CHAPTER I *ATOMIC BONDS*

1.1 Classes of Materials

Traditionally, solid materials are classified into three categories:

1) metals
2) ceramics
3) polymers

Biological tissues can also be added to this list because of their increasing importance in materials science research. Also, specific proteins can crystallize and form unique compounds important in many functions and have widespread industrial and commercial applications and significance. Protein crystallography and crystallization research used for determining protein structure, properties, and design of protein crystals for pharmaceutical and food industries is a broad subject area and rich in material physics. However, its discussion deserves a separate, dedicated course (if not multiple) beyond the subject matter and the theoretical treatment in this course.

The combination of two or more of these material classes forms composite materials.

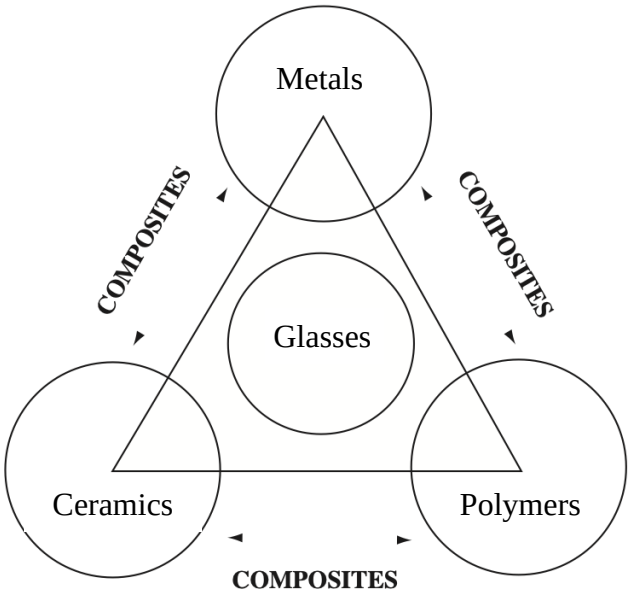


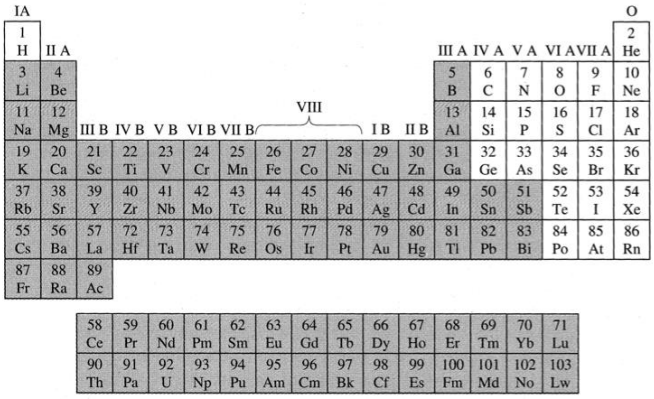
Figure 1-1: *Material classes*

These classes are recognizable from their physical properties, summarized in Table I-1. However, what truly defines them more systematically is the chemical composition of the material.

Table I-1: *Properties of the different classes of materials*

Metals	Ceramics	Polymers
Ductile, good electrical and thermal conductors. They form crystalline alloys with each other. Secondary phases can improve strength	Fragile, very resistant to chemical corrosion and heat. They have poor electrical and thermal conductivity.	Low Young modulus of elasticity, ductile, poor thermal resistance, but good corrosion resistance.

a)



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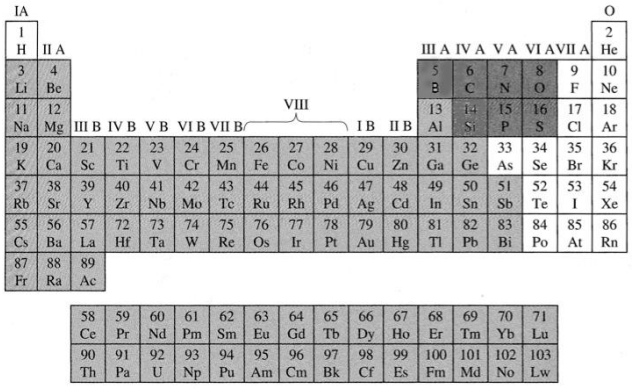


c)

