
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 are not a subset of polymers and should be included in this list due to their growing importance in materials science research. 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, which is used to determine protein structure, properties, and design protein crystals for pharmaceutical and food industries, is a broad subject area rich in material physics. However, their discussion deserves a separate, dedicated course (or multiple courses) that extends beyond the subject matter and theoretical treatment in this course.

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

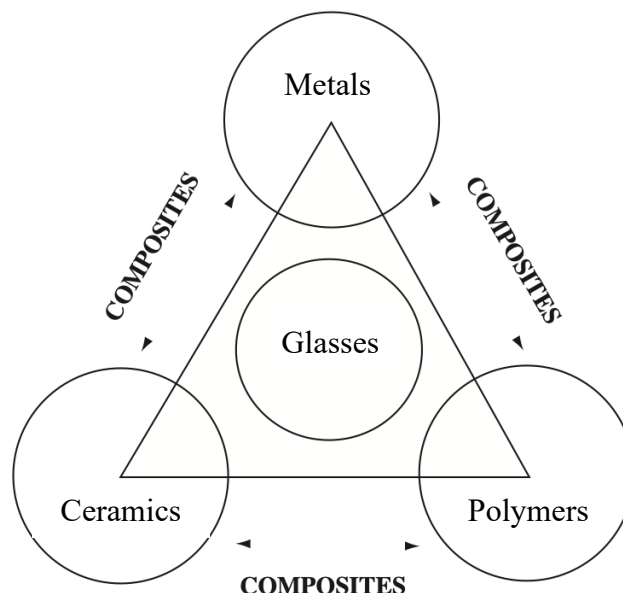


Figure 1-1: Material classes

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)

1	2																	10
3	4																	10
11	12																	18
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
87	88	89																
Fr	Ra	Ac																

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

b)

1	2																	10
3	4																	10
11	12																	18
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
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90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

c)

1	2																	10
3	4																	10
11	12																	18
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
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58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

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

Metals are compounds comprising pure elements or combinations of elements that form alloys with unique properties. Their primary characteristics and properties arise from their bonding behavior and 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 is determined by 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 constituent parts into neutral atoms:

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

The value of this cohesive energy indicates the strength of the bonds between atoms 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 approach each other, which involves solving the wave functions according to the energy equation.

$$(H_0 + H_1) \cdot \Psi = (E_0 + \Delta E) \cdot \Psi \quad (1.2)$$

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

Most elements in nature, except for noble gases, readily form ions. Their atoms tend to donate or accept electrons to achieve stable electronic configurations. This tendency can be quantified by two fundamental properties: ionization energy and electron affinity (Figure 1-3). Ionization energy is the energy required to remove an electron from an atom, while electron affinity describes the change in energy when an atom captures an electron. If the electron affinity is negative, the atom releases energy when it gains an electron, corresponding to an exothermic process.

