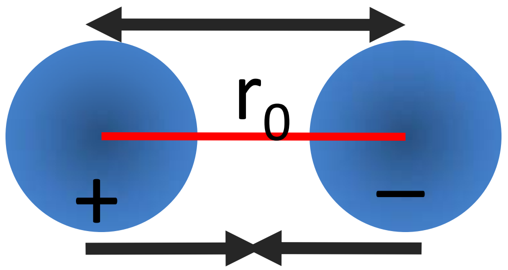
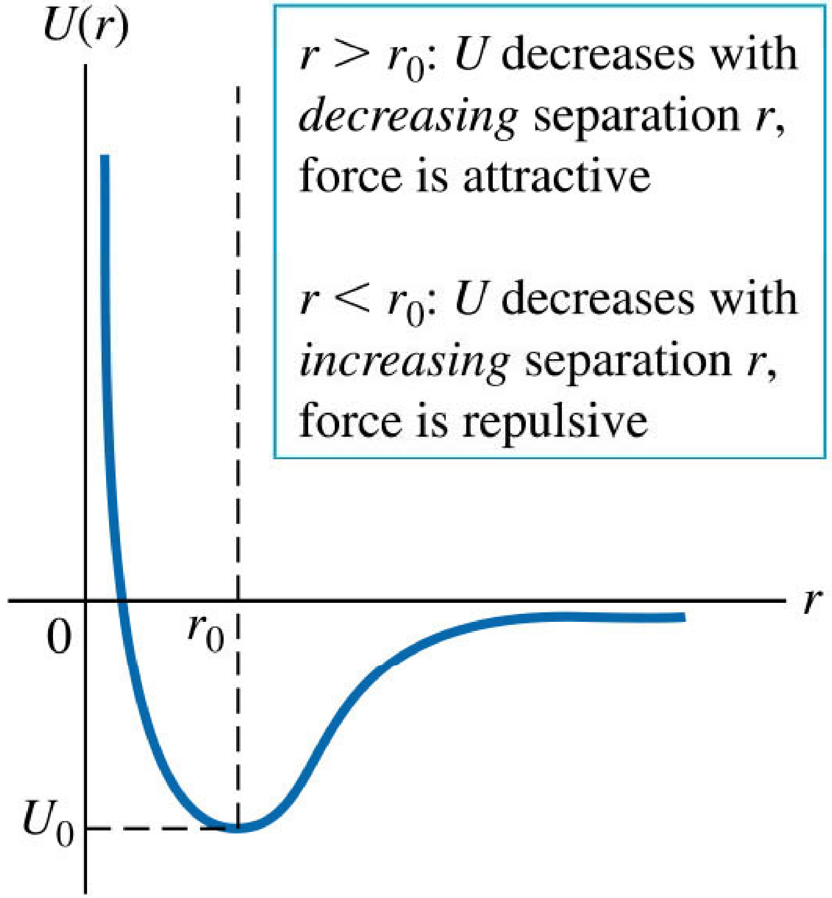
Chapter 42
Molecules and condensed matter

1. Types of molecular bonds
2. Molecular spectra
3. Structure of solids
4. Energy bands
5. Free electron model of metals
6. Semiconductors
7. Semiconductor devices
8. Superconductivity

Potential energy of two oppositely charged particles

What happens when small perturbations from the r_0 is made?





$r > r_0$: U decreases with *decreasing* separation r, force is attractive

$r < r_0$: U decreases with *increasing* separation r, force is repulsive

The Harmonic Oscillator
A Newtonian analysis

The harmonic oscillator in Newtonian mechanics:

A conservative force acts on a particle: $F_x = -k'x$

The force constant: k'

Equilibrium position $x = 0$

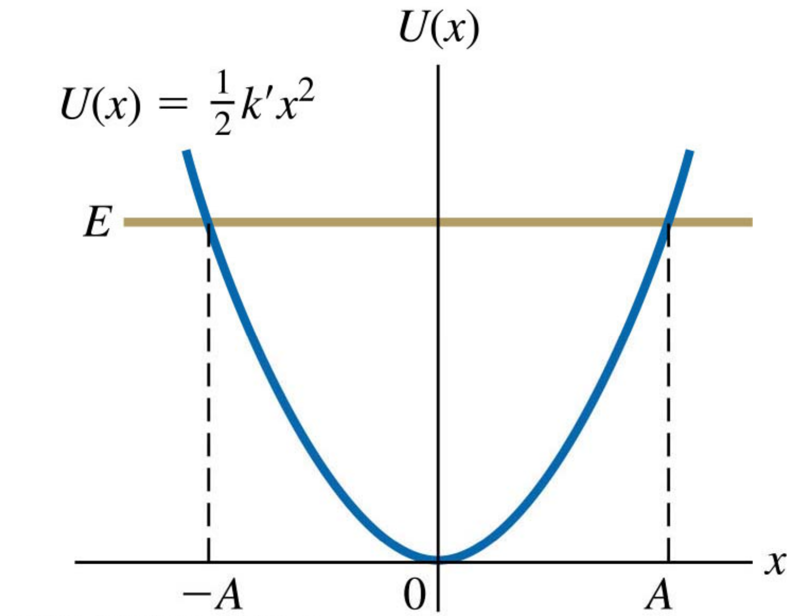
The potential energy function: $U(x) = \frac{1}{2}k'x^2$

Small dispacements from the equilibrium psition generates a restoring force to bring the particle back and initiates an oscillatory motion.

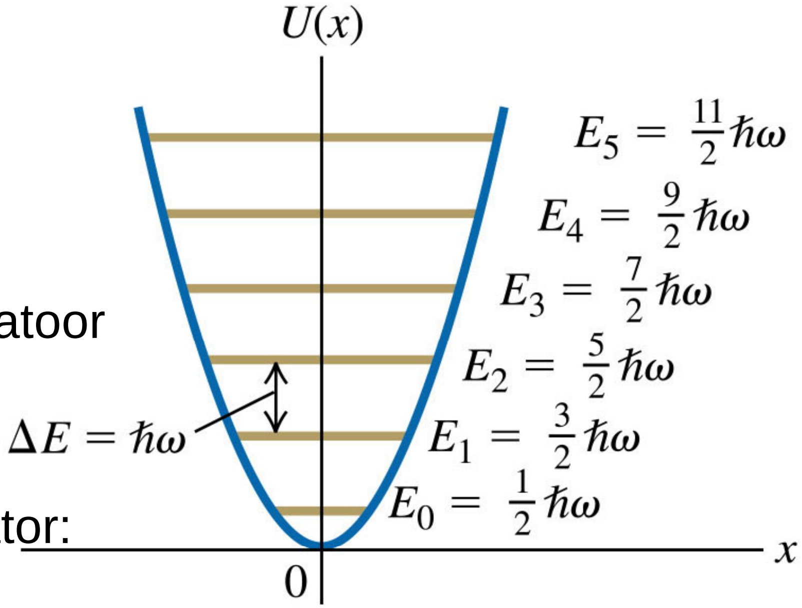
Amplitude of oscillations: A

Frequency of oscillations: $\omega = \sqrt{\frac{k'}{m}}$

$$\underbrace{\frac{1}{2}k'A^2}_{\text{Total energy}} = \underbrace{\frac{1}{2}kx^2}_{\text{Potential energy}} + \underbrace{\frac{1}{2}mv^2}_{\text{Kinetic energy}}$$



The Harmonic Oscillator
A Quantum Mechanical analysis



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The ome-dimentional Schrodinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U(x)\psi = E\psi$$

Solving the problem with the harmonic oscillatoor

potential: $U(x) = \frac{1}{2}k'x^2$

We get the energy levels of harmonic oscillator:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad (n = 0, 2, 3, \ldots)\ \&\ \omega = \sqrt{\frac{k'}{m}}$$

The main differences with classical mechanics:

1) The energy levels are quantized

2) The energy of the ground state is not zero.

