

## Molecular Orbital (MO) Theory of the H<sub>2</sub> molecule:

Following the MO treatment of H<sub>2</sub><sup>+</sup>, assume the (normalized) ground electronic state wavefunction is given by:

$$\Psi_{gs} = \psi_+(1)\psi_+(2) [\alpha(1)\beta(2) - \beta(2)\alpha(1)] / \sqrt{2}$$

with:

$$\psi_+(1)\psi_+(2) = \frac{1}{2(1+S)} [1s_A(1) + 1s_B(1)][1s_A(2) + 1s_B(2)] \equiv \psi(\vec{r}_1, \vec{r}_2)$$

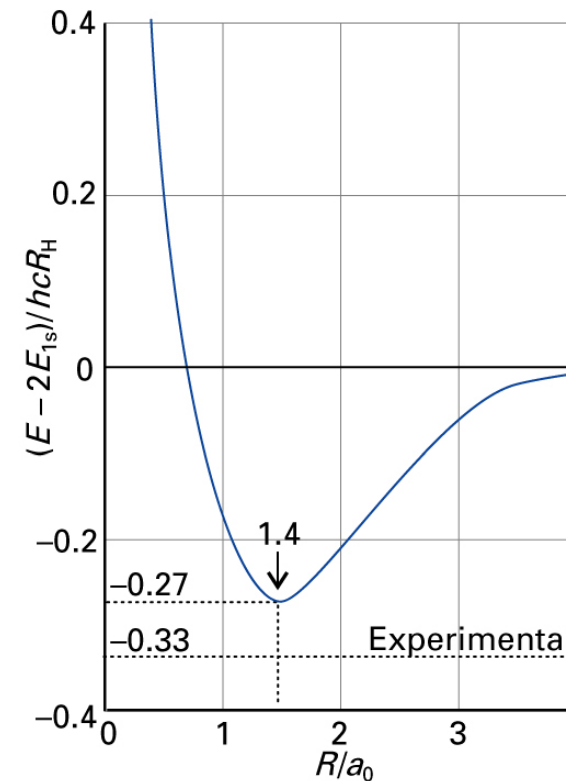
Evaluate the ground state electronic energy based on this presumed (approximate) eigenfunction:

$$E_{gs} = \int d\vec{r}_1 d\vec{r}_2 \psi(\vec{r}_1, \vec{r}_2) H_{el} \psi(\vec{r}_1, \vec{r}_2) = 2E_{1s} + \frac{j_0}{R} - \frac{2j' + 2k'}{1+S} + \frac{j + 2k + m + 4l}{2(1+S)^2}$$

with: 
$$j_0 \equiv \frac{e_0^2}{4\pi\epsilon_0}$$

... and  $j'(R)$ ,  $k'(R)$ ,  $m(R)$ ,  $l(R)$  defined explicitly in Atkins.

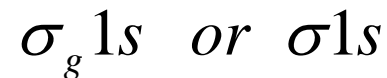
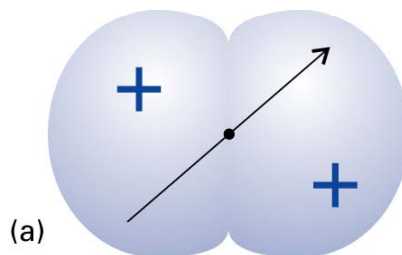
Here is the result obtained  
For  $E_{gs}(R)$  via Eq. [1]:



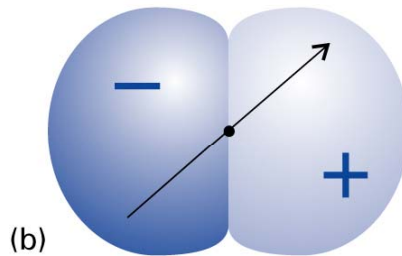
## Configuration Interaction:

Within the two basis orbital approximation, the following electronic configurations are possible:

- 1) Two electrons in Molecular Orbital  $\psi_+$
- 2) One electron in MO  $\psi_+$  and one electron in MO  $\psi_-$
- 3) Two electrons in MO  $\psi_-$ .



