

Ch1A Recitation Section 9 Handout (Oct. 1, 2009)

TA: Eric Olmon (olmon@caltech.edu, ericolmon@gmail.com)

Dimensional Analysis (a.k.a. factor-label method, unit-label method, straight line method) is a useful system for keeping track of units.

Example: Given 0.15 moles of a gas at 25.0 °C that occupies a volume of 10.00 cm³, what is its pressure in atm?

$$PV = nRT \rightarrow P = \frac{n}{V} RT$$

$$P = \frac{0.15 \text{ mol}}{10.00 \text{ cm}^3} 8.31447 \frac{\text{J}}{\text{mol K}} (25.0 + 273.15) \text{K} \left(\frac{100 \text{ cm}}{1 \text{ m}} \right)^3$$

$$= 3.7184388 \times 10^7 \frac{\text{mol kg m}^2}{\text{cm}^3 \text{ mol K}} \text{K} \frac{\text{cm}^3}{\text{m}^3}$$

$$= 3.7 \times 10^7 \frac{\text{kg}}{\text{s}^2 \text{ m}}$$

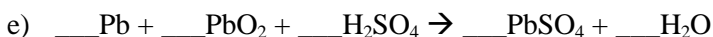
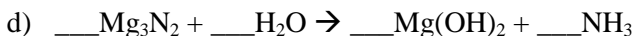
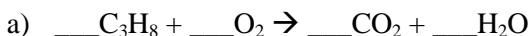
$$= 3.7 \times 10^7 \frac{\text{kg}}{\text{s}^2 \text{ m}} \left(\frac{1 \text{ N}}{\text{kg} \frac{\text{m}}{\text{s}^2}} \right) = 3.7 \times 10^7 \frac{\text{N}}{\text{m}^2}$$

But a N/m² is a Pascal (Pa). Convert from Pa to atm:

$$P = 3.7184388 \times 10^7 \text{ Pa} \left(\frac{1 \text{ atm}}{1.01325 \times 10^5 \text{ Pa}} \right) = 3.6698138 \times 10^2 \text{ atm} = \mathbf{3.7 \times 10^2 \text{ atm}}$$

Chemical Equations and Reactions

1) Balance the following equations



2) Calculate the molecular weight to 5 significant figures of: H₂O, H₂SO₄, CH₄, NaBF₄, P₄O₁₀, BrCl, KMnO₄

3) Starting with 1.2 kg of reactant in problem 1a above, calculate the amount of the first product produced if the reaction goes to completion.

4) In problem 1a above, what volume of water is produced (density water = 1 gm/mL) and if it is frozen on a 1 km² surface how deep is it in cm? (Density of ice, ρ_{ice} = 0.92 g/cm³)

- 5) A solution is made by mixing A and B. Calculate the various concentrations by filling in the following table ($\rho_{\text{H}_2\text{O}} = 1 \text{ g/cm}^3$; $\rho_{\text{CH}_3\text{CH}_2\text{OH}} = 0.789 \text{ g/cm}^3$, density of 50:50 solution by volume of $\text{CH}_3\text{CH}_2\text{OH}$ is 0.96 g/cm^3):

A	B	Molarity Moles per Liter solution	Molality Moles per kg solvent	Mole fraction of solute	% Mass of solute	% Volume of solute
100 mL H_2O	--					
100 mL H_2O	0.010 g H_2					
100 mL H_2O	100 mL $\text{CH}_3\text{CH}_2\text{OH}$					

Working with pressure

- 6) A barometer reads 3 ft of Hg. What is the pressure in Pascals and in psi? (Density of Hg is $1.36 \times 10^4 \text{ kg/m}^3$; $g = 9.807 \text{ m s}^{-2}$)
- 7) When you measure the pressure of your remote-controlled blimp, the gauge reads 5.00 psi. How many moles of H_2 are in your blimp if the volume is 22.4 L and the temperature is $25.0 \text{ }^\circ\text{C}$?

Colligative properties

Vapor pressure lowering	$\Delta P_1 = -X_2 P_2^o$
Boiling point elevation	$\Delta T_b = K_b m$
Freezing point depression	$\Delta T_f = K_f m$
Osmotic pressure	$\pi = \rho gh$ $\pi = cRT$

K_b and K_f are the molal boiling point elevation and freezing point depression constants.

m is expressed as molality (moles solute/kg solvent).

- 8) Add 0.01 kg CaCl_2 to 1 L of water. What is the change in freezing point? ($K_f 1.86 \text{ K mol}^{-1} \text{ kg}$).
- 9) What is freezing point of 1.00 L vodka (50% ethanol by volume)? Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$ has a density of 0.789 g/cm^3). The mixture actually starts to freeze at $-29 \text{ }^\circ\text{C}$. Does this agree with your calculation?

Do the same calculation for 1% alcohol by volume. The actual freezing point is $-0.33 \text{ }^\circ\text{C}$.

Answers

- 1) a. 1, 5, 3, 4; b. 1, 2, 2, 1; c. 1, 2, 2, 1, 1; d. 1, 6, 3, 2; e. 1, 1, 2, 2, 2
 2) 18.015, 98.078, 16.042, 109.79, 283.89, 115.36, 158.03 g mol⁻¹
 3) 3.6 kg
 4) 1.961, 2.1×10⁻⁷ cm thick
 5)

55.5	55.5	1	100	100
5.0×10 ⁻²	5.0×10 ⁻²	0.00090	0.010	--
≈9.2	17.1	.236	44.1	50

- 6) 1.22 × 10⁵ N/m² or 3.00 psi

$$7) n = \frac{PV}{RT} = \frac{\left[5.00 \text{ psi} \left(\frac{1 \text{ atm}}{14.696 \text{ psi}}\right) + 1 \text{ atm}\right] 22.4 \text{ L}}{0.0820574 \frac{\text{L atm}}{\text{mol K}} 298.15 \text{ K}} = 1.22708 \text{ moles} = 1.23 \text{ moles H}_2$$

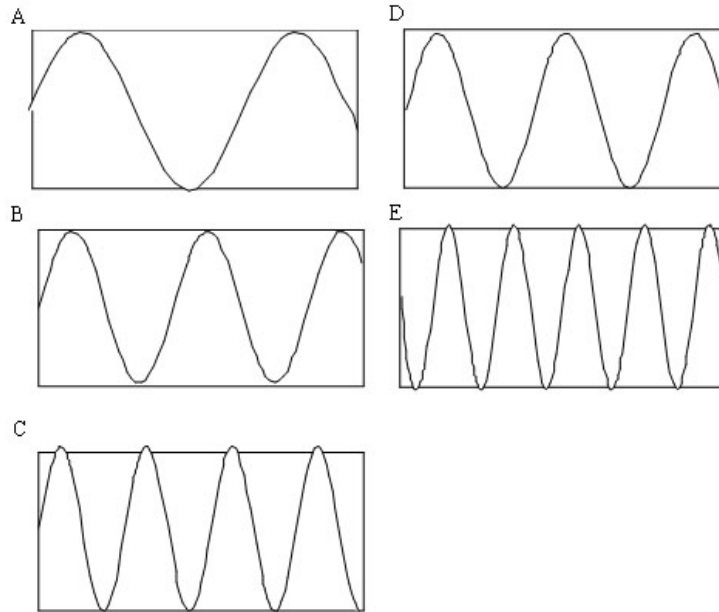
- 8) -0.503 K; CaCl₂ is a strong electrolyte and dissociates completely to yield 3 ions (Ca²⁺, Cl⁻, Cl⁻) for every mole of CaCl₂.
 9) (-31.9 °C not quite right why?)

Ch1A Recitation Section 9 Handout (Oct. 8, 2009)

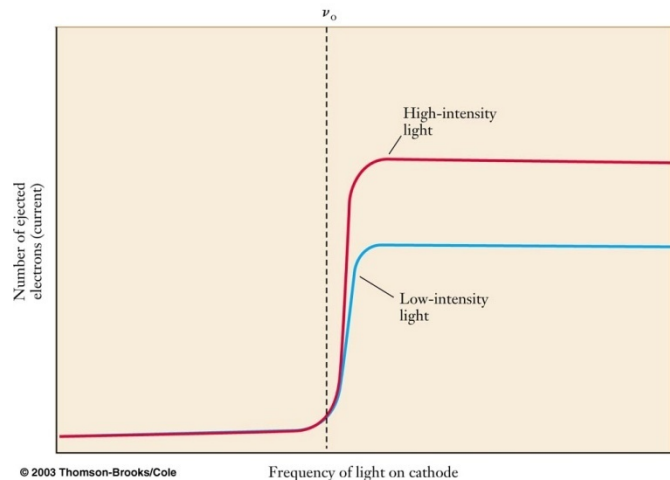
TA: Eric Olmon (olmon@caltech.edu, ericolmon@gmail.com)

- 1) What was the radical idea that Bohr used to construct his model of the atom? Why was it radical?
- 2) Why does Gray say $F = -\frac{e^2}{r^2}$ but Lewis says $F = -\frac{Ze^2}{4\pi\epsilon_0 r^2}$?
- 3) For the Bohr atom, show that the radius of an orbit is inversely related to the square of its velocity.
- 4) From the Bohr angular momentum requirement you can derive that: $r = \frac{nh}{mv}$. Does this contradict your answer in question 3?
- 5) The Rydberg constant is 13.6 eV. What is it in cm^{-1} and J?
- 6) What is the energy of 900 nm light in J, cm^{-1} , and eV?
- 7) When an H atom goes from $n=3$ to $n=1$, what is the change in energy and what is the related wavelength of light? Is the light emitted or absorbed?
- 8) If a H atom absorbs a photon of wavelength 90 nm what happens to the atom?
- 9) How much energy (in eV) is required to ionize the last electron in B^{4+} (boron ion)?
- 10) A Ru complex absorbs light at 450 nm and emits light at 600 nm. What is the energy difference (in cm^{-1}) between the absorbed and emitted light?
- 11) Under ordinary light levels, when molecules emit light they almost always do it at a wavelength longer than the wavelength at which they absorb light. Why?
- 12) What is the de Broglie wavelength of an electron travelling at 1 m/s? What about 1×10^8 m/s (use the relativistic relationship $p = m_0 v / \sqrt{1 - v^2/c^2}$)? What is the de Broglie wavelength of a proton travelling at 1×10^8 m/s?
- 13) We can write the uncertainty relationship for position and momentum as $\Delta x \Delta p \geq h/4\pi$. We know that $E = p^2/2m$ and that the uncertainty in x can be related to the uncertainty in the momentum (or velocity) by $\Delta x = v \Delta t = p \Delta t / m$. Can you use these equations to derive the uncertainty principle in terms of time and energy?
- 14) Consider an atom that has absorbed green light with a wavelength of approximately 500 nm. It stays in an excited state for a very short amount of time, and then it emits light with a wavelength somewhere between 600.0 nm and 602.0 nm. What is the uncertainty of the excited state energy level? What is the lifetime of the excited state?

15) Which of the waves below are standing waves? How many nodes do the standing waves have?



16) When you shine light on a metal you can sometimes get electron to come off of the metal. This is called the *photoelectric effect*. The figure at right shows the number of electrons observed as you change the frequency of light. Can you explain why the number of electrons is 0 for frequencies less than ν_0 and constant above ν_0 ? Why when you increase the light intensity does the number of electrons observed increase? Can you write an equation for the energy of the electrons that are emitted in terms of the energy of the light? Draw a graph of the kinetic energy of the electrons vs. the frequency of the incident light.



