CMP
Lecture 4

School of Physics
The University of Sydney

THE UNIVERSITY OF
SYDNEY

Covalent bonding

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

The covalent bond

A covalent bond is a bond where electrons are shared roughly equally between two atoms.

Particle in a Box Picture
Let us model a hydrogen atom as a box of size L for an electron (for simplicity, let us think about a one-dimensional system).

Then the energy of a single electron in a box is: $E = \dfrac{\hbar^2 \pi^2}{2mL^2}$

$$E = \frac{\hbar^2 \pi^2}{2mL^2}$$

Now suppose two such atoms come close together. An electron that is shared between the two atoms can now be delocalized over the positions of both atoms, thus it is in a box of size 2L and has lower energy.
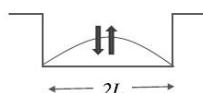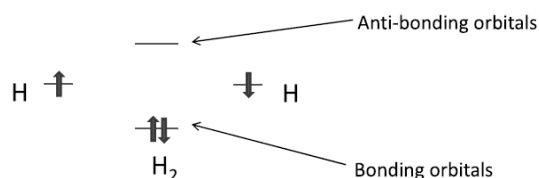
$$E_{bonding} = \frac{\hbar^2 \pi^2}{2m(2L)^2}$$

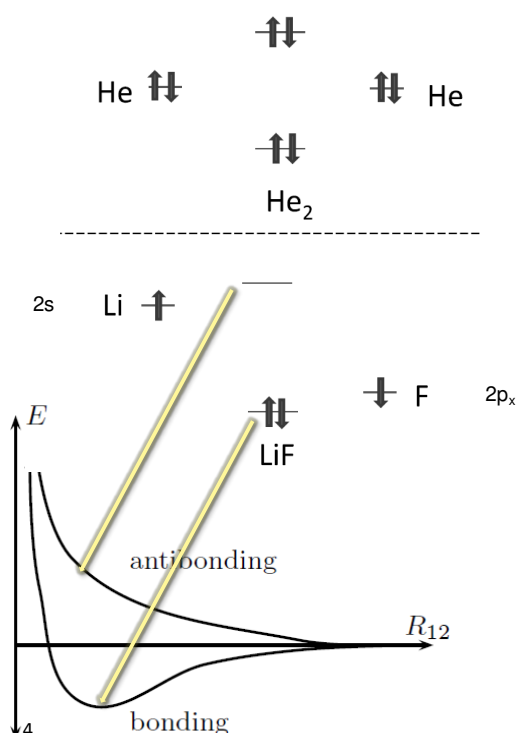$$E_{anti-bonding} = \frac{\hbar^2 (2\pi)^2}{2m(2L)^2}$$

This reduction in energy that occurs by delocalizing the electron is the driving force for forming the chemical bond.
- The new ground-state orbital is known as a **bonding orbital**
- The first excited state is known as the **antibonding orbital**

Anti-bonding orbitals

H

H

H_2

Bonding orbitals

3

The covalent bond

He   He

He_2

2s   Li

E

F $2p_x$

LiF

antibonding

R_{12}

bonding

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For helium, since there are two electrons per atom, the bonding orbitals are filled, and the antibonding orbitals must be filled with two electrons as well.
Therefore, the total energy is not reduced by the two helium atoms coming together and thus helium does not form He_2.
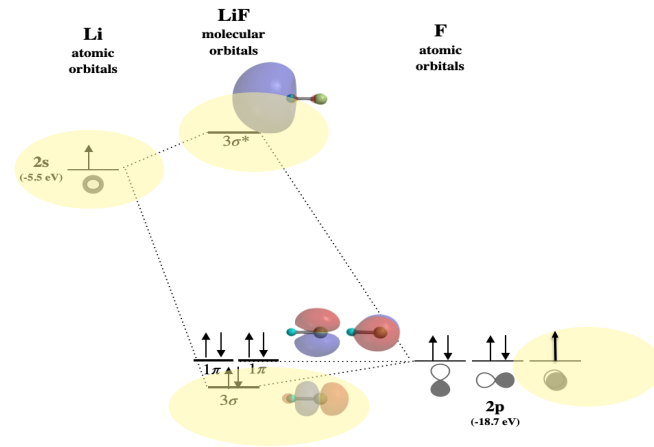
For LiF, the energies of the lithium and the fluorine orbitals are different. Therefore, the bonding orbital is mostly composed of the orbital on the F atom – meaning that the bonding electrons are mostly transferred from Li to F – forming a more ionic bond.

MO for LiF

In the case of LiF, the energy of 2s AO of Li is higher than the energy of 2p of F.

The MOs are derived from the combination of 2s AO of Li and 2p AO of F.

σ and σ* are derived from this interaction, and the two 2p orbitals are not involved. These are non-bonding orbitals or pairs.

Li atomic orbitals

LiF molecular orbitals

F atomic orbitals

2s (-5.5 eV)

3σ*

1π 1π

3σ

2p (-18.7 eV)

2σ

2s (-46.37 eV)

Particle in a box

A particle in a 1-dimensional box is a fundamental quantum mechanical approximation describing the translational motion of a single particle confined inside an infinitely deep well from which it *cannot* escape.

Introduction

The particle in a box problem is a common application of a quantum mechanical model to a simplified system consisting of a particle moving horizontally within an infinitely deep well from which it cannot escape. The solutions to the problem give possible values of E and ψ that the particle can possess. E represents allowed energy values and $\psi(x)$ is a wavefunction, which when squared gives us the probability of locating the particle at a certain position within the box at a given energy level.

To solve the problem for a particle in a 1-dimensional box, we must follow our **Big, Big recipe for Quantum Mechanics:**

1. Define the Potential Energy, V
2. Solve the Schrödinger Equation
3. Define the wavefunction
4. Define the allowed energies

Step 1: Define the Potential Energy V
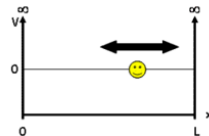
A particle in a 1D infinite potential well of dimension L.

The potential energy is *0 inside the box* (V=0 for 0<x<L) and *goes to infinity at the walls of the box* (V=∞ for x<0 or x>L). We assume the walls have infinite potential energy to ensure that the particle has zero probability of being at the walls or outside the box. Doing so significantly simplifies our later mathematical calculations as we employ these **boundary conditions** when solving the Schrödinger Equation.

