ELECTRONIC STRUCTURE
OF
ORGANIC SEMICONDUCTORS
SMALL MOLECULES AND POLYMERS

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FOREWORD

This text is only a draft of some notes on the electronic structure of organic semiconductors for the exclusive use of researchers of the Organic Electronics Group of IT/Lisbon, and part of it was compiled from pre-existing texts, notes and extracts from papers. It should also be noted that this text was written in the perspective of an experimental chemist.

We tried to put together some fundamentals from chemistry, solid state theory and quantum chemistry, to help understanding the electronic and optical properties of organic semiconductors, both small molecules and polymers.

There is an enormous amount of literature concerning these subjects which can be read. We also suggest a visit to the website of the Linz Institute for Organic Solar Cells (LIOS), and download Alan Heeger’s and other remarkable scientists’ lectures on video\(^1\).

http://www.jku.at/ipc/content/e175559/e175566


1. INTRODUCTION

Organic electronics emerged as a technological paradigm as a result of the discovery, in the 1960’s, and subsequent R&D development of organic materials with conducting and semiconducting properties. The subsequent discovery of organic conducting polymers (or plastics) brought many expectations as they represented an important addition to the pervasive world of plastics, which already cover many fields of applications, including solar photovoltaic cells.

The design and synthesis of novel conjugated polymer semiconductors based on the chemical intuition of synthetic chemists has had significant success in the past, but is ultimately timeconsuming due to the nearly limitless number of promising candidate materials. A more rational and more efficient approach consists in the combination of chemical intuition with the application of predictive computational design, based on quantum chemical calculations. The use of such methods to predict the electronic properties offers significant advantages: it is inherently more time and cost-efficient; and it can greatly reduce the number of potential targets for experimental synthesis. An important domain where theory can specifically contribute is the comprehensive prediction of how different chemical functional groups modulate electronic and optical properties in order to ultimately guide the organic synthesis.

\(^1\) Alan Heeger, Hideki Shirakawa and Alan MacDiarmid, Nobel Prize in Chemistry, 2000, for their contributions to the development of conducting polymers.
2. SOME BASIC QUESTIONS IN SOLID STATE PHYSICS

Drude Model

The Drude model of electrical conduction was proposed in 1900 by Paul Drude to explain the transport properties of electrons in metals. In Drude’s model\(^2\) the valence electrons of a metal are independent and free, and the positive ions are fixed in the lattice. In a metal, the nuclei and the core electrons keep their equilibrium positions in the crystal, but the valence electrons separate and move freely as particles in a gas—the *electron gas* (Fig.1).

![Figure 1 Trajectory of a conduction electron which colides with the ions in a metal according to Drude’s model.](image)

In this model all electron-electron and electron-ion interactions are neglected. The electron gas is then considered similar to a common gas and the ideas of thermodynamics’ perfect gas can be used, as well as the kinetic theory, and consequently the concepts of *mean free path*, \(\ell\)—the mean distance between successive collisions; and the *mean free time between collisions*, \(\tau\). The velocity can be derived from the kinetic energy, which in kinetic theory is \(3/2 k_B T\).

When an electric field \(E\) is applied, the electrons, which in the absence of the field move randomly (with a resulting null velocity), drift in the opposite direction to the field with a drift velocity, \(v_d\). According to Ohm’s law, \(R = V/I\), where \(R\) is the electrical resistance, \(V\) is the voltage and \(I\), the current. We can also write

\[
j = \sigma E
\]

where \(j\) is the current density and \(\sigma\), the conductivity. The conductivity is proportional to the electron density, \(n\), (number of electrons per unit volume), the electron charge, \(-e\), and the drift velocity \(v_d\):

\[
j = -nev_d
\]

\(2\) Note that the electron had been discovered just three years before by Joseph Thomson
We can also consider, that the Lorentz force is the reason for the existence of the drift velocity, i.e., \( \mathbf{F} = -e \mathbf{E} = m \frac{d \mathbf{v}_d}{dt} \), or that, (considering average values), \( -e \mathbf{E} = m \frac{\mathbf{v}_d}{\tau} \), and get \( \mathbf{v}_d = -\frac{e \tau}{m} \mathbf{E} \).

Rewriting equation (1) as
\[
\mathbf{j} = -ne \mathbf{v}_d = \frac{ne^2 \tau}{m} \mathbf{E}
\]
we get for the conductivity
\[
\sigma = \frac{ne^2 \tau}{m}
\]
If we consider that the drift velocity is proportional to the field
\[
\mathbf{v}_d = -\mu \mathbf{E}
\]
we can define \( \mu \) as the mobility:
\[
\mu = \frac{e \tau}{m}
\]
Note that the mobility has units of \([\mu] = \left[ \frac{m^2}{V \cdot s} \right] = m^2 V^{-1} s^{-1} \) or \( cm^2 V^{-1} s^{-1} \).

The concept of mobility is very important, even today. It measures how quickly an electron can move through a metal or semiconductor, when pulled by an electric field. It is even usual to keep the concepts defined in this model, for example, introducing the notion of effective mass, \( m^* \), as the mass that an electron appears to have when responding to a field.

If an electron is excited into a higher state it leaves a hole in its old state. This meaning is used in solid state physics and in chemistry. In crystals, electronic band structure calculations lead to an effective mass for the electrons, which typically is negative at the top of a band. The negative mass is an unintuitive concept, and in these situations a more familiar picture is found by considering a positive charge, a hole, with a positive mass.

For electrons or holes in a solid, the effective mass is usually stated in units of the true mass of the electron, \( m_e \) (9.11 × 10\(^{-31}\) kg).

**Can a Conducting Polymer be Transparent?**

To answer that question we have to consider the electronic polarisability and permittivity.

Electrons in a metal under an electric field will be displaced from their equilibrium positions giving rise to a dipole moment
\[
\mathbf{\mu}_i = -e \mathbf{r} = \varepsilon_0 \alpha \mathbf{E}
\]
Where \( \mathbf{r} \) is the displacement and \( \alpha \) the polarizability. \( \varepsilon_0 \) is the electrical permittivity of the vacuum.
On the other hand, the movement equation for the position vector \( \mathbf{r} \) under the field is

\[
m \left( \frac{d^2 \mathbf{r}}{dt^2} + \frac{1}{\tau} \frac{d\mathbf{r}}{dt} \right) = \mathbf{F} = -e \mathbf{E}
\]

(3)

the first term being the acceleration, the second the friction coefficient (proportional to \( 1/\tau \)) and \( \mathbf{F} = -e \mathbf{E} \), the Lorentz force.

In an oscillating field \( \mathbf{E} = \mathbf{E}_0 e^{i\omega t} \) there will be oscillations in \( \mathbf{r} \), of the form \( \mathbf{r} = \mathbf{r}_0 e^{i\omega t} \). Doing the derivatives in equation (3) we obtain

\[
m \left( -\omega^2 + i \frac{\omega}{\tau} \right) \mathbf{r} = -e \mathbf{E}
\]

giving

\[
\mathbf{r} = -\frac{e}{m} \frac{1}{-\omega^2 + i \frac{\omega}{\tau}} \mathbf{E}
\]

In the Drude model, there are \( n \) free electrons with relaxation time \( \tau \), giving a polarization of the form \( \mathbf{P} = n \mu_\mathbf{i} = -n e \mathbf{r} \), or

\[
\mathbf{P} = \frac{n e^2}{m} \frac{1}{-\omega^2 + i \frac{\omega}{\tau}} \mathbf{E}
\]

Considering equation (2), \( \mathbf{P} = n \mu_\mathbf{i} = \varepsilon_0 n \alpha \mathbf{E} \), from which we get

\[
n \alpha = \frac{n e^2}{\varepsilon_0 m} \frac{1}{-\omega^2 + i \frac{\omega}{\tau}}
\]

giving the permittivity,

\[
\varepsilon = \varepsilon_0 \left( 1 + n \alpha \right)
\]

(4)

We have several situations:

For low frequencies \( \omega \ll \frac{1}{\tau} \) (note that \( \tau \approx 10^{-13} \text{ s} \)), gives

\[
\varepsilon = \varepsilon_0 \left( 1 - i \frac{n e^2 \tau}{\varepsilon_0 m \omega} \right)
\]

The \( n \) electrons give the Drude conductivity

\[
\sigma_0 = -\text{Im} \varepsilon(\omega) = \frac{n e^2 \tau}{m}
\]

(5)
For high frequencies $\omega \gg \frac{1}{\tau}$ the $n$ electrons give a permittivity

$$
\varepsilon = \varepsilon_0 \left( 1 - \frac{ne^2}{\varepsilon_0 m \omega^2} \right)
$$

or

$$
\varepsilon = \varepsilon_0 \left( 1 - \frac{\omega_p^2}{\omega^2} \right)
$$

(6)

in which $\omega_p$ is the plasma frequency given by

$$
\omega_p^2 = \frac{ne^2}{\varepsilon_0 m}
$$

(7)

If, in (6), $\omega > \omega_p$, then $\varepsilon > 0$ and real, the metal is transparent. That is the case of alkali metals, which are transparent in the UV. In Fig. 2, we represent $\varepsilon$ as a function of frequency.

Using $\omega = 2\pi \nu$ and $\lambda = c/\nu$, we can calculate the wavelength corresponding to the plasma frequency.

To know if a conductor (with free electrons in Drude’s sense) is transparent or not, we can, in a first approximation, calculate its plasma frequency and see if it is below or above the frequency of the light incident on the material.

When $\omega < \omega_p$, the permittivity is negative and light is totally reflected, since $R \approx 1 - \frac{2n_r}{Re(n_r)}$ with $n_r = \sqrt{\frac{\varepsilon}{\varepsilon_0}}$. Alkali metals (Na, K, etc.) with

---

**Figure 2** Schematic representation of $\varepsilon$ and reflectance $R(\omega)$ as a function of frequency.
\[ n \sim 10^{23} \text{ electrons per cm}^3 (10^{29} \text{ electrons per m}^3) \text{ will give } \omega_p = \sqrt{\frac{ne^2}{\varepsilon_0 m}} \]

values of the order of \(10^{16} \text{ rad/s} \), or \( \lambda_p \approx 100 \text{ nm} \), and since the VIS spectrum is in the range of 380 nm (3.2 eV) to 750 nm (1.6 eV) typical metals reflect VIS light, but are transparent in the UV.

