The polymer as a chain

Some intuition in case you are used to QWs or optical waveguides

If we go back and remember what happens in a quantum well system. In a quantum well one finds a given electrical potential which in the case of a quantum well is square in the direction of the well (Z). When such a system is excited it is convenient to describe the excitation (usually electrons) as a combination of a set of states. The obvious choice is the set of eigen states derived using the Schrödinger equation. Such a choice defines energy levels for each state and a probability function (or wavefunction). If one is used to optic rather then solid state physics one can find a very similar situation when one evaluates the properties of a waveguide and the Schrödinger equation is replaced by the scalar wave equation. In this case the eigen-states are the optical modes of the waveguide and each mode is associated with a propagation constant. To construct a confining structure one makes use of at least two type of materials: one for the well [waveguide core] (as InGaAs) and one for the barrier [cladding] (as InP).
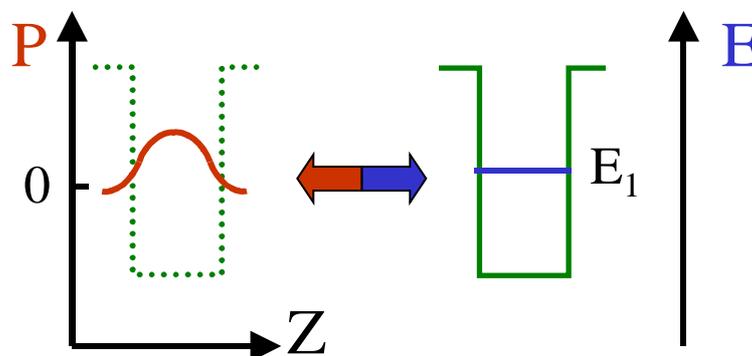

Figure 1. The electrical potential of a quantum-well (right). The first energy level of such a system is denoted as E_1. On the left, the spatial probability function associated with such a state. Note that this is a confining potential.

In a system that contains more than one confining potential (as multiple QWs or waveguides) there could be coupling between two potentials (states). In such a case one has to solve for a more global potential which contains the various quantum-wells. If the two wells are similar one would expect to find that the states of each isolated well will couple together to give rise to new states of the combined system. This is illustrated in the figure below.
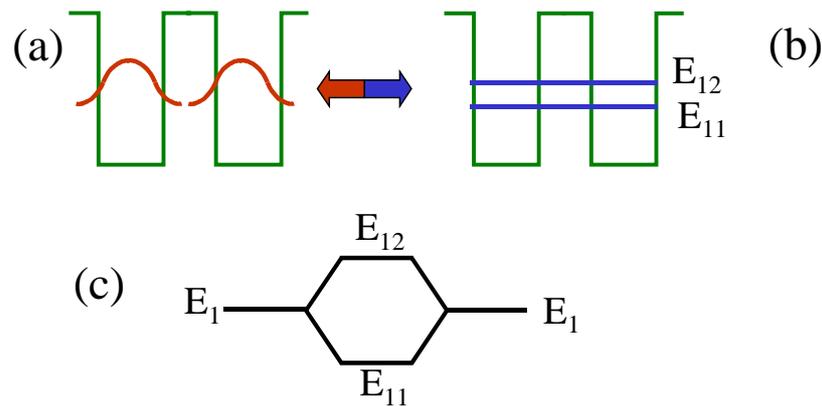
Figure 2. (a) Spatial proximity of two wells leads to overlap of wave functions and to an effective coupling. (b) The energy level of the combined system has now split into two energy levels. (c) Schematic representation of the two separate systems combining to give a final split energy levels.

The spacing between the two new levels is a measure for the degree of coupling between the two original states. For example, if the spacing is large, placing a carrier on the right side will results in a swift transfer to the left (and vice versa). In the system described in Figure 2 this is called resonant tunnelling where the tunnelling time is inversely proportional to the energy spacing ($\Delta E = E_{12} - E_{11}$). In the above we have confined our discussion to the first eigen state but one should remember that there could be more states with a more complicated probability function (or wave function).

In the discussion of Figure 1 we mentioned the use of materials to form the well structure. It was assumed that the reader is well aware that each of these materials has an energy-gap (band-gap) that enabled the formation of the well. We did not go into the details of the band-gaps but one should remember that these energy gaps arise from the close coupling of the constituent atoms that make up the material lattice. In other words, the InP semiconductor is a result of close coupling of atomic potentials giving rise to electronic continuity on one hand and to an energy gap on the other.

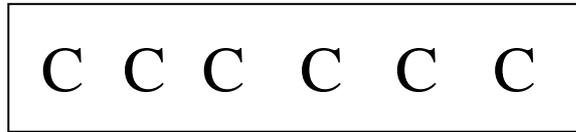## Placing carbon atoms together

Figure 3. One dimensional lattice structure which is the schematic description of an organic (hence the carbon) polymer.

