

CMP Lecture 3

School of Physics
The University of Sydney



The free electron (Sommerfeld) model

Does treat properly the fact that electrons are fermions.
Compared to Drude theory, Sommerfeld theory obtains electron velocity
 ~ 10 times larger, but heat capacity per electron ~ 100 times smaller.
This leaves the Wiedemann–Franz ratio roughly unchanged from Drude.

Drude's classical gas treatment was incorrect – resulting in huge
overestimation of the heat capacity per particle and underestimation of
the typical velocity of particles.

Shortcomings of the free electron model

- Having found v_F is very large, and being able to measure the scattering time τ we can obtain a scattering length $\lambda = v_F \tau$ which can be as large as 100 Å – why then do the electrons not scatter from the atoms?
- Assumes one free electron per atom.
- No explanation of why the Hall coefficient sometimes has a negative sign.
- Does not explain optical spectra, e.g. varying absorption at some frequencies – different metals look different colours.
- The specific heat of electrons, although more correct than in Drude theory, is still off by factors as large as 10 for some metals.
- Magnetism is not explained, i.e. for no applied magnetic field we can still get magnetisation (ferromagnetism, anti-ferromagnetism).
- Electron-electron interaction is not included (e.g. ignored the Coulomb interactions between electrons).

NEED to take into account the ATOMIC STRUCTURE

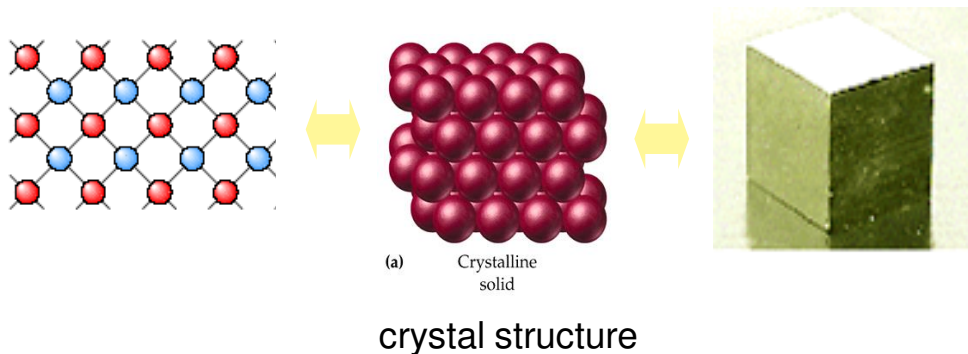
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Types of Matter

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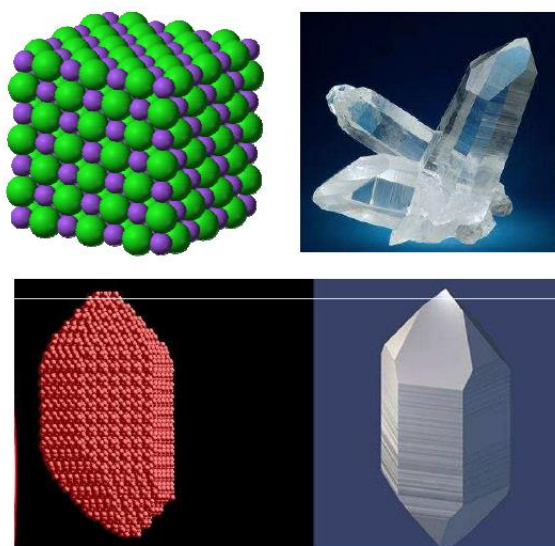
Crystalline solids

- Crystalline solid is the solid form of a substance in which the **atoms or molecules** are arranged in a definite, repeating pattern in three dimensions.
- Single crystals, ideally **have a high degree of order**, or regular geometric periodicity, throughout the **entire volume of the material**.



