Teoría de Orbitales Moleculares (OM)

- Se deriva de la teoría cuántica
- CLOA (Combinación Lineal de Orbitales Atómicos)

$$\text{Átomos} \xrightarrow{\text{CLOA}} \text{Moléculas}$$

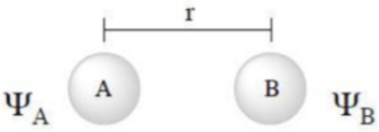
$$\Psi \qquad\qquad \Psi$$

$$s, p, d, f, \ldots \qquad\qquad \sigma, \pi, \delta, \phi, \ldots$$

$$\Downarrow$$

- Principio de exclusión de Pauli
- Regla de Hund

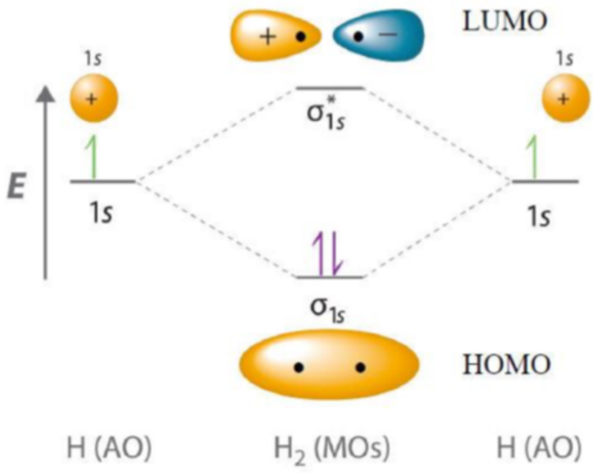
Para una molécula A — B, se combinan dos OA para obtener dos OM:



$\Psi_b = \Psi_A + \Psi_B \longrightarrow$ b = bonding (enlace)

$\Psi_a = \Psi_A - \Psi_B \longrightarrow$ a = antibonding (antienlace)

Diagrama de Orbitales Moleculares:


LUMO
+
−
1s
1s
σ^*_{1s}
E
1s
1s
σ_{1s}
HOMO
H (AO)
H_2 (MOs)
H (AO)

(Orbital molecular más bajo desocupado)

(Orbital molecular más alto ocupado)

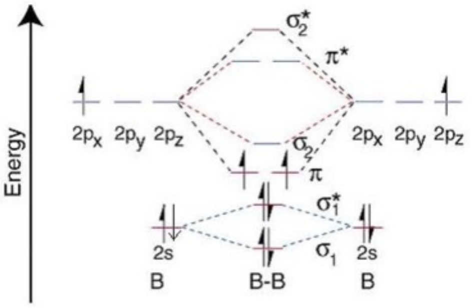
Orden de Enlace (OE):

$$OE = \frac{1}{2}(N_b - N_a)$$

N_b = número de electrones de enlace

N_a = número de electrones de antienlace

OE (H_2) = ½(2 – 0) = 1 → H — H


Energy
σ₂*
π*
2px 2py 2pz
2px 2py 2pz
σ₂
π
σ₁*
σ₁
2s
2s
B
B-B
B

Un diagrama de OM **no correlacionado** se construye a partir de los OA ns, np cuyos niveles de energía no interfieren entre ellos. Los niveles energéticos de los OM resultantes siguen la secuencia:

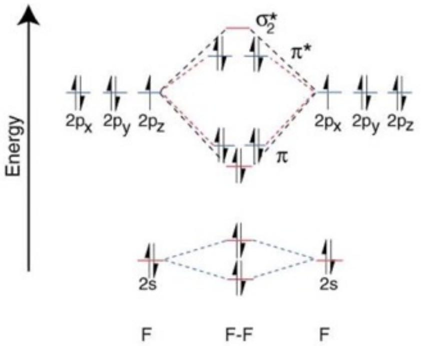
$\sigma_s < \sigma_s^* < \sigma_z\ ,\ (\pi_x, \pi_y) < (\pi_x^*, \pi_y^*) < \sigma_z^*$

Un diagrama de OM **correlacionado** se construye a partir de los OA ns,np cuyos niveles de energía están muy próximos entre ellos. Los niveles energéticos de los OM resultantes siguen la secuencia:

$\sigma_s < \sigma_s^* < (\pi_x, \pi_y) < \sigma_z < (\pi_x^*, \pi_y^*) < \sigma_z^*$

Las moléculas diatómicas homonucleares del segundo y tercer período tienen un diagrama de OM correlacionado, con excepción del O_2, F_2, Ne_2.