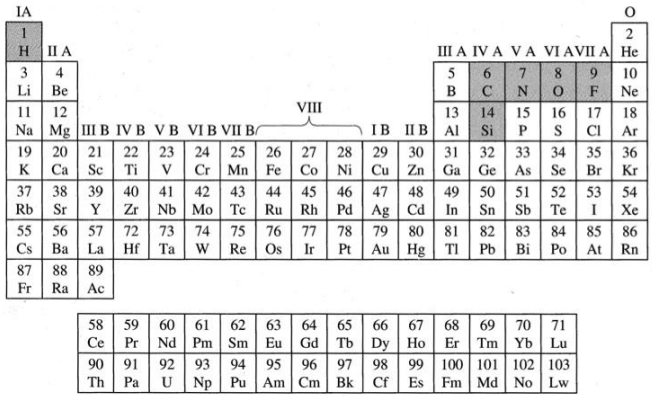


Figure 1-2: *The elements in the periodic table that form: a) metals, b) ceramics, c) polymers.*

Metals are compounds of pure elements and their alloys. Their characteristic is the ability to give between 1 and 3 valence electrons. That is, most metals are electron donors and tend to oxidize quickly. Most ceramics are made from compounds of metal and nonmetal elements (C, N, O, P, S, Si, B). Finally, polymers are formed by the many repetitions of the same base molecule (monomer), which gives them a chain structure. Most polymers comprise chains of covalently bonded carbon atoms, though other elements, like silicones with chains of covalently bonded Si atoms, can make up the chain. Chains of atoms can be weakly bonded (Van der Waals) to form dense or crystalline materials.

Generally, the structure of solid metals and ceramics is crystalline, defined by a periodic repetition in three dimensions of the same base pattern. Nevertheless, metallic and ceramic materials exist that do not have a long-range ordered periodic structure and belong to the categories of glasses and quasicrystals. Only in a few cases do polymers have a long-range ordered crystal structure.

1.2 Atomic bonds

Why are solids stable in a specific range of temperatures?
How can we explain the elastic properties of solids (linear reversible deformation)?
How can the crystal structure be interpreted?

Analyzing the cohesive forces within solids is necessary to answer these questions. In practice, the cohesion of matter comes from the electrostatic attraction between electrons and nuclei. As in many physics problems, the stability of specific configurations lies in a decrease in the overall system's energy.

The bond energy of a crystal is defined as the energy that must be supplied to separate its constituting parts into neutral atoms:

$$E_b = (E_{at,free} - E_{at,bound}) \tag{1.1}$$

The value of this cohesive energy indicates how strong the bonds between the atoms are in a solid. Atomic bonds derive essentially from variations in the distributions of electrons induced by the proximity of other atoms. Quantum mechanics calculations can determine this bond energy by computing the perturbation of the Hamiltonian of isolated atoms when they come close together, which consists of computing the wave functions of the energy equation,

$$(H_0 + H_1)\cdot\Psi = (E_0 + \Delta E)\cdot\Psi \tag{1.2}$$

where H_1 and ΔE are the perturbations of the Hamiltonian and the energy, respectively.

In solid bodies, four main kinds of interaction are found: Ionic, Van der Waals, Covalent, and Metallic bonding.

1.2.1 Ionic bond

The majority of atoms in nature do not have a neutral state. Noble gases are excluded, and atoms of the other elements tend to accept or donate electrons. This tendency can be quantified by ionization energy and electron affinity (Figure 1-3). The first one characterizes the energy necessary to extract one electron, and the second term accounts for the variation in energy resulting from the capture of an electron. If the electron affinity is negative, the atom loses energy by capturing an electron, and an exothermic reaction occurs.

