Cohesive Energy

energy required to disassemble a solid into "elementary" parts

can be: neutral atoms, ions, molecules — as convenient building blocks

I. Molecular crystals: the noble gases

Potential of interaction between two atoms: neutral, in the ground state

nearest-neighbor distance

$$\phi(r) = -\frac{A}{r^6} + \frac{B}{r^{12}}$$

van der Waals

mimics repulsion at short distances; manifestation of the Pauli exclusion pr. (closed shells are hard to deform)

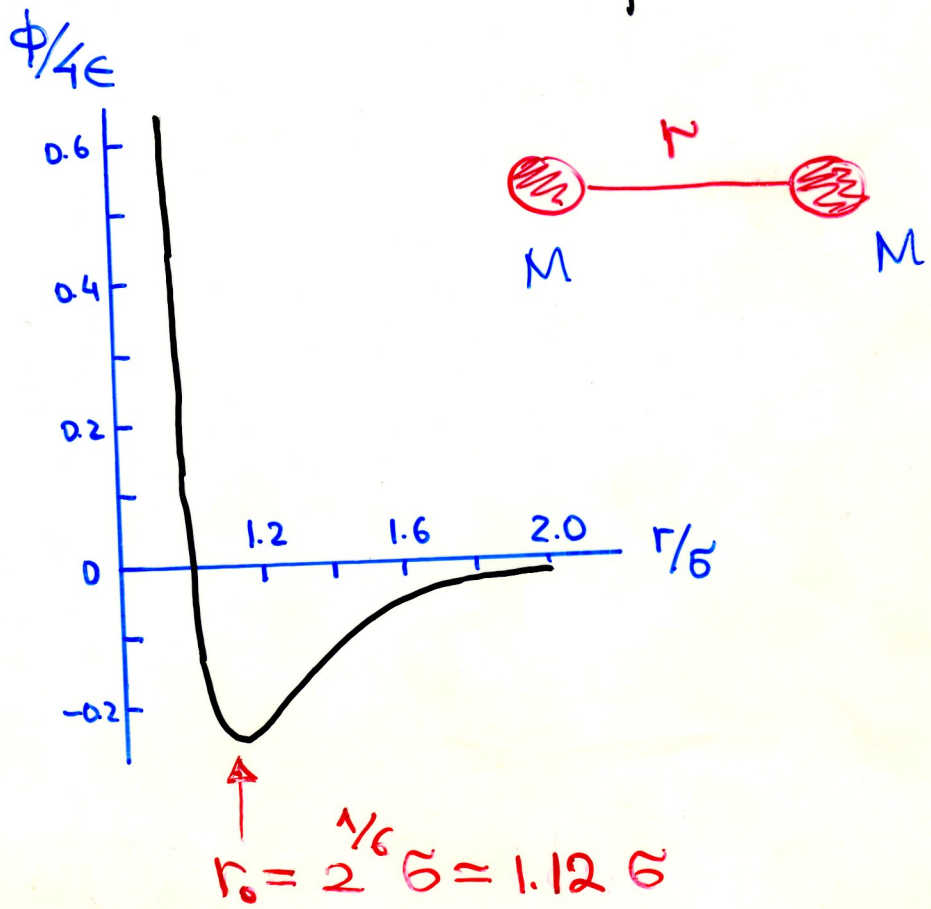
Cast $\phi(r)$ into another form:

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

$\sigma = \left(\frac{B}{A}\right)^{1/6}$, characteristic length

$4\epsilon = \frac{A^2}{B}$, characteristic energy

two-parameter potential, known as "Lennard-Jones 6-12 potential"



$r_0 = 2^{1/6}\sigma = 1.12\,\sigma$

$\left.\frac{\partial \phi}{\partial r}\right|_{r_0} = 0$; minimum $\phi(r_0) = -\epsilon$

Classical or quantum description?

zero-point energy $\dfrac{\hbar^2}{M*(\text{typical size})^2}$ ← σ

characteristic potential energy ← ϵ

Dimensionless ratio: $\dfrac{\hbar^2/M\sigma^2}{\epsilon}$

de Boer parameter $\Lambda = \dfrac{\hbar}{\sigma\sqrt{\epsilon M}}$

	^{3}He	^{4}He	Ne	Ar	Kr	Xe
Λ	3.1	2.6	0.59	0.19	0.10	0.064
	quantum description		← → classical description			
$\epsilon/10^{-2}$ (eV)			0.3	1.04	1.40	2.0
σ (Å)			2.74	3.40	3.65	3.98

deduced from properties of low-density gases

binary collisions

$$P = \frac{NT}{V}\left\{1 + \underbrace{B(T)}_{\text{2nd}}\frac{N}{V} + \underbrace{C(T)}_{\text{3rd}}\left(\frac{N}{V}\right)^2 + \dots\right\}$$

.. virial coef.

