UNIVERSITÀ
DEGLI STUDI DI TRIESTE

Scienza dei Materiali
- lecture 5-

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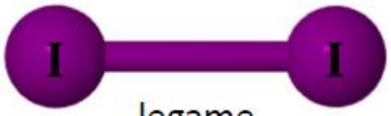
Legame chimico (ripasso)

Legami Primari (tra atomi)

forze intramolecolari

- si manifestano all'interno di una molecola (o insieme atomi/ioni)
- più forti *(150-4000 kJ/mol)*
- fortemente direzionali
- a corto raggio
- determinano le proprietà CHIMICHE della materia

interazione tra ***atomi***



legame covelente

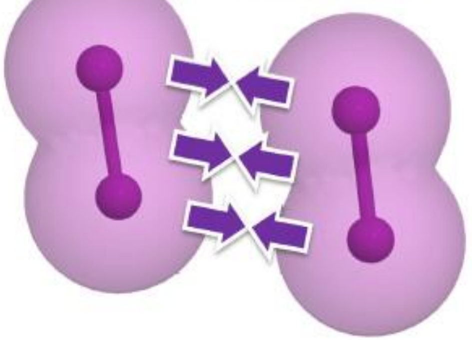
Importanti per i solidi inorganici

Legami Secondari (tra molecole)

forze intermolecolari

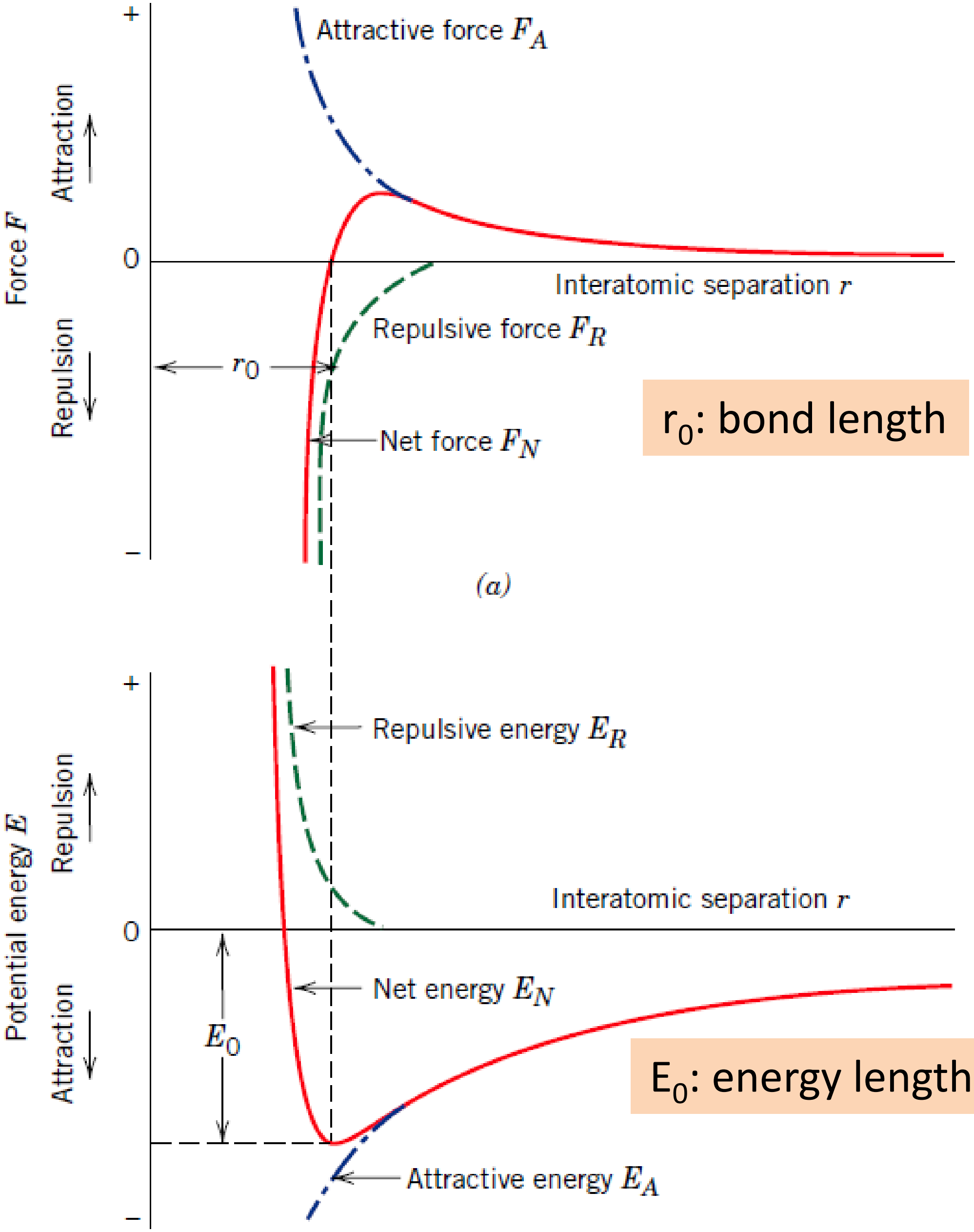
- forze che si manifestano tra entità molecolari (uguali o diverse tra loro)
- più deboli *(0.05- 30 kJ/mol)*
- meno (non-) direzionali
- ad ampio raggio
- determinano le proprietà FISICHE della materia

interazione tra ***molecole***



Importanti nei polimeri

Potential energy and Bond Force



r_0: bond length

E_0: energy length

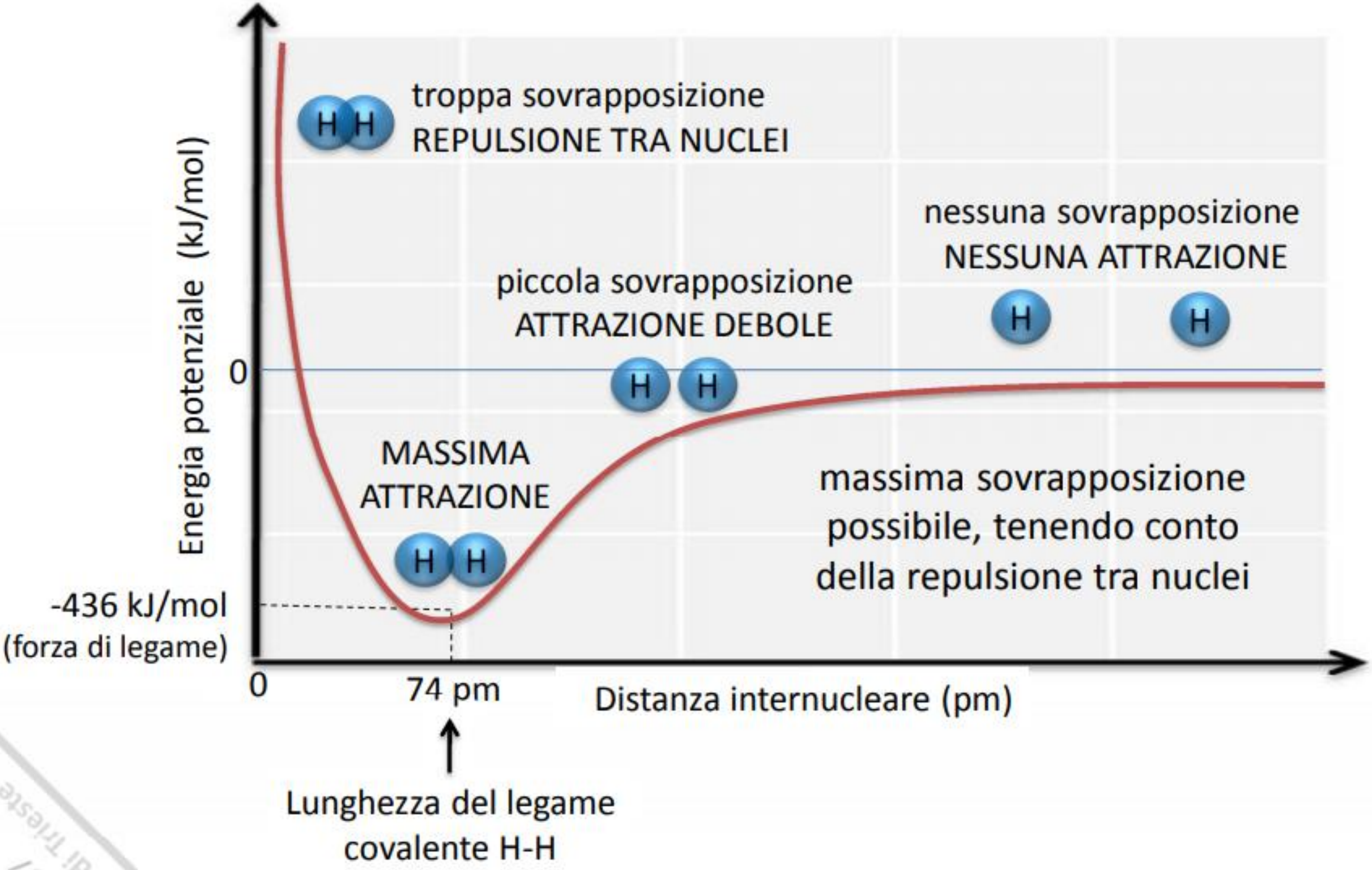
$$F_N = F_A + F_R$$

$$E_N = \int_\infty^r F_N\,dr$$

$$= \int_\infty^r F_A\,dr + \int_\infty^r F_R\,dr$$

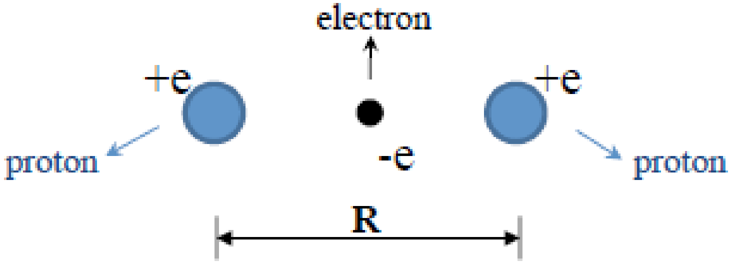
$$= E_A + E_R$$

Energia potenziale per coppie di atomi interagenti



COVALENT BOND

We start from the simplest covalently bonded system: the H_2^+ molecular ion



A simple electrostatic estimate, using Coulomb's energy $U_{12} = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r_{12}}$ gives:

$$U_{TOT} = U_{P_1P_2} + U_{P_1E} + U_{P_2E}$$

$$= \frac{1}{4\pi\varepsilon_0} e^2 \left[\frac{1}{R} - \frac{1}{R/2} - \frac{1}{R/2} \right] = \boxed{-\frac{1}{4\pi\varepsilon_0}\frac{3e^2}{R}} < 0$$

➡ with ***-e*** charge in the middle, the molecular ion IS stable

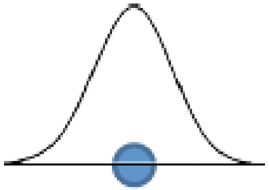
THE “ LCAO” MODEL

To make some progress, we will combine ORBITALS (i.e. electron states) from atoms to describe the molecular orbitals in the molecule.

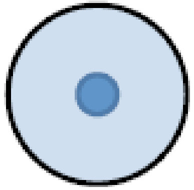
H atom: $1s^1$

the energy is:

$$\varepsilon \cong -13,6058 eV$$

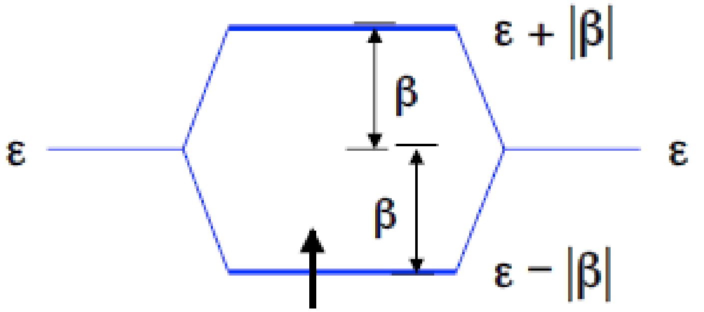


Exponential
(radial)



Symmetry
(angular)

If we place the two protons close to each other, the two orbitals may mix, giving two new states, with different energies (an energy level “doublet”)



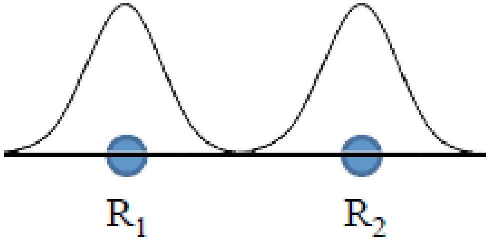
The electron occupies the lowest energy level, i.e., $\varepsilon - |\beta|$

→ a new Ground State

THE “ LCAO” TECHNIQUE

A technique to construct “molecular orbitals” which the electrons occupy when chemical bonds are established. They are obtained as Linear Combination of Atomic Orbitals:

$$\Phi_1(\vec{\mathbf{r}}) = \Phi_{1S}(\vec{\mathbf{r}} - \vec{\mathbf{R}}_1)$$



$$\Phi_2(\vec{\mathbf{r}}) = \Phi_{1S}(\vec{\mathbf{r}} - \vec{\mathbf{R}}_2)$$

$$\boxed{\Psi = C_1\Phi_1 + C_2\Phi_2} \Longleftarrow \text{LCAO}$$

Using as “basis set” just these two orbitals, the “molecular orbital” Ψ is expressed by just 2 real coefficients.

$$\Psi \longleftrightarrow \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

