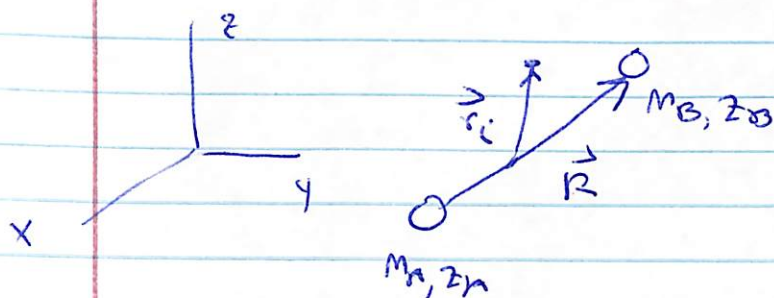


①

# DIATOMIC MOLECULES

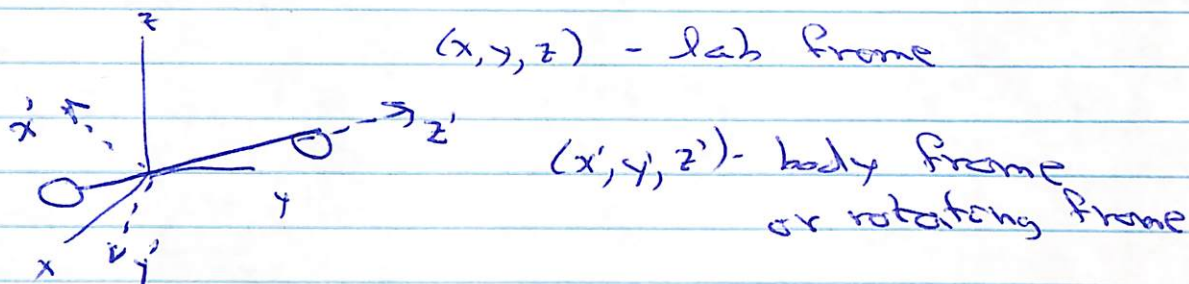
two ions,  $Z_A, Z_B$

lots of electrons ( $=1, \dots, N$ )



Big idea: nuclei are heavy & slow  
electrons are light & fast

⇒ pick reference frame centered on nuclear  
COM, rotating with nuclei



related by Euler angles

$$\psi = (\varphi, \theta, \gamma)$$

spherical  
coords of  
molecular axis

rotation  
around  
that axis

Basis set (lab frame:)

$$\underbrace{|j, m\rangle}_{\text{ang. momentum}} \times \underbrace{Y_{N, N}(\vec{r})}_{\text{rotation of nucl. axis}} \times \underbrace{\frac{1}{R} \psi(\vec{r}, R)}_{\text{depends on } R, \text{ e coordinates}}$$

(2)

Remark - these are generally not good quantum numbers of the molecule

total angular momentum is:

lab:

$$|jN\rangle_{JM} \Big|_{\text{lab}} = \sum_{mN} |jm\rangle Y_{NM_N}(\hat{r}) \langle jm N M_N | JM \rangle$$

To go to the rotating frame, 3 facts:

$$1) |jm\rangle_{\text{lab}} = \sum_{m\omega} D_{m\omega}^{j*}(\hat{r}) |j\omega\rangle$$

Wigner matrix

$\omega$  = projection of  $j$  onto body frame

$$2) Y_{NM_N} = \sqrt{\frac{2N+1}{8\pi^2}} D_{M_N 0}^{N*}$$

$\nearrow$  nuclei have no projection of  $\vec{N}$  onto body axis

3) addition theorem:

$$D_{m\omega}^{j*} D_{m\omega}^{N*} = \sum_J \langle jm N M_N | JM \rangle \langle j\omega N 0 | JM \rangle D_{m\omega}^{J*}$$

$$M = m + M_N \quad \omega = \omega + 0$$

it's like adding angular momenta in lab & body frames simultaneously



(3)

after some algebra:

$$|(jN)JM\rangle_{lab} = \sum_{\omega} |j; JM_{\omega}\rangle (-1)^{j-\omega} \langle j\omega JM_{\omega} | N \rangle \sqrt{\frac{2j+1}{2JM}}$$

where body-frame basis states are

$$|j; JM_{\omega}\rangle_{body} = |j_{rot}\rangle \times \sqrt{\frac{2J+1}{8\pi^2}} D_{M_{\omega}}^{J*}$$