Conjugated polymers, with electron densities of the order of \(2 \times 10^{21}\) to \(4 \times 10^{21} \text{ electrons per cm}^3\), as can be predicted for a polymer chain where there are two electrons per double bond, the situation is completely different. The plasma frequency values, (taking \(n = 2 \times 10^{21}/\text{cm}^3\)) are of the order of \(\omega_p = 2.5 \times 10^{15} \text{ rad s}^{-1}\) and \(\lambda_p = 747 \text{ nm}\), which implies that the wavelength of the plasma is bigger than the wavelength of VIS light (the plasma frequency lies below that that of VIS light) (see figure 2). The polymer is practically transparent in the VIS.

**Sommerfeld Model**

In the Sommerfeld model (1928), quantum mechanics is introduced and the Pauli exclusion principle is considered (implying the Fermi-Dirac distribution).

We can visualize this model in a very simple way, considering a one-dimensional metal. The problem can be solved as the one of a particle in a one-dimensional box: one electron in a chain.

We write the Shrödinger equation

\[
\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi(x) = E \psi(x)
\]

By solving this equation, we get the energy

\[
E = \frac{\hbar^2 k^2}{2m}
\]

where

\[
k = \frac{2\pi}{L} n \quad (n = 1, 2, \ldots)
\]

The wave functions are plane waves

\[
\psi = \frac{1}{\sqrt{L}} e^{ikx}
\]

There are several important ideas (or concepts) in this model, which are still used today.

One is that we can describe the electronic properties of a metal in such a simple model: the energy levels form, for all practical purposes, a continuous
energy band, in which the energy of the electrons can be described by a function of $k$ (eq: 8) (note that $k = 2\pi/\lambda$ where $\lambda$ is the wavelength of the plane waves which describe the electrons movement.)

Other aspects are, for example, the concept of Fermi level as the last occupied level at $T = 0$, and $k_F$ which will define the velocity of the electrons (in this free electron model $\hbar k = p = mv$). In more sophisticated models we will call $k$, the crystal momentum, (which does not give the velocity of the electrons).

A very important aspect is that we can keep the description of the electrons in, for example, a semiconductor, using equation (8) but substituting the mass $m$ by an effective mass $m^*$, which may be a function of $k$, i.e., $m^*(k)$.

Although we could further explore this model to define some other concepts, we will go to a more sophisticated type of description.

3. FROM ORBITALS TO BANDS

Orbitals in a Chain of Atoms

It is trivial knowledge that the electronic structure of the hydrogen molecule H$_2$ can be described, in a first approximation, in terms of molecular orbital theory, using a linear combination of the 1s orbitals of each atom (Fig.4):

$$\psi(\mathbf{r}) = c_1 s_A + c_2 s_B$$

To find the energy values and the coefficients of the linear combination we must solve the eigenvalue equation

$$H \psi(\mathbf{r}) = \varepsilon \psi(\mathbf{r})$$

Which in a basis of the 1s orbitals of the two hydrogen atoms, can be
Figure 4 Electronic Structure of the H$_2$ molecule in terms of molecular orbitals. 

$\varepsilon_s = h_{AA} = h_{BB}$ is the energy of one electron in the $s$ orbital of an hydrogen atom; 

$V = h_{AB} = h_{BA}$ is the transfer or resonance integral.

written, in matrix representation, as

$$[H - S\varepsilon]c = 0$$

Or in expanded notation,

$$\sum_q (h_{pq} - \varepsilon S_{pq}) c_q = 0 \quad (9)$$

where $H$ is the hamiltonian matrix, of elements $h_{pq}$. Matrix $S$, of elements $S_{pq}$, is called the overlap matrix, and will be defined below. This equation has a non trivial solution ($c \neq 0$), if and only if

$$\det(H - \varepsilon S) = 0$$

or

$$\det[h_{pq} - \varepsilon S_{pq}] = 0 \quad (10)$$

Making

$$h_{AA} = h_{BB} = \langle 1s_A | h | 1s_A \rangle = \langle 1s_B | h | 1s_B \rangle = \varepsilon_s$$

$$h_{AB} = h_{BA} = \langle 1s_A | h | 1s_B \rangle = V$$

To simplify, we can make $S = S_{AB} = S_{BA} = \langle 1s_A | 1s_B \rangle = 0$ and $S_{AA} = S_{BB} = \langle 1s_A | 1s_A \rangle = \langle 1s_B | 1s_B \rangle = 1$

and write

$$\begin{vmatrix} \varepsilon_s - \varepsilon & V \\ V & \varepsilon_s - \varepsilon \end{vmatrix} = 0$$
Solving for $\varepsilon$, we get:

\[
\begin{align*}
\varepsilon_1 &= \varepsilon_s + V \rightarrow \text{Ground State} \\
\varepsilon_2 &= \varepsilon_s - V \rightarrow \text{First Excited State}
\end{align*}
\]

Considering that $V < 0$, the energy of the ground state (GS) is $\varepsilon_1$, and that of first excited state is $\varepsilon_2$.

Substituting the values of $\varepsilon$ in equations (9) we get the wave functions which represent the molecular orbitals.

Let us now consider a linear chain of $N$ hydrogen atoms. The wave functions will be of the form

\[\psi(\mathbf{r}) = \sum_i^N c_i u_i\]

We could solve the secular equations to get the energy levels and the orbitals. There will be $N$ energy levels from a lowest value $\varepsilon_s + V$ to a highest value $\varepsilon_s - V$ (note that $V < 0$). We can call $V$ a transfer integral—it is the energy associated with the transfer of one electron between adjacent atoms. There will be $N$ values of $V$ (actually they could be indexed as $V_{i,j>i}$—one for each transfer integral between atom $i$ and atom $j$. Their values will decrease as the distance between atoms $i$ and $j$ increases. In the limit of large $N$, $V_{i,j>i} \rightarrow 0$, as the separation increases (Fig.5).

![Electronic Structure of the H$_N$ chain](image)

**Figure 5** Electronic Structure of the H$_N$ chain; $\psi(\mathbf{r}) = \sum_i^N c_i u_i$: energy band.

If we now consider that each hydrogen atom contributes with one electron, there will be $N$ electrons in the chain, and they will occupy (at $T = 0$) the lowest $N/2$ energy levels.

In the limit of large $N$ the separation between energy levels will become smaller and smaller—they will become dense, almost as in a continuum, and form, what is called an energy band.
Since the band is half filled, the chain of hydrogen atoms will become a metal—an electron in the highest occupied level (Fermi level) will easily move (acquire some kinetic energy) when an electric field is applied, since there are very close empty levels available. In fact there are reports on the probable existence of metallic hydrogen, under extreme conditions of pressure and low temperatures.

4. BAND THEORY

Electrons in a Periodic Potential. Bloch Theorem

The translational symmetry of finite crystal lattices requires some conditions for the states of the electrons moving in such lattices. In an independent electron approximation, (e.g., mean field) these conditions are satisfied by the use of a monoelectronic effective potential \( V(r) \) of spherical symmetry. The choice of the form of such an effective potential is a complex matter. At this stage, we will consider, that whatever its detailed form, in a perfect crystal lattice, it must satisfy a condition of translational symmetry

\[
V(r + T) = V(r)
\] (13)

for any translation \( T \) of the lattice. From this fact, we can immediately draw some important conclusions.

Qualitatively, a typical potential will have a form such as the one represented in fig. 6. The periodicity of the crystal potential implies some general properties for the one electron Schrödinger equation

\[
-\frac{\hbar^2}{2m} \nabla^2 + V(r) \psi(r) = E \psi(r)
\] (14)

The independent electrons, which individually satisfy the monoelectronic Schrödinger equation (14), with a periodic potential, are called Bloch electrons, as opposed to free electrons for which \( V(r) = 0 \).
The Bloch theorem\(^3\) shows that the wave function for an electron in the crystal can be chosen as a product of a plane wave \(e^{i\mathbf{k}.\mathbf{r}}\), with an appropriate function (e.g., an orbital) \(u_{nk}(\mathbf{r})\) with the periodicty of the lattice (Fig. 7):

\[
\psi_{nk}(\mathbf{r}) = u_{nk}(\mathbf{r}) e^{i\mathbf{k}.\mathbf{r}} \tag{15}
\]

\[
u_{nk}(\mathbf{r} + \mathbf{T}) = u_{nk}(\mathbf{r}) \tag{16}
\]

The \(\psi_{nk}(\mathbf{r})\), functions which can also be written as \(|\mathbf{k}\rangle\), as in equation (15) are called Bloch functions. The subscript \(n\) is a quantum number which represents each of the many solutions of the Schrödinger equation.

\[u(\mathbf{r})e^{i(\mathbf{k}.\mathbf{r})}\]

\[|\mathbf{k}\rangle\]

\[\psi(\mathbf{r})_{nk} = |\mathbf{k}\rangle.\]

A Bloch electron is represented by a plane wave modulated by the periodicity of the crystal lattice.

**Figure 7** Representation of the wave functions \(u_{k}(\mathbf{r})\), plane wave, \(e^{i(\mathbf{k}.\mathbf{r})}\) and crystalline wave function, \(\psi(\mathbf{r})_{nk} = |\mathbf{k}\rangle\). A Bloch electron is represented by a plane wave modulated by the periodicity of the crystal lattice.

**Bloch Theorem:** The nondegenerate solutions of the Schrödinger equation (14), \(\psi_{nk}(\mathbf{r})\), and appropriate linear combinations are also eigenfunctions of the translation operator \(\mathbf{T}\) with eigenvalues \(e^{i\mathbf{k}.\mathbf{T}}\).

