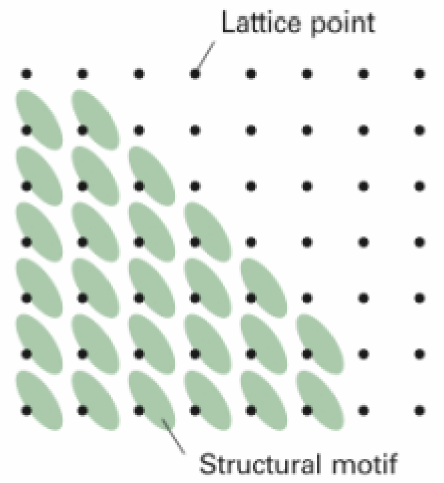
Physical Chemistry

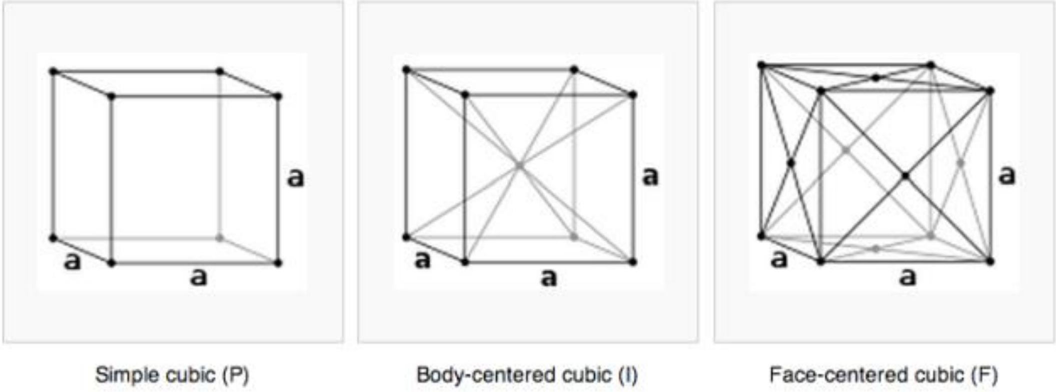
Mechanical Properties of Solids

Crystalline Solids

A crystal is built up from regularly repeating 'structural motifs' (atoms, molecules, or groups of atoms, molecules, or ions). A space lattice is the pattern formed by points representing the locations of these motifs. The space lattice is, in effect, an abstract scaffolding for the crystal structure. A given crystal structure is obtained by associating with each lattice point an identical structural motif.

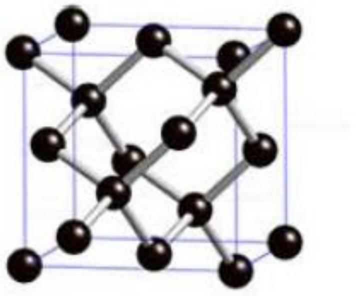


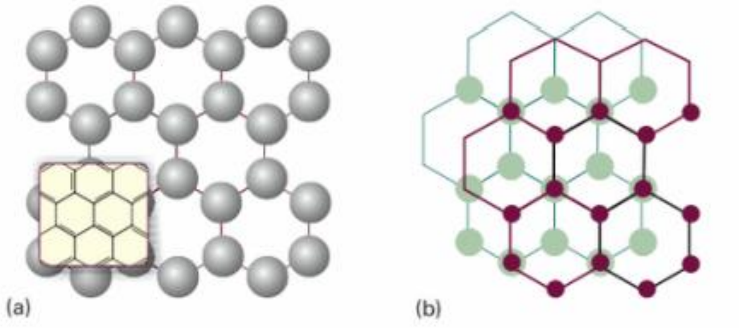
The unit cell is a small box containing one or more atoms arranged in 3-dimensions. The unit cells stacked in three-dimensional space describe the bulk arrangement of atoms of the crystal.



Covalent Network Solids

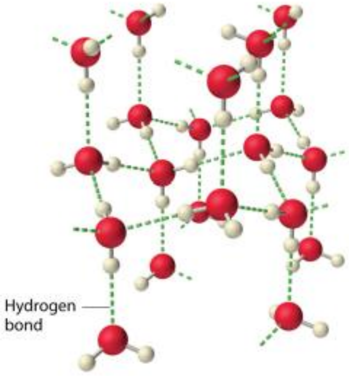
In covalent network solids, covalent bonds in definite spatial orientation link atoms in a network extending through the crystal. Examples include silicon, red phosphorus, boron nitride, and diamond, graphite, and carbon nanotubes.

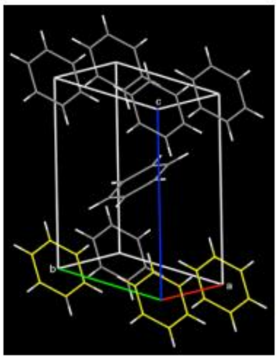


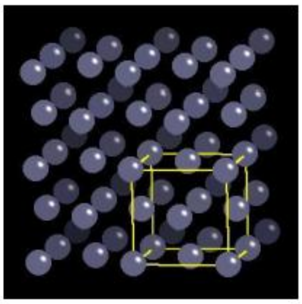


Molecular Solids

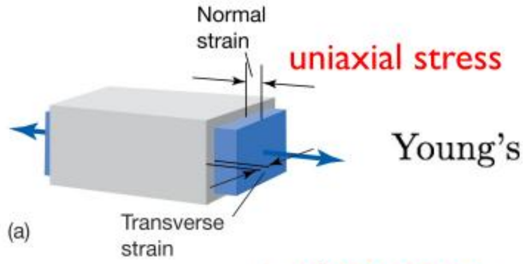
Molecular solids are held together by van der Waals interactions. Crystal structure results from condensing objects of various shapes into an aggregate of minimum energy. Because these dipole forces are weaker than covalent or ionic bonds, molecular solids are soft and have relatively low melting temperature.



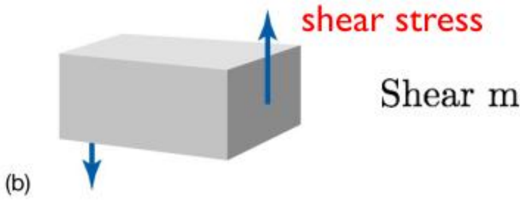




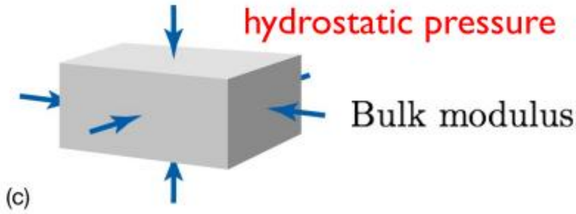
Stresses and Strains



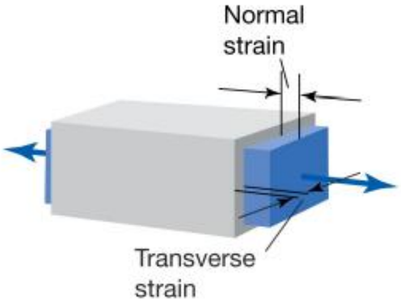
Young's modulus: $E = \frac{\textit{normal stress}}{\textit{normal strain}}$



Shear modulus: $G = \frac{\textit{shear stress}}{\textit{shear strain}}$



Bulk modulus: $K = \frac{\textit{pressure}}{\textit{fractional change in volume}}$



Poisson's modulus: $\nu_p = \frac{\textit{transverse strain}}{\textit{normal strain}}$

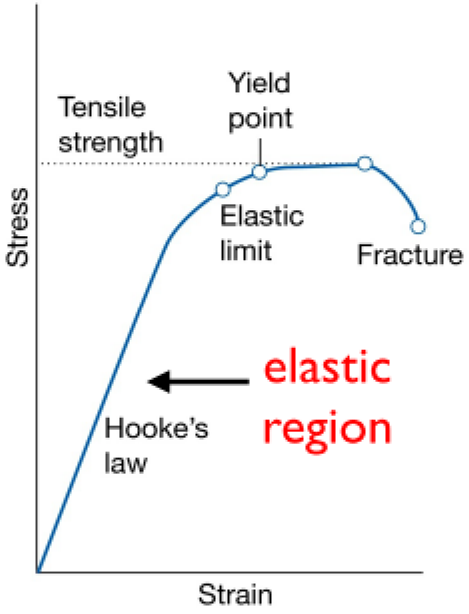
Relationship between moduli.

$$G = \frac{E}{2(1+\nu_p)}$$

$$K = \frac{E}{3(1-2\nu_p)}$$

The Elastic Limit

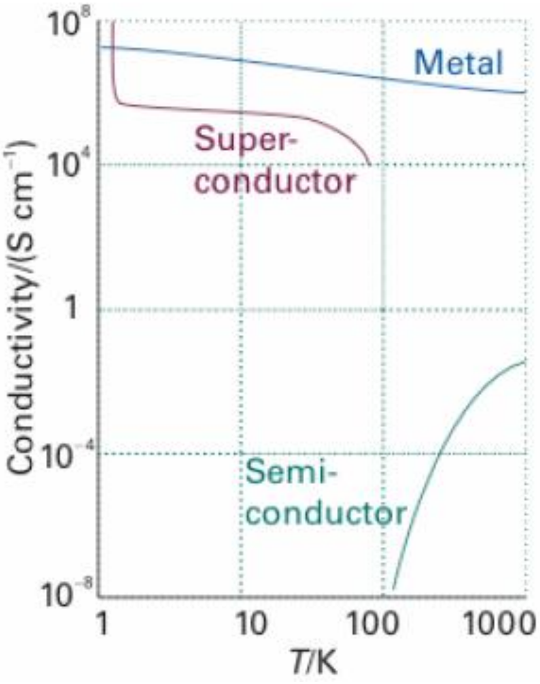
Elastic limit refers to the maximum stress or force per unit area within a solid material that can arise before the onset of permanent deformation. When stresses up to the elastic limit are removed, the material resumes its original size and shape. Stresses beyond the elastic limit cause a material to yield or flow. For such materials the elastic limit marks the end of elastic behaviour and the beginning of plastic behaviour. For most brittle materials, stresses beyond the elastic limit result in fracture with almost no plastic deformation.