$\underbrace{\quad}_{e \text{ on body frame}} \quad \underbrace{\quad}_{\text{rigid rotor}}$

Remark - angular momentum around molecular axis is entirely due to electrons

notation:  $\omega = \lambda + \sigma$  for each electron

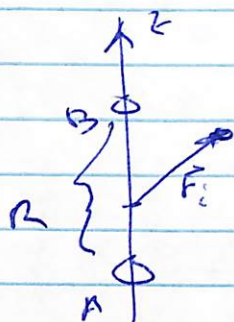
$\uparrow \quad \quad \uparrow$   
 orbital spin

Schrödinger equation:

$$\left[ -\frac{\hbar^2}{2M} \nabla_R^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + V(\vec{r}_i, \vec{R}) \right] \psi = E \psi$$

$M =$  nuclei reduced mass

$$V = \frac{Z_A Z_B e^2}{R} - \sum_i \frac{Z_A e^2}{|\vec{r}_i - \vec{r}_A|} - \sum_i \frac{Z_B e^2}{|\vec{r}_i - \vec{r}_B|}$$



$$+ \sum_{i < j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

ADDENDUM

in body frame, each electron has ang. momentum



$$\omega_i = \lambda_i + \sigma_i \quad \vec{j} = \vec{L} + \vec{S}$$

$\vec{L}$  orbital
spin

$$\text{total: } \Lambda = \sum_i \lambda_i \quad \Sigma = \sum_i \sigma_i$$

$$J = \Lambda + \Sigma$$

general wave function is

$$\underbrace{\sqrt{\frac{2J+1}{8\pi^2}} D_{M, -J}^{J*}}_{\text{rotation}} \times \frac{1}{R} \underbrace{\psi_{\Lambda\Sigma}(\vec{r}_1, \dots, \vec{r}_N; R)}_{\substack{\text{subject to} \\ \text{fixed } \Lambda, \Sigma}} \quad \uparrow \text{nuclear separation}$$



SIMPLIFICATION - nuclei are massive, nuclear kinetic energy negligible at first

$\Rightarrow$  Born-Oppenheimer approximation  
set  $R$  to a fixed value, solve the electronic structure problem

$$\left[ -\frac{\hbar^2}{2m_e} \nabla_{\vec{r}_e}^2 + V(\vec{r}_e; R) \right] \phi_n(\vec{r}_e; R) = U_n(R) \phi_n(\vec{r}_e; R)$$

eigen-energies  
are a function of  $R$

REMARK - This is hard; leave it to chemists,  
2) cylindrical symmetry  $\Rightarrow$  total electronic  
angular momentum projection

$$-2 = \sum_i m_i \quad \text{is conserved.}$$

Total wave function is then

$$\psi(\vec{r}_e, R) = \sum_n F_n(R) \phi_n(\vec{r}_e; R)$$

to a pretty good (B.O.) approximation,  
treat each one separately.