In other words, the eigenstates of the hamiltonian \(H = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r})\) in which \(V(\mathbf{r}) = V(\mathbf{r} + \mathbf{T})\) for all \(\mathbf{T}\) (in a Bravais lattice) can be chosen as a product of a plane wave and a function with the periodicity of the lattice (equations 15 and 16).

Note that this expressions implies

\[T\psi_{nk}(\mathbf{r}) = \psi_{nk}(\mathbf{r} + \mathbf{T}) = e^{i\mathbf{k}.\mathbf{T}} \psi_{nk}(\mathbf{r})\]

in agreement with Bloch Theorem.

The wave vector $k$ is given by the expression

$$k = \frac{m_1}{N_1} \mathbf{g}_1 + \frac{m_2}{N_2} \mathbf{g}_2 + \frac{m_3}{N_3} \mathbf{g}_3$$  \hspace{1cm} (17)$$

in which $\mathbf{g}_1$, $\mathbf{g}_2$, $\mathbf{g}_3$ are the basis vectors of the reciprocal lattice (which define the Brillouin zone, i.e., the primitive cell in reciprocal or $k$ space); $N_1$, $N_2$, $N_3$, the number of primitive cells along its axis $a$, $b$, $c$, respectively; and $m_1$, $m_2$, $m_3$ are integers in the range $[-\frac{N_1}{2}, \frac{N_1}{2}]$.

The Bloch Theorem introduces a wave vector $k$ which has a role similar to that of the wave vector of the free electrons in the Sommerfeld model. However, for Bloch electrons, $k$ is not proportional to the momentum $p$ as for free electrons for which $k = p/h$ with $p = mv$.

The wave vector $k$ for Bloch electrons (electrons in a periodic potential) is called the \textit{crystal momentum} and, for our purposes, it is just an index characteristic of the translational symmetry associated to the quantum numbers $m_1$, $m_2$, $m_3$.

The index $n$ appears in these equations because there are many solutions of the Schrödinger equation for each $k$. In fact, if we take $\psi(r) = u(r) e^{i k \cdot r}$ in which $k$ is fixed and $u(r)$ has the periodicity of the lattice, and substitute in the Schrödinger equation, we can see that $u(r)$ is determined by an eigenvalue equation of the form

$$H_k u_k(r) = E_k u_k(r)$$  \hspace{1cm} (18)$$

with the condition $u_k(r) = u_k(r + T)$.

We can therefore consider equation (18) as an eigenvalue equation relative to the primitive unit cell of the crystal. Since this equation refers to a given volume, we expect an infinite set of solutions with discrete eigenvalues $E_k$, with index $n$ as in the problem of the electron in a box.

Note that in equation (18), $k$ appears only as a parameter in the hamiltonian $H_k$. It is therefore expected that for a given $k$, each energy level $E_k$ will vary continuously with $k$. In this way, we arrive at a description of the energy levels for an electron in a periodic potential in terms of a family of continuous functions $E_n(k)$. The fact that $m_1$, $m_2$, $m_3$ are integers in the range $[-\frac{N_1}{2}, \frac{N_1}{2}]$ for $m_1$, etc. does not affect the continuity of $E_n(k)$ as a continuous function of $k$, since no reference is made to the size of the crystal and it is well defined for any value of $k$. It should be noted that the set of the $k$ values becomes dense in $k$ space, in the limit of an infinite crystal. Since a real macroscopic crystal has of the order of $10^{23}$ atoms or molecules, it can be considered infinite in this context.

The complete set of energy levels of a crystal can be described in terms of $k$ restricted to the Brillouin zone.
The energy levels of an electron in a periodic potential is then described in terms of a family of continuous wave functions $E_{n,k}$ or $E_n(k)$. The information content of these wave functions is called the band structure of the solid.

For each value of $n$, the set of levels specified by $E_n(k)$ is called an energy band. The energy of each state, $E_{n,k}$, can be calculated by the expression

$$E_{n,k} = \frac{\langle n|H|n\rangle}{\langle n|n \rangle}$$  \hspace{1cm} (19)

In figure 8a) we represent $E_{1,k}$, $E_{1,k+G}$, $E_{1,k-G}$ and $E_{2,k}$ (where $G$ is a vector of the reciprocal lattice, or $k$ space, of the form $G = h\mathbf{g}_1 + k\mathbf{g}_2 + \ell\mathbf{g}_3$, $h, k, \ell$ being the Miller indexes) in the extended zone representation (with all $k$ values). It is easily seen that $E_{n,k+G} = E_{n,k}$. In b) we show the reduced band representation, which corresponds to the first Brillouin zone (or simply the Brillouin zone).

**Figure 8** Typical representation of the energy bands of a crystal. The different energy bands, $E_n(k)$, can be identified by the index $n$. a) Representation of $E_n(k)$ in the extended scheme along $k_x$. The $E_{1,k}$, $E_{1,k+G}$, $E_{1,k-G}$ and $E_{2,k}$ bands are shown. It can easily be seen that $E_{n,k+G} = E_{n,k}$. b) Reduction to the first Brillouin zone. Since $E(k) = E(-k)$, we can represent the energy bands for positive values of $k$ alone.

Since $E(k) = E(-k)$, the bands can be represented for positive $k$ only—the representation for both $k$ and $-k$ is redundant and $k$ stays in the Brillouin zone.

It is convenient to introduce the notion of density of states, as the number of states per unit of energy at each energy level that are available to be occupied by electrons:

$$D(E) = \frac{dN}{dk} \frac{dk}{dE} \propto \frac{1}{dE/dk}$$

and that of effective mass as follows:
If we take the expression for the energy as $E(k) = \frac{\hbar^2 k^2}{2m^*}$, and do the second derivative, we get

$$\frac{dE}{dk} = \frac{\hbar^2 k}{m^*} \rightarrow \frac{d^2E}{dk^2} = \frac{\hbar^2}{m^*}$$

(20)

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2E}{dk^2}$$

(21)

which gives the effective mass in terms of the curvature of the energy bands.

**Energy Bands as Linear Combinations of Orbitals**

Our purpose is to solve the problem of an electron in a periodic potential. A general approximation consists in taking a basis of known functions, (e.g., orbitals), allow some perturbations (e.g., a mixture of simple basis functions) and, finally, get diagonalizable matrices to obtain the eingenvalues of the energy.

A first simplification consists in considering basis functions which satisfy Bloch theorem, in order to reduce the problem to just one value of $k$. We could even choose plane waves. For our purposes it is better to consider linear combinations (LC) of basis functions, such as atomic or molecular orbitals (which can be themselves LC of atomic orbitals). This approximation is generally good if we choose an appropriate set of basis functions. If the basis is a set of atomic orbitals this approximation is generally called the *tight binding* approximation and was historically used to describe the core electrons.

The LC method is conceptually very simple and is based on the idea that the crystal wave function can be a linear combination of, for example, its atomic orbitals. It is also a monoelctronic method (mean field). This means that the calculation is based of the idea that there is only one electron in the crystal and that it feels a mean field due to all other electrons. The wave functions describe the various possible states of such an electron. Once the band structure calculation is done, it is acceptable to fill the bands with the total number of electrons of the crystal. All interactions are included in the mean field potential.

Let us consider a crystal with $N$ cells and only one atom (with only one orbital) per primitive cell.

The wave function of the crystal is of the form

$$\psi(r) = \sum_{i=1}^{N} c_i \phi(r - R_i)$$

(22)

where the $c_i$ are the coefficients of the linear combination and $\phi(r - R_i)$ the individual atoms (and respective orbital) in their positions $R_i$. 
We know that the wave functions $\psi(r)$ has to satisfy the Bloch theorem:

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

which enables a choice for the $c_i$ coefficients to be of the form

$$c_i = \frac{1}{\sqrt{N}} e^{i\mathbf{k} \cdot \mathbf{R}_i} \quad \text{(23)}$$

where $\frac{1}{\sqrt{N}}$ is a normalization factor.

If we solve equation (19) by a variational method we obtain $N$ solutions for the energy, $E_k$, and $N$ wave functions $\psi_k(r)$.

It is probably easier to use a matrix representation and write $\Psi$ as a matrix whose $N$ columns are the $N$ solutions, i.e.:

$$\Psi = \Phi \mathbf{C} \quad \text{(24)}$$

in which $\Psi = (\psi_1 \ldots \psi_q \ldots \psi_N)$

$$\Phi = \begin{pmatrix} \phi_1 & \ldots & \phi_i & \ldots & \phi_N \end{pmatrix}$$

$$\mathbf{C} = \begin{pmatrix} c_1 & \ldots & c_q & \ldots & c_N \end{pmatrix} = (c_{iq})$$

$$\mathbf{c}_q = \begin{pmatrix} \vdots & \vdots & c_{iq} & \vdots & \vdots \end{pmatrix}$$

The energy values can be obtained by diagonalization of the matrix

$$\langle \Psi | H | \Psi \rangle = E \quad \text{(25)}$$

of diagonal elements $E_{qq}$.

Substituting (24) in (25) one obtains

$$\mathbf{C}^\dagger \langle \Phi | H | \Phi \rangle \mathbf{C} = E$$

or

$$\mathbf{C}^\dagger \mathbf{H} \mathbf{C} = E \quad \text{(26)}$$

with

$$\mathbf{H} = \langle \Phi | H | \Phi \rangle \quad \text{(27)}$$
and \( \mathbf{C}^\dagger = (c_{qi}^*) \); \( \mathbf{H} = (H_{ij}) \); \( \mathbf{E} = (E_{qq}) \).

