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 \( H_2^+ \) \( \sigma \) states,

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

three lowest \( m = 0 \) hydrogenlike functions

For the symmetry of the homonuclear diatomic molecule

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

\( + \): even (g) states

\( _{-} \): odd (u) states
The relative magnitudes of the coefficients:

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

\[ c_1 \gg c_2 \text{ and } c_3 \]

\( c_2 \text{ and } c_3 \text{ vanish in the limit of } R \text{ going to infinity} \)

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

As a first approximation,

\[
\phi = c_1 (1s_a \pm 1s_b)
\]

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.

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

\[ c_2 \gg c_1 \text{ and } c_3 \]

\( c_1 \text{ and } c_3 \text{ vanish in the limit of } R \text{ going to infinity} \)

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

As a first approximation,

\[
\phi = c_2 (2s_a \pm 2s_b)
\]

LCAO functions

To find rigorous upper bounds to the energies of these two \( \text{H}_2^+ \) states, we must use the upper trial function and solve the appropriate secular equation

contour diagrams
\[ (2p_0)_a \pm (2p_0)_b = (2p_2)_a \pm (2p_2)_b \]

\[ \sigma \text{ MOs even though they correlate with } 2p \text{ separated AOs, since they have } m = 0. \]

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

In the R→ \( \infty \) 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<sub>+</sub> and 2p<sub>-</sub> complex functions or the 2p<sub>x</sub> and 2p<sub>y</sub> real functions:

\((2p_+)_a + (2p_+)_b\)
\((2p_+)_a - (2p_+)_b\)
\((2p_-)_a + (2p_-)_b\)
\((2p_-)_a - (2p_-)_b\)

inversion of the electron's coordinates in \(H_2^+\)
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, \hspace{1cm} \text{an unstarred (bonding) orbital.}

\[ (2p_{+1})_a + (2p_{+1})_b = \pi_{2p_{+1}} \]

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

\[
\frac{\partial^2 e^{i\phi}}{\partial \phi^2} = \frac{\partial^2 e^{-i\phi}}{\partial \phi^2}
\]

\[\psi = |e^{i\phi}| \quad \rightarrow \quad \pi_u^2 p_{+1} \text{ and } \pi_u^2 p_{-1} \text{ MOs}
\]

have the same shapes,

do not give charge buildup between the nuclei

\[\pi_g^2 p_{+1}, \pi_g^2 p_{-1}\]
the more familiar alternatives:

\[
\begin{align*}
(2p_x)_a + (2p_x)_b & \quad \pi_2 p_x \\
(2p_x)_a - (2p_x)_b & \quad \pi^*_g p_x
\end{align*}
\]

Bonding (u) antibonding (g)

\[
\begin{align*}
\pi_2 p_x & \quad \text{and} \quad \pi_2 p_y \quad \text{have the same energy.} \\
\pi^*_g p_x & \quad \text{are not eigenfunctions of } L_z \\
\pi^*_g p_y & \quad \text{are eigenfunctions of } L_z \\
\pi^*_g p_x & \quad \text{are not eigenfunctions of } L_z \\
\pi^*_g p_y & \quad \text{are eigenfunctions of } L_z
\end{align*}
\]
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:

\[
\sigma_u^\pi 1s < \sigma_u^\pi 2s < \sigma_g^\pi 2s < \pi^\pi_2 p_{+1} = \pi_u^\sigma 2p_{-1} < \sigma_u^\sigma 2p < \pi_u^\pi 2p_{+1} = \pi_g^\pi 2p_{-1} < \sigma_g^\sigma 2p
\]
Molecular-Orbital Nomenclature for Homonuclear Diatomic Molecules

<table>
<thead>
<tr>
<th>Separated-Atoms Description</th>
<th>United-Atom Description</th>
<th>Numbering by Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{1s}$</td>
<td>$1s\sigma_g$</td>
<td>$1\sigma_g$</td>
</tr>
<tr>
<td>$\sigma_{2s}$</td>
<td>$2s\sigma_g$</td>
<td>$2\sigma_g$</td>
</tr>
<tr>
<td>$\sigma_{3s}$</td>
<td>$3s\sigma_g$</td>
<td>$3\sigma_g$</td>
</tr>
<tr>
<td>$\sigma_{4s}$</td>
<td>$4s\sigma_g$</td>
<td>$4\sigma_g$</td>
</tr>
<tr>
<td>$\pi_{1p}$</td>
<td>$1p\pi_u$</td>
<td>$1\pi_u$</td>
</tr>
<tr>
<td>$\pi_{2p}$</td>
<td>$2p\pi_u$</td>
<td>$2\pi_u$</td>
</tr>
<tr>
<td>$\pi_{3p}$</td>
<td>$3p\pi_u$</td>
<td>$3\pi_u$</td>
</tr>
<tr>
<td>$\pi_{4p}$</td>
<td>$4p\pi_u$</td>
<td>$4\pi_u$</td>
</tr>
</tbody>
</table>

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 $\sigma$, $\pi$, $\delta$, ....

$s$, $d$, $g$, ... 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.
Homonuclear diatomic MOs formed from 1s, 2s, and 2p AO’s.

Molecular electronic configurations
terms, levels, and states

\[ \text{H}_2^+ \quad \sigma_g^* 1s \]
\[ \text{H}_2 \quad (\sigma_g 1s)^2 \quad D_e = 4.75 \text{ eV} \]
\[ \text{He}_2 \quad (\sigma_g 1s)^2(\sigma_g^* 1s)^2 \quad \text{no net bonding,} \]

- 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.

\[ \text{He}_2^+ \quad (\sigma_g 1s)^2(\sigma_g^* 1s) \]
Li$_2$ & $(\sigma^s_1s)^2(\sigma^*_{1s})^2(\sigma_g^s_{2s})^2$ & a single bond

KK$(\sigma_g^s_{2s})^2$ & indicate the negligible change in inner-shell orbital energies on molecule formation

Be$_2$ & $KK(\sigma_g^s_{2s})^2(\sigma^*_{2s})^2$ & no net bonding electrons.