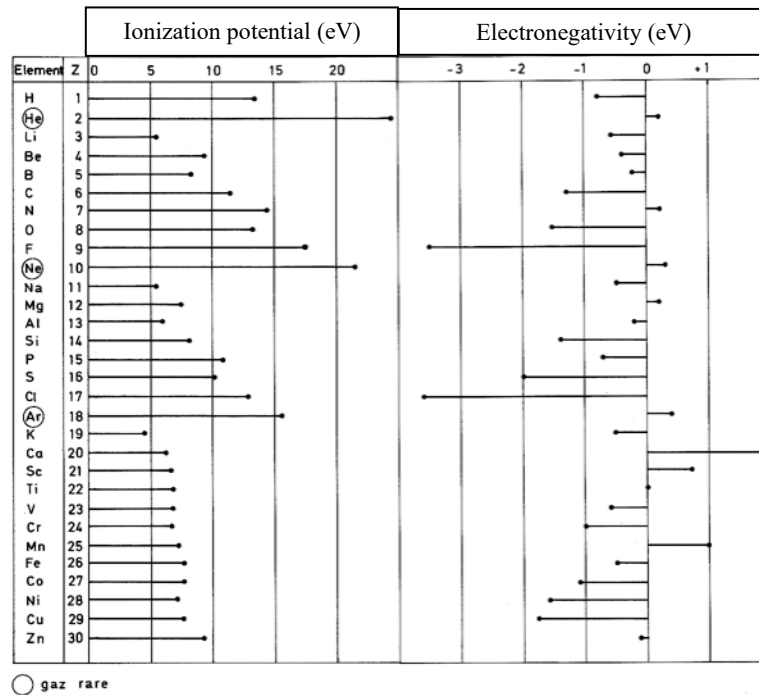


Figure 1-3: Ionization potential and electron affinity for different elements

In ionic crystals, charge transfer occurs between atoms with low ionization energies (which easily lose electrons) and atoms with high electron affinities (which readily accept electrons). For example, chlorine has an electron affinity of -3.6 eV, while sodium's is -0.55 eV. Their combination yields the ionic compound NaCl, whose structural units consist of Na^+ and Cl^- ions. The bond energy in such a crystal can be modeled as the sum of a long-range Coulomb attraction between oppositely charged ions and a short-range repulsion that arises when electron clouds overlap. The latter originates from the Pauli exclusion principle, which forbids electrons from occupying the same quantum state, and produces a strong repulsive force that is independent of the charge sign. The interaction potential energy for ion i can be written as:

$$U_i = \sum_j U_{ij} \quad (1.3)$$

$$U_{ij} = \lambda \exp\left(\frac{-r_{ij}}{\rho}\right) \pm \frac{q^2}{4\pi\epsilon_0 r_{ij}}$$

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

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 the ion distance, and ϵ_0 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:
$$\sum_i \pm \frac{1}{r_{ij}} = \frac{\alpha}{R} \tag{1.5}$$

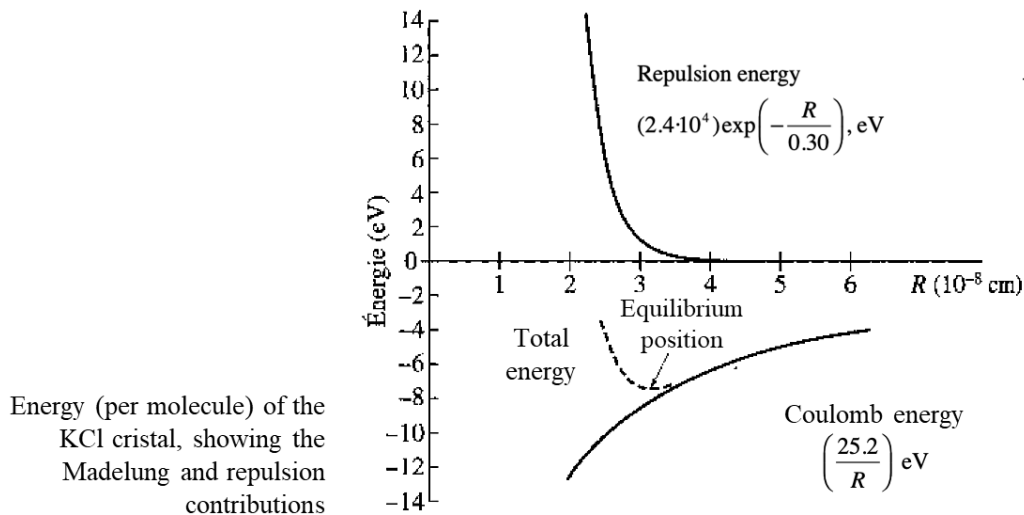


Figure 1-4: Ionic bond potential

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 $\alpha = 1.75$ $R_0 = 2.81 \cdot 10^{-10}$ 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:

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

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: $Na + Cl \rightarrow NaCl$.

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 the 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.

