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

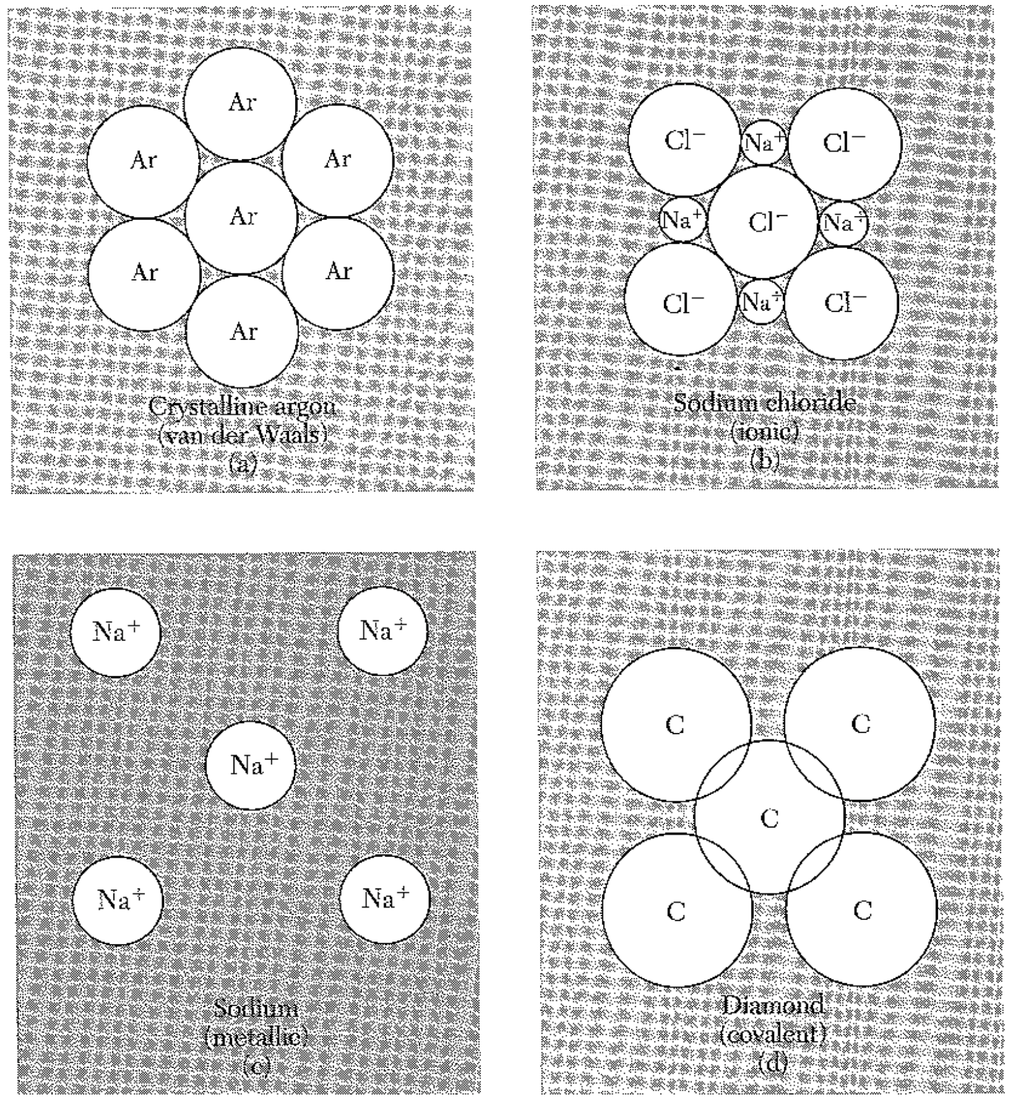
Periodic Table, with the Outer Electron Configurations of Neutral Atoms in Their Ground States

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 momentum 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.

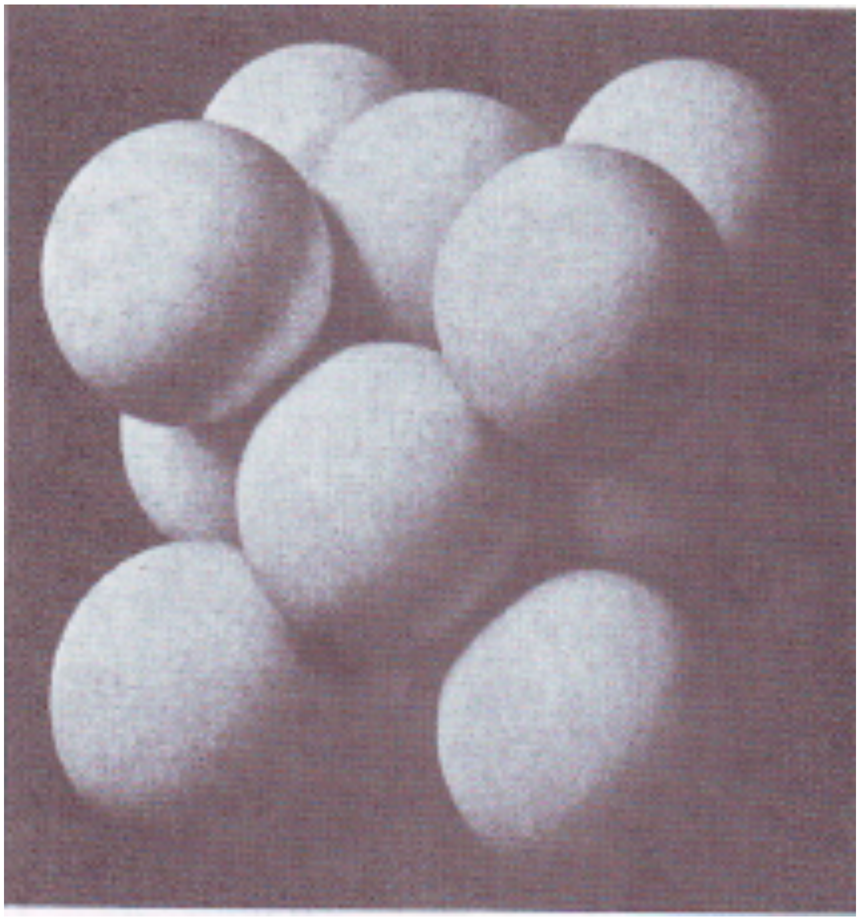
H^{1} $1s$																	He^{2} $1s^2$
Li^{3} $2s$	Be^{4} $2s^2$											B^{5} $2s^22p$	C^{6} $2s^22p^2$	N^{7} $2s^22p^3$	O^{8} $2s^22p^4$	F^{9} $2s^22p^5$	Ne^{10} $2s^22p^6$
Na^{11} $3s$	Mg^{12} $3s^2$											Al^{13} $3s^23p$	Si^{14} $3s^23p^2$	P^{15} $3s^23p^3$	S^{16} $3s^23p^4$	Cl^{17} $3s^23p^5$	Ar^{18} $3s^23p^6$
K^{19} $4s$	Ca^{20} $4s^2$	Sc^{21} $3d$ $4s^2$	Ti^{22} $3d^2$ $4s^2$	V^{23} $3d^3$ $4s^2$	Cr^{24} $3d^5$ $4s$	Mn^{25} $3d^5$ $4s^2$	Fe^{26} $3d^6$ $4s^2$	Co^{27} $3d^7$ $4s^2$	Ni^{28} $3d^8$ $4s^2$	Cu^{29} $3d^{10}$ $4s$	Zn^{30} $3d^{10}$ $4s^2$	Ga^{31} $4s^24p$	Ge^{32} $4s^24p^2$	As^{33} $4s^24p^3$	Se^{34} $4s^24p^4$	Br^{35} $4s^24p^5$	Kr^{36} $4s^24p^6$
Rb^{37} $5s$	Sr^{38} $5s^2$	Y^{39} $4d$ $5s^2$	Zr^{40} $4d^2$ $5s^2$	Nb^{41} $4d^4$ $5s$	Mo^{42} $4d^5$ $5s$	Tc^{43} $4d^6$ $5s$	Ru^{44} $4d^7$ $5s$	Rh^{45} $4d^8$ $5s$	Pd^{46} $4d^{10}$ –	Ag^{47} $4d^{10}$ $5s$	Cd^{48} $4d^{10}$ $5s^2$	In^{49} $5s^25p$	Sn^{50} $5s^25p^2$	Sb^{51} $5s^25p^3$	Te^{52} $5s^25p^4$	I^{53} $5s^25p^5$	Xe^{54} $5s^25p^6$
Cs^{55} $6s$	Ba^{56} $6s^2$	La^{57} $5d$ $6s^2$	Hf^{72} $4f^{11}$ $5d^2$ $6s^2$	Ta^{73} $5d^3$ $6s^2$	W^{74} $5d^4$ $6s^2$	Re^{75} $5d^5$ $6s^2$	Os^{76} $5d^6$ $6s^2$	Ir^{77} $5d^9$ –	Pt^{78} $5d^9$ $6s$	Au^{79} $5d^{10}$ $6s$	Hg^{80} $5d^{10}$ $6s^2$	Tl^{81} $6s^26p$	Pb^{82} $6s^25p^2$	Bi^{83} $6s^26p^3$	Po^{84} $6s^26p^4$	At^{85} $6s^26p^5$	Rn^{86} $6s^26p^6$
Fr^{87} $7s$	Ra^{88} $7s^2$	Ac^{89} $6d$ $7s^2$															