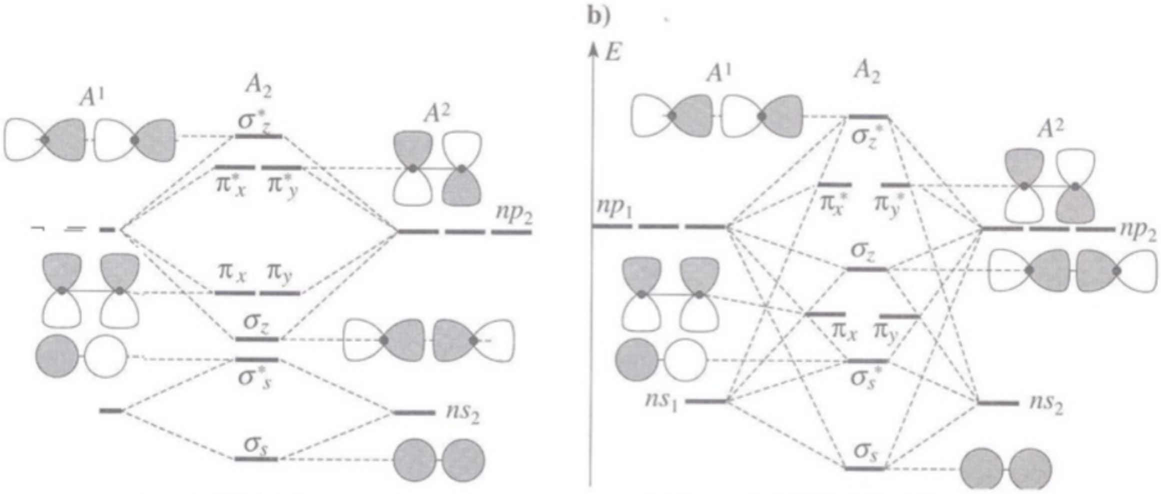
El siguiente diagrama para el F_2 es representativo de las moléculas diatómicas homonucleares con Z>7.


Energy
σ₂*
π*
2px 2py 2pz
2px 2py 2pz
π
2s
2s
F
F-F
F

A continuación se enlistan los OM de las moléculas diatómicas homonucleares del 2do. Período:

H_2	σ_{1s}^{2}
He_2	$\sigma_{1s}^{2}\sigma_{1s}^{*\,2}$
Li_2	σ_{2s}^{2}
Be_2	$\sigma_{2s}^{2}\sigma_{2s}^{*\,2}$
B_2	$\sigma_{2s}^{2}\sigma_{2s}^{*\,2}\ \pi_{2p}^{2}$
C_2	$\sigma_{2s}^{2}\sigma_{2s}^{*\,2}\ \pi_{2p}^{4}$
N_2	$\sigma_{2s}^{2}\sigma_{2s}^{*\,2}\ \pi_{2p}^{4}\ \sigma_{z}^{2}$
O_2	$\sigma_{2s}^{2}\sigma_{2s}^{*\,2}\ \ \sigma_{z}^{2}\ \ \pi_{2p}^{4}\ \pi_{2p}^{*2}$
F_2	$\sigma_{2s}^{2}\sigma_{2s}^{*\,2}\ \ \sigma_{z}^{2}\ \ \pi_{2p}^{4}\ \pi_{2p}^{*4}$
Ne_2	$\sigma_{2s}^{2}\sigma_{2s}^{*\,2}\ \ \sigma_{z}^{2}\ \ \pi_{2p}^{4}\ \pi_{2p}^{*4}\sigma_{z}^{*2}$

$$\sigma_s < \sigma_s^* < (\pi_x, \pi_y) < \sigma_z < (\pi_x^*, \pi_y^*) < \sigma_z^* .$$