Step 2: Solve the Schrödinger Equation

The time-independent Schrödinger equation for a particle of mass m moving in one direction with energy E is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \qquad (1)$$

with

- $\hbar$ is the reduced Planck Constant where $\hbar = \frac{h}{2\pi}$
- m is the mass of the particle
- $\psi(x)$ is the stationary time-independent wavefunction
- V(x) is the potential energy as a function of position
- E is the energy, a real number

- $\psi(x)$ is the stationary time-independent wavefunction
- V(x) is the potential energy as a function of position
- E is the energy, a real number

This equation can be modified for a particle of mass m free to move parallel to the x-axis with zero potential energy (V = 0 everywhere) resulting in the quantum mechanical description of free motion in one dimension:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \tag{2}$$

This equation has been well studied and gives a general solution of:

$$\psi(x) = A\sin(kx) + B\cos(kx) \tag{3}$$

where A, B, and k are constants.

Step 3: Define the wavefunction

The solution to the Schrödinger equation we found above is the general solution for a 1-dimensional system. We now need to apply our **boundary conditions** to find the solution to our particular system. According to our boundary conditions, the probability of finding the particle at x=0 or x=L is zero. When $x = 0$, $\sin(0) = 0$, and $\cos(0) = 1$; therefore, B *must equal 0* to fulfill this boundary condition giving:

$$\psi(x) = A\sin(kx) \tag{4}$$

We can now solve for our constants (A and k) systematically to define the wavefunction.

Solving for k

Differentiate the wavefunction with respect to x:

$$\frac{d\psi}{dx} = kA\cos(kx) \tag{5}$$

$$\frac{d^2\psi}{dx^2} = -k^2A\sin(kx) \tag{6}$$

Since $\psi(x) = A sin(kx)$, then

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$$\frac{d^2\psi}{dx^2} = -k^2\psi \tag{7}$$

If we then solve for k by comparing with the Schrödinger equation above, we find:

$$k = \left(\frac{8\pi^2 mE}{h^2}\right)^{1/2} \tag{8}$$

Now we plug k into our wavefunction:

$$\psi = A\sin\left(\frac{8\pi^2 mE}{h^2}\right)^{1/2} x \tag{9}$$

Solving for A

To determine A, we have to apply the boundary conditions again. Recall that the *probability of finding a particle at x = 0 or x = L is zero.*

When $x = L$:

$$0 = A\sin\left(\frac{8\pi^2 mE}{h^2}\right)^{1/2} L \tag{10}$$

This is only true when

$$\left(\frac{8\pi^2 mE}{h^2}\right)^{1/2} L = n\pi \tag{11}$$

where n = 1,2,3...

Plugging this back in gives us:

$$\psi = A\sin\frac{n\pi}{L}x \tag{12}$$

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To determine A, recall that the total probability of finding the particle inside the box is 1, meaning there is no probability of it being outside the box. When we find the probability and set it equal to 1, we are *normalizing* the wavefunction.

$$\int_0^L \psi^2 dx = 1 \tag{13}$$

For our system, the normalization looks like:

$$A^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = 1 \tag{14}$$

Using the solution for this integral from an integral table, we find our normalization constant, A:

$$A = \sqrt{\frac{2}{L}} \tag{15}$$

Which results in the normalized wavefunction for a particle in a 1-dimensional box:

$$\psi = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \tag{16}$$

Step 4: Determine the Allowed Energies

Solving for E results in the allowed energies for a particle in a box:

$$E_n = \frac{n^2 h^2}{8mL^2} \tag{17}$$

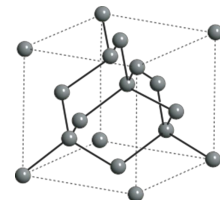This is an important result that tells us:

1. The energy of a particle is quantized and
2. The lowest possible energy of a particle is **NOT** zero. This is called the **zero-point energy** and means the particle can **never be at rest**

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The covalent bond

Directional bond character, electron sharing, strong bonds
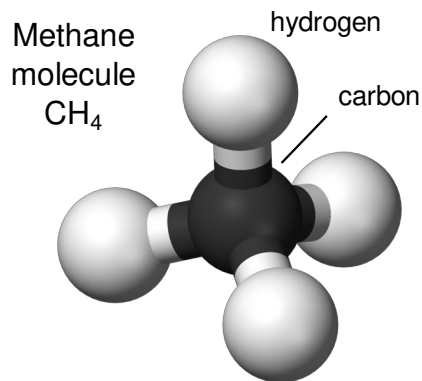
e.g. diamond [He] 2s^2 2p^2 Carbon atoms

- Electron configuration: 2s and 2p electrons

- Formation of four sp^3 hybrid orbitals as linear combination between the s and three p orbitals

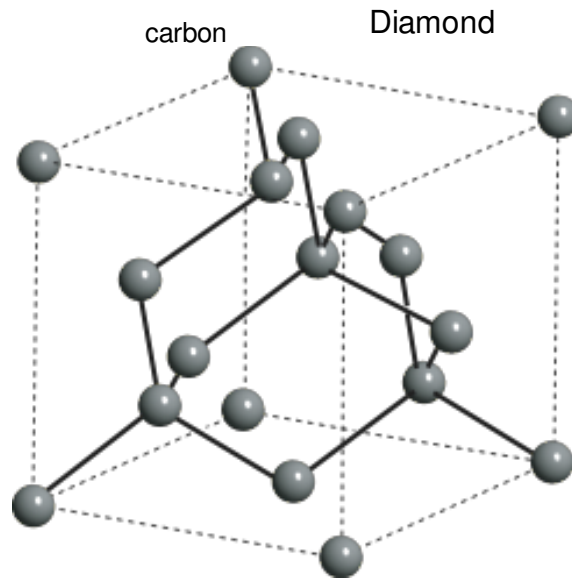- Directional character of p orbitals is also found in sp^3 orbitals.

