

LECTURE 20/36 OCT/25/02

HOMO NUCLEAR DIATOMIC MOL.

HETERO NUCLEAR DIATOMIC MOL.

READ: CH3 → GRAY

NEXT LEC. CH4 → GRAY

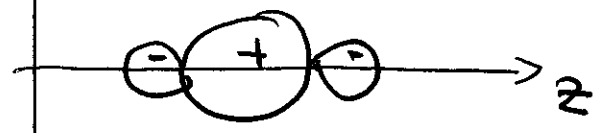
PS # 5

GRAY CH 2 problem
20 - u, r, y, w, z
23
24

DUE
FRIDAY
NOV 1st
8am

CH 3. - PROBLEMS
3, 4, 7, 9, 10, 12, 13

$$2p_z \pm 2p_z$$



R₂ SYM ⇒ σ

INV SYM ⇒ g

$$2p_z - 2p_z$$

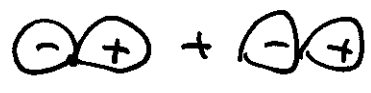
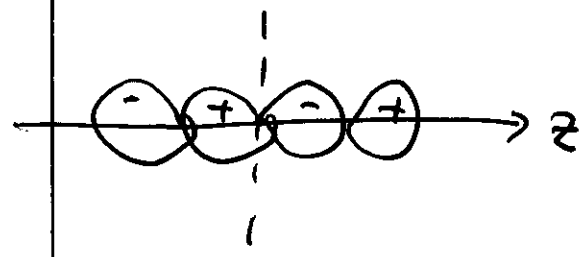
$$[\ominus \oplus - \oplus \ominus]$$



