

Structure and Bonding in Organic Compounds

Class Outline

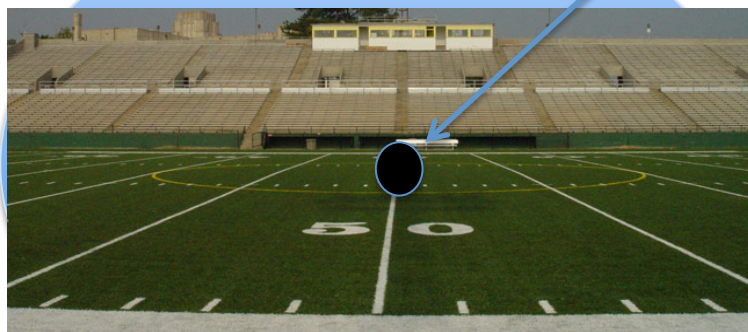
- Introduction
- Atomic structure and Carbon
- Drawing Carbon based Chemicals
- Introduction to ChemDraw and SciFinder
- The difference between “Vitalism”, Organic Chemistry and Organic Food
- Electrons and electron configurations
- Electrons as waves and shapes
- Valence Bond Theory
- Hybridization of carbon (sp^3 , sp^2 and sp hybrid orbitals)
- sigma and pi bonds
- Hybridization of heteroatoms (N, P, O, S)
- Molecular orbital theory

The atom and the Super Bowl

Atomic Number

- = number of protons (or e-s)
- = number on the periodic table
- for Carbon, $Z = 6$

Nucleus (+ charge)
 10^{-15} meter diameter
all mass is here
(protons and neutrons)



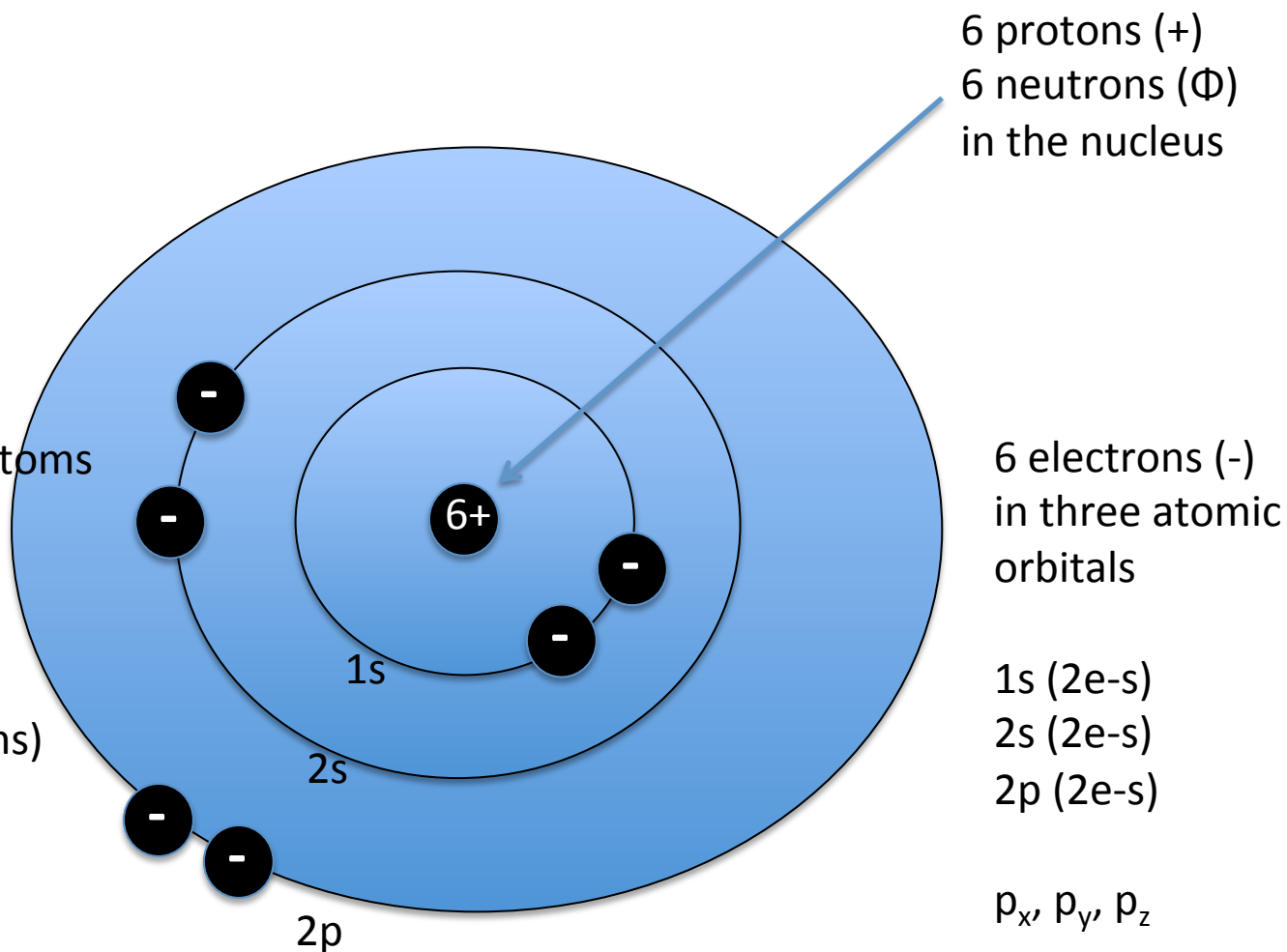
Electron cloud (- charge)
* Negligible mass

Atomic Mass

- = number of protons *and* neutrons
- = used to calculate stoichiometry
(and reaction yields)
- = average isotopic abundance
- for C, atomic mass = 12.011 g/mol

Diameter of typical atom = 2×10^{-10} m (200 pm)

Atom structure of carbon



6 protons (+)
6 neutrons (Φ)
in the nucleus

6 electrons (-)
in three atomic
orbitals

1s (2e-s)
2s (2e-s)
2p (2e-s)

p_x, p_y, p_z

Group 4A
- 4 valence e-s
- 4 covalent bonds

Can bond with other
C atoms and/or other atoms

50 million known
carbon compounds
- methane (1C atom)
- DNA (1 million C atoms)

Drawing Compounds of Carbon

- Lines represent bonds (single, double, triple)
- Corners represent atoms
 - If unlabeled, carbon atom is implied
 - If corner is not carbon, atom must be specified (O, N, S, P, Si, etc)

Bonds to hydrogen atoms are not typically drawn unless they are involved in a *reaction mechanism*

Drawing organic structures

- H with 1 bond = neutral
- hydride (H^-) and proton (H^+)

- C with 4 bonds = neutral = no lone pairs
- C with 3 bonds = carbanion (-ve) or carbocation (+ve)

- N/P with 3 bonds and one lone pair = neutral
- N/P with 4 bonds and zero lone pairs = nitride/phosphide
- N/P with 2 bonds and two lone pairs = nitronium/phosponium

- O/S with 2 bonds and 2 lone pairs = neutral
- O/S with 1 bond, 2 lone pairs and -ve charge = oxide/sulfide
- O/S with 3 bonds, 1 lone pair and + charge = oxonium/sulfonium

- Halogens with 1 bond, 3 lone pairs, neutral
- Halogens with 0 bonds, 4 lone pairs, -ve charge = halides
- Halogens with 2 bonds, two lone pairs, +ve charge = haloniums

ChemDraw and SciFinder

- Used to draw structures for formal presentation/papers and link these structures to a database of published reactions, topics and commercial sources
- Can rapidly determine molecular mass
 - Useful for fragmentation analysis when using mass spectrometry (MS)
- Can predict H and C nuclear magnetic resonance (NMR) spectra
- ChemDraw 3D can predict compound stabilities and produce energy min/max plots

What is Organic?



- Of, relating to, or arising from a *bodily organ or organism*
- ***Of, relating to, or containing carbon-based compounds***
- Forming an integral element of a whole, having systematic coordination of parts
- Of, relating to, or **constituting the law by which a government or organization exists**

Organic Chemicals are Everywhere...

- Every living organism is made of organic chemicals (DNA, protein, fats, vitamins)
- Food (protein, fats, carbohydrates)
- Medicines (pharmaceuticals, nutraceuticals)
- Fuels (natural gas, ethanol, gasoline, diesel, biodiesel, jet)
- Plastics, fabrics, paints, paper, etc...



“Organic” food



Food that is “Certified Organic” is food produced by national and international guidelines for organic farming such as the USDA or the European Commission

Synthetic pesticides and chemical fertilizers are prohibited.* Foods are not processed with irradiation, industrial solvents or synthetic food additives.

Animals for meats are not fed with animal by-products, genetically engineered and cannot receive growth hormones or antibiotics.

*synthetic herbicides for weed control can be selected from an approved list of substances

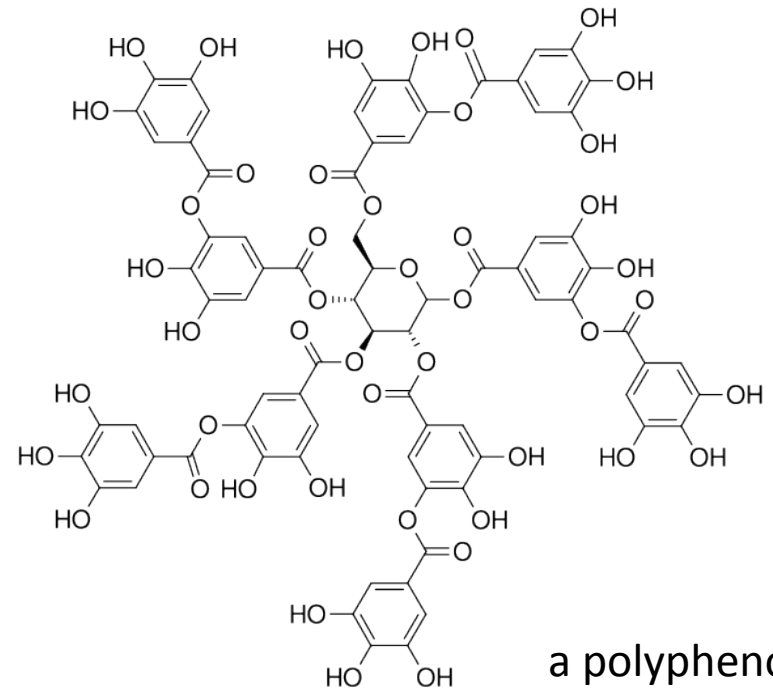
Organic Food Chemistry

“In 2014 an analysis of 343 studies showed that organic food contained 17% greater polyphenol content as compared to conventionally grown crops.”¹

Polyphenols = Antioxidants

4 x less cadmium

Less pesticide residues



¹ British J. Nutrition 2014, 112 (5) 1-18

Case 1 Against Vitalism: The Wöhler Synthesis

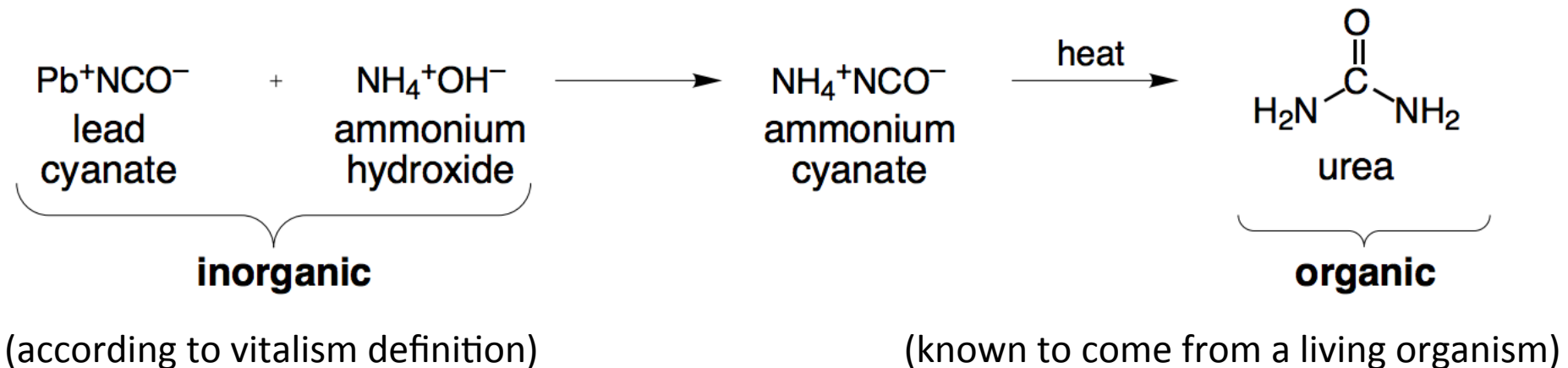
“Organic from Inorganic”

