\text{Y}^-} \times 100$

Equation or Concept	Info About Equation/Concept
Octet rule	An atom satisfies the octet rule if it has eight valence electrons. The octet rule most strongly applies to atoms in row two of the periodic table and atoms in group 14-18, and may be relaxed for other rows and columns. Atoms satisfying the octet rule are generally in low energy electronic configurations, such atoms form stable compounds. The rule: if (number of lone pair electrons) + (number of bonding electrons) = 8, then the atom has a complete octet. The octet rule is the most important property when determining the stability of a molecule.
Exceptions to the octet rule	Atoms in row two of the periodic table may NOT exceed an octet of valence electrons without becoming extremely unstable. Atoms in row three and beyond have access to low lying higher energy orbitals (e.g. <i>d</i> orbitals) and therefore may exceed the octet rule without losing much stability, becoming hypervalent. Transition metals are especially prone to higher numbers of valence electrons. Elements in group 13 only have three valence electrons when neutral, and often only form three bonds. The repulsive cost to add 5 more electrons to the valence shell of these atoms is not overcome by the electron-nucleus binding energy. As a result, such elements are commonly <b>electron deficient</b> .
Radicals	Radicals are species that contain at least one unpaired valence electron. They are often (but not always) unstable and highly reactive species. For example, the oxygen molecule O <sub>2</sub> is actually a <b>diradical</b> (has two unpaired electrons) in its ground state, but is fairly stable.
Formal charge	Formal charge is a bookkeeping device that allows us to keep track of electrons in molecules. To calculate: (number of valence electrons in neutral atom) - (lone pair valence electrons on atom) - (bonding electrons ÷ 2). A formal charge can be assigned to every atom in a molecule. High absolute values of formal charges are usually unstable. The best Lewis dot structure for a molecule will have as little formal charge as possible while still maintaining the octet rule on as many atoms as possible (apart from the exceptions). For maximum stability, negative formal charges should be on more electronegative species, while positive formal charges should be on less electronegative species. The sum of formal charges on every atom in a molecule will always be the same as the overall charge of the molecule.
Resonance structure	When a chemical species has more than one plausible arrangement of electrons around the atoms, we can think of the real (experimental) structure as a weighted combination of all of the valid Lewis structures. Lewis structures that are more stable contribute more to the overall real electronic structure. Positions and connectivity of the atomic nuclei are always the same for all resonance structures of a species, but lone pairs and multiple bonds (and therefore formal charges) may rearrange.
Valid resonance structure	Definition: any structure where the octet rule is satisfied on all atoms (except for atoms which can be electron deficient or can expand their octet).
Best resonance structure	The valid resonance structure that has minimal formal charges, and any formal charges that exist are placed on the best possible atoms (i.e. negative charges on the most electronegative species and positive charges on the least electronegative species).
Chemically reasonable structure	Any valid resonance structure where formal charges are kept fairly low (e.g. no more than a formal charge of ±2 on any single atom). Chemically reasonable resonance structures contribute significantly to the overall electronic structure.
Isomer	Chemical species that have the same overall empirical chemical formula, but differ in the arrangement of atoms and bonds. Isomers are not the same as resonance structures.
Oxidation state	The oxidation state of ions is just the charge on the ion. For covalently bonded atoms, the oxidation state is the charge that would result from moving all bonded electrons to the most electronegative atom in each bond (as opposed to formal charge, where bonded electrons are shared equally). The sum of all oxidation states in a compound must always equal the total charge of the compound.
Brønsted-Lowry acids and bases	In Brønsted-Lowry acid-base theory, acids are species that donate protons. Bases are species that accept protons.

## Chapter 3 - Shapes and Polarity of Chemical Species

Equation or Concept	Info About Equation/Concept
VSEPR Theory	Valence Shell Electron Pair Repulsion Theory. This theory approximately describes the 3D arrangement of valence electrons around atoms, generally quite well. It assumes that the only force that determines the positions of valence electrons is the Coulombic repulsive force with other electrons.
Dashed and Solid Wedges	Dashed wedges indicate covalent bonds that point into the page. Solid wedges indicate covalent bonds that point out of the page toward the reader.
Parent Shape	The lowest energy 3D arrangement of all lone pair and bonding pair electrons, minimizing electrostatic repulsion.
Axial and Equatorial	In VESPR theory, axial positions are the positions that point “up” and “down” with respect to the atom in question. They are only defined for atoms with more than 5 bonded groups and/or lone pairs. There are only two axial positions and they are always 180° separated from one another. The equatorial positions are those positions that are 90°, 120°, or 180° from one another. Axial and Equatorial positions are always 90° from each other.


		Electronegativity increases 																		
Period																				
1	H 2.20																	He		
2	Li 0.98	Be 1.57													B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31													Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00		
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.6		
6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn		
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo		
Lanthanides	*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27				
Actinides	**	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3				

Figure 1: Table of electronegativities using the Pauling scale.<sup>1</sup>

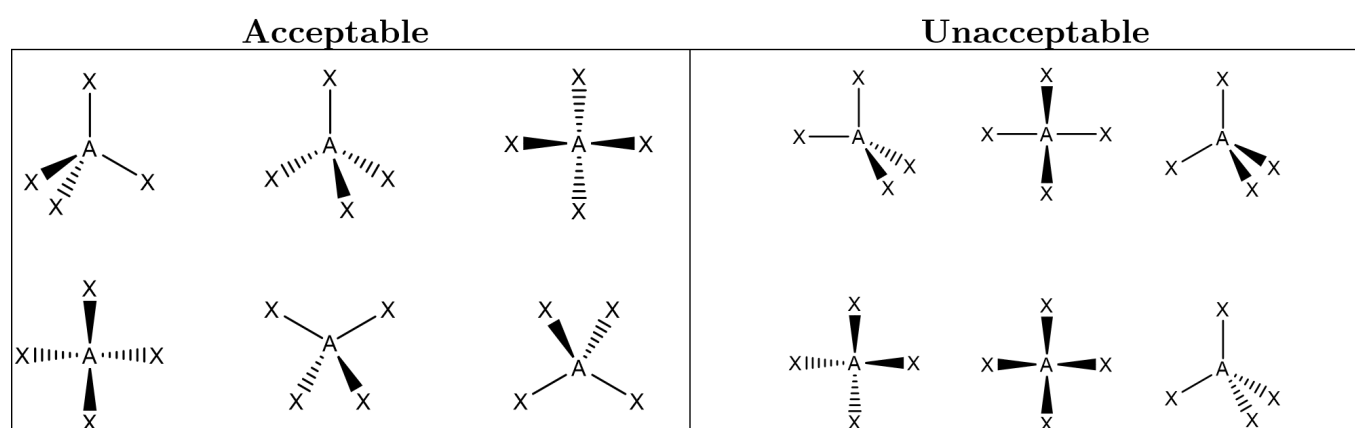
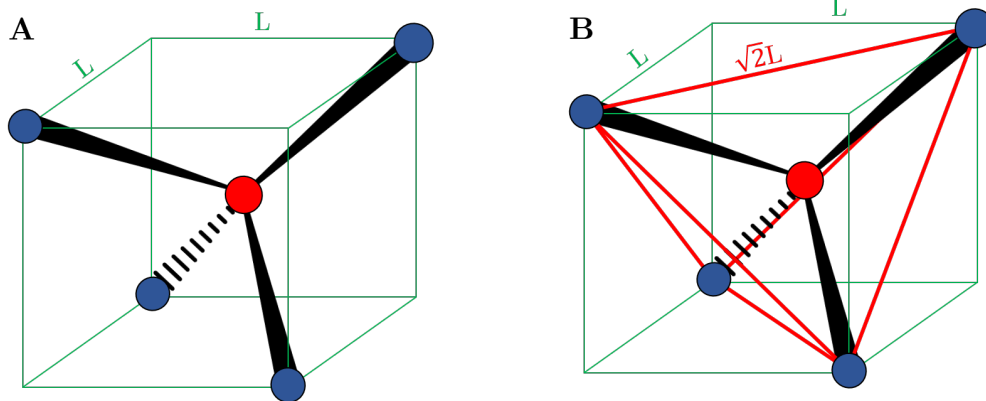


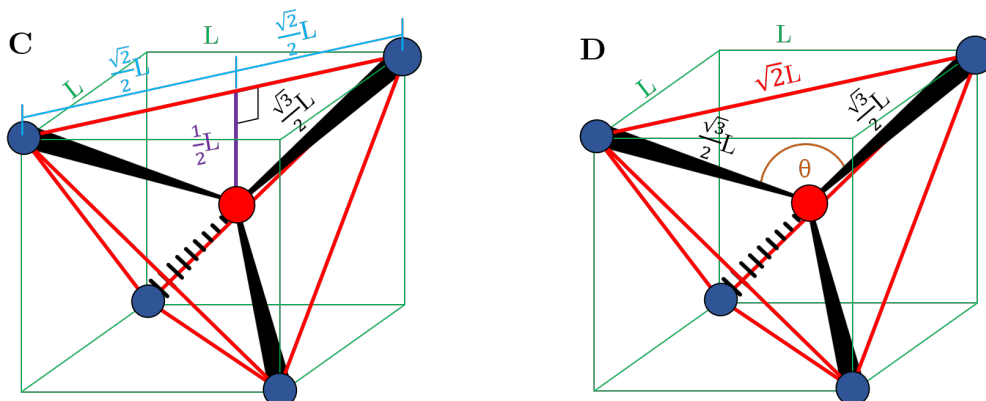
Figure 2: Examples of how to (and how not to) properly draw tetrahedral structures. All bond angles are  $\approx 109.5^\circ$

<sup>1</sup>Image by Aini Norhidayah. <http://ocw.ump.edu.my/course/view.php?id=479>

## Geometric Proof that the Bond Angles of a Perfect Tetrahedral Molecule are $109.5^\circ$



- A. Begin by drawing a perfect cube with side length  $L$ . In the *exact center* of the cube, place the central atom. Place four attached terminal atoms at the vertices of the cube such that they are separated by two vertices from every other atom.
- B. As can be seen above, the distance between every terminal atom will simply be the diagonal of a face of the cube. Since this is a perfect cube, the distance between every pair of terminal atoms can be found through the Pythagoras theorem:  $\sqrt{L^2 + L^2} = \sqrt{2}L$ . Since each of the distances between terminal atoms is the same, each face of the resulting polygon shown in red above is an equilateral triangle of the same size. Hence, the red polygon is a perfect tetrahedron, and the molecule is perfectly tetrahedral.



- C. Draw a **line** out from the central atom to the exact center of the any face of the cube. The length of this line will simply be half the length of any side of the box,  $\frac{1}{2}L$ . A right triangle is then generated between the central atom, one of the terminal atoms, and the center of chosen cube face. Since we are cutting the diagonal in half with this triangle, its length will be half the diagonal, or  $\frac{\sqrt{2}}{2}L$ . Once again, we can use the Pythagorean theorem to find the bond length:  $\sqrt{(\frac{\sqrt{2}}{2}L)^2 + (\frac{1}{2}L)^2} = \sqrt{\frac{2}{4}L^2 + \frac{1}{4}L^2} = \frac{\sqrt{3}}{2}L$ .
- D. Since all the bond lengths must be the same, a new isosceles triangle has been generated with all side lengths now known. The angle  $\theta$  can be calculated using the law of cosines,  $c^2 = a^2 + b^2 - 2ab \cos C$ . All that is left to do is to set the angle  $C = \theta$  and solve for  $\theta$ :

$$\begin{aligned}
 (\sqrt{2}L)^2 &= \left(\frac{\sqrt{3}}{2}L\right)^2 + \left(\frac{\sqrt{3}}{2}L\right)^2 - 2\left(\frac{\sqrt{3}}{2}L\right)\left(\frac{\sqrt{3}}{2}L\right) \cos \theta \\
 2L^2 &= \frac{3}{4}L^2 + \frac{3}{4}L^2 - 2\frac{3}{4}L^2 \cos \theta = \frac{6}{4}L^2 - \frac{6}{4}L^2 \cos \theta \\
 \frac{2}{4}L^2 &= -\frac{6}{4}L^2 \cos \theta \\
 -\frac{2}{6} &= \cos \theta \rightarrow \theta = \cos^{-1}\left(-\frac{1}{3}\right) \approx 109.5^\circ
 \end{aligned}$$

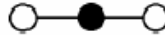
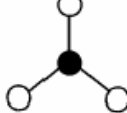
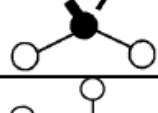
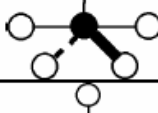


Number of electron pairs around central atom		Full description of the molecule					
BONDING (B)	LONE (E)	Example	Bond angles °	Geometry of Electron Pairs	Geometry of Atoms	3D Shape	Type
2	0	BeCl <sub>2</sub>	180	Linear	Linear		AB <sub>2</sub>
3	0	BF <sub>3</sub>	120	Trigonal planar	Trigonal Planar		AB <sub>3</sub>
2	1	SO <sub>2</sub>	Slightly less than 120	Trigonal planar	Bent or V Shaped		AB <sub>2</sub> E
4	0	CH <sub>4</sub>	109.5	Tetrahedral	Tetrahedral		AB <sub>4</sub>
3	1	NH <sub>3</sub>	107.5	Tetrahedral	Trigonal Pyramidal		AB <sub>3</sub> E
2	2	H <sub>2</sub> O	104.5	Tetrahedral	Bent or V Shaped		AB <sub>2</sub> E <sub>2</sub>
5	0	PCl <sub>5</sub>	120 in plane. 90 perpendicular to plane	Trigonal bipyramidal	Trigonal Bipyramidal		AB <sub>5</sub>
4	1	SF <sub>4</sub>	Complex	Trigonal bipyramid	Seesaw		AB <sub>4</sub> E
3	2	ClF <sub>3</sub>	Approx. 90	Trigonal bipyramidal	T-Shaped		AB <sub>3</sub> E <sub>2</sub>
2	3	XeF <sub>2</sub>	180	Trigonal bipyramid	Linear		AB <sub>2</sub> E <sub>3</sub>
6	0	SF <sub>6</sub>	90	Octahedral	Octahedral		AB <sub>6</sub>
5	1	BrF <sub>5</sub>	Approx. 90	Octahedral	Square Pyramidal		AB <sub>5</sub> E
4	2	XeF <sub>4</sub>	90	Octahedral	Square Planar		AB <sub>4</sub> E <sub>2</sub>

Figure 3: VSEPR Summary.<sup>2</sup>

<sup>2</sup>Taken from <https://gatorchem.wordpress.com/2014/08/06/1-4-bond-angles-and-shapes-of-molecules/>

