Organic Molecules
~ Structure and Nomenclature ~

- Determining the structure of organic compounds

- Carbon
- Covalent bond (Lewis structure formalism)
- Molecular geometry (bond length, bond angle)

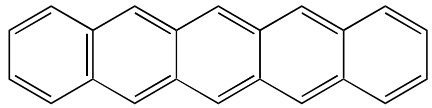
- Electronic structure of atoms and molecules (1^{st} pass)
- σ and π bonds

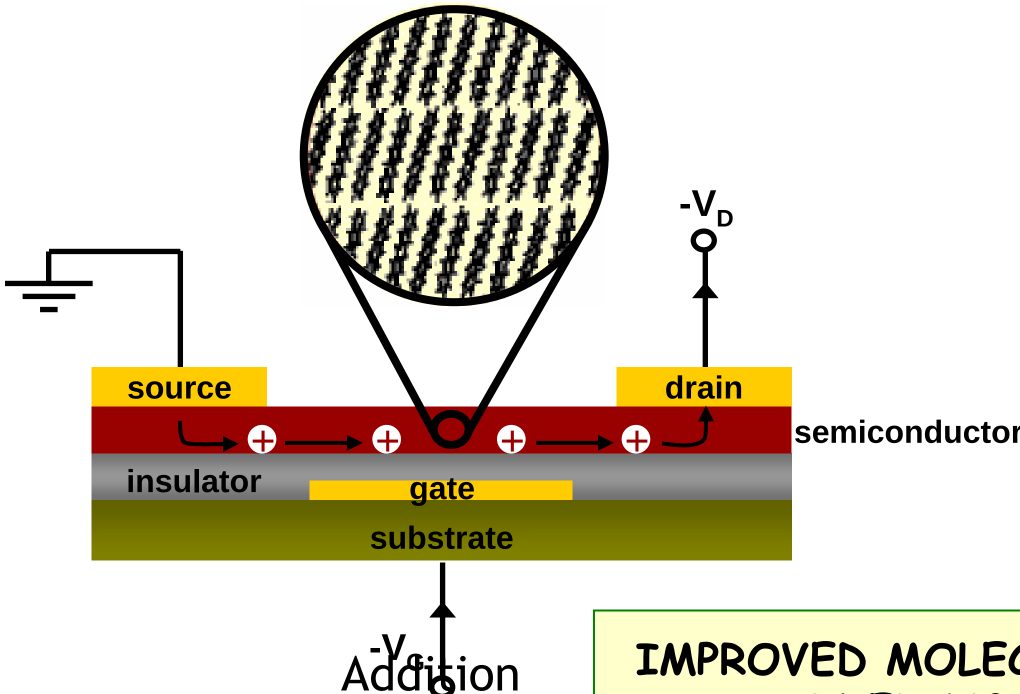
looe @ MIT

Organic Field Effect Transistors

Charge carrier mobility is dependent on molecular order within the semiconducting thin film

pentacene





Addition

Current modulation is achieved by electric field-induced charge build-up at the interface between the organic semiconductor and the insulator

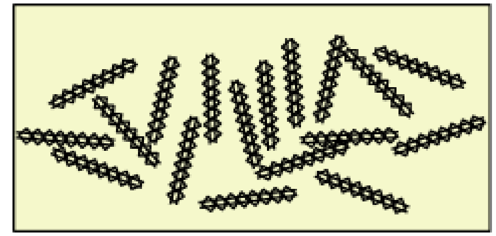
IMPROVED MOLECULAR ORDERING

⇩

Larger grain sizes
Lower defect densities

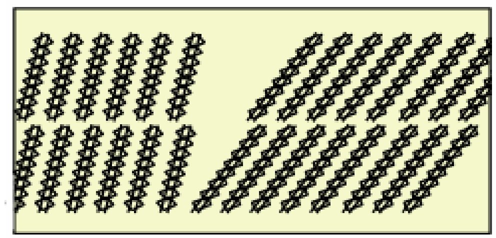
⇩

Enhanced mobility



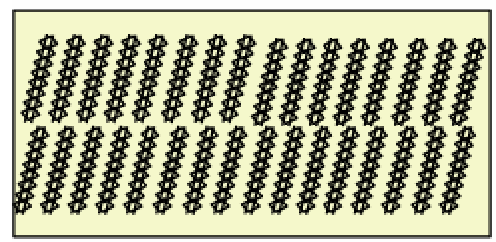
T$_{sub}$=-196 °C, DR=0.5 Å/sec

¼~10^{-8} cm^2 V^{-1} s^{-1}



T$_{sub}$=55 °C, DR=0.25 Å/sec

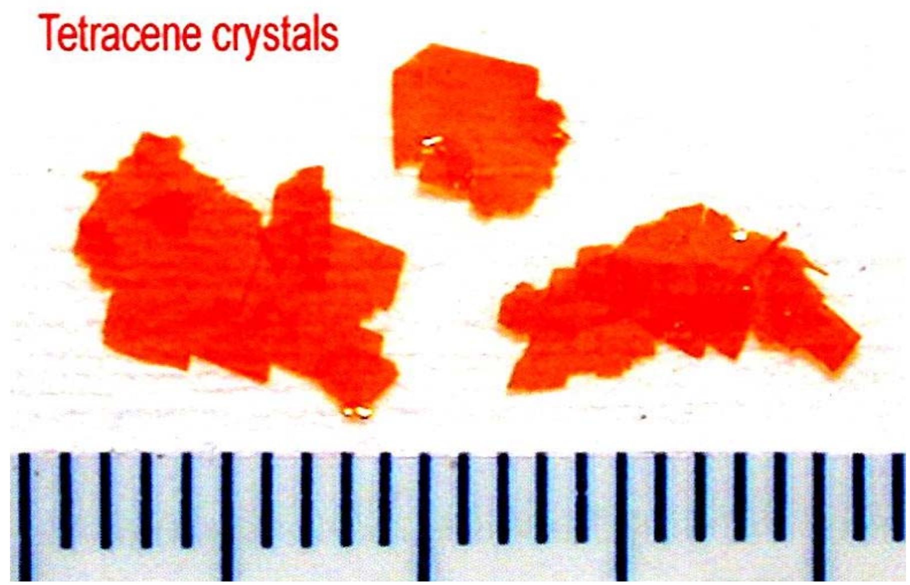
¼~10^{-6} cm^2 V^{-1} s^{-1}



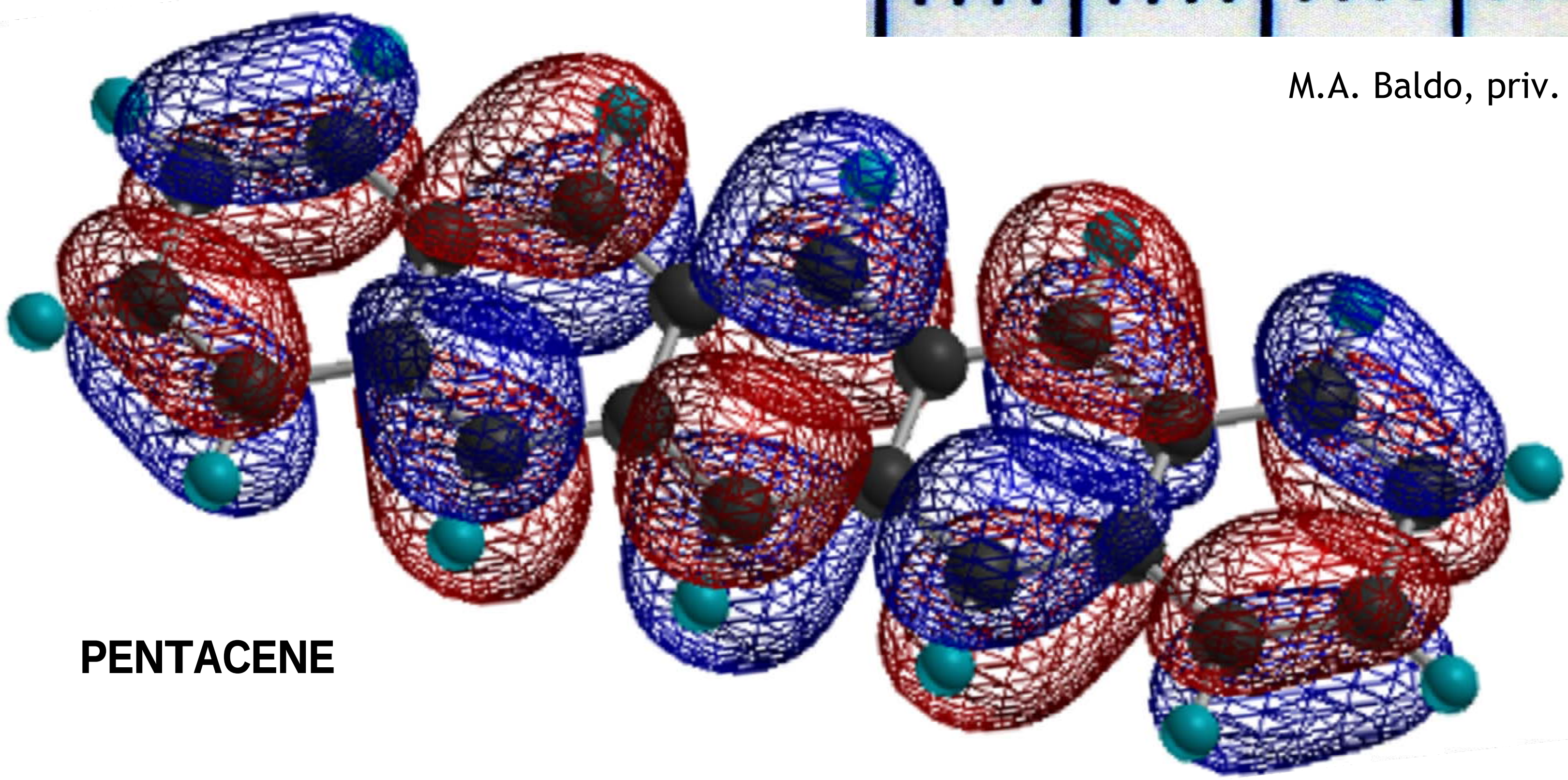
T$_{sub}$=27 °C, DR=1.0 Å/sec

¼~0.6 cm^2 V^{-1} s^{-1}

Dimitrakopoulos, et. al., *IBM J. Res. and Devel.* **45**, 11 (2001).