1780: Organic compounds very complex and only obtained from living sources (vitalism)

Vitalism: Belief that a "magic" vital force, present in plants and animals, is necessary for the synthesis of organic compounds

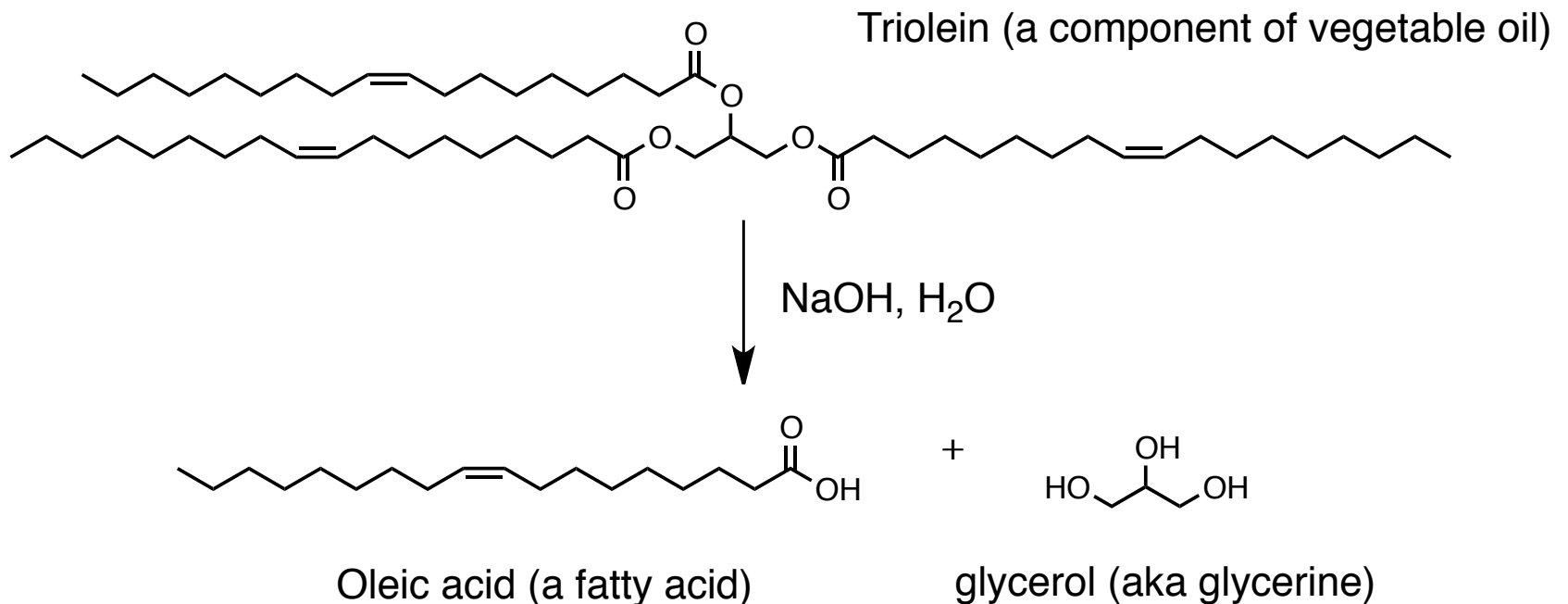
1789: Antoine Laurent Lavoisier observed that organic compounds are composed primarily of carbon and hydrogen

1828: Friedrich Wohler synthesized an organic compound (urea) from inorganic compounds (lead cyanate and ammonium hydroxide).



Case 2 Against Vitalism: Synthesis of Soap “Organic to Organic”

Michel Chevreul (1816) also disproved “vitalism” by showing that biological substances (fats and oils) can be converted into other biological substances (fatty acids and glycerol, a.k.a. soaps)



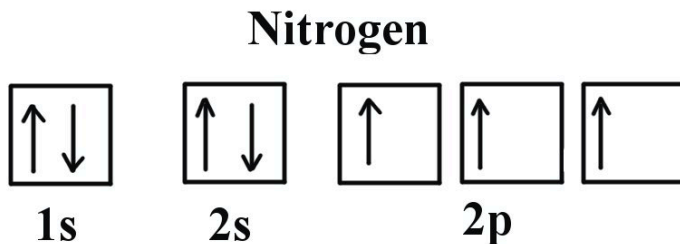
Why Study Electrons?

- Their transition energies are fundamental to many *physical* phenomenon (electricity, magnetism, thermal conductivity)
- They bond atoms together to form molecules and this is the basis of all *chemistry*
- *Applications* (electronics, welding, microscopy, lasers, etc) are the basis of many technical industries

Intrinsic Property of Electrons: Spin

Hund's Rule

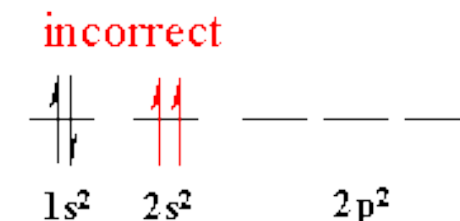
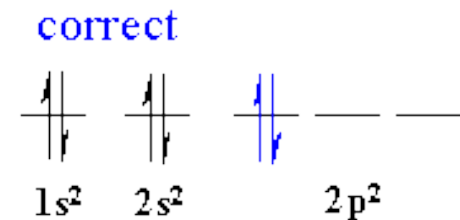
“Every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin.”



Pauli's Rule

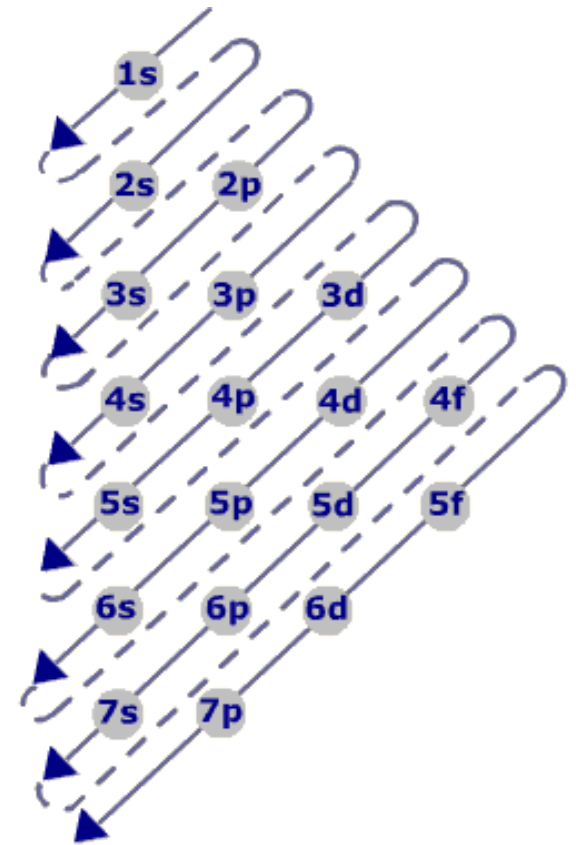
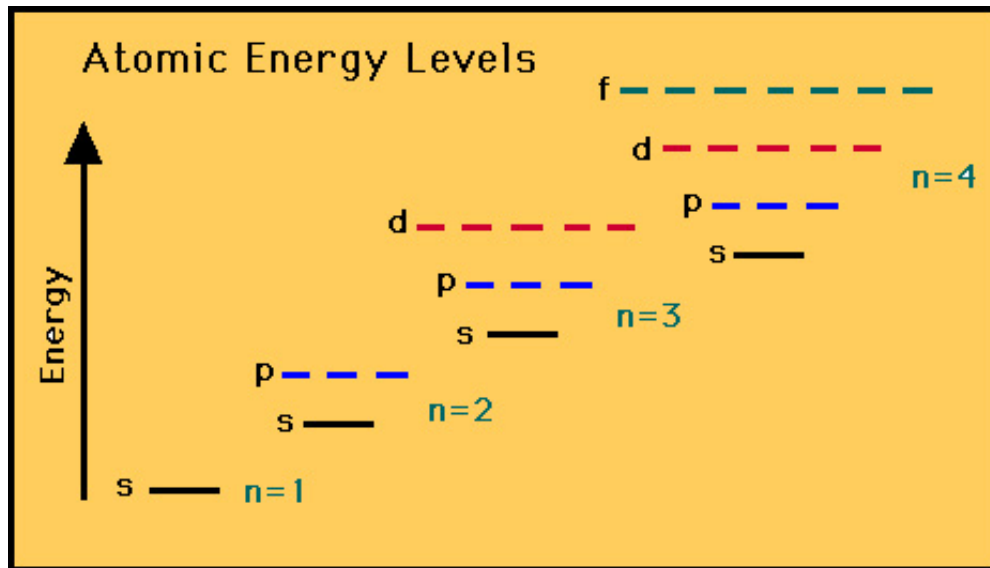
“Two identical [electrons] cannot occupy the same [orbital] simultaneously”

i.e. electrons must be “spin paired”



The Aufbau “building up” Principal

- Lowest energy orbitals fill 1st
- Note that 4s orbital fills before 3d orbitals because it 4s is lower in energy



Atomic Structure: Shells, Subshells and Orbitals

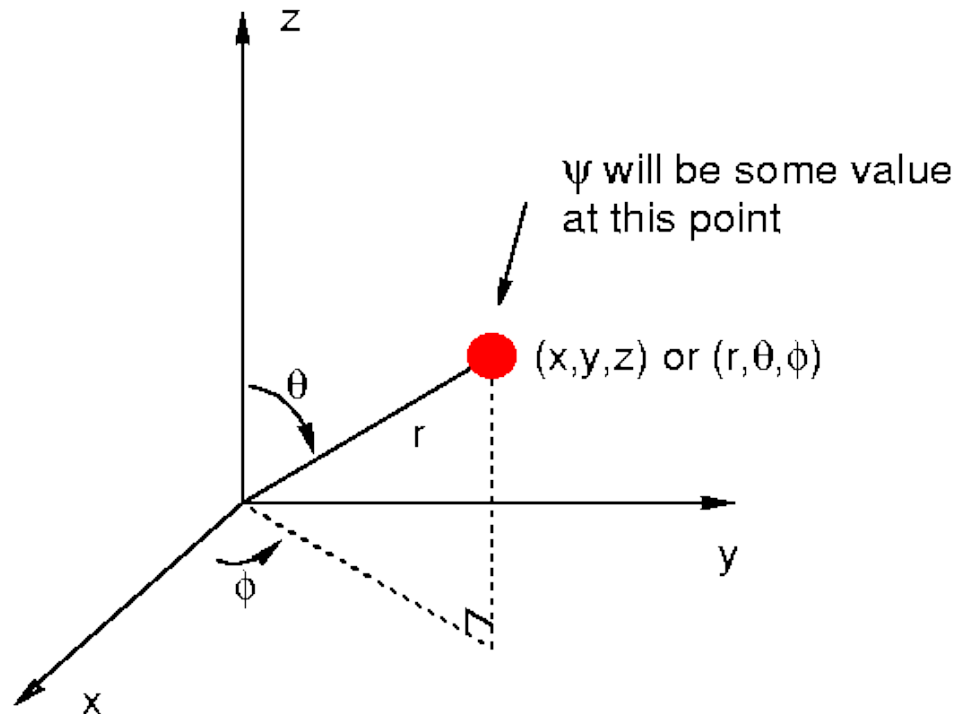
- **Quantum mechanical model of the atom:** the behavior of a *specific electron* in an atom can be described by a wave equation (like a wave in a fluid)
- The wave equation is a differential equation and its solution is called the wave function (Ψ)
- Ψ^2 is a 3D plot used to describe the ***probability*** of locating an electron in a given time and place
- These 3D plots are called “orbitals”

The Schrödinger equation for a single particle in 3D

Used to describe the probability of finding an electron in an orbital

(orbital = a space orbiting the nucleus)

$$i\hbar \frac{\partial}{\partial t} \psi = -\frac{\hbar^2}{2m} \nabla^2 \psi + V(x, y, z) \psi$$