ACCUMULATION IN CENTER
⇒ BONDING

$$\sigma_g^b 2p_z$$

$$2p_z + 2p_z$$

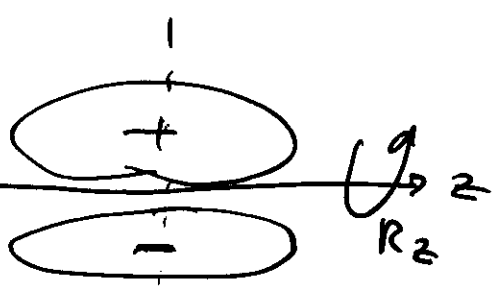


NO ACCUMULATION IN
THE CENTER ⇒ ANTI BONDING

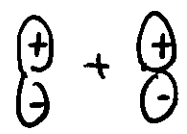
$$\sigma_u^* 2p_z$$

R₂ SYM ⇒ σ

NO INV SYM ⇒ u



$$2p_x + 2p_x$$



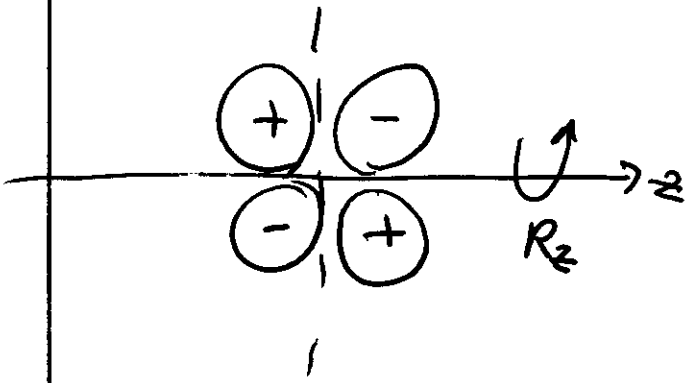
NO R₂ SYM ⇒ π

NO INV SYM ⇒ u