## Chapter 4 - Fundamentals of Quantum Mechanics

Equation or Concept	Info About Equation/Concept
$\vec{p} = m\vec{v}$	The exact momentum for non-relativistic objects with constant mass. Notice that momentum has a size and direction; it is a vector quantity.
$E_K = \frac{1}{2}mv^2 = \frac{p^2}{2m}$	The (non-relativistic) kinetic energy of a particle with mass $m$ and velocity $v$ .
$\lambda = \frac{h}{p}$	The De Broglie wavelength equation. This equation relates a quantum object's momentum with it's wavelength.
$p = h\nu$	The De Broglie wavelength equation in terms of the frequency $\nu$ .
$v = \nu\lambda$	The relationship between the speed of a wave $v$ , it's frequency $\nu$ , and it's wavelength $\lambda$ . For electromagnetic waves, $v = c$ .
Nodes	The points of a standing wave where the amplitude is precisely zero at all times. The sign of the wave always changes when passing through a node. Boundary conditions that are set to zero are not considered nodes. The particle-in-a-box always has $n - 1$ nodes, where $n$ is known as the quantum number and may be any integer greater than 0.
$\Delta x \Delta p \geq \frac{\hbar}{2}$	The mathematical formulation of the Heisenberg uncertainty principle. The product of the uncertainty in a quantum object's momentum and the uncertainty in it's position cannot be arbitrarily small. At a certain well-defined point ( $\frac{\hbar}{2}$ ), increased knowledge of the precision in a particle's position necessarily requires a decrease in the knowledge of the precision of it's momentum. This follows directly from the wave-nature of quantum objects, since position and momentum are Fourier pairs.
$-\frac{\hbar^2}{8\pi^2m} \frac{d^2\Psi(x)}{dx^2} + V(x)\Psi(x) = E\Psi(x)$	The time-independent Schrödinger equation. The solutions $\Psi(x)$ to this differential equation are the quantum-mechanical wavefunctions for a (1 dimensional) particle under the influence of some unchanging potential energy surface $V(x)$ . The values $E$ are the total energies associated with each particular wavefunction $\Psi(x)$ . The Schrödinger equation was not derived from some more fundamental principles, but was instead postulated. It has since found to be in very good agreement with experimental observation.
$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$	The wavefunctions for a particle in a 1-dimensional box with infinite walls of length $L$ . Here, $n$ is the quantum number. It is any integer greater than zero—but not including zero. If $n$ were zero, the wavefunction would be zero, and the probability of finding the particle anywhere would also be zero. The factor $\sqrt{\frac{2}{L}}$ is called a normalization constant, and comes from insisting that the integral of the square of the wavefunction between 0 and $L$ must be precisely 1. In other words: the particle must exist somewhere within the box with 100% certainty. The values of $n$ must be integers because this ensures that the boundary conditions of the particle-in-the-box are fulfilled (the wavefunction falls to 0 at $x = 0$ and $x = L$ ).
$E_n = \frac{\hbar^2 n^2}{8mL^2}$	The total energy for a particular solution of the particle-in-a-box with quantum number $n$ . This is obtained by solving the Schrödinger equation with the particle-in-a-box of length $L$ .
$P(x) = \Psi^2(x)$	This is the probability density function, it gives the probability of finding the quantum particle as a function of it's position. It is simply the square of the wavefunction. This statement is generally true and is a postulate of quantum mechanics (applying to any wavefunction). It is not derived from any deeper principles. However, experimental evidence suggests that it is indeed true. Notice that nodes are conserved by this function, and become areas of zero probability density.
Zero-point energy	The energy of the lowest possible energy state for a quantum particle. For confined systems this value is not usually 0, but some small finite value. A system exhibiting its zero point energy is said to be in the lowest energy level or ground state.
Quantum confinement	In quantum mechanics, confinement <i>causes</i> the quantization of energies. Free particles have no restrictions on their possible energy states, they are said to have a continuous energy spectrum. Hence a free electron may have any value for its total energy, but an electron confined to an atom may only have specific well-defined total energies.

Equation or Concept	Info About Equation/Concept
$\lambda = \frac{2L}{n}$	The wavelength of a quantum-mechanical particle-in-a-box in terms of the box length $L$ and the quantum number $n$ .
$\Delta E = E_{n+1} - E_n = \frac{h^2(2n+1)}{8mL^2}$ $\Delta E = E_n - E_{n-1} = \frac{h^2(2n-1)}{8mL^2}$	The equation for the difference in energy between energy level $n$ of the quantum mechanical particle in a box and its next or previous energy level.
Addition, subtraction, or multiplication of wavefunctions	Because wavefunctions are solutions to a linear differential equation, any linear combination (scaled sum) of wavefunctions is also a solution to the Schrödinger equation. Therefore, it is possible to sum wavefunctions together to create new wavefunctions. In fact, this happens all the time in nature. Summation of wavefunctions is done by adding together the (scaled) values of the two wavefunctions at every point in space separately to create a new function. Mathematically, for two solutions $\Psi_a(x)$ and $\Psi_b(x)$ we can generate a new wavefunction (up to a multiplicative constant) through $\Psi(x) = A\Psi_a(x) + B\Psi_b(x)$ where $A$ and $B$ are arbitrary constants.

## Chapter 5 - Electronic Structure of Atoms and Ions

Equation or Concept	Info About Equation/Concept
$V(r) = k_e \frac{q_1 q_2}{r}$	Coulombs law for two charged point particles separated by $r$ . Here, $V(r)$ is the electric potential energy, and $k_e = \frac{1}{4\pi\epsilon_0}$ is Coulomb's constant. $q_1$ and $q_2$ are the electric charges of the two particles whose electric potential energy we wish to measure. To obtain forces between the two particles, $F(r) = -\frac{dV(r)}{dr} = k_e \frac{q_1 q_2}{r^2}$ .
$\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$	The total wavefunction for a one-electron species can be mathematically separated into two components: the radial wavefunction $R(r)$ , which only depends on the distance $r$ from the nucleus; and the spherical harmonic $Y(\theta, \phi)$ which only depends on the orientation.
$n = 1, 2, 3, \dots$	As was the case for the particle-in-the-box, the principal quantum number $n$ for real atoms may be any integer greater than zero.
$0 \leq \ell \leq n - 1$	The angular momentum quantum number defines the total angular momentum of an electron, it can take on values from 0 up to one below the principal quantum number. A specific value of $n$ and $\ell$ defines a subshell. For each value of $n$ , there are $n$ allowed values of $\ell$ and $\sum_{\ell=0}^{n-1} 2\ell + 1 = n^2$ total orbitals. Different values of $\ell$ have historical names: $\ell = 0$ is the $s$ subshell; $\ell = 1$ is the $p$ subshell; $\ell = 2$ is the $d$ subshell; $\ell = 3$ is the $f$ subshell. Subsequent subshells are named alphabetically starting at $g$ .
$-\ell \leq m_\ell \leq \ell$	The magnetic quantum number describes the angular momentum component of an electron with respect to any particular direction of measurement. It can be any integer whose absolute value is not greater than the total angular momentum quantum number, including negative numbers. Specific values of $n$ , $\ell$ , and $m_\ell$ together define an orbital. For each value of $\ell$ , there are $2\ell + 1$ values of $m_\ell$ .
$m_s = \frac{1}{2}$ or $-\frac{1}{2}$	$m_s$ is the spin quantum number. It defines the direction of intrinsic spin angular momentum with respect to any particular direction of measurement. Note that quantum mechanical spin is not real physical rotation. $m_s$ can only have one of two possible values, known as spin up ( $m_s = \frac{1}{2}$ ) or spin down ( $m_s = -\frac{1}{2}$ ).
Angular Nodes	Angular nodes occur at a specific value of $\theta$ or $\phi$ . Generally, angular nodes appear as cones or planes in 3D space. When an angular node happens to occur at $\theta = 90^\circ$ or any specific $\phi$ , then the angular node is a nodal plane, otherwise it is a cone. The total number of angular nodes in an orbital is always the equal to the quantum number $\ell$ .
Radial Nodes	Radial nodes occur at specific values of $r$ . Therefore, radial nodes appear as spherical shells with well defined radii. Since there are always $n - 1$ total nodes, there are always $n - 1 - \ell$ radial nodes.
Shell	Electrons with a particular value of $n$ are in the $n^{\text{th}}$ shell.
Subshell	Electrons with particular values of $n$ and $\ell$ are in a particular subshell.
Orbital	Electrons with particular values of $n$ , $\ell$ , and $m_\ell$ are in a particular orbital. An orbital can hold two electrons, one for each value of $m_s$ .

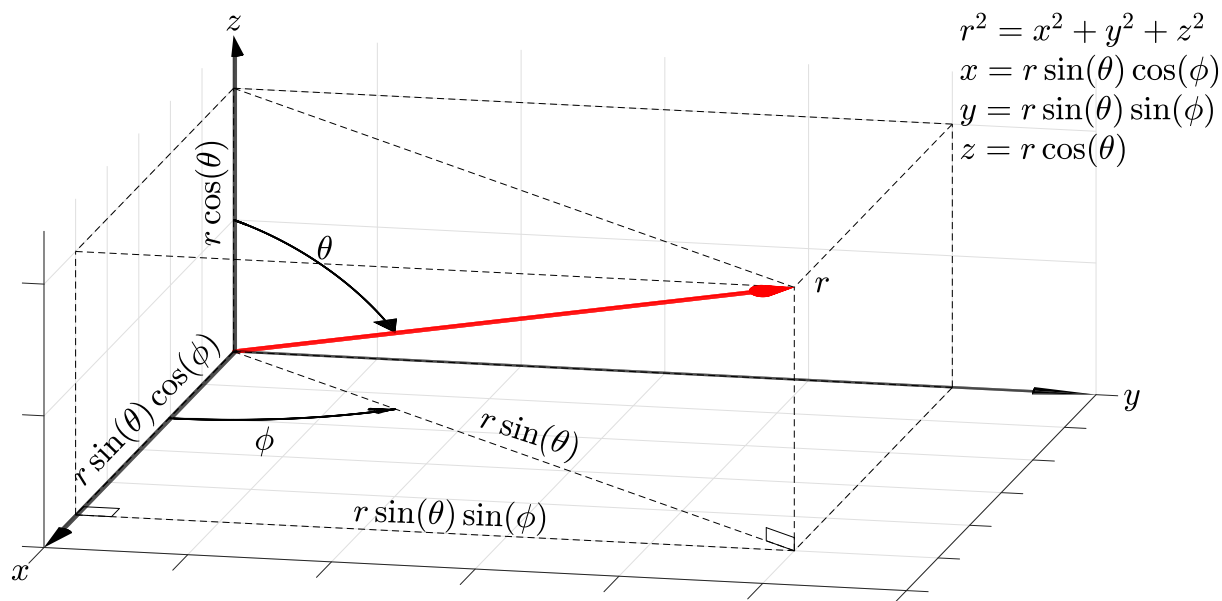


Figure 4: A diagram showing the conversion between Cartesian and spherical polar coordinates

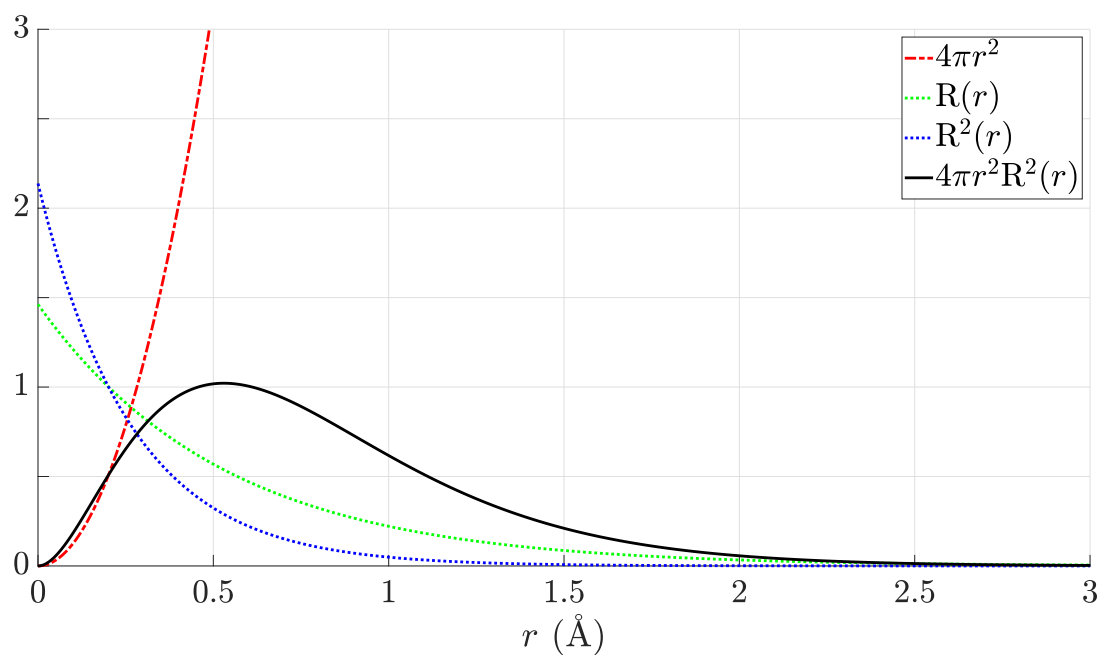


Figure 5: The radial part of the 1s wavefunction  $R$  as a function of distance from the nucleus  $r$ . The wavefunction squared multiplied by  $4\pi r^2$  yields the probability density of finding the electron in a spherical shell of radius  $r$  around the nucleus. At distances far from the nucleus, both the wavefunction and probability density decay exponentially.



Equation or Concept	Info About Equation/Concept
Spin Orbital	Electrons with particular values of $n$ , $\ell$ , $m_\ell$ , and $m_s$ are in a particular spin orbital. According to the Pauli Exclusion Principle, only one electron may occupy a particular spin orbital of an atom or molecule.
$\sum_{i=1}^{n-1} i = \frac{1}{2}(n^2 - n)$	This is the total number of possible transitions resulting in emission of a photon from a shell with principal quantum number $n$ to lower energy levels. True only <i>for 1 electron species</i> because all subshells are degenerate in this case, so transitions between orbitals within the same shell do not change the energy of the system.
$E_n = -R_H \frac{Z^2}{n^2}$	The orbital energy of an electron in a single-electron atom or ion. The energies only depend on the principal quantum number $n$ and the charge of the nucleus, not on the other quantum numbers. All orbitals within a shell are degenerate for single-electron atoms. This is not the case for multi-electron atoms and molecules. $R_H$ is called the Rydberg constant.
$\Delta E = -R_H Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$	The change in energy $\Delta E = E_{final} - E_{initial}$ as a result of an electron moving from one shell $n_i$ to another shell $n_f$ in a single-electron atom or ion.

## Chapter 6 - Interactions Between Light and Matter

Equation or Concept	Info About Equation/Concept
$c = \nu\lambda$	The relationship between an electromagnetic wave's frequency $\nu$ and its wavelength $\lambda$ . Their product is always the speed of light $c$ .
Monochromatic light	Light that consists of photons that all have the same or nearly the same wavelength (i.e. a very narrow distribution of wavelengths). Monochromatic light (in the visible region) will appear as a very specific colour. Monochromatic light is not necessarily coherent.
Coherent light	Light in which the waves and troughs of the photons are all spatially and temporally aligned. Coherent light is always monochromatic, otherwise it would rapidly lose coherence. An example of a coherent light source is a laser. Coherent light is not necessarily polarized.
Linearly polarized light	Light in which the direction of the oscillating electric and magnetic field vectors of the photons are aligned. Polarized light has many uses, and is usually generated with a polarizing filter. Polarizers work by blocking all light except that of a specific electric field orientation.
$E = pc = \frac{hc}{\lambda} = h\nu$	The Planck relation. It is the relationship between a photon's energy $E$ , momentum $p$ , wavelength $\lambda$ , and frequency $\nu$ .
Compton Scattering	Sometimes when a photon of light interacts with a charged particle (such as an electron) it will impart some energy onto the particle and change its momentum. The path of the photon and the particle of matter will both be altered in a way that is best explained by thinking of light as a particle.
Photoelectric Effect	When high energy light is incident on a substance, it may eject electrons. Light will not eject any electrons if its energy per photon is lower than the first ionization energy of the substance. If the energy per photon of light (i.e. its colour, not intensity) is higher than the substance's first ionization energy, then electrons will be ejected with kinetic energy equal to the difference between the photon's energy and the substance's first ionization energy. The intensity of light does not determine whether or not electrons will be ejected (or with what velocity), but will determine the rate of electron ejection if the energy per photon is high enough.
Electronic Transitions	When electrons change state, their energy will change as well (unless the transition is between two degenerate states). This energy must come or go in some form. One form of energy transfer is through electromagnetic radiation, or light. When electrons in atoms or molecules absorb a photon of light containing just the right energy, they become excited and may reach a higher energy level or — if the photon is high enough energy — become ionized entirely. Excited electrons decay back to their ground state very quickly, and in doing so release energy. Electrons may release this energy in the form of a photon of light whose energy is equal to the difference in energy between the initial and final states of the electron undergoing the transition.