Answers

- Bohr's radical idea was that the energies of electrons are quantized; that is, the energies can only take on discrete (integer multiples of some fundamental energy) values. This was a radical idea because in classical mechanics, all quantities are thought to be continuous (energy, mass, velocity, momentum, etc. can take on any value).
- This is a difference in units. Gray uses electrostatic units, while Lewis uses mks (meter-kilogram-second) units. A third unit system is cgs (centimeter-gram-second). Note that the variables that really matter, charge and distance, appear in both versions.
- We know that $\frac{Ze^2}{4\pi\epsilon_0 r^2} = m \frac{v^2}{r}$, which can be arranged to get $r = \frac{Ze^2}{4\pi\epsilon_0 mv^2}$
- No. The relationship shown above is not only between r and v since there n is also in the equation. In order for r to change both n and v must also change. Thus it does not contradict the above answer since it is a relationship between three variables, not two.
- $c = 2.997925 \times 10^8 \text{ m s}^{-1}$; $h = 6.6262068 \times 10^{-34} \text{ J s}$; $e = 1.602176 \times 10^{-19} \text{ C}$ (Note that $1 \text{ eV} = 1.602176 \times 10^{-19} \text{ J}$. Why is the conversion from eV to J just the charge on the electron?)
- $2.21 \times 10^{-19} \text{ J}$, $1.11 \times 10^4 \text{ cm}^{-1}$, 1.38 eV
- $9.75 \times 10^{-6} \text{ cm}^{-1}$, emits 102 nm
- This is 13.8 eV. The atom ionizes.
- $E = 13.6 \text{ eV} \frac{Z^2}{n^2}$ and $Z = 5$ and $n = 1$, so $E = 13.6 \text{ eV} \frac{5^2}{1^2} = 340 \text{ eV}$
- $5.55 \times 10^3 \text{ cm}^{-1}$
- Conservation of energy requires that the absorbed energy plus the energy of the atom must be equal to the emitted energy plus the energy of the atom after it emits. Thus, if the atom is in its lowest energy state at the beginning, then the most energy that can be emitted is equal to the absorbed energy (the atom ends in its ground state). However, in most cases, the atoms ends up in a vibrationally excited state (the molecule is "heated up") following emission, so the light that comes out must be less than what went in. You'll learn more about this in Ch1B.

12.

$$\lambda_{\text{slow electron}} = \frac{h}{p} = \frac{h}{m_e v} = \frac{6.626068 \times 10^{-34} \text{ J s}}{(9.109382 \times 10^{-31} \text{ kg})(1 \text{ m/s})} = 7.3 \times 10^{-4} \text{ m}$$

$$\lambda_{\text{fast electron}} = \frac{h}{p} = \frac{h}{m_0 v / \sqrt{1 - v^2/c^2}} = 6.9 \times 10^{-12} \text{ m}$$

$$\lambda_{\text{fast proton}} = \frac{h}{p} = \frac{h}{m_0 v / \sqrt{1 - v^2/c^2}} = 3.7 \times 10^{-15} \text{ m}$$

13.

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

Substitute for Δx :

$$\frac{p \Delta t}{m} \Delta p \geq \frac{h}{4\pi}$$

Differentiate E in the given definition:

$$E = \frac{p^2}{2m}$$

$$\frac{dE}{dp} = \frac{p}{m}$$

Differentials can be approximated by differences:

$$\frac{dE}{dp} \approx \frac{\Delta E}{\Delta p}$$

Solve for Δp :

$$\Delta p = \frac{m}{p} \Delta E$$

Substitute for Δp :

$$\left(\frac{p\Delta t}{m}\right) \left(\frac{m\Delta E}{p}\right) \geq \frac{h}{4\pi}$$

$$\Delta E \Delta t \geq \frac{h}{4\pi}$$

14.

$$E_{green} = \frac{1}{500 \text{ nm}} \frac{10^7 \text{ nm}}{1 \text{ cm}} = 2 \times 10^4 \text{ cm}^{-1}$$

$$E_{600} = \frac{1}{600.0 \text{ nm}} \frac{10^7 \text{ nm}}{1 \text{ cm}} = 1.6667 \times 10^4 \text{ cm}^{-1}$$

$$E_{602} = \frac{1}{602.0 \text{ nm}} \frac{10^7 \text{ nm}}{1 \text{ cm}} = 1.6611 \times 10^4 \text{ cm}^{-1}$$

$$\Delta E = E_{600} - E_{602} = 56 \text{ cm}^{-1}$$

Converting to Joules we get

$$\Delta E = hc\tilde{\nu} = 6.626068 \times 10^{-34} \text{ J s} \times \frac{2.997925 \times 10^8 \text{ m}}{\text{s}} \times \frac{100 \text{ cm}}{1 \text{ m}} \times \frac{56}{\text{cm}} = 1.11 \times 10^{-21} \text{ J}$$

$$\Delta E \Delta t \geq \frac{h}{4\pi}$$

$$\Delta t \geq \frac{h}{4\pi \Delta E} = \frac{6.626068 \times 10^{-34} \text{ J s}}{4\pi \times 1.11 \times 10^{-21} \text{ J}} = 4.75 \times 10^{-14} \text{ sec}$$

15. A (2 nodes), D (4 nodes), and E (9 nodes) are standing waves. Only these go to zero at the endpoints.

16. The energy of the electrons on the metal is quantized. Incoming photons must have energy greater or equal to a certain threshold energy, called the work function, in order for them to cause electrons to be ejected from the metal. If the energy of the incoming photons is greater than the work function, the extra energy will be imparted to the ejected electrons as kinetic energy. If the energy of the incoming photons is less than the work function, no electrons are ejected. Each metal has a different work function. An increase in light intensity is just an increase in the number of photons hitting the metal surface, so more electrons are emitted, assuming the energy of the photons is greater than the work function. The photoelectric effect was viewed as a paradox of classical mechanics, since under classical assumptions, photons of any energy, supplied in sufficient number, should cause ejection of electrons from metal.

Ch1A Recitation Section 9 Handout

Week 3 (Oct. 13, 2009)

TA: Eric Olmon (olmon@caltech.edu, ericolmon@gmail.com)

What is a wave function? A wave function is a mathematical function denoted by Ψ that describes the amplitude of an electron wave at all positions. Instead of using x, y, and z coordinates, the spherical coordinates r, θ , and Φ are typically used. The square of the wave function gives a new function, Ψ^2 , which describes the probability of finding the electron at any given position.

What is an electron orbital? An electron orbital is a three-dimensional plot of Ψ^2 . In other words, it is a description of the probability of an electron being in a certain place. Depending on the energy and angular momentum of the electron, the orbital takes on a different shape. The shapes and energies of orbitals can be determined by quantum mechanics. As with classical systems, an orbital with more nodes describes an orbital of higher energy.

There are two types of nodes in atomic orbitals: **angular nodes** and **radial nodes**. An angular node is a plane at a particular angle where the amplitude of the wave function is zero. A radial node is a sphere of a particular radius centered around the nucleus where the amplitude of the wave function is zero.

Orbitals are described by four quantum numbers which follow different rules:

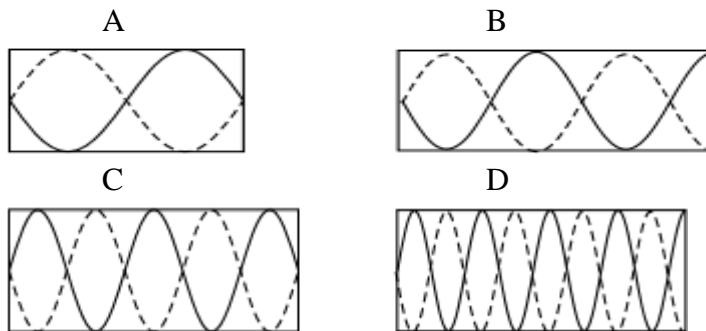
Name	Symbol	Relates to...	Rules
Principle quantum number	n	Energy	= total # nodes + 1 Integer $n > 0$
Angular quantum number	ℓ	Shape	= # angular nodes Integer $0 \leq \ell < n$
Magnetic quantum number	m_ℓ	Orientation of orbital	Integer Range from -1 to +1
Spin quantum number	m_s	Direction of e^- spin	Either $+1/2$ (up) or $-1/2$ (down)

Pauli exclusion principle: Each electron in an atom must have a unique set of quantum numbers. This means that each orbital (which are described by n, ℓ , and m_ℓ) may hold up to two electrons (one for each m_s value).

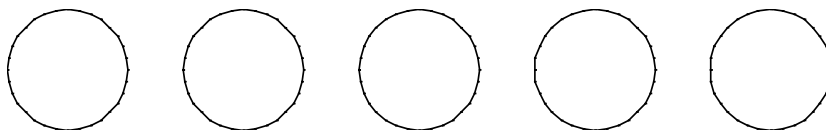
The Aufbau Principle: When placing electrons into orbitals, place them into the lowest energy orbitals first.

Hund's rule: When placing electrons into orbitals, every member of a degenerate set is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin (up or down).

1. Which of the waves below are standing waves? How many nodes do the standing waves have?



2. Draw the nodes in the first six modes of a round drum, indicating the number of radial and angular nodes for each (assume that for this system, each angular node contributes less energy than each radial node):



Which modes are degenerate?

3. Fill in the table below.

total # nodes	# radial nodes	# angular nodes	n	ℓ	Designation
4	2	2	5	2	5d
	8		12		
	1		2		
		2	4		
	4		7		
8	3				
5		1			
	3	2			
					12p
			3	2	
			7	4	
			5	1	

4. Plot the following for the 1s, 3d, 2p, 3p, and 2s orbitals:

$$\Psi \text{ vs. } r \qquad \Psi^2 \text{ vs } r \qquad r^2 R^2 \text{ vs. } r$$

5. Draw the shapes of the 3d, 2p, 4p, and 5s orbitals.
 6. Compare the shapes of the 3s, 3p and 3d orbitals.
 7. Draw an energy level diagram for orbitals up to $n=5$. (Plot n on the x-axis and energy on the y-axis, then make a line at the appropriate energy for each orbital: 1s, 2s, 2p, etc.)
 8. Penetration: Put the following orbitals into the order in which they penetrate the 1s orbital best:

$$2s, 2p \ 3s, 3p, 3d, 4s$$

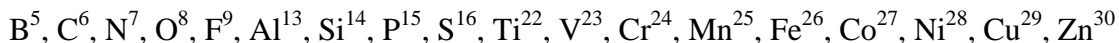
9. Which has lower energy:

- 3p or 4s
- 4p or 5s
- 3d or 4p
- 5d or 4f or 5p

10. State:

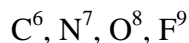
- The Pauli Exclusion Principle
- the Aufbau Principle
- Hund's rule. Why is it true?

11. Write the electron configuration for the following atoms:



12. Write the electron configuration for these ions: C^{2+} , Cl^- , Ti^{2+} , Cr^+ , Co^{3+} , Cu^+ , Cr , Nb

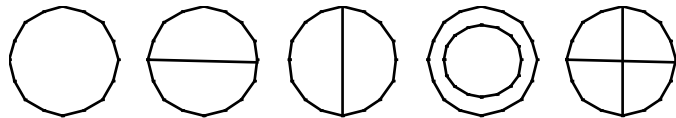
13. The rule we use for the magnetic quantum number is $m_l = -\ell, -\ell + 1, \dots, \ell - 1, \ell$. What if instead, $m_l = 0, 1, 2, \dots, \ell$ but the rules for n , ℓ , and m_s were the same? What would the first 3 noble gases be? Give the ground state and first excited state configurations for:



Answers

1. A) yes, 1; B) No; C) yes, 4; D) no

2.



