Course of lectures «Contemporary Physics: Part2»

Lecture №12

Molecules and Solids. Molecular Bonds. Energy States and Spectra of Molecules. Bonding in Solids. Free-Electron Theory of Metals. Band Theory of Solids. Electrical Conduction in Metals, Insulators, and Semiconductors. Semiconductor Devices. Superconductivity.

Molecular Bonds

A potential energy function that can be used to model a molecule should account for two known features of molecular bonding:

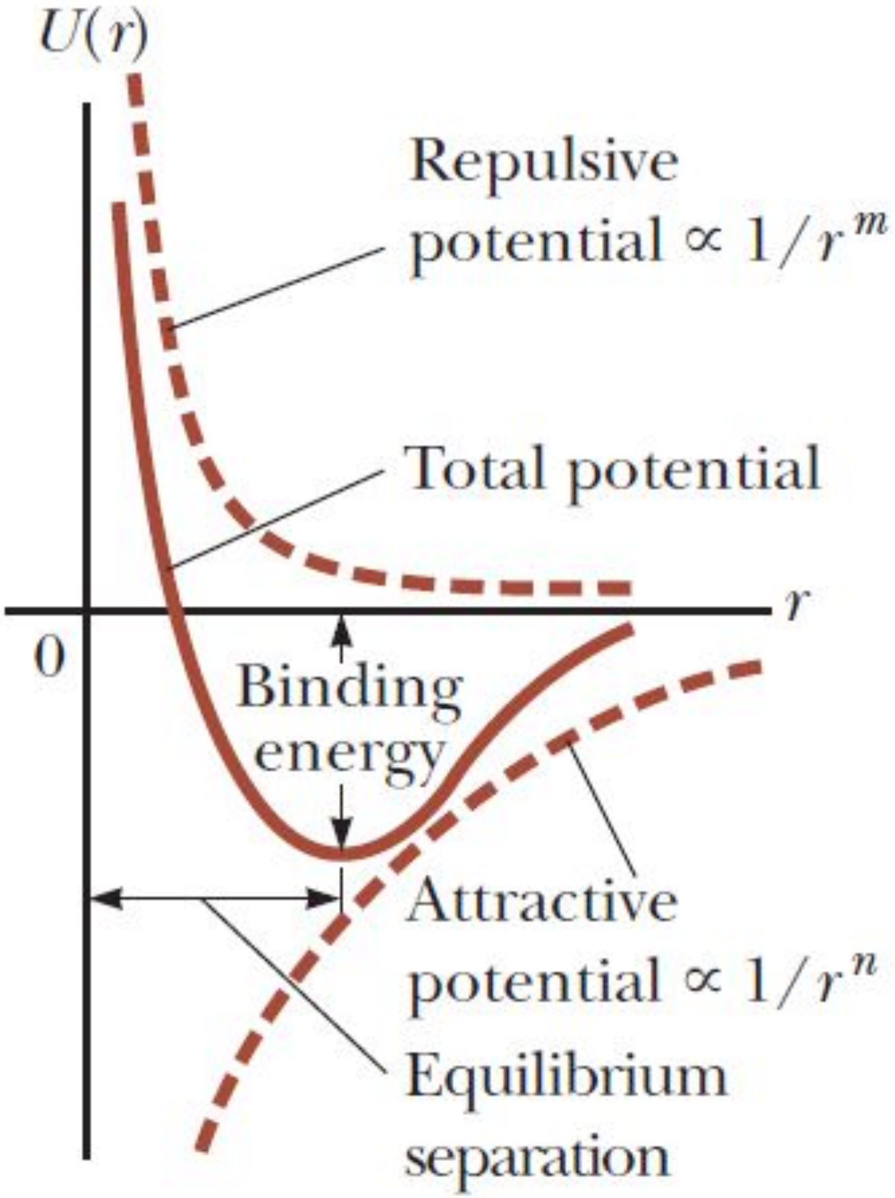
1. The force between atoms is repulsive at very small separation distances. When two atoms are brought close to each other, some of their electron shells overlap, resulting in repulsion between the shells. This repulsion is partly electrostatic in origin and partly the result of the exclusion principle. Because all electrons must obey the exclusion principle, some electrons in the overlapping shells are forced into higher energy states and the system energy increases as if a repulsive force existed between the atoms.

2. At somewhat larger separations, the force between atoms is attractive. If that were not true, the atoms in a molecule would not be bound together.

Taking into account these two features, the potential energy for a system of two atoms can be represented by an expression of the form

$$U(r) = -\frac{A}{r^n} + \frac{B}{r^m}$$

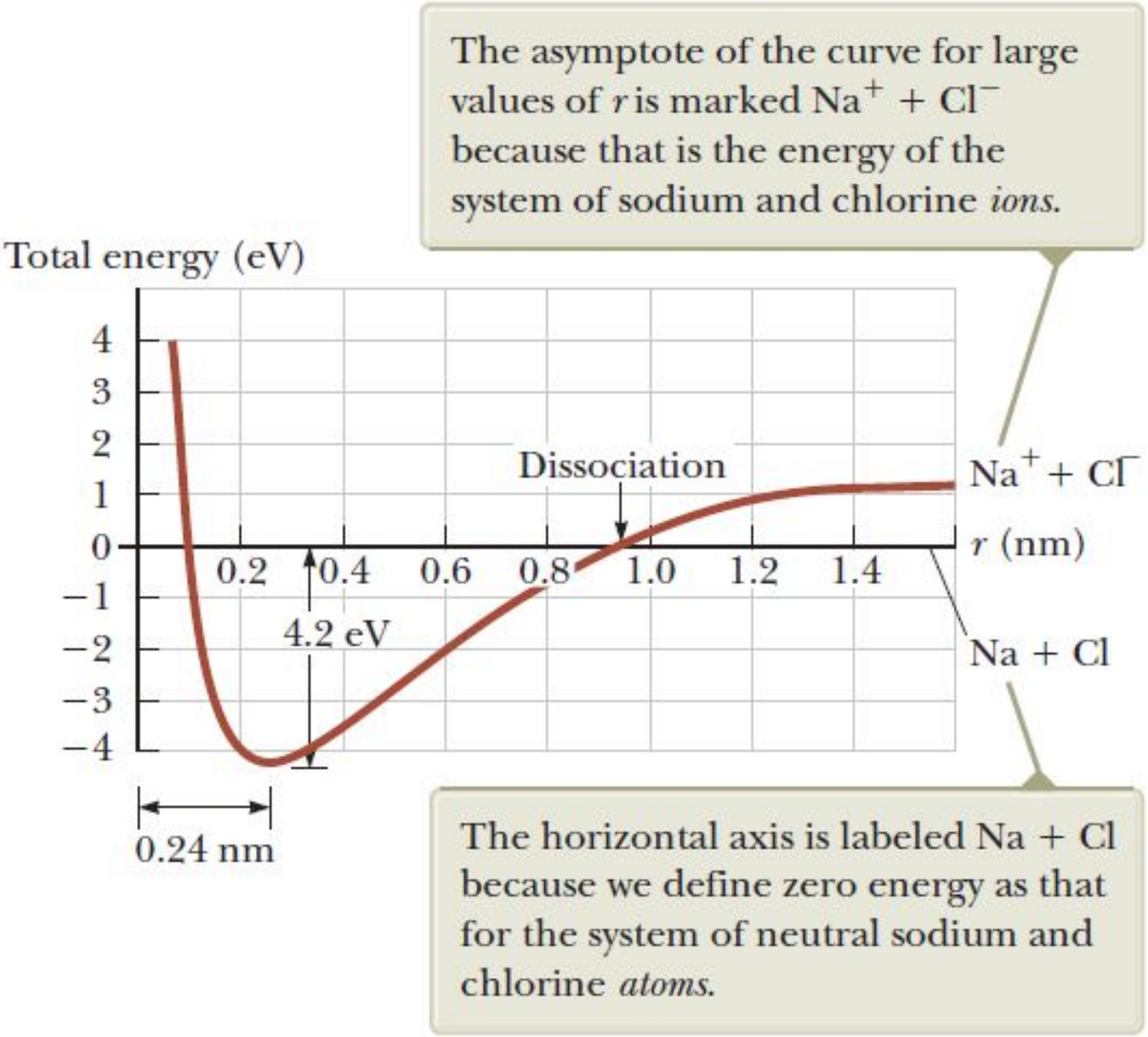
Molecular Bonds



Potential energy versus internuclear separation distance for a two-atom system is graphed in Figure. At large separation distances between the two atoms, the slope of the curve is positive, corresponding to a net attractive force. At the equilibrium separation distance, the attractive and repulsive forces just balance. At this point, the potential energy has its minimum value and the slope of the curve is zero.

Molecular Bonds

Ionic Bonding



The asymptote of the curve for large values of *r* is marked $Na^+ + Cl^-$ because that is the energy of the system of sodium and chlorine *ions*.

The horizontal axis is labeled Na + Cl because we define zero energy as that for the system of neutral sodium and chlorine *atoms*.

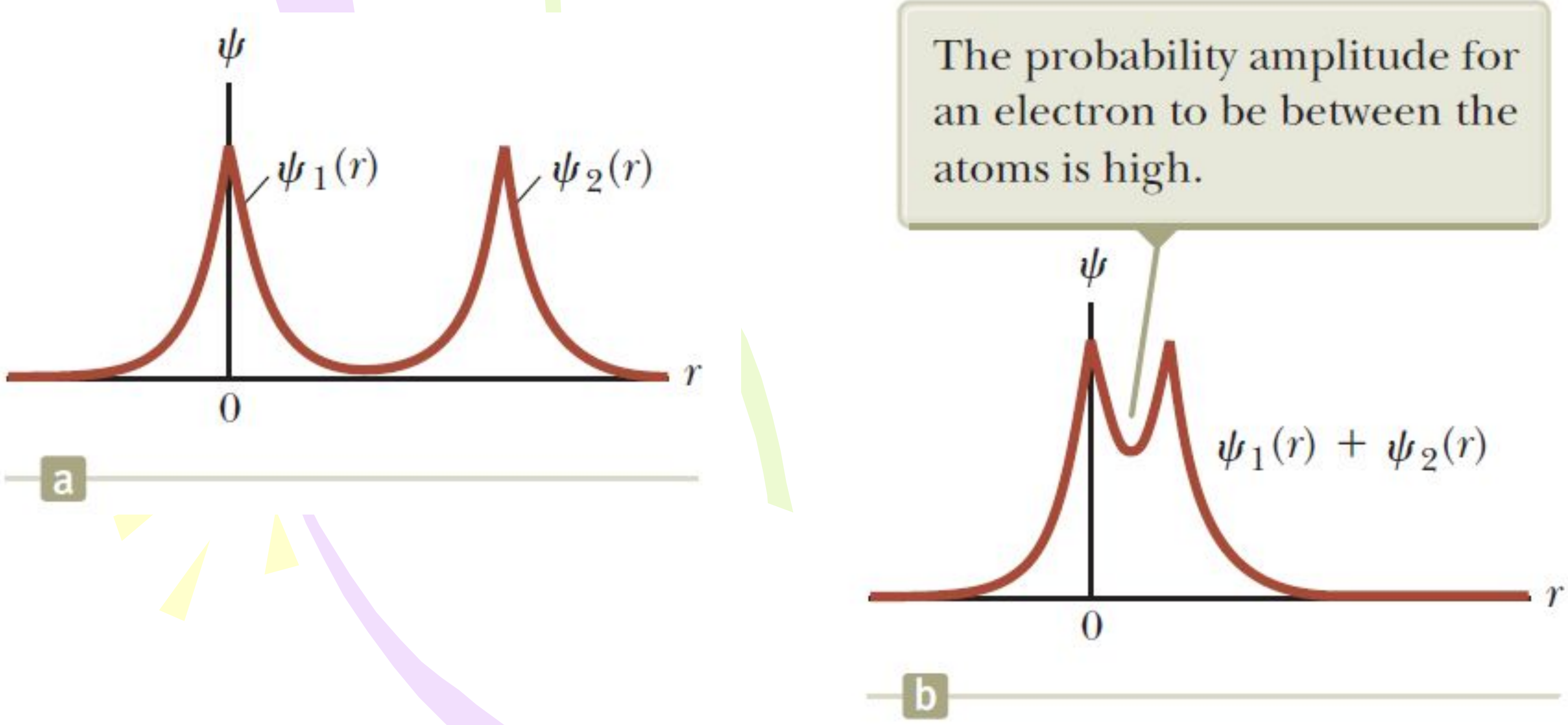
Total energy versus internuclear separation distance for Na^+ and Cl^- ions.

Molecular Bonds

Covalent Bonding

A **covalent bond** between two atoms is one in which electrons supplied by either one or both atoms are shared by the two atoms.

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi a_0^{\,3}}}\, e^{-r/a_0}$$



The probability amplitude for an electron to be between the atoms is high.

Molecular Bonds

Van der Waals Bonding

You might think that two neutral molecules would not interact by means of the electric force because they each have zero net charge. They are attracted to each other, however, by weak electrostatic forces called **van der Waals forces.**

There are three types of van der Waals forces. The first type, called the *dipole–dipole force,* is an interaction between two molecules each having a permanent electric dipole moment. For example, polar molecules such as HCl have permanent electric dipole moments and attract other polar molecules.