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Crystalline solids



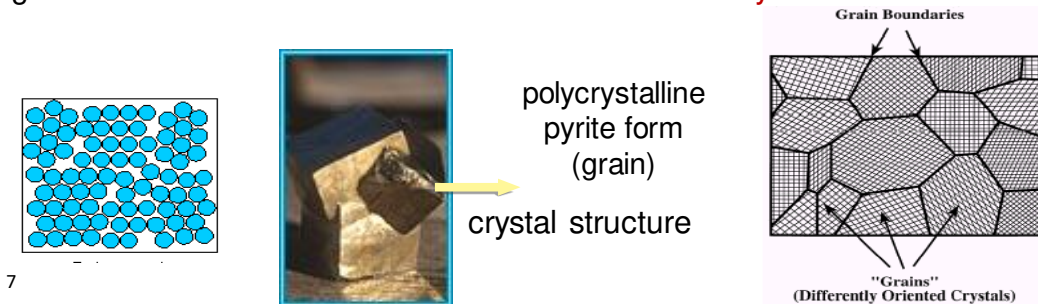
Small units reproduced periodically to form a crystal. This particular figure depicts NaCl (table salt), with the larger spheres being Cl⁻ ions and the smaller spheres being Na⁺ ions.

The macroscopic morphology of a crystal often will reflect the underlying microscopic (atomic) structure.

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Polycrystalline solids

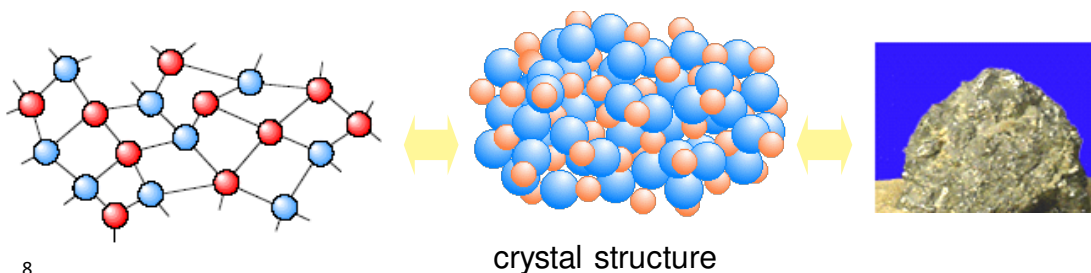
- A polycrystal is a material made up of an aggregate of *many small single crystals* (also called crystallites or grains).
- Polycrystalline materials **have a high degree of order over many atomic or molecular dimensions**.
- These *ordered regions*, or single crystal regions, **vary in size and orientation** wrt one another.
- These regions are called *grains (domains)* and are separated from one another by *grain boundaries*. *The atomic order can vary from one domain to the next*.
- The grains are usually *100 nm - 100 microns in diameter*. Polycrystals with grains that are *<10 nm in diameter* are called **nanocrystalline**.



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Amorphous solids

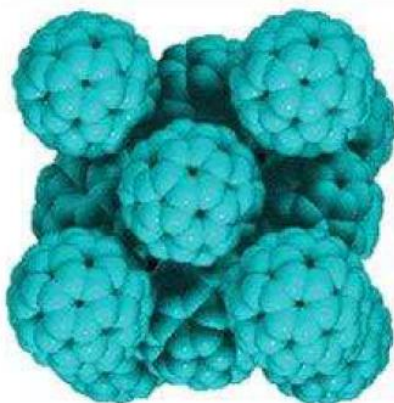
- Amorphous (non-crystalline) solids are composed of randomly orientated atoms, ions, or molecules that do not form defined patterns or lattice structures.
- Amorphous materials have order only within a few atomic or molecular dimensions.
- Amorphous materials do not have any long-range order, but they have varying degrees of short-range order.
- Examples of amorphous materials include amorphous silicon, plastics, and glasses.
- Amorphous silicon can be used e.g. in solar cells and thin film transistors.