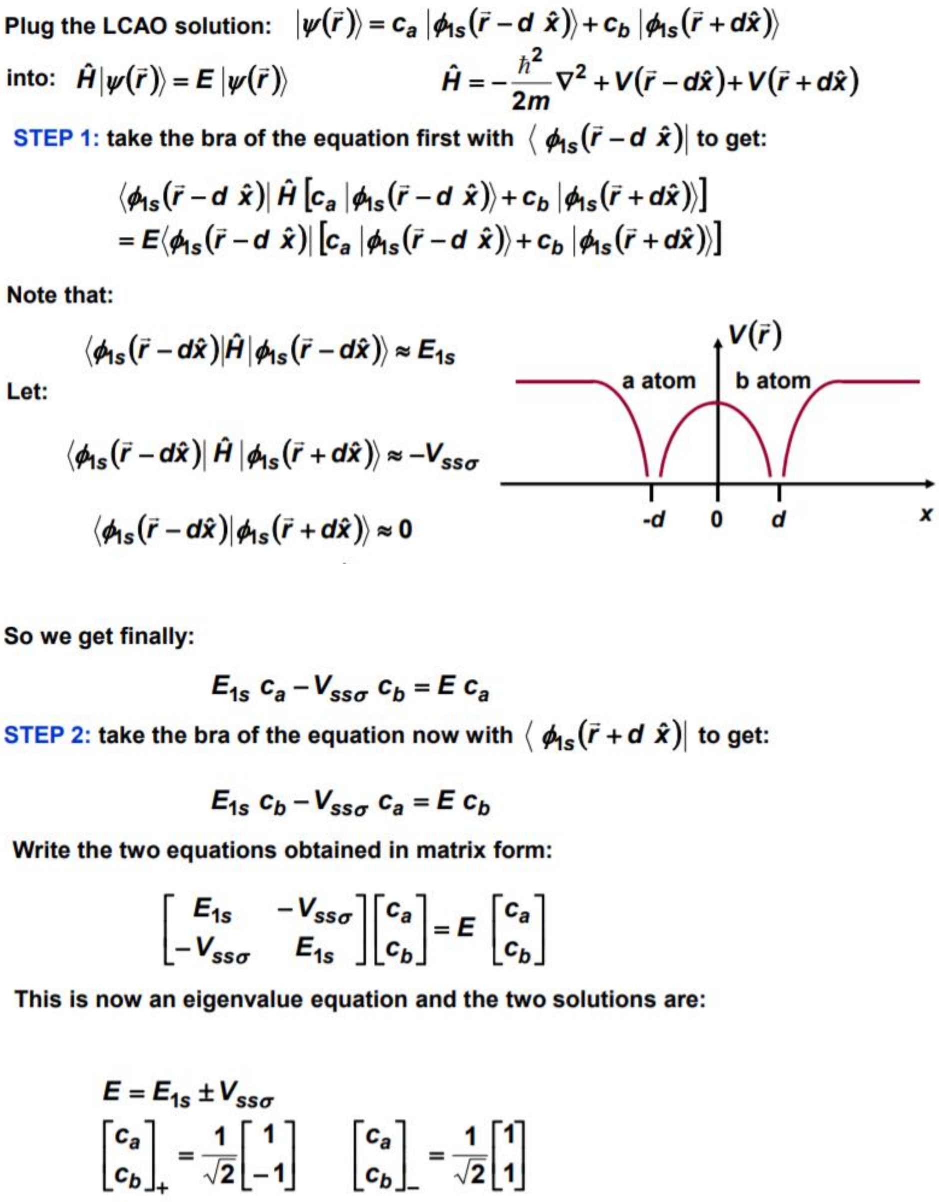
SCHRÖDINGER EQUATION $E\Psi = \hat{H}\Psi \Longrightarrow E\Psi(\vec{r}) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right)\Psi(\vec{r})$

This as we saw is the full equation we would usually solve, but on our simplified basis the differential Hamiltonian operator $\hat{\mathbf{H}}$ will just act on those two coefficients…

$$\begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

$\Longrightarrow$ …it will be a 2x2 MATRIX!!

Note di calcolo su come ottenere il sistema di equazioni lineari che poi possiamo scrivere in forma matriciale (facoltativo). Occhio alla notazione diversa!



Plug the LCAO solution: $|\psi(\vec{r})\rangle = c_a\,|\phi_{1s}(\vec{r}-d\,\hat{x})\rangle + c_b\,|\phi_{1s}(\vec{r}+d\hat{x})\rangle$

into: $\hat{H}|\psi(\vec{r})\rangle = E\,|\psi(\vec{r})\rangle$ $\qquad \hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}-d\hat{x}) + V(\vec{r}+d\hat{x})$

STEP 1: take the bra of the equation first with $\langle\,\phi_{1s}(\vec{r}-d\,\hat{x})|$ to get:

$$\langle\phi_{1s}(\vec{r}-d\,\hat{x})|\,\hat{H}\,[c_a\,|\phi_{1s}(\vec{r}-d\,\hat{x})\rangle + c_b\,|\phi_{1s}(\vec{r}+d\hat{x})\rangle]$$
$$= E\langle\phi_{1s}(\vec{r}-d\,\hat{x})|\,[c_a\,|\phi_{1s}(\vec{r}-d\,\hat{x})\rangle + c_b\,|\phi_{1s}(\vec{r}+d\hat{x})\rangle]$$

Note that:

$$\langle\phi_{1s}(\vec{r}-d\hat{x})|\hat{H}|\phi_{1s}(\vec{r}-d\hat{x})\rangle \approx E_{1s}$$

Let:

$$\langle\phi_{1s}(\vec{r}-d\hat{x})|\,\hat{H}\,|\phi_{1s}(\vec{r}+d\hat{x})\rangle \approx -V_{ss\sigma}$$

$$\langle\phi_{1s}(\vec{r}-d\hat{x})|\phi_{1s}(\vec{r}+d\hat{x})\rangle \approx 0$$

So we get finally:

$$E_{1s}\,c_a - V_{ss\sigma}\,c_b = E\,c_a$$

STEP 2: take the bra of the equation now with $\langle\,\phi_{1s}(\vec{r}+d\,\hat{x})|$ to get:

$$E_{1s}\,c_b - V_{ss\sigma}\,c_a = E\,c_b$$

Write the two equations obtained in matrix form:

$$\begin{bmatrix} E_{1s} & -V_{ss\sigma} \\ -V_{ss\sigma} & E_{1s} \end{bmatrix}\begin{bmatrix} c_a \\ c_b \end{bmatrix} = E\begin{bmatrix} c_a \\ c_b \end{bmatrix}$$

This is now an eigenvalue equation and the two solutions are:

$$E = E_{1s} \pm V_{ss\sigma}$$
$$\begin{bmatrix} c_a \\ c_b \end{bmatrix}_+ = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -1 \end{bmatrix} \qquad \begin{bmatrix} c_a \\ c_b \end{bmatrix}_- = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

THE “ LCAO” TECHNIQUE

We next *guess* a 2x2 Hamiltonian matrix:

$$H = \begin{pmatrix} \varepsilon & \beta \\ \beta & \varepsilon \end{pmatrix}$$

The H_{12} term is an energy β CONNECTING the two atoms

$\Longrightarrow \beta < 0$

The diagonal term is a single site energy: the energy of an isolated if the other is pulled far away.

NOTE: the matrix has to be symmetric, like the molecule.

We recover an *eigenvalue problem*, representing the Schrödinger Equation on the Φ_1, Φ_2 basis:

$$\underline{\underline{H}}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = E\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} \Longrightarrow \begin{pmatrix} \varepsilon & \beta \\ \beta & \varepsilon \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = E\begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

NOTE: in quantum mechanics, the density of probability for the electron to be found at some place **r** is the square modulus of the “wave function” Ψ(**r**).

$$\left|\Psi(r)\right|^2 \quad \text{with} \quad \int_{volume} \left|\Psi(r)\right|^2 d^3r = 1$$

Normalization condition for the probability

Here, we will just have $\left|C_1\right|^2 + \left|C_2\right|^2 = 1$

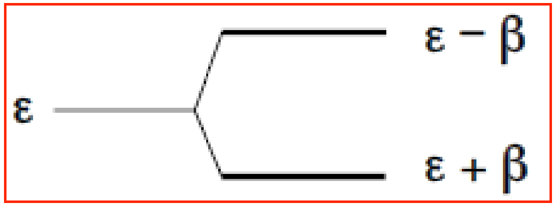
THE “ LCAO” TECHNIQUE

Let’s solve the eigenvalue problem:

$$\det\begin{vmatrix}\varepsilon - E & \beta \\ \beta & \varepsilon - E\end{vmatrix} = 0 \Longrightarrow (\varepsilon - E)^2 - \beta^2 = 0 \Longrightarrow E_{1,2} = \varepsilon \pm \beta$$

note: $\beta < 0$

$E_{1,2} \Longrightarrow$ eigenvalues



Two electron levels

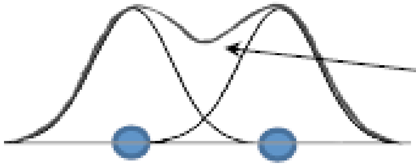
Q: To what states do they correspond?

1) Ground State: $\varepsilon + \beta$

$$\begin{pmatrix}\varepsilon & \beta \\ \beta & \varepsilon\end{pmatrix}\begin{pmatrix}x \\ y\end{pmatrix} = (\beta + \varepsilon)\begin{pmatrix}x \\ y\end{pmatrix} \Rightarrow \varepsilon x + \beta y = \beta x + \varepsilon x$$

$\Rightarrow x = y$ and the same for the 2nd equation.

Normalizing $x = y = \frac{1}{\sqrt{2}} \Rightarrow \boxed{\Psi = \frac{1}{\sqrt{2}}(\Phi_1 + \Phi_2)}$

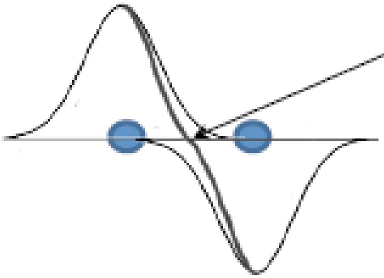


Bonding: since it is adding up in the middle

2) Excited State: $\varepsilon - \beta$

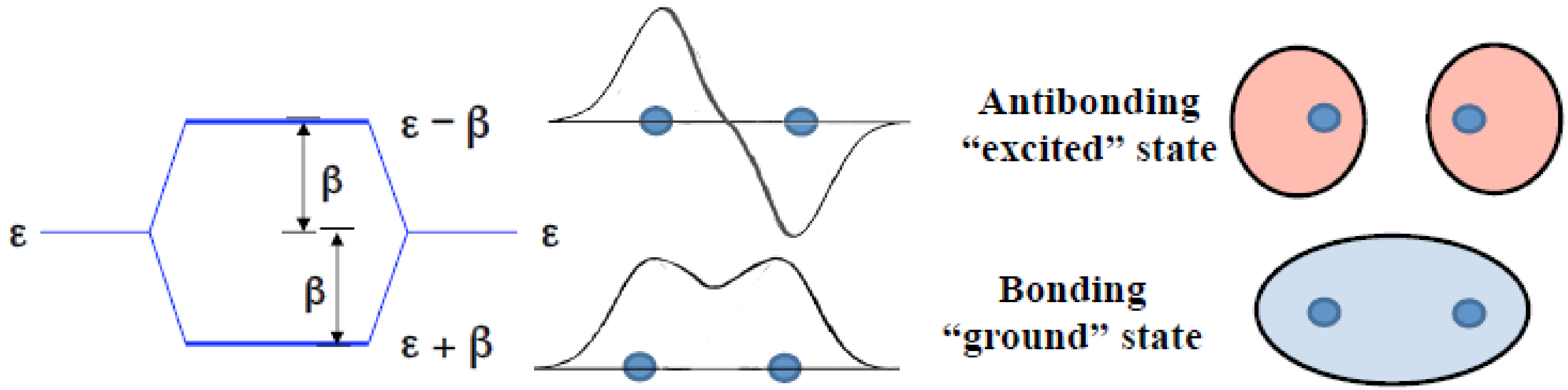
We can show that

$$\boxed{\Psi = \frac{1}{\sqrt{2}}(\Phi_1 - \Phi_2)}$$



A node!! no charge in the middle → antibonding state

THE “ LCAO” TECHNIQUE

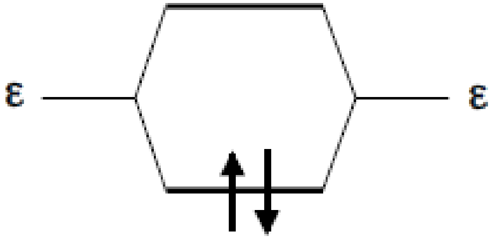


Antibonding
“excited” state

Bonding
“ground” state

For H_2 we should take into consideration the repulsion between the two electrons, but if we ignore this, we can just use the same model.

H_2 molecule:

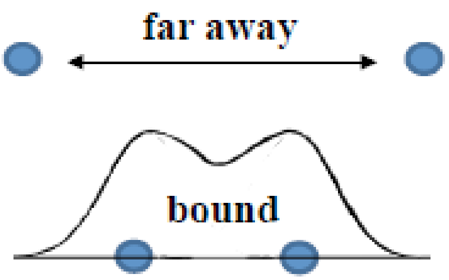


We put **TWO** electrons in the bonding state, which is allowed as they have **OPPOSITE** SPIN.

⟹ **Pauli Exclusion Principle**: “*Two electrons cannot be in the same state with the same spin*”

THE “ LCAO” TECHNIQUE

Q: Which is the cohesive energy E_c (bond energy) of the H_2molecule?

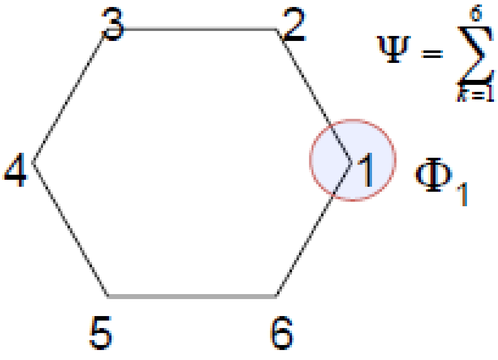


$$E_{2H} = E_H + E_H = 2\varepsilon$$

$$E_{H_2} = 2(\varepsilon + \beta)$$

$$\Longrightarrow \; E_c = E_{H_2} - E_{2H} = 2\beta < 0 \qquad {E_c}/{electron} = \beta < 0$$

Exercise: try again with benzene



$$\Psi = \sum_{k=1}^{6} c_k \Phi_k$$

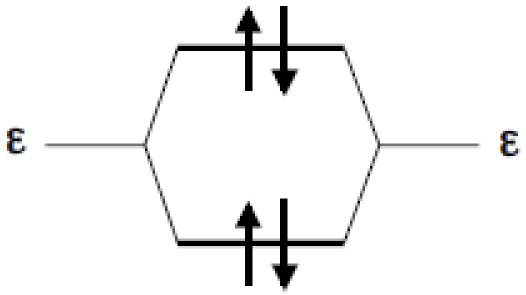
$$\begin{pmatrix} \varepsilon & \beta & 0 & 0 & 0 & \beta \\ \beta & \varepsilon & \beta & 0 & 0 & 0 \\ 0 & \beta & \varepsilon & \beta & 0 & 0 \\ 0 & 0 & \beta & \varepsilon & \beta & 0 \\ 0 & 0 & 0 & \beta & \varepsilon & \beta \\ \beta & 0 & 0 & 0 & \beta & \varepsilon \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \\ C_5 \\ C_6 \end{pmatrix} = E \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \\ C_5 \\ C_6 \end{pmatrix}$$

find the “SPECTRUM” of energy levels (Hint: it will have to be a multiplet with six states!)

