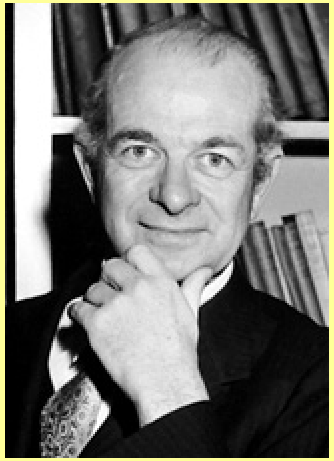
Molecules and binding



Linus Pauling
Nobel 1954

Max Born
Nobel 1954

Robert Oppenheimer

The Nature of the Chemical Bond

The Born-Oppenheimer Approximation

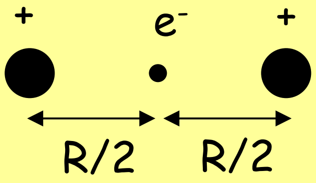
Molecules and binding

Stability
Variety
Complexity

due to chemical bonds → electromagnetic forces +
subtle quantum phenomena

→ lowering of energy if bond is formed

H_2^+ classical and static model:



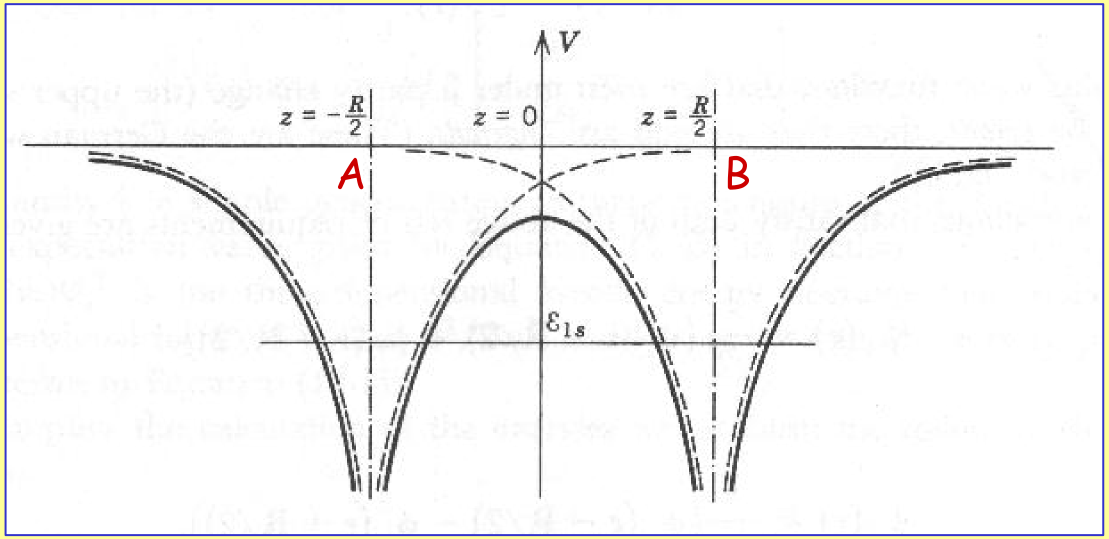
$$V_{\text{Coulomb}} = \frac{+e^2}{4\pi\varepsilon_0 R} - 2\frac{e^2}{4\pi\varepsilon_0 (R/2)} = -3\frac{e^2}{4\pi\varepsilon_0 R}$$

→ centered electron keeps
positively charged nuclei together

Born-Oppenheimer Approximation

Nuclei <u>fixed</u> in a frame: use $k = \dfrac{1}{4\pi\varepsilon_0}$

Schrödinger equation: $$\left\{ \underbrace{-\frac{\hbar^2}{2m_e}\nabla_r^2}_{T} \underbrace{-\frac{ke^2}{|\vec{r}+R/2|}}_{V_b} \underbrace{-\frac{ke^2}{|\vec{r}-R/2|}}_{V_a} + \underbrace{\frac{ke^2}{R}}_{V_R} \right\}\Psi_e(r) = \varepsilon_e \Psi_e(r)$$



Solutions, for the case of only one potential:

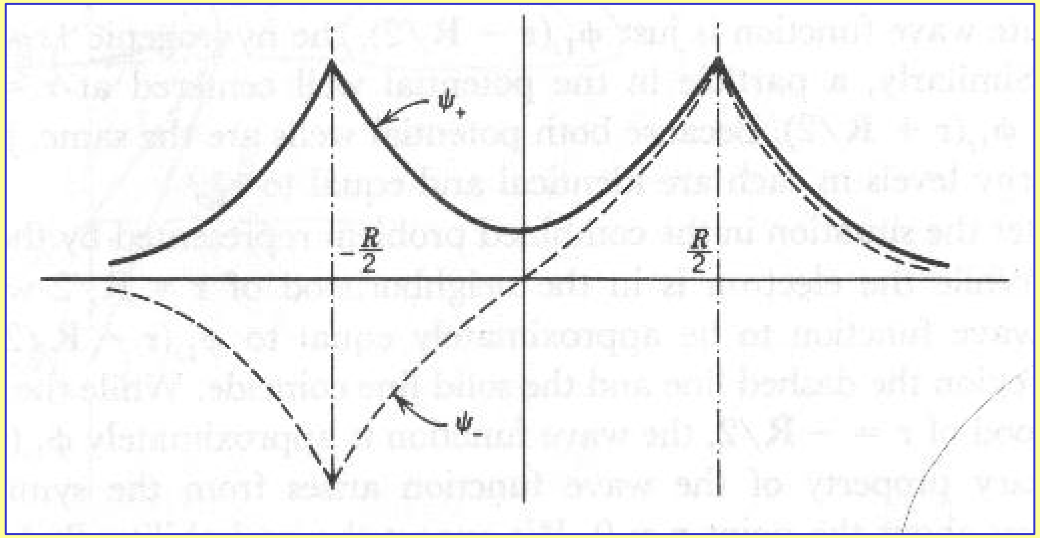
$$\phi_{1s}^A(r - R/2)$$

$$\phi_{1s}^B(r + R/2)$$

ϕ_{1s} not exact approximations

Symmetric and anti-symmetric wave functions

Define: $\Psi_+(r) = \frac{1}{\sqrt{2}}\left(\phi_{1s}^A + \phi_{1s}^B\right)$ and $\Psi_-(r) = \frac{1}{\sqrt{2}}\left(\phi_{1s}^A - \phi_{1s}^B\right)$



Two hydrogenic wave functions for 1s orbital: $\phi \propto e^{-a(r \pm R/2)}$

Linear combinations of single $1s$ orbital solutions

Insert in SE: $\Psi_+(r) = \frac{1}{\sqrt{2}}\left(\phi_{1s}^{A} + \phi_{1s}^{B}\right)$ and $\Psi_-(r) = \frac{1}{\sqrt{2}}\left(\phi_{1s}^{A} - \phi_{1s}^{B}\right)$

$$\langle \varepsilon \rangle = \varepsilon_{\pm} = \frac{1}{2}\int \left(\phi^{A} \pm \phi^{B}\right)\left[T + V_a + V_b + V_R\right]\int \left(\phi^{A} \pm \phi^{B}\right) dV =$$

$$\frac{1}{2}\int \left(\phi^{A} \pm \phi^{B}\right)\left[\underline{(T + V_a)\phi_A} \pm \underline{(T + V_b)\phi_B}\right] dV$$

$$+\frac{1}{2}\int \underline{\phi_A^2\left(V_b + V_R\right) dV} + \frac{1}{2}\int \underline{\phi_B^2\left(V_a + V_R\right) dV}$$

$$\pm\frac{1}{2}\int \phi_A\left(V_a + V_R\right)\phi_B dV \pm \frac{1}{2}\int \phi_B\left(V_b + V_R\right)\phi_A dV$$

1. $(T + V_a)\phi_A = \varepsilon_{1s}\phi_A$ $\quad (T + V_b)\phi_B = \varepsilon_{1s}\phi_B$ ⟶ solutions with hydrogen wave functions

2. Define: $\int \phi_A^2\left(V_b + V_R\right) dV = \int \phi_B^2\left(V_a + V_R\right) dV = G$ ⟶ direct Coulomb energy

↓ electron at A

↓ Coulomb pot with B

Evaluation of energies in H_2^+ system

$$\langle \varepsilon \rangle = \frac{1}{2}\int \left(\underline{\phi^A \pm \phi^B\right)\left[(T+V_a)\phi_A} \pm \underline{(T+V_b)\phi_B}\right] dV \longrightarrow = \frac{1}{2}\varepsilon_{1s} + \frac{1}{2}\varepsilon_{1s}$$

$$+\frac{1}{2}\int \underline{\phi_A^2 \left(V_b + V_R\right)} dV + \frac{1}{2}\int \underline{\phi_B^2 \left(V_a + V_R\right)} dV \longrightarrow = \frac{1}{2}G + \frac{1}{2}G$$

$$\pm\frac{1}{2}\int \underline{\phi_A \left(V_a + V_R\right)\phi_B dV} \pm \frac{1}{2}\int \underline{\phi_B \left(V_b + V_R\right)\phi_A dV} \longrightarrow = \pm\frac{1}{2}S \pm \frac{1}{2}S$$