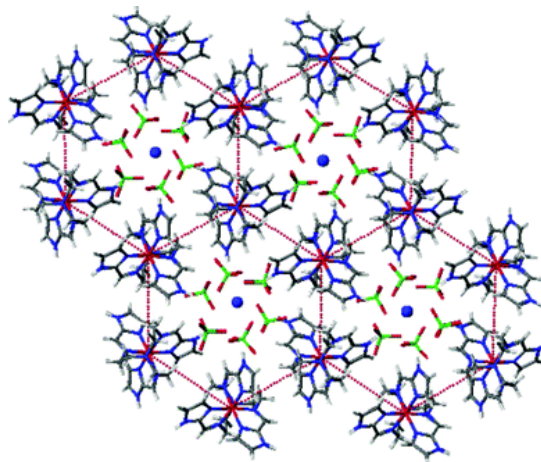
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Molecular crystals

60 carbon atoms bind together to form a large molecule known as a “Buckyball” or “Fullerene”, the full name being Buckminsterfullerene



Buckyballs stick together by weak van der Waals bonds to form a
9 molecular crystal



A molecular lattice of 1·KClO₄

Buckminsterfullerene, C₆₀, “Bucky balls”

Was first generated in 1984 by Eric Rohlfing, Donald Cox and Andrew Kaldor. In 1985 their work was repeated by Harold Kroto, James R. Heath, Sean O'Brien, Robert Curl, and Richard Smalley at Rice University, who recognized the structure of C₆₀ as buckminsterfullerene. Kroto, Curl and Smalley were awarded the 1996 **Nobel Prize** in Chemistry.

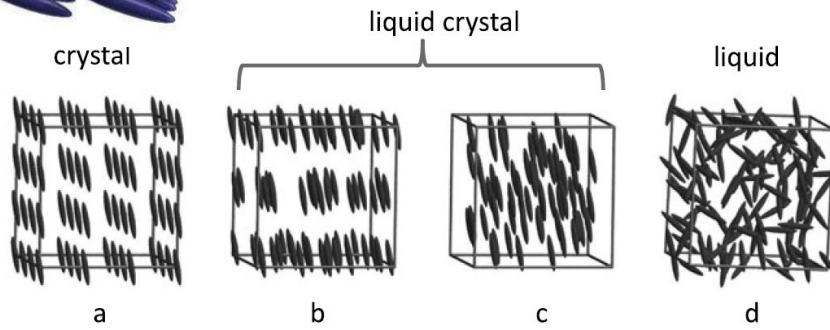
*Name inspired by
Richard Buckminster Fuller, an
American architect, systems theorist,
author, designer, inventor, and futurist.
who designed geodesic domes
e.g. Montreal Biosphère*



Liquid crystals



Liquid crystals – the system orders in some ways and remains disordered in other ways.



Crystal of molecules, all positionally ordered and all are oriented in the same direction.

Retain orientation, and retain some of their positional order, but within each layer, disordered "*smectic-C phase*"

Positional order lost, but orientation remains, "*nematic phase*"

True liquid, no positional order or orientational order

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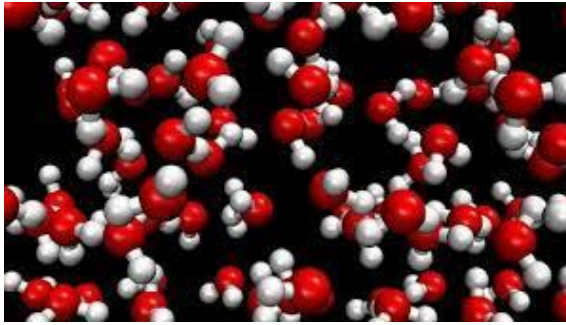
Liquid crystals

LCD by far, the most widely produced and sold television display type.



Liquids

Here, atoms are attracted to each other, but not so strongly that they form permanent bonds. They are disordered configurations of molecules where the molecules are free to move around into new configurations (e.g. water below).