HOMONUCLEAR DIATOMIC MOLECULES

Extension other diatomic homonuclear molecules:

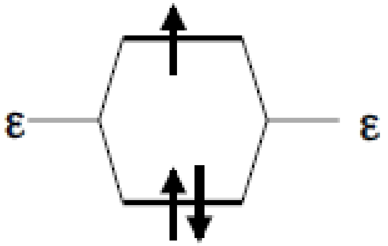
- **He** atoms: $1s^2$



For He_2, we have again a doublet (while of course ε and β will have different values), but 4 electrons to fit in these two states .

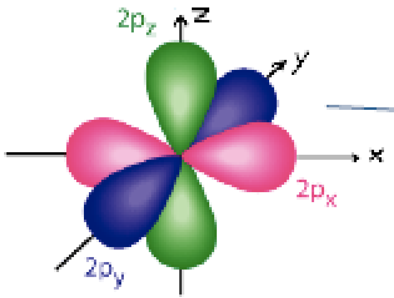
…**NO energy gain!** ⟹ the molecule does **NOT** bind.

But note that He_2^+ (another molecular ion) is stable!



$$E_c = 2\beta - \beta = \beta < 0$$

- With **B, C, …** we must have LCAO with ***p*** electrons

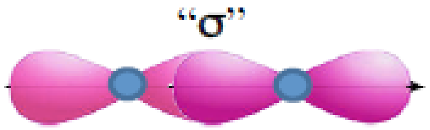


The three ***p*** electronic states

These combine to form bonds in **two** ways,
depending if they “point” along or orthogonal to the bond axis

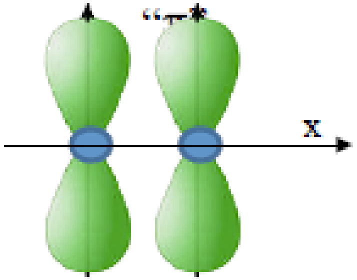
HOMONUCLEAR DIATOMIC MOLECULES

1) p_x is along the line joining the atoms



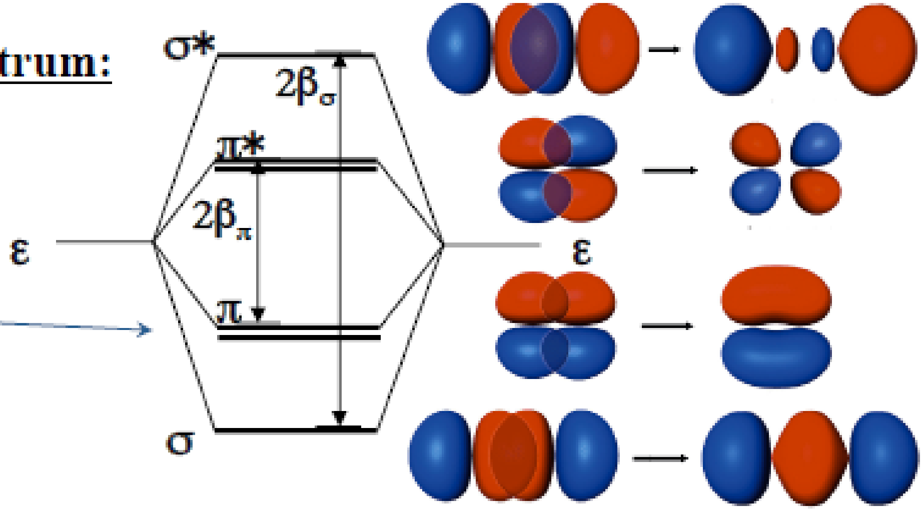
→ **big overlap** in the middle will yield a larger β_σ

2) using p_y, p_z



Small overlap in the middle β_π will be less!

The energy spectrum:



the two π levels are doubly – degenerate since we have the y and z direction.

Note the “nodes” in the wavefunction (molecular orbitals) so obtained

⟹ We thus get **6 MOs** overall, which is ok as we started from **6 AOs**.

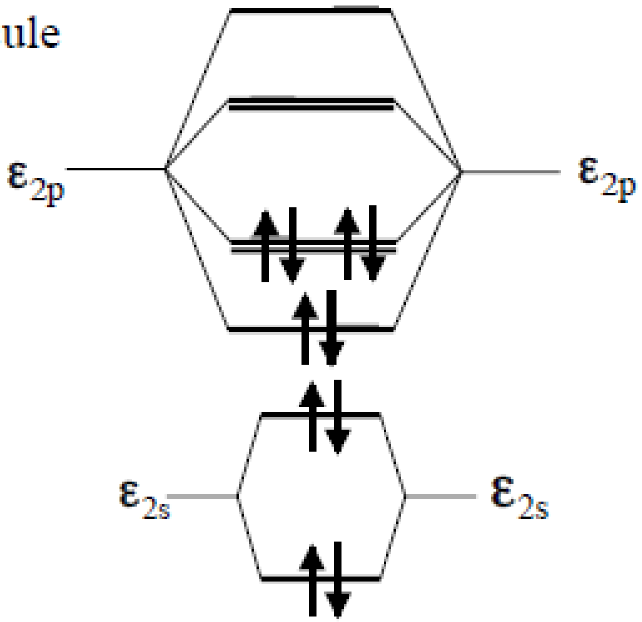
HOMONUCLEAR DIATOMIC MOLECULES

Covalent "bond order"

Three electrons in the *p*-multiplet

- **N** atom: $1s^2\ 2s^2\ 2p^3$

N_2 molecule

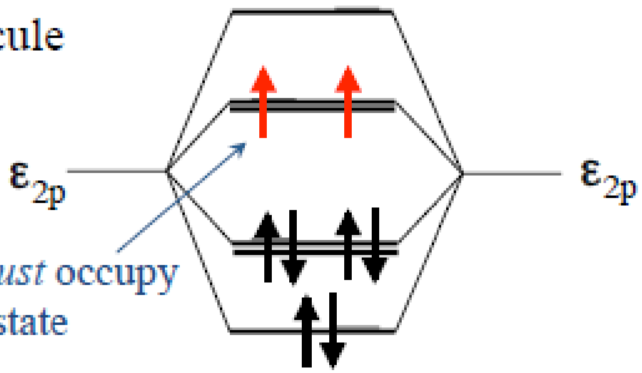


Three fully completed (↑↓) BONDING states

⟹ **TRIPLE** BOND $N \equiv N$

- **O** atom: $1s^2\ 2s^2\ 2p^4$

O_2 molecule



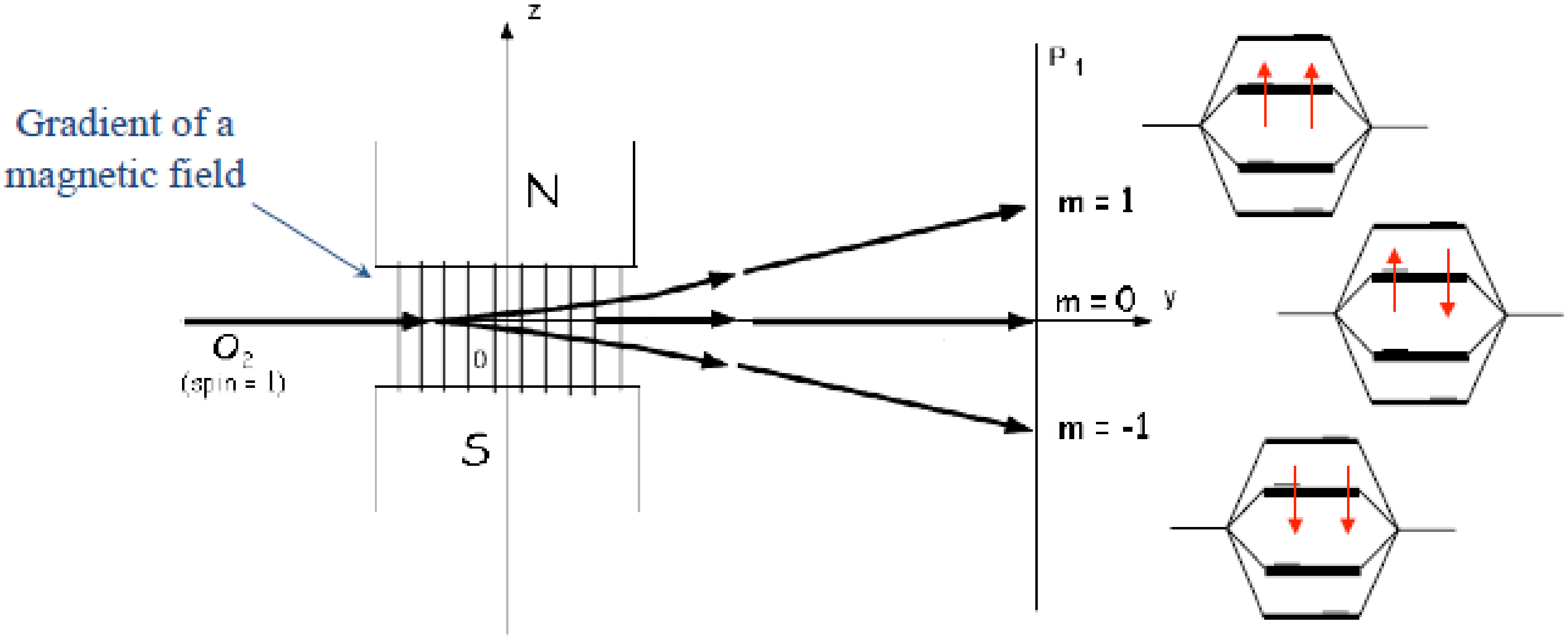
For **O_2** we *must* occupy antibonding state

We put the two electrons in different MO states, i.e., more far away from each other (lower energy, as they repel each other!)

⟹ Now the **spins** can **be the same** (and will, due **Hund's Rule**)

- **O_2** bond order: $3_{bonding} - 1_{antibonding} = 2$
- Total **spin**: $2 \times \frac{1}{2} = 1$ ⟹ the molecule is **paramagnetic**

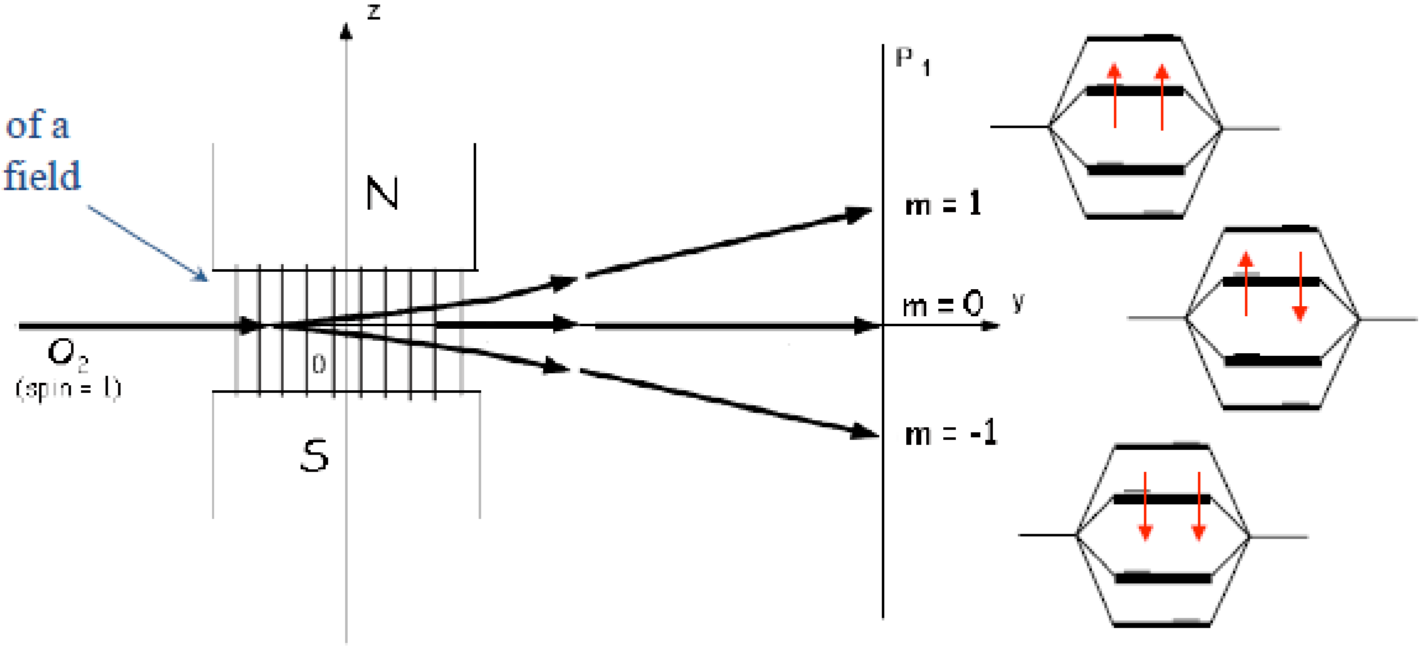
THE STERN-GERLACH EXPERIMENT



Gradient of a magnetic field

There are various (3) lines, as the **s = 1** is a quantized angular momentum!