Electrical Properties of Solids

Classes of Electrical Behaviour

- A conductor is a substance with high conductivity that *decreases* as temperature is raised
- Semiconductors have a lower conductivity that *increases* as temperature is raised
- Insulators are semiconductors with very low electrical conductivities
- Superconductors are solids that conducts electricity without resistance



The Tight-binding Approximation

This is an approach to the calculation of electronic band structure using an approximate set of wave functions based upon superposition of wave functions for isolated atoms located at each atomic site.

Suppose each atom has one s orbital available for forming molecular orbitals. We can construct LCAO-MOs by adding N atoms in succession and generate electronic structure using aufbau principle.

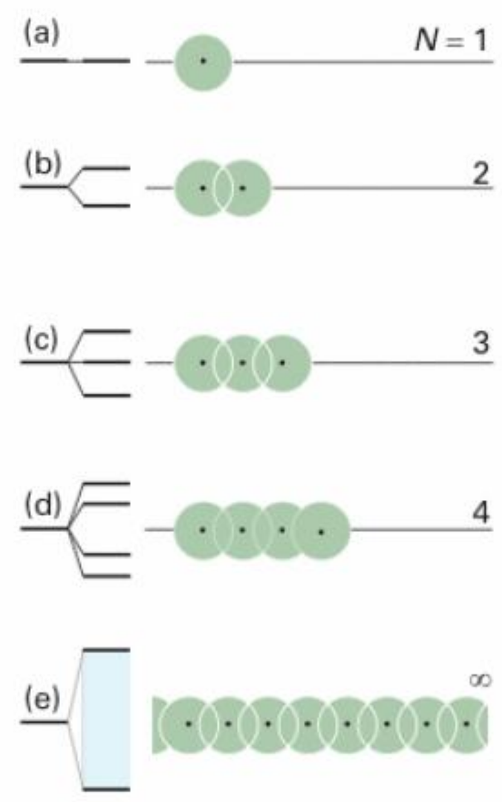
One atom contributes one s orbital at a certain energy. When a second atom is brought up it overlaps the first and forms bonding and antibonding orbitals. The effect of adding successive atoms is to spread the range of energies covered by MOs, and to fill the range of energies with more and more MOs (one more for each atom). When N is infinitely large, the difference between neighbouring energy levels (the energies corresponding to k and k + 1) is infinitely small, but the band still has finite width.

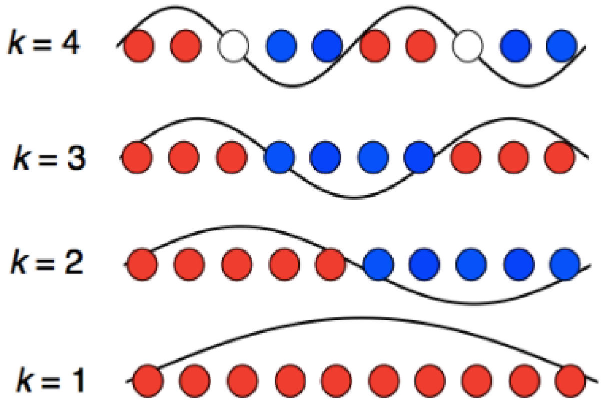
By solving the Huckel determinant, we find that the energy levels are:

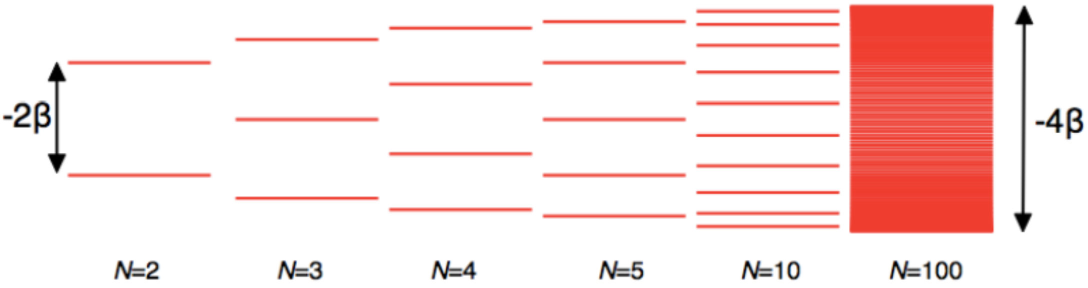
$$E_R = \alpha + 2\beta \cos\left(\frac{k\pi}{N+1}\right), \text{with } k = 1,2,\dots,N$$

In the limit where $N \rightarrow \infty$ we find the total band gap width is:

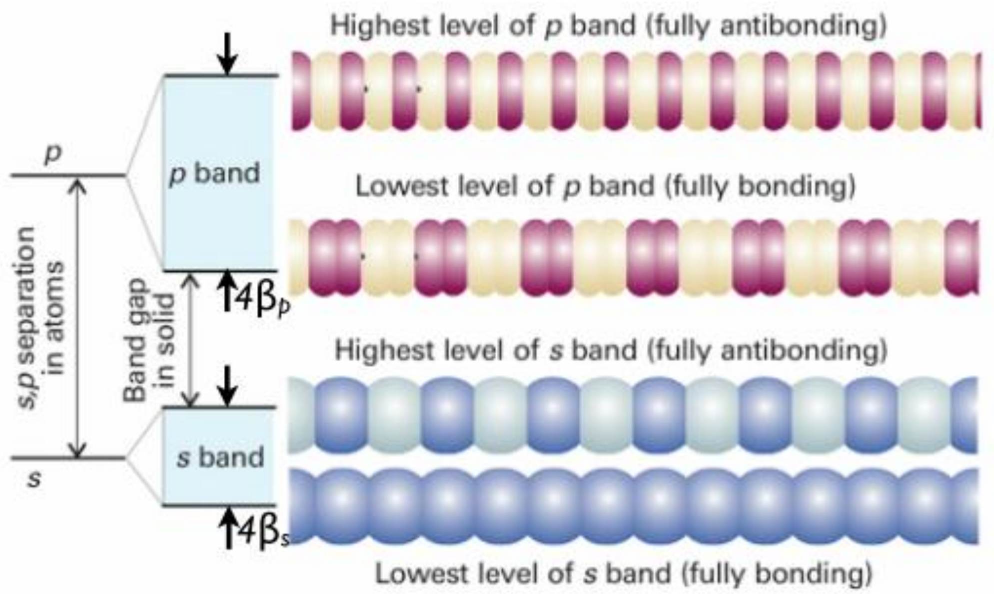
$$\begin{aligned} E_N - E_1 &= \lim_{N\rightarrow\infty}\left(\alpha + 2\beta\cos\left(\frac{N\pi}{N+1}\right)\right) - \lim_{N\rightarrow\infty}\left(\alpha + 2\beta\cos\left(\frac{\pi}{N+1}\right)\right) \\ &= \alpha + 2\beta\cos(\pi) - \alpha - 2\beta\cos(0) \\ &= -2\beta - 2\beta \\ \Delta E &= -4\beta \end{aligned}$$





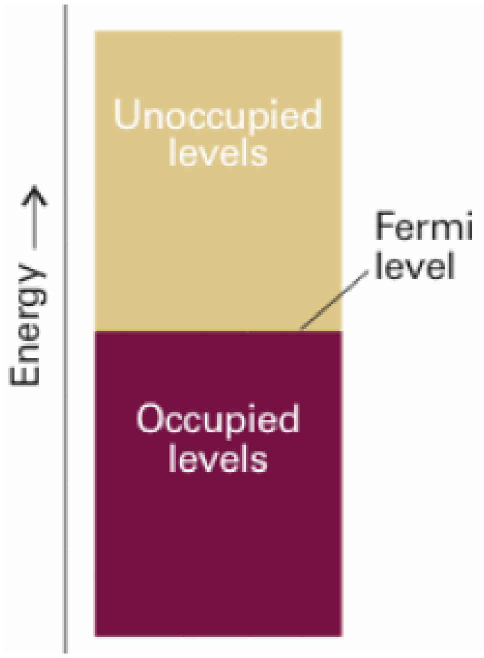


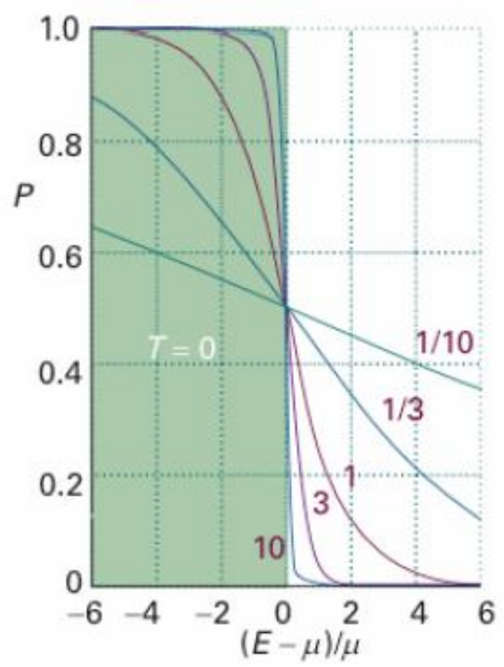
Can think of band as consisting of N different molecular orbitals, the lowest-energy orbital (k=1) being fully bonding, and highest-energy orbital (k=N) being fully antibonding between adjacent atoms. The band formed from overlap of s orbitals is called s band. If atoms have p orbitals available, same procedure leads to a p band. There may be a band gap between s band and p band, a range of energies to which no orbital corresponds, or the s and p bands may be contiguous or overlap.



Occupation of Orbitals

Consider the electronic structure of a solid formed from alkali metal atoms, each contributing one valence electron. There are N atomic orbitals and therefore N molecular orbitals forming an apparently continuous band to accommodate N electrons. When N electrons occupy a band of N orbitals, the band is only half full. At T = 0, only the lowest ½N molecular orbitals are occupied, and the HOMO is called the Fermi level. As, there are empty orbitals close in energy to Fermi level, it requires very little energy to excite uppermost electrons. Some of the electrons are therefore very mobile and give rise to electrical conductivity.





