

PY4T01 Condensed Matter Theory: Lecture 3

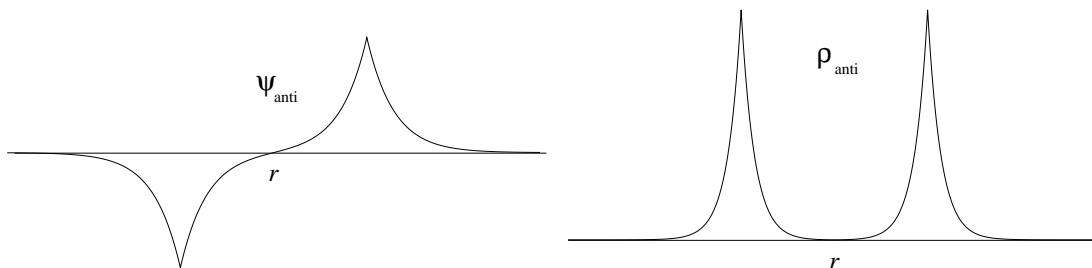
The H₂ molecule

$$E_{\text{bond}} = \epsilon_0 + \gamma \quad |\psi_{\text{bond}}\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$$

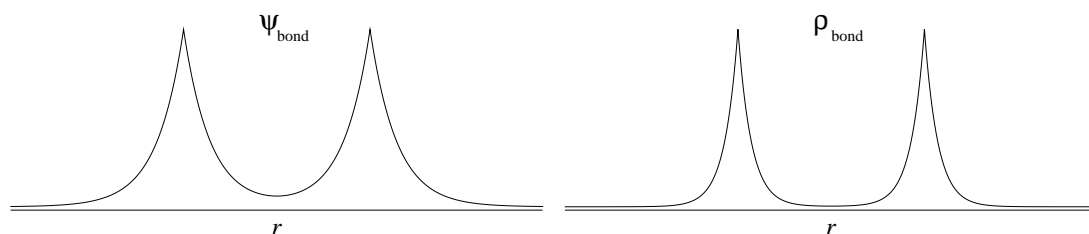
$$E_{\text{anti}} = \epsilon_0 - \gamma \quad |\psi_{\text{anti}}\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle)$$

How does the charge distribute in space?

Antibonding State: no charge between the two atoms



Bonding State: charge between the two H atoms



In fact the charge density associated with two electrons in the bonding state is:

$$\rho = 2\langle\psi_{\text{bond}}|\psi_{\text{bond}}\rangle$$

$$\begin{aligned}\rho(\vec{r}) &= 2\langle\psi_{\text{bond}}|\vec{r}\rangle\langle\vec{r}|\psi_{\text{bond}}\rangle = 2|\psi(\vec{r})_{\text{bond}}|^2 = \\ &= \rho_1(\vec{r}) + \rho_2(\vec{r}) + \rho_{\text{B}}(\vec{r})\end{aligned}$$

with

$$\rho_{\text{B}}(\vec{r}) = 2\psi_1(\vec{r})\psi_2(\vec{r})$$

Time dependent Schrödinger equation

$$i\hbar \frac{d|\psi\rangle}{dt} = H|\psi\rangle$$

Again we expand the wave function on the atomic wave functions

$$|\psi(t)\rangle = \psi_1(t)|1\rangle + \psi_2(t)|2\rangle$$

We obtain the equations of motion for the coefficients $\psi_i(t)$

$$\begin{cases} i\hbar \frac{d\psi_1}{dt} = \epsilon_0\psi_1 + \gamma\psi_2 \\ i\hbar \frac{d\psi_2}{dt} = \gamma\psi_1 + \epsilon_0\psi_2 \end{cases}$$