Following the usual convention for matrix multiplication (line×column) in (26), and starting from right to left, one obtains \( \mathbf{H} \mathbf{C}^\dagger = \mathbf{H}' = (H_{iq}') \), with \( H_{iq}' = \sum_j^N H_{ij} c_{jq} \) which one multiplies on the left by \( \mathbf{C}^\dagger = (c_{qi}^*) \) giving directly the \( N \) elements \( E_{qq} \) of the diagonal matrix \( \mathbf{E} \).

\[
E_{qq} = \sum_i^N c_{qi}^* H_{iq}' = \sum_i^N \sum_j^N c_{qi}^* c_{jq} H_{ij}
\]

(28)

Substituting (23) in (28), one obtains

\[
E_{qq} = \sum_i^N \sum_j^N \frac{1}{N} e^{i\mathbf{k}(\mathbf{R}_j - \mathbf{R}_i)} H_{ij} = \sum_i^N \frac{1}{N} \sum_j^N e^{i\mathbf{k}(\mathbf{R}_j - \mathbf{R}_i)} H_{ij}
\]

Or, considering orbital \( i \) and extending the sum to all its neighbors, including itself \( (j = i) \):

\[
E_{qq} = \sum_j^N e^{i\mathbf{k}(\mathbf{R}_j - \mathbf{R}_i)} H_{ij}
\]

with \( \mathbf{R}_j - \mathbf{R}_i \) as the distance vectors of orbital \( j \) to orbital \( i \).

Note that, as mentioned above, the set of all discrete values of \( \mathbf{k} \) becomes dense in the limit of an infinite crystal, allowing the identification of the set of eigenvalues \( E_{qq} \equiv E_\mathbf{k} \) with the functions \( E(\mathbf{k}) \):

\[
E(\mathbf{k}) = \sum_j^N e^{i\mathbf{k}(\mathbf{R}_j - \mathbf{R}_i)} H_{ij}
\]

one for each \( i \)

(29)

One can, therefore, conclude that in the case of \( N \) primitive cells (one atom, one orbital per cell), the diagonalization of the (25) matrix leads us to energy bands, \( E(\mathbf{k}) \), of the form (29), which depends on the distances between atoms (where the orbitals are located) and on the \( H_{ij} \) integrals.

The matrix elements \( H_{ij} \) are the Coulomb integrals (if \( i = j \)) and the transfer integrals (if \( i \neq j \)):

\[
H_{ij} = \langle \phi_i | H | \phi_j \rangle = \int \phi^*(\mathbf{r} - \mathbf{R}_i) H \phi(\mathbf{r} - \mathbf{R}_j) d\tau
\]

(30)

More precisely, the Coulomb integrals are of the form

\[
H_{ii} = \langle \phi_i | H | \phi_i \rangle = \int \phi^*(\mathbf{r} - \mathbf{R}_i) \left[ -\frac{\hbar^2}{2m} \nabla + V(\mathbf{r}) \right] \phi(\mathbf{r} - \mathbf{R}_i) d\tau
\]

(31)
If $V(r)$ were the exact atomic potential and $\phi_i$ an exact atomic orbital, this term would give the atomic energy $\varepsilon_0$ (the energy of the orbital in an isolated atom). Note, however, that the atomic orbitals in (22) are not the isolated atom orbitals since in a crystal the local wave functions (those which should be in 22) are not the exact wave functions of the isolated atom. The exact local wave functions should be of the form

$$\phi_i = \phi(r - R_i) = \frac{1}{\sqrt{N}} \sum_k e^{-i k R_i} |\psi_k\rangle$$  (32)

obtained by inverting expression (22) and considering that the $c_i$ are given by (23).

The functions (32) are called Wannier functions and can be obtained by self-consistent methods. In practice one can use several types of approximations which enable band calculations by the LC method with a desired approximation (and corresponding difficulty). For the time being, $H_{ii} = \varepsilon_i$, considering that one can obtain its value by means of a calculation or from databases.

The integrals $H_{ij} \neq j$ are of the form

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle = \langle \phi_i | -\frac{\hbar^2}{2m} \nabla + V(r) | \phi_j \rangle$$

$$= \varepsilon' \langle \phi_i (r - R_i) | \phi_j (r - R_j) \rangle + \langle \phi_i (r - R_i) | V(r) | \phi_j (r - R_j) \rangle$$  (33)

The first term includes the overlap integral $\langle \phi_i (r - R_i) | \phi_j (r - R_j) \rangle$. Note that it is the overlap of two wave functions centred at $R_i$ and $R_j$, respectively. In principle, they can be calculated, although not always easily. Anyway, their values are only meaningful if $i$ and $j$ are sufficiently close; they are practically zero for far away neighbours.

The second term is a transfer integral and corresponds to the energy associated with the transfer of the electron between orbitals centred at $R_i$ and $R_j$. The integrals between close neighbours are the most relevant. In a first approximation, it is reasonable to neglect all overlap integrals and transfer integrals between far away neighbours, keeping only

$$H_{ij} = \langle \phi_i (r - R_i) | V(r) | \phi_j (r - R_j) \rangle = V_{ij}$$  (34)

In the following we will give some simple examples.

Energy Bands in a One Dimensional Crystal

One atom per unit cell
Let us consider a one-dimensional crystal of lattice parameter $a$, with an atom per unit cell (Fig.9), and take only one $s$ type orbital of each atom to build
the linear combination. A real system would be a linear chain of hydrogen ions, \( H^+ \), and just one electron which can move along it.

Note that the calculation is made, starting from the hypothesis that there is only one electron in the whole crystal and that the wave functions describe the various possible states of such electron. Once the energy band calculation is done, it is acceptable to occupy the states of the bands with the total number of electrons of the crystal, putting two electrons in each state. All interactions are included in the mean field potential. In our calculation, we will neglect all overlap integrals and take only the exchange integrals between adjacent (first) neighbours.

Expression (29) gives \( E(k) \) directly

\[
E(k) = \sum_{j} e^{i\mathbf{k} (\mathbf{R}_j - \mathbf{R}_i)} H_{ij}
\]

In the first neighbour approximation one considers

\[
H_{ii} = \varepsilon_0 \quad \text{(Coulomb integral)}
\]

\[
H_{i,i\pm1} = V \quad \text{(transfer integral)}
\]

The Coulomb integral is the energy of the electron in the orbital and the transfer integral is the energy required to transfer the electron from one orbital to one of its first neighbours, \( i + 1 \) or \( i - 1 \). The integrals between far away neighbours are neglected: \( H_{i,j':|i|+1} = 0 \). Making the corresponding substitutions, one obtains

\[
E(k) = e^{i\mathbf{k}a} V + \varepsilon_0 + e^{-i\mathbf{k}a} V = \varepsilon_0 + 2V \cos(ka)
\]

\[
k = \frac{2\pi}{Na}; \quad m = \frac{-N}{2}, 0, \frac{N}{2}
\]

which is represented in figure 10. On the right hand side, the free electron band is represented for comparison. Such a comparison may help getting the orders of magnitude of the transfer integrals and its dependence on the
distance between atoms.

This band structure would be typical of, for example, a linear chain of hydrogen atoms, each with its electron. There will then be \( N \) electrons to occupy the \( N \) states in the energy band. Since each state can be occupied by two electrons, (with antiparallel spins), the band will be half filled at zero temperature \((T = 0)\), and this chain would correspond to the electronic structure of a one-dimensional metal\(^4\).

**Two atoms per unit cell**

If one considers two identical atoms per primitive cell (e.g., by dimerization of the previous chain), and therefore with two orbitals per cell, as shown in figure 11a) one will have to consider two distinct transfer integrals, \( V_1 \) and \( V_2 \).

\[
\begin{align*}
H_{i,j} &= -V_1 \\
H_{j,i+1} &= -V_2
\end{align*}
\]

with \( V_1 > V_2 \).

Writing down and solving the corresponding equations (29) for this case, one gets the band structure which is represented in figure 11b). Note that from equation (29) we would have to consider the diagonalization of a two by two matrix for various values of \( k \) from \( k = 0 \) to \( k = \pi/2a \) to obtain the energy bands.

In the case of a chain of hydrogen atoms with two atoms per cell one fills

---

4) Metallic hydrogen in the liquid state has been reported in 2011, at static pressures of 260–300 GPa, but such claim has been questioned.
Figure 11  a) Representation of a linear chain (one-dimensional solid) with two atoms (with one orbital each) per unit cell, of length \( b = 2a \) (lattice parameter). This situation can be considered as the dimerization of the equally spaced linear chain of atoms (Fig. 9). b) Since the primitive cell doubled, \( b = 2a \), the new Brillouin zone is halved—the new boundaries being \( \pm \pi/2a \),—there will be two energy bands separated by an energy gap.

the first band, at \( T=0 \). This would correspond to the electronic structure of a one-dimensional semiconductor.

Instabilities in One-dimensional Solids. Peierls Transition

For a deeper study of this subject we recommend the review article of D. Jérome e H. J. Schulz: D. Jérome and H. J. Schulz, "Organic Conductors and Superconductors", Advances in Physics, 51:1, 293-479; http://dx.doi.org/10.1080/00018730110116362

In solids of extreme anisotropy, such as observed in organic conductors and semiconductors, both in molecular materials and in conjugated polymers, the electron-electron interactions mediated by phonons give rise to structural instabilities and phase transitions, of metal-insulator type and spin transitions, as well as appearance of superconductivity. The formalism to treat these instabilities is essentially identical to that of superconductivity, and all these are critical phenomena that can be treated within a common formalism.

In quasi one-dimensional solids, the ion-ion, electron-electron and electron-phonon interactions can be very different for different directions in the crystal. Most organic conductors and semiconductors, including small molecule solids and polymers fall in this category.

The anisotropy in the properties of these solids can reach very high values. For example, the conductivity can be \( 10^3 \) or \( 10^5 \) times higher along a chain, in which there are \( \pi - \pi \) interactions between stacked molecules, or along conjugated polymer chains.

In a strictly one-dimensional (1D) solid there are several instabilities, which make these systems very rich on the point of view of their physics and chemistry:

- In the presence of electron-phonon interactions, the ground state is unstable relative to the appearance of charge density waves, CDW, or spin
density waves, SDW (*Peierls instabilities*). This instability competes with superconductivity—BCS instability.

- In a 1D system with short range interactions, the thermal fluctuations destroy long range order at \( T > 0 \).
- An arbitrary small quantity of desordem may induce electron localisation and transform a 1D metal into an insulator.

In quasi-1D metals, at low \( T \), the elastic energy cost to modulate the lattice is less than the gain in conduction electron energy, so the CDW state is the ground state. In these conditions it is common to see the opening of a gap in the energy band at \( k = k_F \), as represented in Fig. 12.