Total energy of the solid?

taken as FCC BL

1 atom: $\sum_{\vec{R}\neq 0} \phi(|\vec{R}|)$ — BL vectors

N atoms: $\frac{1}{2} N \sum_{\vec{R}\neq 0} \phi(|\vec{R}|)$ — cohesive en.

Energy per particle $u = \frac{1}{2} \sum_{\vec{R}\neq 0} \phi(|\vec{R}|)$

$|\vec{R}| = \alpha(\vec{R}) \cdot r$ — nearest-n. distance

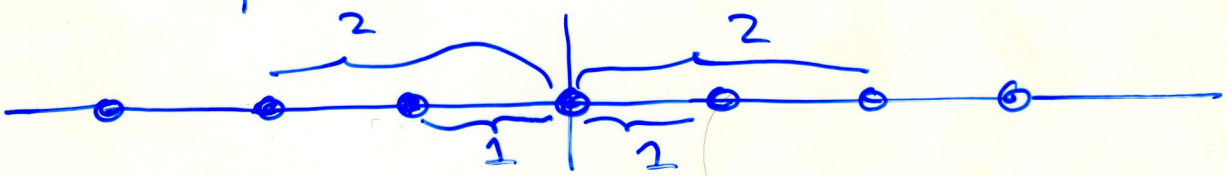
↓ dimensionless, depends on BL

$$u = 2\epsilon \cdot \left[A_{12}\left(\frac{\sigma}{r}\right)^{12} - A_6\left(\frac{\sigma}{r}\right)^{6} \right]$$

$$A_n = \sum_{\vec{R}\neq 0} \frac{1}{\alpha(\vec{R})^n}$$

depends only on BL

Example: 1D chain



$$A_n^{(1D)} = 2\sum_{k=1}^{\infty} \frac{1}{k^n} = 2\,\zeta(n)$$

Riemann's ζ-function

$A_6^{(1D)} = 2.0346$

$A_{12}^{(1D)} = 2.0004$

$$A_6^{(FCC)} = 14.45 \qquad A_{12}^{(FCC)} = 12.13$$

$A_n \xrightarrow[n\to\infty]{}$ coordination number

$$A_n\Big|_{n\gg 1} = \left(\text{nearest neighbors}\right) + \left(\text{next to nearest n.}\right) + \dots$$

Equilibrium position in a crystal: $\left.\frac{\partial u}{\partial r}\right|_{r_0} = 0$

$$r_0 = \left(\frac{2A_{12}}{A_6}\right)^{1/6}\sigma = 1.09\sigma$$

Eq. cohesive energy

$$u(r_0) = -\frac{\epsilon A_6^2}{2A_{12}} = -8.6\,\epsilon$$

Bulk modulus $B = -V\left(\frac{\partial P}{\partial V}\right)_T$

$$B = \frac{4\epsilon}{\sigma^3} A_{12}\left(\frac{A_6}{A_{12}}\right)^{5/2} = \frac{75\epsilon}{\sigma^3}$$

		Ne		Xe
r_0 (Å)	Ex.	3.13	....	4.33
	Th.	2.99		4.34
u_0 ($\frac{eV}{atom}$)	Ex.	-0.02		-0.17
	Th.	-0.027	....	-0.172
B ($\frac{10^{10}\,dyne}{cm^2}$)	Ex.	1.1	...	3.6
	Th.	1.81		3.81

$\hbar\omega \sim 10^{-1} - 10^{-2}$ eV small !

Bulk modulus (compressibility)

$$B = -V\left(\frac{\partial P}{\partial V}\right)_T \qquad K = \frac{1}{B}$$

$$dU = -P\,dV$$

energy $U = Nu$ volume $V = Nv$

$$B = -Nv\,\frac{\partial}{\partial Nv}\left(-\frac{\partial Nu}{\partial Nv}\right)$$

$$B = v\,\frac{\partial^2 u}{\partial v^2}$$

$u = u(r)$ — nearest-n. distance

$$\Rightarrow \quad v = \frac{a^3}{4} = \frac{r^3}{\sqrt{2}} \quad (\text{FCC}) \qquad a = \sqrt{2}r$$

