Physics 0551 Lecture #9

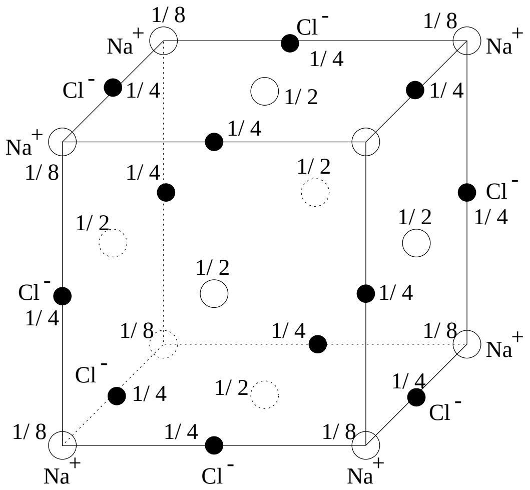
Title: Madelung constants, Metallic bonding, Defects

The process of calculating the Madelung constant is complicated by the fact that the $1/p_{ij}$ lattice sums are conditionally convergent.

One of the simplest methods was introduced by Evjen. (More complicated and general method are discussed elsewhere, see for example Appendix B of Kittel, Introduction to Solid State Physics.) Evjen's method requires an iterative summation of ever larger neutral cells with *no* accumulation of surface charge. This method constructs the sum so that only dipole and higher moments are used. Thus, rapid convergence is guaranteed.

Example: FCC Na^+Cl^- with its two atoms/unit cell.

$$\alpha = A^1 + A^2 + A^3 + \ldots.$$

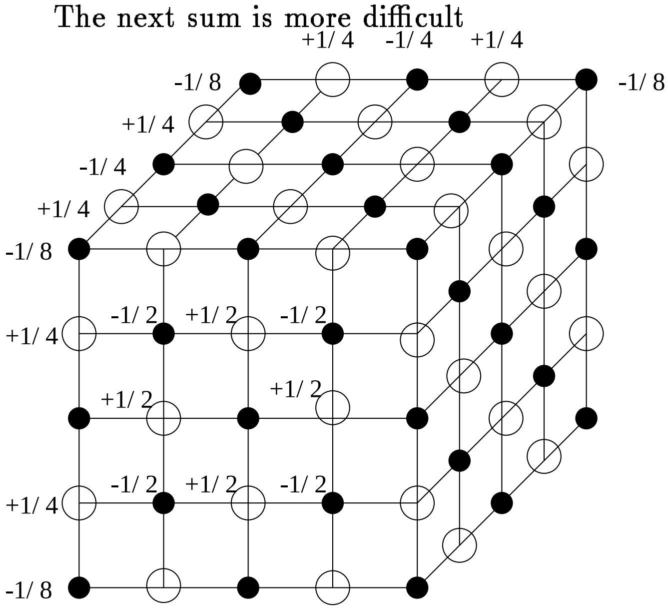


Cl^- in the center Use fraction of atoms within cube

#	fraction	p_{ij}
6	+1/2	1
12	−1/4	$\sqrt{2}$
8	+1/8	$\sqrt{3}$

$$A^1 = \frac{6 \cdot 1/2}{1} - \frac{12 \cdot 1/4}{\sqrt{2}} + \frac{8 \cdot 1/8}{\sqrt{3}} = 1.456$$

The next sum is more difficult



Outside "wall"
(Inner surface)

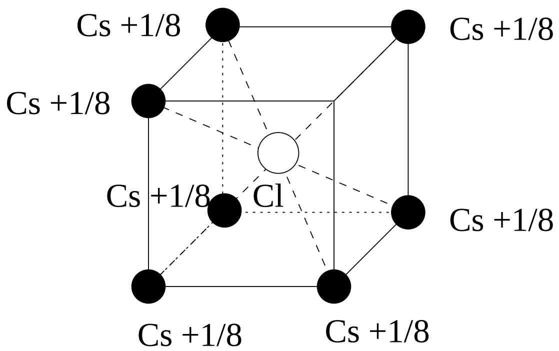
#	frac.	p_{ij}
6	$-1/2$	2
24	$+1/2$	$2\sqrt{5/4}$
24	$+1/4$	$2\sqrt{9/4}$
12	$-1/4$	$2\sqrt{2}$
8	$-1/8$	$2\sqrt{3}$
24	$-1/2$	$2\sqrt{3/2}$