The second and third form a degenerate set.

3. Fill in the table below.

Total # nodes	# radial nodes	# angular nodes	n	l	designation
4	2	2	5	2	5d
11	8	3	12	3	12f
1	1	0	2	0	2s
3	1	2	4	2	4d
6	4	2	7	2	7d
8	3	5	9	5	9h
5	4	1	6	1	6p
5	3	2	6	2	6d
11	10	1	12	1	12p
2	0	2	3	2	3d
6	2	4	7	4	7g
4	5	1	5	1	5p

4. See H radial plots handout or look at:

<http://winter.group.shef.ac.uk/orbitron/admin/references.html>

http://www.uky.edu/~holler/html/orbitals_2.html

<http://www.orbitals.com/orb/>

<http://www.orbitals.com/orb/orbtable.htm>

5. Draw the shape of the 3d, 2p, 4p, and 5s orbitals.

See handout H orbital pictures.

Download the program Orbital viewer from <http://www.orbitals.com/orb/>.

Look at the websites:

<http://winter.group.shef.ac.uk/orbitron/admin/references.html>

http://www.uky.edu/~holler/html/orbitals_2.html

<http://www.orbitals.com/orb/>

<http://www.orbitals.com/orb/orbtable.htm>

6. See above.

7. See Gray, pg. 36

8. 2s 2p 3s 3p 4s 3d

9. 3p, 4p, 3d, 5p

10.

- The Pauli Exclusion Principle: No two electrons can have same 4 quantum numbers
- The Aufbau Principle: Electrons go into the lowest energy orbital available
- Hund's rule: When two states are possible that only differ by electron spin, the state with the highest spin is lowest in energy. Why is it true? They occupy different regions of space so their interaction energy is lower.

11.

- B^5 , $1s^2 2s^2 3p^1$
 C^6 , $1s^2 2s^2 3p^2$ (2 unpaired spins)
 N^7 , $1s^2 2s^2 3p^3$, (3 unpaired spins)
 O^8 , $2s^2 3p^4$ (2 unpaired)
 F^9 , $1s^2 2s^2 3p^5$, (1 unpaired)
 Al^{13} , $1s^2 2s^2 3p^6 3s^2 3p^1$ (1 unpaired)
 Si^{14} , $1s^2 2s^2 3p^6 3s^2 3p^2$ (2)
 P^{15} , $1s^2 2s^2 3p^6 3s^2 3p^3$ (3)
 S^{16} , $1s^2 2s^2 3p^6 3s^2 3p^4$ (2)
 Ti^{22} , $1s^2 2s^2 3p^6 3s^2 3p^6 4s^2 3d^2$ (2)
 Fe^{26} , $1s^2 2s^2 3p^6 3s^2 3p^6 4s^2 3d^6$ (4)
 Cu^{29} , $1s^2 2s^2 3p^6 3s^2 3p^6 4s^2 3d^9$ (1)

12. C^{2+} ($1s^2 2s^2$)

- $Cl^-(1s^2 2s^2 3p^6 3s^2 3p^6)$
 $Ti^{2+}(1s^2 2s^2 3p^6 3s^2 3p^6 3d^2)$
 $Cr^+(1s^2 2s^2 3p^6 3s^2 3p^6 3d^4)$
 $Co^{3+}(1s^2 2s^2 3p^6 3s^2 3p^6 3d^6)$
 $Cu^+(1s^2 2s^2 3p^6 3s^2 3p^6 3d^{10})$
 $Cr(1s^2 2s^2 3p^6 3s^2 3p^6 4s^1 3d^5)$
 $Nb(1s^2 2s^2 3p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^5)$

13. First 4 noble gases: He, (N=2), O (N=0), Si (N=14), Ni (N=28)

- C^6 , $1s^2 2s^2 2p^2$ (2 unpaired) $1s^2 2s^2 2p^2$ (0 unpaired)
- N^7 , $1s^2 2s^2 2p^3$ (1 unpaired) $1s^2 2s^2 2p^2 3s^1$ (1 unpaired but 2 electrons in their own orbitals)
- O^8 , $1s^2 2s^2 2p^4$, (0 unpaired) $1s^2 2s^2 2p^3 3s^1$ (2 unpaired)
- F^9 , $1s^2 2s^2 2p^4 3s^1$, (1 unpaired) $1s^2 2s^2 2p^3 3s^2$ (1 unpaired but 3 electrons in their own orbital).

Ch1A Recitation Section 9 Handout (Oct. 22, 2009)

TA: Eric Olmon (olmon@caltech.edu, ericolmon@gmail.com)

Single-electron and Multi-electron systems

Single electron systems are composed of only two bodies, the electron and the nucleus, and their interactions and energies can be calculated easily considering the electrostatic attraction between them.

Important points about single electron orbitals:

- The zero energy is defined as the energy of an electron and a nucleus as the distance between them approaches infinity.
- All orbitals have negative energies on this scale.
- In single electron systems, all atomic orbitals with the same principle quantum number have the same energy.
- The presence of a node causes electron density to squish out closer to and further from the nucleus.

Multi-electron systems are more complicated. Interaction energies between one electron and the nucleus are influenced by the presence of additional electrons. Instead of seeing the full nuclear charge Z , electrons in multi-electron systems see an effective nuclear charge, Z_{eff} , which is lower than Z .

Important points about multi-electron orbitals:

- Orbital energies depend not only on the principle quantum number, but on the angular momentum as well.
- The presence of a node may enable the electron density of an outer electron to penetrate the electron density of an inner electron, making its energy lower than expected.
- The presence of a node may also push more electron density further from the nucleus in one orbital than another, making an electron in the orbital containing a node more reactive (it is “seen” first by an approaching atom).

1. Consider the following orbitals: 2s, 2p, 3s, 3p, 3d, 4s, 4p
Place the orbitals in order of:
 - a. Which extend farthest from the nucleus
 - b. Which see the largest effective nuclear charge
 - c. Which screen other electrons best

Wavefunctions

Wavefunctions describe the amplitude of electron wave occupancy around a nucleus at a given instant in time. Wavefunctions generally depend on three coordinates (r , θ , and ϕ) and can be factored into two functions: the radial wavefunction $R(r)$, and the angular wavefunction $Y(\theta, \phi)$:

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

2. Consider the orbital:

$$\psi(r, \theta, \phi) = \left(\frac{4}{81\sqrt{30}}\right) \left(\frac{Z}{a_0}\right)^{3/2} (\sigma^2) \exp(-\sigma/3) \sqrt{\frac{5}{16\pi}} (3 \cos^2\theta - 1)$$

where $\sigma = Zr/a_0$.

- a. Factor this wavefunction into $R(r)$ and $Y(\theta, \phi)$.
- b. How many angular nodes are there?
- c. How many radial nodes are there?

3. For the orbital

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi) = \left(\frac{1}{\sqrt{4\pi}}\right) \left(\frac{2}{81\sqrt{3}}\right) \left(\frac{Z}{a_0}\right)^{3/2} (27 - 18\sigma + 2\sigma^2) \exp(-\sigma/3)$$

- Calculate the positions of any radial nodes for $Z = 3$ and $a_0 = 0.529 \text{ \AA}$.
- Does this wave function have any angular nodes?
- What type of orbital is this (e.g. 4f)?

Quantum numbers

There are four quantum numbers: n , l , m_l , and m_s . See the Week 3 handout for rules pertaining to the values these quantum numbers can hold.

4. Which of the following combinations of quantum numbers are allowed for an electron in a one-electron atom? For those that are not allowed, explain why.

	n	l	m_l	m_s	Allowed?	Reason:
a)	2	2	1	$1/2$	_____	_____
b)	3	1	0	$-1/2$	_____	_____
c)	5	1	2	$1/2$	_____	_____
d)	4	-1	0	$1/2$	_____	_____
e)	3	2	1	0	_____	_____
f)	2	0	0	$-1/2$	_____	_____
g)	7	2	-2	$1/2$	_____	_____

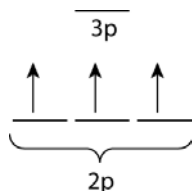
Filling orbitals in multi-electron atoms

There are three rules that govern the filling of orbitals: the *Aufbau Principle*, the *Pauli Exclusion Principle*, and *Hund's rule*. These are defined on the Week 3 handout.

5. Finish the orbital filling order: 1s, 2s, 2p, 3s, ...

There are several exceptions to the orbital filling order. These exceptions have to do with the proximity of some orbitals and a balance between the following:

- Electrons usually prefer to go into the lowest energy orbital possible
 - Pairing two electrons in a single orbital is less stable (results in a higher energy atom) than keeping them unpaired.
 - Filling or half-filling a p or d orbital results in bonus stabilization.
6. The figure shown below is an orbital occupation diagram of the ground state of N. Draw a diagram illustrating three different excited states of N.



- What two 1st row transition metals are exceptions to the orbital filling order?
- The following elements are exceptions to the general rule on orbital filling. Explain each:

Nb, Pd, Mo, Ag, Ru, Rh

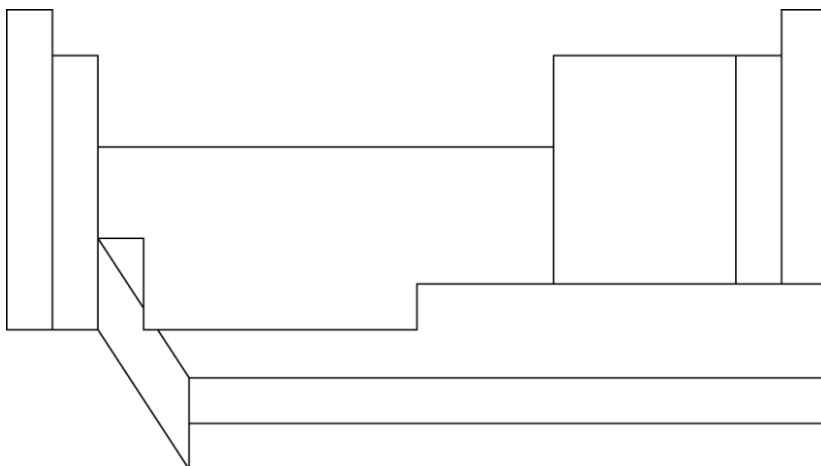
9. Which atoms with $Z < 18$ are paramagnetic (have unpaired electrons)?