Once we accept the above concepts, it is straightforward to consider the formation of a polymer chain as an electronic entity. Each carbon atom creates a local electrical potential. This type of potential has a well-defined eigen states, wave functions, and probability functions. The coupling between atoms and the formation of the polymer chain is a result of an overlap between neighbouring atomic wave functions.

Although the nature of the carbon atom is rarely used in the device-physics field (just as In or P atoms in III-V), for completeness we will briefly describe its electronic nature and schematically show how a few atoms form a chain. Like any other atom it has a positive inner core surrounded by electrons which orbit around it and maintain the overall charge neutrality. The orbital or the wave functions of the electrons are again the eigen states of the system (atom). The electrons are grouped into shells and Figure 4 illustrates the growth in the number of shells as the atomic number (number of protons) increases. For the carbon atom we note that it has two shells and in the outer shell it has **4** electrons, which is half the possible occupancy of this shell.

First Shell — H, He

Second Shell — Li, Be, B, C
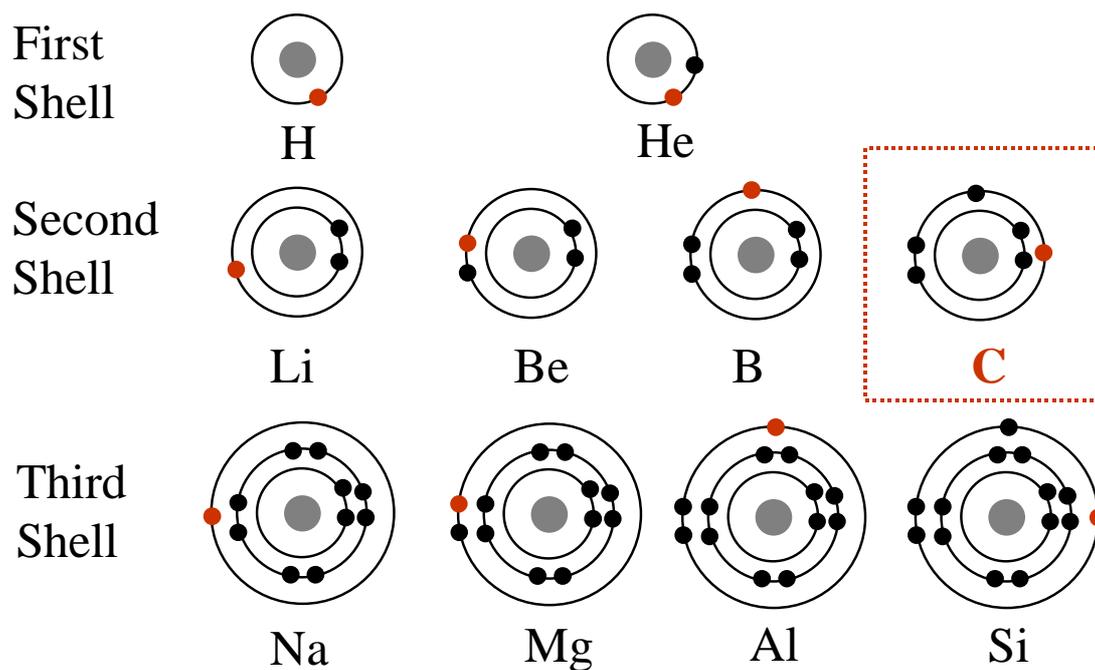
Third Shell — Na, Mg, Al, Si

Figure 4. Electronic structure of atoms

Since we want to build a structure (chain) consisting of overlapping carbon atoms, we are interested in the wave functions that are in the outer-shell (they are most likely to overlap first). The carbon has four electrons that can be used to build the chain and hence we are interested in four wave functions.
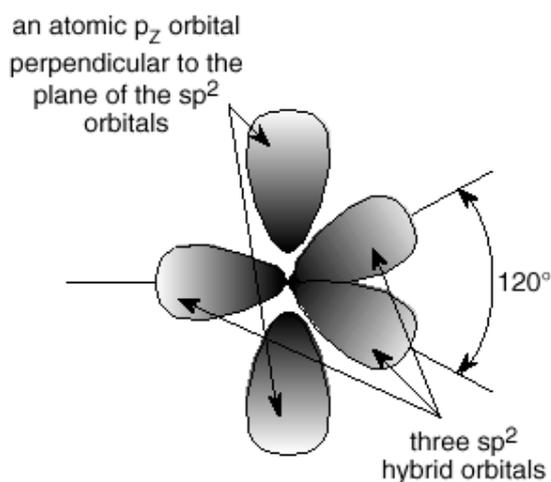

an atomic p_z orbital perpendicular to the plane of the sp^2 orbitals

120°

three sp^2 hybrid orbitals

Figure 5. The 4 orbitals of a carbon atom in the form which allows it to couple to other atoms (in order to make a chain).