At temperatures above absolute zero, electrons can be excited by the thermal motions of the atoms. The population P of the level with energy E is given by the Fermi–Dirac distribution, a version of the Boltzmann distribution that takes into account the Pauli principle (2 electrons in each level).

$$P(E) = \frac{1}{e^{E-E_F/k_BT}+1}$$

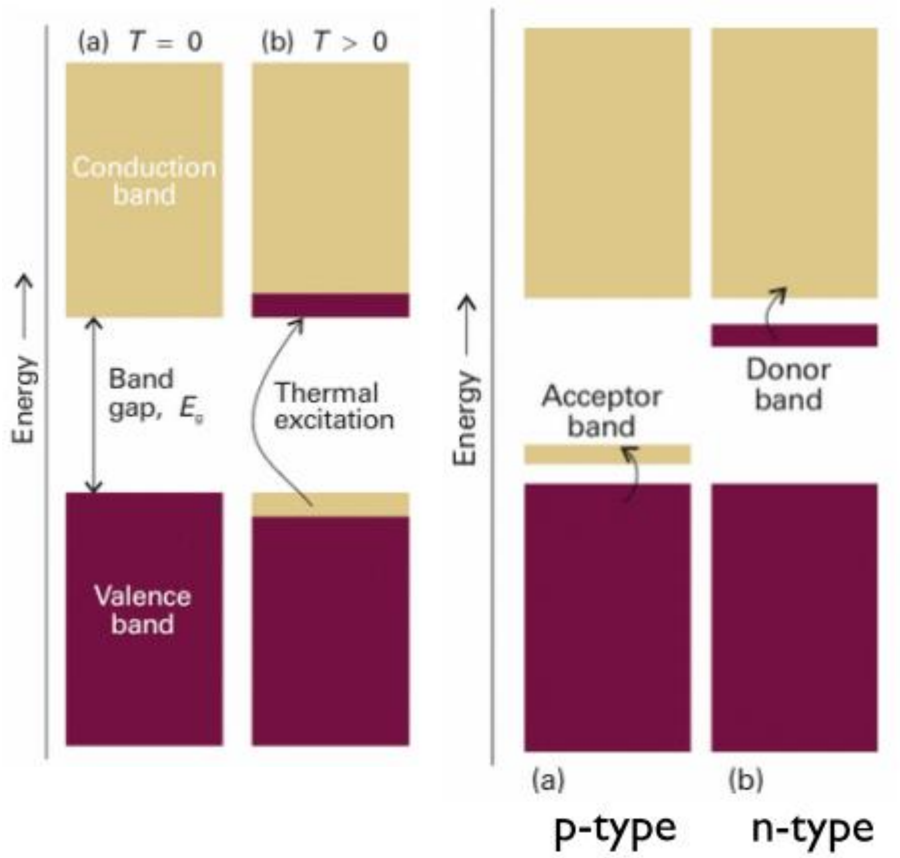
The fermi energy (E_F) corresponds to energy at which $P(E) = 0.5$ (i.e. there is 50% probability that level is occupied). The fermi level corresponds to highest occupied level at T=0 K. For energies well above the fermi level, the distribution approximates the Boltzmann distribution:

$$P(E) \approx e^{-E/kT}$$

Metal Conductivity

Metals are good conductors because they do not have band gaps, and so electrons can always be promoted into higher energy levels. Their conductivity decreases with temperature, however, owing to the fact that higher temperature causes more vigorous thermal motion of atoms, so collisions between moving electrons and atoms are more likely, thus electrons are scattered as they move through the solid, inhibiting efficient movement of charge.

Semiconductors have band gaps, which means they can only conduct electricity when the thermal energy excites electrons through the band gap to the conduction band. The distinction between an insulator and semiconductor is not absolute, but related to the size of band gap.



Doped Semiconductors

An intrinsic semiconductor is one in which semiconduction is a property of the band structure of the pure material (e.g. Si & Ge). An extrinsic semiconductor is one in which charge carriers are present as a result of the replacement of some atoms (about 1 in a billion) by dopant atoms (atoms of another element).

P-type semiconductors have dopants which are introduced to trap electrons, withdrawing electrons from filled band, leaving holes which allow remaining electrons to move. “p” indicates that holes are positive relative to electrons in band (e.g. silicon doped with indium).

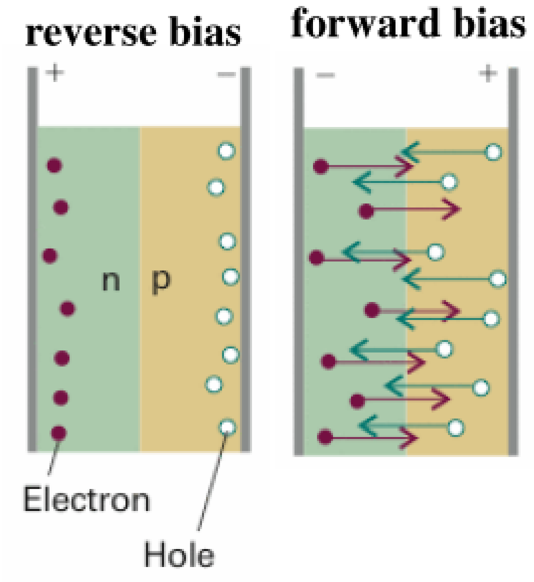
N-type semiconductors have dopants which are introduced that carry excess electrons (for example, P atoms introduced into Si). Additional electrons occupy otherwise empty bands and carry charge.

p-n Junctions

A p-n junction gives control over magnitude and direction of current, which is essential for transistors and diodes. For reverse bias, the negative electrode is attached to p-type semiconductor and the positive electrode to n-type semiconductor. Positively charged holes in p-type semiconductor are attracted to negative electrode and negatively charged electrons in n-type semiconductor are attracted to positive electrode, so charge does not flow across the junction.

For forward bias, the positive electrode is attached to p-type semiconductor and the negative electrode is attached to n-type semiconductor. Charge flows across junction, with electrons in n-type semiconductor moving toward positive electrode and holes moving in opposite direction. Recombination of holes and electrons occurs at the junction, releasing energy and producing what is called a depletion region. As long as forward bias is applied, the flow of charge from electrodes to the semiconductor replenishes the electrons and holes, so the junction sustains current.

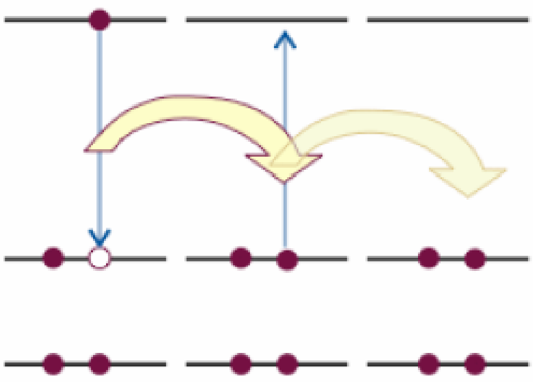
In the depletion region at junction, electrons from n-type semiconductor recombine with holes from p-type semiconductor. Reduction in density of mobile charge carriers causes depletion region to act as insulator.



Optical Properties of Solids

Light absorption by molecular solids

Absorption of a photon can create an electron-hole pair in a material with a band gap. This electron–hole pair can migrate through a solid lattice as an excitation hops from molecule to molecule. Electron and hole can jump together from molecule to molecule as they migrate. A migrating excitation of this kind is called Frenkel exciton. Electron and hole can also be on different molecules, but in each other's vicinity. Migrating excitation of this kind, which is now spread over several molecules or ions, is a Wannier exciton.

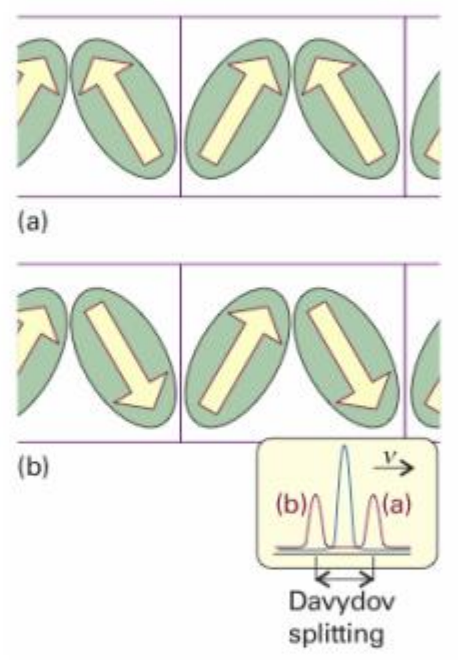


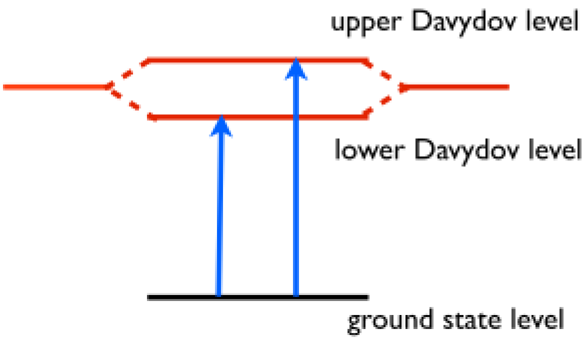
Migration of excitons implies there is an interaction between species that constitute the crystal, which affects system's energy levels. Interaction strength governs rate for exciton propagation through crystal: strong interaction gives fast migration, and vanishingly small interaction leaves exciton localised on original molecule.

The mechanism by which excitons migrate through a lattice is the interaction between transition dipole moments of excitation. When an exciton forms, there is a shift in the electric dipole of the molecule, which exerts a force on the charges of an adjacent molecule, which in turn responds by shifting its own charge.