Molecular Bonds

Van der Waals Bonding

The second type, the *dipole–induced dipole force,* results when a polar molecule having a permanent electric dipole moment induces a dipole moment in a nonpolar molecule. In this case, the electric field of the polar molecule creates the dipole moment in the nonpolar molecule, which then results in an attractive force between the molecules.

The third type is called the *dispersion force,* an attractive force that occurs between two nonpolar molecules. In this case, although the average dipole moment of a nonpolar molecule is zero, the average of the square of the dipole moment is nonzero because of charge fluctuations. Two nonpolar molecules near each other tend to have dipole moments that are correlated in time so as to produce an attractive van der Waals force.

Molecular Bonds

Hydrogen Bonding

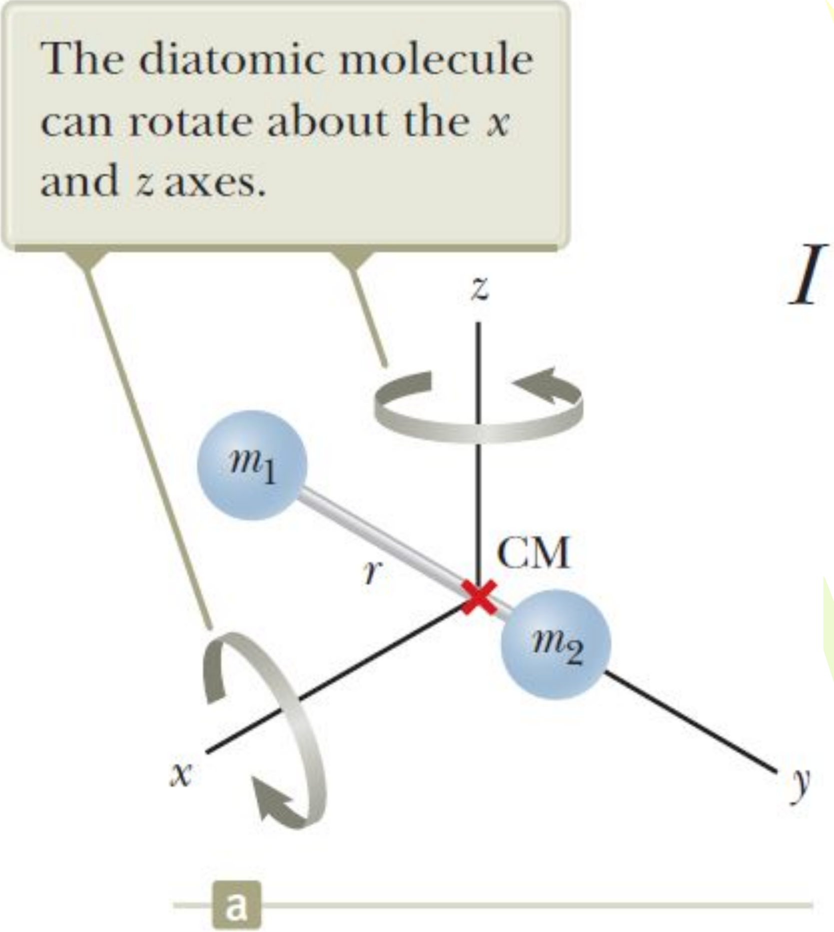
Because hydrogen has only one electron, it is expected to form a covalent bond with only one other atom within a molecule. A hydrogen atom in a given molecule can also form a second type of bond between molecules called a **hydrogen bond.**

DNA molecules are held together by hydrogen bonds

Energy States and Spectra of Molecules

$$E = E_{\text{el}} + E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}}$$

Rotational Motion of Molecules



The diatomic molecule can rotate about the *x* and *z* axes.

$$E_{\text{rot}} = \frac{1}{2} I \omega^2$$

$$I = \left(\frac{m_1 m_2}{m_1 + m_2} \right) r^2 = \mu r^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

the **reduced mass of the molecule**

Energy States and Spectra of Molecules

Rotational Motion of Molecules

$$L = I\omega$$

$$L = \sqrt{J(J+1)}\,\hbar \qquad J = 0, 1, 2, \ldots$$

J is the **rotational quantum number**

$$E_{\text{rot}} = \tfrac{1}{2}I\omega^2 = \frac{1}{2I}(I\omega)^2 = \frac{L^2}{2I} = \frac{\left(\sqrt{J(J+1)}\,\hbar\right)^2}{2I}$$

$$E_{\text{rot}} = E_J = \frac{\hbar^2}{2I}J(J+1) \qquad J = 0, 1, 2, \ldots$$

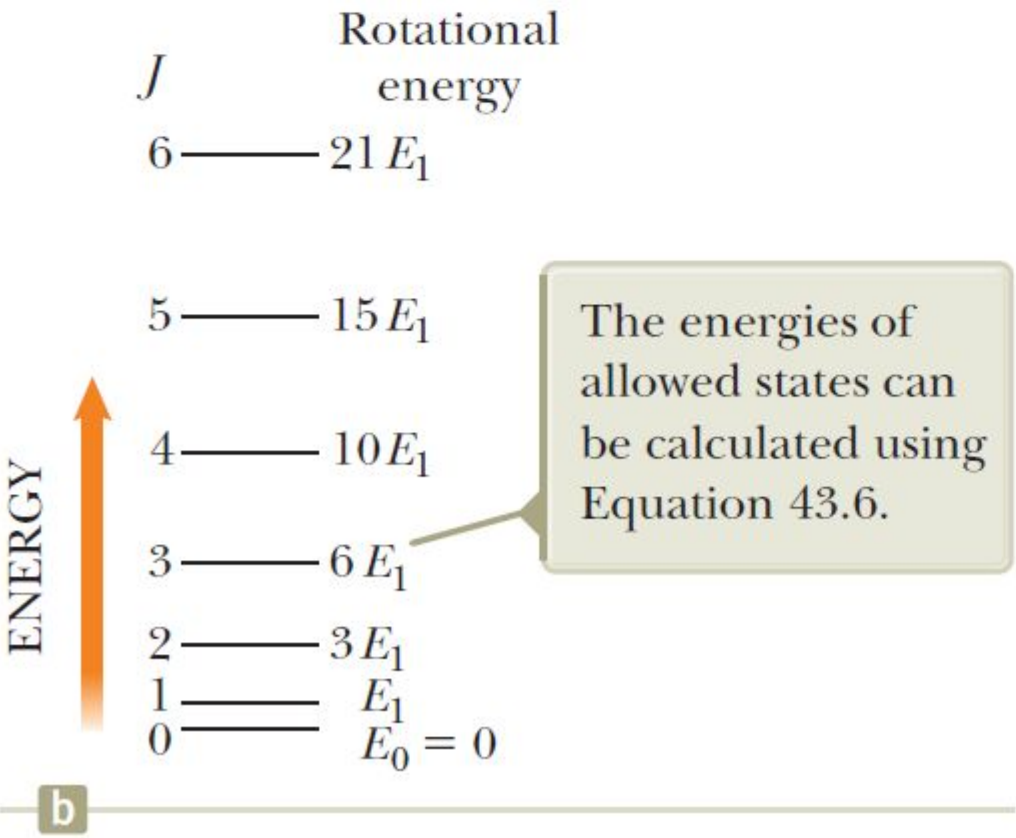
Energy States and Spectra of Molecules

Rotational Motion of Molecules

$$\Delta J = \pm 1$$

$$E_J - E_{J-1},$$

$$J = 1, 2, 3, \ldots .$$



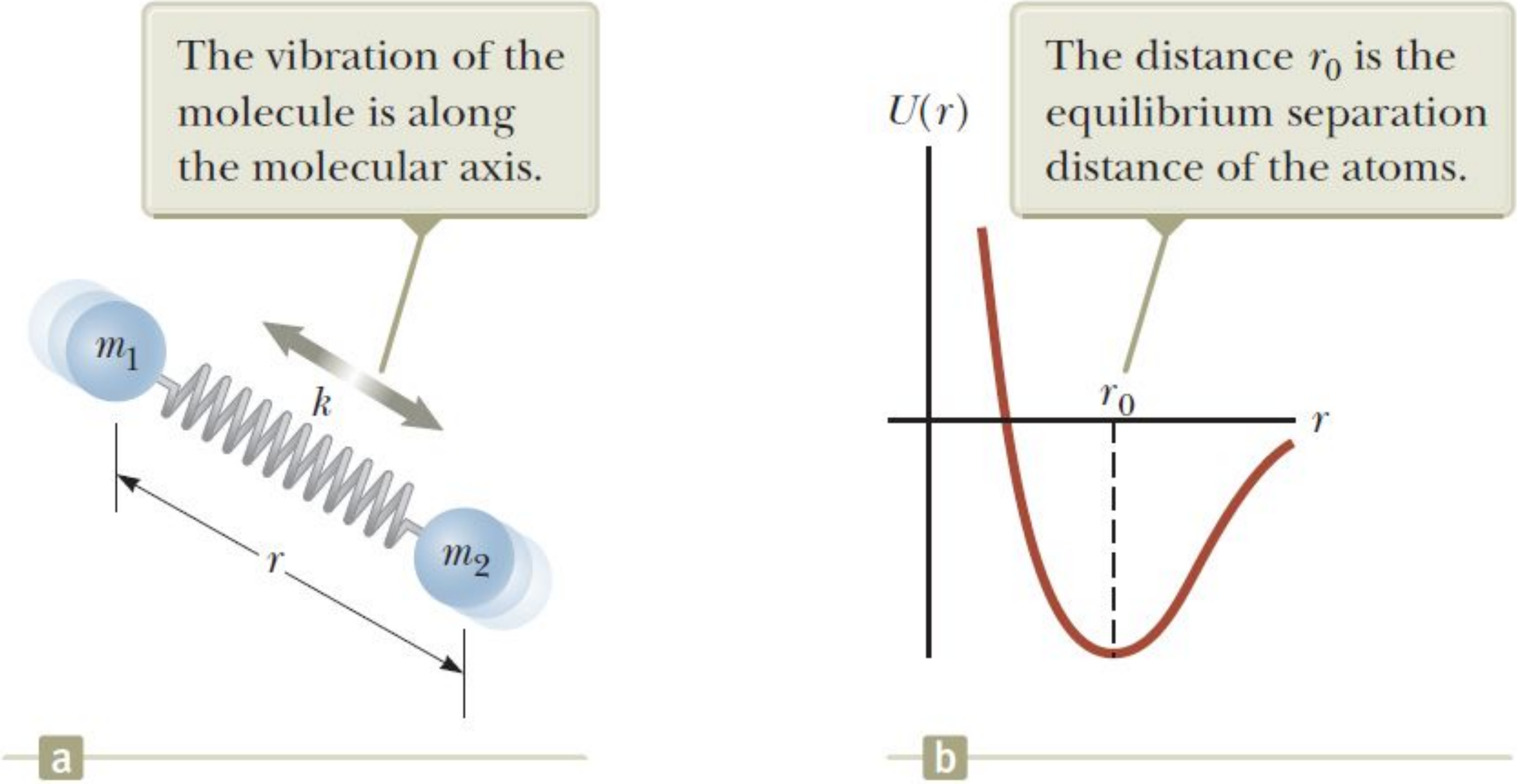
The energies of allowed states can be calculated using Equation 43.6.

$$E_{\text{photon}} = \Delta E_{\text{rot}} = E_J - E_{J-1} = \frac{\hbar^2}{2I}[J(J+1) - (J-1)J]$$

$$E_{\text{photon}} = \frac{\hbar^2}{I}J = \frac{h^2}{4\pi^2 I}J \qquad J = 1, 2, 3, \ldots$$

Energy States and Spectra of Molecules

Vibrational Motion of Molecules


The vibration of the molecule is along the molecular axis.

The distance r_0 is the equilibrium separation distance of the atoms.