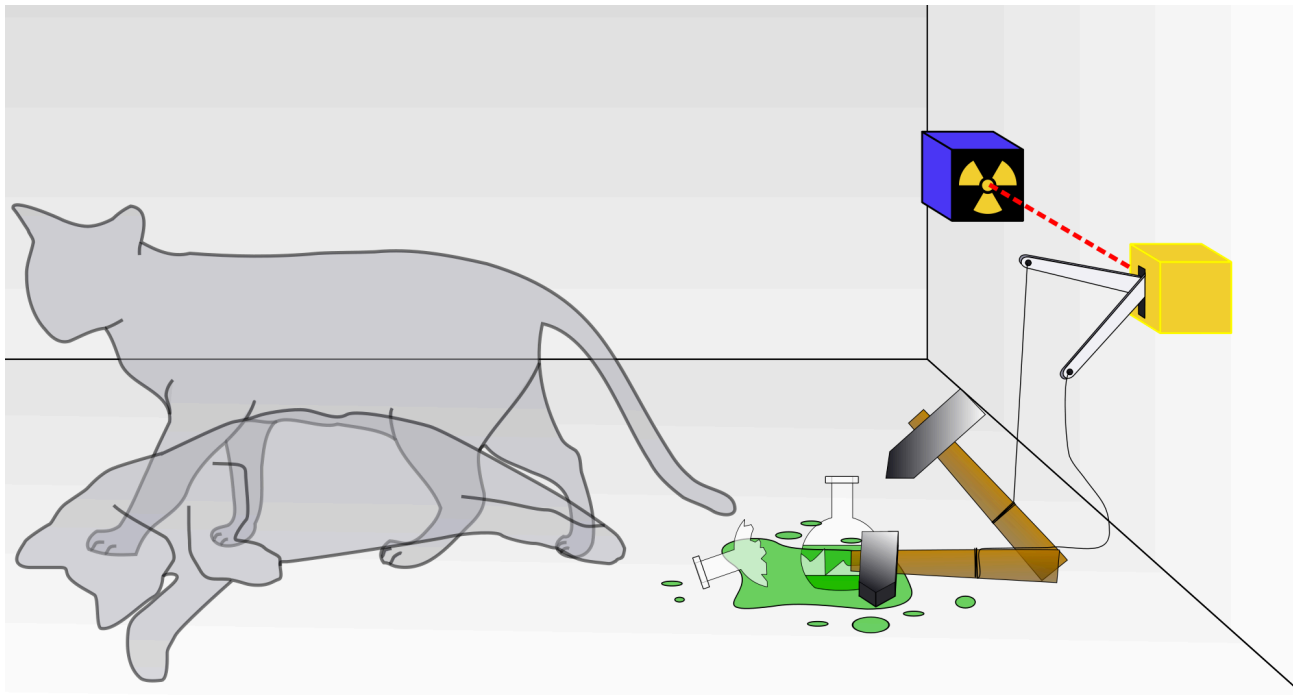
Ψ = the wave function (amplitude for particle)

m = mass of particle

$V(x, y, z)$ = potential Energy of particle in each position

The Schrödinger Cat and Heisenberg's Uncertainty Principle

- Because all particles (including electrons) have a dual nature (they behave as both waves and particles), you can not know position (x,y,z) and momentum at the same time



Electron Locations

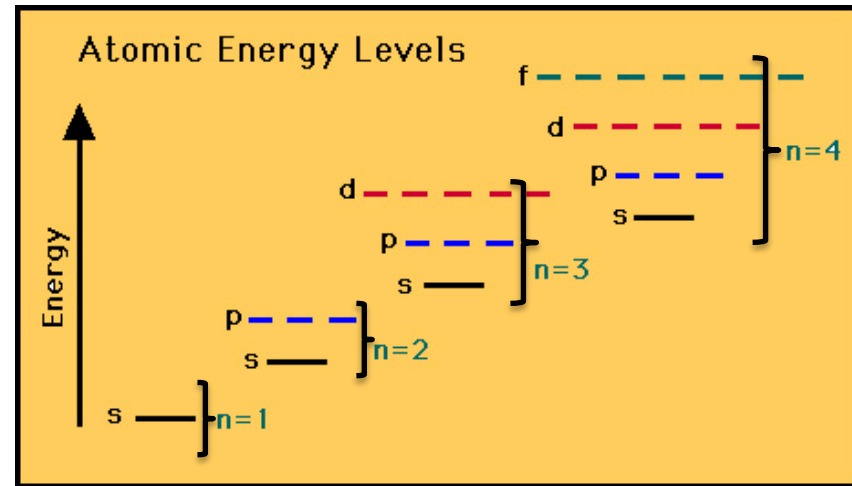
- **Shells** “The Building”

- Principal Quantum Number (n)

- 2 carbon e-'s have $n = 1$

- 4 carbon e-'s have $n = 2$

- the $n = 2$ electrons are “bonding” (valence) electrons



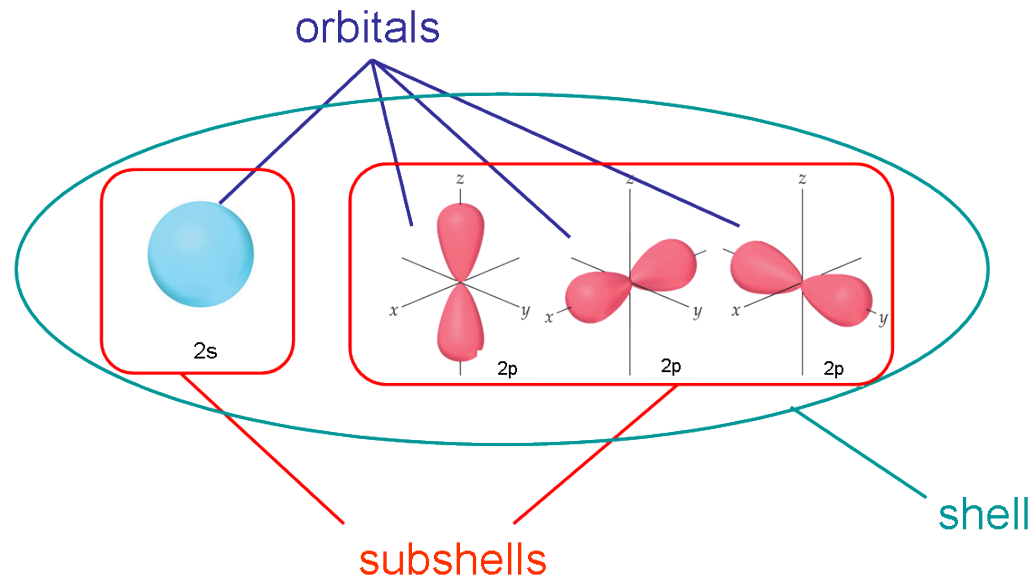
- **Subshells** “The Apartment”

- i.e. 1s, 2s or 2p

- 2s and 2p are valence

- **Orbitals** “The Bedroom”

- i.e. $2p_x$



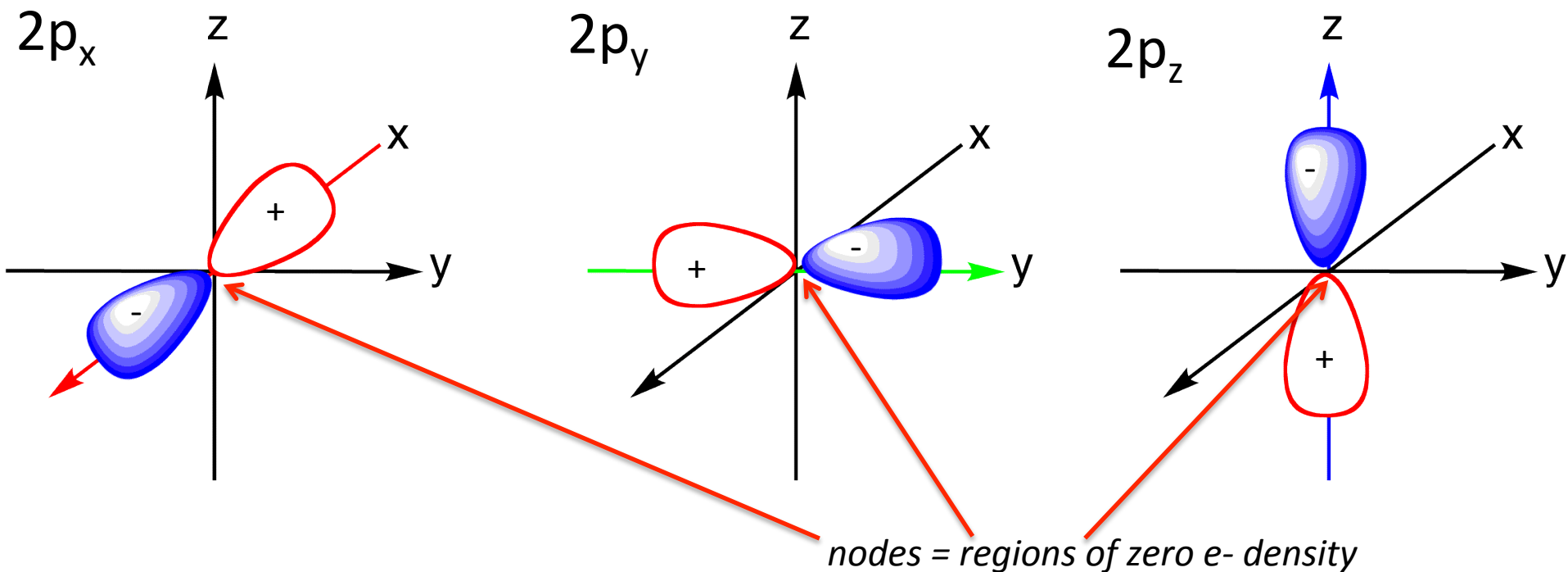
Subshells and orbitals determine the *shape* of the bond

Electronic orbitals

	Subshell	Shape	Total # of orbitals	Total # of electrons
Organic chemistry	<i>s</i>	<i>spherical</i>	1	2
	<i>p</i>	<i>dumb-bell</i>	3	6
Inorganic chemistry	d	clover leafed	5	10
	f	complex	7	14

Note * the s subshell has only 1 orbital

2p orbitals of carbon



- Three 2p orbitals (2p_x, 2p_y and 2p_z) are aligned “orthogonally” (along perpendicular axes).
- For each 2p orbital: $n = 2$ and $l = 1$
- Each p-orbital therefore has one angular node and zero radial nodes
- The two orbital regions separated by a node have different algebraic signs (+ and -)
- **These regions (lobes) represent the opposite phases of the a wave function and have different reactivity and bonding abilities**