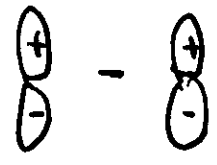
ACCUMULATION CENTER
⇒ BONDING



$$\pi_u^b 2p_x$$



$$2p_x - 2p_x$$



NO $R_z \Rightarrow \pi$

INV SYM $\Rightarrow g$

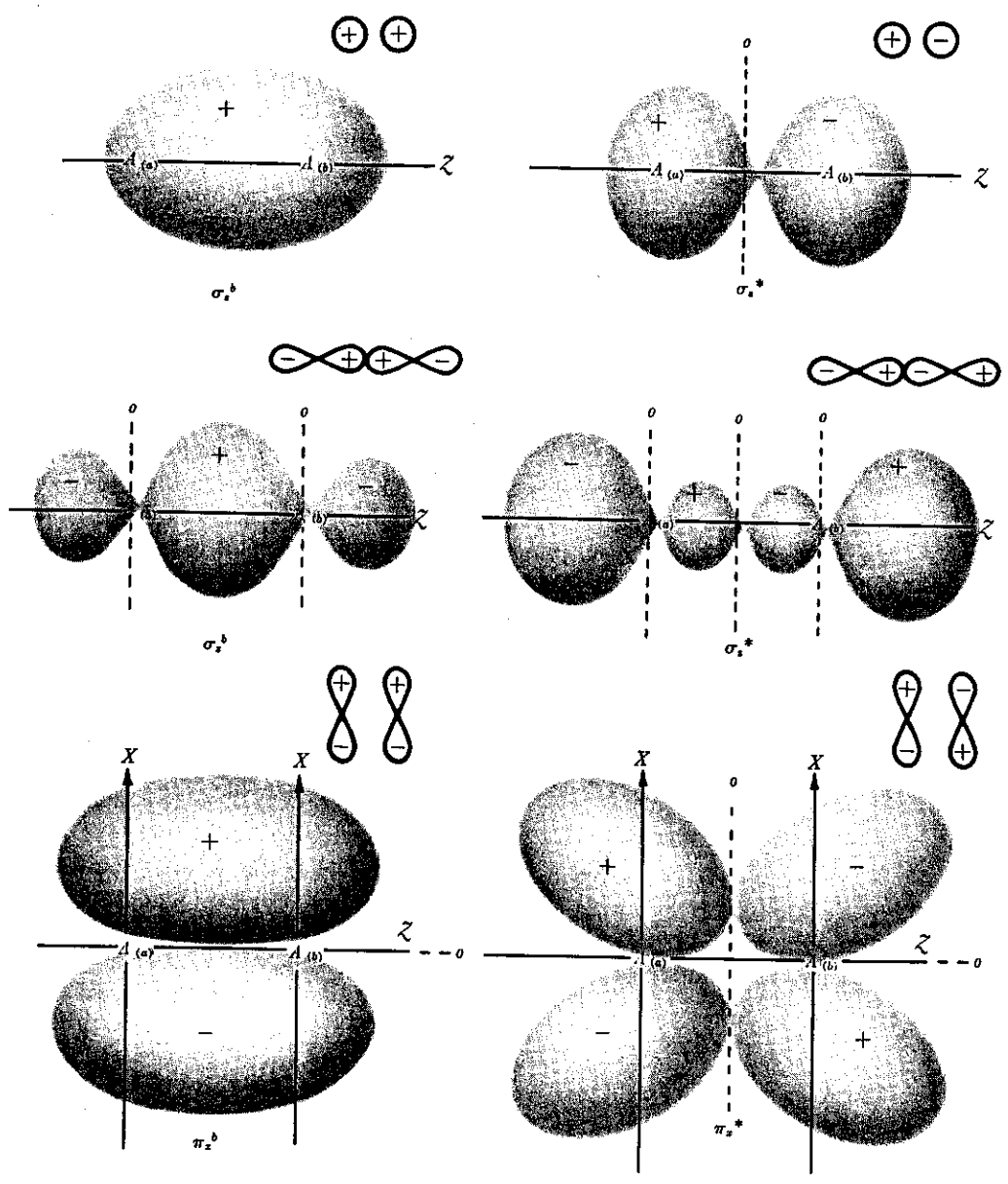
NO ACCUMULATION CENTER
 \Rightarrow ANTI BONDING

$\pi_g^* 2p_x$

ALSO

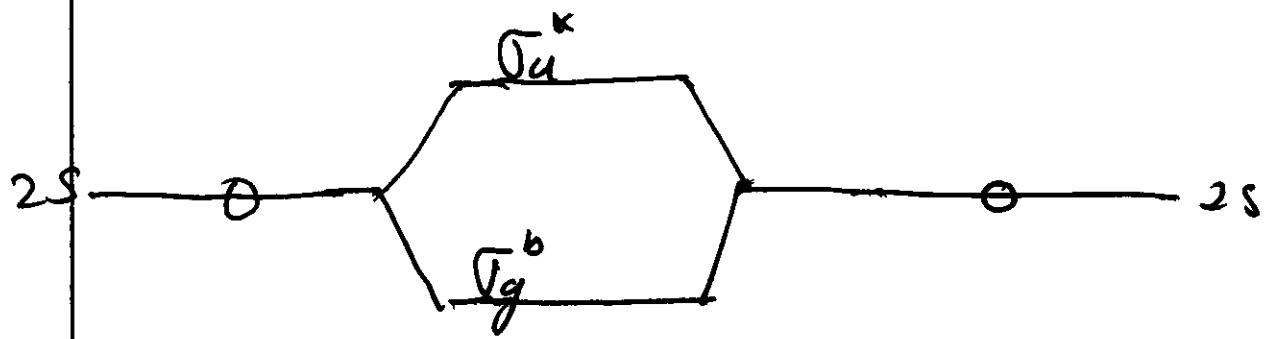
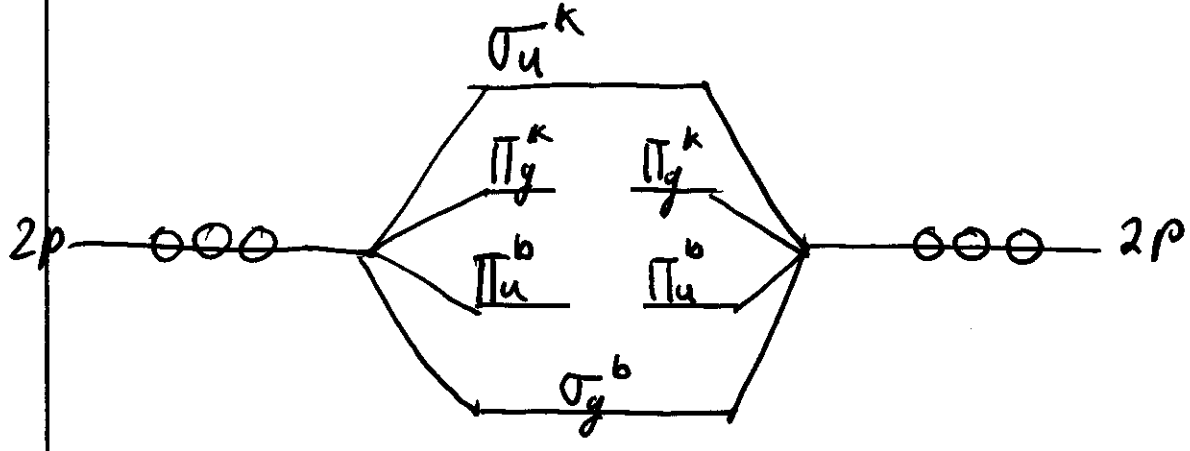
$$\pi_u^b 2p_y$$

