Error: Eqn 2.6 factor in brackets

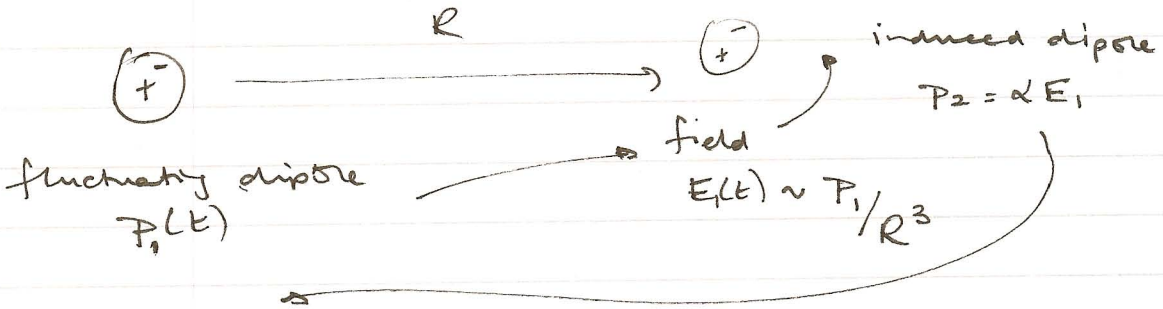
$$-\frac{1}{2}\left[\frac{e^2}{4\pi\varepsilon_0 R^3}\cdot\frac{1}{m\omega_0^2}\right]^{1/2}$$

# Lecture 1

## Binding of Crystals. Fig. on p 57. Kittel.

Inert gases: filled electronic shells
large ionisation energy

Attraction: Van der Waals




$$\frac{p_2}{R^3} \alpha = \frac{\alpha p_1}{R^6} \longrightarrow \text{Energy } p_1 E_1 = \boxed{-\frac{\alpha \langle p_1^2 \rangle}{R^6}} = -\frac{A}{R^6}$$

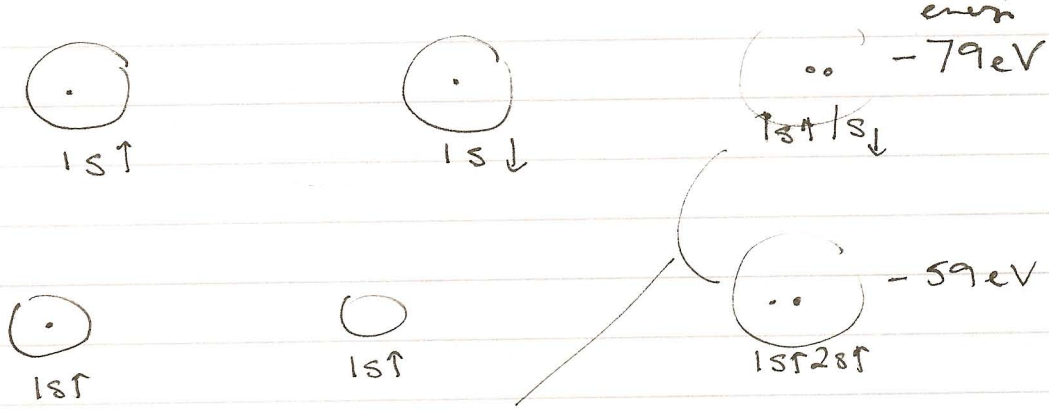
N.B. $\langle p_1 \rangle = 0$

$\langle p_1^2 \rangle \neq 0$ $\longrightarrow$

Actually this is change in zero point energy of 2 coupled oscillators → see prob 1.

Repulsion: Coulomb from e-e overlap.
Pauli Exclusion

Compare $H + H \longrightarrow He$




Model by short range $\frac{1}{R^{12}}$ or $e^{-\lambda r}$

## Ionic Crystals eg NaCl.

$$Na + 5.14\,eV \longrightarrow Na^+ + e^- \qquad \text{Ionization energy } I$$

$$e^- + Cl \longrightarrow Cl^- + 3.61\,eV \qquad \text{Electron Affinity. } A$$

$$Na^+ + Cl^- \longrightarrow (Na^+Cl^-)_{\text{solid}} + 7.9\,eV. \qquad \text{Electrostatic attraction}$$

$$E_{coh} = 7.9 - 5.1 + 3.6 = 6.4 \text{ eV/molecule.}$$

Stable filled shell → small ionization energy $I$
→ large electron affinity $A$

Computing madelung constant

Coulomb energy $U_c = \frac{1}{2}\sum_{ij}{}' U_{ij}$ (double counting)

