

SCHAUM'S OUTLINE OF

THEORY AND PROBLEMS

of

ORGANIC CHEMISTRY

by

HERBERT MEISLICH, Ph.D.
HOWARD NECHAMKIN, Ph.D.

and

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São Paulo Singapore Sydney Tokyo Toronto

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0-07-041457-2

3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 SH SH 7 8 3 2 1 0 9

Library of Congress Cataloging in Publication Data

Meislich, Herbert.

Schaum's outline of theory and problems of organic chemistry.

(Schaum's outline series)

Includes index.

1. Chemistry, Organic—Problems, exercises, etc.
2. Chemistry organic. I. Nechamkin, Howard, 1918– joint author. II. Sharefkin, Jacob George, 1909– joint author. III. Title.

QD257.M44 547 77-9318

ISBN 0-07-041457-2

Preface

The beginning student in Organic Chemistry is often overwhelmed by facts, concepts, and new language. Each year, textbooks of Organic Chemistry grow in quantity of subject matter and in level of sophistication. This Schaum's Outline was undertaken (initially by the senior author, J. S.) to give a clear view of first-year Organic Chemistry through the solution of illustrative problems. Completely worked-out problems make up over 80% of the book, the remainder being a concise presentation of theory. The reader learns by thinking and doing rather than by being told.

This outline can be used in support of a standard text, as a text to supplement a good set of lecture notes, as a review book for taking professional examinations, and as a vehicle for self-instruction.

Our thanks and appreciation to Mr. Larry Alemany for his expert criticism from a student's viewpoint and for his careful proofreading, to Mr. David Beckwith for his editorial assistance, and to Mrs. Joyce Gaiser for her meticulous typing.

HERBERT MEISLICH
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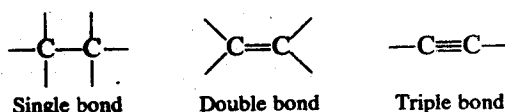
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Chapter 1

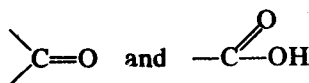
Structure and Properties

1.1 ORGANIC COMPOUNDS

Organic chemistry is the study of carbon (C) compounds. Most organic compounds consist of individual molecules whose atoms are held together by covalent bonds but some also have ionic bonds. Carbon atoms can bond to each other to form chains as in **open-chain (acyclic)** compounds or to form rings as in **cyclic** compounds. Both types can also have branches of C atoms. Cyclic compounds having at least one atom other than C (a **heteroatom**) are called **heterocyclic**. The heteroatoms are usually oxygen (O), nitrogen (N) or sulfur (S). C's can be bonded to each other by:



Hydrocarbons contain only C and hydrogen (H). H's in hydrocarbons can be replaced by other atoms or groups of atoms. These replacements, called **functional groups**, are the reactive sites in molecules. The C to C double and triple bonds are considered to be functional groups. Some common functional groups are the halogens, $-\text{OH}$, $-\text{NH}_2$,



Compounds with the same functional group form a **homologous series** having similar chemical properties and often exhibiting a regular gradation in physical properties with increasing molecular weight.

Organic compounds show a widespread occurrence of **isomers**, which are compounds having the same **molecular** formula but different **structural** formulas and therefore different properties. **Structural formulas** show the arrangement of atoms in a molecule. These formulas are written by assigning the following numbers of bonds: 1 for H and halogen, 2 for O, 3 for N, and 4 for C. These numbers are the **valences** of the atoms.

Most carbon-containing molecules have three-dimensional shapes. In methane, the bonds of C make equal angles of 109.5° with each other, and each of the four H's is at a corner of a regular tetrahedron whose center is occupied by the C atom. The spatial relationship is indicated as in Fig. 1-1(a) (Newman projection) or in Fig. 1-1(b) ("wedge" projection).