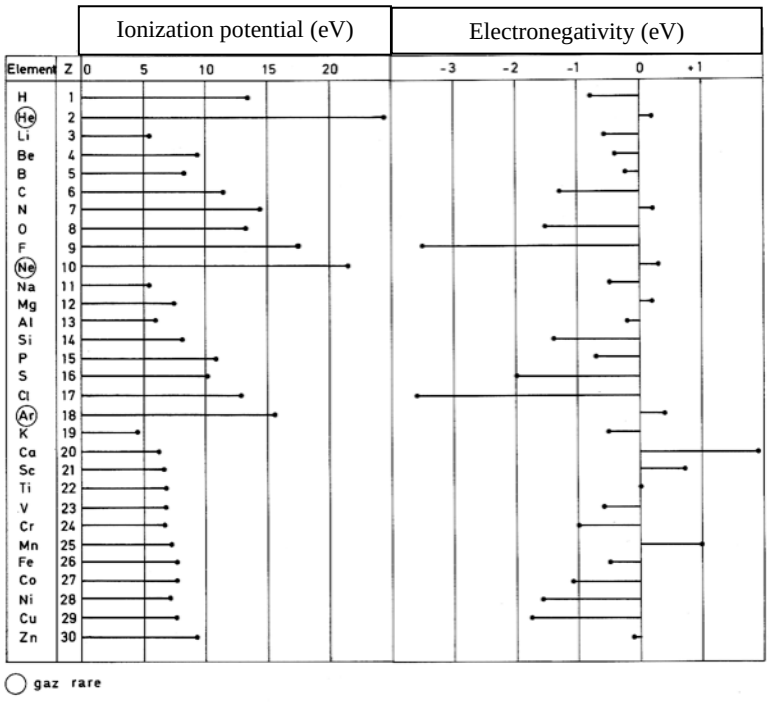


Figure 1-3: *Ionization potential and electron affinity for different elements*

In ionic crystals, electric charge transfer occurs between atoms with low electron affinity (neutral or positively charged stable atoms) and atoms with strong electron affinity. For example, Cl has an affinity of -3.6 eV, whereas Na has an electron affinity of -0.55 eV. An ionic crystal is formed with base units of two charges, one positive (Na^+) and one negative (Cl^-). The bond energy is calculated considering the coulombic interaction between atoms, consisting of an attractive potential between opposite charges and a repulsive potential between ions of the same sign. However, suppose two atoms come too close. The overlapping of the electron clouds creates conditions that violate Pauli's exclusion principle, which determines a repulsive, short-distance force independent of the sign of the charges. The interaction potential for the ion *i* is of the form:

$$U_i = \sum_i U_{ij} \tag{1.3}$$

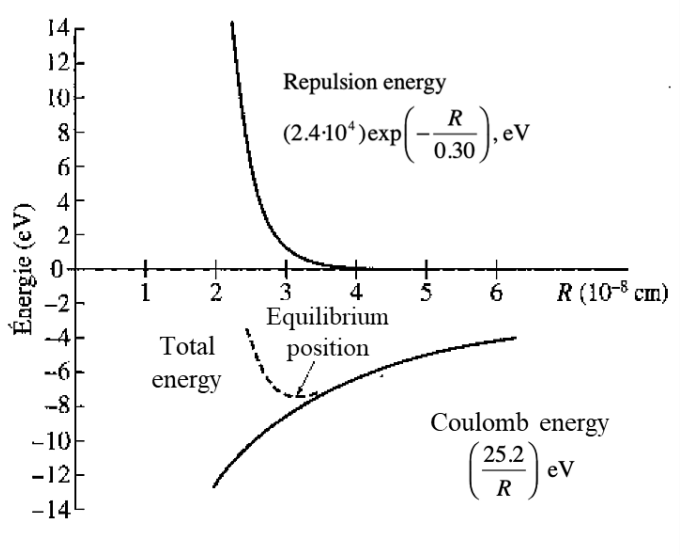
$$U_{ij} = \lambda \exp(\frac{-r_{ij}}{\rho}) \pm \frac{q^2}{4\pi\varepsilon_0 r_{ij}}$$

Thus, the repulsion term is, $$\sum_i \lambda \exp(\frac{-r_{ij}}{\rho}) = \lambda z \exp(\frac{-R}{\rho}) \tag{1.4}$$

where λ is a constant, ρ is the compressibility constant, z is the number of the closest neighboring ions since long-range interactions are negligible, q is the electron charge, r_{ij} is ion distances, and ε_o is the permittivity constant. The value of the coulombic term can be computed as the sum of a convergent series, the value of which is called the Madelung constant (α):