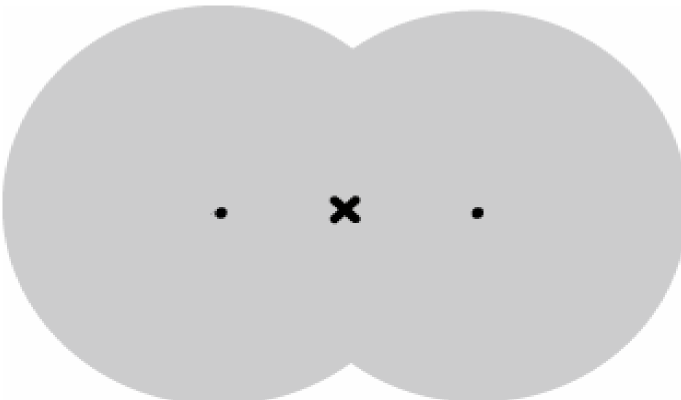


M.A. Baldo, priv. comm.

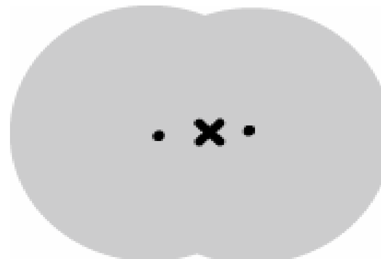


PENTACENE

MOLECULE – derived form “molecula” - meaning small mass
(a smallest unit of chemical compound that still exhibits all its properties)



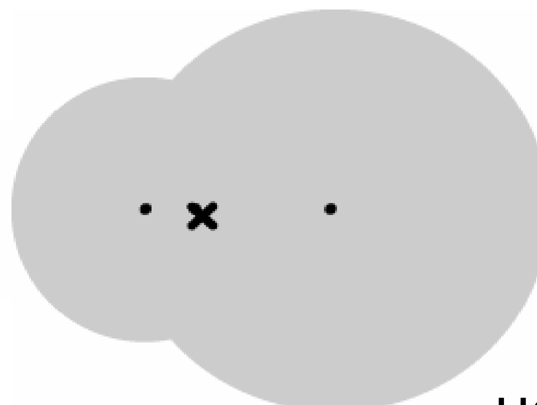
Cl_2



H_2

HOMONUCLEAR
diatomic molecules

Electron distributions in the small molecules H_2, Cl_2, HCl. The nuclear separations are 0.74 Å H_2, 1.27 Å in HCl, and 1.99 Å in Cl_2

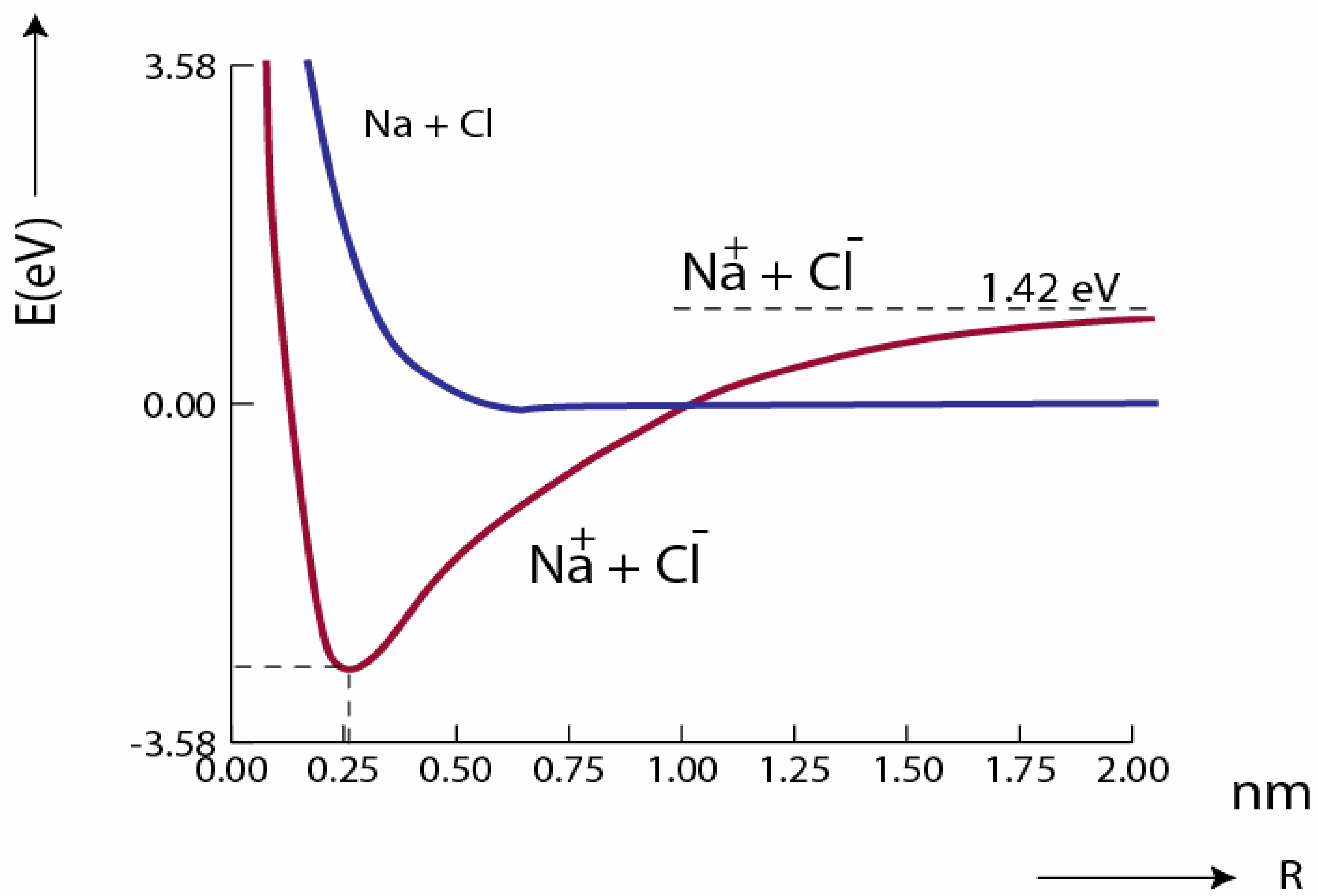


HCl

HETERONUCLEAR

Adapted from Molecular Physics and Elements of Quantum Chemistry by H. Haken and H.C. Wolf

Potential Energy as a Function of Internuclear Distance, R



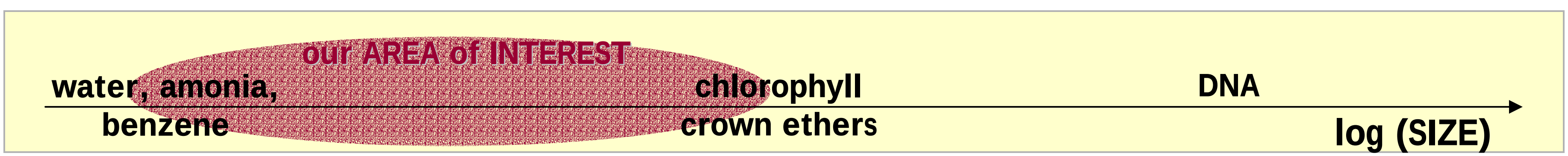
Adapted from *Molecular Physics and Elements of Quantum Chemistry* *by H. Haken and H.C. Wolf*

The Size of the System

Photosynthetic Process

The reaction center for bacterial photosynthesis as a molecular functional unit. The schematic drawing shows the photoactive molecules, which are embedded in a larger protein unit. The latter in turn is embedded in a cell membrane. Light absorption by the central chlorophyll dimer is the first step in the charge separation which sets off the chemical process of photosynthesis. The picture is based on the x-ray structure by Deisenhofer, Huber, and Michel (Nobel Prize 1988), is taken from the newspaper “Die Zeit”

Adapted from Figure 1.3 caption of ***Molecular Physics and Elements of Quantum Chemistry*** *by H. Haken and H.C. Wolf*



Seeing the shape of molecules

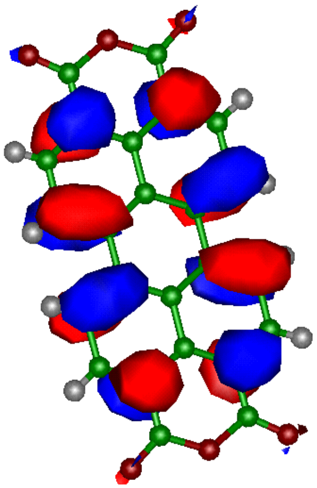
with Transmission Electron Microscope (TEM)

An electron microscope image of hexadecachloro copper phthalocyanine molecules. The molecules form a thin, oriented layer which serves as substrate. The image was made with a high-resolution 500kV transmission electron microscope and was processed using special image-enhancement methods. The central copper atoms and the 16 peripheral chlorine atoms may be most clearly recognized. (This picture was kindly provided by Prof. N. Uyeda of Kyoto University.)