If it was it would have been violating the uncertainty principle sine it would have meant knowing position of the particel at $x = 0$ with 100% accuracy.

Ionic bonds: interaction between oppositely charged ionized atoms with large difference in electron affinity
Strong with typical bonding energies 1-5 eV

- Find the electric potential energy of the NaCl molecule separated by 0.24 nm

Ionization energy +5.138eV

Electron affinity -3.613eV

+5.138eV-3.613eV=1.525eV
Higher than ground state energy of both particles.

Energy of the charge $-e$ in the field of charge $+e$

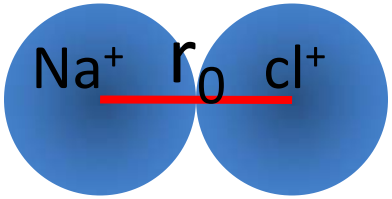
$$U = Eq = -\frac{1}{4\pi\varepsilon_0}\frac{e}{r_0}(-e)$$

$$U = -\left(9.0\times10^{9}\,N.m^2/C^2\right)\frac{1.6\times10^{-19}}{0.24\times10^{-9}}$$

$$U = -9.6\times10^{-19}\,J = -6.0eV$$

Ionization energy +5.138eV

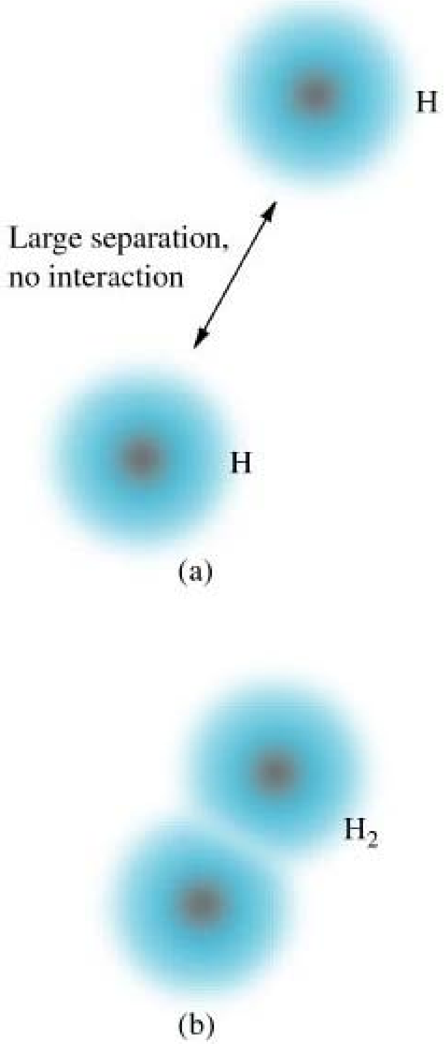
Electron affinity -3.613eV



U =-5.7eV of NaCl at r_0 from each other.
Net energy released: -5.7eV+1.525eV=-4.2eV
A much more stable system than the original atoms.

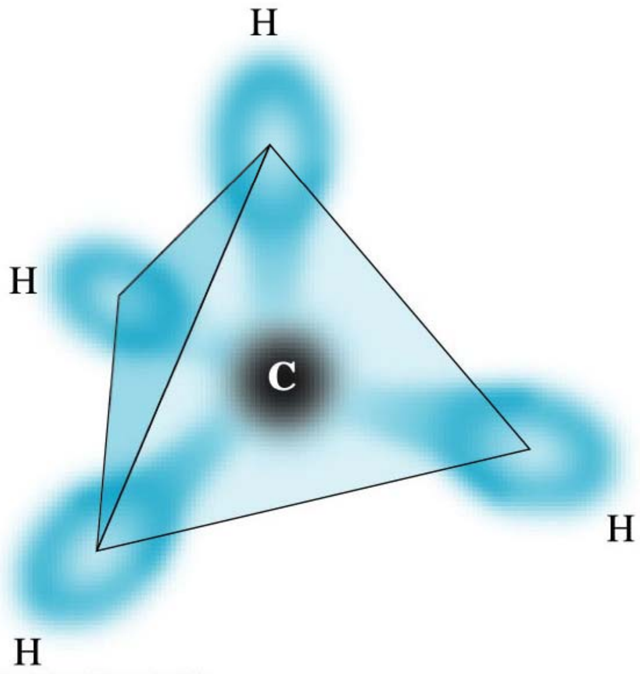
Covalent bonds:

- Sharing of the electronic cloud between two atoms that may be of the same kind or not as different in electron affinity as the atoms participating in ionic bonds.
- E of the H_2 atom is -4.48eV a much more stable structure than the two H atoms.
- Exclusion principle forbids the electrons in H_2 atom from occupying the same orbitals. So maximum two hydrogen atoms can participate in this bond.
- Covalent bonds are highly directional due to symmetry properties of the orbitals participating in the bond.
- H_2 is not directional since only s orbitals participate in the bond.
- Strong with typical bonding energies 1-5 eV



A directional covalent bond

- Methane CH_4
- C has 2 electrons in s and 2 in P orbitals (wavefunctions) of L shell. So two types of bond is expected but as we see the molecule has tetrahedron shape with all bonds the same.
- The s and three p orbitals mix to generate the hybrid four sp orbitals each extruding from the center twards the corner of the tetrahedron.
- The interaction potential energy is very sensitive to the distance and drops with $1/r^6$
- Very important in organic chemistry

