Structure of Matter II

Ellis de Wit

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1 Valence Bond Theory

A bond forms when an electron in an *atomic orbital* on one atom pairs its spin with that of an electron in an *atomic orbital* on another atom, this can be described by valence bond theory.

1.1 The Born–Oppenheimer Approximation

We will adopt the **Born–Oppenheimer approximation** in which it is supposed that the nuclei, being so much heavier than an electron, move relatively slowly and may be treated as stationary while the electrons move in their field.

1.2 Diatomic molecules

First we'll look at molecular hydrogen, H_2. The wave function of electrons 1 and 2 on two widely separated H atoms is given by

$$\Psi(1,2) = \psi_{\mathrm{H1s}_A}(r_1)\psi_{\mathrm{H1s}_B}(r_2)$$

When the atoms are close together, it is not possible to know which electron is which. A better description of the molecule than either wavefunction alone is one of the (unnormalized) linear combinations

$$\Psi(1,2) = \psi_A(1)\psi_B(2) \pm \psi_A(2)\psi_B(1).$$

The combination with lower energy turns out to be the one with a + sign, so the valence-bond wavefunction of the electrons in an H2 molecule is

$$\Psi(1,2) = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1).$$

The reason why this linear combination has a lower energy than either the separate atoms or the linear combination with a negative sign can be traced to the constructive interference between the wave patterns represented by the two terms.

σ **bond.** A covalent bond that has cylindrical symmetry around the internuclear axis (often the z axis) is called a σ bond. When viewed along the internuclear axis, it resembles a pair of electrons in an s orbital.

A chemist's picture of a covalent bond is one in which the spins of two electrons pair as the atomic orbitals overlap. The bond can only be formed by two spin-paired electrons ($\uparrow\downarrow$).

The **Pauli principle** requires the overall wavefunction of two electrons, the wavefunction including spin, to change sign when the labels of the electrons are interchanged. Is that happening here?
The overall VB wavefunction for two electrons is

$$\Psi(1,2) = \left[\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)\right]\sigma(1,2),$$

with $\sigma(1,2)$ being the spin component. Interchanging the labels gives:

$$\Psi(2,1) = \left[\psi_A(2)\psi_B(1) + \psi_A(1)\psi_B(2)\right]\sigma(2,1)$$
$$= \left[\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)\right]\sigma(2,1).$$

Like said before the Pauli requires that $\Psi(1,2) = -\Psi(2,1)$, which thus requires that $\sigma(1,2) = -\sigma(2,1)$. Two paired electron spins luckily have this property:

$$\sigma_-(1,2) = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right].$$

π **bond.**   Covalent bonds where two lobes of an orbital on one atom overlap two lobes of an orbital on another atom and this overlap occurs laterally are called pi-bonds. It is so called because, viewed along the internuclear axis, a π bond resembles a pair of electrons in a p orbital.

Let's look at another homonuclear diatomic molecule, N_2, for instance. N_2 has a valence electron configuration of $2s^1 2p_x^1 2p_y^1 2p_z^1$. The internuclear axis is by convention the z-axis. For this molecule an σ bond will be formed by spin pairing between the two electrons in the two $2p_z$ orbitals. Two π bonds will also be formed, one formed by spin pairing in two neighbouring $2p_x$ orbitals and the other by spin pairing in two neighbouring $2p_y$ orbitals.

1.3   Resonance

Resonance is the superposition of the wavefunctions representing different electron distributions in the same nuclear framework. This principle can, for example, be used to give a VB description of a HCl molecule. This molecule can be expressed in different ways: the purely covalent, H-Cl, the ionic, H^+-Cl^-, and the very unlikely other ionic H^--Cl^+. Each of these descriptions has their own wavefunction:

$$\Psi_{\text{H-Cl}} = \psi_{\text{H1s}}(1)\psi_{\text{Cl3p}}(2) + \psi_{\text{H1s}}(2)\psi_{\text{Cl3p}}(1)$$
$$\Psi_{\text{H}^+\text{-Cl}^-} = \psi_{\text{Cl3p}}(1)\psi_{\text{Cl3p}}(2)$$

The H^--Cl^+ possibility will be neglected. These wavefunctions together give an (un-normalized) wavefunction, which is called a **resonance hybrid**:

$$\Psi_{HCl} = \Psi_{\text{H-Cl}} + \lambda\Psi_{\text{H}^+\text{-Cl}^-},$$

with λ numerical coefficient. In this case, where one structure is pure covalent and the other pure ionic, it is called **ionic–covalent resonance**.

A systematic way of calculating the value of λ is provided by the **variation principle**:

<blockquote>
If an arbitrary wavefunction is used to calculate the energy,

then the value calculated is always higher than the true energy.
</blockquote>

The arbitrary wavefunction is called the **trial wavefunction**.
This implies that if the energy is calculated for various trial wavefunctions, then the best value of λ is the one that results in the lowest energy. The ionic contribution to the resonance is then proportional to λ^2.

1.4   Polyatomic molecules

Each σ bond in a polyatomic molecule is formed by the spin pairing of electrons in atomic orbitals with cylindrical symmetry around the relevant internuclear axis. Likewise, π bonds are formed by pairing electrons that occupy atomic orbitals of the appropriate symmetry.
Resonance plays an important role in the VB description of polyatomic molecules. The wavefunction is improved by allowing resonance because it allows the electrons to adjust into a distribution of lower energy. This lowering is called the **resonance stabilization** of the molecule. Resonance always lowers the energy, and the lowering is greatest when the contributing structures have similar energies.

1.4.1   Promotion

A deficiency of this initial formulation of VB theory is its inability to account for the common tetravalence of carbon (or the valence of any other atoms). Its ground-state configuration, $2s^2 2p_x^1 2p_y^1$, suggests that a

carbon atom should be capable of forming only two bonds, not four.

This can be overcome by allowing **promotion**; this is the notional excitation of an electron to an empty orbital to enable the formation of additional bonds. In carbon the promotion of a 2s electron to a 2p orbital can give the $2s^1 2p_x^1 2p_y^1 2p_z^1$ configuration, which has four unpaired electrons in separate orbitals.

It is important to remember that promotion is not a 'real' process in which an atom somehow becomes excited and then forms bonds: it is a notional contribution to the overall energy change that occurs when bonds form.

1.4.2   Hybridization

The description of carbon is still not complete, even with the addition of promotion. When looking at CH_4 all four bonds should be the same, but we have three σ bonds with C2p orbitals and one σ bond with a C2s orbital. Thus the bonds are different symmetry wise.

This problem is overcome by using **hybridization**, this is the blending together of atomic orbitals on the same atom to achieve the appropriate directional properties and enhanced overlap.

A *hybrid orbital* has enhanced amplitude in the internuclear region, which arises from the constructive interference between the s orbital and the positive lobes of the p orbitals. This causes a greater bond strength. The hybridization of N atomic orbitals always results in the formation of N hybrid orbitals, which may either form bonds or may contain **lone pairs** of electrons, pairs of electrons that do not participate directly in bond formation.

sp^3 hybridization

In sp^3 hybridization one s orbital and three p orbitals are used to make each **sp^3 hybrid orbital**:

$$h_1 = s + p_x + p_y + p_z$$
$$h_2 = s - p_x - p_y + p_z$$
$$h_3 = s - p_x + p_y - p_z$$
$$h_4 = s + p_x - p_y - p_z$$

These are four equivalent hybrid orbitals to describe CH_4. The hybrid orbitals are orthogonal and each have contains a single unpaired electron; an H1s electron can pair with each one, giving rise to a σ bond pointing to a corner of a tetrahedron. This gives a tetrahedral molecule containing four equivalent C–H bonds.

sp^2 hybridization

In sp^2 hybridization each C atom is regarded as being promoted to a $2s^1 2p^3$ configuration. Instead of using all four orbitals to form hybrids, one s orbital and two p orbitals are used to make each **sp^2 hybrid orbital**:

$$h_1 = s + 2^{1/2} p_y$$
$$h_2 = s + \left(\frac{3}{2}\right)^{1/2} p_x - \left(\frac{1}{2}\right)^{1/2} p_y$$
$$h_3 = s - \left(\frac{3}{2}\right)^{1/2} p_x - \left(\frac{1}{2}\right)^{1/2} p_y$$

This hybridization is used to describe the structure of an ethene molecule, $H_2C{=}CH_2$, and the torsional rigidity of double bonds. An ethene molecule is planar, with HCH and HCC bond angles close to 120°. The $2p_z$ orbital is not included in the hybridization; it lies along an axis perpendicular to the plane formed by the hybrids.

sp hybridization

A similar description applies to sp hybridization, here only one s and one p orbital are used to make each **sp hybrid orbital**:

$$h_1 = s + p_z$$
$$h_2 = s - p_z$$

This hybridization is used to describe the structure of ethyne, HC≡CH, a linear molecule. These two hybrids lie along the internuclear axis (conventionally the z-axis in a linear molecule). The electrons in these hybrid orbitals can pair with either the other C atom or a H1s electron. The electrons in the two remaining p orbitals on each atom, which are perpendicular to the molecular axis, pair to form two perpendicular π bonds.

1.4.3   Which hybridization?

You can find the hybridization of an atom by finding its steric number. The **steric number** gives the number of regions of electron density. This is the number of atoms bonded to the atom + the number of lone pairs the atom has.

Steric number $\longrightarrow$ Hybridization:

- $2 \longrightarrow$ sp
- $3 \longrightarrow$ sp^2
- $4 \longrightarrow$ sp^3

2   Molecular Orbital Theory

In **molecular orbital theory** (MO theory), electrons do not belong to particular bonds but spread throughout the entire molecule.

2.1   The Hydrogen Molecule-Ion

First we look at the simplest molecular species of all, the hydrogen molecule-ion, H_2^+, to introduce the essential features of the theory. These can then be used to describe the structures of more complex systems.

2.1.1   Linear combinations of atomic orbitals

The Hamiltonian for the single electron in H_2^+ is:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 + V \quad V = -\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{A1}} + \frac{1}{r_{B1}} - \frac{1}{R}\right).$$

r_{A1} and r_{B1} are the distances of the electron from the two nuclei A and B and R is the distance between the two nuclei. The one-electron wavefunctions obtained by solving the Schrödinger equation $\hat{H}\psi = E\psi$ are called **molecular orbitals**. These are like atomic orbitals, but spread throughout the molecule.

The construction of linear combinations   The Schrödinger equation can be solved analytically for H_2^+, but it's easier to look at a more approximate procedure, since this will be easier to extended to other molecules.

If an electron can be found in an atomic orbital ψ_A belonging to atom A and also in an atomic orbital ψ_B belonging to atom B, then the overall wavefunction is a **linear combination of atomic orbitals** (LCAO), a superposition of the two atomic orbitals:

$$\psi_\pm = N_\pm\left(\psi_A \pm \psi_B\right).$$

For H_2^+, ψ_A and ψ_B are 1s atomic orbitals and $N_\pm$ is a normalization factor. An approximate molecular orbital formed from a linear combination of atomic orbitals is called an LCAO-MO.
A $\boldsymbol{\sigma}$ **orbital**, like the one being discussed, is a molecular orbital that has cylindrical symmetry and zero orbital angular momentum around the internuclear axis.

Bonding orbitals   According to the Born interpretation, the probability density of the electron at each point in H_2^+ is proportional to the square modulus of its wavefunction at that point. Then using ψ_+ from the LCAO we get:

$$\psi_+^2 \propto \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B$$

This shows that the total probability density is proportional to the sum of:

- ψ_A^2, the probability density if the electron were confined to atom A;

- ψ_B^2, the probability density if the electron were confined to atom B;

- $2\psi_A\psi_B$, an extra contribution to the density from both atomic orbitals, the **overlap density**.

The overlap density represents an enhancement of the probability of finding the electron in the internuclear region, which comes from the constructive interference of the two atomic orbitals. This observation is summarized as: *bonds form as a result of the build-up of electron density where atomic orbitals overlap and interfere constructively.*

Shifting an electron away from a nucleus into the internuclear region raises its potential energy. At the same time as the electron shifts into the internuclear region, the atomic orbitals shrink. This orbital shrinkage improves the electron–nucleus attraction more than it is decreased by the migration to the internuclear region, so there is a net lowering of potential energy. The kinetic energy of the electron is also modified because the curvature of the wavefunction is changed, but this change is dominated by the change in potential energy.

The σ orbital just described is an example of a bonding orbital, an orbital which, if occupied, helps to bind two atoms together. An electron that occupies a σ orbital is called a **σ electron**, and if that is the only electron present in the molecule, then the configuration of the molecule is σ^1.