Coulombic term becomes:

$$\sum_i \pm \frac{1}{r_{ij}} = \frac{\alpha}{R} \tag{1.5}$$



Energy (per molecule) of the KCl cristal, showing the Madelung and repulsion contributions

Figure 1-4: *Ionic bond potential*

For N molecules, we can write:

By calculating $\frac{dU_i}{dR}$, we can derive the equilibrium radius R_0 and thus the bond energy:

When $\frac{\rho}{R_0} \approx 0.1$; the coulomb energy is, therefore, dominant.

$$U_i = \left(z\lambda e^{\frac{-R}{\rho}} - \frac{\alpha q^2}{4\pi\epsilon_0 R} \right) \tag{1.6}$$

Application: NaCl $\alpha = 1.75$ $R_0 = 2.81\ 10^{-10}$ m, $E_c = -7.9$ eV/molecule

$$U_{tot} = -\frac{N\alpha q^2}{4\pi\epsilon_0 R_0}\left(1 - \frac{\rho}{R_0}\right) \tag{1.7}$$

This energy is calculated with respect to the energy of free ions. Keeping in mind that:

$E_{ionisation}(Na) = 5.1$ eV and $E_{electronaffinity}(Cl) = -3.6$ eV

We find that the bond energy is $E_b = -7.9 + 5.1 - 3.6 = -6.4$ eV/molecule.

This value corresponds to the decrease in energy in the state of a molecule for isolated atoms or, in other words, to the heat released during the reaction: Na+Cl->NaCl.

1.2.2 Van der Waals interactions

If we consider neutral atoms, like noble gases, the electron charge distribution around the nucleus is perfectly symmetric. Nevertheless, if atoms in this molecule are brought closer, the electron cloud of one atom is attracted by neighboring nuclei. The result of this close proximity is the formation of two electric dipoles. These can be represented as two charged harmonic oscillators.

Figure 1-5: Model of two charged harmonic oscillators

The Hamiltonian of the system at rest is:

$$H_0 = \frac{1}{2m}p_1^2 + \frac{1}{2}kx_1^2 + \frac{1}{2m}p_2^2 + \frac{1}{2}kx_2^2 \tag{1.8}$$

The energy of the system in its fundamental state is $h\omega_0$, $\omega_0 = \sqrt{k/m}$ being the resonance frequency of each one of the oscillators. Coulombic interaction between the two oscillators generates an attractive force. By solving for eigenvalues of energy, the following expression is obtained (exercise):

$$-h\omega_0 \frac{1}{32\pi^2\epsilon_0^2}\left(\frac{e^2}{kR^3}\right)^2 \tag{1.9}$$

This result justifies the form used to calculate the bond energy within solids starting from the classical example related to noble gases: Lennard-Jones potential. By neglecting thermal agitation, the bond energy is given by an attractive term relative to Van der Waals force and by a repulsive term that arises because of Pauli's exclusion principle when the electron clouds come closer together. It is written as follows,

$$U = \left(\frac{A}{R^{12}} - \frac{B}{R^6}\right) = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6\right] \tag{1.10}$$

and the total potential becomes:

$$U_{tot} = \frac{1}{2}N(4\epsilon)\left[\sum_{ij}\left(\frac{\sigma}{p_{ij}R}\right)^{12} - \left(\frac{\sigma}{p_{ij}R}\right)^6\right] \tag{1.11}$$

The sums $\sum_{ii}\left(\frac{1}{p_{ij}}\right)^{12}$ and $\sum_{ii}\left(\frac{1}{p_{ij}}\right)^6$ are – similar for calculating the Madelung constant - convergent series that can be calculated for every crystal structure.

For an FCC structure, we obtain:

$$\sum_{ii}\left(\frac{1}{p_{ij}}\right)^{12}=12.13188 \quad \text{and} \quad \sum_{ii}\left(\frac{1}{p_{ij}}\right)^{6}=14.45392 \tag{1.12}$$

We calculate the equilibrium position R_0 taking $\frac{dU}{dR}=0$ It can easily be shown that the ratio, $R_0/\sigma=1.09$, is a constant. Experimental measures (table I-2) confirm the theory to a remarkable extent. Observed deviations may result since quantum kinetic energy is neglected.

