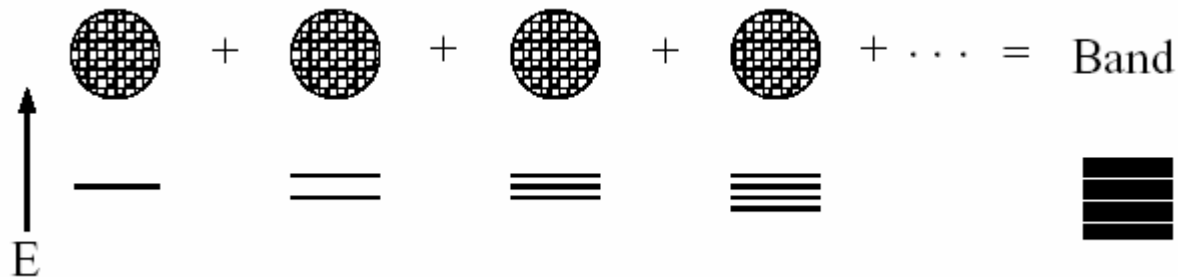


# Atomic Orbitals and Chemical Bonding

□ Solids are composed of elements with multiple orbitals that produce multiple bonds. Now imagine what happens if we have several orbitals on each site (s,p,d, etc.), as we reduce the separation between the orbitals and increase their overlap, these bonds increase in width and may eventually overlap, forming bands.

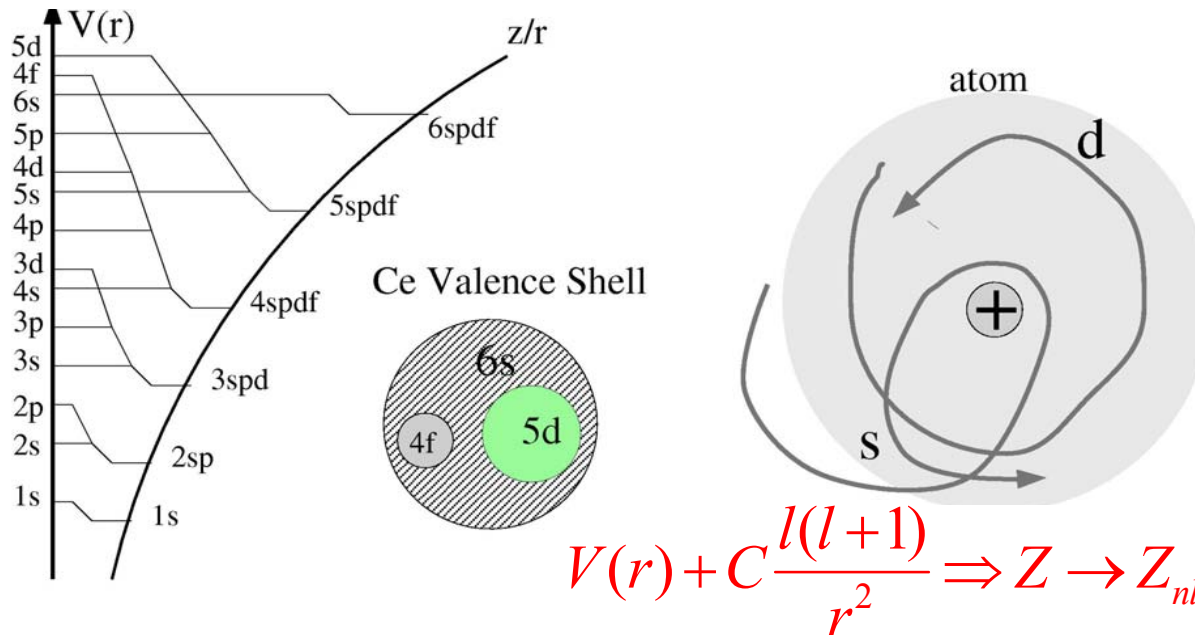


□ **Valence orbitals**, which generally have a greater spatial extent, will overlap more so their bands will broaden more. **They dominate the bonding mechanism.**

□ Eventually we will stop gaining energy from bringing the atoms closer together, due to overlap of the cores ) Once we have reached the optimal point we fill the states 2 particles per, until we run out of electrons.

□ **Electronic correlations**  $n_{\uparrow} n_{\downarrow}$  complicate this simple picture of band formation since they strive to keep the orbitals from being multiply occupied.

# Atomic Level Crossing and Screening



For large  $n$ , the orbitals do not fill up simply as a function of  $n$  as we would expect from a simple Hydrogenic model with

$$E_n = -\frac{m e^4}{2 \hbar^2 n^2} Z^2$$

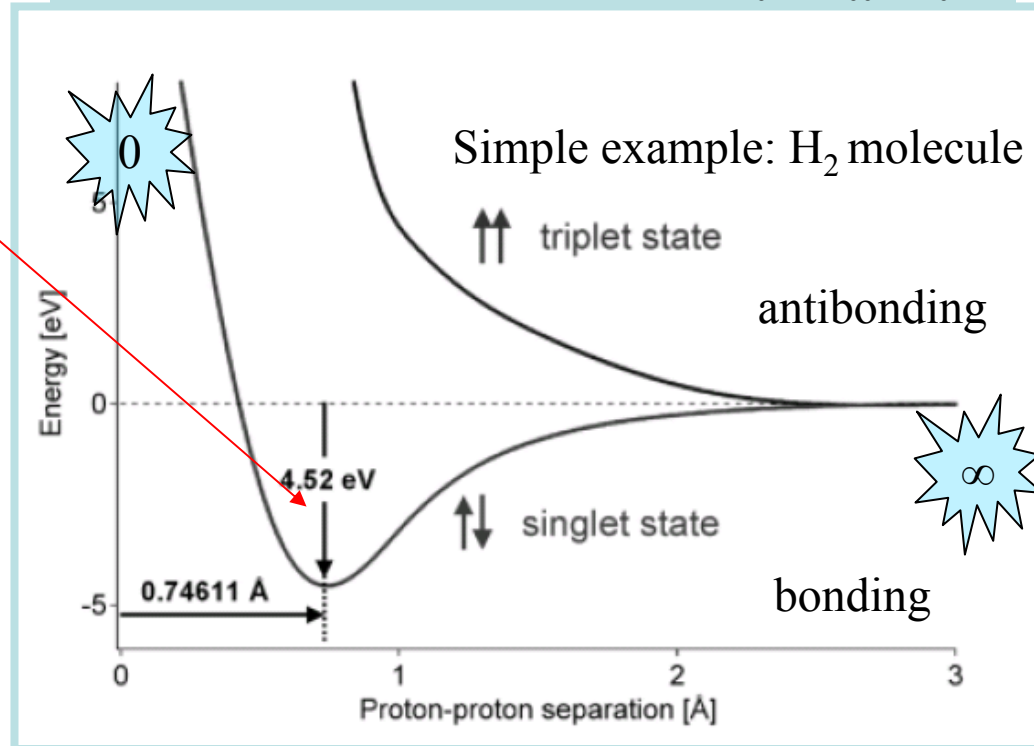
□ Level crossings due to atomic screening. **The potential felt by states with large  $l$  are screened since they cannot access the nucleus.** Thus, orbitals of different principle quantum numbers can be close in energy. For example, in elemental Ce ( $4f^1 5d^1 6s^2$ ) both the 5d and 4f orbitals may be considered to be in the valence shell, and form metallic bands. However, the 5d orbitals are much larger and of higher symmetry than the 4f ones. Thus, electrons tend to hybridize (move on or off) with the 5d orbitals more effectively. The Coulomb repulsion between electrons on the same 4f orbital will be strong, so these electrons on these orbitals tend to form magnetic moments.