Davydov Splitting

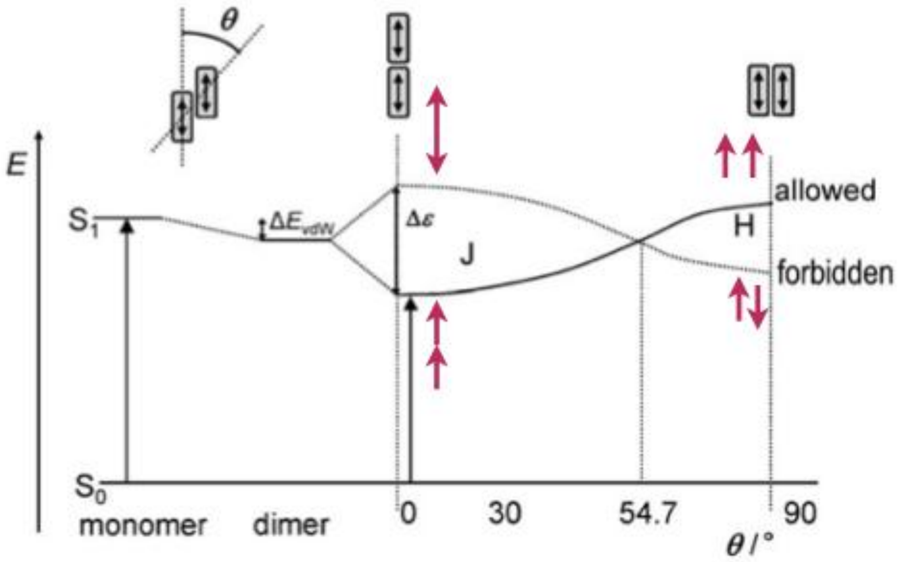
If there are N molecules per unit cell, there are N exciton bands in spectrum (if all of them are allowed). Splitting between bands is Davydov splitting. Suppose N=2. Radiation stimulates collective excitation of transition dipoles that are in-phase between neighbouring unit cells. Within each unit cell transition dipoles may be arrayed in two different ways shown in illustration. Since the two orientations correspond to different interaction energies, with interaction repulsive in one and attractive in other, the two transitions appear in the spectrum at two bands of different frequencies.





J-aggregate is a supramolecular assembly of dye molecules whose absorption is shifted to longer wavelength than the individual dye molecule (bathychromic shift).

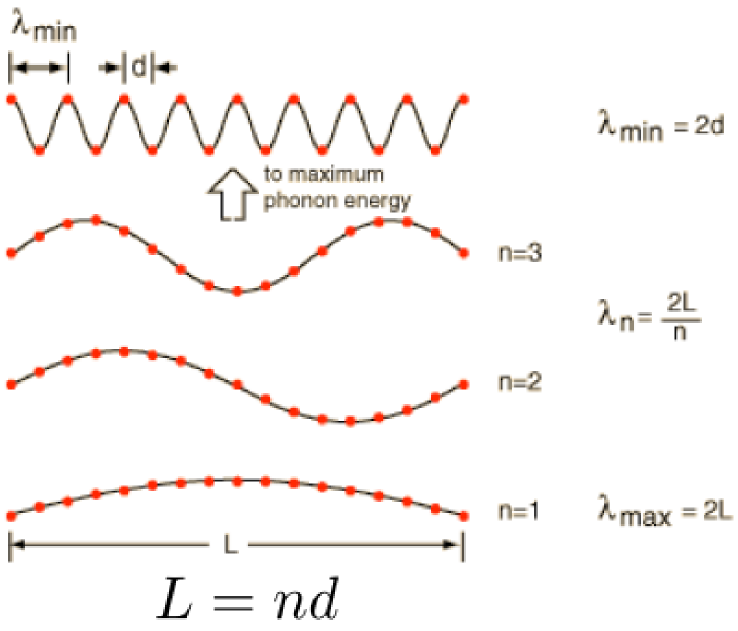
H- aggregate is a supramolecular assembly of dye molecules whose absorption is shifted to shorter wavelength than individual dye molecule (hypsochromic shift).



Phonons

Phonon is a quantum mechanical description of a lattice vibration, in which lattice elements uniformly oscillate at same frequency. Any arbitrary vibrational motion of a lattice can be considered as a superposition of phonons (normal modes) with various frequencies. At absolute zero, crystal lattice is in ground state, and contains no phonons. Energy fluctuations are associated with random lattice vibrations, which can be viewed as a gas of phonons.

Lattice vibrations (phonons) have discrete wavelengths with maximum and minimum values that depend on the crystal's dimensions and lattice spacing.



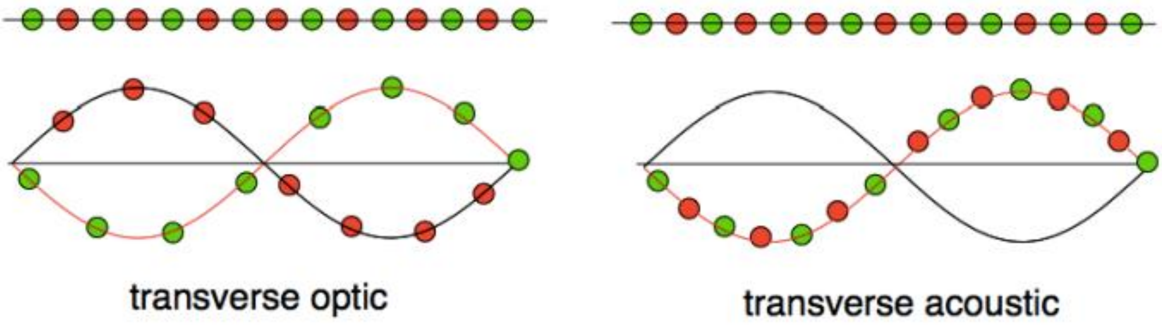
Frequency ω_k and wavenumber k are related by the dispersion relationship:

$$\omega_k = \sqrt{2w_0^2(1-\cos(kd))} = 2w_0 \left|\sin\left(\frac{kd}{2}\right)\right|$$

Energy levels of phonons are given by:

$$E_k = \hbar\omega_k\left(n_k + \frac{1}{2}\right), n_k = 0,1,2, \ldots$$

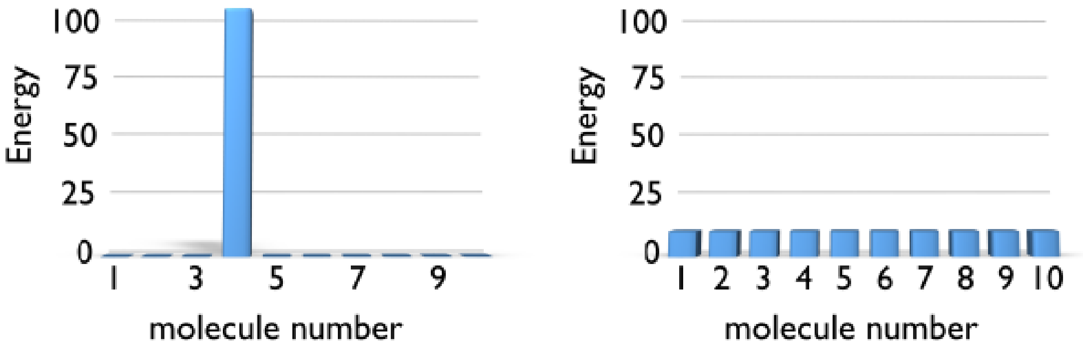
A solid can support transverse and longitudinal oscillations. Furthermore, if unit cell contains 2 atoms or molecules, the crystal can have acoustic or optical phonons depending on whether the two components move in or out of phase.



Statistical Thermodynamics

Distribution of Molecular States

If we consider a system of N molecules, there are many different configurations of energy states that system could be in.



The same macroscopic state can usually be generated by more than one microstate, so the number of microstates corresponding to a particular macrostate is known as that state's multiplicity. The system's configuration at a particular moment in time can be written as the number of particles in each possible state: $\{N-2,2,0,0,\ldots\}$.

The weight of a configuration in which n_0 molecules are in state ϵ_0, n_1 molecules are in state ϵ_1, etc, is given by:

$$W = \frac{N!}{n_0!\,n_1!\,n_2!\ldots}$$

The Partition Function

The probability of finding n_i molecules in state with energy ϵ_i is given by:

$$\begin{aligned} p_i &= \frac{n_i}{N} \\ &= \frac{e^{-\frac{\epsilon_i}{kT}}}{\sum_i g_i e^{-\frac{\epsilon_i}{kT}}} \\ p_i &= \frac{e^{-\frac{\epsilon_i}{kT}}}{q} \end{aligned}$$

This function q is called the partition function, and is very useful:

$$q = \sum_i g_i e^{-\epsilon_i/kT}$$

The sum over energy levels i, multiplied by the weight (multiplicity) of each level g_i.

Planck–Einstein Relation

The energy of a particle is proportional to its frequency:

$$E = hf = hc\tilde{\nu}$$

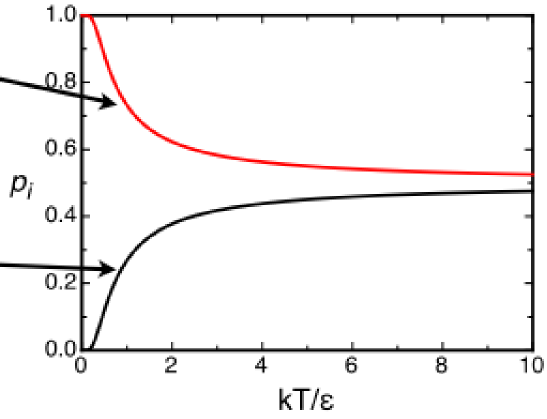
Two Level System

Suppose we have a system of two singly degenerate energy levels at $\epsilon_0 = 0$ and $\epsilon_1 = \epsilon$.

$$\begin{aligned} q &= \sum_i g_i e^{-\epsilon_i/kT} \\ &= \sum_i e^{-\epsilon_i/kT} \\ q &= 1 + e^{-\epsilon/kT} \end{aligned}$$

$$p_{lower} = \frac{1}{q} = \frac{1}{(1+e^{\frac{-\epsilon}{kT}})}$$

$$p_{upper} = \frac{e^{\frac{-\epsilon}{kT}}}{q} = \frac{e^{\frac{-\epsilon}{kT}}}{(1+e^{\frac{-\epsilon}{kT}})}$$



At low temperature (kT<<ε), lower state is almost exclusively populated

At high temperature (kT>>ε), upper and lower states have almost equal populations

In the unusual case where $\frac{p_1}{p_0} > 1$, it must be the case that T<0. This is known as a population inversion.

