

Ira N. Levine, Quantum Chemistry

MOLECULAR ORBITALS FOR H_2^+ EXCITED STATES

we construct approximate functions for further excited states so as to build up a supply of H_2^+ -like molecular orbitals.

We shall then use these MOs to discuss many-electron diatomic molecules qualitatively, (just as hydrogenlike AOs).

we can use the linear-variation-function method:

we add in more AOs to the previous linear combination.

for the six lowest H_2^+ σ states,

$$\phi = c_1 1s_a + c_2 2s_a + c_3 (2p_0)_a + c_4 1s_b + c_5 2s_b + c_6 (2p_0)_b$$

three lowest $m = 0$ hydrogenlike functions

For the symmetry of the homonuclear diatomic molecule

$$\phi = [c_1 1s_a + c_2 2s_a + c_3 (2p_0)_a] \pm [c_4 1s_b + c_5 2s_b + c_6 (2p_0)_b]$$

$+$: even (g) states

$-$: odd (u) states

The relative magnitudes of the coefficients:

For the two states that dissociate into a 1s hydrogen atom:

$$c_1 \gg c_2 \text{ and } c_3$$

(c_2 and c_3 vanish in the limit of R going to infinity)

$$\phi = [c_1 1s_a + c_2 2s_a + c_3 (2p_0)_a] \pm [c_1 1s_b + c_2 2s_b + c_3 (2p_0)_b]$$

As a first approximation,

$$\phi = c_1 (1s_a \pm 1s_b) \quad \text{LCAO functions}$$

From the viewpoint of perturbation theory:

if we take the separated atoms as the unperturbed problem, the above functions are the correct zeroth-order wave functions.

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for the two states that dissociate to a 2s hydrogen atom

$$c_2 \gg c_1 \text{ and } c_3$$

(c_1 and c_3 vanish in the limit of R going to infinity)

$$\phi = [c_1 1s_a + c_2 2s_a + c_3 (2p_0)_a] \pm [c_1 1s_b + c_2 2s_b + c_3 (2p_0)_b]$$

As a first approximation,

$$\phi = c_2 (2s_a \pm 2s_b) \quad \text{LCAO functions}$$

To find rigorous upper bounds to the energies of these two H_2^+ states, we must use the upper trial function and solve the appropriate secular equation

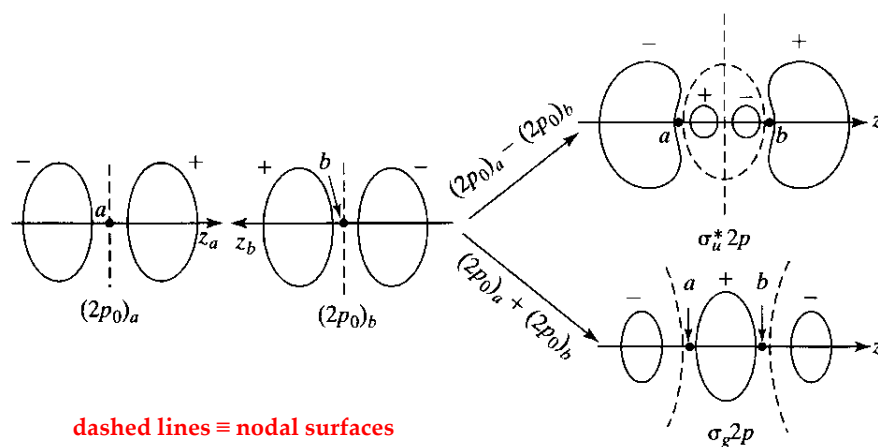
contour diagrams

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$$(2p_0)_a \pm (2p_0)_b = (2p_z)_a \pm (2p_z)_b$$

σ MOs even though they correlate with 2p separated AOs, since they have $m = 0$.



For the hydrogen atom, the 2s and 2p AOs are degenerate, and so ...

In the $R \rightarrow \infty$ limit, H_2^+ consists of an H atom perturbed by the essentially uniform electric field of a far-distant proton.

for the $n = 2$ levels

$$2^{-1/2}(2s + 2p_0), 2^{-1/2}(2s - 2p_0), 2p_1, \text{ and } 2p_{-1}.$$

the correct zeroth-order functions

For molecules that dissociate into many-electron atoms, the separated-atoms 2s and 2p AOs are not degenerate but do lie close together in energy. Hence, ...

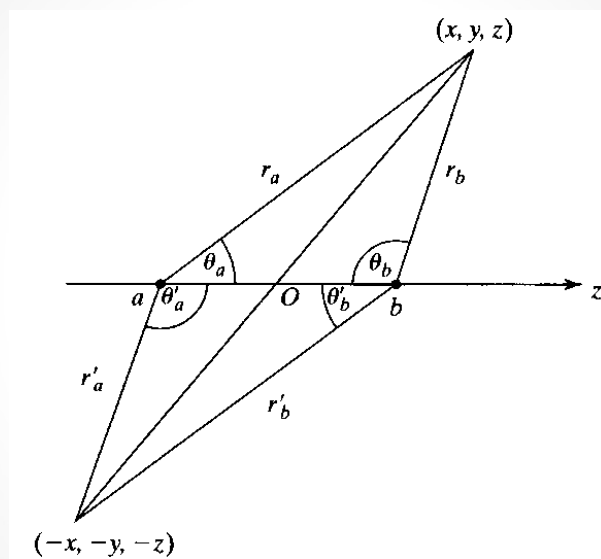
For the other two 2p atomic orbitals, we can use either the $2p_{+1}$ and $2p_{-1}$ complex functions or the $2p_x$ and $2p_y$ real functions.

$$(2p_{+1})_a + (2p_{+1})_b$$

$$(2p_{+1})_a - (2p_{+1})_b$$

$$(2p_{-1})_a + (2p_{-1})_b$$

$$(2p_{-1})_a - (2p_{-1})_b$$



inversion of the electron's coordinates in H_2^+

$$(2p_{+1})_a + (2p_{+1})_b$$

↓ $\phi_a = \phi_b = \phi$

$$(2p_{+1})_a + (2p_{+1})_b = \frac{1}{8}\pi^{-1/2}(r_a e^{-r_a/2} \sin \theta_a + r_b e^{-r_b/2} \sin \theta_b) e^{i\phi}$$

$\lambda = |m| = 1 \longrightarrow$ a π orbital

inversion of the electron's coordinates

$$r_a \rightarrow r_b, \quad r_b \rightarrow r_a, \quad \phi \rightarrow \phi + \pi$$

$$e^{i(\phi + \pi)} = (\cos \pi + i \sin \pi) e^{i\phi} = -e^{i\phi}.$$

$$\theta_a \rightarrow \theta_b, \quad \theta_b \rightarrow \theta_a$$

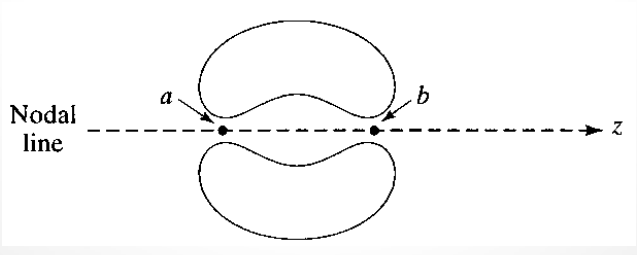
a u orbital.

Reflection in the plane perpendicular to the axis and midway between the nuclei:

$$r_a \rightarrow r_b, \quad r_b \rightarrow r_a, \quad \phi \rightarrow \phi, \quad \theta_a \rightarrow \theta_b, \quad \theta_b \rightarrow \theta_a$$

unchanged, \longrightarrow an unstarred (bonding) orbital.

$$(2p_{+1})_a + (2p_{+1})_b \equiv \pi_u 2p_{+1}$$



$|e^{i\phi}| = 1$

$$(2p_{-1})_a + (2p_{-1})_b \equiv \pi_u 2p_{-1}$$

$$\partial^2 e^{i\phi} / \partial \phi^2 = \partial^2 e^{-i\phi} / \partial \phi^2$$

the $\lambda = 1$ energy levels are doubly degenerate,
corresponding to $m = \pm 1$

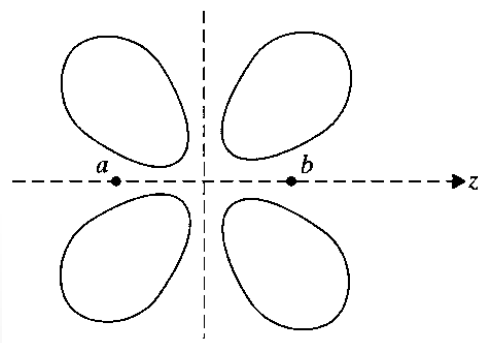
$$|e^{i\phi}| = |e^{-i\phi}| \longrightarrow \pi_u 2p_{+1} \text{ and } \pi_u 2p_{-1} \text{ MOs}$$

have the same shapes,

$$(2p_{+1})_a - (2p_{+1})_b \longrightarrow \pi_g^* 2p_{+1}$$

$$(2p_{-1})_a - (2p_{-1})_b \longrightarrow \pi_g^* 2p_{-1}$$

do not give charge buildup between the nuclei



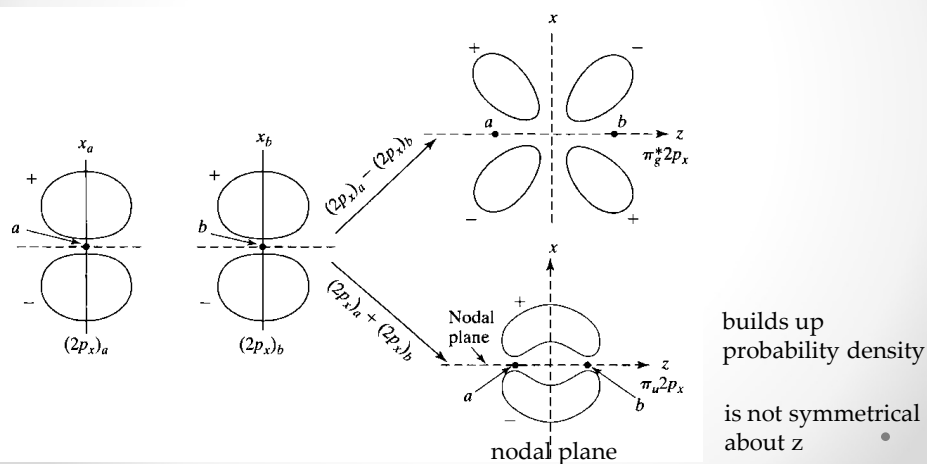
the more familiar alternatives:

$$(2p_x)_a + (2p_x)_b$$

$$\pi_u 2p_x$$

$$(2p_x)_a - (2p_x)_b$$

$$\pi_g^* 2p_x$$



$$(2p_y)_a + (2p_y)_b$$

$$\pi_u 2p_y$$

Bonding (u)

$$(2p_y)_a - (2p_y)_b$$

$$\pi_g^* 2p_y$$

antibonding (g)