# Cohesive Energy in Solids

- Coulomb interactions: electrons, nuclei → bonding, antibonding states
- Real materials: potential wells in  $U(r)$ , depth = bonding strength (cohesive  $E$ ).
- **Cohesive energy = energy required to overcome bonding, separate constituents**
- In real materials – many body Schrödinger equation. Many – body problem, technical difficulty

Mechanism	Valence electrons
Metallic	Delocalized throughout
Covalent	Delocalized, electron density high between pairs
Van der Waals	Atoms neutral, closed shell configuration
Ionic	Transfer
Hydrogen	Mixed Ionic and Covalent

Interatomic potential energy  $U(r)=U_{en}+U_{ee}+U_{en} ?$



# Cohesive Energy in Solids 1

## IMPORTANCE OF KINETIC ENERGY (VIRIAL THEOREM)

Covalent bond (example H<sub>2</sub>) is **not** purely electrostatic phenomenon: electron kinetic energy contributes to total molecular energy

□ Born-Oppenheimer Approximation in calculation of molecular wavefunctions:

$T_{nucl} = 0$  in molecular  $\hat{H}$ , nuclear positions are parameters, Coulomb interaction is felt by electrons

$$\hat{H}(\vec{r}_1^{nucl}, \dots, \vec{r}_N^{nucl}) |\Psi(\vec{r}_1^{nucl}, \dots, \vec{r}_N^{nucl})\rangle = E(\vec{r}_1^{nucl}, \dots, \vec{r}_N^{nucl}) |\Psi(\vec{r}_1^{nucl}, \dots, \vec{r}_N^{nucl})\rangle$$

$$\langle T_{electron} \rangle + \langle V \rangle = E(\vec{r}_1^{nucl}, \dots, \vec{r}_N^{nucl}) \rightarrow V_{ee} + V_{en}(\vec{r}_1^{nucl}, \dots, \vec{r}_N^{nucl}) + V_{nn}(\vec{r}_1^{nucl}, \dots, \vec{r}_N^{nucl})$$

1. Consider normalized eigenfunction:  $\psi(x) \rightarrow \gamma^{1/2} \psi(\gamma x) = \psi_\gamma(x)$ ;  $\exists \langle \psi_\gamma | \psi_\gamma \rangle = \int |\psi_\gamma(x)|^2 dx = \gamma \int |\psi(\gamma x)|^2 dx = \int |\psi(y)|^2 dy$

2. Example: a molecule where  $\hat{H}_e = \hat{T} + V(\vec{r}, \vec{R}) = \left(-\frac{1}{2} \nabla_r^2\right) + \left(-\frac{Z}{|r-R|}\right)$  and introduce scaling  $\psi_\gamma[\vec{R}](\vec{r}) = \gamma^{3N_e/2} \psi[R](\gamma\vec{r})$

Kinetic energy scaling:

$$T_\gamma[\vec{R}] = \langle \psi_\gamma | \hat{T} | \psi_\gamma \rangle = \int \psi_\gamma[\vec{R}](\vec{r}) \left(-\frac{1}{2} \nabla_r^2\right) \psi_\gamma[\vec{R}](\vec{r}) d^{3N_e} r = \gamma^{3N_e} \int \psi[\vec{R}](\gamma\vec{r}) \left(-\frac{1}{2} \nabla_r^2\right) \psi[\vec{R}](\gamma\vec{r}) d^{3N_e} r = \gamma^2 \int \psi[\vec{R}](\vec{s}) \left(-\frac{1}{2} \nabla_s^2\right) \psi[\vec{R}](\vec{s}) d^{3N_e} s = \gamma^2 T[\vec{R}]$$

Potential energy scaling:

$$V_\gamma[R] = \langle \psi_\gamma | \hat{V} | \psi_\gamma \rangle = \int \psi_\gamma(\vec{r}, \vec{R})^2 V(\vec{r}; \vec{R}) d^{3N_e} r = \gamma^{3(N_e)} \int \psi(\gamma\vec{r}, \vec{R})^2 V(\vec{r}; \vec{R}) d^{3N_e} r = \int \psi(\vec{s}, \vec{R})^2 V(\gamma^{-1}\vec{s}; \vec{R}) d^{3N_e} s = \gamma \int \psi(\vec{s}, \vec{R})^2 V(\vec{s}; \gamma\vec{R}) d^{3N_e} s = \gamma V[\gamma\vec{R}]$$

We have:  $E_\gamma[R] = \gamma^2 T[R] + \gamma V[\gamma R] \longrightarrow$  For ground state energy  $\frac{d}{d\gamma} E[\psi_\gamma]_{\gamma^*=1} = 0 = 2\gamma T[\vec{R}] + V[\gamma\vec{R}] + \gamma(\vec{R}\nabla V)[\gamma\vec{R}]$