Define: $\boxed{\int \phi_A \left(V_a + V_R\right)\phi_B dV = \int \phi_B \left(V_b + V_R\right)\phi_A dV = S}$

S

- is a quantum interference, or an overlap integral
- it contributes if electron has density at A *and* B
- integral contributes if electron is near $z=0$

Energies in H_2^+: $\boxed{\langle \varepsilon \rangle = \varepsilon_{1s} + G \pm S}$

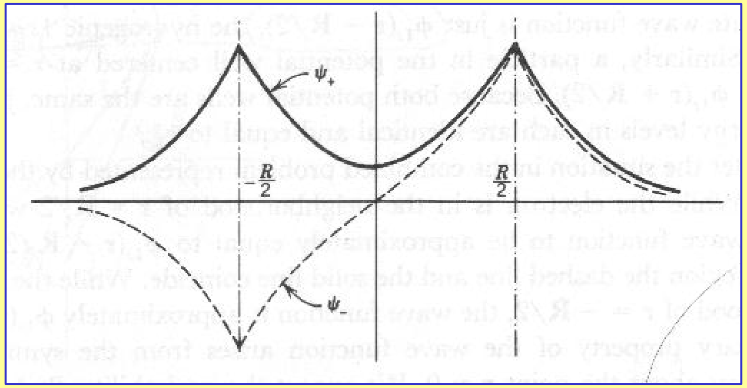
Bonding in a molecule as a result of S integral

Energies in H_2^+: $\langle \varepsilon \rangle = \varepsilon_{1s} + G \pm S$

Integral calculations show that: $|S| > |G|$ interference integral is larger

One of the two gives binding $+S$ or $-S$

(can be calculated that S is negative, but)



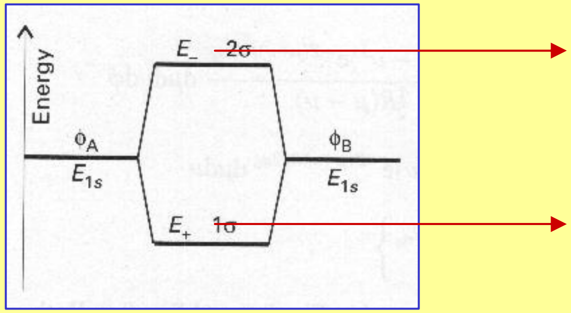
$\Psi_+(r)$ must be the bonding state

$\Psi_-(r)$ is then higher in energy by $2S$

Bonding and anti-bonding in H_2^+

$$\varepsilon_+ = \varepsilon_{1s} + G - S$$

$$\varepsilon_- = \varepsilon_{1s} + G + S$$

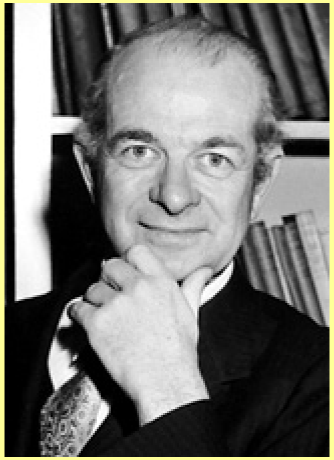


σ* anti-bonding

σ bonding

The Nature of the Chemical bond:

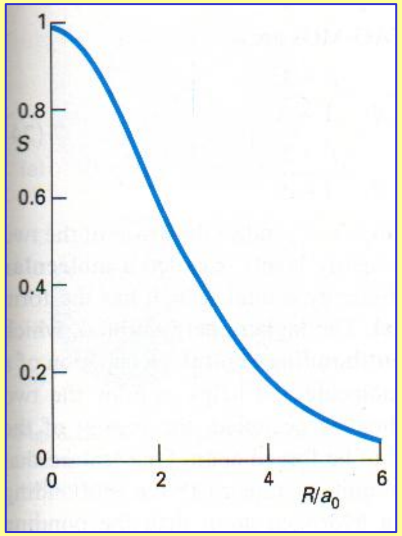
Wave function overlap of identical orbitals give rise to chemical stability