The energy E_σ of the σ orbital is:

$$E_\sigma = E_{\mathrm{H1s}} + \frac{j_0}{R} - \frac{j+k}{1+S}$$

where E_{H1s} is the energy of a H1s orbital, j_0/R is the potential energy of repulsion between the two nuclei, j_0 is shorthand for $e^2/4\pi\varepsilon_0$, and

$$S = \int \psi_A\psi_B \; \mathrm{d}\tau = \left\{ 1 + \frac{R}{a_0} + \frac{1}{3}\left(\frac{R}{a_0}\right)^2 \right\} \mathrm{e}^{-R/a_0}$$

$$j = j_0 \int \frac{\psi_A^2}{r_B} \; \mathrm{d}\tau = \frac{j_0}{R}\left\{ 1 - \left(1 + \frac{R}{a_0}\right)\mathrm{e}^{-2R/a_0} \right\}$$

$$k = j_0 \int \frac{\psi_A\psi_B}{r_B} \; \mathrm{d}\tau = \frac{j_0}{a_0}\left(1 + \frac{R}{a_0}\right)\mathrm{e}^{-R/a_0}$$

Note that

$$\frac{j_0}{a_0} = \frac{e^2}{4\pi\varepsilon_0 a_0} = \frac{e^2}{4\pi\varepsilon_0} \times \frac{\pi m_e e^2}{\varepsilon_0 h^2} = \frac{m_e e^4}{4\varepsilon_0^2 h^2} = 2hc\tilde{R}_\infty = 27.21 \text{ eV}$$

All three integrals are positive and decline towards zero at large internuclear separations. The integral j is a measure of the interaction between a nucleus and electron density centred on the other nucleus. The integral k is a measure of the interaction between a nucleus and the excess electron density in the internuclear region arising from overlap.

Antibonding orbitals   The linear combination ψ_- has higher energy than ψ_+, and for now it is labelled σ^* because it is also a σ orbital. At the mid-point of this bond ψ_A and ψ_B cancel exactly. The probability density is

$$\psi_-^2 \propto \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B$$

Due to the term $-2\psi_A\psi_B$ there is a reduction in probability density between the nuclei, this is because of destructive interference where the two atomic orbitals overlap.

The σ^* orbital is an example of an **antibonding orbital**, an orbital that, if occupied, contributes to a reduction in the cohesion between two atoms and helps to raise the energy of the molecule relative to the

separated atoms.

The energy E_{σ^*} of the σ^* antibonding orbital is

$$E_{\sigma^*} = E_{\text{H1s}} + \frac{j_0}{R} - \frac{j-k}{1-S}.$$

With the same integrals S, j and k as before.

In effect, whereas a bonding electron pulls two nuclei together, an antibonding electron pulls the nuclei apart. Another important conclusion is:

$$|E_{\sigma^*} - E_{\text{H1s}}| > |E_\sigma - E_{\text{H1s}}|,$$

which indicates that *the antibonding orbital is more antibonding than the bonding orbital is bonding.* This stems in part from the presence of the nucleus–nucleus repulsion (j_0/R): this contribution raises the energy of both molecular orbitals.

2.1.2   Orbital notation

For homonuclear diatomic molecules (molecules consisting of two atoms of the same element), it proves helpful to label a molecular orbital according to its **inversion symmetry**, the behaviour of the wavefunction when it is inverted through the centre of the molecule. The parity of an orbital is even (gerade) if its wavefunction is unchanged under inversion through the centre of symmetry of the molecule, but odd (ungerade) if the wavefunction changes sign. Heteronuclear diatomic molecules do not have a centre of inversion, so for them the g, u classification is irrelevant.

Gerade symmetry is denoted by a subscript g, as in σ_{g}. **Ungerade symmetry** is denoted by a subscript u, as in σ_{u}.

2.2   Homonuclear Diatomic Molecules

2.2.1   Electron configurations

Molecular orbital theory (MO theory) of bonding in diatomic molecules (and ions) starts with the construction of molecular orbitals as linear combinations of the available atomic orbitals. Following from that a building-up principle can be used to establish their ground-state electron configurations:

- The aim is to get the lowest overall energy, while respecting the Pauli exclusion principle that no more than two electrons may occupy a single orbital.

- If several degenerate orbitals exist, then single occupancy is preferred, since this minimizes electron–electron repulsion.

- According to Hund, if two electrons do occupy different degenerate orbitals, then a lower energy is obtained if their spins are parallel.

σ Orbitals and π orbitals   In general, from N atomic orbitals N molecular orbitals can be built. The molecular orbitals can be drawn in a **molecular orbital energy level diagram**, which shows the energies of the atomic orbitals and the energies of the molecular orbitals.

In H_2, for example, each H atom contributes a 1s orbital, which form $1\sigma_{\text{g}}$ bonding and $1\sigma_{\text{u}}^*$ antibonding orbitals. With two electrons to accommodate, the ground-state will be $1\sigma_{\text{g}}^2$ with both electrons in the $1\sigma_{\text{g}}$ orbital by pairing their spins.

This argument also shows why helium does not form diatomic molecules. Each H atom contributes a 1s orbital, so $1\sigma_{\text{g}}$ and $1\sigma_{\text{u}}^*$ molecular orbitals can be formed. With four electrons to accommodate, the ground-state will be $1\sigma_{\text{g}}^2 1\sigma_{\text{u}}^{*2}$. Since $|E_{\sigma^*} - E_{\text{H1s}}| > |E_\sigma - E_{\text{H1s}}|$, this is unstable and it will not form.

Only the orbitals of the valence shell are used to form molecular orbitals so, for molecules formed with atoms from Period 2 elements, only the 2s and 2p atomic orbitals are considered.

A general principle of MO theory is that *all orbitals of the appropriate symmetry contribute to a molecular orbital.* For σ bonds of Period 2 elements these are the 2s and $2p_z$ orbitals.

This gives the LCOA-MO:

$$\psi = c_{\text{A2s}}\psi_{\text{A2s}} + c_{\text{B2s}}\psi_{\text{B2s}} + c_{\text{A2p}_z}\psi_{\text{A2p}_z} + c_{\text{B2p}_z}\psi_{\text{B2p}_z}$$

Because the 2s and 2p orbitals on each atom have such different energies, they may be treated separately

$$\psi_1 = c_{A2s}\psi_{A2s} + c_{B2s}\psi_{B2s} \rightarrow 1\sigma_g, 1\sigma_u^*$$

$$\psi_2 = c_{A2p_z}\psi_{A2p_z} + c_{B2p_z}\psi_{B2p_z} \rightarrow 2\sigma_g, 2\sigma_u^*$$

The energies of each orbital on both atoms is the same; $|c_A| = |c_B|$, the possible difference in sign creates the bonding and the antibonding orbitals.

Now consider the $2p_x$ and $2p_y$ orbitals of each atom. These orbitals are perpendicular to the internuclear axis and overlap broadside-on when the atoms are close together. This overlap may be constructive or destructive and results in a bonding or an antibonding π orbital. A π orbital looks like a p orbital and has one unit of orbital angular momentum around the internuclear axis.

$$\left.\begin{array}{l} 2p_x \rightarrow \pi_x \\ 2p_y \rightarrow \pi_y \end{array}\right\} \text{ degenerate}$$

A bonding π orbital has odd parity (u) and the antibonding π^* orbital has even parity (g).

The overlap integral

Period 2 diatomic molecules   To construct the molecular orbital energy level diagram for Period 2 homonuclear diatomic molecules, eight molecular orbitals are formed from the eight valence shell orbitals. Now what is the order of the MOs? The relative order is controlled by the energy separation of the 2s and 2p orbitals in the atoms, which increases across the period. The change in the order of the $2\sigma_g$ and $1\pi_u$ orbitals occurs at about N_2.

For O_2 and F_2 For Li_2, Be_2, ..., N_2
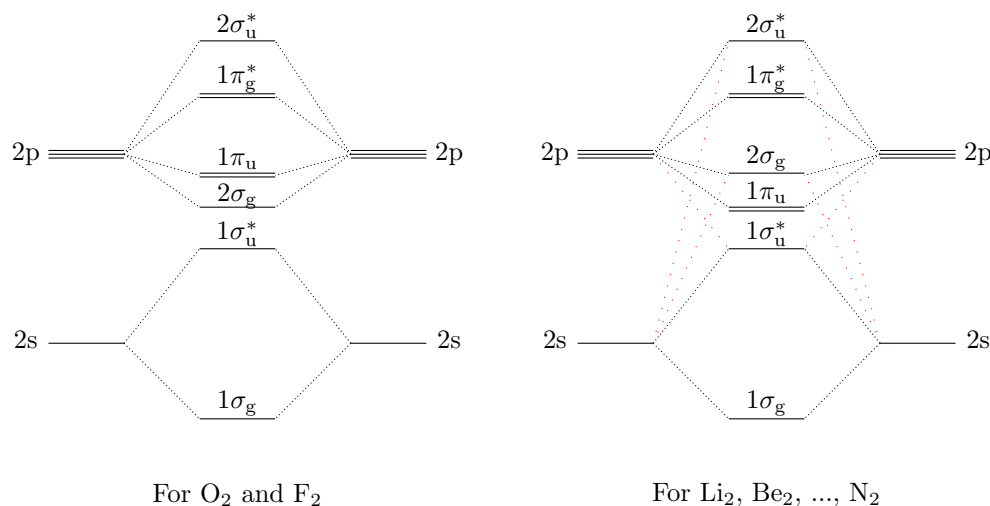
As can be seen in the figure, for Li_2, Be_2, ..., N_2 the 2s and 2p orbitals contribute to all four σ orbitals, since 2s and $2p_z$ lie closer to each other. These diagrams can now be used to determine the probable ground-state configurations of the molecules by adding the appropriate number of electrons to the orbitals and following the building-up rules. Anionic species (such as the peroxide ion, O_2^{2-}) need more electrons than the parent neutral molecules; cationic species (such as O_2^+) need fewer.

A measure of the net bonding in a diatomic molecule is its **bond order**, b:

$$b = \frac{1}{2}(N - N^*)$$

where N is the number of electrons in bonding orbitals and N^* is the number of electrons in antibonding orbitals.

The bond order is a useful parameter for discussing the characteristics of bonds, because it correlates with bond length and bond strength. For bonds between atoms of a given pair of elements:

- The greater the bond order, the shorter the bond.

- The greater the bond order, the greater the bond strength.

2.2.2   Photoelectron spectroscopy

Photoelectron spectroscopy (PES) measures the ionization energies of molecules when electrons are ejected from different orbitals, by absorption of a photon of known energy. This process is given by:

$$h\nu = \frac{1}{2}m_e v^2 + I_i$$

Here $h\nu$ is the energy of the photon, which, because of conservation of energy, is equal to the sum of the kinetic energy of the **photoelectron** and I_i, the ionization energy for ejection of an electron from an orbital i.

The **Koopmans' Theorem** states that the ionization energy I_i is equal to the orbital energy of the ejected electron. This approximation helps to interpret the photoelectron spectra.

Depending on the amount of energy needed, there are different subcategories of PES, much work has been done with radiation generated by a discharge through helium, which rise to the technique of **ultraviolet photoelectron spectroscopy** (UPS). When core electrons are being studied, photons of even higher energy are needed to expel them, which leads to **X-ray photoelectron spectroscopy** (XPS).

2.3   Heteronuclear Diatomic Molecules

The electrons in a covalent bond in a heteronuclear diatomic species are not distributed equally over the atoms. This imbalance results in a **polar bond**, a bond in which the bonding electron density is shared unequally between the bonded atoms. The accumulation of bonding electron density near the one atom results in that atom having a net negative charge, which is called a **partial negative charge** and denoted δ^-. There is a matching **partial positive charge**, δ^+, on the other atom.

2.3.1   Polar bonds and electronegativity

A polar bond consists of two electrons in a bonding molecular orbital of the form:

$$\psi = c_A \psi_A + c_B \psi_B,$$

with unequal coefficients. A nonpolar bond has $|c_A| = |c_B|$, and a pure ionic bond has one coefficient equal to zero (so the species A^+B^- would have $c_A = 0$ and $c_B = 1$). The atomic orbital with the lower energy makes the larger contribution to the bonding molecular orbital. The opposite is true of the antibonding orbital, for which the dominant component comes from the atomic orbital with higher energy.

The distribution of partial charges in bonds is commonly discussed in terms of the **electronegativity**, χ (chi), of the elements involved. The bonding MO is mainly composed of the atomic orbital of the more electronegative atom. For antibonding this is the other way around. To be able to define the **Mulliken electronegativity scale** we first have to define some other things.

As we know from before, the ionisation energy, I, is the minimum amount of energy required to remove an electron from a molecule. The electron affinity, E_{ea}, is the energy that is released when an electron attaches. The two extremes that an (neutral) atom X can be in are X^+ and X^-, these extremes are linked by the ionisation energy and electron affinity:
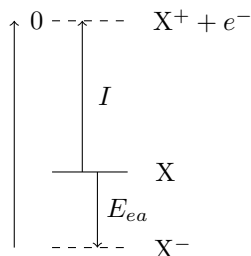
This relation gives an approximate energy of $-\frac{1}{2}(I + E_{ea})$. Following from this we get the Mulliken electronegativity scale. Mulliken argued that an element is likely to be highly electronegative if it has a high ionization energy (so it will not release electrons readily) and a high electron affinity (so it is energetically favourable to acquire electrons).

$$\chi_M = \frac{1}{2}(I + E_{ea})/\text{eV}$$

The greater the value of the Mulliken electronegativity the greater is the contribution of that atom to the electron distribution in the bond.

Pauling has a different approach to the electronegativity, he proposed that the difference in electronegativities could be expressed as:

$$|\chi_A - \chi_B| = \left\{ hc\tilde{D}_0(\text{AB}) - \frac{1}{2}\left[hc\tilde{D}_0(\text{AA}) + hc\tilde{D}_0(\text{BB})\right] \right\}^{1/2} /\text{eV}$$

This expression gives differences of electronegativities; to establish an absolute scale Pauling chose individual values that gave the best match to the values obtained from the equation. Electronegativities based on this definition are called **Pauling electronegativities**.