H's project toward viewer
H's project away from viewer

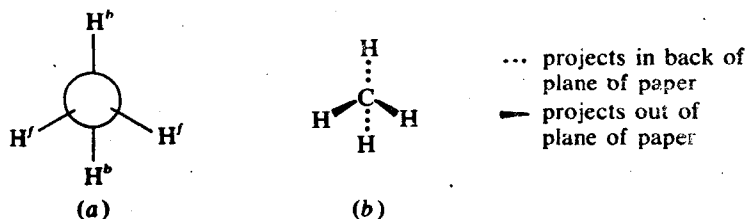
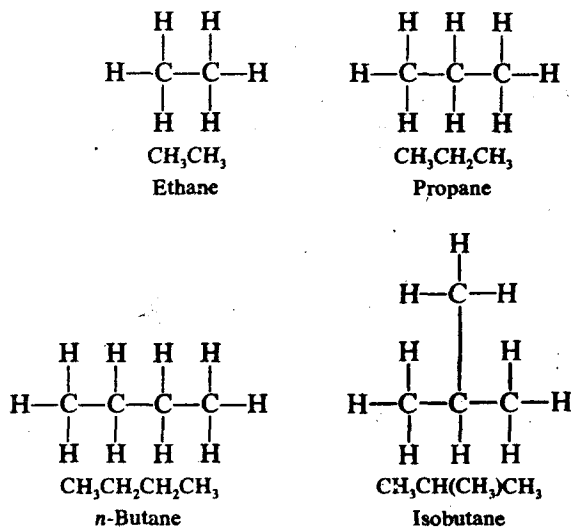


Fig. 1-1

Structural formulas for some hydrocarbons are:



These are flat projections of the three-dimensional structures. **Condensed** structural formulas are shown beneath the molecular formulas. **Lewis (electron-dot)** structural formulas show all shared and unshared pairs of electrons, e.g.



Problem 1.1 Why are there so many compounds that contain carbon? ◀

Bonds between C's are covalent and strong, so that C's can form long chains and rings, both of which may have branches. C's can bond to almost every element in the periodic table. Also, the number of isomers increases as the organic molecules become more complex.

Problem 1.2 How do the boiling points, melting points and solubilities of covalent organic compounds differ from those of inorganic salts? Account for the differences. ◀

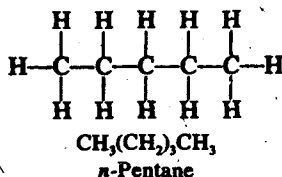
Covalent organic compounds have much lower boiling and melting points because the forces attracting molecules to each other are weak. The electrostatic forces attracting the oppositely charged ions in inorganic salts are very strong. The forces of attraction between the atoms within a covalent molecule are, however, very strong. Inorganic salts are generally soluble in water because water aids in the separation of the ions. Inorganic salts are *not* soluble in organic solvents such as ether and benzene. Most organic compounds are insoluble in water but dissolve in organic solvents.

Problem 1.3 Give four differences in chemical reactivity between an organic compound, such as a hydrocarbon, and an inorganic salt. ◀

1. Ionic reactions often occur *instantaneously*. Reactions between covalent organic molecules proceed *more slowly*; they often need higher temperatures and/or catalysts.
2. Many reactions of organic compounds give *mixtures of products*.
3. Organic compounds are *less stable* to heat. They usually decompose at temperatures above 700 °C, which break many of their covalent bonds.
4. Organic compounds are more *susceptible to oxidation*. Hydrocarbons burn in O₂ to give CO₂ and H₂O. Inorganic compounds generally remain unchanged even after intense heating.

Problem 1.4 Write structural and condensed formulas for the three isomers of pentane, C_5H_{12} .

Carbon forms four covalent bonds; hydrogen forms one. The carbons can bond to each other in a chain:



or they can be "branches" (shown circled in Fig. 1-2) on the linear backbone (shown in a rectangle).

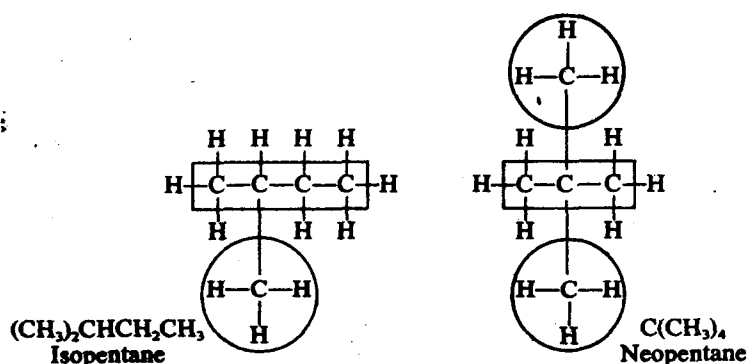


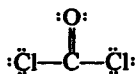
Fig. 1-2

Problem 1.5 Write structural formulas for: (a) hydrazine (N_2H_4), (b) carbonyl chloride ($COCl_2$), (c) nitrous acid (HNO_2).