$\pi_u 2p_x$ and $\pi_u 2p_y$ have the same energy.

are not eigenfunctions of L_z

linear combinations of

$$\pi_u 2p_{+1}$$

$$\pi_u 2p_{-1}$$

are eigenfunctions of L_z

$\pi_g^* 2p_x$ and $\pi_g^* 2p_y$ have the same energy.

are not eigenfunctions of L_z

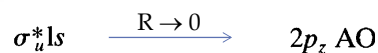
linear combinations of

$$\pi_g^* 2p_{+1}$$

$$\pi_g^* 2p_{-1}$$

are eigenfunctions of L_z

how H_2^+ MOs correlate with the united-atom AOs.



$$\hat{H}' = \hat{H}_{\text{mol}} - \hat{H}_{\text{UA}} \quad ?$$

$$E_{\text{el}} = E_{\text{UA}} + aR^2 + bR^3 + cR^4 + dR^5 + eR^5 \ln R + \dots$$

MO CONFIGURATIONS OF HOMONUCLEAR DIATOMIC MOLECULES

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

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.

the order in which the MOs fill as we go across the periodic table:

$$\sigma_g 1s < \sigma_u^* 1s < \sigma_g 2s < \sigma_u^* 2s < \pi_u 2p_{+1} = \pi_u 2p_{-1} < \sigma_g 2p < \pi_g^* 2p_{+1}$$

$$= \pi_g^* 2p_{-1} < \sigma_u^* 2p$$

Molecular-Orbital Nomenclature for Homonuclear Diatomic Molecules

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

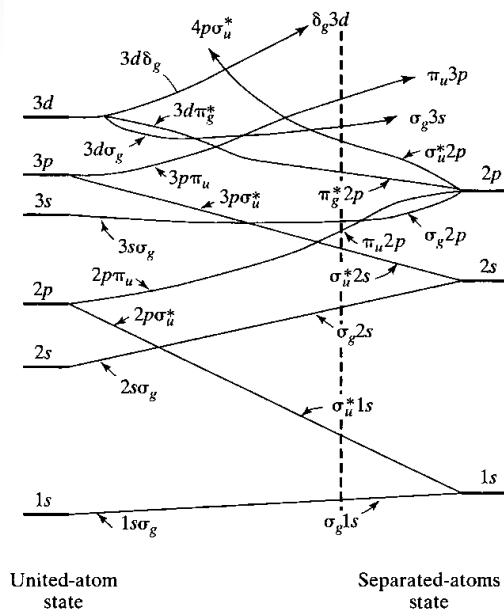
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the noncrossing rule:
the energies of MOs
with the same
symmetry cannot
cross.

symmetry refers to
whether the orbital is
g or u and whether it
is σ , π , δ

s, d, g,... united-atom AOs
(even) correlate with g MOs,
p, l, h,... AOs (odd) correlate
with u MOs.

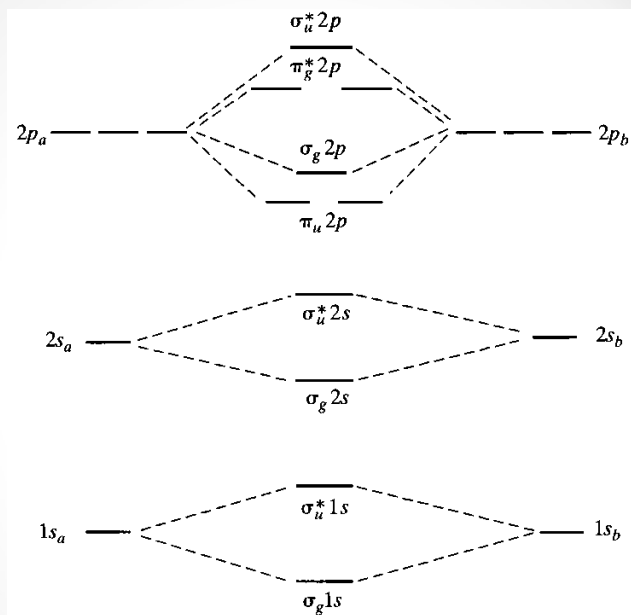


Correlation diagram for homonuclear diatomic
MOs.

this diagram is not quantitative.

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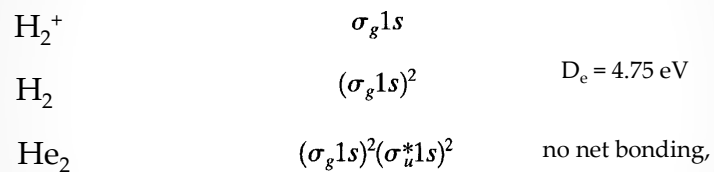
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- Homonuclear diatomic MOs formed from 1s, 2s, and 2p AO's. •

Molecular electronic configurations

terms, levels, and states



- ✓ It has bound excited electronic states,
- ✓ about two dozen such bound excited states of He_2 have been spectroscopically observed in gas discharge tubes.
- ✓ such excited states decay to the ground electronic state, and then the molecule dissociates.



Li_2	$(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2$	a single bond
	$KK(\sigma_g 2s)^2$	indicate the negligible change in inner-shell orbital energies on molecule formation
Be_2	$KK(\sigma_g 2s)^2 (\sigma_u^* 2s)^2$	no net bonding electrons.
B_2	$KK(\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^2$	two net bonding electrons
	one electron in the $\pi_u 2p_{+1}$ MO and the other in the $\pi_u 2p_{-1}$ MO,	
	is at variance with the notion that single bonds are always σ bonds.	
	the electron-spin-resonance spectrum showed that the ground term is a triplet with $S = 1$	

C_2	$KK(\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^4$	with four net bonding electrons
	the $\pi_u 2p$ and $\sigma_g 2p$ MOs have nearly the same energy in many molecules.	
	$KK(\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^3 (\sigma_g 2p)$	giving a triplet term.
	$(\pi_u 2p)^4$	a singlet term.
	the ground term by a small margin (0.09 eV)	

N_2	$KK(\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^4 (\sigma_g 2p)^2$	a triple bond
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O_2	$KK(\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\sigma_g 2p)^2 (\pi_u 2p)^4 (\pi_g^* 2p)^2$	a double bond.
	Spectroscopic evidence indicates that in O_2 (and in F_2) the $\sigma_g 2p$ is lower in energy than the $\pi_u 2p$ MO.	
	The paramagnetism of O_2	

F_2	$\dots (\pi_g^* 2p)^4$	a single bond.
Ne_2	$\dots (\pi_g^* 2p)^4 (\sigma_u^* 2p)^2$	no net bonding electrons
Na_2	$KKLL(\sigma_g 3s)^2$	
Al_2	$\left\{ \begin{array}{l} \dots (\sigma_g 3p)(\pi_u 3p) \\ \dots (\pi_u 3p)^2 \end{array} \right.$	0.02 eV below
Si_2	$\left\{ \begin{array}{l} \dots (\sigma_g 3p)^2 (\pi_u 3p)^2 \\ \dots (\sigma_g 3p)(\pi_u 3p)^3 \end{array} \right.$	0.05 eV below

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Molecule	Ground Term	Bond Order	D_e/eV	$R_e/\text{\AA}$	$\tilde{\nu}_e/\text{cm}^{-1}$
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	3.0	
Li_2	$1\Sigma_g^+$	1	1.07	2.67	351.4
Be_2	$1\Sigma_g^+$	0	0.10	2.45	
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	892
Ne_2	$1\Sigma_g^+$	0	0.0036	3.1	14

the harmonic
vibrational
frequency

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Bonding MOs produce charge buildup between the nuclei, whereas antibonding MOs produce charge depletion between the nuclei.

Usually, removal of an electron from:
 a bonding MO decreases D_e
 an antibonding MO increases D_e

$N_2 \rightarrow N_2^+$: the dissociation energy decreases
 $O_2 \rightarrow O_2^+$: the dissociation energy increases

Energy is always required to ionize a stable molecule, no matter which electron is removed.

Are interaction between two ground-state He atoms strictly repulsive ?
 helium gas can be liquefied !

van der Waals forces: all kinds of intermolecular forces.

For example: London or dispersion force

Except for highly polar molecules: the dispersion force is the largest contributor to intermolecular attractions.

van der Waals molecules

Ar_2 van der Waals molecules: $D_e = 0.012$ eV and $R_e = 3.76$ Å;
 Ar_2 has seven bound vibrational levels ($v = 0, \dots, 6$).

Examples of diatomic van der Waals molecules:

	R_e	D_e
Ne_2 :	3.1 Å	0.0036 eV
HeNe :	3.2 Å	0.0012 eV
Ca_2 :	4.28 Å	0.13 eV
Mg :	2,3.89 Å	0.053 eV

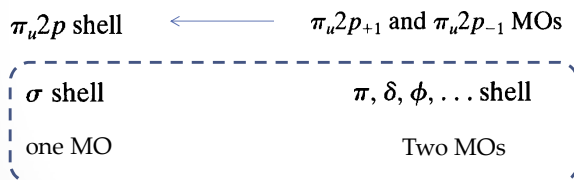
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ELECTRONIC TERMS OF DIATOMIC MOLECULES

For atoms, each set of degenerate atomic orbitals constitutes an **atomic subshell**.

For molecules, each set of degenerate molecular orbitals constitutes a **molecular shell**.



a molecular electronic configuration \rightarrow giving the number of electrons in each shell

$$(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^3$$

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For a many-electron diatomic molecules:

\hat{L}_z commutes with \hat{H}

$L_z = M_L \hbar$, where $M_L = 0, \pm 1, \pm 2, \pm \dots$

$$\Lambda \equiv |M_L|$$

Λ	0	1	2	3	4
letter	Σ	Π	Δ	Φ	Γ

$\Lambda \neq 0 \longrightarrow M_L: +\Lambda \text{ and } -\Lambda$

electronic energy depends on $M_L^2 \rightarrow$ double degeneracy

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The magnitude of S : $[S(S + 1)]^{1/2} \hbar$

$S = 0, 1/2, 1, 3/2, \dots$

The component of S along an axis = $M_s \hbar$, where $M_s = S, S - 1, \dots, -S$.

$2S + 1$ is called the spin multiplicity

$$2S+1\Lambda$$

Diatomic electronic states that arise from the same electron configuration and that have the same value for Λ and the same value for S are said to belong to the same electronic **term**.