Table I-2: *Equilibrium distance in noble gases normalized for Lennard-Jones potential*

	Ne	Ar	Kr	Xe
R_0/σ	1.14	1.11	1.1	1.09

1.2.3 Covalent bond

The covalent bond derives from forming local common orbitals from merging isolated separate orbitals. The electrons occupy the new orbitals compatibly with the exclusion principle. Thus, the partially free valence orbitals do contribute to atomic bonds. Even in the simple case of molecular hydrogen, the calculations, which follow the principles of quantum mechanics of molecular energy, are rather complex and are not presented here for brevity. However, it can be shown, for example, that the computation of the energy of a two electrons and two protons system leads to two possible states (see C. Cohen-Tannoudji and others - Complement Gxi): one high energy antibonding state A (antisymmetric to the exchange of electrons - parallel spins) and a bonding state (symmetric to the exchange of electrons - opposite spins) with lower energy than the two atoms taken singularly with an energy minimum corresponding to the equilibrium distance between the atoms in the molecule.

It is interesting to note that the wave functions of molecular orbitals can be constructed starting from the electron orbitals of the hydrogen atom. Thus, 1s states or $2p_z$ give rise to states called σ (as s) with an angular momentum Lz corresponding to $|m|=0$. The states $2p_x$ and $2p_y$ give rise to states with $|m|=1$ called π (as pi).

Example: Bonds in organic materials

Carbon atoms have six electrons: 2 in the sub-shell 1s, 2 in the sub-shell 2s, and 2 in the sub-shell 2p. We expect only the electrons in 2p to be involved in atomic bonds. However, when carbon atoms bind with other atoms, one of the 2s electrons can occupy the third 2p orbital. In this case, the valence electrons would be 4: 2s, $2p_x$, $2p_y$, and $2p_z$. The wave functions of these electrons derive from a linear combination of the wave functions of these orbitals, and these hybrid orbitals are used to explain the geometry and bonding characteristics of molecules.

sp hybridization is a linear combination of one s (spherical-shaped- sigma) wavefunction and one p (dumbbell-shaped- pi) wavefunction (Figure 1-7). This hybridization results in two sp orbitals in which an atom forms a double bond with another atom. The two sp hybrid orbitals are linearly oriented at 180 degrees to each other, creating a linear molecular geometry. Examples of molecules that have sp hybridization include carbon dioxide (CO_2) and acetylene ($C2H_2$). We refer to sp^2

hybridization when two p wavefunctions combine with one s wavefunction (Figure 1-9) and form a trigonal planar arrangement, such as in molecules with a double bond and no lone pairs of electrons around the central atom. The three sp^2 hybrid orbitals are arranged in a trigonal planar geometry with bond angles of approximately 120 degrees. Examples of molecules that undergo SP2 hybridization include ethene (C_2H_4) and formaldehyde (CH_2O). There are 3 orbitals for sp^2 hybridization and 4 orbitals for sp^3 (Figure 1-10). The four sp^3 hybrid orbitals are arranged tetrahedrally around the central atom, with bond angles of approximately 109.5 degrees. Methane (CH_4), water (H_2O), and ammonia (NH_3) are examples of molecules having sp^3 hybridization.

