\[ \langle n\ell m_\ell | n\ell m_\ell \rangle \]
\[ \sum_i |i\rangle \langle i| = 1 \]
\[ \beta = \langle 1| \hat{H} |2 \rangle \]
$H_2$: a homonuclear diatomic molecule
2 H atoms, 1s orbitals only

$\sigma^*$ antibonding molecular orbital

$\sigma$ bonding molecular orbital

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Goal: find these molecular orbitals, and their energies, $E$

$$ |\Psi\rangle = \langle 1,1s | \Psi \rangle |1,1s\rangle + \langle 2,1s | \Psi \rangle |2,1s\rangle $$

$$ |\Psi\rangle = c_1 |1,1s\rangle + c_2 |2,1s\rangle $$

We know these atomic orbitals, and their energy => basis kets.
Assume orthogonal $\langle 1,1s | 2,1s \rangle = 0$
Overlap of atomic orbitals on different atoms

A large overlap integral requires spatial overlap, but spatially overlapping orbitals can still have zero overlap if the signs are appropriately arranged. e.g. 2s is orthogonal to 2p on same atom.
We want to find these molecular orbitals, and their energies, $E$

$$\hat{H} |\Psi\rangle = E |\Psi\rangle$$

$$|\Psi\rangle = c_1 |1,1s\rangle + c_2 |2,1s\rangle$$

$$\hat{H} \left[ c_1 |1,1s\rangle + c_2 |2,1s\rangle \right] = E \left[ c_1 |1,1s\rangle + c_2 |2,1s\rangle \right]$$

On-site matrix element $\hat{H}_{11} = E_0$ (assume known)

Project onto basis ket #1

$$c_1 \langle 1,1s | \hat{H} |1,1s\rangle + c_2 \langle 1,1s | \hat{H} |2,1s\rangle$$

$$= E \left[ c_1 \langle 1,1s | 1,1s \rangle + c_2 \langle 1,1s | 2,1s \rangle \right]$$

Hopping matrix element $\hat{H}_{12} = \beta$ (assume known)
We want to find these molecular orbitals, and their energies, \( E \).

\[
\begin{align*}
    c_1E_0 + c_2\beta &= Ec_1 \\
    c_1\beta + c_2E_0 &= Ec_2
\end{align*}
\]

Project onto basis kets

\[
\begin{vmatrix} E_0 - E & \beta \\ \beta & E_0 - E \end{vmatrix} = 0
\]

Linear algebra \( \Rightarrow \) quadratic eqn

\[
\begin{align*}
    E_a &= E_0 - \beta \\
    E_b &= E_0 + \beta
\end{align*}
\]

\[
\beta = \langle 1, 1s \mid V_2(r) \mid 2, 1s \rangle < 0
\]

For overlapping \( s \) orbitals, \( \beta \) is negative. This is because \( s \) orbitals are +ve everywhere and \( V_2 < 0 \) (attractive potential)
We want to find these molecular orbitals, and their energies, $E$

\[ c_1E_0 + c_2\beta = Ec_1 \]
\[ c_1\beta + c_2E_0 = Ec_2 \]

Now we can find the $c$’s for each of $E_b$ and $E_a$, and hence the corresponding $\Psi_b$ and $\Psi_a$.

\[
\Psi_a = \frac{1}{\sqrt{2}}(\ket{1,1s} - \ket{2,1s})
\]
\[
\Psi_b = \frac{1}{\sqrt{2}}(\ket{1,1s} + \ket{2,1s})
\]
H₂ molecule

constructive combination

electron density between nuclei

nucleus of the hydrogen atom

phase of the orbital

destructive combination

electron density outside of nuclei

node
H$_2$ molecule

Bonding is a quantum mechanical phenomenon that results from the interference of quantum waves!

To view bonding as the “sharing” of electrons, we can show (Sutton p33-31) that an electron oscillates from atom #1 to atom #2 at a frequency $2\beta/h$. How does it overcome the large ionization potential? It tunnels! Again a quantum mechanical phenomenon.
σ bonding with ρ-orbitals

Why is the –ve sign associated with the bonding orbital in this example?

\[
\Psi_a = \frac{1}{\sqrt{2}} (|1, p\rangle + |2, p\rangle)
\]

\[
\Psi_b = \frac{1}{\sqrt{2}} (|1, p\rangle - |2, p\rangle)
\]
π bonding with p-orbitals
MO diagram for $p$-orbitals
H\textsubscript{2} molecule has 2 atoms and the 2 molecular orbitals are (relatively) close in energy, one higher and one lower than the energy of the atomic orbital.

The hopping term represents tunneling of electrons across the potential barrier between atoms (see Sutton). The faster the tunneling, the stronger the interaction, and the bigger the splitting.