$U_{ij} = \pm \frac{q^2}{R_{ij}}$ ($+q$, $-q$)


In 1D: $\sum_j U_{0j} = +2\left[-\frac{1}{R} + \frac{1}{2R} - \frac{1}{3R} + \frac{1}{4R} \cdots -\right]$

[Conditionally convergent series]

$$= -\frac{2}{R}\left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots\right]$$

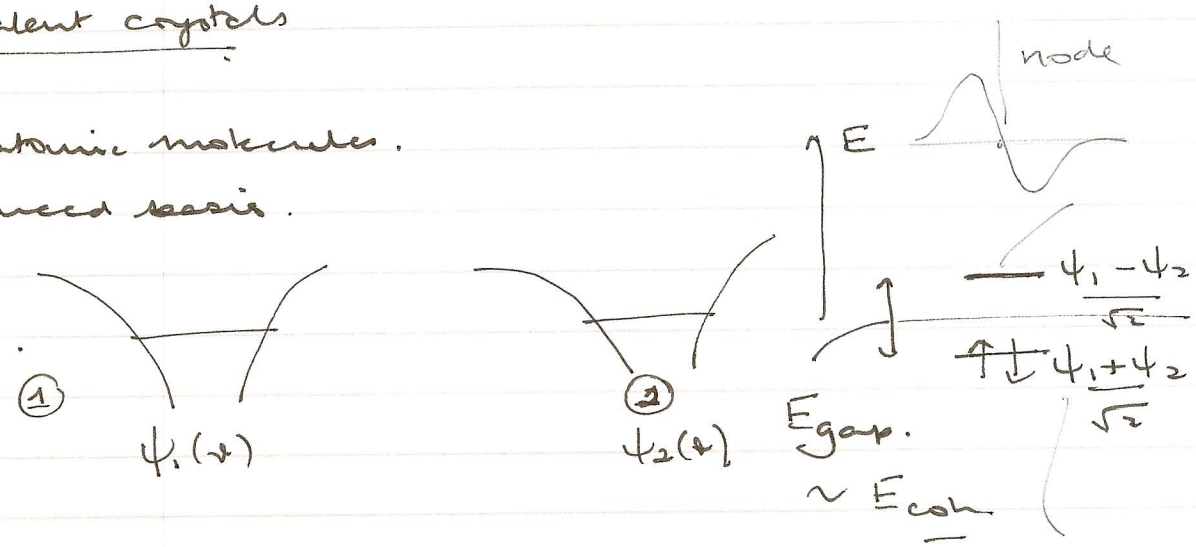
$$= -\frac{2\ln 2}{R}$$

Madelung const.

In general. $U_e/\text{atom} = -\frac{1}{2}\alpha\frac{q^2}{R}$

## Covalent crystals

Diatomic molecules.
Reduced basis.




$$E_{gap} = \langle \psi_1 | \cancel{H} - \frac{\hbar^2}{2m}\nabla^2 + V_1 + V_2 | \psi_2 \rangle$$

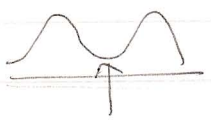
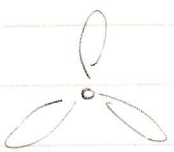



Fig: Diamond.

Diamond structure : $sp^3$ hybrids.

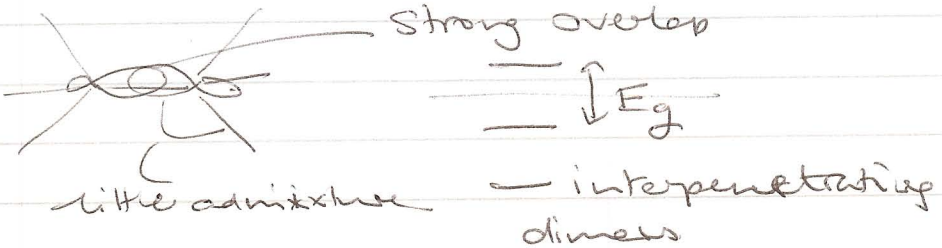
Tetrahedral arrangement:



C. — 4 electrons/atom. 1s. 3p.
— Suppose instead use a new basis $sp^3$.

| S | + $P_x$ | + $P_y$ | + $P_z$ | |
|---|---|---|---|---|
| | | | + | (111) |
| | − | − | + | (11$\bar{1}$) |
| | − | + | − | (1$\bar{1}$1) |
| | + | − | − | (1$\bar{1}\bar{1}$) |

Hamiltonian no different — but note




Qu 2.2 Si → GaAs → ZnS
III - V II - VI
} 8 electrons/pair "octet" rule.

increasing ionic component to bonding

C → Si → Ge → Sn — increasing energy sep of s & p orbitals
distances. $sp^3$ hybrids.