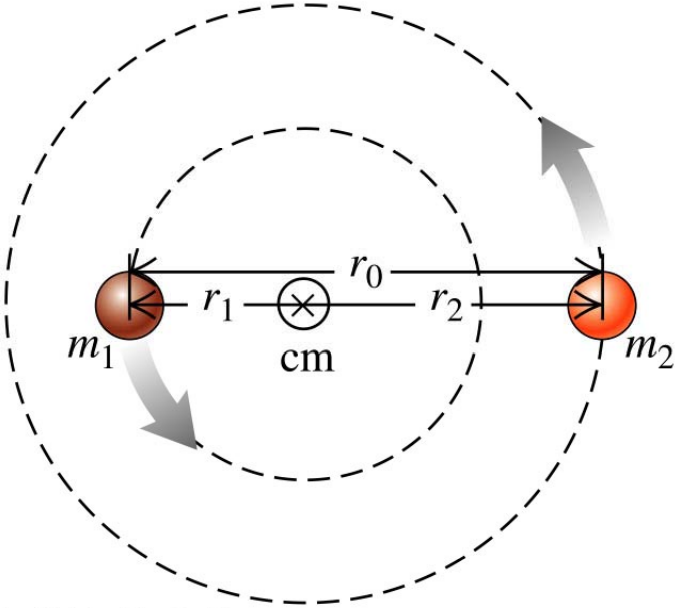


Hydrogen bond

- A H^+ atom with no electron cloud gets between the two atoms and polarizing their electron clouds and attracting them to each other.
- This only happens with hydrogen because other + ions have their own elctronic cloud and can’t achieve this with efficiency of the hydrogen atom.
- The interaction energy is < 0.5 eV. A weak bond.
- Important in organic chemistry and polymer crosslinking

Moment of inertia of a diatomic molecule

The two-body problem of the electron-nucleus can be reduced to two one-body problems



1) $m_{CM}\ddot{R} = F_{ext}$ where $m_{CM} = m_1 + m_2$ & $R = \dfrac{m_1 r_1 + m_2 r_2}{m_1 + m_2}$

2) $m_r \ddot{r}_0 = F_{mutual}$ where $m_r = \dfrac{m_1 m_2}{m_1 + m_2}$ is the reduced mass

and r_0 is the reltive distance of the two particles.

$r_1 = \dfrac{m_1}{m_1 + m_2} r_0$ & $r_2 = \dfrac{m_2}{m_1 + m_2} r_0$ are the coordinates of the electron and nucleus in the center-of-mass system

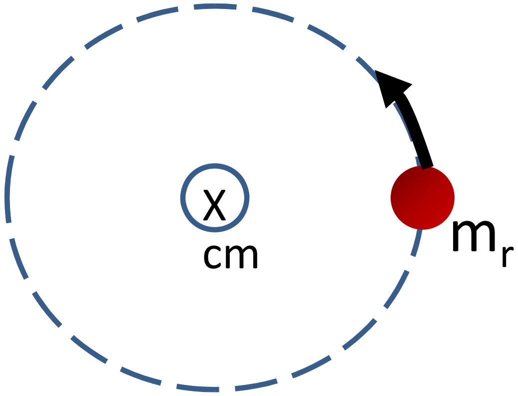
The moment of inertia of the system: $I = m_1 r_1^2 + m_2 r_2^2$

$$I = m_1 \left(\frac{m_1}{m_1 + m_2} r_0 \right)^2 + m_2 \left(\frac{m_2}{m_1 + m_2} r_0 \right)^2 = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = m_r r_0^2$$

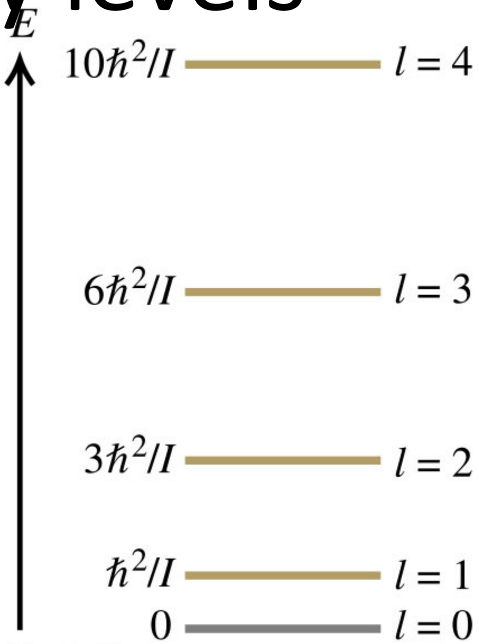
Moment of inertia of a diatomic molecule:

$\boxed{I = m_r r_0^2}$ for hydrogen atom $m_r = 0.99946 m_e$

So we can reduce the two-body problem to a one electron with reduced mass m_r rotating around a stationary nucleus.



Molecular spectra of the diatomic moleules: Rotational energy levels



We model a diatomic molecule as a dumbell rigid body with masses of m_1 and m_2 and separation of r_0. For this system:

$$\left.\begin{array}{l}\text{Kinetic energy: } K = \frac{1}{2} I\omega^2 \\ \text{Angular momentum: } L = I\omega\end{array}\right\} K = \frac{L^2}{2I} \text{ with } I = m_r r_0^{\,2} \rightarrow$$

$$\left.\begin{array}{l} K = \dfrac{L^2}{2m_r r_0^{\,2}} \\ U = 0 \end{array}\right\} H = K + U = \frac{L^2}{2m_r r_0^{\,2}} \rightarrow H\psi = E\psi$$

the energy operator does not depend on θ, ϕ, and the solutions of the Schrodinger equation are simmilar to that of hydrogen atom.

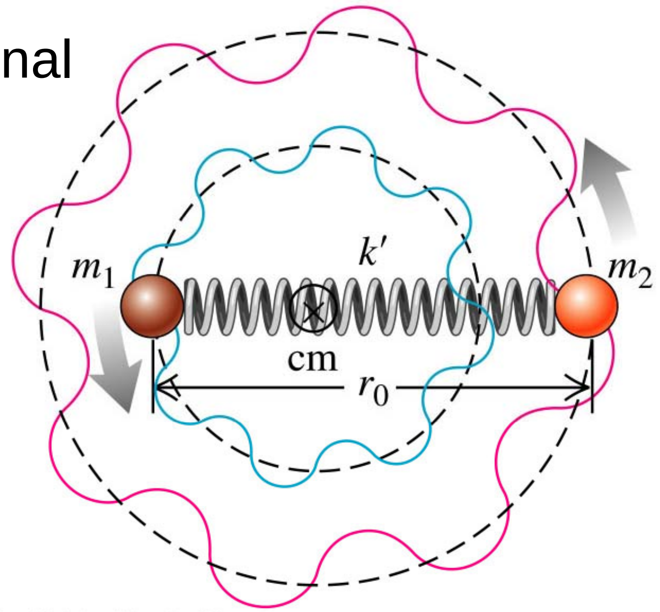
The angular momentum is quantized:

$$L^2 = l\left(l+1\right)\hbar^2, \quad \left(l = 0,1,2,3,\ldots\right)$$

Rotational energy levels of a diatomic molecule:

$$\boxed{E_l = l\left(l+1\right)\frac{\hbar^2}{2I} = l\left(l+1\right)\frac{\hbar^2}{2m_r r_0^{\,2}}, \ \left(l = 0,1,2,3,\ldots\right)}$$

