

# Interatomic Forces

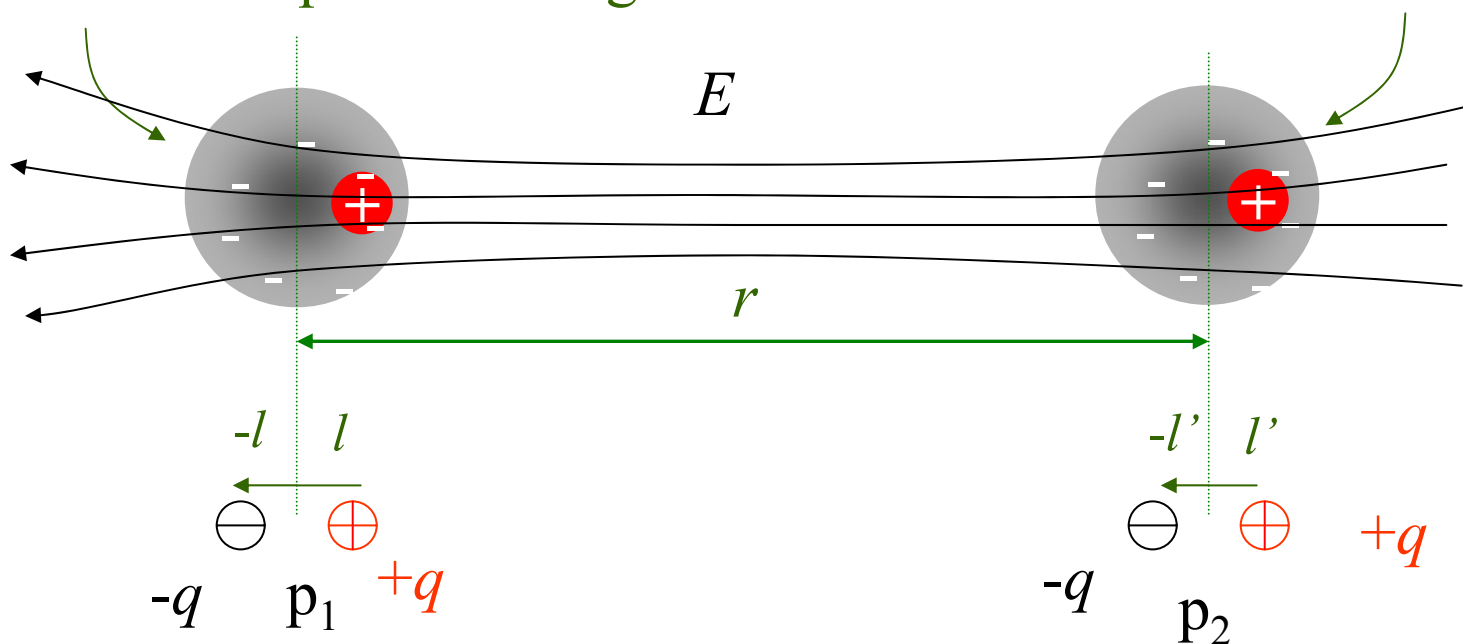
## Overview

- Van der Waals (short range  $V \sim 1/r^6$ , weak  $\sim 0.01-0.1$  eV)
- Ionic (long range,  $V \sim 1/r$ , strong  $\sim 5-10$  eV)
- Metallic (no simple dependence,  $\sim 0.1$  eV)
- Covalent (no simple dependence, directional,  $\sim 3$  eV)
- Hydrogen (partially ionic and covalent)