B$_2$ & $KK(\sigma_g^s_{2s})^2(\sigma^*_{2s})^2(\pi^u_{2p})^2$ & two net bonding electrons

one electron in the $\pi^u_{2p}$ MO and the other in the $\pi^a_{2p}$ MO,

is at variance with the notion that single bonds are always $\sigma$ bonds.

the electron-spin-resonance spectrum showed that the ground term is a triplet with $S = 1$

C$_2$ & $KK(\sigma_g^s_{2s})^2(\sigma^*_{2s})^2(\pi^u_{2p})^4$ & with four net bonding electrons

the $\pi^u_{2p}$ and $\sigma^a_{2p}$ MOs have nearly the same energy in many molecules.

$KK(\sigma_g^s_{2s})^2(\sigma^*_{2s})^2(\pi^u_{2p})^2(\sigma^a_{2p})$ & giving a triplet term.

$(\pi^u_{2p})^4$ & a singlet term.

the ground term by a small margin (0.09 eV)

N$_2$ & $KK(\sigma_g^s_{2s})^2(\sigma^*_{2s})^2(\pi^a_{2p})^4(\sigma^g_{2p})^2$ & a triple bond

O$_2$ & $KK(\sigma_g^s_{2s})^2(\sigma^*_{2s})^2(\sigma^a_{2p})^2(\pi^u_{2p})^2(\pi^a_{2p})^2$ & a double bond.

Spectroscopic evidence indicates that in O$_2$ (and in F$_2$) the $\sigma^a_{2p}$ is lower in energy than the $\pi^u_{2p}$ MO.

The paramagnetism of O$_2$
\[
\begin{align*}
\text{F}_2 & \quad \ldots (\pi^* \pi^2)^4 \quad \text{a single bond.} \\
\text{Ne}_2 & \quad \ldots (\pi^* \pi^2)^4(\sigma^* \pi^2)^2 \quad \text{no net bonding electrons} \\
\text{Na}_2 & \quad KKL\ell(\sigma_3s)^2 \\
\text{Al}_2 & \quad \begin{cases} 
\ldots (\sigma_3p)(\pi_3p) \\
\ldots (\pi_3p)^2 
\end{cases} \quad 0.02 \text{ eV below} \\
\text{Si}_2 & \quad \begin{cases} 
\ldots (\sigma_3p)(\pi_3p)^2 \\
\ldots (\sigma_3p)(\pi_3p)^3 
\end{cases} \quad 0.05 \text{ eV below}
\end{align*}
\]
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 $D_e$

\[ \text{N}_2 \rightarrow \text{N}_2^+ : \text{the dissociation energy decreases} \]
\[ \text{O}_2 \rightarrow \text{O}_2^+ : \text{the dissociation energy increases} \]

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\textsubscript{2} van der Waals molecules: $D_e = 0.012$ eV and $R_e = 3.76$ Å;
Ar\textsubscript{2} has seven bound vibrational levels ($v = 0, ..., 6$).
Examples of diatomic van der Waals molecules:

<table>
<thead>
<tr>
<th>Molecule</th>
<th>R_0 (Å)</th>
<th>D_e (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne_2</td>
<td>3.1</td>
<td>0.0036</td>
</tr>
<tr>
<td>HeNe</td>
<td>3.2</td>
<td>0.0012</td>
</tr>
<tr>
<td>Ca_2</td>
<td>4.28</td>
<td>0.13</td>
</tr>
<tr>
<td>Mg</td>
<td>2, 3.89</td>
<td>0.053</td>
</tr>
</tbody>
</table>

**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**.

\[
\begin{align*}
\pi_\sigma^2p \text{ shell} & \quad \text{and } \pi_\sigma^2p_{\pm 1} \text{ MOs} \\
\sigma \text{ shell} & \quad \pi, \delta, \phi, \ldots \text{ shell} \\
\text{one MO} & \quad \text{Two MOs}
\end{align*}
\]

A molecular electronic configuration \( \rightarrow \) giving the number of electrons in each shell

\[
(\sigma^2_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^3
\]

Ali Ebrahimi
For a many-electron diatomic molecules:

\[ \hat{L}_z \text{ commutes with } \hat{H} \]

\[ L_z = M_L \hbar, \text{ where } M_L = 0, \pm 1, \pm 2, \pm \ldots \]

\[ \Lambda = |M_L| \]

<table>
<thead>
<tr>
<th>( \Lambda )</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>letter</td>
<td>( \Sigma )</td>
<td>( \Pi )</td>
<td>( \Delta )</td>
<td>( \Phi )</td>
<td>( \Gamma )</td>
</tr>
</tbody>
</table>

\( \Lambda \neq 0 \) \quad \Rightarrow \quad M_L: +\Lambda \text{ and } -\Lambda

electronic energy depends on \( M_L^2 \rightarrow \text{double degeneracy} \)

The magnitude of \( S \):

\[ [S(S + 1)]^{1/2} \hbar \]

\( S = 0, 1/2, 1, 3/2, \ldots \)
The component of \( S \) along an axis = \( M_s \hbar \), where \( M_s = S, S - 1, \ldots, -S \).