# Cohesive Energy in Solids 2

## IMPORTANCE OF KINETIC ENERGY (VIRIAL THEOREM)

Hellmann-Feynmann

$$0 = 2T[R] + V[R] + R \nabla_R V \rightarrow (E = T + V, \nabla_R V \stackrel{\downarrow}{=} \nabla_R E) \rightarrow T(R) = -E(R) - R \frac{dE(R)}{dR}; V(R) = 2E(R) + R \frac{dE(R)}{dR}$$

Molecular electronic energy as a function of nuclear separation – Example H<sub>2</sub> molecule

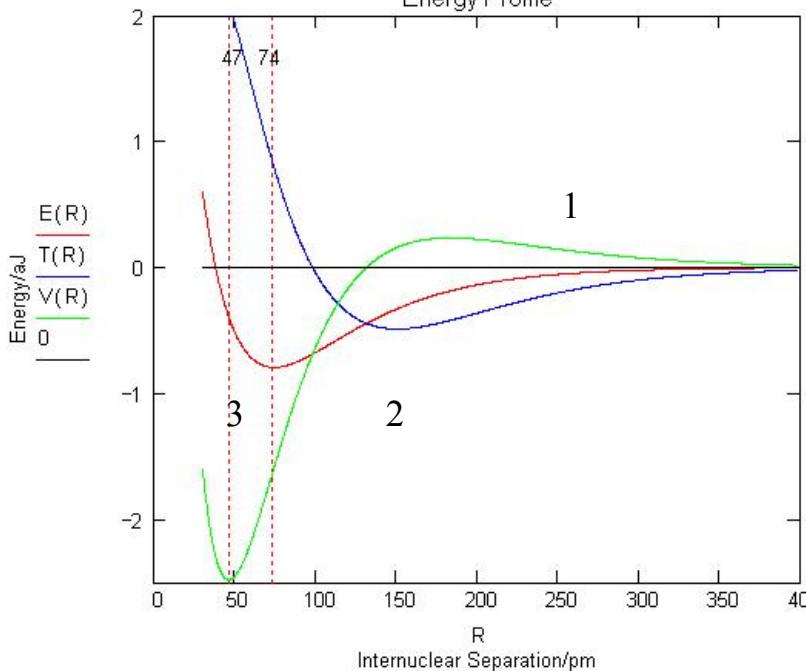
power series function

$$E(R) = e_0 \lambda^2 \left( 1 + \sum_{n=2}^{\infty} e_n \lambda^n \right) + E(R_e)$$

$$\lambda = 1 - (R_e / R)^p$$

H<sub>2</sub> Molecule

Energy Profile



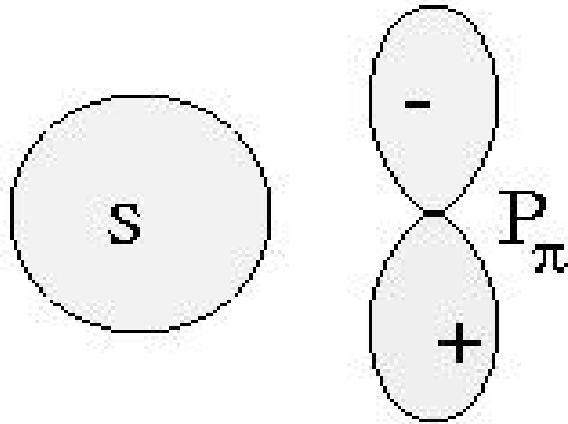
1. As the atoms approach, the **potential energy rises** (electrons are moving away from the nuclei), and the **kinetic energy falls** (delocalization begins). Thus, a decrease in kinetic energy funds the initial build-up of charge between the nuclei that is traditionally associated with chemical bond formation.

2. At R ~ 150 pm, the **potential energy begins to decrease** and the **kinetic energy increases**, while the total energy continues to decrease gradually. This is an atomic effect, not a molecular one → **transfer of charge away from the nuclei and into the bond region allows the atomic orbitals to contract** causing a large **decrease in potential energy** because the electron density is moved, on average, closer to the nuclei. The **kinetic energy increases** because the atomic orbitals are smaller and kinetic energy is inversely proportional to the square of the average orbital radius. The orbital contraction causes some electron density to be withdrawn from the bonding region and returned to the nuclei.

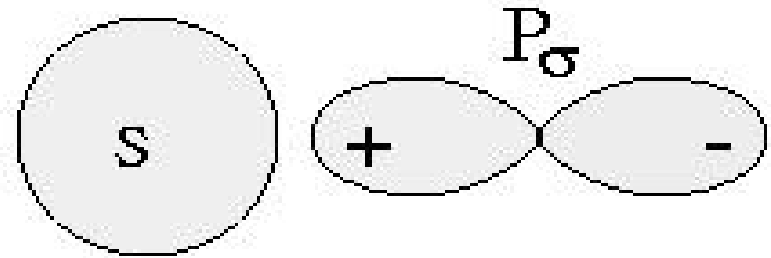
3. **An energy minimum is reached while the potential energy is still in a significant decline**, indicating that **kinetic energy, which is increasing rapidly, is the immediate cause of a stable bond** and the molecular ground state in H<sub>2</sub>. The **final increase in potential energy** is mainly due to nuclear-nuclear repulsion. It begins when the inter-nuclear separation is less than 50 pm, while the equilibrium bond length is 74 pm.