Equation or Concept	Info About Equation/Concept
$n$ -Shell Energy Splitting	In multi-electron species, electron-electron repulsion destroys the degeneracy of the subshells within a shell. Orbitals within subshells are still degenerate in unperturbed multi-electron atoms.
$Z_{eff}$ : Effective Nuclear Charge	This is the effective quantity of charge “felt” by a valence electron as a result of the positive nuclear charge combined with the shielding of core electrons.
$Z_{eff} \approx Z - S$	An approximation of the effective nuclear charge is obtained by subtracting the number of core electrons $S$ from the total nuclear charge $Z$ . This is only a weak approximation and becomes less accurate from left to right along the periodic table.
$m_s$ : Spin Quantum number	The fourth and final quantum number of electrons bound within atoms. $m_s$ describes the spin component of an electron with respect to the particular axis of measurement. It takes on one of two possible values: $+\frac{1}{2}$ (up) or $-\frac{1}{2}$ (down).
Pauli Exclusion Principle	No two fermions (of which an electron is a member) can have all four quantum numbers exactly the same within the same atom or molecule. In other words, two electrons cannot occupy the same quantum state at the same time. The Pauli Exclusion principle is a direct result of the fact that all electrons are indistinguishable particles, and the total wavefunction of a system of fermions must be antisymmetric to exchange of any two electrons, i.e. $\psi(\vec{r}_1, \vec{r}_2) = -\psi(\vec{r}_2, \vec{r}_1)$ .
Aufbau Principle	The aufbau (building up) principle is an empirical principle that rationalizes how the electronic orbitals of atoms are filled up in the ground state. The principle states that for ground state atomic species, electrons fill up the lowest available energy levels completely before occupying higher energy levels in order. See figure 6 for the general trend. Note that the aufbau principle is only a guide, and there are exceptions to it.
Hund’s Rule	Hund’s rule is used to determine the ground electronic state of multi-electron species in which the highest occupied orbitals are degenerate. The rule has two parts. First, electrons occupy degenerate orbitals singly until all such orbitals are singly occupied, after which electron pairing may begin. Second, all electrons in singly occupied orbitals have matching spins (all up or all down). The first part of the rule is due to the fact that the repulsive interaction between two electrons in the same orbital is greater than between electrons in different orbitals. The second part of the rule is due to a quantum mechanical interaction which occurs only between electrons with matched spins and similar energies called the exchange interaction. Exchange energy is always negative, and occurs due to the fact that such electrons are indistinguishable.
Exceptions to Regular Orbital Filling	The electronic configurations of chromium and copper are not exactly as one might expect by following the aufbau principle and Hund’s rule. Instead of $[\text{Ar}]4s^23d^4$ for chromium, the experimentally observed ground state is $[\text{Ar}]4s^13d^5$ . In copper, $[\text{Ar}]4s^13d^{10}$ is observed. In both cases, the reduction in Coulombic repulsion combined with the increased exchange energy is greater than the difference between the $4s$ and $3d$ orbital energies. This is often succinctly stated as “there is extra stability associated with half full or completely full $3d$ subshells.” Another exception occurs in fourth row transition metal ions: when an electron is removed (ionized) from these transition metals, the valence $4s$ and $3d$ orbitals rearrange in energy, with the $3d$ orbital slightly lower than the $4s$ orbital. Therefore, in these transition metal ions, all remaining electrons will fill up the outermost $3d$ orbital before the outermost $4s$ orbital.
Spin Pairing Energy	This is the positive (repulsive) energy associated with pairing two electrons in the same orbital. It arises due to the repulsive Coulombic interaction between electrons forced into an orbital together. Spin pairing energy is higher for smaller orbitals (e.g. $1s$ , $2s$ , $2p$ ). Although spin pairing energy is generally quite small compare with the difference in energy between orbitals, it is responsible for the first part of Hund’s rule.
Exchange Energy	Electrons are indistinguishable particles., If two or more electrons with degenerate energies have the same spin quantum number $m_s$ , they can be exchanged without changing the quantum state. It turns out that this exchange interaction <i>lowers</i> the total energy of the system when possible. The exchange energy is entirely quantum-mechanical in nature and is responsible for the second part of Hund’s rule.

Equation or Concept	Info About Equation/Concept
Excited State	Any of the infinite number of electronic configurations which are not the ground state are considered excited states. This includes flipping electron spins, moving electrons to higher energy orbitals, or both. Excited electronic states generally decay to the ground state extremely rapidly. An electron may absorb energy (e.g. from a photon of light) and become excited, which changes the chemical properties of the species. An excited state will never violate the Pauli exclusion principle.
Diamagnetism	Species that contain all paired electrons are governed by the quantum mechanical diamagnetic interaction. Diamagnetic species are weakly repelled by magnetic fields.
Paramagnetism	Species that contain at least one unpaired electron are said to be paramagnetic. In such species, the weak diamagnetic force is overcome by the much stronger magnetic interaction of the unpaired electron(s). Hence, paramagnetic species are weakly attracted to magnetic fields.
Ferromagnetism	In some chemical species with particularly strong paramagnetism, magnetic domains form in which the spins of all the unpaired electrons are aligned to generate a much larger magnetic field. When most of the magnetic domains within such a species are aligned, a macroscopic magnetic field is generated. Ferromagnetic species are strongly attracted to magnetic fields.
Covalent Radius	One method of estimating the radius of atoms. The covalent radius is only well-defined for species that form single homonuclear bonds. For example, the covalent radius of hydrogen is simply half the bond length of $H_2$ . The covalent radius of other species that form heteronuclear single bonds can be estimated by subtracting the covalent radius of the known species in the bond.
Ionic Radius	A measure of the radius of ions within a crystal lattice, usually determined by crystallographic measurements (i.e. using X-ray crystallography).
Van Der Waals Radius	A measure of the radius of non-bonded atoms, which is found by finding the distance at which Van Der Waals dispersion interaction is no longer attractive.
Atomic Size Trend	Atomic radii tend to increase down the periodic table and from right to left across the periodic table. The downward trend is easily explained by the increasing range of electron density found in the radial distribution functions of orbitals with higher principal quantum number $n$ . The trend from right to left is explained by the relatively increased shielding and therefore reduced $Z_{eff}$ of atoms as one moves from right to left across the table. This is due to the higher proportion of core electrons (which contribute more to shielding) in elements on the left side of the periodic table.
Atomic Size of Ions	Cations have at least one fewer electron than neutral species and hence have a smaller atomic radius. Anions have one or more electrons than neutral species and are therefore larger than neutral species. Additionally, between two isoelectronic species with different nuclear charges, the species with the higher nuclear charge will always have a smaller atomic radius.
Ionization Energy	Ionization energy is the minimum energy required to remove a single electron from an atom, ion, or molecule. Clearly this quantity increases for species with more tightly bound electrons. Ionization energy depends on both the electronic configuration before ionization as well as after. Since valence orbitals are closer to the nucleus for atoms on the right side of the periodic table, ionization energy generally increases left to right. Ionization energy decreases down the periodic table, as the size of valence orbitals increases and their corresponding orbital energies increase.
Electron Affinity	Electron affinity is the energy released or spent when an electron is added to an isolated atom, molecule, or ion from infinitely far away. This quantity is usually negative (i.e. is exothermic), although may be positive for species that are already negatively charged or for noble gases. The <i>magnitude</i> (i.e. absolute value) of electron affinity follows ionization energy and electronegativity trends: it is larger from left to right across the periodic table, as well as top to bottom down the periodic table. The electron affinity of noble gases is difficult to measure and probably small but positive.

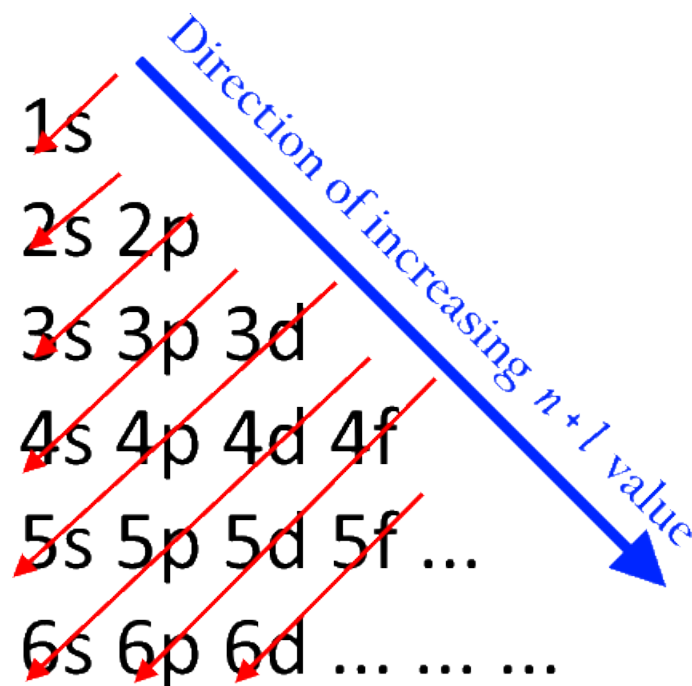


Figure 6: The Aufbau Principle: a diagram of the usual order of electron orbital filling. This does not include the exceptions to that occur in chromium, copper, transition metal ions, and other heavy elements.<sup>4</sup>

<div>1 (#e<sup>-</sup> = 1) H 1s<sup>1</sup></div>				<div>2 (#e<sup>-</sup> = 2) He 1s<sup>2</sup></div>			
<div>3 Li 1s<sup>2</sup> 2s<sup>1</sup></div>	<div>4 Be 1s<sup>2</sup> 2s<sup>2</sup></div>	<div>5 B 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>1</sup></div>	<div>6 C 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>2</sup></div>	<div>7 N 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>3</sup></div>	<div>8 O 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>4</sup></div>	<div>9 F 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>5</sup></div>	<div>10 Ne 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup></div>
<div>11 Na 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>1</sup></div>	<div>12 Mg 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup></div>	<div>13 Al 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>1</sup></div>	<div>14 Si 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>2</sup></div>	<div>15 P 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>3</sup></div>	<div>16 S 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>4</sup></div>	<div>17 Cl 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>5</sup></div>	<div>18 Ar 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup></div>
<div>19 K 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 4s<sup>1</sup></div>	<div>20 Ca 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 4s<sup>2</sup></div>						
		<div>31 Ga 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>10</sup> 4s<sup>2</sup> 4p<sup>1</sup></div>	<div>32 Ge 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>10</sup> 4s<sup>2</sup> 4p<sup>2</sup></div>	<div>33 As 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>10</sup> 4s<sup>2</sup> 4p<sup>3</sup></div>	<div>34 Se 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>10</sup> 4s<sup>2</sup> 4p<sup>4</sup></div>	<div>35 Br 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>10</sup> 4s<sup>2</sup> 4p<sup>5</sup></div>	<div>36 Kr 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>10</sup> 4s<sup>2</sup> 4p<sup>6</sup></div>
<div>21 Sc 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 4s<sup>2</sup> 3d<sup>1</sup></div>	<div>22 Ti 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 4s<sup>2</sup> 3d<sup>2</sup></div>	<div>23 V 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 4s<sup>2</sup> 3d<sup>3</sup></div>	<div>24 Cr 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 4s<sup>1</sup> 3d<sup>5</sup></div>	<div>25 Mn 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 4s<sup>2</sup> 3d<sup>5</sup></div>	<div>26 Fe 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 4s<sup>2</sup> 3d<sup>6</sup></div>	<div>27 Co 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 4s<sup>2</sup> 3d<sup>7</sup></div>	<div>28 Ni 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 4s<sup>2</sup> 3d<sup>8</sup></div>
	<div>29 Cu 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 4s<sup>1</sup> 3d<sup>10</sup></div>						<div>30 Zn 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 4s<sup>2</sup> 3d<sup>10</sup></div>

Figure 7: Electronic configurations for the first four rows of the periodic table, note the exceptions to the trend found in chromium (24) and copper (29).<sup>5</sup>

<sup>4</sup>Taken from [https://en.wikipedia.org/wiki/Aufbau\\_principle](https://en.wikipedia.org/wiki/Aufbau_principle)

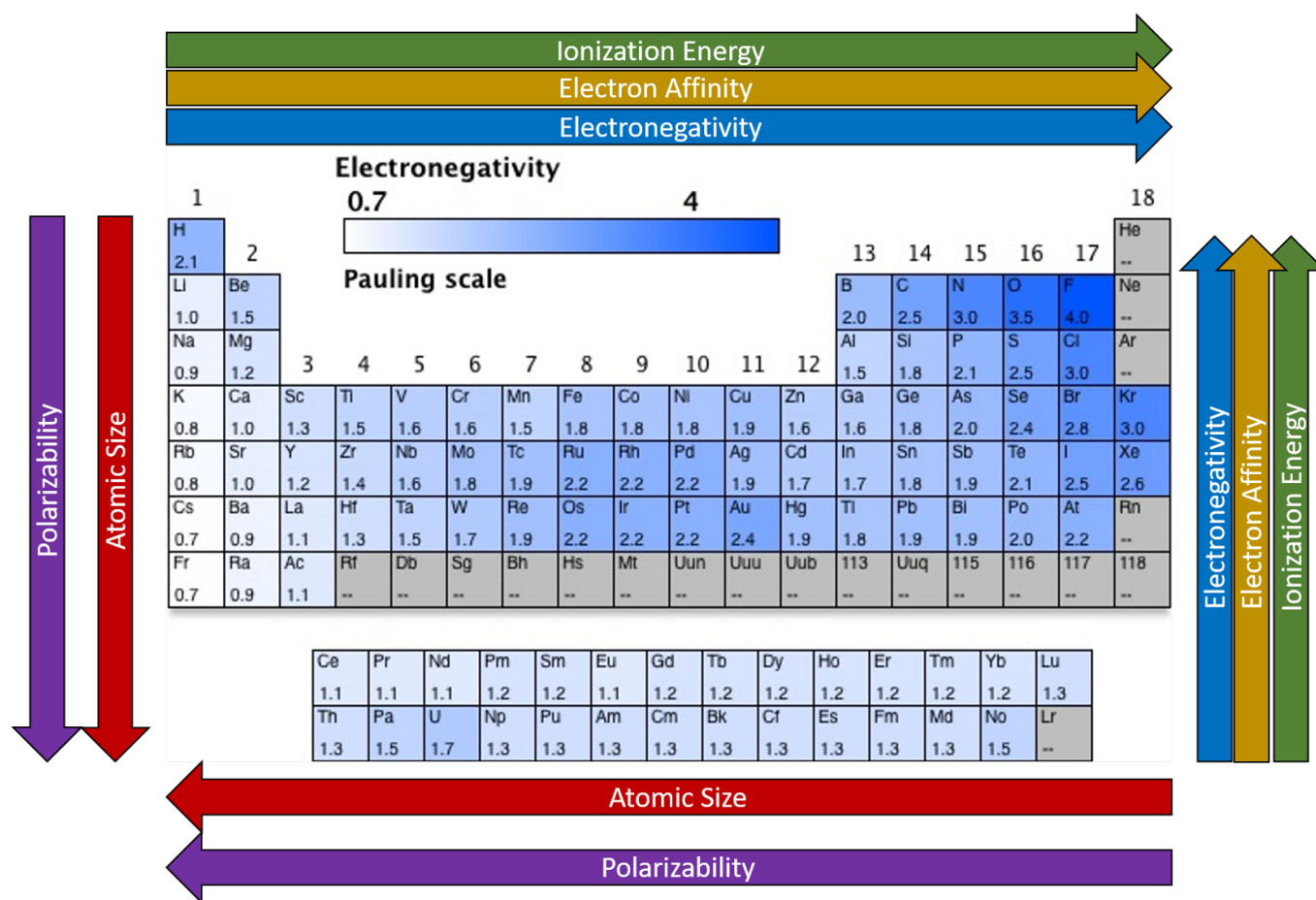


Figure 8: Summary of the periodic trends.<sup>6</sup>

## Chapter 8 - Molecular Orbital Theory

Equation or Concept	Info About Equation/Concept
Molecular Orbital Theory	Molecular orbital (MO) theory is an extension of atomic orbital theory onto molecules. MO theory treats electrons within molecules as waves, unlike Lewis theory. In MO theory, molecular orbitals are constructed from combinations of atomic orbitals with the correct symmetry to allow maximal overlap of regions with the same phase. MOs can only be formed between atomic orbitals (AOs) that have similar energies. For example, a 1s orbital usually does not form an MO with a 2s orbital due to the large energy difference between them. MO theory takes into account all possible overlaps between all orbitals on all atoms within a molecule, and can become very complex for large molecules.
Valence Bond Theory	Valence Bond Theory (VBT) is a simplification of MO theory which considers the molecular orbitals of individual types of bonds separately. VBT is less accurate than MO theory, but much simpler for larger molecules. VBT is more accurate than Lewis and VSEPR theories.
Wave Superposition	When atomic orbitals are brought together, electron orbitals can interfere constructively or destructively. When the phases of the orbitals are matched, the electrons interfere constructively and the energy is lowered: a bonding MO is formed. When the phases of orbitals are opposite, electrons interfere destructively and the energy is raised: an antibonding MO is formed. When there is greater overlap between orbitals, the energy change is greater (i.e. lower for bonding orbitals and higher for antibonding orbitals).
Conservation of Orbitals	When constructing MOs from AOs, the number of input AOs always equals the number of output MOs.