The wave functions or orbitals, which describe the electrons surrounding the carbon atom, may have more then one form. In Figure 5 we show the configuration which is most suitable for coupling to the next carbon on the chain. We find 3 lobes in one plane (sp^2) and one (p_z) is perpendicular to the plane.
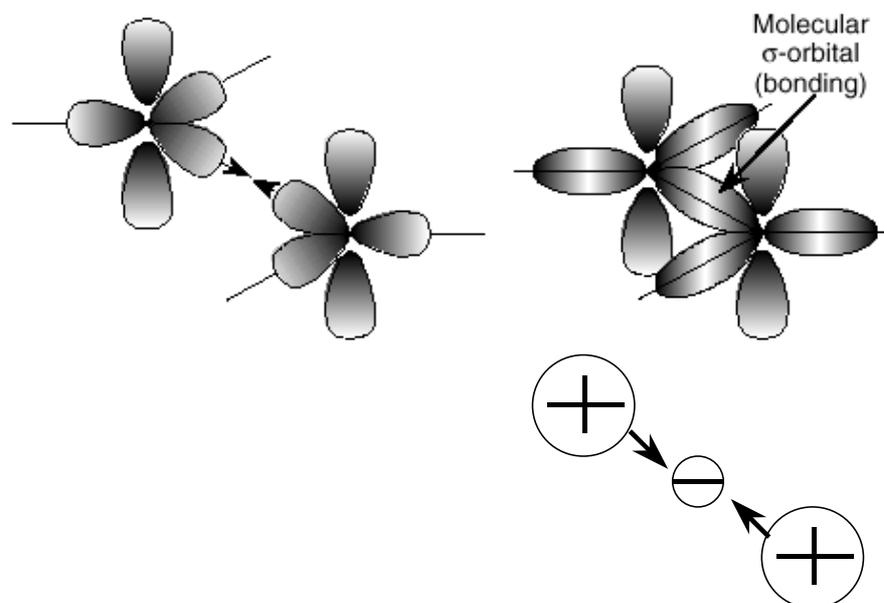
Figure 6. When two atoms are brought together the wavefunctions which are in the plane overlap and couple. The bottom picture illustrates the attraction (stabilisation) introduced by the overlap.

The in plane orbitals, named sp^2, are those which readily overlap when two carbon atoms are brought together. This is a very strong overlap that enhances the amount of negative charge in the space between the two atoms (in phase interference of the wave functions). Namely, a configuration of [+ - +] is created which bonds the two atoms (see Figure 6). This strong bond is called a σ bond and it forms the skeleton of the polymer chain. As can be seen in Figure 6 the two electrons which participate in bonding the two atoms are highly localised between the two atoms and hence one would not expect them to contribute to any electrical conductivity. In order to create a conductivity or an electrical continuity it has to be an electron (orbital) which is symmetric with respect to atoms on both sides. This is the type that will successfully couple to his two neighbours and provide the electrical continuity. Examining Figure 5 and Figure 6 we see that the p_z orbital, which is perpendicular to the plane of the atoms, fulfil this requirement. The orbitals (states) which are created through the coupling of the perpendicular (p_z) wavefunctions are called π orbitals (see Figure 7).
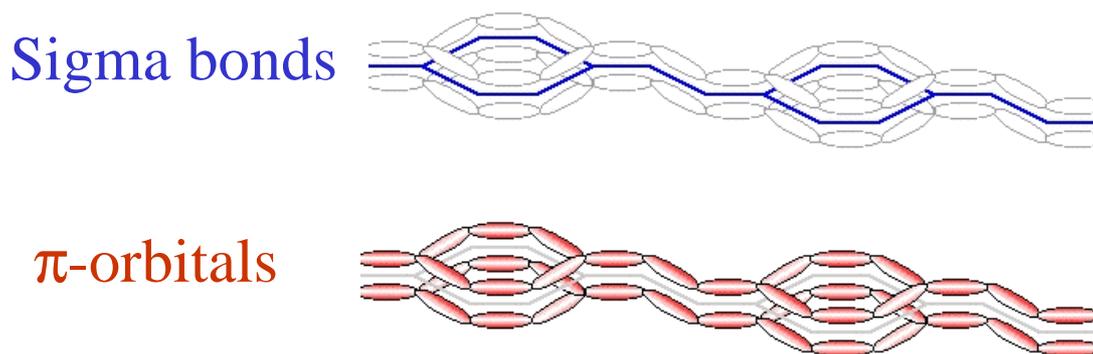
Sigma bonds

π-orbitals

Figure 7. Schematic description of the polymer skeleton (σ) and the delocalised electrons (π).