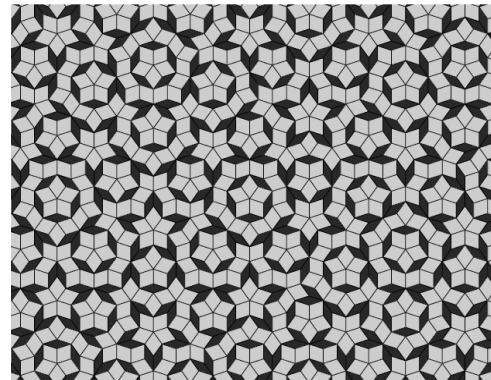
<https://www.youtube.com/watch?v=ZI74NCVbA5A>

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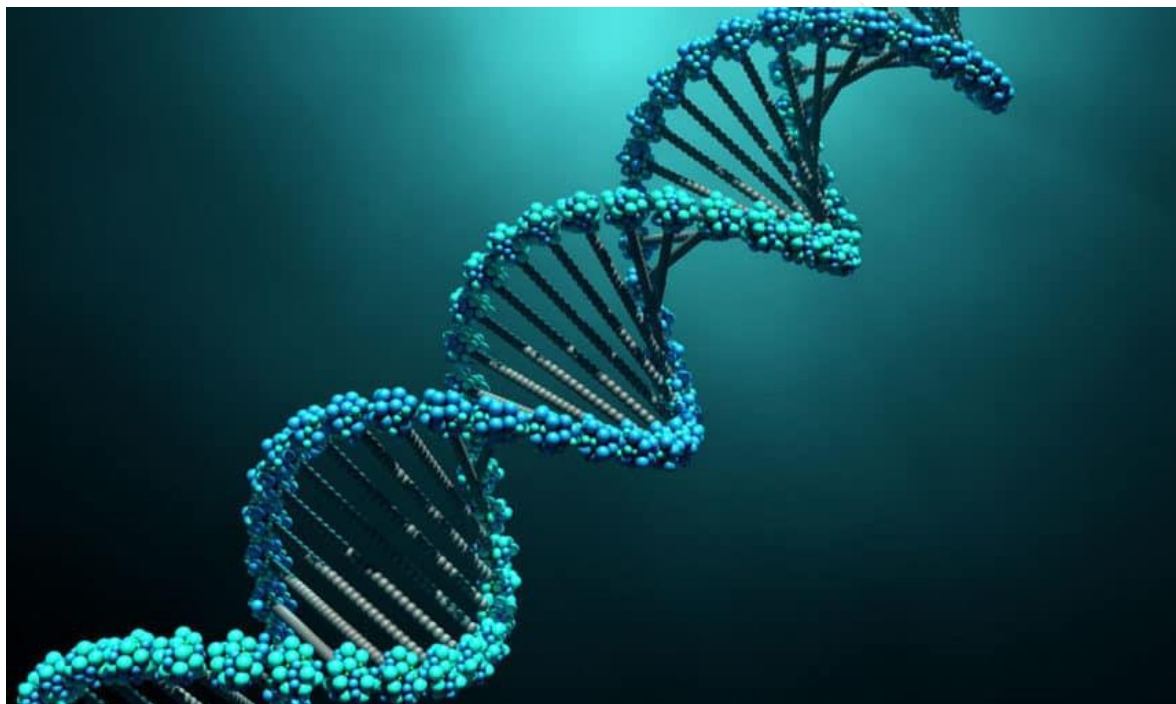
Quasicrystals

Quasi-crystals are ordered but nonperiodic. In a quasi-crystal, units are assembled together with a set of regular rules which appears to make a periodic structure, but in fact the pattern is non-repeating.