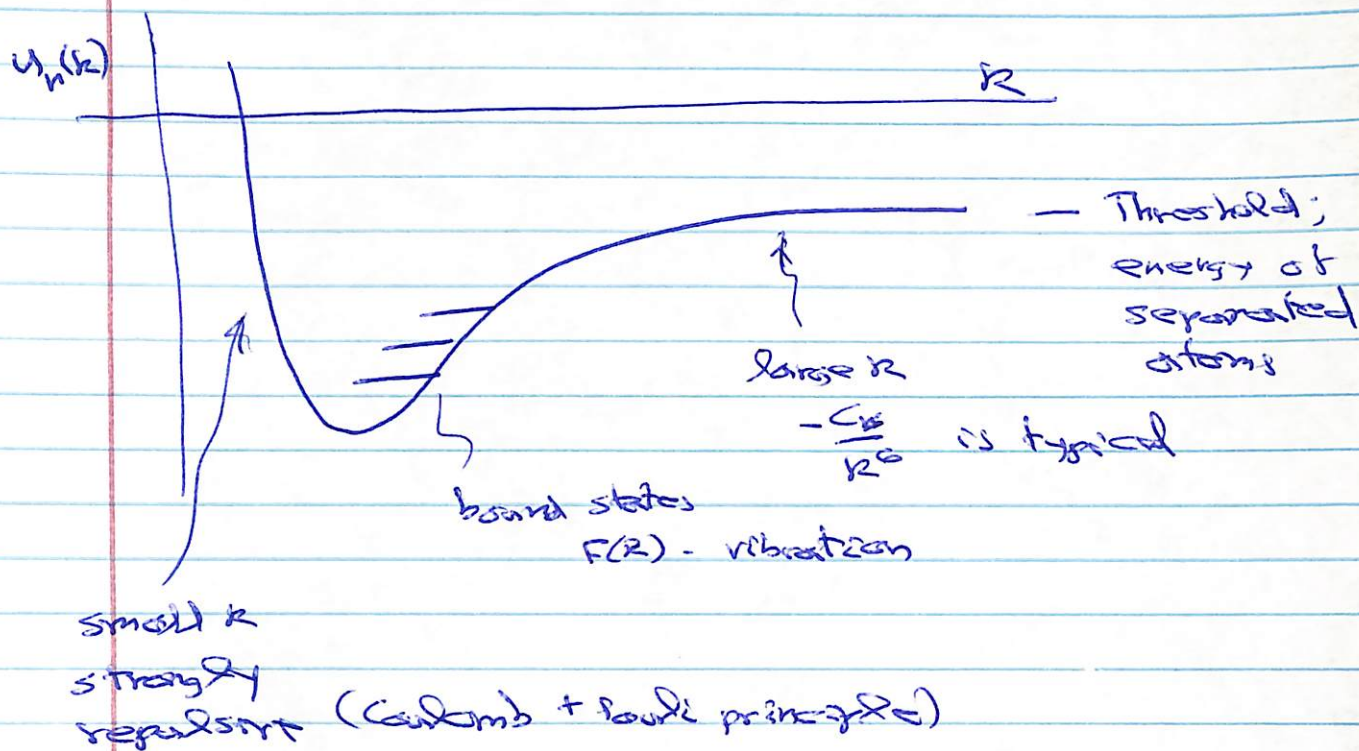
Then, for a given electronic state  $n$ ,  
vibrational Schrödinger eqn for  $R$  is

$$\left[ -\frac{\hbar^2}{2M} \frac{d^2 F_n}{dR^2} + \underbrace{\left( \frac{\hbar^2}{2M} \frac{\chi(R)}{R^2} \right)}_{\text{centrifugal}} + U_n(R) \right] F_n(R) = E F_n(R)$$

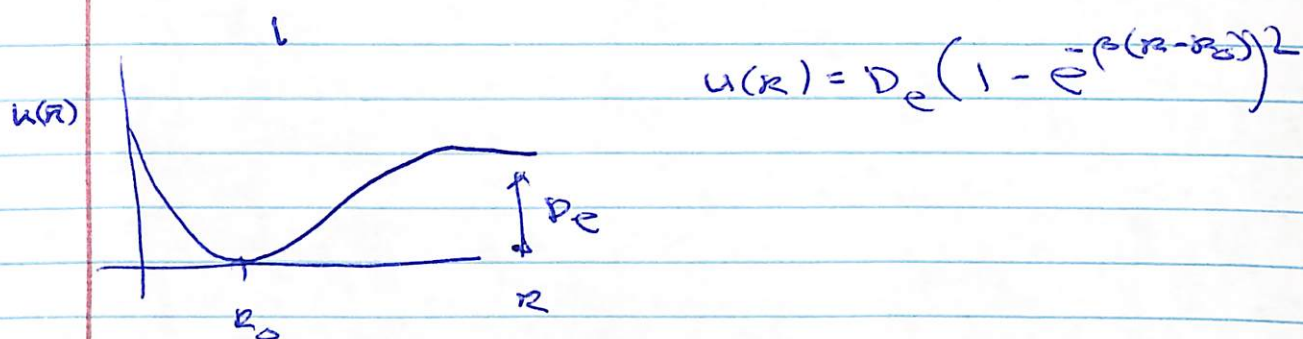
centrifugal; this is a pretty good approx.