Figure 1.4 caption from Molecular Physics and Elements of Quantum Chemistry by H. Haken and H.C. Wolf

Seeing the shape of molecules

with Scanning Tunneling Microscope (STM)
or Atomic Force Microscope (AFM)



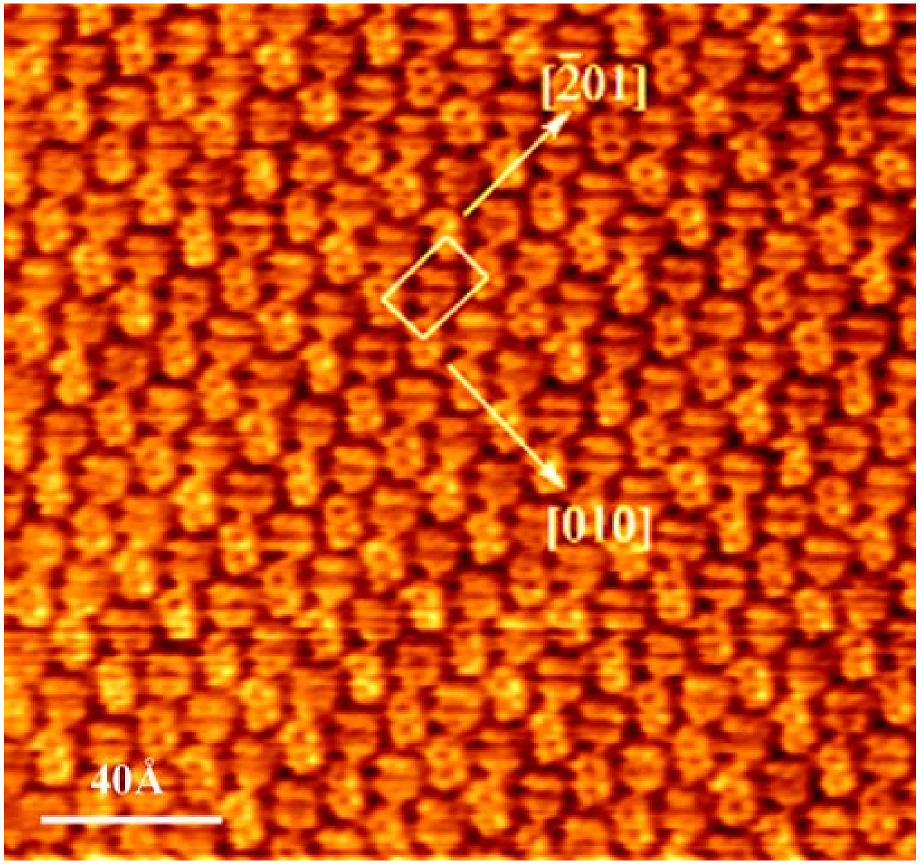
molecular orbital calculation of the electron density in the highest occupied molecular orbital of a PTCDA molecule

Agreement between the calculation and the experiment exemplifies maturity of detailed understanding of electronic arrangement on molecules.

However, …

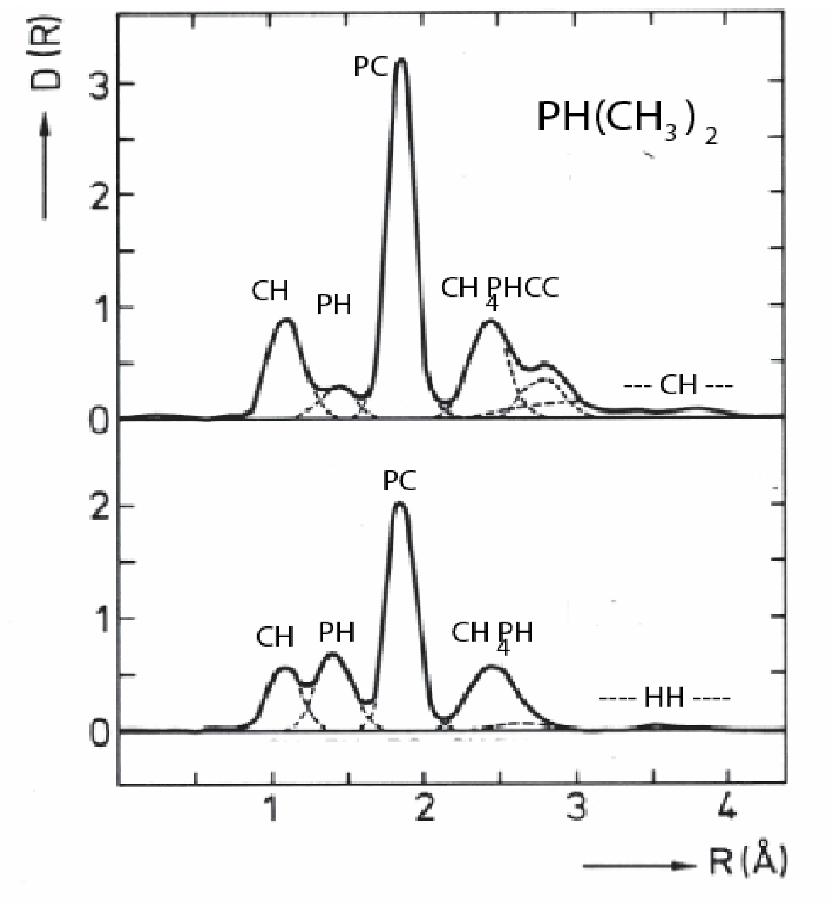
DYNAMIC ELECTRONIC PROCESSES in MOLECULES and MOLECULAR ASSEMBLIES are NOT WELL UNDERSTOOD and present a topic of our research

STM scan of ordered PTCDA monolayer on HOPG



Seeing the shape of molecules

with electron diffraction



Radial distribution functions *D* describing the electron density as a function of the bond length *R* between atomic nuclei in the molecules $PH(CH_3)_2$ and PH_2CH_3, obtained from electron diffraction patterns. The maxima in the distribution functions can be correlated with the inter-nuclear distances indicated. [After Bartell, J. Chem. Physics. 32, 832 (1960)]

Quoted from Figure 2.1 of *<u>Molecular Physics and Elements of Quantum Chemistry</u>* *by H. Haken and H.C. Wolf*

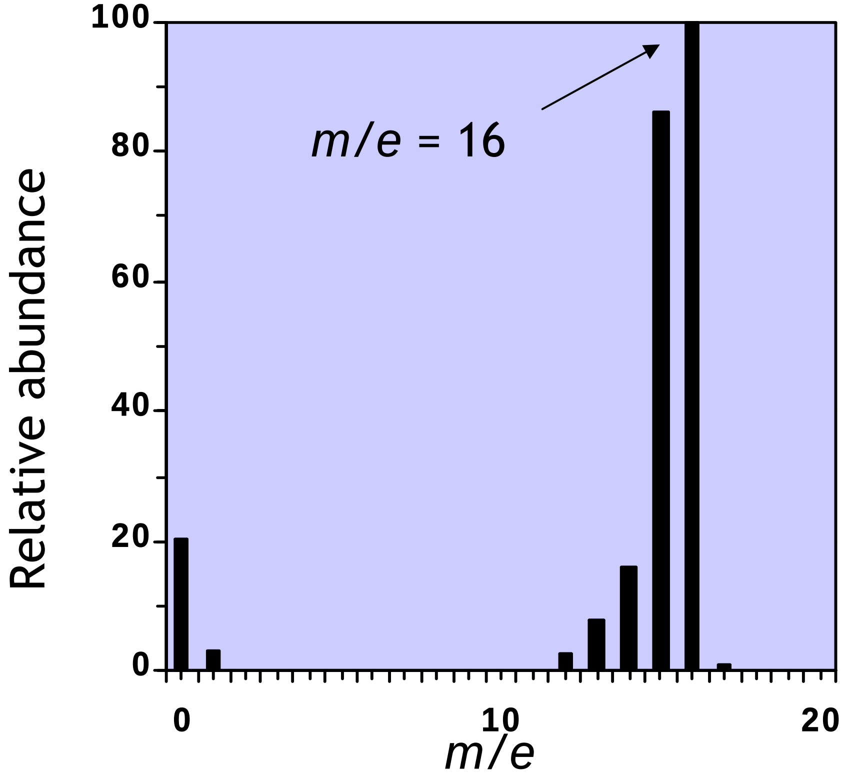
Seeing the shape of molecules

with x-ray diffraction

An simulated electron density diagram of the porphyrine molecule. The H atoms are not visible, since they are poorly detected by X-ray diffraction methods compared to atoms with higher electron densities, such as nitrogen. The contour lines represent the electron density. Their interval corresponds to a density difference of one electron per $Å_2$, and the dashed lines represent an absolute density of 1 electron per $Å_2$.

Quoted from Figure 2.1 of Molecular Physics and Elements of Quantum Chemistry by H. Haken and H.C. Wolf

Mass Spectroscopy

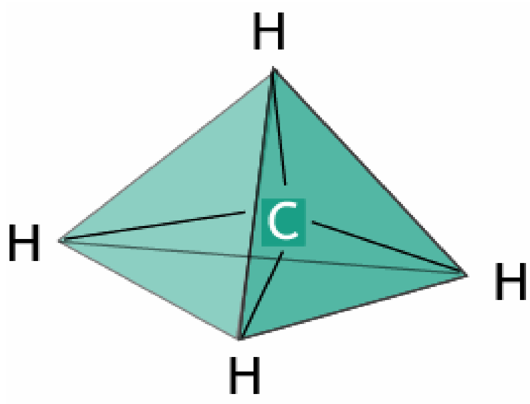


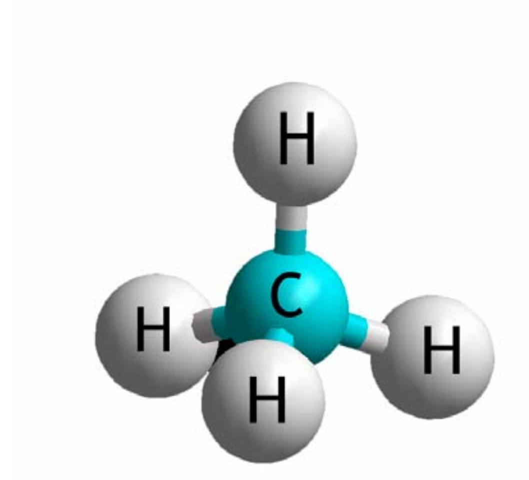
methane

m/e	Relative Abundance
1	*3.36*
12	*2.80*
13	*8.09*
14	*16.10*
15	*85.90*
16	*100.00*
17	*1.11*

Image of a mass spectrometer showing its internal organs.