THE STERN-GERLACH EXPERIMENT



Gradient of a magnetic field

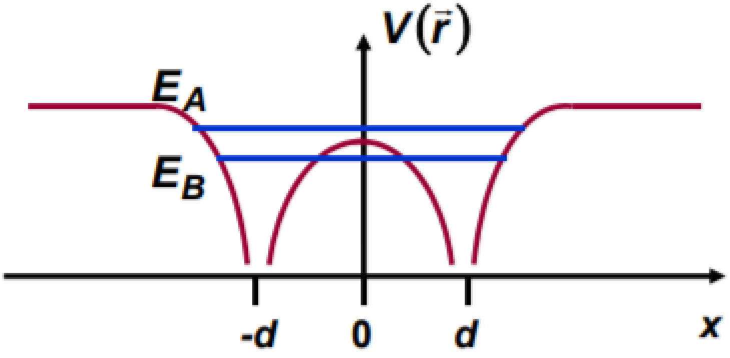
There are various (3) lines, as the **s = 1** is a quantized angular momentum!

Other examples:

- **H atoms** would generate 2 lines, as there is only one state, with spin up or down
- **N_2 molecule** would yield only 1 line: the total electronic angular momentum is 0

Bonding and Anti-Bonding Orbitals

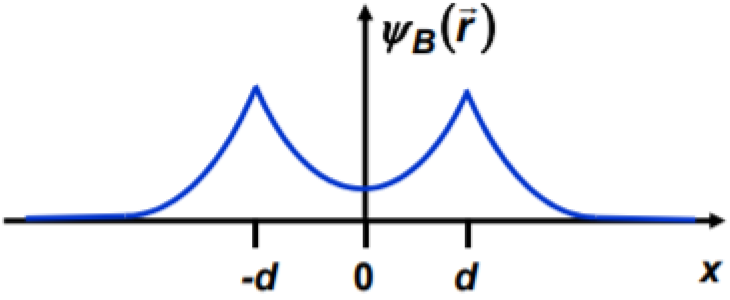
For the lower energy solution we have:



$$E_B = E_{1s} - V_{ss\sigma}$$

$$|\psi_B(\vec{r})\rangle = \frac{1}{\sqrt{2}}\left[\,|\phi_{1s}(\vec{r} - d\,\hat{x})\rangle + |\phi_{1s}(\vec{r} + d\hat{x})\rangle\,\right]$$

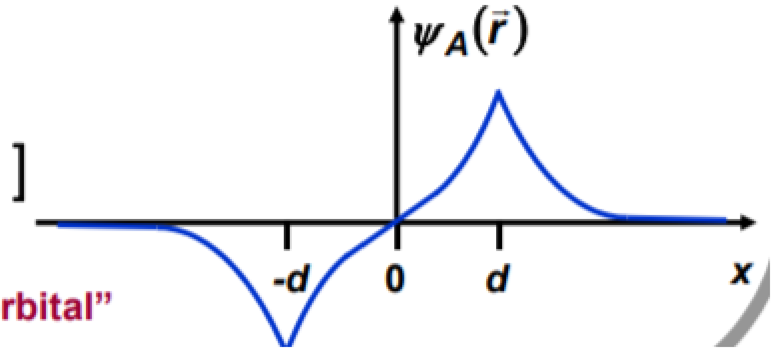
This is called the "Bonding molecular orbital"



For the higher energy solution we have:

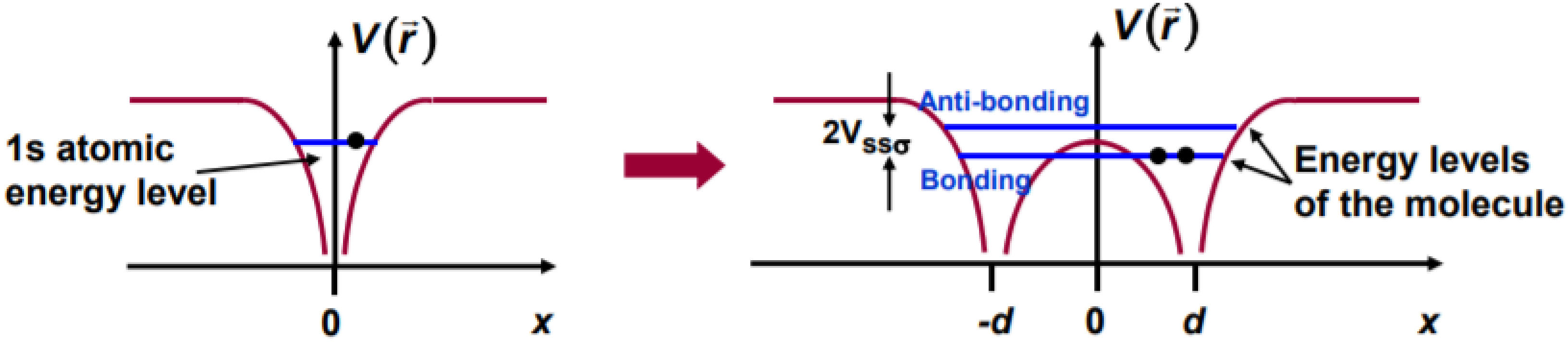
$$E_A = E_{1s} + V_{ss\sigma}$$

$$|\psi_A(\vec{r})\rangle = \frac{1}{\sqrt{2}}\left[\,|\phi_{1s}(\vec{r} - d\,\hat{x})\rangle - |\phi_{1s}(\vec{r} + d\hat{x})\rangle\,\right]$$



This is called the "Anti-bonding molecular orbital"

LCAO: Energy Level Splitting and the Energy Matrix Element



Energy level diagram going from two isolated atoms to the molecule:

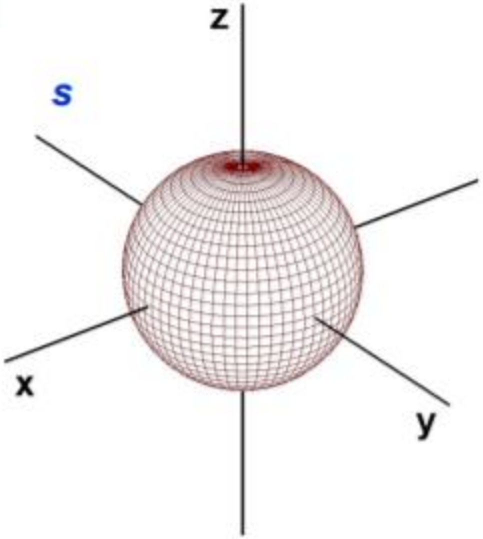
The total energy is lowered when Hydrogen atoms form a Hydrogen molecule

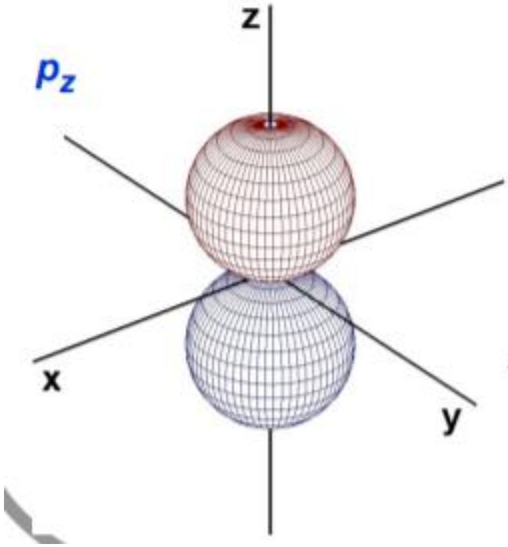
The two 1s orbitals on each Hydrogen atom combine to generate two molecular orbitals – the bonding orbital and the anti-bonding orbital – with energy splitting related to the energy matrix element:

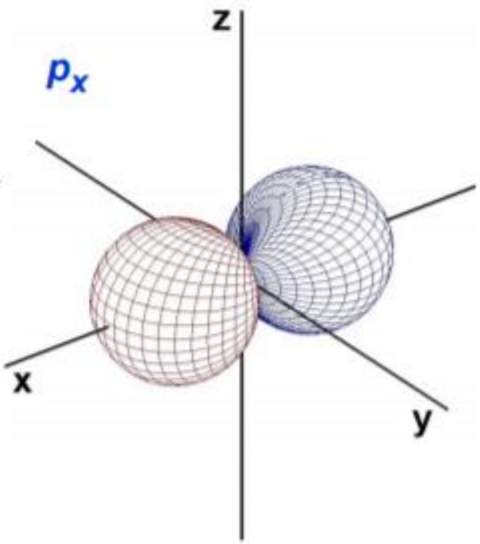
$$\langle \phi_{1s}(\vec{r} - d\hat{x}) | \hat{H} | \phi_{1s}(\vec{r} + d\hat{x}) \rangle \approx -V_{ss\sigma}$$

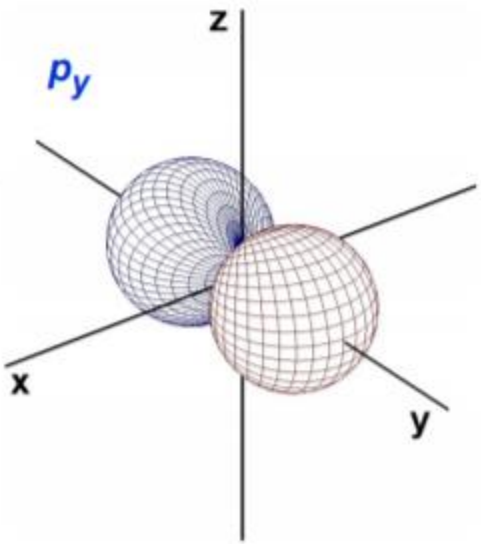
Atomic Orbitals

- Wavefunction amplitudes of the atomic s and p orbitals in the angular directions are plotted
- The s-orbital is spherically symmetric
- The p-orbitals have +ve and –ve lobes and are oriented along x-axis, y-axis, and z-axis





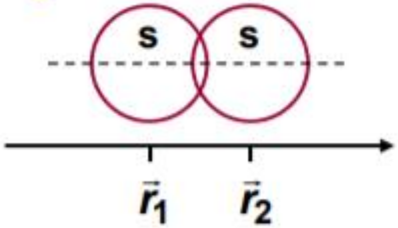




Orbitals and Bonding

There are two main types of co-valent bonds: sigma bonds (or σ-bonds) and pi-bonds (or π-bonds)

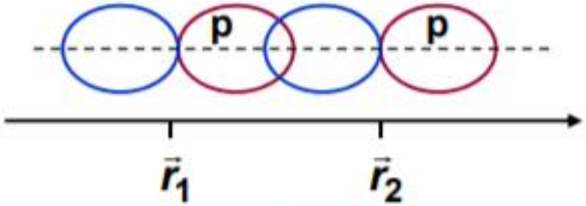
(1) Sigma bonds (or σ-bonds):



s-s σ-bond

(Example: Hydrogen molecule, semiconductors)

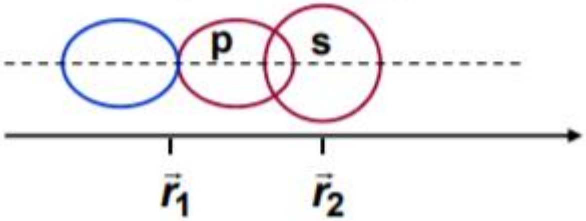
$$\langle \phi_s(\vec{r}-\vec{r}_1) | \hat{H} | \phi_s(\vec{r}-\vec{r}_2) \rangle \approx -V_{ss\sigma}$$



p-p σ-bond

(Example: Semiconductors)

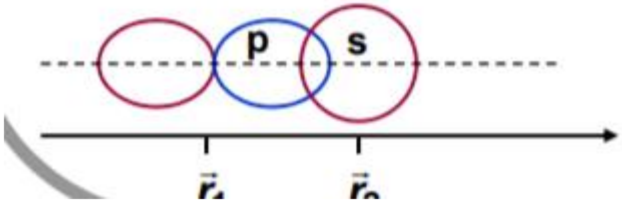
$$\langle \phi_p(\vec{r}-\vec{r}_1) | \hat{H} | \phi_p(\vec{r}-\vec{r}_2) \rangle \approx V_{pp\sigma}$$



s-p σ-bond

(Example: Semiconductors)

$$\langle \phi_p(\vec{r}-\vec{r}_1) | \hat{H} | \phi_s(\vec{r}-\vec{r}_2) \rangle \approx -V_{sp\sigma}$$



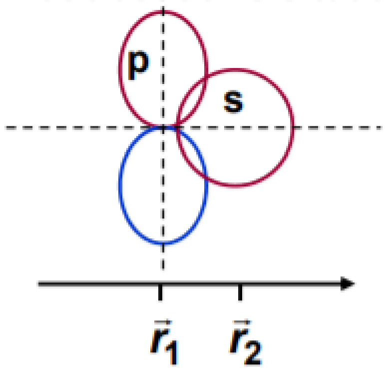
s-p σ-bond

(Example: Semiconductors)

$$\langle \phi_p(\vec{r}-\vec{r}_1) | \hat{H} | \phi_s(\vec{r}-\vec{r}_2) \rangle \approx V_{sp\sigma}$$

Orbitals and Bonding

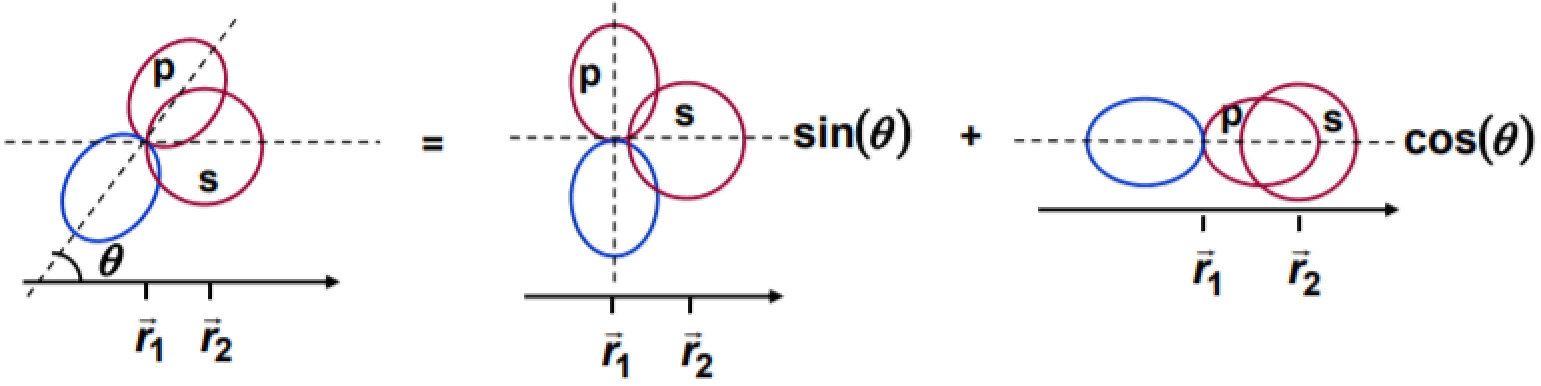
What about this situation?