\( 2S + 1 \) 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 \( \Lambda \) and the same value for \( S \) are said to belong to the same electronic term.
for a filled-shell molecular configuration:

\[ M_s = \sum m_s, \text{values} = 0 \rightarrow S = 0 \]

A filled \( \sigma \) shell: \( M_L = \sum m = 0 \)

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

A filled \( \delta, \phi, \ldots \) shell: \( M_L = \sum m = 0 \)

A closed-shell molecular configuration: \( S = 0 \), \( \Lambda = 0 \)

only a \(^1\Sigma\) term

ground electronic configuration of \( \text{H}_2 \)

A single \( \sigma \) electron: \( s = \frac{1}{2} \rightarrow S = \frac{1}{2} \rightarrow ^2\Sigma \)

A single \( \pi \) 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:

\( ^1\Sigma \) and \(^3\Sigma\)

\( ^1\Pi \) and \(^3\Pi\)
\[\delta \text{ configuration,} \]
\[\pi \text{ electron: } m = \pm 1\]
\[\delta \text{ electron: } m = \pm 2\]
\[M_L = +3, -3, +1, -1 \quad \Lambda = 3 \text{ or } 1\]
\[^3\Pi, ^3\Pi', \Phi, \Phi'.\]

\[\pi \pi \text{ configuration,} \]
\[\pi \pi \text{ configuration, each electron has } m = \pm 1\]
\[M_L \text{ values } 2, -2, 0, 0 \quad \Lambda = 2, 0, \text{ and } 0\]
\[^1\Delta, ^3\Delta, ^1\Sigma, ^3\Sigma, ^1\Sigma' \text{ and } ^3\Sigma'\]

apart from spin degeneracy:  degenerate states nondegenerate

---

**Forms of the wave functions for the terms**

\[M_L = +2 \quad \text{two } \pi \text{ subshells: } \pi \text{ and } \pi' \]
a subscript indicates the m value

For the \(\Delta\) 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

\[^1\Delta: \quad \pi_{+1}(1)\pi_{+1}(2) + \pi_{+1}(2)\pi_{+1}(1)\]
\[^3\Delta: \quad \pi_{+1}(1)\pi_{-1}(2) - \pi_{+1}(2)\pi_{-1}(1)\]
both electrons having $m = +1$  
\[
\begin{align*}
1\Delta: & \quad \pi_{-1}(1)\pi_{+1}(2) + \pi_{+1}(2)\pi_{-1}(1) \\
3\Delta: & \quad \pi_{+1}(1)\pi_{+1}(2) - \pi_{-1}(2)\pi_{+1}(1)
\end{align*}
\]
both electrons having $m = -1$  
\[
\begin{align*}
1\Delta: & \quad \pi_{+1}(1)\pi_{-1}(2) + \pi_{-1}(2)\pi_{+1}(1) \\
3\Delta: & \quad \pi_{-1}(1)\pi_{-1}(2) - \pi_{-1}(2)\pi_{-1}(1)
\end{align*}
\]
symmetric or antisymmetric with respect to exchange of electron  
\[
\begin{align*}
1\Delta: & \quad \pi_{+1}(1)\pi_{+1}(2) + \pi_{+1}(2)\pi_{-1}(1) \\
1\Delta: & \quad \pi_{-1}(1)\pi_{-1}(2) + \pi_{-1}(2)\pi_{+1}(1)
\end{align*}
\]
two states  
\[
\begin{align*}
3\Delta: & \quad \pi_{+1}(1)\pi_{+1}(2) - \pi_{+1}(2)\pi_{+1}(1) \\
3\Delta: & \quad \pi_{-1}(1)\pi_{-1}(2) - \pi_{-1}(2)\pi_{-1}(1)
\end{align*}
\]
six states  
\[
\begin{align*}
\alpha(1)\alpha(2) \\
2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \\
2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\
\beta(1)\beta(2)
\end{align*}
\]

For the $\Sigma$ terms: one electron with $m = +1$ and one with $m = -1$.  
\[
\begin{align*}
\pi_{+1}(1)\pi_{-1}(2), & \quad \pi_{+1}(2)\pi_{-1}(1), \\
\pi_{-1}(1)\pi_{+1}(2), & \quad \pi_{-1}(2)\pi_{+1}(1)
\end{align*}
\]
Combining them to get symmetric and antisymmetric functions,  
\[
\begin{align*}
1\Sigma^+: & \quad \pi_{+1}(1)\pi_{-1}(2) + \pi_{+1}(2)\pi_{-1}(1) + \pi_{+1}(1)\pi_{+1}(2) + \pi_{-1}(2)\pi_{+1}(1) \\
1\Sigma^-: & \quad \pi_{+1}(1)\pi_{-1}(2) + \pi_{+1}(2)\pi_{-1}(1) - \pi_{+1}(1)\pi_{-1}(2) - \pi_{-1}(2)\pi_{+1}(1) \\
3\Sigma^+: & \quad \pi_{+1}(1)\pi_{-1}(2) - \pi_{+1}(2)\pi_{-1}(1) + \pi_{+1}(1)\pi_{+1}(2) - \pi_{-1}(2)\pi_{+1}(1) \\
3\Sigma^-: & \quad \pi_{+1}(1)\pi_{-1}(2) - \pi_{+1}(2)\pi_{-1}(1) - \pi_{+1}(1)\pi_{-1}(2) + \pi_{-1}(2)\pi_{+1}(1)
\end{align*}
\]
These functions have eigenvalue +1 or -1 with respect to reflection of electronic coordinates in the xz (σv) symmetry plane containing the molecular (z) axis; the superscripts + and - refer to this eigenvalue.

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

Two states

\[ \begin{align*}
\Sigma^+: & \quad \pi_{+1}(1)\pi_{-1}'(2) + \pi_{+1}(2)\pi_{-1}'(1) + \pi_{-1}(1)\pi_{+1}'(2) + \pi_{-1}(2)\pi_{+1}'(1) \\
\Sigma^-: & \quad \pi_{-1}(1)\pi_{+1}'(2) + \pi_{+1}(2)\pi_{-1}'(1) - \pi_{-1}(1)\pi_{+1}'(2) - \pi_{-1}(2)\pi_{+1}'(1)
\end{align*} \]

Six states

Previous Δ terms are not eigenfunctions of the symmetry operator \( \hat{O}_{\sigma_v} \).

\[ \hat{O}_{\sigma_v} \text{ commutes with the Hamiltonian} \]

\[ \hat{O}_{\sigma_v} \text{ eigenvalues} \]

\[ \begin{align*}
\pi_{+1}(1)\pi_{+1}'(2) + \pi_{+1}(2)\pi_{+1}'(1) & \quad +1 & 1^\Delta^+ & \text{same energy} \\
\pi_{+1}(1)\pi_{+1}'(2) + \pi_{+1}(2)\pi_{+1}'(1) & \quad -1 & 1^\Delta^- & \text{same energy}
\end{align*} \]