Point of notation:



Spin-orbitals of type 1 and 3 have the same symmetry, and therefore can “mix” (to give improved wavefunctions and energy eigenvalues):

$$\Psi_1 = \psi_+(1)\psi_+(2)[\alpha(1)\beta(2) - \beta(2)\alpha(1)] / \sqrt{2}$$

$$\Psi_2 = \psi_+(1)\psi_+(2)[\alpha(1)\beta(2) - \beta(2)\alpha(1)] / \sqrt{2}$$

Consider the trial wavefunction:

$$\Psi_{tr} = c_1\Psi_1 + c_2\Psi_2 \quad [1]$$

Inserting this trial function into the Raleigh-Ritz Variational Principle ...

we will determine (c1,c2) that minimize the expectation value of the Electronic Hamiltonian operator with this trial function. This will provide us with improved values of the ground state energy (which must be lowered by this variational calculation) and the ground state energy eigenfunction.

Note the flexibility of the trial (spatial) wavefunction. Modulo normalization:

$$c_1\psi_+(1)\psi_+(2) + c_2\psi_-(1)\psi_-(2)$$

$$= c_1[1s_A(1) + 1s_B(1)][1s_A(2) + 1s_B(2)] + c_2[1s_A(1) - 1s_B(1)][1s_A(2) - 1s_B(2)]$$

Note the reductions for specific  $c_1, c_2$  coefficient choices:

$$c_1 = 1, c_2 = -1 \Rightarrow 1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)$$

Covalent bonding  
configuration

$$c_1 = 1, c_2 = 1 \Rightarrow 1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)$$

Ionic bonding  
configuration

Thus, the trial function  $\psi_{tr}$  in Eq. [1] confers considerable additional flexibility to the wavefunction shape, hence leading to a more accurate solution of the Schrodinger Eq.

## Performance of various level of electronic structure theory for H<sub>2</sub>:

TABLE 9-1  
Results of Various Calculations for H<sub>2</sub>

	Wave function	Effective nuclear charge	Total energy/au	Dissociation energy/au	Bond length/au	Vibrational frequency/10 <sup>3</sup> cm <sup>-1</sup>
(VB) <sup>a</sup>	1s <sub>A</sub> (1)1s <sub>B</sub> (2) + 1s <sub>B</sub> (1)1s <sub>A</sub> (2)	1.000	-1.1160	0.1160	1.64	4.08
(VB) <sup>b</sup>	1s <sub>A</sub> (1)1s <sub>B</sub> (2) + 1s <sub>B</sub> (1)1s <sub>A</sub> (2)	1.166	-1.1389	0.1389	1.39	4.18
(MO) <sup>c</sup>	[1s <sub>A</sub> (1) + 1s <sub>B</sub> (1)][1s <sub>A</sub> (2) + 1s <sub>B</sub> (2)]	1.000	-1.0990	0.0990	1.61	4.16
(MO) <sup>c</sup>	[1s <sub>A</sub> (1) + 1s <sub>B</sub> (1)][1s <sub>A</sub> (2) + 1s <sub>B</sub> (2)]	1.197	-1.1282	0.1282	1.38	4.58
	Hartree-Fock <sup>d</sup>	—	-1.1336	0.1336	1.40	—
(VB + ionic) <sup>e</sup>	c[1s <sub>A</sub> (1)1s <sub>B</sub> (2) + 1s <sub>B</sub> (1)1s <sub>A</sub> (2)] + [1s <sub>A</sub> (1)1s <sub>A</sub> (2) + 1s <sub>B</sub> (1)1s <sub>B</sub> (2)]	1.000	-1.1187	0.1187	1.67	—
(VB + ionic) <sup>e</sup>	c[1s <sub>A</sub> (1)1s <sub>B</sub> (2) + 1s <sub>B</sub> (1)1s <sub>A</sub> (2)] + [1s <sub>A</sub> (1)1s <sub>A</sub> (2) + 1s <sub>B</sub> (1)1s <sub>B</sub> (2)]	1.193	-1.1478	0.1478	1.43	4.75
(VB) <sup>f</sup>	φ <sub>A</sub> (1)φ <sub>B</sub> (2) + φ <sub>B</sub> (1)φ <sub>A</sub> (2) φ = 1s + λ2p <sub>z</sub>	1.19	-1.1484	0.1484	1.416	—
(VB + ionic) <sup>e</sup>	c[φ <sub>A</sub> (1)φ <sub>B</sub> (2) + φ <sub>B</sub> (1)φ <sub>A</sub> (2)] + [1s <sub>A</sub> (1)1s <sub>A</sub> (2) + 1s <sub>B</sub> (1)1s <sub>B</sub> (2)]	1.190	-1.1514	0.1514	1.41	—
	φ = 1s + λ2p <sub>z</sub>					
	Equation 9-95 13 terms <sup>g</sup>		-1.1735	0.1735	1.40	—
	Equation 9-95 100 terms <sup>h</sup>	1.072	-1.174475	0.174475	1.40	—
	MO-CI 28 configurations <sup>i</sup>		-1.16724	0.16724	1.40	4.385
	experimental <sup>j</sup>		-1.174	0.174	1.4006	4.401

