# Chapter 42: molecules and condensed matter

- Types of molecular bonds
- Molecular spectra
- Structure of solids
- Energy bands
- Free electron model of metals
- Semiconductors
- Semiconductor devices
- Superconductivity

Molecular bonds and energy

When a molecule is bonded to another molecule, the total energy of the system is lower than if the two molecules where separated. Thus, it takes energy to separate the distance between two atoms and "break" the molecular bond.

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.

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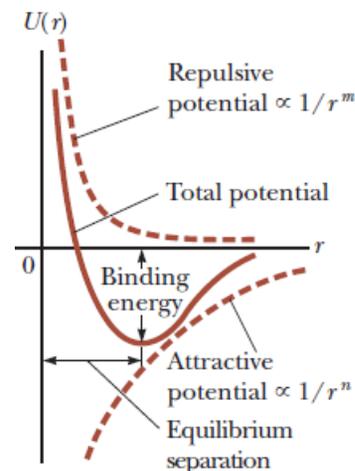
Ionic Bonds

An **ionic** bond is an interaction between oppositely charged ionized atoms. Note that ionic bonds can allow for the formation of crystalline structured materials.

Cl⁻

Na⁺

1 nm

Example: Sodium chloride

Removal of the outermost electron from a sodium atom (the 3s electron) to expose the filled interior shell creates an energy difference of 5.138 eV (the ionization energy).

Adding an electron to the chlorine atom to fill the 3p shell causes an opposing energy difference of 3.613 eV (electron affinity).

Thus, the transfer of an electron from a sodium atom to a chlorine atom requires an energy of 5.138 eV − 3.613 eV = 1.525 eV.

When these two atoms are ionized, they have a strong attraction via the electric force. The minimum energy before the repulsive force begins to dominate occurs at a separation distance of 0.24 nm. This energy is −5.70 eV.

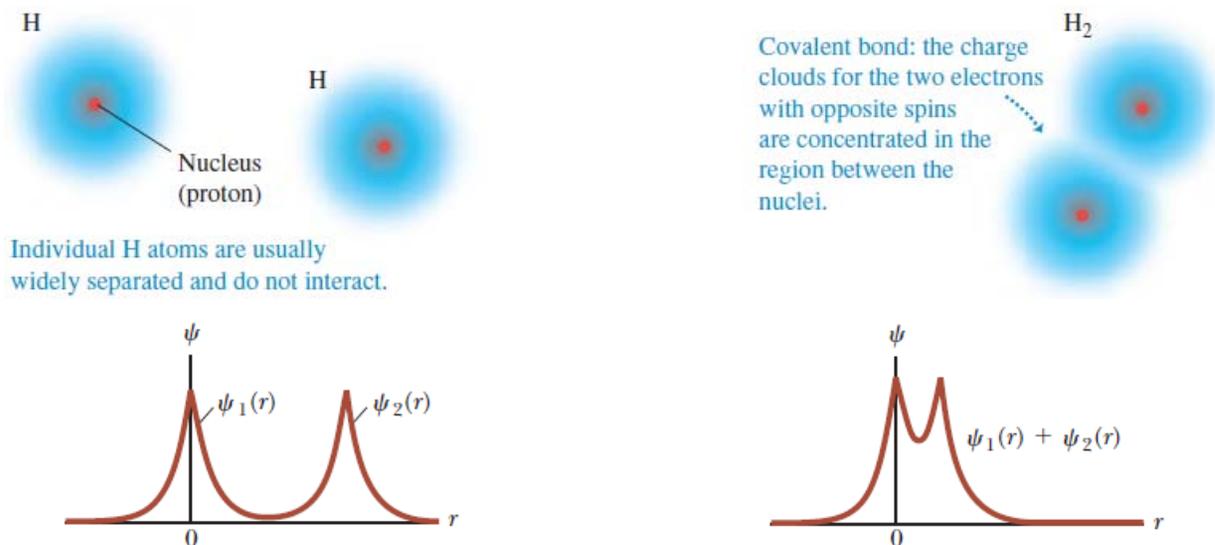The energy to separate the bond follows as 5.70 eV − 1.525 eV = 4.18 eV.
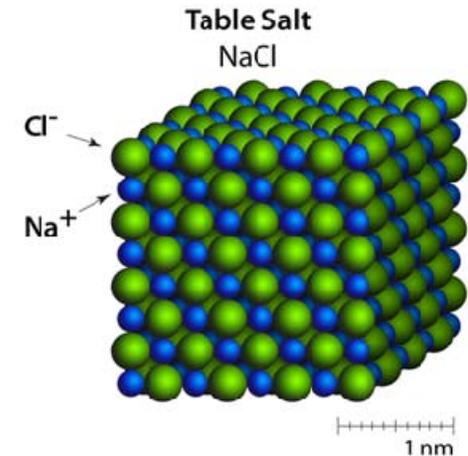
Covalent bonds

For **covalent bonds**, as separate atoms come together, the outer shell electron wave functions become distorted with a higher probability of finding an electron in the region between the two nuclei.

The net attraction of the covalently bonded electrons for each nuclear charge balances the repulsion of the two nuclear charges and of the covalent bound electrons.

H

H

Nucleus
(proton)

Individual H atoms are usually widely separated and do not interact.

H_2

Covalent bond: the charge clouds for the two electrons with opposite spins are concentrated in the region between the nuclei.

ψ

$\psi_1(r)$ $\psi_2(r)$

r

0

ψ

$\psi_1(r) + \psi_2(r)$

r

0

Thus, the attractive interaction is then supplied by a pair of electrons, one contributed by each atom. The energy of the covalent bond in the hydrogen molecule H_2 is -4.48 eV.

van der Waals bond

The **van der Waals bond** is an interaction between the electric dipole moments of atoms or molecules.

The van der Waals bond is a type of weak molecular bond. The amount of energy necessary to separate this type of bond is typically less than a few tenths of an electron Volt.

In addition to molecules with permanent dipole moments, fluctuating charge distributions can lead to fluctuating dipole moments. These induced dipole moments cause an attractive force between the two atoms or molecules.
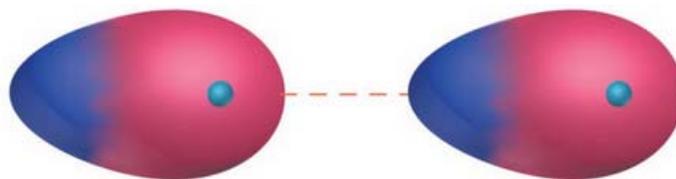
The liquefaction and solidification of the inert gases and of small molecules such as H_2, O_2, and N_2 are due to induced dipole van der Waals interactions. Not much thermal-agitation energy is needed to break these weak bonds.