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for a filled-shell molecular configuration:

$$M_s = \sum m_s \text{ values} = 0 \rightarrow S = 0$$

A filled σ shell : $M_L = \sum m = 0$

A filled π shell : $M_L = \sum m = (-1) + (+1) = 0$

A filled δ, ϕ, \dots shell : $M_L = \sum m = 0$

a closed-shell molecular configuration: $S = 0, \Lambda = 0$

only a $^1\Sigma$ term

ground electronic configuration of H_2

A single σ electron: $s = \frac{1}{2} \rightarrow S = \frac{1}{2} \rightarrow ^2\Sigma$

A single π electron: $s = \frac{1}{2} \rightarrow S = \frac{1}{2} \rightarrow ^2\Pi$

....

more than one electron:

Nonequivalent : Electrons that are in different molecular shells

Equivalent : Electrons that are in same molecular shells

two nonequivalent electrons:

$\sigma\sigma$ configuration

$$M_L = 0$$

$$\text{Each } s = \frac{1}{2}$$

$$S = 1 \text{ or } 0$$

$$\rightarrow ^1\Sigma \text{ and } ^3\Sigma$$

$\sigma\pi$ configuration:

$$M_L = 1$$

$$\text{Each } s = \frac{1}{2}$$

$$S = 1 \text{ or } 0$$

$$\rightarrow ^1\Pi \text{ and } ^3\Pi$$

$\pi\delta$ configuration,

π electron: $m = \pm 1$ $M_L = +3, -3, +1, -1$ $\Lambda = 3 \text{ or } 1$

δ electron: $m = \pm 2$

$^1\Pi, ^3\Pi, ^1\Phi, ^3\Phi.$

$\pi\pi$ configuration, each electron has $m = \pm 1$ M_L values 2, -2, 0, 0

$\Lambda = 2, 0, \text{ and } 0$

$^1\Delta, ^3\Delta, ^1\Sigma, ^3\Sigma, ^1\Sigma, \text{ and } ^3\Sigma$

apart from spin degeneracy: degenerate states nondegenerate

Forms of the wave functions for the terms

$M_L = +2$ two π subshells: π and π'
a subscript indicates the m value

For the Δ terms: both electrons have $m = +1$ or both have $m = -1$.

the spatial factor in the wave function is

$$\pi_{+1}(1)\pi'_{+1}(2) \text{ or } \pi_{+1}(2)\pi'_{+1}(1)$$

neither symmetric nor antisymmetric with respect to ... and are **unacceptable**

$$^1\Delta: \pi_{+1}(1)\pi'_{+1}(2) + \pi_{+1}(2)\pi'_{+1}(1)$$

$$^3\Delta: \pi_{+1}(1)\pi'_{+1}(2) - \pi_{+1}(2)\pi'_{+1}(1)$$

$$\begin{array}{l}
 \text{both electrons} \\
 \text{having } m = +1
 \end{array}
 \left\{
 \begin{array}{ll}
 {}^1\Delta: & \pi_{+1}(1)\pi'_{+1}(2) + \pi_{+1}(2)\pi'_{+1}(1) \quad \text{symmetric} \\
 {}^3\Delta: & \pi_{+1}(1)\pi'_{+1}(2) - \pi_{+1}(2)\pi'_{+1}(1) \quad \text{antisymmetric}
 \end{array}
 \right.$$

$$\begin{array}{l}
 \text{both electrons} \\
 \text{having } m = -1
 \end{array}
 \left\{
 \begin{array}{ll}
 {}^1\Delta: & \pi_{-1}(1)\pi'_{-1}(2) + \pi_{-1}(2)\pi'_{-1}(1) \quad \text{symmetric} \\
 {}^3\Delta: & \pi_{-1}(1)\pi'_{-1}(2) - \pi_{-1}(2)\pi'_{-1}(1) \quad \text{antisymmetric}
 \end{array}
 \right.$$

symmetric or antisymmetric with respect to exchange of electron

$$\left.
 \begin{array}{l}
 {}^1\Delta: \pi_{+1}(1)\pi'_{+1}(2) + \pi_{+1}(2)\pi'_{+1}(1) \\
 {}^1\Delta: \pi_{-1}(1)\pi'_{-1}(2) + \pi_{-1}(2)\pi'_{-1}(1)
 \end{array}
 \right\} \times 2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad \text{two states}$$

$$\left.
 \begin{array}{l}
 {}^3\Delta: \pi_{+1}(1)\pi'_{+1}(2) - \pi_{+1}(2)\pi'_{+1}(1) \\
 {}^3\Delta: \pi_{-1}(1)\pi'_{-1}(2) - \pi_{-1}(2)\pi'_{-1}(1)
 \end{array}
 \right\} \times \left\{
 \begin{array}{l}
 \alpha(1)\alpha(2) \\
 2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\
 \beta(1)\beta(2)
 \end{array}
 \right\} \quad \text{six states}$$

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For the Σ terms: one electron with $m = +1$ and one with $m = -1$.

$$\pi_{+1}(1)\pi'_{-1}(2), \quad \pi_{+1}(2)\pi'_{-1}(1), \quad \pi_{-1}(1)\pi'_{+1}(2), \quad \pi_{-1}(2)\pi'_{+1}(1)$$

Combining them to get
symmetric and antisymmetric
functions,



$$\begin{array}{ll}
 {}^1\Sigma^+: & \pi_{+1}(1)\pi'_{-1}(2) + \pi_{+1}(2)\pi'_{-1}(1) + \pi_{-1}(1)\pi'_{+1}(2) + \pi_{-1}(2)\pi'_{+1}(1) \\
 {}^1\Sigma^-: & \pi_{+1}(1)\pi'_{-1}(2) + \pi_{+1}(2)\pi'_{-1}(1) - \pi_{-1}(1)\pi'_{+1}(2) - \pi_{-1}(2)\pi'_{+1}(1)
 \end{array}
 \left.
 \begin{array}{l}
 \\
 \end{array}
 \right\} \text{symmetric}$$

$$\begin{array}{ll}
 {}^3\Sigma^+: & \pi_{+1}(1)\pi'_{-1}(2) - \pi_{+1}(2)\pi'_{-1}(1) + \pi_{-1}(1)\pi'_{+1}(2) - \pi_{-1}(2)\pi'_{+1}(1) \\
 {}^3\Sigma^-: & \pi_{+1}(1)\pi'_{-1}(2) - \pi_{+1}(2)\pi'_{-1}(1) - \pi_{-1}(1)\pi'_{+1}(2) + \pi_{-1}(2)\pi'_{+1}(1)
 \end{array}
 \left.
 \begin{array}{l}
 \\
 \end{array}
 \right\} \text{antisymmetric}$$

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$$\left. \begin{array}{l} {}^1\Sigma^+: \pi_{+1}(1)\pi'_{-1}(2) + \pi_{+1}(2)\pi'_{-1}(1) + \pi_{-1}(1)\pi'_{+1}(2) + \pi_{-1}(2)\pi'_{+1}(1) \\ {}^1\Sigma^-: \pi_{+1}(1)\pi'_{-1}(2) + \pi_{+1}(2)\pi'_{-1}(1) - \pi_{-1}(1)\pi'_{+1}(2) - \pi_{-1}(2)\pi'_{+1}(1) \end{array} \right\} \times$$

$$2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad \text{two states}$$

$$\left. \begin{array}{l} {}^3\Sigma^+: \pi_{+1}(1)\pi'_{-1}(2) - \pi_{+1}(2)\pi'_{-1}(1) + \pi_{-1}(1)\pi'_{+1}(2) - \pi_{-1}(2)\pi'_{+1}(1) \\ {}^3\Sigma^-: \pi_{+1}(1)\pi'_{-1}(2) - \pi_{+1}(2)\pi'_{-1}(1) - \pi_{-1}(1)\pi'_{+1}(2) + \pi_{-1}(2)\pi'_{+1}(1) \end{array} \right\} \times$$

$$\left\{ \begin{array}{l} \alpha(1)\alpha(2) \\ 2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\ \beta(1)\beta(2) \end{array} \right\} \quad \text{six states}$$

These functions have eigenvalue +1 or -1 with respect to reflection of electronic coordinates in the xz (σ_v) symmetry plane containing the molecular (z) axis; the superscripts + and - refer to this eigenvalue.

Previous Δ terms are not eigenfunctions of the symmetry operator \hat{O}_{σ_v}

a twofold
degeneracy



\hat{O}_{σ_v} commutes with the
Hamiltonian

\hat{O}_{σ_v} eigenvalues

$$\left. \begin{array}{ll} \pi_{+1}(1)\pi'_{+1}(2) + \pi_{+1}(2)\pi'_{+1}(1) + \pi_{-1}(1)\pi'_{-1}(2) + \pi_{-1}(2)\pi'_{-1}(1) & +1 \quad {}^1\Delta^+ \\ \pi_{+1}(1)\pi'_{+1}(2) + \pi_{+1}(2)\pi'_{+1}(1) - \pi_{-1}(1)\pi'_{-1}(2) - \pi_{-1}(2)\pi'_{-1}(1) & -1 \quad {}^1\Delta^- \end{array} \right\} \text{same energy}$$

are not eigenfunctions of L_z but are superpositions of L_z
eigenfunctions with eigenvalues +2 and -2.

Δ -type doubling: a very slight splitting of the two states of a ${}^1\Delta$
term by the interaction between the molecular rotational angular
momentum and the electronic orbital angular momentum

equivalent electrons:

π^2 configuration

$^1\Sigma^+, ^3\Sigma^-, ^1\Delta$

m_1	m_2	m_{s1}	m_{s2}	M_L	M_S	S
+1	+1	-1/2	1/2	2	0	•
-1	-1	-1/2	1/2	-2	0	•
+1	-1	1/2	1/2	0	1	✓
+1	-1	-1/2	-1/2	0	-1	✓
+1	-1	1/2	-1/2	0	0	1
+1	-1	-1/2	1/2	0	0	•

$$M_L = 2, -2 \rightarrow \Lambda = 2 \rightarrow ^1\Delta$$

$$S = 0$$

$$M_L = 0 \rightarrow \Lambda = 0 \rightarrow ^3\Sigma$$

$$S = 1 \text{ (for } M_S = -1, 0, 1)$$

$$M_L = 0 \rightarrow \Lambda = 0 \rightarrow ^1\Sigma$$

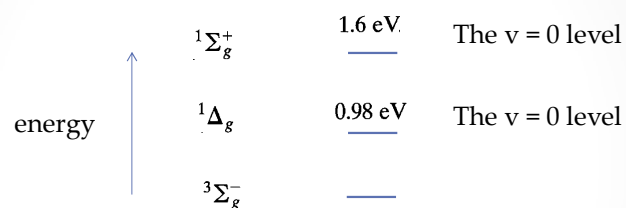
$$S = 0 \text{ (for } M_S = 0)$$

Configuration	Terms
$\sigma\sigma$	$^1\Sigma^+, ^3\Sigma^+$
$\sigma\pi; \sigma\pi^3$	$^1\Pi, ^3\Pi$
$\pi\pi; \pi\pi^3$	$^1\Sigma^+, ^3\Sigma^+, ^1\Sigma^-, ^3\Sigma^-, ^1\Delta, ^3\Delta$
$\pi\delta; \pi^3\delta; \pi\delta^3$	$^1\Pi, ^3\Pi, ^1\Phi, ^3\Phi$
σ	$^2\Sigma^+$
$\sigma^2; \pi^4; \delta^4$	$^1\Sigma^+$
$\pi; \pi^3$	$^2\Pi$
π^2	$^1\Sigma^+, ^3\Sigma^-, ^1\Delta$
$\delta; \delta^3$	$^2\Delta$
δ^2	$^1\Sigma^+, ^3\Sigma^-, ^1\Gamma$

For homonuclear diatomic molecules, a g or u right subscript is added to the term symbol to show the parity of the electronic states belonging to the term.

