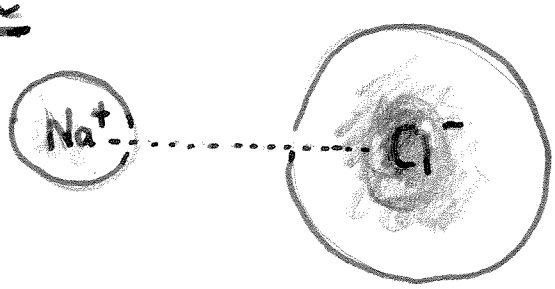
LECTURE 17. MOLECULES AND CONDENSED MATTER.

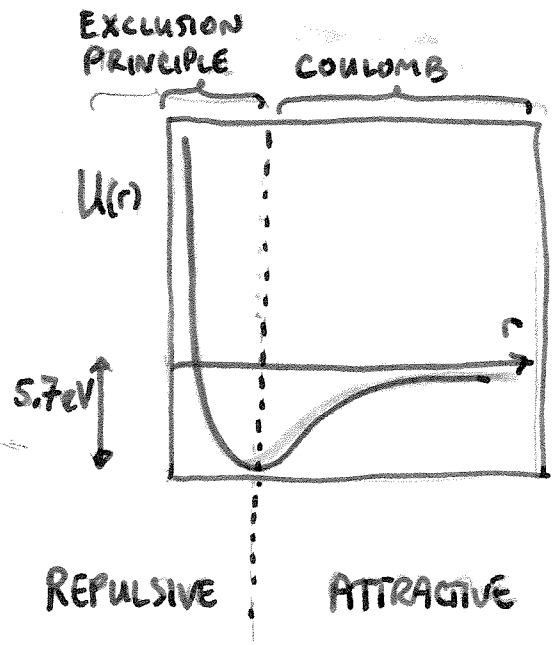
The orbital picture of electrons in atoms can be extended, first to molecules, then to crystals. Remarkably, the same laws which work for one, two, ten electrons, continue working, as far as we know, to vast assemblies of electronic matter — even life itself. We call such matter "condensed matter".

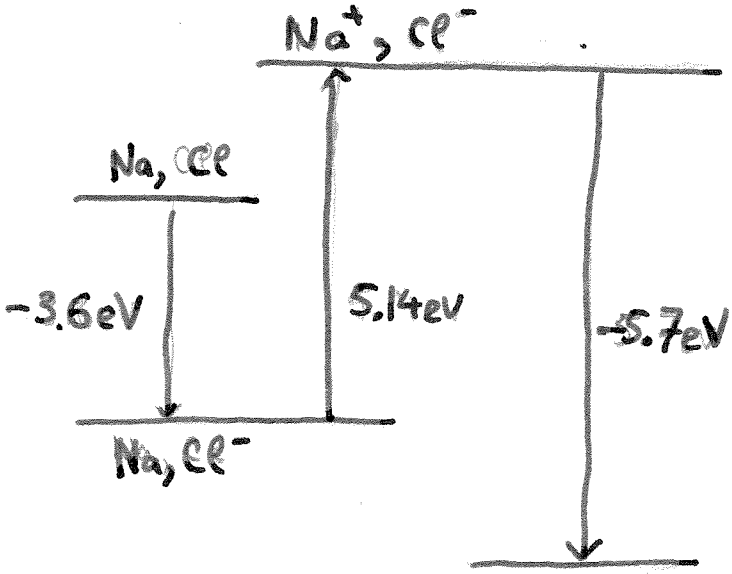
Today we will learn about the nature of the chemical bond, about molecules and the concept of electron energy bands.