Hydrogen bonds

In a **hydrogen bond**, a proton (H+ ion) is located between two atoms. The presence of the hydrogen ion polarizes the molecules and attracts them by inducing dipole moments.

This type of bond is unique to hydrogen-containing compounds because only hydrogen has a singly ionized state with no remaining electron cloud.

The hydrogen bond energy is usually less than 0.5 eV.
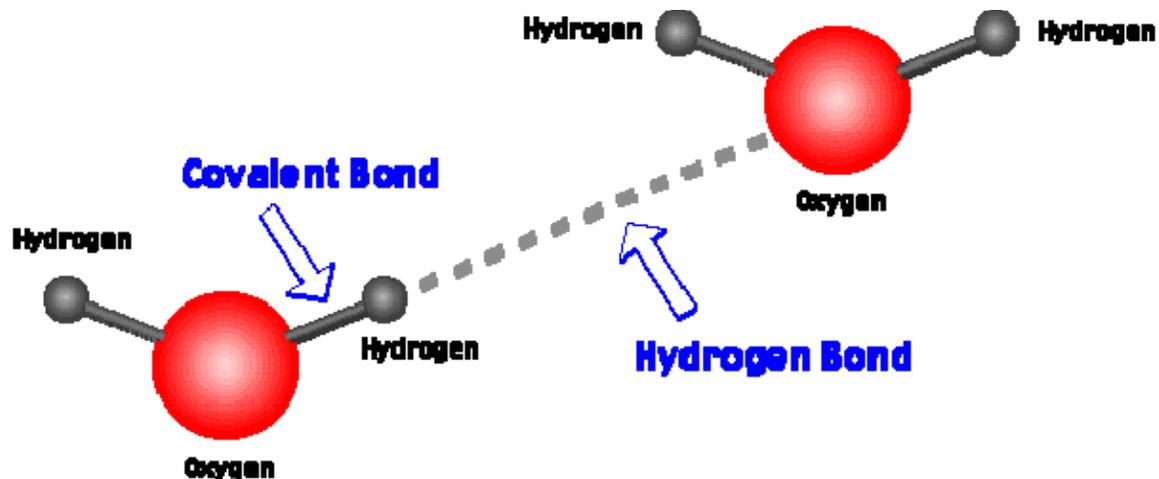
The hydrogen bond binds water molecules in ice with molecular distances much closer than those from van der Waals interactions.

Ionic bonding is due to

A. atoms bonding to hydrogen molecules.

B. the transfer of electrons between atoms.

C. the sharing of electrons between atoms.

D. atoms bonding to oxygen molecules.

Covalent bonding is due to

A. the sharing of electrons between atoms.

B. atoms bonding to hydrogen molecules.

C. atoms bonding to oxygen molecules.

D. the transfer of electrons between atoms.

How are van der Waals bonds formed?

A. Van der Waals bonds are formed as a result of the sharing of electrons between atoms.

B. Van der Waals bonds are formed as a result of the bonding of atoms to hydrogen molecules.

C. Van der Waals bonds are formed as a result of the unequal charge distributions around neutral molecules.

D. Van der Waals bonds are formed as a result of the transfer of electrons between atoms.

Rotational energy levels

A diatomic molecule can be modeled as a rigid dumbbell with two point masses m_1 and m_2 separated by a constant distance r_0.

The simple molecule can rotate about the axes through its center of mass, perpendicular to the line joining the atoms.

When there is no potential energy acting on the molecule, there is only the kinetic energy K, which is equal to the total mechanical energy E,
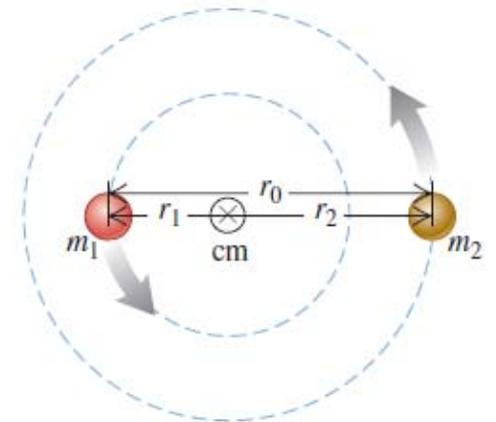
$$E = \frac{L^2}{2I}$$

From quantum mechanics, we found that $L = \sqrt{l(l+1)}\hbar$. Thus, we may write the rotational energy as

$$E = \frac{\hbar^2}{2I}l(l+1)$$

We may finally write the rotational energy in terms of the reduced mass $m_r = \dfrac{m_1 m_2}{m_1 + m_2}$, which gives

$$E = \frac{\hbar^2}{2m_r r_0^2}l(l+1) \quad \text{where} \quad I = m_r r_0^2$$

Vibrational energy levels

A more realistic model of a diatomic molecule models the connection between atoms as a spring instead of a rigid rod.

For small oscillations, the restoring force can be taken as proportional to the displacement from the equilibrium separation r_0 (aka Hooke's law). Thus, we may use our knowledge of the quantum harmonic oscillator.