Terms arising from an electron configuration that has an odd number of electrons in molecular orbitals of odd parity are odd (u); all other terms are even (g).

O₂ has a π^2 configuration:



Singlet O₂ is a reaction intermediate in many organic, biochemical, and inorganic reactions.

Most stable diatomic molecules: $1\Sigma^+$ ground term

Exceptions: B₂, Al₂, Si₂, and O₂, and NO 2Π ground

Spectroscopists prefix the ground term of a molecule

the symbol X

terms of the same spin multiplicity as the ground term

are designated as A, B, C, ...,

excited terms of different spin multiplicity

are designated as a, b, c

Exceptions are C₂ and N₂

ground terms $1\Sigma_g^+$

But, A, B, C, ... are used for excited triplet terms

spin-orbit interaction can split a molecular term into closely spaced energy levels

The projection of the total electronic spin S on the molecular axis is $M_s\hbar$.

In molecules the quantum number M_s is called Σ

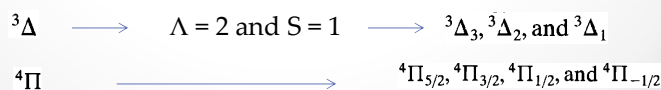
$$\Sigma = S, S - 1, \dots, -S$$

total axial component of electronic angular momentum $(\Lambda + \Sigma)\hbar$

$$\Lambda + S, \Lambda + S - 1, \dots, \Lambda - S$$

is written as a right subscript to the term symbol

$$\Omega \equiv |\Lambda + \Sigma|$$



The spin-orbit interaction energy in diatomic molecules

$$\text{spin-orbit interaction energy} \approx A\Lambda\Sigma$$

A depends on Λ and S but not on $\Sigma \rightarrow$ spacing between levels = cte.

$A > 0 \rightarrow$ the multiplet is **regular** \rightarrow level with the lowest $\Lambda + \Sigma$ lies lowest

$A < 0 \rightarrow$ the multiplet is **inverted**

$\Lambda \neq 0 \rightarrow 2S + 1 =$ the number of multiplet components

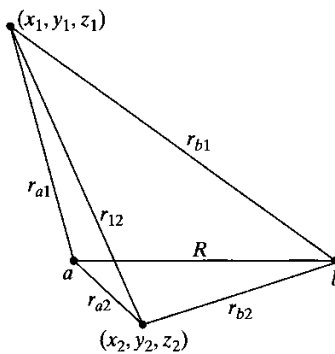
with $\Lambda \neq 0$, levels are doubly degenerate (for two values of M_L).

Spin-orbit interaction splits the ${}^3\Delta$ term into three levels, each doubly degenerate, which is removed by the Λ -type doubling.

For Σ terms, the spin-orbit interaction is very small (quantum numbers Σ and Ω are not defined).

Σ terms \rightarrow single nondegenerate energy level.

THE HYDROGEN MOLECULE



Interparticle distances in H_2 .

purely electronic Hamiltonian for H_2 is:

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{a1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} - \frac{1}{r_{b2}} + \frac{1}{r_{12}}$$

1 and 2 for electrons
a and b for nuclei

prevents the equation from being separable
↓
approximation methods

1) the molecular-orbital approach:

ground-state electronic configuration $(\sigma_g 1s)^2$

approximate wave function:

$$\frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_g 1s(1)\alpha(1) & \sigma_g 1s(1)\beta(1) \\ \sigma_g 1s(2)\alpha(2) & \sigma_g 1s(2)\beta(2) \end{vmatrix} = \sigma_g 1s(1)\sigma_g 1s(2)2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$= f(1)f(2)2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$\sigma_g 1s = f$$

omission of the spin factor does not affect the variational integral.
we want to choose f so as to minimize:

$$\frac{\iint f^*(1)f^*(2)\hat{H}f(1)f(2) dv_1 dv_2}{\iint |f(1)|^2|f(2)|^2 dv_1 dv_2} \quad \text{over spatial coordinates of two electrons.}$$

Ideally, f should be found by an SCF calculation.
For simplicity, we can use an H_2^+ -like MO.

if we omit the $1/r_{12} \rightarrow \hat{H} = \text{sum of two } H_2^+ \text{ Hamiltonians}$

a good approximation to the ground-state H_2^+ wave function (last sections):

$$\frac{k^{3/2}}{(2\pi)^{1/2}(1 + S_{ab})^{1/2}} (e^{-kr_a} + e^{-kr_b})$$

•

•

variation function = the product of two such LCAO functions

$$\phi = \frac{\zeta^3}{2\pi(1 + S_{ab})} (e^{-\zeta r_{a1}} + e^{-\zeta r_{b1}})(e^{-\zeta r_{a2}} + e^{-\zeta r_{b2}})$$

$$\phi = \frac{1}{2(1 + S_{ab})} [1s_a(1) + 1s_b(1)][1s_a(2) + 1s_b(2)]$$

the effective nuclear charge ζ will differ from k for H_2^+ .

$$\hat{H} = \hat{H}_1^0 + \hat{H}_2^0 + 1/r_{12}$$



$$\iint \phi^* \hat{H} \phi dv_1 dv_2 = 2W_1 + \iint \frac{\phi^2}{r_{12}} dv_1 dv_2$$

$$W_1 = -\frac{1}{2}\zeta^2 + \frac{\zeta^2 - \zeta - R^{-1} + R^{-1}(1 + \zeta R)e^{-2\zeta R} + \zeta(\zeta - 2)(1 + \zeta R)e^{-\zeta R}}{1 + e^{-\zeta R}(1 + \zeta R + \frac{\zeta^2 R^2}{3})}$$

•

•

Coulson,

$R_e = 0.732 \text{ \AA}$ (true value = 0.741 \AA)

$D_e = 3.49 \text{ eV}$ (true value = 4.75 eV)

ζ (at 0.732 \AA) = $1.197 < k$ for H_2^+ .

the screening of the nuclei from each electron by the other electron.

Kolos and Roothaan improved the results.

They expanded f in elliptic coordinates.

f is a function of ξ and η (Since $m = 0$ for the ground state, the $e^{im\phi} = 1$)

$$f = e^{-\alpha\xi} \sum_{p,q} a_{pq} \xi^p \eta^q$$

p and q are integers and α and a_{pq} are variational parameters.

The Hartree-Fock results:

$R_e = 0.733 \text{ \AA}$ and $D_e = 3.64 \text{ eV}$, which is not much improvement over the the simple LCAO molecular orbital.

• we must go beyond the SCF approximation of writing $f(1)f(2)$. •

configuration interaction (CI):

we include contributions from SCF (or other) functions for all the excited states with the same symmetry as the ground state.

configuration $(\sigma_g 1s)^2 \longrightarrow {}^1\Sigma_g^+$

first exs configuration $(\sigma_g 1s)(\sigma_u^* 1s) \xrightarrow{g \times u \rightarrow \text{odd}} {}^1\Sigma_u^+ \text{ and } {}^3\Sigma_u^+ \quad \text{odd parity}$

$(\sigma_u^* 1s)^2 \longrightarrow {}^1\Sigma_g^+$

To simplify things, we will use the LCAO-MOs as approximations to the MOs.

$$\phi = \sigma_g 1s(1)\sigma_g 1s(2) + c\sigma_u^* 1s(1)\sigma_u^* 1s(2)$$

c is a variational parameter.

Weinbaum,

$R_e = 0.757 \text{ \AA}$; $D_e = 4.03 \text{ eV}$; $\zeta = 1.19$

• a considerable improvement over the HF result •

We can improve on this result by using a better form for the MOs of each configuration and by including more configuration functions.

James and Coolidge, use of r_{12} in H_2 trial functions:

$$\exp[-\delta(\xi_1 + \xi_2)] \sum c_{mnjkp} [\xi_1^m \xi_2^n \eta_1^j \eta_2^k + \xi_1^n \xi_2^m \eta_1^k \eta_2^j] r_{12}^p$$

variational parameters : δ and the c_{mnjkp}
function is symmetric with respect to interchange of electrons 1 and 2 (antisymmetric ground-state spin function).

With 13 terms:

$D_e = 4.72$ eV, only 0.03 eV in error.

THE VALENCE-BOND TREATMENT OF H_2

the **valence-bond (VB)** theory, by Heitler and London

more closely related to the chemist's idea of molecules (atomic cores + bonding)

first step : approximate the molecule as two ground-state hydrogen atoms.

$$f_1 = 1s_a(1)1s_b(2)$$

1 and 2 for electrons ; a and b for nuclei

Also:
$$f_2 = 1s_a(2)1s_b(1)$$

the trial variation function

$$c_1 f_1 + c_2 f_2 = c_1 1s_a(1)1s_b(2) + c_2 1s_a(2)1s_b(1)$$

trial variation function $c_1 f_1 + c_2 f_2 = c_1 1s_a(1)1s_b(2) + c_2 1s_a(2)1s_b(1)$

determinantal secular equation $\det(H_{ij} - S_{ij}W) = 0$

$H_{11} = \langle f_1 | \hat{H} | f_1 \rangle, S_{11} = \langle f_1 | f_1 \rangle, \dots$

We can also consider the problem using perturbation theory:

two neutral ground-state hydrogen atoms $\xrightarrow{\text{perturbation}}$ molecule

$1s_a(1)1s_b(2)$
 $1s_a(2)1s_b(1)$ } $c_1 1s_a(1)1s_b(2) + c_2 1s_a(2)1s_b(1)$
 correct zeroth-order wave functions

↓

secular determinant

$(H_{ij} - S_{ij}W) = 0$

Hamiltonian is Hermitian, all functions are real, f_1 and f_2 are normalized

$H_{12} = H_{21} \quad S_{12} = S_{21} \quad S_{11} = S_{22} = 1$

$H_{11} = \langle 1s_a(1)1s_b(2) | \hat{H} | 1s_a(1)1s_b(2) \rangle$
 $H_{22} = \langle 1s_a(2)1s_b(1) | \hat{H} | 1s_a(2)1s_b(1) \rangle$

$\begin{vmatrix} H_{11} - W & H_{12} - WS_{12} \\ H_{12} - WS_{12} & H_{11} - W \end{vmatrix} = 0$

$W_1 = \frac{H_{11} + H_{12}}{1 + S_{12}}, \quad W_2 = \frac{H_{11} - H_{12}}{1 - S_{12}}$

$\phi_1 = \frac{f_1 + f_2}{\sqrt{2}(1 + S_{12})^{1/2}}, \quad \phi_2 = \frac{f_1 - f_2}{\sqrt{2}(1 - S_{12})^{1/2}}$

$f_1 \pm f_2 = 1s_a(1)1s_b(2) \pm 1s_a(2)1s_b(1)$

$S_{12} = \int f_1^* f_2 dv = \iint 1s_a(1)1s_b(2)1s_a(2)1s_b(1) dv_1 dv_2$

$S_{12} = \langle 1s_a(1) | 1s_b(1) \rangle \langle 1s_a(2) | 1s_b(2) \rangle = S_{ab}^2$

the ground state of H_2 is a Σ state with the antisymmetric spin factor and a symmetric spatial factor. Hence ϕ_1 must be the ground state.