He:1s^2

109,5° 109,5° 109,5°

s   p$_x$ p$_y$ p$_z$

combined to generate four sp^3 hybrid orbitals
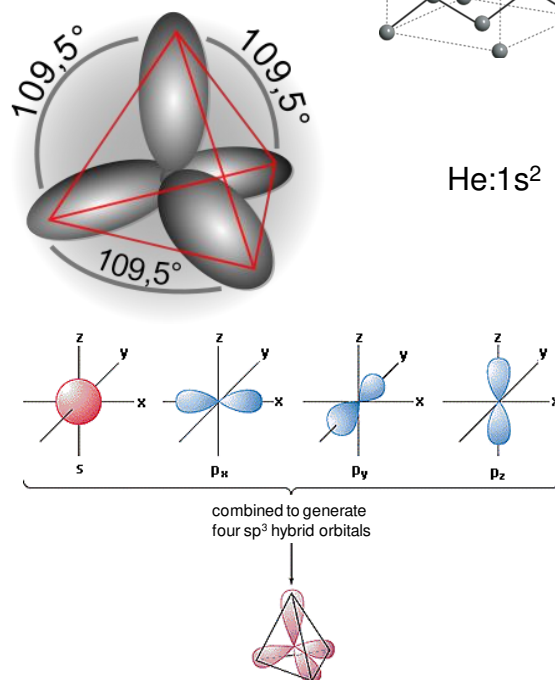
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The covalent bond: sp^3 bonding

Methane molecule CH_4

hydrogen
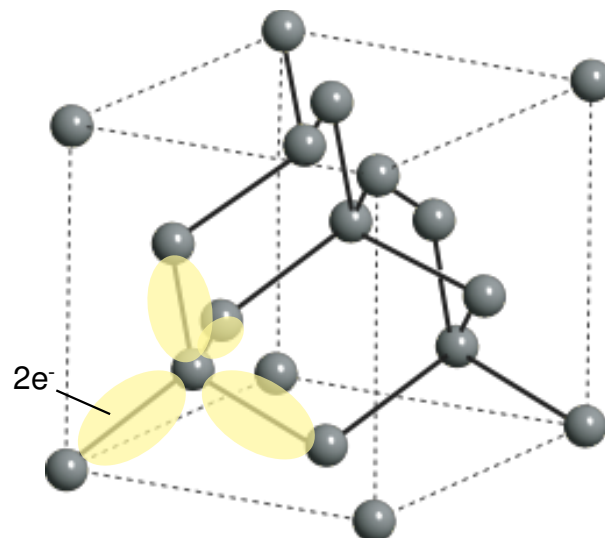
carbon

Very stable molecule

Directional character is maintained and important: it is found in all solids and molecules of sp^3 bonding

carbon

Diamond
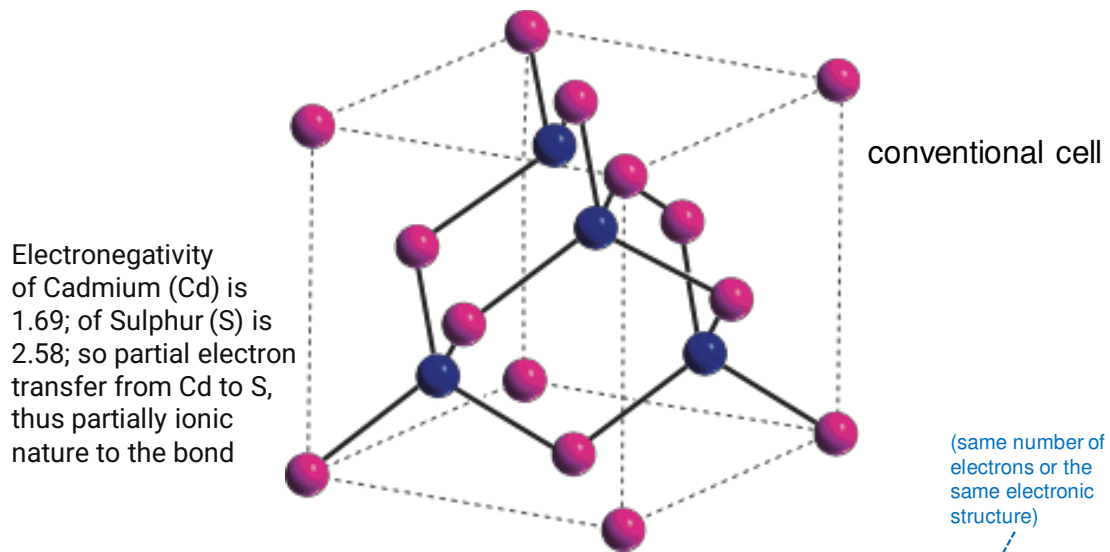
Bonding in most semiconductors

2 electrons in each of the four sp^3 bonds, one from each C atom

$2e^-$

- Tetrahedral (sp^3) configuration almost ubiquitous: diamond, Si, Ge, III-V (GaAs, AlAs, InP), II-VI (CdS, CdTe)

Bonding in most semiconductors

conventional cell

Electronegativity of Cadmium (Cd) is 1.69; of Sulphur (S) is 2.58; so partial electron transfer from Cd to S, thus partially ionic nature to the bond

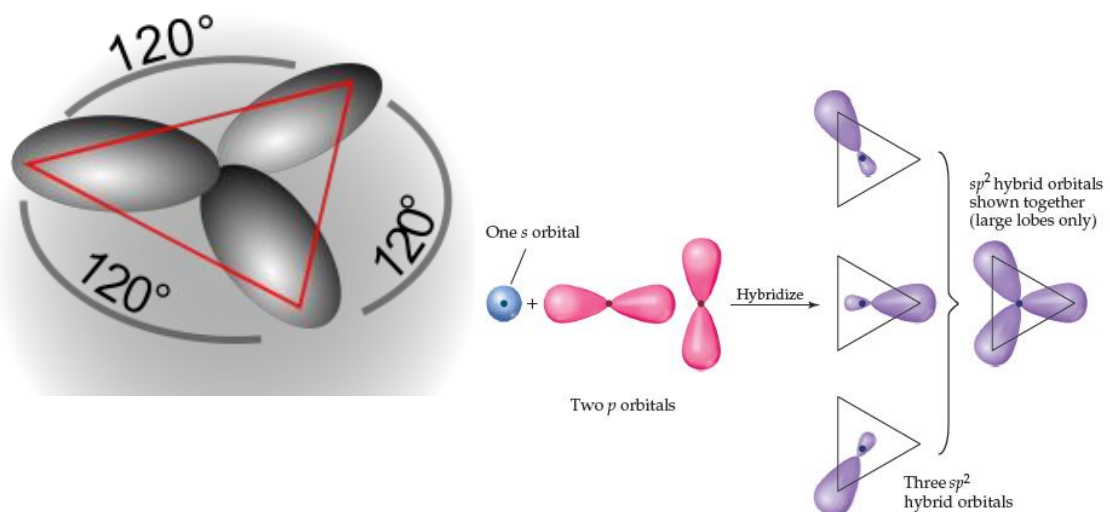(same number of electrons or the same electronic structure)