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

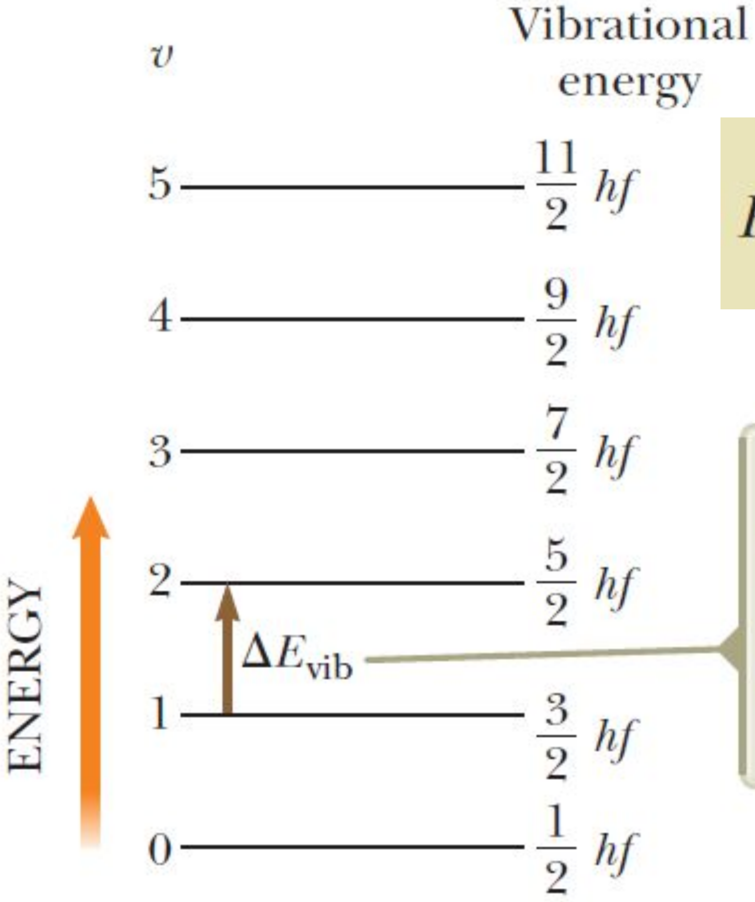
$$E_{\text{vib}} = \left(v + \tfrac{1}{2}\right)hf \qquad v = 0, 1, 2, \ldots$$

v is the **vibrational quantum number**

Energy States and Spectra of Molecules

Vibrational Motion of Molecules

$$E_{\text{vib}} = \left(v + \tfrac{1}{2}\right) \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \qquad v = 0, 1, 2, \ldots$$



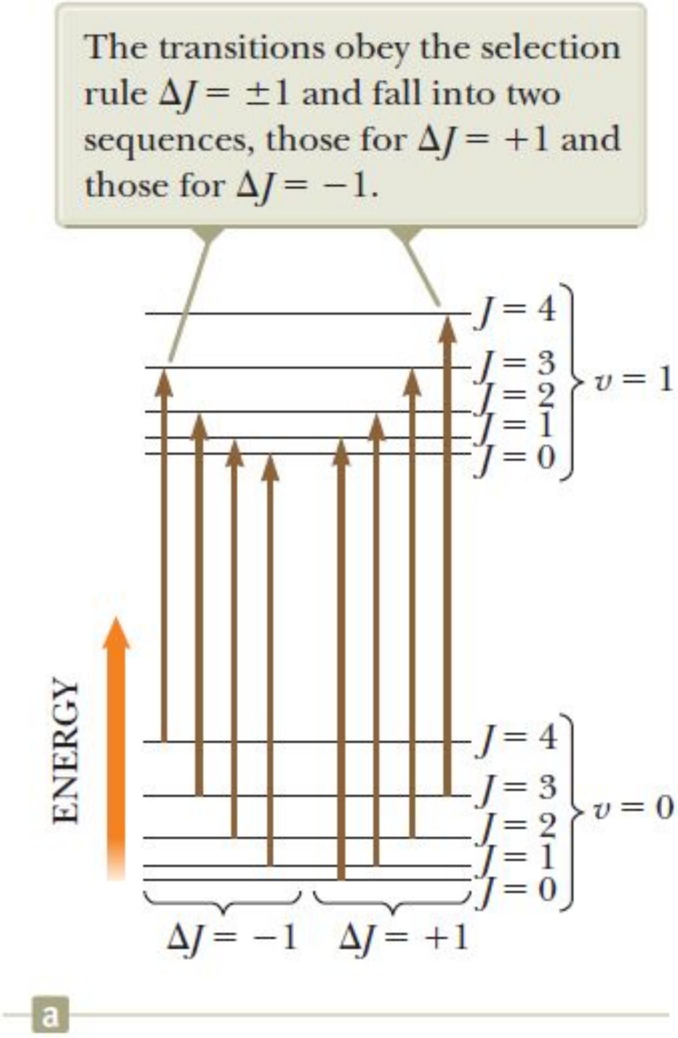
The spacings between adjacent vibrational levels are equal if the molecule behaves as a harmonic oscillator.

$$\Delta v = \pm 1$$

$$E_{\text{photon}} = \Delta E_{\text{vib}} = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

Energy States and Spectra of Molecules

Molecular Spectra



The transitions obey the selection rule $\Delta J = \pm 1$ and fall into two sequences, those for $\Delta J = +1$ and those for $\Delta J = -1$.

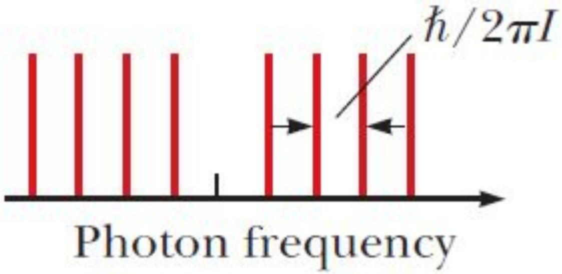
In general, a molecule vibrates and rotates simultaneously. To a first approximation, these motions are independent of each other, so the total energy of the molecule for these motions is

$$E = \left(v + \tfrac{1}{2}\right)hf + \frac{\hbar^2}{2I} J(J + 1)$$

The energy levels of any molecule can be calculated from this expression, and each level is indexed by the two quantum numbers *v* and *J*.

Energy States and Spectra of Molecules

Molecular Spectra



The lines to the right of the center mark correspond to transitions in which J changes by $+1$; the lines to the left of the center mark correspond to transitions for which J changes by -1.

b

When a molecule absorbs a photon with the appropriate energy, the vibrational quantum number *v* increases by one unit while the rotational quantum number *J* either increases or decreases

Therefore, the molecular absorption spectrum consists of two groups of lines:

$\Delta J = +1$ $\qquad$ $\Delta J = -1$

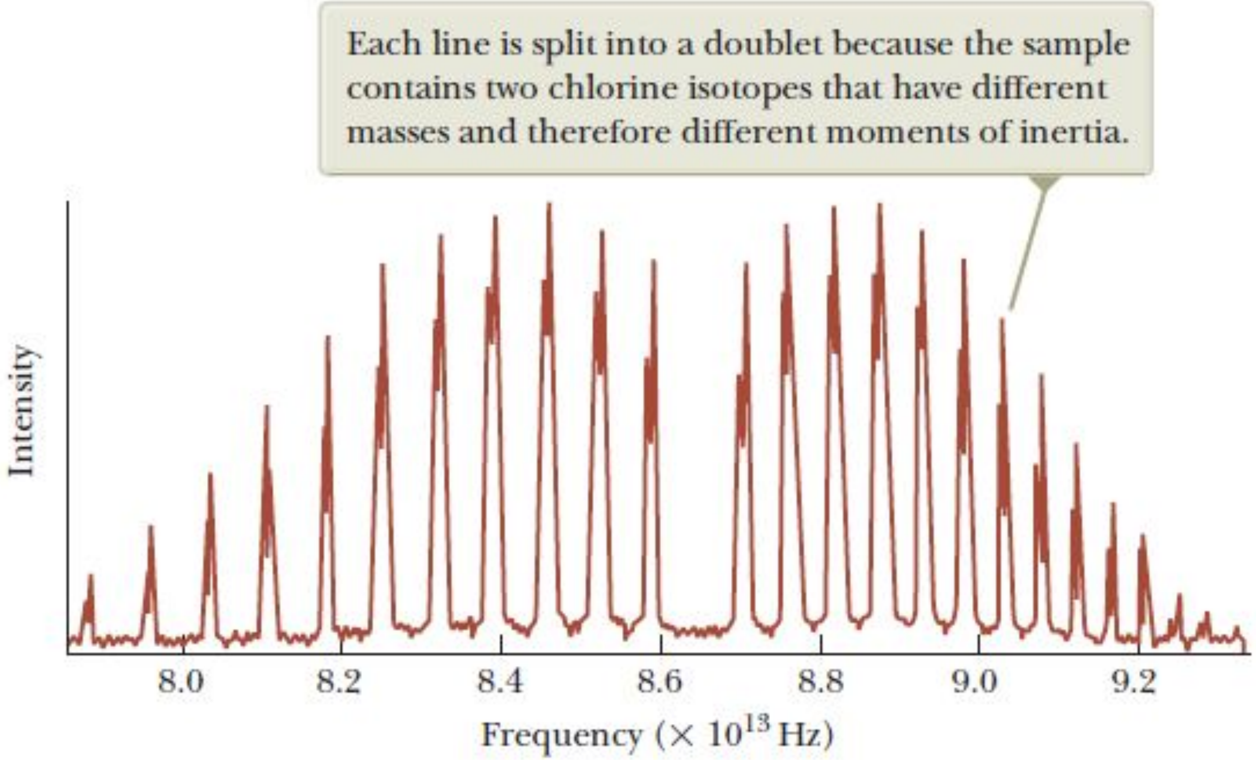
$\Delta v = +1$ $\qquad$ $\Delta v = +1$

$$E_{\text{photon}} = \Delta E = hf + \frac{\hbar^2}{I}(J+1) \qquad J = 0, 1, 2, \ldots \qquad (\Delta J = +1)$$

$$E_{\text{photon}} = \Delta E = hf - \frac{\hbar^2}{I}J \qquad J = 1, 2, 3, \ldots \qquad (\Delta J = -1)$$

Energy States and Spectra of Molecules

Molecular Spectra



Each line is split into a doublet because the sample contains two chlorine isotopes that have different masses and therefore different moments of inertia.