5

## General form of the potential



In spectroscopy, often approximate the potential



vibrations are almost harmonic, but

$$E_{S,v} = h\nu_e(v + \frac{1}{2}) - h\nu_e x_e(v + \frac{1}{2})^2 + B_e J(J+1) - D_e [J(J+1)]^2 - \alpha_e(v + \frac{1}{2}) J(J+1)$$



②

where

$\omega_e$  = effective oscillator

$\omega_e x_e$  = anharmonic correction

$B_e = \frac{\hbar^2}{2I_e}$  = rotation const =  $\langle \phi_n | \frac{\hbar^2}{2mR^2} | \phi_n \rangle$

$D_e$  = centrifugal distortion

$\alpha_e$  = Coriolis, probably

### MORE DETAILS OF ELECTRONIC STRUCTURE

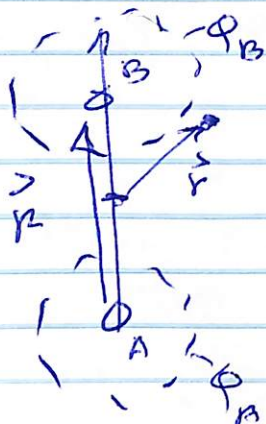
RECALL HARTREE-FOCK: each electron  $\vec{r}_i$

sets its own molecular orbital  $\psi_i(\vec{r}_i)$   
total wave function is a Slater  
determinant

$$\Psi(\vec{r}_1, \dots, \vec{r}_N) = \det \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_1(\vec{r}_2) & \dots \\ \vdots & \vdots & \ddots \\ \psi_N(\vec{r}_1) & \psi_N(\vec{r}_2) & \dots \end{vmatrix}$$

So, let's look at molecular orbitals

set  $Z_A = Z_B$  (homonuclear)  $m_A = m_B$



sensible approximation

linear combination of  
atomic orbitals (LCAO)

$\phi_A$  = hydrogenic wf centered at A

$\phi_B$  =

"

B

(7)

write orbital for a single electron as

$$\psi_{s,u} = \phi_A\left(\vec{r} - \frac{\vec{R}}{2}\right) \pm \phi_B\left(\vec{r} - \frac{\vec{R}}{2}\right)$$

$+$  = "gerade" = even



$-$  = "ungerade" = un-even  
odd



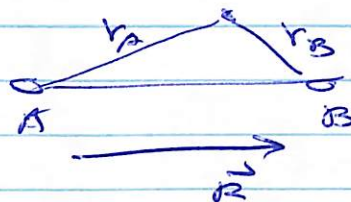
(necessarily zero in the middle)

Remark:  
amount to  
reflection  
symmetry  
thru origin

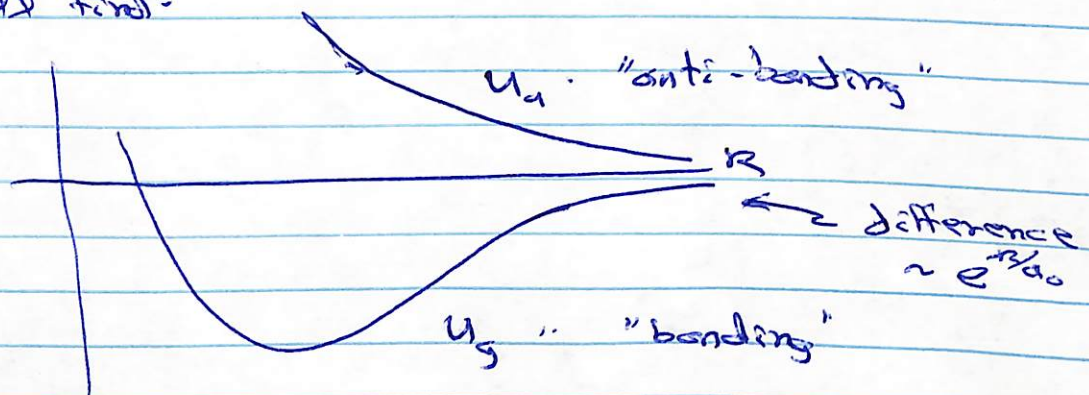
you can evaluate the B.O. energy variationally,