- Tetrahedral (sp^3) configuration almost ubiquitous: diamond, Si, Ge, III-V (GaAs, AlAs, InP), II-VI (CdS, CdTe)

    Note: the II/VI or III/V semiconductors may be isoelectronic but the bonding is not purely covalent anymore. It is partly ionic.
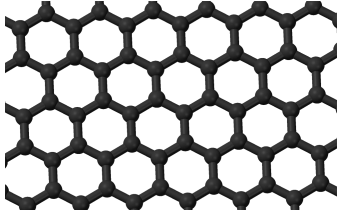
The covalent bond: sp^2 bonding

120°

120°

120°

One s orbital

Two p orbitals

Hybridize

sp^2 hybrid orbitals shown together (large lobes only)

Three sp^2 hybrid orbitals

- Formation of three sp^2 hybrid orbitals as linear combination between the s and two p orbitals. One p-orbital remains.
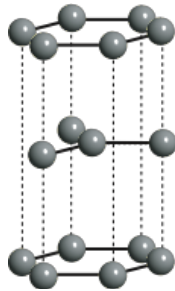
The covalent bond: sp^2 bonding

graphene / graphite
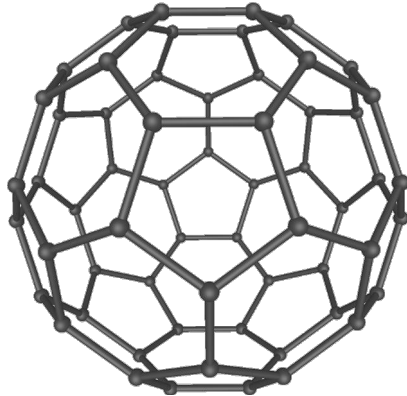
bucky-balls

Graphite good conductor
unlike diamond

Nanotubes conductors or not
depending on how they are
rolled up

carbon nanotubes
(rolled-up graphene)

C_{60} can be made
into a solid - insulator
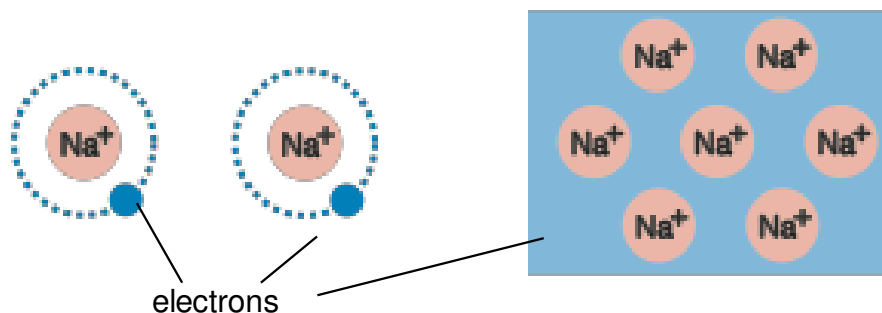
Metallic bonding

Metals / non-metals

- the boundaries can be disputed
- simple metals, transition metals, noble metals

Metallic bonding (simple metals)

- Outer electrons are delocalized and act as "glue" between positively charged ion cores.
- Generally found for elements with one, two or three valence electrons.
- Cohesive energies in the eV range.

Electronic configuration of sodium, Na is: [Ne] $3s^1$

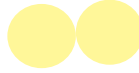electrons

Electrons become "delocalised" and form an "electron sea"

Metallic bonding (simple metals): more characteristics

- Smaller cohesive energies than in ionic crystals.

- Electrons are delocalized throughout crystal, "provide glue" that hold together +ion cores.

- Larger ionic radii, e.g. for Na: 3.82 Å (metal) and 1.94 Å (NaCl)
  Qualitative measure of how big the atom is, via its radius, in a given solid environment

- Bonding has no directional preference

- Closed-packed atomic configurations are preferred: best possible overlap between the orbitals
  face-centred-cubic, hexagonal close-packed

Recall ionic: each ion (Na^+, Cl^-) is strongly attracted by its neighbours (at least by the nearest neighbours).

Here: all ions (Na^+) repel each other (but they are of course still embedded in average one valence electron). It is not nearly as clear where the energy gain comes from.

Metallic bonding: why is this so favorable?

$$-\frac{\hbar^2 \nabla^2}{2m}\Psi(r) + U(r)\Psi(r) = E\Psi(r)$$

Can think of: kinetic energy $\propto$ (negative) average curvature of wave function
"flatter" wave function -> lower energy

(momentum $\boldsymbol{p}=-i\hbar\nabla$)

$$\Delta x \Delta p \geq \hbar/2$$

Heisenberg uncertainty principle

or   less localization so larger Δx -> smaller p variation smaller kinetic energy

If we force the electron to be localized in a small orbit around a single atom, the curvature is high. If we de-localize the electron over the whole solid (or some larger fraction), the average curvature is smaller.

Transition metals

- 4s and 3d have very similar energies

- 4s electrons form delocalized metallic bonds

- 3d electrons form more local (covalent-like) bonds

- higher cohesive energies

Why gold is the noblest of all the metals
B Hammer, JK Norskov
Nature 376, 238-240 (1995)
over 2500 citations!
(ab initio quantum mechanical calculations)

Noble metal, filled d-shell: e.g. gold, Au: [Xe] 4f^{14} 5d^{10} 6s^1

resists chemical action, does not corrode

Transition metal, partially filled d-shell: e.g. ruthenium Ru: [Kr] 4d^7 5s^1

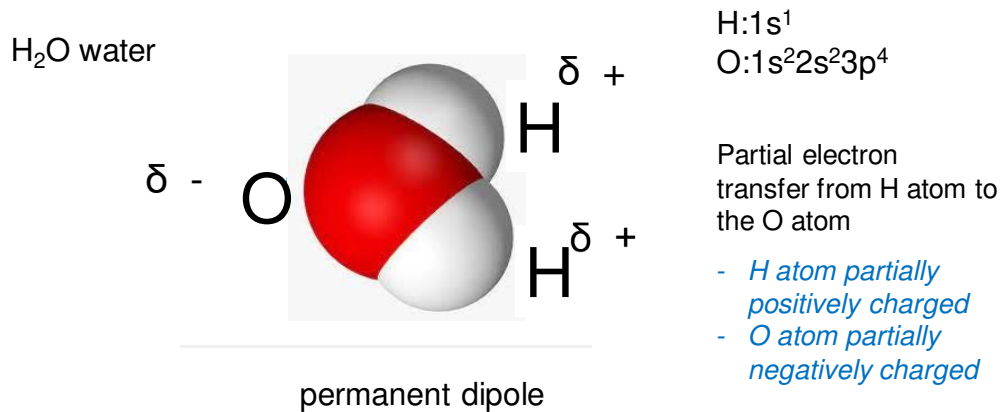# Bonds between molecules

(Hydrogen bonding)