Ce^{58} $4f^2$ $5s^2$	Pr^{59} $4f^3$ $6s^2$	Nd^{60} $4f^4$ $6s^2$	Pm^{61} $4f^5$ $6s^2$	Sm^{62} $4f^6$ $6s^2$	Eu^{63} $4f^7$ $6s^2$	Gd^{64} $4f^7$ $5d$ $6s^2$	Tb^{65} $4f^8$ $5d$ $6s^2$	Dy^{66} $4f^{10}$ $6s^2$	Ho^{67} $4f^{11}$ $6s^2$	Er^{68} $4f^{12}$ $6s^2$	Tm^{69} $4f^{13}$ $6s^2$	Yb^{70} $4f^{14}$ $6s^2$	Lu^{71} $4f^{14}$ $5d$ $6s^2$
Th^{90} – $6d^2$ $7s^2$	Pa^{91} $5f^2$ $6d$ $7s^2$	U^{92} $5f^3$ $6d$ $7s^2$	Np^{93} $5f^5$ $7s^2$	Pu^{94} $5f^6$ $7s^2$	Am^{95} $5f^7$ $7s^2$	Cm^{96} $5f^7$ $6d$ $7s^2$	Bk^{97}	Cf^{98}	Es^{99}	Fm^{100}	Md^{101}	No^{102}	Lr^{103}

Types of Bonding



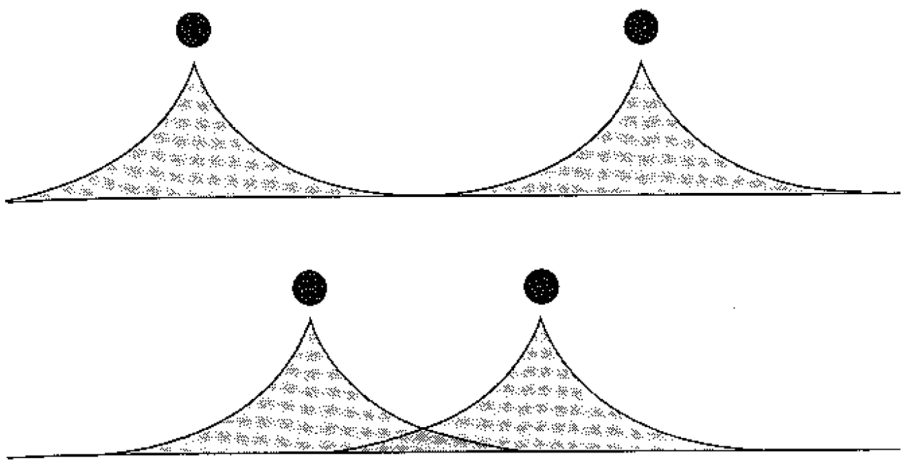
fcc structure of inert gases

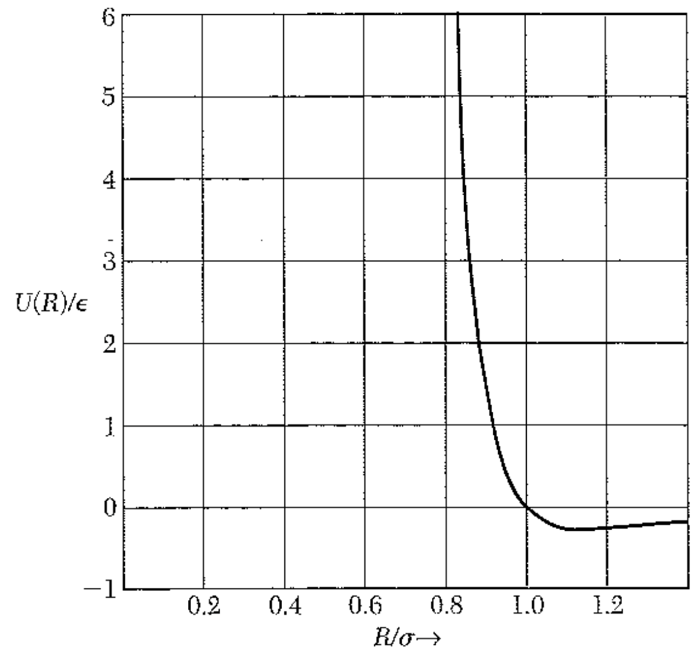


Consider two inert gas atoms at a separation R apart. The two atoms talk to each other by inducing a dipole moment.