Periodic trends

Trends appear as one moves across or down the periodic table. Trends are observed in:

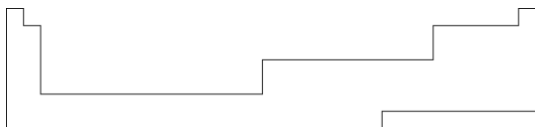
- atomic radius
- ionization energy: the amount of energy required to pull an electron off of an atom
- electron affinity:
- electronegativity: $EN = (I.E. + E.A) / 2$

10. In the blank periodic table below, label the names of the various functional blocks:

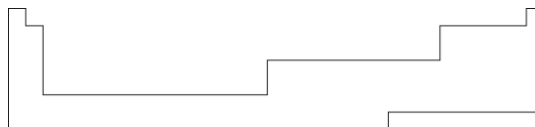


11. For each periodic trend, indicate which direction the property increases on the periodic tables below:

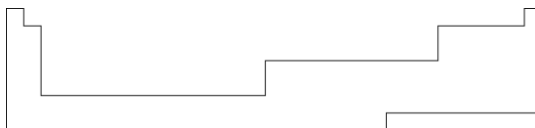
Atomic Radius:



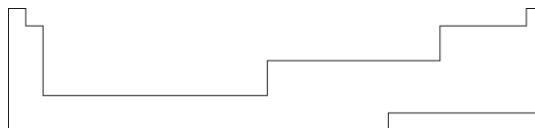
Ionization Energy:



Electron Affinity:



Electronegativity:



12. Which of each pair of the following has the higher ionization energy?

a. Ni, Ni⁺

b. Ne, Ar

c. Ne, Na⁺ F, Ar

Answers:

1.

- $4s > 4p > 3s > 3p > 3d > 2s > 2p$
- $2s > 2p > 3s > 3p > 4s > 3d > 4p$
- $2s > 2p > 3s > 3p > 3d > 4s > 4p$

2.

- $R(r) = \left(\frac{4}{81\sqrt{30}}\right) \left(\frac{Z}{a_0}\right)^{3/2} (\sigma^2) \exp(-\sigma/3); Y(\theta, \phi) = \sqrt{\frac{5}{16\pi}} (3 \cos^2\theta - 1)$
- The only angular variable in $Y(\theta, \phi)$ is θ , which is only defined from 0 to π . Solving for θ in $Y(\theta, \phi) = 0$ yields two roots, so there are two angular nodes.
- Solving $R(r) = 0$ yields only one root, at $r = 0$. This is really only an effect of the angular nodes, so there are no radial nodes.

3.

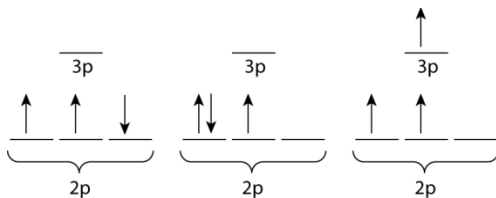
- $r = 0.34$ and 1.25 \AA . These values are found by determining where $\psi(r, \theta, \phi) = 0$.
- This function has no angular nodes because there is no theta or phi dependence.
- 3s (no angular nodes, two radial nodes)

4.

	n	l	m_l	m_s	Allowed?	Reason:
a)	2	2	1	$\frac{1}{2}$	No	$l > n$
b)	3	1	0	$-\frac{1}{2}$	Yes	
c)	5	1	2	$\frac{1}{2}$	No	$m_l > l$
d)	4	-1	0	$\frac{1}{2}$	No	$l < 0$
e)	3	2	1	0	No	$m_s = \pm \frac{1}{2}$
f)	2	0	0	$-\frac{1}{2}$	Yes	
g)	7	2	-2	$\frac{1}{2}$	Yes	

5. 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p,...

6.



7. Cr and Cu. In these atoms, one electron is promoted from 4s to 3d in order to half fill or fill the 3d set.

8. Nb: Steals two 5s electron to attain half-full 4d shell

Pd: steals two 5s electrons to attain full 4d shell

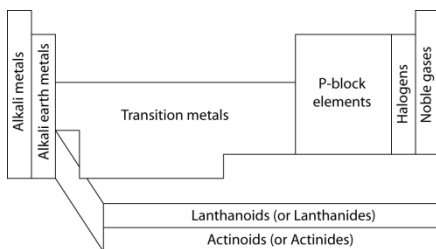
Mo: steals one 5s electron to attain half-full 4d shell

Ag: steals one 5s electron to attain full 4d shell

Ru, Rh: steal a 5s electron to add another electron to the 4d shell

9. A paramagnetic element has unpaired electrons. The following are the paramagnetic elements with $Z < 18$. H, Li, B, C, N, O, F, Na, Al, Si, P, S, Cl. If an element has no unpaired electrons, it is diamagnetic.

10.



11. Atomic radius increases down and to the left; Ionization energy increases up and to the right; Electron affinity increases up and to the right; EN increases up and to the right

12. a. $\text{Ni} < \text{Ni}^+$; b. $\text{Ar} < \text{Ne}$; c. $\text{Ne} < \text{Na}^+$; d. $\text{Ar} < \text{F}$

How to solve Lewis dot problems:

1. Count the number of electrons contributed by each atom. Account for charges. This is the number of electrons that are available to work with.
2. Pick a central atom.
3. Build up the molecule following a few rules:
 - Form octets if possible.
 - Maximize bonding (instead of having a lone pair on an atom, see if you can use it in a bond).
 - Distribute formal charges in a reasonable way:
 - Minimize charges if possible.
 - Put negative charges on more electronegative atoms.
 - Never put the same sign on neighboring atoms.
4. Look for possible resonance structures.
5. Double check! Count the number of electrons in your drawing and make sure it matches the total number of electrons you calculated in step 1.

Some tips:

- Central atom: If there is a C atom in the molecule, this is a good choice. If not, look to see if the molecule has only one atom of a certain element. For example, in H_3PO_4 , P is a good choice for the central atom.
- Forming octets: C, N, O, and the halogens generally accommodate only eight electrons. 3rd row elements like P and S can often accommodate more than an octet (but they prefer to only have an octet).
- Atoms in the same group bond similarly. For example, O and S often have 2 bonds connected to them.
- Number of bonds: C likes to have 4 bonds; O likes to have 2 bonds and 2 lone pairs; H and Li like to have 1 bond; N often has 3 or 4 bonds and one lone pair; the halogens usually make just 1 bond.
- Charges: Atoms almost never have a +3 or -3 charge. Even +2 or -2 is stretching it in most cases. Almost always, atoms to the left of N can have positive charges but not negative charges, and atoms to the right of O can have negative charges but not positive charges.
- The types of molecules you will be dealing with will often fall into one of three categories:
 1. *Organic molecules*. These consist mainly of C, N, O, and sometimes S or halogens. For molecules like these, C is usually the central atom, and if there is more than one C atom, there is usually a bond (or double bond or triple bond) between them.
 2. *Oxoacids*. These are H_2SO_4 , HSO_4^- , H_3PO_4 , H_2PO_4^- , etc., as listed on slide VI-17. Most of them have many resonance structures and consist of one atom surrounded by O atoms which also bind H or hold negative charges. Become familiar with the list of oxoacids so that you can recognize them.
 3. *Expanded octets*. Atoms like P, S, and As can have more than an octet of electrons.

Drawing Lewis dot structures in a methodical way (from Oxtoby):

1. Count the total number of valence electrons available by first using the group numbers to add the valence electrons from all the atoms present. If the species is a negative ion, add the absolute value of the total charge; if it is a positive ion, subtract the value of the charge.
2. Calculate the total number of electrons that would be needed if each atom had its own noble-gas shell of electrons around it (two for hydrogen, eight for carbon and heavier elements).
3. Subtract the number in step 1 from the number in step 2. This is the number of shared (or bonding) electrons present.
4. Assign two bonding electrons (one pair) to each bond in the molecule or ion.
5. If bonding electrons remain, assign them in pairs by making some of the bonds double or triple bonds. In some cases there may be more than one way to do this. In general, double bonds form only between atoms of the elements C, N, O, and S. Triple bonds are usually restricted to C, N, or O.
6. Assign the remaining electrons as lone pairs to the atoms, giving octets to all atoms except hydrogen.
7. Determine the formal charge on each atom and write it next to that atom. Check that the formal charges add up to the correct total charge on the molecule or ion.

Ch1A Recitation Section 9 Handout (Oct. 29, 2009)

TA: Eric Olmon (olmon@caltech.edu, ericolmon@gmail.com)

1. For each of the following pairs of atoms or ions, state which is larger:

- | | | | |
|-----------|------------------------|--------------------------------------|-------------------------------------|
| a. Na, K | b. Cs, Cs ⁺ | c. K, Ca | d. Sm, Sm ³⁺ |
| e. Mg, Ca | f. I ⁻ , Xe | g. O ²⁻ , S ²⁻ | h. O ⁻ , S ²⁻ |

2. Put the following sets in order of increasing size:

- N³⁻, O²⁻, F⁻, Ne, Na⁺
- Mg²⁺, Al³⁺
- N, O, F
- F⁻, Cl⁻, Br⁻
- Li⁺, Be

3. State which of the following has the greater electron affinity:

- | | | | |
|----------|-----------|----------|-----------|
| a. O, F | b. Al, Si | c. Si, P | d. Cu, Zn |
| e. S, Sl | f. K, Ca | g. H, Li | H. As, Ge |

4. Write the Lewis dot structures for:

- | | | | | | |
|----------------------------------|----------------------------------|----------------------------------|-----------------------------------|-----------------------------------|--|
| a. CO | b. SO ₂ | c. CO ₂ | d. CN ⁻ | e. SF ₆ | f. CH ₄ |
| g. C ₂ H ₂ | h. C ₂ H ₄ | i. C ₆ H ₆ | j. C ₆ H ₁₂ | k. C ₈ H ₁₄ | l. C ₆ H ₅ CH ₃ |

Oxoacids

Oxoacids are molecules in which a central atom is bound to two or more oxygen atoms, which are themselves bound to acidic hydrogens. Three factors affect the acidity of oxoacids:

- Electronegativity: a more electronegative central atom can stabilize the negative charge on an O atom that results from loss of a proton, so oxoacids with more electronegative central atoms are more acidic.
- Resonance structures: if loss of a proton results in an increase in the number of resonance structures, then loss of the proton is favorable and the species is more acidic.
- Net charge: a net negative charge on the molecule prevents loss of a positively-charge proton due to electrostatic attraction between the two, making the species less acidic.

5. Put the following in order of increasing acid strength:

6. Write resonance structures for the conjugate bases of the above oxoacids: H₂PO₄⁻, HSO₄⁻, ClO₄⁻

ANSWERS

1. K; Cs; K; Sm; Ca; Γ^- ; S^{2-} ; S^{2-} 2. Na^+ ; Ne, F^- , O^{2-} , N^{3-} ; Al^{3+} , Mg^{2+} ; F, O, N; F^- , Cl^- , Br^- ; Li^+ , Be3. $F > O$; $Si > Al$; $Si > P$; $Cu > Zn$; $Cl > S$; $K > Ca$; $H > Li$; $Ge > As$

4.

a.

b.

c.

d.

e.

f.

g.

h.

i.

j.