![Peierls transition](https://example.com/peierls_transition.png)

**Figure 12** Peierls transition. In a 1D metal, at low temperature, the lowering in the electronic energy is bigger than the elastic (phonon) energy and the band opens a gap at \( k = k_F \). If \( k_F = a/2\pi \) the opening of the gap leads to a dimerization of the lattice.

This leads to a phase transition called the Peierls transition—it was predicted by Rudolf Peierls\(^5\).

Most of the organic semiconductors of technological interest (both small molecules and polymers) are already in a state below the Peierls transition temperature and that is why they are semiconductors—they have a gap, and the conduction band is separated from the valence band (Figs. 13 to 16).

A molecule of interest is pentacene which is commonly used in thin films, Figs. 15 and 16. In both cases there are two molecules per unit cell. Note that the molecules are arranged in stacks and the \( \pi - \pi \) interaction between adjacent molecules in the stacks is responsible for the semiconducting behaviour.

### 5. ELECTRONIC STRUCTURE OF CONJUGATED POLYMERS

Although there is some controversy concerning the applicability of band theory to conjugated polymers, the theory is of great help to understand

Figure 13 a) Stacking of molecules along a chain, where the arrow represents the Peierls transition—with dimerization of the lattice. $V_1$ and $V_2$ represent the transfer integrals; $V_1 > V_2$. b) Polyacetylene, is a semiconductor with a gap, generated by the Peierls instability. The lattice is distorted and the single bonds are slightly longer than the double bonds—dimerization occurred.

Figure 14 Unit cell for (CH)$_x$ in the P21/a space group. The chain direction is along the $a$ axis. The P21\n cell is obtained by translating the central chain along $g$ by $c/2$. Ref: Solid State Communications, Vol. 83, No. 3, PP. 179-183, 1992

Figure 15 Pentacene crystal structure. a) Electron-density projection along the $b$-axis. b) Projection of the structure along [010]. Ref: Acta Cryst. (1961). 14, 705
the properties of such materials. The argument comes from the fact that conjugated polymers are, in general, non-crystalline and soft, and it is common to talk only about density of states. In fact, the density of states is an observable, in general, more accessible than the energy bands, and for non-crystalline solids more reliable, when it can be measured. In any case, the concept of energy band, as a set of a great number of very close energy levels—almost a continuum—, it is of great convenience, and of common use, especially among physicists. Chemists, and especially spectroscopists, prefer, generally, to talk about energy levels, especially the frontier levels—the HOMO and the LUMO. In a solid, there are always bands, larger or narrower, depending on the degree of delocalization. It is, in the end, a question of language, and we will use one or the other, according to convenience.

Conjugated polymers are linear chains in which the interactions along the chain are dominant, while the interactions between chains are of less importance, negligible, in many contexts, and considered as perturbations in quantum calculations.

In this context, it is common to consider a conjugated polymer as a one-dimensional solid. In the end of the 1960s and during the 1970s, a great number of one-dimensional materials came into being, both molecular crystals (or charge transfer), and polymers.

We will now introduce the use of band theory in conjugated polymers.

**Energy Bands in Conjugated Polymers**

The problem of the band structure calculation in a solid with several atoms per primitive cell, can always be reduced to the diagonalization of a matrix
\( H \) of dimension \( sN \times sN \) in which \( s \) is the number of orbitals per cell which are considered and \( N \) is the number of cells in the crystal. The matrix \( H \) is reducible to \( s \times s \) blocks of sub-matrices \( N \times N \), and considering that \( H_{k'k}^{ij} = 0 \) for \( k' \neq k \), we can write:

\[
H = \begin{pmatrix}
H(k)^{11} & H(k)^{12} & \cdots & H(k)^{1s} \\
H(k)^{21} & \cdots & \cdots & \cdots \\
\cdots & \cdots & \cdots & \cdots \\
H(k)^{s1} & \cdots & \cdots & H(k)^{ss}
\end{pmatrix}
\]

(35)

where \( k \) acts as a parameter, and each block can be reduced to a continuous function of the form \( H_{\alpha\beta}(k) \):

\[
H_{\alpha\beta}(k) = \sum_{j} e^{i k (R_j - R_i)} H_{ij}
\]

(36)

Identical to equation (29).

The indexes \( \alpha \) and \( \beta \) refer to various orbitals in the cell (\( \alpha, \beta = 1, 2\ldots s \)), \( R_i \) and \( R_j \) refer to the positions of the atoms to which the \( \alpha \) e \( \beta \) orbitals are associated. Note that \( H_{\alpha\beta}(k) \) depends only on the distances \( (R_j - R_i) \) and on the nature of the orbitals. The number of orbitals to be considered depends on the approximation we choose.

To calculate the energy bands, \( E(k) \), we just have to diagonalize the matrix \( s \times s \) of elements \( H_{\alpha\beta}(k) \). We will obtain \( s \) energy bands of the form \( E_n(k) \) where \( n = 1, 2, \ldots s \).

We can now apply these concepts to some conjugated polymers, like polyacetylene and poly(p-phenylene vinylene), PPV.

**Energy Bands in Polyacetylene**

Firstly, we have to choose the basis for the linear combinations. In conjugated polymers, usually the carbon atoms are held by \( \sigma \) chemical bonds involving the three \( sp^2 \) hybrid orbitals, with one electron each, and a \( \pi \) bond involving the \( p_z \) orbital which keeps one electron (Fig. 17).

In polyacetylene, \((CH)_x\), the \( sp^2 \) hybrid orbitals will form the backbone of the chain, with two of the orbitals making the bond to the adjacent carbon atoms and the third orbital forming the bond to the hydrogen atom. The \( p_z \) orbitals of adjacent carbons will combine to form the \( \pi \) bonds (Fig.18).

In a naive view of the problem, we could be led to consider polyacetylene \((CH)_x\) with equal bond lengths (one CH unit per unit cell). In a band structure calculation the \( \sigma \) orbitals would give a full \( \sigma \) band, and the \( p_z \) would give a half-filled \( \pi \) band since there would be only one \( p_z \) orbital per cell. It would then be expected polyacetylene to be a metal. This is not true as we know,
Figure 17 The carbon atom has the electronic configuration \([1s^2 2s^2 2p^2]\). In conjugated polymers the two \(p\) orbitals in the \(xy\) plane (i.e., \(p_x\) and \(p_y\)) will combine with the \(2s\) orbital to give an \(sp^2\) hybridization—three directed bonds at angles of 120º, with one electron each—, leaving the \(p_z\) orbital with one electron.

Figure 18 a) Electronic structure of a polyacetylene chain with single and double bonds of slightly different bond lengths. b) Hybrid \(sp^2\) and \(p_z\) orbitals, which are a basis for the linear combinations to form the energy bands. c) and d) HOMO and LUMO orbitals.

although we can get highly conducting poliacetylene when it is doped \(^6\).

In trans-polyacetylene, the C—C bond lengths are not exactly equal as described above. In a first approximation we could consider that there are two (CH) units per cell, and calculate the \(\pi\) energy bands of type

\[
E_k = \pm \sqrt{\varepsilon_k^2 + \Delta^2} \quad \varepsilon_k = 2t \cos ka
\]

Since there is one electron per CH unit and therefore two electrons per cell, band \(\pi\), the valence band is full, and band \(\pi^*\) (conduction band) is empty.

Fig. 19 show a schematic representation of the energy bands of polyacetylene and the density of states.

\(^6\) For a long time polyacetylene was thought to be a metal, which led researchers to purify it as much as possible, but, contrary to expected, the higher the degree of purity, the more insulating it would become. In a happy chance of serendipity, a student from Professor Shirakawa group polymerised acetylene with a thousand times more catalyst than usually, and obtained a conducting and golden film on the walls of the reactor. Later on, Shirakawa collaborated with Alan J. Heeger and Alan MacDiarmid, and in 1976, they discovered that the oxidation of polyacetylene with iodine increased the conductivity by a factor of \(10^8\). For the discovery, the three professors got the Nobel Prize in Chemistry, in 2000. The student is an illustrious unknown.
**Figure 19** Left: Band structure of polyacetylene, showing the $\sigma$ and $\sigma^*$ bands, which result from the combination of the $sp^2$ hybrids, and the $\pi$ and $\pi^*$ resulting from the combination of the $p_z$ of each carbon atom. Center: $\pi$ and $\pi^*$ as a function of $k$. Right: Density of states relative to the $\pi$ and $\pi^*$ bands.

In figure 20 the results of 1D trans-(CH)$_x$ ETB (Extended Thigh Binding—LCAO) calculations are compared for three different carbon-carbon bond lengths. For the uniform bond length case shown in a), the Fermi level passes through the degeneracy point at the zone edge and the system is intrinsically metallic.

**Figure 20** Band structure of trans-(CH)$_x$ for different carbon-carbon lengths: a) uniform (1.39 Å); b) early alternating (C=C: 1.36 Å, C—C: 1.43 Å); and c) strongly alternating (C=C: 1.34 Å, C—C: 1.54 Å). Note the lifting of the degeneracy at $Y$ as bond alternation occurs. Ref: P.M. Grant and P. Batra, "Band Structure of polyacetylene, (CH)$_x", Solid State Comm. Vol 29, (1979) pp. 225-229.

**Energy Bands in PPV**

The band structure of PPV (poly(p-phenylene vinylene)), can be considered as the superposition of the bands of benzene and those of ethylene (Fig. 21).
Since there are $8 \pi$ electrons per cell, the four first bands are full.

![Graph showing band structure of benzene and PPV](image)

**Figure 21** The band structure of PPV can be considered as the superposition of the bands of benzene with those of ethylene. a) Band structure of benzene. b) Band structure of PPV.

The electronic spectrum of PPV (Fig. 22) can be understood with the help of the band structure. As in a molecule, the spectrum is due to transitions between the ground state and the first excited states. In the scheme of figure 21, these transitions are vertical, starting from the lower energy separation, which corresponds to $k = 0$ (the optical gap), and extending up to the highest values of the separation between the two bands.