- Molecular solids are very common (but not at RT)

- Ice (water molecules, H_2O)

- Plastic

- DNA

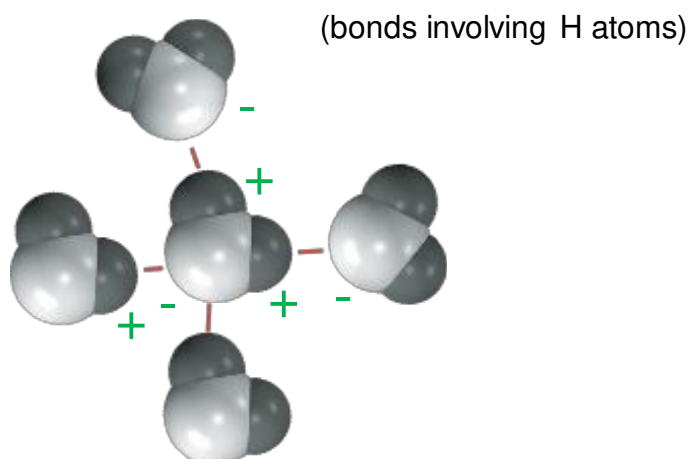- What makes molecules bond to each other?

Hydrogen bonds

The hydrogen atom is extremely special due to its very small size. As a result, the bonds formed with hydrogen atoms are qualitatively different from other bonds. When the hydrogen atom forms a covalent or ionic bond with a larger atom, being small, the hydrogen nucleus (a proton) simply sits on the surface of its partner.

This then makes the molecule (hydrogen and its partner) into a dipole. These dipoles can then attract charges, or other dipoles, as usual.

H_2O water

$H:1s^1$
$O:1s^22s^23p^4$

δ +

H

δ - O

δ +

H

Partial electron transfer from H atom to the O atom

- *H atom partially positively charged*
- *O atom partially negatively charged*

permanent dipole

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Bonds between molecules: hydrogen bonds

(bonds involving H atoms)

-

+

-

+

+

-

-

- H is positively charged but also very small: another "real" bond cannot be established without overlap of electron clouds (in this sense it is too big in this drawing).

- Hydrogen bonding is extremely important in biological molecules where, for example, hydrogen bonds hold together strands of DNA.

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# Van der Waals, fluctuating dipole forces, or molecular bonding

Also known as "Dispersion Forces"

For two atoms/molecules far apart, there is attraction due to van der Waals forces. Both atoms have a dipole moment which may be zero on average, but can fluctuate momentarily.

If one atom obtains a momentary dipole moment, p_1
Gives rise to an electric field that second atom experiences:
$$E = \frac{p_1}{4\pi\epsilon_0 r^3}$$

The second atom can polarize, obtaining a dipole moment p_2 to lower its energy, $p_2 = \chi E$
where χ is known as the polarizability or electric susceptibility.
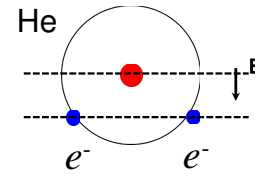
This type of bonding between atoms is very typical of inert atoms (such as noble gases: He, Ne, Kr, Ar, Xe) whose electrons do not participate in covalent bonds or ionic bonds.
It is also typical of bonding between inert molecules such as nitrogen molecules N_2.
This bonding is weak compared to covalent or ionic bonds, but it is also long ranged.

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Van der Waals, fluctuating dipole forces, or molecular bonding

Consider two such atoms, separated by a distance r in the $\hat{x}$ direction.
Suppose one atom momentarily has a dipole moment $\mathbf{p}_1$ and assume the dipole moment is in the $\hat{z}$ direction. Then the second atom will feel an electric field in the negative $\hat{z}$ direction and develop a dipole moment $\mathbf{p}_2$.
The potential energy between these two dipoles is,

$$U = \frac{-|p_1||p_2|}{4\pi\epsilon_0 r^3} = \frac{-p_1\chi E}{(4\pi\epsilon_0)r^3} = \frac{-|p_1|^2\chi}{(4\pi\epsilon_0 r^3)^2} \propto \frac{1}{r^6}$$
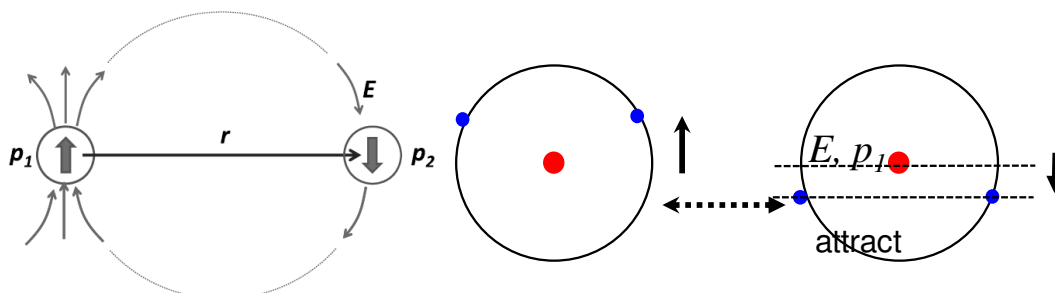
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Van der Waals force allows geckos to climb on smooth surfaces, e.g. glass – or even hang by one toe!