The Heitler-London ground-state wave function:

$$\frac{1s_a(1)1s_b(2) + 1s_a(2)1s_b(1)}{\sqrt{2}(1 + S_{ab}^2)^{1/2}} \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

for the three states of the lowest $^3\Sigma$ term are:

$$\frac{1s_a(1)1s_b(2) - 1s_a(2)1s_b(1)}{\sqrt{2}(1 - S_{ab}^2)^{1/2}} \begin{cases} \alpha(1)\alpha(2) \\ 2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\ \beta(1)\beta(2) \end{cases}$$

•

•

the ground-state energy expression:

$$\hat{H} = \hat{H}_a(1) + \hat{H}_b(2) + \hat{H}'$$

$$\hat{H}_a(1) = -\frac{1}{2}\nabla_1^2 - \frac{1}{r_{a1}}, \quad \hat{H}_b(2) = -\frac{1}{2}\nabla_2^2 - \frac{1}{r_{b2}}, \quad \hat{H}' = -\frac{1}{r_{b1}} - \frac{1}{r_{a2}} + \frac{1}{r_{12}}$$

$$H_{11} = \langle 1s_a(1)1s_b(2) | \hat{H}_a(1) + \hat{H}_b(2) + \hat{H}' | 1s_a(1)1s_b(2) \rangle$$

$$\begin{aligned} & \langle 1s_a(1)1s_b(2) | \hat{H}_a(1) | 1s_a(1)1s_b(2) \rangle \\ &= \langle 1s_a(1) | \hat{H}_a(1) | 1s_a(1) \rangle \langle 1s_b(2) | 1s_b(2) \rangle \end{aligned}$$

$$Q \equiv \langle 1s_a(1)1s_b(2) | \hat{H}' | 1s_a(1)1s_b(2) \rangle$$

Coulomb integral

The Heitler-London calculation does not introduce an effective nuclear charge into the 1s function. Hence $1s_a(1)$ is an eigenfunction of $\hat{H}_a(1)$ with eigenvalue $-1/2$ hartree,

$$H_{11} = Q - 1$$

•

•

$$H_{12} = H_{21} = \langle 1s_a(2)1s_b(1) | \hat{H}_a(1) + \hat{H}_b(2) + \hat{H}' | 1s_a(1)1s_b(2) \rangle$$

$$\langle 1s_a(2) | 1s_b(2) \rangle \langle 1s_b(1) | \hat{H}_a(1) | 1s_a(1) \rangle = -\frac{1}{2} S_{ab}^2$$

$$A \equiv \langle 1s_a(2)1s_b(1) | \hat{H}' | 1s_a(1)1s_b(2) \rangle$$

$$H_{12} = A - S_{ab}^2$$

$$W_1 = \frac{H_{11} + H_{12}}{1 + S_{12}}$$

$$\downarrow$$

$$W_1 = -1 + \frac{Q + A}{1 + S_{ab}^2}$$

$$W_2 = \frac{H_{11} - H_{12}}{1 - S_{12}}$$

$$\downarrow$$

$$W_2 = -1 + \frac{Q - A}{1 - S_{ab}^2}$$

To obtain the U(R) potential-energy curves, we add the internuclear repulsion 1/R to these expressions.

Many of the integrals have been evaluated in the treatment of H_2^+

The only new integrals are those involving $1/r_{12}$.

two-center, two-electron exchange integral:

$$\iint 1s_a(1)1s_b(2) \frac{1}{r_{12}} 1s_a(2)1s_b(1) dv_1 dv_2$$

Two-center : the integrand contains functions centered on two different nuclei

two-electron : the coordinates of two electrons occur in the integrand

This must be evaluated using an expansion for $1/r_{12}$ in confocal elliptic coordinates

Heitler-London treatment : $D_e = 3.15$ eV, $R_e = 0.87$ Å
 the experimental values : $D_e = 4.75$ eV, $R_e = 0.741$ Å

In this treatment, most of the binding energy is provided by the exchange integral A.

Improvements on the Heitler-London function

Wang introduced an orbital exponent ζ in the 1s function:

$$\zeta_{\text{opt}} = 1.166, R_e = 3.78 \text{ eV}, D_e = 0.744 \text{ \AA}$$

Rosen: mixing in some $2p_z$ character into the atomic orbitals (hybridization).

to improve the Heitler-London-Wang function

$$\phi = \phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)$$

$$\phi_a = e^{-\zeta r_a}(1 + cz_a)$$

allows for the polarization of the AOs on molecule formation ($D_e = 4.04 \text{ eV}$)

Another improvements:

- 1) the use of ionic structures
- 2) the generalized valence-bond method

COMPARISON OF THE MO AND VB THEORIES

The H_2 ground state:

the spatial factor of the unnormalized LCAO-MO wave function

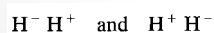
$$[\phi_a(1) + \phi_b(1)][\phi_a(2) + \phi_b(2)] \quad \phi_a \text{ an atomic orbital centered on nucleus a}$$

simplest treatment: ϕ is a 1s AO

$$\phi_a(1)\phi_a(2) + \phi_b(1)\phi_b(2) + \phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)$$

the physical significance of the terms:

$$\underbrace{\phi_a(1)\phi_a(2) + \phi_b(1)\phi_b(2)}_{\text{ionic terms,}} + \underbrace{\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)}_{\text{covalent terms,}}$$



Two terms occur with equal weight,

We remedy this; the simplest procedure is to omit the ionic terms of the MO function.

$$\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2) \quad \text{As the Heitler-London function}$$

there is some probability of finding both electrons near the same nucleus,

$$\phi_{\text{VB,imp}} = \phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2) + \delta[\phi_a(1)\phi_a(2) + \phi_b(1)\phi_b(2)]$$

↑
variational parameter

- ✓ represents **ionic-covalent resonance**.
- ✓ a time-independent mixture of covalent and ionic functions.
- ✓ $\delta(\infty) = 0$

Weinbaum's calculation:

$$\delta(R_e) = 0.26; \zeta = 1.19; D_e = 4.03 \text{ eV}$$

•

•

$$\delta = 0 : \phi_{\text{VB,imp}} \rightarrow \text{VB function} ; \delta = 1 \phi_{\text{VB,imp}} \rightarrow \text{LCAO-MO function}$$

$\delta(R_e) = 0.26$ is closer to zero than to 1, and, in fact, the Heitler-London-Wang VB function gives a better dissociation energy than the LCAO-MO function.

compare the imp VB trial function with the simple LCAO-MO function improved by CI.

The LCAO-MO CI trial function (unnormalized):

$$\phi_{\text{MO,imp}} = [\phi_a(1) + \phi_b(1)][\phi_a(2) + \phi_b(2)] + \gamma[\phi_a(1) - \phi_b(1)][\phi_a(2) - \phi_b(2)]$$

multiplying it by $1/(1-\gamma)$



$$\phi_{\text{MO,imp}} = \phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2) + \frac{1+\gamma}{1-\gamma}[\phi_a(1)\phi_a(2) + \phi_b(1)\phi_b(2)]$$

$$\delta = (1 + \gamma)/(1 - \gamma)$$

• improved MO function and the improved VB function are identical. •

- ✓ The MO function underestimates electron correlation (ec can be introduced by CI)
- ✓ The VB function overestimates electron correlation (ec is reduced by ionic-covalent resonance)
- ✓ at large R, the simple VB is more reliable than the simple MO method

How VB and MO methods divide the H_2 electronic Hamiltonian into unperturbed and perturbation Hamiltonians?

For the MO method,

$$\hat{H} = \underbrace{\left[\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{a1}} - \frac{1}{r_{b1}} \right) + \left(-\frac{1}{2}\nabla_2^2 - \frac{1}{r_{a2}} - \frac{1}{r_{b2}} \right) \right]}_{\text{unperturbed Hamiltonian (sum of two } H_2^+ \text{ Hamiltonians)}} + \frac{1}{r_{12}}$$

•

•

the zeroth-order MO wave function is a product of two H^{2+} -like wave functions (approximate as LCAOs)

The effect of the $1/r_{12}$ perturbation is taken into account in an average way through use of self-consistent-field molecular orbitals

instantaneous electron correlation can be taken into account by (CI)
LCAO-MO SCF CI

For the valence-bond method,

$$\hat{H} = \left[\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{a1}} \right) + \left(-\frac{1}{2}\nabla_2^2 - \frac{1}{r_{b2}} \right) \right] - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} + \frac{1}{r_{12}}$$

or

$$\hat{H} = \left[\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{b1}} \right) + \left(-\frac{1}{2}\nabla_2^2 - \frac{1}{r_{a2}} \right) \right] - \frac{1}{r_{a1}} - \frac{1}{r_{b2}} + \frac{1}{r_{12}}$$

unperturbed system: two hydrogen atoms

We have two zeroth-order functions (belong to a degenerate level)

The correct ground-state zeroth-order function is the linear combination

MO is computationally much simpler than the VB method.

- The MO method was developed by Hund, Mulliken, and Lennard-Jones in the late 1920s.

•

MO AND VB WAVE FUNCTIONS FOR HOMONUCLEAR DIATOMIC MOLECULES

- ✓ The **MO approximation** puts the electrons of a molecule in molecular orbitals (is approximated by LCAOs) which extend over the whole molecule.
- ✓ The **VB method** puts the electrons in AOs and constructs the molecular wave function by allowing for "exchange" of the valence electron pairs between the atomic orbitals of the bonding atoms.

The ground state of He₂:

- ✓ The separated helium atoms: closed-subshell configuration (1s²).
- ✓ unpaired electrons = 0
- ✓ VB wave function: antisymmetrized product of the AO functions.

VB wave function

$$\frac{1}{\sqrt{24}} \begin{vmatrix} 1s_a(1) & \overline{1s_a}(1) & 1s_b(1) & \overline{1s_b}(1) \\ 1s_a(2) & \overline{1s_a}(2) & 1s_b(2) & \overline{1s_b}(2) \\ 1s_a(3) & \overline{1s_a}(3) & 1s_b(3) & \overline{1s_b}(3) \\ 1s_a(4) & \overline{1s_a}(4) & 1s_b(4) & \overline{1s_b}(4) \end{vmatrix}$$

spin function β .