Molecular orbitals and energy states

So far we have described how when two atoms are brought together a new state is formed. However, we already know (see Figure 2) that in fact there should be two new states. We have clearly discussed only one of them and we now need to show how the other state is formed. In the discussion thus far we have not considered that the electronic wavefunction have a phase associated with it and that two wavefunctions can either interfere in a constructive or destructive manner. This is illustrated in Figure 8 where the top part shows the phase associated with the p_z orbital.
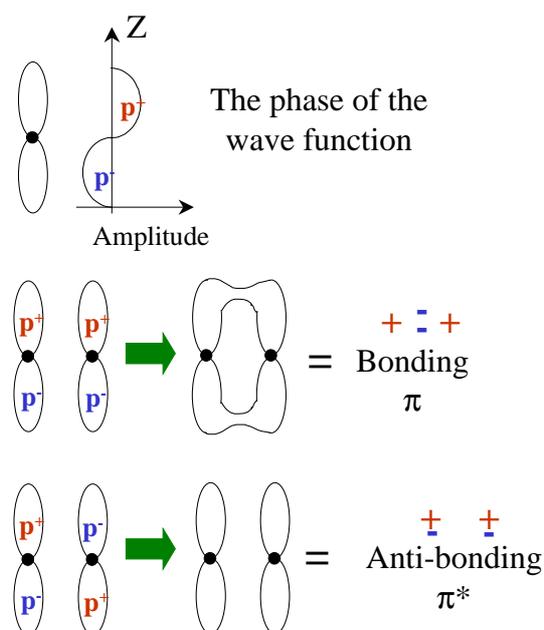
Figure 8. Schematic description of the formation of low energy (bonding) and high energy (anti-bonding) states through in-phase or out of phase coupling, respectively.

The centre part of Figure 8 shows that when the positive (p^+) and negative (p^-) parts are constructively aligned the constructive interference, taking place in between the two atoms, raises the electron density and gives rise to a stabilised [+ - +] configuration. The bottom of Figure 8 shows that when the phases are anti-parallel the coupling is reduced and the bond is less stabilised (the molecule is at a higher energy state). This is farther illustrated in
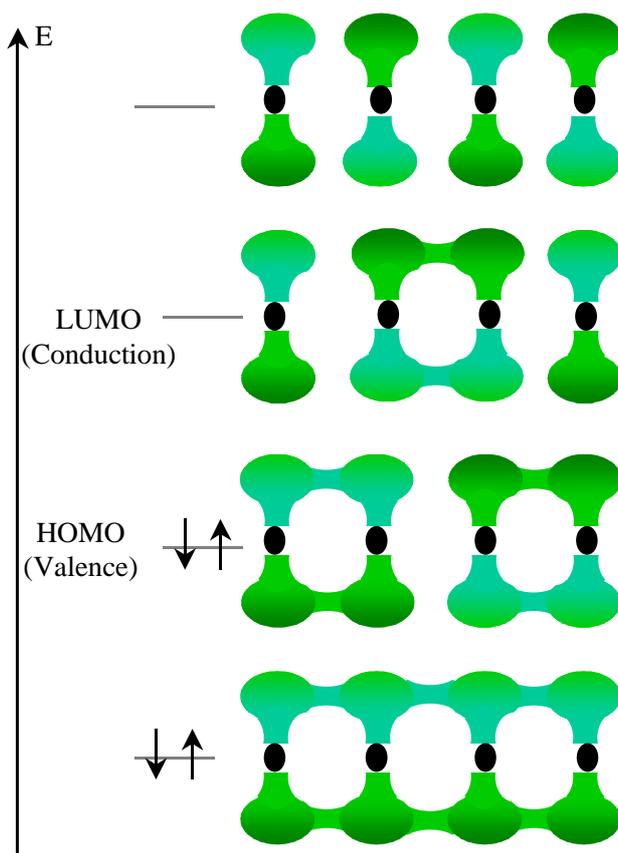

Figure 9. Schematic description of molecular orbitals and their relative energetic position, for a molecule made of 4 carbon atoms.