Have hair on their feet that makes close contact with the atoms of the surface

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van der Waals Layered Materials: Opportunities and Challenges

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ABSTRACT: Since graphene became available by a scotch tape technique, a vast class of two-dimensional (2D) van der Waals (vdW) layered materials has been researched intensively. What is more intriguing is that the well-known physics and chemistry of three-dimensional (3D) bulk materials are often irrelevant, revealing exotic phenomena in 2D vdW materials. By further constructing heterostructures of these materials in the planar and vertical directions, which can be easily achieved via simple exfoliation techniques, numerous quantum mechanical devices have been demonstrated for fundamental research and technological applications. It is, therefore, necessary to review the special features in 2D vdW materials and to discuss the remaining issues and challenges. Here, we review the vdW materials library, technology relevance, and specialties of vdW materials covering the vdW interaction, strong Coulomb interaction, layer dependence, dielectric screening engineering, work function modulation, phase engineering, heterostructures, stability, growth issues, and the remaining challenges.
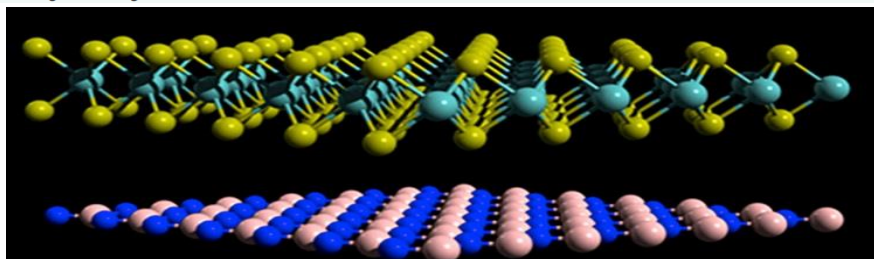
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The idea of energy bands: Na
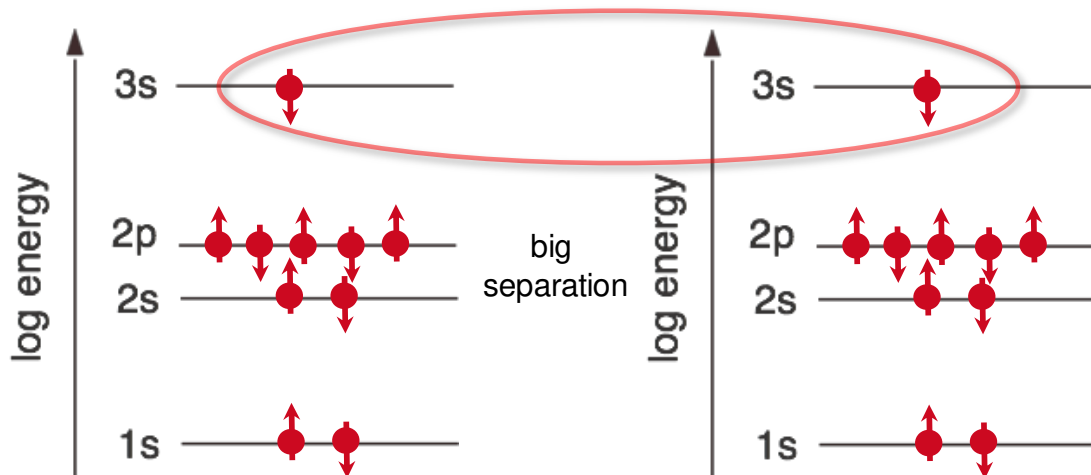
consider one atom of Na: 11 electrons

Valence electron, weakly bound

core electrons, strongly bound
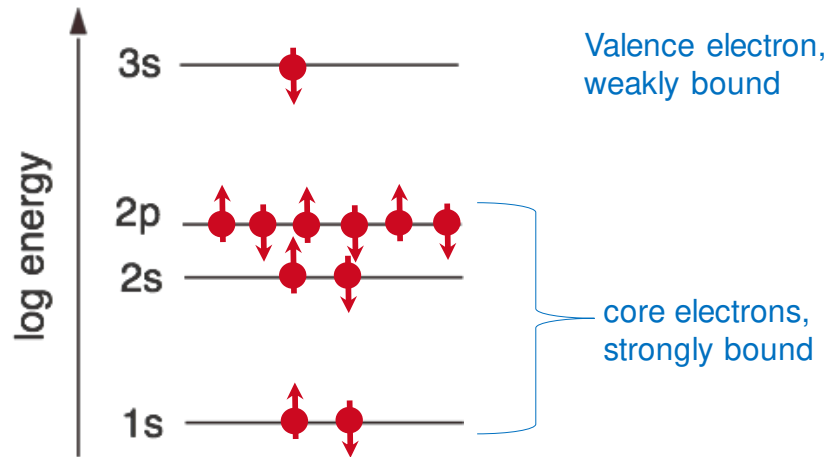
An intuitive picture - think of the solid as built from atoms

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The idea of energy bands: Na

consider two Na atoms / one Na_2 molecule: 22 electrons
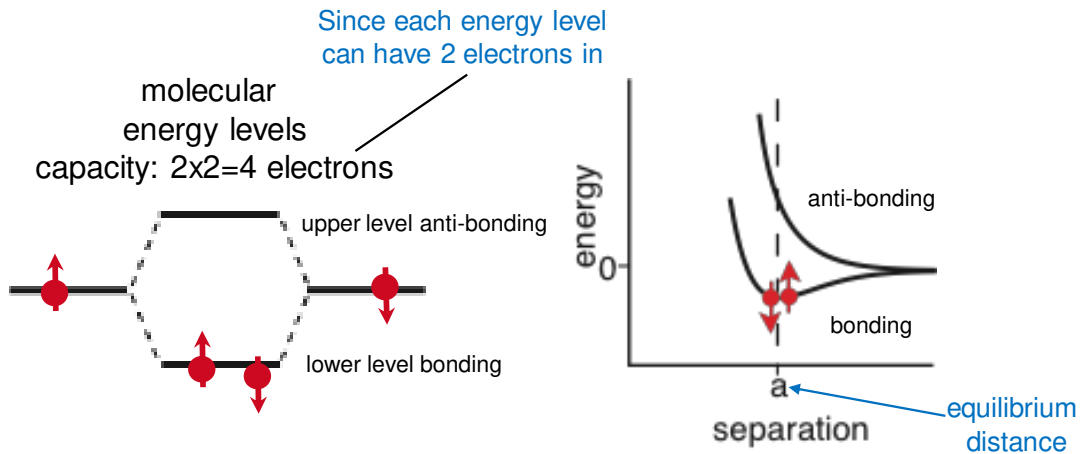

big separation

- Focus only on the valence (outer) electrons (3s).

- What happens when we move them together?