(a) N needs three covalent bonds and H needs one. Each N is bonded to the other N and to two H's:



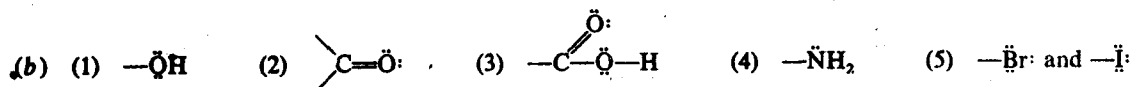
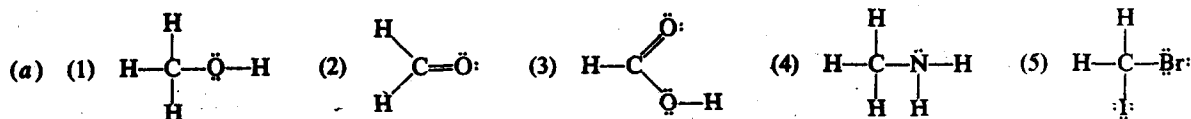
(b) The tetravalent C is bonded to divalent O by a double bond and to each Cl by a single bond:



(c) The valences of one, two and three for H, O and N, respectively, are satisfied by one bond of O to H and another of the same O to N. The second O is double-bonded to N: $H-\ddot{O}-\ddot{N}=\ddot{O}$.

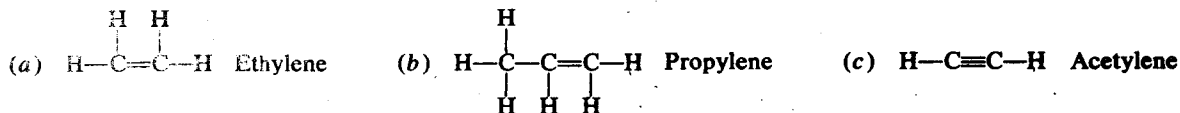
Problem 1.6 (a) Write possible structural formulas for (1) CH_4O , (2) CH_2O , (3) CH_2O_2 , (4) CH_5N , (5) CH_2BrI . (b) Indicate the functional group in each case.

The atom with the higher valence is usually the one to which most of the other atoms are bonded.



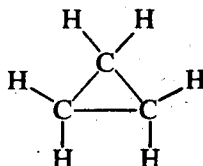
Problem 1.7 Write structural formulas for (a) C_2H_4 , (b) C_3H_6 , (c) C_2H_2 .

In each case there is at least one bond between the two C atoms. There are not enough H's to satisfy the valence of C. Multiple bonds must be used.



Problem 1.8 Is propylene the only compound with the formula C_3H_6 ?

The valence of four for C can be met if the bonding C's form a ring instead of using a double bond. Cyclopropane,



is an isomer of propylene.

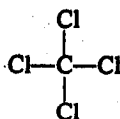
Problem 1.9 What physical properties are used to determine the purity of liquids and solids?

For liquids, the physical properties are boiling point, refractive index, density, and various spectra such as ultraviolet, infrared, nuclear magnetic resonance and mass. Melting points and spectra are most frequently used for solids.

Problem 1.10 Use the Lewis-Langmuir octet rule to write Lewis electron-dot structures for: (a) HCN, (b) CO_2 , (c) CCl_4 and (d) $\text{CH}_3\text{CH}_2\text{OH}$.

According to the octet rule, elements tend to combine so as to acquire the electron configuration of the nearest noble gas. This configuration is 2 for H and Li, which are close to He, and is 8 (octet) for elements of the second and third periods of the periodic table.