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

Van der Waals Bonding





At equilibrium ($R=R_0$),

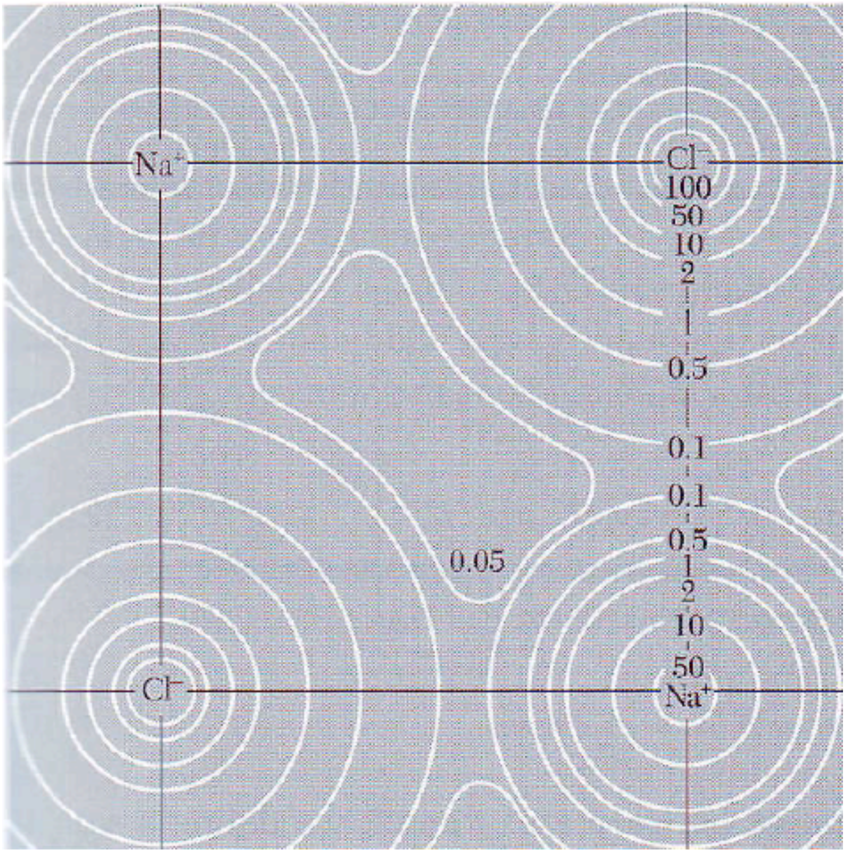
-- Lennard-Jones potential

$$U(R_0) = -2.15(4N\varepsilon)$$

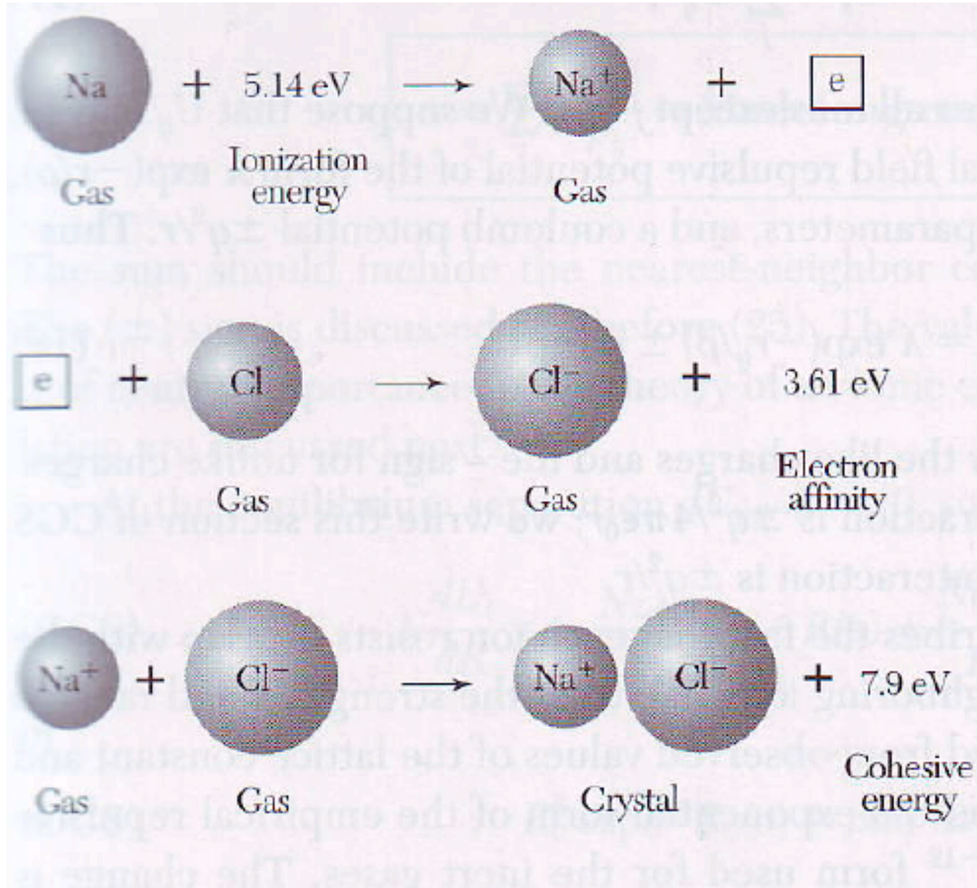
$$U(R) = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right]$$