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The idea of energy bands: Na

consider two Na atoms / one Na$_2$ molecule: 2 3s electrons

Since each energy level
can have 2 electrons in

molecular
energy levels
capacity: 2x2=4 electrons

upper level anti-bonding

lower level bonding

anti-bonding

energy
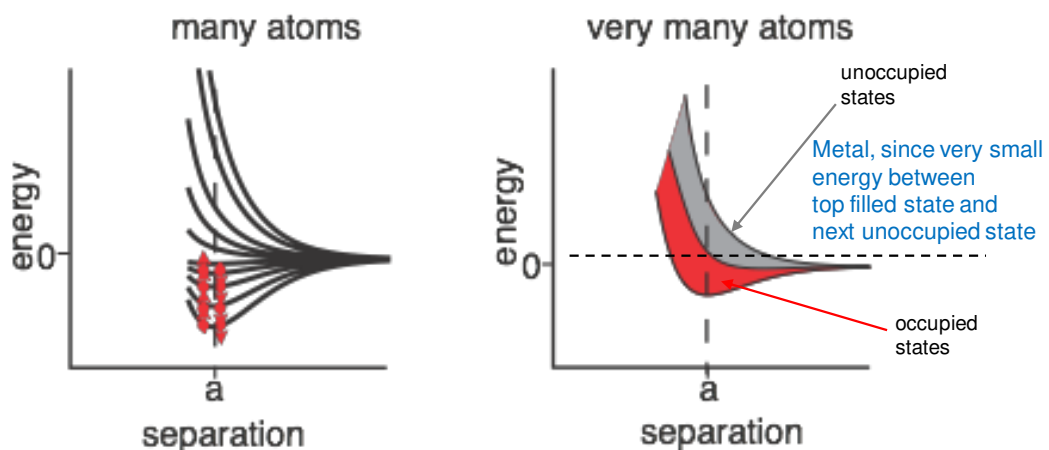
0

bonding

a

separation

equilibrium
distance

- Levels split up in bonding and anti-bonding molecular orbitals and are occupied according to the Pauli principle.

- The distance between the atoms must be such that there is an energy gain.

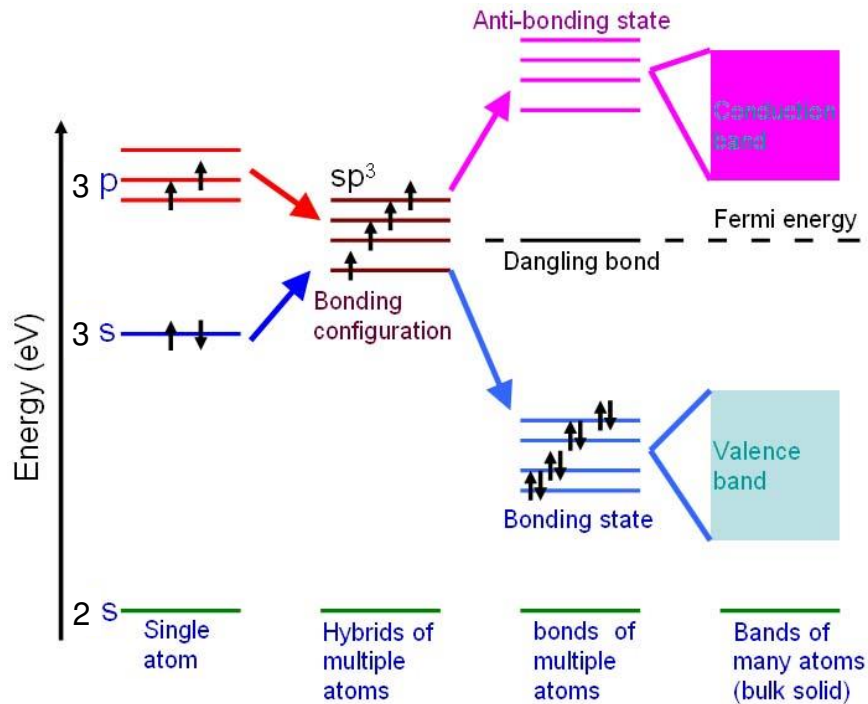# The idea of energy bands: Na

consider many (N) Na atoms (only 3s level)

many atoms

very many atoms

energy

0

a

separation

energy

0

a

separation

unoccupied
states

Metal, since very small
energy between
top filled state and
next unoccupied state

occupied
states

- N levels with very similar energies, like in a super-giant molecule. We can speak of a "band" of levels.