↓

helium-atom 1s

{ Ideally: is an SCF atomic function
Approximatly: a hydrogenlike function with effective nuclear charge.

predicts no bonding

shorthand notation: $|1s_a \overline{1s_a} 1s_b \overline{1s_b}|$

MO approximation to the wave function:

the ground-state configuration: $(\sigma_g 1s)^2 (\sigma_u^* 1s)^2$

No bonding is predicted,

MO wave function: $|\sigma_g 1s \overline{\sigma_g 1s} \sigma_u^* 1s \overline{\sigma_u^* 1s}|$

The simplest way to approximate the (unnormalized) MOs is LCAOs:

$$\begin{aligned}\sigma_g 1s &= 1s_a + 1s_b \\ \sigma_u^* 1s &= 1s_a - 1s_b\end{aligned}$$

$$|(1s_a + 1s_b)(\overline{1s_a + 1s_b})(1s_a - 1s_b)(\overline{1s_a - 1s_b})|$$

$$|(1s_a + 1s_b)(\overline{1s_a + 1s_b})(1s_a - 1s_b)(\overline{1s_a - 1s_b})|$$

add column 1 to column 3
and column 2 to column 4

$$4|(1s_a + 1s_b)(\overline{1s_a + 1s_b})1s_a \overline{1s_a}|$$

subtract column 3 from
column 1 and column 4 from
column 2

$$4|1s_b \overline{1s_b} 1s_a \overline{1s_a}|$$

interchange of columns 1 and 3
and of 2 and 4 multiplies by $(-1)^2$

$$4|1s_a \overline{1s_a} 1s_b \overline{1s_b}|$$

is identical to the VB
function

the simple VB and simple LCAO-MO methods give the same approximate wave functions for diatomic molecules formed from atoms with completely filled atomic subshells.

trial function: $|1s_a \overline{1s_a} 1s_b \overline{1s_b}|$



the variational integral



repulsive curve for the interaction of two gs He atoms

the Heitler-London VB functions (gs) for H_2 as Slater determinants:

$$\frac{1s_a(1)1s_b(2) + 1s_a(2)1s_b(1)}{\sqrt{2}(1 + S_{ab}^2)^{1/2}} \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$



$$\frac{1}{2}(1 + S_{ab}^2)^{-1/2} \left\{ \begin{vmatrix} 1s_a(1)\alpha(1) & 1s_b(1)\beta(1) \\ 1s_a(2)\alpha(2) & 1s_b(2)\beta(2) \end{vmatrix} - \begin{vmatrix} 1s_a(1)\beta(1) & 1s_b(1)\alpha(1) \\ 1s_a(2)\beta(2) & 1s_b(2)\alpha(2) \end{vmatrix} \right\}$$

$$= (2 + 2S_{ab}^2)^{-1/2} \{ |1s_a \overline{1s_b}| - |\overline{1s_a} 1s_b| \}$$



electron on a is paired with an electron of opposite spin on b (Lewis structure H—H)

HL functions for the **lowest H_2 triplet state**:

$$\begin{aligned} \text{Singlet:} & \quad |1s_a \overline{1s_b}| - |\overline{1s_a} 1s_b| \\ \text{Triplet:} & \quad \begin{cases} |1s_a 1s_b| \\ |1s_a \overline{1s_b}| + |\overline{1s_a} 1s_b| \\ |\overline{1s_a} \overline{1s_b}| \end{cases} \end{aligned}$$

- Li_2 :
- ✓ gs configuration $1s^2 2s$,
 - ✓ the Lewis structure is $Li-Li$ (two $2s$ Li electrons paired and the $1s$ electrons remaining in the inner shell of each atom)

the gs VB function:

$$|1s_a \overline{1s_a} 1s_b \overline{1s_b} 2s_a \overline{2s_b}| - |1s_a \overline{1s_a} 1s_b \overline{1s_b} \overline{2s_a} 2s_b|$$

Exercise: show that it is an eigenfunction of the spin operators \hat{S}^2 and \hat{S}_z with eigenvalue zero for each operator,

To save space:

$$|1s_a \overline{1s_a} 1s_b \overline{1s_b} \overbrace{2s_a 2s_b}^{\text{pairing (bonding) of the } 2s_a \text{ and } 2s_b \text{ AOs}}|$$

pairing (bonding) of the $2s_a$ and $2s_b$ AOs

MO wave function (gs)

$$|\sigma_g 1s \overline{\sigma_g 1s} \sigma_u^* 1s \overline{\sigma_u^* 1s} \sigma_g 2s \overline{\sigma_g 2s}|$$

approximate the two lowest MOs by $1s_a \pm 1s_b$

$$|1s_a \overline{1s_a} 1s_b \overline{1s_b} \sigma_g 2s \overline{\sigma_g 2s}|$$

Recall the notation $KK(\sigma_g 2s)^2$ for gs configuration

The N_2 ground state:

the VB treatment:

The lowest configuration of N $1s^2 2s^2 2p^3$

The Lewis structure : $:N \equiv N:$

the VB wave function?

three pairs of orbitals and two ways to give opposite spins. Hence, there are $2^3 = 8$ possible Slater determinants that we can write.

$$D_1 = |1s_a \overline{1s_a} 2s_a \overline{2s_a} 1s_b \overline{1s_b} 2s_b \overline{2s_b} 2p_{xa} \overline{2p_{xb}} 2p_{ya} \overline{2p_{yb}} 2p_{za} \overline{2p_{zb}}|$$

In all eight determinants, the first eight columns will remain unchanged

$$D_1 = |\cdots 2p_{xa} \overline{2p_{xb}} 2p_{ya} \overline{2p_{yb}} 2p_{za} \overline{2p_{zb}}|$$

$$D_2 = |\cdots \overline{2p_{xa}} 2p_{xb} 2p_{ya} \overline{2p_{yb}} 2p_{za} \overline{2p_{zb}}|$$

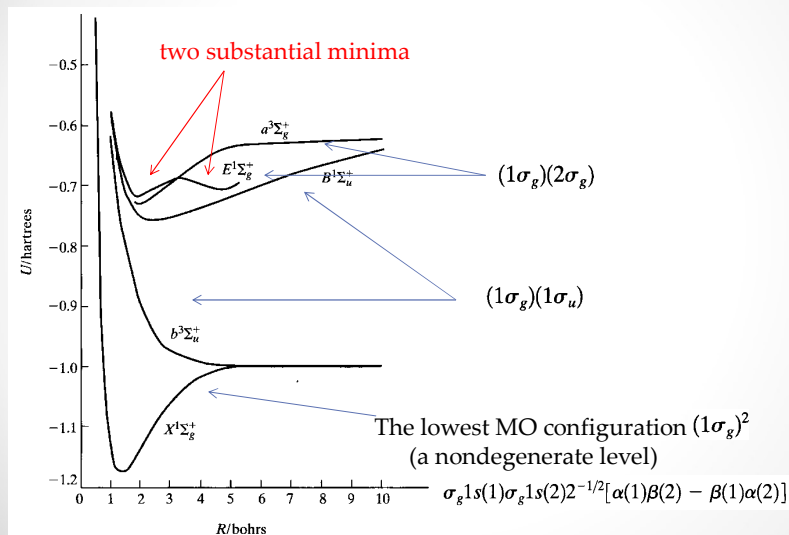
There are six other determinants

The **VB wave function** is a linear combination of eight determinants .

Rule in the combination?

The single-determinant gs N_2 MO function is easier to handle than the eight-determinant VB function.

EXCITED STATES OF H₂



LCAO-MO functions

triply degenerate

$$b^3\Sigma_u^+: 2^{-1/2}[1\sigma_g(1)1\sigma_u(2) - 1\sigma_g(2)1\sigma_u(1)] \begin{cases} \alpha(1)\alpha(2) \\ 2^{-1/2}[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \\ \beta(1)\beta(2) \end{cases}$$

nondegenerate

$$B^1\Sigma_u^+: 2^{-1/2}[1\sigma_g(1)1\sigma_u(2) + 1\sigma_g(2)1\sigma_u(1)]2^{-1/2}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

$$1\sigma_g \approx N(1s_a + 1s_b) \quad 1\sigma_u \approx N'(1s_a - 1s_b)$$

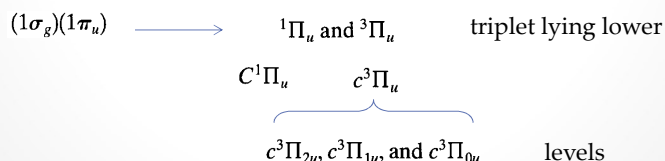
- ✓ one bonding and one antibonding electron, and repulsive p-e curves are expected .
- ✓ Actually, the B level has a minimum in its U(R) curve.

The Heitler-London wave functions

$$\frac{1s_a(1)1s_b(2) - 1s_a(2)1s_b(1)}{\sqrt{2}(1 - S_{ab}^2)^{1/2}} \begin{cases} \alpha(1)\alpha(2) \\ 2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\ \beta(1)\beta(2) \end{cases}$$

$$\frac{1s_a(1)1s_b(2) + 1s_a(2)1s_b(1)}{\sqrt{2}(1 + S_{ab}^2)^{1/2}} \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

- ✓ going across the periodic : $2\sigma_u$ MO fills before the two $1\pi_u$
- ✓ in H_2 : $1\pi_u < 2\sigma_u$



Each level is twofold degenerate (eight electronic states)

SCF WAVE FUNCTIONS FOR DIATOMIC MOLECULES

- Some examples of SCF MO WFs for diatomic molecules.
- The spatial orbitals ϕ_i in an MO WF are each expressed as a linear combination of a set of one-electron basis functions χ_s

$$\phi_i = \sum_s c_{si} \chi_s$$
- For SCF calculations on diatomic molecules, one can use STOs centered on the various atoms of the molecule as the basis functions.
- Complete set of AO basis functions \equiv an infinite number of STOs
- True molecular HF wave function can be closely approximated with a reasonably small number of carefully chosen STOs.
- A minimal basis set (MBS) for a molecular SCF calculation consists of a single basis function for each inner-shell AO and each valence-shell AO of each atom.
- An extended basis set (EBS) is a set that is larger than a minimal set.
- MBS SCF calculations are easier than EBS calculations, but the latter are much more accurate.

SCF WAVE FUNCTIONS FOR DIATOMIC MOLECULES

Examples of SCF wave functions for diatomic molecules:

1) the SCF MOs for the ground state of Li_2 at $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2]$
 $R = \text{Re}$:

$$\begin{aligned} 1\sigma_g &= 0.706(1s_a + 1s_b) + 0.009(2s_{\perp a} + 2s_{\perp b}) + 0.0003(2p\sigma_a + 2p\sigma_b) \\ 1\sigma_u &= 0.709(1s_a - 1s_b) + 0.021(2s_{\perp a} - 2s_{\perp b}) + 0.003(2p\sigma_a - 2p\sigma_b) \\ 2\sigma_g &= -0.059(1s_a + 1s_b) + 0.523(2s_{\perp a} + 2s_{\perp b}) + 0.114(2p\sigma_a + 2p\sigma_b) \end{aligned}$$

- ✓ The AO functions in these equations are STOs, except for $2s_{\perp}$.
- ✓ A ST $2s$ AO has no radial nodes and is not orthogonal to a $1s$ STO.
- ✓ The HF $2s$ AO has one radial node ($n - l - 1 = 1$) and is orthogonal to the $1s$ AO.

$$2s_{\perp} = (1 - S^2)^{-1/2}(2s - S \cdot 1s) \quad \text{By Schmidt orthogonalization}$$

S is the overlap integral $\langle 1s | 2s \rangle$.