\( \Delta \)-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:

$\pi^2$ configuration

$$
\begin{array}{|c|c|c|c|c|c|c|}
\hline
m_1 & m_2 & m_{s1} & m_{s2} & M_s & M_L & S \\
\hline
+1 & +1 & -1/2 & 1/2 & 2 & 0 & 1 \\
-1 & -1 & -1/2 & 1/2 & -2 & 0 & 1 \\
+1 & -1 & 1/2 & 1/2 & 0 & 1 & 1 \\
+1 & -1 & -1/2 & -1/2 & 0 & -1 & 1 \\
+1 & -1 & 1/2 & -1/2 & 0 & 0 & 1 \\
+1 & -1 & -1/2 & 1/2 & 0 & 0 & 1 \\
\hline
\end{array}
$$

\[ M_L = 2, -2 \rightarrow \Lambda = 2 \rightarrow \Sigma \]
\[
S = 0
\]
\[ M_L = 0 \rightarrow \Lambda = 0 \rightarrow \sum
\]
\[
S = 1 \text{ (for } M_s = -1, 0, 1) \]
\[ M_L = 0 \rightarrow \Lambda = 0 \rightarrow \sum
\]
\[
S = 0 \text{ (for } M_s = 0) \]

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 $\pi^2$ configuration:

- $^1\Sigma_g^+$
  - Energy: $1.6 \text{ eV}$
  - The $v = 0$ level

- $^1\Delta_g$
  - Energy: $0.98 \text{ eV}$
  - The $v = 0$ level

- $^3\Sigma_g^-$

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 $^3\Pi$ 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 $\Sigma$

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

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

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

is written as a right subscript to the term symbol

$$\Omega = |\Lambda + \Sigma|$$

$^3\Delta \rightarrow \Lambda = 2$ and $S = 1 \rightarrow ^3\Delta_3, ^3\Delta_2,$ and $^3\Delta_1$

$^4\Pi \rightarrow ^4\Pi_{3/2}, ^4\Pi_{3/2}, ^4\Pi_{1/2},$ and $^4\Pi_{1/2}$

The spin-orbit interaction energy in diatomic molecules

spin-orbit interaction energy $\approx A\Lambda\Sigma$

$A$ depends on $\Lambda$ and $R$ 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 $\Lambda$-type doubling.

For $\Sigma$ terms, the spin-orbit interaction is very small (quantum numbers $\Sigma$ and $\Omega$ are not defined).

$\Sigma$ terms $\rightarrow$ single nondegenerate energy level.
THE HYDROGEN MOLECULE

Interparticle distances in $\text{H}_2$.

purely electronic Hamiltonian for $\text{H}_2$ 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

1) the molecular-orbital approach:

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

approximate wave function:

$$
\frac{1}{\sqrt{2}} \left| \sigma_g 1s(1)\alpha(1) \quad \sigma_g 1s(1)\beta(1) \right| = \sigma_g 1s(1)\sigma_g 1s(2)2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]
$$

$$
= f(1)f(2)2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]
$$
\[\sigma_8 1s = f\]

omission of the spin factor does not affect the variational integral.

we want to choose \(f\) so as to minimize:

\[
\iint f^*(1)f^*(2)\hat{H}f(1)f(2)
\,dv_1\,dv_2
\]

\[
\iint |f(1)|^2|f(2)|^2
dv_1\,dv_2
\]

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 \(l/r_{12} \rightarrow \hat{H} = \) sum of two \(H_2^+\) Hamiltonians

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

\[
\frac{k^{3/2}}{(2\pi)^{1/2}(1 + S_{ab})^{1/2}}\left(e^{-kr_1} + e^{-kr_2}\right)
\]

variation function = the product of two such LCAO functions

\[
\phi = \frac{\zeta^3}{2\pi(1 + S_{ab})} (e^{-ir_{1\mu}} + e^{-ir_{2\nu}})(e^{-ir_{1\nu}} + e^{-ir_{2\mu}})
\]

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

the effective nuclear charge \(\zeta\) will differ from \(k\) for \(H_2^+\).

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

\[
\iint \phi^* \hat{H} \phi
\,dv_1\,dv_2 = 2W_1 + \iint \frac{\delta^2}{r_{12}}
\,dv_1\,dv_2
\]

\[
W_1 = -\frac{\zeta^2}{2} + \frac{\zeta^2 - \zeta - R^{-1} + R^{-1}(1 + \zeta R)e^{-2\zeta R} + \zeta (\zeta - 2)(1 + \zeta R)e^{-\zeta R}}{1 + e^{-\zeta R}(1 + \zeta R + \zeta R^2/3)}
\]
Coulson,
\[ R_e = 0.732 \text{ Å} \text{ (true value = 0.741 Å)} \]
\[ D_e = 3.49 \text{ eV} \text{ (true value = 4.75 eV)} \]
\[ \zeta \text{ (at 0.732 Å) = 1.197} \text{ Å} \text{ for H}_2^+ \]

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 \( \xi \) and \( \eta \) (Since \( m = 0 \) for the ground state, the \( e^{im\varphi} = 1 \))

\[
f = e^{-a\xi} \sum_{p,q} a_{pq} \xi^p \eta^q
\]

\( p \) and \( q \) are integers and \( a \) and \( a_{pq} \) are variational parameters.

The Hartree-Fock results:
\[ R_e = 0.733 \text{ Å} \text{ and } D_e = 3.64 \text{ eV}, \text{ which is not much improvement} \]

over 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.