- Every band has N levels. We can put 2N electrons into it (but we have only N electrons from N Na atoms).
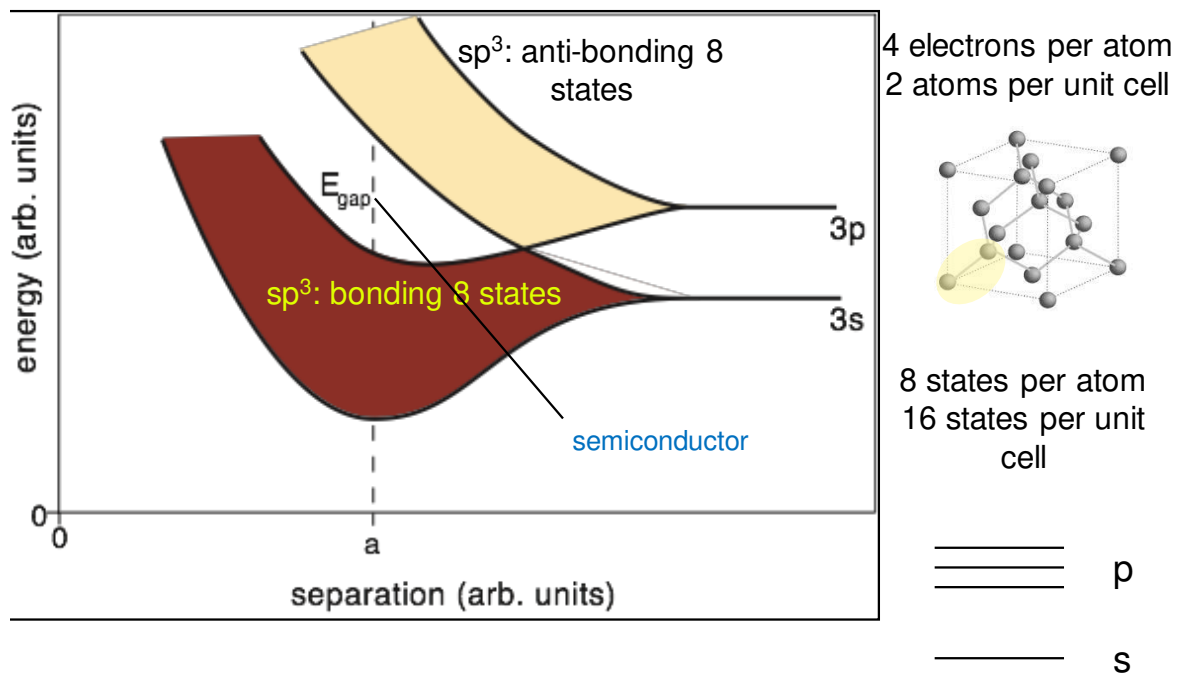
Can see why this (Na) is metallic: band half filled
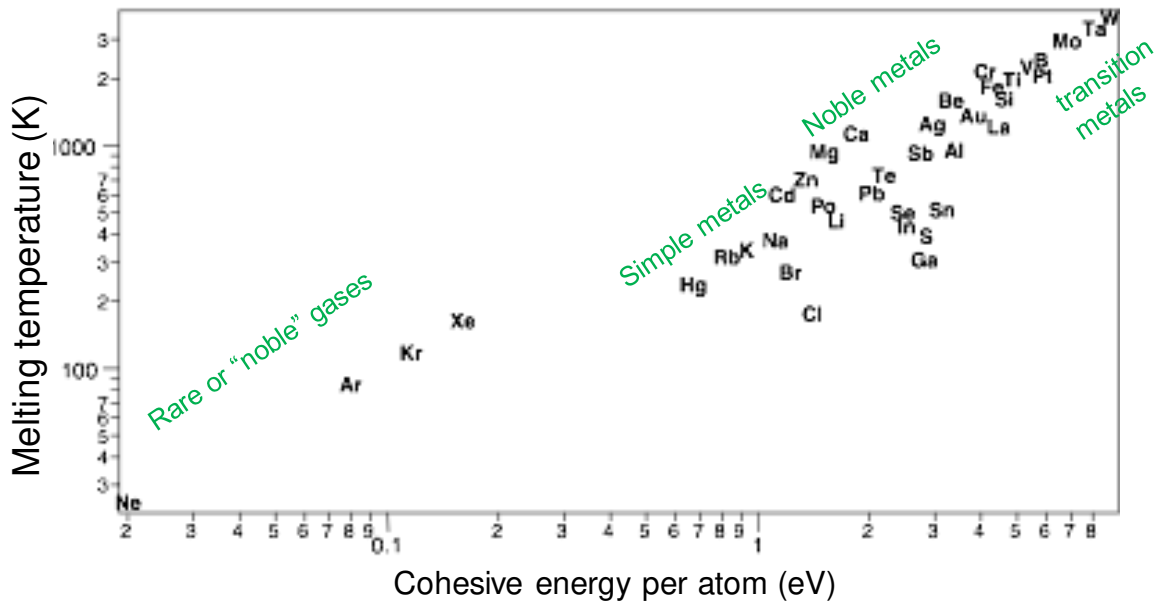
The idea of energy bands: Si or diamond

Labels in figure: Anti-bonding state, 3 p, sp³, Conduction band, Fermi energy, Dangling bond, 3 s, Bonding configuration, Energy (eV), 2 s, Valence band, Bonding state, Single atom, Hybrids of multiple atoms, bonds of multiple atoms, Bands of many atoms (bulk solid)

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The idea of energy bands: Si or diamond

Si: $1s^2 2s^2 2p^6 \mathbf{3s^2 3p^2}$

4 electrons per atom
2 atoms per unit cell

sp³: anti-bonding 8 states

E_{gap}

sp³: bonding 8 states

3p

3s

semiconductor

8 states per atom
16 states per unit cell

energy (arb. units)

separation (arb. units)

p

s

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Bond type and physical properties

Lowest melting temperature: rare-gas solids Ne, Ar, Kr, Xe: only van der Waals bonding, less than room temperature; then simple metals and noble metals and finally, transition metals.

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Summary

- We have looked at different types of bonding: ionic, metallic, covalent, H-bonds, van der Waals bonds.

- In reality, intermediate bonding scenarios are often found.

- We have some ideas about the relation between the bonding type and the physical properties (at least for the melting point).
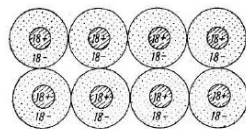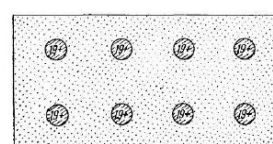

Argon crystal, molecular (fluctuating dipole) bonds. No transfer of charge.
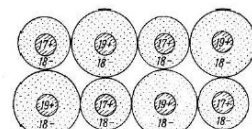
Potassium chloride (KCl). Ionic crystal. An electron is transferred from the K to the Cl to make K+ and Cl⁻ which then attract each other.
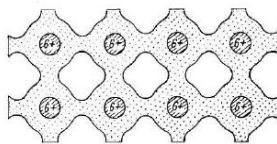
Carbon crystal (covalent bonds). Each atom shares electrons with its neighbors.

Metallic bonding in Potassium. Electrons are completely delocalized into an electron gas which holds together the ions.

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Summary

Type of Bonding	Description	Typical of which compounds	Typical Properties
Ionic	Electron is transferred from one atom to another, and the resulting ions attract each other	Binary compounds made of constituents with very different electronegativity: Ex, group I-VII compounds such as NaCl.	• Hard, Very Brittle • High Melting Temperature • Electrical Insulator • Water Soluble
Covalent	Electron is shared equally between two atoms forming a bond. Energy lowered by delocalization of wave-function	Compounds made of constituents with similar electronegativities (ex, III-V compounds such as GaAs), or solids made of one element only such as diamond (C)	• Very Hard (Brittle) • High Melting Temperature • Electrical Insulators or Semiconductors
Metallic Bonds	Electrons delocalized throughout the solid forming a glue between positive ions.	Metals. Left and Middle of Periodic Table.	• Ductile, Maleable (due to non-directional nature of bond. Can be hardened by preventing dislocation motion with impurities) • Lower Melting Temperature • Good electrical and thermal conductors.
Molecular (van der Waals or Fluctuating Dipole)	No transfer of electrons. Dipole moments on constituents align to cause attraction. Bonding strength increases with size of molecule or polarity of constituent.	Noble Gas Solids, Solids made of Non-Polar (or slightly polar) Molecules Binding to Each Other (Wax)	• Soft, Weak • Low Melting Temperature • Electrical Insulators
Hydrogen	Involves Hydrogen ion bound to one atom but still attracted to another. Special case because H is so small.	Important in organic and biological materials	• Weak Bond (stronger than VdW though) • Important for maintaining shape of DNA and proteins

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End

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