

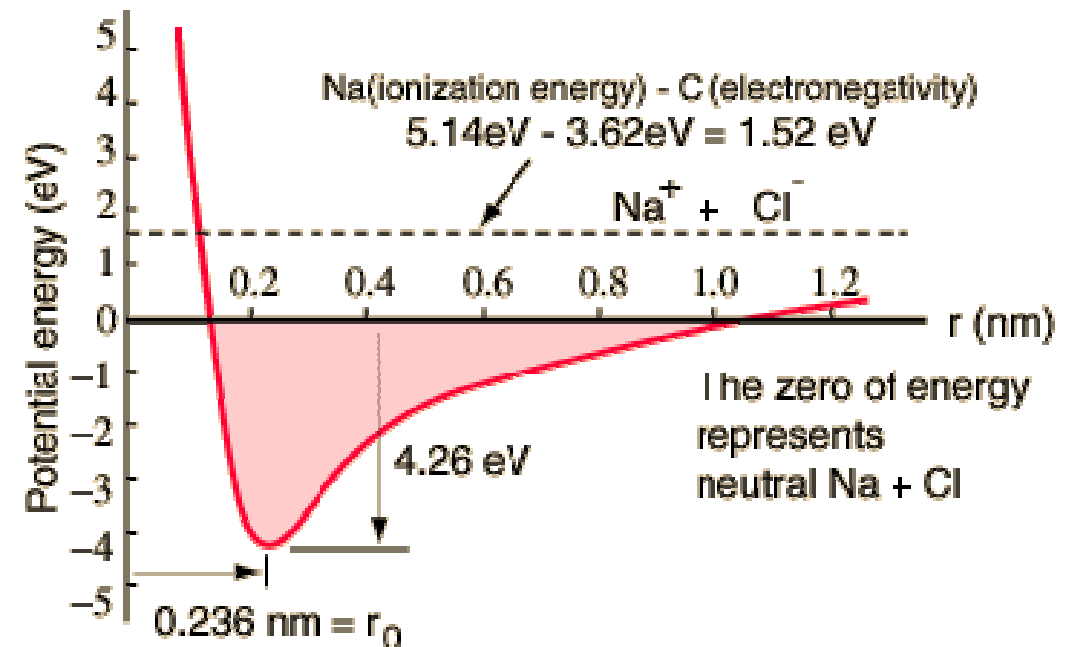
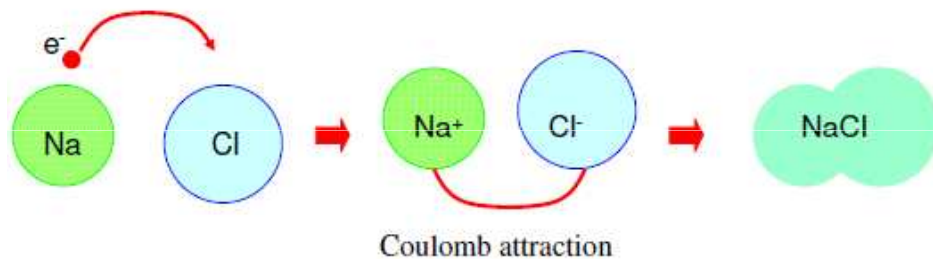
# Intramolecular bonding

Intramolecular bonding:

- 1.heteropolar bonding (ionic)
- 2.homopolar bonding (covalent)

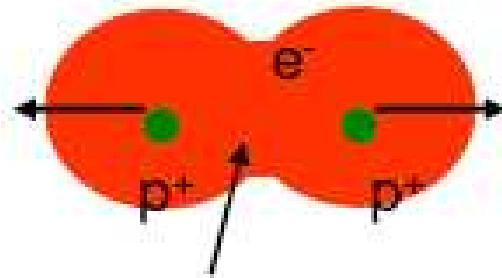
## 1. Heteropolar bonding: NaCl molecule