The vibrational energy levels from the quantum harmonic oscillator are

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \quad \text{for} \quad n = 0, 1, 2, \ldots$$

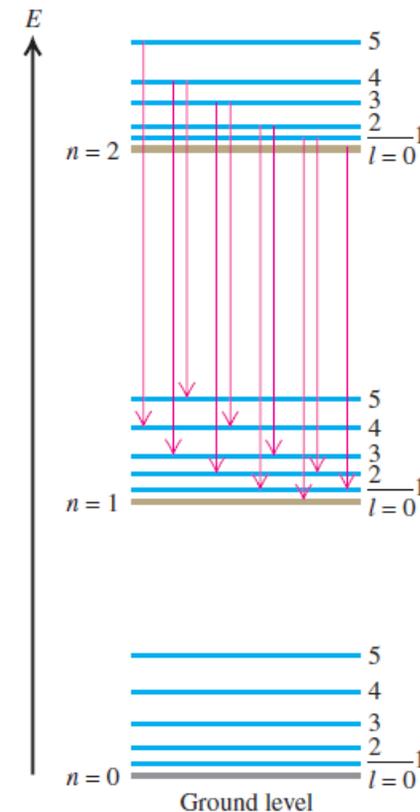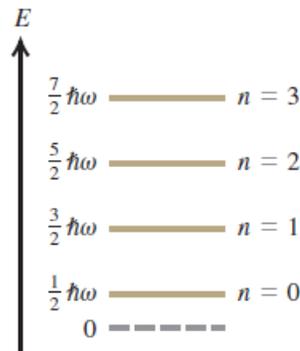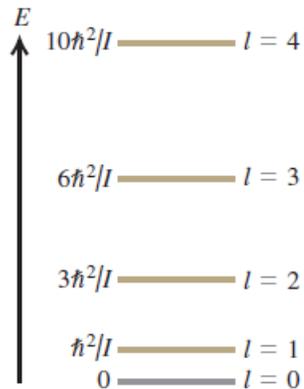We may rewrite this in terms of the spring constant k', and replace the mass m by the rest mass m_r to get

$$E_n = \left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k'}{m_r}}$$
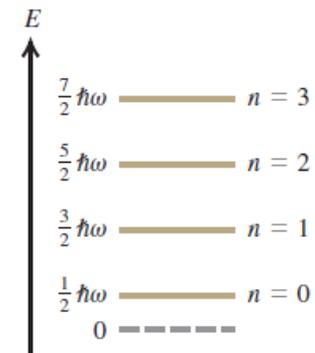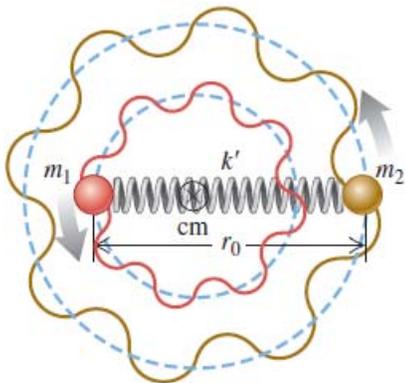
Combined energy from vibrations & rotations

Including both rotational and vibrational energies, we may write the diatomic molecule energy levels as

$$E_{nl} = l\,(l+1)\,\frac{\hbar^2}{2m_r r_0^2} + \left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k'}{m_r}}$$

A rotating diatomic molecule in its $l = 1$ quantum state has energy E. What is the energy of the same molecule in its $l = 2$ quantum state?

A. $2E$

B. $3E$

C. $4E$

D. $6E$

A vibrating diatomic molecule in its ground state has energy E. What is the energy of the same molecule in its second excited state?

A. $2E$

B. $3E$

C. $5E$

D. $9E$

A vibrating diatomic molecule has vibrational quantum number n. The energy difference between <u>adjacent</u> energy levels

A. is independent of n.

B. decreases as n increases.

C. increases as n increases.

D. increases until a threshold n, and then decreases.

Molecular spectra

The energy transitions must obey the selection rule $\Delta l = \pm 1$ in order to conserve angular momentum.

An additional selection rule for the quantum harmonic oscillator states that if the vibrational level changes, the vibrational quantum number must either increase by 1 (absorb a photon) or decrease by 1 (emit a photon).

Transitions between states with various pairs of n-values give different series of spectrum lines, and the resulting spectrum has a series of "bands."

A typical molecular band spectrum.

Note that all molecules can have excited states of the electrons in addition to the rotational and vibrational states just described.

Also note that a molecule with three or more atoms will have several different kinds or modes of vibratory motion.

Bending mode   Symmetric stretching mode   Asymmetric stretching mode
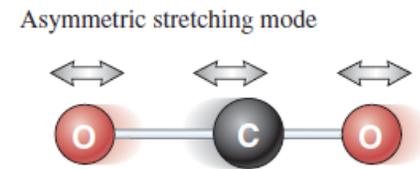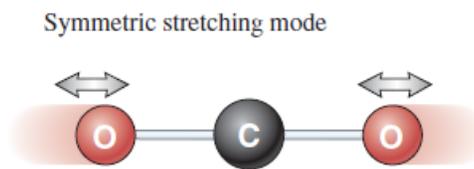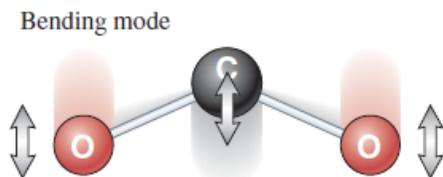
Crystal lattices and structure

A crystal lattice is a repeating pattern of mathematical points that extends throughout space. Some examples of crystal lattices follow:

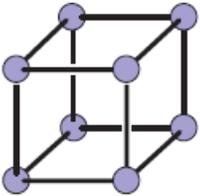The simple cubic lattice (sc) has a lattice point at each corner of a cubic array
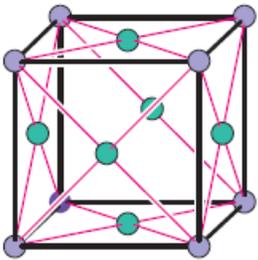
The face-centered cubic lattice (fcc) is like the simple cubic but with an additional lattice point at the center of each cube face.
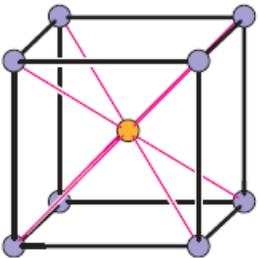
The body-centered cubic lattice (bcc) is like the simple cubic but with an additional point at the center of each cube.
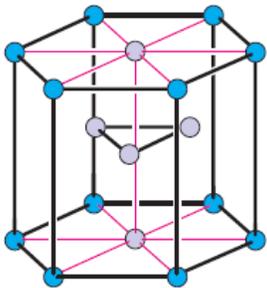
The hexagonal close-packed lattice has layers of lattice points in hexagonal patterns, each hexagon made up of six equilateral triangles.

Types of crystals

Covalent crystals are formed by covalent bonds. An example of such a crystal is the diamond structure. Diamonds can be formed Group IV elements in the periodic table such as carbon, silicon, germanium, and tin.

Ionic crystals are formed by ionic bonds, where common table salt is an ionic crystal made of sodium and chlorine atoms.