The configuration co-ordinate

In the above we have seen that a given arrangement (spacing) of carbon atoms gives rise to electronic states (wavefunctions). We also mentioned that the electronic states take an active part in binding the carbon atoms together. The states (orbitals) which enhance the overall binding and stabilise the chain are by nature the lower energy states (bonding or "valence" states). Those which, when occupied, destabilise the chain are by the same token are higher energy states (anti-bonding or 'conduction" states). Not only does the arrangement of carbon atoms define the molecular states but also the occupation of various states affects the arrangement of the carbon atoms (filling of an anti-bonding state will increase the spacing between atoms). Namely, there is a close coupling between the spatial arrangement (configuration co-ordinate and the electronic states).
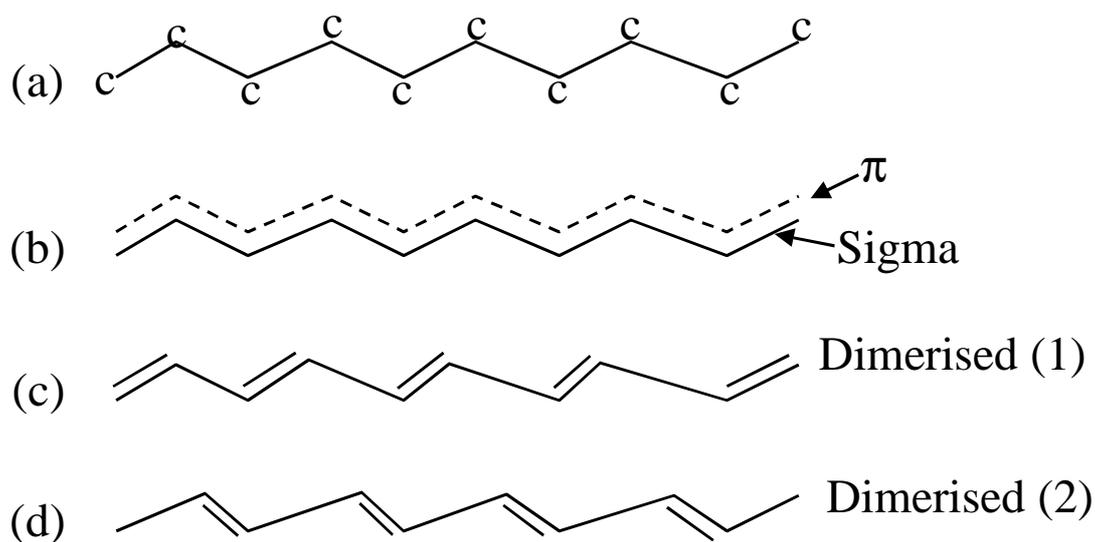

Figure 10. Schematic description of the interaction between the spatial configuration of the atoms and the electronic distribution [wave]function. (a) General description of a simple chain. (b) The configuration when the π electrons are uniformly distributed along the chain. (c) The configuration when the π electrons are not uniformly distributed along the chain. (d) A symmetric configuration with respect to (c). Note that the p electrons reduce the distance (bond length) between atoms.

The spatial configuration of a chain can be driven to change through a change in its electronic occupancy. This can happen when, (a) an electron is promoted to an upper level (as in light absorption), (b) an electron is added to a chain to occupy an upper state or an electron is extracted from a lower state (electron or hole injection). The other cause is the thermal motion of the molecule, which can be separated into

discrete phonon modes in the form of vibration or rotation of the molecule. Let us first consider the latter case which does not include electronic excitation. For example the molecule described in Figure 10 may change its configuration going form (c) through (b) to (d). This is depicted in Figure 11 where the [potential] energy of the molecule is plotted as a function of its spatial arrangement.
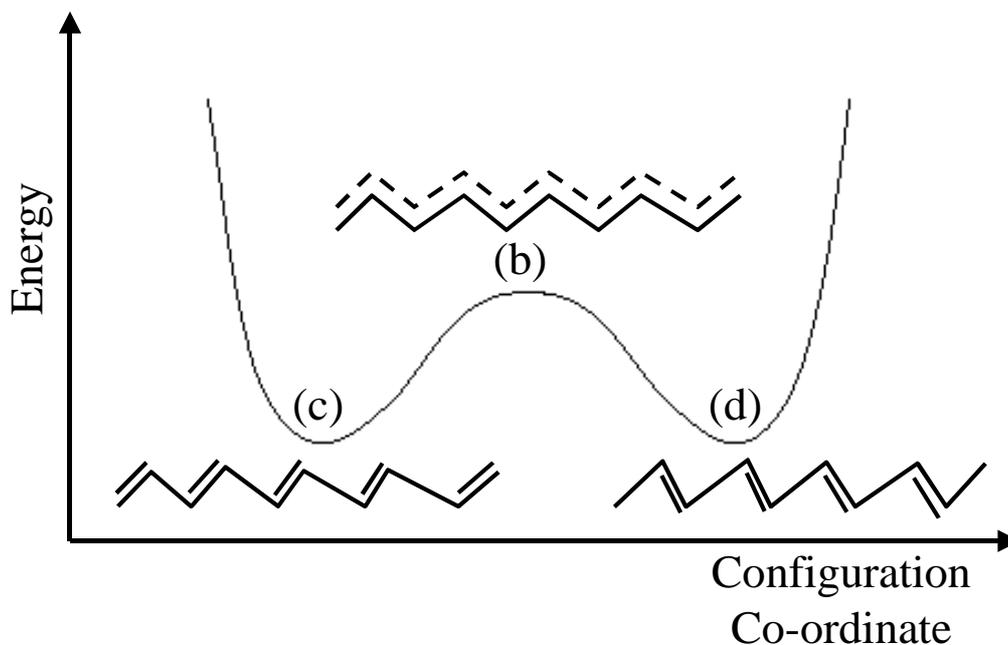

Figure 11. The [potential] energy stored in the molecule as a function of its spatial organisation. We note that the dimerised configuration is more stable and that due to symmetry the two low states are degenerate (of equivalent energy).