Inside "wall"
(Outer surface)

#	frac.	p_{ij}
6	$+1/2$	1
12	$-3/4$	$\sqrt{2}$
8	$+7/8$	$\sqrt{3}$

$A^1 + A^2 = 1.752$
$A^1 + A^2 + A^3 = 1.747$
$\mathrm{A} = 1.74756$

Note: This method requires care. Example CsCl simple Cubic

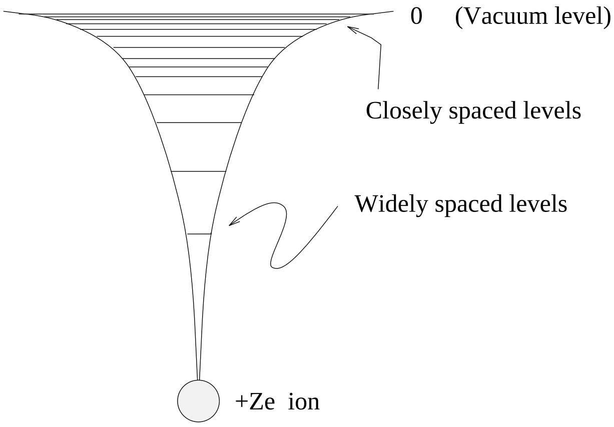


It appears to be a proper cell. However A^{2n} and A^{2n+1} differ by π! Notice the accumulation of surface charge.
$\alpha = \mathrm{A} = \mathrm{A}^1 + \mathrm{A}^2 + ... = 2.0354$
For this a rhombic dodecahedron is necessary.

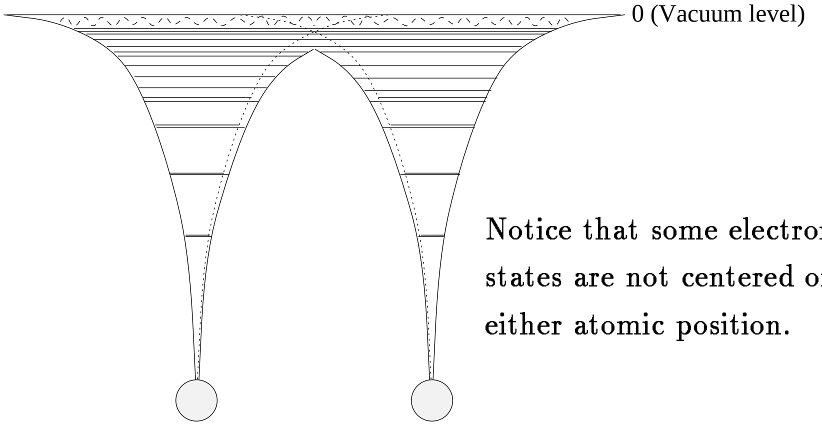
Metallic Bonding: Due to global sharing of charge.

Since this topic will be covered later, the discussion will be abbreviated here.

For one atom the potential is V(r):

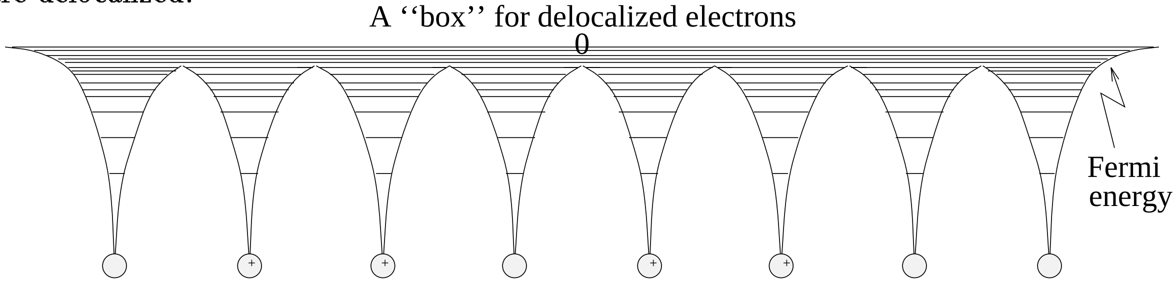


For two atoms:

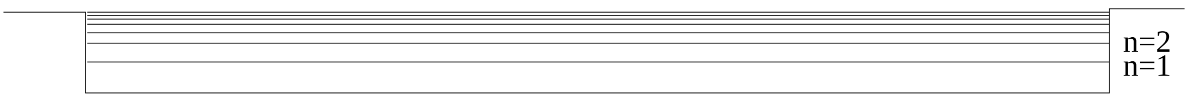


Notice that some electron states are not centered on either atomic position.