- (a) The covalencies of H, N and C are one, three and four, respectively, and the structural formula is $\text{H}-\text{C}\equiv\text{N}$. H and C both have completed their outer shells with two and eight electrons, respectively, but N has only six electrons. This formula shows only eight outer electrons (two in each bond). It should have ten, since H, C and N are in families I, IV and V of the periodic table, and their outer electron shells have one, four and five electrons, respectively. The missing pair of electrons is placed on N to give $\text{H}:\text{C}::\text{N}:$, thereby also completing the octet of N.
- (b) The valences 2 for O and 4 for C are used to deduce the structural formula $\text{O}::\text{C}::\text{O}$. There are 4 bonding electrons in each of the two double bonds between O and C. C has an octet, but each O has only 4 electrons. The octet of each O may be completed by adding two unshared electron pairs to each. There are 16 electrons in the complete electron-dot formula, $:\ddot{\text{O}}::\text{C}::\ddot{\text{O}}:$, in agreement with the total number of outer electrons (4 from one C and 6 from each of the two O's).
- (c) The structural formula

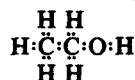


is deduced from the covalencies of 1 for Cl and 4 for C. C has an octet but each Cl shares only 2 electrons. Three unshared electron pairs are placed on each of the four Cl's to provide the complete electron-dot structure

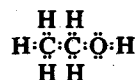


The 32 electrons in this structure agrees with the sum of 4 electrons from C and 28 from 4 Cl's, each of which has 7 outer electrons.

- (d) The procedure outlined in Problem 1.5 gives the formula

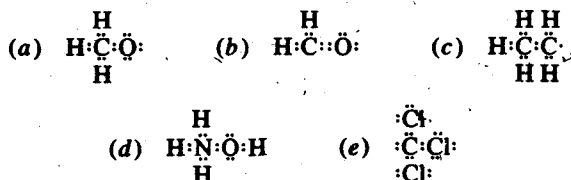


Only O with 4 electrons lacks an octet. Placing two unshared electron pairs on O gives the complete formula



This shows 20 outer electrons, which agrees with the sum of 8 electrons from C (2×4), 6 from H (6×1) and 6 from O.

Problem 1.11 Determine the positive or negative charge, if any, on the following species:



The charge on a species equals the sum of the outer electrons minus the total number of electrons shown.

- (a) The sum of the outer electrons (6 for O, 4 for C, and 3 for three H's) is 13. The electron-dot formula shows 14 electrons. The net charge is -1 ($13 - 14$) and the species is the methoxide anion, $\text{CH}_3\ddot{\text{O}}^-$.
- (b) There is no charge on the formaldehyde molecule because the 12 electrons in the structure equals the number of outer electrons, i.e. 6 for O, 4 for C, and 2 for two H's.
- (c) This species is neutral because there are 13 electrons shown in the formula and 13 outer electrons: 8 from two C's and 5 from five H's.
- (d) There are 15 outer electrons: 6 from O, 5 from N, and 4 from four H's. The Lewis dot structure shows 14 electrons. It has a charge of $+1$ ($15 - 14$) and is the hydroxylammonium cation, $[\text{H}_3\text{NOH}]^+$.
- (e) There are 25 outer electrons, 21 from three Cl's and 4 from C. The Lewis dot formula shows 26 electrons. It has a charge of -1 ($25 - 26$) and is the trichloromethide anion, CCl_3^- .

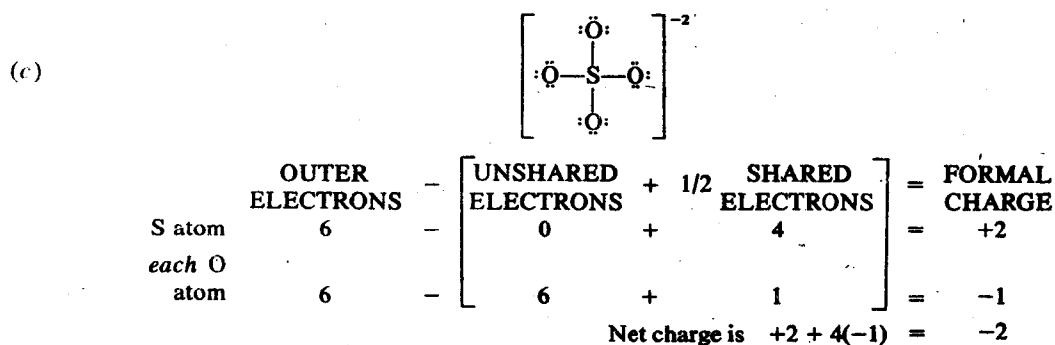
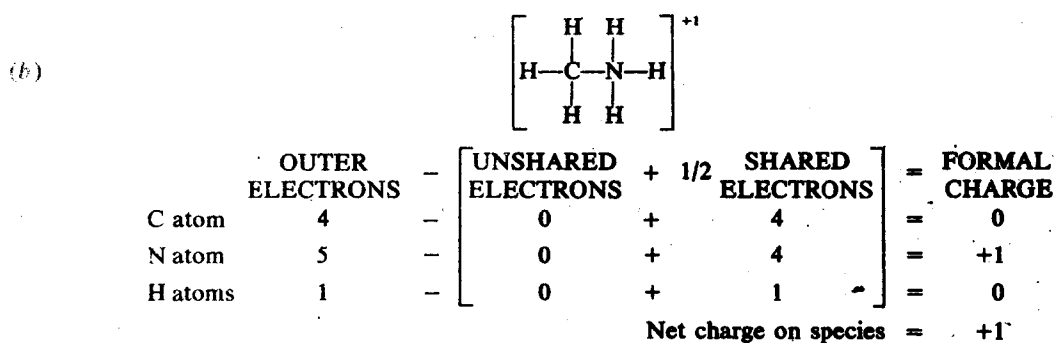
Problem 1.12 Determine the formal charge on each atom in the following species: (a) H_3NBF_3 , (b) CH_3NH_3^+ and (c) SO_4^{2-} .