(J. C. Slater, "The Virial and Molecular Structure", Journal of Chemical Physics, 687 (1993); Frank Rioux, "The covalent bond examined using the virial theorem", Chemical Educator 8, 10-12 (2003)); J. S. Winn, J. Chem. Phys. 74, 608 (1981)

# Chemical Bonds in Solids: Covalent



No bonding



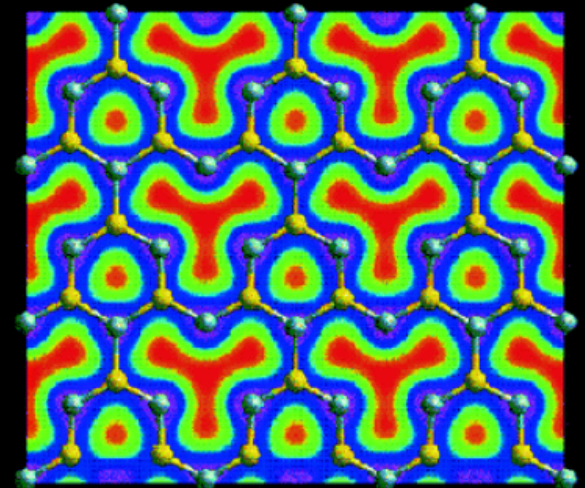
Bonding

- ❑ Formed when electrons in well defined directional orbitals, which can be thought as linear combinations of the original atomic orbitals, have strong overlap with similar orbitals in neighboring atoms.
- ❑ Attractive interaction arises from the attraction of each nucleus toward the enhanced electron charge density centered midway between nuclei.
- ❑ Solids produced in this way are semiconductors or insulators.
- ❑ Example: sharing of valence electrons between pairs of atoms (bonding molecular orbital). Each bond has two electrons  $\downarrow\uparrow$  (hydrogen, silicon, germanium..)

# Covalent Bonding

- Covalent bonding dominates in solids when number of NN's  $\leq$  number of valence electrons/atom  $\rightarrow$  **well defined bonding orbitals directonal in space are formed**
- Excess valence electrons form “lone pairs” or delocalized bond (V, VI)
- In IV group elements overlap of bonds in energy and space broadens energy levels of covalent bonds into continuous energy bands
- Crystal structure is derived from bonding
- Bonds can be also be derived by hybrid orbitals (sp, sp<sup>2</sup>..)
- (IV) Graphite: sp<sup>2</sup> – planar structure, strong  $\sigma$  (*planar* cohesive bonds in plane) and weak  $\pi$  (delocalized over the plane of C atoms).
- (V) P, As, Sb.: s<sup>2</sup>p<sup>3</sup> valence electrons, *pyramidal* bonding with 3 NN's + 2 electrons/atom in nonbonding orbitals
- (VI) S, Se, Te: s<sup>2</sup>p<sup>4</sup> valence electrons, *chain* bonding with 2 NN's + 4 electrons/atom in nonbonding orbitals
- B: complex structures, icosahedra B<sub>12</sub>, cubic, rhombohedral, tetragonal

Covalent bonds in C<sub>3</sub>N<sub>4</sub>  
electron density highest between pairs of NN atoms



# Covalent Bonding

**Coordination number (local bonding units)  $CN = 8 - N$  [ $N = \text{valence electrons/atom}$ ]**

	Group	CN	Local structure
B	III	5	Icosahedra
C(diamond)	IV	4	Tetrahedra
C(graphite)	IV	3	Planar hex
P, As, Sb	V	3	Nonplanar hex
S, Se, Te	VI	2	Rings, chains
F, Cl, Br, I	VII	1	Diatomic molecules



# Chemical Bonds in Solids: Van der Waals

❑ **Van der Waals bonding:** formed by atoms that do not have valence electrons available for sharing (**the noble elements and crystals or organic molecules**) – “fluctuating dipole” (zero-point motion) of van der Waals interaction is due to slight polarization of the electronic wave function in one atom due to the surrounding atoms.

❑ **Lowering of zero-point energy by dipole dipole interaction.** Present in other bonding types but is a small correction

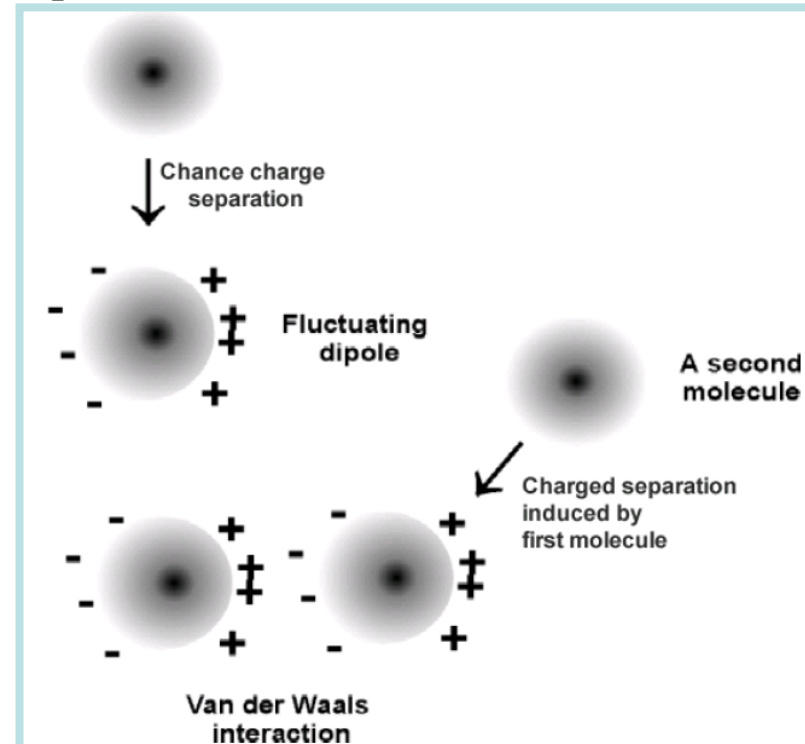
❑ Usually filled shell, inert gas solids, between graphite planes, chains of atoms in Se, Te based materials. Weaker than other types.

