Electrons in Solids

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\cdot\psi(x) = E\cdot\psi(x)$$

Hydrogen atom $\psi(r,\theta,\varphi)$ $V = V(r) = \frac{-Ze^2}{4\pi\epsilon_0 r}$

→ exact solutions → 1s, 2s, 2p etc.

Hydrogen molecule $\tilde{\psi}^s = \psi^a + \psi^b$ LCAO

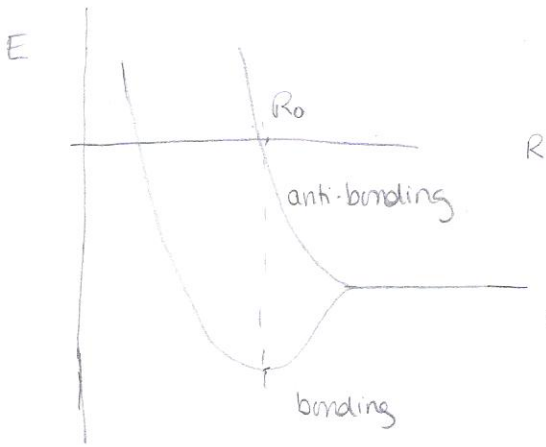
$\tilde{\psi}^A = \psi^a - \psi^b$

s orbitals → symmetric ≡ bonding
(σ bond) antisymmetric ≡ anti bonding

p_z orbitals (σ) → opposite

symmetric

antisymmetric



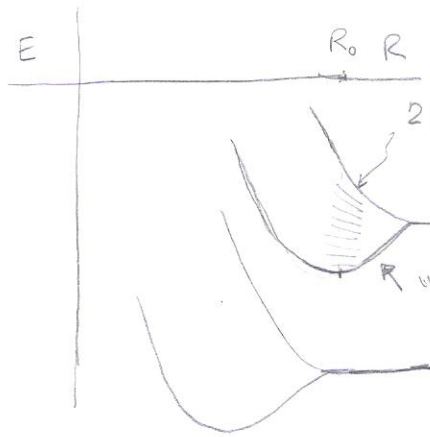
$\psi^*\psi$ symmetric

H_2: covalent bond

- directional
- typical of molecules.

N atom Solid - single element

example: Li (#3) $1s^2\ 2s^1$ → 3N electrons total



2s: no interaction; 2 states/atom; 2N states. N electrons

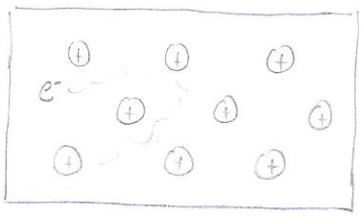
1s: 2 states/atom; 2N states fill w/ 2N electrons.

at equilibrium R_0 → 1s not affected

2s → band of states, ½ states filled

partially filled band → METAL

alternative picture



fixed atom cores

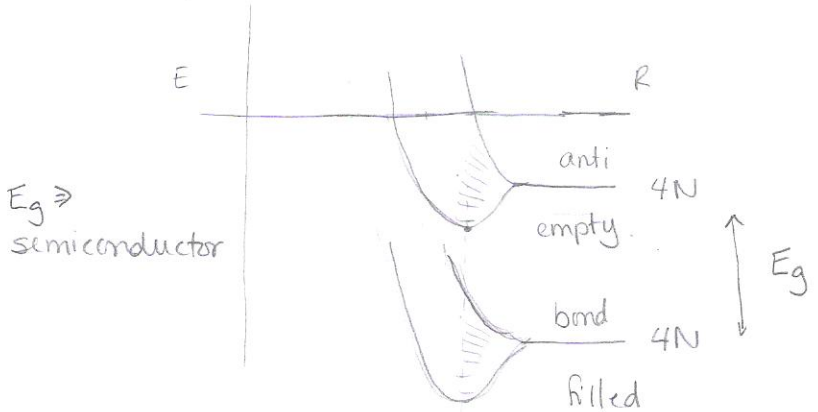
free electron gas

3s → 2N states } 8N
3p → 6N states }

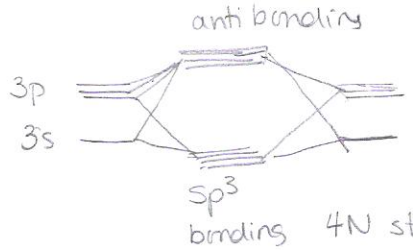
example: Si (#14) $1s^2\ 2s^2\ 2p^6$ $3s^2\ 3p^2$ 4N bonding electrons