<sup>5</sup>Taken from <https://chem.libretexts.org/>

<sup>6</sup>Adapted from Work by Synergy Creations <http://chemistry-reference.com/pditable/default.asp>

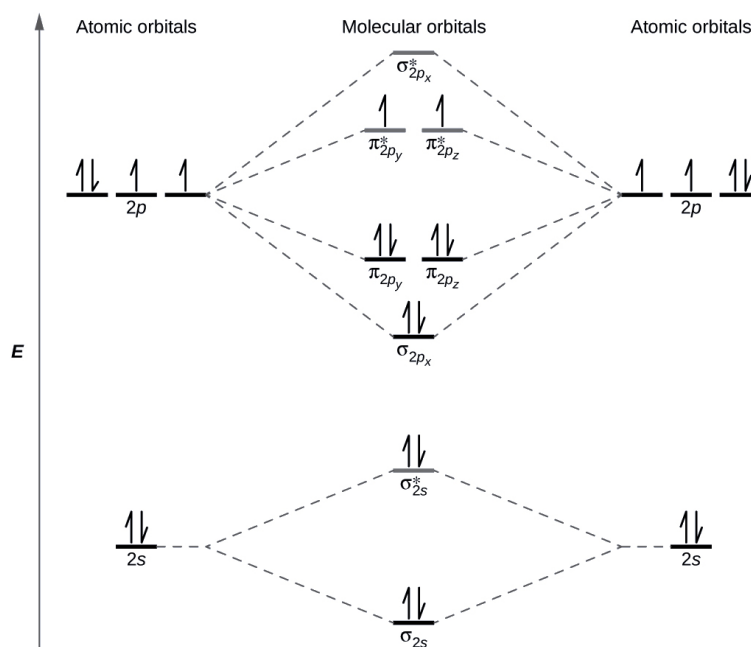


Figure 9: An orbital interaction diagram for the  $O_2$  molecule. The diagram shows that the number of orbitals is conserved such that the number of input AOs equals the number of output MOs. Placing the electrons in agreement with the aufbau principle, Pauli exclusion principle, and Hund's rule explains why the ground state of diatomic oxygen is paramagnetic. Note that the core electrons do not overlap as much as the valence electrons, and also contain an equal number of bonding and antibonding electrons. Hence core electrons do not contribute significantly to bonding and are often not shown. Molecular orbitals are labeled as  $\sigma$  if they are cylindrically symmetric, or as  $\pi$  if they instead have a plane of symmetry containing the bond vector. The label contains an asterisk (\*) if it is an antibonding orbital. The label also contains a subscript that denotes from which AOs the MO originated.<sup>7</sup>

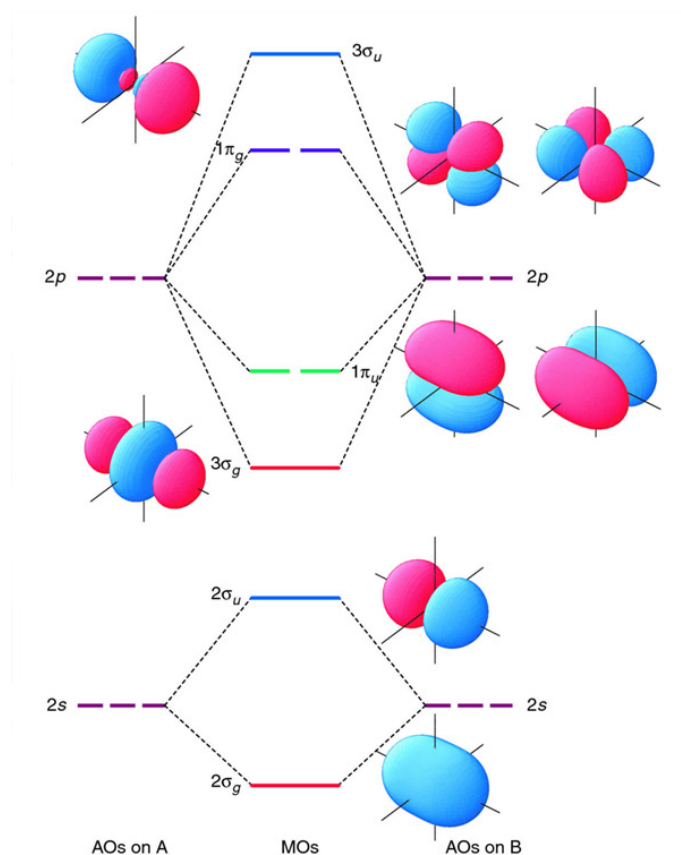


Figure 10: The shapes of  $O_2$  molecular orbitals.<sup>8</sup>

<sup>7</sup>Adapted from <https://opentextbc.ca/chemistry/chapter/8-4-molecular-orbital-theory/>

<sup>8</sup>Taken from [http://www.forgottenplanet.com/studyguide/chem210/chem210\\_ch3.html](http://www.forgottenplanet.com/studyguide/chem210/chem210_ch3.html)

Equation or Concept	Info About Equation/Concept
Nodes in Molecular Orbitals.	When two AOs are combined to form two MOs, the resulting MO with fewer nodes is the bonding orbital, and the MO with more nodes is the antibonding orbital.
$BO = \frac{e_{\text{bonding}} - e_{\text{antibonding}}}{2}$	Here, $BO$ refers to bond order, a measure of the strength of an inter-atomic bond. When electrons occupy bonding orbitals, energy is lowered with respect to the separated atomic orbitals. However, when electrons occupy anti-bonding orbitals, energy is raised.
HOMO	Highest Occupied Molecular Orbital. This is the highest energy molecular orbital that contains at least one electron.
LUMO	Lowest Unoccupied Molecular Orbital. This is the lowest energy molecular orbital that contains no electrons. The HOMO and LUMO of a molecule are generally the orbitals that are most important to the chemistry of the molecule.
MO Energy Levels for Diatomics	The MO energy levels for second row heteronuclear diatomic molecules decrease from left to right across the period (see figure 11). This follows the trend of increasing $Z_{\text{eff}}$ due to decreased shielding in the atoms the make up the molecule. Another important point is that between $\text{N}_2$ and $\text{O}_2$ , a reversal in the relative energies of the $\sigma_{2p}$ and $\pi_{2p}$ MOs is observed. This occurs due to the mixing of $2s$ and $2p_z$ AOs when constructing the $\sigma$ MOs in the diatomic molecules before $\text{O}_2$ , raising the energy of the $\sigma_{2p_z}/\sigma_{2p_z}^*$ MOs and lowering the energy of the $\sigma_{2s}/\sigma_{2s}^*$ MOs. Beyond $\text{O}_2$ , the energy gap between $2s$ and $2p$ is too large to allow such mixing, so the energy of the $\sigma_{2p_z}$ MO is lowered.

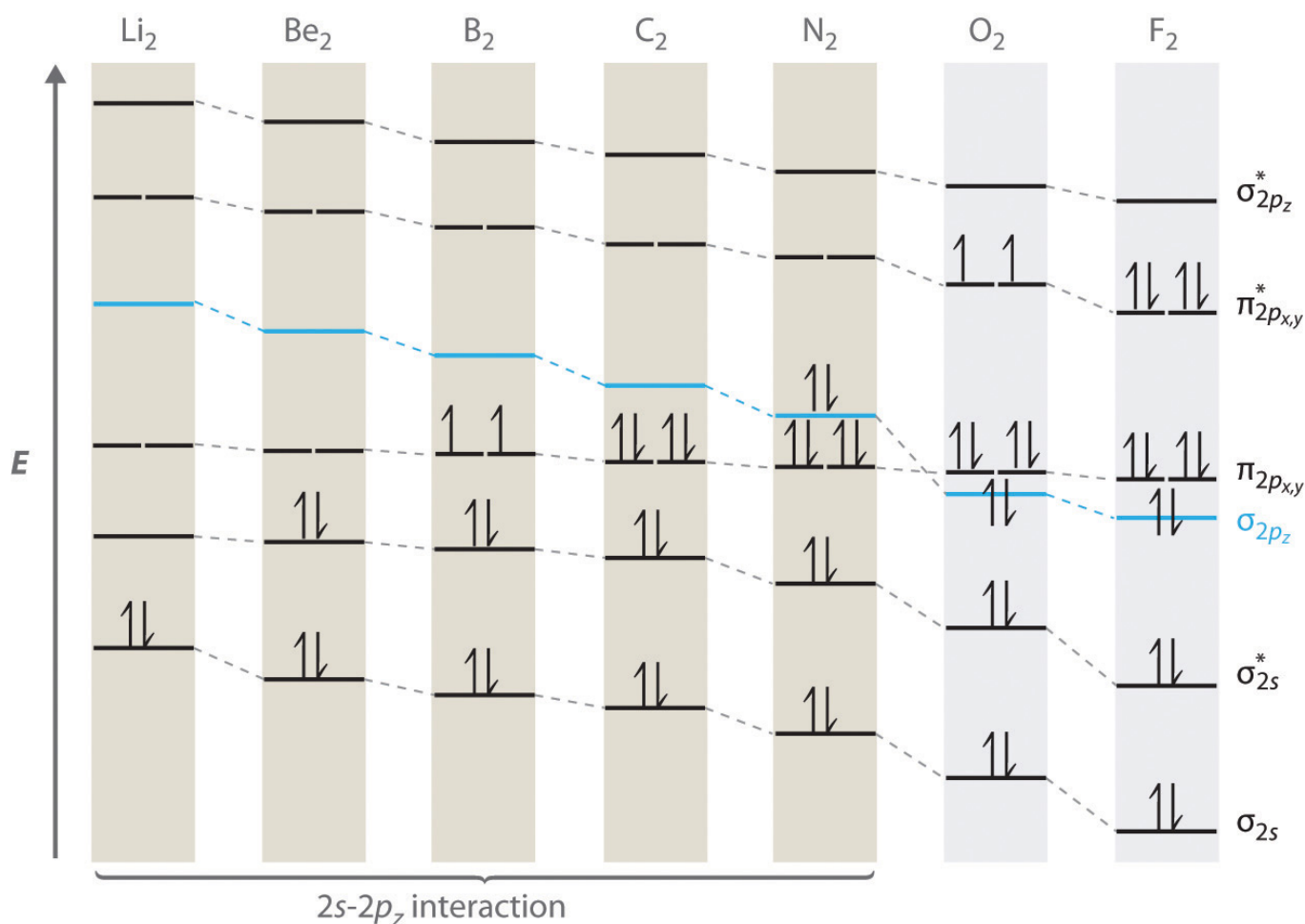


Figure 11: The energy levels of the MOs of the second row heteronuclear diatomic molecules. In the first five molecules, mixing between the  $2s$  and  $2p_z$  AOs of different atoms lowers the energy of the  $\sigma_{2s}$  orbitals but raises the energy of the  $\sigma_{2p_z}$  orbitals enough that it is higher than the  $\pi_{2p_{x,y}}$  orbitals. By the time we reach  $\text{O}_2$ , the  $2s$  and  $2p$  orbitals are well enough separated in energy that the relative energies of the resulting  $\sigma_{2p_z}$  and  $\pi_{2p_{x,y}}$  MOs are reversed.<sup>9</sup>

<sup>9</sup>Taken from <https://chem.libretexts.org/>



## Chapter 9 - Valence Bond Theory

Equation or Concept	Info About Equation/Concept
Approximations of VBT	<ol style="list-style-type: none"> <li>1. Each covalent bond is treated as an independent interaction involving overlap of atomic orbitals between the bonding atoms. This approximation works fairly well except when conjugation (resonance) is present.</li> <li>2. Only the overlap between singly-occupied valence atomic orbitals on each atom are considered. Ignore core electrons and lone pair contributions to bonding.</li> <li>3. Assumes no electrons enter into antibonding orbitals. Hence, we ignore antibonding orbitals and each bond in VBT contributes one to the total bond order. This is usually true for “well-behaved” organic molecules.</li> </ol>
Hybridization	<p>Hybridization (see table 1) is the combination of pure atomic orbitals into new hybrid orbitals for the purposes of bonding. By creating linear combinations of pure atomic orbitals on the same atom, we can produce hybrid atomic orbitals with the correct symmetry to produce a bonding pattern in agreement with the observed ground state molecular geometries. For example, we can create a set of two <math>sp</math> orbitals with major lobes pointing along the <math>x</math>-axis in opposite directions by the addition and subtraction of the <math>2s</math> and <math>2p_x</math> orbitals, <math>sp = \sqrt{\frac{1}{2}}(2s + 2p_x)</math> and <math>sp = \sqrt{\frac{1}{2}}(2s - 2p_x)</math>. The factor of <math>\sqrt{\frac{1}{2}}</math> is included to ensure that the orbitals stay <i>normalized</i>, i.e. that the integration over of the square of the entire hybrid wavefunction equals unity. We must keep in mind that orbitals are still probability distributions. During hybridization, atomic orbitals cannot be created or destroyed, so the number of hybrid orbitals is always equal to the number of atomic orbitals that make it up. As usual in quantum mechanics, hybridization only works between orbitals of similar energies (e.g. <math>2s</math> and <math>2p</math> orbitals or <math>3s</math>, <math>3p</math>, and <math>3d</math> orbitals). The energies of a set of hybrid orbitals are all identical, and are the average of the energies of the atomic orbitals that were used to create them (i.e. energy is conserved). Hybrid orbitals are always used to form sigma bonds and/or lone-pair orbitals.</p>
Unhybridized Orbitals	When more valence orbitals are available than are needed for sigma bonding, the remaining electrons are found in unhybridized atomic orbitals. These electrons can be used to form $\pi$ - or even $\delta$ -bonds.
$\sigma$ -Bond	$\sigma$ (sigma) bonds are defined as covalent bonds that are cylindrically symmetric about rotation along the internuclear axis. That is to say, rotations about the vector that points between the nuclei of the bonded atoms will not change the shape of sigma bond orbitals. $\sigma$ -bonds generally have more orbital overlap than other types of bonds, and hence are stronger. Any bond involving hybrid orbitals will always be a $\sigma$ -bond.
$\pi$ -Bond	$\pi$ (pi) bonds are covalent bonds that contain a plane of symmetry directly along the internuclear axis. $\pi$ orbitals contain a nodal plane between two lobes that appear above and below the internuclear axis. $\pi$ -bonds usually occur from overlap between $p$ orbitals that are pointing perpendicular to the internuclear axis, but may also involve $d$ orbitals of the correct symmetry.
$\delta$ -Bond	$\delta$ (delta) bonds are covalent bonds containing four separate lobes of electron density. These are created only from overlap between $d$ or $f$ orbitals of the correct symmetry.