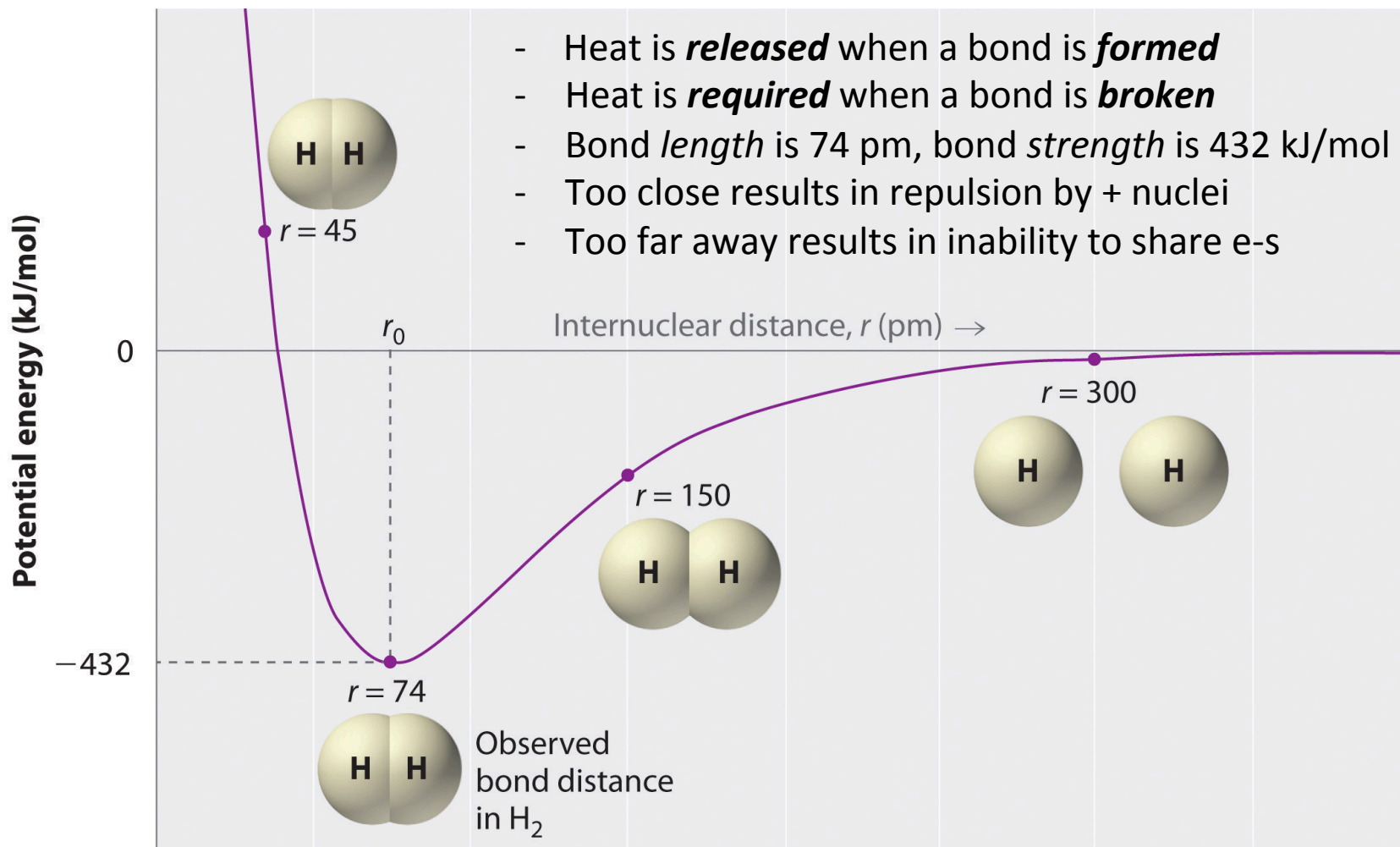
Organic Electronics Review

- Orbitals of atoms are organized into different electronic “shells” that are centered around the nucleus and have successively larger size and energies.
- Different shells have a different number and kinds of orbitals
- Each orbital has max of 2 e-s
- Organic chemistry is focused mainly on s and p-shaped orbitals in the second shell of carbon, nitrogen and oxygen and can include silicon, phosphorus, sulfur and the halogens.
- Hydrogen has one electron in one 1 s subshell/orbital and is present in most organic compounds

Chemical Bond Theory

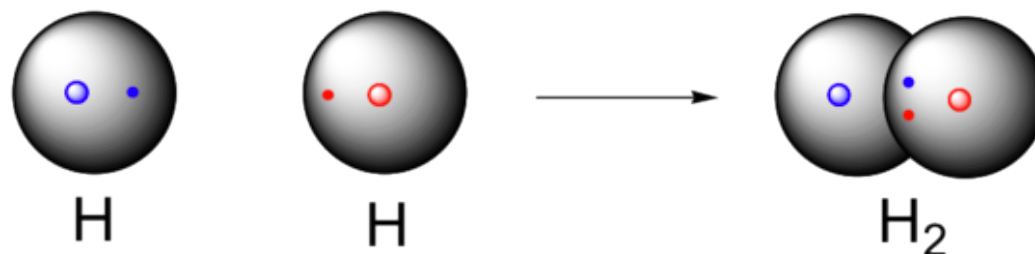
- Kekulé (1858) predicts a tetravalent carbon (4 bonds) and ring structures
- Van't Hoff (1874) predicts carbon sits in the middle of a regular tetrahedron
- ***Atoms are bound together because the resulting compound is more stable and lower E than the individual separate atoms***
- Ionic bonds *transfer* e-s to achieve octet
- Covalent bonds *share* electrons to achieve octet
- **Valence Bond Theory** - *atomic orbital overlap* to account for e- sharing
- **Molecular Orbital Theory** – *molecular orbitals* formed to share e-s. A *mathematical combination of wave functions*

Energetics of the H-H bond



Valence Bond Theory and Sigma Bonds

- A covalent bond forms when two atoms approach each other closely and a singly-occupied orbital of one atom overlaps with that of another



- e-s are now paired in the overlapping orbitals and attracted to the nuclei of both atoms
- **Sigma bonds (σ)** are formed by the head-on overlap of two atomic orbitals (*s-s or s-p_n*)

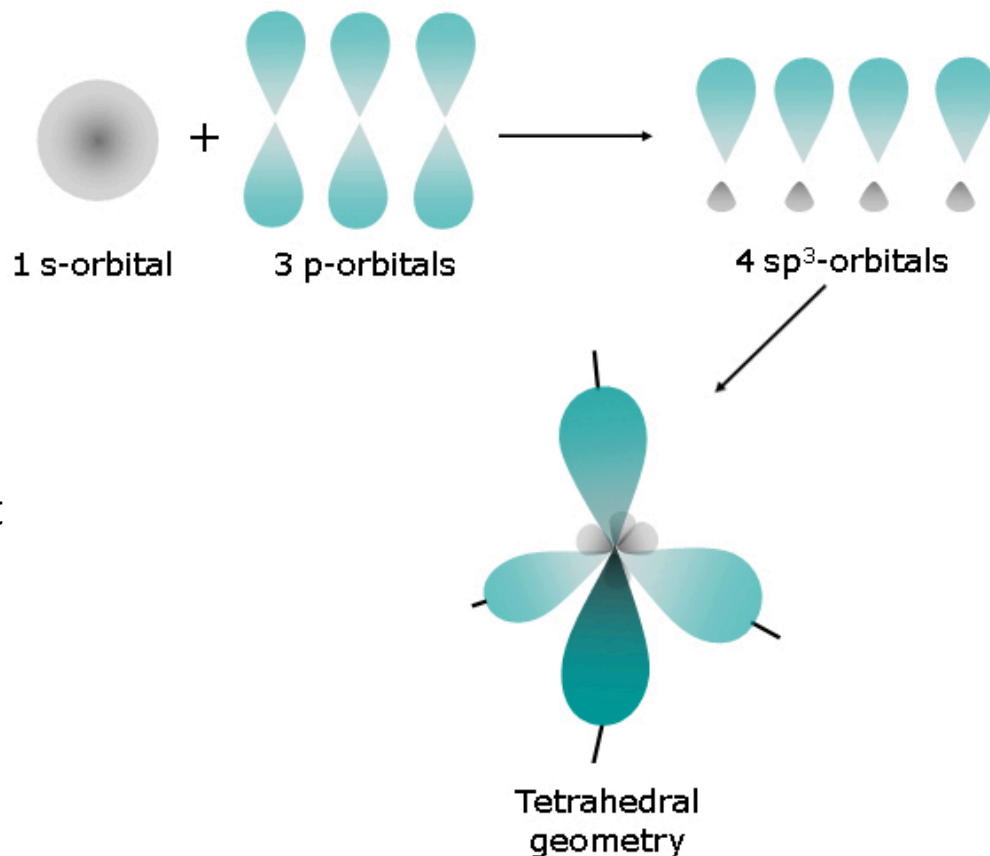
Hybrid Atomic Orbitals

- s and p orbitals combine to form *hybrid atomic orbitals*

- These new types of orbitals are involved in forming most covalent bonds

- Electron clouds repel to assume the most distant geometry (e.g. tetrahedral, 109.5°)

- When drawing structures they should have correct bond angles!



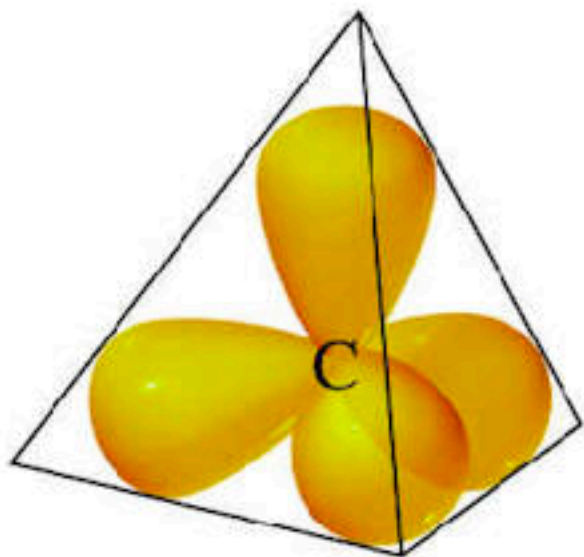
Sigma bonds (σ) are also formed by the head-on overlap of *two hybrid atomic orbitals*, or *the overlap of an atomic orbital (i.e. $1s$ of hydrogen) with a hybrid atomic orbital*

Examples = methane (CH_4) and ethane (CH_3CH_3)

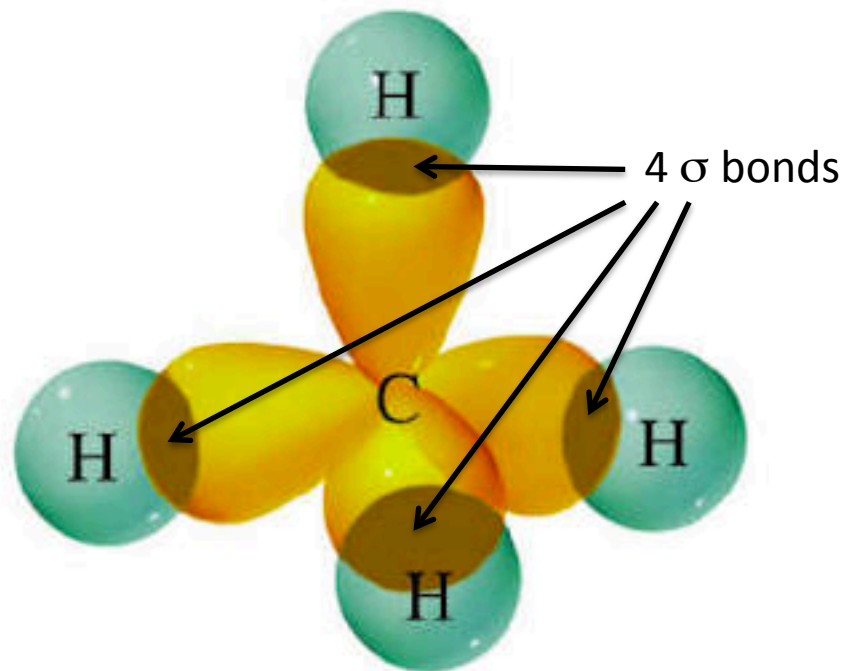
sp^3 hybrid orbitals and the structure of methane

- Methane = simplest organic molecule
- Hybridization of two 2s and one $2p_x$ and one $2p_y$ electrons to form four sp^3 hybrid orbitals
- sp^3 hybrid orbitals are “asymmetric” about the nucleus with larger lobes extending out to form bonds
- Extended lobes can overlap more effectively with other hybrid atomic orbitals to form bonds (σ bonds, for example)
- Bonds from hybrid orbitals are stronger than those of un-hybridized s or p orbitals

Methane (CH₄)

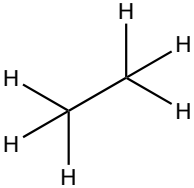
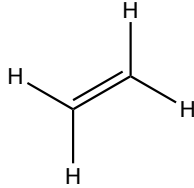
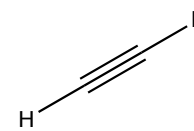


(a)



(b)