$$U_{s,u}(R) = \frac{\langle \psi_{s,u} | H | \psi_{s,u} \rangle}{\langle \psi_{s,u} | \psi_{s,u} \rangle}$$

$$H = \underbrace{\frac{p^2}{2m}}_{\text{electron}} + \frac{1}{R} - \frac{e^2}{r_A} - \frac{e^2}{r_B}$$



you will find:





(8)

Remark - gerade allows the electron to exist in the space between nuclei

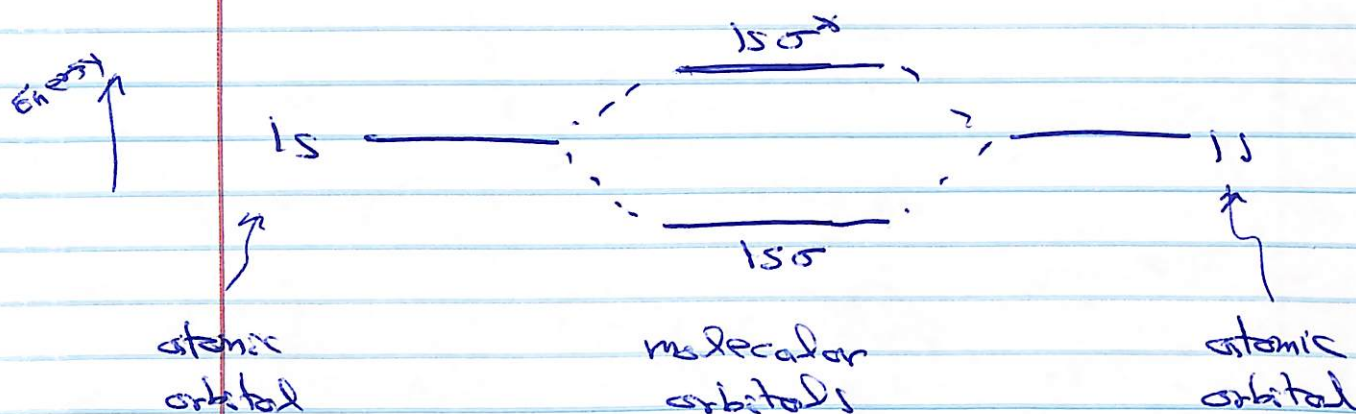
simplest possible picture:  $Z_A = Z_B = 1$



Potential energy: 
$$+\frac{e^2}{R} - \frac{e^2}{R/2} - \frac{e^2}{R/2} = -\frac{3e^2}{R} < 0$$

\* conclusion:  $H_2^+$  can be bound  
extrapolation: for larger nuclear charges it takes more electrons, but they can be bound, too!