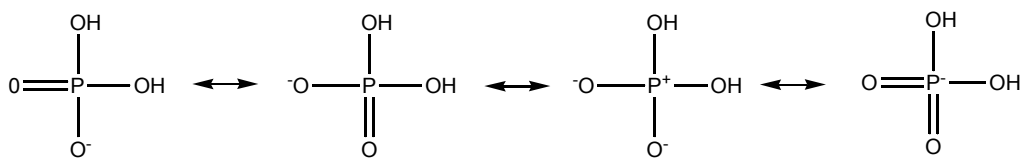
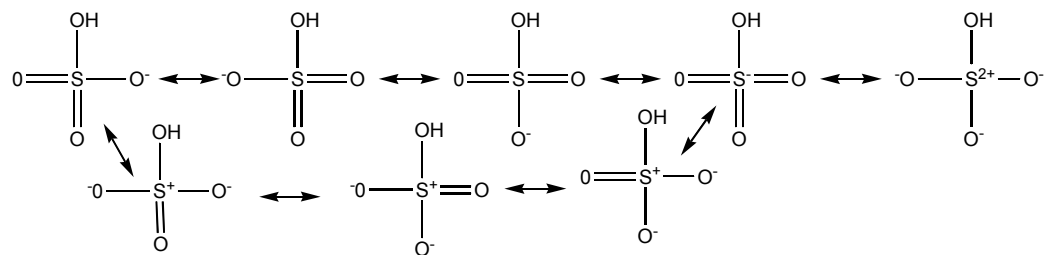
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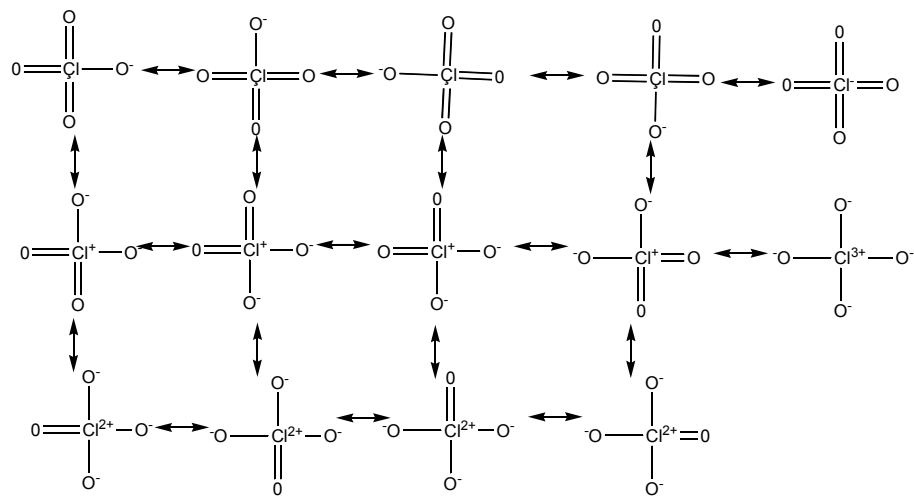
l.

For help with Lewis structures, see:

<http://www.kentchemistry.com/links/bonding/lewisdotstruct.htm>5. H_3PO_4 , H_2SO_4 , $HClO_4$

6.





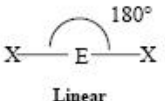
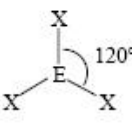
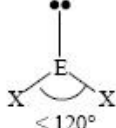
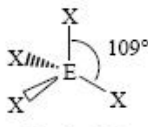
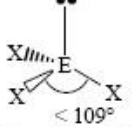

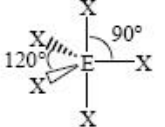
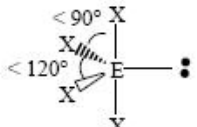
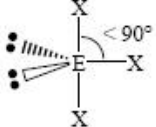
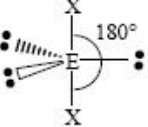
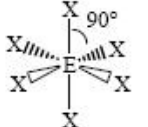
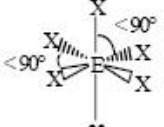
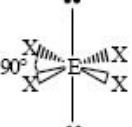
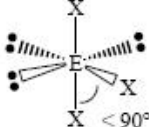
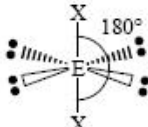
VSEPR – Valence Shell Electron Pair Repulsion Theory: *Statement of theory:* the shape of a molecule is predominantly determined by the number of bonding and lone pairs of electrons associated with each atom. This statement comes about from the general tendency of electrons to repel each other. In three-dimensional space, they will get as far away from one another as possible.

Steric number: the sum of the number of atoms bonded to the central atom and the number of lone pairs on the central atom. The steric number determines the **basic geometry** or **electronic geometry** of the molecule, while the actual shape of the molecule (what it really looks like) is given by the **molecular geometry** or **molecular shape**. Sometimes the basic geometry is the same as the molecular geometry; sometimes it is not.

Note that ideal angles are based on fully symmetrical molecules like BH_3 or CH_4 , etc. Lone pairs are FAT, so if a lone pair is present, it will tend to reduce the angles between bonded atoms.

How to determine molecular geometry using VSEPR theory:

1. Draw the best Lewis dot structure of the molecule.
2. Assign a steric number to the structure.
3. Place the atoms and lone pairs as far apart as possible (while still keeping them connected to the central atom).
4. Deduce the molecular geometry by ignoring the positions of the lone pairs.
5. Remember, lone pairs are FAT.

VSEPR Geometries					
Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal Planar	 Bent or Angular			
4	 Tetrahedral	 Trigonal Pyramid	 Bent or Angular		
5	 Trigonal Bipyramid	 Sawhorse or Seesaw	 T-shape	 Linear	
6	 Octahedral	 Square Pyramid	 Square Planar	 T-shape	 Linear

http://upload.wikimedia.org/wikipedia/commons/a/a9/VSEPR_geometries.PNG

Factors that affect bond angles:

1. **Lone pairs:** lone pairs are fatter than bonded pairs, so there is a greater repulsion between a lone pair and a bonded pair than between a bonded pair and another bonded pair. The presence of a lone pair causes the angle between bonded pairs to decrease.
2. **Size of the central atom:** as the size of the central atom increases, its lone pairs get fatter, causing a decrease in the expected bond angle.
3. **Size of bound (ligand) atoms:** as the size of bound atoms increases, the distance between them must increase due to size constraints, resulting in a greater angle between them.

VSEPR example problems

1. Predict the shapes of:



2. Of the three molecules above, which has the largest bond angle? Why?
3. What is the shape around each of the C atoms in H_3CCOOH ?
4. Fill in the following table:

Molecule	SN	Lone Pairs	Geometry of Electrons	Molecular Geometry
IF_4^-	6	2	Octahedral	Square Planar
PF_3				
XeF_2				
SO_2				
SO_4^{2-}				
PF_5				
BF_3				
CS_2				
SO_3				
ICl_3				
CBr_4				
SiH_4				
SF_2				
SeF_6				
PF_3				

VSEPR ANSWERS

1. CH₄: tetrahedral; NH₃: trigonal pyramidal; H₂O: bent or angular
2. CH₄ has the largest bond angle because it has no lone pairs repulsing the bonded pairs.
3. H₃C: tetrahedral; COOH: trigonal planar.
- 4.

Molecule	SN	Lone Pairs	Geometry of Electrons	Molecular Geometry
IF ₄ ⁻	6	2	Octahedral	Square Planar
PF ₃	4	1	Tetrahedral	Trigonal Pyramidal
XeF ₂	5	3	Trigonal Bipyramidal	Linear
SO ₂	3	1	Trigonal Planar	Bent or Angular (angle < 120)
SO ₄ ²⁻	4	0	Tetrahedral	Tetrahedral
PF ₅	5	0	Trigonal Bipyramidal	Trigonal Bipyramidal
BF ₃	3	0	Trigonal Planar	Trigonal Planar
CS ₂	2	0	Linear	Linear
SO ₃	3	0	Trigonal Planar	Trigonal Planar
ICl ₃	5	2	Trigonal Bipyramidal	T-shaped (bent)
CBr ₄	4	0	Tetrahedral	Tetrahedral
SiH ₄	4	0	Tetrahedral	Tetrahedral
SF ₂	4	2	Tetrahedral	Bent or Angular
SeF ₆	6	0	Octahedral	Octahedral
PF ₃	4	1	Tetrahedral	Trigonal Pyramidal

Molecular Orbital (MO) theory: *Statement of Theory:* the electronic structures of molecules can be described by molecular wave functions which are derived from linear combinations of atomic orbitals (LCAOs).

One way to think of MOs:

Imagine two atoms that are separated by a large distance. As those two atoms are brought closer and closer together, the electrons from one will start to be influenced by the nucleus of the other, and vice versa. At a very close distance, the electrons from the first atom will not be able to distinguish between the nucleus of the first atom and the nucleus of the second atom. At this point, a bond has formed. The electron is no longer described by an atomic orbital since it is influenced by two different nuclei; instead, the position of the electron in space is described by a molecular orbital.

Another way to think of them:

We built up atomic orbitals by considering the influence of a point positive charge (the nucleus) on a wave-like negative charge (the electron) and determining the mathematical form of the electron wave that would fit our quantization rules. We can build up molecular orbitals in the same way by considering the influence of several point positive charges on an electron. Like atomic orbitals, molecular orbitals have mathematical forms that fit quantization rules. These mathematical forms resemble linear combinations of atomic orbitals.

Bonding MOs: when filled with electrons, these result in stronger bonds between atoms. These can be signified by appending a subscript “b” to the name of the orbital (but sometimes the b is left off). Ex) σ_b .

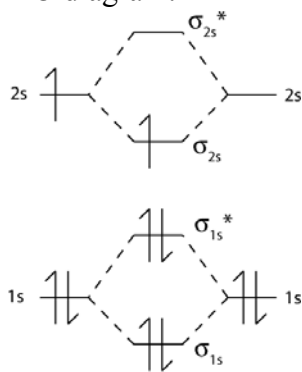
Antibonding MOs: when filled with electrons, these orbitals will weaken the bonds between atoms. Antibonding MOs are generally higher in energy than their related bonding MOs. These are notated with an * appended to the name of the orbital. Ex) σ_{2s}^* . In antibonds, a planar node exists between the nuclei.

Exercises:

1. Draw the molecular orbital diagram for Li_2^+ . What is the bond order of this ion? Is it diamagnetic or paramagnetic?
2. Sketch the bonding MO for H_2 . Sketch the antibonding MO and label any nodes and the sign (+ or -) of each lobe.
3. We can generate σ MOs by taking linear combinations of s AOs. Knowing this, can you predict what π MOs might look like (they are linear combinations of p AOs)? By convention, the intermolecular axis (the axis connecting the nuclei) is usually assigned as the z -axis of both atoms. Can you draw a MO diagram that includes the MOs derived from $2p$ orbitals?

MO ANSWERS:

1. MO diagram:

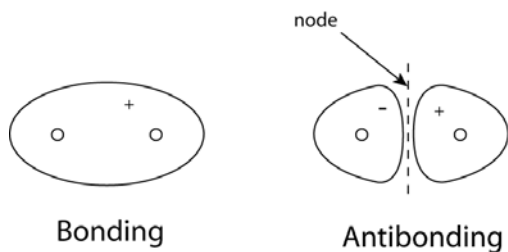


Li

Li⁺

Bond order: 0.5; paramagnetic

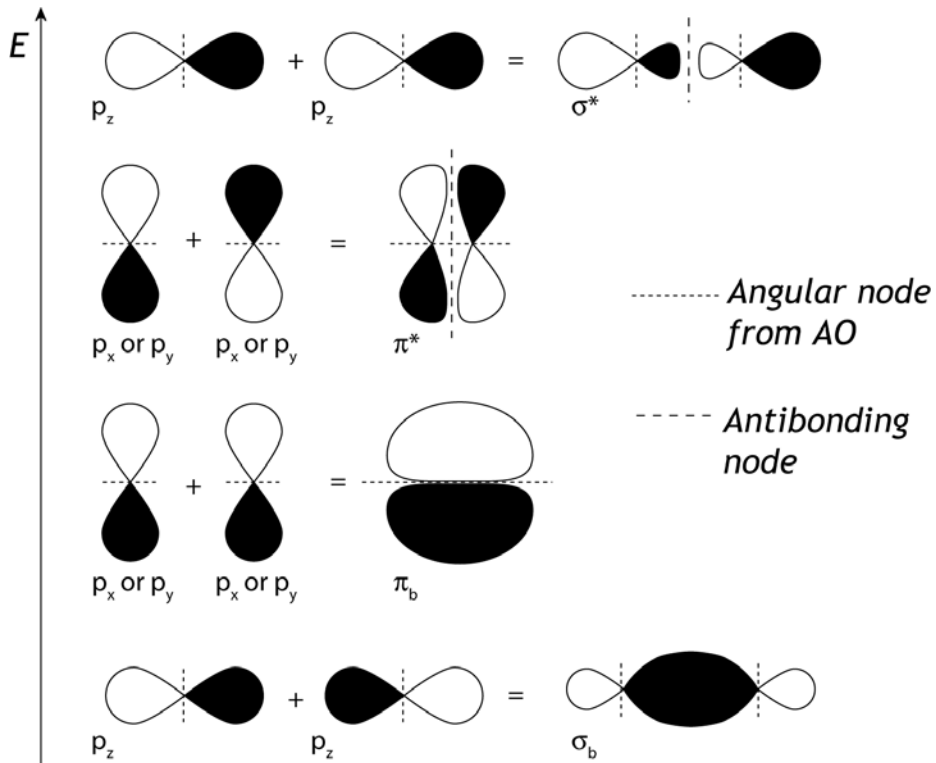
2.