-- cohesive energy at T=0

Ionic Crystals



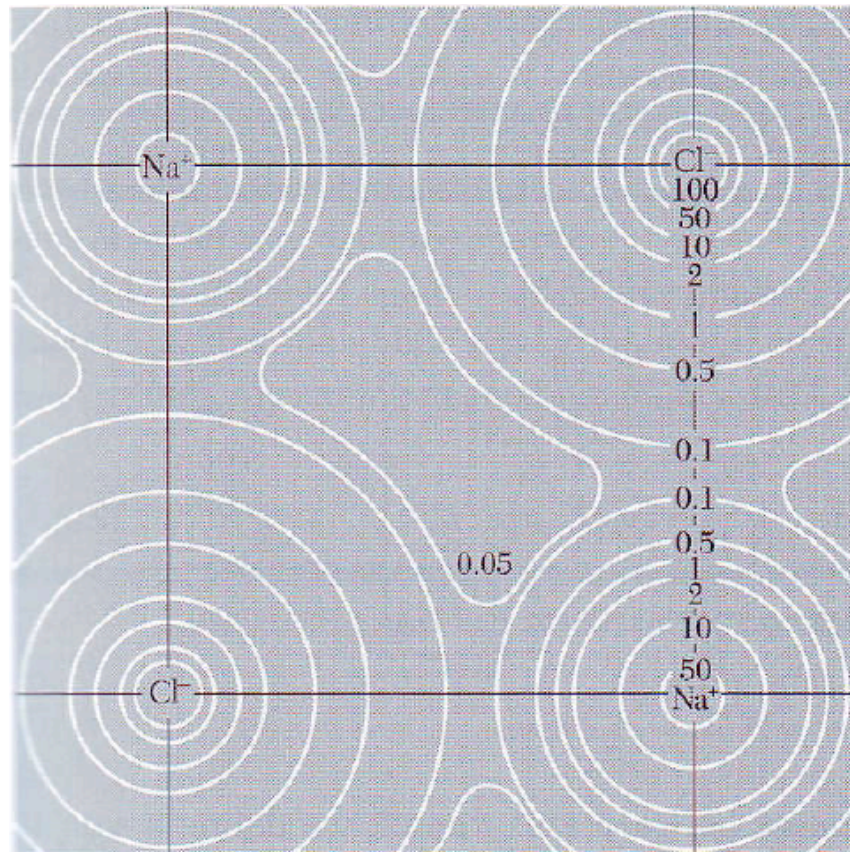
Electron density in NaCl: x-ray data



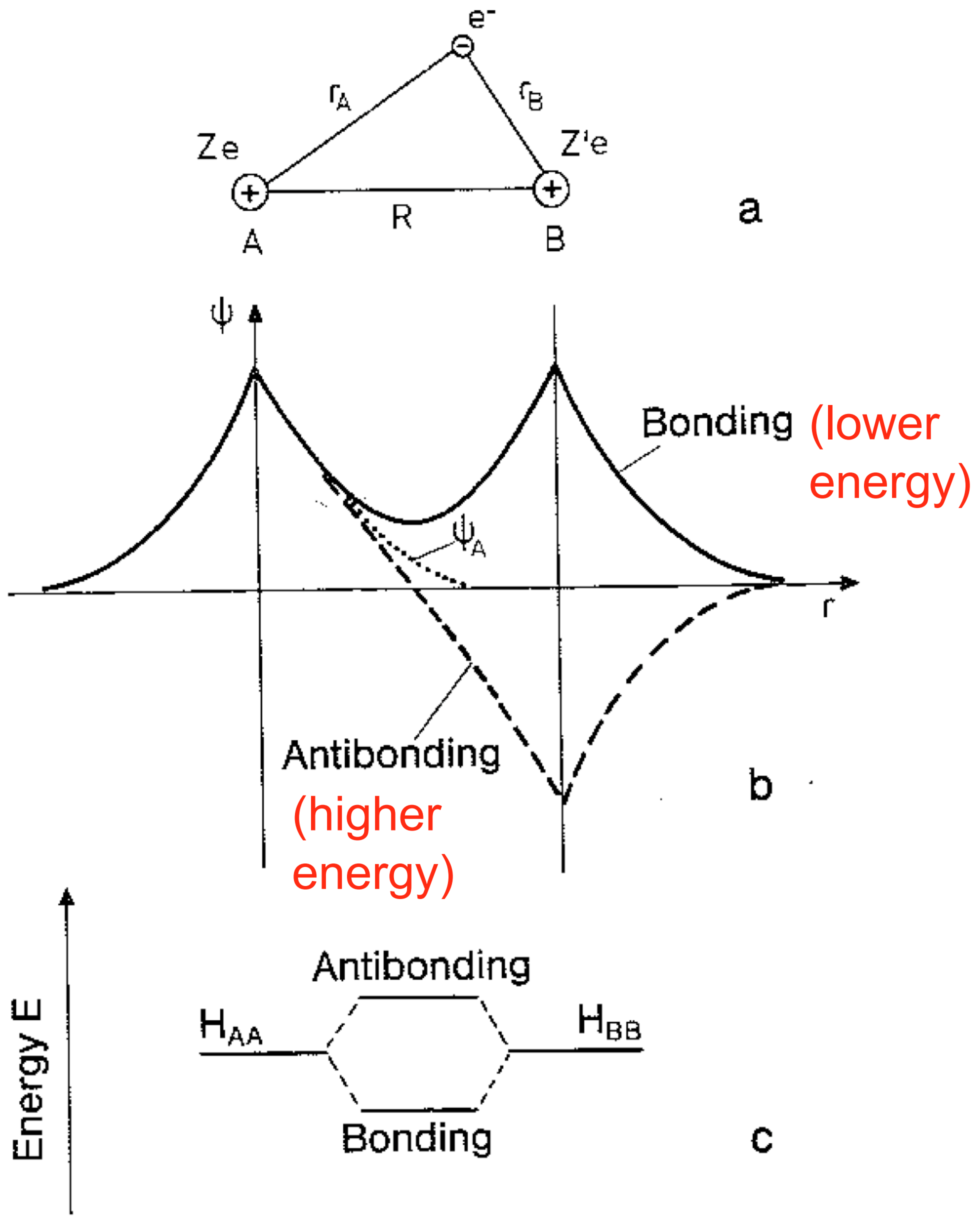
Picture showing the calculation of the Cohesive energy for NaCl.