The internal energy for a two level system:

$$E = -\frac{N}{q}\frac{dq}{d\beta}$$
$$q = \left(1 + e^{-\beta\epsilon}\right)$$

$$E = -\left(\frac{N}{1 + e^{-\beta\epsilon}}\right)\frac{d}{d\beta}\left(1 + e^{-\beta\epsilon}\right)$$
$$E = \frac{N\epsilon}{1 + e^{\epsilon/kT}}$$

Vibrational Partition Function

Vibrational energy levels can be modelled as if they are produced by a harmonic oscillator:

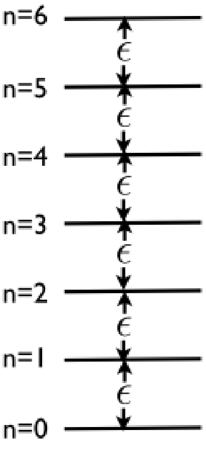
$$e_i = n\epsilon, g_i = 1$$

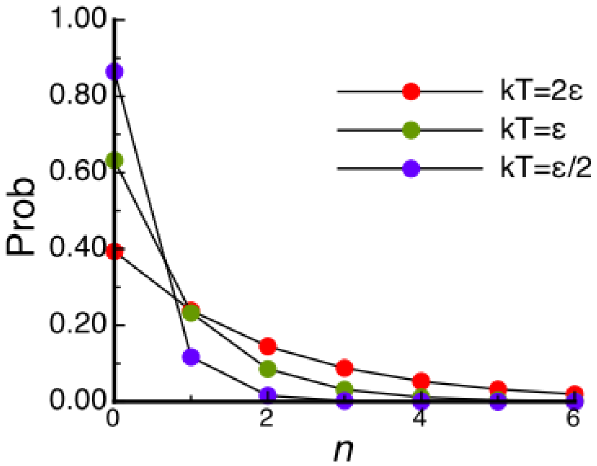
The partition function is given by:

$$q = \sum_{n=0}^{\infty} e^{-\frac{n\epsilon}{kT}}$$
$$= \sum_{n=0}^{\infty} \left(e^{-\frac{\epsilon}{kT}}\right)^n$$
$$q = \frac{1}{1 - e^{-\frac{\epsilon}{kT}}}$$

Thus the boltzmann distribution for vibrational energy modes:

$$p_n = \frac{e^{-n\epsilon/kT}}{q} = \frac{e^{-\frac{n\epsilon}{kT}}}{1 - e^{-\frac{\epsilon}{kT}}}$$





Internal energy given by:

$$E = -\frac{N}{q}\frac{dq}{d\beta}$$

$$= -\frac{N}{\left(\frac{1}{1-e^{-\frac{\epsilon}{kT}}}\right)}\frac{d}{d\beta}\left(\frac{1}{1-e^{-\epsilon\beta}}\right)$$

$$= -N\left(1-e^{-\epsilon\beta}\right)(-1)\left(\epsilon e^{-\epsilon\beta}\right)\left(\frac{1}{1-e^{-\epsilon\beta}}\right)^2$$

$$= N\left(\epsilon e^{-\epsilon\beta}\right)\left(\frac{1}{1-e^{-\epsilon\beta}}\right)$$

$$= N\left(\frac{\epsilon}{e^{\epsilon\beta}-1}\right)$$

$$E = N\left(\frac{hcv}{e^{\frac{hcv}{kT}}-1}\right)$$

For high temperatures (small x as $kT \gg hcv$) use the approximation $e^x \approx 1 + x$, yielding:

$$E = N\left(\frac{hcv}{\left(1+\frac{hcv}{kT}\right)-1}\right)$$

$$E = NkT$$

Rotational Partition Function

Linear molecules have quantised rotational energy levels that depend on the angular moment quantum number J.

$$E(J) = hcBJ(J+1), g_J = 2J+1$$

Thus the partition function is given by:

$$q = \sum_{J=0}^{\infty} g_J e^{-\frac{E(J)}{kT}}$$

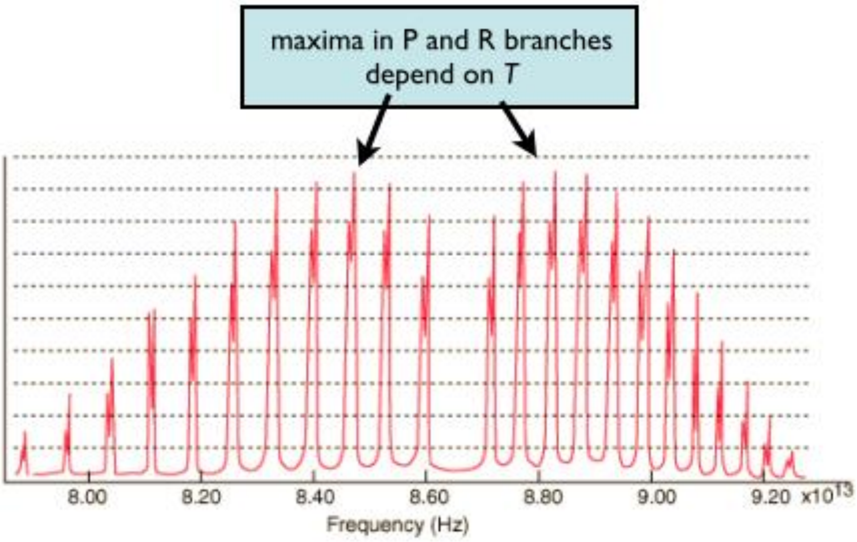
$$q = \sum_{J=0}^{\infty} (2J+1)\, e^{-\frac{hcBJ(J+1)}{kT}}$$

Where B is given by:

$$B = \frac{h}{8\pi^2 c\mu r^2}, \mu = \frac{m_1 m_2}{m_1 + m_2}$$

The peak of the spectrum is given by:

$$J_{max} = \sqrt{\frac{kT}{2B}} - \frac{1}{2}$$



Translational Partition Function

Partition function for particle of mass m free to move in a one-dimensional container of length X can be evaluated by considering particle-in-a-box model. Energy levels are given by:

$$E(n) = \frac{n^2h^2}{8mX^2}, g_i = 1$$

$$q = \sum_i g_i\, e^{-\epsilon_i/kT} = \sum_{n=1}^{\infty} e^{-\frac{n^2h^2}{8mX^2kT}}$$

Since the energy levels are very close together, we can replace the sum by an integral:

$$\sum_{n=1}^{\infty} e^{-\frac{n^2h^2}{8mX^2kT}} \approx \int_0^{\infty} e^{-\frac{n^2h^2}{8mX^2kT}}\, dn$$

$$q = \sqrt{\frac{2\pi mkT}{h^2}}X$$

Partition function for translational motion increases with length of box and mass of particle. In each case, separation of energy levels becomes smaller and more levels become thermally accessible. This applies to each of three dimensions:

$$\begin{aligned} q_T &= q_X q_Y q_Z \\ &= \sqrt{\frac{2\pi mkT}{h^2}}X\sqrt{\frac{2\pi mkT}{h^2}}Y\sqrt{\frac{2\pi mkT}{h^2}}Z \\ &= \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V \\ q_T &= \frac{V}{\Lambda^3} \end{aligned}$$

Where Λ is called the thermal wavelength (measured in length), which is defined by:

$$\Lambda = \frac{h}{\sqrt{2\pi mkT}}$$

Internal energy given by:

$$\begin{aligned}
E &= -\frac{N}{q}\frac{dq}{d\beta} \\
&= -\frac{N}{\left(\frac{2\pi m}{h^2\beta}\right)^{3/2} V}\frac{dq}{d\beta}\left(\frac{2\pi m}{h^2\beta}\right)^{3/2} V \\
&= -N\beta^{3/2}\frac{dq}{d\beta}\beta^{-3/2} \\
&= -N\beta^{3/2}(-3/2)\beta^{-5/2} \\
E &= \frac{3}{2}NkT
\end{aligned}$$

Overall Partition Function

The overall partition function is found as a function of individual partition functions:

$$\epsilon_i = \epsilon_i^T + \epsilon_i^R + \epsilon_i^V + \epsilon_i^E$$

$$\begin{aligned}
q &= \sum_i e^{-\beta\epsilon_i} \\
&= \sum_i e^{-\beta\epsilon_i^T - \beta\epsilon_i^R - \beta\epsilon_i^V - \beta\epsilon_i^E} \\
&= \sum_i e^{-\beta\epsilon_i^T} \sum_i e^{-\beta\epsilon_i^R} \sum_i e^{-\beta\epsilon_i^V} \sum_i e^{-\beta\epsilon_i^E} \\
q &= q_T q_R q_V q_E
\end{aligned}$$

Chemical Kinetics

Reaction Rates

The rate of a reaction is defined to be:

$$\text{rate} = \frac{\Delta[X]}{\Delta t}$$

Reaction rates are always positive, so are defined with a negative sign out the front for reactants.

