7. Organic semiconductors

7.0 Introduction

7.1 Absorption and Fluorescence

7.2 Molecular orbitals

7.3 Transfer of charge

7.4 Transfer of energy

7.5 Organic light emitting devices (OLED)

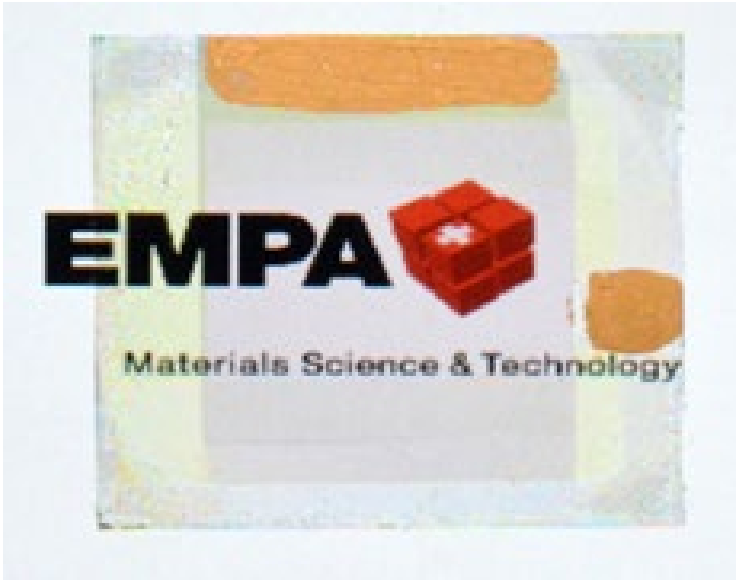
7.6 Organic solar cells (OPV)

Organic electronics – Printed electronics – Flexible electronics – Stretchable electronics - Plastic electronics

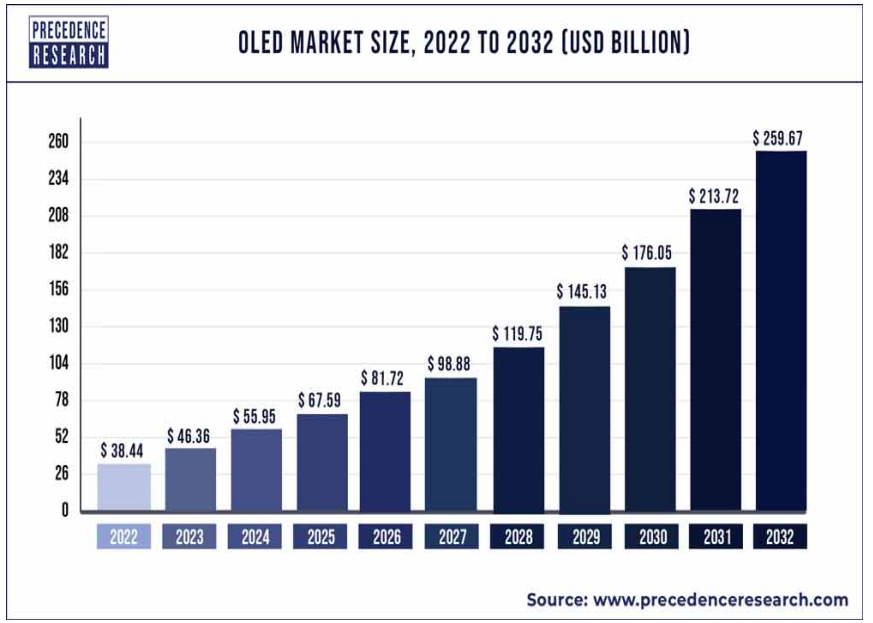
OPV single junction Record Power Conversion Efficiency: 19.3 %