$$\pi_g^* 2p_y$$



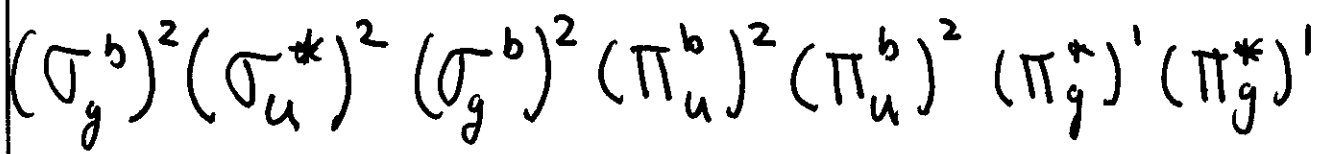
HOMONUCLEAR DIATOMIC MOL

$E_{2p} \gg E_{2s}$



MOLECULAR ORBITALS FOR O₂ AND F₂

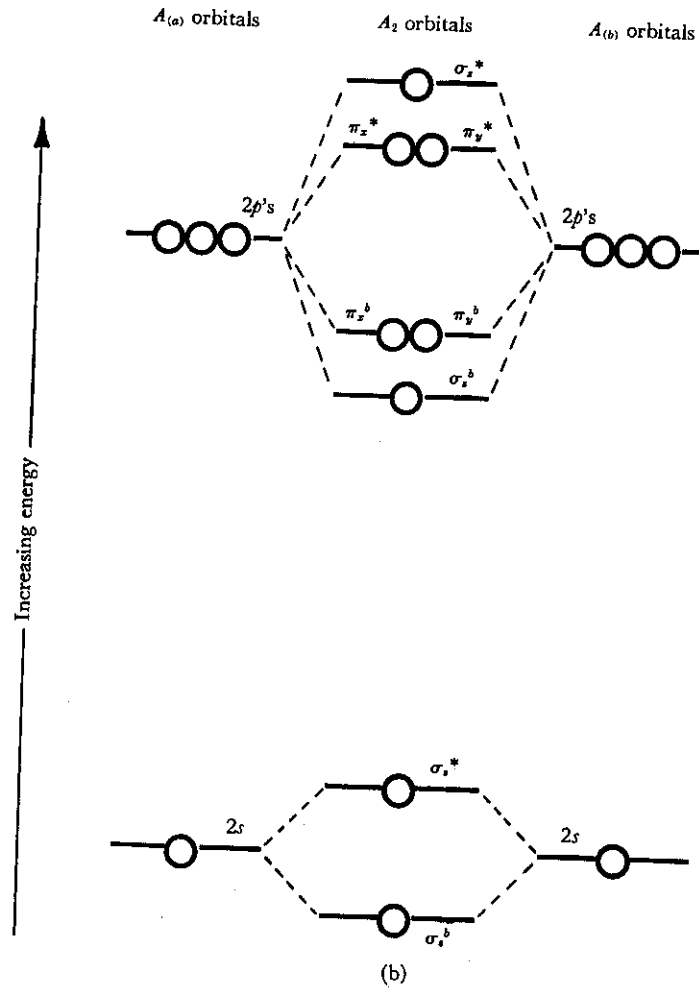
O₂ HAS 12 e⁻



2 UNPAIRED e⁻ ⇒ PARAMAGNETIC

$$\begin{aligned} \text{BOND ORDER} &= \frac{1}{2} [\# \text{ BONDING } e^- - \# \text{ ANTI BONDING } e^-] \\ &= \frac{1}{2} [8 - 4] = 2 \end{aligned}$$