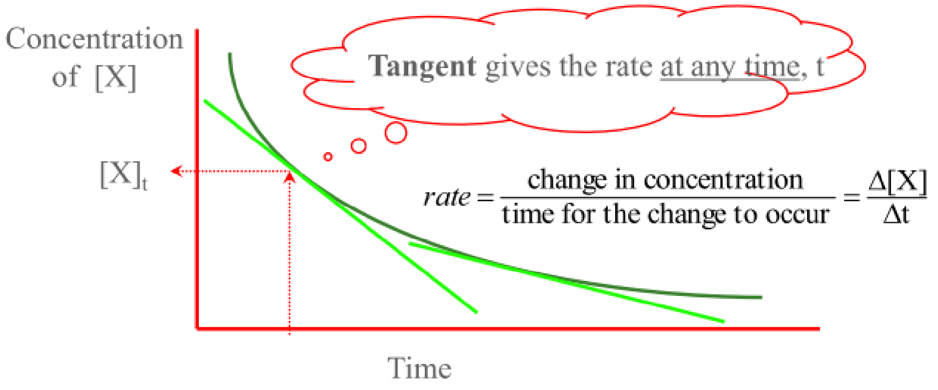
When the stoichiometric coefficients differ, we define the rate as follows:

$$\text{rate} = \frac{1}{\mathrm{n_J}}\frac{d[J]}{dt}$$

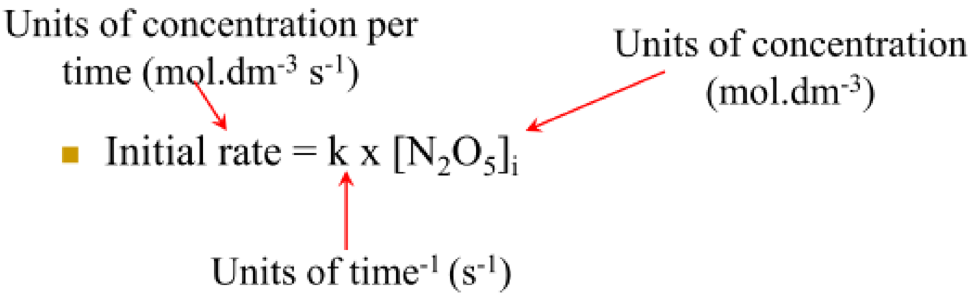
$$\mathrm{A + 2\,B \rightarrow 2\,C + 3\,D}$$

$$rate = -\frac{1}{1}\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = +\frac{1}{2}\frac{d[C]}{dt} = +\frac{1}{3}\frac{d[D]}{dt}$$

- As a reaction progresses the rate of reaction will decrease



$$rate = \frac{\text{change in concentration}}{\text{time for the change to occur}} = \frac{\Delta[X]}{\Delta t}$$


Units of concentration per time ($mol.dm^{-3}\ s^{-1}$)

Units of concentration ($mol.dm^{-3}$)

- Initial rate = k x $[N_2O_5]_i$

Units of time^{-1} (s^{-1})

Note that the units of the rate constant vary in order to ensure that the rate itself is always measured in Ms^{-1}.

Half life equation:

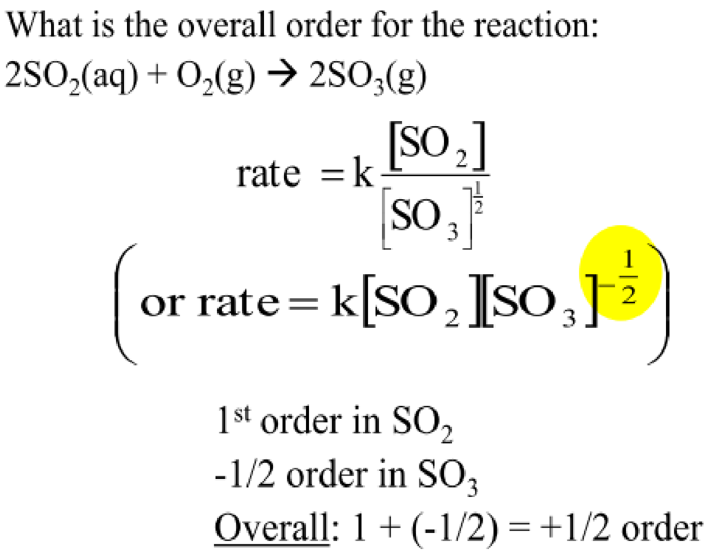
$$N(t) = N_0 e^{-t/\tau}$$

Order of Reactions

The order of a reaction is the sum of the powers on the concentrations that determine the rate:

$$\text{rate} = k[\text{reactant}]^n$$

Note that n can be positive, negative, zero, or a fraction. It can only be determined experimentally.



What is the overall order for the reaction:
$2SO_2(aq) + O_2(g) \rightarrow 2SO_3(g)$

$$\text{rate} = k\frac{[SO_2]}{[SO_3]^{\frac{1}{2}}}$$

$$\left(\text{or rate} = k[SO_2][SO_3]^{-\frac{1}{2}}\right)$$

1st order in SO_2
-1/2 order in SO_3
<u>Overall</u>: 1 + (-1/2) = +1/2 order

First Order Integrated Rate Law

$$\frac{d[A]}{dt} = k[A]$$
$$\frac{1}{[A]}\frac{d[A]}{dt} = k$$
$$\int \frac{1}{[A]}\frac{d[A]}{dt}dt = \int k\,dt$$
$$\int \frac{1}{[A]}d[A] = kt$$
$$\ln[A]_t - \ln[A]_0 = kt$$

$$t_{1/2} = \frac{1}{k}\ln\left(\frac{[A]_0}{0.5[A]_0}\right) = \frac{\ln(2)}{k}$$

Second Order Integrated Rate Law

$$\frac{d[A]}{dt} = k[A]^2$$
$$\frac{1}{[A]^2}\frac{d[A]}{dt} = k$$
$$\int \frac{1}{[A]^2}d[A] = kt$$
$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$t_{\frac{1}{2}} = \frac{1}{k}\left(\frac{1}{0.5[A]_0} - \frac{1}{[A]_0}\right) = \frac{1}{k[A]_0}$$

Pseudo-First Order

If there is a reaction of the type: $A + B \rightarrow P$ with rate late $k[A][B]$, it may be possible to choose conditions such that $[B]_0 \gg [A]_0$, in which case the rate law can be simplified:

$$\text{rate} = k'[A]$$

Second Order with Two Reactants

$$A + 2B \rightarrow P, \qquad \text{rate} = k[A][B]$$

$$\left(\frac{1}{[B]_0 - 2[A]_0}\right) \ln\left(\frac{[A]_0([B]_0 - 2x)}{[B]_0([A]_0 - x)}\right) = kt$$

Where x is the concentration reacted so far, so $x = [A]_0 - [A]$

Reaction Mechanisms

Collision Theory

For a reaction to occur, chemical species must collide together with sufficient energy and in the correct orientation. Collision volume density depends on molecular size and velocity:

$$z = \pi d^2 c_{rel} N_A N_B = \sigma c_{rel} N^2$$

Where z is the collision frequency and σ is the collision cross section πd^2. The relative velocity is given by:

$$c_{rel} = \sqrt{\frac{8kT}{\pi\mu}}$$

The fraction of collisions with sufficient energy to react increases with temperature in accordance with the Boltzmann distribution:

$$f = \frac{1}{N} e^{-\frac{E_a}{RT}}$$

The fraction of collisions of the appropriate orientation is indicated by the steric factor p. Combining these factors we arrive at the final rate:

$$\begin{aligned} \text{rate} &= p\sigma\sqrt{\frac{8kT}{\pi\mu}} N e^{-\frac{E_a}{RT}}[A][B] \\ &= p\sigma c_{rel} N^2 \left(\frac{1}{N} e^{-\frac{E_a}{RT}}\right)[A][B] \\ &= pze^{-\frac{E_a}{RT}}[A][B] \\ \text{rate} &= k[A][B] \end{aligned}$$

The rate constant k is given by the Arrhenius equation where A is the frequency factor:

$$k = Ae^{-\frac{E_a}{RT}}$$

Molecularity of Reactions

Molecularity is the number of molecules that come together to react in an elementary reaction and is equal to the sum of stoichiometric coefficients of reactants in this elementary reaction. Unimolecular reactions are first order, while bimolecular reactions are second order.

Reactions can take place in a series of elementary steps called a reaction mechanism. Mechanisms must satisfy two criteria: the sum of elementary steps must give the overall balanced equation for the reaction, and the mechanism must agree with the experimentally determined rate law.

$$NO_2(g) + NO_2(g) \xrightarrow{k_1} NO_3(g) + NO(g) \quad (1)$$

$$NO_3(g) + CO(g) \xrightarrow{k_2} NO_2(g) + CO_2(g) \quad (2)$$

$$\boxed{\text{overall : } NO_2(g) + CO(g) \xrightarrow{k} NO(g) + CO_2(g)}$$

Mechanisms can include intermediate species, which are neither reactants nor products.

Steady State Approximation

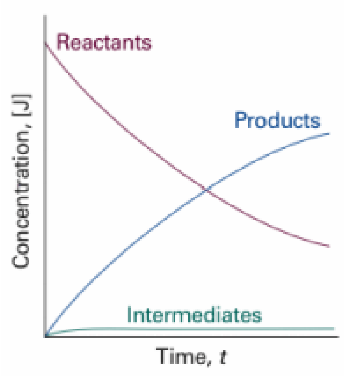
The overall reaction rate is limited by the rate of the slowest step in the sequence. Often to make calculations easier we use what is called the steady state approximation, which involves setting the rate of change of the intermediate to zero.

$$A \xrightarrow{k_a} I \xrightarrow{k_b} P$$

$$\frac{d[A]}{dt} = -k_a[A] \qquad \frac{d[P]}{dt} = k_b[I]$$

$$\frac{d[I]}{dt} \approx 0 \qquad \rightarrow \qquad k_a[A]-k_b[I] \approx 0$$

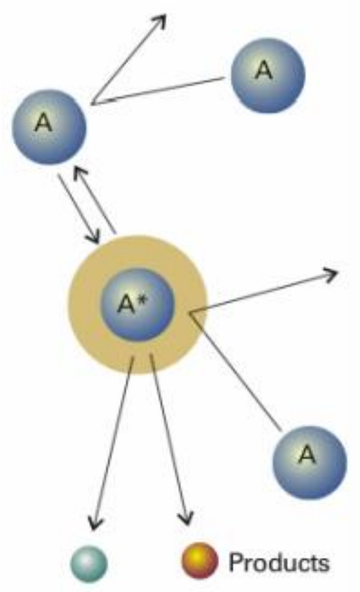
$$[I] \approx \frac{k_a}{k_b}[A]$$



$$\frac{d[P]}{dt} \approx k_a[A]$$

Lindemann-Hinshelwood Mechanism

Used to model first order decomposition reactions through activation of products.



$$A + A \xrightarrow{k_a} A^* + A \quad \text{(activation)}$$

$$A^* + A \xrightarrow{k_a'} A + A \quad \text{(deactivation)}$$

$$A^* \xrightarrow{k_b} P$$

$$\frac{d[P]}{dt} = k_b[A^*]$$

$$\frac{d[A^*]}{dt} = 0 = k_a[A]^2 - k_a'[A^*][A] - k_b[A^*]$$

$$[A^*] = \frac{k_a[A]^2}{k_a'[A] + k_b}$$

$$\frac{d[P]}{dt} = \frac{k_a k_b [A]^2}{k_a'[A] + k_b}$$

$$\frac{1}{k_1} - \frac{1}{k_2} = \frac{1}{k_a}\left(\frac{1}{[A]_1} - \frac{1}{[A]_2}\right)$$