42.1 Molecular Bonds

IONIC

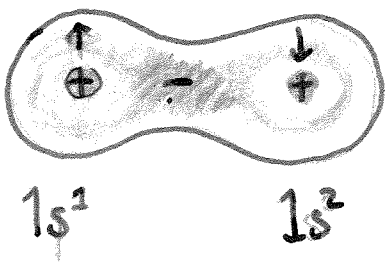






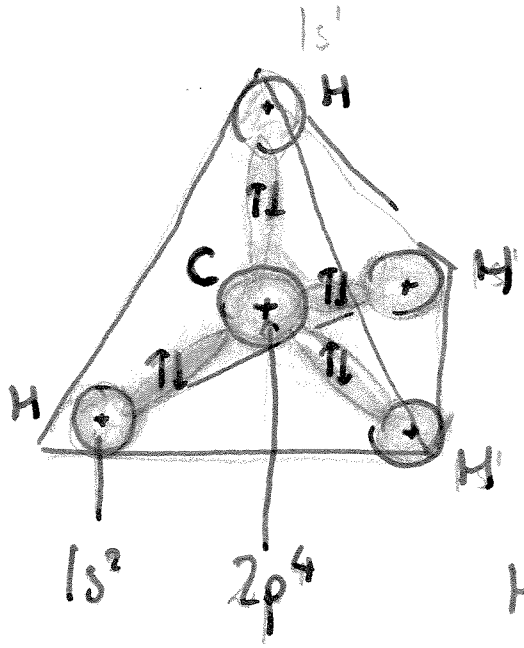
COVALENT

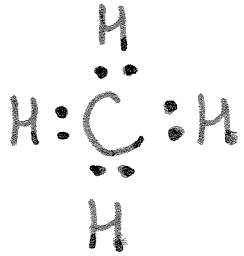
H_2



H : H

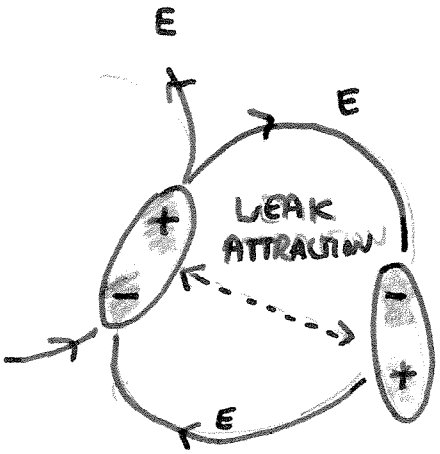
CH_4.





Van der Waals

No dipole moment in isolation



Fluctuations in dipole moment

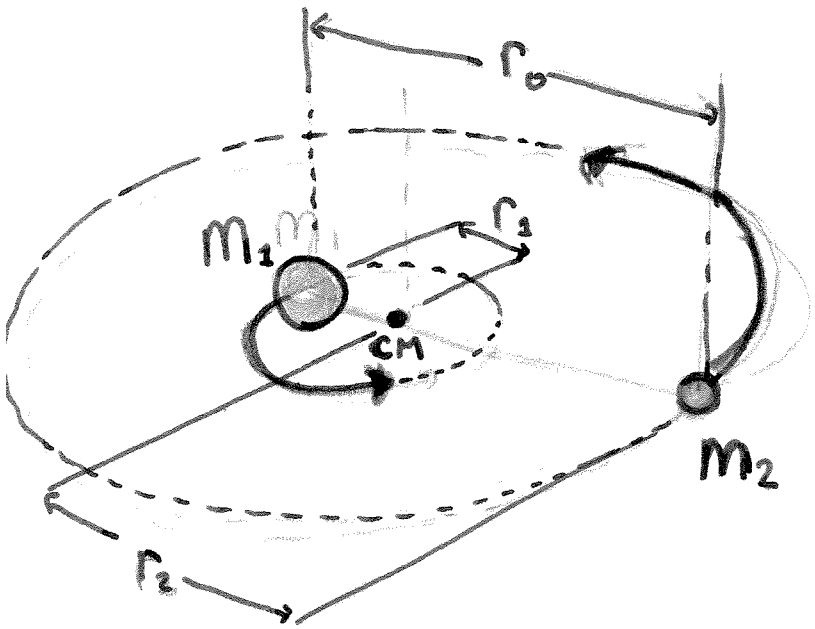
→ ATTRACTION $U \sim -\frac{1}{r^6}$

$U_{\text{ionic, covalent}} \sim 5\ eV$

$U_{VDW} \sim 1/10\text{th}\ eV$

42.2 Molecular Spectra

ROTATION

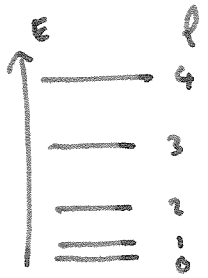


$E = \frac{1}{2} I \omega^2$; $L = I\omega$

$$E = \frac{L^2}{2I}$$

$$L^2 = \hbar^2 \ell(\ell+1)$$

$$E_\ell = \frac{\hbar^2}{2I} \ell(\ell+1)$$



$(\ell = 0, 1, 2, 3 \ldots)$

REDUCED MASS

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

Both atoms rotate about the CENTER OF MASS.