Vibrational energy levels



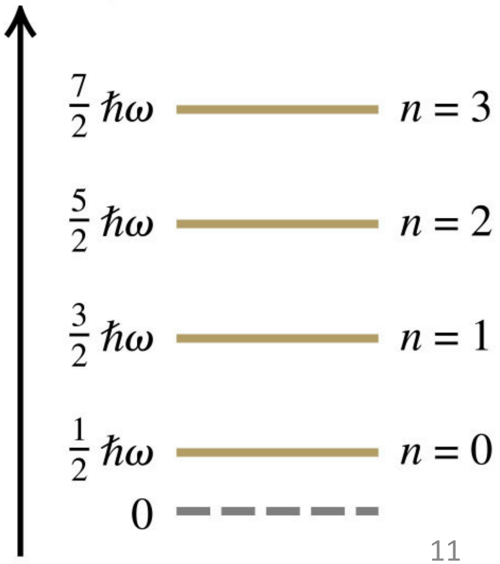
Molecules are never rigid and can have vibrational motion around their equilibrium position. Vibrational motion of the molecules can be modeled as a harmonic oscillator if the perturbations from the equilibrium position are small. The asociated energy levels are:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega = \left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k'}{m_r}}$$

Angular frequency: $\omega = \sqrt{\frac{k'}{m_r}}$

Spring constant: k'; Reduced mass: $m_r = \frac{m_1 m_2}{m_1 + m_2}$

Difference between conesquitive levels: $\Delta E = \hbar\omega$



Rotational spectrum of the carbon monoxide and its force constant

- Two nuclei of the carbon monoxide molecule are 0.1128 nm apart. m_C=12u=1.993x10^{-26}kg m_O=15.995u=2.656x10^{-26}kg.
- Find the energies of the lowest 3 rotational energy levels.
- Express the results in eV
- Find the wavelength of the photon emitted in the transition from *l=2* to *l=1*
- *Find the force constant of the CO atom if spacing of the vibrational energy levels is 0.2690 eV*

$$a)\ \ m_r = 1.139 \times 10^{-26} kg$$

$$I = m_r r_0^{\ 2} = 1.449 \times 10^{-46}$$

$$E_l = l\left(l+1\right)\frac{\hbar^2}{2I} = l\left(l+1\right)0.2395 \times 10^{-3} eV$$

$$E_0 = 0;\ E_1 = 0.479 meV;\ E_2 = 1.437 meV$$

$$b) E = E_2 - E_1 = 0.958 meV$$

$$\lambda = \frac{hc}{E} = 1.29 mm$$

Compare this to the atomic transitions?

Does the result make sence?

Suggest a method for measuring the moment of inertia of the molecules, measuring the distances between the atoms in a molecule.

$$k' = m_r \left(\frac{\Delta E}{\hbar}\right)^2 = 1902 \frac{N}{m}$$

Rotation and vibration combined

When we include both rotation and vibration, the energy levels for the diatomic molecule are:

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

Energies of the visible spectrum $1.77 - 3.10\ eV$

The spacing between the vibrational levels is of the order of hundreds of meV

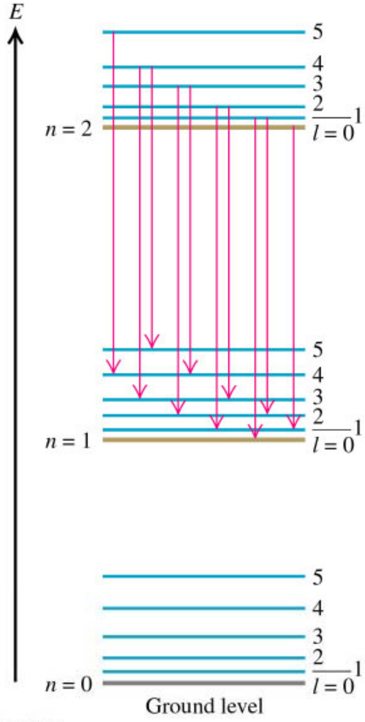
The spacing between the rotational levels are of the order of fraction of meV or hunrdeds of μeV.

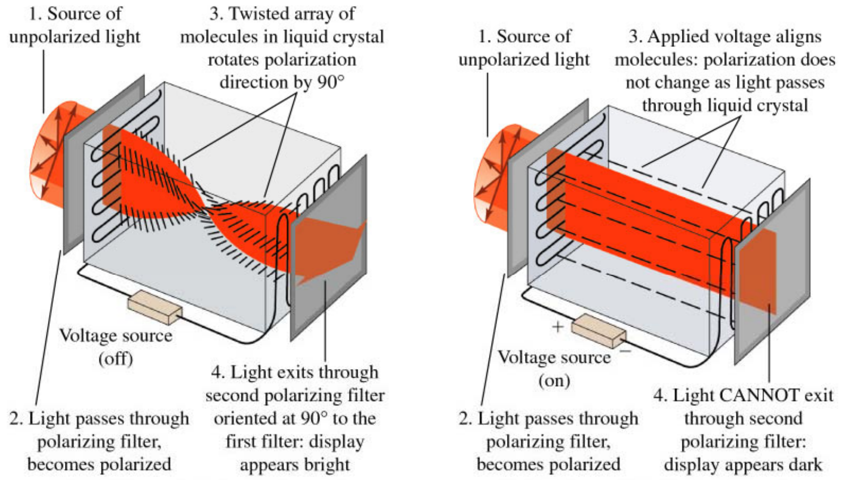
Combining the two we can graph the sectrum of the diatomic molecules.

Same selection rules apply as seen in hydrogen atom. Why?

$$\Delta l = \pm 1$$

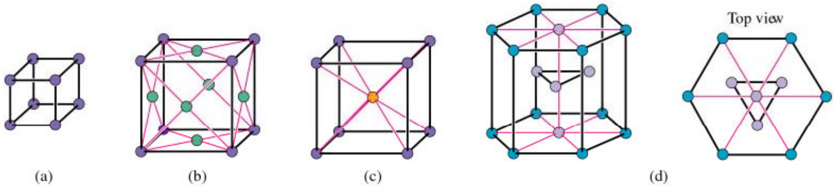
$$\begin{cases} \Delta n = +1 \text{ if a photon is absorbed} \\ \Delta n = -1 \text{ if a photon is emitted} \end{cases}$$