Materials formed from ionic and covalent bonds are often <u>polycrystalline,</u> composed of many small single crystals bonded together at <u>grain boundaries</u>.

Metallic crystals are formed when one or more of the outermost electrons in each atom become detached from the parent metal atom. These "free" electrons are not localized near the individual ions, and the corresponding electron wave functions extend over many atoms.

This sea of electrons has many of the properties of a gas, where it is sometimes modeled as an electron-gas in metallic solids.

Positive
ions
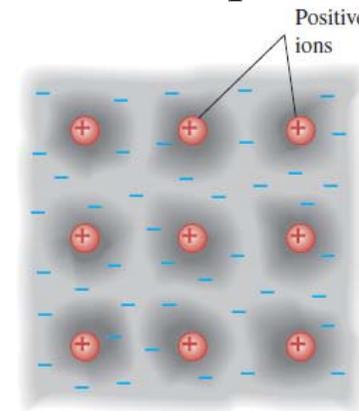
Which of the following are characteristics of metallic bonds?

A. Free electrons are shared by all atoms.

B. Electrons are stolen from one atom by another.

C. Unequal charge distributions around neutral atoms create strong bonds.

D. Atoms bond to hydrogen molecules.

Insulators, semiconductors and conductors

The **valence band**, at absolute zero temperature, is the highest band that is completely filled.

The **conduction band** is the next higher energy band above the valence band.

In <u>insulators</u>, the valence band is completely filled and is also the highest band that has any electrons in it.

<u>Semiconductors</u> are similar to insulators in that the conduction band at absolute zero temperature is also vacant. The energy difference between the valence band and conduction band (**band gap**) is much smaller for semiconductors than insulators.

<u>Conductors</u> have electrons in the conduction band at absolute zero temperature.
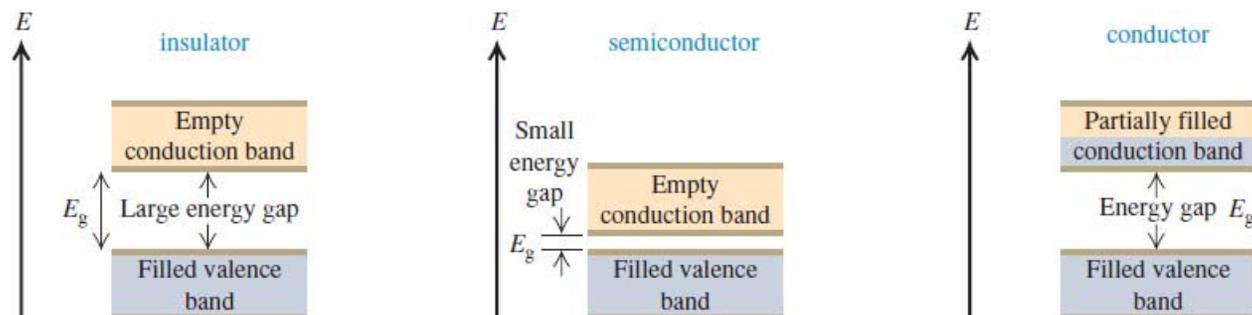
Electron concentration and free energy

The probability that a particular state having energy E is occupied by one of the electrons in a solid is given by the Fermi-Dirac distribution function,

$$f(E) = \frac{1}{1 + e^{(E - E_F)/kT}}$$

where E_F is called the Fermi energy.

At absolute zero temperature, $f(E) = 0$ for $E < E_F$ and $f(E) = 1$ for $E > E_F$. As the temperature increases, the curve becomes a smooth sigmoidal function.
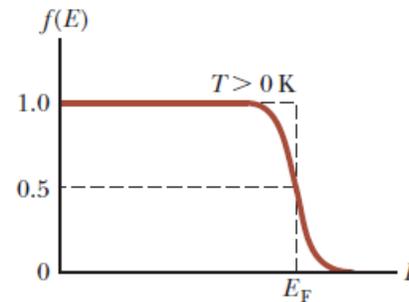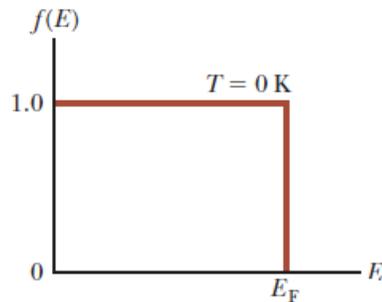
If an electron is assumed to be "free" within a cube-like region of a conductor, then it can be modeled as a three-dimensional particle-in-a-box with energies

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2mL^2} \left(n_x^2 + n_y^2 + n_z^2 \right)$$

Electron concentration and free energy (cont.)

Because of the macroscopic size L of the box, the energy levels for the electrons are very close together, where we can approximate the quantum numbers as continuous variables.

The number of allowed states that have energies between E and $E + dE$ is

$$g\left(E\right)\,dE = \frac{dN}{dE}\,dE = \frac{\sqrt{2}m^{\frac{3}{2}}L^3}{\pi^2\hbar^3}E^{\frac{1}{2}}\,dE$$

where the function $g(E)$ is called the density-of-states. Note that in some books, the density of states is defined such that there is no volume L^3 appearing in the density-of-states by looking at the change in electron number density per unit change in energy.

If a metal is in thermal equilibrium, the number of electrons is equal to the product of the number of allowed states and the probability that a state is occupied, $dN = g(E)f(E)dE$. Thus, we may write

$$dN = \frac{\sqrt{2}m^{\frac{3}{2}}L^3}{\pi^2\hbar^3}\frac{E^{\frac{1}{2}}}{1 + e^{(E-E_F)/kT}}\,dE$$

Electron concentration and free energy (cont.)

