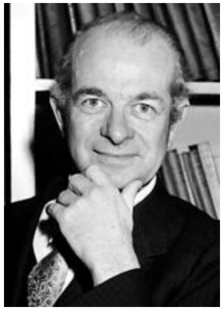
Bonds in molecules

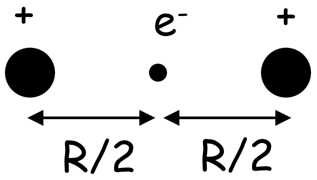


Linus Pauling,
Nobel 1954

"for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances"

Molecules and binding: classical

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

Max Born

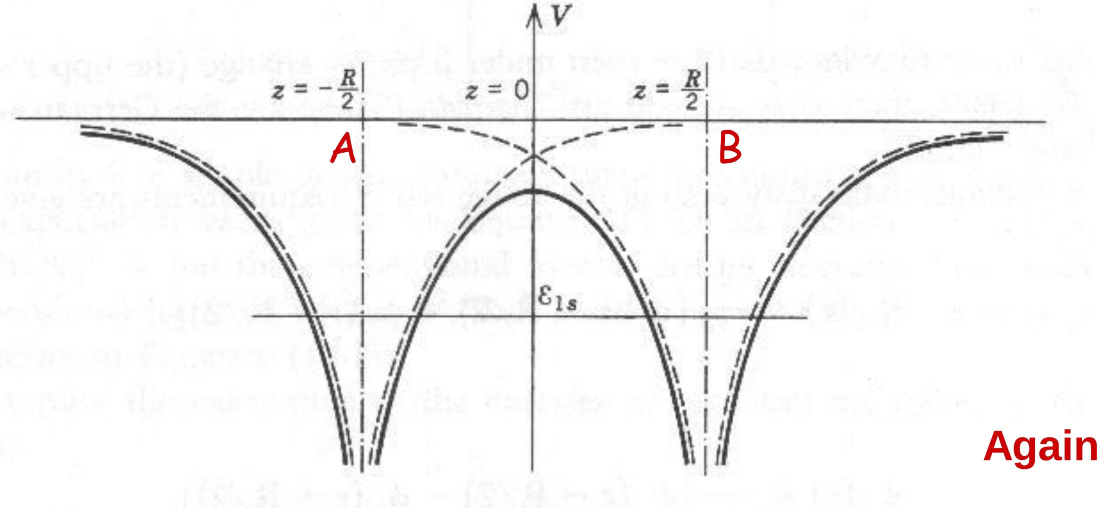
Robert Oppenheimer

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

Schrödinger equation:

$$\left\{ -\frac{\hbar^2}{2m_e}\nabla_r^2 - \frac{ke^2}{\left|\vec{r}+R/2\right|} - \frac{ke^2}{\left|\vec{r}-R/2\right|} + \frac{ke^2}{R} \right\} \Psi_e(r) = \varepsilon_e \Psi_e(r)$$

T V_b V_a V_R



Solutions, for the case of only one potential:

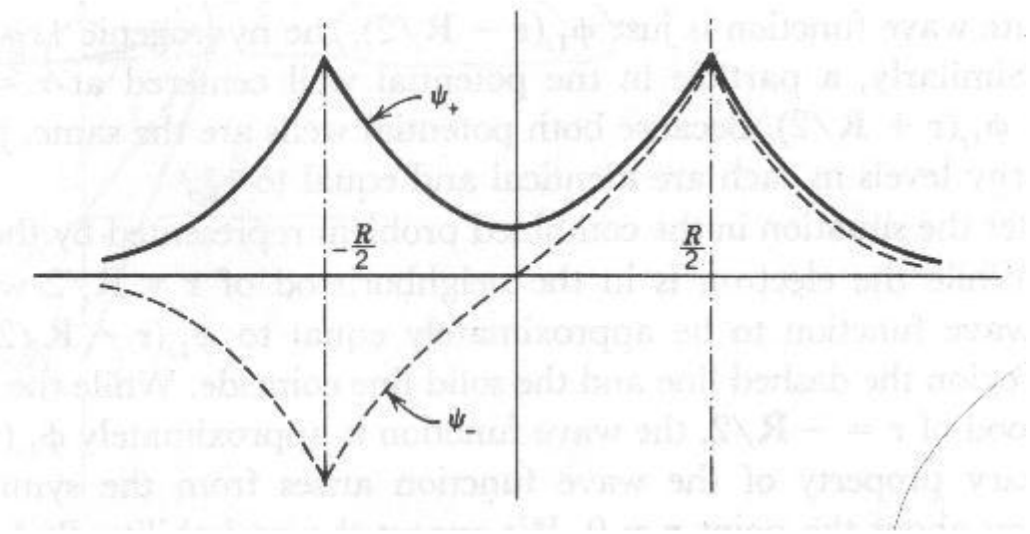
$$\phi_{1s}^{A}(r - R/2)$$

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

Again; the known H wave functions

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: $\phi \propto e^{-a(r \pm R/2)}$