![Graph showing absorption spectra](image)

**Figure 22** The VIS/UV spectra of PPV can be understood with the help of the band structure (Fig. 21). It is due to vertical electronic transitions from the valence band (D1) to the conduction band (D1*), starting from the lowest energy, corresponding in this case to the optical gap ($k = 0$) up to the highest energy values separating the energy bands, along the Brillouin zone. a) Onset of absorption at the optical gap vs. frequency. b) Onset of absorption at the optical gap vs. wavelength as in the spectra on c).
6. COMPUTATIONAL METHODS

There are many computational methods for the calculation of energy levels and orbitals in molecules, as well as for energy bands in solids. Here we will mention briefly the general principles which support computational methods, based on the Hartree-Fock approximation and on the density functional theory (DFT). We will consider the electronic structures of molecules first, and then that of solids.

Hartree-Fock theory

In the Hartree-Fock approximation, the interactions of each electron with all the other $N - 1$ are reduced to a mean field potential, $V(r)$, which depends only on its own coordinates (Fig. 23).

![Figure 23](image-url) In the Hartree-Fock approximation, the interactions of each electron with all the other $N - 1$ are reduced to a mean field potential, $V(r)$, which depends only on its own coordinates. In the figure, $r$ are the electrons coordinates, and $R$ are the coordinates of the nuclei. $r_1$ are the coordinates of the electron in orbital $i$ and $r_2$ are the coordinates of the electron in orbital $k$. Electrons 1 and 2 exchange through the exchange operator $K$.

In the Hartree-Fock theory of many-electron systems, the occupied orbitals are the only orbitals physically relevant; but since we usually obtain the occupied orbitals from some kind of eigenvalue equations which give us more orbitals than needed to accommodate the electrons of the system, we have the so-called virtual orbitals. In many cases, they have no use and accordingly they are simply ignored.

There are certain cases, however, in which we do need to use those virtual orbitals resulting from the Hartree-Fock eigenvalue equation. Among them are the configuration interaction calculations and the perturbation calculations based on the Hartree-Fock solutions.

The Hartree-Fock method is based on the one-electron equations

$$ f \chi_a = \varepsilon_a \chi_a $$

$$ [a = 1, 2, ..., n] \quad (37) $$

where $f$ is the Fock operator. $\chi_a$ are the spin orbital functions which are the product of the spatial wave functions $\psi_a(r)$ with the spin functions $\sigma_a(\omega)$:

$$ \chi_a(x) = \psi_a(r)\sigma_a(\omega) $$
For the general case of a system of $N$ electrons and $M$ nuclei, and noting
that the sum extends to all *occupied spin orbitals* (occso), we have for the
Fock operator

$$f = h + \sum_{b=1}^{\text{occso}} (J_b - K_b)$$  \hspace{1cm} (38)$$

with\(^7\) $h = -\frac{1}{2} \nabla^2 + \sum_A^M \frac{Z_A}{|r - R_A|}$, in which the first and second terms are the
kinetic and the attractive electron-nuclei potential, respectively. $J$ and $K$ are
the Coulomb and exchange integrals:

$$J_b = \int |\psi_b(r_2)|^2 \frac{1}{r_{12}} d\tau_2$$  \hspace{1cm} (39)$$

$$K_b = \int \psi_b^*(r_2) \psi_a(r_2) \frac{1}{r_{12}} d\tau_2$$  \hspace{1cm} (40)$$

Note that in these integrals, and since we consider the interactions of each
electron with each one of the others, it is common to designate electron 1, of
coordinates $r_1$, the electron which ”is” in the reference position, and electron
2, of coordinates $r_2$, the other one, whose interaction electron 1 is feeling. For
a system of $N$ electrons we can write $V_{ee}(1) \equiv V_{ee}(r_1) \equiv V_{ee}(r)$, see Figure 23).

Note, also, that in (38) the sum goes from $b = 1$ and extends to all *occupied
spin orbitals* (occso), including $b = a$ (the reference orbital, where electron
1 ”is”). Introducing $b = a$, which means to account for the self-interaction,
does not bring any problem, since, if we make $b = a$ in (39) and (40) we get
$J = K$, which cancel in $V_{ee}$.

The hamiltonian for a system of $N$ electrons and $M$ nuclei can be written
as a sum of Fock operators:

$$H = \sum_{i=1}^N f(i)$$  \hspace{1cm} (41)$$

where the *spin orbitals* $\chi(a)$, are the solutions of the Hartree-Fock equations,
of the form

$$f \chi_a = \varepsilon a \chi_a \hspace{1cm} [a = 1, 2, ..., n]$$  \hspace{1cm} (42)$$

The problem is now reduced to building the $f$ operator (38), for which we
need the $\chi_a$ which are the solutions of the Hartree-Fock equations. To do

7) In computational quantum chemistry methods, *atomic units* are used to make computation easier.
that we need to follow an iteration procedure, starting with a set of chosen spin orbitals \( \{ \chi_a \} \).

From the known \( \{ \chi_a \} \) spin orbitals, we can write an expression for the energy, considering that:

- the one-electron integrals contribute with a term \( h_{aa} \) for each electron in spin orbital \( a \)
- the two-electron integrals contribute a term \( J_{ab} \) for each pair of electrons, and a term \(-K_{ab}\) for each pair of electrons with parallel spins.

We could now proceed to distinguish between closed shell systems and open shell systems to get the so called Restricted Hartree-Fock (RHF) or Unrestricted Hartree-Fock (URHF) versions.

In any case, to solve the Hartree-Fock equations of the form

\[
f \psi_a = \varepsilon_a \psi_a
\]

(43)

where \( \psi_a \) is the spatial part of \( \chi_a \), we need a basis of functions (e.g., Slater type orbitals, STO, and Gaussian type orbitals, GTO) to build the linear combinations. The iterative calculation proceeds with the diagonalization of the Fock matrix \( F \), of all matrix elements of the Fock operator.

In figure 24 we show diagrams of the energy levels in the Unrestricted Hartree-Fock (UHF) and in the Restricted Hartree-Fock (RHF) versions.

![Figure 24](image)

**Figure 24** Diagrams of the molecular energy levels in the Unrestricted Hartree-Fock (UHF) and in the Restricted Hartree-Fock (RHF) versions. The RHF can be used for closed shell systems, and the UHF has to be used for systems with incomplete shells.

The \( \varepsilon_a \) values have a physical meaning. According to Koopmans theorem, \( \varepsilon_a \) is the ionization potential (energy needed to remove one electron from orbital \( \chi_a \), (Fig.25), i.e.,

\[
IP = -\varepsilon_a
\]

(44)
The electron affinity is

$$EA = -\varepsilon_v$$  \hspace{1cm} (45)$$
i.e., the energy needed to put one electron in orbital $\chi_v$.

In quantum chemistry, the electronic structure of atoms and molecules can therefore be described in terms of orbitals and energy levels calculated for one electron which moves in the field of the nuclei and in the mean field of the interactions with all other electrons. The distribution of the electrons by the spacial orbitals is the electronic configuration. The electronic states resulting from these configurations are the terms of the configurations. The many-electron states can only be described in terms of eigenfunctions of total angular momentum, since the individual angular momentum of each electron is not an observable—the interactions of various types, namely the Coulomb, spin and exchange, do not allow that the many-electron wave function be simple products of the one-electron wave functions. It is therefore pertinent to distinguish between levels (and orbitals, electronic configurations and electronic states), which are illustrated in figure 26. It is also important to consider the notation: lower case for levels (and orbitals) and upper case for many-electron states. For molecules, the corresponding notation is in greek letters.

Equation (41) may suggest that the wave function for the $N$ electron system could be a product of all occupied $\chi_a$. But all electrons are identical and can exchange (consider the $K$ integrals)—one electron can simultaneously occupy
all orbitals—and are correlated—entangled in Shrödinger’s words\(^8\), meaning that the knowledge about one of them is inextricably linked to the knowledge about others—, and therefore the wave function has to be written as an anti-symmetrized product of all permutations, or a Slater determinant:

\[
\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\chi_a(x_1) & \chi_b(x_1) & \cdots & \chi_n(x_1) \\
\chi_a(x_2) & \chi_b(x_2) & \cdots & \chi_n(x_2) \\
\vdots & \vdots & \ddots & \vdots \\
\chi_a(x_N) & \chi_b(x_N) & \cdots & \chi_n(x_N)
\end{vmatrix}
\]

(46)

where the \(x_i\) are the space+spin coordinates of the electrons.

Figure 26 Illustration of the differences between orbital energy levels, electronic configurations and electronic states.

In the HF method, the Fock operator is of the form

\[
f = \frac{1}{2} \nabla^2 - \sum_A \frac{Z_A}{|r-R_A|},
\]

in the basis of the spin orbitals \(\chi\), with

\[
h = -\frac{1}{2} \nabla^2 - \sum_A \frac{Z_A}{|r-R_A|},
\]

implying that the total electronic energy will be given by

\[
E_{HF} = \sum_a h_{aa} + \frac{1}{2} \sum_{ab} (J_{ab} - K_{ab})
\]

(47)

In the \(\Phi\) basis, of the linear combinations, with \(X = \Phi C\) with components \(\chi(x) = \psi(r)\sigma(\omega)\) and taking the density matrix as \(D = CC^\dagger\), we will have,

considering that for any $T$ operator, $\langle T \rangle = \text{tr}(DT)$:

$$E_{HF} = \text{tr}(DH) + \frac{1}{2}\text{tr}(DJ) - \frac{1}{2}\text{tr}(DK)$$  \hspace{1cm} (48)

**A Note on Density Functional Theory, DFT**

Presently, one of the most successful methods for the calculation of the electronic structure of molecules and solids is that of Density Functional Theory, (DFT).

The theory is based on the notion that the total energy of a system, including all interactions (exchange and correlation), is a unique functional of the electron density, and that the minimum of this functional is the energy of the ground state\(^9\).

The appeal of this method lies in the fact that, in principle, the wave function for a system of $N$ electrons, which is a function of $4N$ coordinates ($3N$ space coordinates and $N$ spin coordinates) can be replaced by the electron density, which is a function of only three space coordinates.