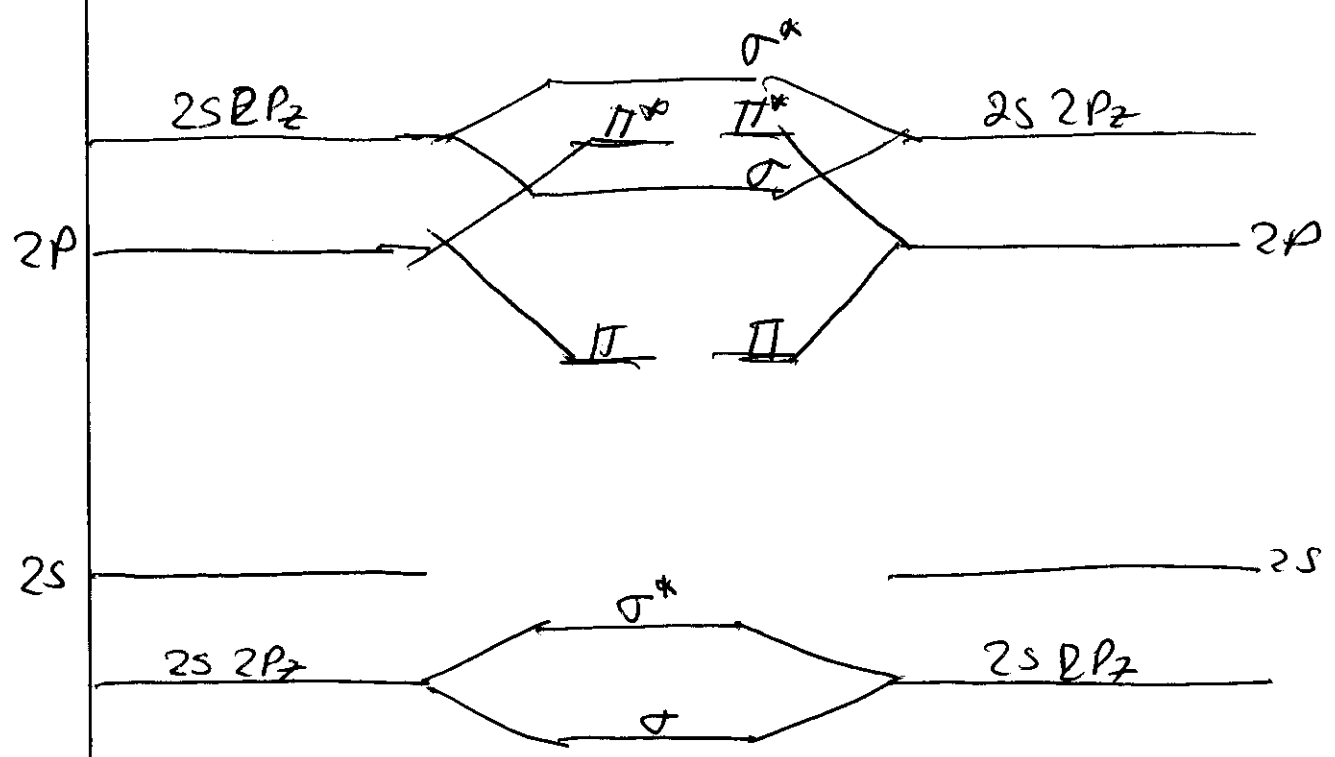
6
20



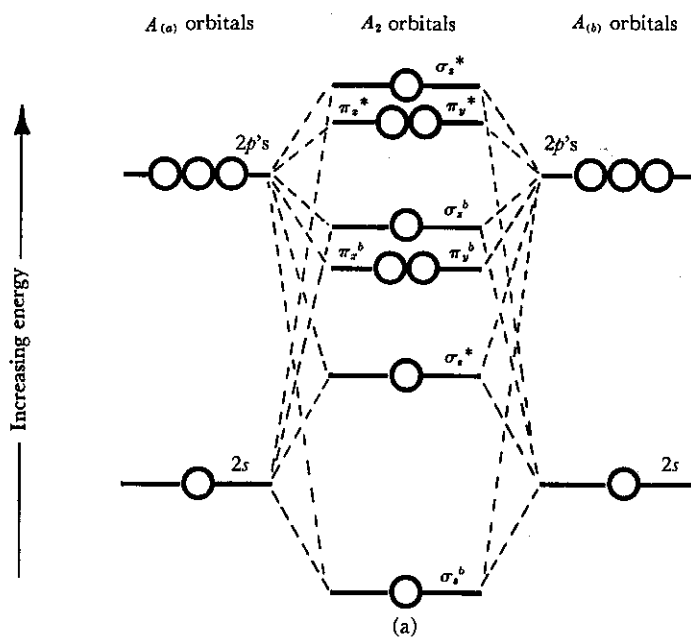
hybridization. This order of energy levels should be observed when the energy separation of the atomic *s* and *p* valence levels is relatively large. Referring to Table 3-3 we see that the large $2s-2p$ energy separation in F atoms makes the F_2 molecule a likely candidate for this scheme of energy levels. Additionally, there is some spectroscopic evidence that the electronic energy levels of the O_2 molecule are consistent with this diagram.

If $E_{2p} \approx E_{2s}$

FIRST COMBINE $2s + 2p_z$ FOR EACH ATOM



B₂ C₂ N₂



3-9

Molecular-orbital energy-level diagrams for homonuclear diatomic molecules. (a) Relative energies of molecular orbitals in the case of appreciable $s-p$ hybridization. This level scheme has been established for most homonuclear diatomic molecules through detailed experiments involving magnetic and spectroscopic properties of molecules. The degree of $s-p$ hybridization becomes smaller as the energy separation of the valence s and p atomic levels becomes larger. (b) Suggested relative order of molecular orbitals in systems with negligible $s-p$

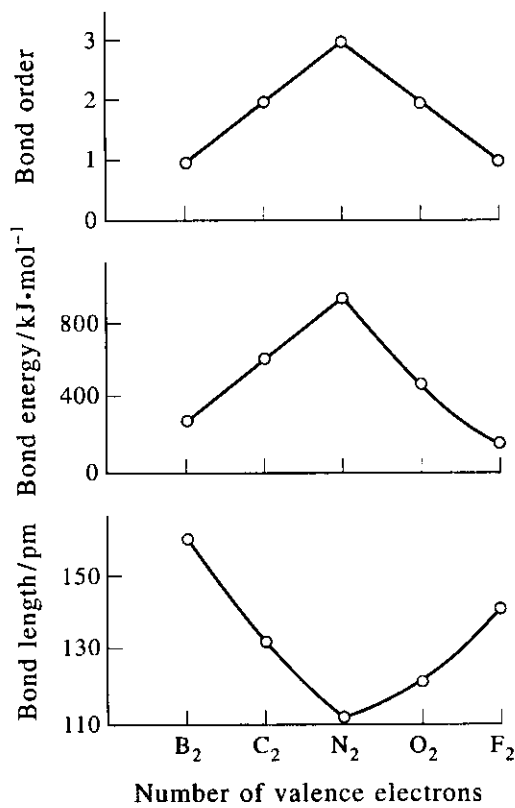


FIGURE 9.15
Plots of various bond properties for the homonuclear diatomic molecules B₂ through F₂.