<sup>a</sup> W. Heitler and F. London, Z. Physik 44, 455 (1927).

<sup>b</sup> S. C. Wang, Phys. Rev. 31, 579 (1928).

<sup>c</sup> C. A. Coulson, Trans. Far. Soc. 33, 1479 (1937).

<sup>d</sup> W. Kolos and C. C. J. Roothaan, Rev. Mod. Phys. 32, 219 (1960).

<sup>e</sup> S. Weinbaum, J. Chem. Phys. 1, 593 (1933).

<sup>f</sup> N. Rosen, Phys. Rev. 38, 2099 (1931).

<sup>g</sup> H. M. James and A. S. Coolidge J. Chem. Phys. 1, 825 (1933).

<sup>h</sup> W. Kolos and L. Wolniewicz, J. Chem. Phys. 41, 3663 (1964); 49, 404 (1968).

<sup>i</sup> S. Hagstrom and H. Shall, Rev. Mod. Phys. 35, 624 (1963).

<sup>j</sup> G. Herzberg, J. Mol. Spectroscopy 33, 147 (1970).

See also A. D. McLean, A. Weiss, and M. Yoshimine, Rev. Mod. Phys. 32, 211 (1960).

[D.A. McQuarrie, Quantum Chemistry]

Testing qualitative MO theory prediction of Bond Order with experiment for homonuclear diatomics made from elements in the 1<sup>st</sup> row of the Periodic Table (using the “Molecular Orbital Aufbau” principle):

$$\text{Bond Order} \equiv [\# \text{bonding } e' s - \# \text{antibonding } e' s] / 2$$

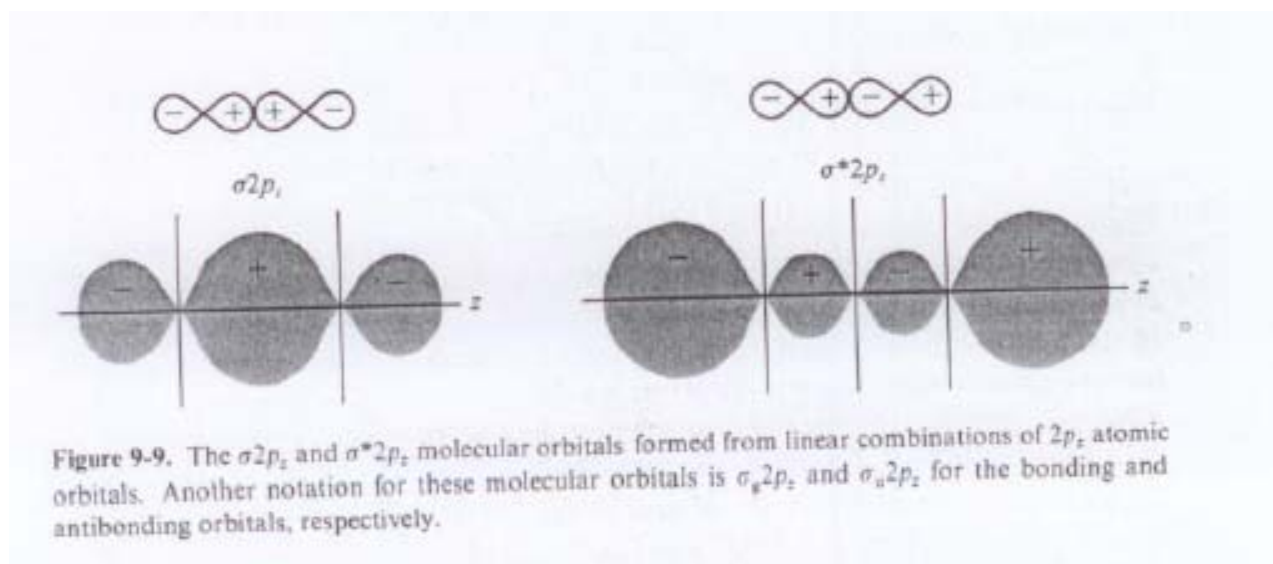
TABLE 9-2  
Molecular Properties of  $H_2^+$ ,  $H_2$ ,  $He_2^+$ , and  $He_2$ .