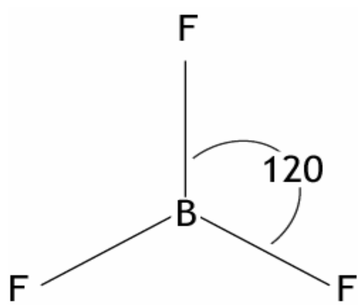
Adapted from Organic Chemistry by G.M. Loudon

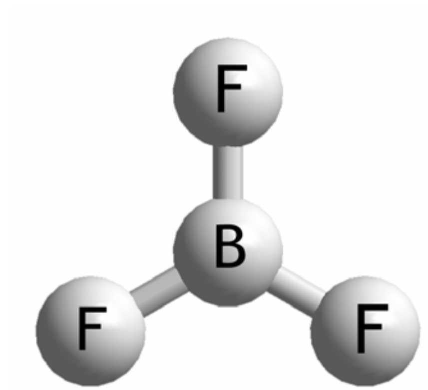




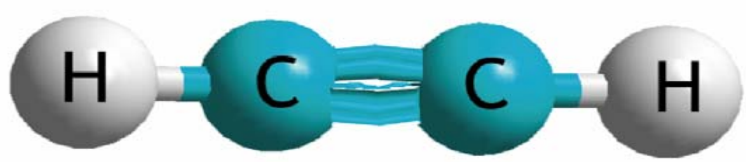
methane

TETRAHEDRAL





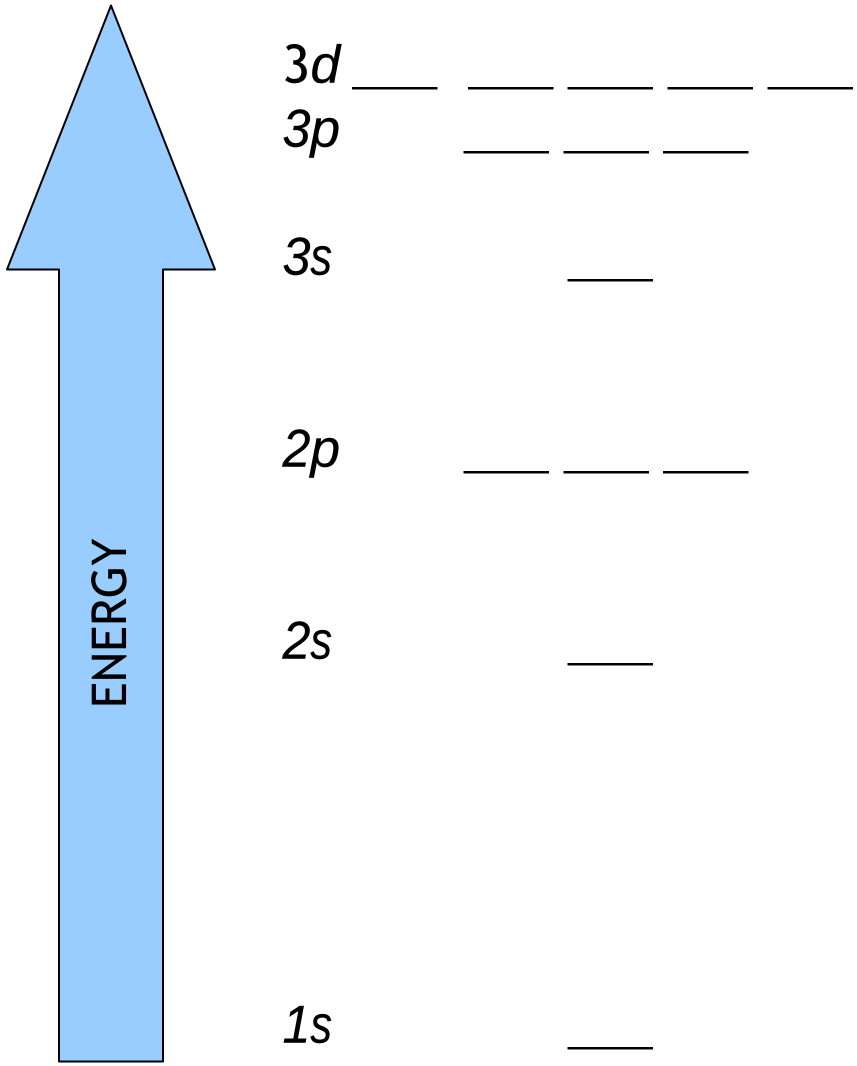
TRIGONAL

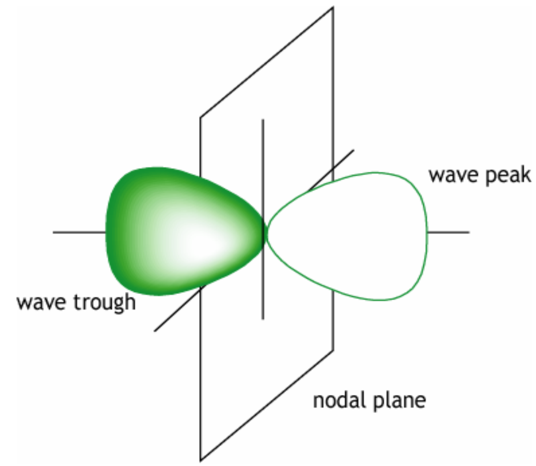


acetylene

LINEAR

Adaped from *<u>Organic Chemistry</u>* *by G.M. Loudon*

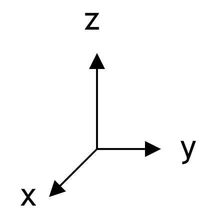


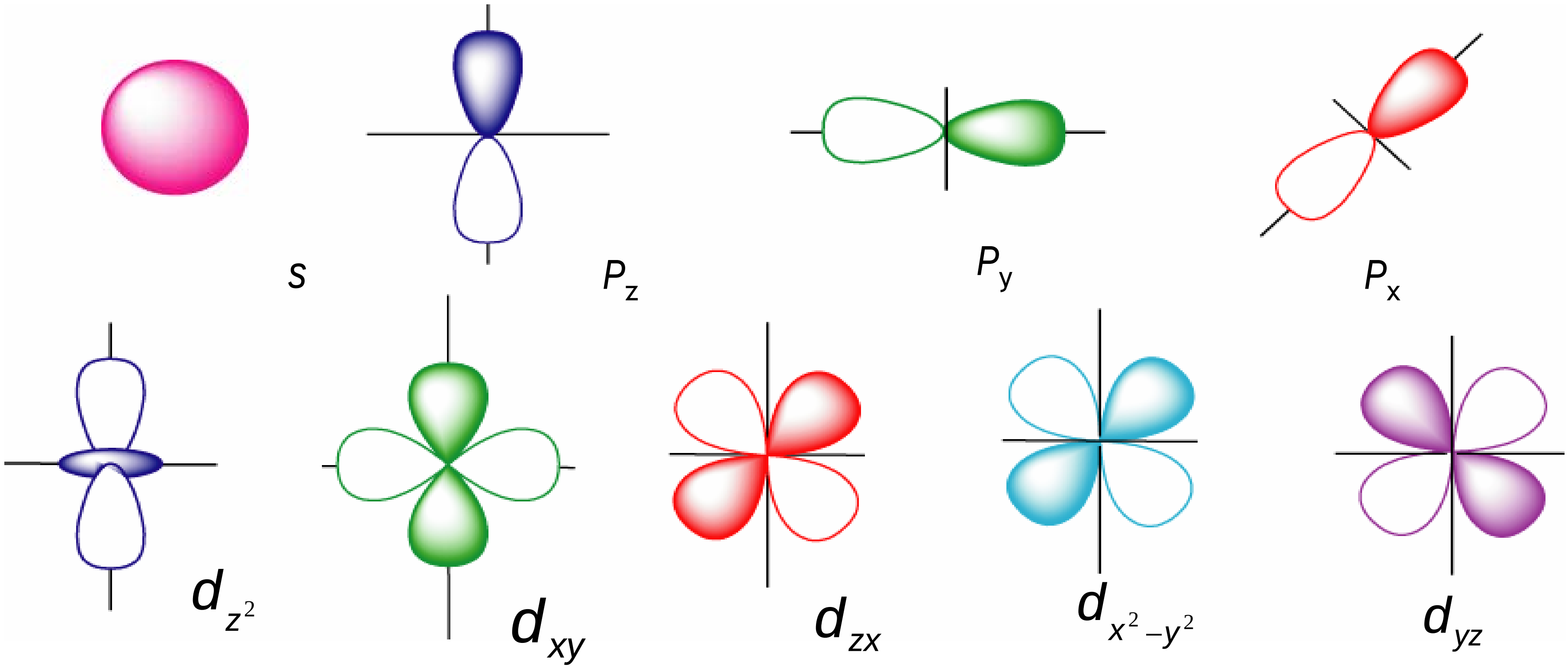


Schematic representation of the relative energies of different orbitals in a many-electron atom. The exact scale varies from atom to atom, but the energy levels tend to be closer together as the principle quantum number increases.