The general solution is

$$\psi_1(t) = A_1 e^{-i\omega t} \quad \text{and} \quad \psi_2(t) = A_2 e^{-i\omega t}$$

$$\begin{cases} \hbar\omega A_1 = \epsilon_0 A_1 + \gamma A_2 \\ \hbar\omega A_2 = \epsilon_0 A_2 + \gamma A_1 \end{cases}$$

which reduces to

$$\begin{pmatrix} \epsilon_0 & \gamma \\ \gamma & \epsilon_0 \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = \hbar\omega \begin{pmatrix} A_1 \\ A_2 \end{pmatrix}$$

with solutions

$$\omega_{\text{bond}} = \frac{\epsilon_0 + \gamma}{\hbar}$$

$$\omega_{\text{anti}} = \frac{\epsilon_0 - \gamma}{\hbar}$$

Therefore the coefficients are:

$$\psi_1(t) = ae^{-i\frac{\epsilon_0+\gamma}{\hbar}t} + be^{-i\frac{\epsilon_0-\gamma}{\hbar}t}$$

$$\psi_2(t) = ae^{-i\frac{\epsilon_0+\gamma}{\hbar}t} - be^{-i\frac{\epsilon_0-\gamma}{\hbar}t}$$

a and b must be fixed from initial conditions. Suppose at $t = 0$ $\psi_1(0) = 1$ and $\psi_2(0) = 0$. Then $a = b = 1/2$

$$\psi_1(t) = e^{-i\epsilon_0/\hbar t} \cos(\gamma t/\hbar)$$

$$\psi_2(t) = e^{-i\epsilon_0/\hbar t} \sin(\gamma t/\hbar)$$

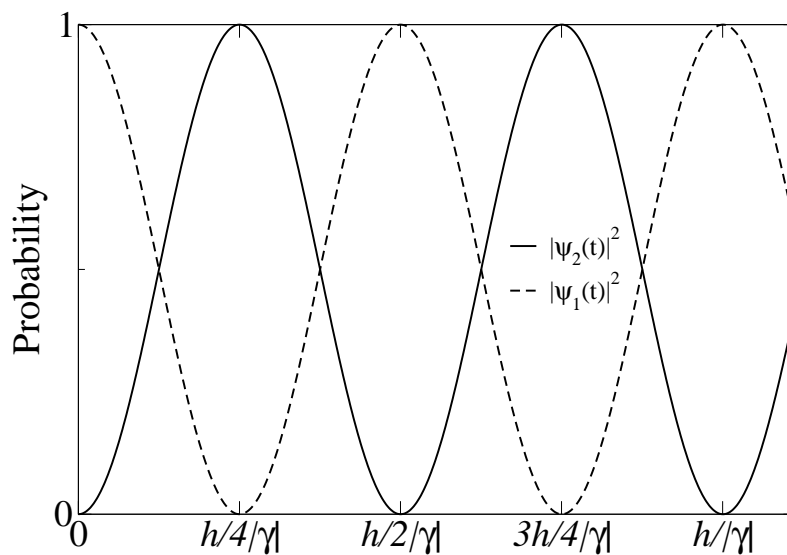
The probability that the molecule is in the state $|1\rangle$ (and $|2\rangle$) is

$$|\psi_1(t)|^2 = \cos^2(\gamma t/\hbar)$$

$$|\psi_2(t)|^2 = \sin^2(\gamma t/\hbar)$$

An electron in the molecule is vibrating back and forth between the two atoms with period

$$T = \frac{h}{2|\gamma|}$$



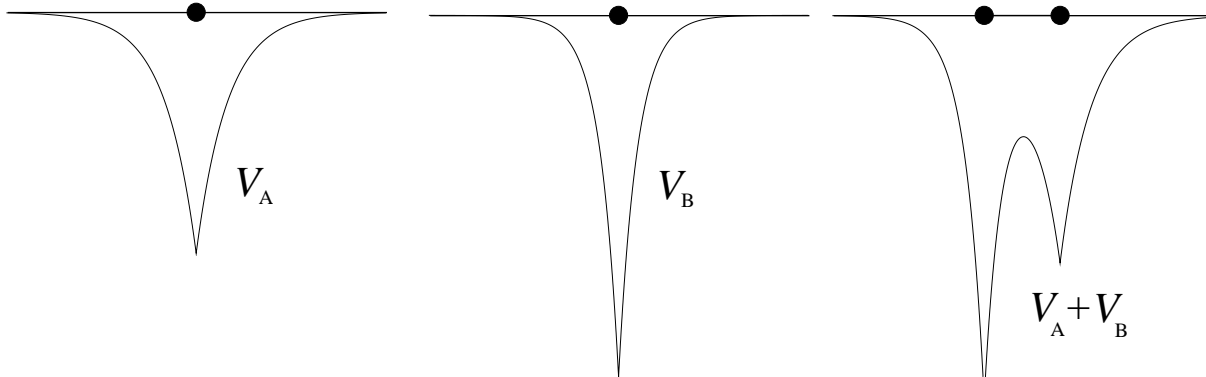
- The ionization energy of H is 13.6 eV. Why do the electrons go back and forth so easily?
- The hopping probability is $2\gamma/h$
- Remember that

$$\gamma = -\langle 1 | \frac{e^2}{|\vec{r} - \vec{R}_B|} | 2 \rangle$$

If the separation between H increases $\gamma \rightarrow 0$. No hopping probability \rightarrow NO BOND