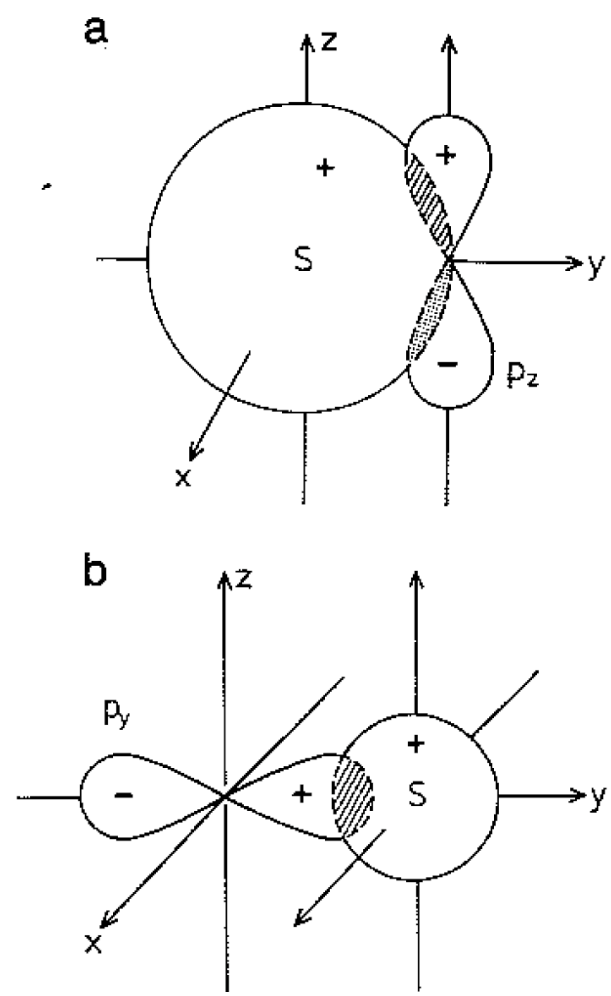
Ionic Crystals

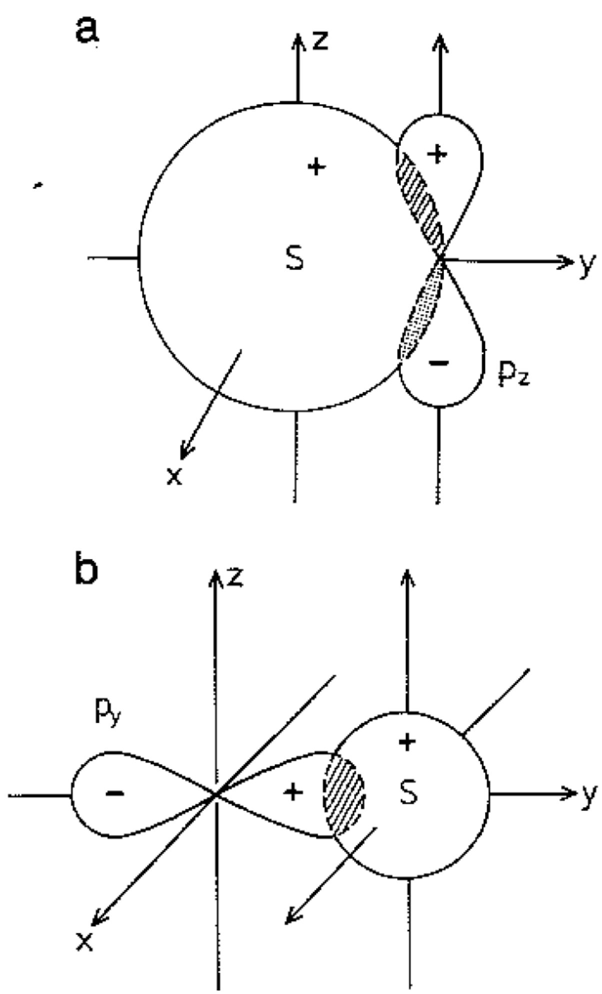
In ionic crystals, it is not possible for the electrons to move about freely between ions unless a large amount of energy (~10 eV) is supplied – it is not conducting.