Lei Zhu et al., Nat. Mat. (2022) *21*, 656

source: Belectric GmbH

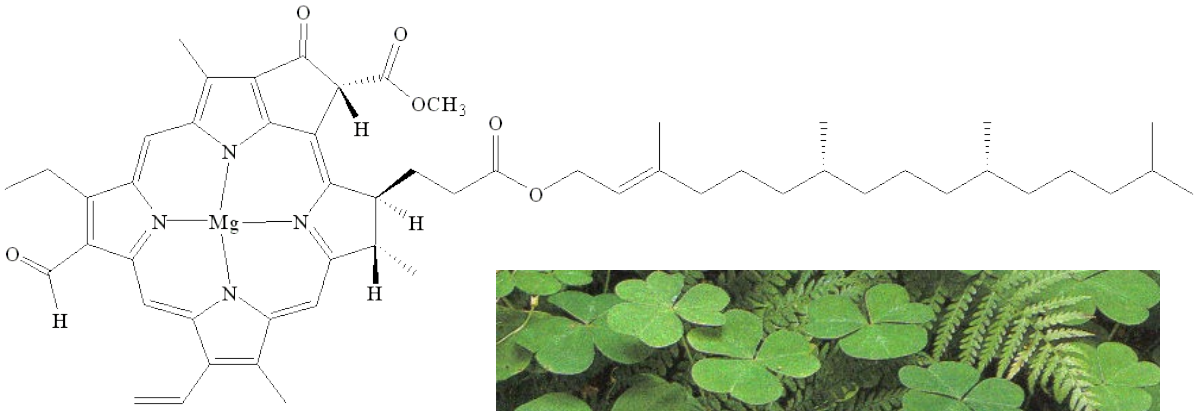


A. C. Véron et al., Org. Lett. (2014) *16*, 4, 1044–1047

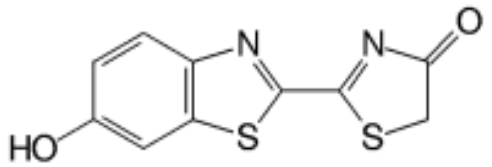


https://www.precedenceresearch.com/oled-market 05.2024

Organic semiconductors ≠ biomaterials

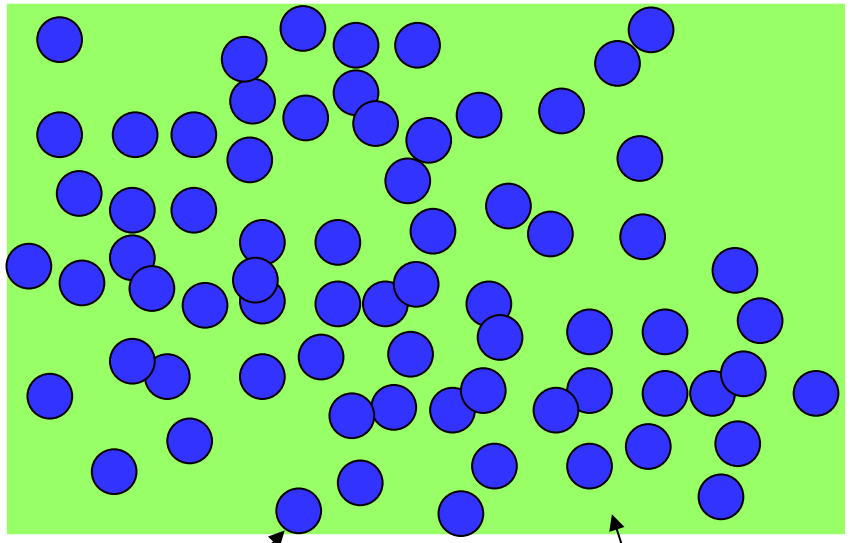


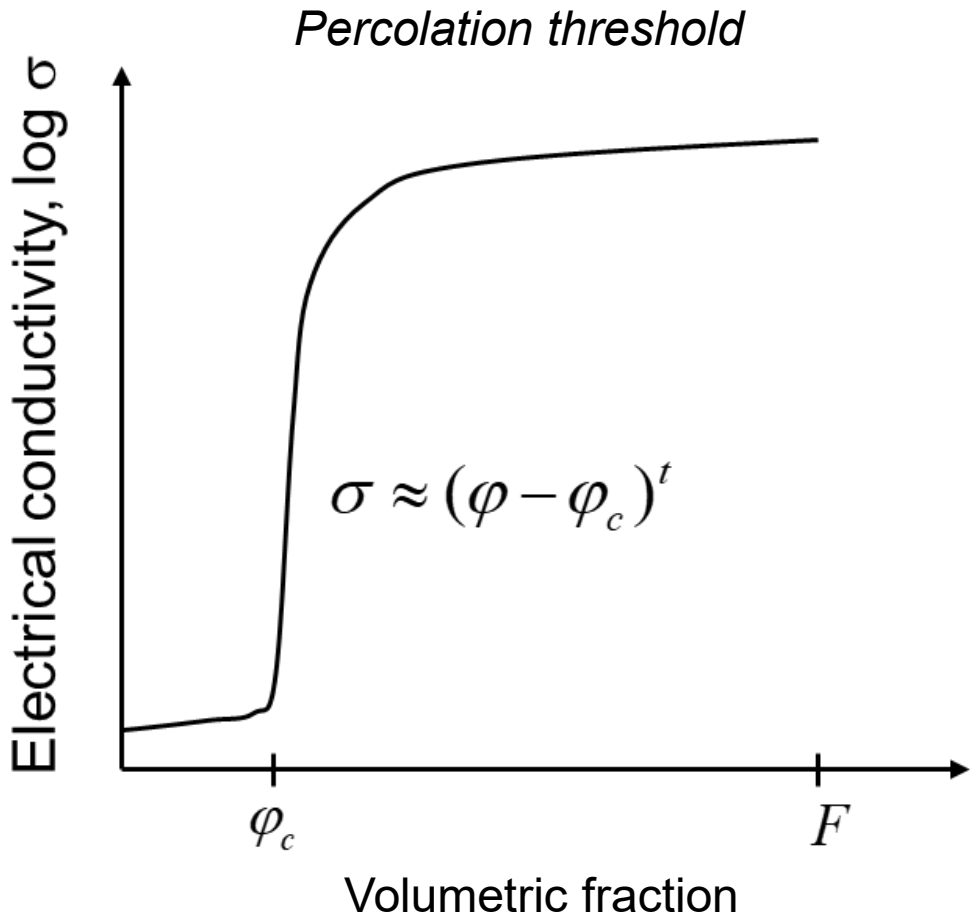
chlorophyll b



oxyluciferin

Organic semiconductors ≠ Polymer composites with metallic fillers



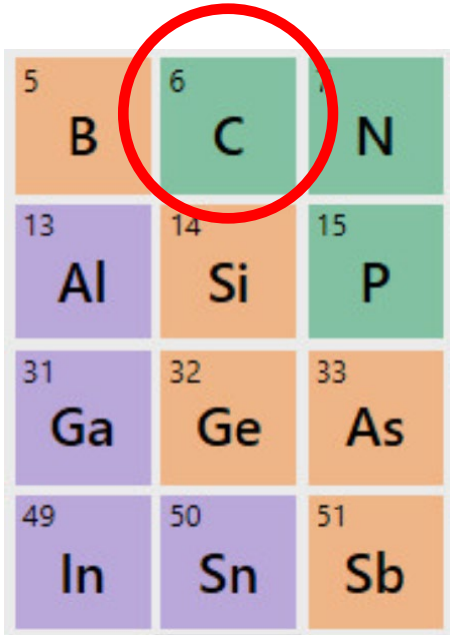


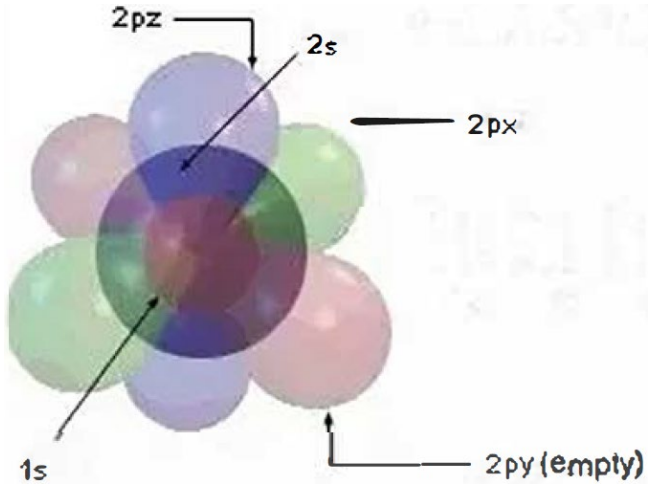
F Maximum loading

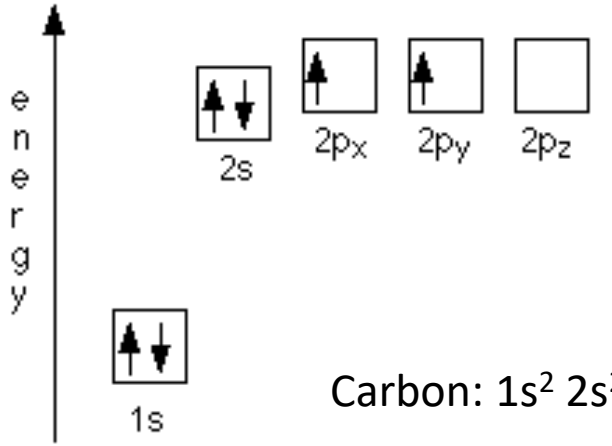
φ_c Critical percolation loading

φ Particle loading

The beauty about carbon





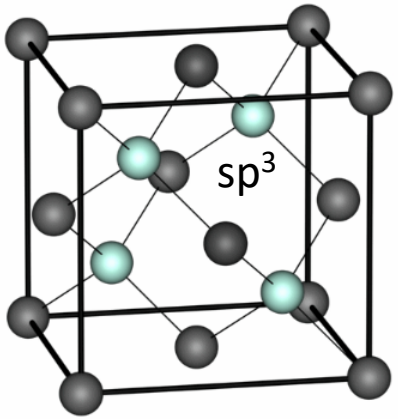


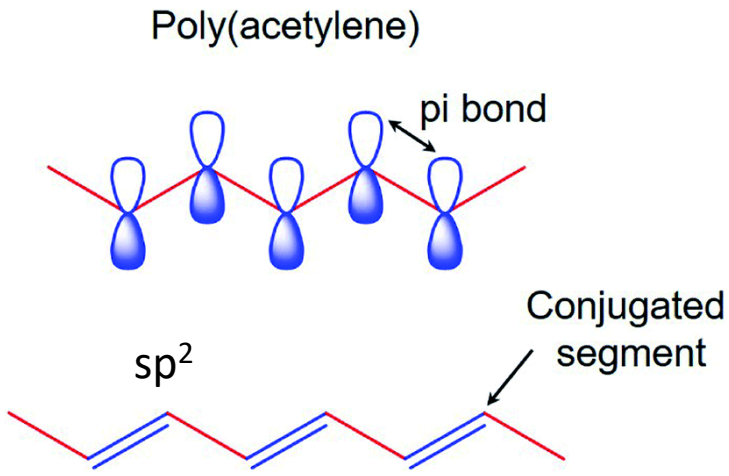
Carbon: $1s^2\ 2s^2\ 2p^2$

Linus Pauling: hybridization of orbitals with the same energy: sp, sp^2, sp^3

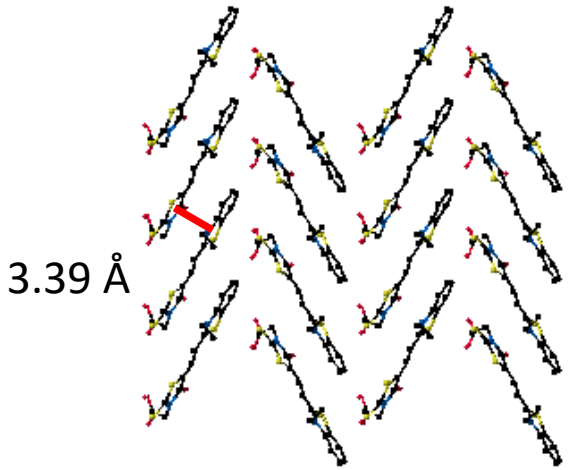
Using diamond?
Bandgap:

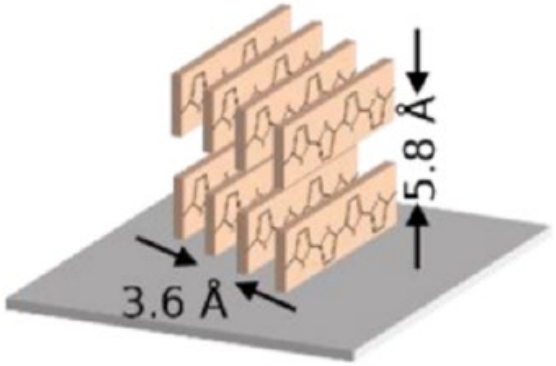
C: 5.47 eV
Si: 1.12 eV
Ge: 0.76 eV

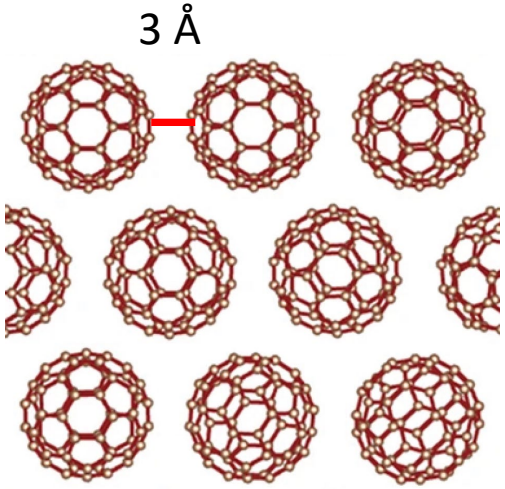


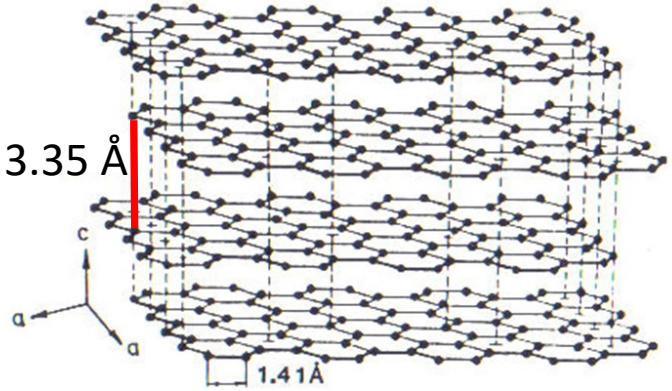


Structure of organic molecular solids





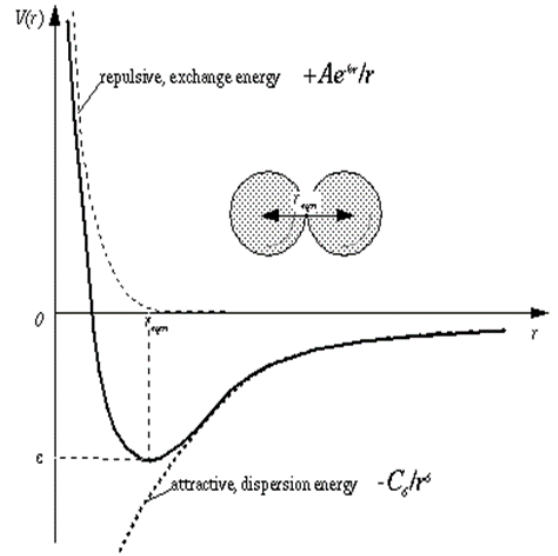




Cohesion forces in molecular solids are Van der Waals forces:

- ❑ Dipole-dipole
- ❑ Dipole-induced dipole
- ❑ Induced dipole-induced dipole (London)

Lennard Jones potential



Carbon-carbon Van der Walls distance: 3.4 A

7.1 Absorption in organic semiconductors

Due to the small interaction between molecules in Van der Waals solids, we make the assumption that intermolecular interactions are rather small. As treated in chapter 1.5 the transition probability P has its maximum at resonance, i.e. when $\omega_{if} = \frac{1}{\hbar}\left(E_f - E_i\right)$, meaning that energy is conserved. E_i and E_f are the initial and final state of the molecule, respectively. At the bandgap the involved states correspond to the Highest Occupied Molecular Orbital (HOMO) φ_{HOMO} and the Lowest Unoccupied Molecular Orbital (LUMO) φ_{LUMO}.

$P \sim \left|\vec{E}\right|^2 \cdot \left|\vec{\mu}_{if}\right|^2$ $\vec{\mu}_{if}$ is the transition dipole moment:

$\vec{\mu}_{if} = \int \psi_i^* \; e \cdot \vec{r} \; \psi_f \; d^3\vec{r}$ the wave functions ψ_i and ψ_f include the spatial, vibrational and spin functions.

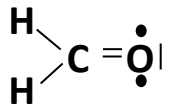
In the **Born-Oppenheimer approximation**, the nuclei are treated as stationary when the electrons move around them. The Schrödinger equation can therefore be solved for the electrons only, keeping the nuclei at defined positions. For small spin-orbit coupling, this allows to factorize the transition dipole moment in the following way: $\psi = N \cdot \varphi \cdot S$, where N is the nuclear wavefunction, φ is the spatial wavefunction (its square corresponds to the orbital) and *S* is the spin wavefunction. Therefore we can write for a HOMO-LUMO transition:

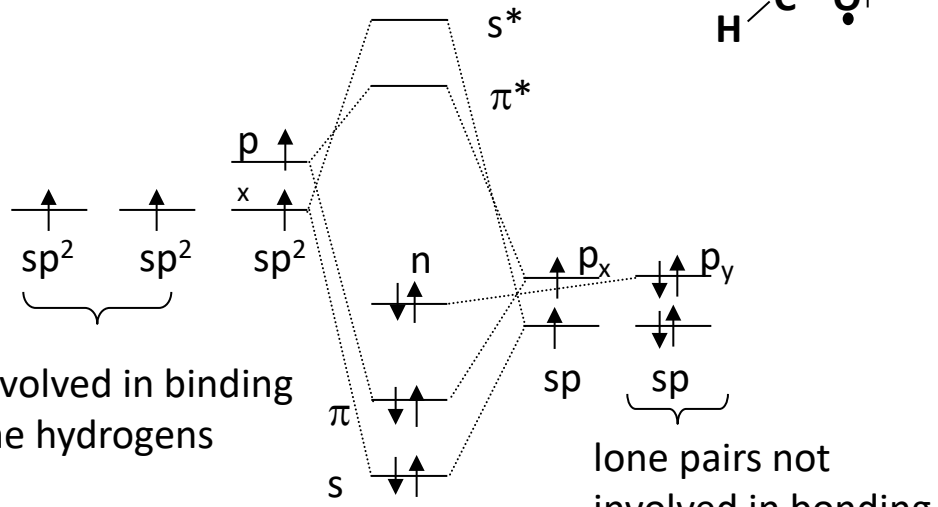
$\vec{\mu}_{if} = \langle \varphi_i | e\vec{r} | \varphi_f \rangle \langle N_i | N_f \rangle \langle S_i | S_f \rangle$ where $\langle \varphi_i | e\vec{r} | \varphi_f \rangle = \int \varphi_i^* \; e \cdot \vec{r} \; \psi_f \; d^3\vec{r}$