\( \text{gs configuration} (\sigma_g 1s)^3 \rightarrow 1\Sigma_g^+ \)

\( \text{first exs configuration} \)

\( (\sigma_g 1s)(\sigma_u 1s) \rightarrow g \times u \rightarrow \text{odd parity} \)

\( (\sigma_u 1s)^2 \rightarrow 1\Sigma_u^+ \text{ and } 3\Sigma_u^+ \)

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,
\[ R_e = 0.757 \text{ Å} ; D_e = 4.03 \text{ eV} ; \zeta = 1.19 \]

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:

\[
\exp \left[ -\delta(\xi_1 + \xi_2) \right] \sum c_{mnpq} \left( \varepsilon_{1m} \varepsilon_{2n} \eta_1 \eta_2 + \varepsilon_{1m} \varepsilon_{2n} \eta_1 \eta_2 \right) r_{12}^p
\]

Variational parameters: \( \delta \) and the \( c_{mnpq} \) 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.

\[
f_1 = 1s_a(1)1s_a(2)
\]

1 and 2 for electrons; \( a \) and \( b \) for nuclei

Also:

\[
f_2 = 1s_b(2)1s_b(1)
\]

The trial variation function

\[
c_1 f_1 + c_2 f_2 = c_1 1s_a(1)1s_b(2) + c_2 1s_b(2)1s_a(1)
\]
We can also consider the problem using perturbation theory:

\[ H_{11} = \langle f_1^* | \hat{H} | f_1 \rangle, \quad S_{11} = \langle f_1 | f_2 \rangle, \ldots \]

two neutral ground-state hydrogen atoms \( \rightarrow \) perturbation \( \rightarrow \) 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

\[ \text{secular determinant} \]

\[ \det (H_{ij} - S_{ij} W) = 0 \]

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

\[ H_{11} = H_{21}, \quad S_{12} = S_{21}, \quad S_{11} = S_{22} = 1 \]

\[ H_{12} = (1s_a(1)1s_b(2)|\hat{H}|1s_a(1)1s_b(2)) \]

\[ H_{22} = (1s_a(2)1s_b(1)|\hat{H}|1s_a(2)1s_b(1)) \]

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

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

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

\[ f_1 \pm f_2 = 1s_a(1)1s_b(2) \pm 1s_a(2)1s_b(1) \]

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

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

Ali Ebrahimi
the ground state of $H_2$ is a $\Sigma$ state with the antisymmetric spin factor and a symmetric spatial factor. Hence $\phi_1$ must be the ground state.

The Heitler-London ground-state wave function:

$$\psi_1 = \frac{1}{\sqrt{2(1 + S_{ab}^2)^{1/2}}} \left[ \alpha(1)\beta(2) - \alpha(2)\beta(1) \right]$$

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

$$\psi_2 = \frac{1}{\sqrt{2(1 - S_{ab}^2)^{1/2}}} \left\{ \begin{array}{l}
\frac{\alpha(1)\alpha(2)}{2^{1/2}} \\
\alpha(1)\beta(2) + \beta(1)\alpha(2) \\
\beta(1)\beta(2)
\end{array} \right\}$$

the ground-state energy expression:

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

$$\hat{H}_a(1) = -\frac{1}{2}\nabla_1^2 - \frac{1}{r_{1a}}, \quad \hat{H}_b(1) = -\frac{1}{2}\nabla_2^2 - \frac{1}{r_{1a}}, \quad \hat{H}^r = -\frac{1}{r_{1a}} - \frac{1}{r_{2a}} + \frac{1}{r_{12}}$$

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

$$Q = \langle 1s_a(1)1s_b(2) | \hat{H}^r | 1s_a(1)1s_b(2) \rangle$$

Coulomb integral

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

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

$$\int \int 1_{s_1(1)}1_{s_2(2)} \frac{1}{r_{12}} 1_{s_1(2)}1_{s_2(1)} \, dv_1 \, dv_2$$

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 $A$. 

\[
\begin{align*}
H_{12} &= H_{51} = (1s_2(2)1s_1(1)\hat{H}_d(1) + \hat{H}_b(2) + \hat{H}^\dagger|1s_1(1)1s_2(2)\rangle \\
\langle 1s_2(2)|1s_2(2)\rangle\langle 1s_1(1)|\hat{H}_d(1)|1s_1(1)\rangle &= -\frac{1}{2}S_{ab}^2 \\
A &= (1s_2(2)1s_1(1)\hat{H}^\dagger|1s_1(1)1s_2(2)\rangle \\
H_{12} &= A - S_{ab}^2 \\
W_1 &= \frac{H_{11} + H_{12}}{1 + S_{12}} \quad W_2 = \frac{H_{11} - H_{12}}{1 - S_{12}} \\
W_1 &= -1 + \frac{Q + A}{1 + S_{ab}^2} \quad W_2 = -1 + \frac{Q - A}{1 - S_{ab}^2}
\end{align*}
\]
Improvements on the Heitler-London function

Wang introduced an orbital exponent $\zeta$ in the 1s function:
$$\zeta_{\text{opt}} = 1.166, \quad R_e = 3.78 \text{ eV}, \quad D_e = 0.744 \text{ Å}$$

Rosen: mixing in some 2p$_z$ character into the atomic orbitals (hybridization),
to improve the Heitler-London-Wang function
$$\phi = \phi_1(1)\phi_n(2) + \phi_n(2)\phi_1(1)$$
$$\phi_2 = e^{-\zeta R}(1 + cz)$$
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

$$[\phi_1(1) + \phi_n(2)] [\phi_1(2) + \phi_n(1)]$$

$\phi_1$ an atomic orbital centered on nucleus a

simplest treatment: $\phi$ is a 1s AO

$$\phi_1(1)\phi_n(2) + \phi_1(2)\phi_n(1) + \phi_n(1)\phi_1(2) + \phi_n(2)\phi_1(1)$$

the physical significance of the terms:

**ionic terms,** $\text{H}^-\text{H}^+$ and $\text{H}^+\text{H}^-$

covalent terms,

Two terms occur with equal weight,
We remedy this; the simplest procedure is to omit the ionic terms of the MO function.

\[ \phi_d(1)\phi_b(2) + \phi_b(1)\phi_d(2) \quad \text{As the Heitler-London function} \]

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

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

* variational parameter

\[ \checkmark \text{represents ionic-covalent resonance.} \]

\[ \checkmark \text{a time-independent mixture of covalent and ionic functions.} \]

\[ \checkmark \delta(\infty) = 0 \]

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):