The heteronuclear diatomic molecule

Now assume atom A and B are different (say H and Li)



“Friendly” basis function \rightarrow Ground state of isolated atoms.

$$\begin{aligned} \epsilon_{2s}^A & \text{ for Li} & (-5.6 \text{ eV}) & \longrightarrow |A\rangle \\ \epsilon_{1s}^B & \text{ for H} & (-13.6 \text{ eV}) & \longrightarrow |B\rangle \end{aligned}$$

where as before:

$$\begin{aligned} H_A |A\rangle &= \epsilon_{2s}^A |A\rangle \\ H_B |B\rangle &= \epsilon_{1s}^B |B\rangle \end{aligned}$$

Then the dimer wavefunction can be written as:

$$|\psi\rangle = \psi_A |A\rangle + \psi_B |B\rangle$$

Following the same procedure than before we end up with the secular equation

$$\begin{pmatrix} \epsilon_A & \gamma \\ \gamma & \epsilon_B \end{pmatrix} \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix} = E \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix}$$

where now

$$\epsilon_A = \epsilon_{2s}^A + \int \rho_A(\vec{r}) V_B(\vec{r}) d\vec{r}$$

$$\epsilon_B = \epsilon_{1s}^B + \int \rho_B(\vec{r}) V_A(\vec{r}) d\vec{r}$$

$$\gamma = \langle A|H|B \rangle = \langle A|V_B|B \rangle$$

Note

In the case of the H atom

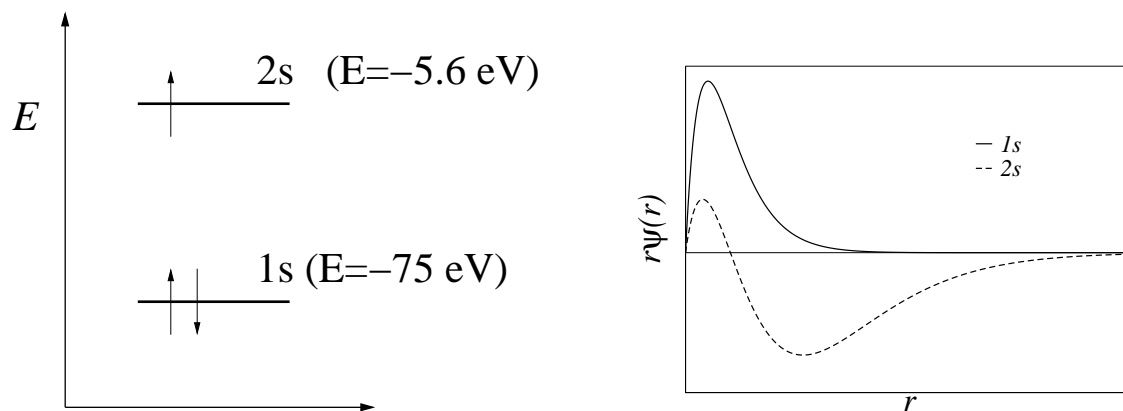
$$V_B(\vec{r}) = -\frac{e^2}{|\vec{r} - \vec{R}_B|}$$

Note:

In our example $A = \text{Li } 2s$ state.

What about the two electrons in the Li 1s state?

$$H = - \sum_j^3 \frac{\hbar^2 \nabla_j^2}{2m} - \frac{1}{2} \sum_i^3 \frac{3e^2}{|\vec{r}_i - \vec{R}|} + \frac{1}{2} \sum_{i \neq j}^3 \frac{e^2}{r_{ij}}$$



Since the 1s state has a much lower energy and it is entirely occupied, we can neglect it and approximate:

$$H = -\frac{\hbar^2 \nabla^2}{2m} + V_A(\vec{r})$$

V_A is the effective potential of the 2s electron (optical electron) due to the 1s states