Note: even if there is only one electron in the system, it can take this form

Intermezzo

Symmetry and the Pauli exclusion principle

Different definitions, but equivalent

1) 2 electrons cannot be in the same quantum state
   2 electron must have different quantum numbers: α and β:
   Pauli exclusion principle

2) Wave function must be anti-symmetric (under interchange of the 2 electrons)

$$\Psi(2,1)=\frac{1}{\sqrt{2}}\left[\psi_{\alpha}(2)\psi_{\beta}(1)-\psi_{\beta}(2)\psi_{\alpha}(1)\right]=-\Psi(1,2)$$

If $\alpha=\beta$ then $\Psi=0$

Two possibilities for having an anti-symmetric wave function:

$$\Psi^{A}(1,2)=\psi^{S}(r_1,r_2)\chi^{A}(1,2)$$
$$\Psi^{A}(1,2)=\psi^{A}(r_1,r_2)\chi^{S}(1,2)$$

spatial ψ and spin χ

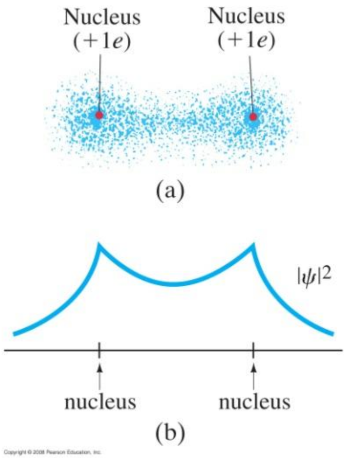
Anti-symmetric spin ↓↑ **S=0 (singlet)**