Species	Number of electrons	Ground-state electron configuration	Bond order	Bond length/pm	Bond energy/ $\text{kJ} \cdot \text{mol}^{-1}$
$H_2^+$	1	$(\sigma 1s)^1$	$\frac{1}{2}$	106	255
$H_2$	2	$(\sigma 1s)^2$	1	74	431
$He_2^+$	3	$(\sigma 1s)^2(\sigma^* 1s)^1$	$\frac{1}{2}$	108	251
$He_2$	4	$(\sigma 1s)^2(\sigma^* 1s)^2$	0	Not observed	

[D.A. McQuarrie, *Quantum Chemistry*]

Going to the 2<sup>nd</sup> row of the Periodic Table ... need to build up MO's from the 2<sup>nd</sup> Lewis Shell:

$p_z$  orbitals can also be "added and subtracted" to form g=gerade and u=ungerade combinations:

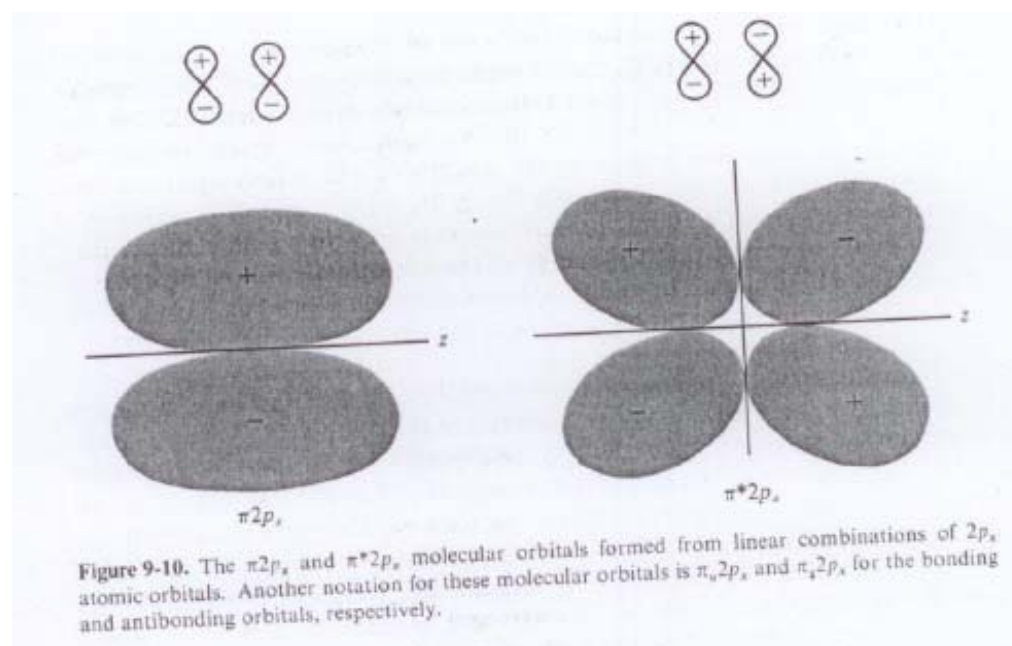


[D.A. McQuarrie, *Quantum Chemistry*]