The solution to the number of electrons from the equation on the previous slide is

$$N = \sqrt{2}\frac{2}{3}\frac{m^{\frac{3}{2}}L^3}{\pi^2\hbar^3}E_{F0}^{\frac{3}{2}}$$

Solving for the Fermi energy at absolute zero temperature E_{F0}, we find

$$E_{F0} = \frac{3^{\frac{2}{3}}\;\pi^{\frac{4}{3}}\hbar^2}{2\;mL^2}N^{\frac{2}{3}}$$

The quantity $\dfrac{N}{V} = \dfrac{N}{L^3}$ is the number of free electrons per unit volume, or <u>free electron concentration</u>, and denoted by n. Therefore, we may finally write the Fermi energy at absolute zero temperature as

$$E_{F0} = \frac{3^{\frac{2}{3}}\pi^{\frac{4}{3}}\hbar^2 n^{\frac{2}{3}}}{2m}$$

Average energy of free electrons

The average free-electron energy in a metal at absolute zero temperature is found via

$$E \, dN = g\left(E\right) f\left(E\right) dE$$

At absolute zero temperature we substitute $f\left(E\right) = 1$ from 0 to E_{F0} and $f\left(E\right) = 0$ for all other energies. Therefore, we may write the total energy of the N electrons, E_{tot}, as

$$E_{\text{tot}} = \int_0^{E_{F0}} E \, g\left(E\right) dE = \int_0^{E_{F0}} \frac{3N E^{\frac{3}{2}}}{2 E_{F0}^{\frac{3}{2}}} \, dE$$

Using $E_{\text{avg}} = \dfrac{E_{\text{tot}}}{N}$, we may find the average energy of a free electron,

$$E_{\text{avg}} = \frac{3}{2 E_{F0}^{\frac{3}{2}}} \int_0^{E_{F0}} E^{\frac{3}{2}} \, dE = \frac{3}{5} E_{F0}$$

In other words, the average free-electron energy equals 3/5 of the Fermi energy at absolute zero .

Electron holes

A semiconductor has an electrical resistivity that is intermediate between those of good conductors and of good insulators.

When an electron is removed from a covalent bond, it leaves a vacancy behind, this vacancy is called a **hole**. Holes can travel through materials in the same way that crystal defects travel through crystals or bubbles travel through water.

An electron is excited to the conduction band leaving a hole in the valence band. There are an equal number of holes and electrons in intrinsic semiconductors (no dopants).

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

● Electrons
● Holes

Conduction band

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.

Valence band

ENERGY

Applied $\vec{E}$ field
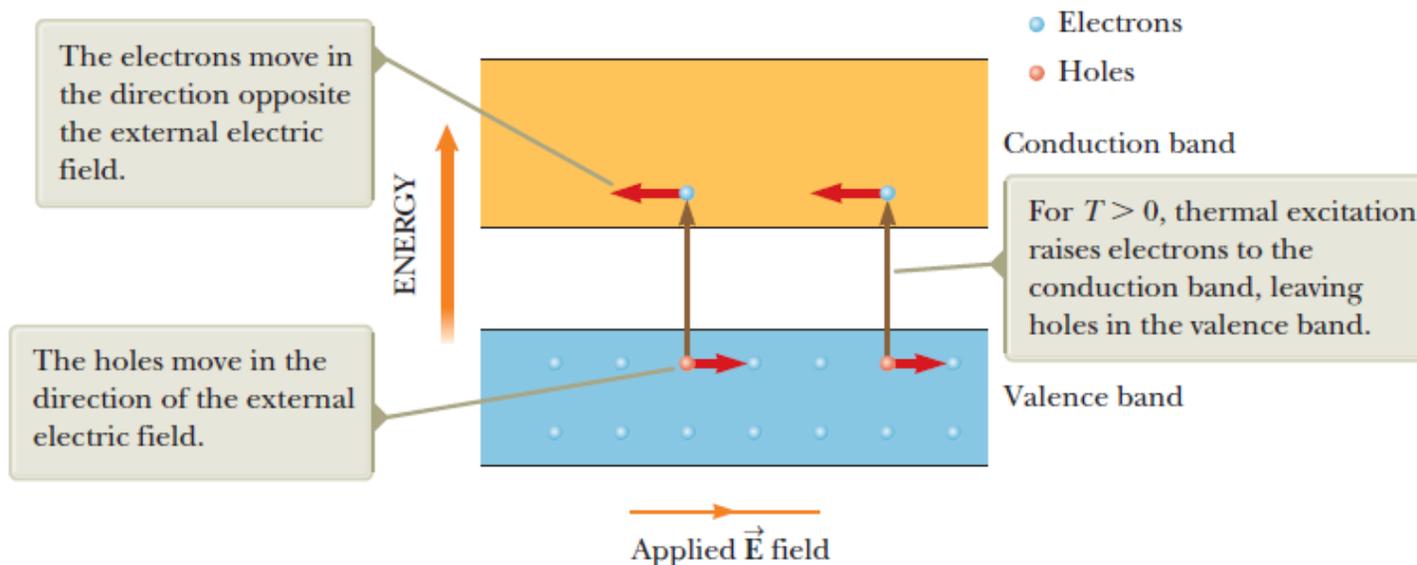
Semiconductor doping

The deliberate addition of an impurity is called **doping**.

Adding a Group V element to a Group IV semiconductor gives an extra "loosely bound" electron. These doped semiconductors are called *n*-type semiconductors.

Adding a Group III element to a Group IV semiconductor causes a bond to be missing an electron. These doped semiconductors are called *p*-type semiconductors.

A donor (*n*-type) impurity atom has a fifth valence electron that does not participate in the covalent bonding and is very loosely bound.

An acceptor (*p*-type) impurity atom has only three valence electrons, so it can borrow an electron from a neighboring atom. The resulting hole is free to move about the crystal.
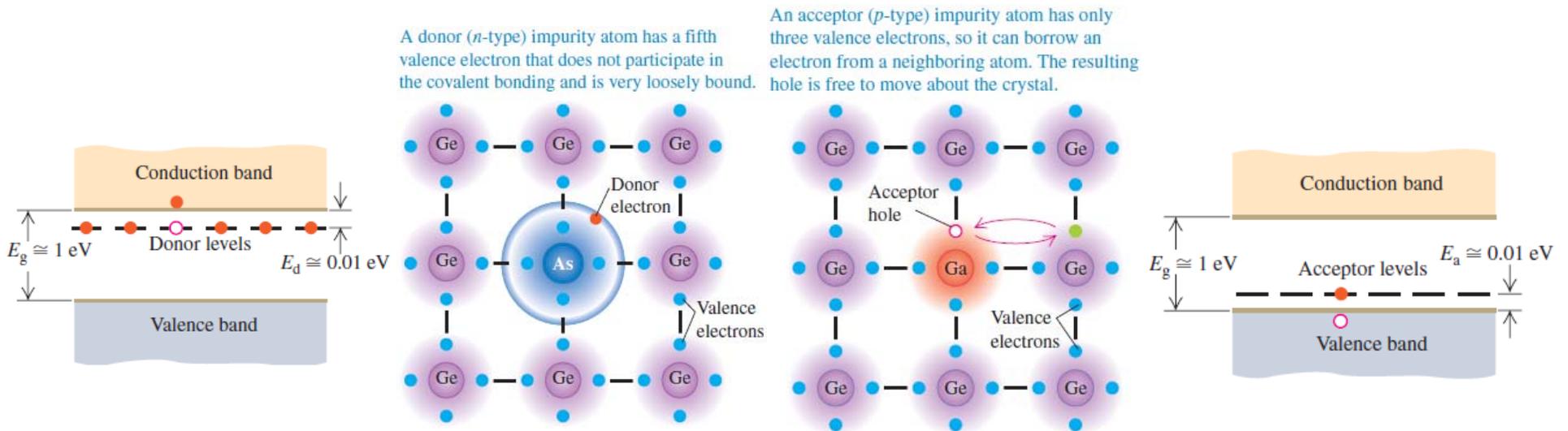
An unfilled electron state in the valence band is called