$$n = n_0 e^{-\hbar^2 J(J+1)/(2I k_B T)}$$

$$I \propto (2J+1) e^{-\hbar^2 J(J+1)/(2I k_B T)}$$

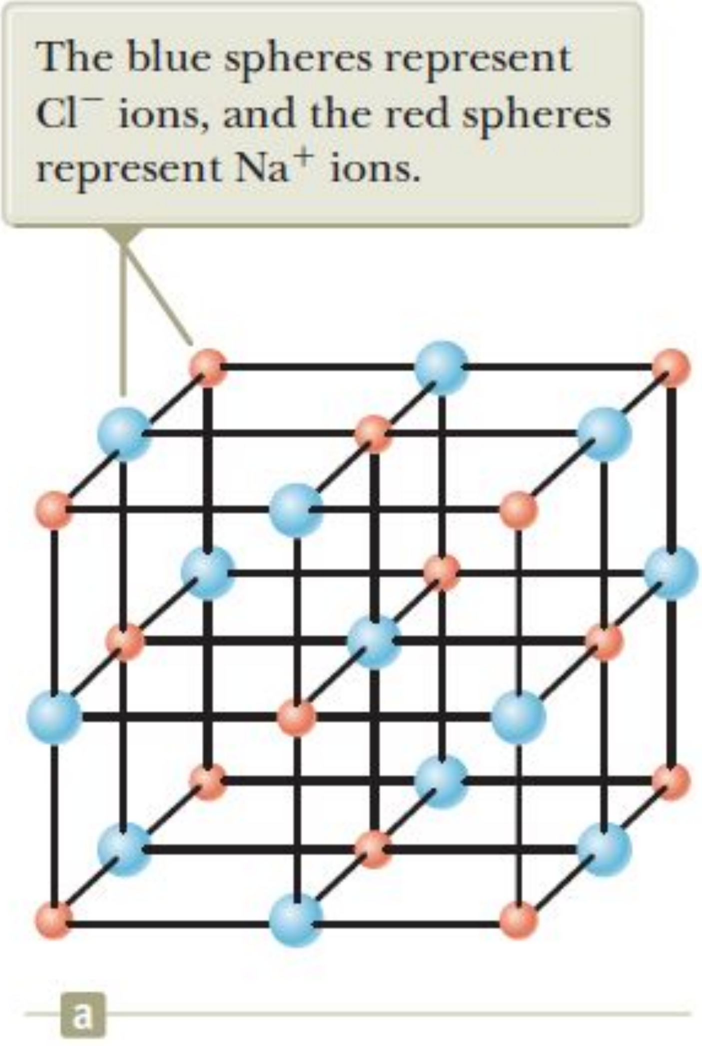
Bonding in Solids

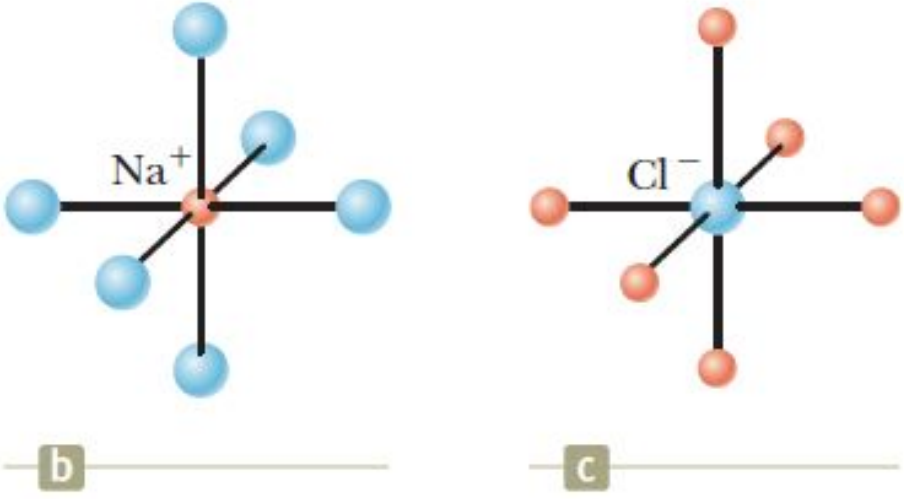
Ionic Solids

$$U_{\text{attractive}} = -\alpha k_e \frac{e^2}{r}$$

α is a dimensionless number known as the **Madelung constant**

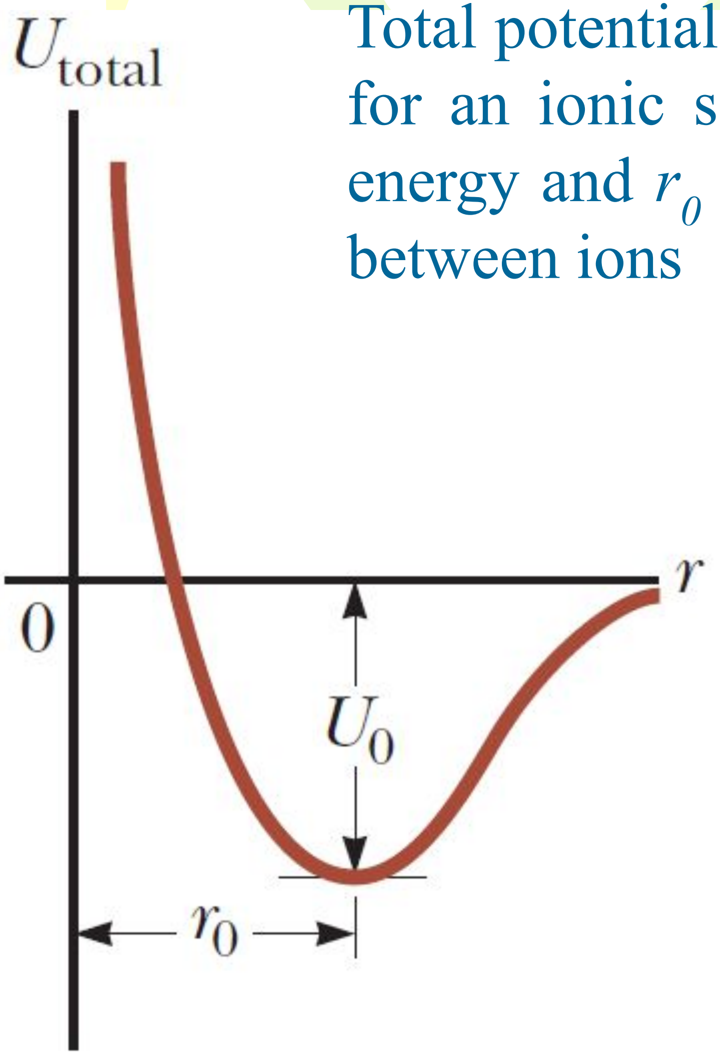
$$U_{\text{total}} = -\alpha k_e \frac{e^2}{r} + \frac{B}{r^m}$$


The blue spheres represent Cl⁻ ions, and the red spheres represent Na⁺ ions.



Bonding in Solids

Ionic Solids



Total potential energy versus ion separation distance for an ionic solid, where U_0 is the ionic cohesive energy and r_0 is the equilibrium separation distance between ions

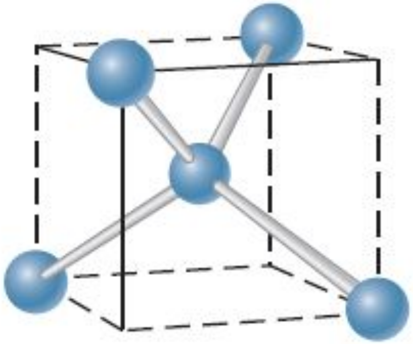
$$U_0 = -\alpha k_e \frac{e^2}{r_0}\left(1 - \frac{1}{m}\right)$$

This minimum energy *U0* is called the **ionic cohesive energy** of the solid, and its absolute value represents the energy required to separate the solid into a collection of isolated positive and negative ions.

The atomic cohesive energy of NaCl is $-7.84\ \text{eV} + 5.14\ \text{eV} - 3.62\ \text{eV} = -6.32\ \text{eV}$

Bonding in Solids

Covalent Solids



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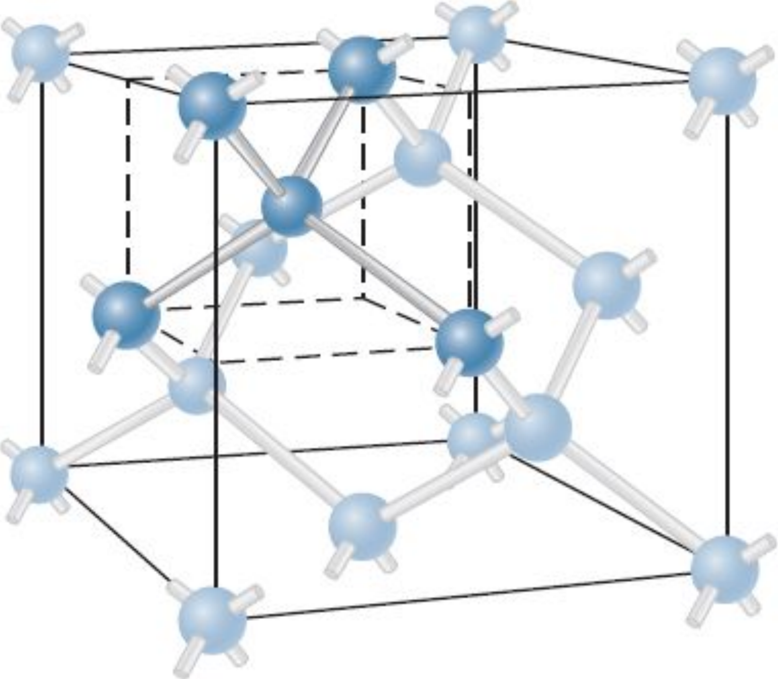

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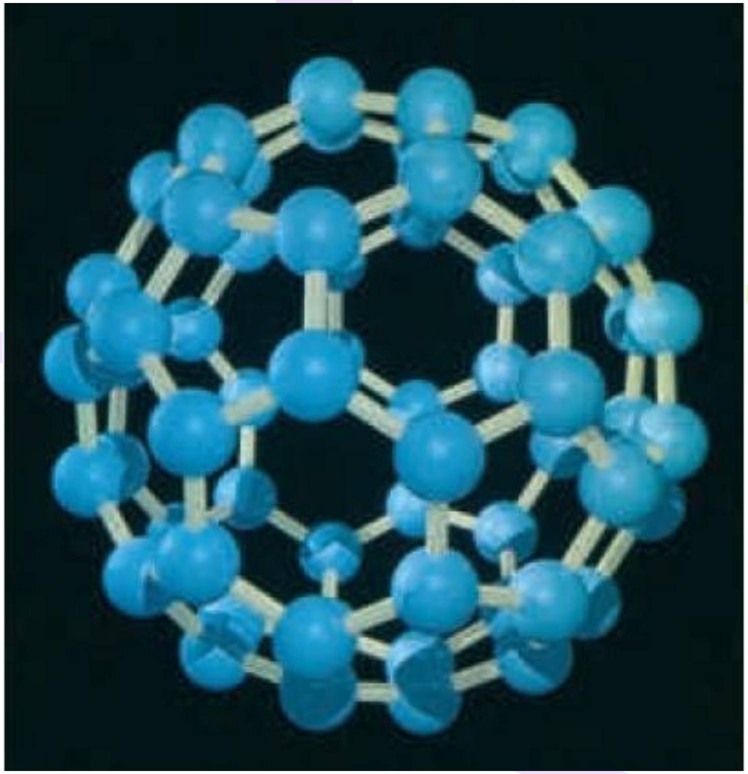
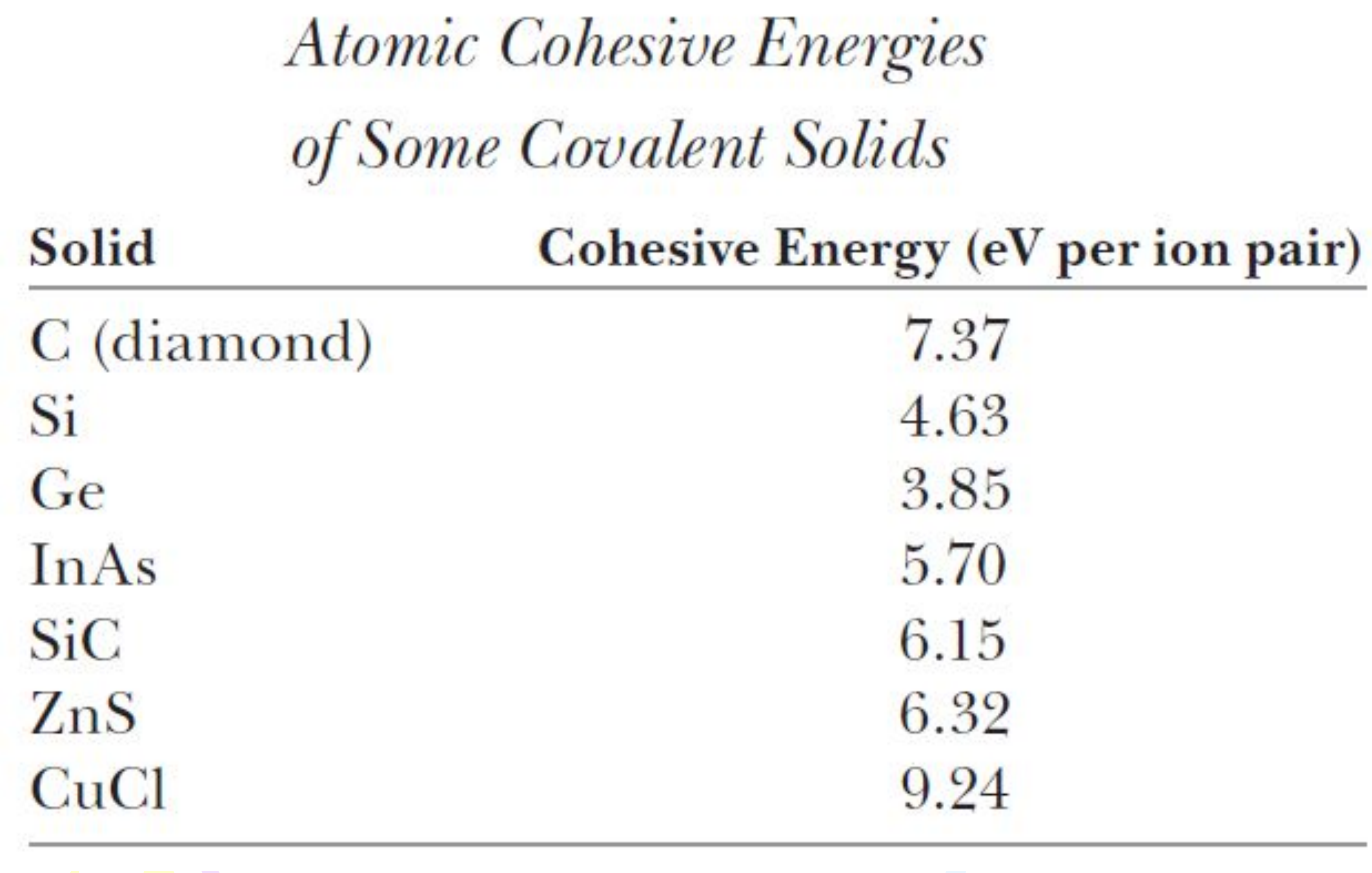


Bonding in Solids

Covalent Solids

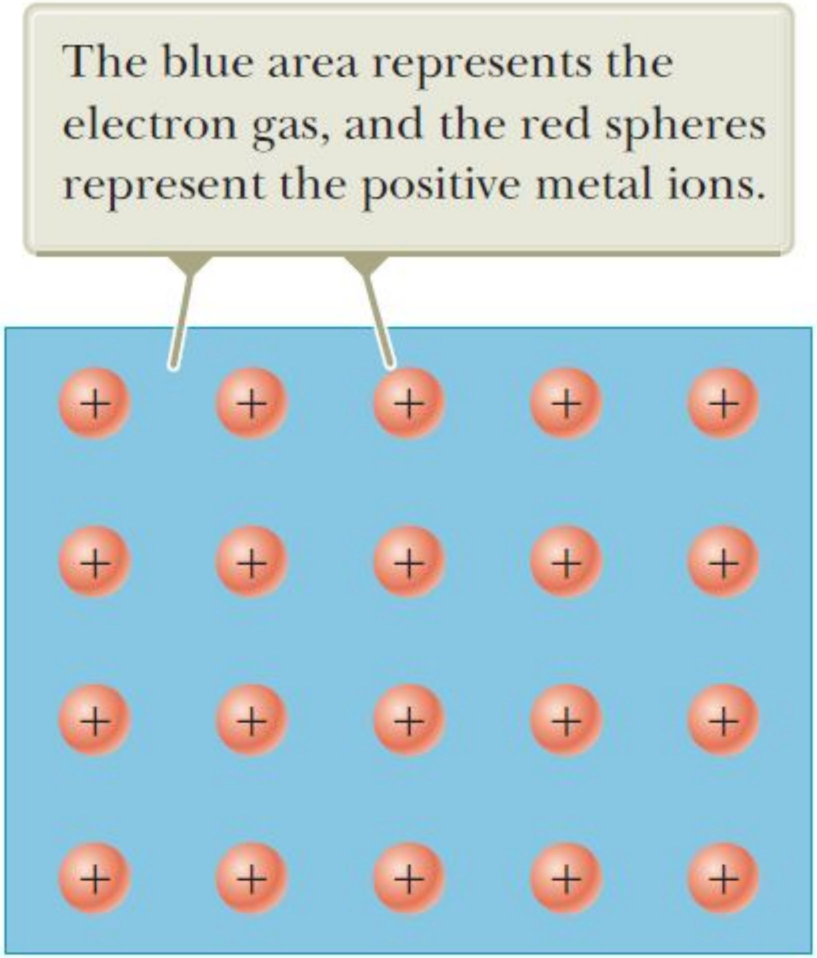


Atomic Cohesive Energies of Some Covalent Solids

Solid	Cohesive Energy (eV per ion pair)
C (diamond)	7.37
Si	4.63
Ge	3.85
InAs	5.70
SiC	6.15
ZnS	6.32
CuCl	9.24

Bonding in Solids

Metallic Solids



The blue area represents the electron gas, and the red spheres represent the positive metal ions.