$$\frac{\partial}{\partial v} = \frac{\partial r}{\partial v}\cdot\frac{\partial}{\partial r}$$

$$\boxed{\frac{\partial v}{\partial r} = \frac{3}{\sqrt{2}}r^2} \qquad \boxed{\frac{\partial}{\partial v} = \frac{\sqrt{2}}{3}r^{-2}\frac{\partial}{\partial r}}$$

$$B = \frac{r^3}{\sqrt{2}}\cdot\frac{\sqrt{2}}{3}r^{-2}\frac{\partial}{\partial r}\left(\frac{\sqrt{2}}{3}r^{-2}\frac{\partial}{\partial r}\right)u(r) = \frac{\sqrt{2}}{9}r\,\frac{\partial}{\partial r}\left(r^{-2}\frac{\partial u}{\partial r}\right)$$

$$B = \frac{\sqrt{2}}{9}r\left[r^{-2}\frac{\partial^2 u}{\partial r^2} - 2r^{-3}\frac{\partial u}{\partial r}\right]\Bigg|_{r=r_0}$$

equilibrium

$$\boxed{B = \frac{\sqrt{2}}{9}r_0^{-1}\left.\frac{\partial^2 u}{\partial r^2}\right|_{r_0}}$$

$$u = 2\epsilon\left[A_{12}\left(\frac{\sigma}{r}\right)^{12} - A_6\left(\frac{\sigma}{r}\right)^6\right]$$

II. Ionic Crystals

e.g KCl: 7.4 eV

Cohesive energy := disassemble to ions

ions treated as charged classical particles localized at some positions $\vec{R}$

$$\phi(r) = u^{core}(r) + u^{coul}(r)$$

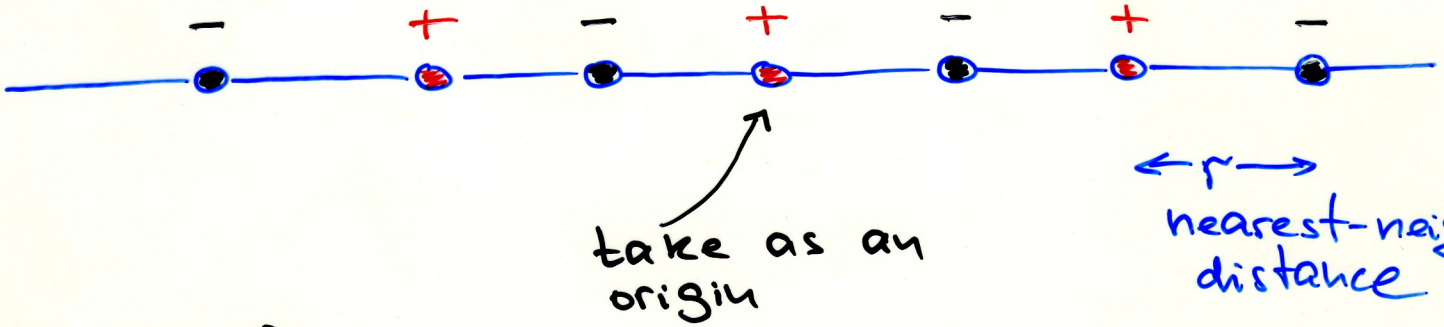
short-range repulsion

long-range Coulomb

main contribution

Coulomb lattice sums

Example: 1D chain



$$u = \frac{e^2}{r} \cdot \left\{ -1 + \frac{1}{2} - \frac{1}{3} + \frac{1}{4} - \dots \right\} * 2 \equiv -\alpha \frac{e^2}{r}$$