Electrons important for bonding \rightarrow VALENCE ELECTRONS

Electrons not important for bonding \rightarrow CORE ELECTRONS

Now solve the secular equation:

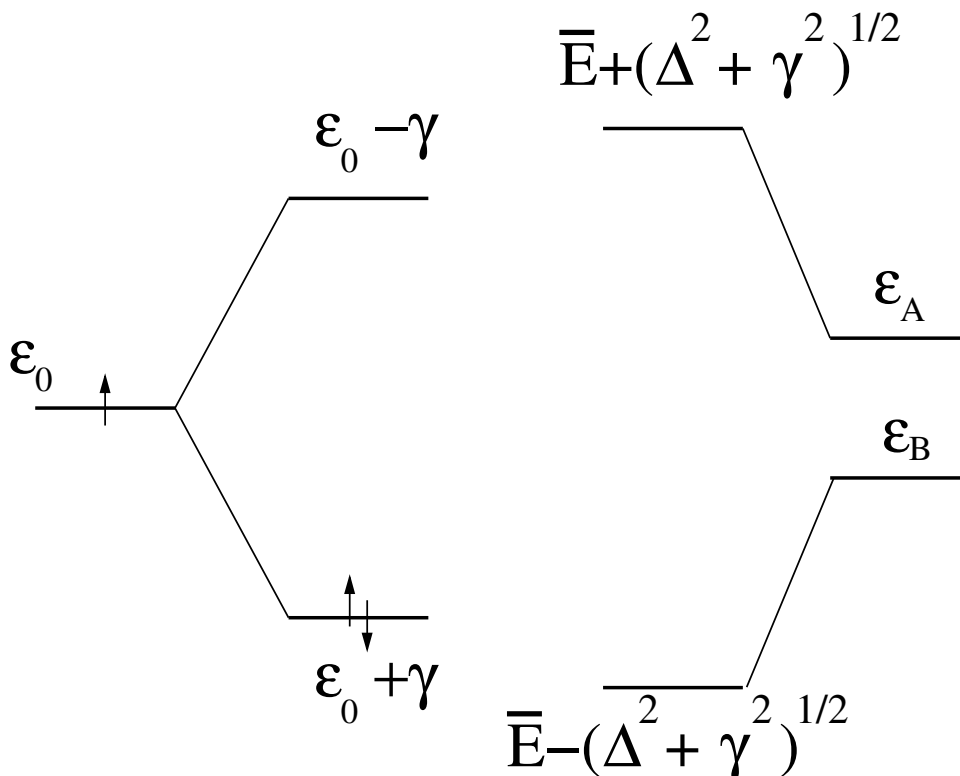
$$E_{\text{bond}} = \bar{E} - (\Delta^2 + \gamma^2)^{1/2}$$

$$E_{\text{anti}} = \bar{E} + (\Delta^2 + \gamma^2)^{1/2}$$

where we have defined

$$\bar{E} = \frac{\epsilon_A + \epsilon_B}{2}$$

$$\Delta = \frac{\epsilon_A - \epsilon_B}{2}$$



The energy difference between bonding and antibonding states is

$$E_{\text{bond}} - E_{\text{anti}} = 2(\Delta^2 + \gamma^2)^{1/2}$$

Note that:

- If $A=B$ then $\Delta = 0 \longrightarrow$ results for homonuclear diatomic molecule
- If $\gamma = 0 \longrightarrow E_{\text{bond}} = \epsilon_B$ and $E_{\text{anti}} = \epsilon_A$ (remember $\epsilon_B < \epsilon_A$)

How does the charge distribute?

We have to calculate ψ_A and ψ_B .