The Mulliken and Pauling scales are approximately in line with each other. A reasonably reliable conversion between the two is

$$\chi_{\text{Pauling}} = 1.35\,\chi_{\text{Mulliken}}^{1/2} - 1.37$$

2.3.2   The variation principle

The big question now is how do we find the coefficients c_A and c_B? The systematic way of discussing bond polarity and finding the coefficients in the linear combinations used to build molecular orbitals is provided by the variation principle: *if an arbitrary wavefunction is used to calculate the energy, then $E_{trial} \geq E_{real}$.* The principle implies that, if the coefficients in the trial wavefunction are varied until the lowest energy is achieved, then those coefficients will be the best for that particular form of trial function.

The procedure   Now how do we we apply this principle to our trial wavefunction $\psi = c_A\psi_A + c_B\psi_B$?

Step 1 *Write an expression for the energy*
To normalize our trial function we can multiply it by $N = 1/\langle\psi|\psi\rangle$, so from now on we will write our trial wavefunction as $\psi/\langle\psi|\psi\rangle$.
The expectation value of the Hamiltonian, the energy, using the normalized real trial function, is

$$E = \frac{\left\langle \psi|\hat{H}|\psi \right\rangle}{\langle\psi|\psi\rangle}$$
$$= \frac{c_A^2\alpha_A + c_B^2\alpha_B + 2c_Ac_B\beta}{c_A^2 + c_B^2 + 2c_Ac_BS}$$

with

$$\alpha_A = \left\langle \psi_A|\hat{H}|\psi_A \right\rangle \qquad \alpha_B = \left\langle \psi_B|\hat{H}|\psi_B \right\rangle \qquad \beta = \left\langle \psi_A|\hat{H}|\psi_B \right\rangle \qquad S = \langle\psi_A|\psi_B\rangle$$

S is the overlap integral we've seen before.

Step 2 *Minimize the energy*
Now we want to find the values of the coefficients that minimize the value of E. This is a standard problem in calculus, and is solved by finding the coefficients for which

$$\frac{\partial E}{\partial c_A} = 0 \quad \frac{\partial E}{\partial c_B} = 0.$$

This gives the **secular equations**:

$$(\alpha_A - E)\, c_A + (\beta - SE)c_B = 0$$
$$(\alpha_B - E)\, c_B + (\beta - SE)c_A = 0$$

$\alpha_{A,B}$ are the **Coulomb integrals**. They're negative and can be interpreted as the energy of the electron when it occupies ψ_A (for α_A) or ψ_B (for α_B). In a homonuclear diatomic molecule, $\alpha_A = \alpha_B$.

β is a **resonance integral**. It vanishes when the orbitals do not overlap, and at equilibrium bond lengths it is normally negative.

The secular equations have a solution if the secular determinant, the determinant of the coefficients, is zero. That is, if

$$\begin{vmatrix} \alpha_A - E & \beta - SE \\ \beta - SE & \alpha_B - E \end{vmatrix} = (\alpha_A - E)(\alpha_B - E) - (\beta - SE)^2$$
$$= \left(1 - S^2\right) E^2 + \{2\beta S - (\alpha_A + \alpha_B)\}\, E$$
$$+ \left(\alpha_A \alpha_B - \beta^2\right) = 0$$

The full solutions of the energies are

$$E_\pm = \frac{\alpha_A + \alpha_B - 2\beta S \pm \left\{(2\beta S - (\alpha_A + \alpha_B))^2 - 4\left(1 - S^2\right)\left(\alpha_A \alpha_B - \beta^2\right)\right\}^{1/2}}{2\left(1 - S^2\right)}.$$

Two cases   **Case 1** *The homonuclear case*
For a homonuclear diatomic, $\alpha_A = \alpha_B = \alpha$ and then

$$E_+ = \frac{\alpha + \beta}{1 + S} \quad E_- = \frac{\alpha - \beta}{1 - S}$$

Case 2 *The zero overlap approximation*
For heteronuclear diatomic molecules, making the approximation that $S = 0$ gives

$$E_\pm = \frac{1}{2}\left(\alpha_A + \alpha_B\right) \pm \frac{1}{2}\left(\alpha_A - \alpha_B\right)\left\{1 + \left(\frac{2\beta}{\alpha_A - \alpha_B}\right)^2\right\}^{1/2}$$

In this approximation the coefficients are given by

$$c_A = \frac{1}{\left\{1 + \left(\frac{\alpha_A - E}{\beta}\right)^2\right\}^{1/2}} \qquad\qquad c_B = \frac{1}{\left\{1 + \left(\frac{\beta}{\alpha_A - E}\right)^2\right\}^{1/2}}$$

The features of the solutions   As the energy difference $|\alpha_B - \alpha_A|$ between the interacting atomic orbitals increases, the bonding and antibonding effects decrease. When $|\alpha_B - \alpha_A| \gg 2|\beta|$ it is possible to use the approximation $(1 + x)^{1/2} \approx 1 + \frac{1}{2}x$ to obtain

$$E_+ \approx \alpha_A + \frac{\beta^2}{\alpha_A - \alpha_B} \qquad\qquad E_- \approx \alpha_B - \frac{\beta^2}{\alpha_A - \alpha_B}$$

The strongest bonding and antibonding effects are obtained when the two contributing orbitals have similar energies.

2.4   Polyatomic Molecules

The molecular orbitals of polyatomic molecules are built in the same way as in diatomic molecules, the only difference being that more atomic orbitals are used to construct them. As for diatomic molecules, polyatomic molecular orbitals spread over the entire molecule. A LCAO-MO has the general form

$$\psi = \sum_i c_i \psi_i$$

where ψ_i is an atomic orbital and the sum extends over all the valence orbitals of all the atoms in the molecule. The coefficients are found by setting up the secular equations, just as for diatomic molecules, then solving them for the lowest possible energies.

2.4.1 Computational chemistry

Density functional theory The functional theory (DFT) focusses on the electron density, $\rho(r)$, rather than the wavefunction, ψ.
The energy of a molecule is a function (functional) of the electron density, written $E(\rho(r))$. The occupied orbitals are used to construct the electron density from

$$\rho(r) = \sum_{m,\text{ occupied}} |\psi_m(r)|^2.$$

First, the electron density is guessed, commonly using a superposition of atomic electron densities. Next, modified versions of the Schrödinger equation, known as the **Kohn–Sham equations**, are solved to obtain an initial set of orbitals, which will give a better approximation to the electron density. This process is then repeated.

3 Molecular spectroscopy

3.1 Recap and connection to SoM 1

Compared to atomic spectra, molecular spectra are more complicated:

Atomic spectra	$\longrightarrow$	Molecular spectra
· Electronic transitions		· Electronic transitions
		+ Rotational changes of state
		+ Vibrational changes of state

3.1.1 Degrees of freedom

Suppose you have N atoms in your molecule, then you have $3N$ degrees of freedom, because each atom can move in 3 directions. This includes any translation, vibration or rotation.

Linear molecules. These molecules have 3 possible translations and 2 possible rotations. Therefore they have $3N - 5$ possible vibrations.

Non-linear molecules. These molecules have 3 possible translations and 3 possible rotations. Therefore they have $3N - 6$ possible vibrations.

3.2 General features of molecular spectroscopy

3.2.1 The absorption and emission of radiation

The separation of rotational energy levels is smaller than that of vibrational energy levels, which itself is smaller than that of electronic energy levels:

UV, Visible, IR	Infrared	Microwave
· Electronic changes of state	· Vibrational changes of state	· Rotational changes of state
$\rightarrow$ eV	$\rightarrow 10^5$ of meV	$\rightarrow$ meV

Stimulated and spontaneous radiative processes. There are three processes by which radiation could be either generated or absorbed by matter as a result of transitions between states.
Stimulated absorption is a transition from a lower energy state l to a higher energy state u. The rate of

such transitions is proportional to the intensity of the incident radiation at the transition frequency and to the number of molecules in the lower state, N_l. The rate of stimulated absorption, $W_{u \leftarrow l}$, can therefore be written

$$W_{u \leftarrow l} = B_{u,l} N_l \rho(\nu).$$

With $\rho(\nu)$ the energy spectral density and $B_{u,l}$ the **Einstein coefficient of stimulated absorption**. Stimulated emission is a transition from a higher energy state u to a lower energy state l, that is induced by radiation. This is proportional to number of molecules in the upper level N_u and the intensity of the radiation at the transition frequency. This gives:

$$W'_{u \rightarrow l} = B_{l,u} N_u \rho(\nu).$$

With $B_{l,u}$ the **Einstein coefficient of stimulated emission**.
Spontaneous emission is a transition from a higher energy state u to a lower energy state l, that is *not* driven by radiation. The rate of this is given by:

$$W''_{u \rightarrow l} = A_{l,u} N_u.$$

With $A_{l,u}$ the **Einstein coefficient of spontaneous emission**.
The total rate of emission is

$$W_{u \rightarrow l} = B_{l,u} N_u \rho(\nu) + A_{l,u} N_u.$$

At equilibrium we have

$$B_{u,l} N_l^{\text{eq}} \rho(\nu) = B_{l,u} N_u^{\text{eq}} \rho(\nu) + A_{l,u} N_u^{\text{eq}}.$$

This gives:

$$\rho(v) = \frac{A_{1,u}/B_{u,1}}{N_1^{\text{eq}}/N_u^{\text{eq}} - B_{1,u}/B_{u,1}} = \frac{A_{1,u}/B_{u,1}}{e^{h\nu/kT} - B_{1,u}/B_{u,1}}.$$

At equilibrium the radiation density is given by the black body radiation:

$$\rho(v) = \frac{8\pi h\nu^3/c^3}{e^{h\nu/kT} - 1}.$$

Thus:

$$A_{l,u} = \left(\frac{8\pi h\nu^3}{c^3} \right) B_{l,u} \text{ and } B_{l,u} = B_{u,l}$$

These are properties of the molecules themselves and are independent of the spectral distribution of the radiation and can thus be used for any energy densities.
What also becomes clear is that at high frequencies spontaneous emission dominates.
The ratio of the rate of spontaneous to stimulated emission is given by

$$\frac{W''_{u \rightarrow l}}{W'_{u \rightarrow l}} = \frac{A_{l,u}}{B_{l,u} \rho(\nu)} = \frac{8\pi h\nu^3}{c^3 \rho(\nu)}$$

Selection rules and transition moments.   A 'selection rule' is a statement about whether a transition is forbidden or allowed. Emission or absorption of a photon requires that the molecule must posses (at least transiently) an electric dipole oscillating at the frequency of the photon. The **transition dipole moment**, $\boldsymbol{\mu}_{\text{fi}}$, is given by:

$$\boldsymbol{\mu}_{\text{fi}} = \int \psi_{\text{f}}^* \hat{\boldsymbol{\mu}} \psi_{\text{i}} d\tau,$$

where $\hat{\boldsymbol{\mu}}$ is the electric dipole moment operator, which is given by $\sum_i q_i \mathbf{r}_i$. For one electron this is $-q\mathbf{r}$. The size of $\boldsymbol{\mu}_{\text{fi}}$ is a measure of the charge distribution associated with the transition. If $|\boldsymbol{\mu}_{\text{fi}}| = 0$, then the transition is not allowed.

3.2.2   Spectral linewidths

Doppler broadening.

Lifetime broadening.

3.3   Rotational spectroscopy

Pure rotational spectra, in which only the rotational state of a molecule changes, can be observed only in the gas phase.

3.3.1   Rotational energy levels

The **moment of inertia**, I, of a molecule about an axis passing through the centre of mass is defined as

$$I = \sum_i m_i x_i^2.$$

- i represents the atoms in the molecule,
- m_i is the mass of these atoms,
- x_i is the perpendicular distance from the axis of rotation.

the rotational properties of any molecule can be expressed in terms of its three principal moments of inertia I_q about three mutually perpendicular axes, $q = x, y, z$. These are also commonly recorded as I_a, I_b, and I_c, with $I_c \geq I_b \geq I_a$.

The energy of a body free to rotate about three axes is

$$E = \frac{1}{2} I_x \omega_x^2 + \frac{1}{2} I_y \omega_y^2 + \frac{1}{2} I_z \omega_z^2$$

Because the classical angular momentum about the axis q is $J_q = I_q \omega_q$, it follows that

$$E = \frac{J_x^2}{2I_x} + \frac{J_y^2}{2I_y} + \frac{J_z^2}{2I_z}$$

The energy levels can be found by first writing the energies in terms of $\mathcal{J}$ and then making the quantum substitution:

$$\mathcal{J}^2 \to J(J+1)\hbar^2$$

with $\mathcal{J}^2 = J_x^2 + J_y^2 + J_z^2$. J is the angular momentum quantum number, which has the values $J = 0, 1, 2, \ldots$.