❑ Consider dipole dipole interaction

$$V(\vec{r}) = \frac{\mu_1\mu_2 - 3(\mu_1\hat{r})(\mu_2\hat{r})}{4\pi\epsilon_0 r^3}$$

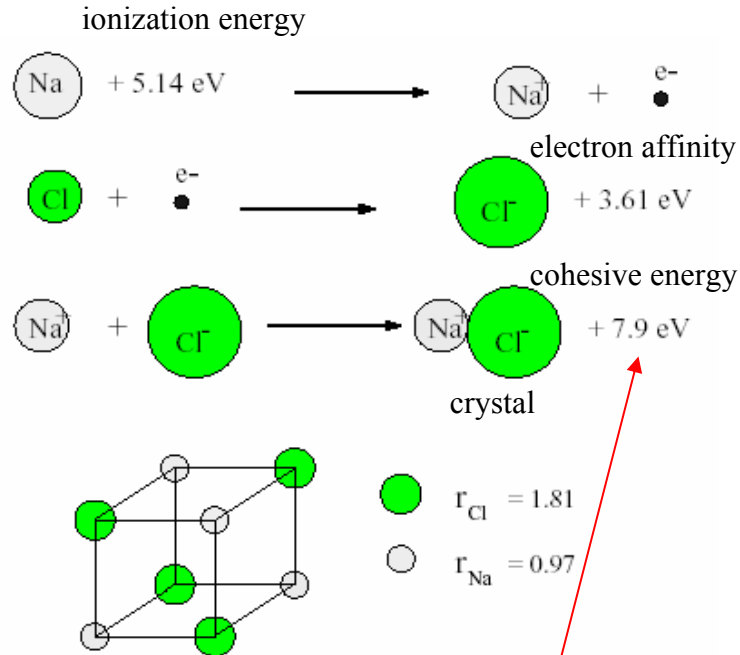
❑ Interaction energy

$$U(r) = -\sum_{nn'} \frac{|\langle nn'|V(\vec{r})|00\rangle|^2}{E_n^1 + E_{n'}^2 - E_0^1 - E_0^2} = -\frac{C}{r^6}$$



# Chemical Bonds in Solids: Ionic

Influence on crystal structure – maximizing NN of opposite type



□ The energy per molecule of a crystal of sodium chloride is  $(7.9 - 5.1 + 3.6) \text{ eV} = 6.4 \text{ eV}$  lower than the energy of the separated neutral *atoms*. The cohesive energy with respect to separated *ions* is  $7.9 \text{ eV}$  per molecular unit. All values on the figure are experimental.

**Madelung constant ( $A=1.748$  for NaCl)**

**Ionic Bonding:** Formed when two different type of atoms are combined, one that prefers to lose some of its valence electrons and become positive ion, and one that prefers to grab electrons from other atoms and become a negative ion. *In practice transfer is incomplete.* Bonding then occurs by Coulomb attraction between the ions. Combinations of such elements are I-VII, II-VI, and III-V. In the first case bonding is purely ionic, in the other two there is a degree of covalent bonding present.

Model electrostatic potential of all ionic pairs: sum of Coulomb potentials + short range repulsions when electronic clouds overlap:

$$\Phi = N_{pairs} \left( -\frac{e}{4\pi\epsilon_0 r} \sum_{i \neq j} \frac{\pm 1}{p_{ij}} + \frac{B}{r^n} \sum_{i \neq j} \frac{1}{p_{ij}^n} \right)$$

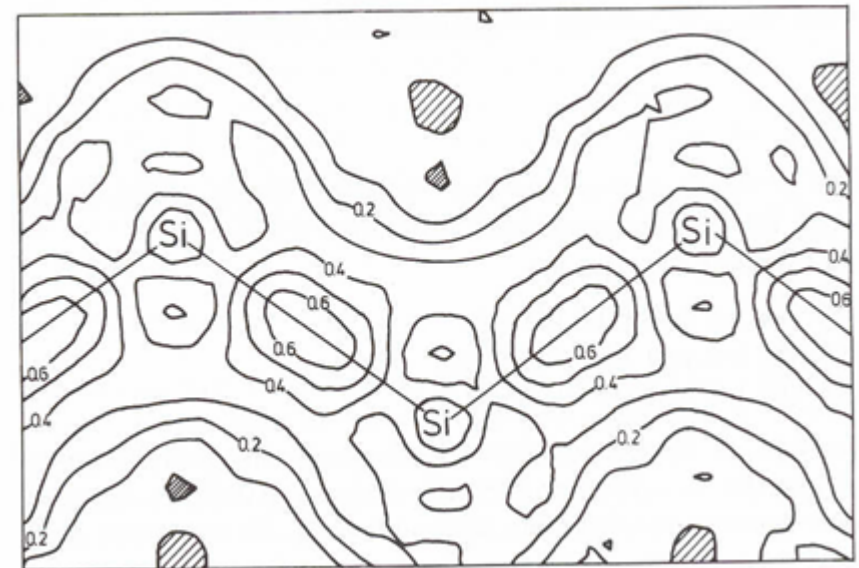
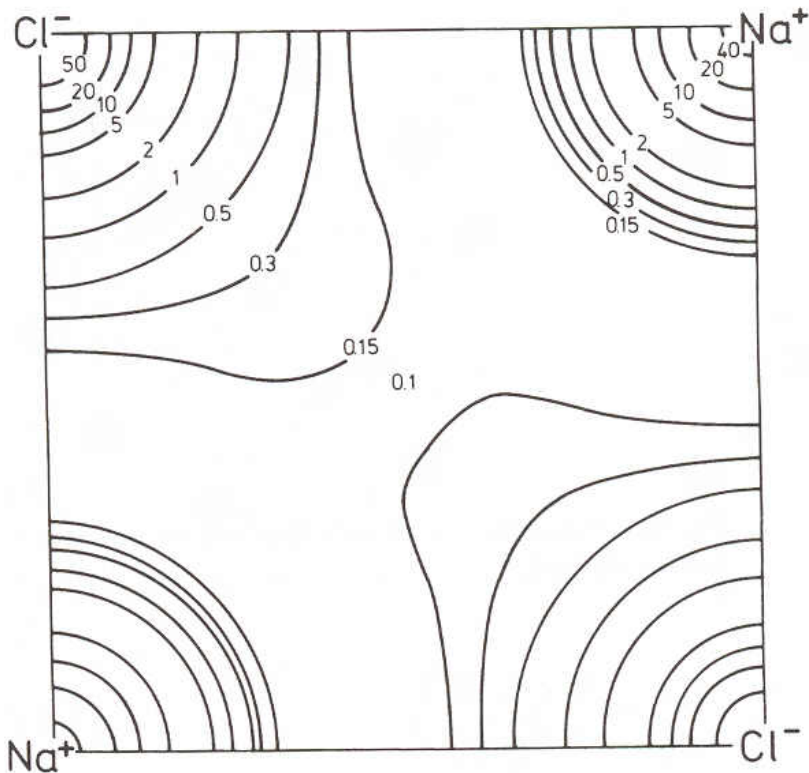
$p_{ij} = |R_i - R_j|$

**Coulomb attraction**

**Repulsion between electron clouds**

# Covalent vs. Ionic Bonding: Valence Charge Density

□ Ionic and covalent bondings are two limiting cases, of which, only the later can exist in solids **composed of a single type** of atom. In majority of cases the bonding is of an intermediate nature representing a mixture of the two extremes.