A. a hole.

B. an empty positron.

C. a positron.

D. an empty electron.

How is an n-type semiconductor produced?

A. By forming a pure crystal of germanium.

B. By forming a pure crystal of arsenic.

C. By doping the host crystal with acceptor impurities.

D. By doping the host crystal with donor impurities.

p-n junction and diodes

A *p-n* junction is the boundary between one region of a semiconductor with *p*-type impurities and another region containing *n*-type impurities.

When a p-n junction is connected to an external circuit and the potential difference across the junction $V_p - V_n = V$ is varied, the current I varies. This variation creates a somewhat "one way" device called a **diode rectifier**.

A simple model of p-n junction gives the current-voltage relationship

$$I(V) = I_S \left(e^{eV/kT} - 1 \right)$$

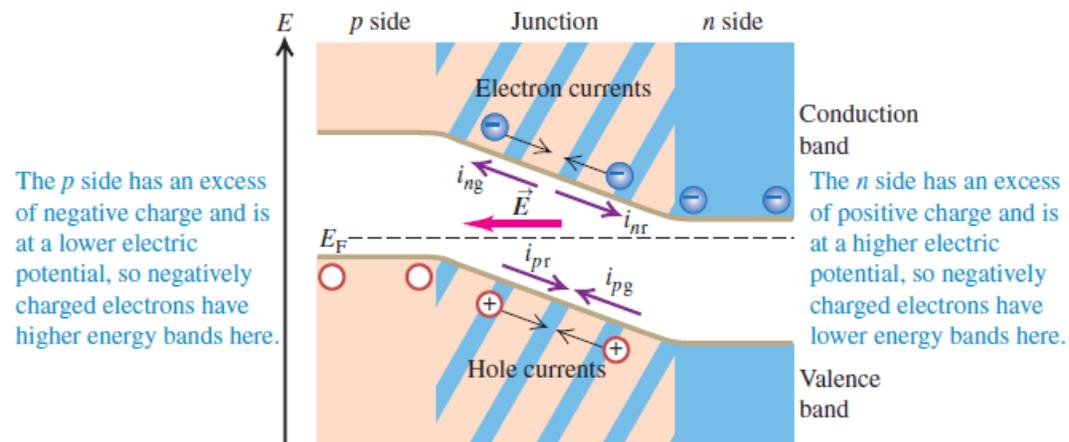where I_S is the saturation current.
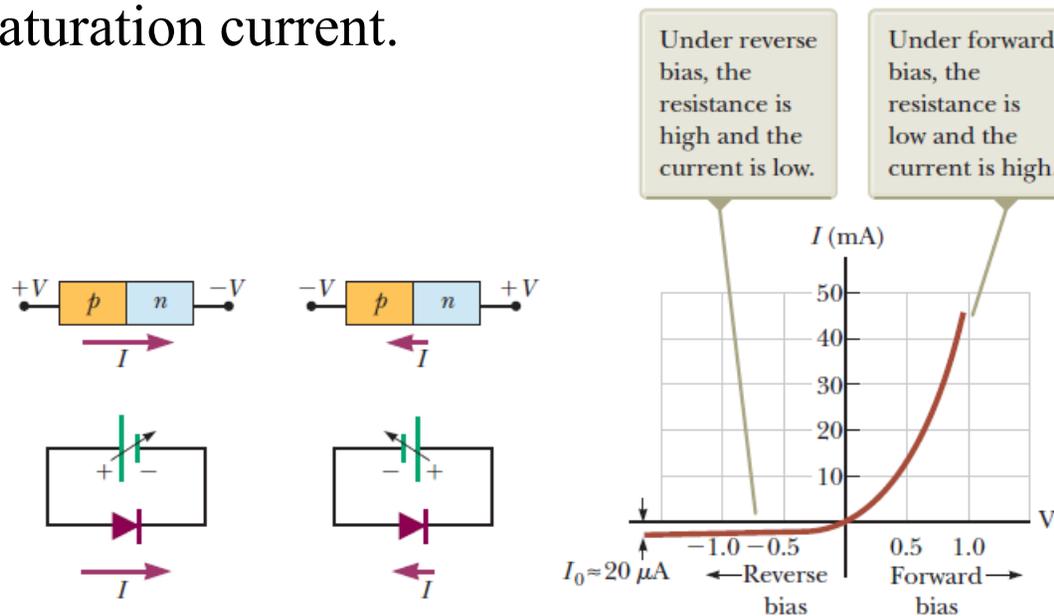
Currents in a *p-n* junction

There are four currents across a *p-n* junction.

Diffusion processes lead to <u>recombination currents</u> of holes and electrons, i_{pr} and i_{nr}.

At the same time the electron-hole pairs are recombining, the pairs are also being generated in the junction region by thermal excitation. The <u>generation currents</u> of holes and electrons are labeled as i_{pg} and i_{ng}.