## Van der Waals: related to dipole-dipole interactions

Fluctuation separates charge

Induced charge separation



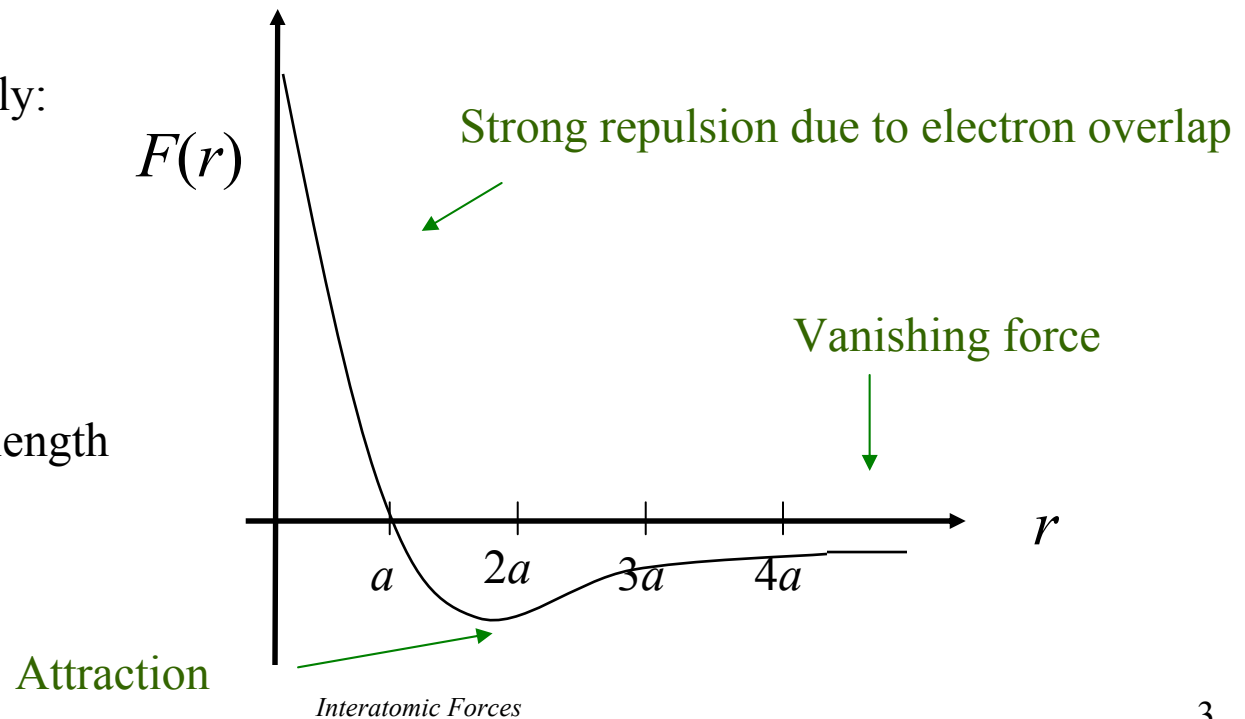
Separate the molecules by some distance, a weak **ATTRACTION** is produced due to molecular structure and Coulomb's law. The internal motion of the nucleus and electron cloud that can give attraction. This force is called the **VAN DER WAALS** force and is the attractive part of the  $L$ - $J$  potential

From observation we know that:

- Molecules repel if too close together due to electrostatic repulsion of electron clouds ( $r \sim 1-2 \text{ \AA}$ )
- In solids and liquids the molecules tend to ‘stick’ together so at some  $r$  molecules must **attract** each other
- At very large  $r$  there is no discernable force

Expressed graphically:

Take some standard length  
 $a$  as a unit of  $r$



Mathematical representation:

$E$  – electric field,  $p$  – dipole moment,  $q$  - charge

$E \sim p_1/r^3$  (follows from  $F \sim qE \sim q^2/r^2$ ), hence

$p_2 \sim \alpha p_1/r^3$ ,  $\alpha$  - polarisability

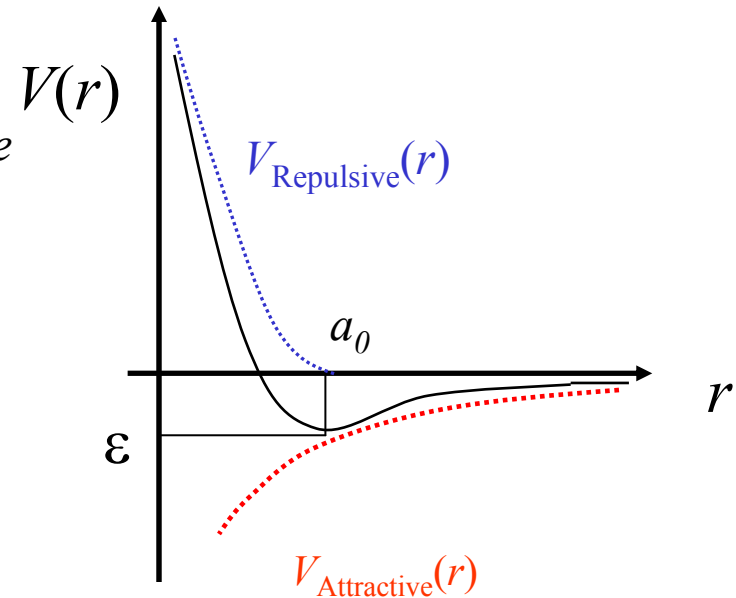
$V \sim pE \sim A/r^6$

$V(r) = V_{\text{Repulsive}}(r) + V_{\text{Attractive}}(r)$

$$V(r) = A \left( \frac{1}{r} \right)^n - B \left( \frac{1}{r} \right)^6, \quad n > 9$$

or

$$V(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^n - \left( \frac{\sigma}{r} \right)^6 \right]$$



Most commonly  $n=12$  is used (“6-12” potential mostly for convenience of calculations). In general symbols  $p$  and  $q$  can be used (“ $p$ - $q$ ” potential) For repulsion  $\sim e^{-r/a}$  dependence is also sometimes used (due to fall off in charge density in the outer edge of electron clouds of each molecule as they overlap)

- The ‘ $p$ - $q$ ’ potential is just one example of an infinite set of mathematical functions that might represent a molecular pair-potential
- For INERT GASES this is a good representation of potential between molecules because these gases comprise single atoms
- Often use the LENNARD-JONES potential (often called the ‘6-12’ potential) to describe inert gases:

$$V(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$

This is sometimes written in terms of the distance  $a$  at which  $V(r)$  is zero

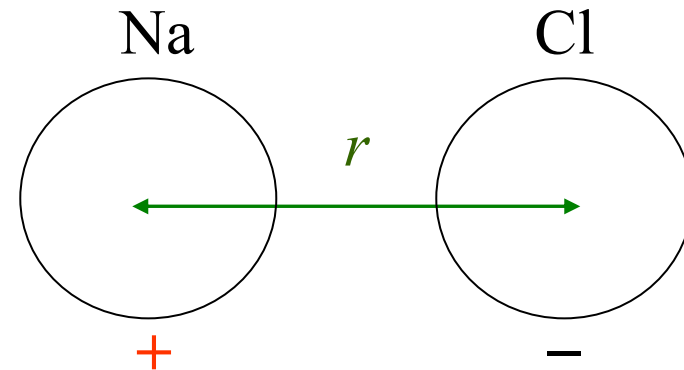
**IONIC FORCES:** in substances like Sodium Chloride or the alkali halides generally, the effect of internal structure is different. Instead of metal Na and Cl atoms, it is energetically favourable for an electron to leave the Sodium cloud to join the chlorine electron cloud leaving two **charged** ions:

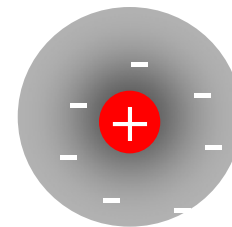
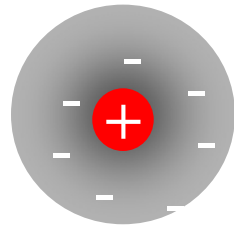
$$F(r) = F_{\text{Repulsion}} + F_{\text{Coulomb}}$$

$$V(r) = V_{\text{Repulsion}} + V_{\text{Coulomb}}$$

$$V(r) = \frac{\lambda}{r^p} - \frac{e^2}{4\pi\epsilon_0 r}$$

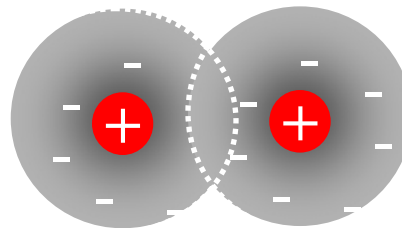
Constants





$$F(r) = \frac{q_1 q_2}{4\pi\epsilon_0 r^2}$$

The fundamental force here is the **ELECTROSTATIC COULOMB** force between point charges.