For the bonding state we have

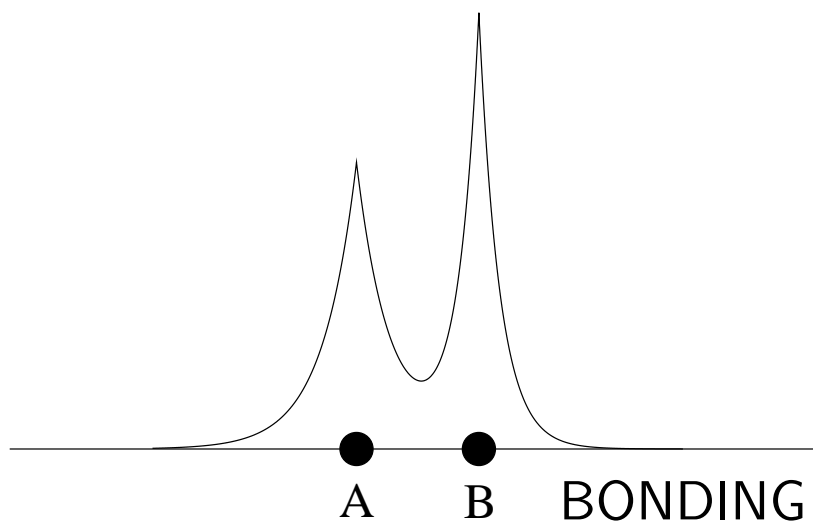
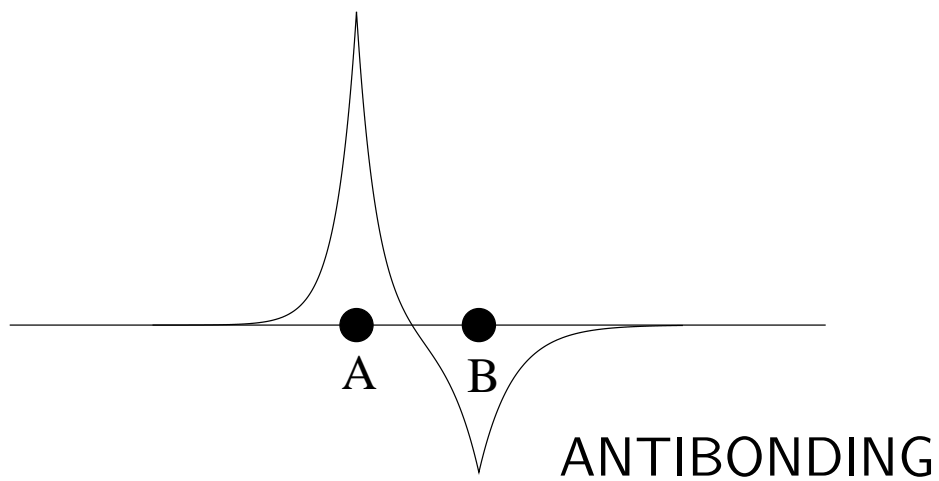
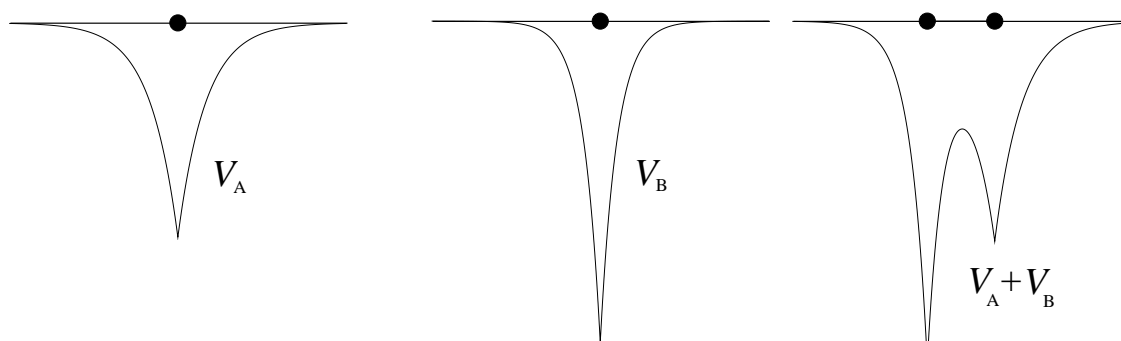
$$\left\{ \begin{array}{l} \psi_A^{\text{bond}} = \frac{1}{\sqrt{2}} \left[1 - \frac{x}{\sqrt{1+x^2}} \right]^{1/2} \\ \psi_B^{\text{bond}} = \frac{1}{\sqrt{2}} \left[1 + \frac{x}{\sqrt{1+x^2}} \right]^{1/2} \end{array} \right.$$

and for the antibonding

$$\left\{ \begin{array}{l} \psi_A^{\text{anti}} = \frac{-1}{\sqrt{2}} \left[1 + \frac{x}{\sqrt{1+x^2}} \right]^{1/2} \\ \psi_B^{\text{anti}} = \frac{1}{\sqrt{2}} \left[1 - \frac{x}{\sqrt{1+x^2}} \right]^{1/2} \end{array} \right.$$