The degenerate nature of the low energy (ground state) is rather unique to the above structure and typically one finds a non-degenerate ground state and Figure 12 describes such an example [the polymer poly(para-phenylene)] where one of its configuration is energetically favoured.
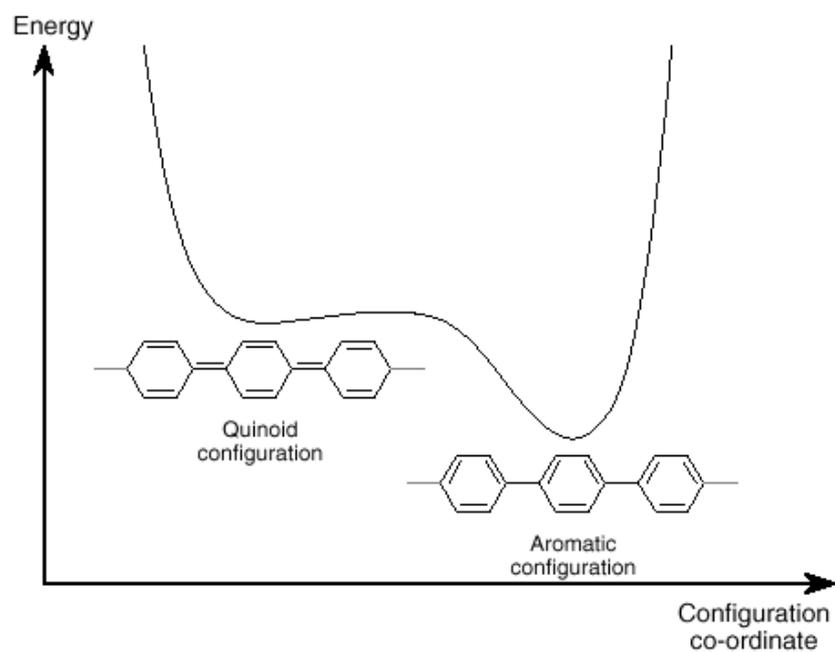
Figure 12. The energy stored in the molecule as a function of its spatial organisation for a non-degenerate ground state polymer [poly(para-phenylene)].

Both Figure 11 and Figure 12 describe the energy stored in a molecule which is not electronically excited and the motion along the curve is through absorption (upward) or emission (downward) of phonons.

The motion along the curves in Figure 11 and Figure 12 does not require any electronic excitation and in fact one such curve describes only one electronic state. When the molecule is excited it gains an overall energy and the energy curve is shifted upward in energy (see Figure 13).
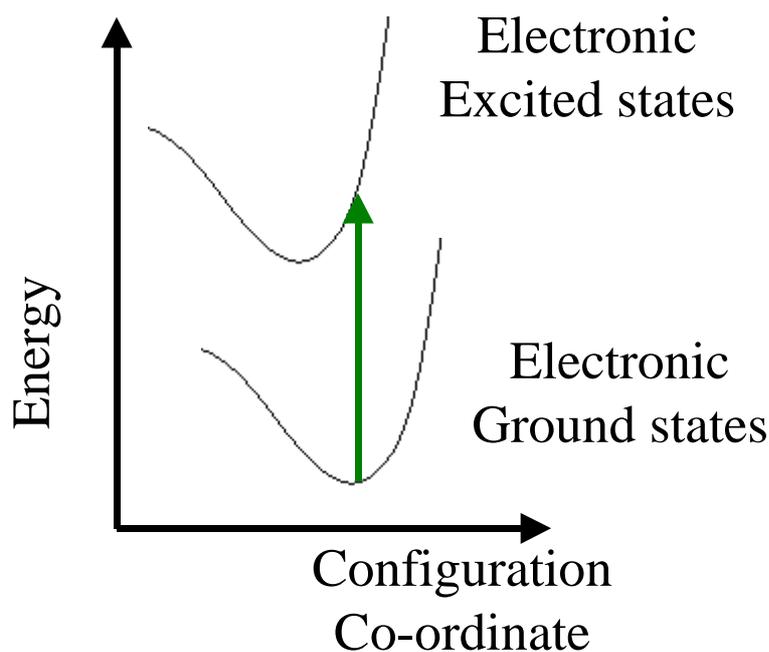
Figure 13. A vertical electronic transition between two molecular energy surfaces.