# Mixed Ionic – Covalent Bonding

- Transfer of valence electrons (partial or complete).

**CsF (ionic)**



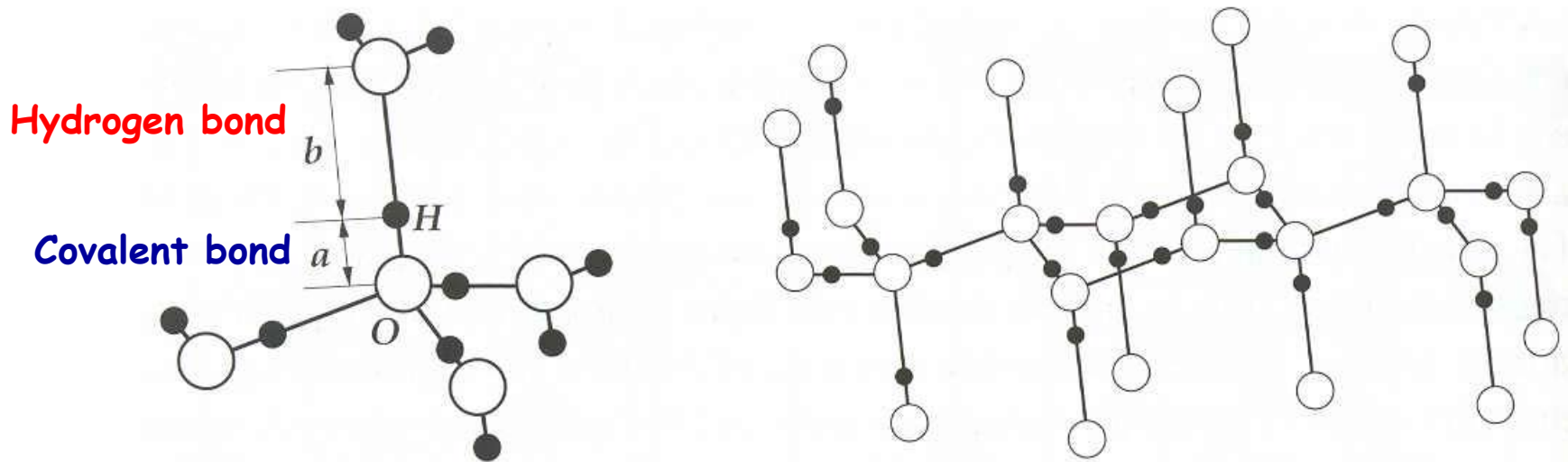
**Ge (covalent)**

- Ionicity of chemical bond:  $f = 0$  (Si) to  $f = 1$  (CsF), influences coordination and crystal structure formation

crystal	Group	$f$
C, Si, Ge	IV	0
SiC	IV - IV	0.18
BN	III-V	0.26
AlN	III-V	0.45
ZnS	II-VI	0.62
HgS	II-VI	0.79
NaCl	I-VIII	0.94



# Chemical Bonds in Solids: Hydrogen



□ **Hydrogen Bonding:** formed when H is present and bounded to two other atoms (**organic molecules, DNA, and water, ice**); this is a special bond due to its lack of core electrons (bare proton left after sharing 1s electron), its light mass (must use quantum mechanics for, e.g., zero-point proton motion) and high ionization energy.

# Orbital Overlap and Crystalline Structures

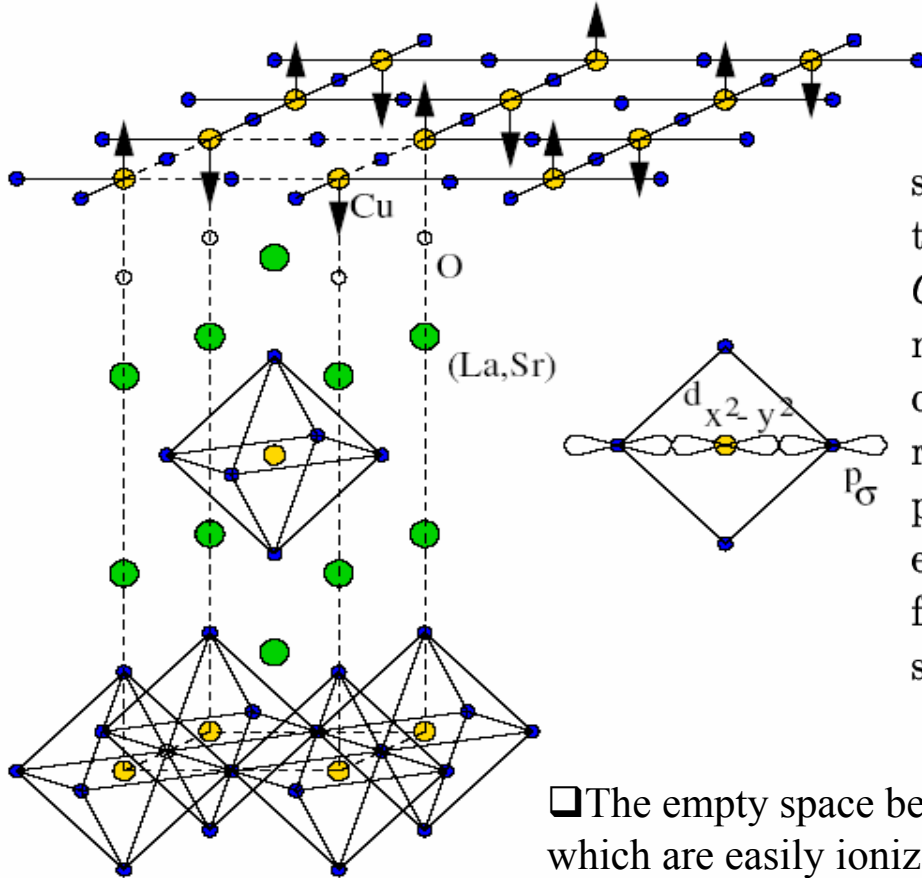
□ The type of bond that forms between two orbitals is dictated largely by the amount that these **orbitals overlap** relative to their separation  $a$ .