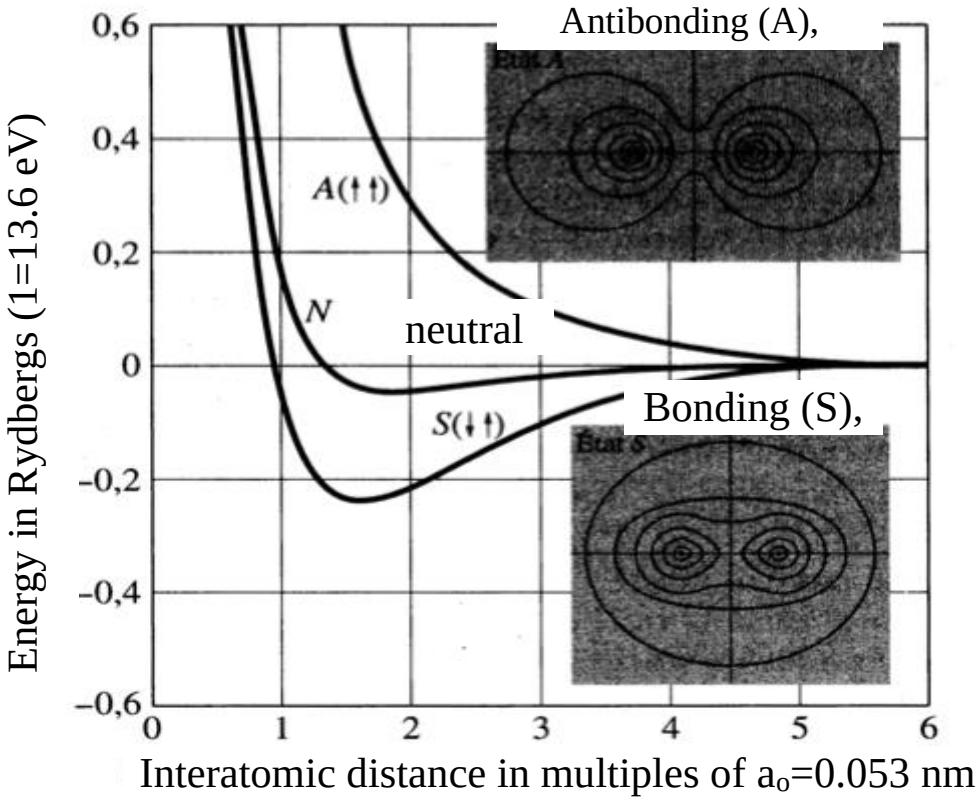
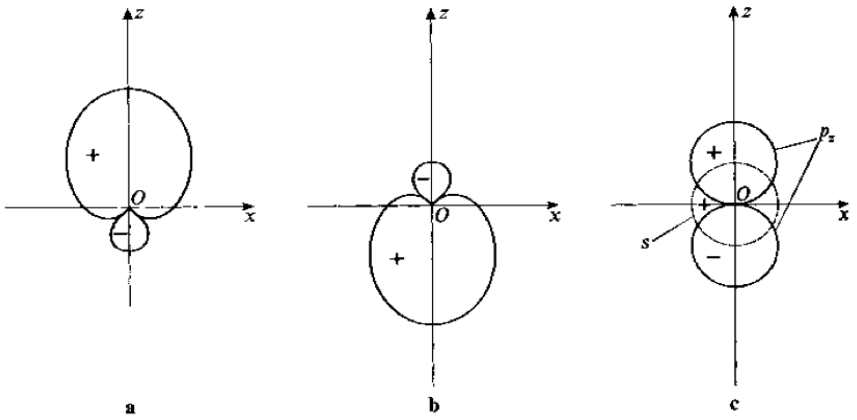


Figure 1-6: *Bonding states (S), antibonding states (A), and neutral atoms potentials for two hydrogen atoms*



Angular dependence of orbital hybridization a) s-p_x b) s-p_z and c)s and p_z ortibals with opposite parity. A hybrid orbital can extend further in certain directions than the pure orbitals from which it originates.