Hybridization	Groups Surrounding Central Atom (Including LP)	Electronic Geometry
$sp$	2	Linear
$sp^2$	3	Trigonal Planar
$sp^3$	4	Tetrahedral
$sp^3d$	5	Trigonal Bipyramidal
$sp^3d^2$	6	Octahedral

Table 1: Summary of the chemically relevant hybrid orbitals.

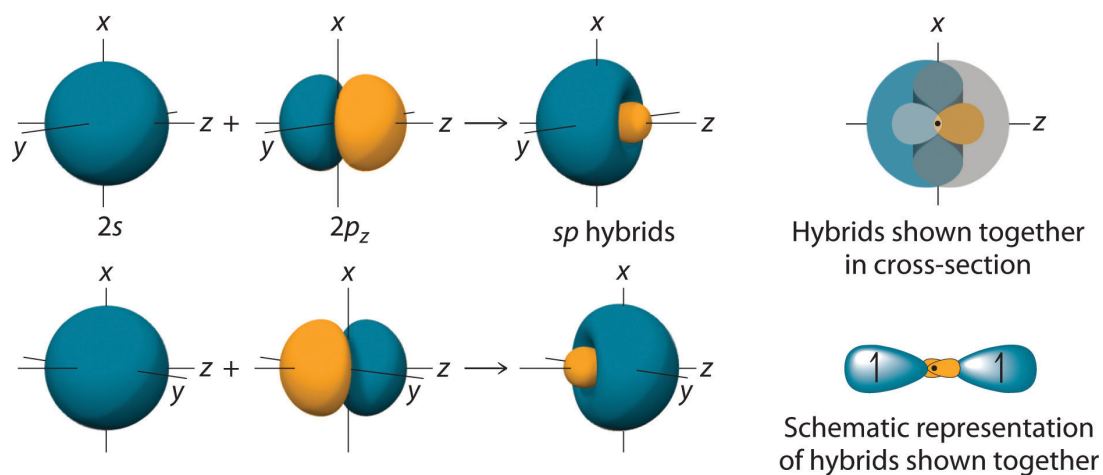


Figure 12:  $sp$  orbitals are created by the summation of one  $s$  orbital and one  $p$  orbital.<sup>10</sup>

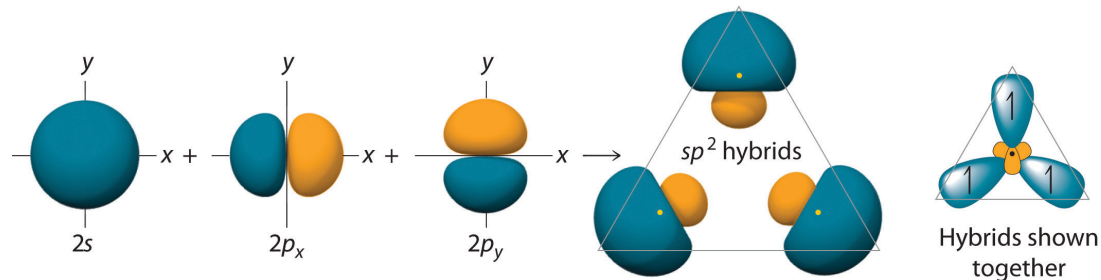


Figure 13:  $sp^2$  orbitals are created by the summation of one  $s$  orbital and two  $p$  orbitals.<sup>10</sup>

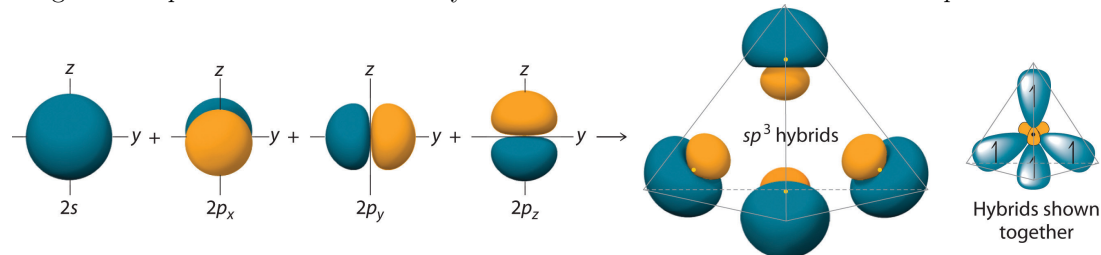


Figure 14:  $sp^3$  orbitals are created by the summation of one  $s$  orbital and three  $p$  orbitals.<sup>10</sup>

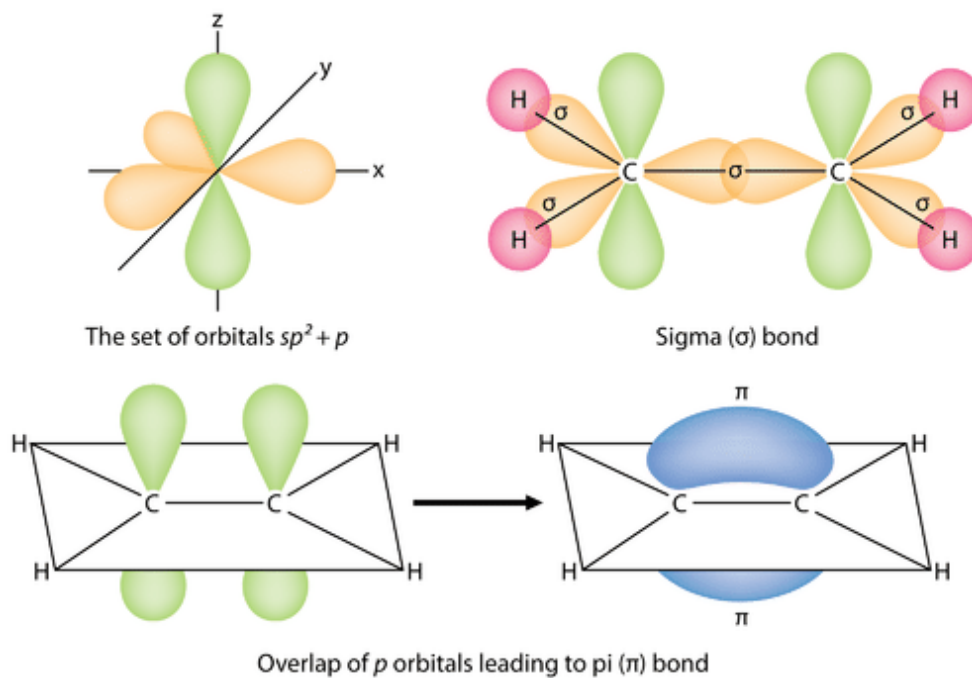
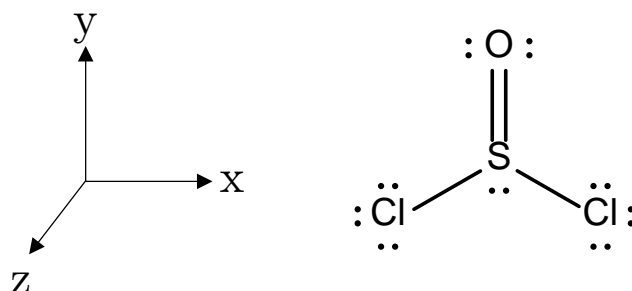


Figure 15: An overview of how hybrid  $sp^2$  orbitals may overlap to form  $\sigma$ -bonds, and how  $p$  orbitals may overlap to form  $\pi$ -bonds.<sup>10</sup>

<sup>10</sup>Taken from <https://chem.libretexts.org/>

## Example of Valence Bond Theory in Practice: $\text{SOCl}_2$

Step 1: Draw the Lewis dot structure of the compound and a reference frame.



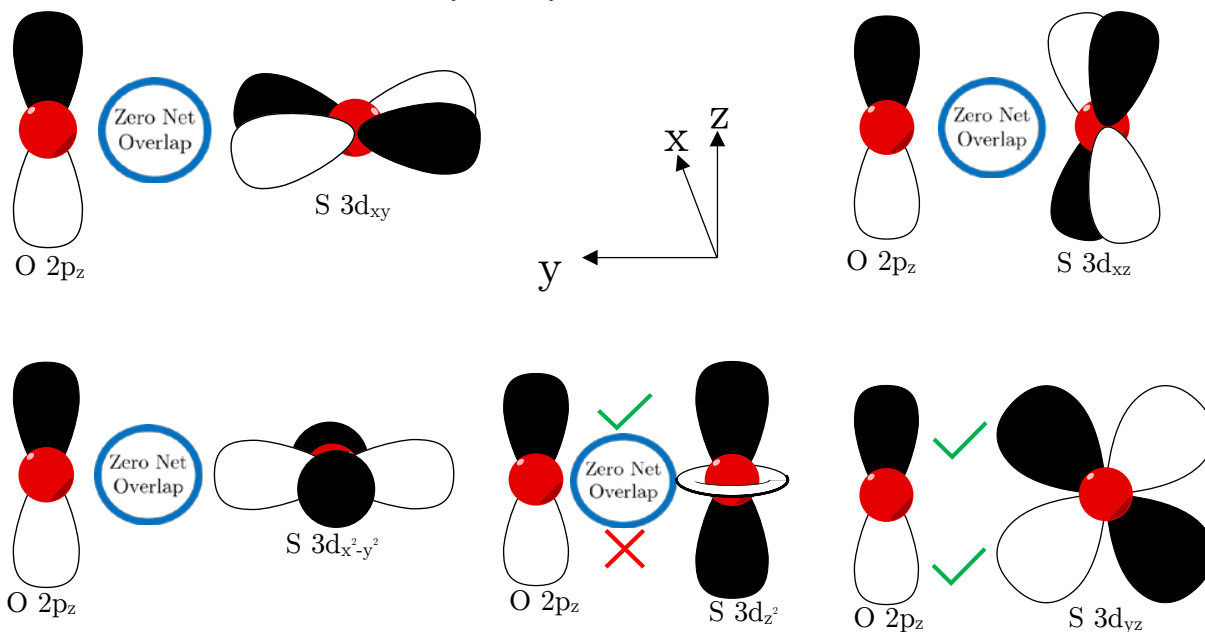
Step 2: Determine the hybridization of each atom by counting the number of bonded groups and lone pairs. Use this to find the parent structure of each atom.

O	1 bonded group + 2 LP $\rightarrow$ $sp^2$ hybrid orbitals $\rightarrow$ Trigonal Planar
S	3 bonded groups + 1 LP $\rightarrow$ $sp^3$ hybrid orbitals $\rightarrow$ Tetrahedral
Cl	1 bonded group + 3 LP $\rightarrow$ $sp^3$ hybrid orbitals $\rightarrow$ Tetrahedral
Cl	1 bonded group + 3 LP $\rightarrow$ $sp^3$ hybrid orbitals $\rightarrow$ Tetrahedral

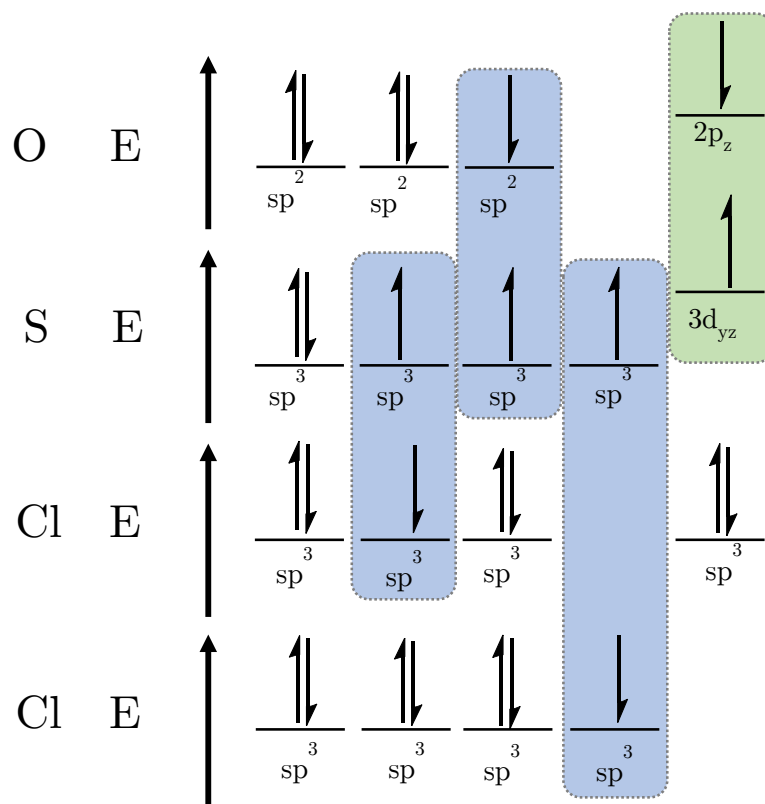
Step 3: For all  $\pi$ -bonds, determine which atomic orbitals are still available for  $\pi$ -bonding.

O	$2s$ , $2p_x$ , and $2p_y$ are used in $\sigma$ -framework $\rightarrow$ $2p_z$ available for $\pi$ -bonding
S	$3s$ , $3p_x$ , $3p_y$ , and $3p_z$ used for $\sigma$ -framework $\rightarrow$ all d orbitals available for $\pi$ -bonding

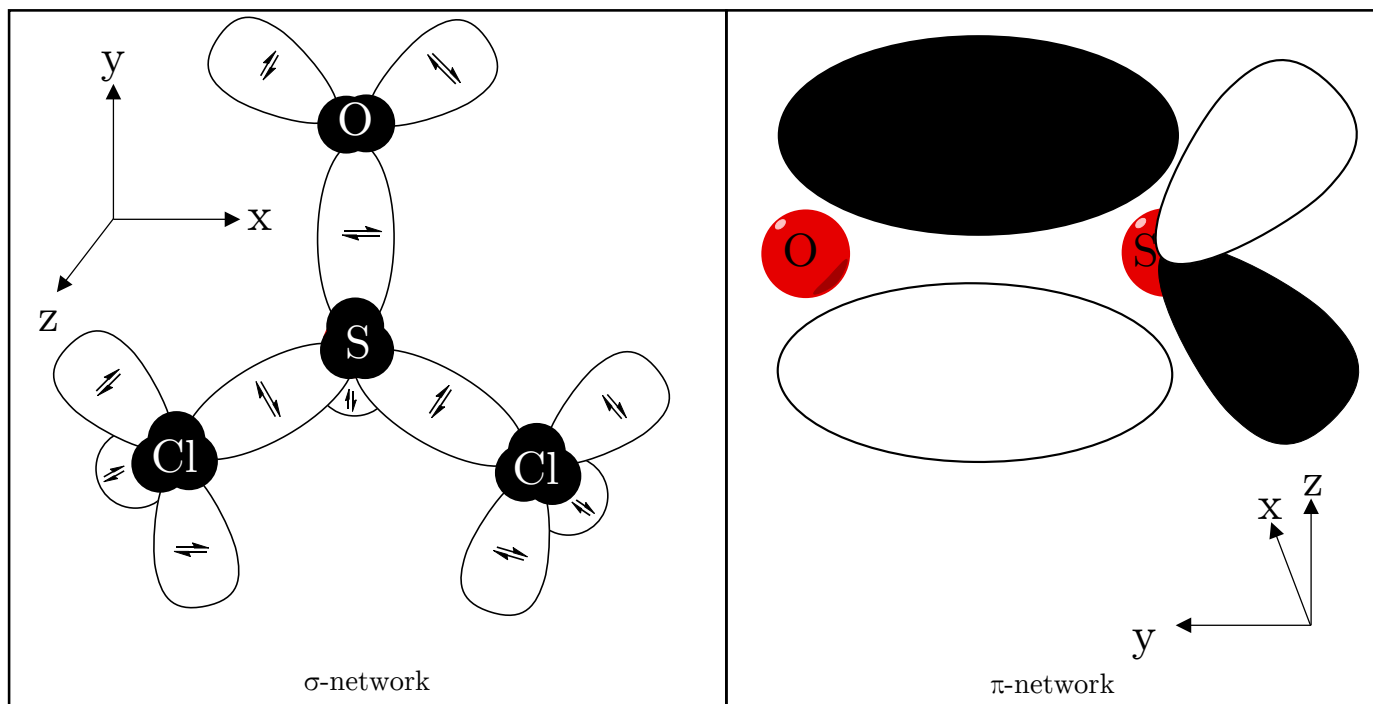
Step 4: If multiple orbitals are available to form  $\pi$ -bonds, find the one with the correct symmetry to form the bond.