Bonding

Antibonding

3.

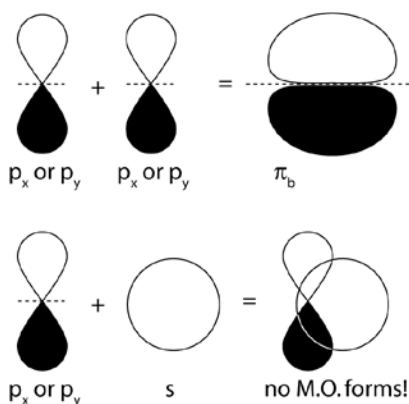


Ch1A Week 7 Handout

TA: Eric Olmon (ericolmon@gmail.com, olmon@caltech.edu)

Molecular Orbital Theory*There are three criteria for the formation of M.O.s:***1. The symmetries of the interacting A.O.s must be the same.**

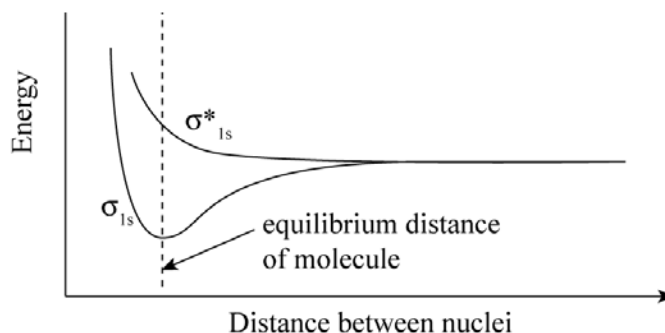
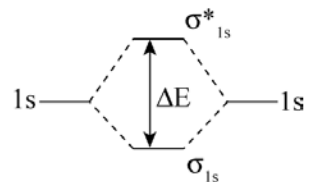
By symmetry, we are referring to the effect of rotating the interacting atomic orbitals around the internuclear axis (defined as the z-axis). Some orbitals are cylindrically symmetric; that is, they do not change in shape or sign (+ or -) when they are rotated about the z-axis by any angle. Examples of these types of orbitals are s orbitals and p_z orbitals. (Can you think of any others?) Some orbitals change sign upon rotation by 180° , like p_x , p_y , d_{xz} , and d_{yz} orbitals. Still others change sign after each 90° rotation, like d_{xy} , $d_{x^2-y^2}$, and some f orbitals.

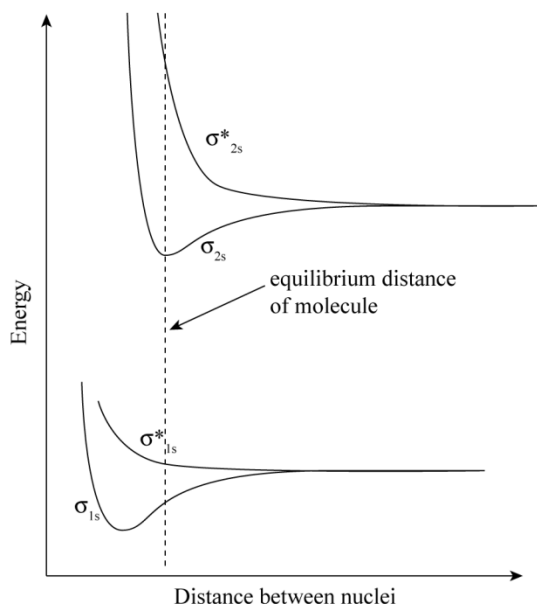


Only orbitals with the same symmetry can interact to form M.O.s. This means that s orbitals may form M.O.s with other s orbitals or with p_z orbitals, but not with p_x , d_{xz} , or f_{xyz} orbitals, for example. This is because any constructive interference attained by overlapping atomic orbitals is offset by an equal amount of destructive interference, resulting in no net stabilization. On the other hand, p_x orbitals may interact with other orbitals of the same symmetry, such as other p_x orbitals or d_{yz} orbitals, to form M.O.s. When two orbitals with cylindrical symmetry interact, they produce an M.O. with cylindrical symmetry called a σ M.O. When two orbitals with p_x -type symmetry (rotation of 180° results in sign exchange) interact, a π orbital, which also has p_x -type symmetry, is formed.

2. The atoms must be separated by an appropriate distance.

When the two $1s$ orbitals of H overlap, they form a bonding and an antibonding orbital with an energy splitting, ΔE , that is shown in the figure. This splitting is dependent on distance. There is some optimal bond distance, called the equilibrium distance, at which ΔE will be maximized. If the nuclei involved are moved closer together or farther apart than this ideal separation, ΔE will decrease. The dependence of energy splitting on distance is shown in the figure below.

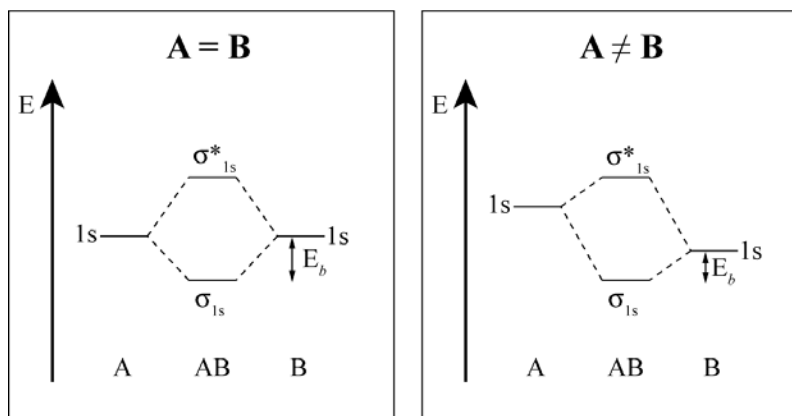




In Li_2 , both the $1s$ and the $2s$ orbitals are involved in forming M.O.s. Since the $2s$ orbitals extend further away from the nucleus than the $1s$ orbitals, the optimal distance will be different for these two orbitals. In Li_2 , the nuclear charge is greater than it is in H_2 , and the nuclei will repel one another to a greater extent, making the bond in Li_2 longer than it is in H_2 . The figure shows that the equilibrium bond length is close to the maximum ΔE for the M.O.s formed from the $2s$ orbitals.

3. The absolute energy levels of the A.O.s must be similar.

For two bonding atoms, A and B, if A and B are the same element, then as they come together, they form a strong bond with bond energy E_b . This is the amount of stabilization that the bond gives the molecule, and it is the amount of energy that is required in order to break the bond.



If the two atoms are not the same, then the change in energy upon forming the bond is skewed so that the lower energy A.O. lies closer in energy to the bonding M.O., and the higher energy A.O. lies closer in energy to the antibonding M.O. In the example shown, we would say that the bonding M.O. more closely resembles the B $1s$ A.O., or that the bonding orbital “has more B character.” In an extreme case, you can imagine that the bonding M.O. has the exact same energy as the lower energy A.O. and that the antibonding M.O. has the same energy as the higher energy A.O. In this case, no bond forms.

Together, this means that any kind of orbital can interact with any other orbital, assuming they have the same symmetry and similar energy. The bond energy of a diatomic molecule will be greater if the energies of the contributing atomic orbitals are more similar.

Drawing M.O. diagrams

1. Draw energy axis and position the atoms.
2. Determine the relative energies of the A.O.s, plot them, and fill in electrons. Only valence A.O.s need to be included on the M.O. diagram.
3. Determine whether either of your atoms lies outside the O or F groups on the periodic table. If so, the σ_{pz} M.O.s will lie higher in energy than the $\pi_{px,y}$ orbitals.
4. Draw the M.O. energy levels and fill them with electrons according to the Pauli Principle and Hund's Rule.

Example problems:

- 1) Sketch the bonding and antibonding orbitals of Li_2 as a function of the distance between the nuclei.
- 2) Place the following in order of increasing bond length:



- 3) Use the following table of ionization energies to draw M.O. diagrams for F_2 , FCl , and FBr . Determine the bond order and magnetic properties for each molecule.

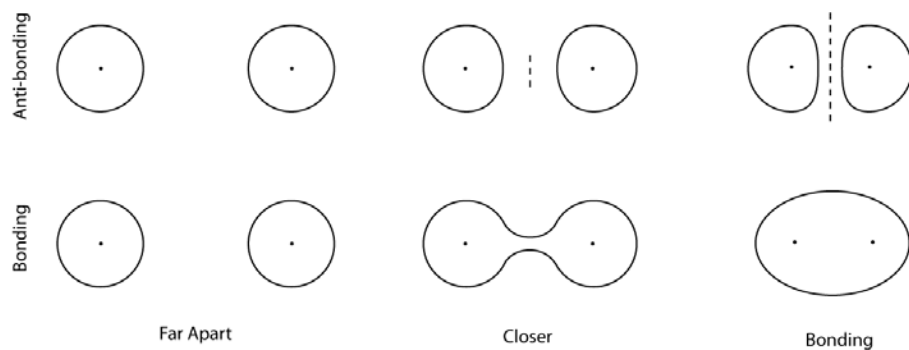
Valence ionization energies in units of 10^3 cm^{-1}

Atom	1s	2s	2p	3s	3p	4s	4p
H	110						
F		374	151				
Cl				204	111		
Br						194	101

- 4) Draw the M.O. diagram for HF without looking at any references.