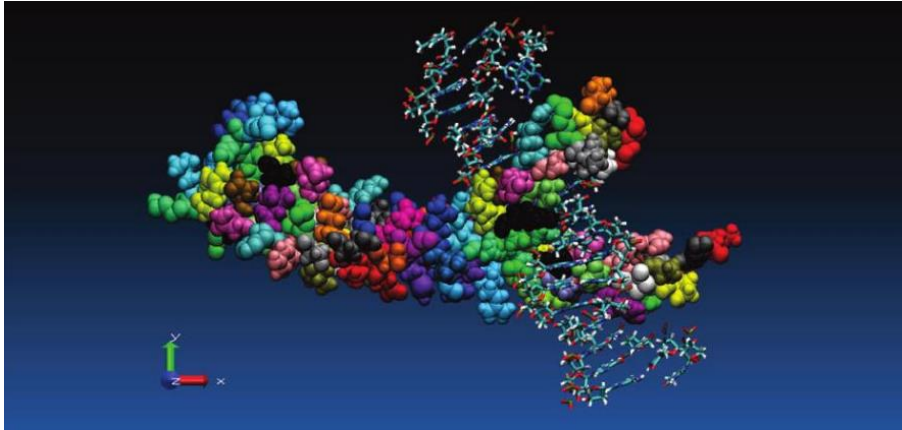
Quasicrystals made of atoms are extremely rare in nature, but there are many man-made quasi-crystalline materials



Polymers



Soft Matter Physics



- A new discipline in Condensed Matter Physics, covers the structure and function of proteins, polymers, DNA and has a major interface with molecular biology.

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Periodic table

The many-particle Schroedinger equation describing the many electrons and many nuclei in a solid is,

$$H\Psi = E\Psi$$

where Ψ is the wavefunction describing the positions and spin states of all the electrons and nuclei in the system, and H the Hamiltonian which includes a kinetic term (with the electron and nuclear masses) as well as a Coulomb interaction term between all the electrons and nuclei.

It is not possible to solve this for the 10^{23} electrons in a real solid, so approximations are made.

An electron in an atomic orbital is labeled by four quantum numbers, $|n, l, l_z, \sigma_z\rangle$

$n = 1, 2, \dots$ *principal quantum number*

$l = 0, 1, \dots, n - 1$ *angular momentum,*

$l_z = -l, \dots, l$ *z-component*

$\sigma_z = -1/2$ or $+1/2$ *z-component of spin*

The $l=0, 1, 2, 3$ are known as s, p, d, f, in atomic language

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Periodic table

The electrons in atoms are filled according to:

Aufbau principle: shells should be filled starting with the lowest available energy state. An entire shell is filled before another shell is started.

Madelung's rule: the energy ordering is from lowest value of $n + l$ to the largest; and when two shells have the same value of $n + l$, fill the one with the smaller n first.

This ordering rule means that shells should be filled in the order:

$$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, \dots$$

e.g. for nitrogen: which has

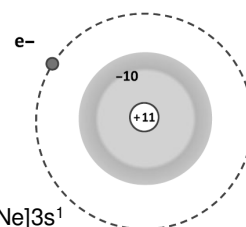
- a filled 1s shell (containing two electrons, one spin-up, one spin-down),
- a filled 2s shell (containing two electrons, one spin-up, one spin-down),
- a 2p shell containing the remaining three electrons

In atomic notation we would write this as $1s^2 2s^2 2p^3$

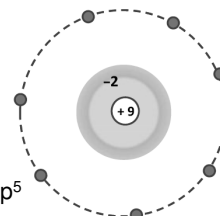
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Periodic table

I II		III IV V VI VII VIII									
Hydrogen 1 1.0079											
Lithium 3 6.941	Beryllium 4 9.0122										
Sodium 11 22.9897	Magnesium 12 24.304	Boron 5 10.811	Carbon 6 12.011	Nitrogen 7 14.007	Oxygen 8 15.999	Fluorine 9 18.998	Neon 10 20.180	Aluminum 13 26.981	Silicon 14 28.086	Phosphorus 15 30.974	Sulfur 16 32.06
Potassium 19 39.098	Calcium 20 40.078	Gallium 31 69.723	Germanium 32 72.61	Arsenic 33 74.922	Selenium 34 78.96	Bromine 35 79.904	Krypton 36 83.80	Indium 49 114.818	Tin 50 118.710	Antimony 51 121.757	Tellurium 52 127.60



For a Na atom, with 1 electron in the outermost (3s) shell, the effective nuclear charge seen by the electron is +1. Thus, weak binding of electron.