Step 5: Draw out an orbital diagram for each atom's valence electrons and form bonds.



Step 6: Draw out the shapes of the resulting  $\sigma$  and  $\pi$  networks separately



## Chapter 10 - Chemical Origins of Colour

Equation or Concept	Info About Equation/Concept
Conjugated Systems	Conjugated systems are planar arrangements of atoms which all have a set of $p$ -orbitals perpendicular to the plane of the atoms. These $p$ orbitals all overlap constructively to create an extended $\pi$ -system. This overlap is called conjugation and always lowers the energy of the system. In Lewis dot structures, conjugated systems are drawn as alternating single and double/triple bonds. Conjugated systems form bonds that are neither single nor multiple bonds, because pairs of conjugated electrons are typically spread out over more than one bond.
Symmetry and Nodes of $\pi$ MOs	When constructing molecular orbitals out of perpendicular $p$ orbitals to form the $\pi$ molecular orbitals, remember that there are always as many output molecular orbitals as input atomic orbitals. The lowest energy MO should have all the $p$ orbitals constructively interfere, and only have the typical $\pi$ node in the plane of the molecule. The highest energy MO will have $N - 1$ additional nodes, where $N$ is the number of contributing atomic orbitals. That is to say, all of the atomic orbitals will destructively interfere to create the highest energy MO. All intermediate MOs can be constructed by increasing the number of planar nodes that are perpendicular to the plane of the molecule by one for each new MO of increasing energy, and maintaining symmetry of the nodes relative to the center of the $\pi$ system. For MOs with an odd number of input atomic orbitals, molecular orbitals with an odd number of nodes will contain a node that cuts the most central atom in half.
Chromophore	The region of a molecule responsible for absorbing or emitting light.
Opsins	Biological molecules found in the eyes of animals responsible for absorption of visible light. Each type of opsin only absorbs a small range of wavelengths, and contributes to the excitation of an optical neuron upon absorption. Normal human eyes contain three types of opsins. One for short wavelengths of visible light (blues), one for middle wavelengths (greens), and one for longer wavelengths (reds). Colorblindness is usually caused by a mutation that prevents proper production/expression of one or more type of opsin in the eyes, but may also be caused by improper transmission of signals sent to the optic nerve or improper interpretation by the brain itself.
RGB vs CMYK Colour Systems	The RGB colour system (red-green-blue) is an <i>additive colour mixing</i> system. All colours are created by combinations of red, green, and blue light. The RGB system is used by our eyes to interpret colour, and represents how light can be added together. The CMYK colour system (cyan, magenta, yellow, and black) is a <i>subtractive colour mixing</i> system. This system is used in paints and pigments to create colours by subtracting particular wavelengths of light from pure white light. Black is not necessary for subtractive colour mixing, but is included in printers to reduce costs.
$\lambda_{\max}$	The wavelength of light that is absorbed best by a particular compound. It corresponds to the peak in an absorbance spectrum. The colour of a compound that absorbs only with $\lambda_{\max}$ will not be the colour corresponding to that wavelength, but will appear as the colour resulting from the removal of that light from pure white light.
Conjugation Length and Colour	Conjugated systems form sets of extended molecular orbitals that span the length of the entire $\pi$ -system. These molecular orbitals, when filled with electrons, can be approximated as a 1D particles-in-a-box. The difference in energy between the HOMO and the LUMO can then be calculated using $\Delta E = \frac{h^2(n_f^2 - n_i^2)}{8m_e L^2}$ where the length is approximated by the summation of all of the bond lengths plus the covalent radii of the terminal atoms.
Azo Dyes	Azo-type dyes have a chromophore made from double bonded nitrogen connected to carbon containing a $\pi$ system. Azo dyes are conjugated systems containing non-carbon atoms.

Equation or Concept	Info About Equation/Concept
Transition Peak Broadening	In absorption or emission spectra of dyes (especially dyes in solution) peaks corresponding to transitions between different energy levels are usually very broad. This broadening is caused by a variety of factors including: the manifold of possible vibrational and rotational transitions that may simultaneously occur during an electronic transition; the local electronic environment which can perturb the energy levels within molecules; the temperature-dependent Doppler shifting of photons caused by the thermal motion of the emitting molecules; and natural peak broadening due to the Heisenberg uncertainty principle.
Vibrational Transitions	Much like the electronic orbitals of atoms and molecules, the possible vibrational states of molecules are quantized (due to quantum confinement). Molecules cannot vibrate at any arbitrary frequency, but may only vibrate at very specific frequencies, which correspond to particular energies. The energy differences between vibrational states generally correspond to light in the infrared region of the electromagnetic spectrum. Infrared spectra of molecules therefore provide information about the vibrational states within the molecule.
Rotational Transitions	Rotation is quantized in molecules due to confinement. Molecules can only rotate at specific allowed frequencies. Generally, rotational transitions within molecules correspond to light in the microwave and radio frequencies. Microwave spectra therefore provide us with details about the rotational states allowed within a molecule.
Quantum Dots	Quantum dots are nanoparticles of semiconductors whose absorbance and emission properties depend on the size of the nanoparticle. Quantum dots are less than 100 nm in size along at least one dimension, and are therefore small enough to introduce quantum confinement. The valence electrons of quantum dots can be modeled with the mathematics of the quantum particle-in-a-box, and as such contain discrete energy levels that are inversely proportional to box length (particle size). Smaller quantum dots <i>fluoresce</i> (emit) at higher energy and shorter wavelengths, while larger quantum dots fluoresce at longer wavelengths. The colour of quantum dot solutions can be <i>tuned</i> by modifying the nanoparticle size, which is changed by modifying the reaction time and temperature. Longer reaction times lead to larger quantum dots.
Types of Radiation	There are many types of radiation, some types are harmless while others are very dangerous. Radiation that contains enough energy to ionize electrons from molecules is known as <b>ionizing radiation</b> . Ionizing radiation includes: ultraviolet light, X-rays, gamma-rays, $\alpha$ and $\beta$ particles emitted from nuclear decay, and high energy neutrons produced from nuclear reactions. Ionizing radiation has the potential to damage biological molecules including cellular DNA. Non-ionizing radiation does not contain enough energy per particle to ionize biological molecules, and hence can only do damage to humans through absorptive heating. Photons with energies less than that of UV light are usually non-ionizing (visible, infrared, microwave, and radio). Visible light may contain enough energy per photon to ionize some molecules.

## Example of Using the Particle-in-a-box Model for Extended Conjugated Systems

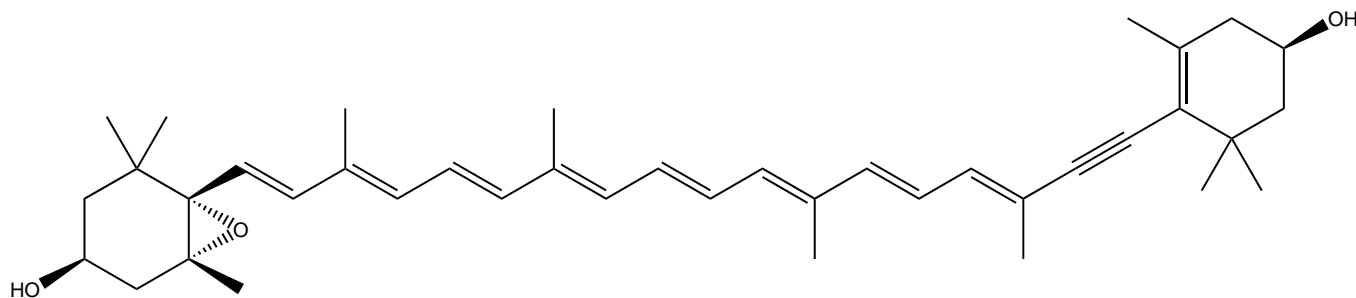


Figure 16: Diadinoxanthin, an orange pigment found in phytoplankton.

Step 1: Locate the atoms which contribute to the extended  $\pi$  system.

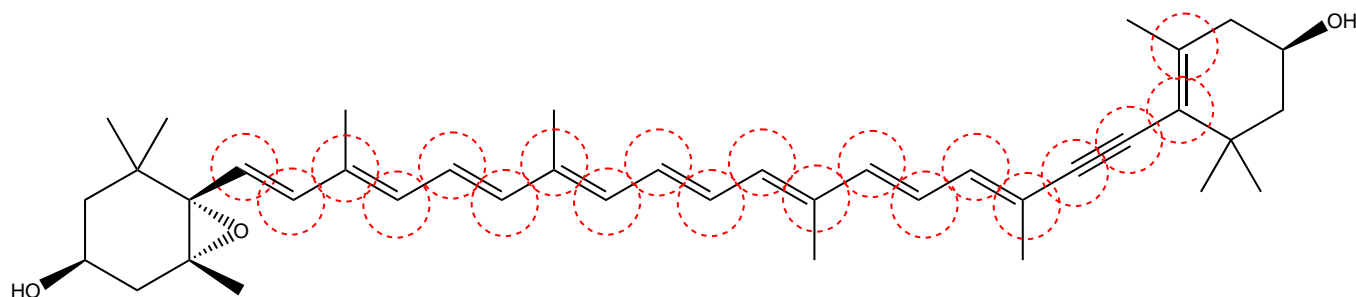


Figure 17: Contributing atoms *must* have unhybridized  $p$ -orbitals with the correct symmetry available to form  $\pi$ -bonds with. Both  $sp^2$  and  $sp$  hybridized atoms may contribute. Non-carbon atoms (often called heteroatoms) can contribute to conjugation. Diadinoxanthin contains 20 carbon atoms that contribute to its extended  $\pi$  system, circled in red above. Therefore, there will be 20  $\pi$  molecular orbitals in the conjugated system.

Step 2: Figure out the quantum numbers of the HOMO and LUMO.

Each carbon atom involved in the conjugated  $\pi$  system contributes one electron to  $\pi$  molecular orbitals. Each  $\pi$  molecular orbital can hold two electrons. Hence, the first 10  $\pi$  molecular orbitals will be fully occupied, making the 10<sup>th</sup> orbital the HOMO. The 11<sup>th</sup> orbital will be the LUMO.

Step 3: Calculate the “box length”.

There are 9 C–C single bonds, 9 C–C double bonds, 1 C–C triple bond, and two terminal carbon atoms. Sum up all of the bond lengths plus the radii of the terminal atoms to obtain an approximate box length:  $9 \times 1.54 \text{ \AA} + 9 \times 1.35 \text{ \AA} + 1 \times 1.20 \text{ \AA} + 2 \times 0.77 \text{ \AA} = 27.98 \text{ \AA} = 2.798 \times 10^{-9} \text{ m}$ .

Step 4: Use the particle-in-a-box energy equation to calculate  $\Delta E$  between the HOMO and LUMO.

$$\begin{aligned}\Delta E = E_f - E_i &\approx \frac{h^2 n_f^2}{8m_e L^2} - \frac{h^2 n_i^2}{8m_e L^2} = \frac{h^2 (n_f^2 - n_i^2)}{8m_e L^2} \\ &= \frac{(6.626 \times 10^{-34} \text{ J s})^2 (11^2 - 10^2)}{8(9.11 \times 10^{-31} \text{ kg})(2.798 \times 10^{-9} \text{ m})^2} = 1.616 \times 10^{-19} \text{ J}\end{aligned}$$

Step 5: Convert the energy to a photon wavelength and determine the colour, compare with the real absorption.

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ m s}^{-1})}{1.616 \times 10^{-19} \text{ J}} = 1.230 \times 10^{-6} \text{ m} = 1230 \text{ nm}$$

This would imply that diadinoxanthin absorbs in the infrared region. In reality, diadinoxanthin absorbs at wavelengths of approximately 400 – 480 nm. The crude approximation used here does not account for many factors!

## Chapter 11 - Physical Properties and Chemical Reactivity

Equation or Concept	Info About Equation/Concept
Boiling	Boiling is the change from liquid to gas. In order to boil a liquid, energy must be absorbed from the surroundings and converted into thermal energy within the liquid; hence, boiling is an endothermic process. This energy is used to overcome the intermolecular forces between liquid particles. Long, heavy molecules tend to have more intermolecular forces than small molecules and so require higher temperatures to boil.
Melting	Melting is the change from solid to liquid. Melting is an endothermic process, much like boiling. Melting occurs when the thermal energy of a solid becomes so great that the particles can overcome the intermolecular forces that kept the particles fixed in place. The molecules then begin to glide past one another.
Intermolecular forces	Intermolecular forces are forces that occur <i>between</i> molecules. Covalent bonds are not intermolecular forces, but are considered <i>intramolecular</i> interactions. There are many types of intermolecular forces. The following is an incomplete list in order from strongest to weakest: ionic forces, ion-dipole forces, hydrogen bonding, dipole-dipole forces, dipole-induced dipole, and London dispersion forces. Additional types of forces can be created by other combinations of ionic, dipolar, and induced dipolar interactions. Substances with stronger intermolecular forces have higher melting and boiling points.
Dipole-Dipole Interaction	Dipole-dipole interactions are attractive intermolecular forces that occur between polar molecules involving interaction between permanent molecular dipole moments. For example, water's permanent dipole moment can interact with polar solutes to help dissolve them by lowering the energy of solvation with an attractive interaction. Dipole-dipole interactions decay proportional to $\frac{1}{r^3}$ with increasing distance $r$ .
Hydrogen Bonding	Hydrogen bonding is an important intermolecular interaction that appears between substances containing hydrogen covalently bonded to a very electronegative element (such as O or F) and a second-row electronegative element with a lone pair. The interaction is similar to a regular dipole-dipole interaction but involves the sharing of significant electron density, and therefore behaves like a very weak covalent bond. Because orbital overlap is involved, hydrogen bonding cannot occur between hydrogen's 1s orbital and elements whose valence electrons lie in the $n = 3+$ shells; the energy difference is too great for significant orbital overlap. Hydrogen bonding is responsible for many of water's unique chemical properties.
London Dispersion Forces	The dispersion force is the weakest of all intermolecular forces. It is caused by an instantaneous dipole moment created by random electron movement that induces a dipole on neighboring atoms or molecules. The result is a very weak electrostatic force. The dispersion force is the dominant intermolecular force only in compounds with no other intermolecular forces, such as non-polar compounds or noble gases. The dispersion force may become significant for very large molecules, where lots of tiny forces add up to a strong interaction (much like in Velcro). Dispersion forces decay proportional to $\frac{1}{r^6}$ .
Solubility	Solubility is the tenacity of a substance to dissolve in a particular solvent. Solvents are fluids that make up the bulk of a solution. Solute are compounds that are added to solvents to make a solution. Dissolution occurs when the intermolecular forces between solvent and solute are stronger than the intermolecular forces between different solute molecules AND different solvent molecules. Polar compounds have relatively strong intermolecular forces (dipole-dipole interactions), and require polar solvents to overcome these. Hence, polar solutes dissolve in polar solvents. Non-polar compounds have very weak intermolecular forces, so non-polar solutes can easily dissolve in non-polar solvents. However, the strong intermolecular forces in polar solvents prevent dissolution of non-polar solutes. Likewise, the strong intermolecular forces in polar solutes prevent their dissolution in non-polar solvents. In summary: "like dissolves like".
Polarizability	This is the ease at which an atom or molecule's electronic cloud can be perturbed, or polarized. Larger atoms with a weaker bond to their outer electrons are more polarizable, especially if negatively charged. Atoms and molecules that are more polarizable have stronger dispersion interactions.