a) *Non corrélé.* b) *Corrélé.*

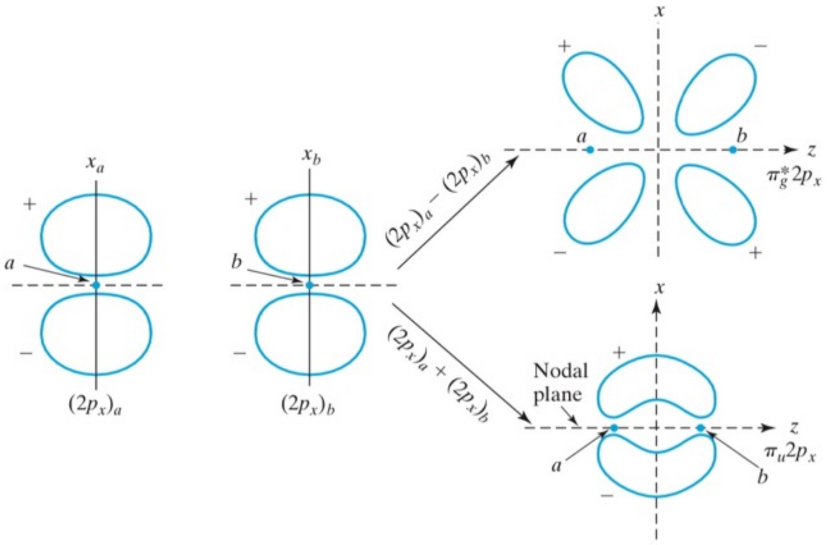


FIGURE 13.15 Formation of the $\pi_u 2p_x$ and $\pi_g^* 2p_x$ MOs. Since $\phi = 0$ in the *xz* plane, the cross sections of these MOs in the *xz* plane are the same as for the corresponding $\pi_u 2p_{+1}$ and $\pi_g^* 2p_{-1}$ MOs. However, the $\pi 2p_x$ MOs are not symmetrical about the *z* axis. Rather, they consist of blobs of probability density above and below the nodal *yz* plane.

Just as the $2p_x$ and $2p_y$ AOs are linear combinations of the $2p_{+1}$ and $2p_{-1}$ AOs [Eqs. (6.118) and (6.120)], the $\pi_u 2p_x$ and $\pi_u 2p_y$ MOs are linear combinations of the $\pi_u 2p_{+1}$ and $\pi_u 2p_{-1}$ MOs. We can use any linear combination of the eigenfunctions of a degenerate energy level and still have an energy eigenfunction. Just as the $2p_{+1}$ and $2p_{-1}$ AOs are eigenfunctions of $\hat{L}_z$ and the $2p_x$ and $2p_y$ AOs are not, the $\pi_u 2p_{+1}$ and $\pi_u 2p_{-1}$ MOs are eigenfunctions of $\hat{L}_z$ and the $\pi_u 2p_x$ and $\pi_u 2p_y$ MOs are not. For the H_2^+ $\pi_u 2p$ energy level, we can use the pair of real MOs (13.80) and (13.82), or the pair of complex MOs (13.73) and (13.75), or any two linearly independent linear combinations of these functions.

We have shown the correlation of the H_2^+ MOs with the separated-atoms AOs. We can also show how they correlate with the united-atom AOs. As R goes to zero, the $\sigma_u^* 1s$ MO (Fig. 13.9) increasingly resembles the $2p_z$ AO, with which it correlates. Similarly, the $\pi_u 2p$ MOs correlate with p united-atom states, while the $\pi_g^* 2p$ MOs correlate with d united-atom states.

An online simulation of H_2^+ MOs is at www.falstad.com/qmmo; you can vary the internuclear distance.

13.7 MO Configurations of Homonuclear Diatomic Molecules

We now use the H_2^+ MOs developed in the last section to discuss many-electron homonuclear diatomic molecules. (**Homonuclear** means the two nuclei are the same; **heteronuclear** means they are different.) If we ignore the interelectronic repulsions, the zeroth-order wave function is a Slater determinant of H_2^+-like one-electron spin-orbitals. We approximate the spatial part of the H_2^+ spin-orbitals by the LCAO-MOs of the last section. Treatments that go beyond this crude first approximation will be discussed later.

The sizes and energies of the MOs vary with varying internuclear distance for each molecule and vary as we go from one molecule to another. Thus we saw how the orbital exponent k in the H_2^+ trial function (13.54) varied with R. As we go to molecules with higher nuclear charge, the parameter k for the $\sigma_g 1s$ MO will increase, giving a more compact MO. We want to consider the order of the MO energies. Because of the variation of these energies with R and variations from molecule to molecule, numerous crossings occur, just

TABLE 13.1 **Molecular-Orbital Nomenclature for Homonuclear Diatomic Molecules**

Separated-Atoms Description	United-Atom Description	Numbering by Symmetry
$\sigma_g 1s$	$1s\sigma_g$	$1\sigma_g$
$\sigma_u^* 1s$	$2p\sigma_u^*$	$1\sigma_u$
$\sigma_g 2s$	$2s\sigma_g$	$2\sigma_g$
$\sigma_u^* 2s$	$3p\sigma_u^*$	$2\sigma_u$
$\pi_u 2p$	$2p\pi_u$	$1\pi_u$
$\sigma_g 2p$	$3s\sigma_g$	$3\sigma_g$
$\pi_g^* 2p$	$3d\pi_g^*$	$1\pi_g$
$\sigma_u^* 2p$	$4p\sigma_u^*$	$3\sigma_u$

as for atomic-orbital energies (Fig. 11.2). Hence we cannot give a definitive order. However, the following is the order in which the MOs fill as we go across the periodic table:

$$\sigma_g 1s < \sigma_u^* 1s < \sigma_g 2s < \sigma_u^* 2s < \pi_u 2p_x = \pi_u 2p_y < \sigma_g 2p < \pi_g^* 2p_x = \pi_g^* 2p_y < \sigma_u^* 2p$$

Each bonding orbital fills before the corresponding antibonding orbital. The $\pi_u 2p$ orbitals are close in energy to the $\sigma_g 2p$ orbital, and it was formerly believed that the $\sigma_g 2p$ MO filled first.