$$\left\langle \phi_p(\vec{r}-\vec{r}_1) \right| \hat{H} \left| \phi_s(\vec{r}-\vec{r}_2) \right\rangle \approx 0$$

The Hamiltonian is up-down symmetric
The s-orbital is up-down symmetric
The p-orbital is up-down anti-symmetric
⇒ The matrix element is zero! No bonding possible

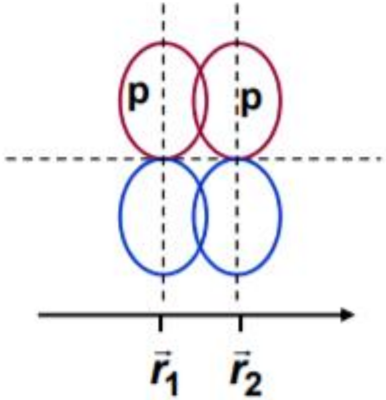
What about this situation? What should be the matrix element?



$$\left\langle \phi_p(\vec{r}-\vec{r}_1) \right| \hat{H} \left| \phi_s(\vec{r}-\vec{r}_2) \right\rangle \approx 0 \,.\, \sin(\theta) + \left(-V_{sp\sigma}\right) . \cos(\theta)$$
$$= -V_{sp\sigma} \cos(\theta)$$

Orbitals and Bonding

(2) Pi bonds (or π-bonds):

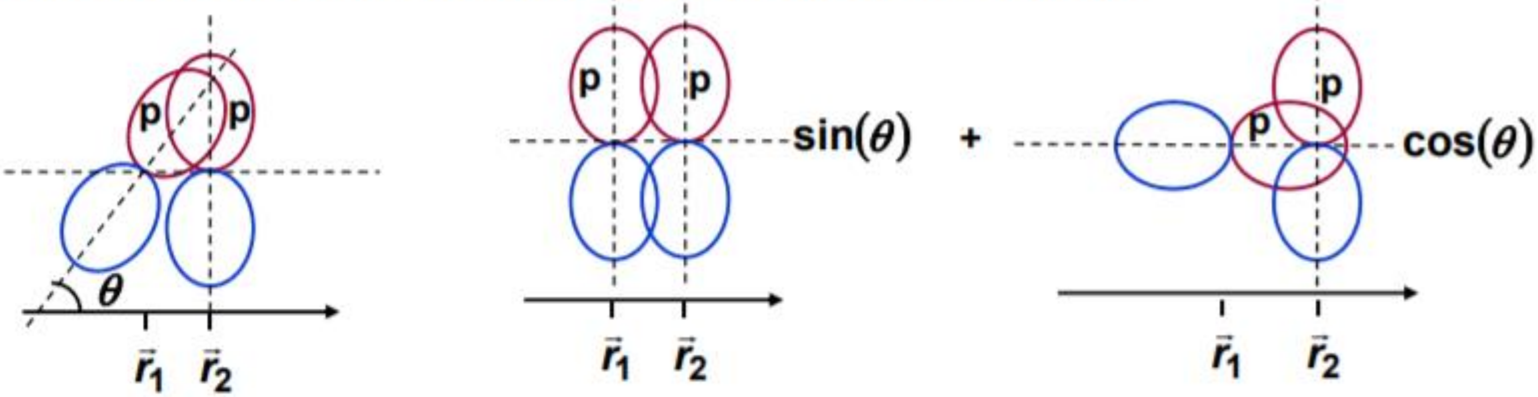


p-p π-bond

(Example: graphene, carbon nanotubes, conjugated conducting molecules)

$$\left\langle \phi_p(\vec{r}-\vec{r}_1) \right| \hat{H} \left| \phi_p(\vec{r}-\vec{r}_2) \right\rangle \approx -V_{pp\pi}$$

What about this situation? What should be the matrix element?



$$\left\langle \phi_p(\vec{r}-\vec{r}_1) \right| \hat{H} \left| \phi_p(\vec{r}-\vec{r}_2) \right\rangle \approx \left(-V_{pp\pi}\right).\sin(\theta) + 0\,.\cos(\theta)$$

$$= -V_{pp\pi}\sin(\theta)$$

van der Waals BONDING

We predicted that the **He_2** molecule is not bound. Actually, at very low temperatures, He does yield a condensed matter phase: it becomes "superfluid" (TRY a LCAO theory for this!).

Another example is **N_2**, liquid below 77°K at normal pressure.

Ne, **Ar**, **Kr**, **Xe** and **Rn** act similarly, and many more materials are just weakly bound.

⇒ **van der Waals "dispersive" forces**

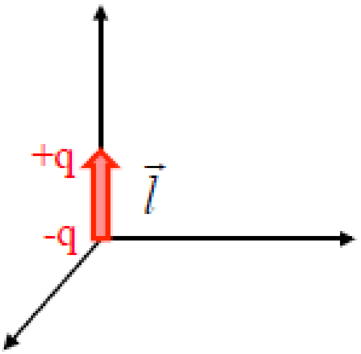
The idea: 3 steps

- even in Ne, a fluctuation may occur in the atom, yielding temporarily a dipole.
- This will exert a field on the other atom, which will polarise.
- The two dipoles will now interact with a strength $\propto -{}^{1}\!/_{R^6}$, an **attraction** measured to be proportional to the inverse *sixth power* of the distance.

⇒ To show it, we need to derive the **potential from a dipole**

THE DIPOLE POTENTIAL

Potential from a dipole



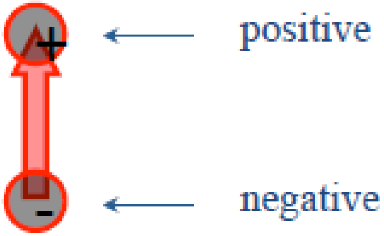
$$\Phi(\vec{r}) = \Phi_c^{+q}(\vec{r} - \vec{l}) + \Phi_c^{-q}(\vec{r})$$

$$\Phi_c(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\frac{q}{r}$$ **Coulomb potential**

if $|\vec{l}| << \vec{r} \implies \Phi(\vec{r} - \vec{l}) \cong \Phi(\vec{r}) + \vec{\nabla}\Phi(-\vec{l})$ with $\boxed{\vec{\nabla}\Phi = -\frac{1}{4\pi\varepsilon_0}\frac{q}{r^2}\frac{\vec{r}}{r}}$

So in the end: $\Phi(\vec{r}) = \Phi_c^{-q}(\vec{r}) + \Phi_c^{+q}(\vec{r}) + \frac{1}{4\pi\varepsilon_0}\frac{q}{r^2}\frac{\vec{r}}{r}\vec{l}$

and if $\vec{p} = q\vec{l} \implies \boxed{\Phi(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\frac{\vec{p}\cdot\vec{r}}{r^3}}$



DIPOLE-DIPOLE INTERACTIONS

Q_1: What is the field $\vec{E}$ associated with an electric dipole?

Q_2: What is the energy of *another* dipole in the field (potential) of a given dipole?

A_2: $q\Phi(\vec{r}) = U =$ energy of a charge q in the external electric potential $\Phi(\vec{r})$

For a dipole, the energy must be:

$$-q\Phi(\vec{r}) + q\Phi(\vec{r}+\vec{l}) \cong -q\Phi(\vec{r}) + q\Phi(\vec{r}) + q\vec{\nabla}\Phi\cdot\vec{l}$$

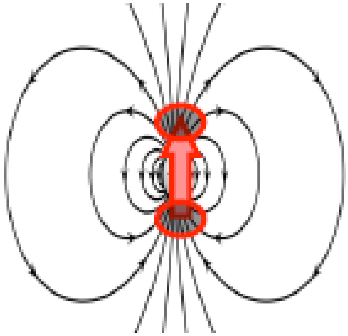
$$= -\vec{E}\cdot\vec{p} \;\Longrightarrow\; \boxed{U = -\vec{E}\cdot\vec{p}}$$

Energy of a dipole
in an external *field*

A_1: $\vec{E} = -\nabla\Phi_{dip} =$ Field from a dipole

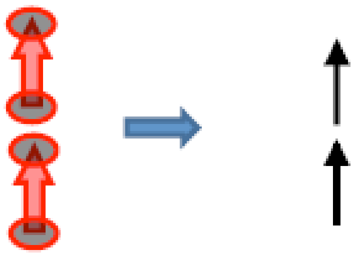
$$= -\nabla\left[\frac{1}{4\pi\varepsilon_0}\frac{\vec{p}\cdot\vec{r}}{r^3}\right] = +\frac{1}{4\pi\varepsilon_0}\left[\frac{-\vec{p}}{r^3} + 3\frac{\vec{p}\cdot\vec{r}}{r^4}\cdot\frac{\vec{r}}{r}\right]$$

$$\Longrightarrow \boxed{\vec{E}_{dip} = \frac{1}{4\pi\varepsilon_0}\left[\frac{-\vec{p}}{r^3} + 3\frac{(\vec{p}\cdot\vec{r})\cdot\vec{r}}{r^5}\right]}$$

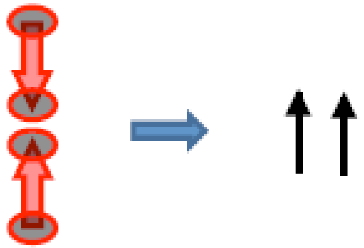


DIPOLE-DIPOLE INTERACTIONS

So:



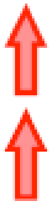
Stable



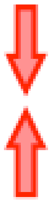
Unstable

… we can compute the energy

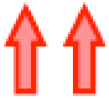
$$U = -\vec{E}_1 \cdot \vec{p}_2 = \frac{1}{4\pi\varepsilon_0}\left[\frac{\vec{p}_1 \cdot \vec{p}_2}{r^3} - 3\frac{(\vec{p}_1 \cdot \vec{r})(\vec{p}_2 \cdot \vec{r})}{r^5}\right]$$



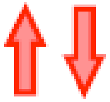
$$U = -2\left(\frac{1}{4\pi\varepsilon_0}\frac{p^2}{r^3}\right)$$



The opposite!



$$U = \frac{1}{4\pi\varepsilon_0}\frac{p^2}{r^3}$$



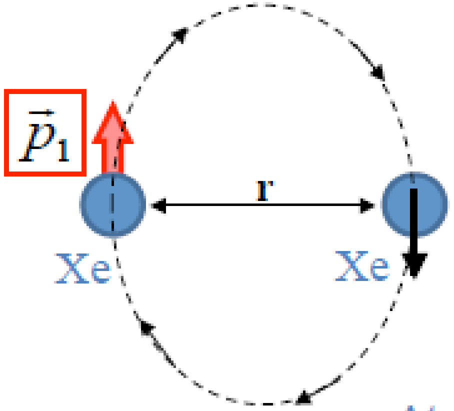
The opposite!

VAN DER WAALS BONDING

So, what is the van der Waals energy?
It must be small, if the liquids boil at very low temperatures!

There is **no** net dipole on **Ne**, **Ar**, **Kr**, **Xe** ,…

But for any *fluctuation* $\Longrightarrow E_1 \propto {}^{1}\!/_{r^3}$



$$\boxed{\vec{E}_1 \propto {}^{1}\!/_{r^3}}$$

$$\boxed{\vec{p}_2 = \propto \vec{E}_1}$$

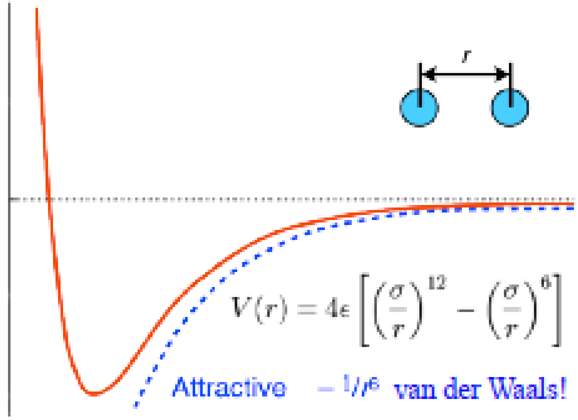
Atoms are polarisable!

So, $|\vec{p}_2| \propto {}^{1}\!/_{r^3}$

$$\Rightarrow \boxed{U = -\vec{E}_1 \cdot \vec{p}_2 \propto -{}^{1}\!/_{r^6}} \quad \text{vdW}$$

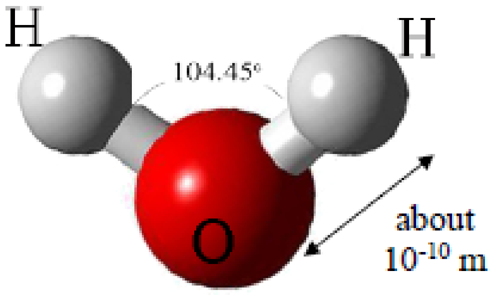
Sometimes we use the Lennard – Jones potential

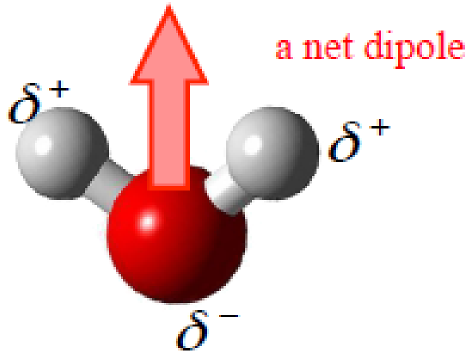
$$\boxed{U = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]}$$

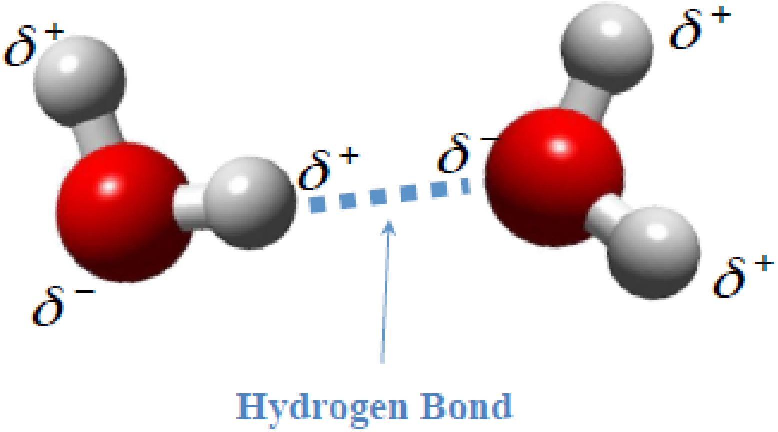


THE HYDROGEN BOND

Sometimes molecules have a **permanent** dipole. Consider e.g., water:







Hydrogen bonds slightly modify the electrostatics of dipoles. They are **directional.**

Furthermore, there are strong **QM effects** in the behaviour of the protons (H atom)

The ElectronVolt

$e =$ fundamental charge unit $e \cong 1{,}60217 \times 10^{-19}$ Coulomb

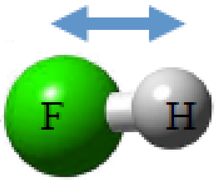
$eV \cong e \cdot 1$ Volt

So $\boxed{1eV \cong 1{,}6 \times 10^{-19} J}$ (the Volt is a IS potential unit) $Volt = \frac{Joule}{Coulomb}$

Typical hydrogen bond energy $\approx 0{,}2 - 0{,}3\ eV$, or higher for $H - F \cdots H - F$
that is, for molecules carrying very strong dipoles

Q: Can we relate the bond energies with the energy corresponding to room <u>temperature</u>?
Why is water a liquid, Si a solid and He a gas at room temperature, T ~ 300K ?