Madelung constant

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \dots$$

$$\alpha = 2\ln 2 \simeq 1.386$$

For an arbitrary BL

$$u^{coul} = -\alpha \frac{e^2}{r}$$

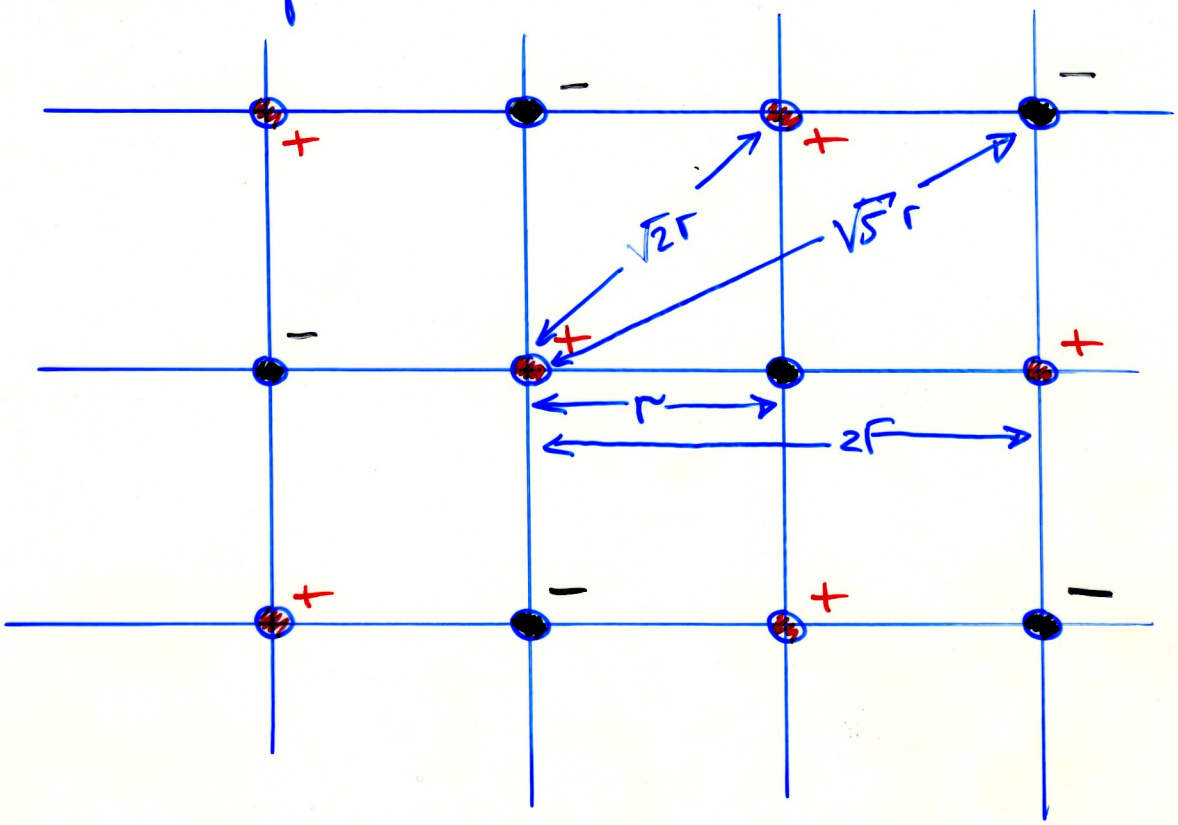
α — Madelung constant

r — nearest-neighb. distance

u^{coul} — energy per ion pair

Problem of finding α

Example: 2D square net



$$u^{coul} = -\frac{e^2}{r}\left\{4\cdot\frac{1}{1} - 4\cdot\frac{1}{\sqrt{2}} + 4\cdot\frac{1}{2} - 8\cdot\frac{1}{\sqrt{5}} + \dots\right\}$$

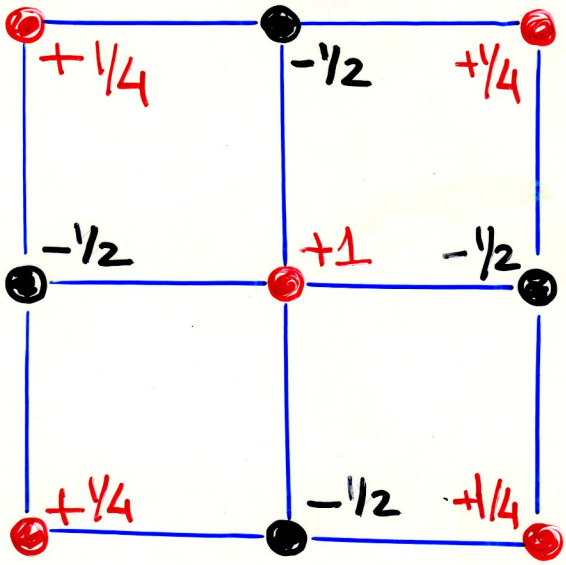
$$= -\frac{e^2}{r}\left\{4 - 2.82 + 2 - 3.57 + \dots\right\}$$

Poor convergence: we deal with charged subsystems; ±

Define a multi-cell:

crystal = a set of multi-cells

Madelung electrostatic energy = inside cell + cell-cell interaction



charge in the corner : 1/4 contribution
charge on the side : 1/2 contribution
charge inside : 1 contribution