Bond	Overlap	Lattice	constituents
Ionic	very small ( $< a$ )	closest unfrustrated packing	dissimilar
Covalent	small ( $\sim a$ )	determined by the structure of the orbitals	similar
Metallic	very large ( $\gg a$ )	closest packed	unfilled valence orbitals



# Complex Solid: Cuprate (High- $T_c$ ) Superconductors

□ A Copper (Cu) atom is surrounded by six Oxygen (O) atoms which form an octahedron; the Cu-O atoms are bonded by strong covalent bonds.



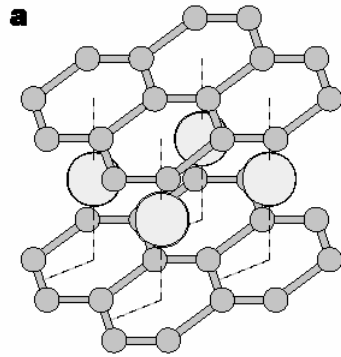
The crystallographic structure of high-temperature superconductors (HTSC) comprises two basic functional elements: (i) layered quasi-two dimensional  $CuO_2$ -lattice planes and (ii) inter-planar regions, mostly containing metallic spacer atoms in a certain concentration ratio (e.g.  $La_{1-x}Sr_x$ ). The essential role of these spacer regions is to provide the  $CuO_2$  planes with a suitable amount of mobile charge carriers. At a favourable charge carrier concentration, and for sufficiently low temperatures, the planes enter a superconducting state with highly unusual properties.

□ The empty space between Cu-O octahedra can accommodate atoms which are easily ionized, to produce **mixed covalent ionic structure**.

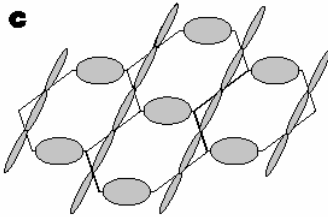
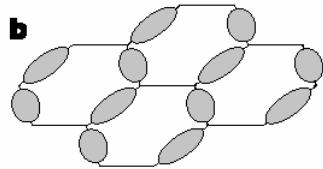


# “Simple Solid” - MgB<sub>2</sub>: Multiple-Bands (Two-Band) Superconductor

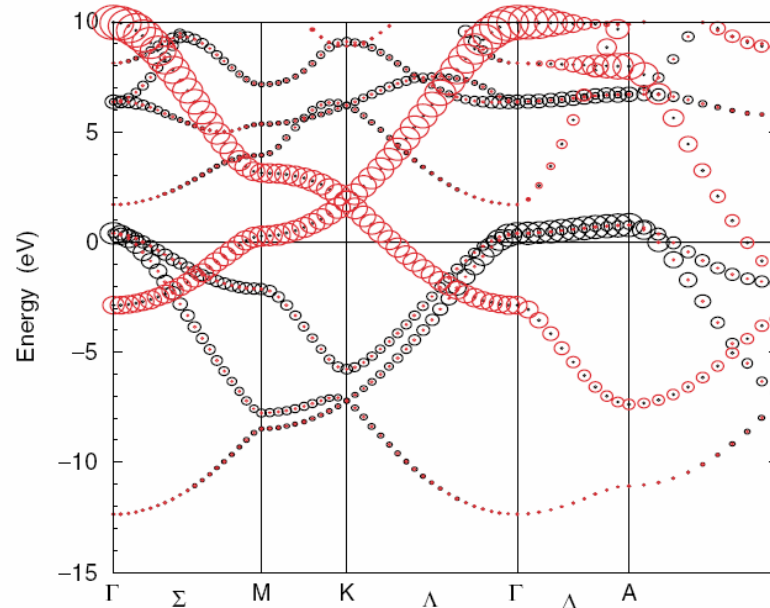
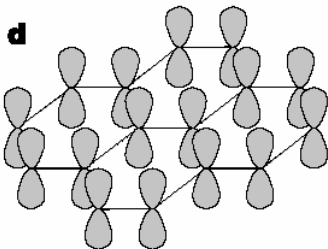
## Structure