Besides the separated-atoms designation, there are other ways of referring to these MOs; see Table 13.1. The second column of this table gives the united-atom designations. The nomenclature of the third column uses $1\sigma_g$ for the lowest σ_g MO, $2\sigma_g$ for the second lowest σ_g MO, and so on.

Figure 13.16 shows how these MOs correlate with the separated-atoms and united-atom AOs. Because of the variation of MO energies from molecule to molecule, this

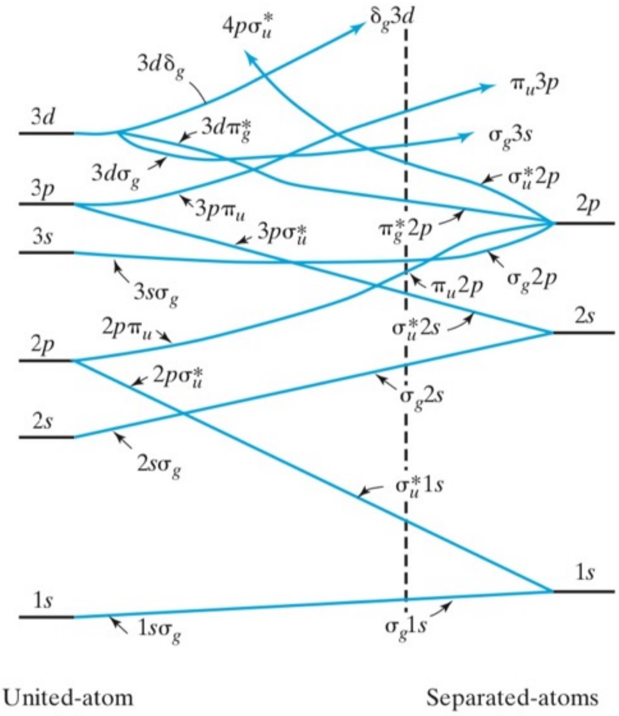

$4p\sigma_u^*$
$\delta_g 3d$
$3d\delta_g$
$\pi_u 3p$
$3d$
$3d\pi_g^*$
$\sigma_g 3s$
$3d\sigma_g$
$\sigma_u^* 2p$
$3p$
$3p\pi_u$
$2p$
$3p\sigma_u^*$
$\pi_g^* 2p$
$3s$
$3s\sigma_g$
$\pi_u 2p$
$\sigma_g 2p$
$2p\pi_u$
$\sigma_u^* 2s$
$2s$
$2p$
$2p\sigma_u^*$
$\sigma_g 2s$
$2s$
$2s\sigma_g$
$\sigma_u^* 1s$
$1s$
$1s$
$1s\sigma_g$
$\sigma_g 1s$
United-atom
Separated-atoms

FIGURE 13.16 Correlation diagram for homonuclear diatomic MOs. (This diagram does not hold for H_2^+.) The dashed vertical line corresponds to the order in which the MOs fill.

holds for potential-energy curves $U(R)$ for different electronic states of a many-electron diatomic molecule.] The proof of the noncrossing rule is a bit subtle; see C. A. Mead, *J. Chem. Phys.*, **70**, 2276 (1979) for a thorough discussion.

Just as we discussed atoms by filling in the AOs, giving rise to atomic configurations such as $1s^2 2s^2$, we shall discuss homonuclear diatomic molecules by filling in the MOs, giving rise to molecular electronic configurations such as $(\sigma_g 1s)^2(\sigma_u^* 1s)^2$. (Recall that with a single atomic configuration there is associated a hierarchy of terms, levels, and states; the same is true for a molecular configuration; see Section 13.8.)

Figure 13.17 shows the homonuclear diatomic MOs formed from the $1s, 2s$, and $2p$ AOs.

For H_2^+ we have the ground-state configuration $\sigma_g 1s$, which gives a one-electron bond. For excited states the electron is in one of the higher MOs.

For H_2 we put the two electrons in the $\sigma_g 1s$ MO with opposite spins, giving the ground-state configuration $(\sigma_g 1s)^2$. The two bonding electrons give a single bond. The ground-state dissociation energy D_e is 4.75 eV.