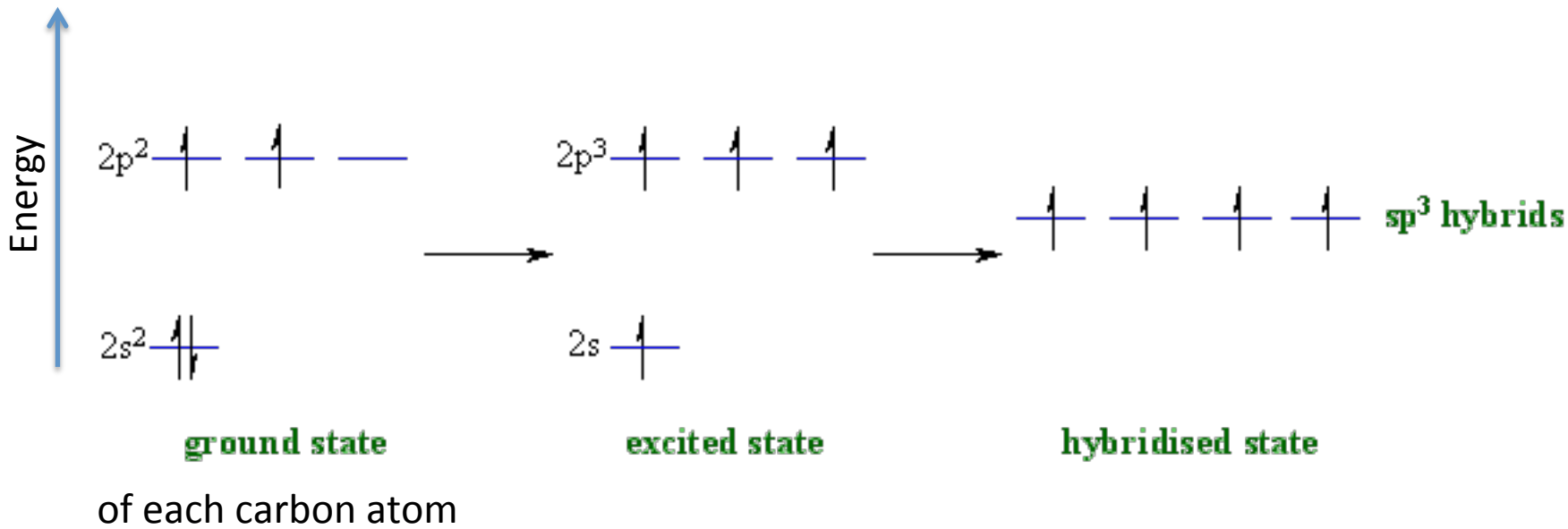
Hybridized Carbon Atoms: sp^3 , sp^2 and sp

Compound (Formula)	Hybrid carbon atom type	Number of s electrons that hybridize*	Number of p electrons that hybridize*	Number of p electrons that do <u>not</u> hybridize*	Number of pi (π) bonds **
 Ethane (C ₂ H ₆)	sp^3	1	3	0	0
 Ethene (C ₂ H ₄)	sp^2	1	2	1	1
 Ethyne (C ₂ H ₂)	sp	1	1	2	2

* = per carbon atom

** = in the entire molecule

sp³ hybridization of ethane (C₂H₆)



Ethane (C_2H_6) has two “sp³ carbons”

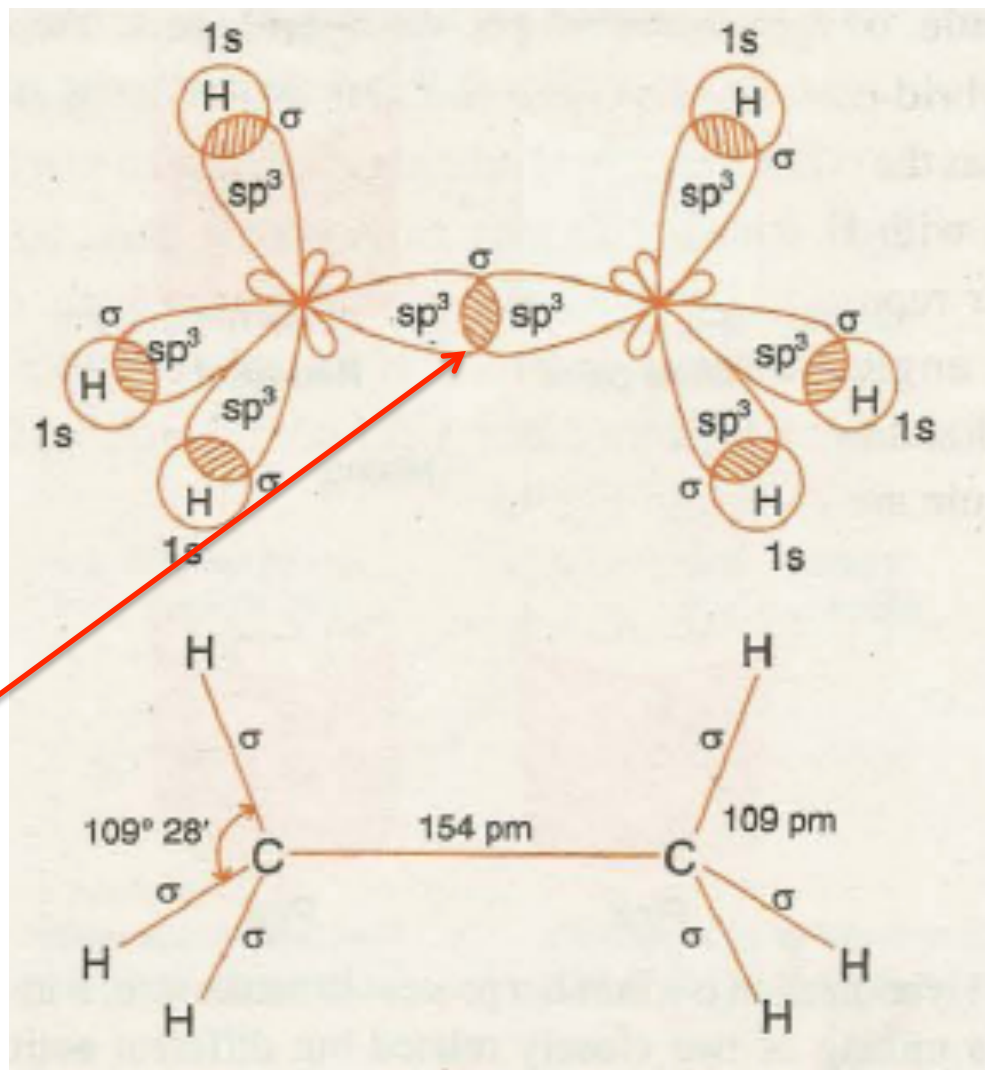
Each carbon has four sp³ hybrid atomic orbitals

Each hydrogen has one (1s) orbital

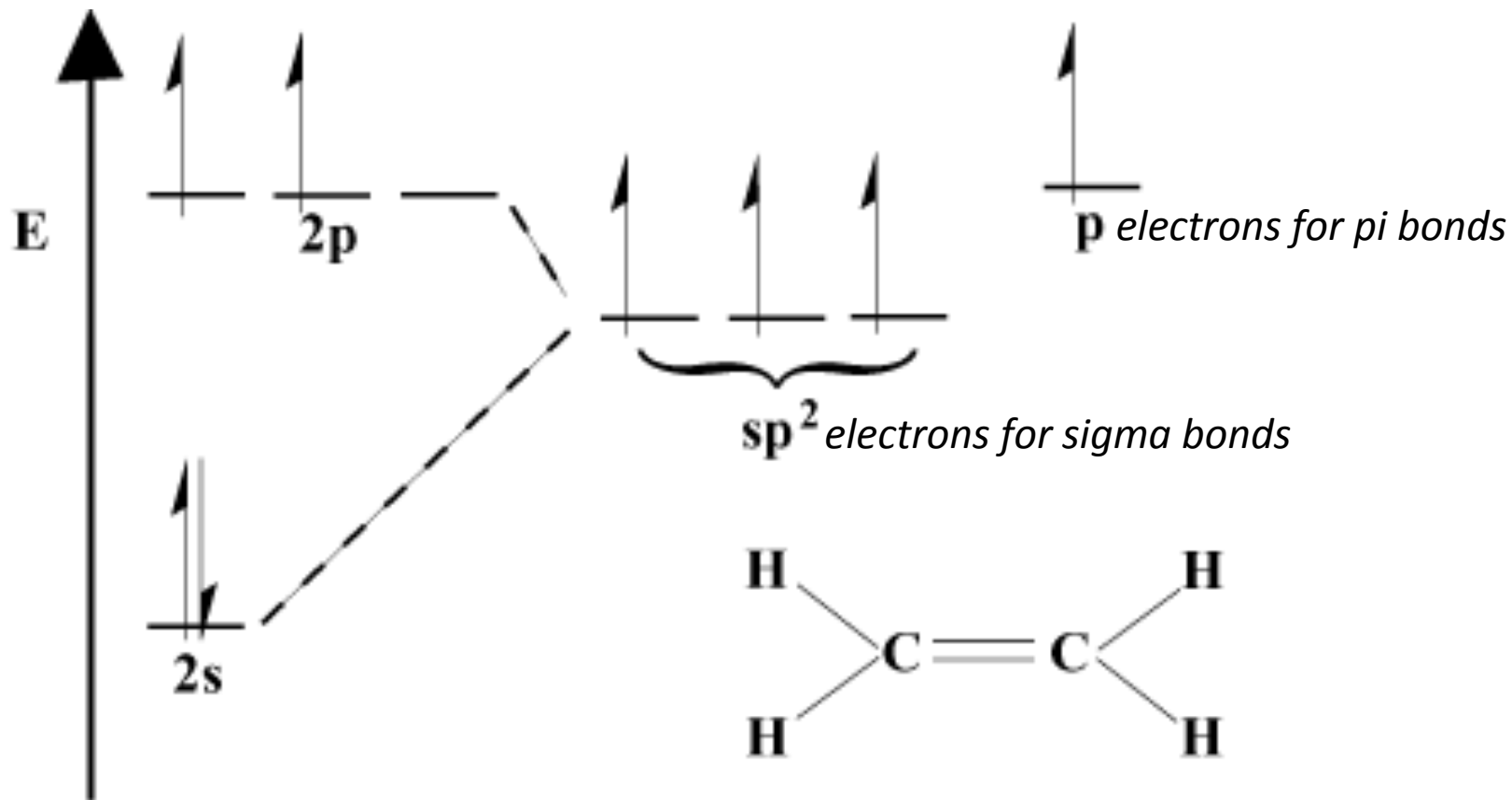
7 sigma (σ) bonds in the entire molecule

109.5° bond angles

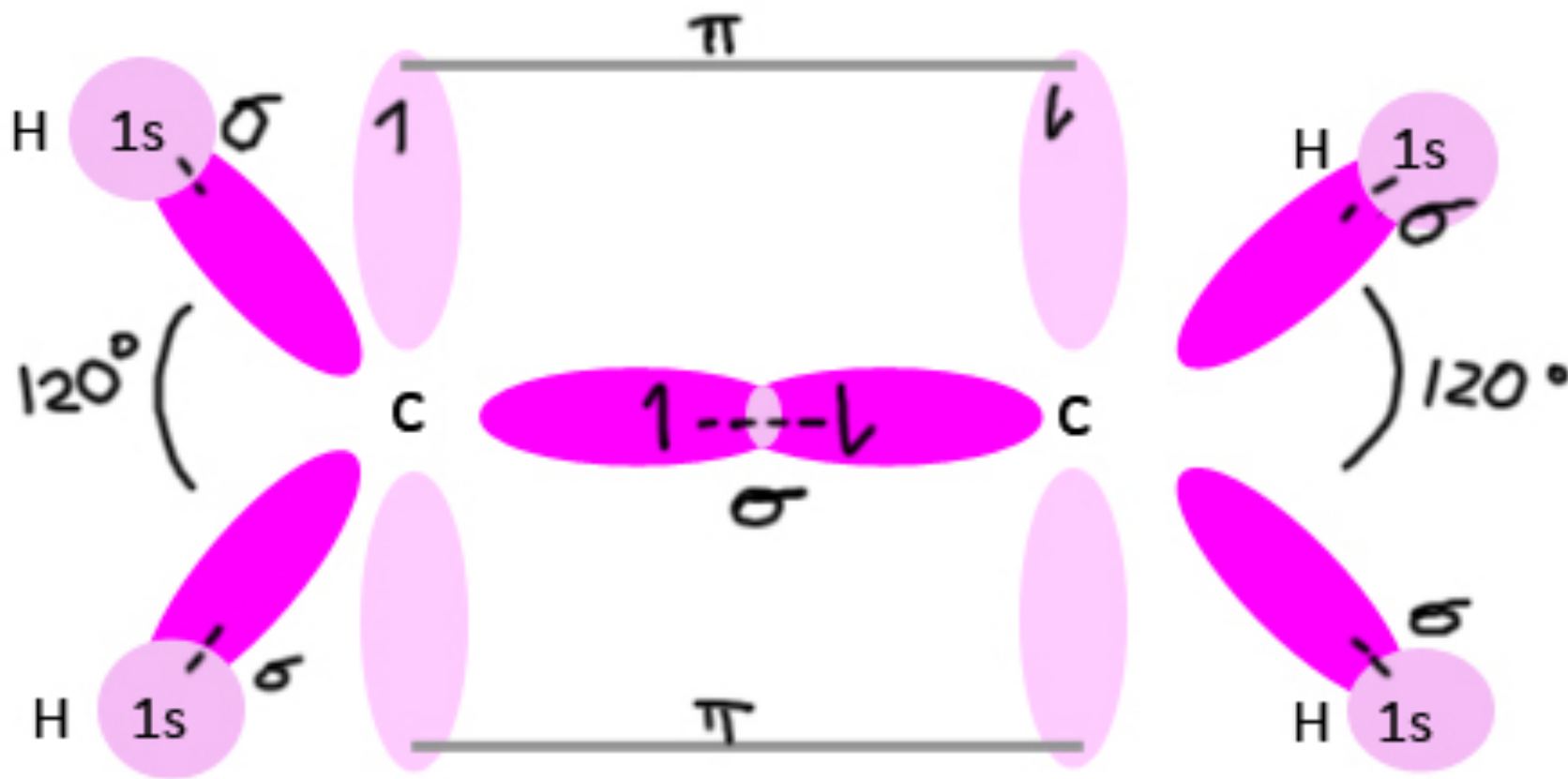
This is first example of a **carbon-carbon single (σ) bond** (154 pm, 377 kJ/mol)



sp² hybridization of ethene (C₂H₄)