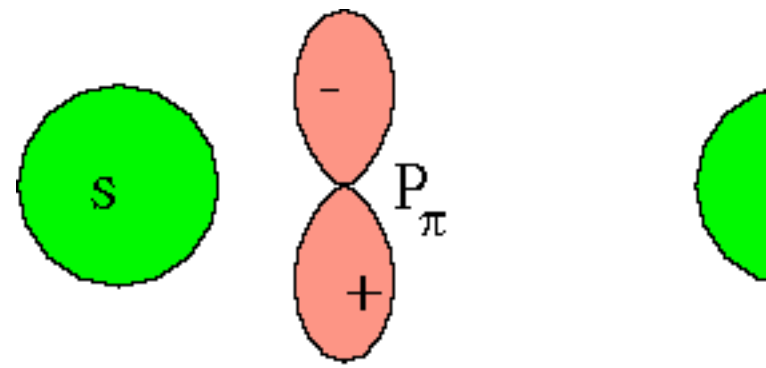


Covalent Crystals



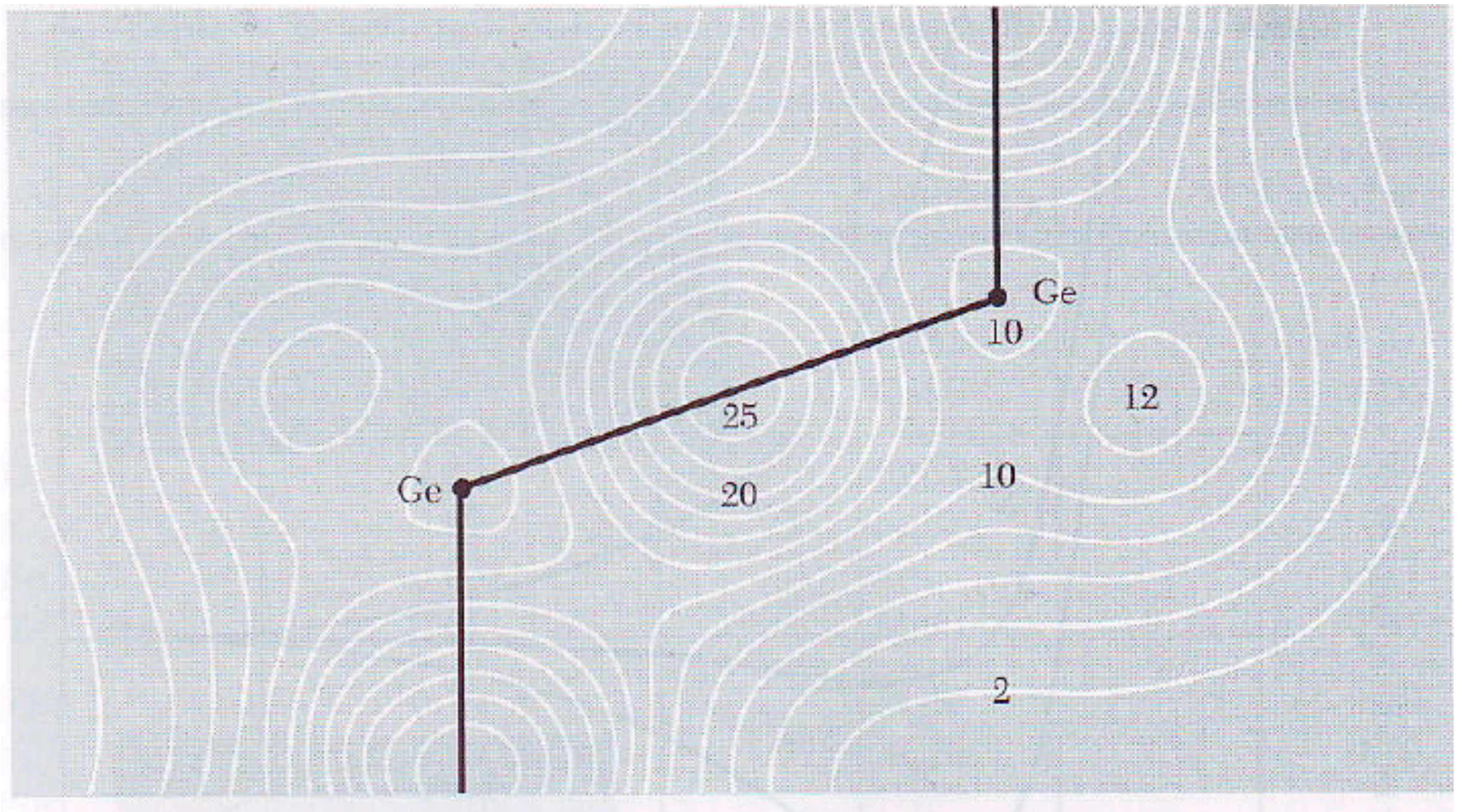






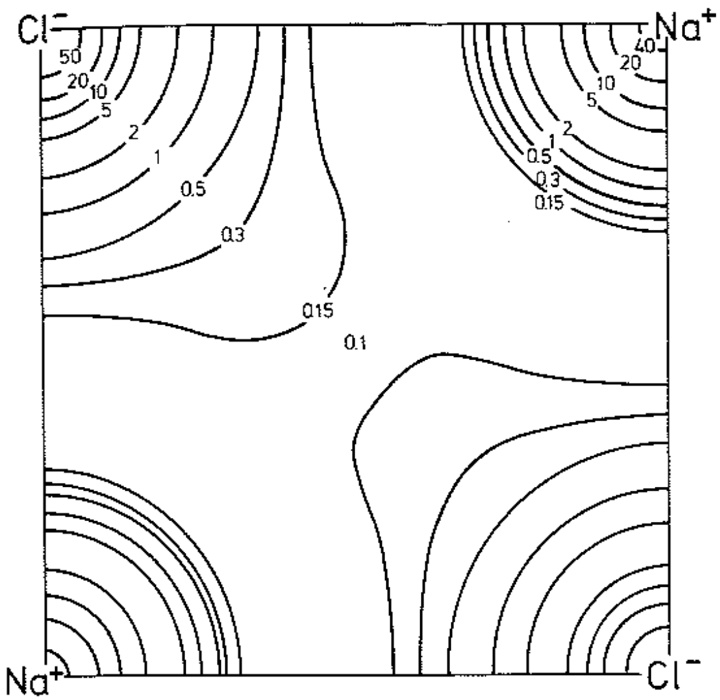
No bonding

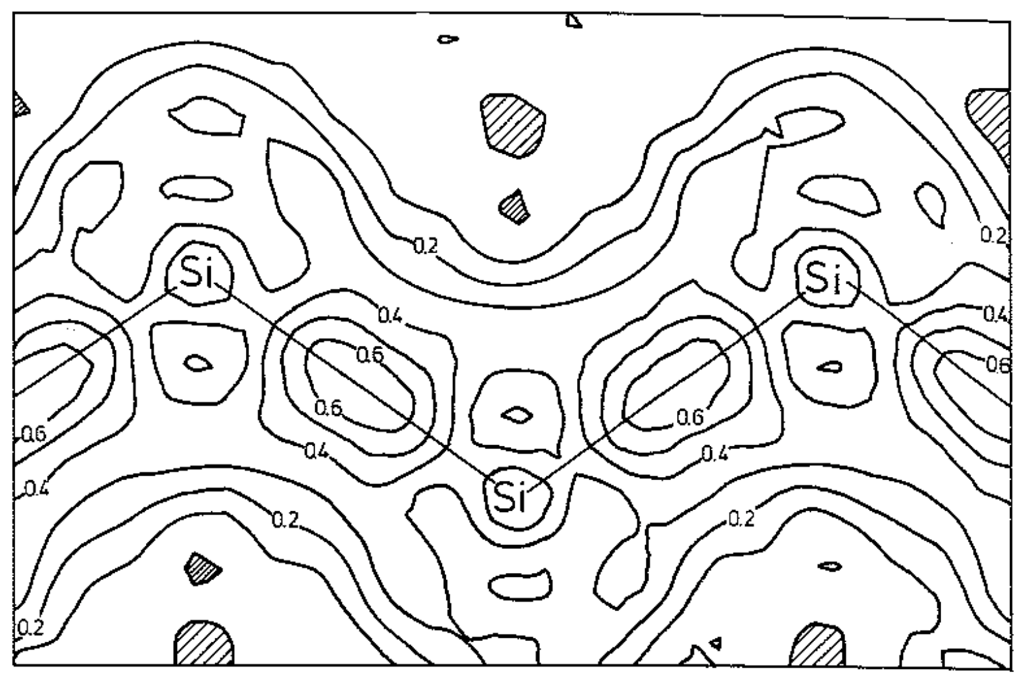
Covalent Crystals



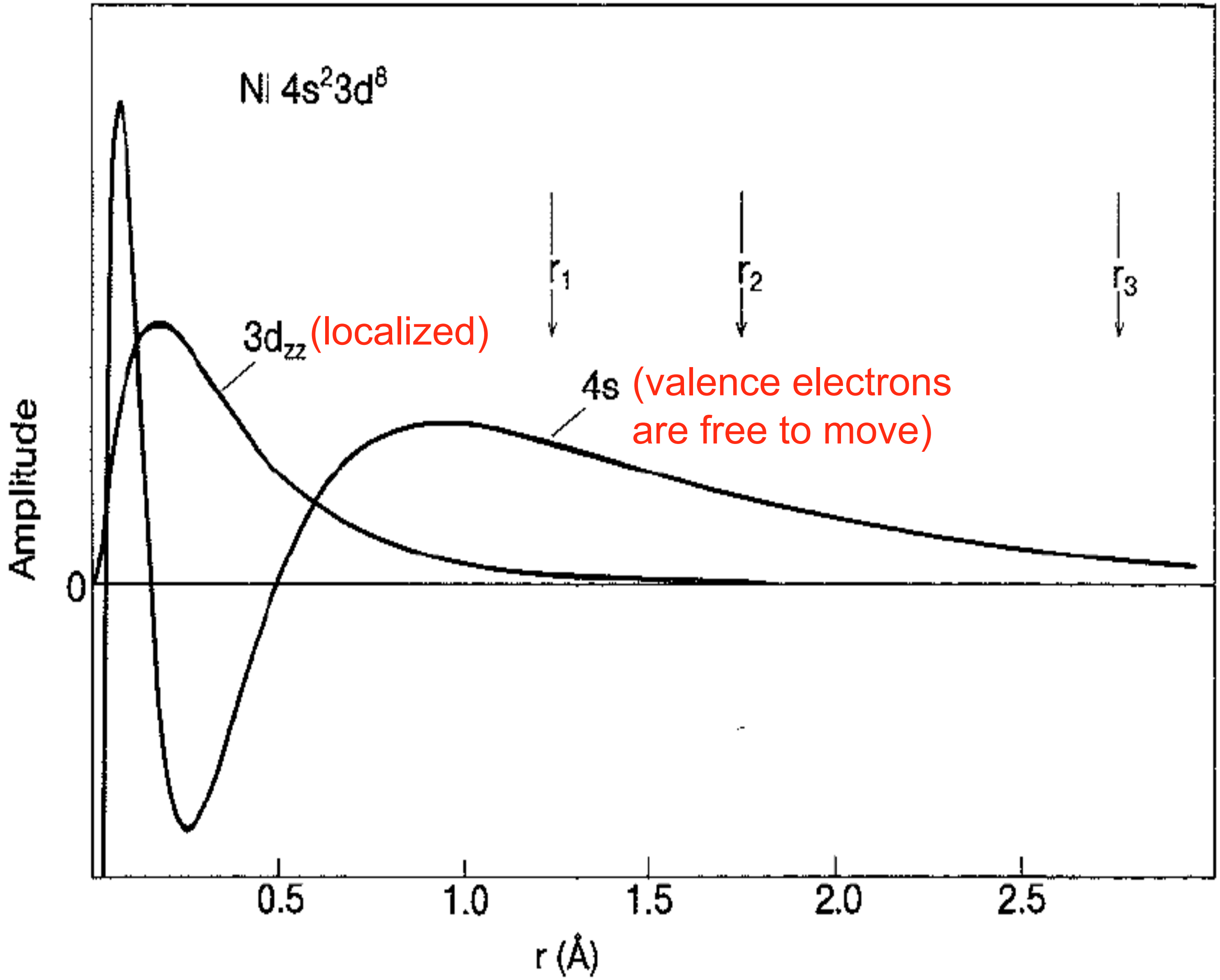
Binding energy: 3.87 eV/atom

Ionic vs. Covalent Bonding





Metallic Bonding



Metallic Bonding

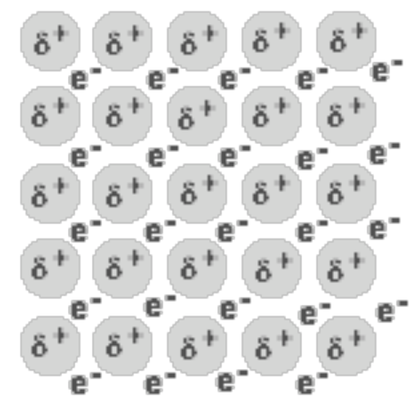