For many atoms closely spaced some of the valence electrons occupy states which are delocalized.



or a schematic representation:



Particles (fermions) in a square box $E \sim 1/L^2$

We can imagine that the delocalized electrons are just particles in an ever larger "box".

$E_{\text{box}} \propto n^2/L^2$ where L = length, $n^2 = n_x^2 + n_y^2 + n_z^2$ and n_x, n_y and n_z are integer associated with quantum states. Since the eigenvalues drop rapidly as the box grows larger, it is energetically favorable to have the largest possible box. In principal, this is the origin of metallic bonding.

Schottky Defects in a Monoatomic Crystal

Since we have been discussing "perfect" crystals, it is perhaps useful to briefly discuss some of the simplest deviations from perfection. Hence, the concepts of Schottky and Frenkel defects are introduced.

At temperatures above absolute zero, it is thermodynamically given that all crystals will develop defects. These defects will take the form of vacancies in the atomic sites. The atoms which are displaced can either migrate to lattice surface and occupy lattice sites: These are called Schottky defects. Alternatively they may sit at interstitial locations: These are called Frenkel defects.

Assume that this process occurs at constant pressure. Hence the Helmholtz free energy F = U - TS is minimized.

1. Crystal consists of N atoms and its coefficient of thermal expansion is zero.
2. The energy W_s of a Schottky defect is temperature independent.
   W_s = (Work to move the atom $\rightarrow\ \infty$) - (energy at the surface)
3. The number of Schottky defects is n_s and they are completely independent of one another.

$$\begin{aligned}
F &= U - TS \\
F &= U_{\text{lattice}} + n_s W_s - k_B T\ \ell n\ \sigma_s \qquad\qquad U_{\text{lattice}} < 0 \\
& \quad k_B = \text{ Boltzmann constant} \\
& \quad \sigma_s = \text{ Number of possible configurations which gives} n_s \\
\sigma_s &= \binom{N}{n_s} = \frac{N!}{(N-n_s)!n_s!} \text{ is the number of combinations}
\end{aligned}$$

Recall ℓn N! $\approx$ N ℓn N - N if N is large

Thus

$\ell n\ \sigma_s\ \approx\ N\ \ell n\ N - (N - n_s)\ \ell n(N - n_s) - n_s \ell n\ n_s$

$\frac{\partial F}{\partial n_s} = 0 = W_s - k_B T\ (1 + \ell n(N - n_s) - 1 - \ell n\ n_s)$

Assume $n_s << \mathrm{N}$

$$0 = \mathrm{W}_s - k_B T\ \ell\mathrm{n}(\mathrm{N}/\mathrm{n}_s)$$
$$\ell n(n_s/N) = W_s/k_B T \rightarrow \qquad n_s = N\exp(-W_s/k_B T)$$

An exponential function.

Frenkel imperfections in a monoatomic crystal

W_F = energy required to bring an atom to an interstitial position. The entropy changes consist of two components

1. n_F vacancies in a crystal of N atoms can be arranged in σ_F ways.
2. The n_F atoms from the vacancies can be distributed in σ_I ways over the N_I interstitial positions.

$$\Delta S_F = k_B[\ell n\frac{N!}{(N-n_F)!n_{F!}} + \ell n\frac{N_{I!}}{(N_I - n_F)!n_{F!}}]$$

so if $n_F << N,\ n_F << N_I$

$$\begin{aligned}
\frac{\partial F}{\partial n_F} &= 0 = W_F - k_B T[\ell n(N/n_F) + \ell n(N_I/n_F)] \\
& \quad\; 0 = W_F + k_B T \ell n\left(\frac{n_F^2}{N N_I}\right) \\
\frac{n_F^2}{N N_I} &= exp(-W_F/k_B T) \\
n_F &= (N N_I)^{1/2} exp(-W_F/2k_B T)
\end{aligned}$$

Very sensitive to N_I.