Figure 13 shows that as a result of an electronic excitation the spatial arrangement of the molecule is modified. We also indicated a vertical transition. Namely, there is a hidden assumption that during the time it takes to make an electronic transition the molecule (its atoms) hasn't changed. This is a reasonable assumption due to the associated time scales (10^{-15} and 10^{-13}) and is known as the Frank-Condon principle.

The curves in Figure 11 to Figure 13 describe a potential energy curve associated with the molecular motion. Just as in Figure 1 we would expect that such a confining potential would give rise to discrete states (see Figure 14). Since these states are associated with the motion (vibration) of the molecule, and not of the electrons, they are called "vibronic states" and a transition will occur between vibronic levels of two electronic states. The probability of the transition depends on the wavefunction overlap between the initial and final states. If we separate this to pure electronic and pure vibronic contributions then the vibronic contribution is called the Franc-Condon factor.
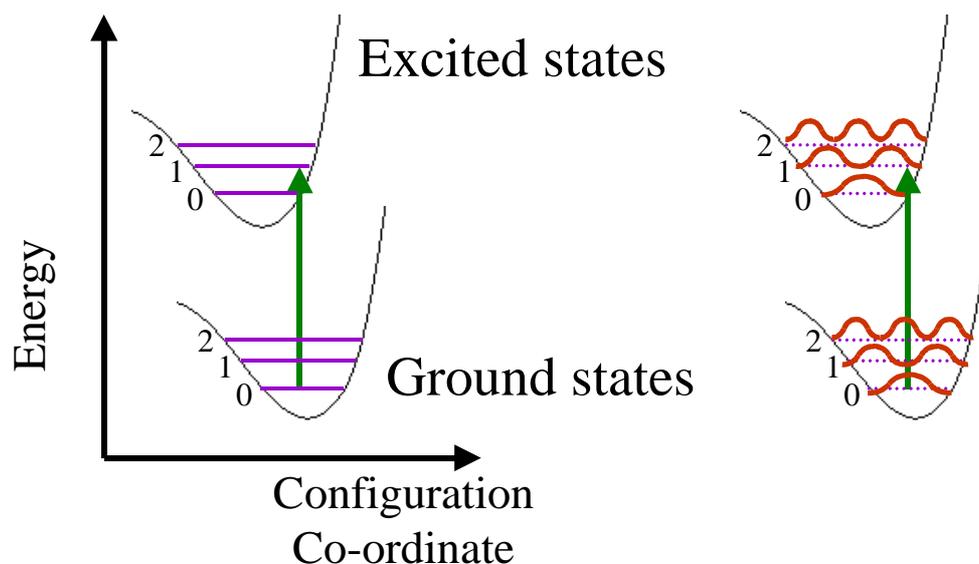
Figure 14. The vibronic energy states (left) and the associated vibronic wave function (right).

In the above discussion we have hinted that the polymer chain does not necessarily look the same after it has been excited (hence the different upper curve). In order to make this visually intuitive we show below the effect a positive charge may have on a chain and we examine the same polymer used in Figure 12. The top of Figure 15 shows that the localised positive charge induces a change in the bond configuration causing part of the chain to change from the aromatic to the quinoid linkage scheme (hence the charge is called a polaron or a defect). However, the quinoid part is of higher energy and hence the molecule will tend to minimise its length. This could be either by pushing the charge (distortion) towards the end of the chain or in the long chain limit in will be favourable to induce another structural defect that will bring the polymer back to its more stable (atomatic) linkage scheme (see Figure 15).
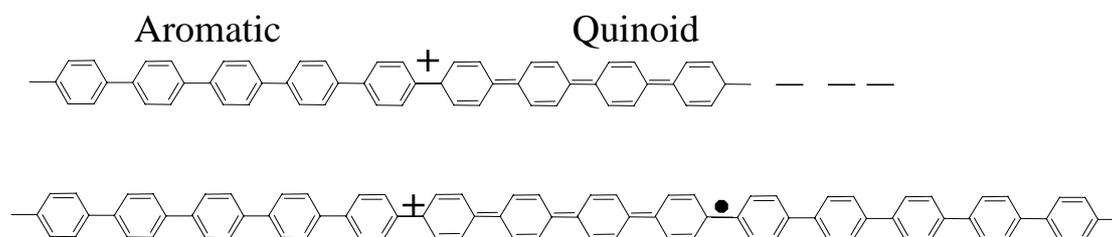

Figure 15. Schematic description of the chain distortion caused by the presence of a charge polaron.