Spherical rotors.   Spherical rotors (such as CH_4 and SF_6) have all three moments of inertia equal and equal to I:

$$E = \frac{J_x^2 + J_y^2 + J_z^2}{2I} = \frac{\mathcal{J}^2}{2I}$$

The corresponding energy levels are then given by:

$$E_J = J(J+1)\frac{\hbar^2}{2I} \quad J = 0, 1, 2, \ldots$$

The energy is normally expressed in terms of the **rotational constant**, $\tilde{B}$ (a wavenumber), of the molecule, where

$$hc\tilde{B} = \frac{\hbar^2}{2I} \quad \text{so} \quad \tilde{B} = \frac{\hbar}{4\pi cI}$$

This gives:

$$E_J = hc\tilde{B}J(J+1) \quad J = 0, 1, 2, \ldots$$

You can also express the rotational constant as a frequency, B, where $B = c\tilde{B}$.

The energy of a rotational state is normally reported as the rotational term, $\tilde{F}(J)$, a wavenumber, by division by hc:

$$\tilde{F}(J) = \tilde{B}J(J+1)$$

To express the rotational term as a frequency, use $F = c\tilde{F}$. The separation of adjacent terms is

$$\tilde{F}(J+1) - \tilde{F}(J) = 2\tilde{B}(J+1)$$

The energy separation between neighbouring levels increases as J increases. Because the rotational constant is inversely proportional to I, large molecules have closely spaced rotational energy levels.

Symmetric rotors.   Symmetric rotors (such as CH_3Cl, NH_3, and C_6H_6) have two equal moments of inertia ($I_{x,y} \to I_\perp$) and a third ($I_z \to I_\parallel$) that is non-zero. The unique axis of a symmetric rotor is its **principal axis**, or *figure axis*.
If the moment of inertia about the principal axis is larger than the other two, the rotor is classified as **oblate** (like a pancake). If the moment of inertia around the principal axis is smaller than the other two, the rotor is classified as **prolate** (like a cigar).
The rotational energy is given by:

$$E = \frac{J_x^2 + J_y^2}{2I_\perp} + \frac{J_z^2}{2I_\parallel}$$
$$= \frac{\mathcal{J}^2 - J_z^2}{2I_\perp} + \frac{J_z^2}{2I_\parallel} = \frac{\mathcal{J}^2}{2I_\perp} + \left(\frac{1}{2I_\parallel} - \frac{1}{2I_\perp}\right) J_z^2$$

This time we can't express the rotational terms with just $\tilde{B}$, due to the factors J_z^2. From QM we know that a component of angular momentum about any axis is restricted to the values $K\hbar$, with $K = 0, \pm 1, \ldots, \pm J$. Using this, we get:

$$\tilde{F}(J, K) = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2$$
$$J = 0, 1, 2, \ldots \quad K = 0, \pm 1, \ldots, \pm J$$

with

$$\tilde{A} = \frac{\hbar}{4\pi c I_\parallel} \quad \tilde{B} = \frac{\hbar}{4\pi c I_\perp}$$

The sign of K does not affect the energy, because opposite values of K correspond to opposite senses of rotation and the energy does not depend on that.
Because the states with K and $-K$ have the same energy, each level, except those with $K = 0$, is doubly degenerate.
The angular momentum of the molecule has a component on an external, laboratory-fixed axis. This component is quantized, and its permitted values are $M_J\hbar$, with $M_J = 0, \pm 1, \ldots, \pm J$. Th energy does not depend on this component. For every J there are $2J + 1$ permitted values of M_J.
Now what is the degeneracy?

$$K = 0 \to 2J + 1$$
$$K \neq 0 \to 2(2J + 1)$$

A spherical rotor can be regarded as a version of a symmetric rotor with $I_\perp = I_\parallel$ and thus $\tilde{A} = \tilde{B}$. Here there is a $(2J + 1)$-fold degeneracy arising from M_J and a $(2J + 1)$-fold degeneracy arising from K. This gives a $(2J + 1)^2$-fold degeneracy.

Linear rotors.   For linear rotors (such as CO_2, HCl, and C_2H_2), the rotation occurs only about an axis perpendicular to the internuclear axis and there is no rotation around that axis. Thus the moment of inertia around the internuclear axis is zero and the two remaining moments of inertia, which are equal, are denoted simply I.
From this follows that $K \equiv 0$ and rotational terms of a linear molecule are

$$\tilde{F}(J) = \tilde{B}J(J+1) \quad J = 0, 1, 2, \ldots$$

The angular momentum of a linear rotor has $2J + 1$ components on an external axis, so its degeneracy is just $2J + 1$.

Centrifugal distortion.   The molecules have been treated as rigid rotors so far, but a molecule does change its shape due to rotation.

The effect of centrifugal distortion on a diatomic molecule is to stretch the bond and hence to increase the moment of inertia. This effect is usually taken into account by including in the energy expression a negative term that becomes more important as J increases:

$$\tilde{F}(J) = \tilde{B}J(J+1) - \tilde{D}_J J^2 (J+1)^2$$

With the **centrifugal distortion constant**:

$$\tilde{D}_J = \frac{4\tilde{B}^3}{\tilde{v}^2}$$

3.3.2   Microwave spectroscopy

Typical values of the rotational constant $\tilde{B}$ for small molecules are in the region of 0.1-10 cm^{-1}. We'll be considering pure rotational changes of state. These rotational transitions can be studied with **microwave spectroscopy**, a technique that monitors the absorption of radiation in the microwave region of the spectrum.

Selection rules   The gross selection rule for the observation of a pure rotational transition is that a molecule *must* have a permanent electric dipole moment. Thus the molecule must be *polar*, because when such a molecule possess a fluctuating dipole when rotating.

Spherical rotors cannot have electric dipole moments unless they become distorted by rotation, so they are rotationally inactive except in special cases.

Molecules like H_2O are very active.

For a linear molecule, the transition moment vanishes unless the following conditions are fulfilled:

$$\Delta J = \pm 1 \quad \Delta M_J = 0, \pm 1$$

The transition $\Delta J = +1$ corresponds to absorption and the transition $\Delta J = -1$ corresponds to emission.

The total $J + 1 \leftrightarrow J$ transition intensity is proportional to

$$|\mu_{J+1,J}|^2 = \left(\frac{J+1}{2J+1} \right) \mu_0^2$$

where μ_0 is the permanent electric dipole moment of the molecule.

For symmetric rotors the selection rules are:

$$\Delta J = \pm 1 \quad \Delta M_J = 0, \pm 1 \quad \Delta K = 0$$

The appearance of microwave spectra.   The wavenumbers of the allowed $J + 1 \leftarrow J$ absorptions are

$$\tilde{v}(J+1 \leftarrow J) = \tilde{F}(J+1) - \tilde{F}(J) = 2\tilde{B}(J+1) \quad J = 0, 1, 2, \ldots$$

With centrifugal distortion taken into account this becomes

$$\tilde{v}(J+1 \leftarrow J) = 2\tilde{B}(J+1) - 4\tilde{D}_J(J+1)^3$$

The intensities of spectral lines increase with increasing J and pass through a maximum before tailing off as J becomes large. The Boltzmann distribution implies that the population of a state decreases exponentially as its energy increases. However, the population of a *level* is also proportional to its degeneracy, and in the case of rotational levels this degeneracy increases with J.

There exists a maximum largest population of level

$$J_{\max} \approx \left(\frac{kT}{2hc\tilde{B}} \right)^{1/2} - \frac{1}{2} \neq 0$$

3.4   Vibrational spectroscopy of diatomic molecules

3.4.1   Vibrational motion

A molecular potential energy curve can be approximated by a parabola near the bottom of the well. Therefore, the first approximation to a molecular potential energy curve is a parabolic potential of the form

$$V(x) = \frac{1}{2}k_{\mathrm{f}}x^2 \quad x = R - R_{\mathrm{e}}$$

With this we can just treat the molecule like a harmonic oscillator. k_{f} is the **force constant** of the bond, a measure of its stiffness:

$$k_{\mathrm{f}} = \left(\frac{\mathrm{d}^2 V}{\mathrm{d}x^2}\right)_0$$

The Schrödinger equation for the relative motion of two atoms of masses m_1 and m_2 with a parabolic potential energy is

$$-\frac{\hbar^2}{2m_{\mathrm{eff}}}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{1}{2}k_{\mathrm{f}}x^2\psi = E\psi$$

where m_{eff} is the **effective mass**:

$$m_{\mathrm{eff}} = \frac{m_1 m_2}{m_1 + m_2}$$

The solutions of this give the vibrational energy levels:

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega \quad \omega = \left(\frac{k_{\mathrm{f}}}{m_{\mathrm{eff}}}\right)^{1/2} \quad v = 0, 1, 2, \ldots$$

The **vibrational terms**, $\tilde{G}(v)$, of a molecule express the energies as wavenumbers, with $E_v = hc\tilde{G}(v)$. Here

$$\tilde{G}(v) = \left(v + \frac{1}{2}\right)\tilde{\nu} \quad \tilde{\nu} = \frac{1}{2\pi c}\left(\frac{k_{\mathrm{f}}}{m_{\mathrm{eff}}}\right)^{1/2}$$

3.4.2   Infrared spectroscopy

The gross selection rule for a change in vibrational state brought about by absorption or emission of radiation is that the electric dipole moment of the molecule must change when the atoms are displaced relative to one another. Therefore a permanent dipole is *not* needed.
Vibrations that change the dipole moment are said to be **infrared active**.
Vibrations that do not affect the dipole moment are said to be **infrared inactive**.
Homonuclear diatomic molecules will be inactive, but heteronuclear diatomic molecules will be active.
The specific selection rule is:

$$\Delta v = \pm 1$$

Transitions for which $\Delta v = +1$ correspond to absorption and those with $\Delta v = -1$ correspond to emission. The wavenumbers of allowed vibrational transitions, which are denoted $\Delta\tilde{G}_{v+\frac{1}{2}}$ for the transition $v+1 \leftarrow v$, are

$$\Delta\tilde{G}_{v+\frac{1}{2}} = \tilde{G}(v+1) - \tilde{G}(v) = \tilde{\nu}$$

Within the harmonic oscillator approximation all emission/ absorption lines have the same energy/ frequency/ wavenumber.
At room temperature $kT/hc \approx 200$ cm^{-1}, but mostly $\tilde{\nu} \gg 200$ cm^{-1}. Therefore most molecules are in their vibrational ground states. So in a spectrum you mostly see the **fundamental transition** $1 \leftarrow 0$, but remember all other transitions have the same energy.

3.4.3   Anharmonicity

At high vibrational excitations the separation of the atoms allows the molecule to explore regions of the potential energy curve where the parabolic approximation is poor. The motion then becomes **anharmonic**, in the sense that the restoring force is no longer proportional to the displacement.

The convergence of energy levels.   The **Morse potential energy** is

$$V(x) = hc\tilde{D}_e \left\{1 - e^{-ax}\right\}^2 \quad a = \left(\frac{m_{\text{eff}}\omega^2}{2hc\tilde{D}_e}\right)^{1/2}$$

At $x = 0$, $V(0) = 0$; at large displacements $V(x)$ approaches $hc\tilde{D}_e$. The resulting Schrödinger Equation can be solved analytically. And now dissocation is included! The vibrational terms are now:

$$\tilde{G}(v) = \left(v + \frac{1}{2}\right)\tilde{v} - \left(v + \frac{1}{2}\right)^2 x_e\tilde{v}$$

$$v = 0, 1, 2, \ldots, v_{\text{max}}$$

$$x_e = \frac{a^2\hbar}{2m_{\text{eff}}\omega} = \frac{\tilde{v}}{4\tilde{D}_e}$$

The positive dimensionless parameter x_e is called the **anharmonicity constant**.
The wavenumbers of transitions with $\Delta v = +1$ are

$$\Delta\tilde{G}_{v+\frac{1}{2}} = \tilde{G}(v+1) - \tilde{G}(v) = \tilde{v} - 2(v+1)x_e\tilde{v} + \cdots$$

Now the overtone transitions $2 \leftarrow 0$, $3 \leftarrow 0$, ... are weakly allowed, where the first one is the **first overtone** and the second one is the **second overtone**.

3.5   Vibrational spectroscopy of polyatomic molecules

Now how can we apply this discussion of diatomic molecules to polyatomic molecules?

3.5.1   Normal modes

The first step in the analysis of the vibrations of a polyatomic molecule is to calculate the total number of vibrational modes. We know this from the previously discussed degrees of freedom:
Linear molecules. These molecules have 3 possible translations and 2 possible rotations. Therefore they have $3N - 5$ possible modes of vibrations.
Non-linear molecules. These molecules have 3 possible translations and 3 possible rotations. Therefore they have $3N - 6$ possible modes of vibrations.
These **modes** are independent as long as the harmonic oscillator approximation holds.
The absorption ranges for many groups within molecules are known and using that molecules can be recognized.

3.5.2   Infrared absorption spectra

3.6   Electronic spectra

Term symbols

Selection rules

Vibrational fine structure

3.6.1   Diatomic molecules

3.7   Decay of excited states

3.7.1   Fluorescence and phosphorescence

8   Electronic Structure of Solids

8.1   Introduction

Matter is considered strictly crystalline if the atoms, ions or molecules that compose it are distributed in the three independent directions of space in a regular and repetitive way. Most metals occur naturally in a crystalline state.
These types of materials can be described using their **lattice**, the periodic structures that underlie most solids.
A free particle (in one dimension) can be described by the wave function

$$\psi(x) = A\mathrm{e}^{\mathrm{i}kx}$$

where the wave vector k is related to the momentum of the particle by the equation

$$p = \hbar k.$$

The free-electron functions are periodic with respect to the crystal lattice if the wave vector k belongs to a lattice called the **reciprocal lattice**.
The unit cell of the reciprocal lattice is called the **Brillouin zone**.