① neutral (count!)
② no dipole (cubic symmetry)

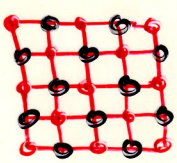
quadrupole-quadr. $\frac{1}{R^5}$ $\Longleftrightarrow$ cell-cell interaction decays off RAPIDLY

$$u_1^{cell} = -\frac{e^2}{r}\left\{4\cdot\frac{1/2}{1} - 4\cdot\frac{1/4}{\sqrt{2}}\right\}$$

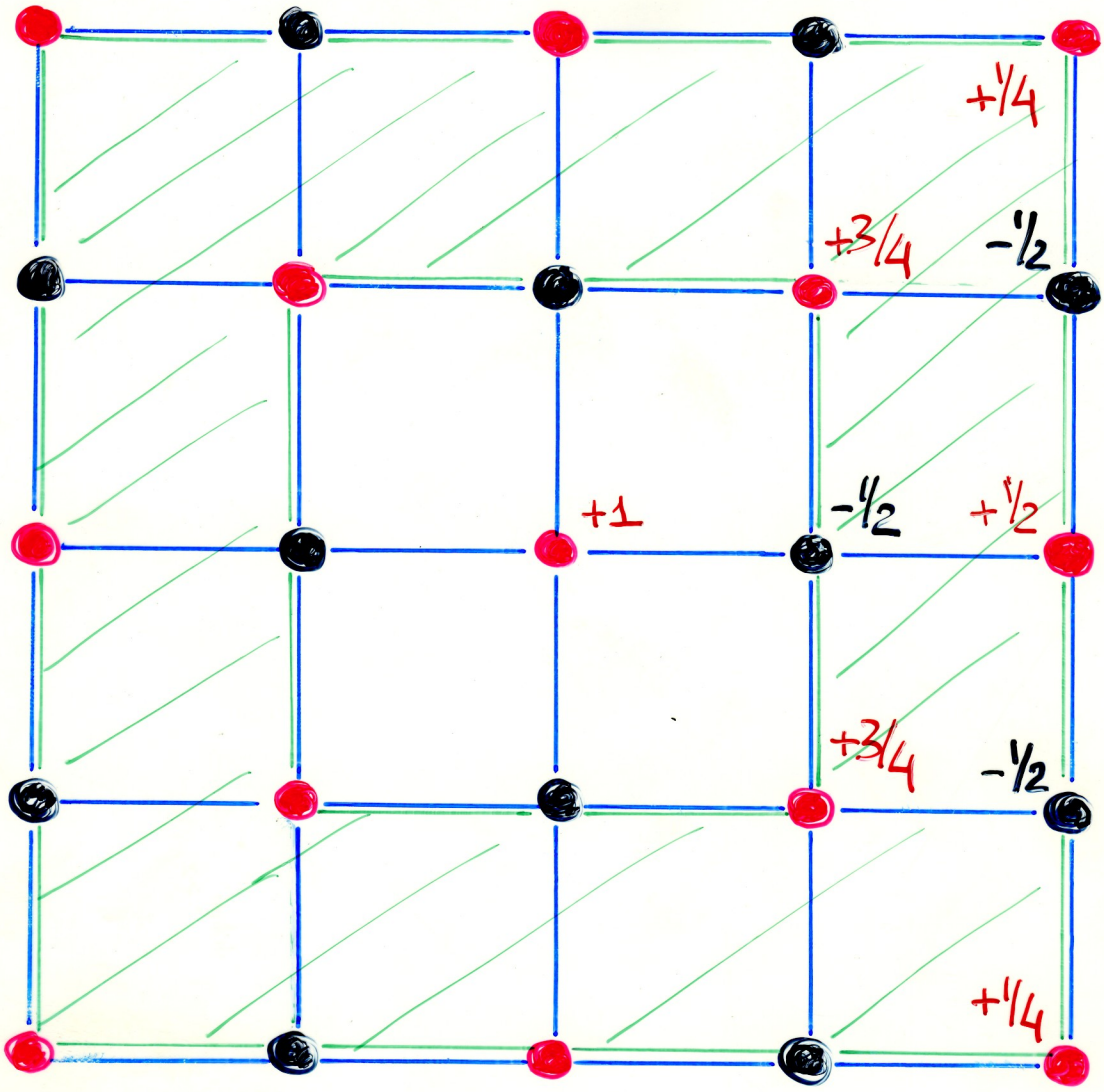
$$\alpha_1 = 2 - \frac{1}{\sqrt{2}} = 1.293$$

Another way of counting ions that surround the origin

Next approximation: take a larger



"Neutral-shell" method (cont'd.)