$$r_1 = \frac{m_2}{m_1+m_2} r_0$$

$$r_2 = \frac{m_1}{m_1+m_2} r_0$$

$$I = m_1 r_1^2 + m_2 r_2^2$$

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

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

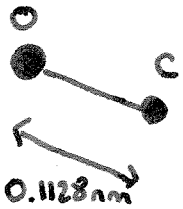
$(m_1 r_1 = m_2 r_2)$

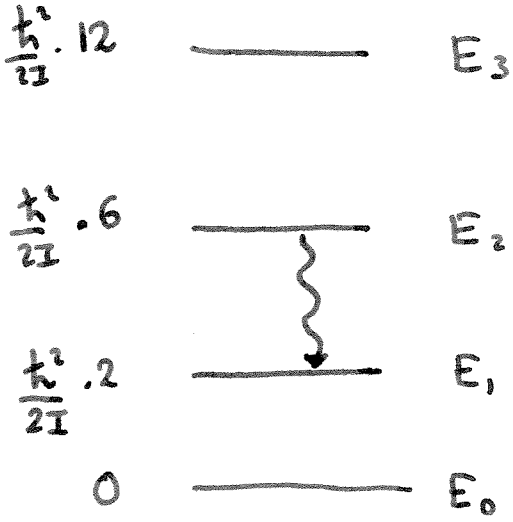
$r_1 + r_2 = r_0$

e.g CARBON MONOXIDE.

$m_O = 2.656 \times 10^{-26}$ kg (12u)

$m_C = 1.993 \times 10^{-26}$ kg (15.995u)





$$m_r = \frac{m_O m_C}{m_O + m_C} = \frac{2.656 \times 1.993}{2.656 + 1.993} \times 10^{-26}$$

$$= 1.139 \times 10^{-26} \text{ kg}.$$

$$I = m_r r_0^2 = 1.139 \times 10^{-26} \text{ kg} \times (0.1128 \times 10^{-9} \text{ m})^2$$

$$= 1.449 \times 10^{-46} \text{ kg m}^2$$

$$\frac{\hbar^2}{2I} = \frac{(1.0546 \times 10^{-34})^2}{2 \times (1.449 \times 10^{-46})} = 3.838 \times 10^{-23} \text{ J}$$

$$E_\ell = \frac{\hbar^2}{2I} \ell(\ell+1)$$

$$\frac{\hbar^2}{2I} = \frac{3.838 \times 10^{-23}}{1.602 \times 10^{-19}} = 0.2395 \times 10^{-4} \text{ eV}$$

$$= 0.2395 \text{ meV}$$

$E_0 = 0$

$E_1 = 0.2395 \times 2 = 0.479$ meV

$E_2 = 0.2395 \times 6 = 1.437$ meV

$E = E_2 - E_1 = 0.958$ meV

$$\lambda = \frac{hc}{E} = \frac{4.136 \times 10^{-15} \text{ eVs} \; (3 \times 10^8)}{0.958 \times 10^{-3} \text{ eV}}$$

$$= 1.29 \times 10^{-3} \text{ m} = \underline{1.29 \text{ mm}}$$

e.g II. What is the frequency of a photon associated with the transition $\ell \to \ell - 1$?

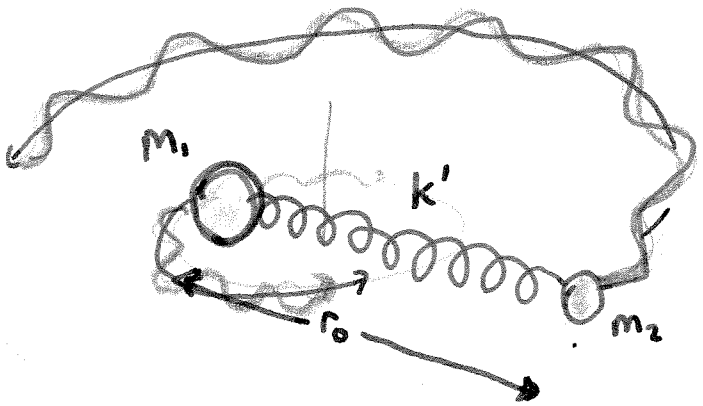
$$\Delta E = E_\ell - E_{\ell-1} = \frac{\hbar^2}{2I}\left[\ell(\ell+1) - (\ell-1)\ell\right]$$

$$= \frac{\hbar^2}{2I}\, 2\ell = \frac{\hbar^2}{I}\,\ell$$

$$hf = \Delta E = 2\pi\hbar f$$

$$f = \frac{\hbar^2}{2\pi\hbar I}\,\ell = \underline{\frac{\hbar}{2\pi I}\,\ell}$$