8.2   The Bravais Lattice

Describing a lattice starts with choosing a point in space, in the crystal. Then you need to identify all points in the crystal that are equivalent to this point. The arrangement of atoms about each of these points is the same and the crystal appears the same from each vantage point. These equivalent points form a lattice known as a **Bravais lattice**.
In 3D there are 14 different Bravais lattices, in 2D this is reduced to 5 possible Bravais lattices.
Any point in the lattice can be specified by the formula

$$\mathbf{l} = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3,$$

where l_1, l_2, and l_3 are integers. The vectors, $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are called **primitive vectors**.
The points in a Bravais lattice that are closest to a given point are called its **nearest neighbors**, the number of nearest neighbors is called the **coordination number** of the lattice. Due to the periodicity of the Bravais lattice, each point has the same number of nearest neighbors.
In 2D, if $|\mathbf{a}_1| = |\mathbf{a}_2|$, then the coordination number is 4 and if $|\mathbf{a}_1| \neq |\mathbf{a}_2|$, then the coordination number is 2.

**The simple cubic lattice**   The simple cubic (sc) lattice has the following structure:
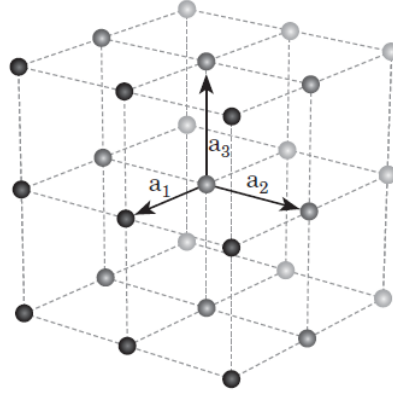
For this lattice the primitive vectors will be

$$\begin{cases} \mathbf{a}_1 &= a\hat{\mathbf{i}} \\ \mathbf{a}_2 &= a\hat{\mathbf{j}} \\ \mathbf{a}_3 &= a\hat{\mathbf{k}} \end{cases}$$

With a being the distance between the lattice points and the usual convention that $\hat{\mathbf{i}}$, $\hat{\mathbf{j}}$, and $\hat{\mathbf{k}}$ are unit vectors pointing along the x-, y-, and z-axes. The simple cubic lattice has a coordination number of 6.

The body-centered cubic lattice   The body-centered cubic (bcc) lattice is another common cubic lattice. It is formed from the simple cubic lattice by adding a single additional atom to the center of each cube. The bcc structure has a coordination number of 8.
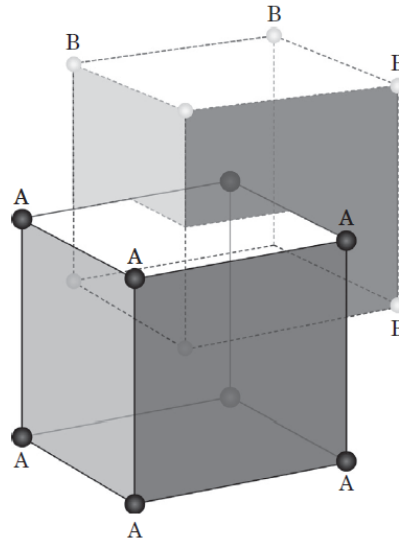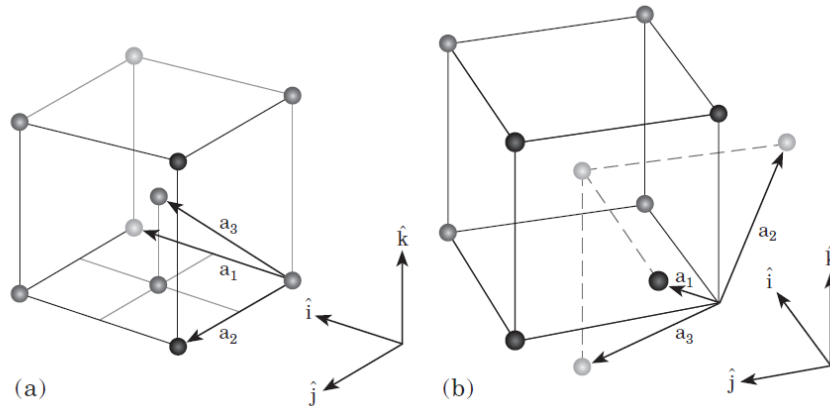

This lattice can be thought of as consisting of two interpenetrating lattices with points A and B. Since each point is a center point in one structure and a corner point in the other structure, all of the points are clearly equivalent. Two choices of primitive vectors are:

$$\mathbf{a}_1 = a\hat{\mathbf{i}}, \quad \mathbf{a}_2 = a\hat{\mathbf{j}}, \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{i}} + \hat{\mathbf{j}} + \hat{\mathbf{k}})$$
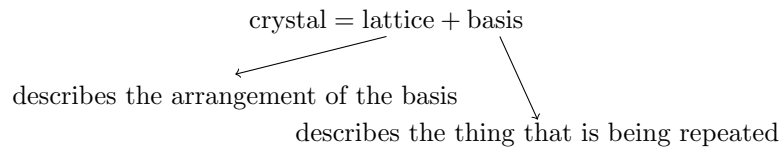
and

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{j}} + \hat{\mathbf{k}} - \hat{\mathbf{i}}), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{k}} + \hat{\mathbf{i}} - \hat{\mathbf{j}}), \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{i}} + \hat{\mathbf{j}} - \hat{\mathbf{k}}),$$

Both are shown here:

(a)   (b)

A crystal can also be described in a different way:

$$\text{crystal} = \text{lattice} + \text{basis}$$

describes the arrangement of the basis

describes the thing that is being repeated

For the bcc structure, the **basis** is given by a unit cell consisting of a corner point and a center point of a single cube

$$0, \quad \frac{a}{2}(\hat{\mathbf{i}} + \hat{\mathbf{j}} + \hat{\mathbf{k}}).$$

and the lattice has the primitive vectors of the original simple cubic lattice. This type of lattice is called a **lattice with a basis**. This description makes the symmetry more apparent.

If a bcc lattice consists of identical atoms, then either way of generating the lattice is entirely acceptable. However, if more than one kind of atom is present, it is necessary to choose a basic unit consisting of more than one atom.
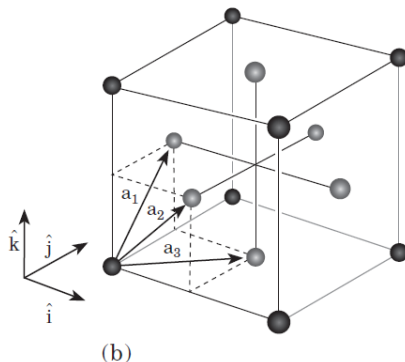
The face-centered cubic lattice   The face-centered cubic (fcc) lattice is another commonly occurring crystal structure. The lattice can be formed from the simple cubic lattice by adding an additional point to each square face. The fcc structure has a coordination number of 12.

(a)
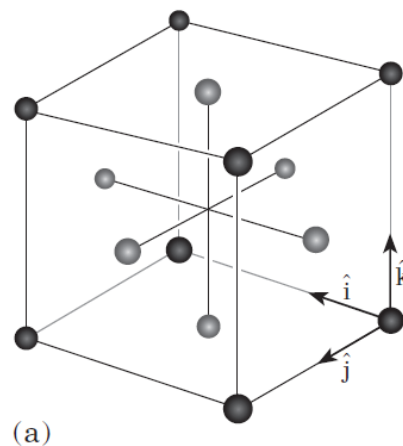
This lattice can be thought of as consisting of interpenetrating lattices. The two of the "face-centered" points can also form a simple cubic lattice, where then the original simple cubic lattice points and the other four "face-centered" points become the new "face-centered" points.

A set of primitive vectors that generates the fcc structure from a single point is:

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{j}} + \hat{\mathbf{k}}), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{k}} + \hat{\mathbf{i}}), \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{i}} + \hat{\mathbf{j}}).$$

(b)

The points of the fcc lattice can be generated using a basis. A four-point basis of the fcc lattice is formed by adding the three primitive vectors to the origin 0:

$$\mathbf{0}, \quad \mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{j}} + \hat{\mathbf{k}}), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{k}} + \hat{\mathbf{i}}), \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{i}} + \hat{\mathbf{j}}).$$

The fcc lattice is obtained from this basis by making the displacement associated with the primitive vectors of the simple cubic lattice.

An **unit cell** is the smallest group of atoms which has the overall symmetry of a crystal, and from which the entire lattice can be built up by repetition in three dimensions. These cells are described by the basis in the lattice with a basis.

The sc lattice has one lattice point per unit cell, the bcc lattice has two lattice point per unit cell and the fcc crystal has four lattice points for every cell.

For many structures, the ions may be considered to be rigid spheres that are stacked together to form the crystals. The **packing fraction** is the volume of these spheres divided by the total volume of the crystal. The packing fraction is the fraction of the volume of space inside the spheres. The packing fractions of the sc, bcc, and fcc structures are 0.52, 0.68, and 0.74, respectively.

A region of space that entirely fills all of space when it is translated in this way is called a **primitive unit cell**. Two common types of primitive unit cells are

- Parralelpiped of $\mathbf{a}_i$ vectors.

- The **Wigner-Seitz cell**. This cell is constructed by drawing perpendicular planes bisecting the lines joining the chosen center to the nearest equivalent lattice cites.

8.3 Additional Crystal Structures

8.3.1 The Diamond Structure

Carbon atoms in naturally occurring diamond crystals occupy the sites of two interpenetrating fcc lattices. The lattice can be regarded as a fcc lattice with a two-point basis located at **0** and $(a/4)(\hat{\mathbf{i}} + \hat{\mathbf{j}} + \hat{\mathbf{k}})$. An important variant of the diamond structure occurs for compounds involving two atomic species. The **zincblende structure** has equal numbers of zinc and sulfur atoms distributed on a diamond lattice in such a way that each atom has four of the atoms of the other species as its nearest neighbors.

8.3.2   The hcp Structure

The hexagonal close packed (**hcp**) structure ranks in importance with the bcc and fcc structures. About 30 elements crystallize in this form. As the name suggests, the hcp lattice can be constructed by stacking hard spheres so that each sphere rests on the spheres below it and touches the spheres next to it on the same level.

8.3.3   The Sodium Chloride Structure

The sodium chloride structure consists of equal numbers of sodium and chloride atoms placed at alternate points of a simple cubic lattice. Each ion has six ions of the other species as its nearest neighbors. The sodium chloride structure may also be described as two interpenetrating fcc structures, one consisting of sodium ions and the other of chloride atoms.

8.4   The Reciprocal Lattice

So far we've looked at the direct lattice, the initial lattice which is usually a periodic spatial function in real-space. Next we want to look at the reciprocal lattice, which represents the Fourier transform of another lattice, our direct lattice in this case.

We begin our study of the properties of the valence electrons in crystals by considering the wave function of a free electron in a periodic environment.

$$\psi(x) = Ae^{ikx}, \quad \text{with } p = \hbar k.$$

Both the potential and the electron density have the periodicity of the lattice. For the wave function this can be satisfied by imposing the periodic boundary condition:

$$\psi(a) = \psi(0),$$

which gives

$$k = \frac{2\pi}{a}n.$$

The wave function thus has the periodicity of the lattice provided that the wave vector k of the particle belongs to this discrete set of values. We can now compare a one-dimensional lattice and the corresponding reciprocal lattice:
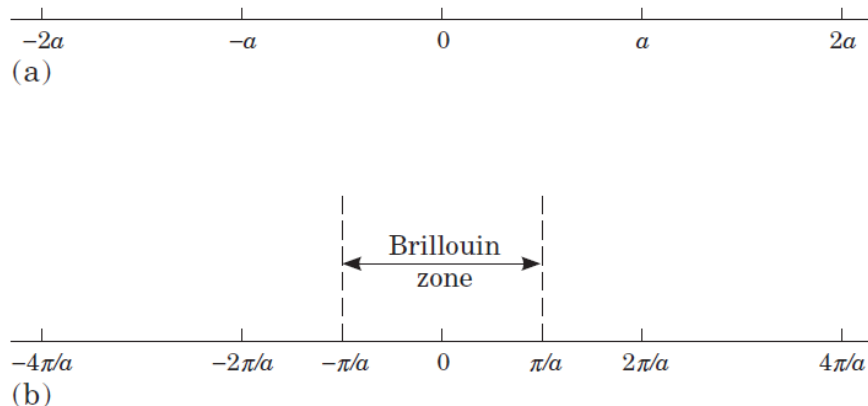
The concept of the reciprocal latticemay be used to state the condition for periodicity: *the free-electron wave function is a periodic function in the Bravais lattice if the value of k to which it corresponds is a member of the reciprocal lattice.* The Wigner-Seitz cell in reciprocal lattice space is called the **Brillouin zone**.