Now consider He_2. Two electrons go in the $\sigma_g 1s$ MO, thereby filling it. The other two go in the next MO, $\sigma_u^* 1s$. The ground-state configuration is $(\sigma_g 1s)^2(\sigma_u^* 1s)^2$. With

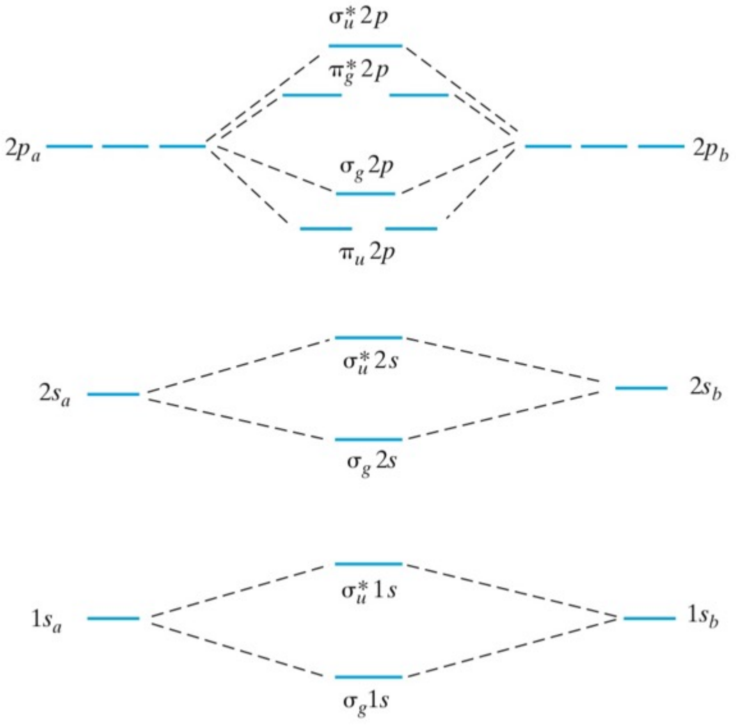


FIGURE 13.17 Homonuclear diatomic MOs formed from 1*s*, 2*s*, and 2*p* AOs.

no chemical bond.

We can go on to describe homonuclear diatomic molecules formed from atoms of the next period. Thus the lowest electron configuration of Na_2 is $KKLL(\sigma_g 3s)^2$. However, there are some differences as compared with the corresponding molecules of the preceding period. For Al_2, the ground term is the triplet term of the $\ldots(\sigma_g 3p)(\pi_u 3p)$ configuration, which lies a mere 0.02 eV below the triplet term of the $\ldots(\pi_u 3p)^2$ configuration [C. W. Bauschlicher et al., *J. Chem. Phys.*, **86**, 7007 (1987)]. For Si_2, the ground term is the triplet term of the $\ldots(\sigma_g 3p)^2(\pi_u 3p)^2$ configuration, which lies 0.08 eV below the triplet term of the $\ldots(\sigma_g 3p)(\pi_u 3p)^3$ configuration [T. N. Kitsopolous et al., *J. Chem. Phys.*, **95**, 1441 (1991)].

Table 13.2 lists D_e, R_e, and $\widetilde{\nu}_e \equiv \nu_e/c$ for the ground electronic states of some homonuclear diatomic molecules, where ν_e is the harmonic vibrational frequency (13.27). (In

TABLE 13.2 **Properties of Homonuclear Diatomic Molecules in Their Ground Electronic States**

Molecule	Ground Term	Bond Order	D_e/eV	R_e/Å	$\widetilde{\nu}_e$/cm^{-1}
H_2^+	$^2\Sigma_g^+$	$\frac{1}{2}$	2.79	1.06	2322
H_2	$^1\Sigma_g^+$	1	4.75	0.741	4403
He_2^+	$^2\Sigma_u^+$	$\frac{1}{2}$	2.5	1.08	1698
He_2	$^1\Sigma_g^+$	0	0.0009	2.97	33
Li_2	$^1\Sigma_g^+$	1	1.07	2.67	351
Be_2	$^1\Sigma_g^+$	0	0.115	2.45	276
B_2	$^3\Sigma_g^-$	1	3.1	1.59	1051
C_2	$^1\Sigma_g^+$	2	6.3	1.24	1855
N_2^+	$^2\Sigma_g^+$	$2\frac{1}{2}$	8.85	1.12	2207
N_2	$^1\Sigma_g^+$	3	9.91	1.10	2358
O_2^+	$^2\Pi_g$	$2\frac{1}{2}$	6.78	1.12	1905
O_2	$^3\Sigma_g^-$	2	5.21	1.21	1580
F_2	$^1\Sigma_g^+$	1	1.66	1.41	917
Ne_2	$^1\Sigma_g^+$	0	0.0036	3.1	14

Fluoruro de hidrógeno

Los 10 electrones nos obligan a definir al menos 5 orbitales
H: 1s
F : 1s,2s,2p

Si el eje Oz pasa por los dúcleos, no consideramos los orbitales $2p_x$ y $2p_y$ del F.
Entonces los orbitales a combinar son 1s,2s,$2p_z$ con el 1s del H para dar orbitales σ.

E_{1s} (H) = - 0.5 u.a.