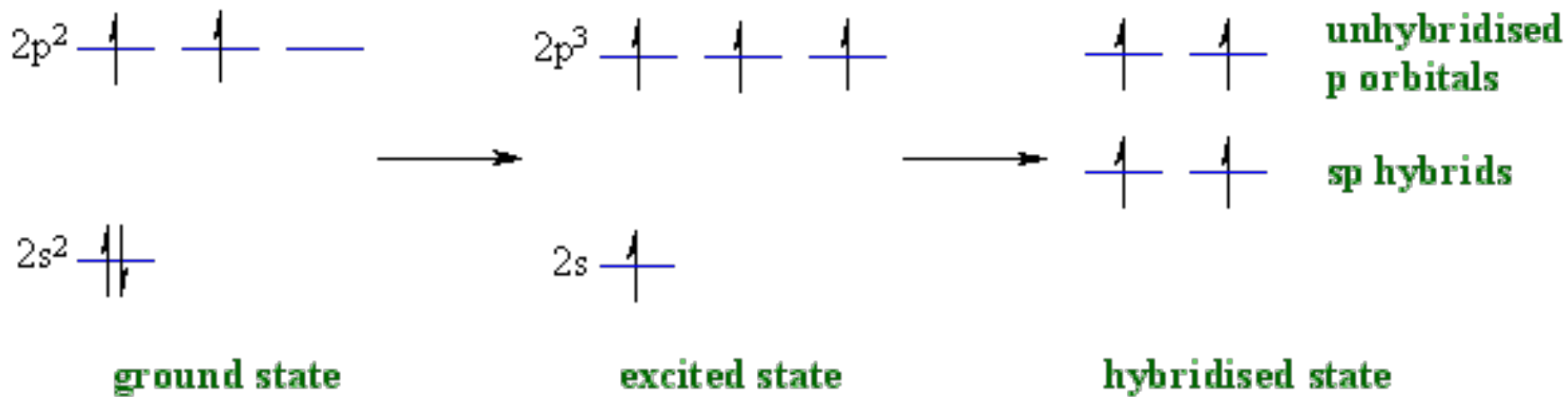


Ethene (C_2H_4) has two “sp² carbons”



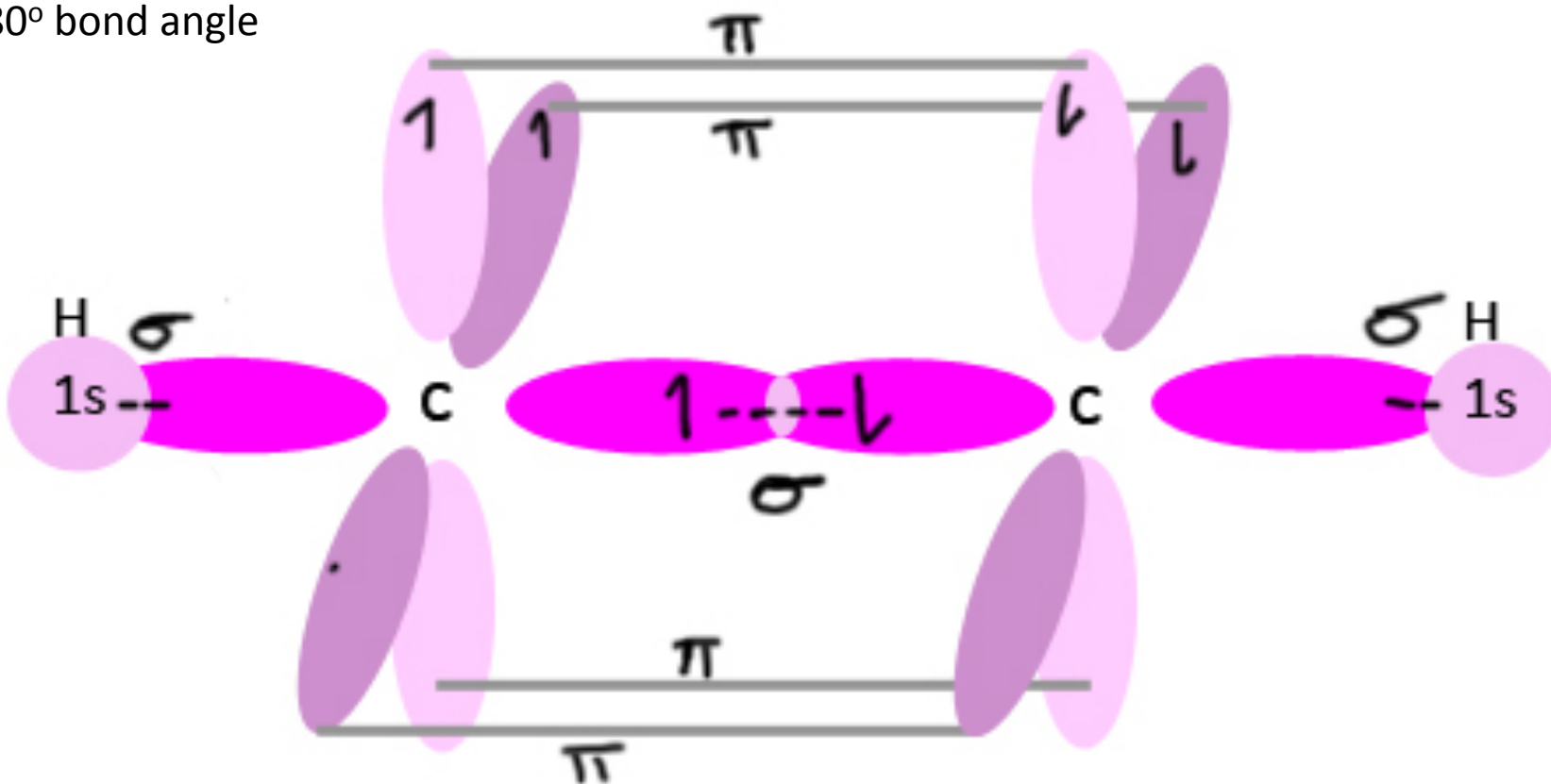
This is an example of a carbon-carbon **double** bond (134 pm, 728 kJ/mol)

sp hybridization of ethyne (C_2H_2)



Ethyne (C_2H_2) has two “sp carbons”

180° bond angle

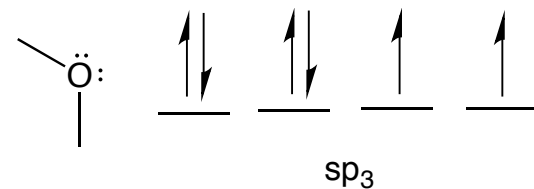
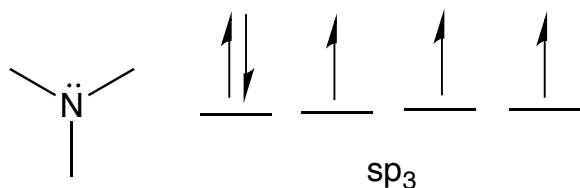
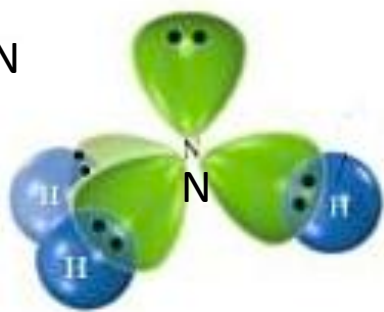


This is an example of a carbon-carbon **triple** bond (120 pm, 965 kJ/mol)

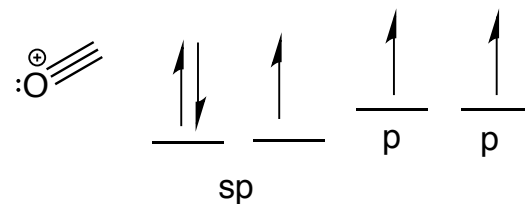
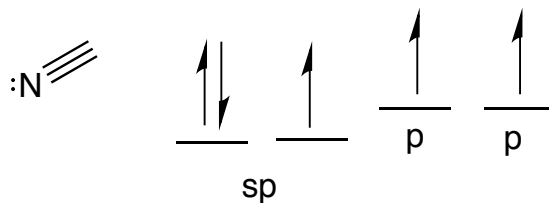
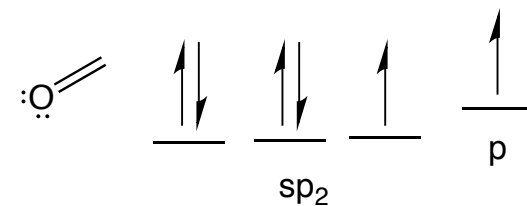
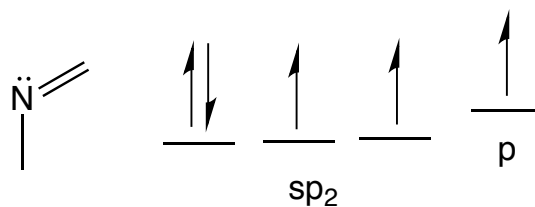
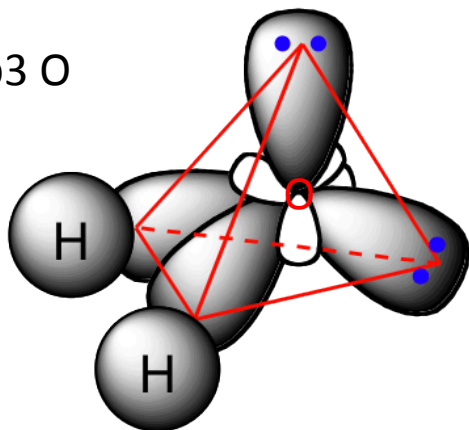
Heteroatoms = Non-Carbon/Hydrogen