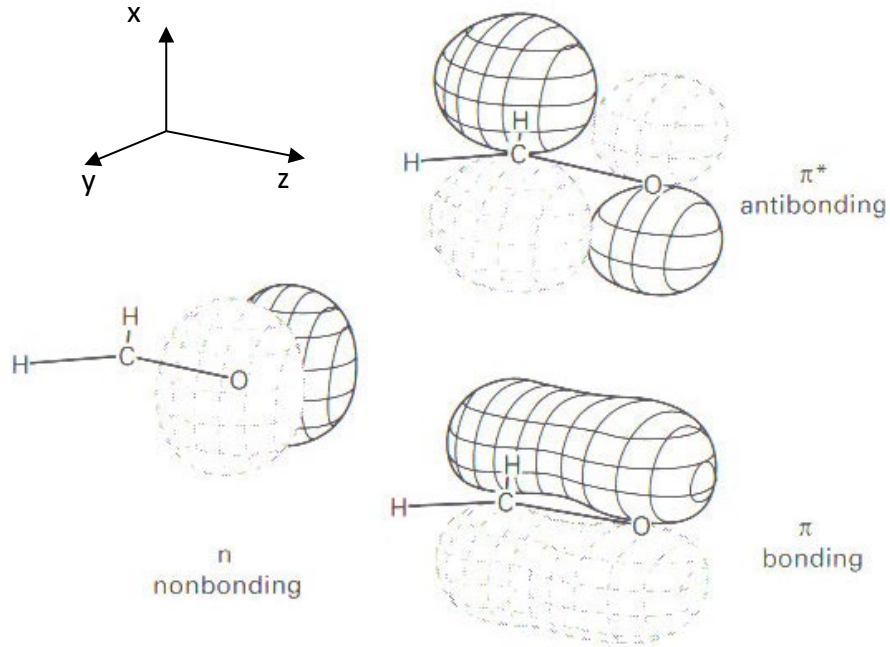
Symmetry allowed/forbidden transitions

A transition is said to be symmetry forbidden, if all the components of $\langle \varphi_i | e\vec{r} | \varphi_f \rangle$ are zero. In general the calculation of such integrals is time consuming. Computational methods could therefore be accelerated if there would be a direct method to determine those integrals that are zero for symmetry reasons.
Group theory is a very powerful mathematical theory that can be applied to a number of fields in physics. It can be used to determine whether an optical transition for a given polarization of the light is allowed or not by considering the orbital symmetry of initial and final orbital. In such a case, the integral $\langle \varphi_i | ex | \varphi_f \rangle$ would vanish or not. However, group theory can not determine the precise value of the integral.

Example: formaldehyde



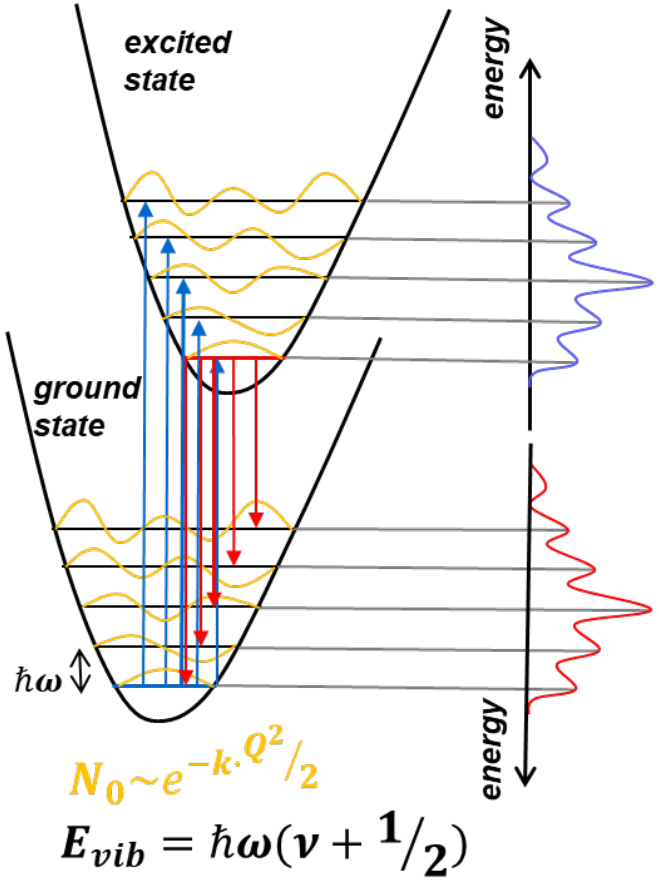




the p-p* transition is allowed, while the n-p* transition is forbidden by symmetry

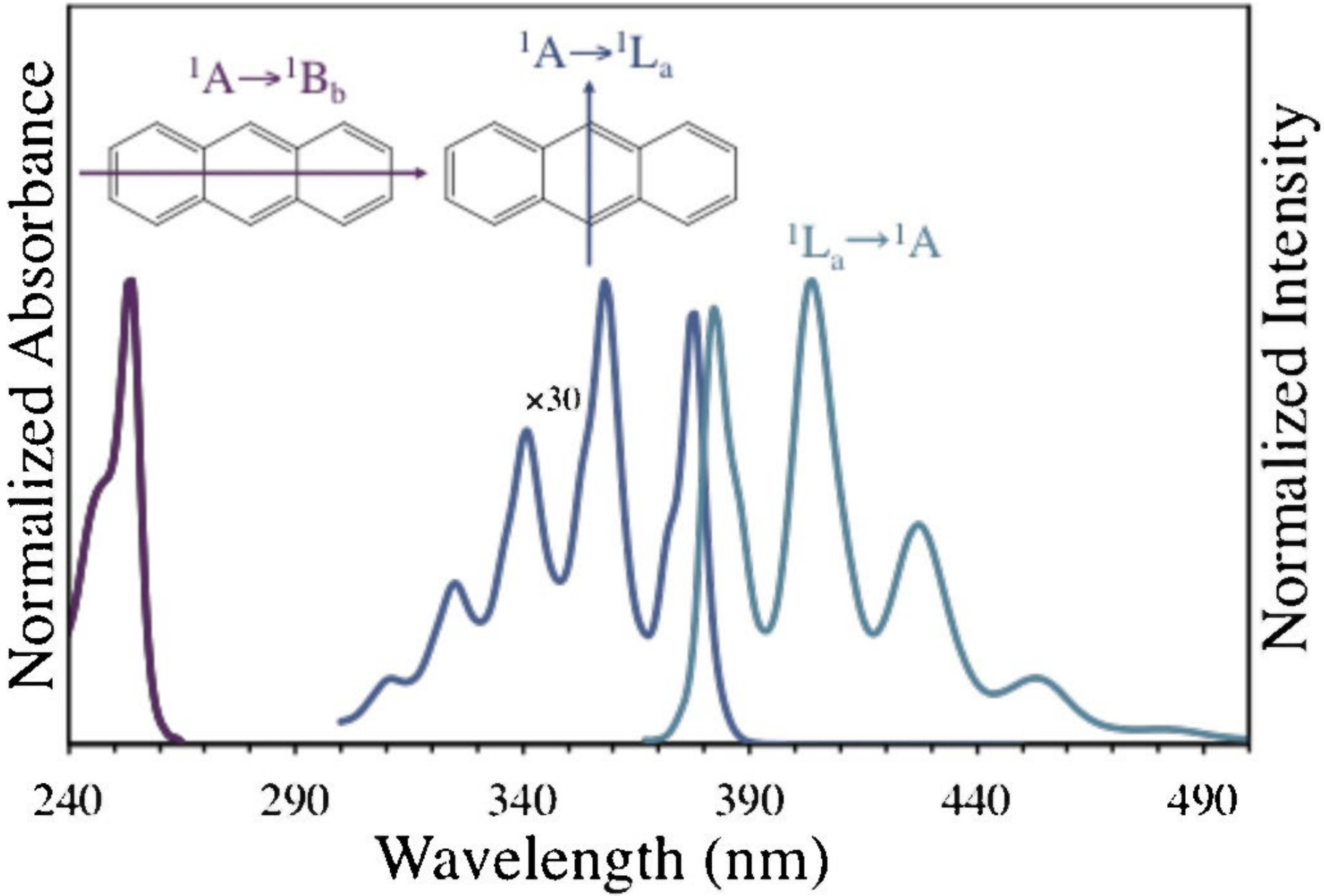
Vibronically allowed transitions - the Franck-Condon principle