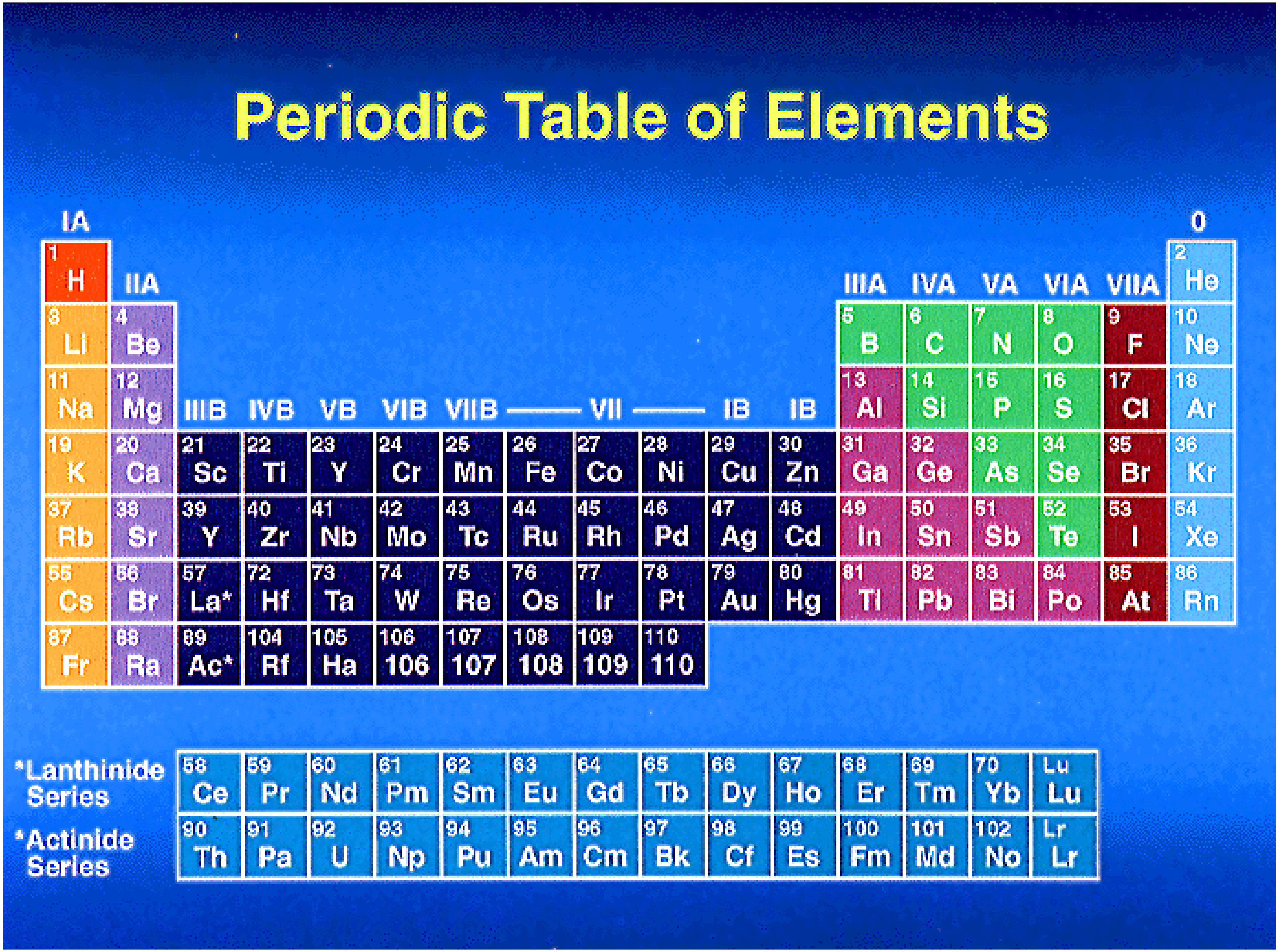
Quoted from Figure 2.6 in <u>Organic Chemistry</u> by G.M. Loudon

Atomic Orbitals





Atoms that constitute typical organic compounds such as
H, C, N, O, F, P, S, Cl
have outermost (valence) electrons in s and p orbitals. When molecules are formed
the **s** and **p** atomic orbitals form σ and π



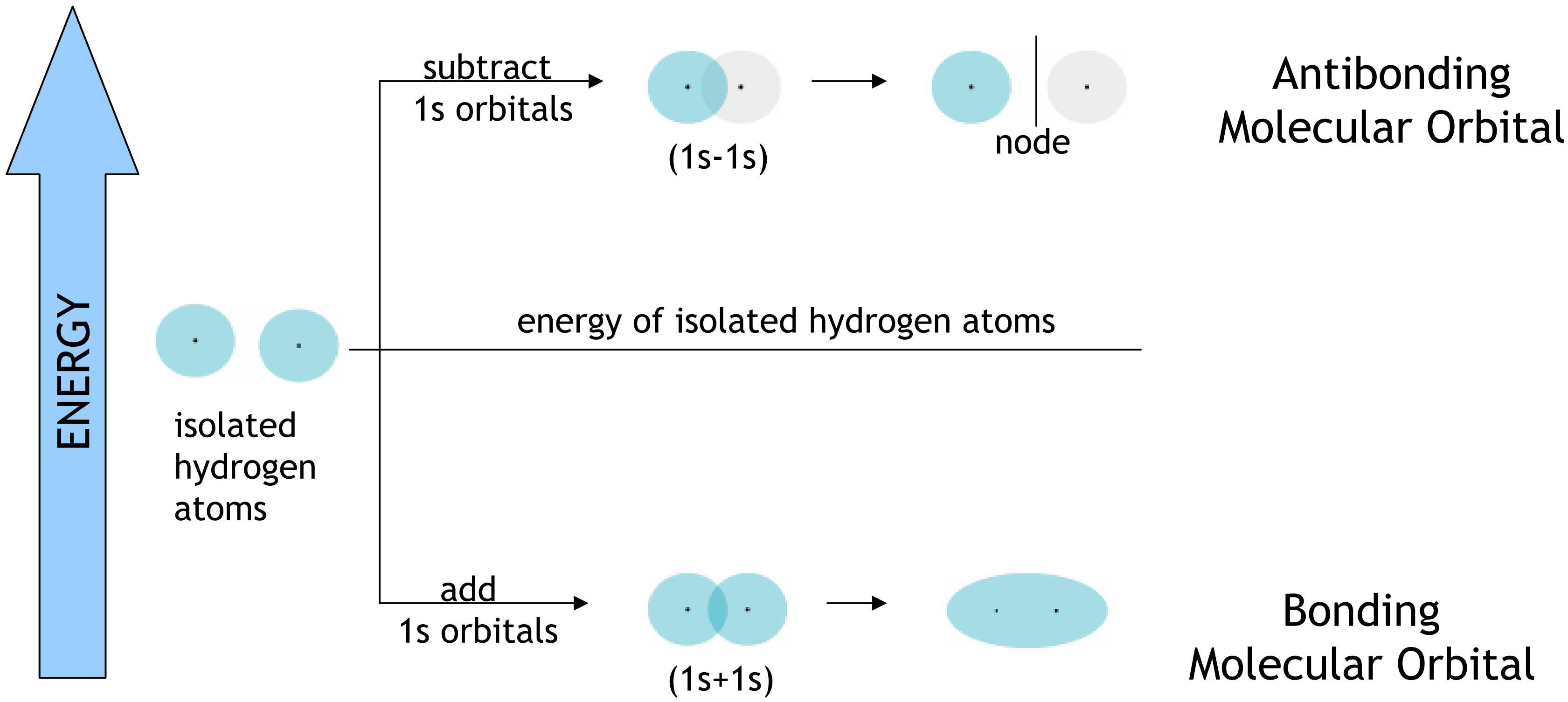
Periodic Table of Elements

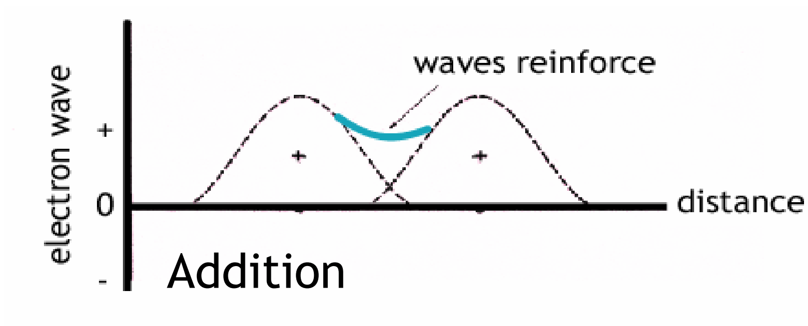
IA	IIA	IIIB	IVB	VB	VIB	VIIB	VII	VII	VII	IB	IB	IIIA	IVA	VA	VIA	VIIA	0
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 Y	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Br	57 La*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac*	104 Rf	105 Ha	106 106	107 107	108 108	109 109	110 110								

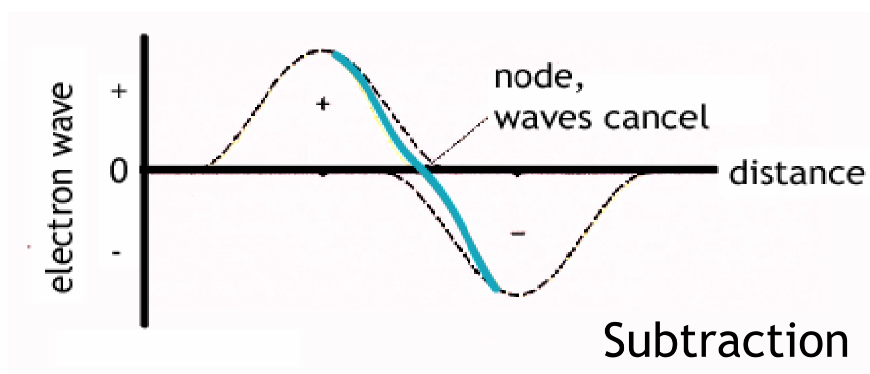
*Lanthinide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	Lu Lu
*Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	Lr Lr

From NASA website

In 0 A.D. 9 elements were known (C, S, Fe, Cu, Ag, Sn, Au, Hg, and Pb)