A: Well, let's assume that the typical "vibration" of an atom carries an energy ≈ **k_bT** (we will prove this later)



Boltzmann Constant $\boxed{k_b = 1{,}3806 \times 10^{-23} \frac{Joule}{molecule \cdot K}}$

$$R = N_a \cdot k_b = 6{,}02 \times 10^{23} \frac{molecules}{mole} \cdot 1{,}38 \times 10^{-23} \frac{Joule}{molecule \cdot K} = 8{,}314 \frac{Joule}{Mole \cdot K}$$

$$\boxed{k_b T} = k_b \cdot 300 = \frac{3 \cdot 1{,}38 \cdot 10^{-21}\, Joule}{1{,}6 \cdot 10^{-19} \frac{Joule}{eV}} \cong \frac{4}{160} eV \cong \boxed{\frac{1}{40} eV}$$

~ a fortieth of an eV
~ room temperature

THE HYDROGEN BOND

Q: So, do we expect hydrogen bonds to break at room temperature? And how soon?

$$\underset{\text{bond breaking frequency}}{\underset{\uparrow}{\begin{pmatrix}\text{Time it takes to}\\ \text{break a bond}\end{pmatrix}^{-1}}} = \underset{\cong 10^{12}}{\underset{\uparrow}{\begin{matrix}\text{frequency of}\\ \text{attempt}\end{matrix}}} \cdot \underset{e^{-\frac{\Delta E}{k_b T}}}{\underset{\uparrow}{\begin{matrix}\text{rate of}\\ \text{success}\end{matrix}}}$$

$\boxed{0,25\ eV}$

Boltzmann law

$\boxed{\frac{1}{40}eV}$

$$10^{12}\cdot e^{-\frac{40}{4}} \cong \boxed{4,5\times 10^{7}}$$

ESTIMATED bond breaking frequency

$$e^{-10} \longrightarrow 10^{-5} < e^{-10} < 10^{-4} \text{ since } e^{-10} \cong 10^{-\frac{10}{2,3}}$$

$\boxed{\ln(10) \cong 2,302585}$

…so it takes less then a millionth of a second to break a 0.25 eV bond!

- and the "ν" attempt rate might be higher then 10^{12}

Q: so, weak covalent bonds also break, surely?

- $\Delta E = 1eV \Longrightarrow 10^{12}\cdot e^{-40} \cong 10^{12}\cdot 10^{-17} \cong 10^{-5}$ So it takes on average ~10^{5} s (~ 1day) to break a 1eV bond

Q: and a strong covalent bond, or an ionic bond?

- $\Delta E = 3eV \Longrightarrow 10^{12}\cdot e^{-120} \cong 10^{12}\cdot 10^{-52} \cong 10^{-40}$ such bonds will effectively **<u>never</u>** break at room temperature

IONIC BONDING I

Typical of oxides, ceramics, etc…
The idea is that **atoms** become **ions** following valence charge displacement

Cations if $q > 0$

Anions if $q < 0$

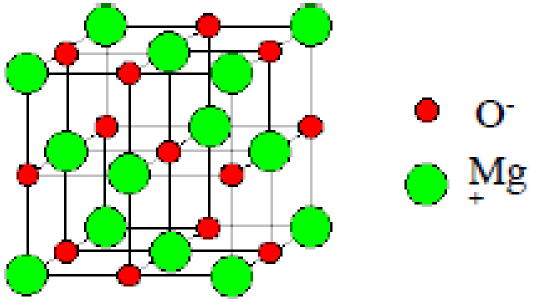
The **stoichiometry** is such that charge neutrality is always achieved

e.g. **MgO**

$\boxed{q = -2e}$

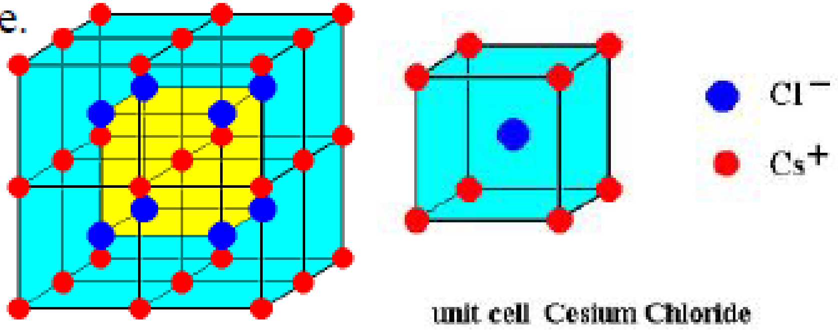
$\boxed{q = 2e}$

MgO involves two "**FCC**" lattices, one next to the other. NaCl does exactly the same.
So this is called the "**sodium chloride**" structure.



e.g. **CsCl**

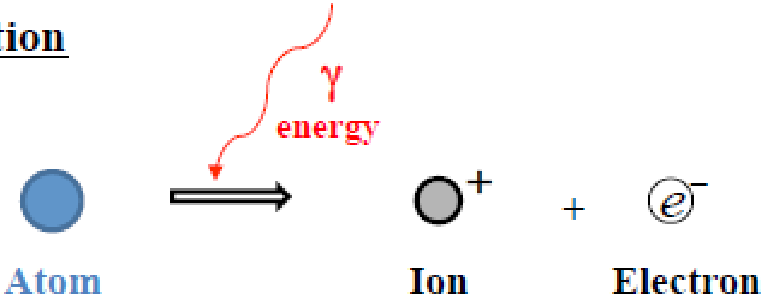
Another structure one is CsCl, corresponding to two SC lattices one inside the other.



we will look at lattices soon enough. Here we focus on ION formation (and why would that happen, at all..!)

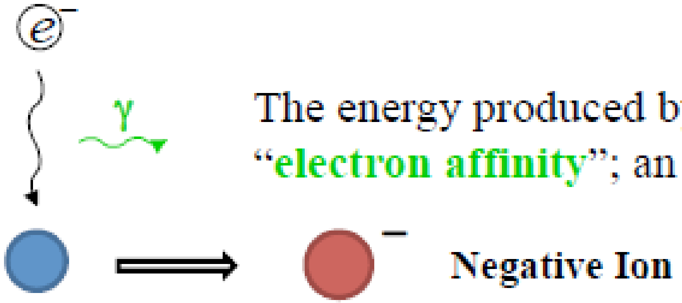
IONIC BONDING II

Ionization



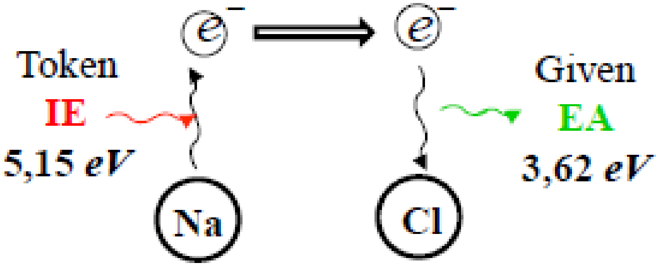
it can happen by light absorption inducing electron-photoemission

the energy necessary to ionise the atom is called “**ionization energy**” or “Ionization Potential”. (for a solid, it’s called “work function” and is surface-dependent)



The energy produced by an electron to a neutral atom, is called “**electron affinity**”; an anion is formed during this process

So:

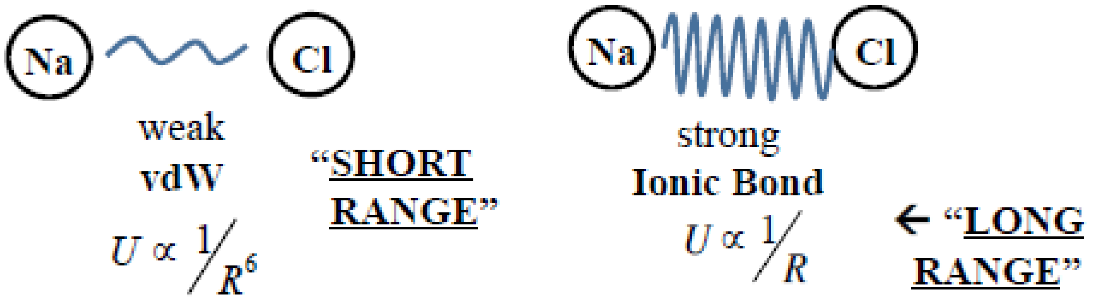


it’s not worth it…!!

… or is it?

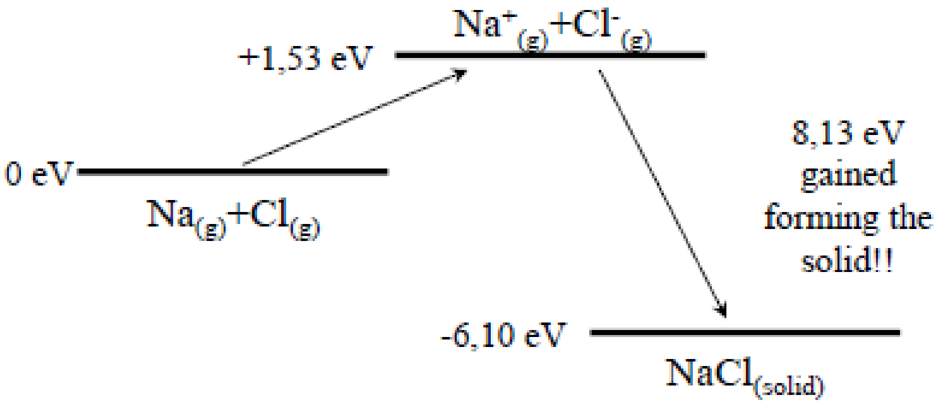
IONIC BONDING III

The process does happen experimentally, due to the stabilising Coulomb energy associated with the formation/interaction of the two ions



This is even more true in solids, where each atom can have several *nearest neighbour* atoms.

we will next attempt to estimate the ELECTROSTATIC ENERGY in solids (periodic = crystalline). The diagram for NaCl was

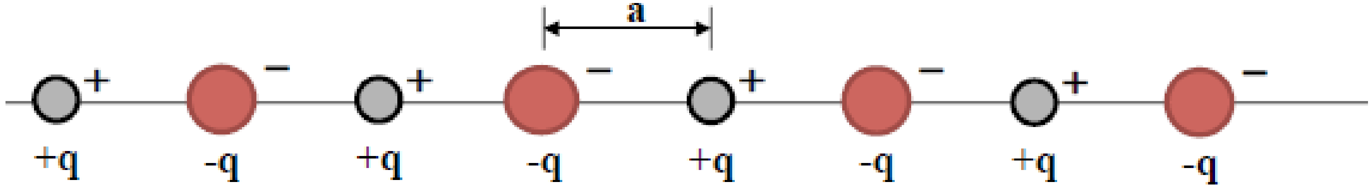


8,13 eV gained forming the solid!!

clearly, the packing of ions is very efficient!