The position of points in a one-dimensional direct lattice can be written

$$l = ma.$$

In the reciprocal lattice this is

$$g = \frac{2\pi}{a}n.$$

This leads to the equation

$$e^{igl} = 1$$

A Fourier series can be used to represent functions with the periodicity of the lattice:

$$f(x) = \sum_n F_n e^{2\pi inx/a}$$
$$= \sum_g F_g e^{igx}$$

Here the coefficients F_g are given by the formula

$$F_g = \frac{1}{a} \int_{\text{cell}} e^{-igx} f(x)\mathrm{d}x$$

where the range of integration extends over a cell of the lattice.

In 3D we get that the wave function of a free electron in three dimensions can be written as

$$\psi_{\mathbf{k}}(\mathbf{r}) = A e^{i\mathbf{k}\cdot\mathbf{r}}, \quad \text{with } \mathbf{p} = \hbar\mathbf{k}.$$

Now the position of points in a direct lattice will be

$$\mathbf{l} = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3$$

and in the reciprocal lattice this is

$$\mathbf{g} = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3.$$

The primitive vectors of the reciprocal lattice can be generated from the three primitive vectors of the direct lattice by the equations

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$
$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$
$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}.$$

The primitive vectors defined above have the property

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$$

A function $f(\mathbf{r})$ having the periodicity of the three-dimensional lattice can be represented by the Fourier series

$$f(\mathbf{r}) = \sum_{\mathbf{g}} F_{\mathbf{g}} e^{i\mathbf{g}\cdot\mathbf{r}}$$

The coefficients $F_{\mathbf{g}}$ are given by the equation

$$F_{\mathbf{g}} = \frac{1}{v_{\text{cell}}} \int_{\text{cell}} f(\mathbf{r}) e^{-i\mathbf{g}\cdot\mathbf{r}} \mathrm{d}V$$

With v_{cell} the volume of a primitive cell of the direct lattice and where, as before, the range of integration extends over a single cell.

8.5   Lattice Planes

In any Bravais lattice, one may identify lattice planes in a variety of different orientations. Each plane contains three or more lattice points that do not lie on a straight line. One can also identify groups of lattice planes, which together contain all of the points in a Bravais lattice. Densely packed planes have the largest distance between the planes.

Certain important features of lattice vectors and families of lattice planes are:

1. A vector extending from one lattice point to another is itself a lattice vector. Suppose we have two vectors pointing to the two lattice points:

$$\mathbf{l} = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3 \quad \text{and} \quad \mathbf{m} = m_1\mathbf{a}_1 + m_2\mathbf{a}_2 + m_3\mathbf{a}_3$$

   The vector extending from the first lattice point to the second is

$$\mathbf{m} - \mathbf{l} = (m_1 - l_1)\mathbf{a}_1 + (m_2 - l_2)\mathbf{a}_2 + (m_3 - l_3)\mathbf{a}_3,$$

   which is also a member of the lattice.

2. Any plane determined by three points in the direct lattice is normal to some vector of the reciprocal lattice. Suppose we have 2 vectors, $\mathbf{l}$ and $\mathbf{m}$, the first pointing from point 1 to 2 and the second from 1 to 3:

$$\mathbf{l} = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3 \quad \text{and} \quad \mathbf{m} = m_1\mathbf{a}_1 + m_2\mathbf{a}_2 + m_3\mathbf{a}_3$$

   A vector which is normal to the plane can be constructed by taking the vector product of these two vectors:

$$\mathbf{n} = \mathbf{l} \times \mathbf{m}$$

   If using the primitive vectors of the reciprocal lattice for $\mathbf{l}$ and $\mathbf{m}$, then the vector $\mathbf{n}$ is parallel to a vector of the reciprocal lattice.

3. Each vector of the reciprocal lattice is normal to a set of lattice planes of the direct lattice. To show this we consider a reciprocal lattice vector and a lattice vector:

$$\mathbf{g} = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3 \quad \text{and} \quad \mathbf{l} = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3$$

   Taking the inner product of these two vectors gives

$$\mathbf{g} \cdot \mathbf{l} = 2\pi(n_1 l_1 + n_2 l_2 + n_3 l_3) = 2\pi N$$

   The projection of the lattice vector $\mathbf{l}$ on the vector $\mathbf{g}$ is

$$d = \mathbf{l} \cdot \frac{\mathbf{g}}{|\mathbf{g}|} = \frac{2\pi N}{|\mathbf{g}|}$$

   Then any lattice vector $\mathbf{l}'$ that satisfies the equation

$$\mathbf{g} \cdot \mathbf{l}' = 2\pi N$$

   will have the same projection on $\mathbf{g}$ and all the points having this property form a lattice plane, which is normal to $\mathbf{g}$.

4. Consider now the reciprocal lattice vector,

$$\mathbf{g} = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3$$

   If the integers (n_1, n_2, n_3) have no common factors, the vector $\mathbf{g}$ is the shortest vector pointing in this direction, and the family of lattice planes normal to $\mathbf{g}$ is separated by the distance

$$d = \frac{2\pi}{|\mathbf{g}|}$$

The correspondence between families of lattice planes and reciprocal lattice vectors provides the basis for the conventional way of describing lattice planes. One describes the orientation of a families of lattice planes by giving the reciprocal lattice vector normal to the planes. For this one uses the **Miller indices**.

The Miller indices of a family of lattice planes are the integer components (n_1, n_2, n_3) of the shortest reciprocal lattice vector normal to the plane. The commas between the integral components are traditionally not written and the minus sign is removed by writing a bar above the integer; $(n_1 \, \bar{n}_2 \, n_3)$. To interpret the indices, one must know which set of primitive vectors is being used (often this is the simple cubic basis).

There is an alternative way to use them. To make contact with their nomenclature, we consider a family of planes normal to the reciprocal lattice vector:

$$\mathbf{g} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3$$

The condition that the position vector,

$$\mathbf{r} = r_1 \mathbf{a}_1 + r_2 \mathbf{a}_2 + r_3 \mathbf{a}_3$$

be directed to a point on a plane which is perpendicular to this vector can be written

$$\mathbf{g} \cdot \mathbf{r} = A$$

where A is a constant.

The three integers for which the plane intercepts the $\mathbf{a}_i$ unit vectors are given by the Miller indices:

$$n_1 = \frac{A}{2\pi x_1}, \quad n_2 = \frac{A}{2\pi x_2}, \quad n_3 = \frac{A}{2\pi x_3}$$

The Miller indices of a plane are thus inversely proportional to the intercepts of the lattice plane with the crystal axes. Crystallographers generally define the Miller indices to be a set of integers with no common factors that are inversely proportional to the intercepts of the lattice plane with the crystal axes

$$n_1 : n_2 : n_3 = \frac{1}{x_1} : \frac{1}{x_2} : \frac{1}{x_3}$$

8.6   Bloch's Theorem

To understand the conditions imposed upon the form of wave functions by the symmetry of the lattice, we consider the effect of a displacement of the coordinate system upon a wave function. Suppose we translate the origin of the coordinate system by the lattice vector $\mathbf{l}$. Then the relation between the original and displaced wavefunction is given by:

$$\mathbf{T}_l \psi(\mathbf{r}) = \psi'(\mathbf{r})$$
$$= \psi(\mathbf{r} + \mathbf{l}).$$

With $\mathbf{T}_l$ a displacement operator.

The wave functions of the electrons in a crystal satisfy the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right) \psi(\mathbf{r}) = E \psi(\mathbf{r})$$

The condition that potential energy has the symmetry of the lattice can be written

$$V(\mathbf{r} + \mathbf{l}) = V(r)$$

where $\mathbf{l}$ is any displacement vector of the Bravais lattice.

A wave function which satisfies the Schrödinger equation with a periodic potential is known as a **Bloch function**. As a consequence of the periodicity of the potential $V(\mathbf{r})$, the wave functions have the following important property:

8.6.1   Bloch's Theorem

For any wave function that satisfies the Schrödinger equation, there is a wave vector $\mathbf{k}$ such that translating the coordinate system by a lattice vector $\mathbf{l}$ is equivalent to multiplying the function by the phase factor $\exp(i\mathbf{k} \cdot \mathbf{l})$

$$\psi(\mathbf{r} + \mathbf{l}) = e^{i\mathbf{k}\cdot\mathbf{l}}\psi(\mathbf{r})$$

The wave function in a cell specified by the lattice vector $\mathbf{l}$ differs from the wave function in the Wigner-Seitz cell near the origin by a phase factor $\exp(i\mathbf{k} \cdot \mathbf{l})$. The electron wave function is entirely determined by the behavior of the function in the unit cell about the origin.

8.6.2   Alternate Form of Bloch's Theorem

Bloch's theorem can be stated a little differently. We define a function $u_{\mathbf{k}}(\mathbf{r})$ by the equation

$$u_{\mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{r}}\psi_{\mathbf{k}}(\mathbf{r})$$

which is periodic, since:

$$u_{\mathbf{k}}(\mathbf{r} + \mathbf{l}) = e^{-i\mathbf{k}\cdot(\mathbf{r}+\mathbf{l})}\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{l}) = e^{-i\mathbf{k}\cdot\mathbf{r}}\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})$$

We may solve for $\psi_{\mathbf{k}}(\mathbf{r})$ obtaining

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r})$$

and state Bloch's theorem as follows:

"The solutions of the Schrödinger equation of an electron in a Bravais lattice can be written as the product of a planewave $e^{i\mathbf{k}\cdot\mathbf{r}}$ and a function $u_{\mathbf{k}}(\mathbf{r})$ having the periodicity of the lattice."

The free-electron wavefunction is given by

$$\psi(x) = A_{\mathbf{k}}e^{ikx}$$

We would expect that the perturbing effects of the ion cores should distort the free-electron wave function. According to the alternate form of Bloch's theorem, however, the distortion of the wave function due to the ion cores can only have the effect of replacing the constant $A_{\mathbf{k}}$ by a periodic function $u_{\mathbf{k}}(\mathbf{r})$.

There is a mathematical device which serves to define the solutions of the Schrödinger equation in a finite region, and which still does not introduce any direct physical effects due to the boundaries. This is to use periodic or Born-von Karman boundary conditions.
To clarify the issues involved, we consider a one-dimensional crystal having N cells, and require that the wave function be periodic over the length of the entire crystal. One can imagine that the ends of the crystal are joined together forming a circle. The periodic boundary condition can be expressed

$$\psi(x + Na) = \psi(x)$$

N is the total number of unit cells in the lattice.
According to Bloch's theorem, there is a wave vector k such that

$$\psi_k(x + Na) = e^{ikNa}\psi_k(x)$$

Comparing the last two equations gives that

$$e^{ikNa} = 1$$

which is satisfied by the following values of k:

$$k = \frac{2\pi n}{Na}$$

where n is an integer.
When comparing the values of k to the reciprocal lattice vector $n2\pi/a$, you can see that k is very finely

spaced. We recall that the reciprocal lattice lengths are those values which the free-electron wave functions have the periodicity of the lattice. By contrast, this new equation defines a much finer grid of k-values for which the wave function is periodic over the length of the entire crystal.

In 3D this becomes

$$\mathbf{k} = \frac{n_1}{N_1}\mathbf{b}_1 + \frac{n_2}{N_2}\mathbf{b}_2 + \frac{n_3}{N_3}\mathbf{b}_3$$

where n_1, n_2, and n_3 are integers, and $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ are the unit vectors of the reciprocal lattice. For each allowed $\mathbf{k}$-value, the free-electron wave functions can be written

$$\psi_{\mathrm{k}}(\mathbf{r}) = \frac{1}{V^{1/2}}e^{i\mathbf{k}\cdot\mathbf{r}}$$

One may show that this wave function is normalized in this large region and that wave functions corresponding to different allowed values of $\mathbf{k}$ are orthogonal

$$\int \psi_{\mathbf{k}'}^*(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r})dV = \left\{ \begin{array}{ll} 1, & \text{for } \mathbf{k}' = \mathbf{k} \\ 0, & \text{for } \mathbf{k}' \neq \mathbf{k} \end{array} \right.$$

8.7   Diffraction of Electrons by an Ideal Crystal

Bragg's law, which was derived using elementary properties of waves, gives the scattering of X-rays by an ideal crystal:

$$2d\sin\theta = n\lambda$$

In this section, we shall consider the elastic scattering of electrons by an ideal crystal.
If a beam of electrons is directed into a crystal, the periodic potential of the ion cores will scatter the electrons into different states.
Suppose that an electron is initially in a free-electron state described by a wave function $\psi_{\mathbf{k}}$, and at time $t = 0$, we allowed the potential $V(\mathbf{r})$ to interact with the electron. The probability that the electron made a transition from its initial state $\psi_{\mathbf{k}}$ to the state described by the wave function $\psi_{\mathbf{k}'}$. is proportional to the absolute value squared of the transition integral. We may write

$$P(\mathbf{k} \rightarrow \mathbf{k}') = \left[\mathbf{I}_{\mathbf{k}',\mathbf{k}}\right]^* \mathbf{I}_{\mathbf{k}',\mathbf{k}}$$

where

$$\mathbf{I}_{\mathbf{k}',\mathbf{k}} = \int \psi_{\mathbf{k}'}^*(\mathbf{r})V(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r})dV$$

This is the transition integral, here the previously defined wavefunctions are used. The potential energy, being periodic, may be expanded in a Fourier series

$$V(\mathbf{r}) = \sum_{\mathrm{g}} V_{\mathrm{g}}e^{i\mathbf{g}\cdot\mathbf{r}}$$

Substituting gives:

$$\mathbf{I}_{\mathbf{k}',\mathbf{k}} = \sum_{\mathbf{g}} V_{\mathrm{g}} \int \frac{1}{V}e^{i(\mathbf{k}+\mathbf{g}-\mathbf{k}')\cdot\mathbf{r}}dV$$

$$= \sum_{\mathbf{g}} V_{\mathrm{g}} \int \psi_{\mathbf{k}'}^*(\mathbf{r})\psi_{\mathbf{k}+\mathbf{g}}(\mathbf{r})dV$$

$$= \left\{ \begin{array}{ll} V_{\mathrm{g}}, & \text{if } \mathbf{k}' = \mathbf{k}+\mathbf{g} \\ 0, & \text{otherwise} \end{array} \right.$$

For a particular value of $\mathbf{k}$, diffracted electrons will be observed in directions corresponding to wave-vectors $\mathbf{k}'$ satisfying

$$\mathbf{k}' = \mathbf{k}+\mathbf{g}$$

For elastic scattering, the energy of the diffracted electrons is the same as the energy of the incident electrons. The vectors $\mathbf{k}$ and $\mathbf{k}'$ thus have the same length ($|\mathbf{k}| = |\mathbf{k}'|$).