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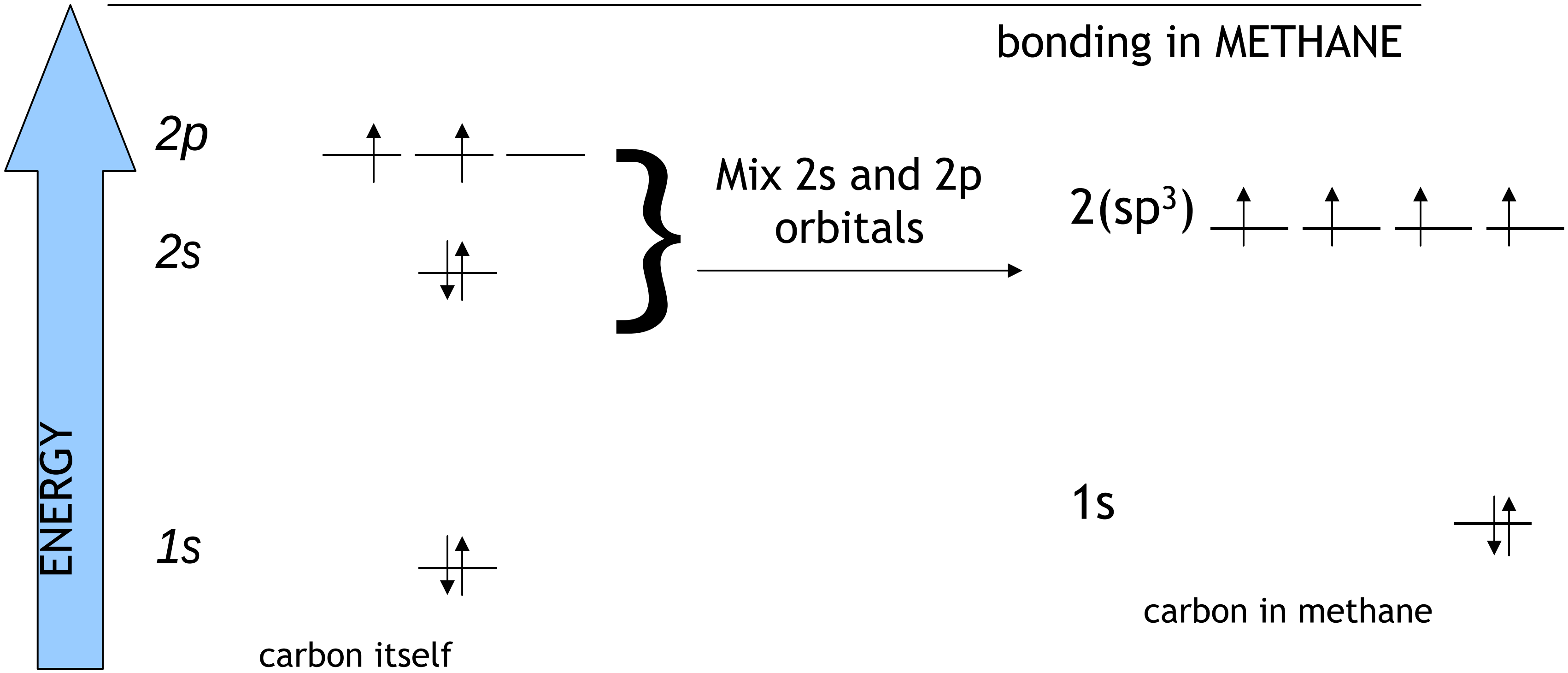
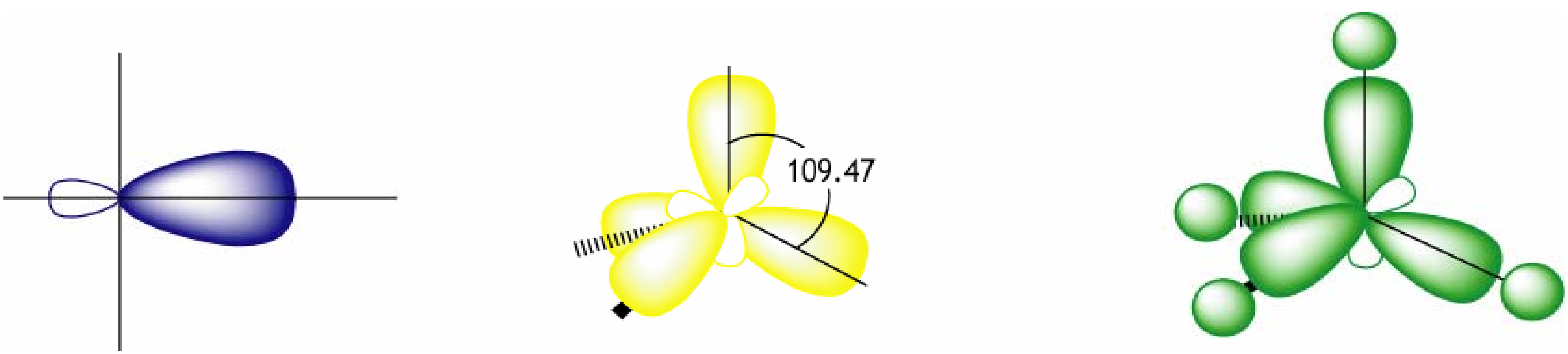
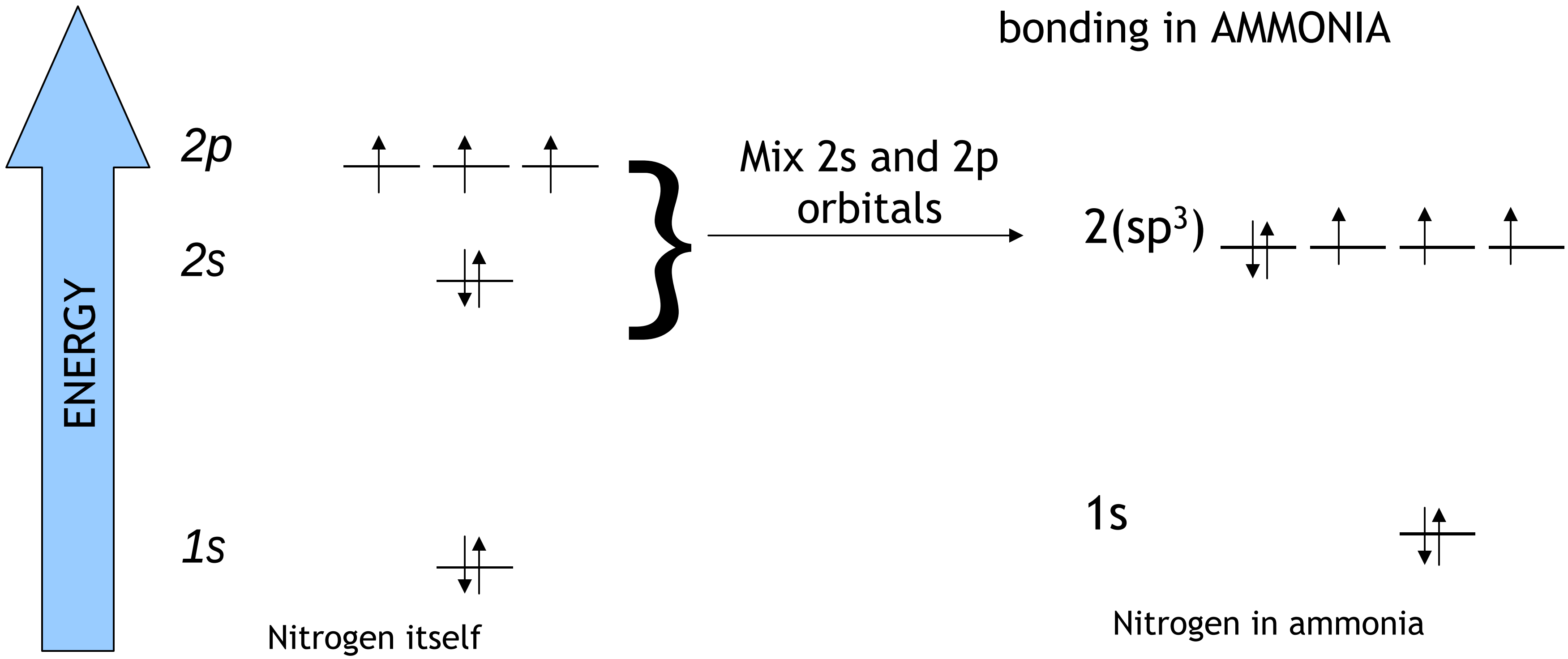
Hybrid Orbitals

