Consider $H_2^+$. 3 bodied problem is intractable.

Solution: remember that nuclei are massive, and that they will move slowly (compared to e-).

Born-Oppenheimer Approx: consider nuclei stationary.

Minimize $E$ at various $R$. 
Consider molecules with many e⁻. Two theories:

- Valence Bond
- Molecular Orbital

<table>
<thead>
<tr>
<th>Electron pairs</th>
<th>Single e⁻</th>
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<tr>
<td>Localized bonds (wave function between 2 nuclei)</td>
<td>MO's spread over entire molecule</td>
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</table>
Valence Bond Theory

Consider \( H_2 \) \( \psi = |s_A(1) \cdot s_B(2)| + |s_A(2) \cdot s_B(1)| \)

only when atoms are separate

put atoms together to make \( H_2 \)

\( \psi = |s_A(1) \cdot s_B(2)| + |s_A(2) \cdot s_B(1)| \) bonding

\( \psi = |s_A(1) \cdot s_B(2)| - |s_A(2) \cdot s_B(1)| \) antibonding

electrons are distinguishable

e- no longer distinguishable
VB theory and Pauli Exclusion Principle:

\[ \psi \text{ must be } -\psi \text{ after exchange.} \]

(e\text{-} are fermions)

however, \( \psi_{\text{bonding}} \) is symmetric.

We fix by multiplying by an anti-symmetric wave function

\[ \psi = \left[ s_A(1)s_B(2) + s_A(2)s_B(1) \right] \left[ \alpha(1)\beta(2) - \alpha(2)\beta(1) \right] \]

since \( \psi_{\text{bonding}} \) is anti-symmetric, it needs a symmetric spin function:

\[ \psi_{\text{antibonding}} = \left[ s_A(1)s_B(2) - s_A(2)s_B(1) \right] \left[ \alpha(1)\beta(2) + \alpha(2)\beta(1) \right] \]
VB and Ionic Bonding

\[ H_2 = \overset{\text{H}^- + \text{H}^+}{\text{H}} \quad \text{and} \quad \overset{\text{H}^- + \text{H}^+}{\text{H}} \]

mixing in ionic states lowers E:

\[ H_A^- \quad H_B^+ \quad H_A^+ \quad H_B^- \]

\[ lS_A(1) lS_A(2) \quad lS_B(1) lS_B(2) \]

\[ \psi_{\text{bonding}} = (lS_A(1) lS_B(2) + lS_A(2) lS_B(1) + \chi [lS_A(1) lS_B(2) + lS_A(2) lS_B(1)]) \]

we vary \( \chi \) to give lowest \( E \).

\[
\% \text{ ionic character} = \frac{\chi^2}{1 + \chi^2} \times 100% 
\]

\[ H_2 \text{ is } \approx 3\% \text{ ionic} \]
MO theory

1) Write wavefunction for entire molecule
2) add e- 

Simplest wavefunction is linear combination of atomic orbitals

LCAO-MO

Consider H₂

*₁₅

*₁₅
bonding $\sigma = 1s_A + 1s_B$

antibonding $\sigma^* = 1s_A - 1s_B$

Bond order =

$\frac{1}{2} (e^- \text{ in bonding orbitals} - e^- \text{ in antibonding orbitals})$

for \( H_2 \), BO = 1
MO

Overall wavefunction

$\psi = \sigma(1) \sigma(2)$

$\psi = N \left[ 1s_{A}(1) + 1s_{B}(1) \right] \cdot N \left[ 1s_{A}(2) + 1s_{B}(2) \right]$ (spin function)

$\psi = N^2 \left[ 1s_{A}(1)1s_{A}(2) + 1s_{A}(1)1s_{B}(2) + 1s_{B}(1)1s_{B}(2) \right]$ (function)

Very similar to VB theory (this won't be true for complicated molecules)

Normalize for 1 e-

$\int N^2(1s_{A} + 1s_{B})^2 \, d^2 \vec{r} = 1$

$N^2 \left[ \int 1s_{A} \cdot 1s_{A} + 1s_{B} \cdot 1s_{B} + 2 \underbrace{1s_{A} \cdot 1s_{B}}_{S, \text{"overlap integral"}} \right] = 1$

$N^2 [2 + 2S] = 1$

$N = \sqrt{\frac{1}{2(1+S)}}$