The angle between $\mathbf{k}$ and $\mathbf{k}'$ is 2θ, and the length of $\mathbf{g}$ is equal to twice the projection of $\mathbf{k}$ upon $\mathbf{g}$

$$|g| = 2|\mathbf{k}|\sin\theta$$

Recalling the distance between planes and that magnitude of the wave vector $\mathbf{k}$ is related to the wave length of the incident wave λ by $|\mathbf{k}| = 2\pi/\lambda$ and substituting leads to the Bragg diffraction law

$$2d\sin\theta = n\lambda$$

$\mathbf{k}' = \mathbf{k} + \mathbf{g}$ is a condition which must be satisfied for scattering to occur. This equation was derived by requiring that the transition integral be nonzero. A condition which we shall find to be more useful, can be derived by requiring that the complex conjugate of the transition integral be nonzero. This leads to the equation $\mathbf{k} = \mathbf{k}' + \mathbf{g}$ or $\mathbf{k}' = \mathbf{k} - \mathbf{g}$. The requirement that the scattering process be elastic is equivalent to the condition

$$|\mathbf{k}| = |\mathbf{k} - \mathbf{g}|$$

This implies that $\mathbf{k}$ lies on the perpendicular bisector of the reciprocal lattice vector $\mathbf{g}$. At this point, we recall that the Wigner-Seitz cell or Brillouin zone is constructed by drawing planes that bisect the reciprocal lattice vectors in the different crystalline directions. We thus conclude that elastic scattering of electrons will occur when $\mathbf{k}$ lies on the boundary of the Brillouin zone.

8.8   The Bandgap

When sodium atoms are brought together to form a solid, the electrons in the inner lying states remain localized around the nuclear centers, while the 3s electrons become conduction electrons described by Block functions that are extended over the entire solid. The wave functions of the outer electrons then satisfy the Schrödinger equation of an electron moving in the potential $V(\mathbf{r})$ of the ion cores.

To the extent that the perturbing effects of the ion cores can be neglected, the conduction electrons can be described by the free-electron wave functions

$$\psi_{\mathrm{k}}(\mathbf{r}) = \frac{1}{V^{1/2}}e^{i\mathbf{k}\cdot\mathbf{r}}$$

and the energy of the electrons is given by the formula

$$\varepsilon^0(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$$

Electrons are diffracted at the zone boundaries in reciprocal lattice space. The diffraction of the electrons can be understood as a mixing effect involving the two free-electron states. These two free-electron states have the same energy, $\varepsilon^0(\mathbf{k}) = \varepsilon^0(\mathbf{k}-\mathbf{g})$. At the zone boundary, the electrostatic field of the crystal combines the two free-electron states with wave vectors $\mathbf{k}$ and $\mathbf{k}-\mathbf{g}$ into two other states with energy ε^+ and ε^-. The separation between these two energy values is known as a **bandgap**.

The equation for the wave function of the lower state is

$$\psi_{\mathrm{k}}^-(\mathbf{r}) = \alpha_{\mathbf{k}}e^{i\left(\mathrm{k}-\frac{1}{2}\ \mathrm{g}\right)\cdot\mathrm{r}}2\cos\left(\frac{1}{2}\ \mathrm{g}\cdot\mathbf{r}\right)$$

The probability of finding an electron at a position $\mathbf{r}$ in space is given by the absolute value squared of the wave function

$$\left|\psi_{\mathbf{k}}^-(\mathbf{r})\right|^2 = |\alpha_{\mathbf{k}}|^2\,4\cos^2\left(\frac{1}{2}\mathbf{g}\cdot\mathbf{r}\right)$$

This function is large near $\mathbf{r} = 0$ and at other sites of the Bravais lattice. Hence, the energy is lowered by the attraction of the electron to the ions of the crystal. Similarly, the wave function $\psi_{\mathbf{k}}^+(\mathbf{r})$ of the upper state is

$$\psi_{\mathbf{k}}^+(\mathbf{r}) = \alpha_{\mathbf{k}}e^{i\left(\mathbf{k}-\frac{1}{2}\mathbf{g}\right)\cdot\mathbf{r}}2i\sin\left(\frac{1}{2}\mathbf{g}\cdot\mathbf{r}\right)$$

The absolute value square of $\psi_{\mathbf{k}}^+$ is

$$\left|\psi_{\mathbf{k}}^+(\mathbf{r})\right|^2 = |\alpha_{\mathbf{k}}|^2 \, 4\sin^2\left(\frac{1}{2}\mathbf{g}\cdot\mathbf{r}\right)$$

This is small near the origin and large in regions of positive potential. This has the effect of raising ε^+ above ε^-.

7 Statistical Physics

7.7 Free-Electron Theory of Metals

The outer electrons of atoms in metals are not bound to individual atoms, but are free to move throughout the metal. These electrons are free and thus have an energy dispersion relation given by:

$$\varepsilon = \frac{\hbar^2 k^2}{2m}$$

here we can also replace m by m^* to indicate the effective mass.
These electrons have a density

$$n = \frac{N}{V}$$

Example: a simple cube has the allowed values of k given by

$$k_x = \frac{2\pi}{Na}n_x = \frac{2\pi}{L}n_x$$

In 3D then our energy dispersion relation becomes

$$\varepsilon = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$$

Now what is the maximum value k can take? What is $k_{\max} = k_F$? We somehow know that

$$N = 2\frac{4}{3}\pi k_F^3 \left(\frac{L}{2\pi}\right)^3$$

thus

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

From the Fermi wave vector we can also get a Fermi velocity:

$$p_F = mv_F = \hbar k_F \quad \rightarrow \quad v_F = \frac{\hbar}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

and a Fermi energy:

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

7.7.1 Density of States

The density of states (D.O.S.) is often represented by either $g(\varepsilon)$ or $D(\varepsilon)$ and is defined as

$$g(\varepsilon) = \frac{\partial N}{\partial \varepsilon}$$

Since we know that $N = 2\frac{4}{3}\pi k_F^3 \left(\frac{L}{2\pi}\right)^3$ and $\varepsilon = \frac{\hbar^2 k^2}{2m}$, we can deduce that

$$g(\varepsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon}$$

Everything we looked at so far was at $T = 0$, but now what if $T > 0$?
This brings us to the Fermi-Dirac distribution function, $f(\varepsilon, \varepsilon_F)$. The amount of electrons within a certain interval of energies is given by:

$$n(\varepsilon)\,\mathrm{d}\varepsilon = g(\varepsilon)f(\varepsilon, \varepsilon_F)\,\mathrm{d}\varepsilon$$

and

$$f(\epsilon) = \frac{1}{e^{(\epsilon - \varepsilon_F)/k_{\mathrm{B}}T} + 1}$$

If you place a metal in an electric field you get a current. The force on a electron is given by:

$$F = m^*\frac{dV}{dt} = \frac{\partial p}{\partial t} = \frac{\partial}{\partial t}(\hbar k) = \hbar\frac{\partial k}{\partial t}$$
$$\rightarrow \hbar\frac{\partial k}{\partial t} = -q\mathbf{E}$$

After a certain amount of time τ, we'll have

$$\Delta\mathbf{k} = \frac{-q\mathbf{E}}{\hbar}\tau.$$

τ is the scattering time, or the average time between scattering events. These scattering events are caused by lattice vibrations and impurities.

$$\tau_{\mathrm{tot}}^{-1} = \tau_{\mathrm{phonon}}^{-1} + \tau_{\mathrm{impurity}}^{-1} + \tau_{e^- - e^-}^{-1}$$

The current density is given by

$$J = \frac{I}{\mathrm{area}} = nqv = \frac{nq^2\tau}{m^*} = \sigma\mathbf{E}$$

and the mobility is given by

$$\mu = \frac{q\tau}{m^*}$$

The conductivity is given by

$$J = \sigma E \quad \rightarrow \quad \sigma = \frac{nq^2\tau}{m^*}$$

And the resistivity is $\rho = \sigma^{-1}$

An electric field results in a shift of the Fermi surface. This shifting is only possible if there are states above the Fermi level, which is the case in metals. In insulators for example it isn't possible. The shift is proportional to:

$$\Delta\mathbf{k} \propto \mathbf{E}\tau$$

8 Electronic Structure of Solids

8.9 Classification of Solids

8.9.1 The Band Picture

The energy levels of a crystal consist of dense bands. The energy bands that occur above 0 eV are called conduction bands, while the bands occurring below zero are known as the valence bands. Electrons in the conduction band are generally free to move about the solid while electrons in the valence band are localized near particular atoms. The conduction and valence bands are separated by a bandgap, which, as we have seen, is associated with scattering at the Bragg planes. An electron excited into a conduction band is called a conduction electron, while an empty state in the valence band is called a hole.

Metals   If a band is not filled, there will be current carrying states available just above the top of the occupied levels. The material will then readily conduct a current, and the conductivity will not depend upon temperature except in so far as temperature affects the scattering of electrons by the ion cores. The solid would then be described as a **metal**.

Semiconductors   If the bandgap $\Delta\varepsilon$ is small, $\sim 0.5 - 3.0$ eV, the distributions of electrons between the energy levels of a solid is described by Fermi-Dirac statistics. At a nonzero temperature T, a small density of electrons will be excited by thermal fluctuations into the upper band. Since these electrons can carry a current, the material then has an observable conductivity, which will increase as the temperature increases. Such a material is called a **semiconductor**.

Insulators   If there is a large bandgap $\Delta\varepsilon$ (> 3 eV) between the occupied and unoccupied states, a prohibitively large amount of energy must be supplied to the electrons to carry them up over the gap into the next band. The solid would then be an **insulator**.

8.9.2   The Bond Picture

Solids can also be classified according to the way in which the atoms are bound together to their neighbors. We shall distinguish five different types of bonding: covalent bonding, ionic bonding, molecular bonding, hydrogen bonding, and metallic bonding.

Covalent Bonding   This type of bonding is like in molecules which we've covered with hybrid orbitals and he sharing of electron pairs in each of the bonding orbitals.
It is instructive to compare the crystal structure of Ge to that of InSb. While germanium is in column IV of the periodic table, indium (In) is in column III, and antimony (Sb) is in column V. The InSb semiconductor forms the same diamond structure as germanium with indium atoms occupying all of the A sites of the crystal and antimony atoms occupying all of the B sites.
However, whereas the four electron pairs occur midway between the germanium atoms in the germanium structure, the electron pairs are drawn more closely to the Sb atom in the InSb lattice. This can be explained with the concept of electronegativity used in modern chemistry. The electronegativity of an atomic species is a measure of the attractive power of the atom for an electron pair. If two atoms, which are bonded together, have the same electronegativity, the bonding electrons are shared equally between them. If, however, one atom is more electronegative than the other, the electron pair is drawn more closely to the atom that is more electronegative and the chemical bond has a polar character.
Depending on the size of their bandgap, covalent crystals can be either insulators or semiconductors.

Ionic Bonding   In an ionic compound, one or more electrons from one of the species is transferred to the other species. In a NaCl crystal, for instance, the outer 3s electron of each sodium atom is drawn over to a chlorine atom with the additional electron completing the outer 3p shell of chlorine. The resulting ionic crystal is composed of Na^+ and Cl^- ions. The distinguishing feature of ionic crystals is that all of the electronic charge is localized near the individual ions. Since the electron charge is well localized, most ionic crystals are insulators.

Molecular Crystals   Molecular crystals consist of individual atoms or molecules drawn together by the weak van der Waals force. The solid phase of the noble gases from column VIII of the periodic table are the best examples of molecular crystals.

Hydrogen-Bonded Crystals   The hydrogen atom has unique properties that give the bonds which it forms with other elements, a special character. The ionization energy of hydrogen (13.59 eV) is much higher than for the other elements from column I of the periodic table. Since it is so difficult to remove an electron completely from hydrogen, the atom does not form ionic crystals as do the other first column elements. Also, since hydrogen only lacks one electron to form a closed shell, it can form only one covalent bond by sharing an electron pair.

In H_2O, each oxygen atom in the figure is joined to two hydrogen atoms by covalent bonds and to two other hydrogen atoms by electrostatic attraction in much the same way as ions are joined to each other in an ionic crystal. The resulting lattice has a tetrahedral bond structure similar to that of covalent crystals.