**Na:**  $1s^2 2s^2 2p^6 3s^1$     **Cl:**  $1s^2 2s^2 2p^6 3s^2 3p^5$

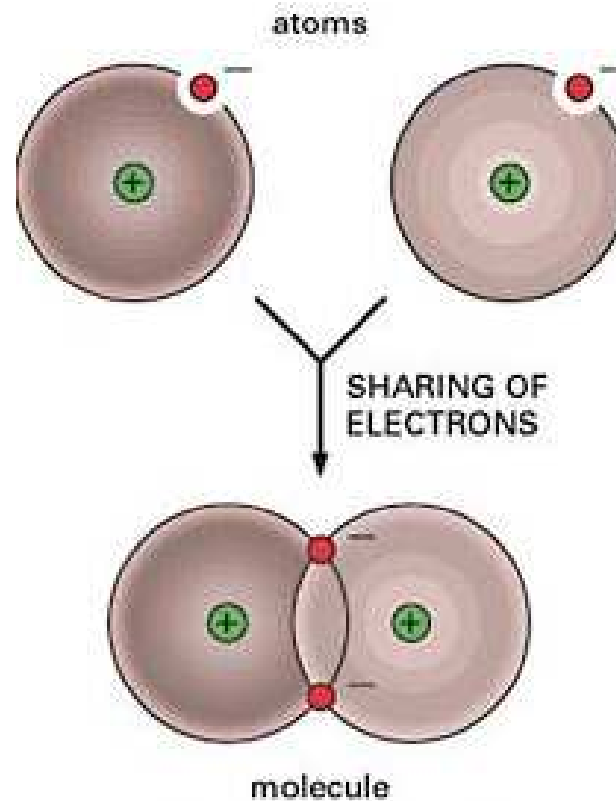


Why is the electron transferred from Na to Cl?

## 2. Homopolar (covalent) bonding: $H_2^+$ molecule



The coulomb repulsion between the protons is reduced by the electron.



# Molecular structure: Born-Oppenheimer approximation

Molecular Schrödinger equation:

$$\sum_{j=1}^r \frac{1}{M_j} \nabla_j^2 \psi + \frac{1}{m_0} \sum_{i=1}^s \nabla_i^2 \psi + \frac{2}{\hbar^2} (E - V) \psi = 0$$

$r$  - nuclei

$M_j$  = mass of  $j^{\text{th}}$  nucleus

$s$  - electrons

$m_0$  = mass of electron

$$V = \sum_{i,i'} \frac{e^2}{4\pi\epsilon_0 r_{ii'}} + \sum_{j,j'} \frac{Z_j Z_{j'} e^2}{4\pi\epsilon_0 R_{jj'}} - \sum_{i,j} \frac{Z_j e^2}{4\pi\epsilon_0 r_{ij}}$$

electron-electron repulsion      nuclear-nuclear repulsion      electron-nuclear attraction

$$\frac{m(H^+)}{m_0} = \frac{1.67 \cdot 10^{-27}}{9.11 \cdot 10^{-31}} \approx 1833$$

**Born-Oppenheimer approximation:**

**The nuclei are stationary and electron motion can be treated separately.**

## Born-Oppenheimer Approximation: wavefunction

$$\psi_{n\nu}(x, \gamma) = \psi_n(x, \gamma) \psi_{n\nu}(\gamma)$$

electronic  
coordinates

nuclear  
coordinates

electronic wavefunction  
depends on electronic  
quantum number,  $n$

nuclear wavefunction  
depends on electronic  
quantum number,  $n$  and  
nuclear quantum number,  $\nu$

# Molecular Schrödinger equations

## electronic Schrödinger equation

$$\sum_{\ddot{u}}^S \nabla_i^2 \psi_n(x, \gamma) + \frac{2M_0}{\hbar^2} [U_n(\gamma) - V(x, \gamma)] \psi_n(x, \gamma) = 0$$

electronic energy depends on the nuclear coordinates and the electronic quantum number.