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

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

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

\[ \delta = (1 + \gamma)/(1 - \gamma) \]

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,
$$\hat{H} = \left[ -\frac{1}{2}\nabla^2_{\alpha} - \frac{1}{r_{\alpha\beta}} \right] + \left[ -\frac{1}{2}\nabla^2_{\beta} - \frac{1}{r_{\alpha\beta}} \right] + \frac{1}{r_{12}}$$

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

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

\[
\begin{pmatrix}
1\sigma_g(1) & \overline{1}\sigma_g(1) & 1\sigma_u(1) & \overline{1}\sigma_u(1) \\
1\sigma_g(2) & \overline{1}\sigma_g(2) & 1\sigma_u(2) & \overline{1}\sigma_u(2) \\
\frac{1}{\sqrt{24}} \sigma_g(3) & \overline{1}\sigma_g(3) & \sigma_u(3) & \overline{1}\sigma_u(3) \\
\sigma_g(4) & \overline{1}\sigma_g(4) & \sigma_u(4) & \overline{1}\sigma_u(4)
\end{pmatrix}
\]

spin function \(\beta\).

helium-atom 1s

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

predicts no bonding

shorthand notation: \( \mid 1\sigma_g \overline{1}\sigma_g 1\sigma_u \overline{1}\sigma_u \mid \)
MO approximation to the wave function:

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

No bonding is predicted,

\[ \left| \sigma_g 1s \sigma_g 1s \sigma_u^* 1s \sigma_u^* 1s \right| \]

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

\[
\begin{align*}
\sigma_g 1s &= 1s_a + 1s_b \\
\sigma_u^* 1s &= 1s_a - 1s_b
\end{align*}
\]

\[
\left| (1s_a + 1s_b)(1s_a + 1s_b)(1s_a - 1s_b)(1s_a - 1s_b) \right|
\]

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

\[
4 \left| (1s_a + 1s_b)(1s_a + 1s_b)(1s_a - 1s_b)(1s_a - 1s_b) \right|
\]

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

\[
4 \left| (1s_b \bar{1s_a}, 1s_a \bar{1s_b}) \right|
\]

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

\[
4 \left| (1s_b \bar{1s_a}, 1s_a \bar{1s_b}) \right|
\]

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.

\[
\text{trial function: } |1s_a \bar{1}s_a 1s_b \bar{1}s_b|
\]

the variational integral

repulsive curve for the interaction of two gs He atoms

the Heitler-London VB functions (gs) for \( \text{H}_2 \) as Slater determinants:

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

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

\[
= (2 + 2S_{ab}^2)^{-1/2} |1s_a\bar{1}s_b| - |\bar{1}s_a1s_b|
\]

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:

Singlet: \[
\begin{aligned}
|1s_a^1s_b^1s_b^-1s_a^1s_b^-| & - |1s_a1s_b^-| \\
1s_a^1s_b^- & 
\end{aligned}
\]

Triplet: \[
\begin{aligned}
|1s_a^-1s_b^-| + |1s_a^-1s_b^1s_b^-| \\
\overline{1s_a^-1s_b^-} & 
\end{aligned}
\]

$Li_2$:  
- gs configuration $1s^22s$,  
- 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:

\[
|1s_a1s_b1s_b1s_b^-2s_a2s_b^-| - |1s_a1s_b1s_b^-2s_a2s_b^-|
\]

**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:

\[
|1s_a1s_b1s_b1s_b^-2s_a2s_b^-|
\]

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

MO wave function (gs)

\[
|\sigma_g^-1s \sigma_g^-1s \sigma_g^1s \sigma_g^1s \sigma_g^-2s \sigma_g^-2s|
\]

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

\[
|1s_a^-1s_b^-1s_b^-2s_a^-2s_b^-|
\]

Recall the notation $KK(\sigma_g^-2s)^2$ for gs configuration
The $N_2$ ground state:

the VB treatment:

The lowest configuration of $N$ is $1s^22s^22p^3$

The Lewis structure: $N≡N$

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.

$$D_1 = \begin{vmatrix} 1s_x & 1s_y & 2s_x & 2s_y & 2p_x & 2p_y & 2p_z & 2p_x \end{vmatrix}$$

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

$$D_1 = \begin{vmatrix} \cdots & 2p_x & 2p_y & 2p_z & 2p_x & 2p_y & 2p_z & 2p_x \end{vmatrix}$$

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 H$_2$

The lowest MO configuration (1σ$_g$)$^2$ (a nondegenerate level)

- two substantial minima
- (1σ$_g$)$^2$(2σ$_g$)
- (1σ$_g$)(1σ$_u$)
- $\sigma^2$$\Sigma^+_g$
- $\pi^2$$\Sigma^+_g$
- $\delta^2$$\Sigma^+_g$
- $\sigma^2$$\Pi$..$

LCAO-MO functions

triply degenerate

$b^3$$\Sigma^+_u$: $2^{-1/2}[1\sigma_g(1)1\sigma_g(2) - 1\sigma_g(2)1\sigma_u(1)]$

\[
\begin{align*}
\alpha(1)\alpha(2) & \quad 2^{-1/2}[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \\
\beta(1)\beta(2) & 
\end{align*}
\]

nondegenerate

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

\[
1\sigma_g \approx N'(1s_e + 1s_u) \quad 1\sigma_u \approx N'(1s_e - 1s_u)
\]

✓ 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

\[
\frac{1s_u(1)1s_u(2) - 1s_u(2)1s_u(1)}{\sqrt{2(1 - S_{\alpha\beta}^2)^{1/2}}} \left( \frac{\alpha(1)\alpha(2)}{2^{1/2}} \alpha(1)\beta(2) + \beta(1)\alpha(2) \right) \\
\frac{1s_u(1)1s_u(2) + 1s_u(2)1s_u(1)}{\sqrt{2(1 + S_{\alpha\beta}^2)^{1/2}}} \frac{1}{\sqrt{2}} \left( \alpha(1)\beta(2) - \alpha(2)\beta(1) \right)
\]

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

✓ in $H_2$: $1\pi_u < 2\sigma_u$

\[(1\sigma_u)(1\pi_u) \rightarrow ^1\Pi_u \text{ and } ^3\Pi_u \text{ triplet lying lower} \]

\[c^1\Pi_u \quad c^3\Pi_u \]

\[c^1\Pi_{2\sigma_u}, c^3\Pi_{1\pi_u} \text{ and } c^3\Pi_{1\sigma_u} \text{ levels} \]

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 $\phi_i$ in an MO WF are each expressed as a linear combination of a set of one-electron basis functions $\chi_s$:
  \[
  \phi_i = \sum c_i^\alpha \chi_i
  \]
- 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 = 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 $R = R_e$:

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

✓ The AO functions in these equations are STOs, except for $2s_{1,a}$.
✓ 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.