$1s^2\ 2s^2\ 2p^6$ = [Ne]

$3s^2\ 3p^2$ → 3 sp^3 → 4 × 2 states / atom

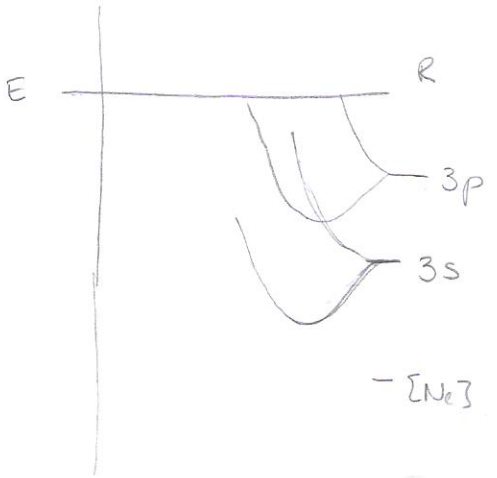


hypothetical Si_2 molecule



degenerate

example Mg #12 $1s^2 2s^2 2p^6 3s^2 (3p^0)$ N atom solid
[Ne]



2N states. → expect a gap,
overlap between 3s & 3p → metal

example multi-element solid - LiF hypothetical ion pair

Li: $1s^2 2s^1 \rightarrow 1s^2 \rightarrow Li^{+1} + e^-$
F: $1s^2 2s^2 2p^5 \rightarrow 2p^6 \Rightarrow F + e^- \rightarrow F^-$

$\Delta E = \Delta E_{ionization} + \Delta E_{coulombic}$,

$\Delta E_{ion} \sim \frac{13.6 Z^2}{n^2}$ $Z_{eff} < Z_{actual}$ due to shielding.

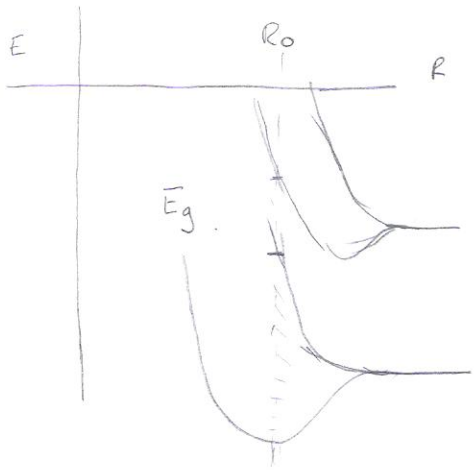
$\Delta E_{Li} \sim \frac{13.6 (Z_{eff}^{Li})^2}{2^2} \rightarrow 5.4\ eV$ (>0) requires energy

$\Delta E_F \sim \frac{-13.6 (Z_{eff}^{F})^2}{2^2} \rightarrow -3.7\ eV$ <0 releases energy.

$\Delta E_{coul} = \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 r} \rightarrow -7.2\ eV$

ΔE to form ion pair: $5.4 - 3.7 - 7.2 = -5.3\ eV$

N atom-pair solid



e: Li (2s) → F (2p) ⇒ $E_{F_{2p}} < E_{L_{2s}}$

2N states. (no electrons)

6N states (6N electrons)

ask: impact of pressure?

Summary

N atom solid → bonding / anti bonding states
→ bands due to exclusion principle

Metal: no energy gap between occupied & unoccupied states
many need to consider orbitals of slightly higher energy.

Semiconductor: hybrid orbitals → bands.
'small' gap between occupied & unoccupied

Ionic: e^- transfer from electropos orbital to electroneg orb.
orbitals → bands
'large' gap between occupied & unoccupied.