➔A metal is a lattice of positive metal "ions" in a "sea" of delocalized electrons.

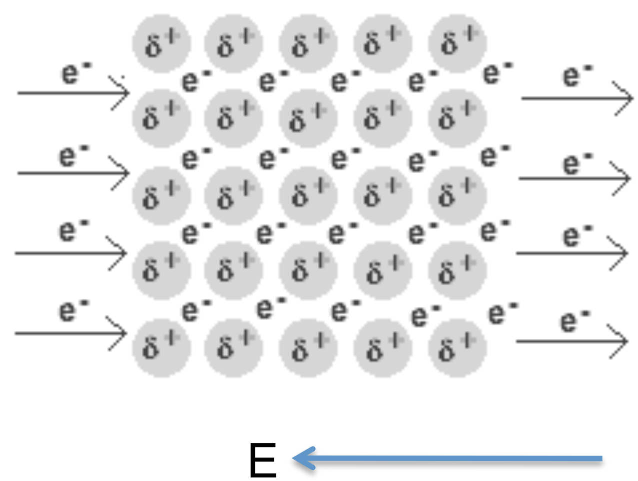
➔Metallic bonding refers to the interaction between the delocalized electrons and the metal nuclei.

➔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)



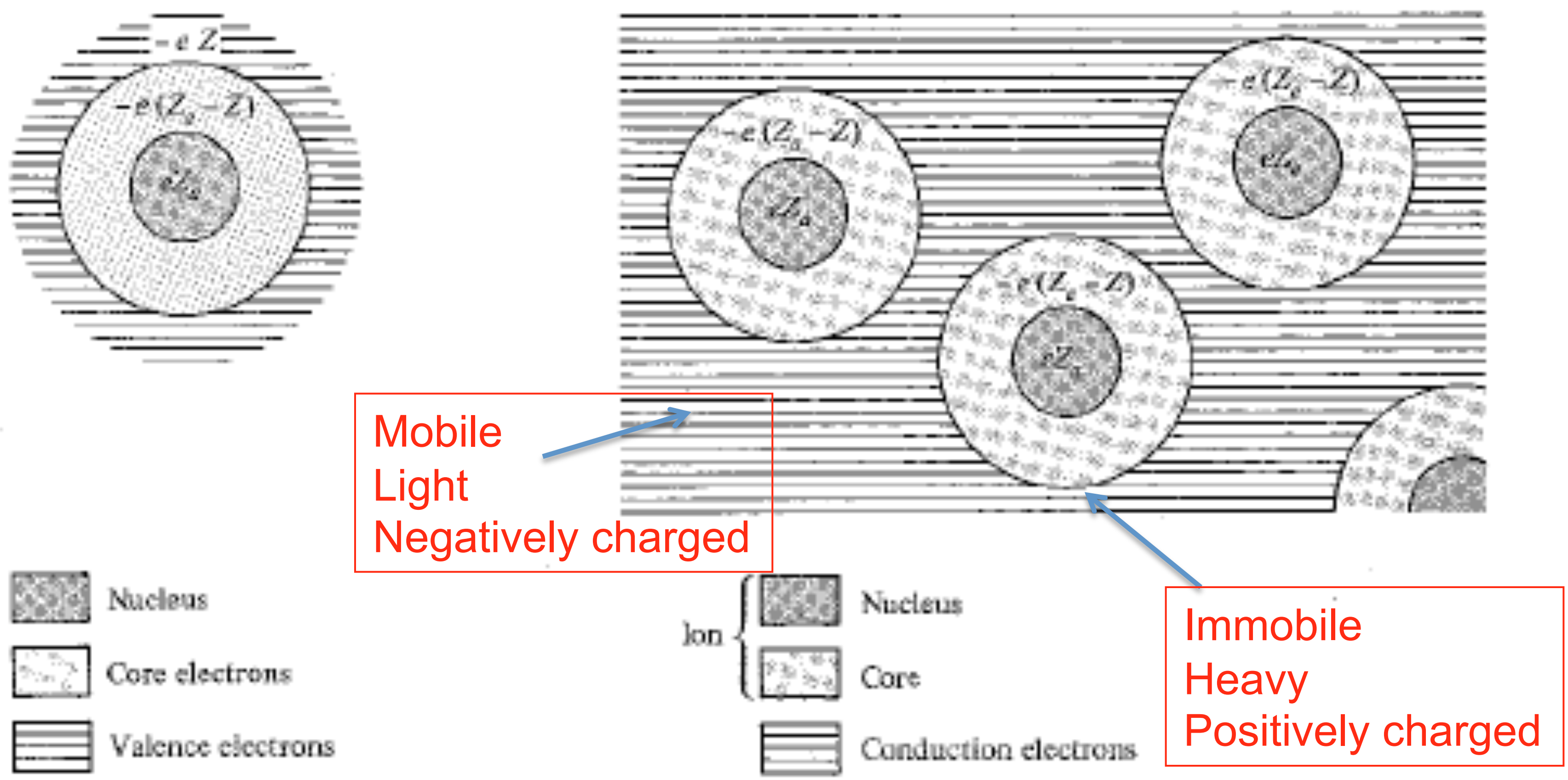


The Drude Theory of Metals

How to describe metallic behavior?