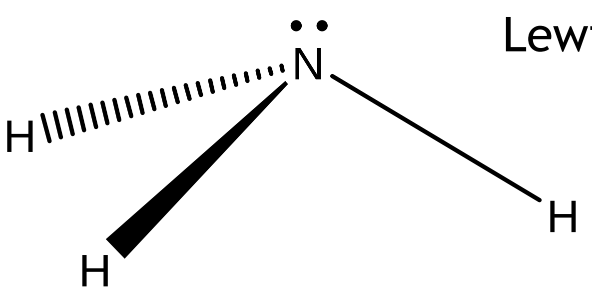




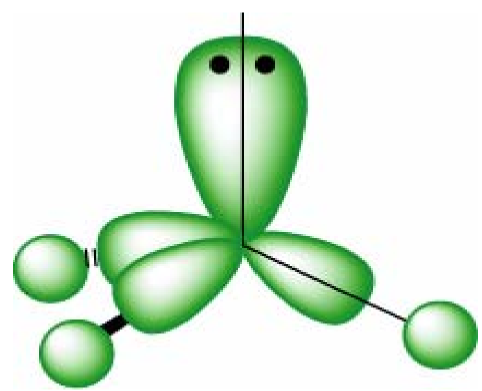
Hybrid Orbitals

bonding in AMMONIA



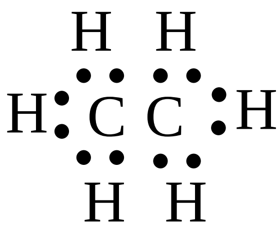


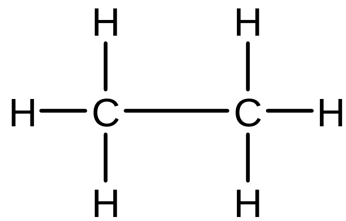
Lewis Structure

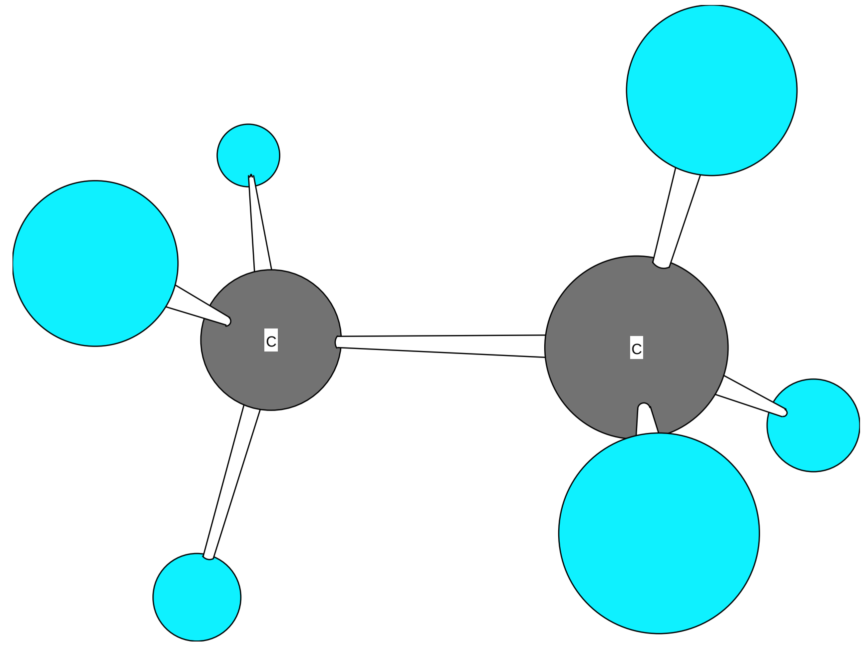


Orbital Picture

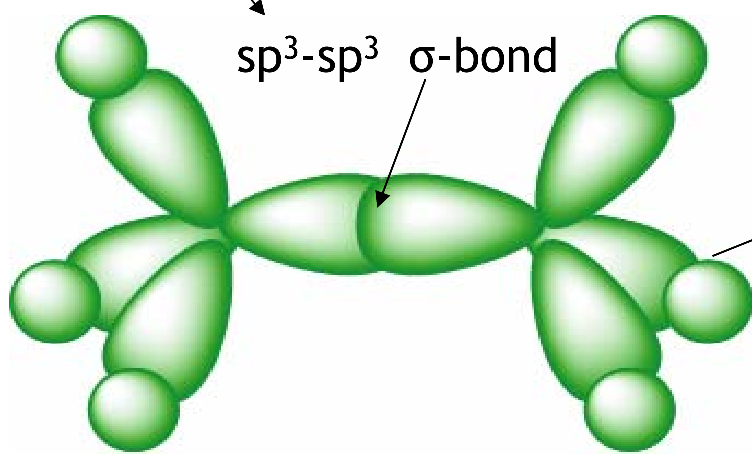
Adapted from Organic Chemistry by G.M. Loudon





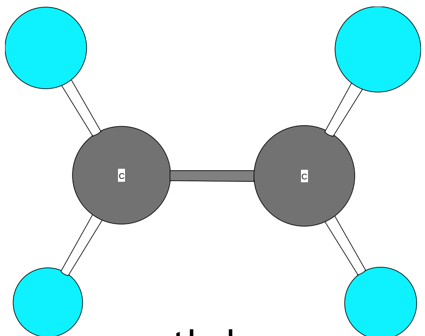


Bonding molecular orbitals in ETHANE

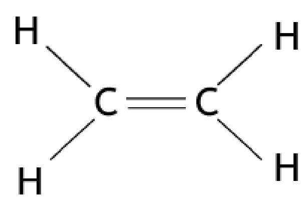


Adapted from Organic Chemistry by G.M. Loudon

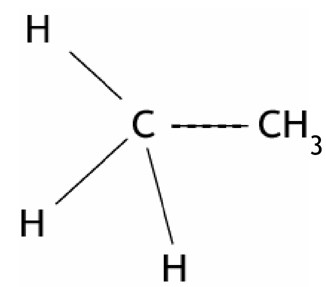
Alkenes, or olefins, are hydrocarbons that contain carbon-carbon double bonds. Ethylene and propylene are the two simplest alkenes.



ethylene



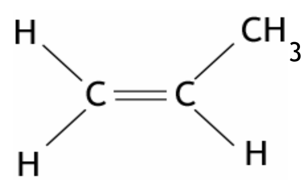
ethylene



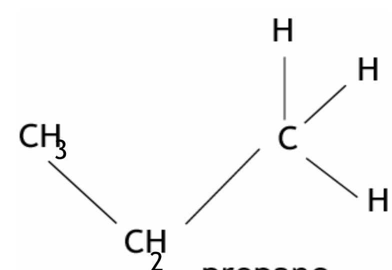
ethane

Structures of ethylene, ethane, propylene, and propane

A DOUBLE BOND



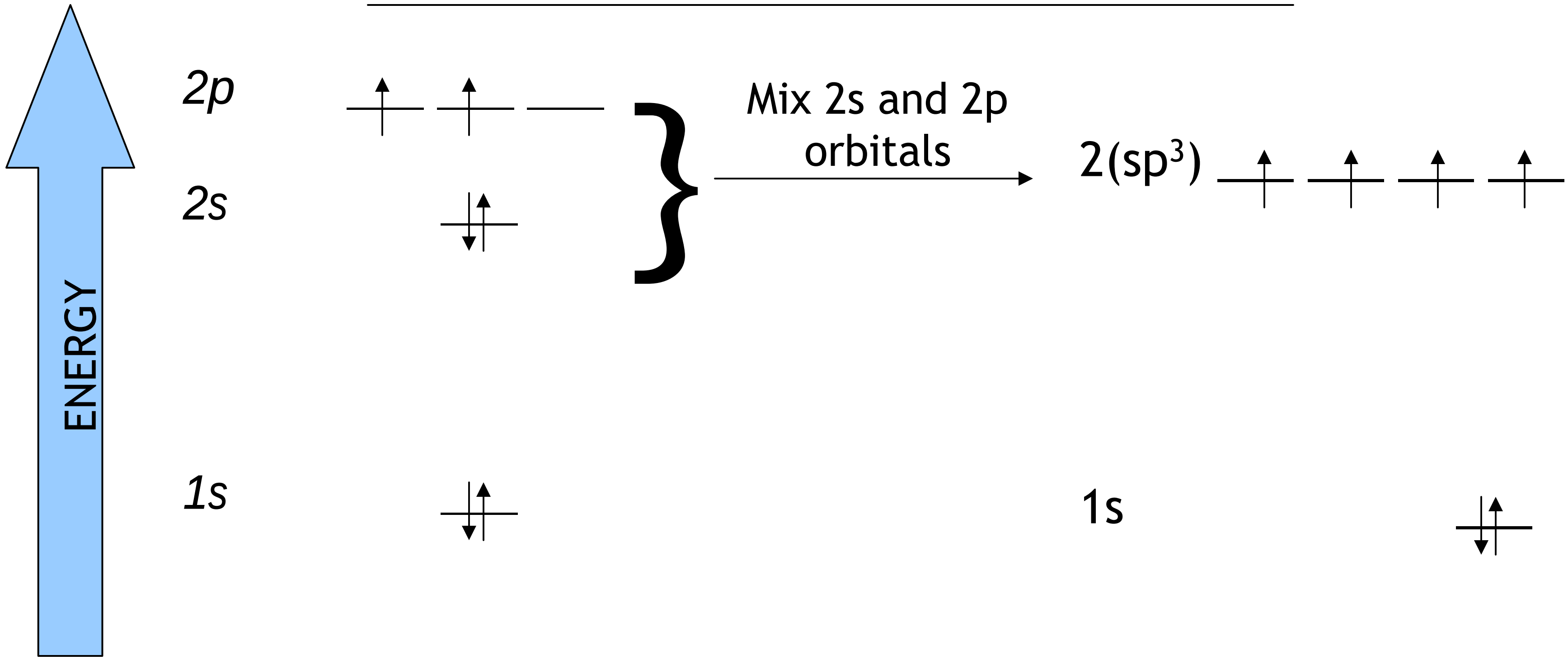
propylene



propane

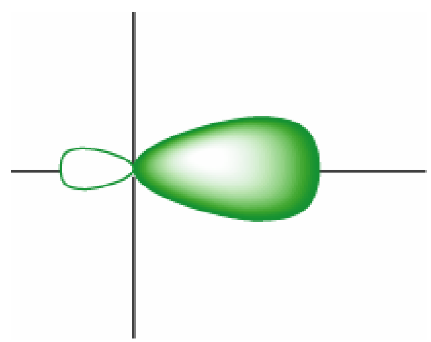
Adapted from <u>Organic Chemistry</u> by G.M. Loudon

Orbitals of a sp³-hybridized carbon

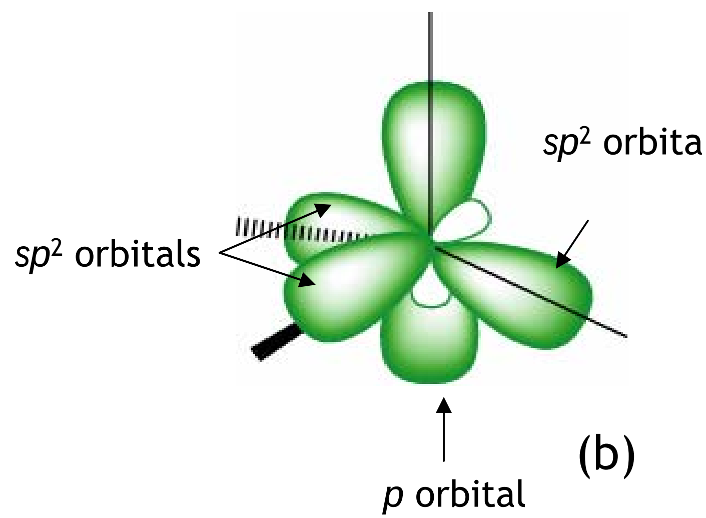


(a) The general shape of an sp² hybrid orbital is very similar to that of an sp³ hybrid orbital, with a large and small lobe of electrons density separated by a node. (b) Spatial distribution of orbital son an sp³-hybridized carbon atom.