The problem of the $N$ electrons can then be solved, by solving the system of self-consistent monoelectronic equations—the Kohn-Sham\(^10\) equations. These equations which are identical to the Hartree-Fock equations can be solved by similar iterative methods.

The Kohn-Sham equations are of the form

$$f^{KS} \chi_a = \varepsilon_a \chi_a$$  \hspace{1cm} (49)

where $f^{KS}$ is the Kohn-Sham operator; $\chi_a$, the Kohn-Sham spin orbitals, and $\varepsilon_a$ is the energy of spin orbital $a$.

The Kohn-Sham operator

$$f^{KS} = T + V_{KS}(r)$$  \hspace{1cm} (50)

is the sum of the kinetic energy $T = -\frac{1}{2}\nabla^2$ and an effective potential called the Kohn-Sham potential, $V_{KS}$, which is a functional of the electron density, $\rho(r)$, and is of the form

$$V_{KS}[\rho(r)] = V_{\text{ext}}(r) + V_{\text{Hartree}}[\rho(r)] + V_{XC}[\rho(r)]$$  \hspace{1cm} (51)

$V_{\text{ext}}(r)$ is an external potential, generally, the attractive potential between the electrons and the nuclei, $V_{ne}$.

$$V_{\text{ext}}(r) = V_{ne}(r) = -\sum_A \frac{Z_A}{|r - R_A|}$$  \hspace{1cm} (52)


$V_{\text{Hartree}}$ is the term relative to the Hartree approximation, i.e., the mean field felt by one electron, due to the Coulomb interactions with all others,

$$V_{\text{Hartree}} = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$  \hspace{1cm} (53)

It is identical to the Coulomb integral $J$ of Hartree-Fock theory, but now a functional of $\rho$, i.e., $V_{\text{Hartree}} = J[\rho]$. Finally, $V_{XC}$ is the exchange-correlation term, or $XC$ and contains all exchange, $V_X$, and correlation $V_C$ contributions; $(V_{XC} = V_X + V_C)$.

It is defined as

$$V_{XC} = \frac{\delta E_{XC}}{\delta \rho}$$  \hspace{1cm} (54)

and is, naturally, the more problematic term. There are many choices available for approximate functionals. One of the simplest is the Local Density Functional, LDF or Local Density Approximation, LDA, for which the exchange-correlation, $E_{XC}$, is the energy of a homogeneous electron gas of constant density $\rho$, of which there are databases from Monte Carlo calculations. We will not go into more details concerning the various $V_{XC}$ potential in this brief note.

The electron density is defined in terms of the Kohn-Sham spin orbitals:

$$\rho_0(\mathbf{r}) = \rho_{KS}(\mathbf{r}) = \sum_{a}^{\text{occso}} |\chi_a(\mathbf{r})|^2$$  \hspace{1cm} (55)

Note that the sum extends over all occupied spin orbitals—(occso).

Expression (49) represents a set of coupled non-linear equations (one for each $a$) that depend on the electron density, which appears in this theory as a fundamental variable.

For the purpose of computational calculations, a procedure can be used, which starts with a density $\rho_0(\mathbf{r})$ appropriately chosen to obtain a first $V_{KS}$. This potential is then introduced in the Kohn-Sham equations, which, when solved, give the orbitals and the energies. From these orbitals a new density $\rho_0(\mathbf{r})$ is calculated and a new $V_{KS}$, and so forth until convergency. The self-consistent cycle is terminated when the pre-established criteria is met. The two most common criteria are based on the differences between the values of the total energies or on the values of the densities for two successive iterations. In other words, when $|E^{(i)} - E^{(i-1)}| < \delta_E$ or $\int |\rho^{(i)} - \rho^{(i-1)}| d\tau < \delta_\rho$ in which $E^{(i)}$ and $\rho^{(i)}$ are the values of the total energy or of the density for iteration $i$, and $\delta_E$ and $\delta_\rho$ are the tolerances defined by the user.
When a basis for the Kohn Sham orbitals is used (Gaussian or Slater type), it is necessary to diagonalize the matrix $F_{KS}$ as in the Hartree-Fock-Rootham method. It should be noted that the minimization of the energy is made using the Lagrange multipliers, in which the restrictive condition, equivalent to normalization is in DFT, $\int \rho(r)d\tau = N$.

In the end, one can calculate the various observables, such as the total energy. From that one can obtain equilibrium configurations (by minimization of $E(R)$, ionization energies, etc. In Kohn Sham theory, the total energy is given by expressions which are similar to those of Hartree-Fock theory, but taking into account the Kohn-Sham operator and the fact the fundamental variable is the electron density.

In DFT we will have, identically to equation (48):

$$E_{DFT} = \text{tr}(DH) + \frac{1}{2}\text{tr}(DJ) + E_X[D] + E_C[D]$$  \hspace{1cm} (56)

in which the terms $E_X[D]$ and $E_C[D]$ are the exchange and correlation terms, respectively, the last being neglected in HF theory. The HF theory is therefore a particular case of DFT, in which $E_X[D] = -\frac{1}{2}\text{tr}(DK)$ and $E_C[D] = 0$.

What is the meaning of the Kohn-Sham spin orbitals\(^{11}\)? In principle, they do not have a physical meaning. They are used as a tool for the calculation of the electron density which is the fundamental variable of the theory. Its unique link to reality is that the sum of all their squares is equal to the real electron density. Note that the molecular orbitals of Hartree-Fock theory are still worse—they do not have taken into account the correlation effects, nor they give the real density.

One should also not mistake Slater determinants built from Kohn-Sham spin orbitals, with the true wave function for the system of $N$ electrons. In DFT there is no exact wave function for the system. Also, the energies $\varepsilon_a$ have no real meaning, since there is no equivalent to Koopmanns theorem to relate the orbital energies to the ionization potentials, except that the $\varepsilon_{\text{max}}$ (HOMO-KS energy) is equal to the first ionization potential:

$$\varepsilon_{\text{HOMO-KS}} = -IP$$  \hspace{1cm} (57)

The HOMO and LUMO levels can be approximately determined experimentally (both in solution or in a solid film) by a simple electrochemical method,

\(^{11}\)See the interesting article: Ralf Stowasser and Roald Hoffmann, "What Do the Kohn-Sham Orbitals and Eigenvalues Mean?", J. Am. Chem. Soc. 1999, 121, 3414-3420
namely *cyclic voltammetry*, from the onset potentials of oxidation and reduction, using a reference system such as ferrocene/ferrocenium (Fc/Fc+) and by assuming that the energy level of this reference is $-4.8 \text{ eV}$ below the vacuum level.

**Molecular Orbitals Calculated by DFT**

In the following, we will give some examples, using hybrid functionals, which are a class of approximations to the exchange–correlation energy functional in DFT that incorporate a portion of exact exchange from Hartree–Fock theory with exchange and correlation from other sources (ab initio or empirical). The exact exchange energy functional is expressed in terms of the Kohn–Sham orbitals rather than the density, so is termed an implicit density functional. One of the most commonly used versions is B3LYP, which stands for Becke, 3-parameter, Lee-Yang-Parr. B3LYP combines the Becke exchange functional and the correlation functional of Lee, Yang and Parr.

In figure 27 we show the HOMO orbital of a chain of 56 CH units, taken here as a simplified model of polyacetylene. The difference between the frontier levels $E_{LUMO} - E_{HOMO}$ gives an approximate value for the band gap.

**Figure 27** The result of a DFT/B3LYP calculation for a chain of 56 CH units gives the following values: $E_{HOMO} = -4.23 \text{ eV}$, $E_{LUMO} = -2.78 \text{ eV}$, band gap=1.45 eV. The figure shows the HOMO orbital.

In figure 28, we give the results for a sequence of six oligomers of p-phenylene vinylene (or phenylene vinylene) (PV), as units of the conjugated polymer Poly(p-phenylene vinylene) (or polyphenylene vinylene), PPV. The sequence starts with one unit and goes up to six units. The HOMO and LUMO orbitals are shown.

**Figure 28** Frontier energy orbitals for 1 to 6 PV units.
The respective energies are given in table 1, and a plot of the levels as a function of the number of PV units is given in figure 28.

Table 1  Molecular orbital frontier levels for PV oligomers

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>E HOMO/eV</th>
<th>E LUMO/eV</th>
<th>Gap/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>PV1</td>
<td>-5.79</td>
<td>-0.67</td>
<td>5.12</td>
</tr>
<tr>
<td>PV2</td>
<td>-5.24</td>
<td>-1.51</td>
<td>3.73</td>
</tr>
<tr>
<td>PV3</td>
<td>-5.04</td>
<td>-1.83</td>
<td>3.21</td>
</tr>
<tr>
<td>PV4</td>
<td>-4.94</td>
<td>-1.99</td>
<td>2.95</td>
</tr>
<tr>
<td>PV5</td>
<td>-4.88</td>
<td>-2.08</td>
<td>2.80</td>
</tr>
<tr>
<td>PV6</td>
<td>-4.86</td>
<td>-2.14</td>
<td>2.72</td>
</tr>
</tbody>
</table>

Figure 29  Values of frontier energy orbitals for 1 to 6 PV units.

This simple exercise shows that the frontier levels tend to stabilize at constant values, as we increase the number of PV units. For six units we get a value for $E_{LUMO} - E_{HOMO} = 2.72$ eV, which is not very far from the real value of 2.5 eV. In fact, PPV is a highly stable conjugated polymer and its yellow color is due to an absorption band centered at 400-420 nm with band gap of 2.5 eV.

Energy Bands Calculated by DFT

The DFT method has been used to calculate band structures, using various exchange and correlation functionals.

Most calculations on conjugated polymers tend to fall into one of two groups: time-dependent (TDDFT) treatments of oligomer excited states, and ground-state DFT band structures of isolated, infinite, periodic, quasione-dimensional (1D) polymer chains.