2nd cell = rest of 1st cell + new charges:

effective charge	# of charges	distance
$-\frac{1}{2}$	4	1
$+\frac{3}{4}$	4	$\sqrt{2}$
$+\frac{1}{2}$	4	2
$-\frac{1}{2}$	8	$\sqrt{2^2+1^2}=\sqrt{5}$
$+\frac{1}{4}$	4	$\sqrt{2^2+2^2}=\sqrt{8}$

Coulomb energy: interaction of the (+1) charge with all (fractional) charges in the 2nd cell

$$u_2^{cell} = -\frac{e^2}{r}\left\{\left[4\cdot\frac{1}{2} - 4\cdot\frac{3}{4}\cdot\frac{1}{\sqrt{2}}\right] + \left[-4\cdot\frac{1}{2}\cdot\frac{1}{2} + 8\cdot\frac{1}{2}\cdot\frac{1}{\sqrt{5}} - 4\cdot\frac{1}{4}\cdot\frac{1}{\sqrt{8}}\right]\right\}$$

$$u_2^{cell} = -\frac{e^2}{r}\cdot\underbrace{\left\{\left[2-\frac{3}{\sqrt{2}}\right]+\left[-1+\frac{4}{\sqrt{5}}-\frac{1}{\sqrt{8}}\right]\right\}}_{\alpha_2 = 0.314}$$

$$=$$

$$u_1^{cell} = -\frac{e^2}{r}\cdot\alpha_1 \qquad \alpha_1 = 1.293$$

$$\alpha = \alpha_1 + \alpha_2 + \dots$$

$$\alpha = \underbrace{1.293 + 0.314}_{1.607} + \dots$$

2D simple square

Coulomb + short-range repulsion

$$u(r) = -\alpha \frac{e^2}{r} + \frac{C}{r^m}$$

total energy per ion

① How to choose m — ?

② contribution ?

Equilibrium: $\left.\frac{\partial u}{\partial r} = +\alpha \frac{e^2}{r^2} - m \frac{C}{r^{m+1}}\right|_{r=r_0} = 0$

$$r_0^{m-1} = \frac{mC}{\alpha e^2}$$

$$u(r_0) = -\alpha \frac{e^2}{r_0} + \frac{1}{m} \cdot \alpha \frac{e^2}{r_0}$$

cohesive energy per ion

slowly varying function of m

We describe anions like Cl^-, F^-...
with excess electron ⇒ lower density of electrons at outer orbitals than for Ne, Ar, ...

Experimentally measurable:
r_0 and bulk modulus B_0

NaCl

$$m = 1 + \frac{18 B_0 r_0^3}{|u^{coul}(r_0)|} = 6 \div 10$$

$|u^{coul}(r_0)| \propto e^2/r_0$

3D Coulomb sums

Consider, e.g., NaCl structure (FCC with a basis)

Negative anions Cl^- at $\vec{R}$

Positive cations at $\vec{R}+\vec{d}$

misplacement $|\vec{d}| = \frac{a}{2}$ along the cube side

$|\vec{d}| = \frac{a}{2} = r$ nearest-neighb. distance

$|\vec{R}| = \alpha(\vec{R})\, r \qquad |\vec{R}+\vec{d}| = \alpha(\vec{R}+\vec{d})\, r$

$\alpha(\vec{R})$: dimensionless, characterizes BL

Potential energy of a single ion

$$u = -\frac{e^2}{r}\left\{ \frac{1}{\alpha(\vec{d})} + \sum_{\vec{R}\neq 0}' \left(\frac{1}{\alpha(\vec{R}+\vec{d})} - \frac{1}{\alpha(\vec{R})} \right) \right\}$$