## nuclear Schrödinger equation: rotation, vibration, translation

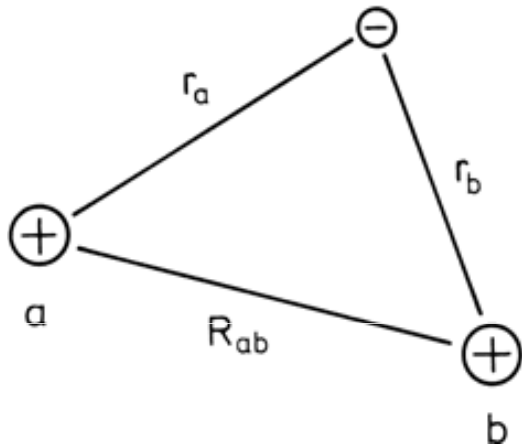
$$\sum_{j=1}^r \frac{1}{M_j} \nabla_j^2 \psi_{nv}(\gamma) + \frac{2}{\hbar^2} [E_{n,v} - U_n(\gamma)] \psi_{nv}(\gamma) = 0$$

the electronic energy acts as the potential energy

total energy of the molecule

# The Hydrogen molecule-ion $H_2^+$

## Linear combination of atomic orbitals (LCAO)



Schrödinger equation for H atom a ( or b):

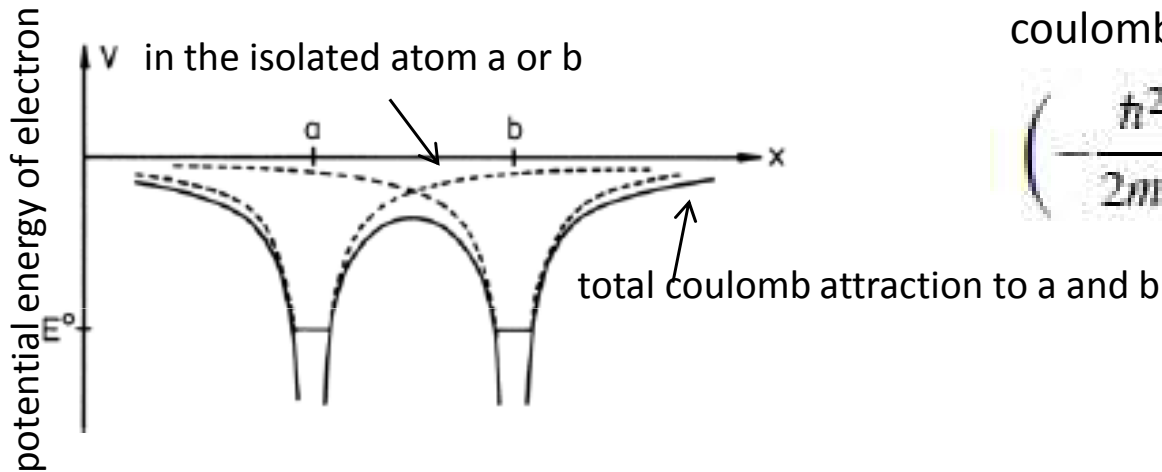
$$\underbrace{\left( -\frac{\hbar^2}{2m_0} \Delta - \frac{e^2}{4\pi\epsilon_0 r_a} \right)}_{H_a} \varphi_a(r_a) = E_a^0 \varphi_a(r_a) \quad (1)$$

$$E_a^0 = E_b^0 = E^0 \quad \text{degeneracy}$$

$$\varphi = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-\frac{Z}{a_0} r}$$

Schrödinger equation for electron sensing the coulomb potential of a and b:

$$\left( -\frac{\hbar^2}{2m_0} \Delta - \frac{e^2}{4\pi\epsilon_0 r_a} - \frac{e^2}{4\pi\epsilon_0 r_b} \right) \psi = E \psi \quad (2)$$



Nucleus b perturbs the energy levels of the electron in atom a and lifts the degeneracy:  
 $\Psi$  as a linear combination:

$$\psi = c_1 \varphi_a + c_2 \varphi_b \quad (3)$$

$c_1$  and  $c_2$  position independent

# The Hydrogen molecule-ion $\text{H}_2^+$ (LCAO)

with (3) in (2) and considering (1):

$$\left( \underbrace{E^0 - E}_{\Delta E} - \frac{e^2}{4\pi\epsilon_0 r_b} \right) c_1 \varphi_a + \left( \underbrace{E^0 - E}_{\Delta E} - \frac{e^2}{4\pi\epsilon_0 r_a} \right) c_2 \varphi_b = 0 \quad (4)$$

$\varphi_a$  and  $\varphi_b$  are ground state wavefunctions of H: are real functions.