IONIC BONDING IV

A 1-Dimensional Model



the energy will be $U = \dfrac{1}{4\pi\varepsilon_0}\left[-\dfrac{q^2}{a} + \dfrac{q^2}{2a} - \dfrac{q^2}{3a} + \dfrac{q^2}{4a} + \ldots\right] \times 2$

for the ion in the origin: $\therefore\ U = \dfrac{-q^2}{2\pi\varepsilon_0 a}\left[1 - \dfrac{1}{2} + \dfrac{1}{3} - \dfrac{1}{4} + \ldots\right]$

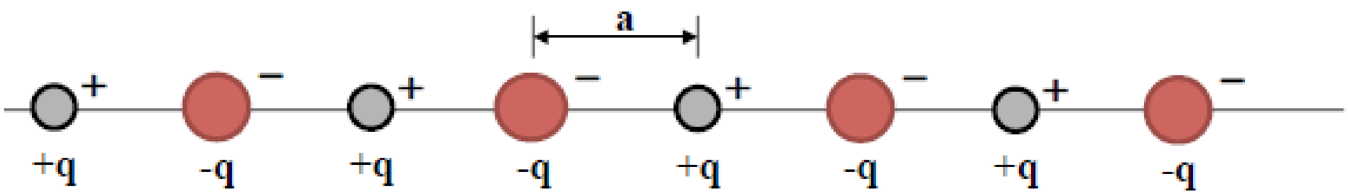
Note: $\therefore\ (1+x)^\alpha = 1 + \alpha x + \dfrac{\alpha(\alpha-1)x^2}{2} + \dfrac{\alpha(\alpha-1)(\alpha-2)x^3}{3!} + \cdots$

$\therefore\ \dfrac{1}{(1+x)} = 1 - x + x^2 - x^3 + \cdots$ $\quad\therefore\ \int \dfrac{1}{(1+x)} = \ln(x+1) = x - \dfrac{x^2}{2} + \dfrac{x^3}{3} - \dfrac{x^4}{4} + \cdots$

$\therefore\ \ln 2 = 1 - \dfrac{1}{2} + \dfrac{1}{3} - \dfrac{1}{4} + \ldots$

$$\Rightarrow \boxed{U = \frac{-q^2}{a} \cdot \left[\frac{\ln 2}{2\pi\varepsilon_0}\right]}$$

THE MADELUNG CONSTANT



$$U = \frac{-q^2}{a}\cdot\boxed{\left[\frac{\ln 2}{2\pi\varepsilon_0}\right]}$$

Madelung Constant

The energy is:

1) proportional to the **square** of the charge
$\Longrightarrow$ MgO has a much higher cohesive energy than NaCl…

2) $\propto \dfrac{1}{a}$ this seems to suggest that halving all distances will *double* the energy, …indefinitely! Not so! Pauli exclusion will kick in at the appropriate "ionic radii" ✪

3) There is a Madelung Constant which depends on the lattice (fcc, bcc, …)

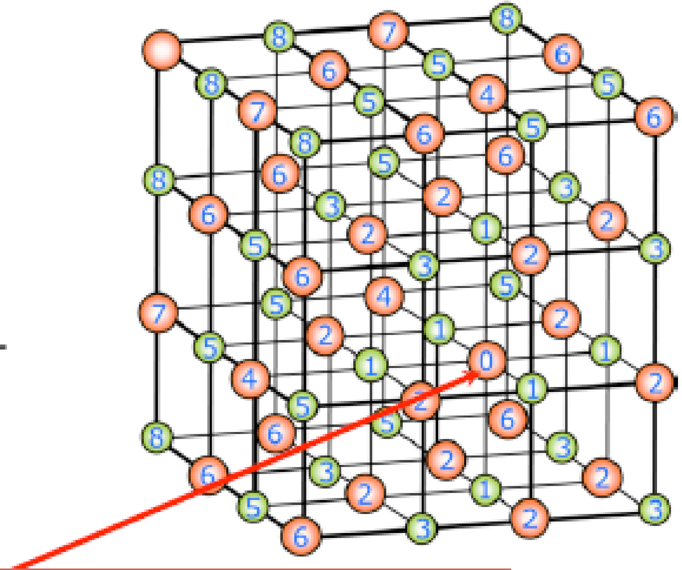
✪ in general, the stoichiometry and the atomic radii will decide the structure of an ionic solid. We next look at crystal lattices.

THE MADELUNG CONSTANT IN 3D

$$U = \frac{-q^2}{a} \cdot M$$

$$M = \sum_{j,k,\ell=-\infty}^{\infty} \frac{(-1)^{j+k+\ell}}{(j^2+k^2+\ell^2)^{1/2}}$$

$$M \cong 1.74756$$

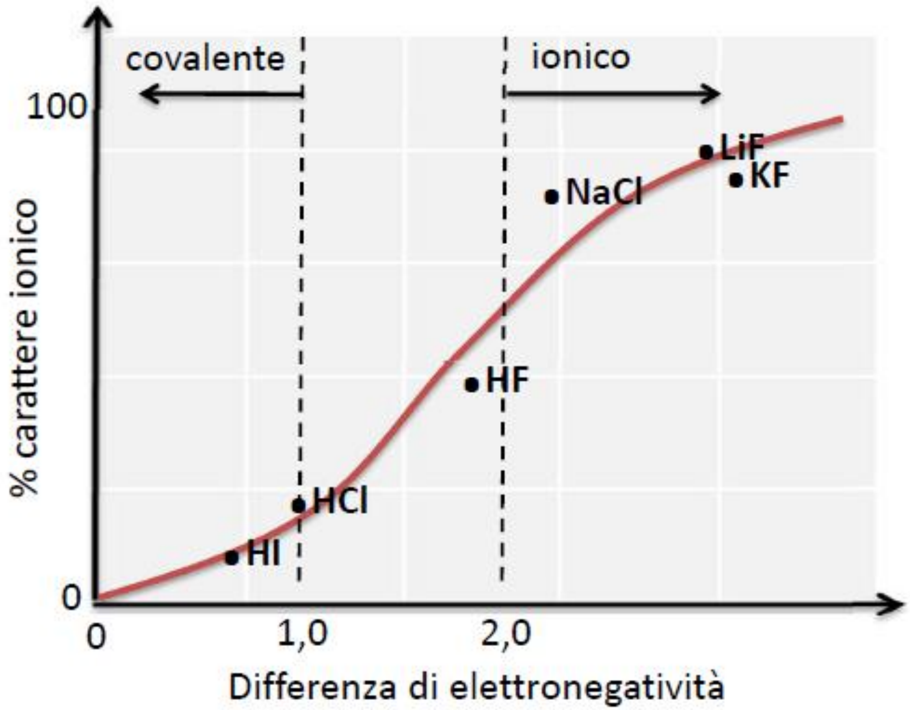


a sum over neighbours of alternated charge sign of the atom at the origin

✪ in general, the stoichiometry and the atomic radii will decide the structure of an ionic solid. We next look at crystal lattices.

Q: would you know how to use a computer to evaluate numerically the Madelung constant *M*? [HINT: you will have to find tricks to save cpu time and speed up converge...]

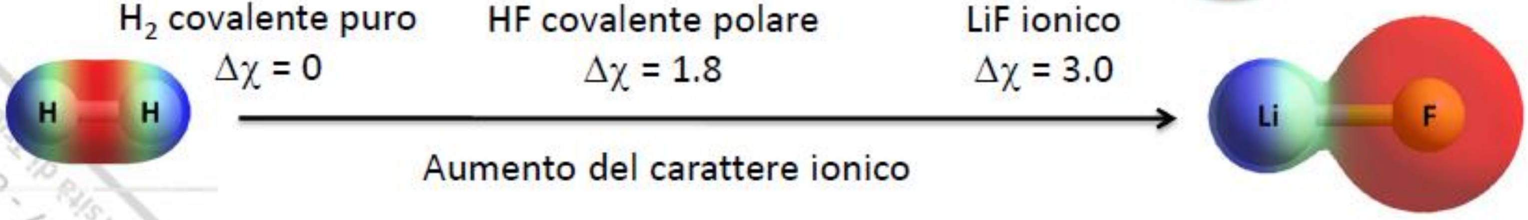
Ionic vs Covalent Bonds



$$\% \text{ ionic character} = \{1 - \exp[-(0.25)(X_A - X_B)^2]\} \times 100$$

$$\mu = Qr$$

se conosco momento dipolare e distanza di legame posso ricavare Q (frazione di carica)



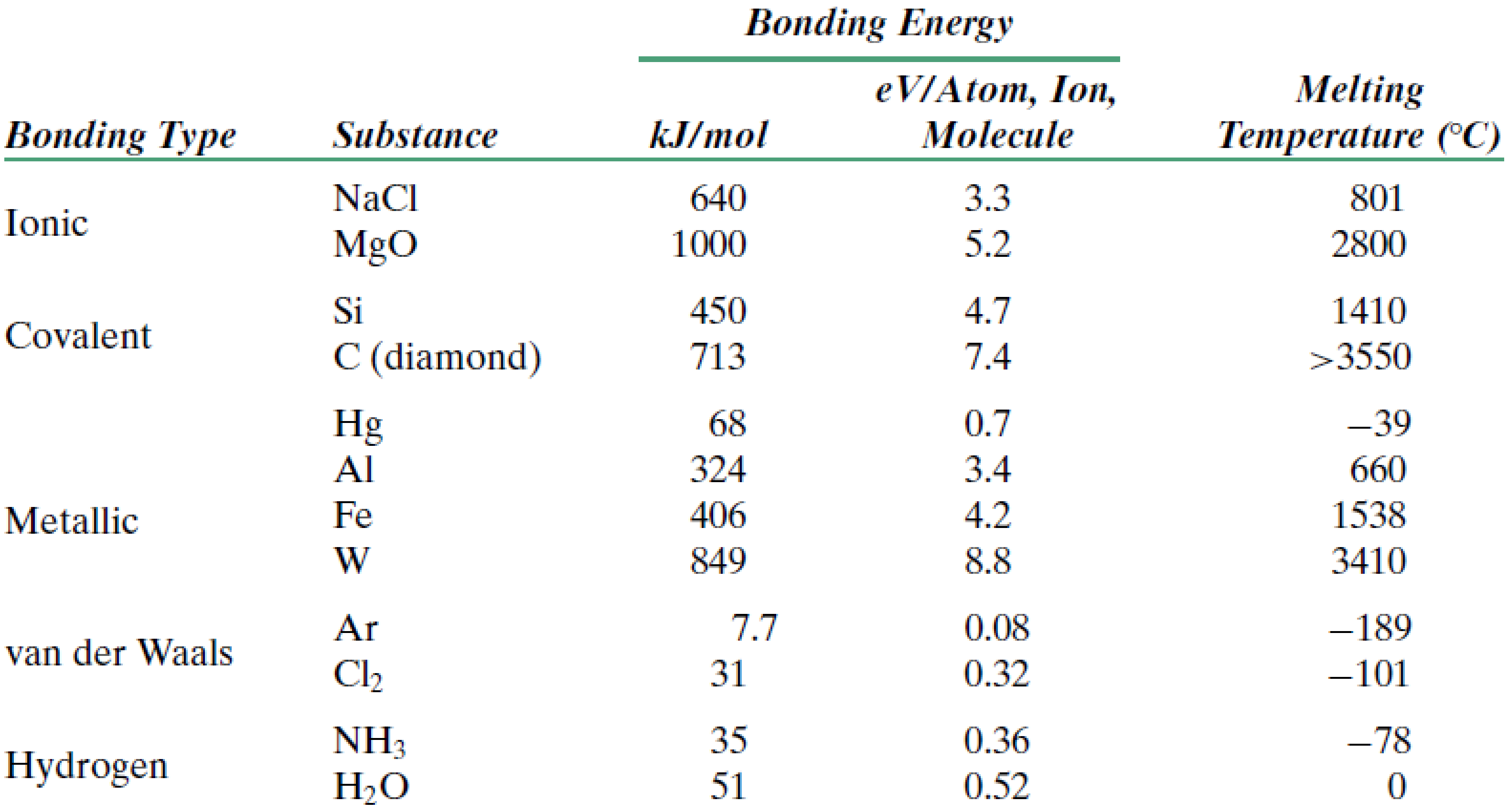
H_2 covalente puro
$\Delta\chi = 0$

HF covalente polare
$\Delta\chi = 1.8$

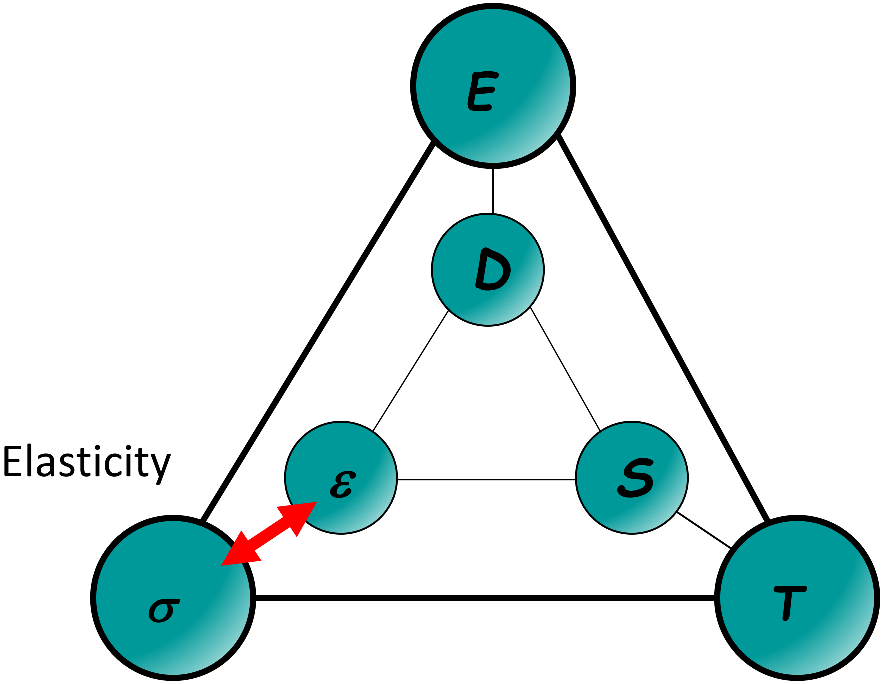
LiF ionico
$\Delta\chi = 3.0$

Aumento del carattere ionico

Comparing Bond Energy

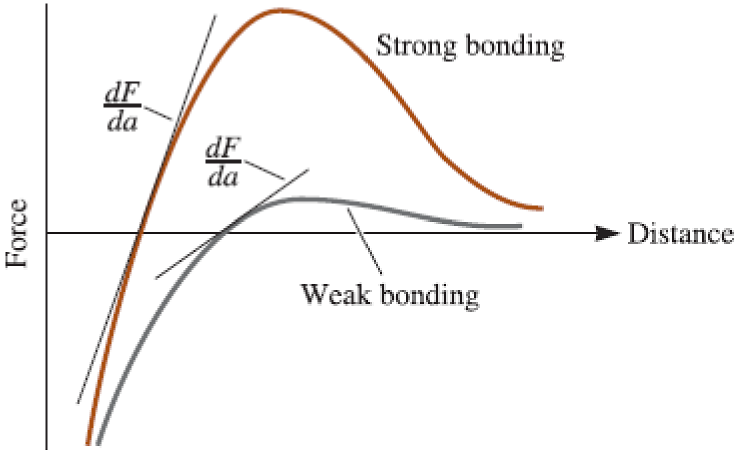


		Bonding Energy		
Bonding Type	**Substance**	**kJ/mol**	**eV/Atom, Ion, Molecule**	**Melting Temperature (°C)**
Ionic	NaCl	640	3.3	801
	MgO	1000	5.2	2800
Covalent	Si	450	4.7	1410
	C (diamond)	713	7.4	>3550
Metallic	Hg	68	0.7	–39
	Al	324	3.4	660
	Fe	406	4.2	1538
	W	849	8.8	3410
van der Waals	Ar	7.7	0.08	–189
	Cl_2	31	0.32	–101
Hydrogen	NH_3	35	0.36	–78
	H_2O	51	0.52	0