CORRELATION DIAGRAMS - get the gist, w/o drawing the potential



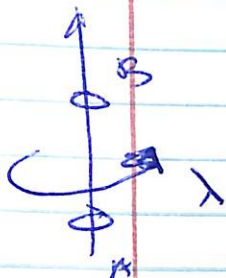
notation:  $1s$  refers to separated atom (limit)  
here, ground state of atomic H

\* : antibonding

9

NOTATION

$\lambda$ : projection of  $l$  orbital angular momentum on axis



RECALL - atoms  $l = 0, 1, 2, 3, \dots$   
 $s, p, d, f$

molecular orbitals  $\lambda = 0, 1, 2, 3, \dots$

$\sigma, \pi, \delta, \phi, \dots$

each molecular orbital can hold 2 electrons

# e's		configuration	"Bond #" $= \frac{1}{2}(\text{e's in bonding} - \text{e's in antibonding})$
1	$H_2^+$	$1s\sigma$	$\frac{1}{2}$
2	$H_2$	$(1s\sigma)^2$	1
3	$He_2^+$	$(1s\sigma)^2(1s\sigma^*)$	$\frac{1}{2}$
4	$He_2$	$(1s\sigma)^2(1s\sigma^*)^2$	0

so in simple chemistry,  $He_2$  is not bound

in real life: yes! binding energy  $26 \times 10^{-10}$  Hartrees  
 $\sim 2 \times 10^{-8}$  eV

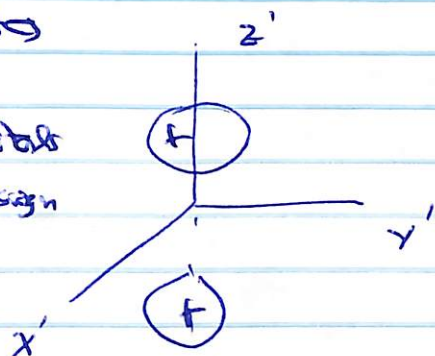
continue the diagram:



# PICTURES OF THE ORBITALS

s-states

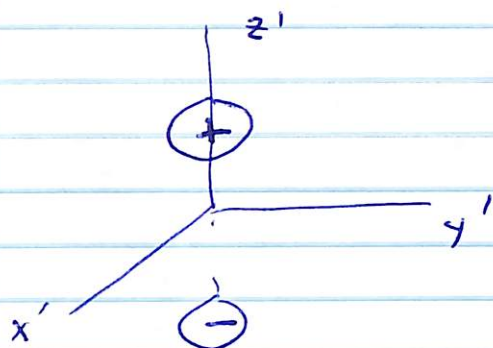
two orbitals  
w/ same sign



$\sigma_g$

here, g means  
even on reflection  
through  ~~$x'$~~  ~~the origin~~  
the origin

opposite  
sign



$\sigma_u$

odd on reflection  
through origin

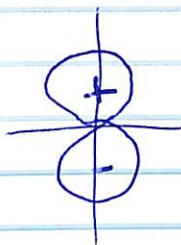
p-states

atomic orbitals have  $Y_{\lambda\mu}$   $\lambda = -1, 0, +1$

$s, \lambda = 0$

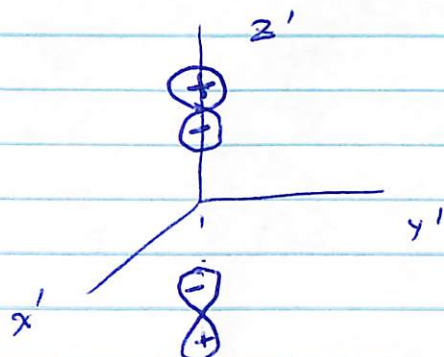
$Y_{10} \propto \cos\theta$

will  
yield  
 $\sigma$  states



molecular orbitals based on these

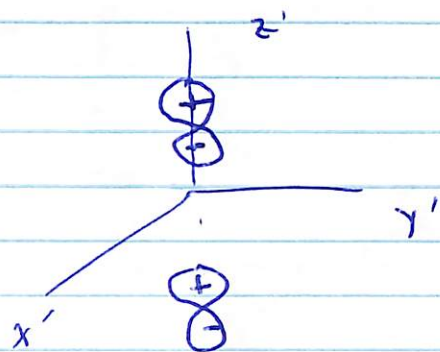
80



$\sigma_g$  : overlap  
bonding



81



$\sigma_u$  : overlap  
antibonding



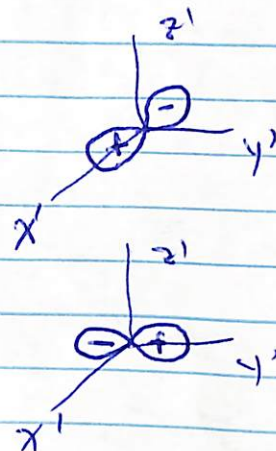
$\lambda=1$

contribute to  $\pi$ -type orbitals  $Y_{\pm 1}$   
Remark - it is convenient (and physically correct)