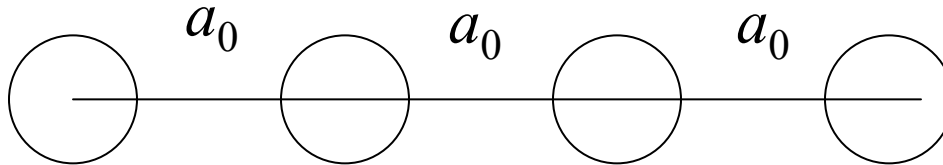


Electron clouds overlap  $\Rightarrow$  **DENSITY** of  $-ve$  charge in the outer edge of the molecule varies rapidly ( $\propto \exp[-r/a]$ )  $\Rightarrow$  strong repulsion

- van der Waals binding energies in the range 0.01 – 0.1 eV
  - Coulomb energy is typical of the energy it takes to pull an electron out of an atom  $\approx 5- 10$  eV
- $\Rightarrow$  IONIC FORCES are much stronger than van der Waals

$$|V_{\text{vdW}}(r)| \ll |V_{\text{Coulomb}}(r)|$$

- $V_{\text{vdW}}(a_0) = -\varepsilon$



$$V_{\text{vdW}}(2a_0) \approx -2\varepsilon \left( \frac{a_0}{2a_0} \right)^6 \approx \frac{-\varepsilon}{32} \approx -0.03\varepsilon$$

$$V_{\text{vdW}}(3a_0) \approx -2\varepsilon \left( \frac{a_0}{3a_0} \right)^6 \approx \frac{-2\varepsilon}{3^6} \approx -0.003\varepsilon$$



$$V_{\text{Coulomb}}(a_0) = \frac{-e^2}{4\pi\epsilon_0 a_0}$$

$$\Rightarrow V_{\text{Coulomb}}(2a_0) = \frac{1}{2} V_{\text{Coulomb}}(a_0)$$

$$\Rightarrow V_{\text{Coulomb}}(10a_0) = \frac{1}{10} V_{\text{Coulomb}}(a_0)$$

Van der Waals forces are SHORT RANGED  
Coulomb forces are LONG RANGED

- A neutral molecule will exert significant force only on its nearest neighbour
- A charged ion can exert a strong force on another ion many neighbours away (causes problems in calculations)

**METALLIC BONDING:** another form of bonding by electron rearrangement. There is no simple  $L-J$  type expression for metallic bonding (some textbooks do use a 6-12 potential but it has no fundamental meaning as is the case for inert gases for example)