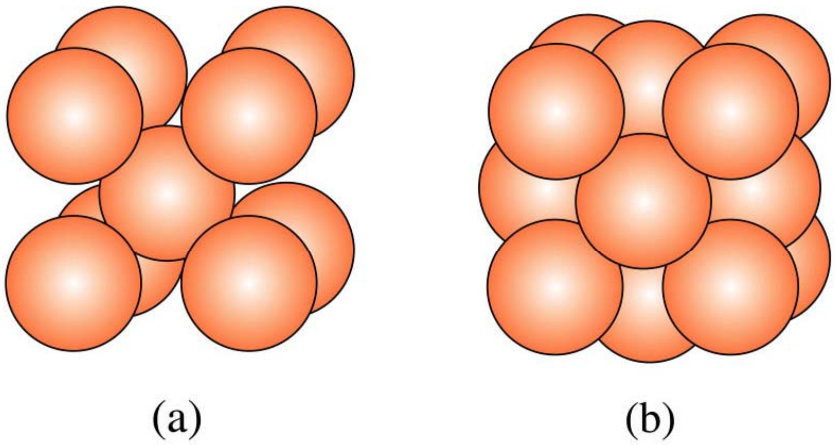


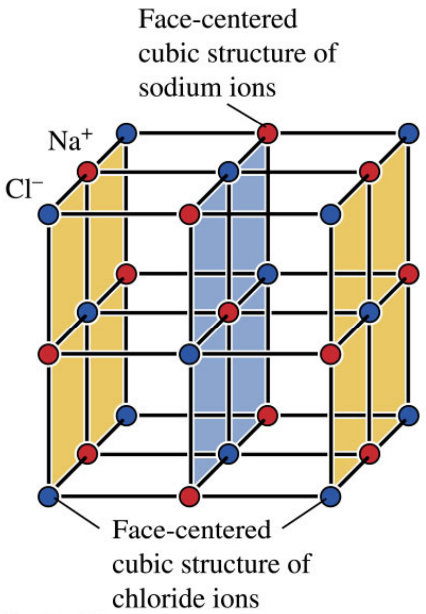


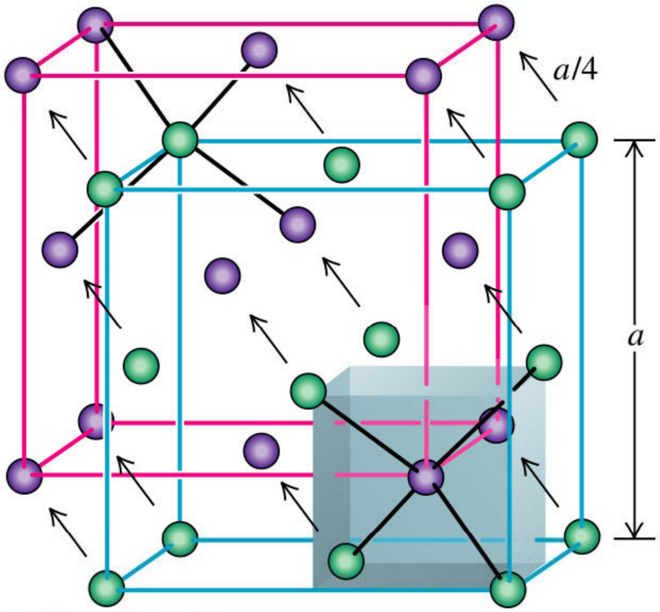
(a) Liquid crystal display (voltage off)

(b) Liquid crystal display (voltage on)


Top view
(a)
(b)
(c)
(d)


(a)
(b)


Face-centered
cubic structure of
sodium ions
Na+
Cl−
Face-centered
cubic structure of
chloride ions



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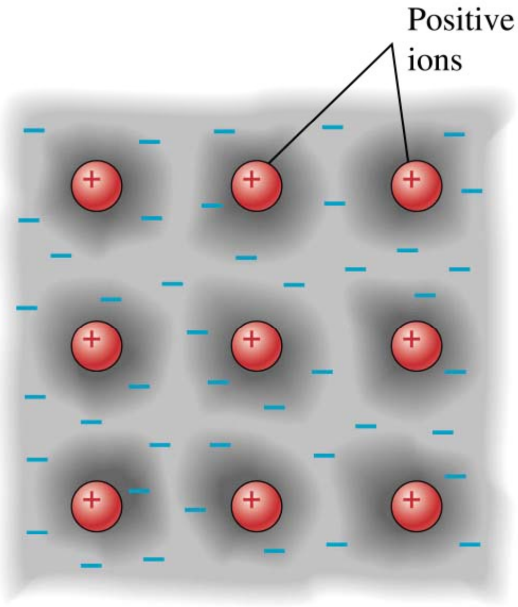
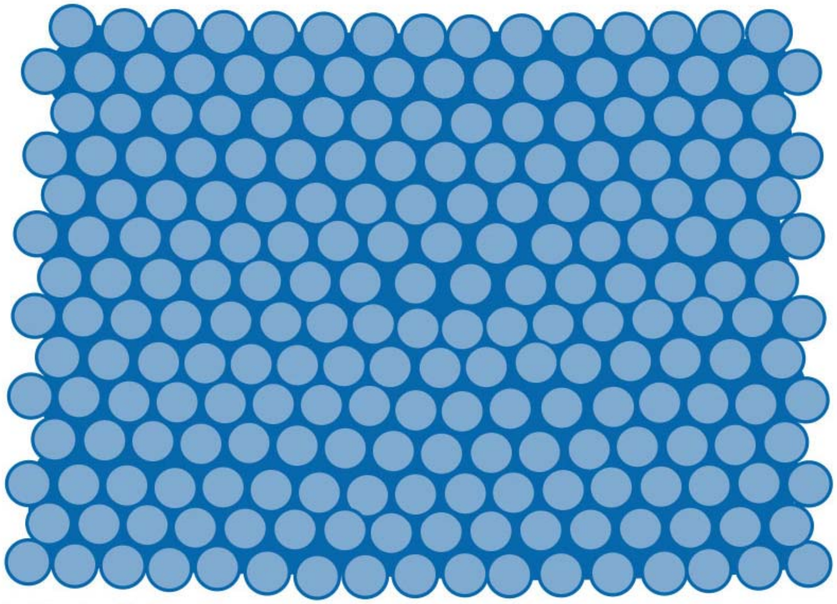
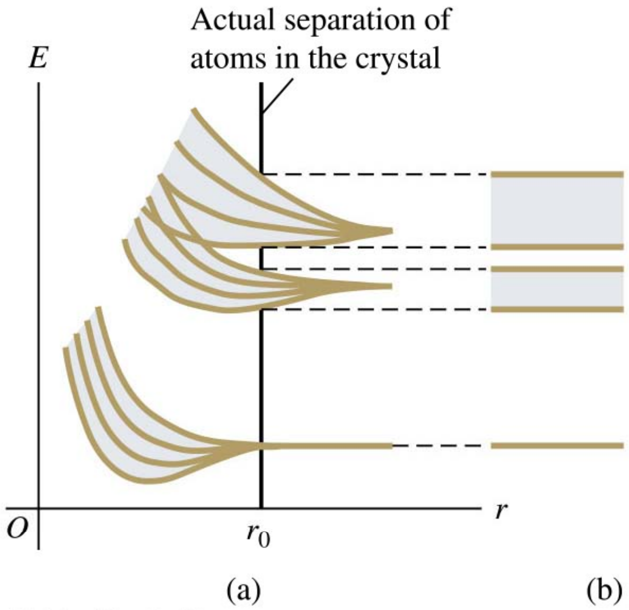
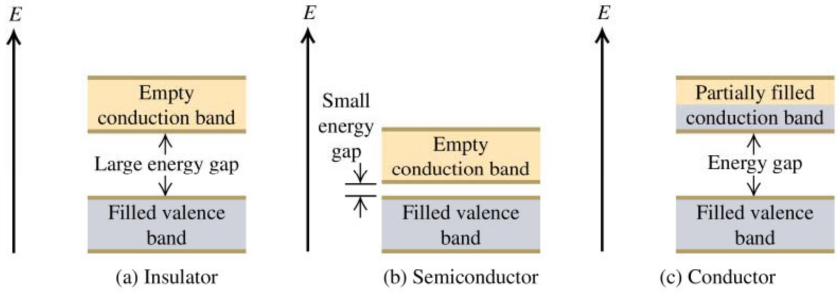
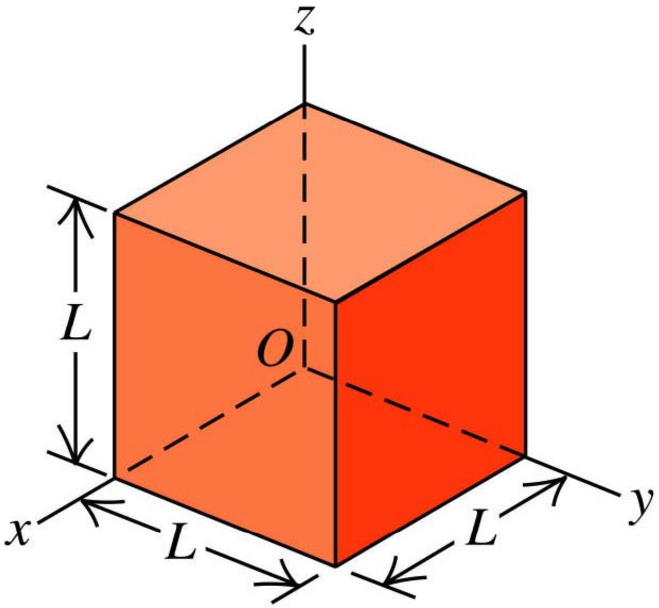
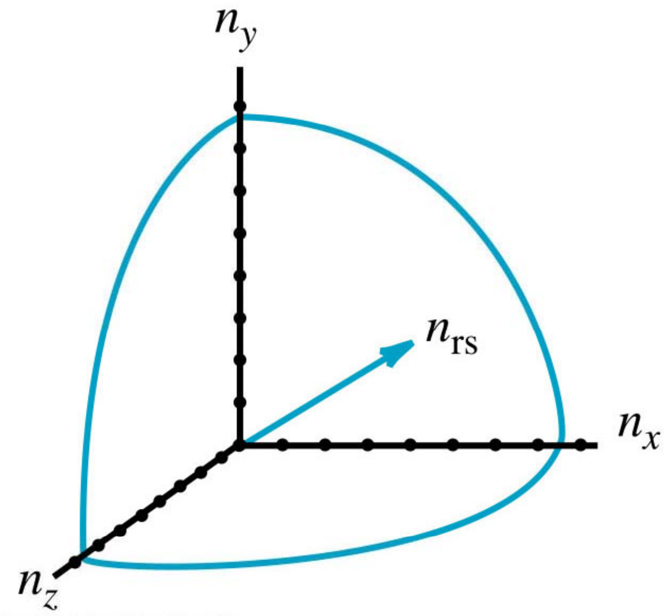