to consider

$$p_x \propto Y_{11} + Y_{1-1} \propto \sin\theta' \cos\phi'$$

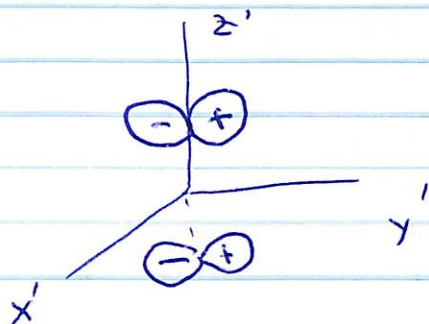
$$p_y \propto Y_{11} - Y_{1-1} \propto \sin\theta' \sin\phi'$$






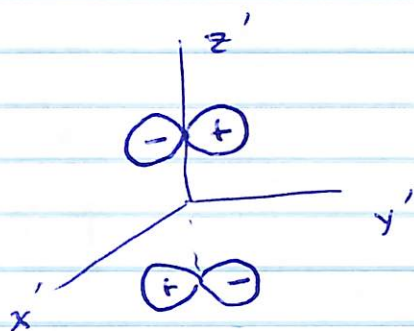
$s=2$  molecular orbitals

$e_g$ , for  $p_y$



$\pi_u$ : overlap 

bonding, but not  
as bonding as  $\sigma_g$



$\pi_g$ : overlap 

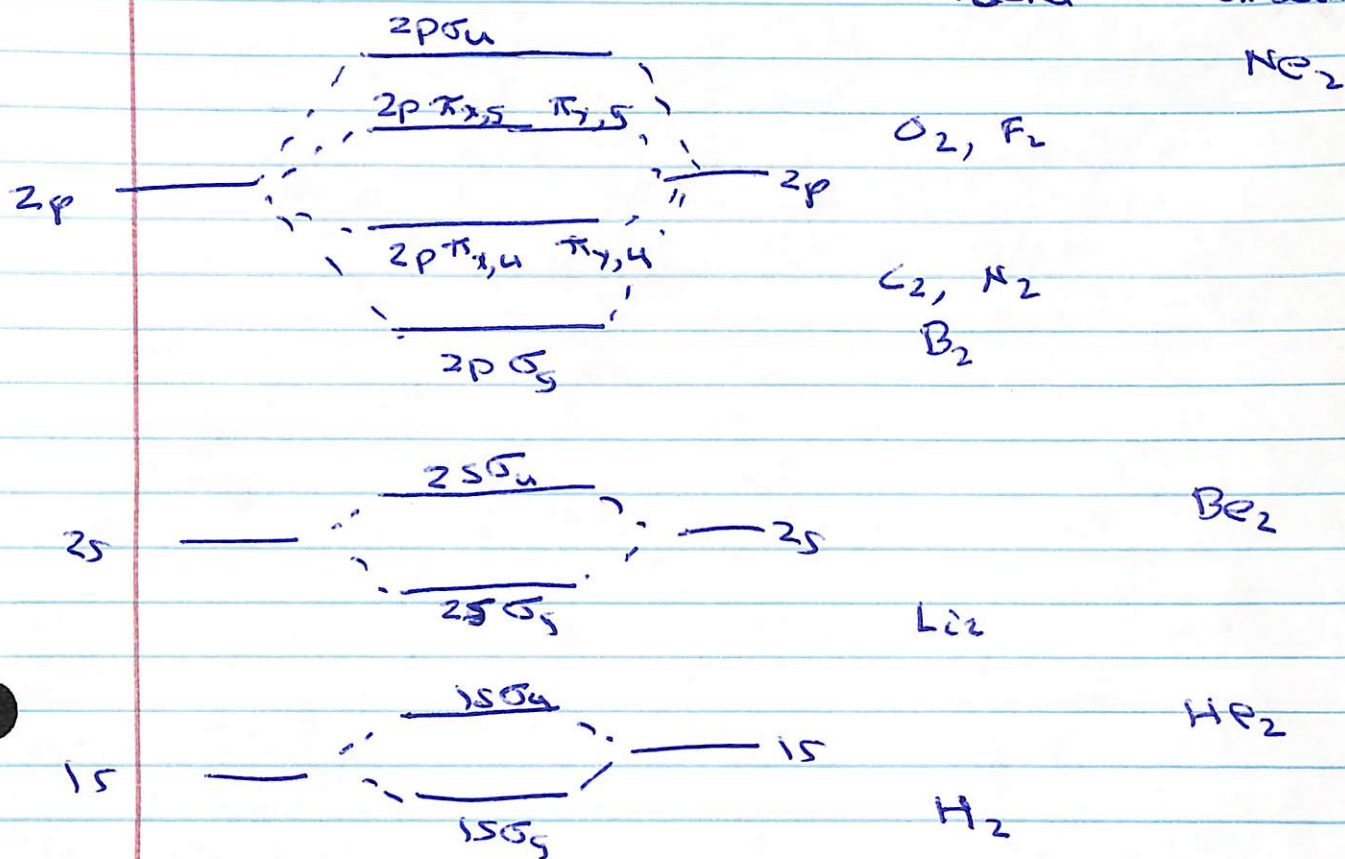
antibonding

and likewise for  $p_x$

(aside: the  $p_x$ ,  $p_y$  orbitals are not quite  
degenerate in energy)

REMARK - each molecular orbital can hold  
2 electrons (Pauli principle)

Summary - small homonuclear, neutral molecular  
 bound unbound



FINAL DETAIL - TERM SYMBOLS

$$\vec{S} = \sum_i \vec{s}_i \quad \text{total } \epsilon \text{ spin; degeneracy } 2S+1$$

$$\Lambda = \sum_i \lambda_i \quad \text{total projection of } \epsilon \text{ orbital}$$

notation  $\Lambda = 0, 1, 2, 3$

$\Sigma \quad \Pi \quad \Delta \quad \Phi, \dots$



diatomic  
 $\Psi$  - molecular wave function is denoted