Equation or Concept	Info About Equation/Concept
Ionic Solids	Ionic solids are compounds that consist of positive and negatively charged ions that are bound together by ionic bonds. These ionic interactions are very strong, so ionic solids have very high melting points and high boiling points. Ionic solids form a 3D network of ionic bonds called a <b>crystal lattice</b> .
Lattice Energy	The difference in energy between free ions and ions in a crystal lattice. It is a description of the totality of the Coulombic interactions that occur within a crystal, per ion pair (or mole of ion pairs). Lattice energy is higher when ions have a larger charge, and when ions are closer together in the crystal lattice (i.e. when ions are smaller).
Metallic Bonding	In metallic compounds, the molecular orbitals that form for the valence electrons are non-local and extremely closely spaced in energy. Electrons are free to move between nuclei in what is described as a “sea of electrons”. The intermolecular interactions within metals are very strong, with an extended covalent character that gives it many of the metallic properties seen in metals. Metals conduct heat and electricity very efficiently, and usually reflect almost all wavelengths of visible light.
Molecular Solid	Molecular solids are non-ionic solid compounds. Their intermolecular forces are strong enough to form a solid. Generally, molecular solids have low melting and boiling points. Molecular solids may be further categorized into polar molecular solids — whose primary intermolecular forces are dipole-dipole interactions — and non-polar molecular solids — whose primary intermolecular forces are dispersion forces. Another type of molecular solid, known as a network covalent solid, is a solid which contains covalent bonds between all neighboring atoms, effectively forming one huge molecule. Network covalent solids have very high melting points.
Allotrope	The different physical forms that an element can exist in. For example, carbon can exist as several allotropes: charcoal, diamond, graphite, and even spherical C <sub>60</sub> molecules known as buckminsterfullerene.
Condensation Reaction	A chemical reaction that produces a new covalent bond between two reactants while simultaneously producing a small molecule (see figure 18).
Soaps	Soaps are compounds made up of molecules with a non-polar chain attached to a charged or highly polar “head”. When dissolved in water, soap molecules arrange themselves into clumps called <b>micelles</b> , with the non-polar chains pointing towards the center of the micelle and the polar heads pointing outwards to interact with the water solvent. Micelles can trap non-polar substances within them, making soaps an effective way to remove non-polar oils and greases. Soaps are created by reacting naturally occurring triacylglycerol (AKA triglycerides) — found in animal fats and plant oils — with a strong base, such as sodium hydroxide (NaOH).
Saturated Fatty Acid	A fatty acid chain containing only C–C single bonds. The chain is saturated with hydrogen atoms.
Unsaturated Fatty Acid	A fatty acid chain containing at least one C–C double bond. Monounsaturated fatty acids contain only one C–C double bond, while polyunsaturated fats contain multiple C–C double bonds.

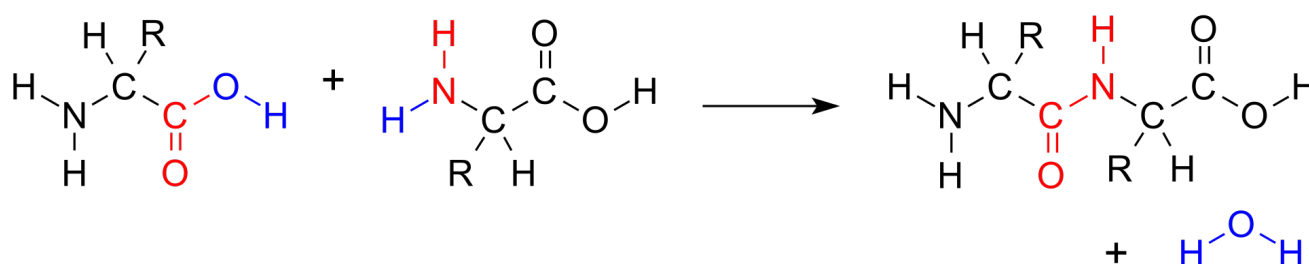


Figure 18: An example of a condensation reaction. Condensation reactions may also occur between carboxylic acids and alcohols to produce a water molecule, or acyl halides and alcohols to produce a hydrogen halide molecule.

## Chapter 12 - Introduction to Polymers

Equation or Concept	Info About Equation/Concept
Polymers	<b>Polymers</b> (Greek “poly” = many, “mer” = parts) are high molecular weight chains of monomers. <b>Monomers</b> are the repeat molecular units of polymers, usually only a few atoms in size. Monomers generally have very different physical and chemical properties than the emergent properties that appear in the polymers they make up. Reactions that produce polymers from monomers are called <b>polymerization</b> reactions. <b>Oligomers</b> are short chain polymers, around 3–10 monomers long. <b>Dimers</b> are bonded pairs of monomers, or oligomers of length two.
Degree of Polymerization	The number of monomers in a polymer chain; the polymer size.
Linear Polymers	Polymers made up predominantly of single linear chains.
Branched Polymers	Polymers made up of many branching chains.
Crosslinked/Network Polymers	Polymers that contain additional covalent bonds between polymer chains (or within chains), leading to extremely high molecular weight polymers and changes in physical and chemical properties. Crosslinked polymers are more rigid and more heat/cold resistant. Crosslinking is often achieved through disulfide linkages, such as in the vulcanization of rubber.
Vulcanization	Vulcanization is the process of crosslinking polymer chains of rubber through addition of S <sub>8</sub> molecules and heat. The process of vulcanization forms sulfur crosslinkages between strands of polymers. The length of sulfur crosslinkages can be between two and eight sulfur atoms long, and depends on the particular conditions of the vulcanization reaction. Rubber with shorter crosslink chains is heat resistant but less flexible. Rubber with long crosslink chains is less heat resistant and more flexible.
Crystallinity	Ordered, organized regions of polymers are called <b>crystalline</b> regions. The degree of crystallinity is a measure of how ordered a region of a polymer is. Non-crystalline regions are called <b>amorphous</b> .
Elastomers	Amorphous polymers that can be stretched and return to their original shape due to crosslinking.
Thermoplastics	Thermoplastics are polymers that are hard at room temperature, but soften when heated due to a weakening of the intermolecular forces holding the individual polymer chains together. <b>Thermosets</b> are plastics that are heavily crosslinked during synthesis. Once formed they cannot be easily re-molded.
HDPE vs LDPE	High density polyethylene (HDPE) is a <b>thermoplastic</b> that has high tensile strength, low density polyethylene (LDPE) is much more flexible with lower tensile strength. HDPE is mostly made of linear chains, whereas LDPE has a heavily branched structure. HDPE is more crystalline, whereas LDPE is very amorphous.
Chain-Growth Polymerization	The type of polymerization reaction that involves the linear growth of a polymer chain after the initial reaction is started by an <b>initiator</b> . Also known as addition polymerization. In chain-growth polymerization, the growing polymer chain contains a reactive site at one end where new monomers attach one at a time. The most common type of chain-growth polymerization begins with a radical initiator (such as peroxide plus light) adding to an alkene, resulting in a reactive radical intermediate that chain-reacts with the next monomer and so on until there are no more monomers available or the reaction is stopped by reaction with another radical (termination). There is much more control over the chain length of polymers which undergo polymerization through chain-growth polymerization, as the starting amount of initiator determines the number of polymer chains that can form. Chain-growth polymerization occurs in three steps: <b>initiation</b> , <b>propagation</b> , and <b>termination</b> (see figure 19).
Step-Growth Polymerization	This type of polymerization reaction involves the addition of monomer units to a polymer chain without the need for an initiator. Step-growth polymerization tends to form a much wider range of molecular weight polymers, it is also known as condensation polymerization. Step-growth polymerization always proceeds by releasing a small molecule as a new monomer-polymer (or monomer-monomer) covalent bond is formed. As such, step-growth polymerization requires monomers with more than one functional group to react together.

Equation or Concept	Info About Equation/Concept
Copolymers	In step-growth polymerization, often two or more monomers are reacted together to form a polymer of alternating monomer types. These monomers are called copolymers.

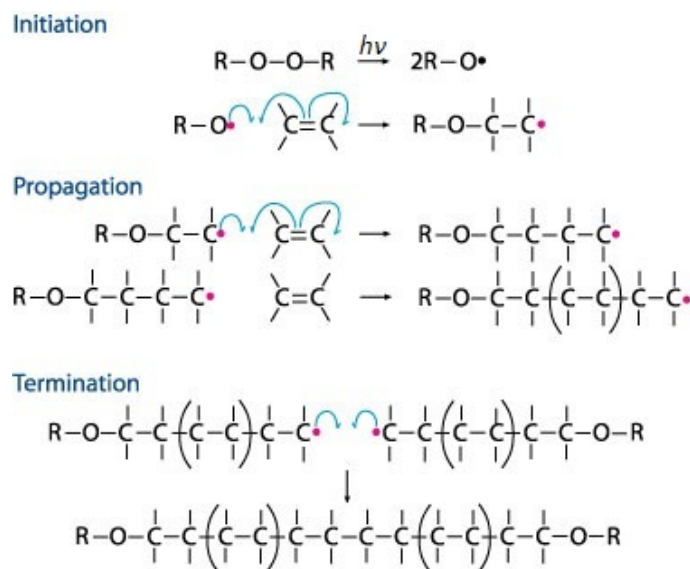


Figure 19: Overview of a chain-growth polymerization reaction, initiated by a peroxide whose single O-O bond is broken by a photon of light with a specific energy  $h\nu$  (usually UV light).<sup>11</sup>

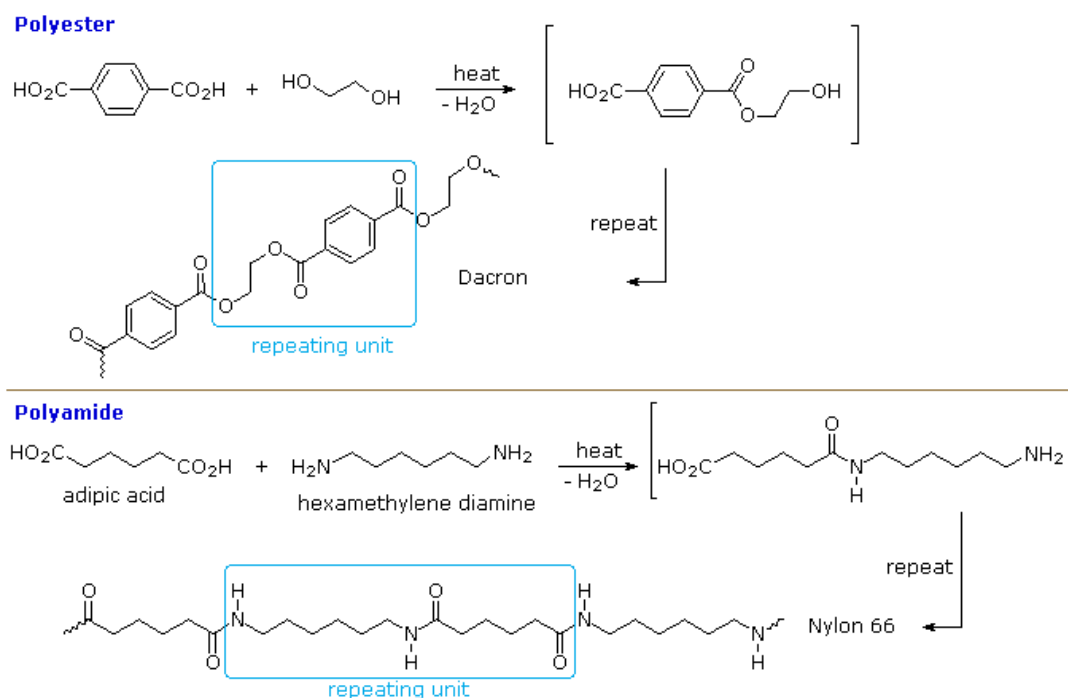


Figure 20: Two examples of step-growth polymerization reactions and their resulting polymers.<sup>12</sup>

<sup>11</sup>Taken from [http://preparatorychemistry.com/Bishop\\_Addition\\_Polymers.htm](http://preparatorychemistry.com/Bishop_Addition_Polymers.htm)

<sup>12</sup>Taken from <https://chem.libretexts.org/>

## Appendix - Why are orbitals with smaller $\ell$ values lower in energy for multi-electron species?

It turns out that the full answer to this question is a fairly complicated. The information in this appendix is not part of the CHEM 121 course, but is included in this study guide to help give a better conceptual understanding of the aufbau principle and its exceptions. If you are content with simply memorizing the aufbau principle and its exceptions, feel free to ignore this section and the next.

### A first Approximation

Let's begin with a somewhat hand-wavy explanation of the simplest possible case: the comparison between the  $2s$  and  $2p$  orbitals. The radial probability distributions of these two orbitals are compared with the  $1s$  orbital in figure 21. Notice that the  $2p$  orbital's most probable  $r$  is actually closer to the nucleus than the  $2s$  orbital; this seems to imply (via Coulomb's law) that the  $2p$  orbital should be lower in energy. However, the  $2s$  orbital has a small lobe of probability density very near to the nucleus—behind the peak of the  $1s$  orbital—that the  $2p$  orbital lacks. In single-electron species, these two facts appear to exactly cancel each other out and both orbitals have identical energy.

In multi-electron species, both the  $2s$  and  $2p$  orbitals are screened by the  $1s$  orbital electrons. However, the  $2s$  orbital's inner lobe penetrates behind the bulk of the electron density of the  $1s$  orbital, and hence has highly reduced screening in this region. This inner lobe acts as a strong Coulombic “anchor” for the  $2s$  orbital, whose energy is substantially lowered compared to the  $2p$  orbital because of this reduced screening.

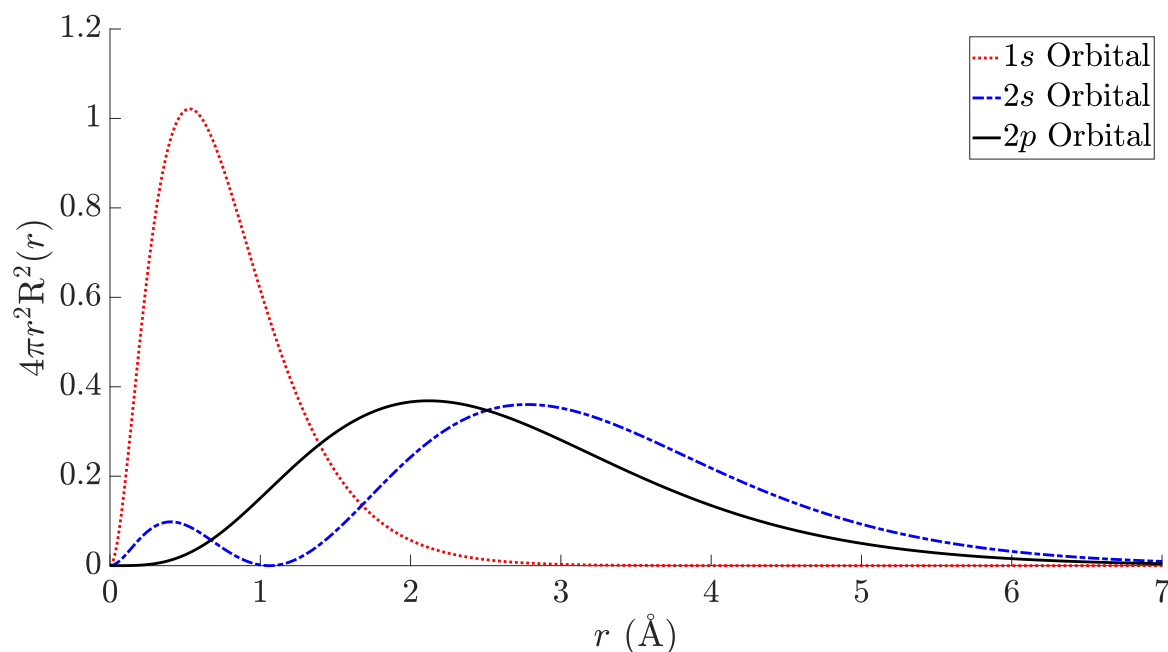


Figure 21: A comparison of the radial probability distributions of  $1s$ ,  $2s$ , and  $2p$  orbitals in the hydrogen atom; i.e. the probability density of finding an electron in a spherical shell at any given distance  $r$  from the nucleus. The total area under each of these curves has been *normalized* to exactly 1. For multi-electron species, the radial probability distributions do not have known exact analytical forms, but are only slightly different than the pure H orbitals in their shape and relative physical extent. The relative differences in orbital shape come about because of electron-electron repulsive interactions; increasing the atomic number  $Z$  does not change the shapes and extent of orbitals relative to each other, but “pulls in” all orbitals closer to the nucleus.