- Nitrogen and Phosphorus (2 + 3 valence e-s)
- Oxygen and Sulfur (2 + 4 valence e-s)

sp³ N



sp³ O

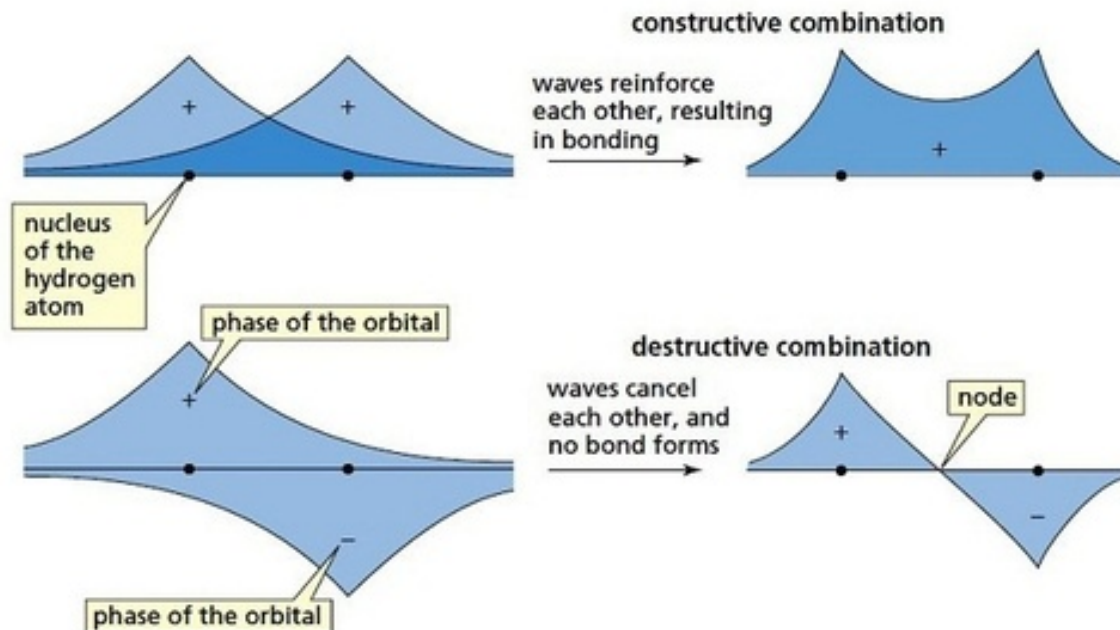


Molecular Orbital Theory

- Treat all electron orbits in the same molecule as one
- As such, *any* electron in a molecule may be found *anywhere* in the molecule
- High frequency light (or other energy input) can excite all electrons to a higher energy state
- This accounts for color of highly “conjugated” pi systems. The molecules absorb light at low energy (i.e. the visible spectrum)

Bonding and Anti-bonding

- Molecular orbitals have low and high energy regions where electrons can occupy
- Dependent on nodal/wave overlap (constructive or destructive interference)



Nodes = Regions of zero electron density

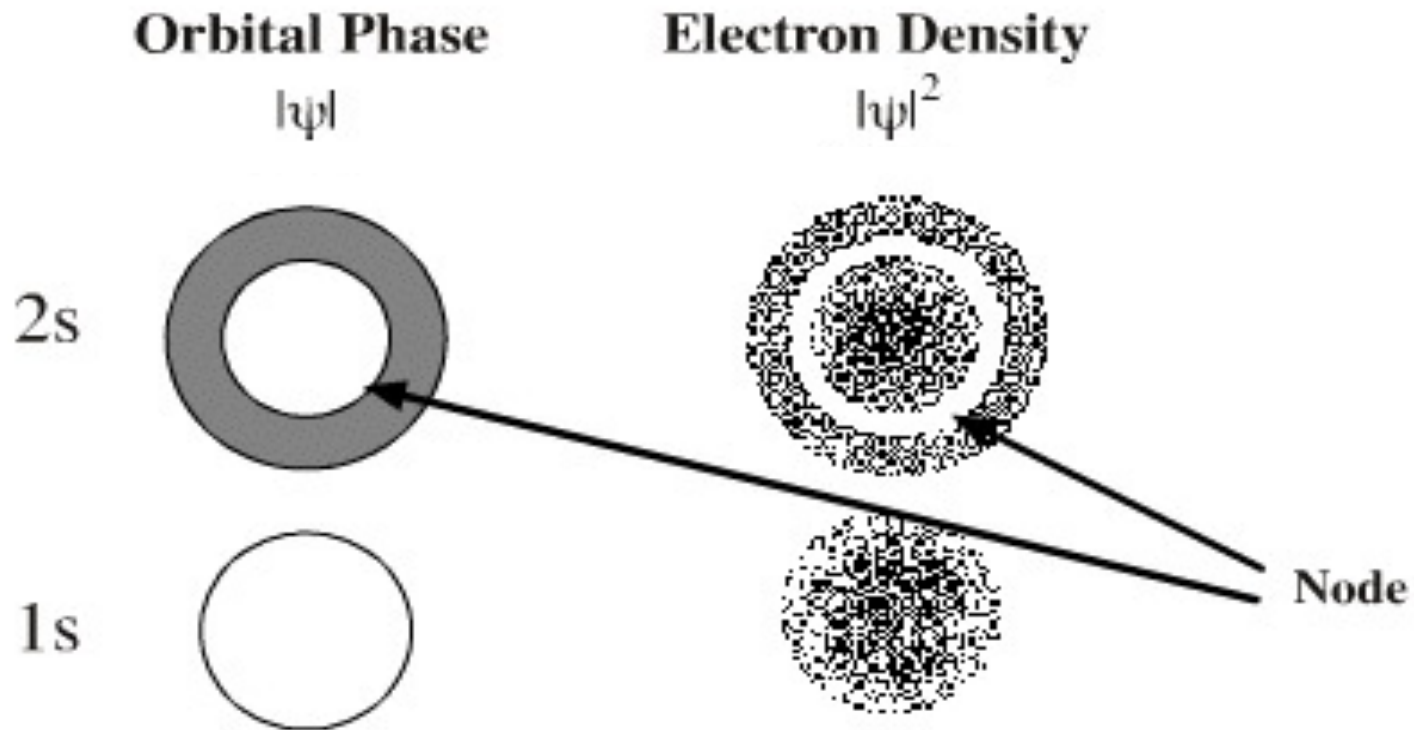
- For a given orbital there are two types of nodes:
 - Angular nodes (aka nodal planes)
 - Calculated: number of angular nodes = l
 - Radial nodes (aka nodal regions)
 - Calculated: number of radial nodes = $n - l - 1$

Where: n = principal quantum number n ($n = 1, 2, 3, 4 \dots \infty$)

l = azimuthal quantum number (aka angular momentum quantum number)

<i>subshell</i>	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>	<i>h</i>	...
<i>l</i>	0	1	2	3	4	5	...

s subshells of carbon

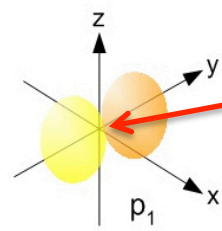
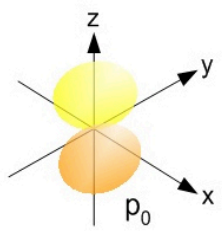
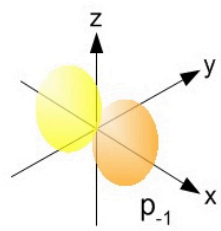
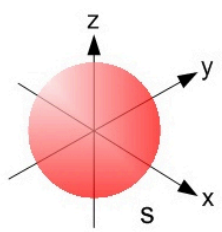


- $n = 1$ for 1s orbital and $n=2$ for 2s orbital
- $l = \text{zero}$ for 1s and 2s orbitals
- 1s orbital has zero angular nodes and zero radial nodes
- 2s orbital has zero angular nodes and one radial node

Orbital shape diagrams and nodes

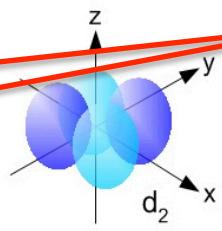
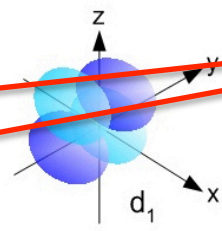
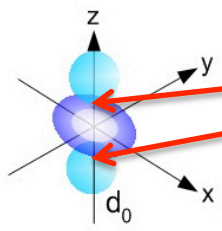
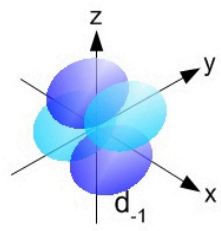
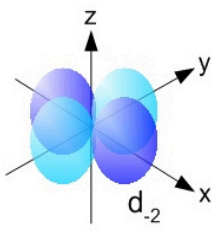
subshell	s	p	d	f	g	h	...
<i>l</i>	0	1	2	3	4	5	...

Organic chemistry

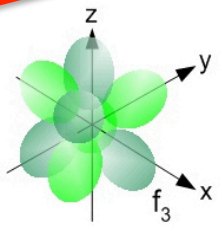
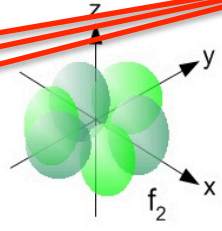
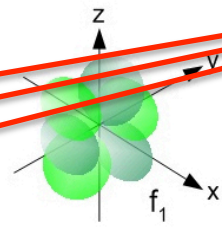
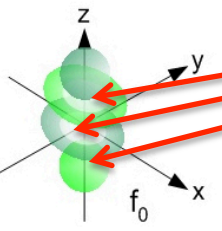
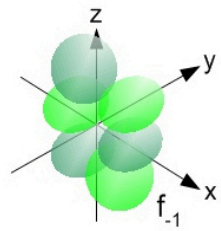
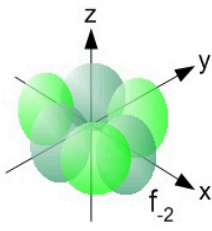
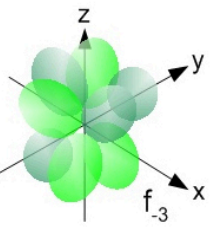