DFT/B3LYP appears to dominate calculations on 1D polymer chains, although KS orbital energies generally underestimate optical and fundamental
bandgaps. TDDFT calculations on such systems tend to converge to the orbital energy gaps. Interestingly, the cancellation among errors in orbital energies, geometries, exciton binding effects, chain packing, and so on, leaves the B3LYP/6-31G* bandgaps of isolated 1D chains quite close to the measured gaps of many conjugated polymers.

Calculations include periodic boundaries only along the chain axis. Geometry optimizations optimize all degrees of freedom including unit cell parameters.

Typical calculations on 1D periodic systems use at least 200 \( k \)-points and integrate the inter-cell energy and potential contributions using at least 100 unit cells. Bandgaps are reported as the minimum indirect gap. Effective masses \( m^* \) are calculated as the inverse curvature of the highest-occupied and lowest-unoccupied crystal orbital (HOCO and LUCO)\(^{12}\) energies around their extrema,

\[
\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2 \epsilon_k}{dk^2}
\]

It has been reported that the B3LYP functional, when compared with other methods, demonstrated better agreement with experimental band gaps of polythiophene (experimental: 2.1 eV, HSE: 1.68 eV, B3LYP: 2.04 eV, BHHLYP: 3.90 eV)\(^{13}\).

The good agreement between B3LYP and experimental band gaps for semiconducting polymers has also been demonstrated very recently in the theoretical study of periodic organic polymers by Janesko\(^{14}\).

In figure 30 we show results obtained by G. R. Hutchison et al\(^{15}\), for the energy levels and density of states, calculated by DFT, for a series of oligomers with one to six thiophene units and for an infinite chain of polythiophene, and in figure 31 we show the corresponding energy bands. The results of the calculation are compared with the experimental values for the lattice parameter, \( a \) and the gap: \( a = 7.71 \text{ Å} \) (exper.: \( a = 7.75 \text{ Å} \)); \( E_g = 1.10 \text{ eV} \) (exp: \( E_g = 1.83 \text{ eV} \), thin film: \( E_g = 2.0 \text{ eV} \)).

\(^{12}\)There is the highest occupied orbital (HOMO made of bonding electrons) and the lowest unoccupied orbital (LUMO consisting of antibonding orbitals). We keep on adding more atoms or molecules and a cluster is formed that now has highest occupied cluster orbitals (HOCO) and lowest unoccupied cluster orbitals (LUCO). We keep on adding and get bands– insulators with a wide band gap, semiconductors with a reasonable bandgap and metals with the Fermi level with no band gap.


Figure 30  Calculated density of states scaling from oligomers (for one to six monomer units) to the infinite polymer structures of polythiophene.

Figure 31  Calculated band structures of polythiophene, plotted relative to the calculated valence band maxima
7. TOPOLOGICAL DEFECTS—SOLITONS AND POLARONS

In polyacetylene there are topological defects called solitons which correspond to non-boning $2p_z$ orbitals, occupied with only one electron. These neutral solitons separate two segments of $(CH)_x$ with the same energy, and they move along the chain (Fig.32), being responsible for charge transport (conductivity). The soliton corresponds to non-bonding levels in the middle of the gap between the $\pi$ and $\pi^*$ bands. Through doping it is possible to create solitons with positive or negative charge, with zero spin, as well as neutral solitons with spin $1/2$ and even with fractional charges as shown in figure 33. Besides polyacetylene, there are also forms of polyaniline with degenerate ground states. Other conjugated polymers have non-degenerate ground states—there is no equivalence between two segments with conjugated double bonds, displaced of one position ($-C_{n-1} = C_n$ to $-C_n = C_{n+1}$). The difference between the two alternate bonds is exemplified in the scheme of figure 34 for poly(p-phenylene vinylene), (PPV). The creation of these topological defects can be followed by techniques such as optical absorption.

**Figure 32** Neutral soliton, separating two $(CH)_x$ segments with opposite directions of the double bond alternation.

**Figure 33** Schematic representation of the creation of a soliton, giving several combinations of charge and spin.
Figure 34 Benzoid conformation (a) and quinoid (b) for a segment of poly(p-phenylene vinylene), (PPV). The energy of the quinoid conformation is higher and therefore less stable. In non-degenerate polymers, the addition or removal of one electron creates a bonding state and an anti-bonding state with a deformation of the chain. These deformations are called polarons or bipolarons.

Figure 35 a) creation of a polaron $P^+$ in a segment of poly(tienylenevinylene) (PTV), by removing an electron, and giving a positive charge and an unpaired electron, which will separate by relaxation of the lattice. b) creation of a bipolaron $BP^{2+}$ by removal of a second electron, leaving two positive charges. Since the bonding level in the gap is occupied in the normal state (without topological defects), we only show the holes.
In the pure state, conjugated polymers are semiconductors (or insulators) as a consequence of the gap between the $\pi$ and $\pi^*$ bands. Doping induces the creation of solitons, or polarons/bipolarons. When the concentration of dopants is high, soliton bands can be formed, as in polyacetylene, and polaron/bipolaron bands in non-degenerate conjugated polymers, giving rise to high conductivities, as in the case of PEDOT/PSS (Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate). A proper metallic state has only been observed in polyaniline, with conductivity values of 300 S cm$^{-1}$ and with $\left(\frac{d\rho}{dT}\right) > 0$ down to 5 K.

Conjugated polymers with high conductivities have been described as disordered metals near a metal-insulator transition. They have a finite density of states near the Fermi level, as can be concluded from the observation of Pauli type magnetic susceptibility, characteristic of metals, as well as a linear temperature dependence of the thermoelectric power and specific heat.

However, the d.c. conductivity is thermally activated (phonon assisted), decreasing as we lower the temperature, or at least with a minimum below room temperature.

**Optical Properties**

The optical properties of conjugated polymers, as electroluminescence and non-linear optical properties are of great interest for many applications. Luminescence—radiative decay of an excited state—can be induced by photo-excitation (photoluminescence) or by electrical excitation (electroluminescence) as shown in figure 36.

The paradigm of electroluminescent polymers is poly(p-phenylene vinylene), PPV, the first conjugated polymer in which electroluminescence was observed in the beginning of the 1990s. The similarity of the emission spectra obtained by photoexcitation and by electrical excitation has been used as a proof that the excited state created by both processes is the same.

Not all conjugated polymers are luminescent. That depends on the relation between the ground state and the excited state—the transition may be forbidden. Polyacetylene and poly(thienylene vinylene) are examples of non-luminescent conjugated polymers. Present research aims at the development of polymers which can emit efficiently not only in the visible but also in the ultra-violet and in the infrared, which is possible by doing gap engineering to modify the HOMO and the LUMO levels.
Figure 36 Illustration of the processes of photoluminescence (PL) and electroluminescence (EL). a) In photoluminescence, an electron, initially in the HOMO (Highest Occupied Molecular Orbital) is excited to the LUMO (Lowest Unoccupied Molecular Orbital) with absorption of a photon $h\nu$ and creates an exciton which is an electron-hole pair that due to a process ofchain relaxationmoves to the interior of the gap where the electron and hole recombine emitting a photon $h\nu'$. b) In electroluminescence, the exciton is created by the combination of an electron (negative polaron) with a hole (positive polaron), which are ejected into the polymer from appropriate electrodes.

9. CASE STUDY: PEDOT:PSS

PEDOT:PSS or Poly(3,4-ethylenedioxythiophene):Polystyrene sulfonate (see Figs.37 and 38 ) is a mixture of two polymers. Poly(3,4-ethylenedioxythiophene) or PEDOT is a conjugated polymer and carries positive charges. The other component is sodium polystyrene sulfonate which is a sulfonated polystyrene. Part of the sulfonyl groups are deprotonated and carry a negative charge.

The most practically useful, polymerization method for EDOT is the so-called BAYTRON P synthesis that was developed at Bayer AG. This method utilizes the polymerization of EDOT in an aqueous polyelectrolyte (most commonly PSS) solution using Na$_2$S$_2$O$_8$ as the oxidizing agent. Carrying this reaction out at room temperature results in a dark blue, aqueous PEDOT/PSS dispersion, which is commercially available from Bayer AG under its trade name BAYTRON P.

PEDOT exhibits an electronic bandgap, defined as the onset of the $\pi \rightarrow \pi^*$ absorption, of 1.6-1.7 eV and a $\lambda_{max}$ of ca. 610 nm, making it deep blue in color. Due to its low oxidation potential, thin films of neutral PEDOT must be handled carefully as they oxidize rapidly in air.

PEDOT was found to be almost transparent in thin, oxidized films and showed a very high stability in the oxidized state. The solubility problem was subsequently circumvented by using a water-soluble polyelectrolyte, poly(styrene sulfonic acid) (PSS), as the charge-balancing dopant during polymerization to yield PEDOT/PSS. This combination resulted in a water-soluble polyelectrolyte system with good filmforming properties, high conductivity (ca. 10 S/cm), high visible light transmissivity, and excellent stability.
PEDOT/PSS can be heated in air at 100 °C for over 1000 h with only a minimal change in conductivity. In figure 38 which represents the most commonly used PEDOT:PSS blend, we can see the PEDOT chain, below the PSS chain, with two positive charges and two localized electrons near those charges. The positive charges of the PEDOT chain are compensated by the two negative charges in the SO$_3$ groups of the PSS chain above.

In PEDOT:PSS only holes contribute to charge transport. Injected electrons will immediately recombine at oxidized PEDOT sites. For highly conductive PEDOT:PSS, the ratio of PEDOT to PSS is 1: 2.5 by weight. The density of solid films is approximately 1. Considering the molecular weight of the monomeric PEDOT and PSS units, 140 and 182 g/mol, respectively, the density of EDOT monomer is of the order of 1021 cm$^{-3}$. From electrochemical measurements, the level of oxidation per monomer is of order of 1 charge per 3 EDOT units. This implies, for PEDOT:PSS films, a density of holes of the order of $p = 3 \times 10^{20}$ cm$^{-3}$. In highly conductive films, conductivity values are of order of 1000 S/cm, implying a hole mobility of $\mu_p = 20$ cm$^2$/V.s.