α

$'$ is conditionally converged only

due to the long-range character of $1/r$

- work with neutral multi-cells
- Ewald's summation

	CsCl	NaCl	Zincblende
α	1.7627	1.7476	1.6381
Z	8	6	4

Cohesion in covalent crystals

Rearrangement of electron orbitals: directional tetrahedral bonds formed

(C, Si, Ge, zincblende ...) valence = 4

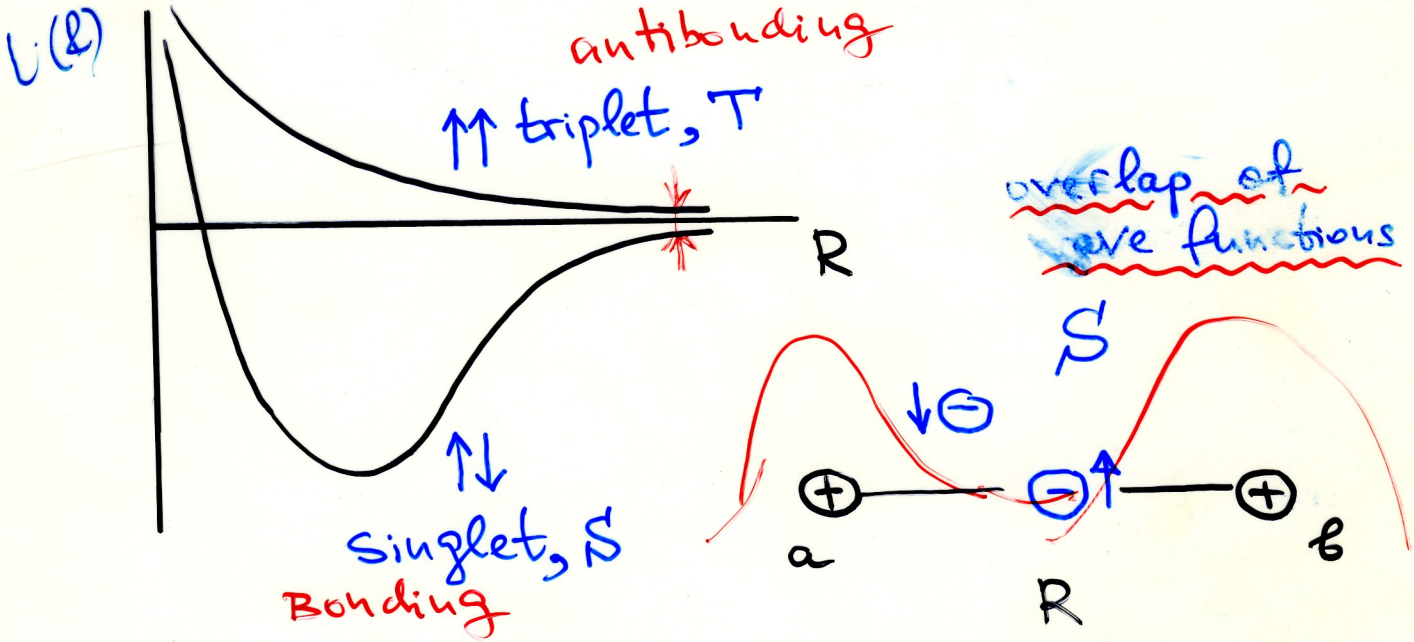
C $1s^2 2s^2 2p^2$ $\xrightarrow{4eV}$ $1s^2 2s\,2p^3$

to form C(=)C bond

7eV

Methods of quantum chemistry needed ...

Simplest example: covalent bonding of H_2



$$\Psi_{S(T)} = A \cdot \left(\phi_a(r_1)\phi_b(r_2) \pm \phi_a(r_2)\phi_b(r_1) \right)$$

Heitler, London 1927

Normalization constant

$$|A|^2_{S(T)} = \langle \Psi_{S(T)} | \Psi_{S(T)} \rangle = 2\left(1 \pm \langle \phi_a(1)\phi_b(2) | \phi_b(1)\phi_a(2) \rangle\right)$$

overlap $S^2 = |\langle \phi_a(1) | \phi_b(1) \rangle|^2$

$$S \sim \int d^3r \; e^{-\frac{|\vec{r}-\vec{R}_a|}{a_B}} \cdot e^{-\frac{|\vec{r}-\vec{R}_b|}{a_B}} \sim e^{-\frac{|\vec{R}_a-\vec{R}_b|}{a_B}}$$

$R \equiv |\vec{R}_a - \vec{R}_b| \gg a_B$

Singlet-triplet splitting

$$E_S - E_T = \frac{\langle \Psi_S | H | \Psi_S \rangle}{\langle \Psi_S | \Psi_S \rangle} - \frac{\langle \Psi_T | H | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle}$$

$$\frac{1}{2}(E_S - E_T) = \int d^3r_1 \int d^3r_2 \; \phi_a(\vec{r}_1)\phi_b(\vec{r}_2) \cdot \left\{ -\frac{e^2}{|\vec{r}_1-\vec{R}_a|} - \frac{e^2}{|\vec{r}_2-\vec{R}_b|} + \frac{e^2}{|\vec{r}_1-\vec{r}_2|} + \frac{e^2}{|\vec{R}_a-\vec{R}_b|} \right\} \cdot \phi_a(\vec{r}_2)\phi_b(\vec{r}_1)$$