Positive ions

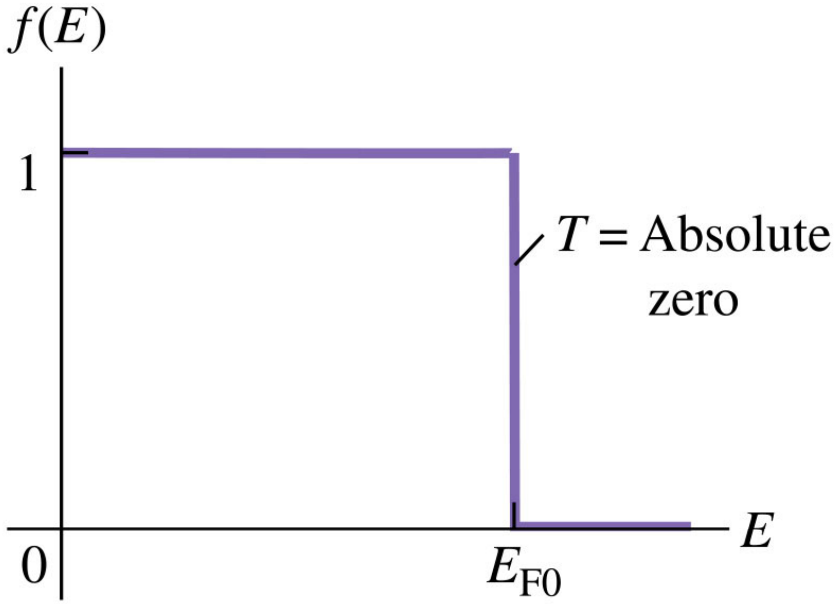


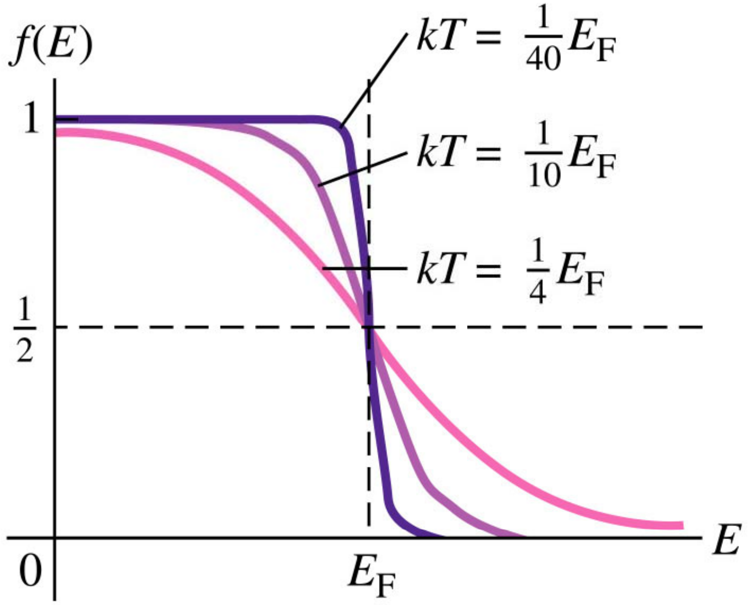

Actual separation of atoms in the crystal
E
O
r_0
r
(a)
(b)

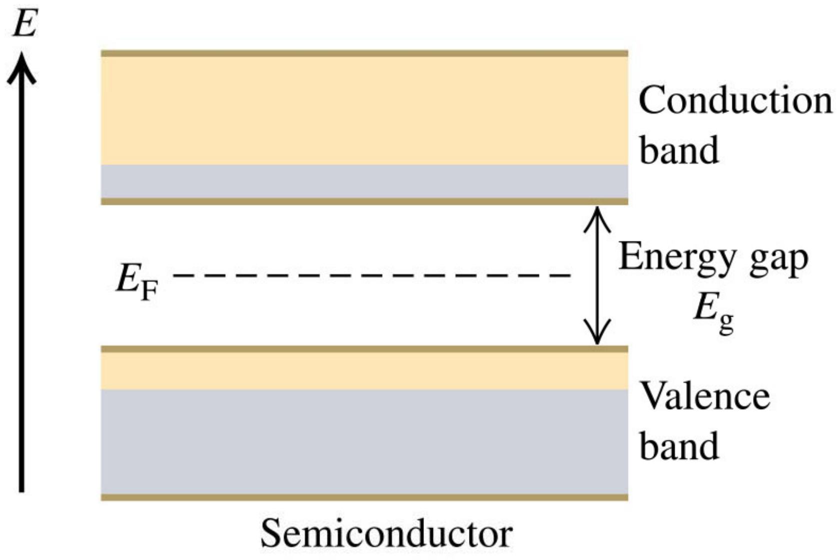

E
Empty
conduction band
Large energy gap
Filled valence
band
(a) Insulator
E
Small
energy
gap
Empty
conduction band
Filled valence
band
(b) Semiconductor
E
Partially filled
conduction band
Energy gap
Filled valence
band
(c) Conductor