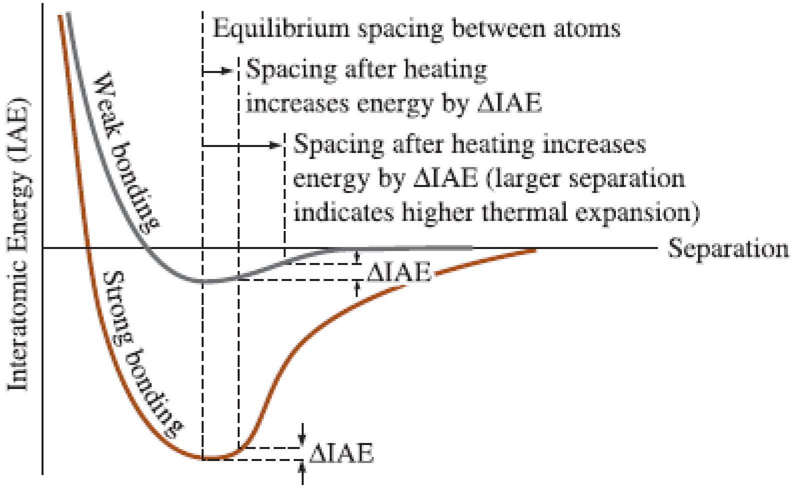

E
D
ε
S
σ
T
Elasticity

Bond and Materials Properties

- an anticipation -

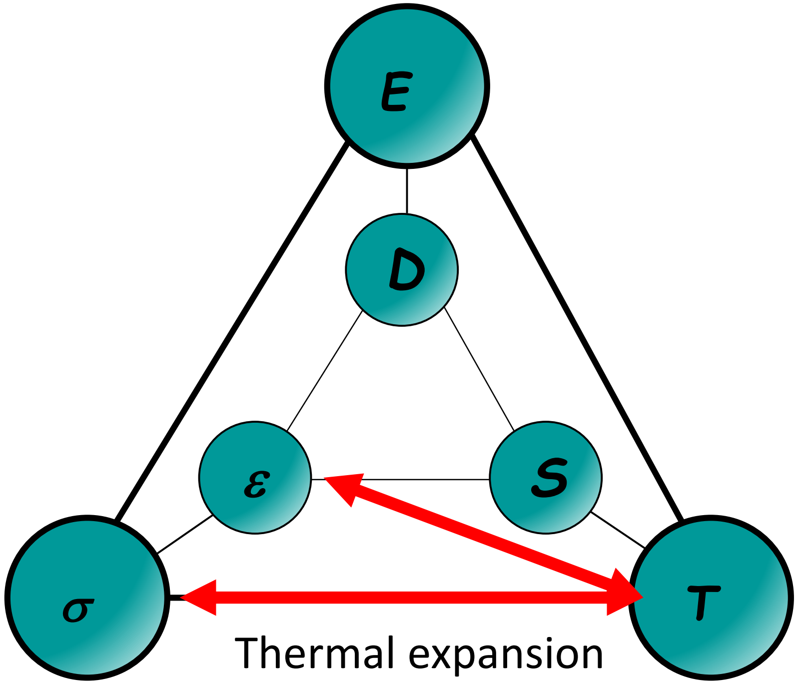


- High slope at r_0: high **stiffness** (Young's modulus)
- Stiffness almost exclusively depends on bond characteristics



- High bond energy E_0: high **melting temperature**

- Deep and narrow curve: low **thermal expantsion**

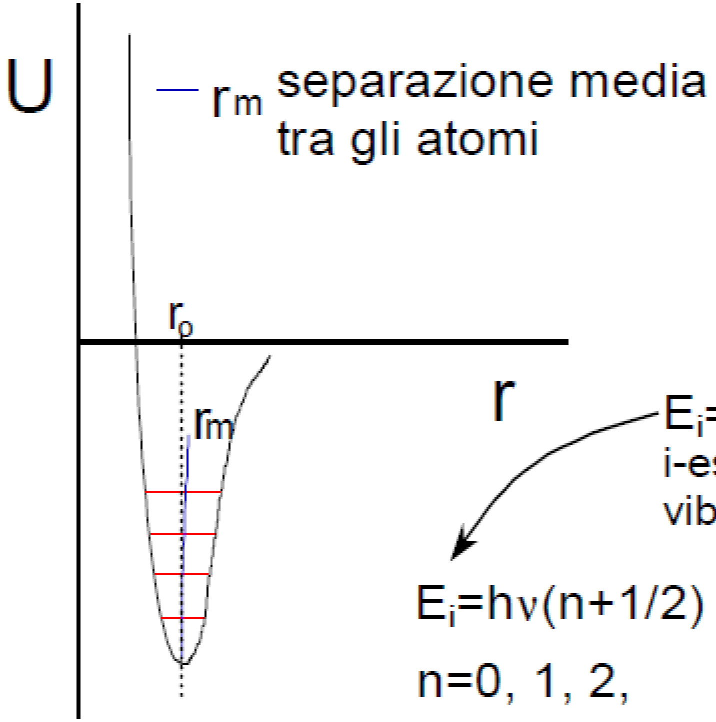


Thermal expansion

Bond and Materials Properties

- an anticipation -

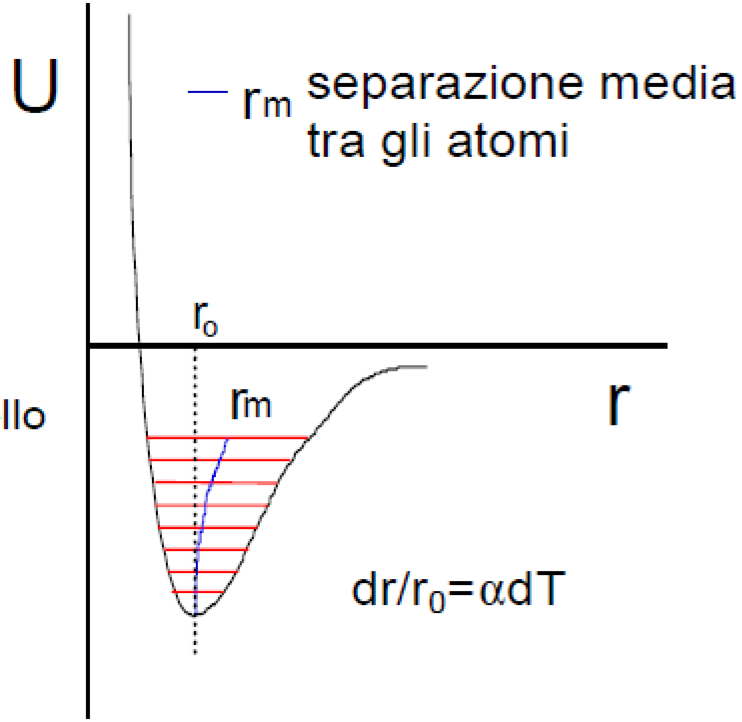
- Deep and narrow curve: low **thermal expantsion**
- Thermal expansion is due to the asymmetry of the curve



E_i=energia dello i-esimo livello vibrazionale

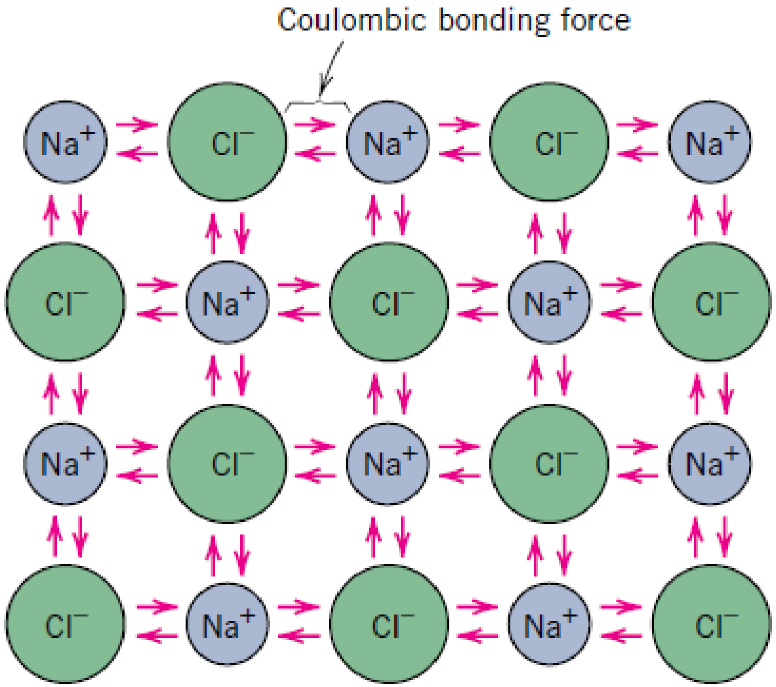
$E_i=h\nu(n+1/2)$

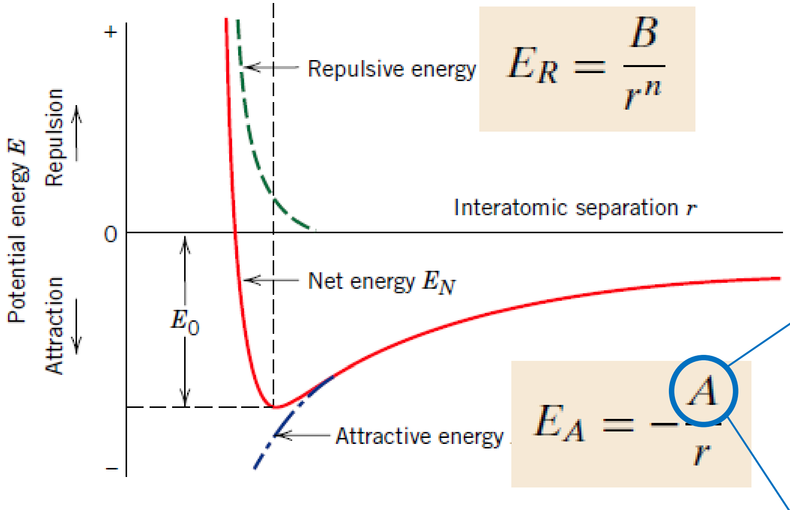
n=0, 1, 2,



$dr/r_0=\alpha dT$

Ionic Bond → Ionic Crystal





$$E_R = \frac{B}{r^n}$$

$n \sim 8$

$$E_A = -\frac{A}{r}$$

Couple of ions:
$$\frac{1}{4\pi\epsilon_0}(Z_1 e)(Z_2 e)$$

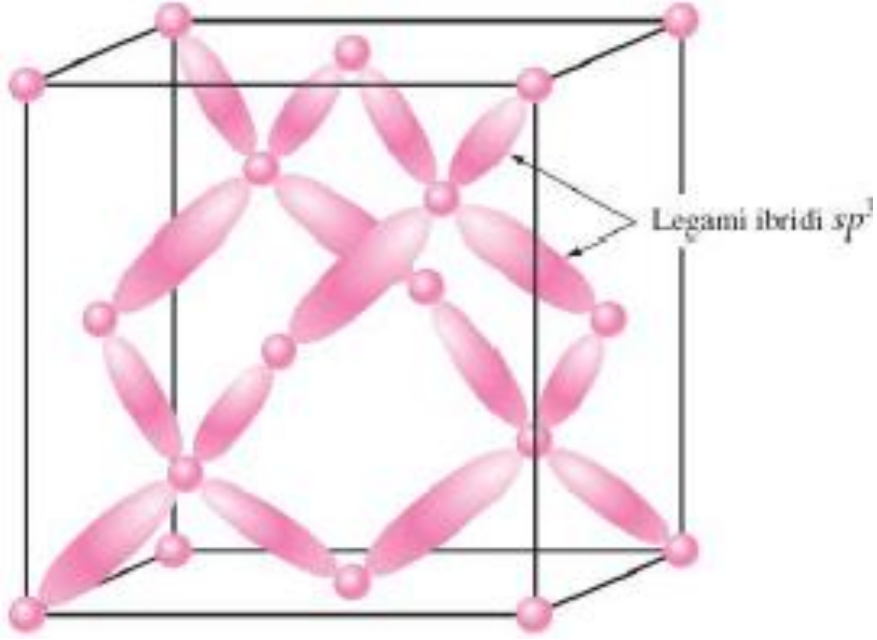
crystal:
$$\alpha e^2$$
α: Madelung

- Non-driectional bond
- High melting point
- Low deformability
- Low electric conduction

Madelung constant:

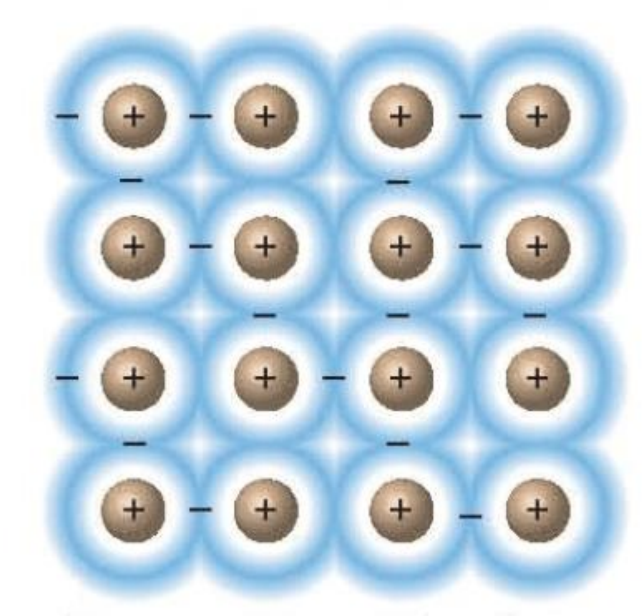
CsCl	1,7627
NaCl	1,7476
ZnS	1,6381

Covalent Bond → Covalent Crystal



- Bond energy can vary widely
- Very directional bonds
- Low deformability
- High hardness
- They often degrade before they melt

Metallic Bond → Metal



legame metallico

legame tra elementi poco elettronegativi (metalli) caratterizzato dalla delocalizzazione degli elettroni di legame su più nuclei ("mare di elettroni")

- Elevata conducibilità elettrica
- Elevata conducibilità termica
- Elevata deformabilità
- Temperatura di fusione dipende da struttura elettronica