where

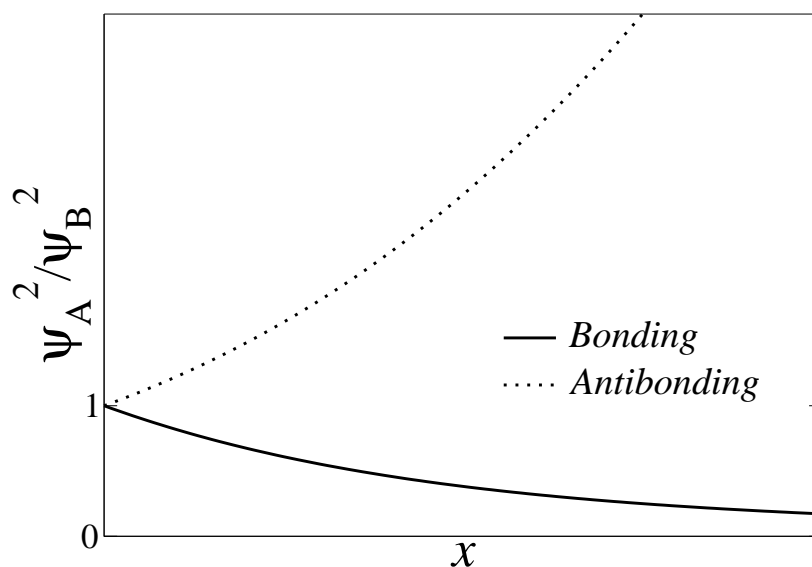
$$x = \Delta/\gamma$$



Consider first the ratio ψ_A^2/ψ_B^2

$$\frac{\psi_A^2}{\psi_B^2} = \frac{1}{1 + 2x^2 + 2x\sqrt{(1+x^2)}} \quad \text{Bonding State}$$

$$\frac{\psi_A^2}{\psi_B^2} = \frac{1}{1 + 2x^2 - 2x\sqrt{(1+x^2)}} \quad \text{Antibonding State}$$



Now look at the charge density:

$$\rho_{\text{bond}}(\vec{r}) = (1 - \alpha_p)\rho_A(\vec{r}) + (1 + \alpha_p)\rho_B(\vec{r}) + \alpha_c\rho_{AB}(\vec{r})$$

with

$$\alpha_p = \frac{x}{\sqrt{1+x^2}} \quad \text{Bond Polarity}$$

$$\alpha_c = \frac{1}{\sqrt{1+x^2}} \quad \text{Bond Covalency}$$

Note that:

- $\alpha_p^2 + \alpha_c^2 = 1$
- If $A=B$, the $x=0 \rightarrow \alpha_p = 0, \alpha_c = 1$, Pure covalent bond
- If $\gamma = 0$, the $x \rightarrow \infty$ then $\alpha_p = 1, \alpha_c = 0$, Pure ionic bond

Electronegativity

Electronegativity: power of an atom to attract electron to itself from neighboring atoms in its environment

How to establish an electronegative scale?

On-site energy is not ideal. Remember in fact that:

$$\epsilon_A = \epsilon_{\text{atomic}}^A + \int \rho_A(\vec{r}) V_B(\vec{r}) d\vec{r}$$

Pauling electronegativity scale

H							
(2.2)							
Li	Be	B	C	N	O	F	
(0.98)	(1.57)	(2.04)	(2.55)	(3.04)	(3.41)	(3.98)	
Na	Mg	Al	Si	P	S	Cl	
(0.93)	(1.31)	(1.61)	(1.90)	(2.19)	(2.58)	(3.16)	
K	Ca		Ge	As	Se	Br	
(0.82)	(1.00)		(2.01)	(2.18)	(2.55)	(2.96)	
Rb						I	
(0.82)						(2.66)	

Mülliken electronegativity

$$\chi_A = \frac{1}{2}(IP_A + EA_A)$$

with IP_A ionization potential atom A, EA_A electron affinity atom A.

A-B is covalent if:

$$\text{Energy } A^+B^- = \text{Energy } A^-B^+$$

or

$$IP_A - EA_B = IP_B - EA_A$$

$$IP_A + EA_A = IP_B + EA_B$$