Absorption and Emission Spectrum

As we have seen above, each level is in fact a combination of several sublevels which are related to the allowed vibrations of the molecule. To understand the emission and absorption spectrum we need to consider transitions between split levels, as shown in Figure 16. To draw the spectrum we introduce the assumption that any relaxation within the sublevels is very fast and that we can assume a thermal equilibrium where only the lower sublevel may be populated. Namely, transitions are only from sublevel "0" but can go to any of the sublevels of the other state. As illustrated in Figure 16 this will result in a mirror image between absorption and emission.
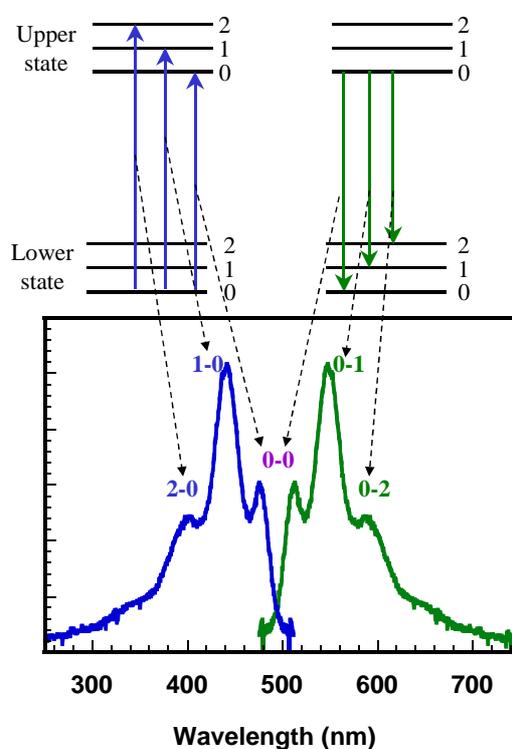

Figure 16. Absorption (blue) and emission (green) between electronic ground state and first electronic excited state.

To make the picture more realistic we must keep in mind that there is always the electron-lattice coupling or that the chains react to electronic excitations. Namely, the set of levels before and after excitations may be slightly different. In such a case one may observe a "stoke shift" which is the difference in energy (wavelength) between the 0-0 transitions in absorption and emission.
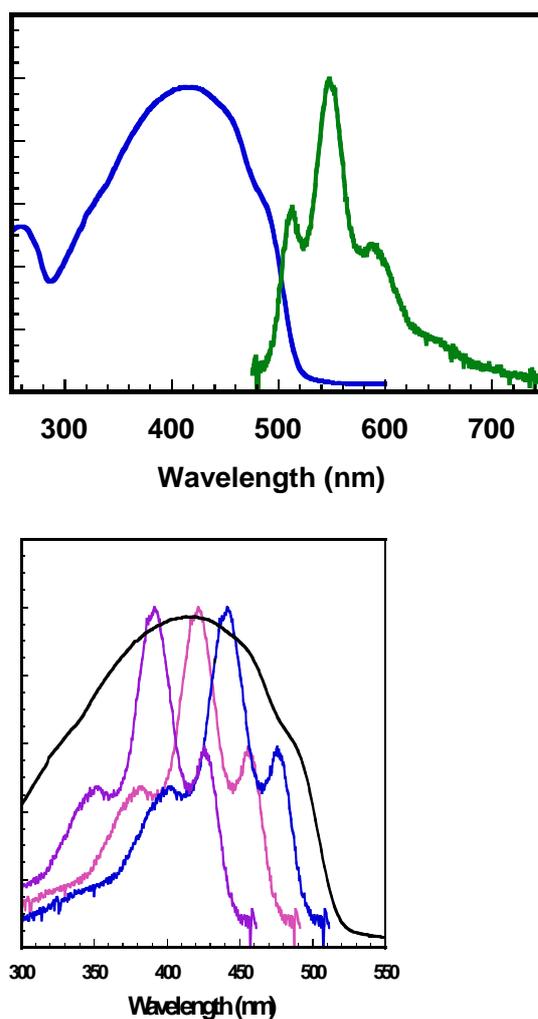
Figure 17. The emission and absorption spectrum of the PPV polymer (top). The bottom figure shows schematically how a distribution in conjugation length may result in a broad absorption spectrum.

Figure 16 shows both the emission and absorption having clear vibronic peaks. However, in reality one often observes such peaks only in the emission spectrum with the absorption spectrum being rather broad. This is usually explained by the distribution of electronic coherence lengths in the chains making up the film. This is the conjugation length which have a similar effect to a quantum-well width of a length of a quantum-wire. The shorter segments (conjugation lengths) have a re shifted to higher energies thus smoothing the absorption spectrum (see Figure 17). Unlike the absorption spectrum, the emission spectrum is not as affected. This is related to the excitation transfer to low energy sites (long conjugation lengths) prior to emissions. Such mechanisms will be described in the next lecture.

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