The formal charge on an atom equals the number of outer electrons minus the number of electrons assigned to the atom in its bonding state. The assigned number is one-half the sum of all shared electrons, plus all unshared electrons.



	OUTER ELECTRONS	-	UNSHARED ELECTRONS	+	1/2 SHARED ELECTRONS	=	FORMAL CHARGE
H atoms	1	-	0	+	1	=	0
F atoms	7	-	6	+	1	=	0
N atom	5	-	0	+	4	=	+1
B atom	3	-	0	+	4	=	-1

The sum of all formal charges equals the charge on the species. In this case, the +1 on N and the -1 on B cancel and the species is an uncharged molecule.



In this book the signs + and - will be used to indicate both formal charge and actual net charge; some texts employ \oplus and \ominus for formal charge.

Chapter 2

Bonding and Molecular Structure

2.1 ATOMIC ORBITALS

An **atomic orbital (AO)** is a region of space about the nucleus in which there is a high probability of finding an electron. An electron has a given energy as designated by: (a) the principal energy level (quantum number), n , related to the size of the orbital; (b) the sublevel, s , p , d , f or g , related to the shape of the orbital; (c) except for the s , each sublevel has some number of equal-energy (**degenerate**) orbitals differing in their spatial orientation; (d) the electron spin, designated \uparrow or \downarrow . Table 2-1 shows the distribution and designation of orbitals.

Table 2-1

Principal Energy Level, n	1	2	3	4
Maximum No. of Electrons, $2n^2$	2	8	18	32
Sublevels	1s	2s, 2p	3s, 3p, 3d	4s, 4p, 4d, 4f
Designation of Filled Orbitals	1s ²	2s ² , 2p ⁶	3s ² , 3p ⁶ , 3d ¹⁰	4s ² , 4p ⁶ , 4d ¹⁰ , 4f ¹⁴
Maximum Electrons per Sublevel	2	2, 6	2, 6, 10	2, 6, 10, 14
Orbitals per Sublevel	1	1, 3	1, 3, 5	1, 3, 5, 7

The s orbital is a sphere around the nucleus, as shown in cross section in Fig. 2-1(a). A p orbital is two spherical lobes touching on opposite sides of the nucleus. The three p orbitals are labeled p_x , p_y , and p_z because they are oriented along the x -, y - and z -axes, respectively (Fig. 2-1(b)). In a p orbital there is no chance of finding an electron at the nucleus—the nucleus is called a **node point**. Regions of an orbital separated by a node are assigned + and – signs. These signs are *not associated with electrical or ionic charges*. The s orbital has no node and is usually assigned a +.

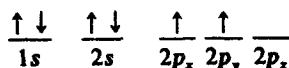
Three principles are used to distribute electrons in orbitals.

1. **“Aufbau” or Building-up Principle.** Orbitals are filled in order of increasing energy: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, etc.
2. **Pauli Exclusion Principle.** No more than two electrons can occupy an orbital and then only if they have opposite spins.
3. **Hund’s Rule.** One electron is placed in each equal-energy orbital so that the electrons have parallel spins, before pairing occurs. (Substances with unpaired electrons are **paramagnetic**—they are attracted to a magnetic field.)