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

$S$ 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

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

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

simple expressions:

\[ 1\sigma_g = 0.706(1s_g + 1s_h) + 0.009(2s_{1s} + 2s_{1s}) + 0.0003(2p\sigma_s + 2p\sigma_s) \]
\[ 1\sigma_u = 0.709(1s_u - 1s_u) + 0.021(2s_{1s} - 2s_{1s}) + 0.0003(2p\sigma_u - 2p\sigma_u) \]
\[ 2\sigma_g = -0.059(1s_g + 1s_h) + 0.523(2s_{1s} + 2s_{1s}) + 0.114(2p\sigma_s + 2p\sigma_s) \]
\[ 2\sigma_u = \sigma_2s = 2^{-1/2}(2s_u + 2s_u) \]

Approximations are good

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

2) the \(3\sigma_g\) MO of the \(F_2\) ground state at \(R_e^e\):

a) using a minimal basis set:

\[ 3\sigma_{g,\text{min}} = 0.038(1s_g + 1s_h) - 0.184(2s_g + 2s_h) + 0.648(2p\sigma_s + 2p\sigma_s) \]
\[ \zeta_{1s} = 8.65, \quad \zeta_{2s} = 2.58, \quad \zeta_{2pv} = 2.49 \]

\[ E_{\text{total}} = -197.877 \text{ hartrees} \]

b) using an extended basis set:

\[ 3\sigma_{g,\text{ext}} = 0.048(1s_g + 1s_h) + 0.003(1s_g^* + 1s_h^*) - 0.257(2s_g + 2s_h) + 0.582(2p\sigma_s + 2p\sigma_s) + 0.307(2p\sigma_s^* + 2p\sigma_s^*) + 0.085(2p\sigma_s^* + 2p\sigma_s^*) \]
\[ - 0.056(3s_g + 3s_h) + 0.046(3d\sigma_s + 3d\sigma_s) + 0.014(4f\sigma_s + 4f\sigma_s) \]
\[ \zeta_{1s} = 8.27, \quad \zeta_{1v} = 13.17, \quad \zeta_{2s} = 2.26 \]
\[ \zeta_{2pv} = 1.85, \quad \zeta_{2pv}^* = 3.27, \quad \zeta_{2pv}^* = 5.86 \]
\[ \zeta_{3s} = 4.91, \quad \zeta_{3dv} = 2.44, \quad \zeta_{4fo} = 2.83 \]

\[ E_{\text{total}} = -198.768 \text{ hartrees} \]

\[ E_{\exp} = -199.670 \text{ hartrees} \]

the correlation energy = -0.90 hartrees = - 24.5 eV.
• $E_{\text{tot}} = -197.877 \text{Eh}$ and $-198.768 \text{Eh}$ 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 - $E_{\text{HF}}$
• The relativistic contribution to $E$ of $F_2$ calculated: $-0.142 \text{Eh}$,
• 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 $-199.530 \text{Eh} + 198.773 \text{Eh} = -0.757 \text{Eh} = -20.6 \text{eV}$.

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.

\[
\begin{align*}
(2p\sigma_a' + 2p\sigma_b') & \quad (2p\sigma_a + 2p\sigma_b) \\
(3d\sigma_a + 3d\sigma_b) & \quad (4f\sigma_a + 4f\sigma_b)
\end{align*}
\]

STOs with different orbital exponents

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 $\sigma$ MO is a linear combination of $1s$, $2s$, $2p_\sigma$, $3s$, $3p_\sigma$, $3d_\sigma$... AOs of the separated atoms.

Ali Ebrahimi
which AOs contribute to a given diatomic MO?

1) only σ-type AOs (s, pσ, dσ,...) can contribute to a σ MO; only π-type AOs (pπ, dπ,...) 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 Li₂ 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 $\rho$. Consequently, such properties are accurately calculated using HF wave functions (for example, the molecular dipole moment).

LiH:
with a near HF $\psi$: 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.

\[ \text{N}_2: \]
\[ \text{HF } D_e = 5.3 \text{ eV} \quad \text{by an extended-bs} \quad \text{(true value } = 9.9 \text{ eV}) \]

\[ \text{F}_2: \]
\[ \text{HF } D_e = -1.4 \text{ eV} \quad \text{(true } D_e = 1.66 \text{ eV}) \]

**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 \( \text{N}_2 \)

gradual transfer of charge from one nucleus to the other.

the original \( \text{N}_2 \) MOs would slowly vary to give finally the CO MOs.