Figure 1-7: *Hybridized orbitals, sp configurations*

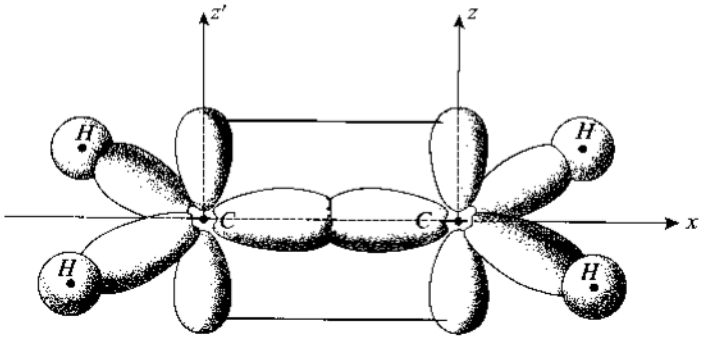


Figure 1-8: *sp hybridization: acetylene molecule*

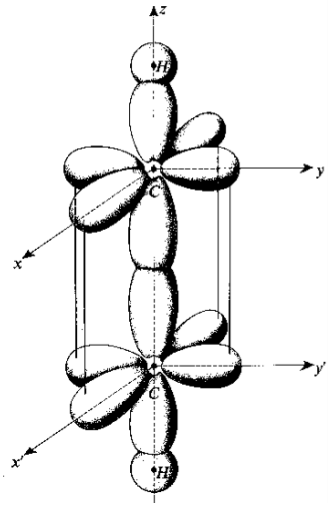


Figure 1-9: *sp^2 hybridization: ethylene molecule*

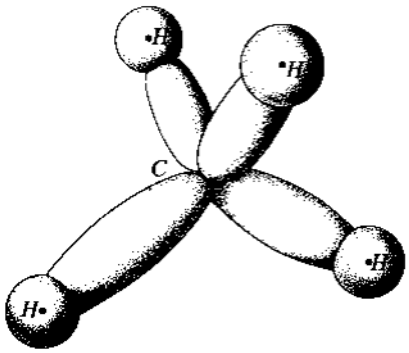


Figure 1-10: *sp^3 hybridization: methane molecule*

In summary, sp, sp^2, and sp^3 hybridization describe the mixing of atomic orbitals that form hybrid orbitals with specific geometries and characteristics. These hybrid orbitals allow atoms to participate in different types of chemical bonding, such as single, double, and triple bonds, and help explain the shapes and structures of molecules.

1.2.4 Metallic bond

The metallic bond can be conceptualized as a lattice of positively charged ions surrounded by a "sea" or cloud of delocalized electrons. Unlike in covalent bonds, where electrons are shared between specific atoms, in metallic bonds, electrons are not associated with any particular ion. Instead, they move freely throughout the metal, creating a strong and flexible bond. The interaction between the positive ions and the electron cloud lowers the energy compared to isolated atoms, similar to how energy is reduced in covalent bonding. However, a key distinction is that the electrons are delocalized in metals, meaning they are free to move and possess kinetic energy. This delocalization is a critical factor in the metallic bond, which is highly isotropic—meaning it has the same properties in all directions—resulting in densely packed and stable crystal structures.

The behavior of electrons in a metal can be described by Bloch wave functions, which are solutions to the Schrödinger equation in a periodic potential, such as that found in a crystal lattice, which takes the form:

$$\psi_k(x) = u_k(x)e^{ikx} \tag{1.13}$$

A Bloch wave function is essentially the product of a plane wave and a function that has the same periodicity as the crystal lattice $u_k(x)$. The function $\psi_k(x)$ that satisfies the border condition $\psi_k(x+L) = \psi_k(x)$, where *L* is the size of the crystal, can be decomposed in the Fourier series:

$$\psi(x) = \sum_k C(k)e^{ikx} \tag{1.14}$$

In the same way, the periodic potential of the crystal can be decomposed in the Fourier series:

$$U(x) = \sum_G U_G e^{iGx} \tag{1.15}$$

where G is the reciprocal lattice vector. The solution of the Schrödinger equation with one electron leads to the eigenvalue problem:

$$\left(\frac{\hbar^2 k^2}{2m} - \epsilon\right)C(k) + \sum_G U_G C(k-G) = 0 \tag{1.16}$$

$$\left(\frac{1}{2m}p^2 + U(x)\right)\psi(x) = \epsilon\psi(x) \tag{1.17}$$

which yields the Bloch functions in the form:

$$\psi_k(x) = \sum_G C(k-G)e^{i(k-G)x} \tag{1.18}$$

Solving the Schrödinger equation for a single electron in this periodic potential leads to an eigenvalue problem, producing the Bloch functions. These functions describe how electrons propagate through the crystal and form the foundation of the theory of energy bands. The wave functions of the atomic orbitals, which take part in the atomic bonds, create, for N atoms, two N states very close to each other that form a continuous band. N states are still available if one atom in the crystalline lattice

gives one electron to the valence band. On the other hand, if each atom gives 2 electrons - or 1 electron with two atoms per cell - the valence band is complete. Incomplete valence bands characterize metals. That is to say, there are available states still with wave vector k. That means the momentum of the electrons can be changed. This incomplete filling allows electrons to change their momentum when an electric field is applied, resulting in a flow of electrical current, which explains why metals are excellent conductors.