The orbitals are bonding (electron density between nuclei tending to draw nuclei together), or antibonding (electron density on opposite sides of nuclei, causing nuclear repulsion).
Heteronuclear diatomic molecule

\[ \langle B | \hat{H} | B \rangle = E_B \quad \langle A | \hat{H} | A \rangle = E_A \]

On-site integrals

\[ \langle A | \hat{H} | B \rangle = \langle B | \hat{H} | A \rangle = \beta \]

Off-site integral

\[ \hat{H} | \Psi \rangle = E | \Psi \rangle \]

General form of MO

\[ | \Psi \rangle = c_A | A \rangle + c_B | B \rangle \]

Schrödinger eigenvalue equation
Want to find these molecular orbitals and their energies, $E$

$$c_A E_A + c_B \beta = E c_A$$

$$c_A \beta + c_B E_B = E c_B$$

Project onto basis kets

$$\begin{vmatrix}
  E_A - E & \beta \\
  \beta & E_B - E
\end{vmatrix} = 0$$

Linear algebra $\Rightarrow$ quadratic eqn

$$E_a = \varepsilon + \left( \Delta^2 + \beta^2 \right)^{1/2}$$

$$E_b = \varepsilon - \left( \Delta^2 + \beta^2 \right)^{1/2}$$
Want to find these molecular orbitals, and their energies, $E$

$$c_A E_A + c_B \beta = E c_A$$
$$c_A \beta + c_B E_B = E c_B$$

Now we can find the c's for each of $E_b$ and $E_a$, and hence the corresponding $\Psi_b$ and $\Psi_a$.

$$\frac{C^{2}_{A,a}}{C^{2}_{B,a}} = \frac{1}{1 + 2(\Delta / \beta)^2 - 2(\Delta / \beta)\left(1 + (\Delta / \beta)^2\right)^{1/2}}$$

$$\frac{C^{2}_{A,b}}{C^{2}_{B,b}} = \frac{1}{1 + 2(\Delta / \beta)^2 + 2(\Delta / \beta)\left(1 + (\Delta / \beta)^2\right)^{1/2}}$$
\[
\frac{c_{A,a}^2}{c_{B,a}^2} = \frac{1}{1 + 2(\Delta / \beta)^2 - 2(\Delta / \beta)(1 + (\Delta / \beta)^2)^{1/2}}
\]

\[
\frac{c_{A,b}^2}{c_{B,b}^2} = \frac{1}{1 + 2(\Delta / \beta)^2 + 2(\Delta / \beta)(1 + (\Delta / \beta)^2)^{1/2}}
\]
# Electronegativity

## TABLE 1.3 The Electronegativities of Selected Elements

<table>
<thead>
<tr>
<th>IA</th>
<th>IIA</th>
<th>IB</th>
<th>IIB</th>
<th>IIIA</th>
<th>IVA</th>
<th>VA</th>
<th>VIA</th>
<th>VIIA</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>1.0</td>
<td>Be</td>
<td>1.5</td>
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<tr>
<td>Na</td>
<td>0.9</td>
<td>Mg</td>
<td>1.2</td>
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<td></td>
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</tr>
<tr>
<td>K</td>
<td>0.8</td>
<td>Ca</td>
<td>1.0</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2.0</td>
<td>C</td>
<td>2.5</td>
<td>N</td>
<td>3.0</td>
<td>O</td>
<td>3.5</td>
<td>F</td>
</tr>
<tr>
<td>Al</td>
<td>1.5</td>
<td>Si</td>
<td>1.8</td>
<td>P</td>
<td>2.1</td>
<td>S</td>
<td>2.5</td>
<td>Cl</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Br</td>
<td>2.8</td>
<td>I</td>
<td>2.5</td>
<td></td>
</tr>
</tbody>
</table>

*Electronegativity values are relative, not absolute. As a result, there are several scales of electronegativities. The electronegativities listed here are from the scale devised by Linus Pauling.*
This commonly shown picture is actually inaccurate. It shows 1s-2p hybridization. One always sees 2s-2p hybridization. 2s electron distribution is different from 1s!

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HF and HCl

Overlap of the bonding sp\(^3\) hybrid orbital of F and Cl with H in HF and HCl. Overlap of the 1s orbital of hydrogen is better with the smaller 2sp\(^3\) hybrid orbital of fluorine than with the larger 3sp\(^3\) hybrid orbital of chlorine, resulting in a shorter, stronger bond in HF than in HCl.

<table>
<thead>
<tr>
<th>Hydrogen halide</th>
<th>Bond length (Å)</th>
<th>Bond strength kcal/mol</th>
<th>Bond strength kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>H—F</td>
<td>0.917</td>
<td>136</td>
<td>571</td>
</tr>
<tr>
<td>H—Cl</td>
<td>1.2746</td>
<td>103</td>
<td>432</td>
</tr>
<tr>
<td>H—Br</td>
<td>1.4145</td>
<td>87</td>
<td>366</td>
</tr>
<tr>
<td>H—I</td>
<td>1.6090</td>
<td>71</td>
<td>298</td>
</tr>
</tbody>
</table>

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