Metallic bonds are generally weaker than ionic or covalent bonds. The outer electrons in the atoms of a metal are relatively free to move throughout the material, and the number of such mobile electrons in a metal is large. The metallic structure can be viewed as a “sea” or a “gas” of nearly free electrons surrounding a lattice of positive ions

Free-Electron Theory of Metals

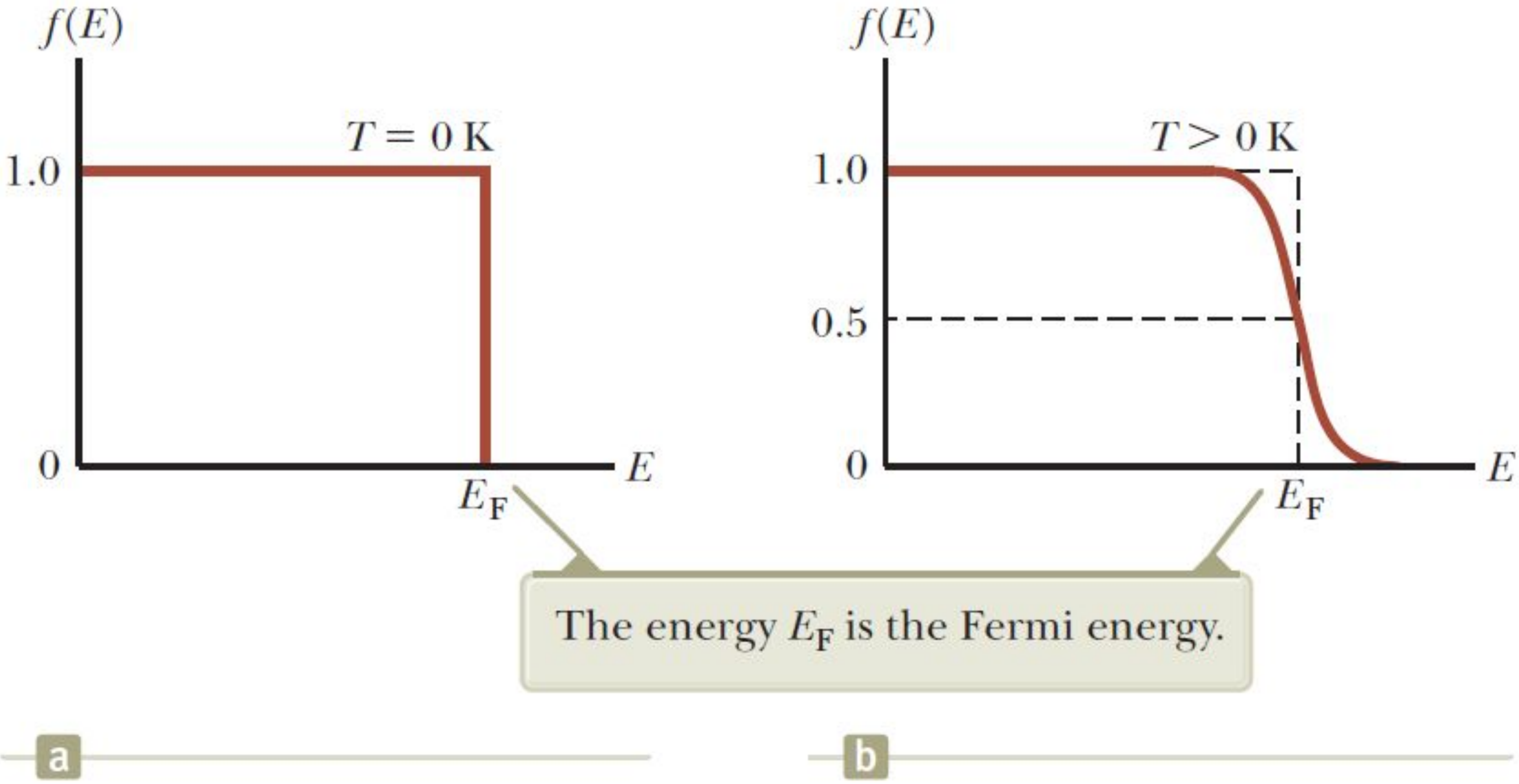
Statistical physics can be applied to a collection of particles in an effort to relate microscopic properties to macroscopic properties. In the case of electrons, it is necessary to use *quantum statistics,* with the requirement that each state of the system can be occupied by only two electrons (one with spin up and the other with spin down) as a consequence of the exclusion principle.

The probability that a particular state having energy E is occupied by one of the electrons in a solid is

$$f(E) = \frac{1}{e^{(E-E_\mathrm{F})/k_\mathrm{B}T} + 1}$$

$f(E)$ is called the **Fermi–Dirac distribution function** and E_F is called **the Fermi energy.**

Free-Electron Theory of Metals



The energy E_F is the Fermi energy.

Free-Electron Theory of Metals

$$E_n = \left(\frac{h^2}{8mL^2}\right)n^2 = \left(\frac{\hbar^2\pi^2}{2mL^2}\right)n^2 \quad n = 1, 2, 3, \ldots$$

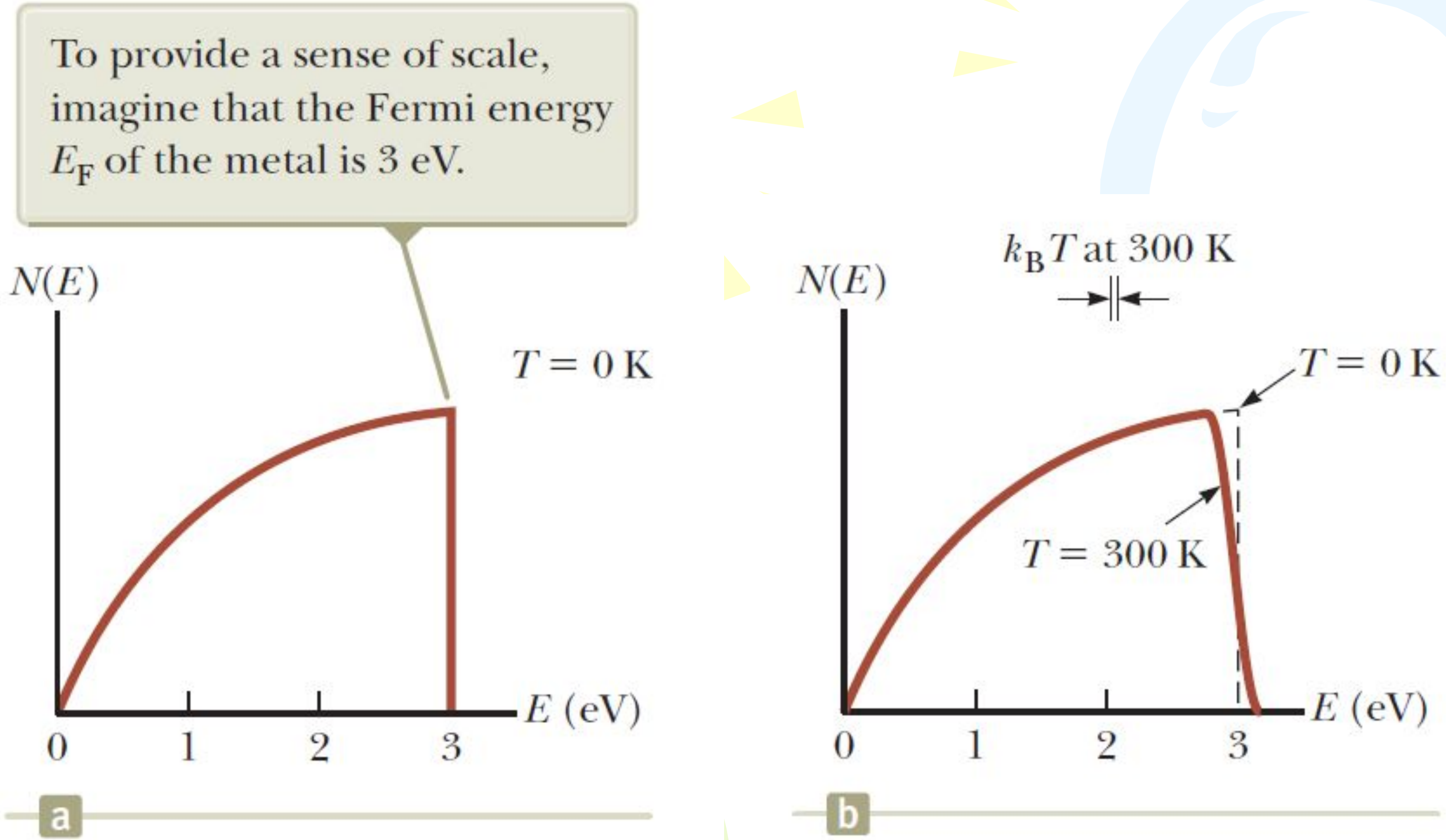
$$E = \frac{\hbar^2\pi^2}{2m_eL^2}(n_x^2 + n_y^2 + n_z^2)$$

$$g(E)\,dE = \frac{8\sqrt{2}\,\pi m_e^{3/2}}{h^3}E^{1/2}\,dE$$

The function *g(E)* is called the **density-of-states function.**

$$N(E)\,dE = \left(\frac{8\sqrt{2}\,\pi m_e^{3/2}}{h^3}E^{1/2}\right)\left(\frac{1}{e^{(E-E_F)/k_BT}+1}\right)dE$$

Free-Electron Theory of Metals



To provide a sense of scale, imagine that the Fermi energy E_F of the metal is 3 eV.

Free-Electron Theory of Metals

$$N(E)\,dE = \left(\frac{8\sqrt{2}\,\pi m_e{}^{3/2}}{h^3}E^{1/2}\right)\left(\frac{1}{e^{(E-E_F)/k_BT}+1}\right)dE$$

$$n_e = \int_0^\infty N(E)\,dE = \frac{8\sqrt{2}\,\pi m_e{}^{3/2}}{h^3}\int_0^\infty \frac{E^{1/2}\,dE}{e^{(E-E_F)/k_BT}+1}$$

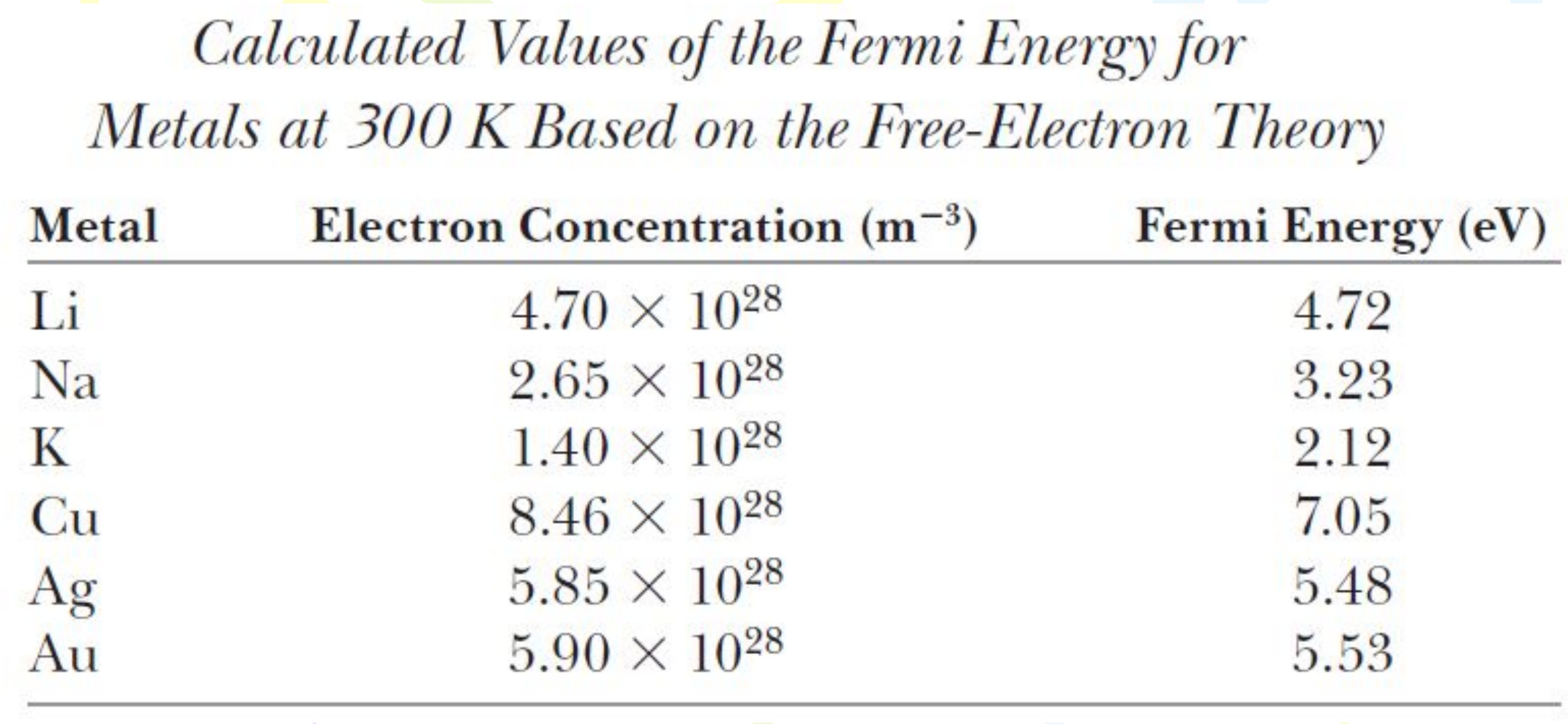
At $T = 0$ K $\quad f(E) = 1$ for $E < E_F$ and $f(E) = 0$ for $E > E_F$