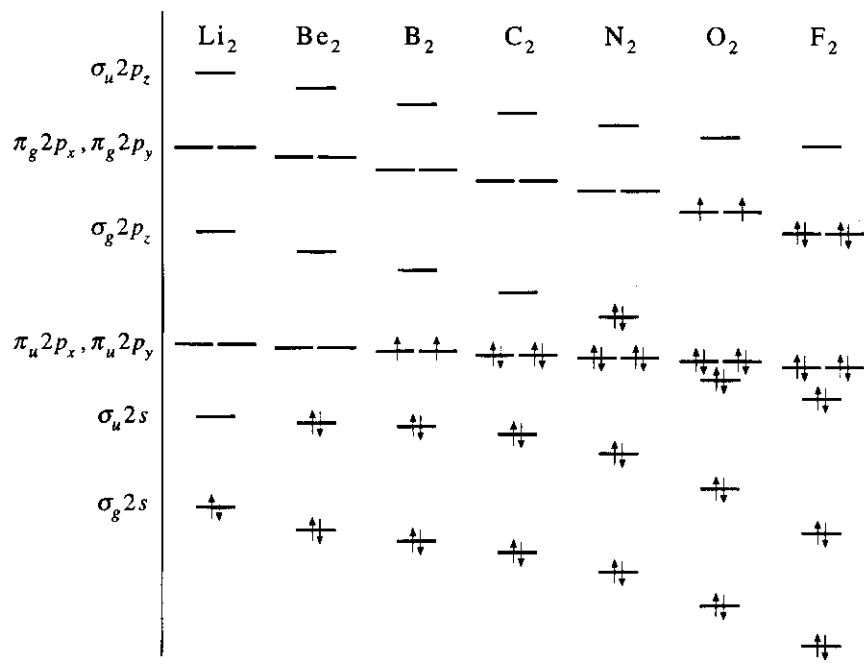
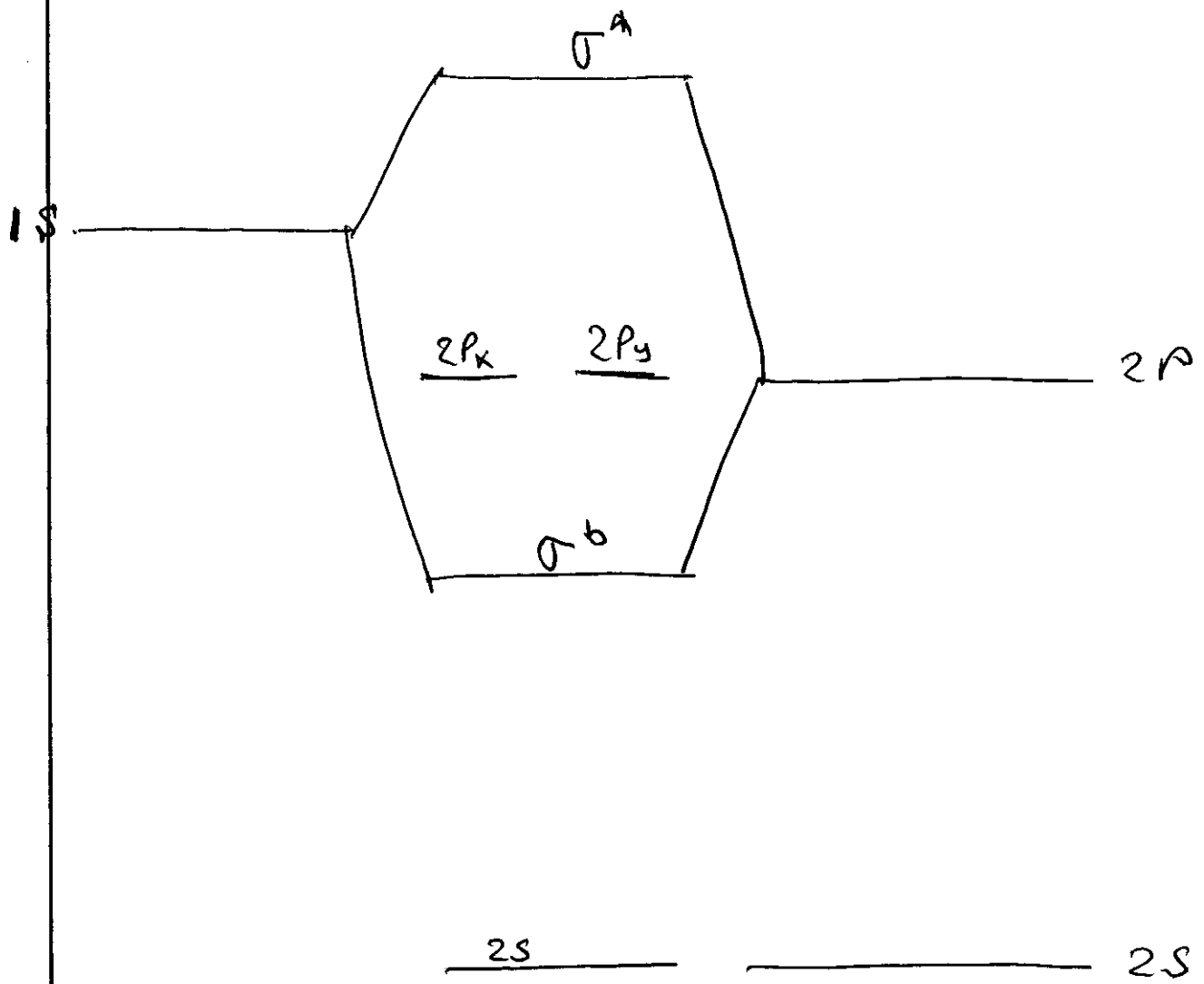


FIGURE 9.13
 The relative energies (not to scale) of the molecular orbitals for the homonuclear diatomic molecules Li₂ through F₂. The $\pi_u 2p_x$ and $\pi_u 2p_y$ orbitals are degenerate, as are the $\pi_g 2p_x$ and $\pi_g 2p_y$ orbitals.