At equilibrium the magnitudes of the generation and recombination currents are equal,

$$\left[\begin{array}{l} |i_{pg}| = |i_{pr}| \\ |i_{ng}| = |i_{nr}| \end{array} \right.$$

E   p side   Junction   n side

Electron currents

The *p* side has an excess of negative charge and is at a lower electric potential, so negatively charged electrons have higher energy bands here.

i_{ng} $\vec{E}$ i_{nr}

E_F

i_{pr} i_{pg}

Hole currents

Conduction band

The *n* side has an excess of positive charge and is at a higher electric potential, so negatively charged electrons have lower energy bands here.

Valence band

p-n junction with forward & reverse bias

A forward bias decreases the electric field in the junction region and decreases the difference between the energy levels on the p and n sides by $\Delta E = -eV$.
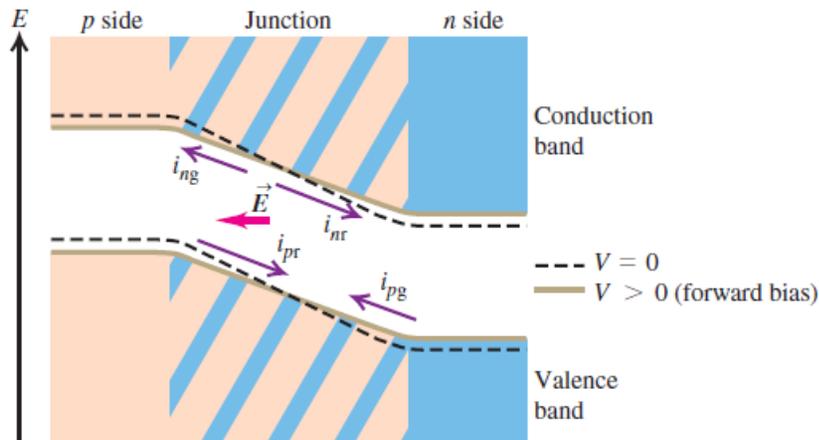
The recombination currents change exponentially while the generation currents are approximately constant,

$$\begin{cases} i_p = i_{pr} - |i_{pg}| = |i_{pg}| \left(e^{eV/kT} - 1 \right) \\ i_n = i_{nr} - |i_{ng}| = |i_{ng}| \left(e^{eV/kT} - 1 \right) \end{cases}$$

$$\Longrightarrow \quad I = i_p + i_n = I_S \left(e^{eV/kT} - 1 \right) \quad \text{where} \quad I_S = |i_{pg}| + |i_{ng}|$$

Although there is little current under reverse bias for low voltage, high voltage can cause an "avalanche breakdown," where carriers can gain enough energy between collisions to create electron–hole pairs during inelastic collisions (and they then gain energy creating even more pairs).

Another type of breakdown, called "Zener breakdown," occurs when electrons tunnel through the junction into the conduction band.

In what direction does current flow when a p-n junction is forward biased?

    A. A current flows through it from the n-side to the p-side.

    B. A current does not flow through it.

    C. A current flows through it from the p-side to the n-side.

    D. A current can flow though it in either direction.

The Fermi level (energy) of a metal is 5.5 eV. What is the number of conduction electrons per unit volume for this metal? ($m_{el} = 9.11 \times 10^{-31}$ kg, 1 eV = 1.60×10^{-19} J, $h = 6.626 \times 10^{-34}$ Js)

A. 3.3×10^{28} m^{-3}

B. 4.1×10^{28} m^{-3}

C. 5.8×10^{28} m^{-3}

D. 6.2×10^{28} m^{-3}

If a metal had a Fermi level (energy) of 5.0 eV, what would be the average energy of the electrons at 0 K?
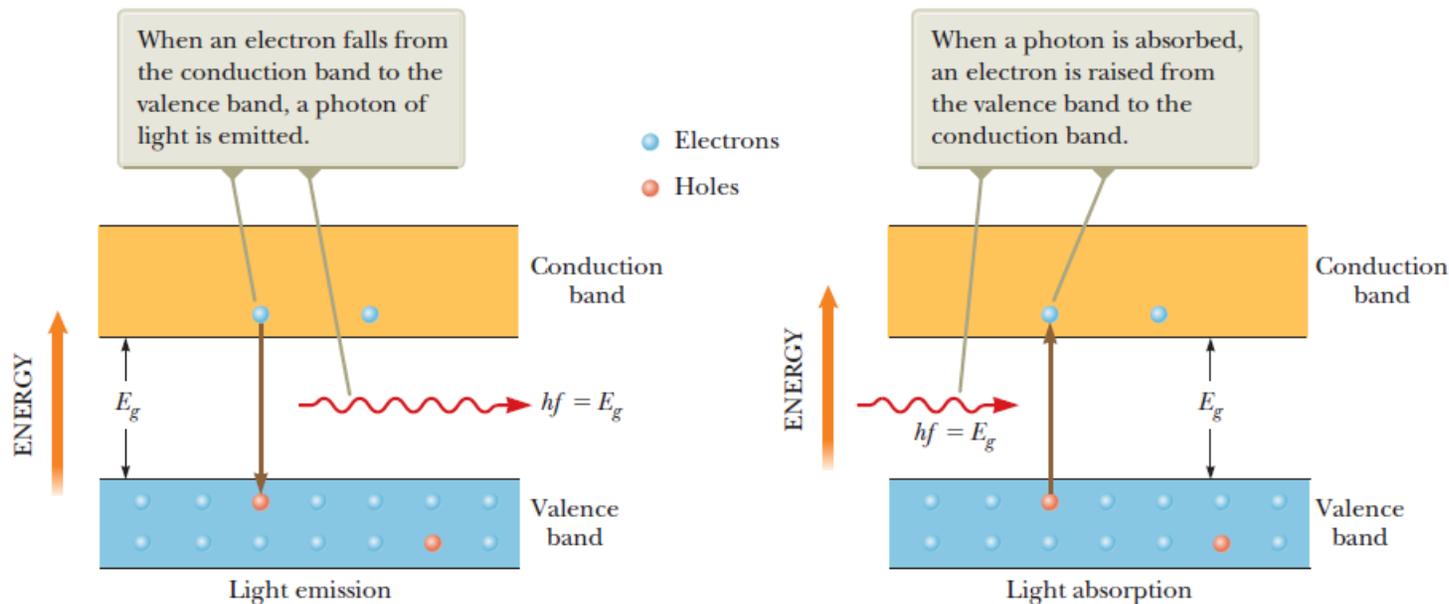
A. 0.0 eV

B. 3.0 eV

C. 5.0 eV

D. 8.0 eV

Light-emitting diodes and solar cells

An electron excited electrically into the conduction band can easily recombine with a hole. As the recombination takes place, a photon of energy E_g is emitted. A device using this concept is the Light Emitting Diode (LED).