$p_x$  and  $p_y$  orbitals can also be “added and subtracted” to form g=gerade and u=ungerade combinations:

ungerade →



← gerade

[D.A. McQuarrie, *Quantum Chemistry*]

Qualitative MO theory orbital diagram for homonuclear diatomics composed of 1<sup>st</sup> or 2<sup>nd</sup> row elements:

difficult to distinguish the ordering of these MOs: {

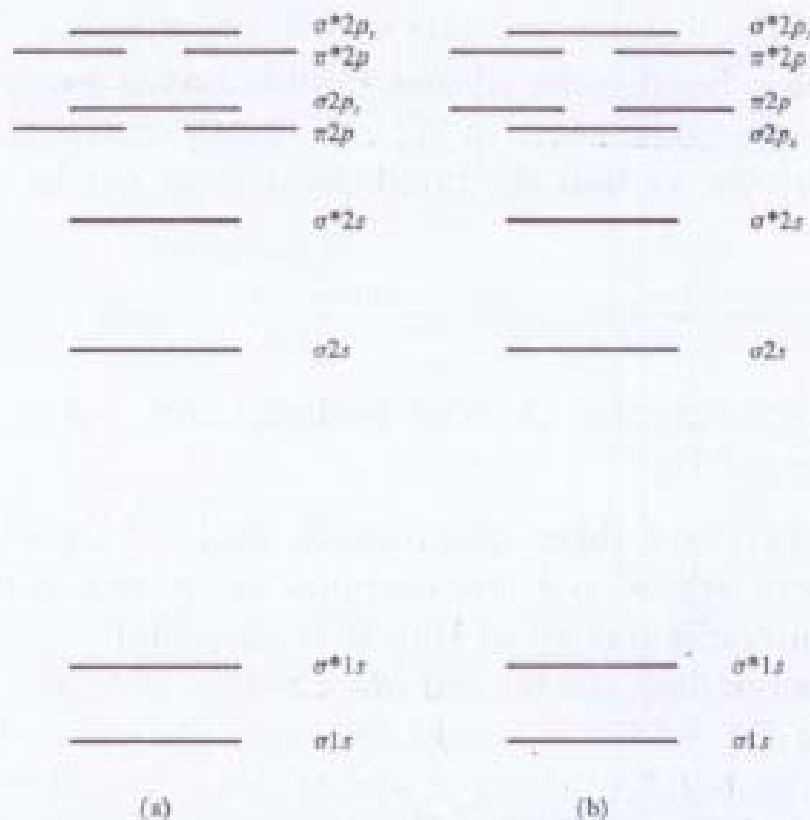


Figure 9-11. Two possible energy-level diagrams for homonuclear diatomic molecules. The separation between the  $\pi_{2p}^*$  and  $\sigma_{2p}^*$  orbitals not only is very small but varies with the atomic number of the nuclei and the internuclear separation. Thus, it is difficult to know beforehand which scheme applies to a given homonuclear diatomic molecule.

[D.A. McQuarrie, *Quantum Chemistry*]

Testing qualitative MO theory prediction of Bond Order with experiment for homonuclear diatomics made from elements in the 2<sup>st</sup> row of the Periodic Table:

TABLE 9-3  
Properties of the Diatomic Molecules  
of Elements in the Second Row of the Periodic Table

<i>Species</i>	<i>Ground-state electron configuration</i>	<i>Bond order</i>	<i>Bond length/pm</i>	<i>Bond energy/ kJ·mol<sup>-1</sup></i>
Li <sub>2</sub>	$KK(\sigma 2s)^2$	1	267	105
Be <sub>2</sub>	$KK(\sigma 2s)^2(\sigma^* 2s)^2$	0	Not observed	
B <sub>2</sub>	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^2$	1	159	289
C <sub>2</sub>	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4$	2	124	599
N <sub>2</sub>	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p_z)^2$	3	110	942
O <sub>2</sub>	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p_z)^2(\pi^* 2p)^2$	2	121	494
F <sub>2</sub>	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p_z)^2(\pi^* 2p)^4$	1	141	154
Ne <sub>2</sub>	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p_z)^2(\pi^* 2p)^4(\sigma^* 2p_z)^2$	0	Not observed	