Quoted from Figure 4.3 of Organic Chemistry by G.M. Loudon



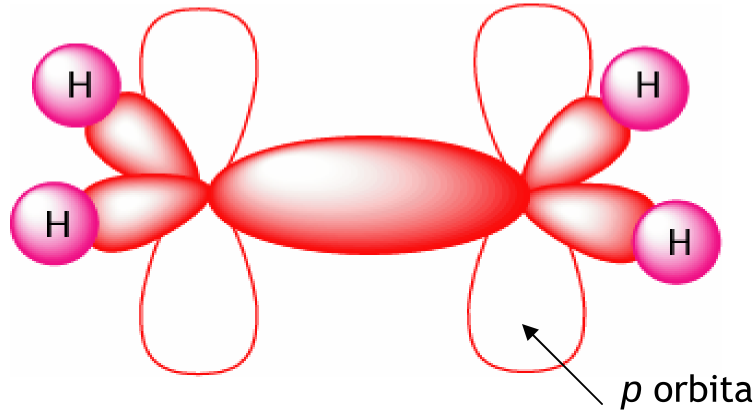
(a)



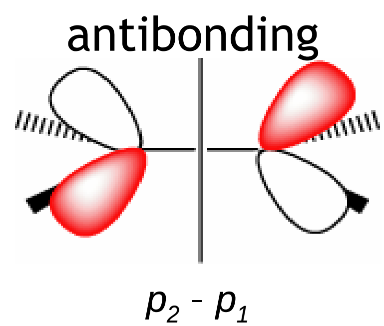
(b)

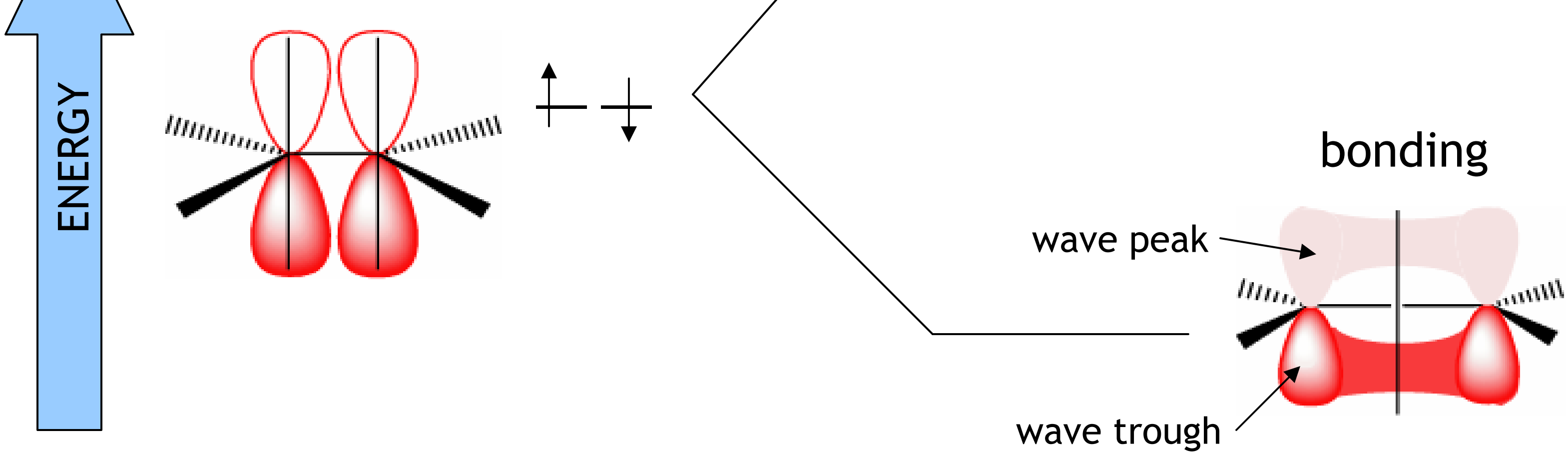
Bonding molecular orbitals in ETHYLENE

The p-bonds in ethylene



Overlap of p orbital to form boding and antibonding π-molecular orbitals. The π-bond is formed when two electrons occupy the bonding π-molecular orbital.





Quoted from Figure 4.5 of <u>Organic Chemistry</u> by G.M. Loudon

Bond Length

The following generalizations can be made about bond length:

1. Bond lengths between atoms of a given type decrease with the amount of multiple bonding. Thus, bond lengths for carbon-carbon bonds are in the order C-C > C =C > C≡C

2. Bond lengths tend to increase with the size of the bonded atoms. This effect is most dramatic as we proceed down the periodic table. Thus, a C-H bond is shorter then a C-F bond, which is shorter then a C-Cl bond. Since bond length is the distance between the center of bonded atoms, it is reasonable that larger atoms should form longer bonds.

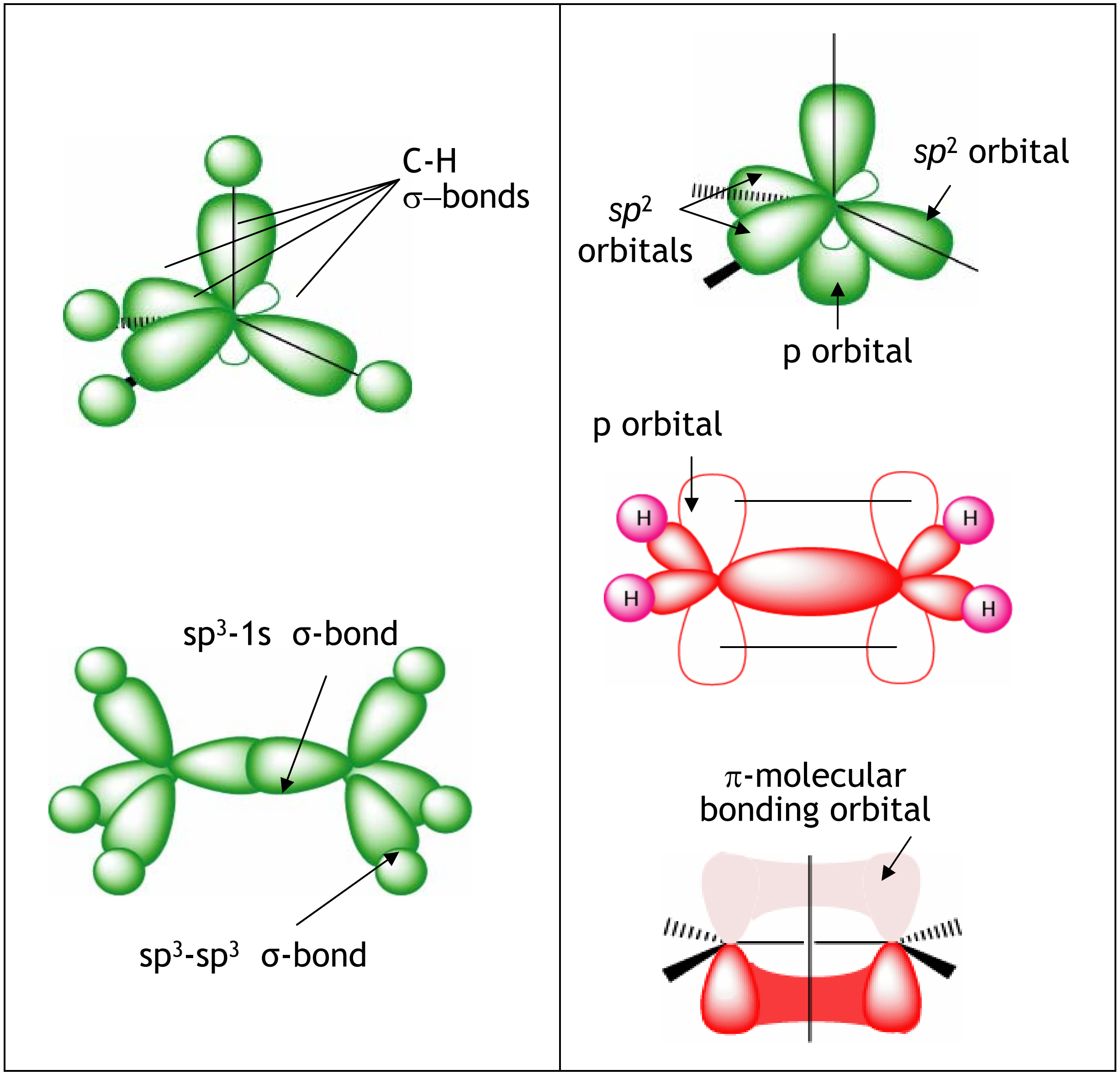
3. When we make comparisons within a given row of the periodic table, bonds of a certain type (single, double, or triple) between a given atom and a series of other atoms become shorter with increasing electro negativity. Thus, the C-F bond in H3C-F is shorter then the C-C bond in H3C-CH3. This effect occurs because a more electronegative atoms has a greater attraction for the electrons of the bonding partner, and therefore 'pulls it closer,' than a less electronegative atom.

Quoted from Organic Chemistry by G.M. Loudon

Bonding in Aliphatic Hydrocarbons

single bonds (alkanes)

double bonds (alkenes)



Adapted from _Organic Chemistry_ *by G.M. Loudon*