**σ States: B p<sub>x,y</sub>**

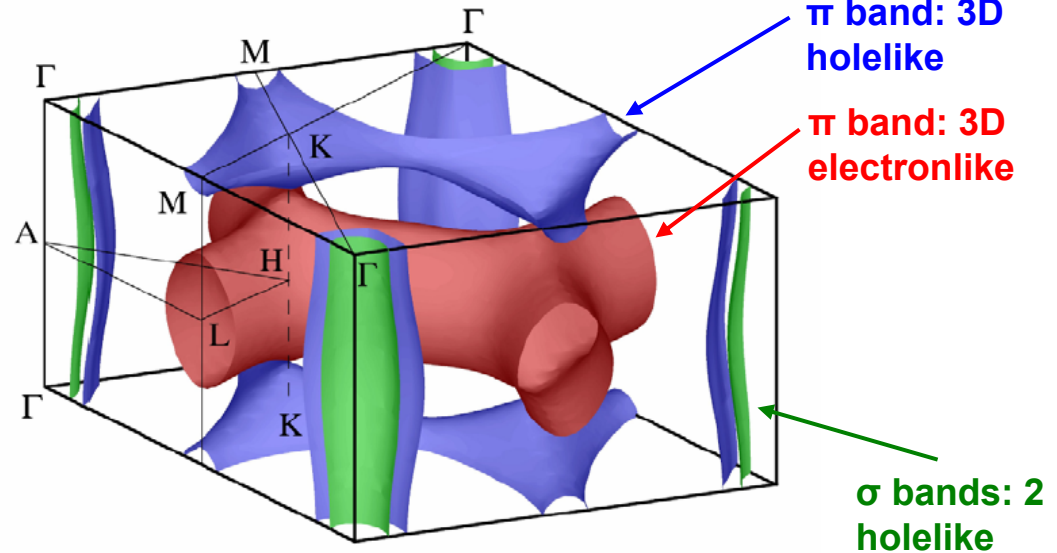


**π State: B p<sub>z</sub>**



**Red: π Bands**  
Contribute 56% of  $N(0)$

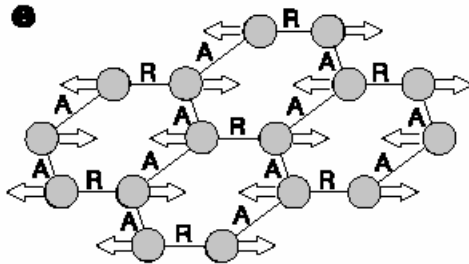
**Black: σ Bands**  
Contribute 44% of  $N(0)$



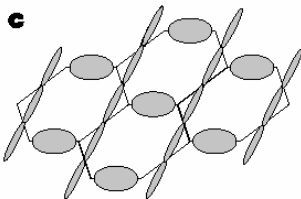
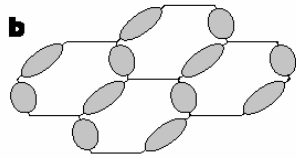
# MgB<sub>2</sub>: Two Superconductors in One Material

## Two Superconducting Gaps

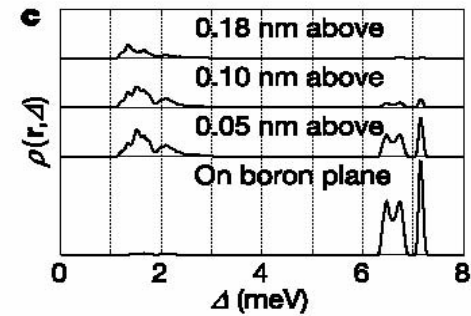
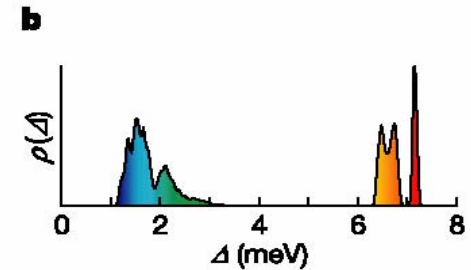
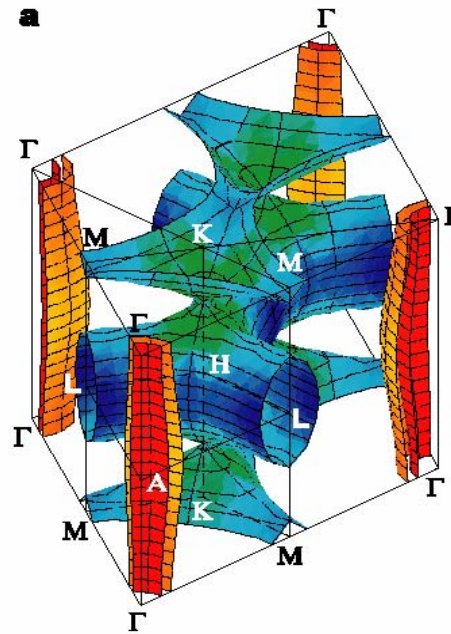
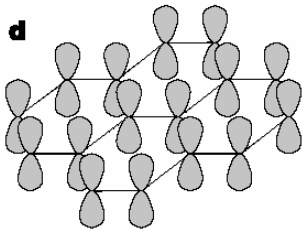
### E<sub>2g</sub> Phonon



### σ States



### π States



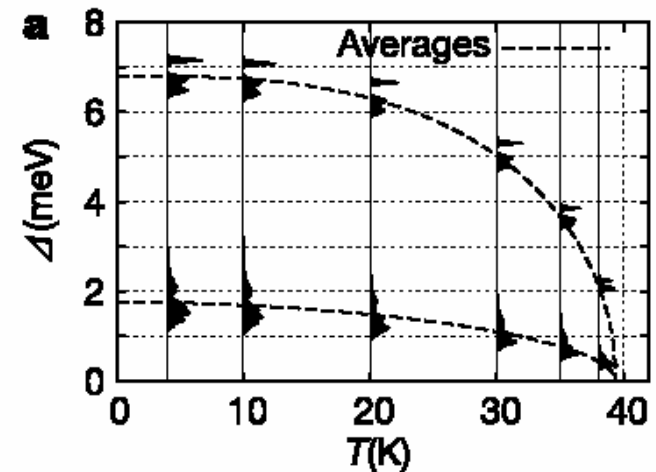
### el-ph Coupling

$$\lambda_{\sigma\sigma}=1.017 \quad \lambda_{\sigma\pi}=0.213$$

$$\lambda_{\pi\sigma}=0.155 \quad \lambda_{\pi\pi}=0.448$$

(Golubov et al. *J. Phys.: Condens. Matter* 14, 1353 (2002).)

### Gaps vs. T



# Cohesive Energy of the Chemical Bond

Bonding	Example	Cohesive E (eV/at.)	properties
Covalent	C, Si, Ge	4-8	Hard, low conduction
Ionic	NaCl, MgO	~5	Low conductivity
Metallic	Na, Fe, La	1-9	High conductivity
Van der Waals	He, Ar, Cl <sub>2</sub>	0.02-0.3	Insulators
Hydrogen	H <sub>2</sub> O, HF	0.1	Low conductivity

- Cohesive energy of the solid:  $\Delta H_C$  – to overcome the bonding and separate constituent atoms at T=0 (standard enthalpy of formation at 0K) = sum of the bond energies

$$\Delta H_C[\text{Si}(s)] = 2N_A E(\text{Si-Si}) \text{ (4NN's (bonds), two Si per bond)}$$

$$E(A-B) = \frac{E(A-A) + E(B-B)}{2} + k(X_A - X_B)^2$$

↑ ↑ ↑  
single bond energies single bond energies ionic contribution  
compound constituent elements To bond energy E(A-B)

Electronegativity (Pauling)