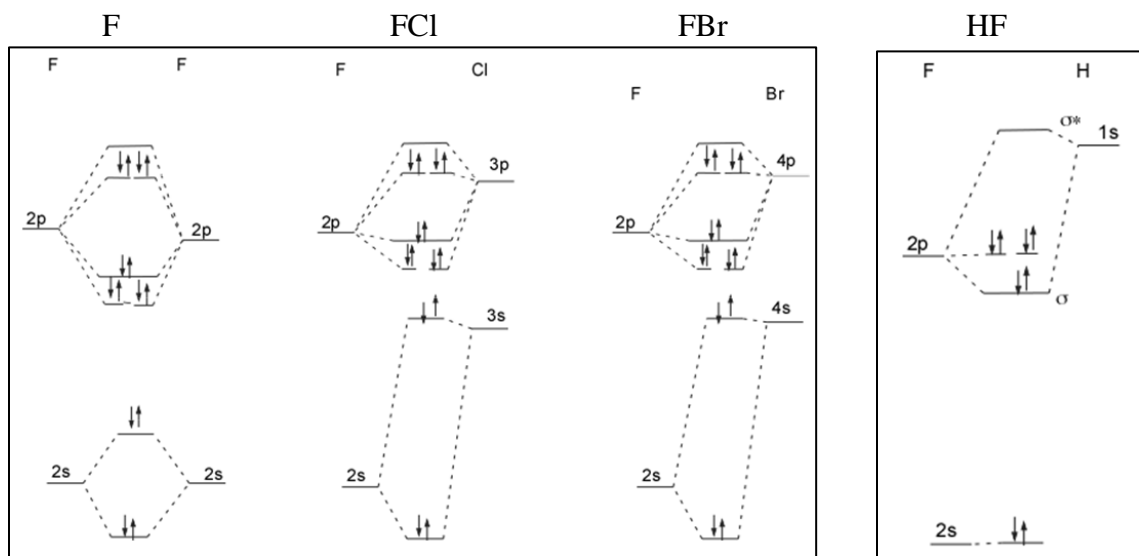
ANSWERS

1) At far separation, the bonding and anti-bonding orbitals of Li_2 are very similar and resemble the individual atomic orbitals in energy and in shape. As the atoms get closer, the distinction between the two nuclei starts to vanish and the bonding and anti-bonding orbitals begins to form. Finally, at the appropriate distance, electrons are shared equally in the bonding case, and a node has developed in the anti-bonding case.



2) Based on the bond order determined by filling electrons in the appropriate M.O. diagrams, it is possible to see that F_2 has a single bond, O_2 has a double bond, and N_2 has a triple bond. Therefore, ordering the molecules in terms of increasing bond length (decreasing bond order), we have: N_2 , O_2 , F_2 .

3) and 4) Using the given ionization energies, it is possible to qualitatively determine the extent to which various orbitals will interact with the orbitals of F. For most halogens, bonding with F creates a skewed M.O. diagram. In HF, however, the 1s orbital of H is so far from the 1s and 2s orbitals of F that bonding with them is impossible. Instead, H bonds with the $2p_z$ orbital of F.



CH1A Section 9 Week 8 handout, Nov. 19, 2009

TA: Eric Olmon (ericolmon@gmail.com, olmon@caltech.edu)

Factors affecting molecule size

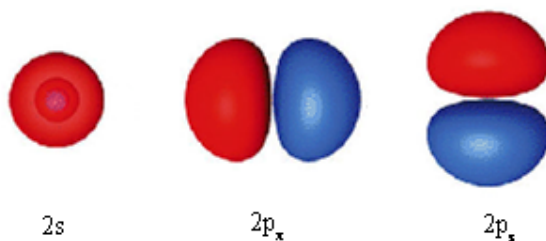
- Atomic size
- Bond length
- Conformation

Hybrid orbitals

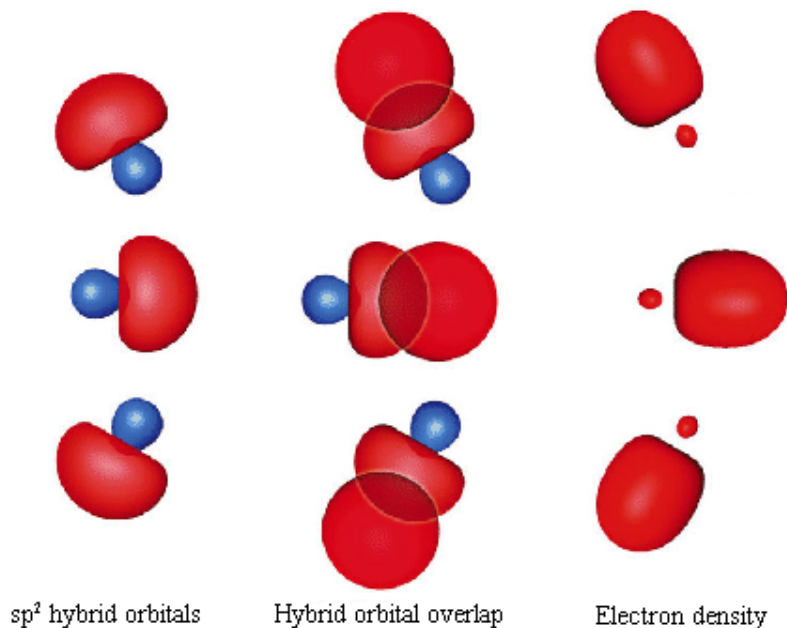
Driving force: by creating hybrid orbitals before bonding, it is possible to increase the overlap between orbitals on bonding atoms.

- Note that a set of hybrid orbitals is just as valid as the atomic orbitals we have been working with for describing the positions of electrons around nuclei. It's just a different formalism.
- Lone pairs are still possible in hybrid orbitals and they are still fat.

Atomic Orbitals



Hybrid Orbitals



Forming M.O.s:

Remember the three criteria for creating molecular orbitals:

- Same symmetry
- Close in space
- Similar energy

Determining shapes of large molecules:

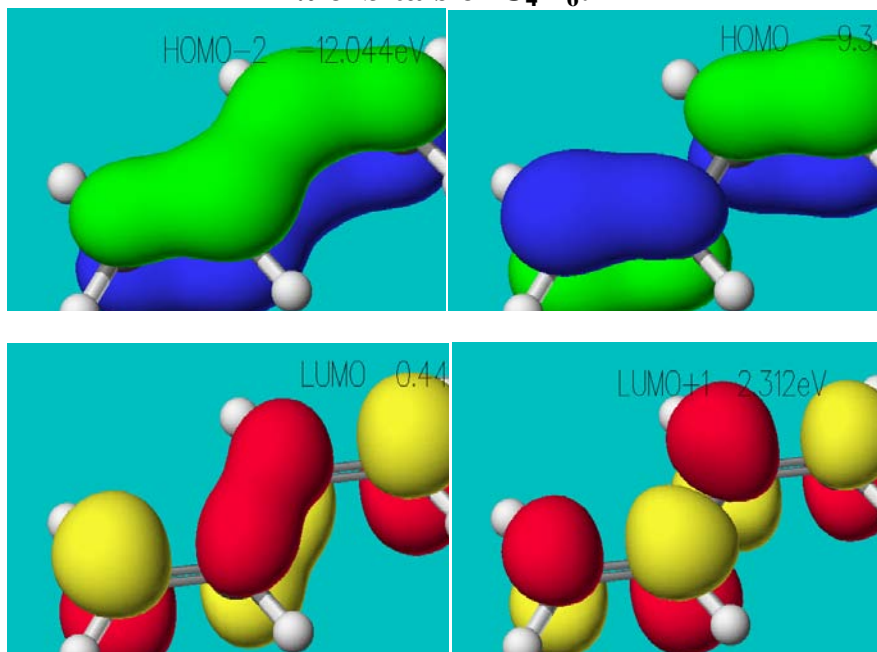
- Use VSEPR to determine the hybridization and bonding at each atom.
- Use the leftover p orbitals to create π bonds
 - Single bonds = 1 σ bond. These allow rotation
 - Double bonds = 1 σ bond + 1 π bond. These do not allow rotation
 - Triple bonds = 1 σ bond + 2 π bonds. These allow rotation

Extended pi systems

For certain types of highly symmetric or repeating molecules, it is possible to figure out what the M.O.s will look like without doing all the math. Because the electrons in these systems are not localized to particular nuclei, conductive polymers can be made from them.

Linear chains of alternating single/double bonds can create a large delocalized system.

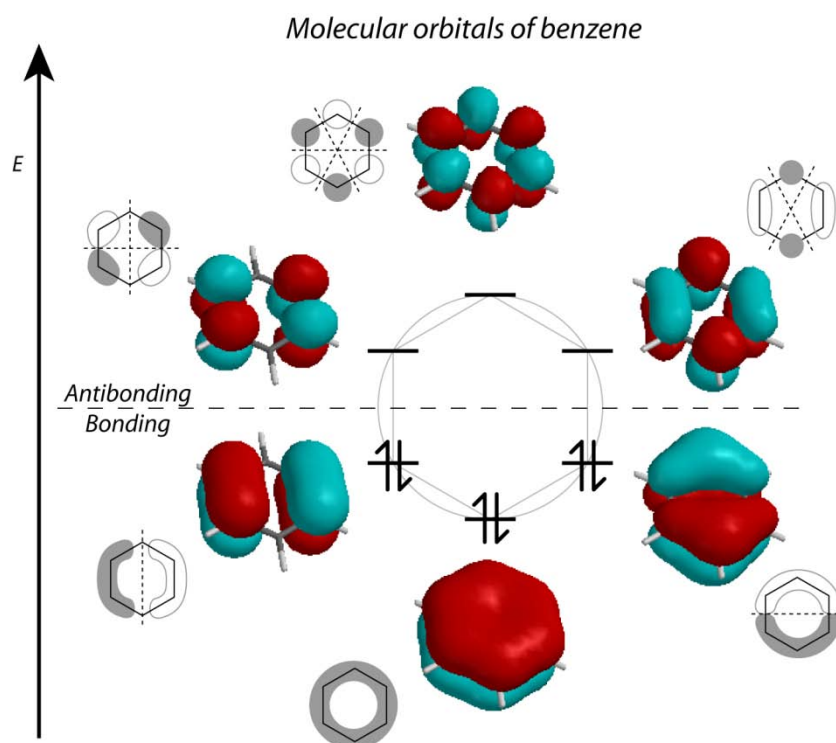
- There are no degenerate orbitals in linear chains
- The number of energy levels is equal to the number of electrons in the π system ($2 e^-$ per double bond)
- Lowest orbital has no nodes
- Highest orbital has nodes between each atom
- Each level in the energy diagram has one more nodes than the level below it
- Nodes should be distributed roughly symmetrically throughout the molecule
- Sometimes, nodes will lie on atoms, sometimes between atoms

 π orbitals of C_4H_6 :

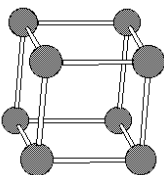
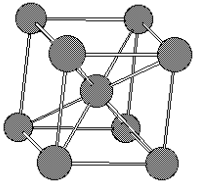
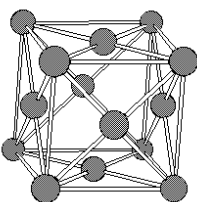
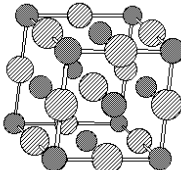
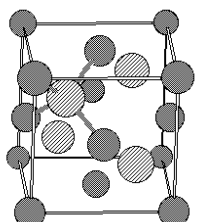
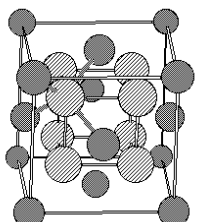
Electron delocalization in ring systems

Similar to linear systems, but this time there will be degeneracy

- Aromaticity: special stability associated with compounds in which electrons are delocalized
- Frost circles
 - Draw a circle and inscribe the cyclic molecule you are working with *point downwards*
 - To the left of the circle, draw an energy axis. Now each vertex of the molecule represents an energy level.
 - All energy levels in the lower half of the diagram will be bonding; all energy levels in the upper half will be antibonding.
 - To determine bond order, fill electrons (follow Hund's Rule) starting with the lowest energy level
 - The lowest energy level has no nodes; the highest has nodes between each atom
 - Each energy level will have one more node than the one below it (don't forget degeneracy!)
 - Sometimes nodes will lie between atoms; sometimes they will lie across atoms.