HETERO NUCLEAR MOLECULES

H F

H	1s	-110000 cm ⁻¹
F	2s	-374 000 cm ⁻¹
	2p	-151 000 cm ⁻¹

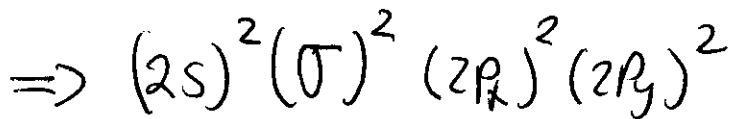


2S AND P_x P_y ARE NON BONDING

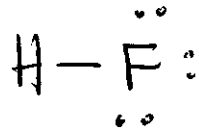
σ BONDING
 σ^* ANTI BONDING

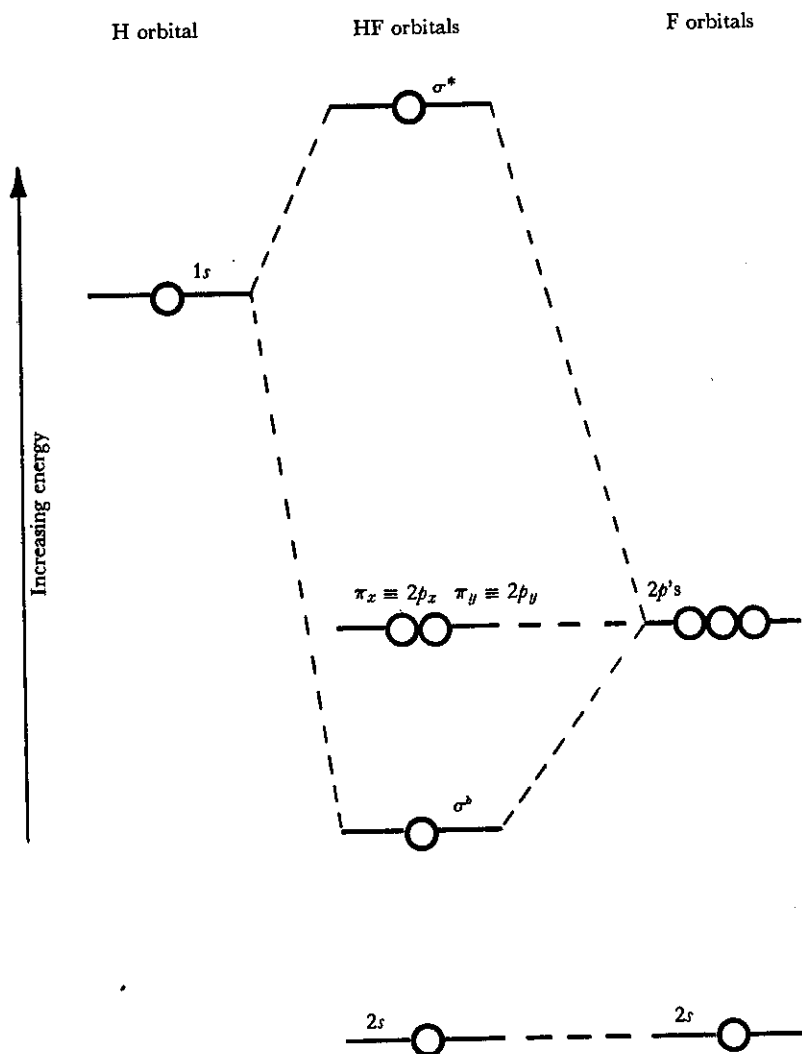
H \rightarrow 1e

F \rightarrow 7e



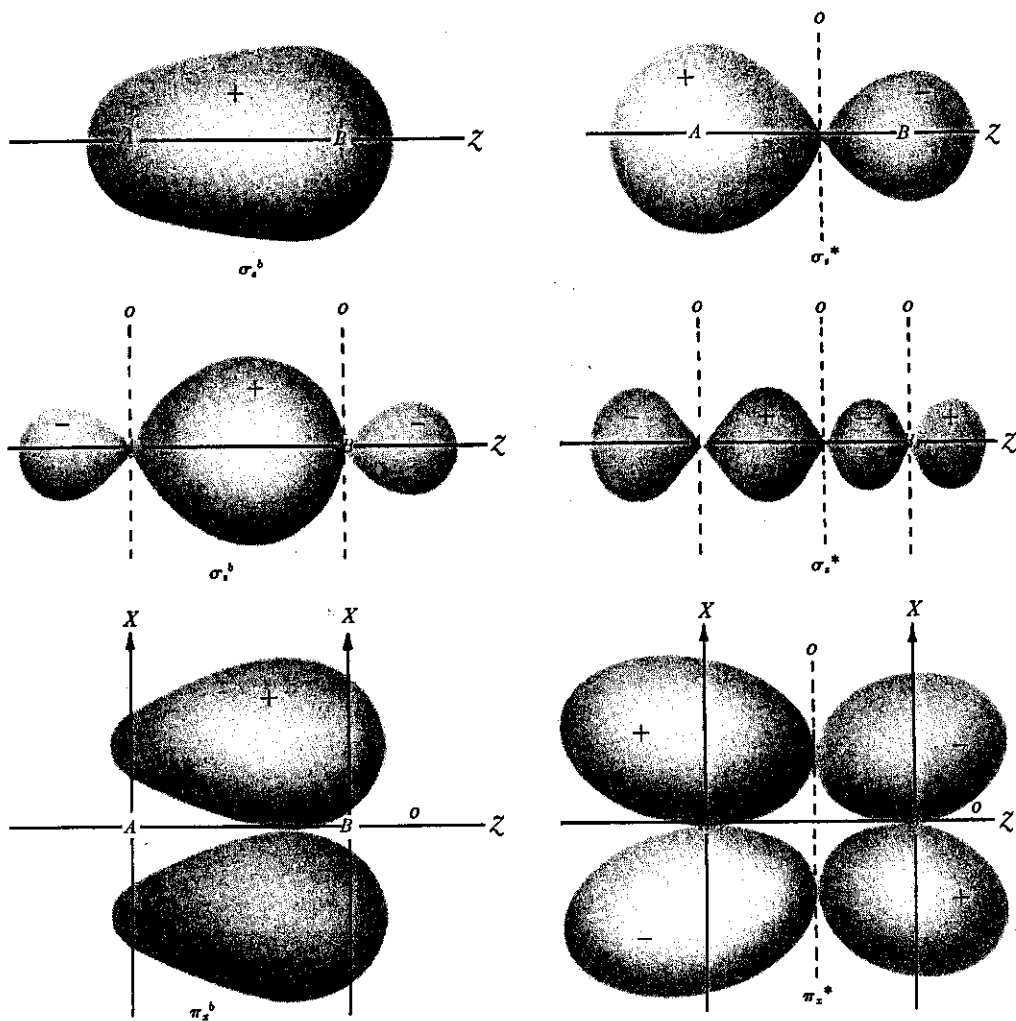
ONE BOND AND 6 PAIRED e^-





3-13

Relative energies of atomic and molecular orbitals in HF. The energy of an electron in atomic hydrogen $1s$ orbital is $-110,000 \text{ cm}^{-1}$ (the first ionization energy of H is $+110,000 \text{ cm}^{-1}$), and the energy in the $2p$ orbitals of F is $-151,000 \text{ cm}^{-1}$ (first ionization energy of F is $+151,000 \text{ cm}^{-1}$). Not drawn to scale because the $2s$ orbital actually is much lower in energy than shown.