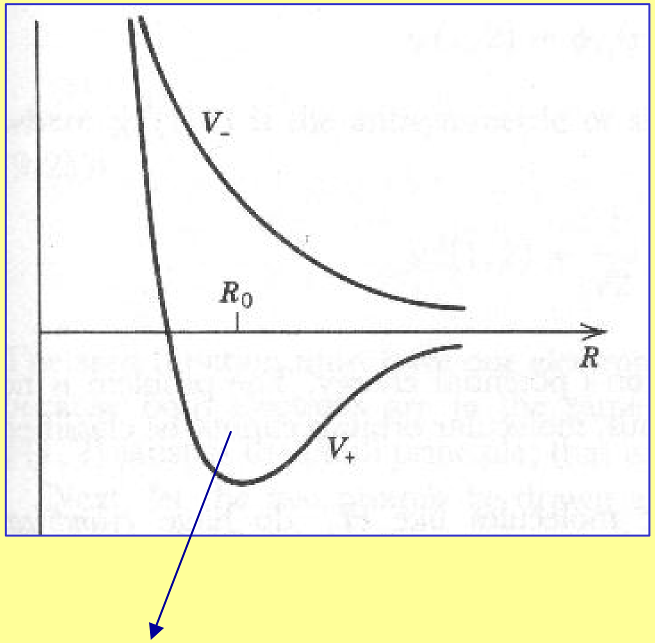
Linus Pauling
Nobel 1954

Molecular “Potential Energy Curves”

S integral is a function of R



Curves for electronic energies

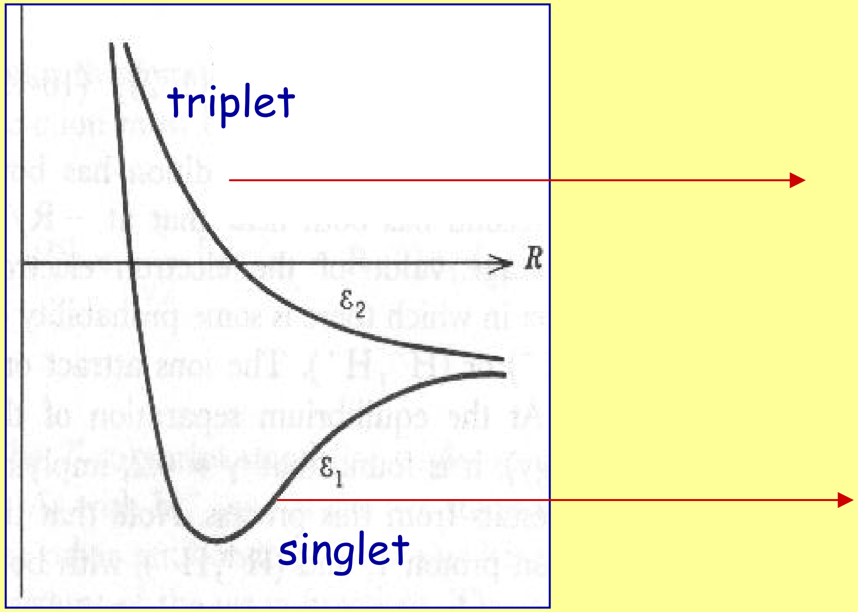


Bound states in a potential well

From H_2^+ to H_2, the hydrogen molecule

Problem is similar, but two electrons occupying the orbitals

$$\langle \varepsilon \rangle = 2\varepsilon_{1s} + G' \pm S'$$



$$\left(\phi_{1s}^{A} - \phi_{1s}^{B}\right)\chi_{spin}^{sym}$$

$$\left(\phi_{1s}^{A} + \phi_{1s}^{B}\right)\chi_{spin}^{anti}$$

Two electrons in a bonding orbital → chemical bond is stronger

Bonding in molecules

H_2^+	(σ_{1s})	
H_2	$(\sigma_{1s})^2$	
He_2^+	$(\sigma_{1s})^2(\sigma_{1s}^*)$	one effective bond
He_2	$(\sigma_{1s})^2(\sigma_{1s}^*)^2$	no effective bond
B_2	$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2$	
C_2	$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^4$	
N_2	$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^6$	→ 6 effective bonds: The most strongly bound molecule
O_2	$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^6(\sigma_{2p}^*)^2$	
F_2	$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^6(\sigma_{2p}^*)^4$	
Ne_2	$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^6(\sigma_{2p}^*)^6$	