E_{1s} (F) = - 37.8 u.a.

Demasiado alejados, los dos electrones 1s del F casi no sufren perturbación (son de la capa interna, se desprecian en el enlace).

E_{ss} (F) = - 1.44 u.a., E_{2pz} (F) = - 0.68 u.a.

Consideramos entonces interacción 1s(H) y $2p_z$(F):

$$\Psi = c_a \varphi_z + c_b \varphi_h$$

con $|c_b/c_a| < 1$

Se obtiene $S \approx 0.300$ para R = 0.917 Å

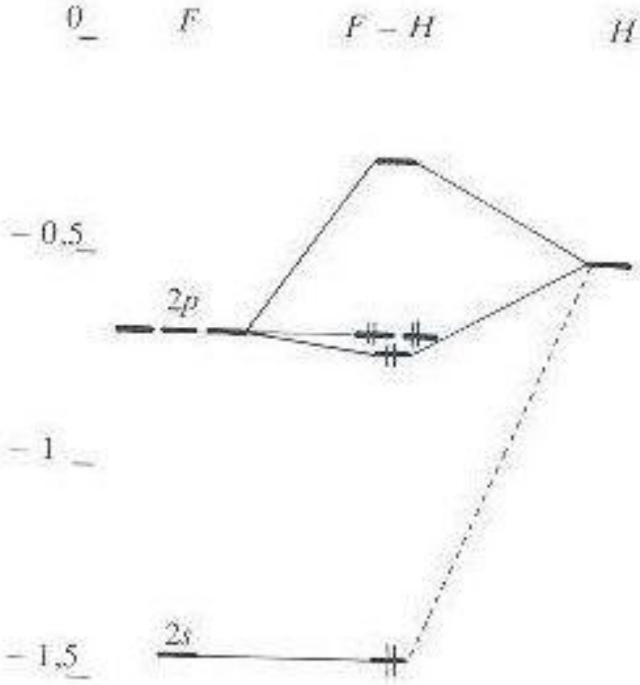
$$H_{ab} = 1.75\left(\frac{e_a{}^0 + e_b{}^0}{2}\right)S$$

lo que da H_{ab}=-0.310 y resolviendo la ecuación secular obtenemos

$$e_- = -0.720u.a., e_+ = -0.372u.a.$$

El càlculo de los coeficientes da:

Ca = 0.8338, Cb = 0.3558


0
F
F – H
H
– 0,5
2p
– 1
2s
– 1,5

POBLACIÓN ELECTRÓNICA – CARGAS ATÓMICAS

El F-H muestra ionicidad parcial.

$\Psi^2 = c_a^2 \varphi_a^2 + c_b^2 \varphi_b^2 + 2c_ac_b \varphi_a \varphi_b$

Aproximación de Mulliken:

$$\varphi_a\varphi_b \approx \frac{(\varphi_a^2\varphi_b^2)}{2} S_{ab}$$

Tendremos:

$$\Psi^2 = (c_a^2 + c_ac_bS_{ab})\varphi_a^2 + (c_b^2 + c_ac_bS_{ab})\varphi_b^2$$

Población electrónica del orbital φ_a

Se define la carga neta del átomo A (2 electrones) como:

$$Q_A = 1 - 2(c_a^2 + c_ac_bS_{ab})$$

Y tendremos para el HF:

$$Q_F = -0.579 \quad u.a.$$

$$Q_H = +0.579 \quad u.a.$$

Lo que corresponde a un momento dipolar de 0.948 u.a. = 2.50 D, muy abajo del valor experimental de 1.82 D.

Ejercicio. Integral de recubrimiento

1. La función de onda que describe al OM enlazante de la molécula de H_2 es:

$$\sigma_s = 0.555(1s_1 + 1s_2)$$

Calcular el valor de S entre los orbitales $1s_1$ y $1s_2$

Por normalización:

$$\iiint \sigma_s{}^2 d\tau = N_+{}^2(1+1+2S) = 1$$

Y por tanto:

$$S = 0.623$$

2. Escribir la expresión analítica de la función antienlazante σ_s^*

$$\sigma_s = N\_(1s_1 - 1s_2)$$

Por normalización se obtiene: N_-=1.152 y por tanto

$$\sigma_s = 1.152(1s_1 - 1s_2)$$

3. La energía de disociación de la molécula es D_{HH}= 431 kj/mol. Calcular en eV el valor de la integral de intercambio β_{12} de los electrones en ésta molécula, la energía del nivel $1s_H$ = -13.6 eV.