Problem 2.1 Show the distribution of electrons in the atomic orbitals of (a) carbon and (b) oxygen. ◀

A dash represents an orbital; a horizontal space between dashes indicates an energy difference. Energy increases from left to right.

(a) Atomic number of C is 6.



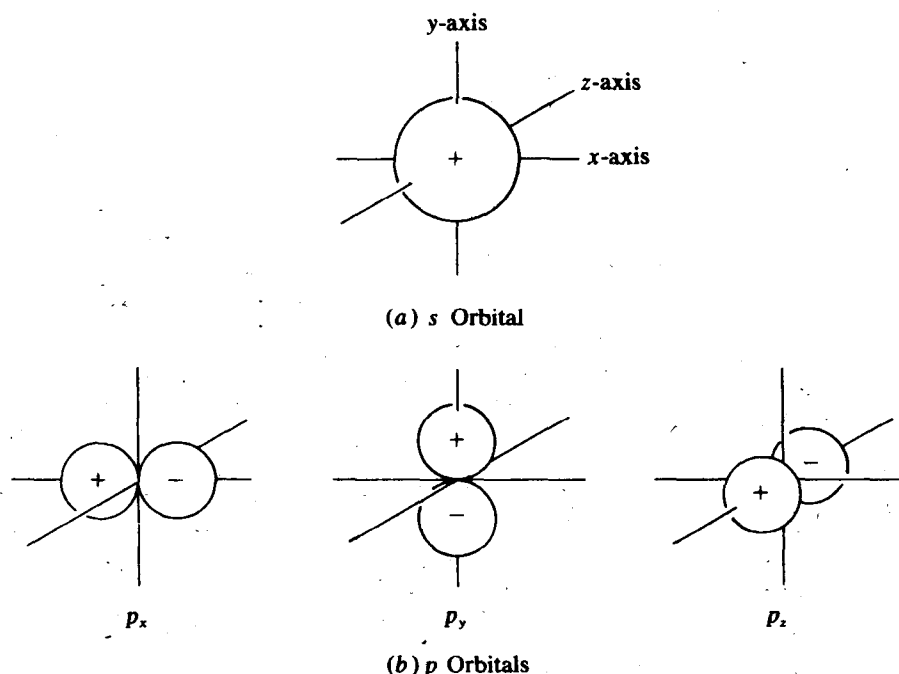
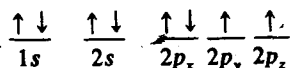


Fig. 2-1

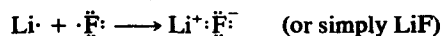
The two 2*p* electrons are unpaired in each of two *p* orbitals (Hund's rule).

(b) Atomic number of O is 8.



Problem 2.2 Show how the ionic compound Li^+F^- forms from atoms of Li and F.

These elements react to achieve a stable noble-gas electron configuration (NGEC). Li(3) has 1 electron more than He and loses it. F(9) has 1 electron less than Ne and therefore accepts the electron from Li. In this transfer of an electron, oppositely charged ions are formed which attract each other to create an ionic bond.



2.2 COVALENT BOND FORMATION—MOLECULAR ORBITAL (MO) METHOD

A covalent bond forms by overlap (fusion) of two AO's—one from each atom. This overlap produces a new orbital, called a **molecular orbital (MO)**, which embraces both atoms. The interaction of two AO's actually creates two MO's. If orbitals with like signs overlap, a **bonding MO** results which has a high electron density between the atoms and therefore has a lower energy (greater stability) than the individual AO's. If AO's of unlike signs overlap, an **antibonding MO*** results which has a node (no electron density) between the atoms and therefore has a higher energy than the individual AO's.

Head-to-head overlap of AO's gives a **sigma (σ) MO**—the bonds are called σ bonds, Fig. 2-2(a). The corresponding antibonding MO* is designated σ^* , Fig. 2-2(b). The imaginary line joining the nuclei of the bonding atoms is the **bond axis**, whose length is the **bond length**.

Two parallel *p* orbitals overlap side-to-side to form a **pi (π) bond**, Fig. 2-3(a), or a π^* bond, Fig. 2-3(b). The bond axis lies in a nodal plane (plane of no electronic density) perpendicular to the cross-sectional plane of the π bond.