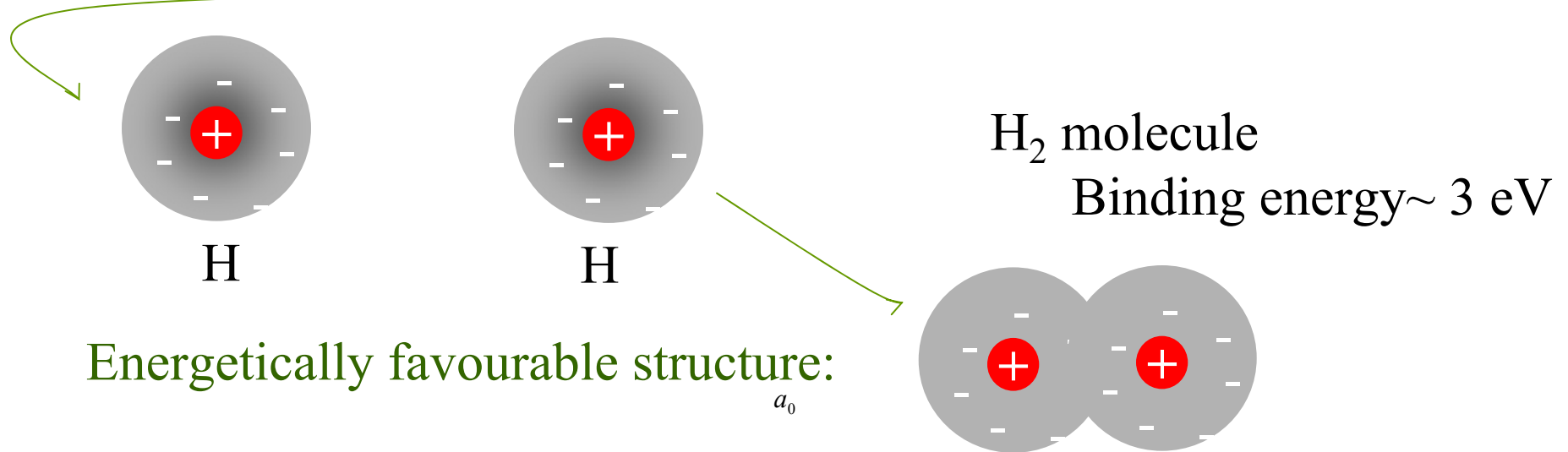
Electron gas 

### Metals:

- One or more loosely bound electrons
- Electrons detach (delocalisation) to form ‘electron gas’ surrounding the +ve ion
- Metal crystal behaves like a single giant molecule
- Repulsion on compression and attraction on extension
- Metallic bonding strong,  $\sim 0.1$  eV

**A FULL EXPLANATION OF METALLIC BONDING REQUIRES  
QUANTUM PHYSICS**

**COVALENT FORCES:** related to electrostatics and the internal structure of the molecules, e.g. H<sub>2</sub> molecule:

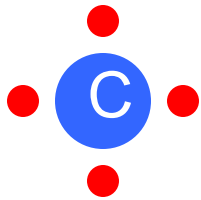


The electron cloud redistributes

The extra electron cloud between the nuclei 'SCREENS' the strong repulsion creating a strong COVALENT force