Vibrational Energy levels



$$\omega = \sqrt{\frac{k'}{m_r}}$$

$$\boxed{E_n = \left(n + \frac{1}{2}\right)\hbar\omega}$$

HARMONIC OSCILLATOR ENERGY LEVELS.

$$\boxed{\Delta E = \hbar\omega}$$

$\frac{7}{2}\hbar\omega$ ——— 3

$\frac{5}{2}\hbar\omega$ ——— 2

$\frac{3}{2}\hbar\omega$ ——— 1

$\frac{1}{2}\hbar\omega$ ——— 0

e.g in CO

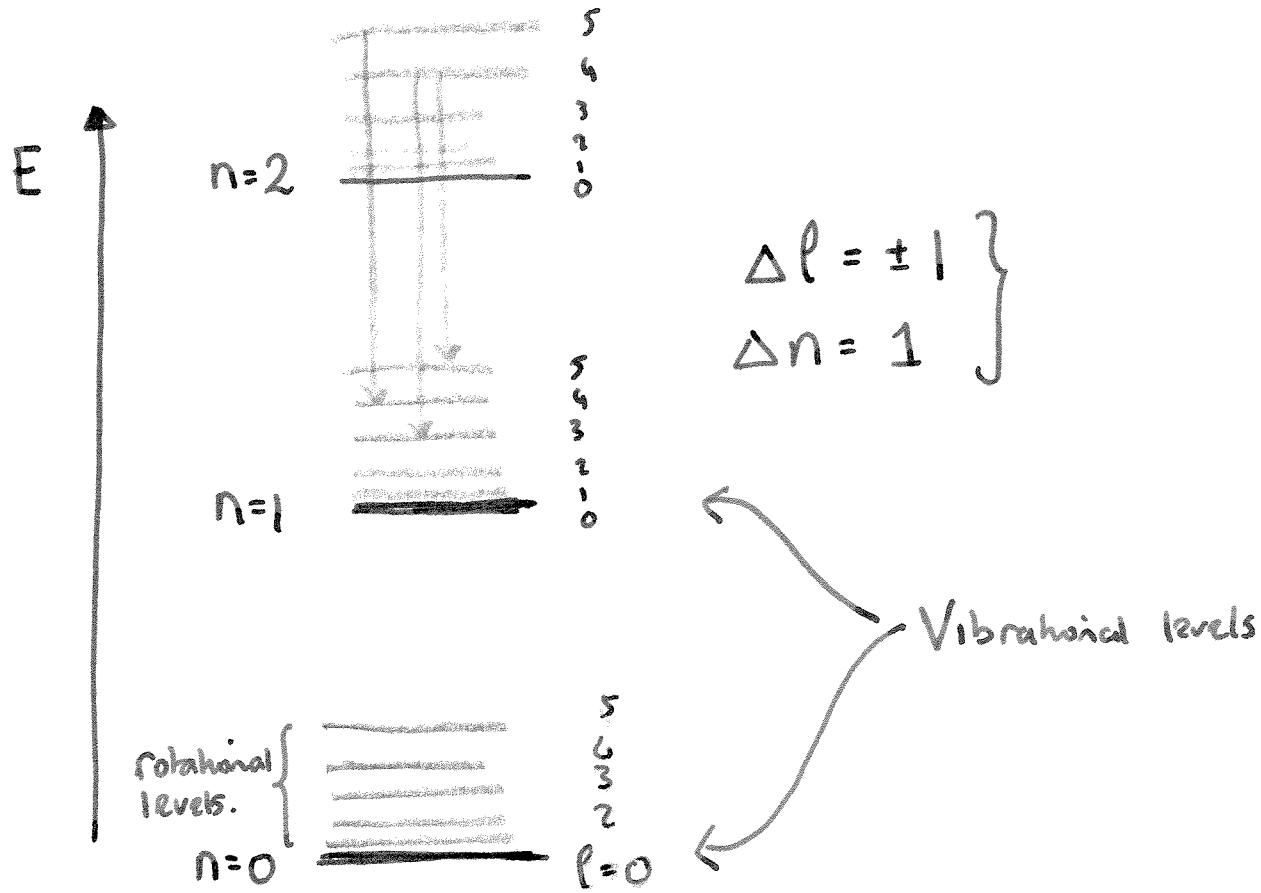
$\Delta E = 0.2690$ eV

What is the force constant?