$2p\sigma$ for an AO \rightarrow the p orbital points along the molecular (z); a $2p_z$ AO
 The $2p_x$ and $2p_y$ AOs are called $2p\pi$ AOs

optimum orbital exponents: $\zeta_{1s} = 2.689$, $\zeta_{2s} = 0.634$, $\zeta_{2p\sigma} = 0.761$

six AOs (as basis functions) \rightarrow approximations for the six lowest MOs of ground-state Li_2 ; only three of these MOs are occupied.

previous simple expressions

$$\begin{aligned} 1\sigma_g &= \sigma_g 1s = 2^{-1/2}(1s_a + 1s_b) \\ 1\sigma_u &= \sigma_u^* 1s = 2^{-1/2}(1s_a - 1s_b) \\ 2\sigma_g &= \sigma_g 2s = 2^{-1/2}(2s_a + 2s_b) \end{aligned}$$

Comparison:

simple expressions:

$$1\sigma_g = 0.706(1s_a + 1s_b) + 0.009(2s_{1a} + 2s_{1b}) + 0.0003(2p\sigma_a + 2p\sigma_b)$$

$$1\sigma_u = 0.709(1s_a - 1s_b) + 0.021(2s_{1a} - 2s_{1b}) + 0.003(2p\sigma_a - 2p\sigma_b)$$

$$1\sigma_g = \sigma_g 1s = 2^{-1/2}(1s_a + 1s_b)$$

$$1\sigma_u = \sigma_u^* 1s = 2^{-1/2}(1s_a - 1s_b)$$

Approximations are good

$$2\sigma_g = -0.059(1s_a + 1s_b) + 0.523(2s_{1a} + 2s_{1b}) + \boxed{0.114(2p\sigma_a + 2p\sigma_b)}$$

$$2\sigma_g = \sigma_g 2s = 2^{-1/2}(2s_a + 2s_b)$$

substantial $2p\sigma$ AO contributions
in addition to the $2s$ AO

the $2s$ and $2p$ AOs are close in energy; the hybridization allows for the polarization of the $2s$ AOs in forming the molecule.

2) the $3\sigma_g$ MO of the F_2 ground state at R_e :

a) using a minimal basis set:

$$3\sigma_{g,\min} = 0.038(1s_a + 1s_b) - 0.184(2s_a + 2s_b) + 0.648(2p\sigma_a + 2p\sigma_b)$$

$$\zeta_{1s} = 8.65, \quad \zeta_{2s} = 2.58, \quad \zeta_{2p\sigma} = 2.49$$

$$E_{\text{total}} = -197.877 \text{ hartrees}$$

b) using an extended basis set:

$$3\sigma_{g,\text{ext}} = 0.048(1s_a + 1s_b) + 0.003(1s'_a + 1s'_b) - 0.257(2s_a + 2s_b) \\ + 0.582(2p\sigma_a + 2p\sigma_b) + 0.307(2p\sigma'_a + 2p\sigma'_b) + 0.085(2p\sigma''_a + 2p\sigma''_b) \\ - 0.056(3s_a + 3s_b) + 0.046(3d\sigma_a + 3d\sigma_b) + 0.014(4f\sigma_a + 4f\sigma_b)$$

$$\zeta_{1s} = 8.27, \quad \zeta_{1s'} = 13.17, \quad \zeta_{2s} = 2.26$$

$$\zeta_{2p\sigma} = 1.85, \quad \zeta_{2p\sigma'} = 3.27, \quad \zeta_{2p\sigma''} = 5.86$$

$$\zeta_{3s} = 4.91, \quad \zeta_{3d\sigma} = 2.44, \quad \zeta_{4f\sigma} = 2.83$$

$$E_{\text{total}} = -198.768 \text{ hartrees}$$

$$E_{\text{exp}} = -199.670 \text{ hartrees}$$

$$\text{the correlation energy} \approx -0.90 \text{ hartrees} = -24.5 \text{ eV.}$$

- $E_{\text{tot}} = -197.877\text{Eh}$ and -198.768Eh for the minimal and extended calculations, respectively
- Extrapolation to larger basis sets: $E_{\text{HF}}(R_e) = -198.773\text{Eh}$
- The experimental energy at R_e : $U(R_e) = -199.672\text{Eh}$.
- The correlation-energy definition: nonrelativistic E of the molecule - E_{HF} .
- The relativistic contribution to E of F_2 calculated: -0.142Eh ,
- exact nonrelativistic E at R_e : $-199.672\text{Eh} + 0.142\text{Eh} = -199.530\text{Eh}$.
- Therefore, the correlation energy in F_2 is $-199.530\text{Eh} + 198.773\text{Eh} = -0.757\text{Eh} = -20.6\text{ eV}$.

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one needs more than one STO of a given n and l in the linear combination of STOs that is to accurately represent the Hartree-Fock MO.

$$(2p\sigma_a + 2p\sigma_b) \quad (2p\sigma'_a + 2p\sigma'_b) \quad (2p\sigma''_a + 2p\sigma''_b)$$

STOs with different orbital exponents

$$(3d\sigma_a + 3d\sigma_b) \quad (4f\sigma_a + 4f\sigma_b)$$

AOs with quantum number $m = 0$, that is, the $3d_0$ and $4f_0$ AOs

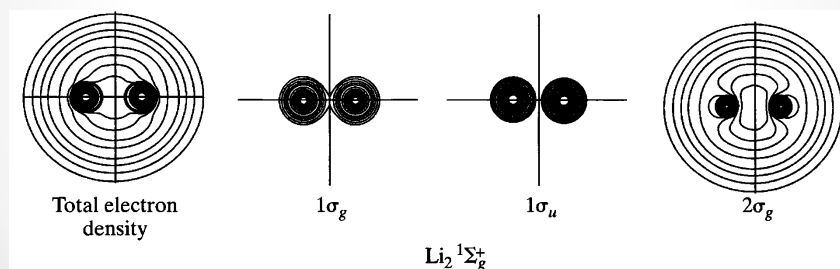
The SCF calculations make clear that all MOs are hybridized to some extent. Thus any diatomic-molecule σ MO is a linear combination of $1s$, $2s$, $2p_0$, $3s$, $3p_0$, $3d_0$, ... AOs of the separated atoms.

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which AOs contribute to a given diatomic MO?

- 1) only σ -type AOs (s, p σ , d σ ,...) can contribute to a σ MO; only π -type AOs (p π , d π ,...) can contribute to a π MO; and so on.
- 2) only AOs of reasonably similar energy contribute substantially to a given MO.



Hartree-Fock MO electron-density contours for the ground electronic state of Li_2 as calculated by Wahl.

Hartree-Fock wave functions are **only approximations to the true wave functions**.

- ✓ a HF wave function gives a **very good approximation** to the **electron probability density** $\rho(x,y,z)$ for equilibrium configuration.
- ✓ A molecular property that **involves only one-electron operators** can be expressed **as an integral involving ρ** . Consequently, such properties are **accurately calculated** using HF wave functions (For example, the molecular **dipole moment**).

LiH :

with a near HF ψ : dipole moment = 6.00 D (experimental value = 5.83 D)

NaCl :

the calculated value = 9.18 D (experimental value 9.02 D)

- ✓ An error of about 0.2 D is typical in such calculations, but **where the dipole moment is small, the percent error can be large**.

CO :

(experimental moment = 0.11 D with the polarity C^-O^+ , the near-HF moment = 0.27 D with the wrong polarity C^+O^-).

- a CI wave function gives 0.12 D with the correct polarity

A major weakness of the Hartree-Fock method is its failure to give accurate molecular dissociation energies.

N_2 :
HF $D_e = 5.3$ eV by an extended-bs (true value = 9.9 eV)

F_2 :
HF $D_e = -1.4$ eV (true $D_e = 1.66$ eV)

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MO TREATMENT OF HETERONUCLEAR DIATOMIC MOLECULES

The treatment is similar to that for homonuclear diatomic molecules.

Suppose: atomic numbers differ only slightly (CO)

CO : isoelectronic with N_2

gradual transfer of charge from one nucleus to the other.

the original N_2 MOs would slowly vary to give finally the CO MOs.

\hat{H}_{el} does not commute with $\hat{\Pi}$ (g, u property of the MOs disappears)

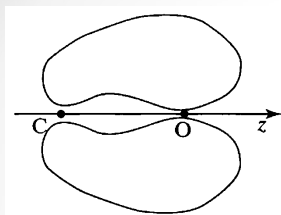
N_2	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$1\pi_u$	$3\sigma_g$	$1\pi_g$	$3\sigma_u$
CO	1σ	2σ	3σ	4σ	1π	5σ	2π	6σ

$$5\sigma = 0.027(1s_C) + 0.011(1s_O) + 0.739(2s_{\perp C}) + 0.036(2s_{\perp O}) \\ - 0.566(2p\sigma_C) - 0.438(2p\sigma_O)$$

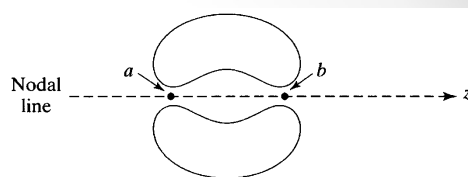
$$1\pi = 0.469(2p\pi_C) + 0.771(2p\pi_O), \quad 2\pi = 0.922(2p\pi_C) - 0.690(2p\pi_O)$$

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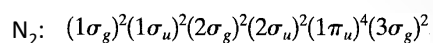
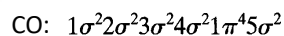


Cross section of a contour of the $1\pi_{\pm 1}$ MOs in CO, determined by an extended-basis-set SCF calculation



Cross section of the $\pi_u 2p_{+1}$ (or $\pi_u 2p_{-1}$) molecular orbital.