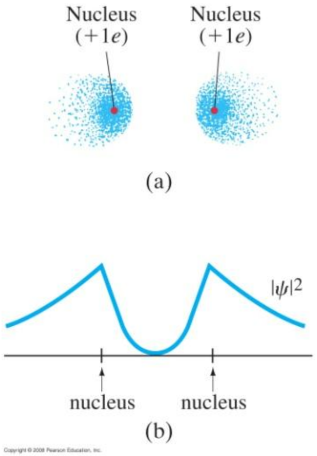
Symmetric spin ↑↑ **S=1 (triplet)**

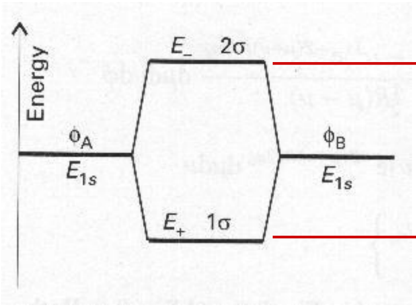
Combine with spatial wave function

Note, for chemical binding we need a Symmetric spatial wave function

Bonding and anti-bonding in H_2^+







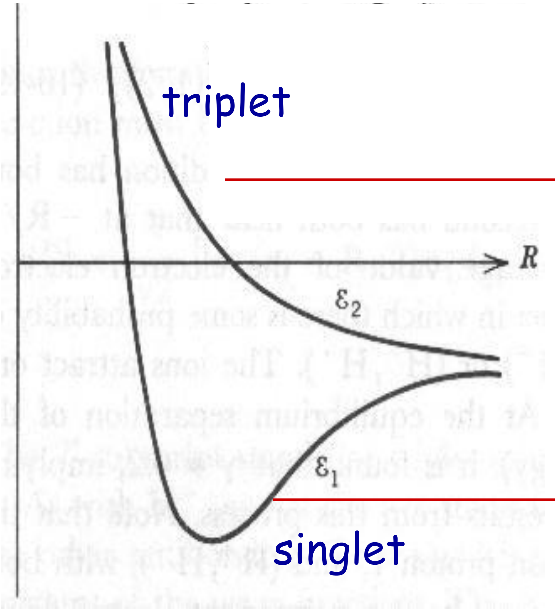
σ^* anti-bonding

σ bonding

Symmetric spatial wave function lowers the energy

From H_2^+ to H_2, the hydrogen molecule

Problem is similar, but two electrons occupying the orbitals



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

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

Two electrons in a bonding orbital → chemical bond is stronger

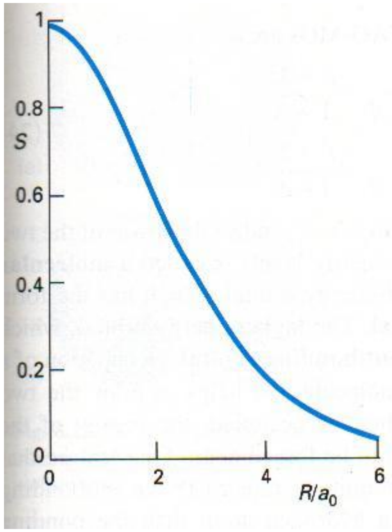
COVALENT Binding in molecules

H_2^+	(σ_{1s})	H_2 better bond than H_2^+
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	$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^6(\sigma_{2p}^*)^6$	

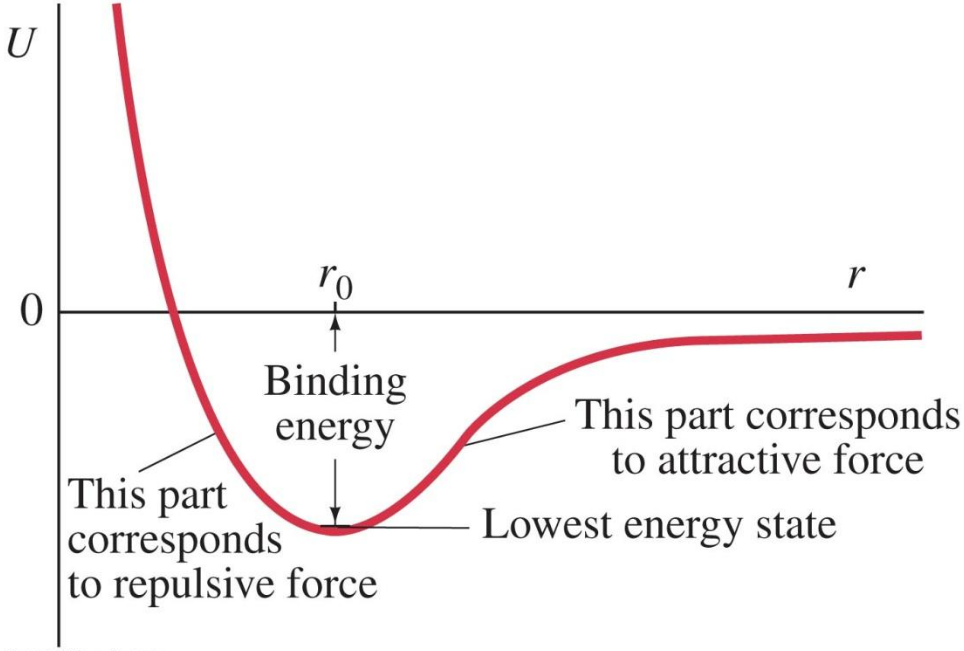
Potential-Energy Diagrams for Molecules

For the hydrogen molecule, the force between the atoms is attractive at large distances. If the atoms are too close, the electrons are too squeezed; therefore, there is a minimum in the potential.