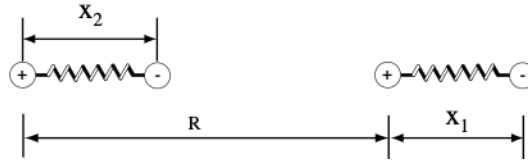


Figure 1-5: Model of two charged harmonic oscillators

The Hamiltonian of the system at rest is:

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

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

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

This result justifies the form used to calculate the bond energy within solids, starting from the classical example related to noble gases: the Lennard-Jones potential. By neglecting thermal agitation, the bond energy is given by an attractive term relative to the 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,

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

and the total potential becomes:

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

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:

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

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 the Lennard-Jones potential

	Ne	Ar	Kr	Xe
R_0/σ	1.14	1.11	1.1	1.09

1.2.3 Covalent bond

A covalent bond arises when atomic orbitals overlap to form molecular orbitals that are shared between two atoms. The electrons occupy these new orbitals in accordance with the Pauli exclusion principle. Thus, valence orbitals, which are only partially filled in isolated atoms, play a central role in bond formation.

Even in the simplest case—the hydrogen molecule—the quantum mechanical treatment of a system with two protons and two electrons is mathematically complex. Nevertheless, it can be shown (see C. Cohen-Tannoudji et al., Complement Gxi) that such a system admits two types of states:

- A bonding state (symmetric with respect to electron exchange, opposite spins), with lower energy than two isolated atoms, and an equilibrium interatomic distance corresponding to the bond length;
- An antibonding state (antisymmetric with respect to electron exchange, parallel spins), with higher energy.

The molecular orbitals of H_2 can be built from linear combinations of hydrogen atomic orbitals. For instance, combining 1s or $2p_z$ orbitals produces σ (sigma) states, which have angular momentum projection $L_z=0$ corresponding to $|m|=0$. By contrast, combinations of $2p_x$ and $2p_y$ orbitals yield with $|m|=1$ referred to as π (pi) states, characterized by $|L_z|=1$.

Example: Bonds in Organic Molecules

Carbon has six electrons: two in the 1s subshell, two in the 2s, and two in the 2p. Although only the 2p electrons are expected to participate in bonding, in practice, one of the 2s electrons is promoted to the empty 2p orbital. This results in four valence electrons available for bonding (2s, $2p_x$, $2p_y$, $2p_z$). The wavefunctions of these orbitals can combine to form hybrid orbitals, which explain the geometry and bonding properties of organic molecules:

- sp hybridization: one s orbital mixes with one p orbital, producing two sp orbitals arranged linearly at 180° . This geometry is found in molecules such as CO_2 and C_2H_2 (acetylene).
- sp^2 hybridization: one s orbital combines with two p orbitals, giving three sp^2 orbitals arranged in a trigonal planar geometry (120° bond angles). Examples include C_2H_4 (ethene) and CH_2O (formaldehyde).
- sp^3 hybridization: one s orbital mixes with three p orbitals, forming four sp^3 orbitals in a tetrahedral arrangement with bond angles of $\sim 109.5^\circ$. Classic examples are CH_4 (methane), H_2O (water), and NH_3 (ammonia).