$$n_e = \frac{8\sqrt{2}\,\pi m_e{}^{3/2}}{h^3}\int_0^{E_F} E^{1/2}\,dE = \tfrac{2}{3}\frac{8\sqrt{2}\,\pi m_e{}^{3/2}}{h^3}E_F{}^{3/2}$$

$$E_F(0) = \frac{h^2}{2m_e}\left(\frac{3n_e}{8\pi}\right)^{2/3}$$

$$E_{\text{avg}} = \tfrac{3}{5}E_F$$

Free-Electron Theory of Metals



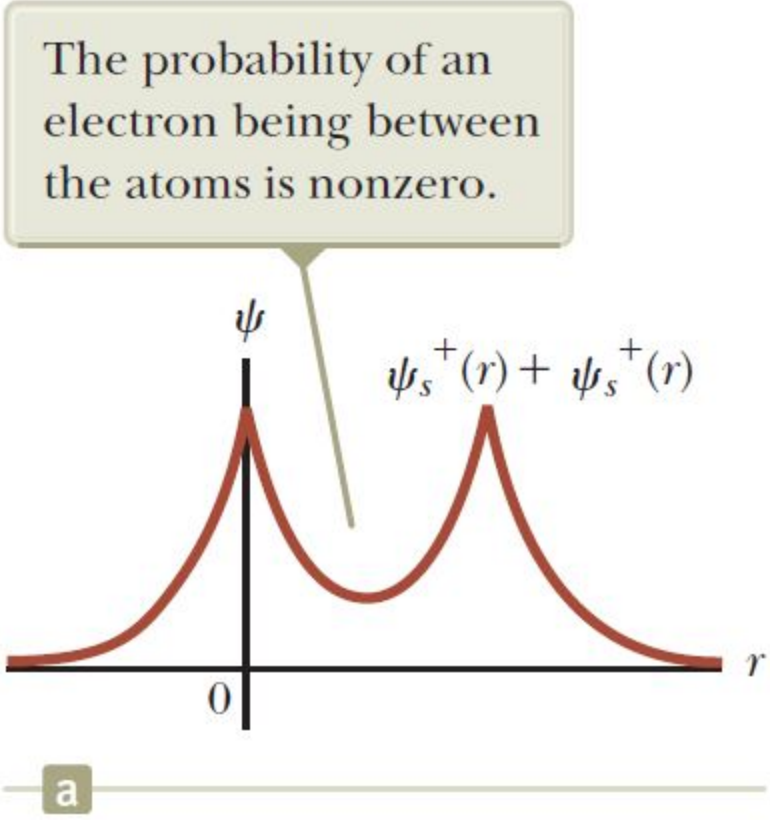
Calculated Values of the Fermi Energy for Metals at 300 K Based on the Free-Electron Theory

Metal	**Electron Concentration (m^{-3})**	**Fermi Energy (eV)**
Li	4.70×10^{28}	4.72
Na	2.65×10^{28}	3.23
K	1.40×10^{28}	2.12
Cu	8.46×10^{28}	7.05
Ag	5.85×10^{28}	5.48
Au	5.90×10^{28}	5.53

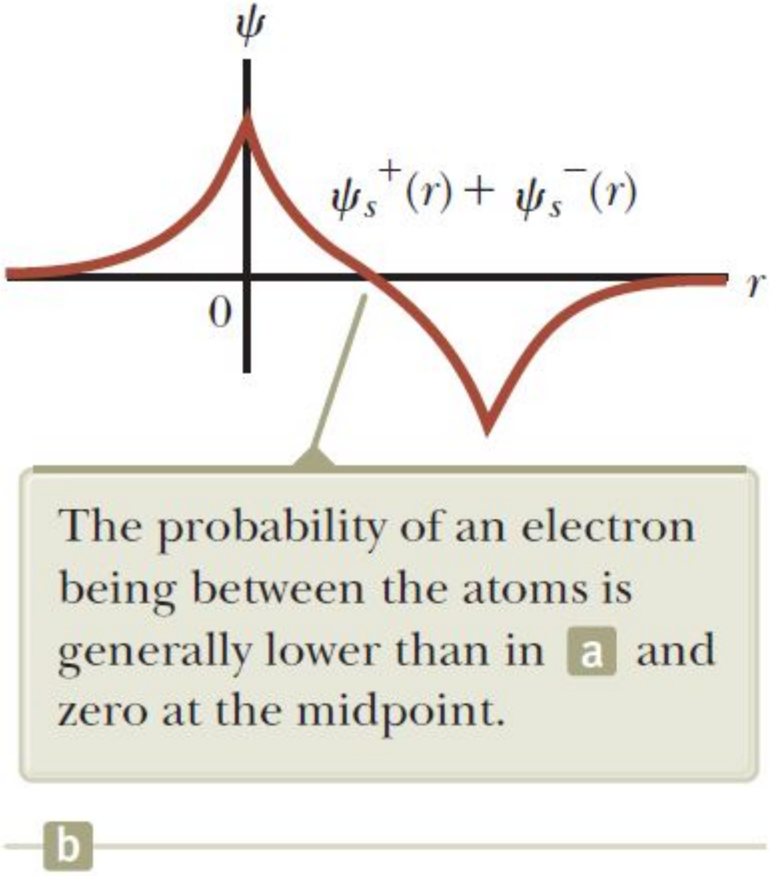
Band Theory of Solids

$$\psi_s^{+}(r) = +Af(r)e^{-Zr/na_0}$$

$$\psi_s^{-}(r) = -Af(r)e^{-Zr/na_0}$$

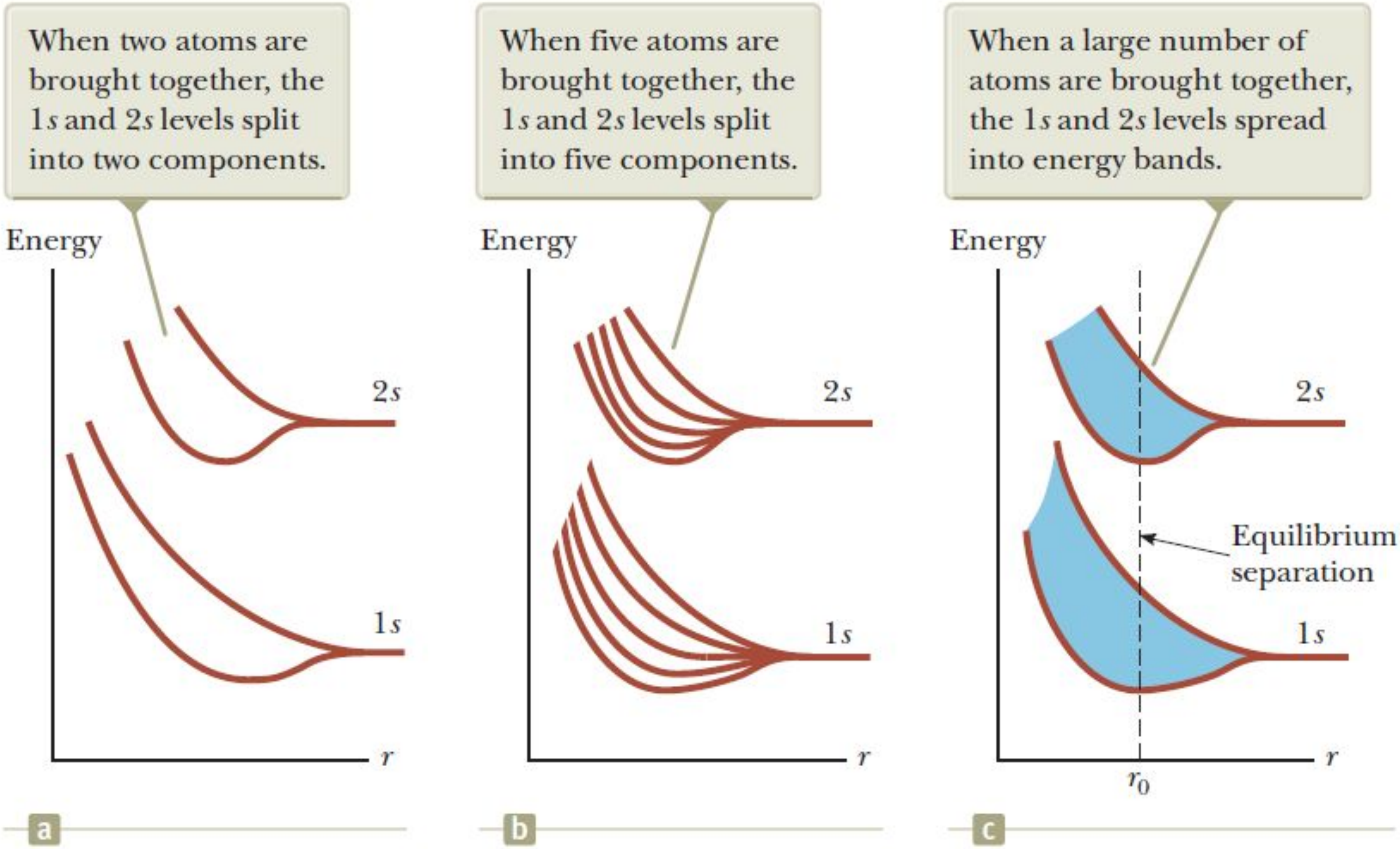


The probability of an electron being between the atoms is nonzero.



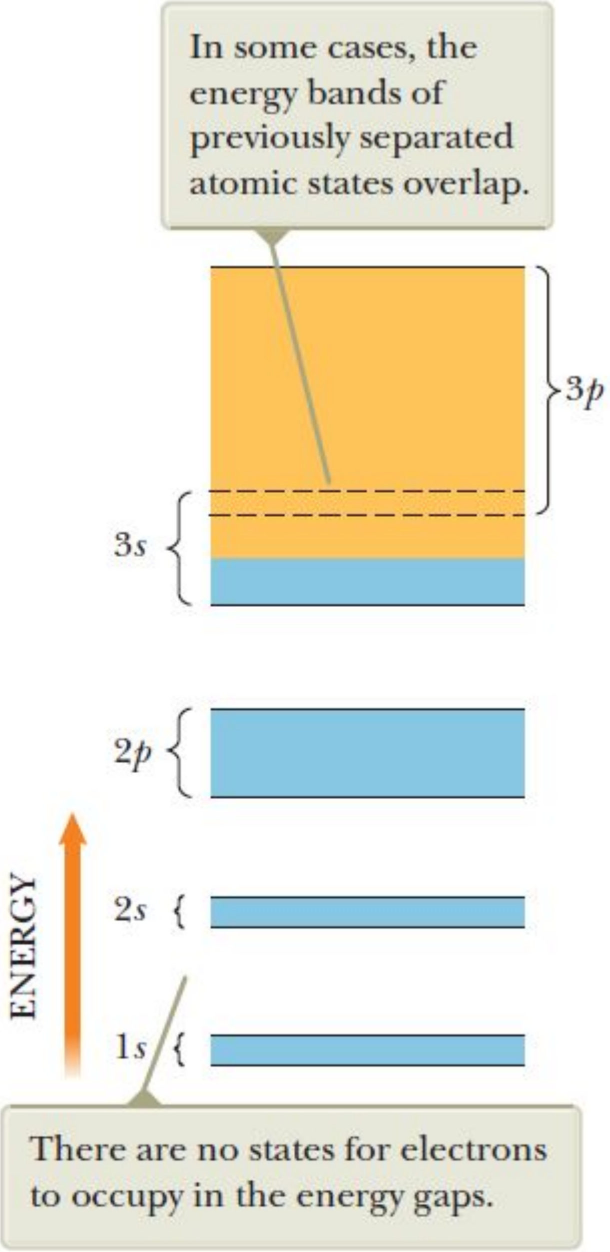
The probability of an electron being between the atoms is generally lower than in **a** and zero at the midpoint.

Band Theory of Solids



Energies of the 1*s* and *2s* levels in sodium as a function of the separation distance *r* between atoms.

Band Theory of Solids



In some cases, the energy bands of previously separated atomic states overlap.