Using the same argument as in the Born-Oppenheimer approximation, we can say that electronic transitions occur rapidly compared to nuclear motion. Thus, the nuclei remain essentially "frozen" in the ground state during the transition. Since the electronically excited state thus generated is likely to have different structural properties compared to the ground state, we expect some changes in the nuclear configuration to take place after the transition has occurred. This is the Franck-Condon principle.

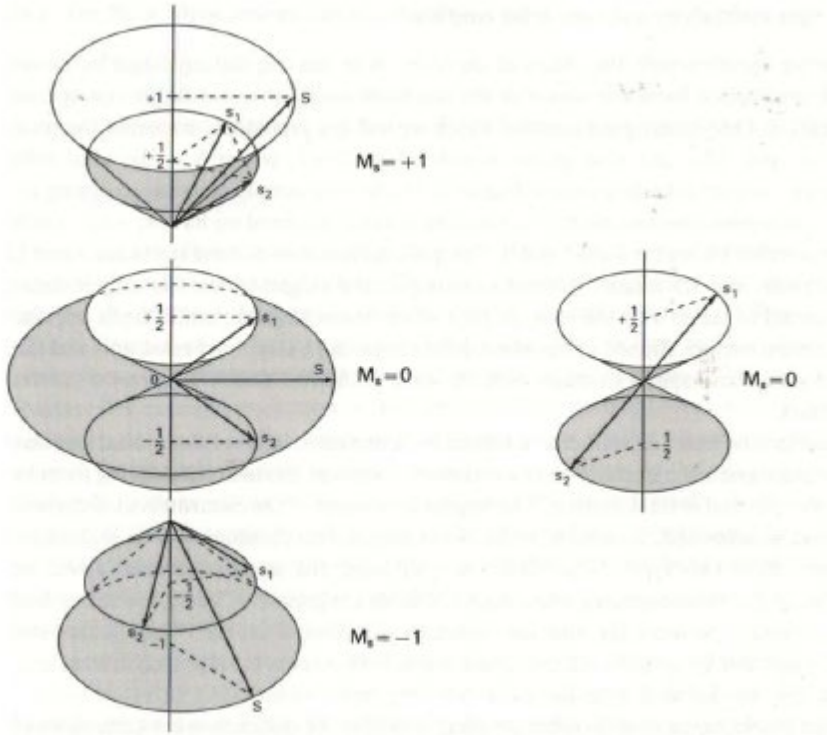


The consequence of this principle is illustrated in the Figure below. In this figure, the potential energy curve of a diatomic molecule in its electronically excited state is displaced to larger equilibrium internuclear separations compared to the ground state. The better the vibronic overlap, the larger will be the nuclear overlap integral $\langle N_i | N_f \rangle$ and the more probable will be the transition.

For a molecule, where the equilibrium geometry in the ground and excited state is similar, the largest vibrational overlap comes from the wavefunctions of the $\nu_{ground} = 0$ and $\nu_{excited} = 0$ levels. For a molecule that possesses a different equilibrium geometry in the excited state compared to the ground state, the largest overlap integral will arise form the vibrational wavefunctions of the levels $\nu_{ground} = 0$ and $\nu_{excited} > 0$. This is illustrated on the left.


$^1A \rightarrow {}^1B_b$
$^1A \rightarrow {}^1L_a$
$^1L_a \rightarrow {}^1A$
×30
Normalized Absorbance
Normalized Intensity
240
290
340
390
440
490
Wavelength (nm)

Spin selection rule



In the ground state of almost all conjugated semiconducting molecules, two electrons fill the HOMO (highest occupied molecular orbital) with antiparallel spins s_1 and s_2 (Pauli exclusion principle). This spin state is antisymmetric and is called singlet. In the excited state, one of 4 possible spin states is allowed, namely 1 singlet state and 3 triplet states. This results from the quantum mechanical treatment of angular momentum. The different two electron spin states are shown to the left. $\alpha(1)$ describes an "up" spin of electron 1, while for example $\beta(2)$ describes "down" spin of electron 2.
For any optical transition, the following spin selection rule holds:

$$\Delta \boldsymbol{S} = \boldsymbol{0}$$

Triplet states:

$$\boldsymbol{S}_{+1} = \boldsymbol{\alpha(1)\alpha(2)}$$

$$\boldsymbol{S}_{-1} = \boldsymbol{\beta(1)\beta(2)}$$

$$\boldsymbol{S}_{+} = {}^{\boldsymbol{1}}/_{\sqrt{\boldsymbol{2}}}\big(\boldsymbol{\alpha(1)\beta(2) + \beta(1)\alpha(2)}\big)$$

Singlet state:

$$\boldsymbol{S}_{-} = {}^{\boldsymbol{1}}/_{\sqrt{\boldsymbol{2}}}\big(\boldsymbol{\alpha(1)\beta(2) - \beta(1)\alpha(2)}\big)$$

In real molecules, the singlet and triplet excited states may be coupled as a consequence of spin – orbit coupling. The magnitude of spin-orbit coupling depends strongly on the atomic number *Z*, *i.e.* ~Z^4.