Tenemos que: $D_{HH} = 2\,E(H) - E(H_2)$
$= 2E_H - 2E_1 = 2\,(E_H - E_1)$

de donde

$E_1 = E_H - D_{HH}/2 = -13.6 - 431/2(96.5) = -\,15.8$ eV

De la ecuación de Shrödinger: $H\sigma_s = E_1\sigma_s$

$$\int \sigma H \sigma d\tau = \int E_1 \sigma^2 d\tau = E_1$$

$$\int N_+(1s_1 + 1s_2) H N_+(1s_1 + 1s_2) d\tau = E_1$$

$$E_1 = N_+{}^2(2E_H + 2\beta_{12})$$

de donde

$$\beta_{12} = -12.1 \quad eV$$

Y la energía del nivel antienlazante es:

$$E_2 = N_-{}^2(2E_H - 2\beta_{12}) = -4.0\,eV$$

MOMENTO DIPOLAR DE LiH

1. Establecer el diagrama de orbitales moleculares del LiH. Dar cualitativamente la expresión general de los OM en función de los OA tipo Slater. Se considera a la molécula sobre el eje Z, el átomo de Li en z = 0 y el de H en z = R.
2. Un cálculo semiempírico del tipo CNDO ha dado el siguiente resultado para el orbital molecular enlazante 2σ que contiene dos electrones

$$\psi_{2\sigma} = 0.4256\varphi_{2sLi} + 0.4278\varphi_{2pzLi} + 0.7974\varphi_{1sH}$$

   Expresar el momento dipolar en función de los coeficientes de los OA en el OM enlazante que contiene 2 electrones y de la integral $< \varphi_{2sLi}|z|\varphi_{2pzLi} >$

3. Calcular la integral $< \varphi_{2sLi}|z|\varphi_{2pzLi} >$ y calcular el momento dipolar de LiH. Comparar con el valor experimental de 5.9 D.

   Los orbitales de Slater normalizados del átomo de Li son:

$$\varphi_{1sLi} = 2.49e^{-2.69r}$$
$$\varphi_{2sLi} = 0.11re^{-0.65r}$$
$$\varphi_{2pzLi} = 0.19rcos\theta e^{-0.65r}$$

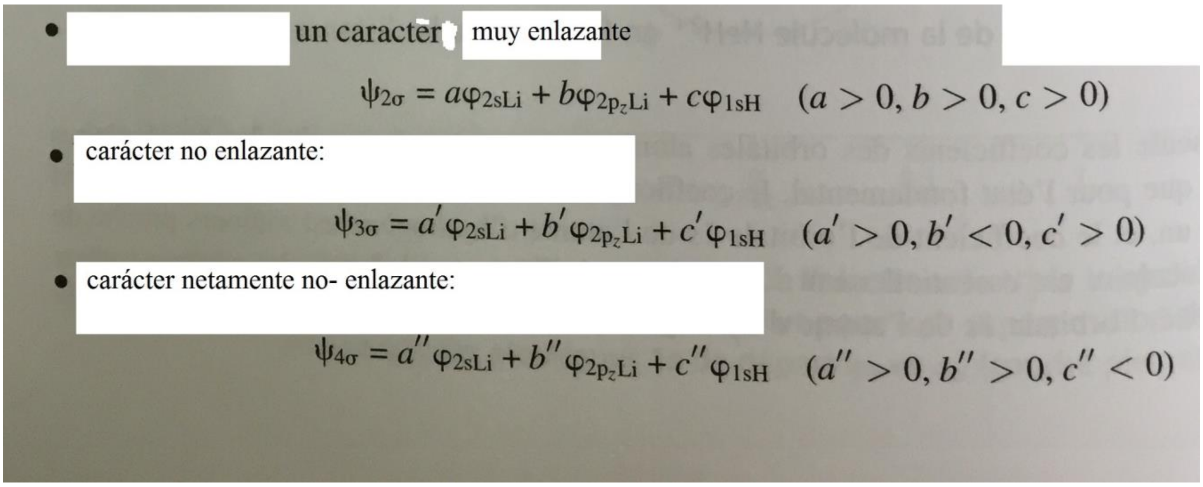
Li: $1s^2 2s^1$ consideramos los OA 1s,2s y 2p para construír los OM

Construímos pues un diagrama de OM con 6 OA

El orbital φ_{1s}(Li) es de energía mucho más baja que el φ_{1s}(H), no se combinan

El orbital φ_{1s}(Li) corresponde a un OM no enlazante de simetría σ: $\psi_{1\sigma} = \varphi_{1s}$(Li)

Los orbitales φ_{2s} (Li), φ_{2pz} (Li) y φ_{is} (H) tienen la misma simetría σ y se pueden combinar en OM σ:



- un caracter muy enlazante

$$\psi_{2\sigma} = a\varphi_{2s\text{Li}} + b\varphi_{2p_z\text{Li}} + c\varphi_{1s\text{H}} \quad (a > 0, b > 0, c > 0)$$

- carácter no enlazante:

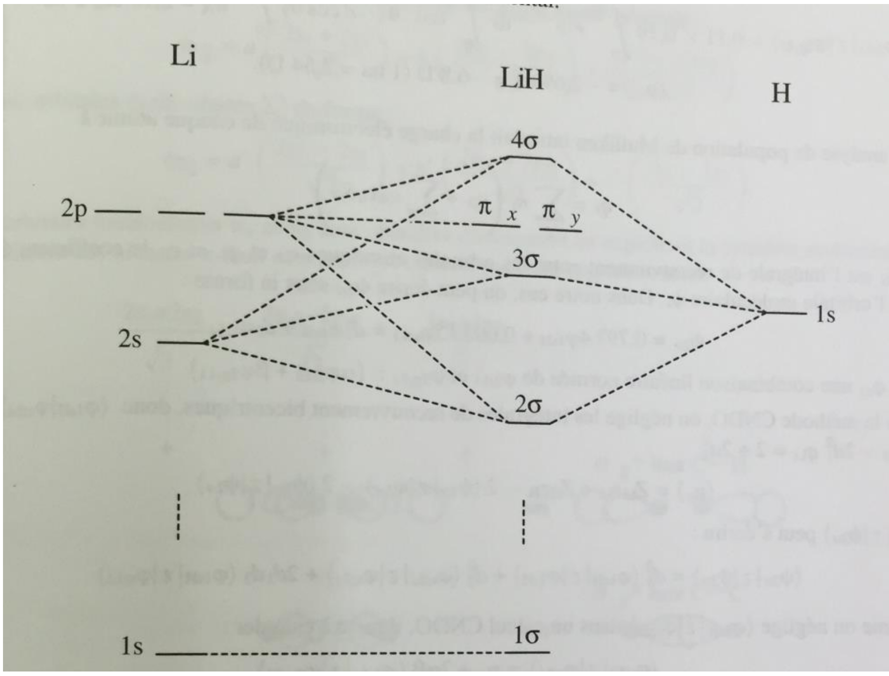
$$\psi_{3\sigma} = a'\varphi_{2s\text{Li}} + b'\varphi_{2p_z\text{Li}} + c'\varphi_{1s\text{H}} \quad (a' > 0, b' < 0, c' > 0)$$

- carácter netamente no- enlazante:

$$\psi_{4\sigma} = a''\varphi_{2s\text{Li}} + b''\varphi_{2p_z\text{Li}} + c''\varphi_{1s\text{H}} \quad (a'' > 0, b'' > 0, c'' < 0)$$

Los orbitales φ_{2px} (Li) y φ_{2py} (Li) constituyen un nivel π no enlazante

$\psi_{\pi x} = \varphi_{2px}$ (Li), $\psi_{\pi} = \varphi_{2py}$ (Li)



2) Momento dipolar: $\langle \overrightarrow{\mu} \rangle = \sum_k Z_k \overrightarrow{R}_k - \sum_i n_i \langle \psi_i | \overrightarrow{r} | \psi_i \rangle$

Donde R_k y Z_k son el vector de posición y la carga del núcleo k, ψ_i es un OM que contiene n_i electrones y r el vector de posición de un electrón.

$\langle \mu_x \rangle = \langle \mu_y \rangle = 0$ por simetría

El átomo de Li en $Z_{Li} = 0$, y $Z_H = R = 3.02$ u.a., entonces:

$$\langle \mu_z \rangle = z_H - 2 \langle \psi_{1\sigma} | z | \psi_{1\sigma} \rangle - 2 \langle \psi_{2\sigma} | z | \psi_{2\sigma} \rangle$$

Como $\psi_{1\sigma}$ es una función de simetría esférica localizada en el átomo de Li:

$$\langle \psi_{1\sigma} | z | \psi_{1\sigma} \rangle = z_{Li} = 0$$

para el orbital $\psi_{2\sigma}$, tendremos:

$$\langle \psi_{2\sigma} | z | \psi_{2\sigma} \rangle = c^2 z_H + 2ab \langle \varphi_{2sLi} | z | (\varphi_{2p_zLi} \rangle$$

Entonces:

$$\langle \mu_z \rangle = z_H \left(1 - 2c^2\right) - 4ab \langle \varphi_{2sLi} | z | \varphi_{2p_zLi} \rangle$$

3) $\langle \varphi_{2sLi} | z | \varphi_{2p_zLi} \rangle = 0{,}11 \times 0{,}19 \int_0^{\infty} r^5 e^{-1{,}3r}\, dr \int_0^{\pi} \cos^2\theta \,(-d \cos\theta) \int_0^{2\pi} d\chi = 2{,}18$ ua,

$\langle \mu_z \rangle = -2{,}69$ ua $= -6{,}8$ D (1 ua = 2,54 D).

que está bastante de acuerdo con el resultado experimental