## Metals

— itinerant electrons. favoured by high density

$$\text{K.E/particle} \sim E_F \sim \frac{\hbar^2}{2m} k_F^2 \sim \frac{\hbar^2}{2ma^2}$$

$$\text{P.E./particle} \sim \frac{e^2}{4\pi\varepsilon_0 a}.$$

↑ high density — small a — KE >> P.E

= ion-ion repulsion?

= however, high density should mean electrons close to ion cores? — SCREENING

$$V_{eff} \sim \frac{Ze}{R} e^{-\lambda R} \qquad \lambda^{-1} \sim 0.1 \text{–} 2 \text{ nm}.$$

$$\lambda \sim (a a_B)^{1/2}$$

⇒ close packing — for given density, max separation of the ions...

— as Z increases (Na Mg Al, Si) eventually metallicity lost ⇒ open structures with some short strong bonds.

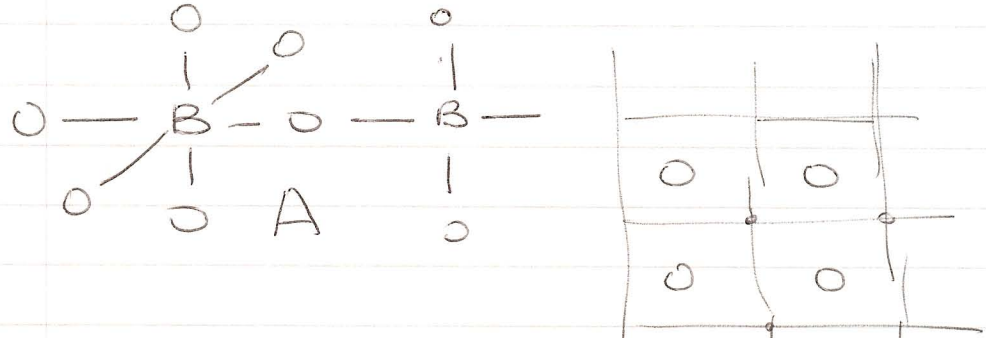
— in transition metals. both s/p & d electrons.

— d orbitals may make localised bonds within s/p shell — strong cohesion in 4d & 5d T.M.

- **Complexity**

Only up to elements & simple compounds.
→ huge complexity → richness. from constructing compounds, ~~out of~~ even with same crystal structure

e.g. ternary oxides. $ABO_3$ $A_2BO_4$.



$LaMnO_3$ ⇒ strong metallic ferromagnet. with phase transition to an insulator

$La_2CuO_{4+}$ ⇒ high temperature superconductor

$BaTiO_3$ ⇒ insulating ferroelectric.

materials become a framework for new model theories.

- Meta-materials.

— Semiconductor heterostructures. (physically tailor the band gap)
— nanomanipulation
— heterointerfaces eg. C nanotube on FM metal

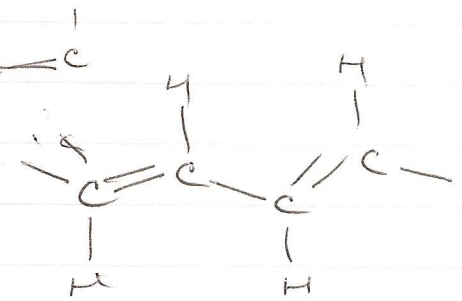
- Non-periodic solids.

Glasses: Crystalline & non crystalline $SiO_2$ are electronically nearly identical — every bond ~~is~~ "saturated"

$SiO_2$ is easy to make into a glass, but not Si
— many configs of Si—O—Si orientation of tetrahedra not fixed

Materials in hierarchies

- Polymers
  - Polyethylene $(CH_2)_n$
  - Polyacetylene (more later).



  - ~~not~~ much interest from structure, but also, recently, for electronics.
    - molecule is a "wire."

- Liquid xtals.
  - Phases of matter intermediate betw. solid & liquid
  - isotropic — nematic — smectic — cholesteric.

- Quasicrystals.
  - crystals with five fold symmetry!
  - long range orientational order
  - "almost" periodic (never repeats)

Projection from higher dim.