How do atoms bond to form solids?

Types of bonding:
• Van der Walls
• Ionic
• Metallic (delocalized)
• Covalent (directional)

The type of bonding in a solid is determined essentially by the degree of overlap between the electronic wavefunctions of the atoms involved.
Electronic configurations

The notation used to describe the electronic configuration of atoms and ions is discussed in all textbooks of introductory atomic physics. The letters s, p, d, ... signify electrons having orbital angular momenta 0, 1, 2, ..., in units \( \hbar \); the number to the left of the letter denotes the principal quantum number of one orbit, and the superscript to the right denotes the number of electrons in the orbit.
Types of Bonding

- Crystalline argon (vander Waals)
- Sodium chloride (ionic)
- Sodium (metallic)
- Diamond (covalent)
Consider two inert gas atoms at a separation $R$ apart. The two atoms talk to each other by inducing a dipole moment.

Fluctuations will produce a dipole moment $p_1$ producing a field $E \sim p_1/r^3$. This polarizes the second atom with polarizability $\alpha$-- $p_2 = \alpha p_1 / r^3$ and the potential is $p_2 \cdot E \sim 1/r^6$. 

fcc structure of inert gases
Van der Waals Bonding

At equilibrium \((R=R_0)\),

\[
U(R_0) = -2.15(4N\epsilon)
\]

-- cohesive energy at \(T=0\)

-- Lennard-Jones potential

\[
U(R) = 4\epsilon \left[ \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^6 \right]
\]
Ionic Crystals

Electron density in NaCl: x-ray data

Picture showing the calculation of the Cohesive energy for NaCl.
Ionic Crystals

In ionic crystals, it is not possible for the electrons to move about freely between ions unless a large amount of energy (~10 eV) is supplied – it is not conducting.
Covalent Crystals

Diagram showing:
- Higher energy antibonding orbitals
- Lower energy bonding orbitals
- Energy levels $E$ with $H_{AA}$ and $H_{BB}$ for bonding and antibonding interactions.
No bonding
Covalent Crystals

Binding energy: 3.87 eV/atom
Ionic vs. Covalent Bonding
Metallic Bonding

Ni $4s^23d^8$

$3d_{zz}$ (localized)

$4s$ (valence electrons are free to move)
Metallic Bonding

A metal is a lattice of positive metal “ions” in a “sea” of delocalized electrons.

Metallic bonding refers to the interaction between the delocalized electrons and the metal nuclei.

The physical properties of metals are the result of the delocalization of the electrons involved in metallic bonding.

The physical properties of solid metals are:
- Conduct heat
- Conduct electricity
- High melting and boiling points
- Strong
- Malleable (can be hammered or pressed out of shape without breaking)
- Ductile (able to be drawn into a wire)
- Metallic luster
- Opaque (reflect light)
The Drude Theory of Metals

How to describe metallic behavior?
Drude Model
-- treat electrons as gas

Mobile
Light
Negatively charged

Immobile
Heavy
Positively charged
Calculations of electron density

Total number of atoms/mole: $6.022 \times 10^{23}$

Mass density: $\rho_m$ (g/cm$^3$)

Atomic mass: A

Number of electrons/volume: 

$$n = Z \left( 6.022 \times 10^{23} \right) \frac{\rho_m}{A}$$

Volume/electron: 

$$\frac{1}{n} = \frac{4 \pi r_s^3}{3}$$

$r_s$: Radius of a sphere, with volume = volume/conduction-electron
Hydrogen atom

carrier concentration =

\[ r_s > a_0 \]

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<th>ELEMENT</th>
<th>Z</th>
<th>( n \times 10^{22}/\text{cm}^3 )</th>
<th>( r_s(\text{\AA}) )</th>
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The density of “electron gas” >> classic gas

Drude Model Assumptions:

• Travel in straight line, ignore e-e interactions (i.e., independent electron approximation)
• Ignore electron-ion interactions (i.e., free electron approximation)
• Collision instantaneously alters the velocity of an electron
• The relaxation time (mean free time) is independent of electron position and velocity
• Achieve thermal equilibrium only through collision
DC Electrical Conductivity $\sigma$

**Definition:**

\[ \mathbf{J} = \sigma \mathbf{E} \]

\[ \mathbf{E} = 0 \Rightarrow v_{\text{average}} = 0 \]

\[ \mathbf{E} \neq 0 \Rightarrow \mathbf{F} = (-e) \mathbf{E} \Rightarrow v_{\text{average}} = \left( \frac{-e \mathbf{E}}{m} \right) \tau \]

\[ \mathbf{J} = (-e) \frac{n(v_{\text{av}} \, dt) A}{(dt) A} = -ne \mathbf{v}_{\text{av}} = \left( \frac{ne^2 \tau}{m} \right) \mathbf{E} \]

**Electrical conductivity:**

\[ \sigma = \frac{ne^2 \tau}{m} \]
Experimental Probe:

$\mathbf{I} = A \mathbf{J}$

Resistivity: 

$$\rho = \frac{1}{\sigma}$$

Resistivity:

$$R = \frac{\Delta V}{I} = \frac{EL}{AJ} = \left( \frac{E}{J} \right) \left( \frac{L}{A} \right) = \rho \left( \frac{L}{A} \right)$$
Being a good metal, the resistivity should be in the order of μΩ-cm
1. For solid H2, one finds from measurements that the Lennard-Jones parameters are $\epsilon=50 \times 10^{-16}$ erg and $\sigma=2.96\text{Å}$. Find the cohesive energy in kJ/mole of H2-do the calculation for an fcc structure.

2. Problem 1(a-d) (page 26) (Ashcroft/Mermin)