[D.A. McQuarrie, *Quantum Chemistry*]

## Qualitative MO theory for Heteronuclear Diatomics:

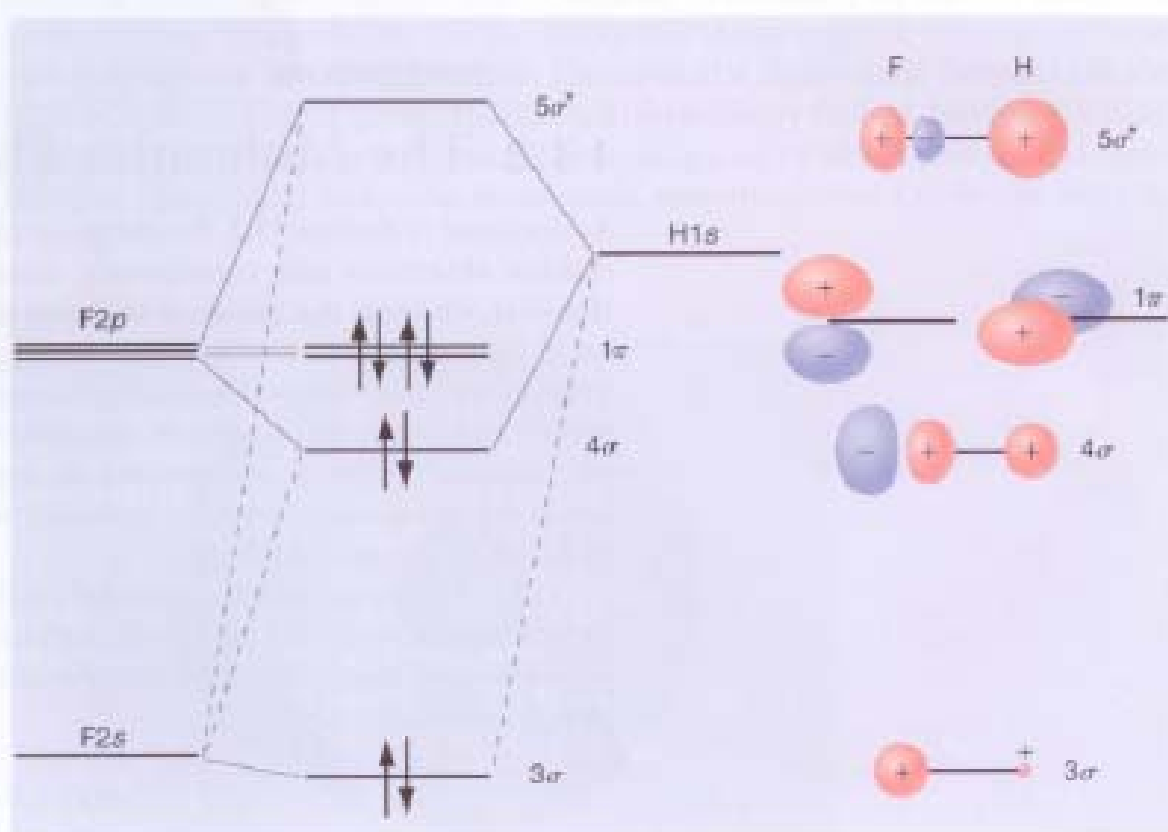
Note: Now the AO's of the two atoms do not line up symmetrically. They have to be carefully aligned, energetically, and then decisions made as to which AO's mix strongly to form MO's.

**FIGURE 13.12**

Schematic energy diagram showing the relationship between the atomic and molecular orbital energy levels for the valence electrons in HF. The degenerate  $p$  and  $\pi$  orbitals are shown slightly offset in energy. The dominant atomic orbital contributions to the MOs are shown as solid lines. Lesser contributions are shown as dashed lines. The MOs are depicted to the right of the figure.

Example: HF

Note: Bond order = 1



[T. Engel, *Quantum Chemistry & Spectroscopy*]