The ground-state configuration:



MOs are approximated as LCAOs. The coefficients are found by solving the Roothaan equations

$$\sum_{s=1}^b c_{si} (F_{rs} - \epsilon_i S_{rs}) = 0, \quad r = 1, 2, \dots, b$$

By a minimal-basis-set SCF calculation using Slater AOs (with nonoptimized exponents given by Slater's rules) for CO:

$$5\sigma = 0.027(1s_C) + 0.011(1s_O) + 0.739(2s_{\perp C}) + 0.036(2s_{\perp O}) \\ - 0.566(2p\sigma_C) - 0.438(2p\sigma_O)$$

$$1\pi = 0.469(2p\pi_C) + 0.771(2p\pi_O),$$

$$2\pi = 0.922(2p\pi_C) - 0.690(2p\pi_O)$$

π MOs are simpler than σ MOs

corresponding MOs in N_2 at $R = R_e$:

$$3\sigma_g = 0.030(1s_a + 1s_b) + 0.395(2s_{\perp a} + 2s_{\perp b}) \\ - 0.603(2p\sigma_a + 2p\sigma_b)$$

$$1\pi_u = 0.624(2p\pi_a + 2p\pi_b)$$

$$1\pi_g = 0.835(2p\pi_a - 2p\pi_b)$$

1σ MO in CO \sim $1s$ oxygen-atom AO

2σ MO in CO \sim $1s$ carbon-atom AO.

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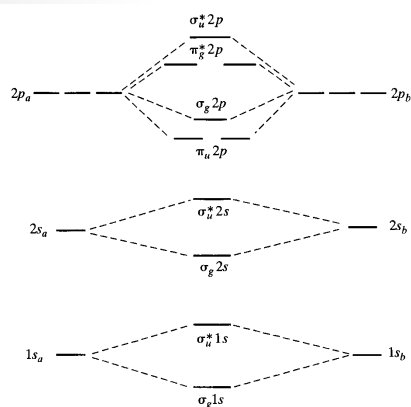
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for **AB**, where the valence AOs :

- ✓ are of s and p type
- ✓ of A do not differ greatly in energy from the valence AOs of B

$$\sigma s < \sigma^* s < \pi p < \sigma p < \pi^* p < \sigma^* p$$

Homonuclear diatomic



Heteronuclear diatomic

each valence AO of the more electronegative atom would lie below the corresponding valence AO of the other atom.



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When the s and p σ valence AOs of B lie below the s valence-shell AO of A:
this affects which AOs contribute to each MO

the molecule BF by a minimal-basis-set calculation:

- ✓ $1\sigma \sim 1s_F$
- ✓ $2\sigma \sim 1s_B$
- ✓ $3\sigma \sim$ predominantly $2s_F$, with small amounts of $2s_B$, $2p\sigma_B$, and $2p\sigma_F$.
- ✓ $4\sigma \sim$ predominantly $2p\sigma_F$, with significant amounts of $2s_B$ and $2s_F$ and a small amount of $2p\sigma_B$
- ✓ $1\pi \sim$ a bonding combination of $2p\pi_B$ and $2p\pi_F$
- ✓ $5\sigma \sim$ predominantly $2s_B$, with a substantial contribution from $2p\sigma_B$ and a significant contribution from $2p\sigma_F$
- ✓ $2\pi \sim$ an antibonding combination of $2p\pi_B$ and $2p\pi_F$.
- ✓ $6\sigma \sim$ important contributions from $2p\sigma_B$, $2s_B$, $2s_F$, and $2p\sigma_F$.

$2p_F$ AO lies well below the $2s_B$ AO, thus:

- ✓ $2p\sigma_F$ AO contribute substantially to lower-lying MOs
- ✓ $2s_B$ AO contribute substantially to higher-lying MOs

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CO:

4σ : very substantial contribution from $2p\sigma_O$

5σ : very substantial contribution from $2s_C$

For AB where each atom has s and p valence-shell AOs and the A and B valence AOs differ widely in energy

$$\sigma < \sigma < \pi < \sigma < \pi < \sigma$$

but it is not so easy to guess which AOs contribute to the various MOs or the bonding or antibonding character of the MOs.

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Diatomic hydrides: H has only a 1s valence AO

HF:

1) a crude qualitative approximation

ground-state configurations, 1s for H and $1s^2 2s^2 2p^5$ for F

1s and 2s F : take little part in the bonding.

2p F electrons are nonbonding

1s AO of H and 2p σ AO of F have the same symmetry (σ) and similar energies, and a linear combination of these two AOs will form a σ MO for the bonding electron pair:

$$\phi = c_1(1s_H) + c_2(2p\sigma_F)$$

F is more electronegative than H, we expect that $c_2 > c_1$.

2) A minimal- basis-set SCF calculation using Slater orbitals with optimized exponents:

$$\begin{aligned} 1\sigma &= 1.000(1s_F) + 0.012(2s_{\perp F}) + 0.002(2p\sigma_F) - 0.003(1s_H) \\ 2\sigma &= -0.018(1s_F) + 0.914(2s_{\perp F}) + 0.090(2p\sigma_F) + 0.154(1s_H) \\ 3\sigma &= -0.023(1s_F) - 0.411(2s_{\perp F}) + 0.711(2p\sigma_F) + 0.516(1s_H) \\ 1\pi_{+1} &= (2p\pi_{+1})_F \\ 1\pi_{-1} &= (2p\pi_{-1})_F \end{aligned}$$

The ground-state configuration of HF : $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4$

Since a single 2s function is only an approximation to the 2s AO of F, we cannot use this calculation to say exactly how much 2s AO character the 3σ HF molecular orbital has.

heteronuclear diatomic molecules:

Accurate MO expressions : the solution of the Roothaan equations
In the crudest approximation: valence MO \approx a linear combination of two AOs

$$c_1\phi_a + c_2\phi_b \quad \text{and} \quad c'_1\phi_a + c'_2\phi_b$$

two AOs, one on each atom

coefficients are not equal (lack of symmetry)

The coefficients are determined by solving the secular equation

$$\begin{vmatrix} H_{aa} - W & H_{ab} - WS_{ab} \\ H_{ab} - WS_{ab} & H_{bb} - W \end{vmatrix} = 0$$

$$\underbrace{(H_{aa} - W)(H_{bb} - W) - (H_{ab} - WS_{ab})^2}_{f(W)} = 0$$

- \hat{H} is some sort of effective one-electron Hamiltonian

Suppose that $H_{aa} > H_{bb}$,

S_{ab} is less than 1 (except at $R = 0$).

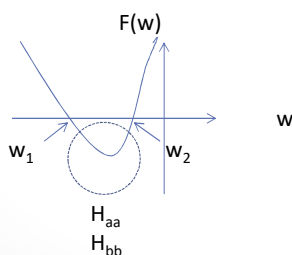
The coefficient of W^2 in $f(W)$ is $(1 - S_{ab}) > 0 \rightarrow f(\infty) = f(-\infty) = +\infty > 0$.

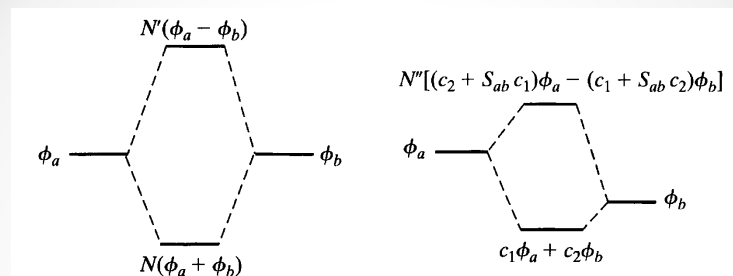
$W = H_{aa}$ or $H_{bb} \rightarrow (H_{aa} - W)(H_{bb} - W) - (H_{ab} - WS_{ab})^2 = 0 \rightarrow f(H_{aa}) < 0$ and $f(H_{bb}) < 0$.

zero

The roots occur where $f(W)$ equals 0

Therefore, the orbital energy of one MO is less than both H_{aa} and H_{bb} and the energy of the other MO is greater than both H_{aa} and H_{bb} .





Formation of bonding and antibonding MOs from AOs in the homonuclear and heteronuclear cases.

These figures are gross oversimplifications, since a given MO has contributions from many AOs

VB TREATMENT OF HETERONUCLEAR DIATOMIC MOLECULES

valence-bond ground state wave function of HF:

The Heitler-London function corresponding to pairing hydrogen 1s electron and 2p σ electron.

$$\phi_{\text{cov}} = |\cdots 1s_H \overline{2p\sigma_F}| - |\cdots \overline{1s_H} 2p\sigma_F|$$

$$\cdots \equiv 1s_F \overline{1s_F} 2s_F \overline{2s_F} 2p\pi_{xF} \overline{2p\pi_{xF}} 2p\pi_{yF} \overline{2p\pi_{yF}}$$

essentially covalent

An ionic valence-bond function has the form $\phi_a(1)\phi_a(2)$

$$\phi_{\text{ion}} = |\cdots 2p\sigma_F \overline{2p\sigma_F}|$$

The VB wave function is then written as

$$\phi = c_1\phi_{\text{cov}} + c_2\phi_{\text{ion}}$$

c_1 and c_2 are found by the variation method

We have ionic-covalent "resonance," involving the structures H-F and H^+F^- .

A term $c_3 |1s_H \overline{1s_H}|$ corresponding to the ionic structure $H^- F^+$ could also be included in the wave function (only slightly)

NaCl (highly ionic molecule):

we expect $c_2 \gg c_1$

$NaCl \xrightarrow{R \rightarrow \infty} Na + Cl$ in the gas phase

$NaCl \xrightarrow{R \rightarrow \infty} Na^+ + Cl^-$ in aqueous solution

$IP(Na) = 5.1 \text{ eV}$, $ea(Cl) = 3.6 \text{ eV}$.

$R \uparrow \rightarrow c_2/c_1 \downarrow$ (becoming zero at $R = \infty$)

For **intermediate R**, the Coulombic attraction between the ions $> 1.5 \text{ eV}$ (difference between the ionization potential and electron affinity)

For **very large R**, the Coulombic attraction between the ions $< 1.5 \text{ eV}$ if the nuclei are pulled apart very rapidly, ..., giving dissociation into ions.

Cs: the lowest ionization potential, 3.9 eV.

Cl: the highest ea, 3.6 eV.

F: $ea = 3.45 \text{ eV}$

$CsCl \rightarrow Cs + Cl$

$CsF \rightarrow Cs + F$

There are cases of excited states of diatomic molecules that dissociate to ions.

THE VALENCE-ELECTRON APPROXIMATION

Cs_2 , which has 110 electrons

In the MO method:

110 X 110 Slater determinant of molecular orbitals

↓
MOs ~ functions containing variational parameters

minimize the variational integral

the valence-electron approximation:

108 core electrons + two 6s valence electrons

molecular energy = core- and valence-electron energies.

1) core electrons \equiv point charges coinciding with the nucleus.

Hamiltonian (for Cs_2) = Hamiltonian for H_2

↓
minimize the variational integral
no restrictions on the valence-electron trial functions,

valence-electrons' MO to "collapse" to the $\sigma_g 1s$ MO

↓
Constraint: variational functions used for the valence electrons be orthogonal to the orbitals of the core electrons.

more work

2) core electrons are treated as a charge distribution (effective repulsive potential for the motion of the valence electrons).

effective Hamiltonian for the valence electrons

The valence-electron approximation is widely used in approximate treatments of polyatomic molecules