For a fluorine atom, more electrons in the outermost shell (2s and p in this case), the effective nuclear charge is larger, e.g. from about +4 to +7. Thus, stronger binding of outer electrons.

Elements with similar chemical properties lie in the same column.

E.g. C, Si, and Ge are similar and each has only two electrons in a partially filled p-shell.

Going from left to right:

- the energy required to remove an electron from an atom, the ionization energy, increases;
- the energy gained by adding an electron to an atom, the electron affinity, also increases from left to right.

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What holds solids together: chemical bonding

- Bonding in general, attractive and repulsive forces, cohesive energy
- Ionic bonding
- Covalent bonding
- Metallic bonding
- Hydrogen bonding and van der Waals bonding
- Relationship between bonding type and some physical properties of a solid (in particular melting point)

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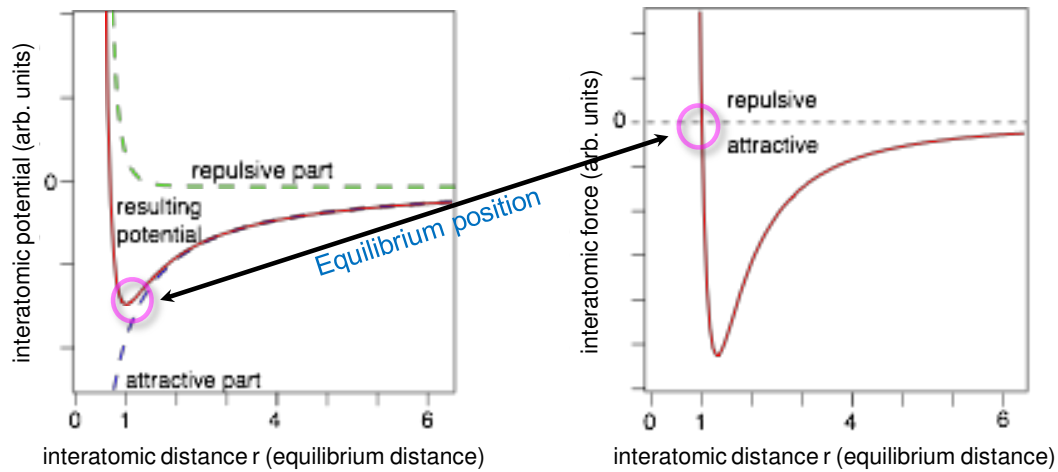
Bonding in solids: the general idea

- Valence electrons (of the outer shell) do most of the bonding.
- Decrease in total energy stabilises the solid (the solid's energy is lower than that of sum of atoms it is made of).
- So the energy gain by the bonding must be higher than the energy it costs to promote electrons from the atomic orbitals to the electronic states of the solid.
- This energy difference is a measure of the strength of the bond. It is called the **cohesive energy**.

Cohesive energy = energy of atoms - energy of solid

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Repulsive force



$$\phi(r) = -\frac{B}{r^m} + \frac{A}{r^n}$$

$$n > m$$

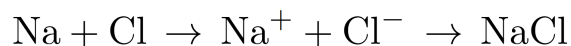
$$\mathbf{F}(\mathbf{r}) = -\text{grad}\phi(\mathbf{r})$$

$$F(r) = -\frac{d}{dr}\phi(r)$$

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Ionic bonds

In an ionic bond it is energetically favorable for an electron to be transferred from one atom to the other, leaving two oppositely charged ions which then attract each other. E.g. the chemical “reaction” for NaCl is,



Ionization Energy = Energy required to remove one electron from a neutral atom to create a positive ion

Electron Affinity = Energy gain for creating a negative ion from a neutral atom by adding an electron

For removing or adding a single electron, these are called first ionization energies and first electron affinities respectively. For removing or adding two electrons these are called the “second” ionization energy and second electron affinity.