11

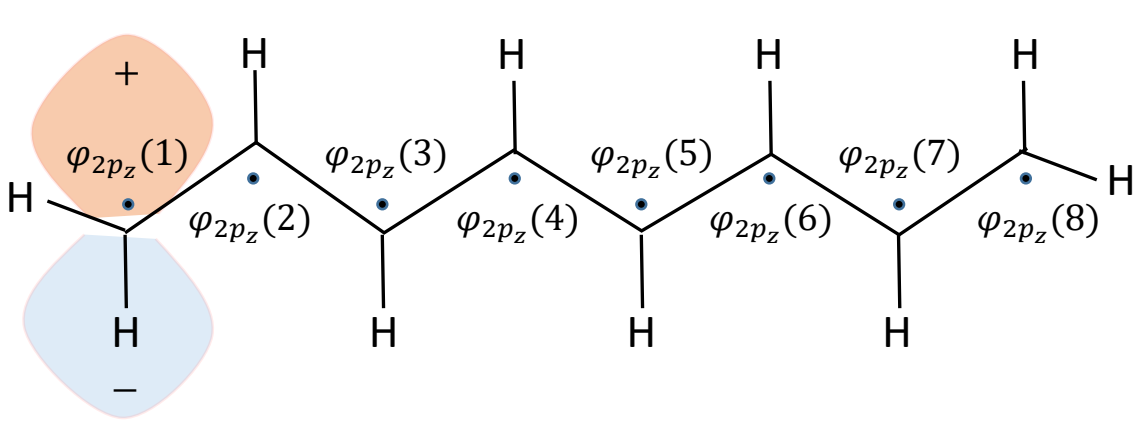
7.2 LCAO approach and the Hückel Molecular Orbitals

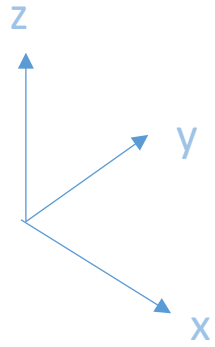
The mathematical problem is to solve the Schrödinger equation for a extremely complex multi-particle system. The Linear Combination of Atomic Orbitals (LCAO) approach considers that the atomic wavefunctions are only weakly perturbed in the molecule (in the solid we call this the tight binding method). Therefore the molecular (crystal) wavefunction can be approximated by a linear combination of atomic orbitals.

To describe π-molecular orbitals (MO), Erich Hückel uses a linear combination of $2p_z$ atomic orbitals, neglecting orbital contributions from 2s, $2p_x$, $2p_y$ states.

$$\hat{H}\psi_\pi = E\psi_\pi \quad \text{with} \quad \psi_\pi = \sum_{n=1}^{N} c_n \varphi_{2p_z}(n)$$

$\hat{H}$ is the Hamiltonian of the electronic system, ψ_π is the π-electron wavefunction (it is a single electron wavefunction) and E is the energy of the π-electron state with wavefunction ψ_π. The π-orbital corresponds to the latter wavefunction and its circumference is generally given by the 90% contour probability (proportional to $|\psi_\pi|^2$) to find the electron within the volume of the orbital.





To find the energies E and MOs ψ_π, the expectation value of the energy $\langle E \rangle$has to be minimized. First ψ_π is normalized:

$$\psi'_\pi = \psi_\pi / \sqrt{\int \psi_\pi^* \, \psi_\pi} \qquad \text{then} \qquad \langle E \rangle = \int \psi'^*_\pi \hat{H} \psi'_\pi = \frac{\int \psi_\pi^* \, \hat{H} \, \psi_\pi}{\int \psi_\pi^* \; \psi_\pi}$$

The variational method for finding the lowest energy value $\langle E \rangle$ consists of calculating the derivatives:

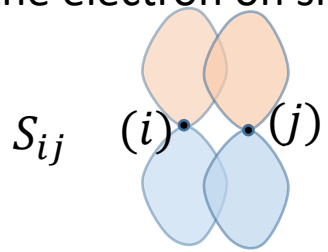
$\frac{\partial \langle E \rangle}{c_1} = 0, \frac{\partial \langle E \rangle}{c_2} = 0, \ldots . \frac{\partial \langle E \rangle}{c_N} = 0.$ This results in a system of N homogeneous linear equations with the following solution:

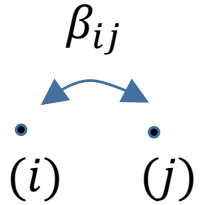
$$Det \begin{bmatrix} \alpha_{11} - E & \beta_{12} - ES_{12} & \beta_{13} - ES_{13} & \cdots & \cdots & \cdots \\ \beta_{21} - ES_{21} & \alpha_{22} - E & \beta_{23} - ES_{23} & \cdots & \cdots & \cdots \\ \beta_{31} - ES_{31} & \beta_{32} - ES_{32} & \alpha_{33} - E & \cdots & \cdots & \cdots \\ & \cdots \; \cdots \; \cdots & & \cdots & \cdots & \cdots \\ & \cdots \; \cdots \; \cdots & & \cdots & \cdots & \cdots \\ & \cdots \; \cdots \; \cdots & & \cdots & \cdots & \cdots \end{bmatrix} = 0$$

$\alpha_{ii} = \int \varphi^*_{2pz}(i) \, \hat{H} \; \varphi_{2p_z}(i)$ <0 : Coulomb integral (the energy of the electron on site i)

$\beta_{ij} = \int \varphi^*_{2pz}(i) \, \hat{H} \; \varphi_{2p_z}(j)$ <0 : Transfer (or resonance) integral

$S_{ij} = \int \varphi^*_{2pz}(i) \; \varphi_{2p_z}(j)$: Overlap integral

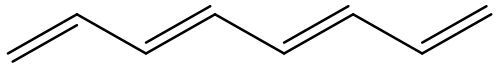




Hückel introduced the following approximation to simplify the computation:

- $\alpha_{11}=\alpha_{22}=\alpha_{33}=\alpha_{44}=\ldots=\alpha$ (all site energies are equivalent)
- All overlap integrals are set to zero $S_{ij}=0$
- All transfer integrals between non neighbors are zero: $\beta_{ij}=0$ for $|i-j|>1$
- All next neighbor transfer integrals are set to β

Linear conjugated chains with N atoms

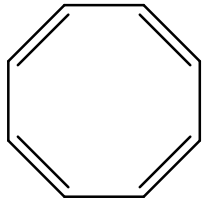


$$Det\begin{bmatrix} \alpha - E & \beta & 0 & 0 & \ldots \\ \beta & \alpha-E & \beta & 0 & \ldots \\ 0 & \beta & \alpha-E & \beta & \ldots \\ 0 & 0 & \beta & \alpha-E & \ldots \\ \ldots & \ldots & \ldots & \ldots & \ldots \end{bmatrix}=0$$

$$E_k=\alpha+2\beta\,cos\left(\frac{k\,\pi}{N+1}\right) \qquad k=1,2,\ldots N$$

$$\psi_k=\sum_{n=1}^{N} c_n^k\;\varphi_{2pz}(n) \qquad with \quad c_n^k=\sqrt{\frac{2}{N+1}}\,sin\left(\frac{kn\,\pi}{N+1}\right)$$