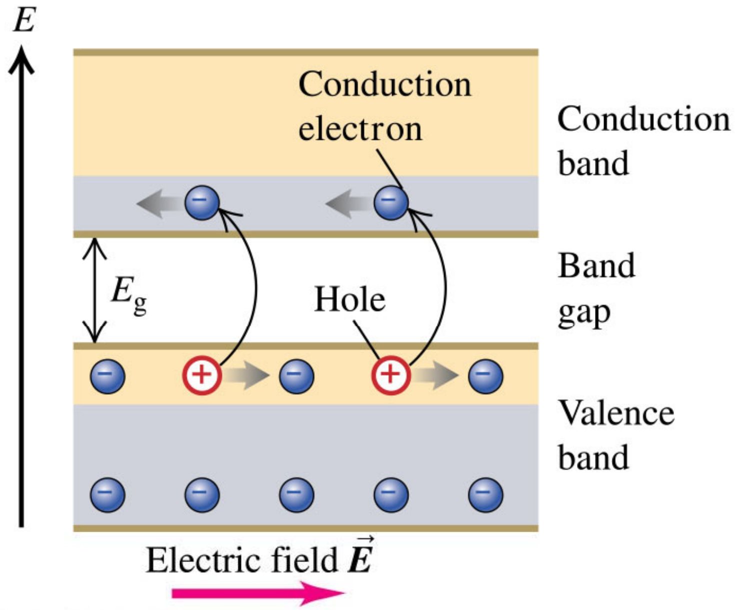

z
L
O
x
L
y
L


n_y
n_{rs}
n_x
n_z

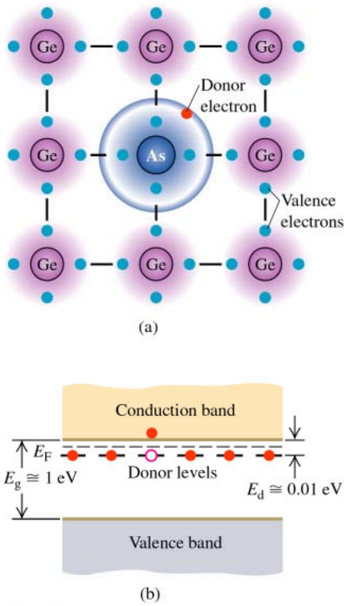

f(E)
1
T = Absolute zero
0
E
E_F0


$f(E)$
$kT = \frac{1}{40}E_F$
1
$kT = \frac{1}{10}E_F$
$kT = \frac{1}{4}E_F$
$\frac{1}{2}$
0
E_F
E


E
Conduction band
Energy gap E_g
E_F
Valence band
Semiconductor

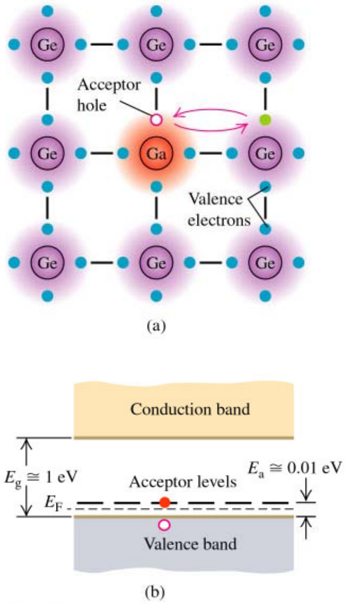


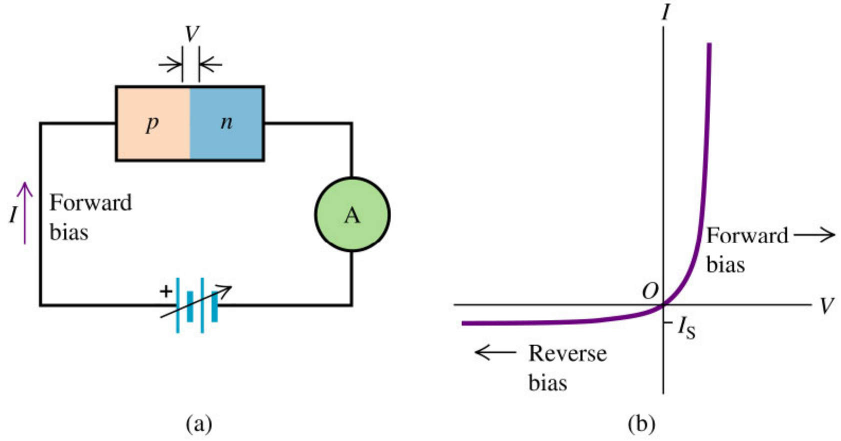
E
Conduction electron
Conduction band
E_g
Hole
Band gap
Valence band
Electric field $\vec{E}$

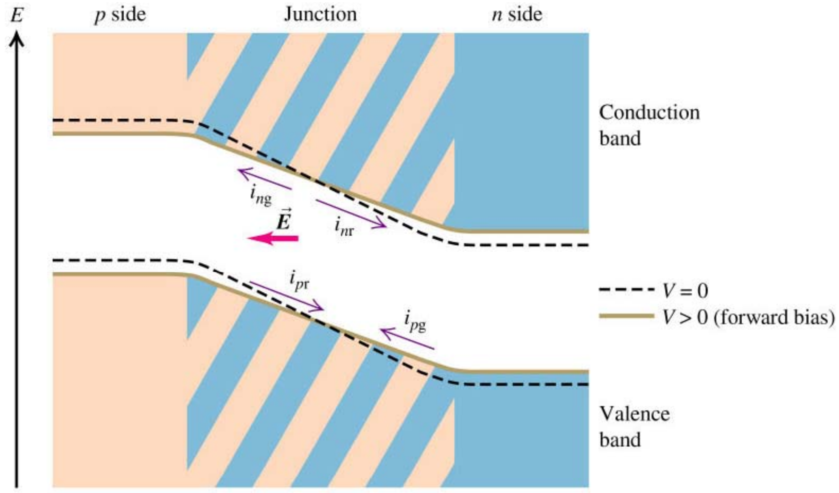

Ge
As
Donor electron
Valence electrons
Conduction band
E_F
$E_g \cong 1$ eV
Donor levels
$E_d \cong 0.01$ eV
Valence band