Crystal Lattices

Name	Picture	Description
Simple cubic		Atoms at each corner of a cube. This shape isn't really found in nature.
Body-centered cubic (BCC)		Fill the central cavity of a simple cubic lattice with one atom. CsCl adopts this type of structure (the Cs is in the center, with Cl on the corners).
Face-centered cubic (FCC)		A simple cubic lattice with atoms placed in the center of each face of the cube. The face atoms may be the same as or different from the corner atoms. There is one octahedral (O_h) hole in the center of this cube, and there are eight tetrahedral (T_d) holes (one in the center of each octant).
Rock salt		Two interpenetrating FCC lattices. This structure may also be created by filling each O_h hole of an FCC lattice with atoms of another type. Table salt, NaCl, and many other solid salts, form this structure.
Zinc blende		This structure is made by filling every other T_d hole in an FCC lattice. If all the atoms are the same, the structure is that of diamond. If the T_d atoms are different, the structure is that of GaAs, InP, or any number of other salts.
Anti-fluorite		An FCC lattice of anions with all of its T_d sites filled by cations. The ratio of anions to cations is 1:2.
Fluorite		An FCC lattice of cations with all of its T_d sites filled by anions. This is the opposite of the anti-fluorite structure. The ratio of anions to cations is 2:1.
Li_3B		An FCC lattice of B with all T_d sites and edge sites filled with Li ions. The ratio of Li to B is 3:1.

Pictures from <http://www.chem.lsu.edu/htdocs/people/sfwatkins/ch4570/lattices/lattice.html>

18 Electron Rule

Just like the octet rule, the 18 electron rule is merely a formalism to help us understand some of the properties of metal complexes, and the results obtained using the rule may not always reflect reality. Also, just like the octet rule, there are many exceptions to the 18 electron rule.

There are two ways to count up to 18! Pick your favorite.

Example: How many electrons does each en ligand donate in $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ if en is a neutral ligand?

The first way (**The Ionic Method//Electron Pair Method**):

- 1) Determine the oxidation state of the metal in the absence of its ligands (take complex ionic charge into account). *We know that each Cl ligand has a -1 charge. Since en is neutral (as given in the problem statement) and the complex has an overall charge of $+1$, we know that the Co atom must have a charge of $+3$.*
- 2) Use the oxidation state you determined in the first step to figure out how many *d* electrons the metal has. Count these toward the 18 that you are trying to account for. *Neutral Co has an electron configuration of $[\text{Ar}]4s^23d^7$. Taking three electrons away to form the Co^{3+} ion leaves us with an electron configuration of $[\text{Ar}]3d^6$. Therefore, 6 of the 18 electrons that we need come from the Co atom.*
- 3) Count up the electrons donated by the ligands of which you know the donation number. To find out how many electrons a common ligand donates, use the table on the next page. (Make sure you are using the correct column!) *According to the table, Cl^- donates 2 electrons. Since there are two of them, together the Cl^- ligands donate a total of 4 electrons to the total. Now our total is 10.*
- 4) To figure out how many electrons are donated by a ligand, subtract the electrons that have been accounted for from 18, then divide the difference by the number of that type of ligand that is in the complex. *10 electrons have been accounted for, so 8 are missing. There are two en ligands in the complex, so each must donate 4 electrons.*

The second way (**The Neutral Ligand Method/Covalent Method**):

- 1) Figure out how many electrons the neutral metal would have. Count these toward the 18 that you are trying to account for. *Neutral Co has 9 valence electrons, so we have accounted for 9 of the 18 electrons.*
- 2) Count up the electrons donated by the ligands for which you know the donation number. Use the table on the next page to how many electrons common ligands donate. *According to the table, Cl^- donates 1 electron when we are using this counting method. Since there are two Cl^- ligands, our total is now 11 electrons.*
- 3) Determine the charge of the complex ion. Subtract this number from the total so far. This will account for the charge of the complex ion. *The complex ion has a $+1$ charge, so we have to subtract this from the 11 we have counted so far, leaving 10 out of 18.*
- 4) To figure out how many electrons are donated by a ligand, divide the number of electrons that are unaccounted for by the number of that type of ligand that is in the complex. *There are still 8 electrons which have not been accounted for, and there are two en ligands in the complex, so each en must donate 4 electrons.*

Electron counting for 18-electron rule

Ligand	Number of e ⁻ donated	
	Ionic Method	Neutral Ligand Method
H ⁻ , CH ₃ ⁻ , CH ₂ CH ₃ ⁻ CN ⁻ , OH ⁻ F ⁻ , Cl ⁻ , Br ⁻ , I ⁻ NO ⁻ η ¹ -CH ₂ CHCH ₂ ⁻ η ¹ -C ₅ H ₅ ⁻	2	1
H ₂ O, SH ₂ NH ₃ , PH ₃ CO HCN η ² -benzene	2	2
η ³ -CH ₂ CHCH ₂ ⁻ η ³ -C ₅ H ₅ ⁻	4	3
cyclobutadienyl butadienyl 1,5-COD η ⁴ -benzene ethylenediamine (en)	4	4
η ⁵ -C ₅ H ₅ ⁻	6	5
η ⁶ -benzene	6	6

Transition Metals Complexes and Crystal Field Splitting

Transition metal complex A molecule made up of a transition metal atom with several smaller molecules (ligands) bound to it, often including counter ions to form a neutral species, and sometimes including some amount of hydration (waters bound loosely).

Complex ion The part of the transition metal complex which includes only the central metal and its inner sphere ligands.

Inner sphere ligands Ligands that are directly bound to the central metal atom.

Outer sphere ligands Additional structures, such as counter ions and hydrating water molecules, which are part of the overall transition metal complex.

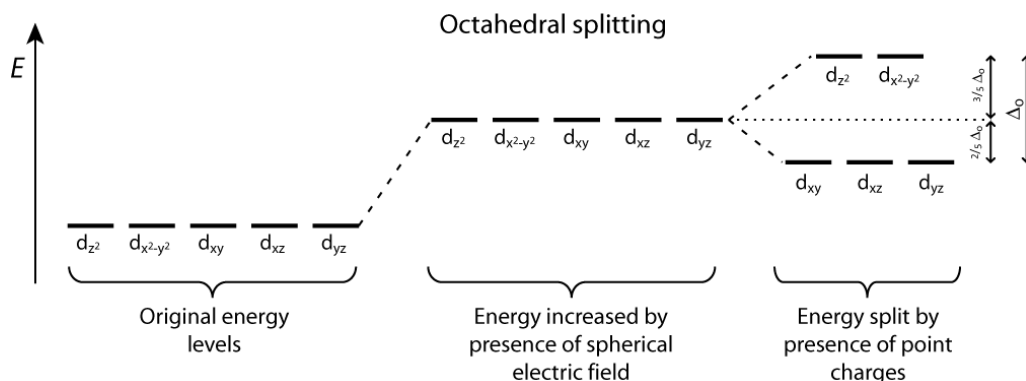
Oxidation number/state The charge on the central metal atom. This term often also refers to the charge of the complex ion.

Coordination number The number of bonds between the central metal atom and its ligands.

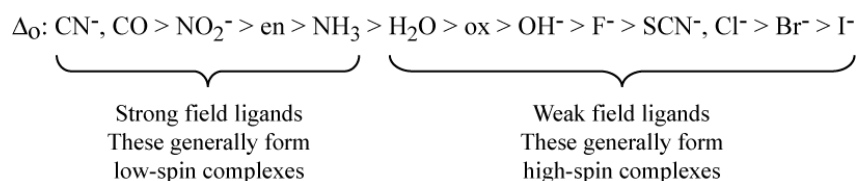
Crystal field theory

As electrons are brought close to a metal atom, the energy levels of that metal atom's electrons will respond. If the electrons were to approach as a diffuse sphere, all of the energies of the d orbitals would increase by the same amount. If the electrons approach as point charges, different d orbitals will be affected in different ways.

The crystal field splitting for octahedral complexes is shown below:



Different complexes show different amounts of crystal field splitting. The amount of splitting is determined partly by the type of ligand bound and partly by the type and oxidation state of the central metal. The *spectrochemical series*, below, shows the relative amount of splitting caused by different ligands. Another series, based on the way metals affect Δ_o , is called the nephelauxetic series (see lecture slide XV-39.)



Transition Metal Complex Examples

Example 1: $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_2$

- a) What is the counter ion?
The counter ion is Cl^-
- b) What is the charge of the complex ion?
Since there are two Cl^- ions to balance the charge, the complex ion must have a charge of $2+$.
- c) What is the oxidation state of the metal?
Since the inner sphere H_2O ligands are neutral, the Fe must have the same charge as the complex ion, so the oxidation state of Fe is $2+$.
- d) Does this complex follow the 18 electron rule?
*Ionic method: 6 (neutral Fe has 8 valent e^- , minus 2 for $2+$) + 2×6 (2 from each H_2O) = 18
Neutral method: 8 (Fe) + 2×6 (H_2O) - 2 (complex ion charge) = 18*
- e) What is the electron configuration of the metal atom?
Neutral Fe has a configuration of $[\text{Ar}]4s^23d^6$. Ionization takes away the s electrons, leaving $[\text{Ar}]d^6$.
- f) Do you expect the complex to be high-spin or low-spin?
The ligands, H_2O , are weak field ligands (although H_2O is right on the border between strong- and weak-field in the spectrochemical series), and Fe^{2+} is in the middle of the nephelauxetic series (meaning Fe^{2+} may not be a strong enough ion to make the complex low-spin), so we can estimate that the complex will be high-spin.
- g) Draw the energy diagram for the complex.
The complex is d^6 high-spin, so its energy diagram looks like this:
- $$\begin{array}{c} \uparrow \quad \uparrow \\ \hline \uparrow\downarrow \quad \uparrow \quad \uparrow \end{array}$$
- h) Is the complex diamagnetic or paramagnetic?
There are unpaired electrons, so the complex is paramagnetic.
- i) What is the ligand field stabilization energy of the complex?
Each electron in the lower three levels contributes $-2/5$ to the LFSE, and each electron in the upper levels contributes $+3/5$ to the LFSE, so the total LFSE is $(-2/5) \times 4 + (3/5) \times 2 = -2/5$

Example 2: Answer the same questions for the complex $[\text{Mn}(\text{CN})_6]\text{K}_3$.

ANSWERS:

- a) K^+
- b) -3 (must balance the charge of the counter ion)
- c) 3+ (each CN^- has a -1 charge)
- d) Ionic: 4 (Mn^{3+}) + 2×6 (CN^-) = 16. Neutral: 7 (Mn) + 1×6 (CN) - (-3) = 16. Does not follow 18 e^- rule.
- e) $[\text{Ar}]3d^4$
- f) Low-spin is a good guess. CN are strong-field ligands.
- g)
- $$\begin{array}{c} \text{---} \text{---} \\ \hline \uparrow\downarrow \quad \uparrow \quad \uparrow \end{array}$$
- h) Paramagnetic.
- i) $(-2/5) \times 4 = -8/5$