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

\[
\begin{array}{c|c|c|c|c|c|c|c|c}
\text{N}_2 & 1\sigma_g & 1\sigma_u & 2\sigma_g & 2\sigma_u & 1\pi_u & 3\sigma_g & 1\pi_g & 3\sigma_u \\
\hline
\text{CO} & 1\sigma & 2\sigma & 3\sigma & 4\sigma & 1\pi & 5\sigma & 2\pi & 6\sigma \\
\end{array}
\]

\[
\begin{align*}
5\sigma &= 0.027(1s_C) + 0.011(1s_O) + 0.739(2s_{1\sigma C}) + 0.036(2s_{1\sigma O}) \\
&- 0.566(2p\sigma_{C}) - 0.438(2p\sigma_{O}) \\
1\pi &= 0.469(2p\pi_{C}) + 0.771(2p\pi_{O}), \quad 2\pi = 0.922(2p\pi_{C}) - 0.690(2p\pi_{O})
\end{align*}
\]
The ground-state configuration:

\[
\text{CO: } 1\sigma^22\sigma^23\sigma^24\sigma^21\pi^5\sigma^2 \\
\text{N}_2: \ (1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_u)^2
\]

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

\[
\sum_{\beta=1}^{b} c_{\beta}(F_{\alpha \beta} - e_{\beta}S_{\alpha \beta}) = 0, \quad r = 1, 2, \ldots, b
\]

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

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

\[
1\pi = 0.469(2p\pi_C) + 0.771(2p\pi_O) \quad \text{π MOs are simpler than σ MOs}
\]

\[
2\pi = 0.922(2p\pi_C) - 0.690(2p\pi_O)
\]
corresponding MOs in N$_2$ at R = R$_e$:

\[
3\sigma_g = 0.030(1s_u + 1s_v) + 0.395(2s_{1u} + 2s_{1v}) \\
- 0.603(2p_{3u} + 2p_{3v}) \\
1\pi_u = 0.624(2p_{4u} + 2p_{4v}) \\
1\pi_g = 0.835(2p_{5u} - 2p_{5v})
\]

1σ MO in CO \sim 1s oxygen-atom AO
2σ MO in CO \sim 1s carbon-atom AO.

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

\[
\begin{array}{c}
\sigma^{2p} \\
\sigma^*p \\
\pi^{2p} \\
\pi^*p \\
\sigma_{2p} \\
\sigma_{3p}
\end{array}
\]

Heteronuclear diatomic

each valence AO of the more electronegative atom would lie below the corresponding valence AO of the other atom.
When the s and p$\sigma$ 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 $2s_B$, with small amounts of $2s_F$, $2p\sigma_B$, and $2p\sigma_F$
- $4\sigma \sim$ predominantly $2p\sigma_B$, 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 $2p\sigma_B$

2$p_F$ 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

CO:

4$\sigma$ : very substantial contribution from $2p\sigma_O$
5$\sigma$ : 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.
Diatomic hydrides: H has only a 1s valence AO

HF:

1) a crude qualitative approximation

Ground-state configurations, 1s for H and 1s^22s^22p^5 for F

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

2pπ F electrons are nonbonding.

Is AO of H and 2pπ 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:

\[ \phi = c_1(1s_H) + c_2(2p_{\pi F}) \]

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:

\[
1\sigma = 1.000(1s_F) + 0.012(2s_{1p_F}) + 0.002(2p_{\sigma F}) - 0.003(1s_H) \\
2\sigma = -0.018(1s_F) + 0.914(2s_{1p_F}) + 0.090(2p_{\sigma F}) + 0.154(1s_H) \\
3\sigma = -0.023(1s_F) + 0.411(2s_{1p_F}) + 0.711(2p_{\sigma F}) + 0.516(1s_H) \\
1\pi^+ = (2p_{\pi^+})_F \\
1\pi^- = (2p_{\pi^-})_F 
\]

The ground-state configuration of HF: \( 1\sigma^22\sigma^23\sigma^21\pi^4 \)

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 ≈ 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

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

\[
(H_{aa} - W)(H_{bb} - W) - (H_{ab} - WS_{ab})^2 = 0
\]

\[ f(w) \]

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

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 \( (1 - S_{ab}) > 0 \) \( \rightarrow f(\infty) = f(-\infty) = +\infty > 0 \).

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

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.

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**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 2pσ electron.

\[
\psi_{\text{cov}} = \prod \left| 1s_1 (2p\sigma)^1 \right| - \prod \left| 1s_1 (2p\sigma)^2 \right|
\]

\[
\prod = 1s_1(2p\sigma)_{x_1} 2s_2(2p\sigma)_{y_2} 2s_2(2p\sigma)_{y_2} 2p\pi_{x_1} 2p\pi_{x_1} 2p\pi_{y_2} 2p\pi_{y_2}
\]

essentially covalent

An ionic valence-bond function has the form \( \psi_{\text{ion}}(1)\psi_{\text{ion}}(2) \)

\[
\psi_{\text{ion}} = \prod \left| 2p\pi_{x_1} 2p\pi_{y_2} \right|
\]

The VB wave function is then written as

\[ \psi = c_1\psi_{\text{cov}} + c_2\psi_{\text{ion}} \]
Cs and Cl are found by the variation method.
We have ionic-covalent “resonance,” involving the structures H–F and H⁺F⁻.
A term $c_1 |1s_i,1s_H⟩$ corresponding to the ionic structure H⁺F⁻ could also be included in the wave function (only slightly).

NaCl (highly ionic molecule):
\[ \text{we expect } c_2 \gg c_1. \]
\[ \text{NaCl} \xrightarrow{\rightarrow \infty} \text{Na} + \text{Cl} \quad \text{in the gas phase} \]
\[ \text{NaCl} \xrightarrow{\rightarrow \infty} \text{Na}^+ + \text{Cl}^- \quad \text{in aqueous solution} \]

IP(Na) = 5.1 eV, ea(Cl) = 3.6 eV.

\[ R \uparrow \quad \rightarrow \quad c_2/c_1 \downarrow \quad \text{(becoming zero at } R = \infty) \]
For intermediate \( R \), the Coulombic attraction between the ions > 1.5 eV (difference between the ionization potential and electron affinity).
For very large \( R \), the Coulombic attraction between the ions < 1.5 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 eV
\[ \text{CsCl} \rightarrow \text{Cs} + \text{Cl} \]
\[ \text{CsF} \rightarrow \text{Cs} + \text{F} \]
There are cases of excited states of diatomic molecules that dissociate to ions.
THE VALENCE-ELECTRON APPROXIMATION

Cs₂, 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 ≡ point charges coinciding with the nucleus.

Hamiltonian (for Cs₂) = Hamiltonian for H₂

minimize the variational integral

no restrictions on the valence-electron trial functions,

valence-electrons' MO to "collapse" to the 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