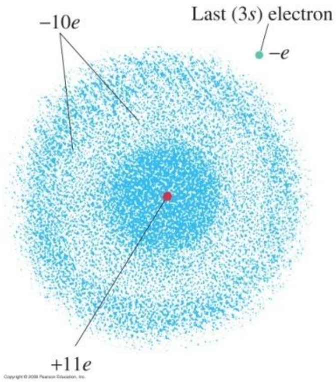
Overlap integral is a function of R



Also account for repulsion of nuclei



Ionic Bonds

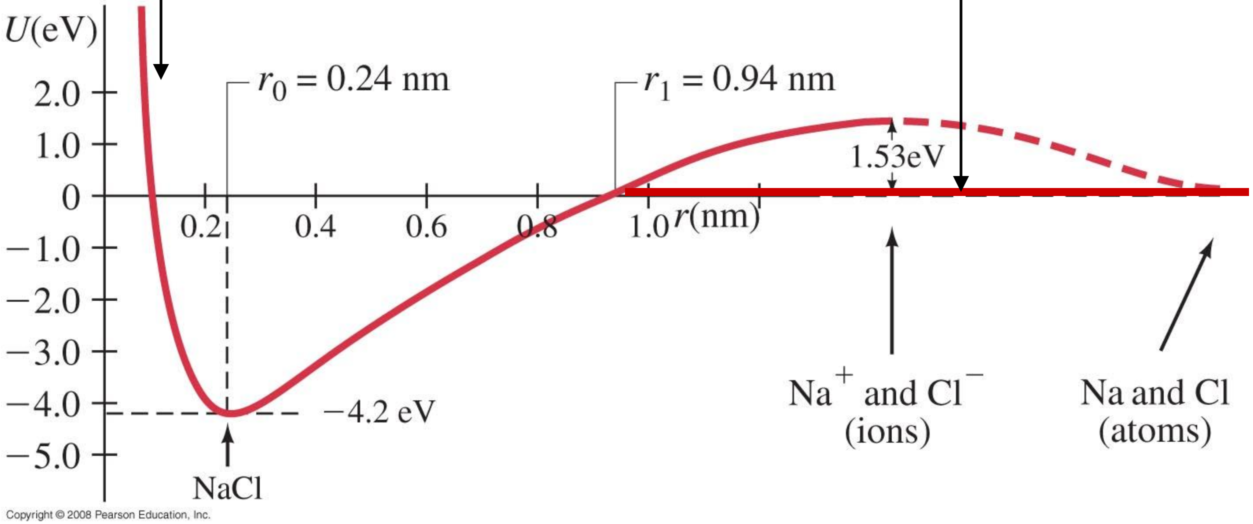


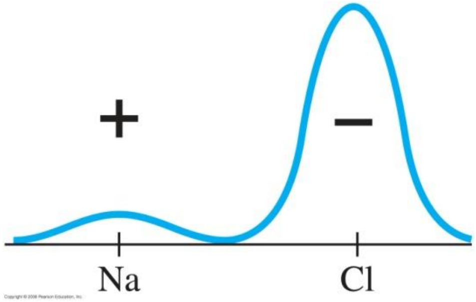
Na (IP) ~ 5.14 eV
Cl (EA) ~ -3.61 eV

1.53 eV required to pruduce Na$^+$Cl$^-$

overlapping of
core electrons

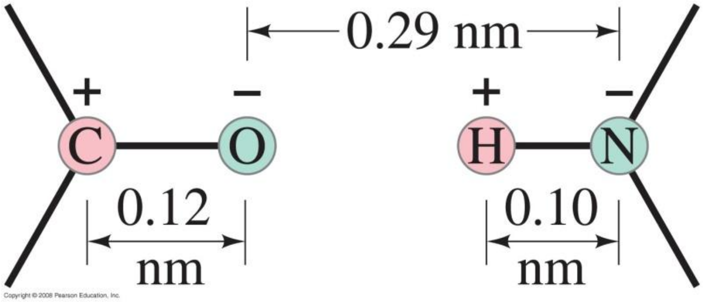
Two uncharged atoms





Van der Waals Bonds

Attraction between molecules that have a dipole moment



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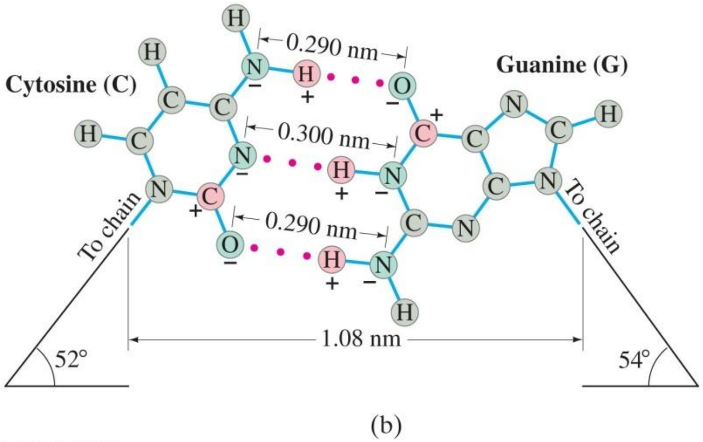
$\vec{p}_i \cdot \vec{p}_j$ **interaction**

Scales like r^{-6}

The basis for the “hydrogen bonding” in nature → weak bonds



(b)

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(a)

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