Conversely, an electron in the valence band may absorb an incoming photon of light and be promoted to the conduction band, leaving a hole behind. An example of a device using this effect is a Photovoltaic (PV) cell, or sometimes referred to as a solar cell.

When an electron falls from the conduction band to the valence band, a photon of light is emitted.

● Electrons
● Holes

ENERGY

Conduction band

E_g

$hf = E_g$

Valence band

Light emission

When a photon is absorbed, an electron is raised from the valence band to the conduction band.

ENERGY

Conduction band

E_g

$hf = E_g$

Valence band

Light absorption

Transistors

A transistor is made from doped semiconductors with either a *p-n-p* or *n-p-n* configuration. The three regions are called the <u>emitter</u>, <u>base</u>, and <u>collector</u>.
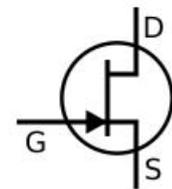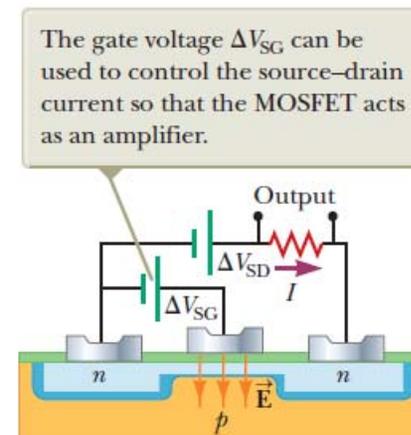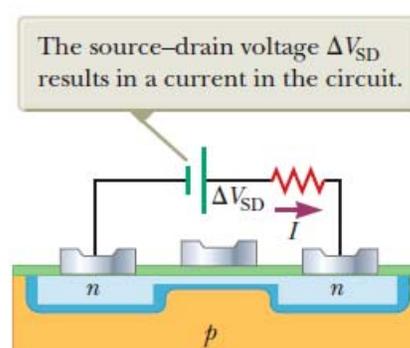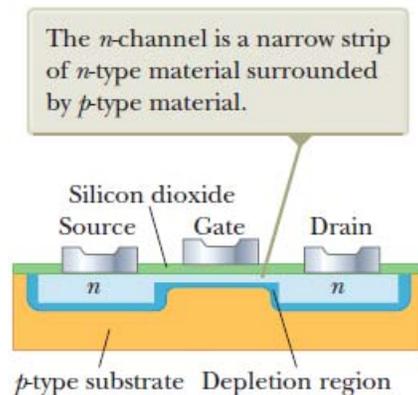
- When $V_e = 0$, the current is very small.
- When a potential V_e is applied between emitter and base, holes travel from the emitter to the base.
- When V_c is sufficiently large, most of the holes continue into the collector.

Emitter   Base   Collector

p   *n*   *p*
Hole flow

I_e I_c R V_e V_c
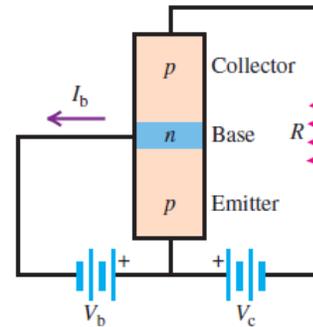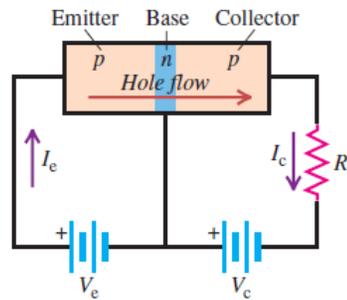
- When $V_b = 0$, I_c is very small, and most of the voltage V_c appears across the base–collector junction.
- As V_b increases, the base–collector potential decreases, and more holes can diffuse into the collector; thus, I_c increases. Ordinarily, I_c is much larger than I_b.

p Collector
n Base R I_c
p Emitter
I_b V_b V_c

B   E   C
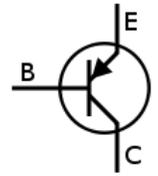
There are other types of transistors. In a Metal-Oxide-Semiconductor Field-Effect Transistor (MOSFET) has three regions called the source, gate, and drain. The current is controlled by applied a potential over the gate, or "charging the gate."

The *n*-channel is a narrow strip of *n*-type material surrounded by *p*-type material.

Silicon dioxide
Source   Gate   Drain
n   *n*
p-type substrate   Depletion region

The source–drain voltage ΔV_{SD} results in a current in the circuit.

ΔV_{SD} I
n   *n*
p

The gate voltage ΔV_{SG} can be used to control the source–drain current so that the MOSFET acts as an amplifier.

Output
ΔV_{SD} I
ΔV_{SG}
n $\vec{E}$ *n*
p

D
G   S

Superconductivity

Superconductivity is the complete disappearance of all electrical resistance at temperatures below the critical temperature T_c.

Two electrons can interact via distortions in the array of lattice ions so that there is a net attractive force between the electrons. The two electrons are bound into a Cooper pair, which behaves like a particle with integral spin (boson). At low temperatures, these pairs can be in there ground state, which allows them to travel without resistance.

$\vec{B} = 0$

$\vec{B}$
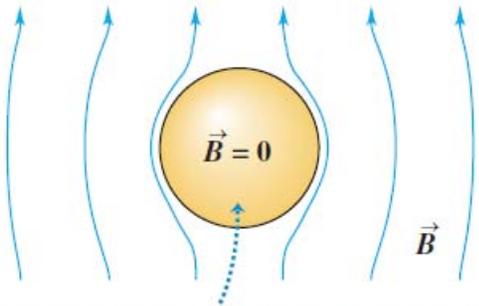
Magnetic flux is expelled from the material, and the field inside it is zero (Meissner effect).

The magnetic flux through a superconducting material is zero. This zero magnetic flux through the superconductor is called the Meissner effect.

Superconducting materials are perfectly diamagnetic below their critical temperature due to the expulsion of the magnetic flux. Therefore, superconducting materials can levitate in a magnetic field. Large magnetic fields applied to a superconductor can reduce T_c.