$$|^{2S+1}\Lambda_{g,u}\rangle = \underbrace{\frac{1}{R} F_v(R)}_{\text{electronic}} \underbrace{\sqrt{\frac{2J+1}{8\pi^2}} D_{M_J}^J}_{\text{vibration}} \underbrace{\quad}_{\text{rotation}}$$

~~note~~  
 aside: for electron spin, write

$$|S\Sigma\rangle \quad \Sigma = \text{body projection} \\ \text{"Hund's case a"} \\ (\text{strong spin-orbit coupling})$$

$$|SM_S\rangle \quad M_S = \text{lab projection} \\ \text{"Hund's case b"}$$

ex/ several electronic states of  $H_2$   
 configuration                      term

$$\underline{(1\sigma_g)^2} \quad B \ ^1\Sigma_g$$

$$\underline{(1\sigma_g)(1\sigma_u^*)} \quad \begin{matrix} A \ ^1\Sigma_u \\ a \ ^3\Sigma_u \end{matrix}$$

$$\underline{(1\sigma_g)^2} \quad X \ ^1\Sigma_g$$

X = ground state

FURTHER READING.

S. GASKOWICZ, QUANTUM PHYSICS  
chap. 20, 21 in the first edition

B. H. BRANSDEN & C. J. JOACHAIN,  
PHYSICS OF ATOMS & MOLECULES, Chap. 10

MORE ADVANCED:

M. MIZUSHIMA, THE THEORY OF ROTATING DIATOMIC  
MOLECULES

J. BROWN AND A. CARBINGTON  
ROTATIONAL SPECTROSCOPY OF DIATOMIC MOLECULES