The total energy change from transferring an electron from atom A to atom B is:

$$\Delta E_{A+B \rightarrow A^+ + B^-} = (\text{Ionization Energy})_A - (\text{Electron Affinity})_B$$

Also we have,

$$\text{Cohesive energy} = \text{Energy gain from } A^+ + B^- \rightarrow AB$$

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Ionic bonds

The **total energy gain** for forming a molecule from the two individual atoms is,

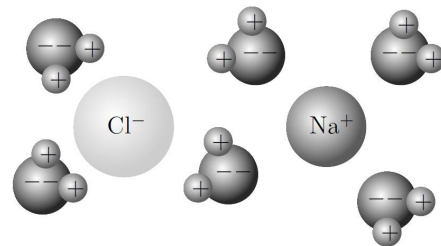
$$\Delta E_{A+B \rightarrow AB} = (\text{Ionization Energy})_A - (\text{Electron Affinity})_B - (\text{Cohesive Energy of } AB)$$

We also define the electronegativity, which describes how much an atom “wants” electrons. Below is the “Mulliken Electronegativity”,

$$\text{Electronegativity} = \frac{\text{Electron Affinity} + \text{Ionization Energy}}{2}$$

Atoms with high electronegativity – upper right of Periodic Table, e.g. O, N

Ionic materials are typically hard and have high melting temperatures. Since water is extremely polar, it can dissolve an ionic solid. This happens by arranging the water molecules such that the negative side of the molecule is close to the positive ions and the positive side of the molecule is close to the negative ions.

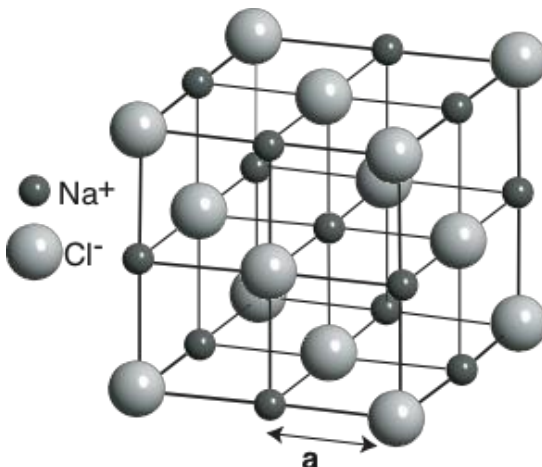


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Ionic bonding

- Form positive and negative ions (here Na^+ and Cl^-)
- Bonding is achieved by electrostatic force and a classical treatment is (partially) meaningful.

example NaCl (rock salt): cubic structure



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Turning atoms in ions

Example: NaCl

How much energy does it cost?

ionization energy Na: 5.1 eV

electron affinity Cl: 3.6 eV

Net energy cost: $(5.1 \text{ eV} - 3.6 \text{ eV}) = 1.5 \text{ eV}$ per pair

Ionization energy: amount of energy required to remove the most loosely bound electron from a neutral atom.

Electron affinity: change in energy of a neutral atom when an electron is added to the atom.

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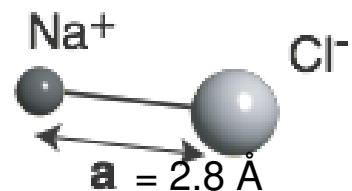
Ionic bonding

Example: NaCl

What is the energy gain?

potential energy:

$$E_{Coulomb} = -\frac{e^2}{4\pi\epsilon_0 a}$$



this amounts to 5.1 eV per pair

So the total gain is
 $5.1 \text{ eV} - 1.5 \text{ eV} = 3.6 \text{ eV}$

Permittivity of free space $\epsilon_0 = \frac{1}{4\pi k} = 8.85 \times 10^{-12} \frac{C^2}{N \cdot m^2}$

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Ionic bonding

Example: NaCl

But this was just a molecule: what about the electrostatic energy gain in the solid?