$$\Delta E = \hbar\sqrt{\frac{k'}{m_r}}$$

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

$$= \left(\frac{0.2690\ \text{eV}}{6.582\times10^{-15}\ \text{eVs}}\right)^2 \times 1.139\times10^{-26}\ \text{kg} = 1902\ \text{N/m}$$

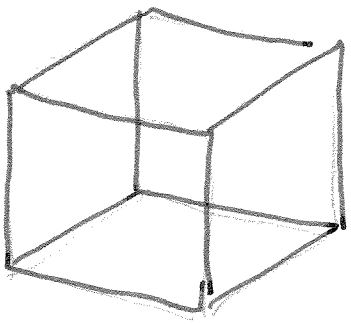


$$E_{nl} = \left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k'}{m_r}} + \frac{\hbar^2}{2I}\,l(l+1)$$

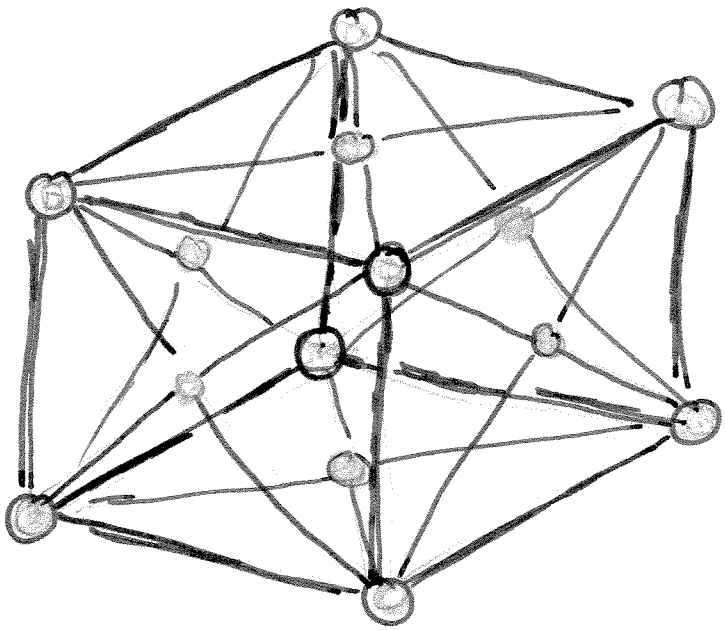
42.3

Crystalline solid	long range order	NaCl
Amorphous solid	short range order	GLASS

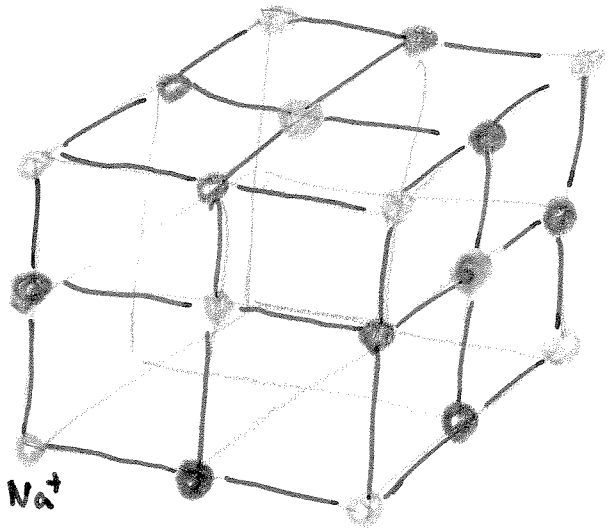
Glass ~ viscous liquid



Simple cubic



face-centered cubic Al, Ca, Cu, Ag



Rock salt NaCl

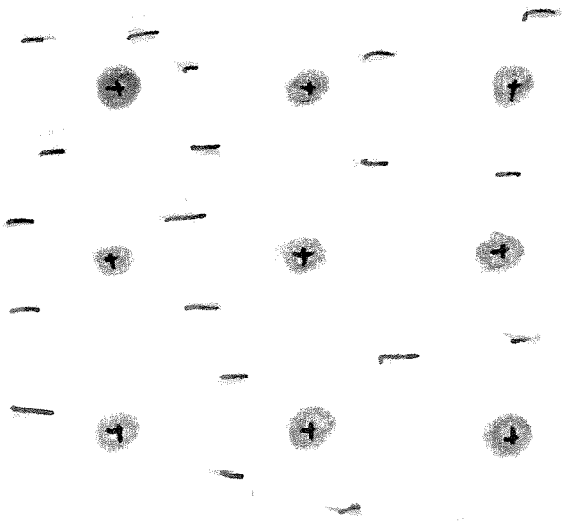
= Two interpenetrating FCC lattices.