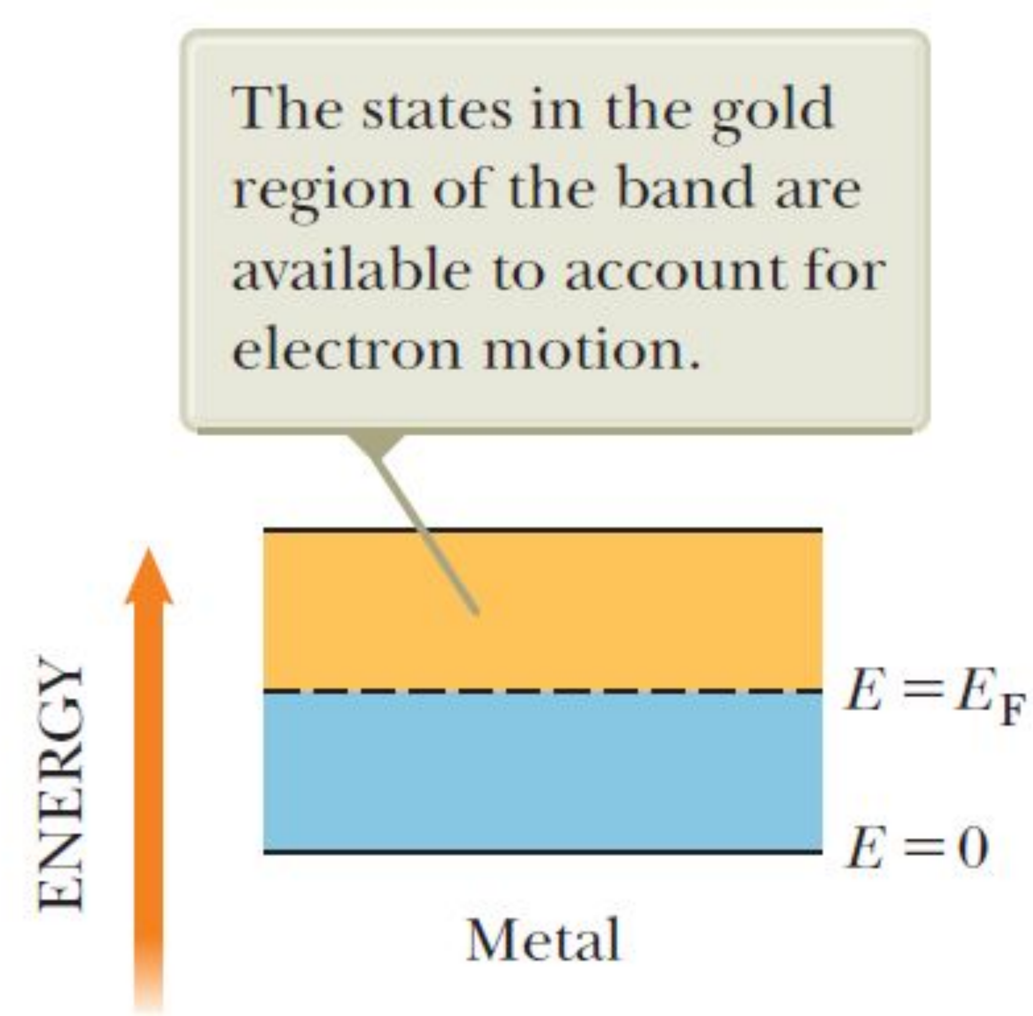
There are no states for electrons to occupy in the energy gaps.

Energy bands of a sodium crystal. Blue represents energy bands occupied by the sodium electrons when the atom is in its ground state. Gold represents energy bands that are empty.

Band theory allows us to build simple models to understand the behavior of conductors, insulators, and semiconductors as well as that of semiconductor devices, as we shall discuss in the following sections.

Electrical Conduction in Metals, Insulators, and Semiconductors

Metals

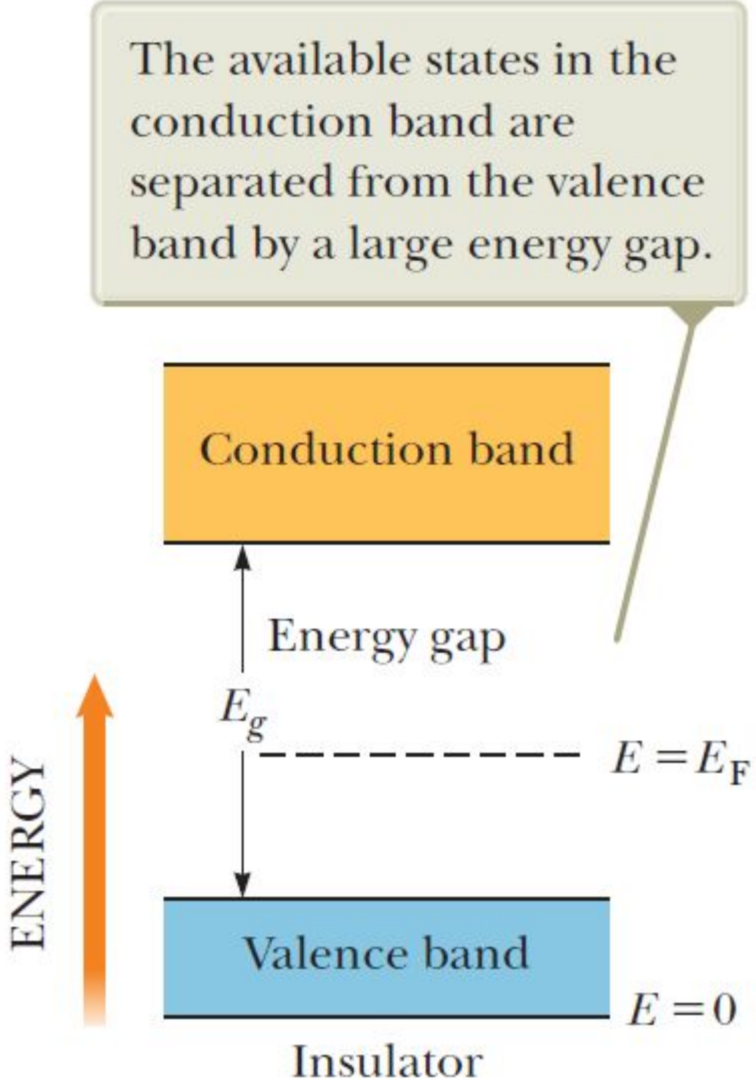


The states in the gold region of the band are available to account for electron motion.

Half-filled band of a metal, an electrical conductor. At *T=0 K*, the Fermi energy lies in the middle of the band.

Electrical Conduction in Metals, Insulators, and Semiconductors

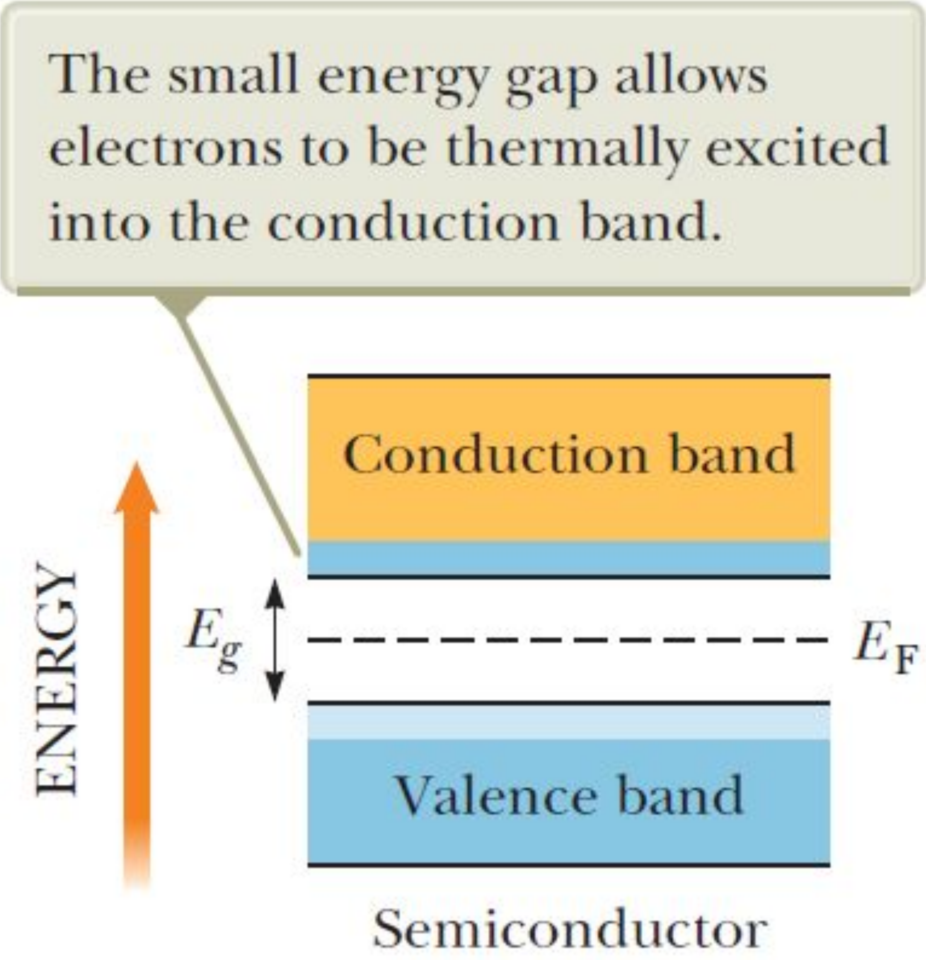
Insulators


The available states in the conduction band are separated from the valence band by a large energy gap.

The lower, filled band is called the **valence band**, and the upper, empty band is **the conduction band.** (The conduction band is the one that is partially filled in a metal.) It is common to refer to the energy separation between the valence and conduction bands as the **energy gap *Eg*** of the material.

Electrical Conduction in Metals, Insulators, and Semiconductors

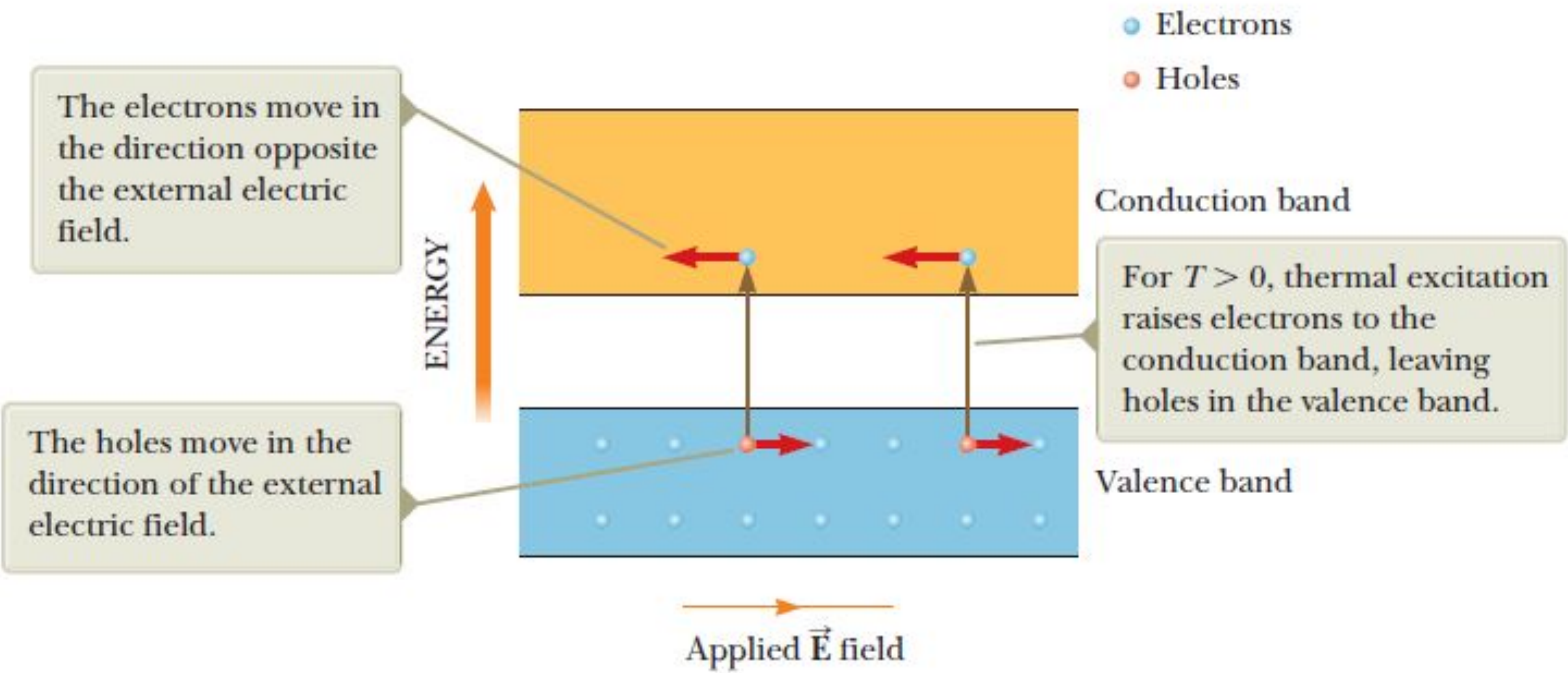
Semiconductors



Semiconductors have the same type of band structure as an insulator, but the energy gap is much smaller, on the order of 1 eV.