Consider the centre Na ion
energy gain from next 6 Cl:

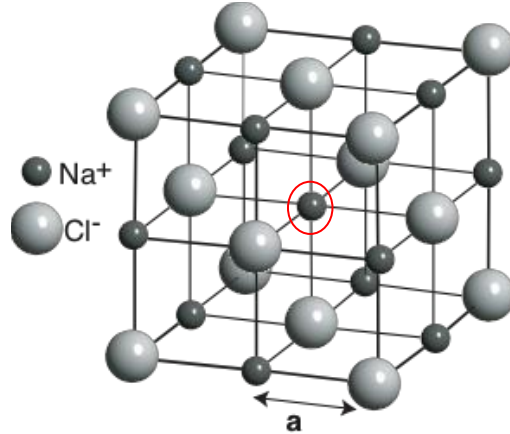
$$E = -6 \frac{e^2}{4\pi\epsilon_0 a}$$

energy loss from next 12 Na:

$$E = +12 \frac{e^2}{4\pi\epsilon_0 a\sqrt{2}}$$

next we get 8 more Cl ions and the total energy becomes

$$E = -\frac{e^2}{4\pi\epsilon_0 a} \times \left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} \right)$$



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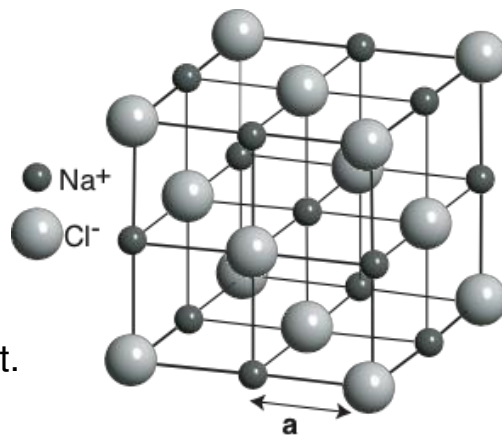
Ionic bonding

Example: NaCl

Eventually the series converges
and we get (for one ion)

$$E = -1.748 \frac{e^2}{4\pi\epsilon_0 a} = -M_d \frac{e^2}{4\pi\epsilon_0 a}$$

M_d is called the Madelung constant.
It is specific for a given structure.



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Ionic bonding

$$E_{\text{Na}} = -1.748 \frac{e^2}{4\pi\epsilon_0 a} = -M_d \frac{e^2}{4\pi\epsilon_0 a}$$

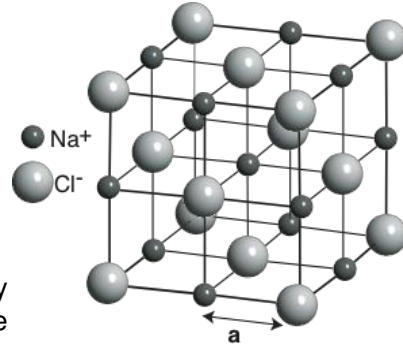
So the total lattice energy for one mole of NaCl is:

because there are Na and Cl ions

Avogadro's number

$$E_{\text{tot}} = \frac{2E_{\text{Na}} \times N_a}{2}$$

to count every pair only once



This gives 861 kJmol^{-1} . The experiment gives 776 kJmol^{-1}

Note: this is the **lattice energy**, not the **cohesive energy**

$$E_{\text{tot}} = E_{\text{Na}} \times N_a = -\frac{e^2}{4\pi\epsilon_0 a} M_d N_a = -\frac{(1.6 \times 10^{-19})^2 \cdot 1.748 \cdot 6.023 \times 10^{23}}{4\pi \cdot 8.85 \times 10^{-12} \cdot 2.8 \times 10^{-10}} = 8.61 \times 10^5 \text{ J mol}^{-1}$$

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Covalent bonding

- Cohesive energies similar to ionic bonding, in the eV range.
- Very directional bonding.

End