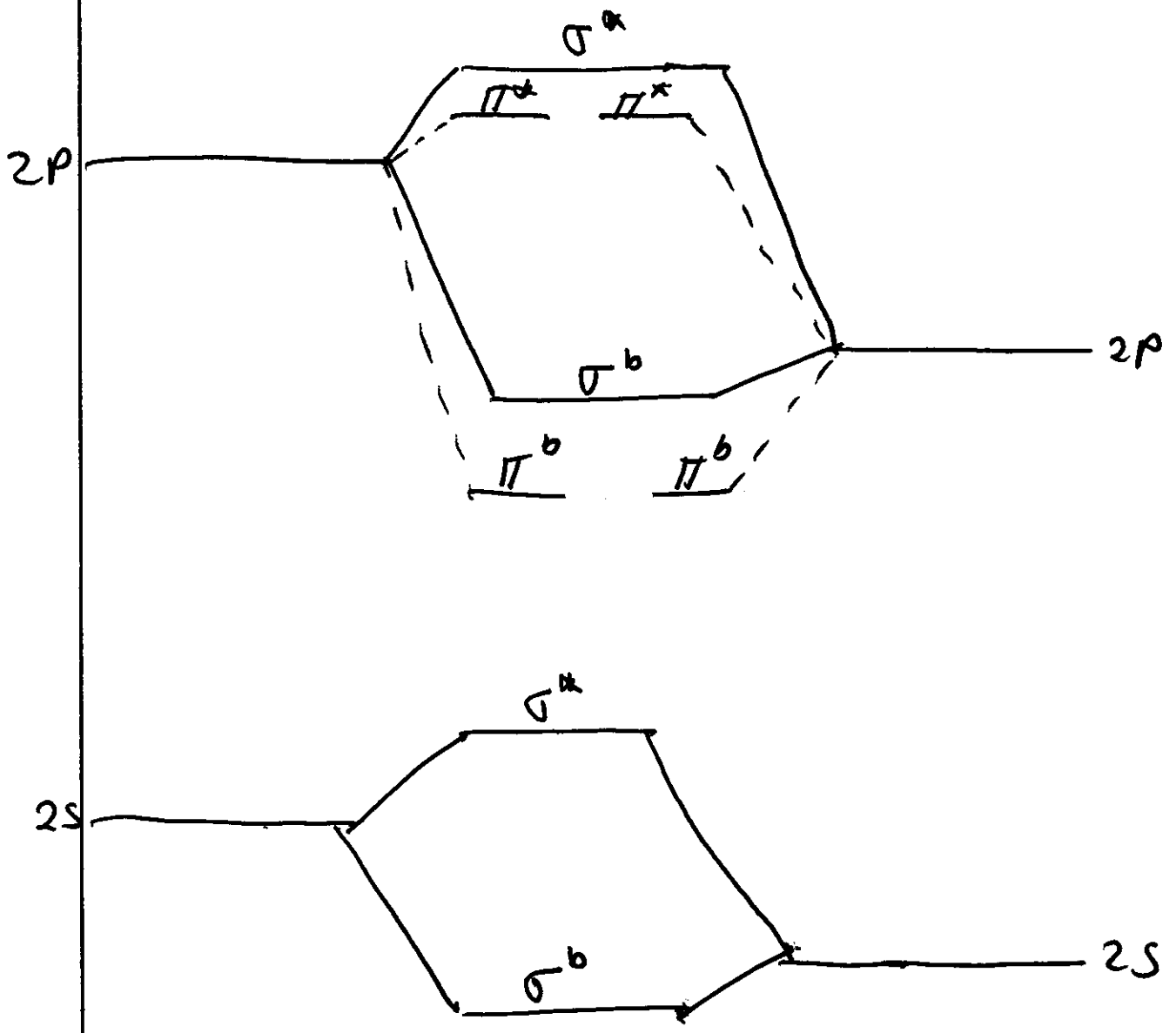
3-15

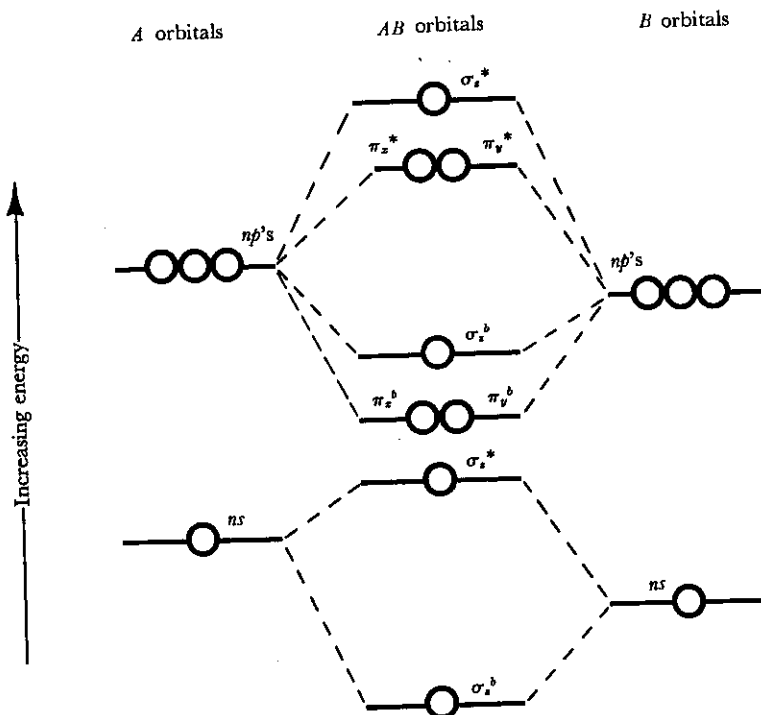
Spatial representation of molecular orbitals for an AB molecule in which B is more electronegative than A. Lines with the letter "o" represent nodal planes of zero electron density.

HETERONUCLEAR DIATOMIC MOLECULE

A

B
(MORE
ELECTRONEGATIVE)





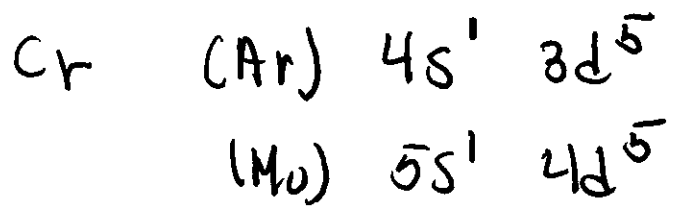
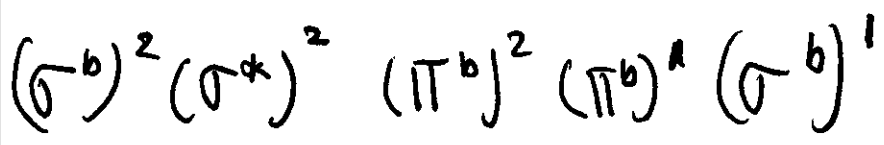
3-14

Relative orbital energies in a general AB molecule in which B is more electronegative than A.

The bond properties of several examples of the heteronuclear diatomic molecules and ions listed in Table 3-5 are discussed in the following paragraphs.

BN (eight valence electrons)

The ground-state electronic configuration for BN is $(\sigma_s^b)^2(\sigma_s^*)^2(\pi_{x,y}^b)^3(\sigma_z^b)^1$, from which we predict two bonds in the molecule. Thus the BN molecule is electronically similar to C_2 , except that for BN the configuration with two unpaired electrons is more stable. The bond lengths of C_2 and BN are 1.243 Å and 1.281 Å, respectively. The BN bond energy of 92 kcal mole⁻¹ is suspiciously low compared with 144 kcal mole⁻¹ for C_2 . Further experimental work is necessary to verify the BN bond energy.



12
20

TABLE 9.3
The correspondence between the various notations for diatomic molecular orbitals.

Simple LCAO-MO		SCF-LCAO-MO
$\sigma 1s$	$\sigma_g 1s$	$1\sigma_g$
$\sigma^* 1s$	$\sigma_u 1s$	$1\sigma_u$
$\sigma 2s$	$\sigma_g 2s$	$2\sigma_g$
$\sigma^* 2s$	$\sigma_u 2s$	$2\sigma_u$
$\pi 2p_x$	$\pi_u 2p_x$	$1\pi_u$
$\pi 2p_y$	$\pi_u 2p_y$	$1\pi_u$
$\sigma 2p_z$	$\sigma_g 2p_z$	$3\sigma_g$
$\pi^* 2p_x$	$\pi_g 2p_x$	$1\pi_g$
$\pi^* 2p_y$	$\pi_g 2p_y$	$1\pi_g$
$\sigma^* 2p_z$	$\sigma_u 2p_z$	$3\sigma_u$