In contrast, semiconductors have completely filled valence bands at absolute zero, with a small energy gap, known as the band gap, between the valence and conduction bands. This gap is small enough that at room temperature, thermal energy or external stimuli (such as photons) can excite electrons into the conduction band, where they become delocalized and contribute to electrical conduction. However, suppose the band gap exceeds around 2 eV. In that case, the material behaves as an insulator because the thermal energy at room temperature is insufficient to excite electrons into the conduction band, preventing the material from conducting electricity. Thus, the electronic structure and band theory explain the differences in conductivity between metals, semiconductors, and insulators.

1.2.5 Atomic bonds and materials

In conclusion, the type of atomic bonds in a solid determines the physical characteristics of materials.

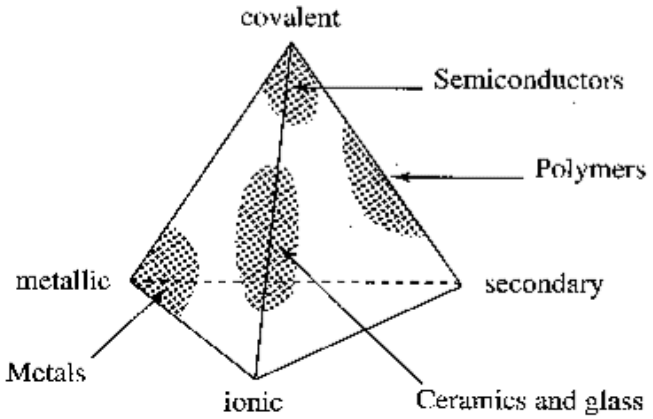


Figure 1-11: Types of bonding intervening in the structure of materials

Metals, by definition, logically, have pure metallic bonds. Other classes of materials generally present mixed types of bonding. Ceramics have ionic, covalent, or mixed types of bonding. Polymers are identified by having covalent main bondings on the axis of the chain structure and Van der Waals bonds between the chains.

Bibliography

Friedel J., “Dislocations”, Pergamon Press, Oxford (1964)

Adda Y. and Philibert J., “La diffusion dans les solides”, Presses Universitaires de France, Paris

Landau Y. and Lifchitz E., "Theory of elasticity," MIR, Editions MIR, Moscow (1967)

Verhoeven J.D., "Fundamentals of physical metallurgy", Wiley & Sons, New York (1975)

Tannoudji C.C., Diu B. and Laloë F., “Mécanique quantique”, Hermann, Paris (1977)

Hirth J.P. and Lothe J., "Theory of dislocations," Wiley & Sons, New York (1982)

Noyan I.C. and Cohen J.B., "Residual stress," Ilschner B. & Grant N.J. editors, Springer-Verlag, New York (1987)

Kurz W., Mercier J.P. and Zambelli G., “Introduction à la science des matériaux”, Presses Polytechniques et Universitaires Romandes, Lausanne (1991)

Philibert J., “Atom movement diffusion and mass transport in solids”, Les éditions de physique, Les Ulis (1991)

Ashby M.F., "Materials selection in Mechanical design," Pergamon Press, Oxford (1992)

Schwarzenbach D., “Cristallographie”, Presses Polytechniques et Universitaires Romandes, Lausanne (1993)

Shackelford J.F., "Introduction to Materials Science for Engineers," Prentice Hall, Upper Saddle River, NJ 07458 (1996)

Porter D.A. and Easterling K.E., "Phase transformations in metals and alloys," Chapman and Hall, London (1997)

Hull D., "Introduction to dislocations," Butterworth-Heinemann, Oxford (1998)

Kittel C., McEuen P., "Introduction to solid state physics," Wiley, Hoboken NJ (2005)