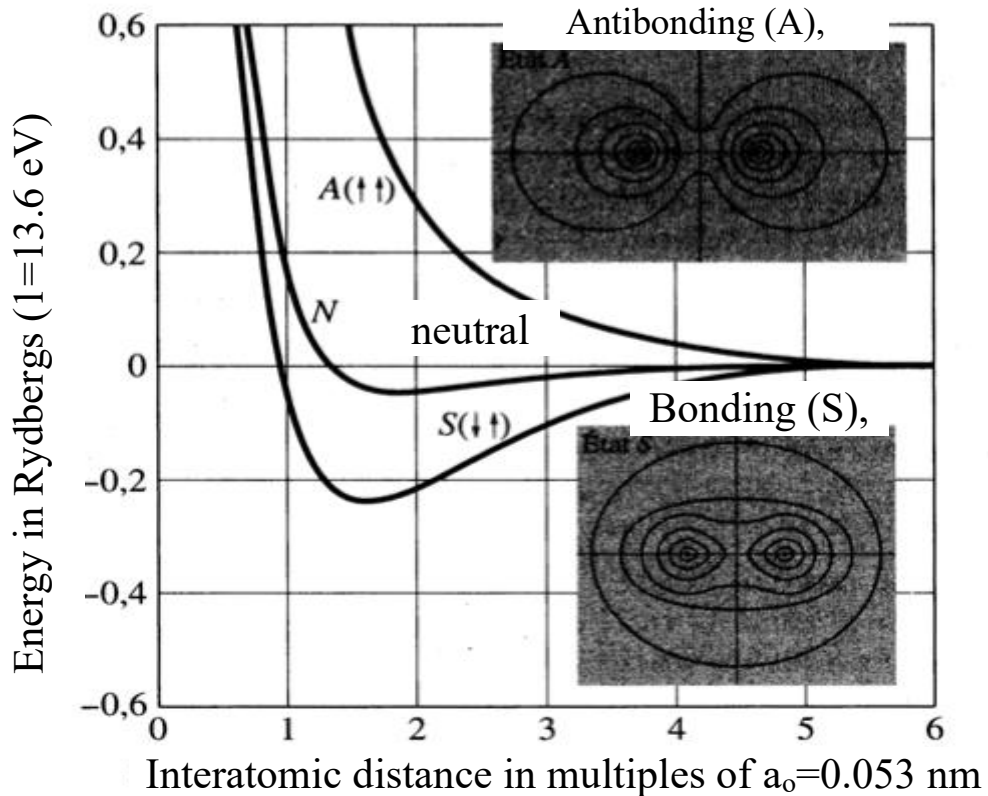
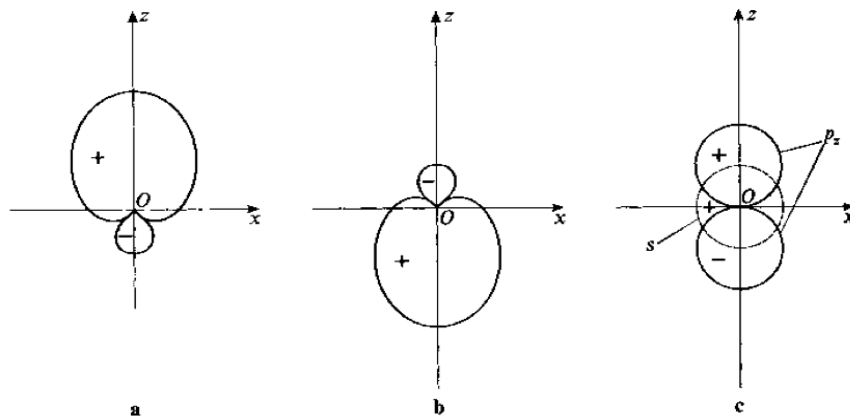


Figure 1-6: Bonding states (S), antibonding states (A), and neutral atom potentials for two hydrogen atoms



Angular dependence of orbital hybridization a) s - p_x b) s - p_z and c) s and p_z orbitals 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