Ionic
Covalent
Metallic
} crystals

Ionic crystals ——— Na^+Cl^-

Covalent crystals ——— diamond C, Si, Ge

Metallic crystals ——— Al, Ca, Cu

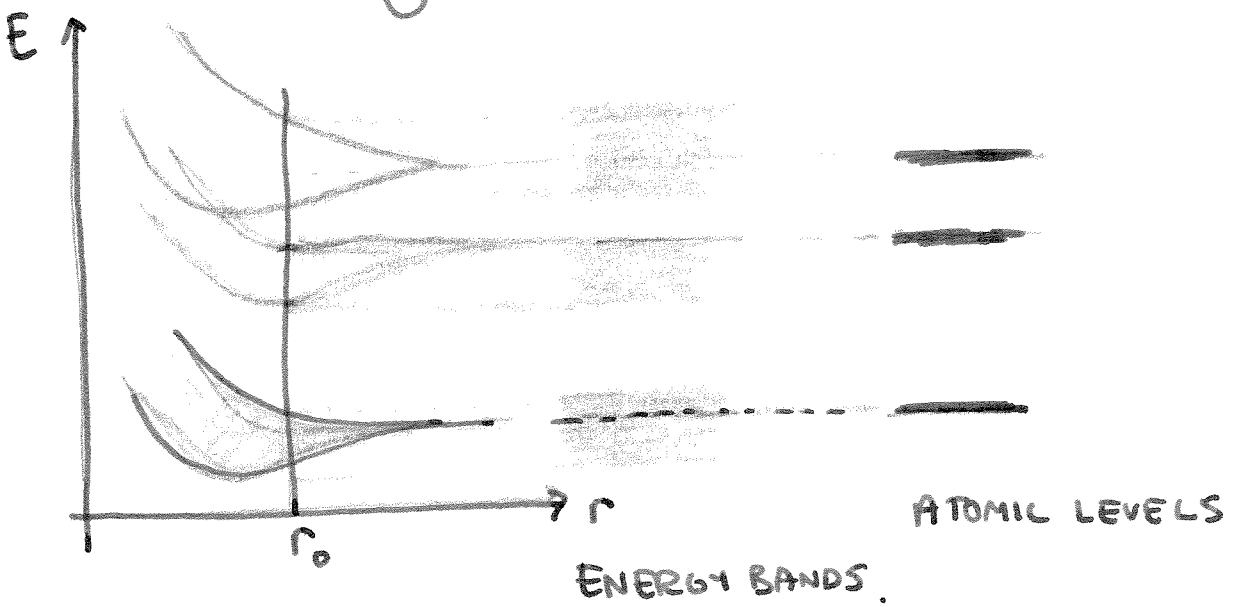


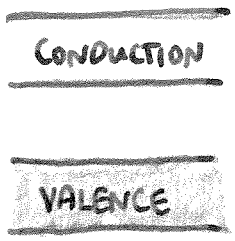
metallic crystal —

negatively charged electrons move freely through the lattice.

42.4 ENERGY BANDS

In isolation, the energy levels of atoms are sharp. When we push the atoms together, the electrons start to "hop" between the atomic states, broadening them into ENERGY BANDS

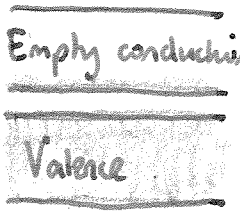




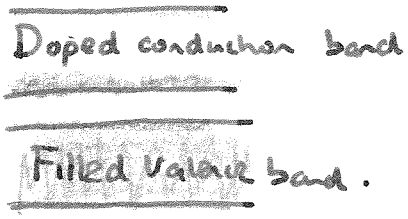
LARGE ENERGY GAP

INSULATOR

(A) INSULATOR



SMALL ENERGY GAP



(B) SEMICONDUCTOR

(D) DOPED SEMICONDUCTOR

Partially Filled conduction band.

Filled Valance Band

(C) METAL