Drude Model

-- treat electrons as gas



Calculations of electron density

Total number of atoms/mole: 6.022×10^{23}

Mass density: ρ_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

$$r_s > a_0$$

carrier concentration = **FREE ELECTRON DENSITIES OF SELECTED METALLIC ELEMENTS**[a]

ELEMENT	Z	$n\ (10^{22}/\text{cm}^3)$	r_s(Å)	r_s/a_0
Li (78 K)	1	4.70	1.72	3.25
Na (5 K)	1	2.65	2.08	3.93
K (5 K)	1	1.40	2.57	4.86
Rb (5 K)	1	1.15	2.75	5.20
Cs (5 K)	1	0.91	2.98	5.62
Cu	1	8.47	1.41	2.67
Ag	1	5.86	1.60	3.02
Au	1	5.90	1.59	3.01
Be	2	24.7	0.99	1.87
Mg	2	8.61	1.41	2.66
Ca	2	4.61	1.73	3.27
Sr	2	3.55	1.89	3.57
Ba	2	3.15	1.96	3.71
Nb	1	5.56	1.63	3.07
Fe	2	17.0	1.12	2.12
Mn (α)	2	16.5	1.13	2.14
Zn	2	13.2	1.22	2.30
Cd	2	9.27	1.37	2.59
Hg (78 K)	2	8.65	1.40	2.65
Al	3	18.1	1.10	2.07
Ga	3	15.4	1.16	2.19
In	3	11.5	1.27	2.41
Tl	3	10.5	1.31	2.48
Sn	4	14.8	1.17	2.22
Pb	4	13.2	1.22	2.30
Bi	5	14.1	1.19	2.25
Sb	5	16.5	1.13	2.14

Hydrogen atom

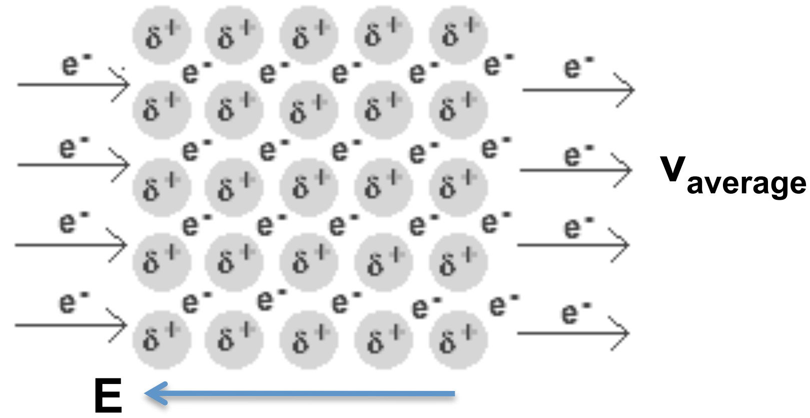
The density of “electron gas” >> classic gas

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 σ

Definition: $\mathbf{J} = \sigma \mathbf{E}$



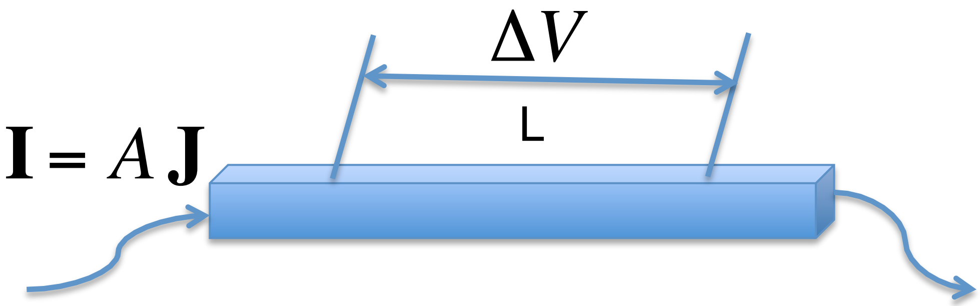
$$\mathbf{E} = 0 \Rightarrow \mathbf{v}_{average} = 0$$

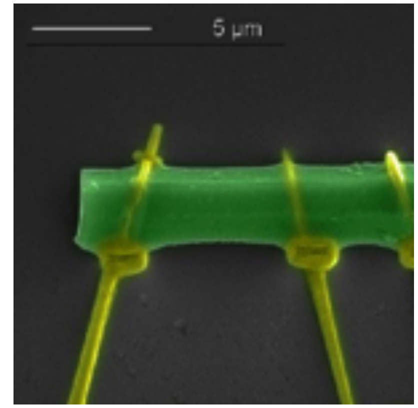
$$\mathbf{E} \neq 0 \Rightarrow \mathbf{F} = (-e)\mathbf{E} \Rightarrow \mathbf{v}_{average} = \left(\frac{-e\,\mathbf{E}}{m}\right)\tau$$

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

Electrical conductivity: $\sigma = \dfrac{ne^2\tau}{m}$

Experimental Probe:





Resistance: $$R = \frac{\Delta V}{I} = \frac{EL}{AJ} = \left(\frac{E}{J}\right)\left(\frac{L}{A}\right) = \rho\left(\frac{L}{A}\right)$$

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

ELECTRICAL RESISTIVITIES OF SELECTED ELEMENTS[a]

ELEMENT	77 K μΩ-cm	273 K μΩ-cm	373 K μΩ-cm	$\frac{(\rho/T)_{373\ K}}{(\rho/T)_{273\ K}}$
Li	1.04	8.55	12.4	1.06
Na	0.8	4.2	Melted	
K	1.38	6.1	Melted	
Rb	2.2	11.0	Melted	
Cs	4.5	18.8	Melted	
Cu	0.2	1.56	2.24	1.05
Ag	0.3	1.51	2.13	1.03
Au	0.5	2.04	2.84	1.02
Be		2.8	5.3	1.39
Mg	0.62	3.9	5.6	1.05
Ca		3.43	5.0	1.07
Sr	7	23		
Ba	17	60		
Nb	3.0	15.2	19.2	0.92
Fe	0.66	8.9	14.7	1.21
Zn	1.1	5.5	7.8	1.04
Cd	1.6	6.8		
Hg	5.8	Melted	Melted	
Al	0.3	2.45	3.55	1.06
Ga	2.75	13.6	Melted	
In	1.8	8.0	12.1	1.11
Tl	3.7	15	22.8	1.11
Sn	2.1	10.6	15.8	1.09
Pb	4.7	19.0	27.0	1.04
Bi	35	107	156	1.07
Sb	8	39	59	1.11

Being a good metal, the resistivity should be in the order of μΩ-cm

Homework today (due on Sept. 9, 2010)

1. For solid H_2, one finds from measurements that the Lennard-Jones parameters are $\varepsilon=50*10^{-16}$ erg and $\sigma=2.96$Å. Find the cohesive energy in kJ/mole of H_2- do the calculation for an fcc structure.

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