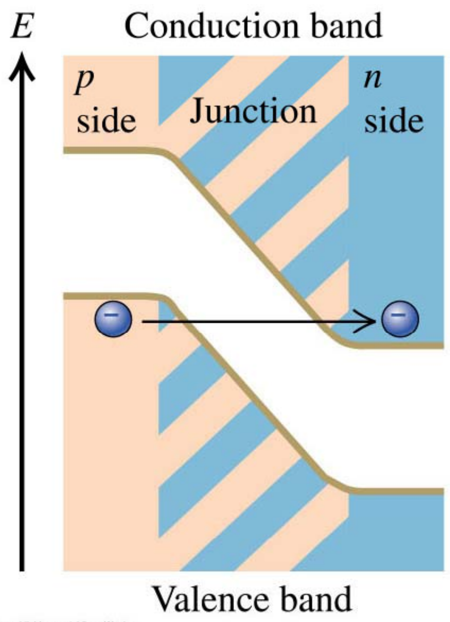
(a)

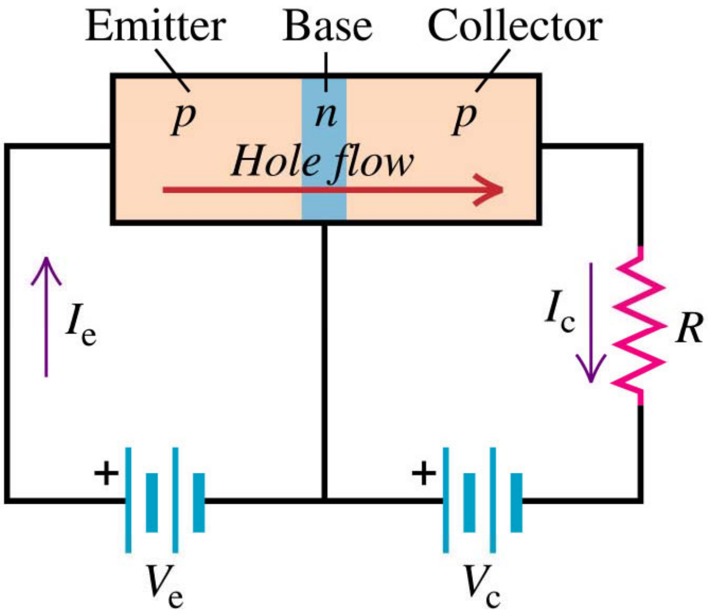
(b)

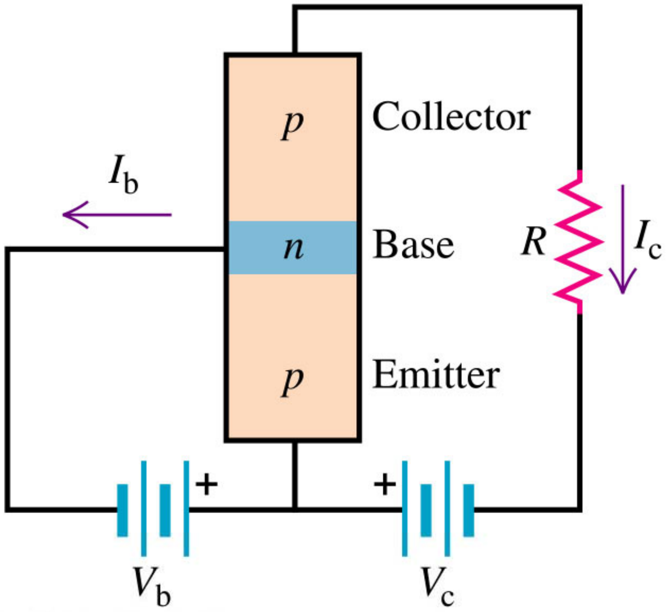

Ge
Ga
Acceptor hole
Valence electrons
(a)
Conduction band
$E_g \cong 1$ eV
E_F
Acceptor levels
$E_a \cong 0.01$ eV
Valence band
(b)

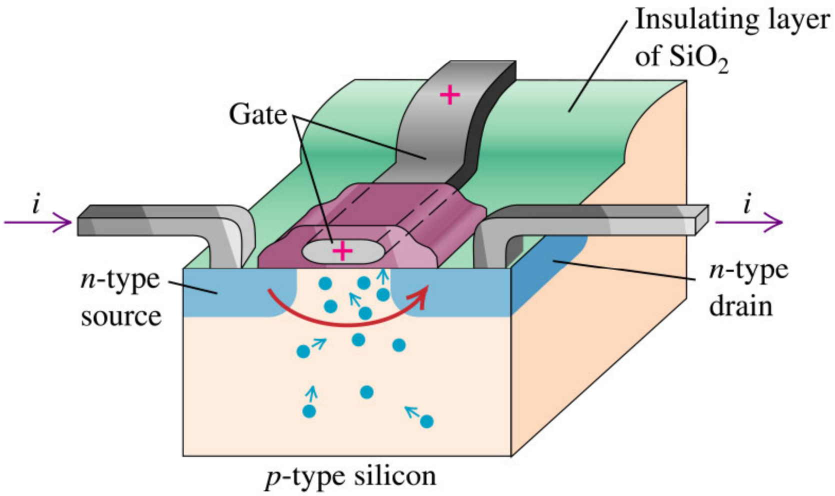
V
p
n
I
Forward bias
A
+
(a)
I
O
V
$-I_S$
Forward bias
Reverse bias
(b)

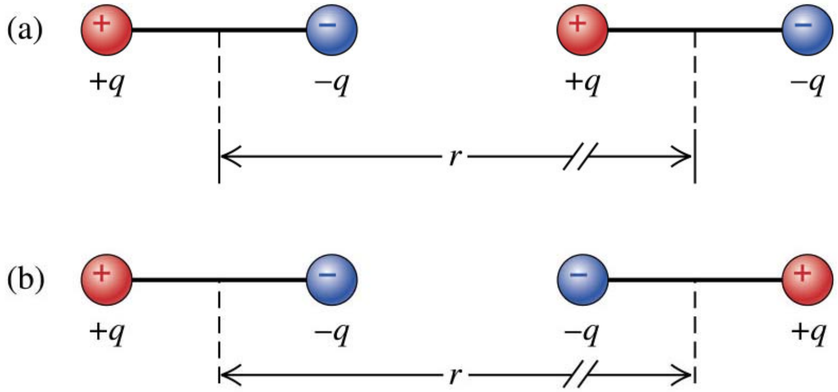

E
p side
Junction
n side
Conduction band
i_{ng}
$\vec{E}$
i_{nr}
i_{pr}
i_{pg}
$V = 0$
$V > 0$ (forward bias)
Valence band


E
Conduction band
p
side
Junction
n
side
Valence band


Emitter
Base
Collector
p
n
p
Hole flow
I_e
I_c
R
+
+
V_e
V_c


p
Collector
I_b
n
Base
R
I_c
p
Emitter
+
+
V_b
V_c


Insulating layer of SiO_2
Gate
+
+
i
i
n-type source
n-type drain
p-type silicon


(a)
+q
−q
+q
−q
r
(b)
+q
−q
−q
+q
r