Conjugated annulenes with N atoms

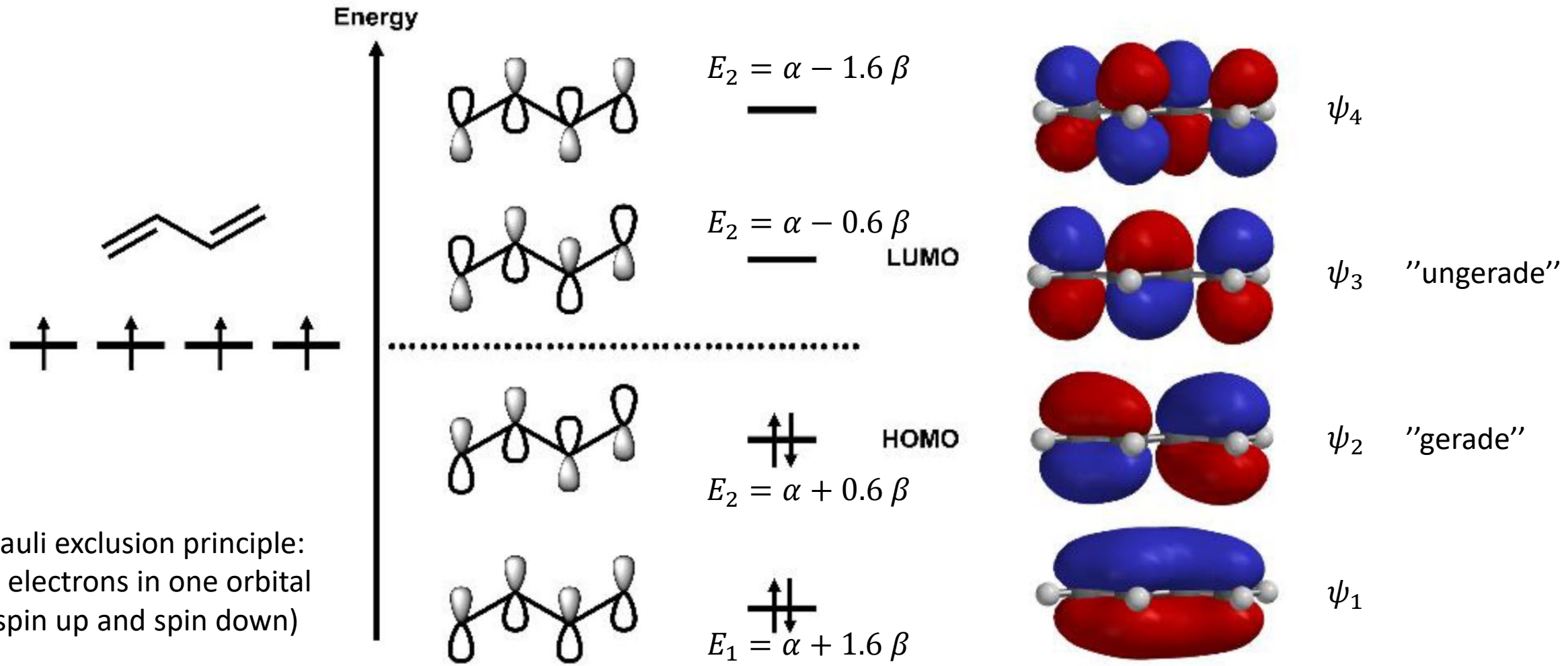


$$Det\begin{bmatrix} \alpha - E & \beta & 0 & 0 & \beta \\ \beta & \alpha-E & \beta & 0 & \ldots \\ 0 & \beta & \alpha-E & \beta & \ldots \\ 0 & 0 & \beta & \alpha-E & \ldots \\ \beta & \ldots & \ldots & \ldots & \ldots \end{bmatrix}=0$$

$$E_q=\alpha+2\beta\,cos\left(\frac{2\pi q}{N}\right) \qquad q=1,2,\ldots N$$

$$\psi_q=\sum_{n=1}^{N} c_n^q\;\varphi_{2pz}(n) \qquad with \quad c_n^q=\sqrt{\frac{1}{N}}\,exp\left(\frac{i\,2\pi qn}{N}\right)$$

Example of butadiene

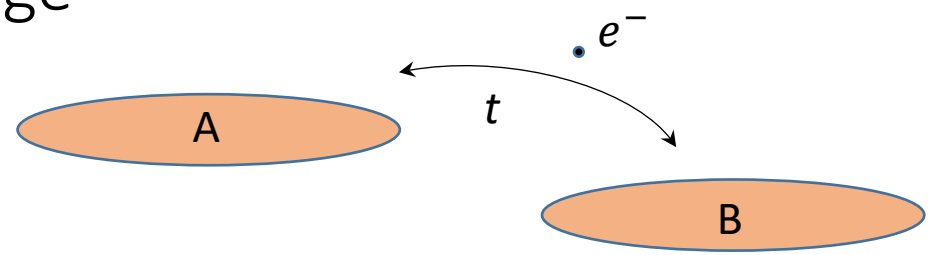


Pauli exclusion principle:
2 electrons in one orbital
(spin up and spin down)

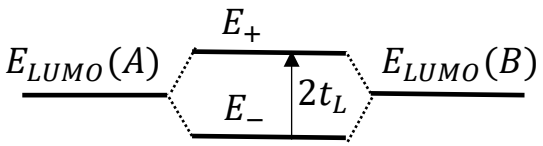
Energy of π – electron system: $E_\pi = 2 \cdot (\alpha + 1.6\,\beta) + 2 \cdot (\alpha + 0.6\,\beta) = 4 \cdot \alpha + 4.4\,\beta$ (stabilization energy: $4.4\,\beta$

$E_{abs} = \psi_{LUMO} - \psi_{HOMO} = 1.2\,\beta$

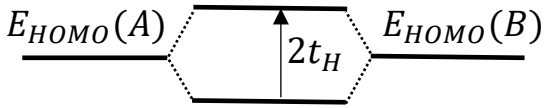
7.3 Transfer of charge



Similar to what we have discussed in the theory of molecular orbitals (Hückel theory) **electronic coupling *t*** between two molecules A and B can be described by using the same approach. As a result, the molecular orbitals of the dimer AB split up according



$$t_{LUMO} = \int \varphi_{LUMO}(A)\hat{H}\varphi_{LUMO}(B)dx$$



$$t_{HOMO} = \int \varphi_{HOMO}(A)\hat{H}\varphi_{HOMO}(B)dx$$

Of course the HOMO orbital of A also interacts with the LUMO orbital of B, but one can show that the splitting due to states with different energy decreases rapidly with the energy difference.

Computationally (e.g. using a HF or DFT calculation) the splitting energy $\Delta E = E_+ - E_-$ is calculated and formally set to $2t$: $\Delta E = E_+ - E_- = 2t$. This is called the **dimer splitting method**.

Similarly to the Hückel theory, we can directly find the energies of the molecular orbital energy levels in a stack of weekly coupled molecules (tight binding approximation). The example below illustrates band formation for the HOMO levels in one dimension (band formation for the coupled LUMO levels is analogous):

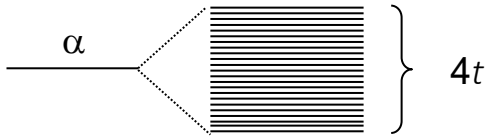
$$E_{HOMO,n} = \alpha + 2tcos\left(\frac{n\pi}{N+1}\right) \quad n = 1,2,\dots,N$$

$$\alpha = \int \varphi_{Homo}(n)\hat{H}\,\varphi_{Homo}(n)\mathrm{dx}$$

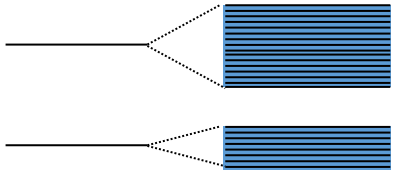
$$t = \int \varphi_{Homo}(n)\hat{H}\,\varphi_{Homo}(n+1)\mathrm{dx}$$

α is the Coulomb integral (site energy) , t is the resonance or transfer integral and $\hat{H}$ is the Hamiltonian of the molecular stack.