Metals As one moves toward the left of the periodic table, covalent bonds expand until there is an appreciable density of electrons throughout the interstitial regions between the positive ions, and the overlap of the energy bands in k-space increases. The material then exhibits the properties of a metal, in which valence electrons are free of their ions, forming a nearly uniform gas. The purest examples of metallic crystals are the alkali metals of column I. Other examples are provided by the alkali earths of column II and by the transition metal elements.

9 Charge Carriers in Semiconductors

When atoms condense to form a solid, the wave functions of electrons in the different atomic shells respond differently to their environment. We can identify 3 different states:

- **Core states**: inner electrons of the atoms, they are only weakly perturbed by the solid-state environment.

- **Valence states**: these are significantly distorted by the solid-state environment and yet remain localized about the atomic center.

- **Conduction states**: these become delocalized over the entire solid.

9.1 Density of Charge Carriers in Semiconductors

The distinctive property of semiconductors is that they have small bandgaps separating valence and conduction states. While electrons can be excited thermally from the valence band into the conduction band of these materials, the number of electron-hole pairs created in this way is quite small.
A perfect semiconductor with no impurities or lattice defects is called an **intrinsic semiconductor**. The generation of a hole in an intrinsic semiconductor is accomplished by breaking a covalent bond of the crystal producing a free electron and a vacancy in the lattice.
The Fermi energy is between the highest occupied level and the lowest unoccupied level. For intrinsic semiconductors, the Fermi energy occurs near the middle of the gap between the valence and conduction bands. Semiconductors with additional charge carriers due to impurities are called extrinsic semiconductors and said to be doped. For extrinsic semiconductors, the Fermi energy may be very close to the bottom of the conduction band or very close to the top of the valence band.
The number of states available to a free electron in the range between ε and $\varepsilon + \mathrm{d}\varepsilon$ for the conduction electrons in a semiconductor is given by:

$$g(\varepsilon)\mathrm{d}\varepsilon = \frac{V4\pi}{h^3} \left(2m_\mathrm{c}\right)^{3/2} \left(\varepsilon - \varepsilon_\mathrm{c}\right)^{1/2} \mathrm{d}\varepsilon$$

The density of electrons in the range between ε and $\varepsilon + \mathrm{d}\varepsilon$ can be written

$$n(\varepsilon)\mathrm{d}\varepsilon/V = f(\varepsilon)g(\varepsilon)\mathrm{d}\varepsilon/V = \frac{4\pi}{h^3} \left(2m_\mathrm{c}\right)^{3/2} \frac{\left(\varepsilon - \varepsilon_\mathrm{c}\right)^{1/2} \mathrm{d}\varepsilon}{\mathrm{e}^{(\varepsilon - \varepsilon_\mathrm{F})/k_\mathrm{B}T} + 1}$$

The expression for the density of charge carriers can be written

$$n(T) = N_c(T)e^{-(\varepsilon_c - \varepsilon_F))/kT}$$

with N_c being the effective density of states for the conduction band;

$$N_\mathrm{c} = 2 \left(\frac{2\pi m_\mathrm{c} k_\mathrm{B} T}{h^2}\right)^{3/2}$$

The density of holes in the valence band is given by

$$p(T) = P_V(T)e^{-(\varepsilon_F - \varepsilon_v))/kT}$$

with

$$P_{\mathrm{v}} = 2 \left(\frac{2\pi m_{\mathrm{v}} k_{\mathrm{B}} T}{h^2} \right)^{3/2}$$

While the density of electrons and holes depends upon the Fermi energy, the product of n and p is independent of the Fermi energy.

$$np = N_{\mathrm{c}} P_{\mathrm{v}} e^{-(\epsilon_{\mathrm{c}} - \epsilon_{\mathrm{v}})/k_{\mathrm{B}} T} = N_{\mathrm{c}} P_{\mathrm{v}} e^{-\epsilon_g/k_{\mathrm{B}} T} = n_i^2$$

n_i is the intrinsic electron density, which is equal to the intrinsic hole density. This relation is called the Law of Mass action and also holds in doped crystals, but only in equilibrium.

9.2   Doped Crystals

The concentration of free electrons and holes in a crystal can be modified by adding impurities to the crystal. Impurities that contribute electrons to the conduction bands are called **donors**, while impurities that contribute holes to the valence bands are called **acceptors**. A semiconductor for which extra free electrons or holes have been introduced by adding impurities is called an **extrinsic semiconductor**, and the process of adding impurities to modify the concentration of free electrons or holes is called **doping**.
A material with additional negative charged carriers (electrons), is said to be **n-doped**. A material with additional positive charged carriers (holes), is said to be **p-doped**. Adding donor or acceptor impurities to a crystal has the effect of adding additional energy levels to the band structure and changes the position of the Fermi level. The additional energy levels are usually within the bandgap.
In doped material, there is always more of one type of carrier than the other and the type of carrier with the higher concentration is called a **majority carrier**, while the lower concentration carrier is called a **minority carrier**.

9.3   A Few Simple Devices

9.3.1   The p-n Junction

A p-n junction is formed by depositing a material doped with either donor or acceptor atoms upon another material with the opposite kind of doping. The junction has two terminals and is thus referred to as a p-n diode.
P-n junctions are used in a lot of applications like rectifiers, LEDs, solar cells, transistors, diodes and more.
Once the p-n junction is formed, electrons in the n-material diffuse across the boundary leaving behind positively charged donor ions, and holes in the p-material diffuse across the boundary leaving behind negatively charged acceptor ions. The majority charge carriers that cross over the boundary recombine with majority carriers in the other material and disappear.
Only fixed ions remain near the junction. Positive ions remain on the n-side, while negative ions remain on the p-side. Because of the lack of charge carriers, this region near the interface between the two materials is called the **depletion zone**.
The charge ions in the depletion zone create an electrostatic potential which eventually becomes strong enough to resist the flow of majority charge carriers across the boundary. Electrons in the n-material are hindered by the electric field due to the negative ions in the p-region, while holes in the p-region are hindered by positive ions in the n-region. Because of the charged ions near the junction, this region is also called the **space-charge region**.

10 Alternative from the Solar Cells Course

10.1 Basics

10.1.1 Semiconductor Materials

Semiconductor materials come from different groups in the periodic table, yet share certain similarities. They are either from group IV, or from a combination of group III and group V (called III-V semiconductors), or of combinations from group II and group VI (called II-VI semiconductors).
The properties of the semiconductor material are related to their atomic characteristics and change from group to group.
Researchers and designers take advantage of these differences to improve the design and choose the optimal material for a PV application.

10.1.2 Semiconductor Structure

Semiconductors are made up of atoms bonded together to form a uniform, regular, periodic structure, a crystal structure. Silicon atoms have four valence electrons which are shared in covalent bond with the four surrounding Si atoms, resulting in that each atom is surrounded by 8 electrons.

10.1.3 Conduction in Semiconductors

Semiconductors act as insulators at low temperatures and conductors at higher temperatures. The electrons in the covalent bonds are held in place by this bond and hence they are localized to the region surrounding the atom.
At elevated temperatures, especially at the temperatures where solar cells operate, electrons can gain enough energy to escape from their bonds. When this happens, the electrons are free to move about the crystal lattice and participate in conduction. Only at absolute zero are all electrons in this "stuck," bonded arrangement, so any temperature above it can be considered an elevated temperature.

10.1.4 Band Gap

The **band gap** (E_G) is the minimum amount of energy required for an electron to break free of its bound state. When the band gap energy is met, the electron is excited into a free state, and can therefore participate in conduction. The band gap determines how much energy is needed from the sun for conduction, as well as how much energy is generated. A **hole** is created where the electron was formerly bound. This hole also participates in conduction.
The band structure of a semiconductor gives the energy of the electrons on the y-axis and is called a **band diagram**. The lower energy level of a semiconductor is called the **valence band** (E_V) and the energy level at which an electron can be considered free is called the **conduction band** (E_C). Electrons sit at bottom of conduction band and holes at top of valence band.

10.1.5 Intrinsic Carrier Concentration

Intrinsic carriers are the electrons and holes that participate in conduction. The concentration of these carriers is called the **intrinsic carrier concentration**, denoted by n_i, and it is contingent upon the temperature and band gap of the material, thus affecting a material's conductivity.
A formula for the intrinsic carrier concentration in silicon as a function of temperature is given by

$$n_i(T) = 5.29 \times 10^{19} \left(\frac{T}{300} \right)^{2.54} e^{-6726/T}$$

10.1.6 Doping

Doping is a technique used to vary the number of electrons and holes in semiconductors. Doping creates **N-type** materials when semiconductor materials from group IV are doped with group V atoms. **P-type**

materials are created when semiconductor materials from group IV are doped with group III atoms. The amount of valence electrons is the determining factor in creating N- or P-type materials.

N-type materials increase the conductivity of a semiconductor by increasing the number of available electrons; P-type materials increase conductivity by increasing the number of holes present.

In doped material, there is always more of one type of carrier than the other and the type of carrier with the higher concentration is called a **majority carrier**, while the lower concentration carrier is called a **minority carrier**.

10.1.7   Equilibrium Carrier Concentration

The densities of the electrons and the holes are given by

$$n(T) = N_C(T)e^{-(\varepsilon_c - \varepsilon_F))/kT}$$
$$p(T) = P_V(T)e^{-(\varepsilon_v - \varepsilon_F))/kT}$$

Here ε_F is the **Fermi level**, a hypothetical energy level of an electron, such that at thermodynamic equilibrium this energy level would have a *50% probability of being occupied at any given time*. The formula to determine the Fermi-level is given by

$$\varepsilon_F = \frac{\varepsilon_c + \varepsilon_v}{2} + \frac{kT}{2}\ln\left(\frac{P_V}{N_C}\right)$$

The **Fermi–Dirac distribution**,
$$f(\varepsilon, \varepsilon_F) \approx e^{-(\varepsilon - \varepsilon_F))/kT},$$

gives the probability that (at thermodynamic equilibrium) a state having energy ε is occupied by an electron.

At equilibrium, the product of the majority and minority carrier concentration is a constant, and this is mathematically expressed by the Law of Mass Action.

$$np = N_C P_V e^{-E_G/kT}$$

This is usually written as

$$np = n_i^2$$

It holds for doped semiconductors and does not hold under illumination or when a bias voltage is applied.

10.2   P-n Junctions

A pn junction separates the electron and hole carriers in a solar cell to create a voltage and useful work.

10.2.1   Formation of a PN-Junction

Joining n-type material with p-type material causes excess electrons in the n-type material to diffuse to the p-type side and excess holes from the p-type material to diffuse to the n-type side. Movement of electrons to the p-type side exposes positive ion cores in the n-type side while movement of holes to the n-type side exposes negative ion cores in the p-type side, resulting in an electron field at the junction and forming the depletion region. A "built-in" potential V_{bi} voltage results from the electric field formed at the junction

10.2.2   P-N Junction Diodes

P-N junction diode is integral for all electronic devices to operate, aggregating all forms of carrier transport, generation, and recombination. Majority carriers can diffuse across the P-N junction depletion region, even though the electric field impedes their crossing. Minority carriers that reach the junction are swept across the depletion region due to drift. At equilibrium, the net current (diffusion and drift current) is zero for both electrons and holes because the diffusion current is equal and opposite to the drift current for both carriers.

10.2.3 Bias of PN Junctions

Semiconductor devices have three modes of operation:

- Thermal Equilibrium:
  At thermal equilibrium there are no external inputs such as light or applied voltage. The currents balance each other out so there is no net current within the device.

- Steady State:
  Under steady state there are external inputs such as light or applied voltage, but the conditions do not change with time. Devices typically operate in steady state and are either in forward or reverse bias.

- Transient:
  If the applied voltage changes rapidly, there will be a short delay before the solar cell responds. As solar cells are not used for high speed operation there are few extra transient effects that need to be taken into account.

Diodes under Forward Bias Forward bias occurs when a voltage is applied across the solar cell such that the electric field formed by the P-N junction is decreased. It eases carrier diffusion across the depletion region, and leads to increased diffusion current.

Carrier Injection and Forward Bias Current Flow In the presence of an external circuit that continually provides majority carriers, recombination increases which constantly depletes the influx of carriers into the solar cell. This increases diffusion and ultimately increases current across the depletion region.

Reverse Bias Reverse bias occurs when a voltage is applied across the solar cell such that the electric field formed by the P-N junction is increased. Diffusion current decreases.

10.2.4 Diode Equation

The diode equation gives an expression for the current through a diode as a function of voltage. The Ideal Diode Law, expressed as:

$$I = I_0 \left(e^{qV/kT} - 1 \right)$$

where: I = the net current flowing through the diode;
I_0 = "dark saturation current", the diode leakage current density in the absence of light;
V = applied voltage across the terminals of the diode;
q = absolute value of electron charge;
k = Boltzmann's constant; and
T = absolute temperature (K).
The "dark saturation current" is an extremely important parameter which differentiates one diode from another. I0 is a measure of the recombination in a device. A diode with a larger recombination will have a larger I_0.

For non-ideal diodes we get

$$I = I_0 \left(e^{qV/nkT} - 1 \right)$$

where n is the ideality factor, a number between 1 and 2 which typically increases as the current decreases.