Multiply (4) by  $\varphi_a$  (or  $\varphi_b$ ) and integrate over the electronic coordinates:

$$(\Delta E + C)c_1 + (\Delta ES + D)c_2 = 0 \quad (5)$$

$$(\Delta ES + D)c_1 + (\Delta E + C)c_2 = 0 \quad (6)$$

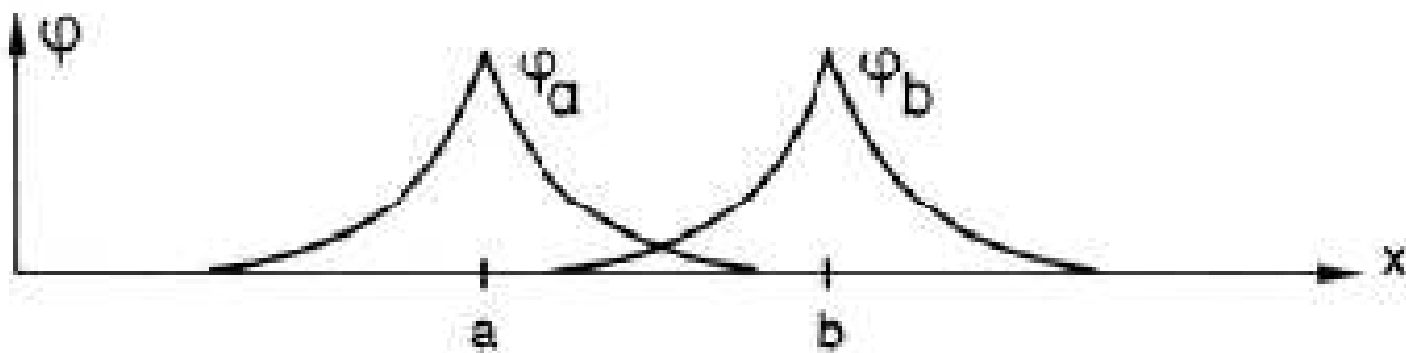
where:

$$\int \varphi_a \varphi_b dV = S \quad \text{overlap integral} \quad (7)$$

$$\int \varphi_a(r_a) \left( -\frac{e^2}{4\pi\epsilon_0 r_b} \right) \varphi_a(r_a) dV = C \quad \text{Coulomb integral} \quad (8)$$

$$\int \varphi_a(r_a) \left( -\frac{e^2}{4\pi\epsilon_0 r_a} \right) \varphi_b(r_b) dV = D \quad \text{exchange integral} \quad (9)$$

## The overlap integral





# The Hydrogen molecule-ion $H_2^+$ (LCAO)

$$(\Delta E + C)c_1 + (\Delta ES + D)c_2 = 0 \quad (5)$$

$$(\Delta ES + D)c_1 + (\Delta E + C)c_2 = 0 \quad (6)$$

The determinant = 0 :

$$(\Delta E + C)^2 - (\Delta ES + D)^2 = 0 \quad \text{quadratic equation for } \Delta E$$

$$(\Delta E + C) = \pm(\Delta ES + D) \quad (10)$$

Inserting (10) in (5) or (6):  $c_1 = \mp c_2 = \mp$  (11)

**Wavefunction:**  $\psi_- = C(\varphi_a - \varphi_b)$  antisymmetric (u ungerade) (12)

$\psi_+ = C(\varphi_a + \varphi_b)$  symmetric (g gerade) (13)

The **electronic energy** corresponding to  $\Psi_- / \Psi_+$  (from (10) with positive / negative sign):

$$E_- = E^0 + \frac{C - D}{1 - S} \quad (14) \quad E_+ = E^0 + \frac{C + D}{1 + S} \quad (15)$$

**The binding energy** considering nuclear repulsion:

$$E_{\text{Bindung}} = \frac{C \pm D}{1 \pm S} + e^2 / 4\pi\epsilon_0 R_{ab} \quad (16)$$