### An advanced explanation

The above explanation may have helped to give a better understanding of the problem, but it is definitely lacking in detail. In this section, I will attempt to give a more advanced physics-based description of why orbitals with the same principle quantum number  $n$  but smaller  $\ell$  are lower in energy for multi-electron species. Perhaps the best starting point to address this question is the  $\ell$  degeneracy of hydrogenic (one-electron) species.

In hydrogenic atoms, the Coulombic potential experienced by the electron in its orbital has the form  $k \frac{e^2 Z}{r}$  where  $e$  is the elementary charge,  $k$  is a constant, and  $Z$  is the nuclear charge. One of

the most famous principles in physics was discovered by a woman that even Einstein considered a genius: Emmy Noether. Her most famous theorem, called Noether's theorem, basically states that all physical symmetries lead to conserved quantities. One example of such a symmetry is translational symmetry, which leads to the conservation of momentum; another is temporal symmetry, which leads to the conservation of energy.

Notice that the potential  $k\frac{e^2Z}{r}$  has rotational symmetry: it has no angular dependence. This rotational symmetry leads to conservation of angular momentum with respect to direction for any rotating object experiencing this potential. The length of the angular momentum vector for electrons in orbitals is defined by the quantum number  $\ell$  for any  $n$ . Hence, the energy of all electronic states with the same value of  $n$  and  $\ell$  does not depend on  $m_\ell$  (which defines the direction of the orbital's angular momentum vector), so long as the potential is rotationally symmetric. This explains  $m_\ell$  degeneracy, but what about  $\ell$  degeneracy in hydrogenic species? There must be some associated symmetry that causes the degeneracy related to the form of the  $\frac{k}{r}$  potential.

The symmetry we are looking for is called the SO(4) symmetry. It is not a geometric symmetry like the rotational symmetry previously discussed, but a so-called dynamic symmetry. This dynamical symmetry conserves a particular quantity known as the Laplace-Runge-Lenz vector  $\vec{M}$ , and it can be shown<sup>13</sup> that this conserved quantity leads to the  $\ell$ -independent energy spectrum with  $E \propto \frac{1}{n^2}$ . As soon as the  $\frac{k}{r}$  type potential form (called a Kepler potential) is perturbed—as is the case when electron-electron repulsion occurs in multi-electron species—the  $\ell$  degeneracy is broken. This tells us why  $\ell$  degeneracy is broken, but why do lower values of  $\ell$  lead to lower energy orbitals?

States of higher angular momentum (i.e. higher values of  $\ell$ ), experience a stronger centrifugal force. We know this from everyday experience: when we rotate an object faster, the object tends to pull itself outward with more force. This centrifugal force increases the average distance of an electron from the nucleus for higher values of  $\ell$ . Hence, it tends to increase the energy of higher  $\ell$  states. At the same time, there is a quantum-mechanical interaction known as Pauli core repulsion that puts an “energy penalty” on states with lower angular momentum.

One of the fundamental postulates of quantum mechanics, the Pauli exclusion principle, forces all electron orbitals to be orthogonal to each other. Orthogonality means that the net overlap (constructive plus destructive interference) of their wavefunctions must be zero. States with different values of  $\ell$  are automatically orthogonal to each other due to the orbital shapes<sup>14</sup>. However, states with the same value of  $\ell$  but different values of  $n$  must also have a net overlap of zero. Take a look at figure 22 and notice that the net overlap between the 1s and 2s orbitals does indeed appear to be zero! The fact that orbitals with different principal quantum number  $n$  and the same value of  $\ell$  must be orthogonal forces the higher principal quantum number orbitals further away from the nucleus. Since electrons further from the nucleus experience a smaller force (Coulomb's law), this core repulsion “force” tends to raise the energy of higher  $n$  orbitals. There are always more orbitals near the core with low values of  $\ell$  (there are no 1p or 1d orbitals after all), hence low  $\ell$  orbitals experience Pauli core repulsion from a greater number of orbitals, which tends to force them further outward. Hence, low  $\ell$  orbitals are more affected by this repulsive force than high  $\ell$  orbitals.

The  $\ell$  degeneracy seen in hydrogenic atoms can be thought of a perfect balance between the effects of the centrifugal force and Pauli repulsion, both of which raise the energies of orbitals with different  $\ell$  values to differently. In multi-electron atoms, electron screening comes into play. The core electrons experience a greater effective charge from the nucleus and hence their orbitals are contracted to a greater degree than the outer electrons. This reduces the Pauli repulsion on the outer orbitals, with a greater effect on low- $\ell$  orbitals. Overall, the energy of low- $\ell$  orbitals is not raised by Pauli core repulsion to the same extent as was seen in hydrogenic atoms. On the other hand, the centrifugal force remains unaffected by electron-electron repulsion, and so raises the energy of high- $\ell$  orbitals just as before. The net effect is that the two forces are no longer in balance, and  $\ell$  degeneracy is broken.

<sup>13</sup><http://hep.uchicago.edu/~rosner/p342/projs/weinberg.pdf>

<sup>14</sup>Think of the net overlap between a 1s orbital and a 2p orbital on the same atom. The constructive overlap is exactly equal to the destructive overlap due to the shapes of the orbitals.

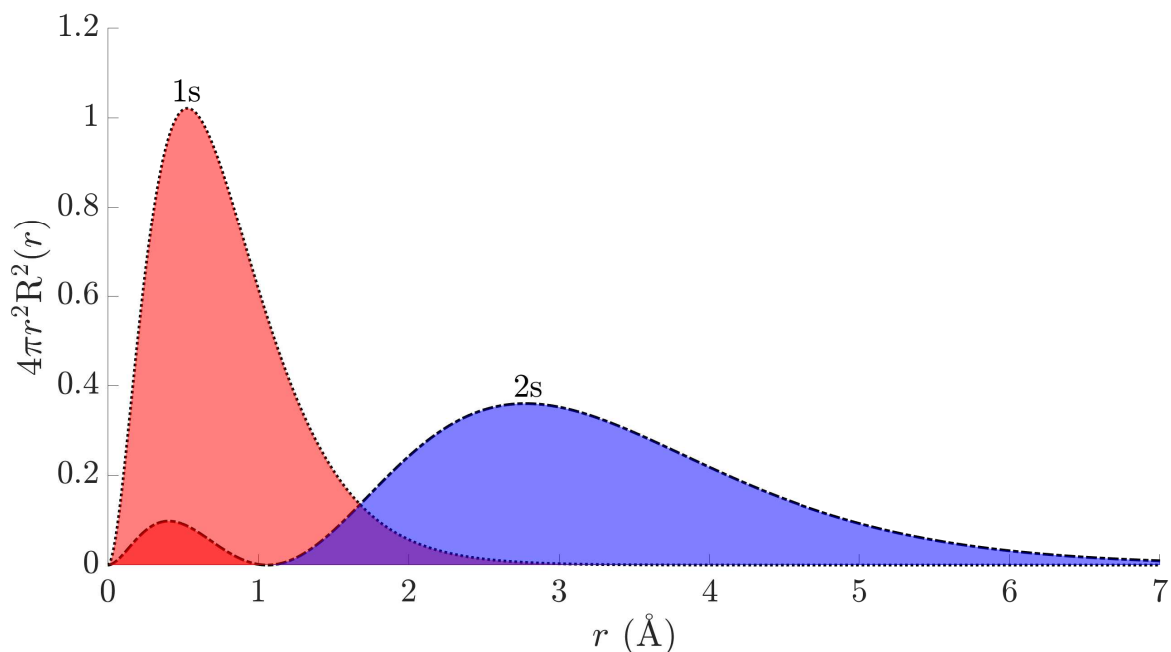


Figure 22: A closer look at the overlap between the 1s and 2s orbitals. Notice the amount of constructive overlap (dark red region) is exactly equal to the amount of destructive overlap (purple region).

### On the exception to the aufbau principle for fourth row transition metal ions

This information in this section is also not part of the CHEM 121 course. I have included it here for general interest. The question I would like to address is the following: why do we observe that, upon ionizing transition metals in the fourth row of the periodic table, the relative energies of the 4s and 3d orbitals are reversed? We see that the 3d orbital becomes lower in energy than the 4s!

As we saw in the previous section, increased screening from core electrons tends to reduce Pauli core repulsion. Since there is a higher number of Pauli interactions for lower  $\ell$  orbitals, the reduction in Pauli core repulsion works to lower the energy of low- $\ell$  orbitals relative to high- $\ell$  ones of the same principal quantum number. So overall, more screening leads to greater  $\ell$ -splitting.

It turns out that for neutral multi-electron species, the 4s and 3d subshells happen to be very close in energy. Because of this, we have to be careful when determining the electronic configuration of atoms whose valence electrons will occupy these orbitals. The 4s orbitals are spherically symmetric and also reach further in extent than 3d orbitals. On the other hand, 3d orbitals are quite compact in comparison. When building up the electronic structure of fourth row transition metals, the 3d orbitals are actually filled up first as they are lower in energy than the 4s orbitals. However, adding electrons into the compact 3d orbitals increases electron-electron repulsions (i.e. screening) more so than adding electrons to the 4s orbital would. When the last electron is added to transition metals (making them neutral) electron-electron repulsion from 3d orbitals reaches a tipping point, and becomes so great that the energy of the more diffuse 4s orbital drops below that of the 3d orbitals. Both of the last two electrons are then found to occupy the “higher energy” 4s orbital due to the reduction in electron-electron repulsion.

Another way of thinking about this problem is to take the limit of a multi-electron species when  $Z \rightarrow \infty$ . In that limit, we expect that the repulsive interaction of all of the electrons becomes absolutely dwarfed by the interaction of the electrons with the nucleus (i.e.  $Z_{eff} \rightarrow \infty$  as well). Essentially, we would expect that the potential energy surface would return to a hydrogenic  $\frac{k}{r}$  form, and the  $\ell$ -degeneracy of shells would be recovered (although the energy levels themselves would all be infinitesimally spaced).

When electrons are removed from multi-electron species, it is like taking a step in the direction towards  $Z_{eff} \rightarrow \infty$ . We are removing electron screening interactions and pushing the electronic structure towards a hydrogenic form. In the hydrogenic atoms, the energy of the 4s orbital is obviously higher than the 3d orbital, because the orbital energy only depends on  $n$ . Hence, although the energy of both 4s and 3d orbitals are lowered by the removal of an electron, the 3d energy is lowered faster. In the fourth row d-block metals, this is observed as an exception to the aufbau principle, which is really just a guideline anyway.

# Physical Constants and Important Relationships (for Reference)

Constant	Value and Units
Atomic mass unit ( $u$ )	$1\text{ u} = 1.660\,538\,9 \times 10^{-24}\text{ g}$ $1\text{ g} = 6.022\,142 \times 10^{23}\text{ u}$
Avogadro's number ( $N_A$ )	$N_A = 6.022\,142 \times 10^{23}\text{ mol}^{-1}$
Boltzmann's constant ( $k_B = R/N_A$ )	$k_B = 1.380\,648\,52 \times 10^{-23}\text{ J K}^{-1}$
Gas constant ( $R = k_B N_A$ )	$R = 8.314\,459\,8\text{ J K}^{-1}\text{ mol}^{-1}$ $= 8.314\,459\,8 \times 10^{-3}\text{ kJ K}^{-1}\text{ mol}^{-1}$ $= 8.314\,459\,8\text{ kg m}^2\text{ s}^{-2}\text{ K}^{-1}\text{ mol}^{-1}$ $= 8.314\,459\,8\text{ m}^3\text{ Pa K}^{-1}\text{ mol}^{-1}$ $= 0.082\,057\,338\text{ L atm K}^{-1}\text{ mol}^{-1}$ $= 1.987\,203\,6 \times 10^{-3}\text{ kcal K}^{-1}\text{ mol}^{-1}$ $= 8.205\,733\,8 \times 10^{-5}\text{ m}^3\text{ atm K}^{-1}\text{ mol}^{-1}$
Mass of electron ( $m_e$ )	$m_e = 5.485\,799 \times 10^{-4}\text{ u}$ $= 9.109\,383 \times 10^{-31}\text{ kg}$
Mass of proton ( $m_p$ )	$m_p = 1.007\,276\,5\text{ u}$ $= 1.672\,621\,7 \times 10^{-27}\text{ kg}$
Mass of neutron ( $m_n$ )	$m_n = 1.008\,664\,9\text{ u}$ $= 1.674\,927\,3 \times 10^{-27}\text{ kg}$
Planck constant ( $h$ )	$h = 6.626\,069 \times 10^{-34}\text{ J s}$
Reduced Planck constant ( $\hbar$ )	$\hbar = h/2\pi = 1.054\,572\,66 \times 10^{-34}\text{ J s}$
Speed of light ( $c$ )	$c = 2.997\,924\,58 \times 10^8\text{ m s}^{-1}$
Rydberg Constant ( $R_H$ )	$R_H = 2.179\,872\,325 \times 10^{-18}\text{ J (energy)}$ $= 1.097\,373\,156\,850\,8 \times 10^7\text{ m}^{-1}\text{ (wavenumber)}$
Bohr Radius ( $a_0$ )	$a_0 = 5.291\,772\,106\,7 \times 10^{-11}\text{ m}$ $= 0.529\,177\,210\,67\text{ \AA}$
Elementary Charge ( $e$ )	$e = 1.602\,176\,62 \times 10^{-19}\text{ C}$
Electron Volt (eV)	$1\text{ eV} = 1.602\,18 \times 10^{-19}\text{ J}$
Joule (J)	$1\text{ J} = 1\text{ kg m}^2\text{ s}^{-2}$
Coulomb's constant ( $k_e = \frac{1}{4\pi\epsilon_0}$ )	$k_e = 8.987\,551\,787\,368\,176\,4 \times 10^9\text{ N m}^2\text{ C}^{-2}$
Vacuum Permittivity ( $\epsilon_0$ )	$\epsilon_0 = 8.854\,187\,817 \times 10^{-12}\text{ F m}^{-1}$
Vacuum Permeability ( $\mu_0$ )	$\mu_0 = 1.256\,637\,061\,4 \times 10^{-6}\text{ N A}^{-2}$
Important Sums	$\sum_{\ell=1}^n \ell = \frac{1}{2}(n^2 + n) \quad ; \quad \sum_{\ell=0}^{n-1} 2\ell + 1 = n^2$
SI unit conversions	$10^{-9}\text{ Gm} = 10^{-6}\text{ Mm} = 10^{-3}\text{ km} = 1\text{ m} = 10^3\text{ mm} =$ $10^6\text{ }\mu\text{m} = 10^9\text{ nm} = 10^{12}\text{ pm} = 10^{10}\text{ \AA}$



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