$k_1 = 2.5 \times 10^{-4}\ s^{-1}$ when $[A]_1$ in terms of P is 1.3 kPa
$k_2 = 2.1 \times 10^{-5}\ s^{-1}$ when $[A]_2$ in terms of P is 12 Pa
k_a (rate constant for the activation step) = $1.9 \times 10^{-6}\ Pa^{-1}\ s^{-1}$

Michaelis-Menten Mechanism

A catalyst speeds up a reaction without itself being consumed. It does this by providing an alternative reaction pathway with lower activation energy. For example the decomposition of hydrogen peroxide is catalised by bromide and water:

$$2H_2O_2\ (aq) \xrightarrow{Br^-, H_3O^+} 2\,H_2O\,(l) + O_2\ (g)$$

Reaction mechanism

$$H_3O^+ + H_2O_2 \rightleftharpoons H_3O_2^+ + H_2O \qquad \text{(fast)}$$

$$H_3O_2+ + Br^- \rightarrow HOBr + H_2O \qquad \text{(slow)}$$

$$HOBr + H_2O_2 \rightarrow H_3O^+ + O_2 + Br^- \qquad \text{(fast)}$$

$$\text{Rate} = k\,[H_3O_2^+][Br^-] \qquad K = \frac{[H_3O_2^+]}{[H_2O_2][H_3O^+]}$$

$$\frac{d[O_2]}{dt} = k_{eff}\,[H_2O_2][H_3O^+][Br^-]; \quad k_{eff} = kK$$

The Michaelis–Menten kinetics is one of the best-known models of enzyme kinetics. It describes the reaction of an enzyme E with a substrate S to produce a product P.

$$E + S \underset{k_a'}{\overset{k_a}{\rightleftharpoons}} ES$$

$$ES \xrightarrow{k_b} P + E$$

$$\text{Rate} = \frac{d[P]}{dt} = k_b\,[ES]$$

$$\text{Using SSA, } \frac{d[ES]}{dt} = k_a\,[E][S] - k_a'\,[ES] - k_b\,[ES] = 0$$

$$[ES] = \left(\frac{k_a}{k_a' + k_b}\right)[E][S]$$

$$K_M = \frac{k_a' + k_b}{k_a} \qquad \text{and} \qquad [E] = [E]_0 - [ES]$$

$$[ES] = \frac{([E]_0\,[S] - [ES]\,[S])}{K_M}$$

Michaelis-Menten constant

$$[\mathrm{ES}] = \frac{\left([\mathrm{E}]_0[\mathrm{S}] - [\mathrm{ES}][\mathrm{S}]\right)}{\mathrm{K_M}}; \qquad \mathrm{K_M}[\mathrm{ES}] = \left([\mathrm{E}]_0[\mathrm{S}] - [\mathrm{ES}][\mathrm{S}]\right)$$

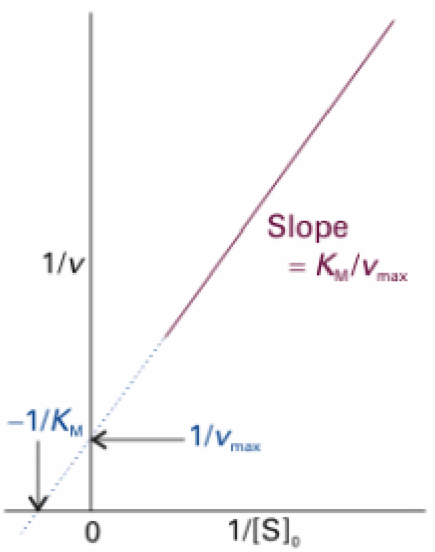
$$\mathrm{K_M}[\mathrm{ES}] + [\mathrm{ES}][\mathrm{S}] = [\mathrm{E}]_0[\mathrm{S}]; \qquad [\mathrm{ES}] = \frac{[\mathrm{E}]_0[\mathrm{S}]}{\mathrm{K_M} + [\mathrm{S}]}$$

$$\mathrm{Rate} = \frac{d[\mathrm{P}]}{dt} = \mathrm{k_b}[\mathrm{ES}] = \frac{\mathrm{k_b}[\mathrm{E}]_0[\mathrm{S}]}{\mathrm{K_M} + [\mathrm{S}]}$$

The rate of this reaction depends upon the concentration of the substrate. As this approaches infinity, the rate of the reaction becomes:

$$\lim_{[S]\to\infty}\left(\frac{k_b[E]_0[S]}{K_m + [S]}\right) = \lim_{[S]\to\infty}\left(\frac{k_b[E]_0}{K_m/[S] + 1}\right) = k_b[E]_0$$

Thus $v_{max} = k_b[E]_0$. We can also manipulate the equation to produce a Lineweaver-Burk Plot:



Chain Reaction Mechanism

A chain reaction is a reaction in which an intermediate reacts to produce another intermediate. They can be described by the Rice-Herzfeld mechanism:

$$\begin{aligned}
CH_3CHO &\rightarrow {}^{\bullet}CH_3 + {}^{\bullet}CHO && \text{initiation}\\
CH_3CHO + {}^{\bullet}CH_3 &\rightarrow CH_3CO^{\bullet} + CH_4 && \text{propagation}\\
CH_3CO^{\bullet} &\rightarrow {}^{\bullet}CH_3 + CO && \text{propagation}\\
{}^{\bullet}CH_3 + {}^{\bullet}CH_3 &\rightarrow CH_3CH_3 && \text{termination}
\end{aligned}$$

$$\text{rate} = k_p\,[CH_3CHO][{}^{\cdot}CH_3]$$

$$\frac{d[{}^{\cdot}CH_3]}{dt} = k_i\,[CH_3CHO] - k_p\,[CH_3CHO][{}^{\cdot}CH_3] + k_p'\,[CH_3CO^{\cdot}] - 2k_t\,[{}^{\cdot}CH_3]^2 = 0$$

$$\frac{d[CH_3CO^{\cdot}]}{dt} = k_p\,[CH_3CHO][{}^{\cdot}CH_3] - k_p'\,[CH_3CO^{\cdot}] = 0$$

The sum of the two equatioins is

$$k_i\,[CH_3CHO] - 2k_t\,[{}^{\cdot}CH_3]^2 = 0$$

$$[{}^{\cdot}CH_3] = \left(\frac{k_i}{2k_t}\right)^{\frac{1}{2}} [CH_3CHO]^{\frac{1}{2}}$$

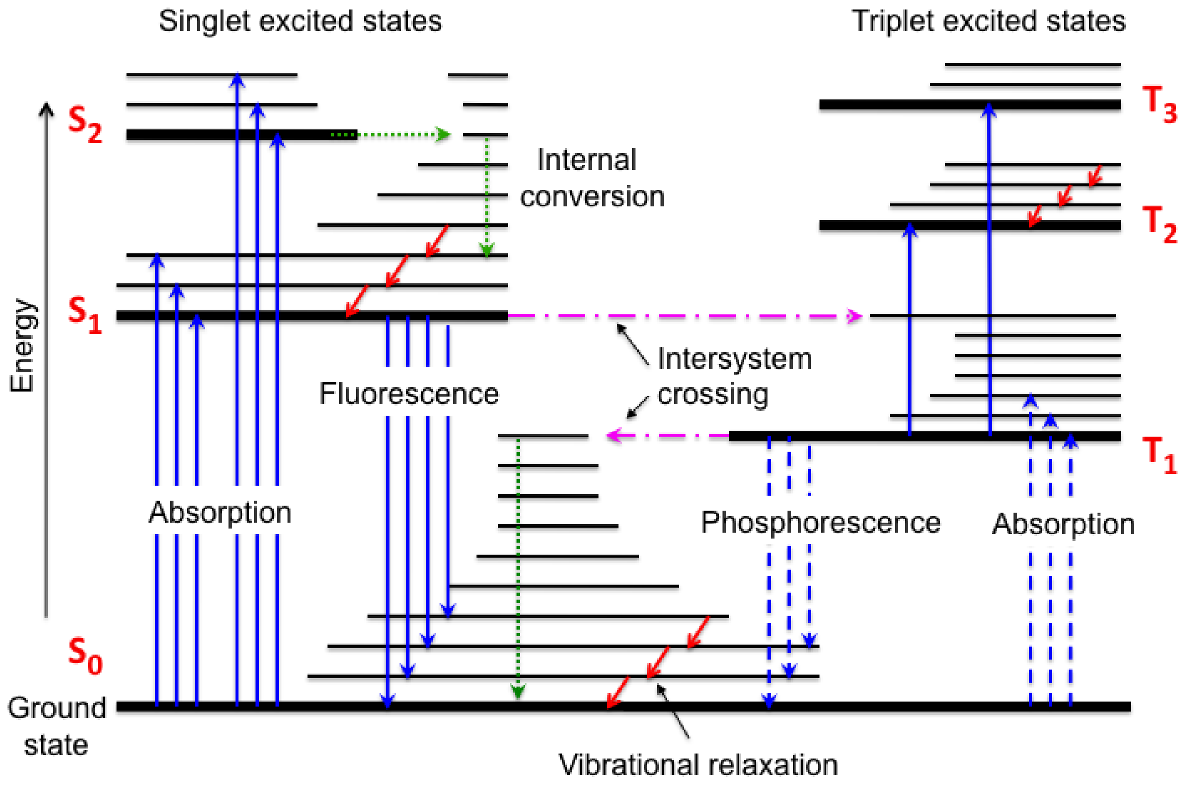
$$\frac{d[CH_4]}{dt} = k_p\,[{}^{\cdot}CH_3][CH_3CHO] = k_p\left(\frac{k_i}{2k_t}\right)^{\frac{1}{2}} [CH_3CHO]^{\frac{3}{2}}$$

Photochemistry

A photochemical reaction is a chemical reaction caused by absorption of light. When a chemical system absorbs light energy there are a number of ways that energy can be released:

- Vibrational relaxation: energy is gradually transferred to translational modes of the same or surrounding molecules, basically dissipating energy as heat into the environment
- Fluorescence: reemission of the photon at a lower wavelength after some amount of vibrational relaxation
- Intersystem Crossing: a radiationless process involving a transition between two electronic states with different spin multiplicity, usually triplet and singlet states
- Internal Conversion: transition from a higher to a lower electronic state in a molecule or atom. It differs from intersystem crossing in that, while both are radiationless methods of de-excitation, the molecular spin state for internal conversion remains the same, whereas it changes for intersystem crossing
- Phosphorescence: a slower version of flourescence which occurs following intersystem crossing. As a result, the energy can become trapped in the triplet state with only classically

"forbidden" transitions available to return to the lower energy state. These transitions still occur in quantum mechanics but only slowly



The quantum yield for any of these processes is simply the number of events of that type divided by the number of absorbed photons:

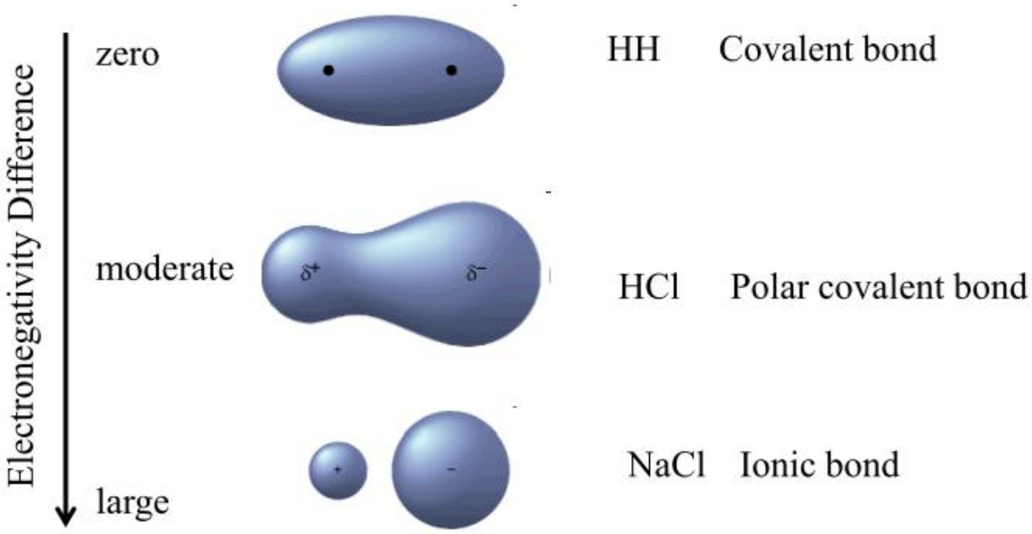
$$\phi_i = \frac{v_i}{I_{abs}}$$

The decay rate for photochemically excited states is given by:

$$S = S_0 e^{(k_f + k_{IC} + k_{ISC})t}$$

Molecular Interactions

Dipole Moments



The electric dipole moment is a measure of the separation of positive and negative electrical charges in a system of electric charges. Its SI unit is column meters, though the old unit debye is sometimes still used, where $1\ D = 3.336 \times 10^{-30}\ C \cdot m$.

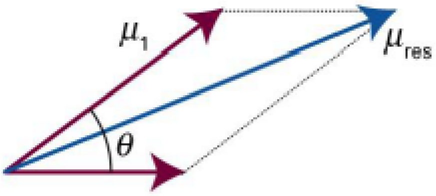
$$\mu = qr$$

By comparing the predicted to the actual dipole moment of a bond, we can determine its ionic character:

$$\%\text{ionic} = \frac{\mu_{meas}}{\mu_{calc}} \times 100$$

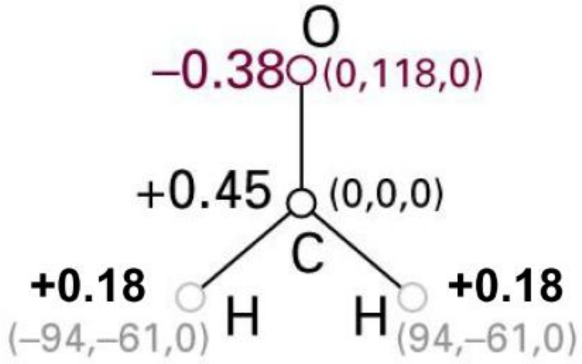
Dipole moments are added by vector addition:

$$\mu_{res} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$$



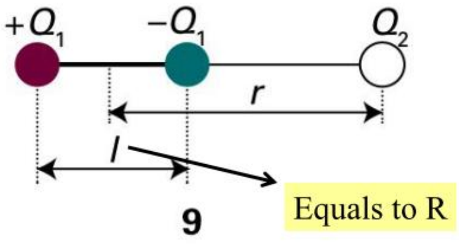
An alternative calculation approach is:

$$\mu_x = \sum_J q_J x_J \qquad \mu_{res} = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{\frac{1}{2}}$$



The Potential Energy of Interaction

Between a dipole and a point charge when $l = r$:

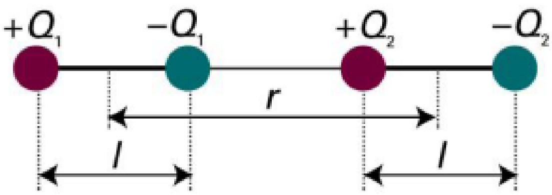


$$V = \frac{q_1 q_2}{4\pi\epsilon_0 r} = \frac{\left(\frac{\mu}{r}\right) q_2}{4\pi\epsilon_0 r} = \frac{\mu q_2}{4\pi\epsilon_0 r^2}$$

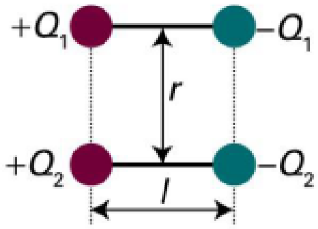
Between a dipole and a point charge when $l \neq r$:

$$\begin{aligned} V &= \frac{q_1 q_2}{4\pi\epsilon_0\left(r + \frac{l}{2}\right)} - \frac{q_1 q_2}{4\pi\epsilon_0\left(r - \frac{l}{2}\right)} \\ &= \frac{q_1 q_2}{4\pi\epsilon_0}\left(\frac{1}{r + \frac{l}{2}} - \frac{1}{r - \frac{l}{2}}\right) \\ &= \frac{q_1 q_2}{4\pi\epsilon_0}\left(\frac{r - \frac{l}{2}}{r^2 + \frac{1}{4}l^2} - \frac{r + \frac{l}{2}}{r^2 + \frac{1}{4}l^2}\right) \\ &= \frac{q_1 q_2}{4\pi\epsilon_0}\left(\frac{-l}{r^2 + \frac{1}{4}l^2}\right) \\ V &\approx -\frac{q_1 q_2 l}{4\pi\epsilon_0 r^2} \end{aligned}$$

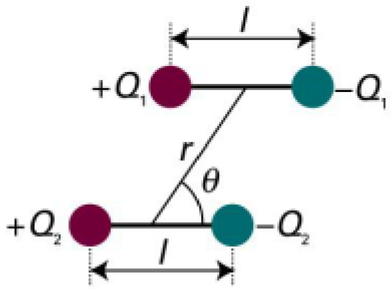
Between two dipoles:



$$V = -\frac{\mu_1\mu_2}{2\pi\epsilon_0 r^3}$$

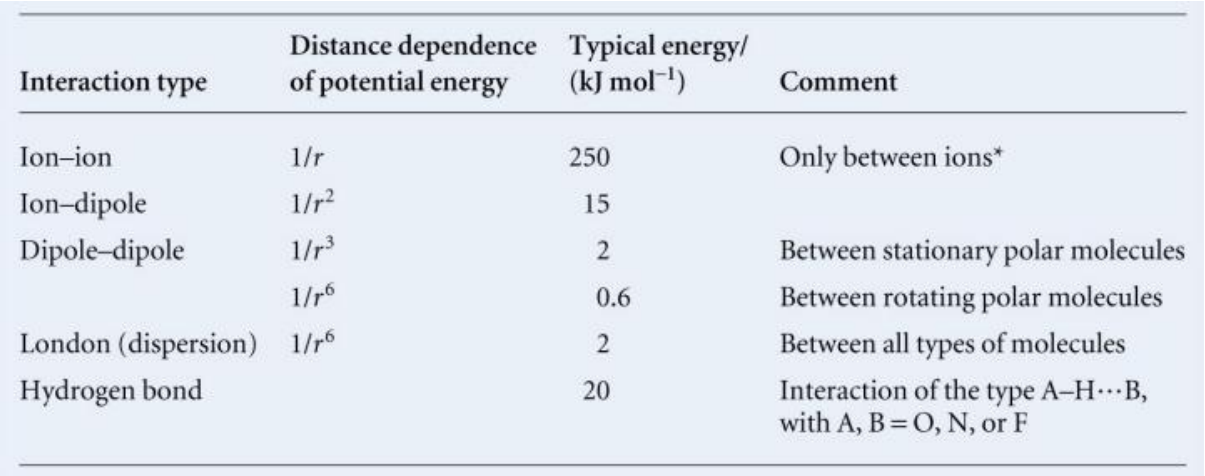


$$V = \frac{\mu_1\mu_2}{4\pi\epsilon_0 r^3}$$



$$V = -\frac{\mu_1\mu_2(1-3\cos^2\theta)}{4\pi\epsilon_0 r^3}$$

Types of Interactions



Interaction type	Distance dependence of potential energy	Typical energy/(kJ mol^{-1})	Comment
Ion–ion	$1/r$	250	Only between ions*
Ion–dipole	$1/r^2$	15	
Dipole–dipole	$1/r^3$	2	Between stationary polar molecules
	$1/r^6$	0.6	Between rotating polar molecules
London (dispersion)	$1/r^6$	2	Between all types of molecules
Hydrogen bond		20	Interaction of the type A–H···B, with A, B = O, N, or F

For the interaction of an n-pole and an m-pole, the potential energy always varies with:

$$V = \frac{1}{r^{n+m-1}}$$

Positive potential energies indicate repulsion; negative indicate attraction.