1 Node

Inorganic chemistry

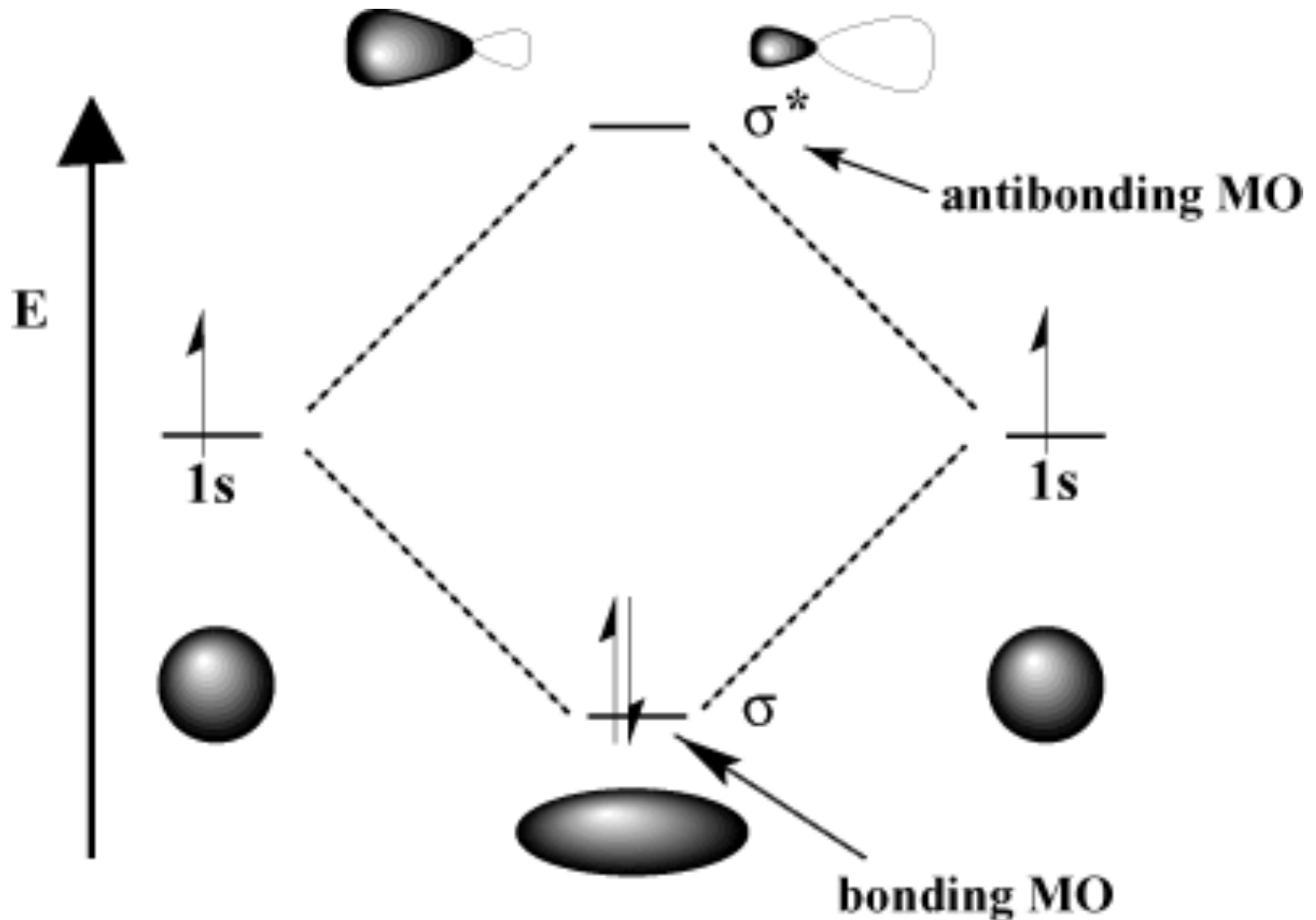


2 Nodes

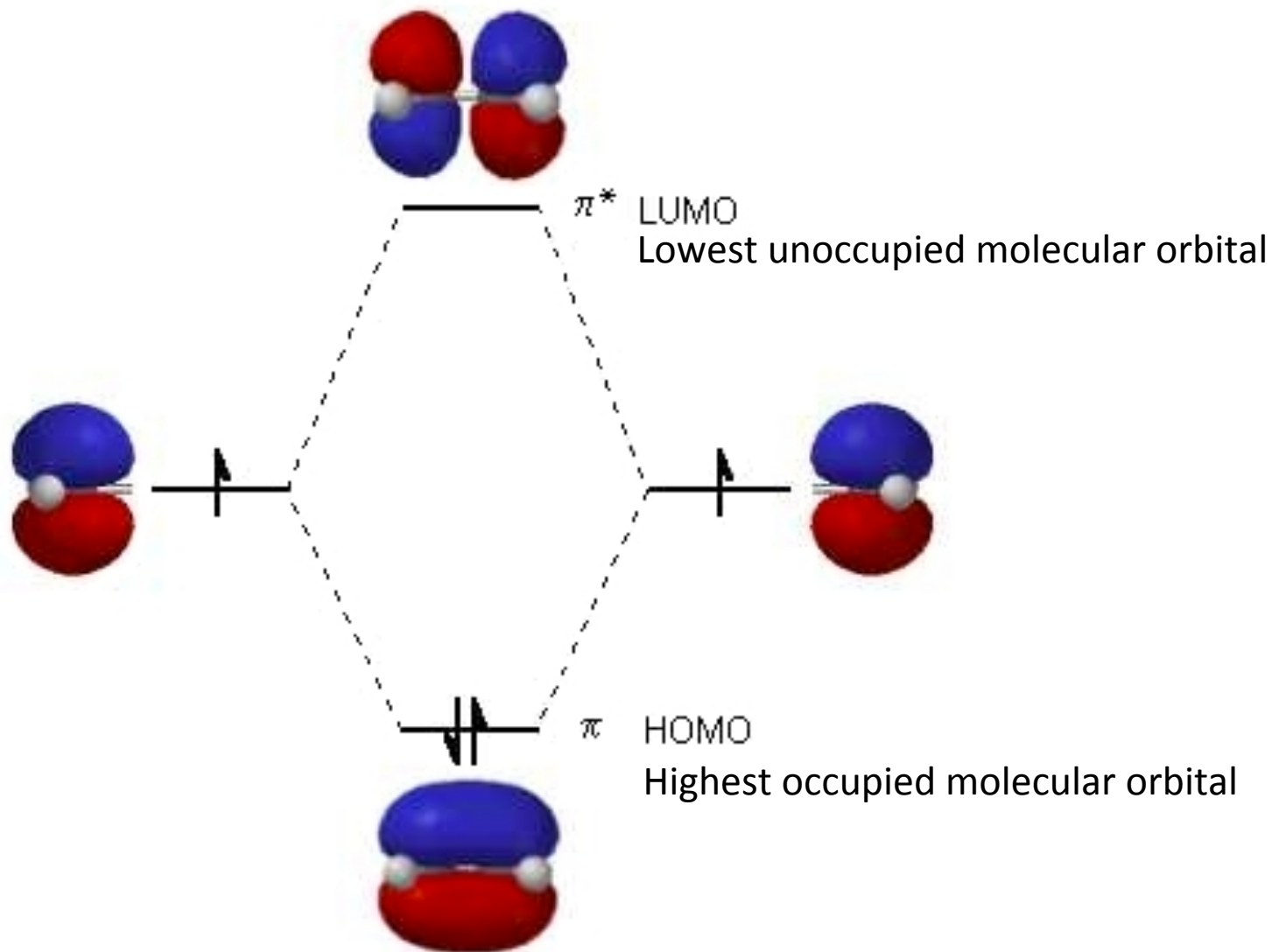


3 Nodes

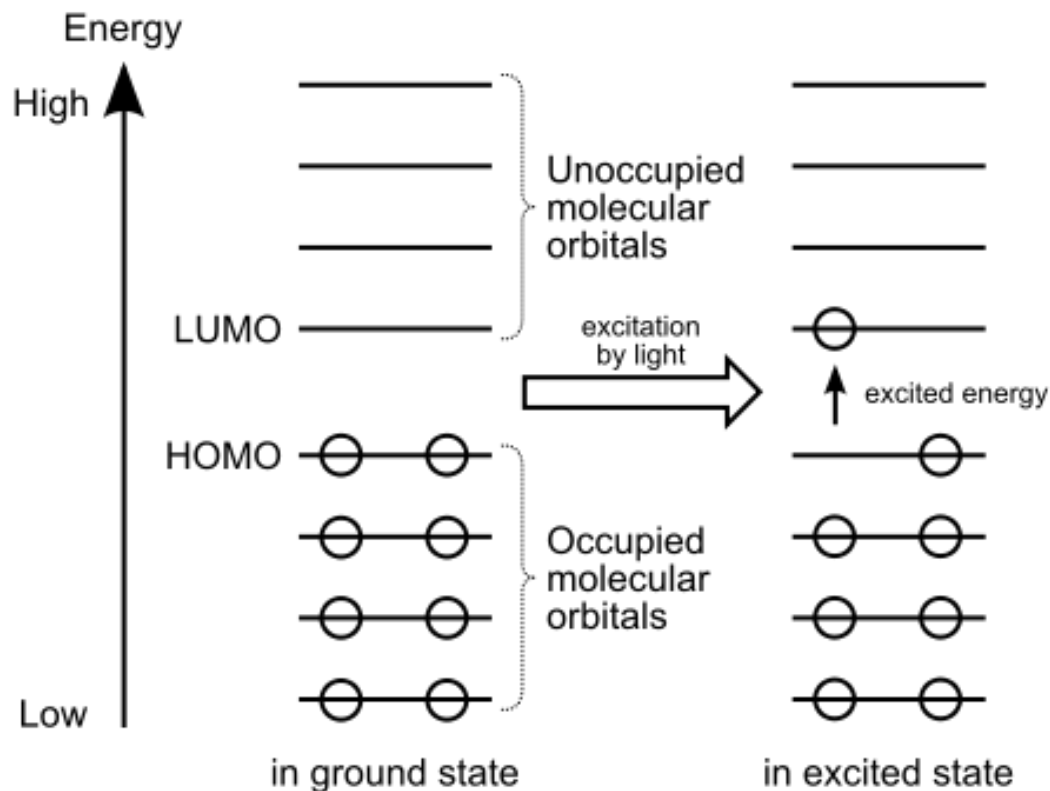
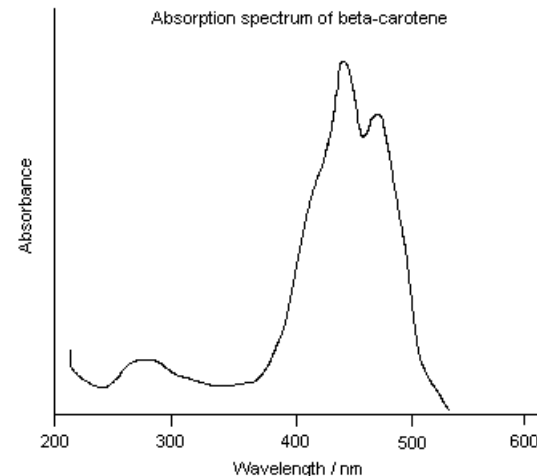
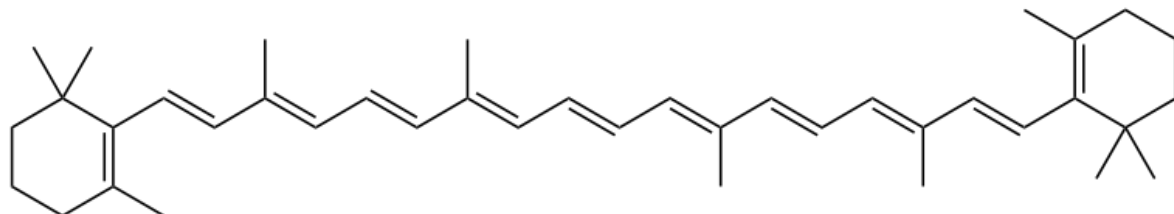
Molecular orbitals of the sigma bond



Molecular orbitals of the π bond



β -carotene: UV max \sim 450 nm

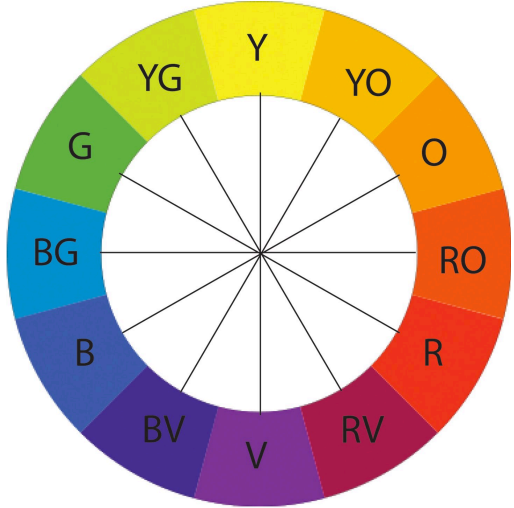
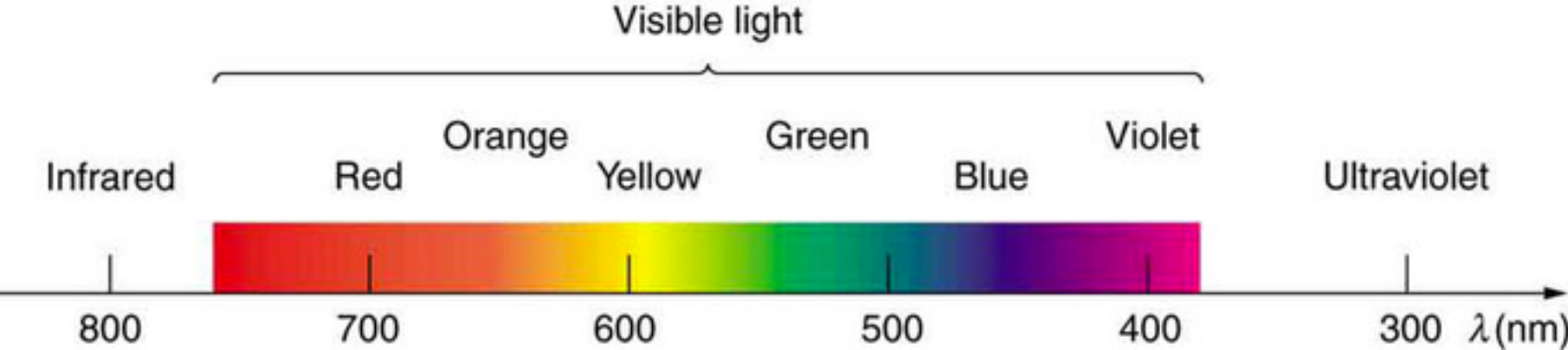


The HOMO/LUMO gap is the energy (i.e. frequency of light) absorbed by the molecule

$$E = hc/\lambda$$

β -carotene absorbs at 450 nm and appears orange because of complimentary colors...

Visible Light and Complimentary colors



Complementary Colors

Draw the following molecules (if possible)

- $\text{CH}_2\text{CH}_2\text{BrCH}_3$
- $\text{NH}_2\text{CH}_2\text{CH}_3$
- H_2SO_4
- CH_3CHN
- CH_3OCH_3
- $\text{CH}_2\text{CHOHCH}_2$
- $\text{CH}_3\text{SiH}_2\text{CH}_2\text{SiH}_3$
- PH_2CH_3

Homework Problems

In text (answers in back of book)

1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 16

End of chapter

35, 36, 37, 39, 42, 43, 49, 50, 51, 52, 53, 57