Molecular Orbital (MO) Theory of the H2 molecule:

Following the MO treatment of H2+, 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:

$$\psi_+(1)\psi_+(2) = \frac{1}{2(1+S)} \left[1s_A(1) + 1s_B(1)\right] \left[1s_A(2) + 1s_B(2)\right] \equiv \psi(r_1, r_2)$$
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: \( j_0 \equiv \frac{e_0^2}{4\pi\varepsilon_0} \)

... 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]:

\( E_{gs}(R) \) versus \( R/a_0 \)
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:

$\sigma_g 1s \quad or \quad \sigma 1s$

$\sigma_u 1s \quad or \quad \sigma^* 1s$
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:

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

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

we will determine \( (c_1,c_2) \) 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:

\[ c_1 \psi_+ (1) \psi_+ (2) + c_2 \psi_- (1) \psi_- (2) \]

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

Note the reductions for specific \( c_1, c_2 \) coefficient choices:

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

Covalent bonding configuration

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

Ionic bonding configuration

Thus, the trial function \( \psi_{\text{tr}} \) 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 H2:

<table>
<thead>
<tr>
<th>Wave function</th>
<th>Effective nuclear charge</th>
<th>Total energy/au</th>
<th>Dissociation energy/au</th>
<th>Bond length/au</th>
<th>Vibrational frequency/10^3 cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>(VB)¹</td>
<td>1sₓ(1)1sᵧ(2) + 1sₓ(1)1sᵧ(2)</td>
<td>1.000</td>
<td>-1.1160</td>
<td>0.1160</td>
<td>1.64</td>
</tr>
<tr>
<td>(VB)²</td>
<td>1sₓ(1)1sᵧ(2) + 1sₓ(1)1sᵧ(2)</td>
<td>1.166</td>
<td>-1.1389</td>
<td>0.1389</td>
<td>1.39</td>
</tr>
<tr>
<td>(MO)³</td>
<td>[1sₓ(1) + 1sᵧ(1)][1sₓ(2) + 1sᵧ(2)]</td>
<td>1.000</td>
<td>-1.0990</td>
<td>0.0990</td>
<td>1.61</td>
</tr>
<tr>
<td>(MO)⁴</td>
<td>[1sₓ(1) + 1sᵧ(1)][1sₓ(2) + 1sᵧ(2)]</td>
<td>1.197</td>
<td>-1.1282</td>
<td>0.1282</td>
<td>1.38</td>
</tr>
<tr>
<td>Hartree-Fock</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(VB + ionic)⁵</td>
<td>c[1sₓ(1)1s₋(2) + 1sₓ(1)1s₋(2)]</td>
<td>1.000</td>
<td>-1.1187</td>
<td>0.1187</td>
<td>1.67</td>
</tr>
<tr>
<td>(VB + ionic)⁶</td>
<td>c[1sₓ(1)1s₋(2) + 1sₓ(1)1s₋(2)]</td>
<td>1.193</td>
<td>-1.1478</td>
<td>0.1478</td>
<td>1.43</td>
</tr>
<tr>
<td>(VB)⁷</td>
<td>ϕₓ(1)ϕₓ(2) + ϕₓ(1)ϕ₋(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ϕ = 1s + λ2pₓ</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(VB + ionic)⁸</td>
<td>c[ϕₓ(1)ϕₓ(2) + ϕₓ(1)ϕ₋(2)]</td>
<td>1.190</td>
<td>-1.1514</td>
<td>0.1514</td>
<td>1.41</td>
</tr>
<tr>
<td>Equation 9.95 13 terms⁹</td>
<td></td>
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<tr>
<td>Equation 9.95 100 terms¹⁰</td>
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<tr>
<td>MO-Cl 28 configurations¹¹</td>
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<tr>
<td>Experimental¹²</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

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¹⁹ See also A. D. McLean, A. Weiss, and M. Yoshimine, Rev. Mod. Phys. 32, 211 (1960).
Testing qualitative MO theory prediction of Bond Order with experiment for homonuclear diatomics made from elements in the 1\textsuperscript{st} row of the Periodic Table (using the “Molecular Orbital Aufbau” principle):

\[
\text{Bond Order} = \left[ \# \text{bonding e'}s - \# \text{antibonding e'}s \right] / 2
\]

<table>
<thead>
<tr>
<th>Species</th>
<th>Number of electrons</th>
<th>Ground-state electron configuration</th>
<th>Bond order</th>
<th>Bond length/pm</th>
<th>Bond energy/\text{kJ}\cdot\text{mol}\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H_2^+)</td>
<td>1</td>
<td>((\sigma 1s)^1)</td>
<td>(\frac{1}{2})</td>
<td>106</td>
<td>255</td>
</tr>
<tr>
<td>(H_2)</td>
<td>2</td>
<td>((\sigma 1s)^2)</td>
<td>1</td>
<td>74</td>
<td>431</td>
</tr>
<tr>
<td>(He_2^+)</td>
<td>3</td>
<td>((\sigma 1s)^2(\sigma^* 1s)^1)</td>
<td>(\frac{1}{2})</td>
<td>168</td>
<td>251</td>
</tr>
<tr>
<td>(He_2)</td>
<td>4</td>
<td>((\sigma 1s)^2(\sigma^* 1s)^2)</td>
<td>0</td>
<td>Not observed</td>
<td></td>
</tr>
</tbody>
</table>

[D.A. McQuarrie, Quantum Chemistry]
Going to the 2\textsuperscript{nd} row of the Periodic Table ... need to build up MO’s from the 2\textsuperscript{nd} Lewis Shell:

p\textsubscript{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:

[Figure 9-10. The \( \pi 2p_z \) and \( \pi^* 2p_z \) molecular orbitals formed from linear combinations of \( 2p_z \) atomic orbitals. Another notation for these molecular orbitals is \( \pi_1 2p_z \) and \( \pi_2 2p_z \) for the bonding and antibonding orbitals, respectively.]

[D.A. McQuarrie, Quantum Chemistry]
Qualitative MO theory orbital diagram for homonuclear diatomics composed of 1\textsuperscript{st} or 2\textsuperscript{nd} row elements:

difficult to distinguish the ordering of these MOs: 

[D.A. McQuarrie, Quantum Chemistry]
Testing qualitative MO theory prediction of Bond Order with experiment for homonuclear diatomics made from elements in the 2nd row of the Periodic Table:

![Table 9-3](image)

[D.A. McQuarrie, Quantum Chemistry]
Qualitative MO theory for Heternuclear Diatomics:

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

**Example:** HF

**Note:** Bond order = 1

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