Electrical Conduction in Metals, Insulators, and Semiconductors

Semiconductors

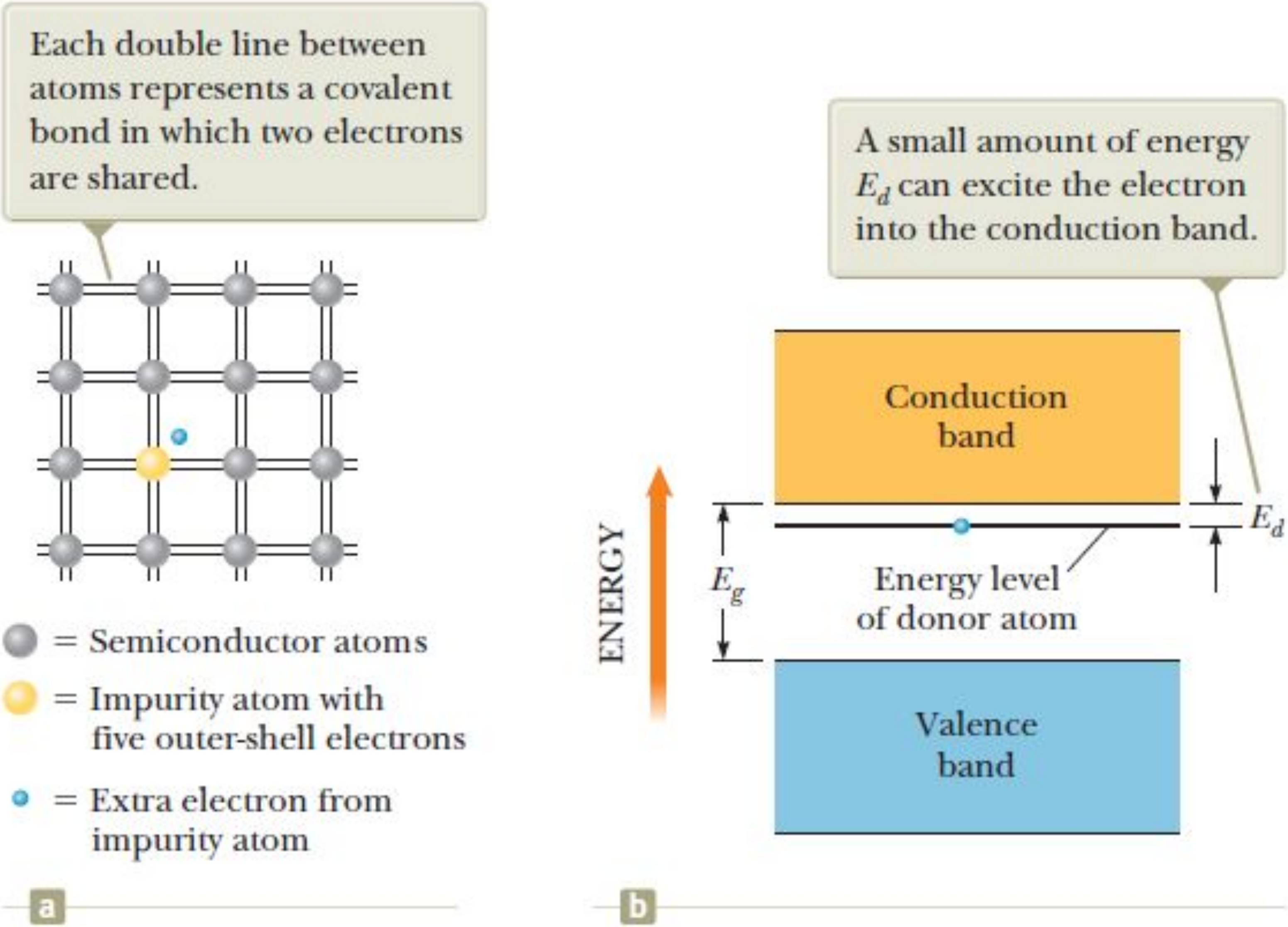

The electrons move in the direction opposite the external electric field.

For $T > 0$, thermal excitation raises electrons to the conduction band, leaving holes in the valence band.

The holes move in the direction of the external electric field.

Electrical Conduction in Metals, Insulators, and Semiconductors

Doped Semiconductors



Each double line between atoms represents a covalent bond in which two electrons are shared.

A small amount of energy E_d can excite the electron into the conduction band.

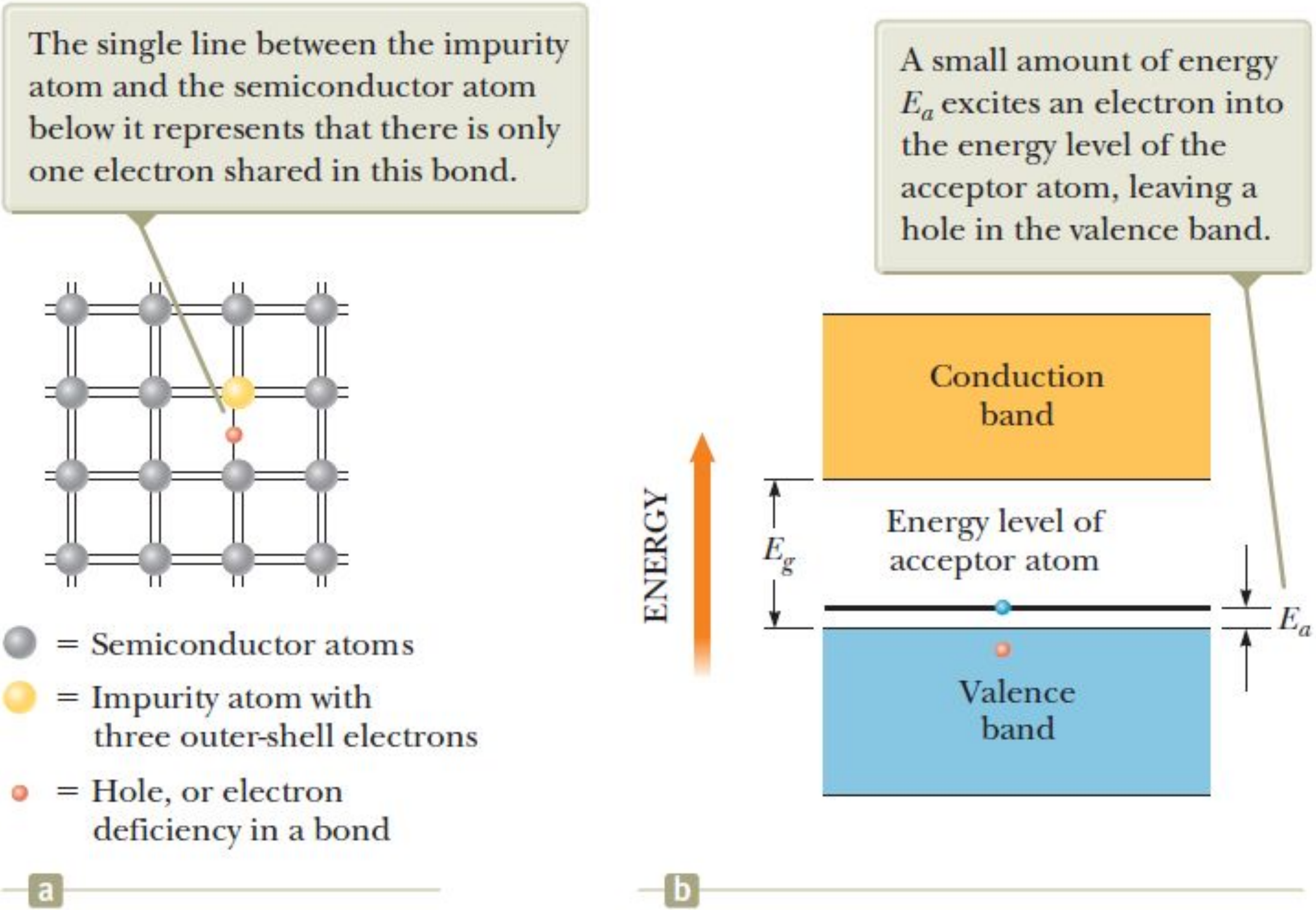
● = Semiconductor atoms

● = Impurity atom with five outer-shell electrons

● = Extra electron from impurity atom

Electrical Conduction in Metals, Insulators, and Semiconductors

Doped Semiconductors

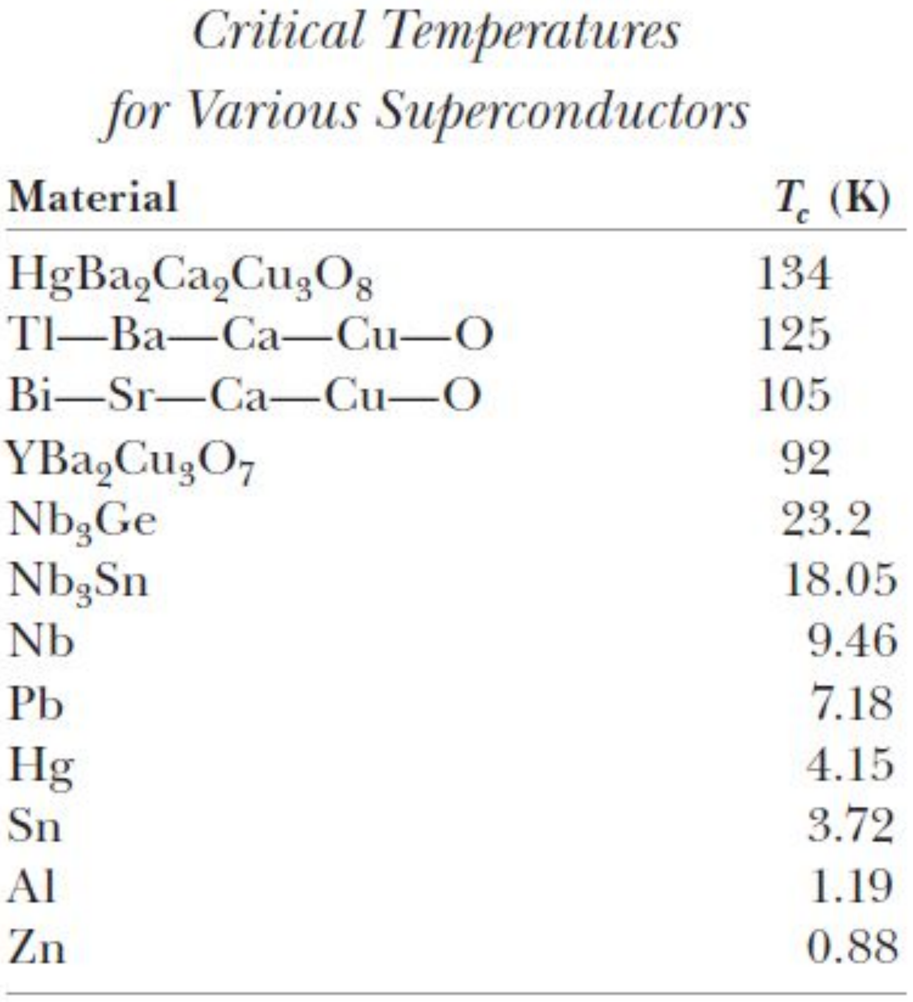


The single line between the impurity atom and the semiconductor atom below it represents that there is only one electron shared in this bond.

A small amount of energy E_a excites an electron into the energy level of the acceptor atom, leaving a hole in the valence band.

Superconductivity

There is a class of metals and compounds known as **superconductors** whose electrical resistance decreases to virtually zero below a certain temperature T_c called the critical temperature.

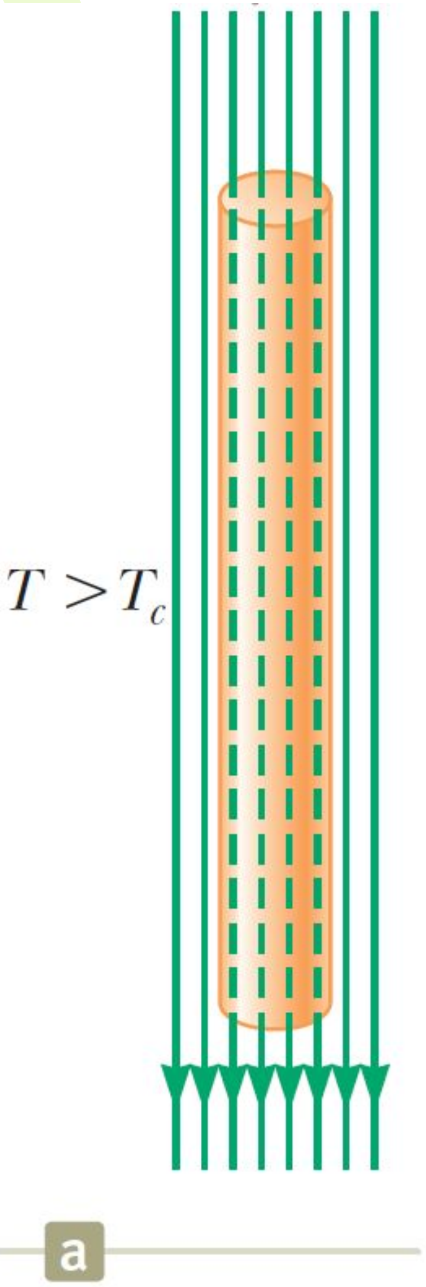


Critical Temperatures for Various Superconductors

Material	T_c (K)
$HgBa_2Ca_2Cu_3O_8$	134
Tl—Ba—Ca—Cu—O	125
Bi—Sr—Ca—Cu—O	105
$YBa_2Cu_3O_7$	92
Nb_3Ge	23.2
Nb_3Sn	18.05
Nb	9.46
Pb	7.18
Hg	4.15
Sn	3.72
Al	1.19
Zn	0.88

Superconductivity

At temperatures above T_c, the field lines penetrate the cylinder because it is in its normal state.



When the cylinder is cooled to $T < T_c$ and becomes superconducting, magnetic flux is excluded from its interior by the induction of surface currents.