← "exchange"

Correct answer for H_2 $R = |\vec{R}_a - \vec{R}_b| \gg a_B$:

$$E_S - E_T = -1.64 \, Ry \cdot \left(\frac{R}{a_B}\right)^{5/2} \exp\left\{-\frac{2R}{a_B}\right\}$$

exponential effect

Cohesion in Free Electron Metals

Model:

ions = point classical ($M=\infty$) charges embedded into a sea of electrons of density n_e: uniform compensating background

Characteristic lengths

Bohr radius $a_0 = \hbar^2/me^2$ (alkali M.)

distance between electrons $r_s = \left(\frac{3}{4\pi}\right)^{1/3} n_e^{-1/3} = 0.62\, n_e^{-1/3}$

$\left(\frac{4\pi}{3} r_s^3 \cdot n_e = 1\right)$

Contribution to energy

1. Coulomb e-ion, (direct e-e repulsion, ion-ion interactions)

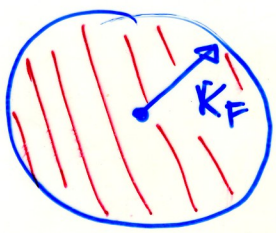
BCC

$$u^{coul} = -\frac{24.35}{r_s/a_0}\ \frac{eV}{atom} \sim n_e^{1/3}$$

classical contribution

2. Electronic kinetic energy

Fermi sphere in k-space



$$\frac{2 \cdot \frac{4\pi}{3} k_F^3 \cdot V}{(2\pi\hbar)^3} = N_e$$

phase-space cells

Fermi momentum $k_F = (3\pi^2 \hbar^3 n_e)^{1/3}$

Fermi energy $E_F = \frac{k_F^2}{2m} \sim \frac{(\hbar^3 n_e)^{2/3}}{m} \sim n_e^{2/3}$

Mean kinetic energy

$$u^{kin} = \frac{3}{5} E_F = \left\langle \frac{k^2}{2m} \right\rangle \sim \frac{(\hbar^3 n_e)^{2/3}}{m}$$ quantum contrib.

$$u^{kin} = \frac{30.1}{(r_s/a_0)^2} \frac{eV}{atom} \sim n_e^{2/3}$$

③ Electron-electron exchange inter. (lowers energy!)

$$u^{ex} = -\frac{12.5}{r_s/a_0} \frac{eV}{atom} \sim n_e^{1/3}$$ quantum effect

↑↑

$$\frac{1}{\sqrt{2}}\left(\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)\right) \cdot \frac{e^2}{r_{12}}$$

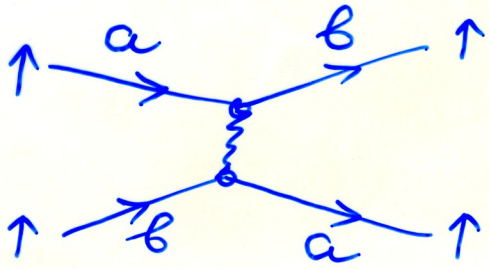
same direction of spins

$$\frac{1}{\sqrt{2}}\left(\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)\right) =$$

$$= \langle \phi_a(1)\phi_b(2) | \frac{e^2}{r_{12}} | \phi_a(1)\phi_b(2) \rangle \leftarrow \text{direct e-e}$$

$$- \langle \phi_a(1)\phi_b(2) | \frac{e^2}{r_{12}} | \phi_a(2)\phi_b(1) \rangle \leftarrow \text{exchange e-e contribution}$$

↑↑ sign!



All contributions together

$$u = \frac{30.1}{(r_s/a_0)^2} - \frac{36.8}{r_s/a_0} \quad \frac{eV}{atom}$$

"Equilibrium" position $\frac{\partial u}{\partial r_s} = 0$ $r_s = 1.6 a_0$

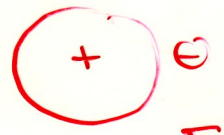
overestimation $|u^{th}| = 11.2 \, eV/atom$

universal for all Alk. M.

In reality r_s ranges from $2a_0$ to $6a_0$ and is not universal

ions have finite radii:

① less volume accessible to electrons
⇒ smaller r_s ⇒ larger u^{kin}

② 

+e

Electrostatic energy gives smaller negative contrib.