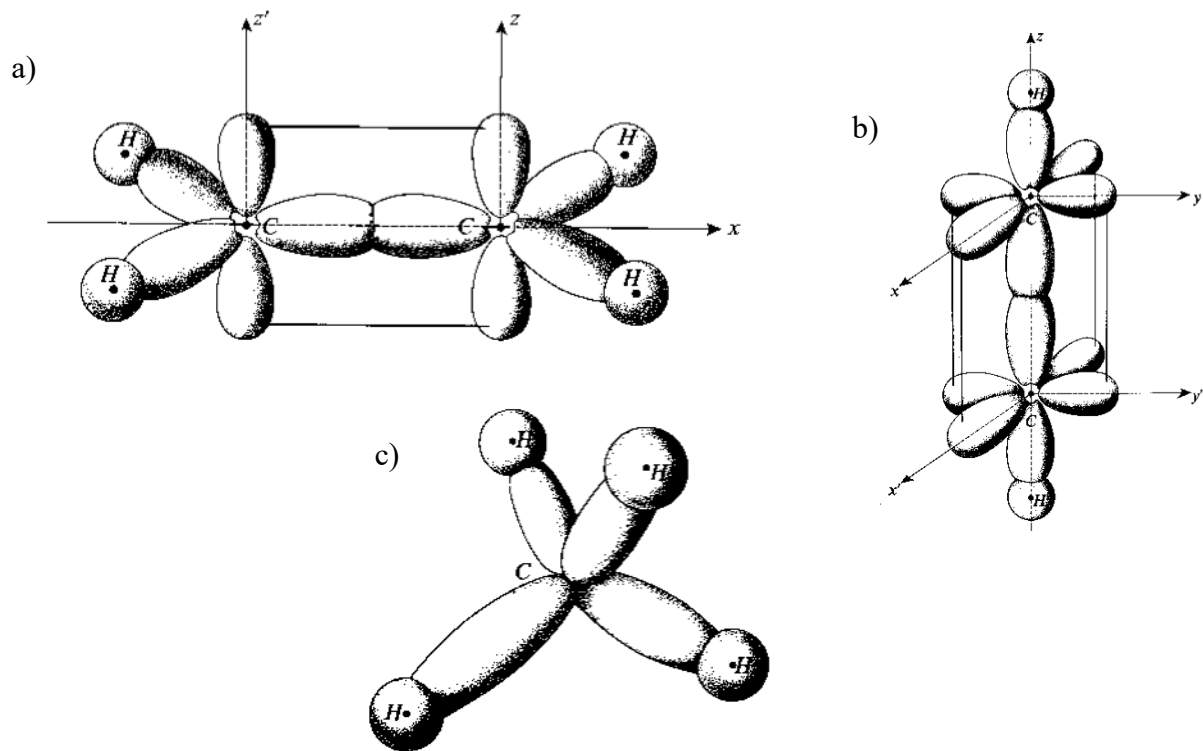


Figure 1-8: a) *sp* hybridization: acetylene molecule, b) *sp*² hybridization: ethylene molecule, and c) *sp*³ hybridization: methane molecule

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 enable atoms to form various types of chemical bonds, including single, double, and triple bonds, and contribute to the understanding of the shapes and structures of molecules.

1.2.4 Metallic bond

Metallic bonds can be understood as a lattice of positively charged ions immersed in a delocalized electron gas. Unlike covalent bonds, where electrons are localized between specific nuclei, the valence electrons in metals are not associated with individual atoms. Instead, they are delocalized across the entire crystal and can be treated as nearly free particles subject to the periodic potential of the ion lattice. This delocalization lowers the total energy of the system relative to isolated atoms, in analogy to covalent bonding, but with a crucial difference: metallic electrons are collective excitations, free to move throughout the crystal. Their mobility accounts for the high electrical and thermal conductivity of metals. Moreover, this delocalization is highly isotropic—meaning it has the same properties in all directions because the bonding is isotropic (not directional, as in covalent bonds), metallic crystals tend to form densely packed, stable structures such as face-centered cubic (FCC), body-centered cubic (BCC), or hexagonal close-packed (HCP) lattices.

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:

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

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 boundary condition $\psi_k(x+L) = \psi_k(x)$, where L is the size of the crystal, can be decomposed into the Fourier series:

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

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

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

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

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

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

which yields the Bloch functions in the form:

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

Solving the Schrödinger equation for a single electron in this periodic potential yields an eigenvalue problem, resulting in the Bloch functions. These functions describe how electrons propagate through the crystal and form the foundation of the theory of energy bands. For N atoms, each atomic orbital that participates in bonding contributes N molecular orbitals. These orbitals are so closely spaced in energy that they form a quasi-continuous energy band.

- Suppose the number of available electrons exactly fills the band (or a set of bands). In that case, the material behaves as an insulator or semiconductor, depending on the presence and size of an energy gap to the next band.
- If the highest occupied band (the valence band) is only partially filled, as in metals, there exist available electronic states at the Fermi energy with different wavevectors, k . This allows electrons to change momentum under an applied electric field, leading to electrical conduction.

Thus, the metallic state is characterized by delocalized Bloch states, partially filled bands, and a Fermi surface separating occupied and unoccupied states. Conversely, at absolute zero, semiconductors and insulators have filled valence bands and empty conduction bands, separated by a band gap (E_g).

- In **semiconductors**, $E_g \lesssim 2$ eV, and thermal excitation at room temperature or external stimulation (e.g., photons) can promote electrons across the gap, generating mobile charge carriers.
- In **insulators**, $E_g \gtrsim 2$ eV, so thermal excitation is insufficient to populate the conduction band, and the material remains non-conducting.