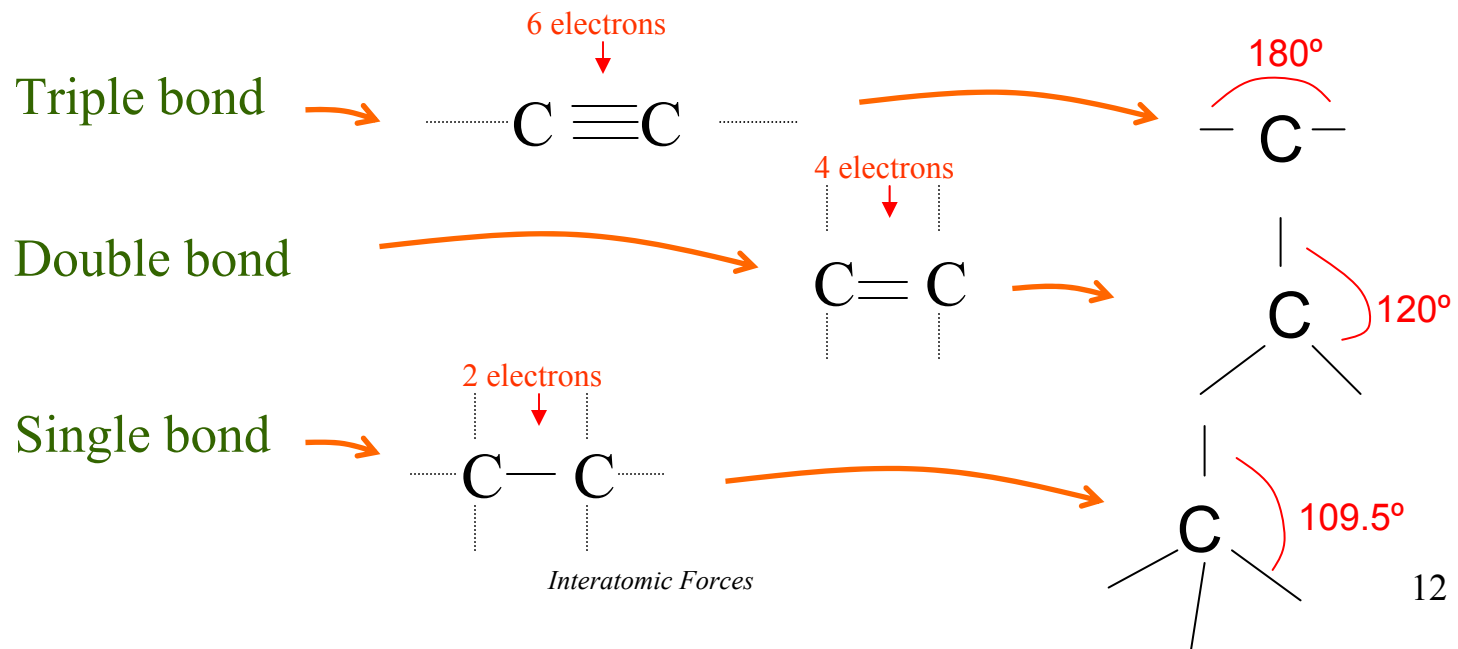
**A FULL EXPLANATION OF COVALENT BONDING REQUIRES QUANTUM PHYSICS**

# E.g. Carbon: covalently bonded material



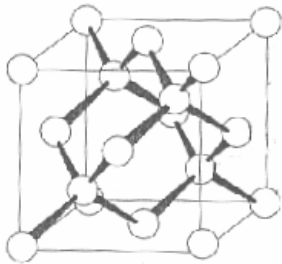
4 moveable  
outer electrons

IA	IIA	IIIB	IVB	VB	VI B	VII B	VIII B
H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar

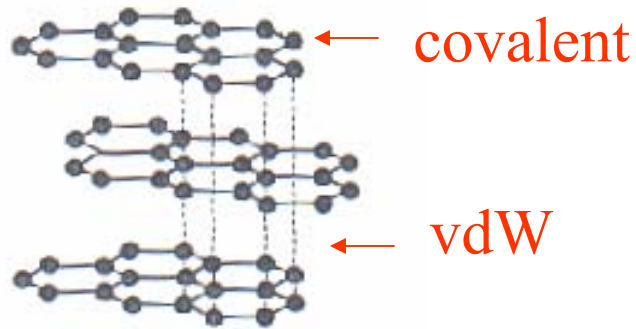


# Carbon allotropes

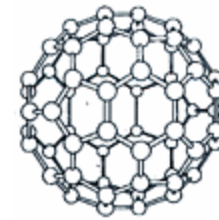
## Diamond



## Graphite



## Fullerenes

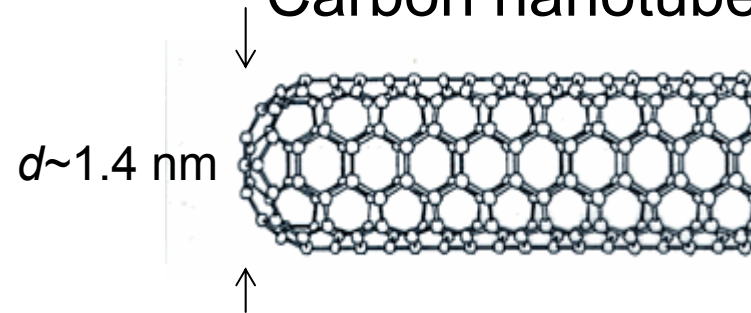


↓  
 $d=0.7 \text{ nm}$   
↑

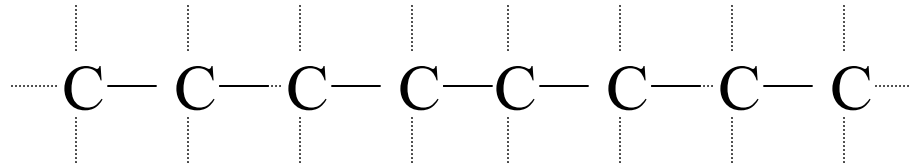
## Carbyne



## Carbon nanotubes



# Polymers

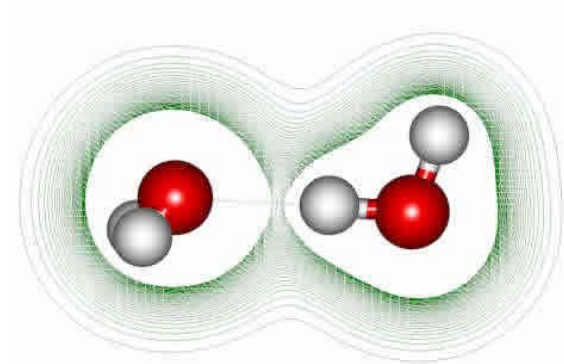
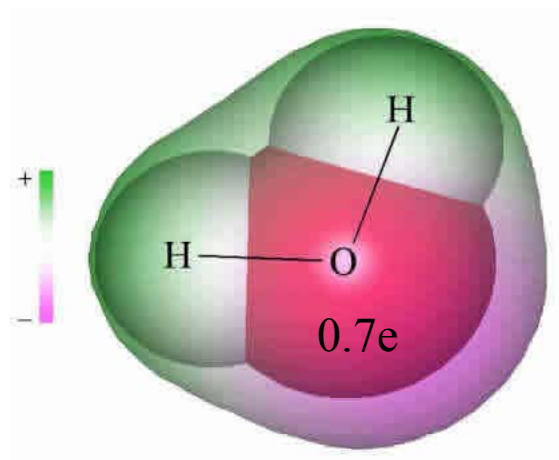
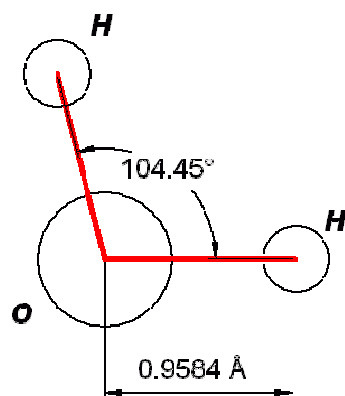


The COVALENT BOND is:

- Due to electron re-arrangement
- Strong
- Highly directional
- Cannot be represented by any simple mathematical force expression

**HYDROGEN BOND:** H atoms form single covalent bond to form  $H_2$ , but fully or partially ionised can form essentially ionic bonds with e.g. O ( $H_2O$ ), N ( $NH_3$ ) or F ( $HF$ ). Bond is part (about 90%) electrostatic and part (about 10%)

## The water molecule



# Summary

## LENNARD-JONES (6-12) POTENTIAL

### VAN DER WAALS bonding

- Between neutral atoms and molecules
- Strength  $\sim 0.01$  eV – 0.1 eV
- Short range
- E.g. Ar, Kr

Origin in fluctuation  
of electron cloud

$$V(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$

### IONIC bonding

- Between charged atoms
- Strength  $\sim 5$  eV
- Long range
- E.g.  $\text{Na}^+$ ,  $\text{Cl}^-$

Origin in electron transfer

$$V(r) = \frac{\lambda}{r^p} - \frac{e^2}{4\pi\epsilon_0 r}$$



# Summary contd.

## COVALENT bonding

- Origin in electron rearrangement (quantum mechanical)
- Strength  $\sim 3$  eV
- Short range
- Directional

## METALLIC bonding

- Origin in electron rearrangement (quantum mechanical)
- Strength  $\sim 0.1$  eV
- Short range

Next Topic: Interatomic forces contd