By contrast, metals have no band gap at the Fermi level; the density of states at E_F is nonzero, enabling conduction even at absolute zero temperature. Thus, the electronic structure and band theory explain the differences in conductivity between metals, semiconductors, and insulators.

The emergence of bands can be understood more concretely through the nearly free electron (NFE) model. If the periodic potential were absent, electrons would behave as free particles with plane-wave states and a quadratic dispersion relation.

$$E(k) = \hbar^2 \vec{k}^2 / 2m \quad (1.19)$$

When the weak periodic potential of the lattice is included, the Schrödinger equation still admits solutions of Bloch form, but important modifications arise near the boundaries of the Brillouin zone. At these boundaries, wavevectors \vec{k} and $\vec{k} + \vec{G}$ (\vec{G} is a reciprocal lattice vector) correspond to degenerate free-electron states. The periodic potential couples these degenerate states, and the resulting hybridization lifts the degeneracy and opens an energy gap of order $|V_G|$, where V_G is the Fourier coefficient of the lattice potential at reciprocal vector, G . In one dimension, this can be seen by considering plane waves with momenta $+k$ and $-k$ near the Brillouin zone edge at $k = \pm\pi/L$. The potential mixes these states to produce new standing-wave solutions, one with maxima on the ion cores and one with minima, leading to a splitting into bonding and antibonding states separated by an energy gap.

The effect of the NFE model is that the free-electron parabola remains a good description of electronic dispersion away from zone boundaries, while at the Brillouin edges, the dispersion bends and forbidden energy regions, or band gaps, appear. This mechanism explains how continuous atomic levels broaden into bands and how the translational symmetry of the lattice naturally produces electronic states grouped into allowed and forbidden energy regions (where Bragg reflections occur). The magnitude of the band gaps depends on the strength of the periodic potential: in weak potentials, the gaps are small and the bands resemble those of a free electron gas; in stronger potentials, the bands become more distorted, and the NFE model provides a stepping stone to the tight-binding picture. The position of the Fermi energy relative to these bands determines the material's electronic behavior. Suppose the Fermi level lies in a gap. In that case, the material is insulating, unless the gap is sufficiently small that thermal or optical excitation can promote carriers into the conduction band, in which case the material is a semiconductor. If the Fermi level intersects a band, the system is metallic, as partially filled states at the Fermi surface allow electrons to accelerate under an applied electric field, resulting in electrical conduction. This incomplete filling defines the metallic state, where the existence of a Fermi surface at the boundary between occupied and unoccupied Bloch states governs most transport and optical properties. In this way, the nearly free electron model provides the essential microscopic explanation for the origin of band structure and the fundamental distinction between metals, semiconductors, and insulators.

1.2.5 Atomic bonds and materials

In conclusion, the type of atomic bonds present in a solid determines its physical characteristics. Metals, by definition, logically, have pure metallic bonds. Other classes of materials typically exhibit a combination of bonding types. Ceramics have ionic, covalent, or mixed types of bonding. Polymers are characterized by having covalent bonds along the axis of their chain structure and Van der Waals bonds between the chains.

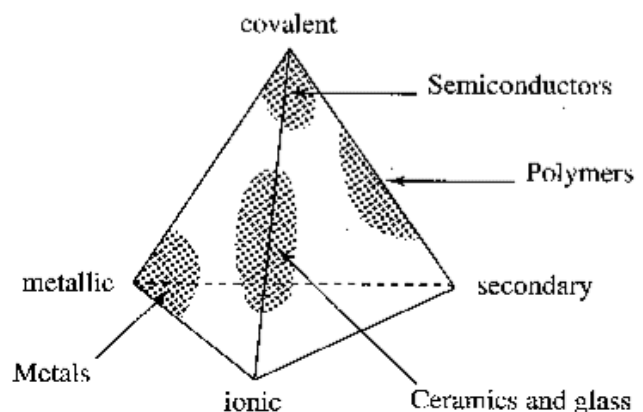


Figure 1-11: Types of bonding intervening in the structure of materials

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," Ilshner 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)