For very large *N*, the levels *E(n)* become very dense and form a band with a width of 4*t*. :



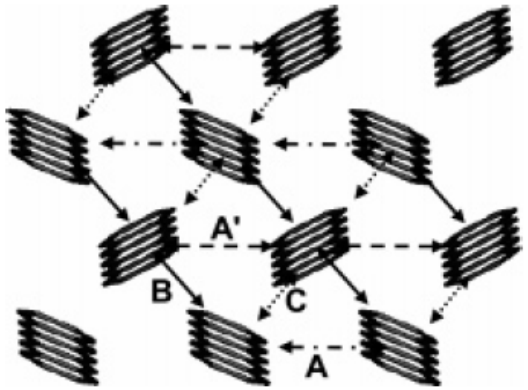
If each molecule in the periodic lattice would contribute to the band with two electrons, the band would be completely filled (apart from thermally excited carriers). This is the case for an insulator or semiconductor.



insulator at *T*=0

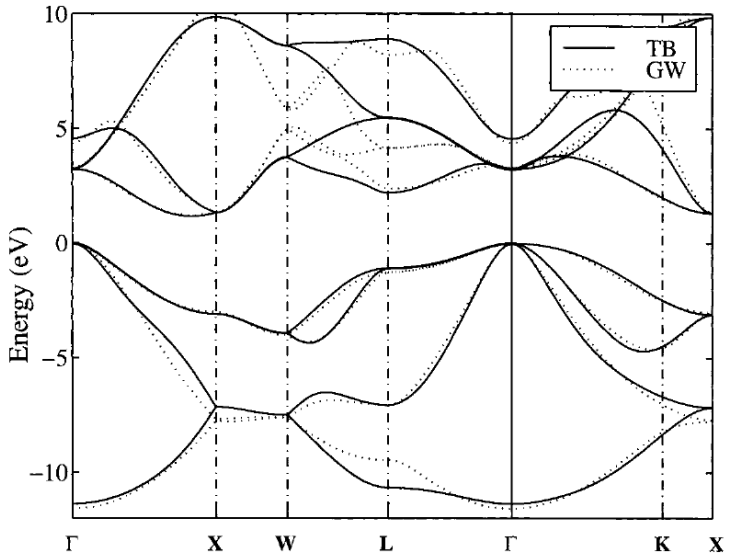
If each molecule contributes with just one electron (for example in the case of a heavily doped semiconductor), the band would be half filled. This is the case of a good conductor (e.g. charge transfer salts).

Energy bands in organic semiconductors compared to the bandstructure of inorganic semiconductors



Pentacene		
	t (cm^{-1})	t (meV)
A	455	56
A’	477	59
B	-616	76
C	983	122
Anthracene		
A	-630	78
B	477	59

Calculated transfer integrals for different directions A’, A, B, C in the case of anthracene and pentacene at(300K)
Troisi et al. (*J. Phys. Chem. A, Vol. 110, No. 11, 2006)*

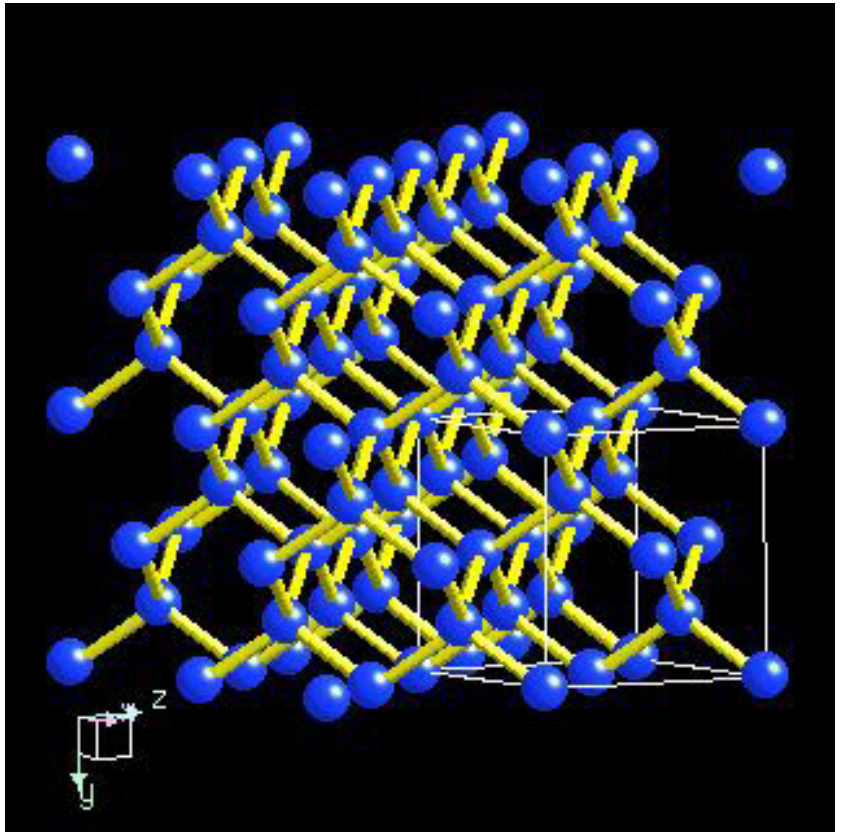


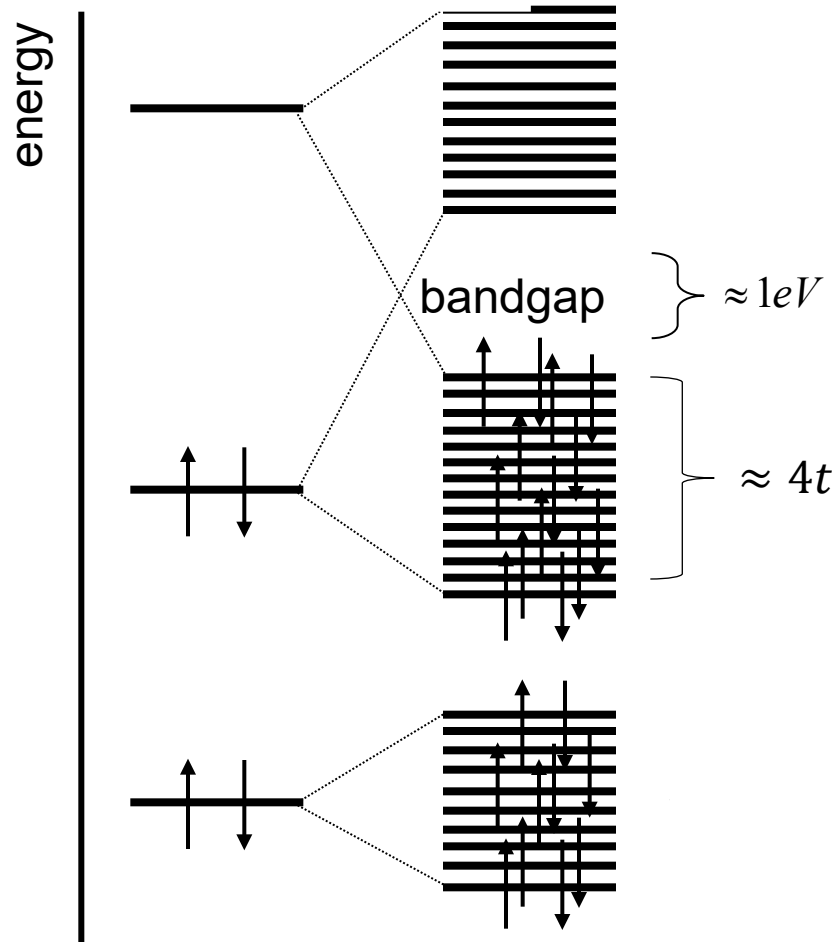
Band structure of silicon calculated by the tight binding method and Green’s Function approach. C. Delerue, M. Lannoo, G. Allan, Phys. Stat. Sol. , 227 (1), p. 115-149, 2001.

In comparison to organic *molecular* semiconductors, the transfer integral t between nearest neighbors (NN) in diamond, silicon or germanium is higher by one to two orders of magnitude:

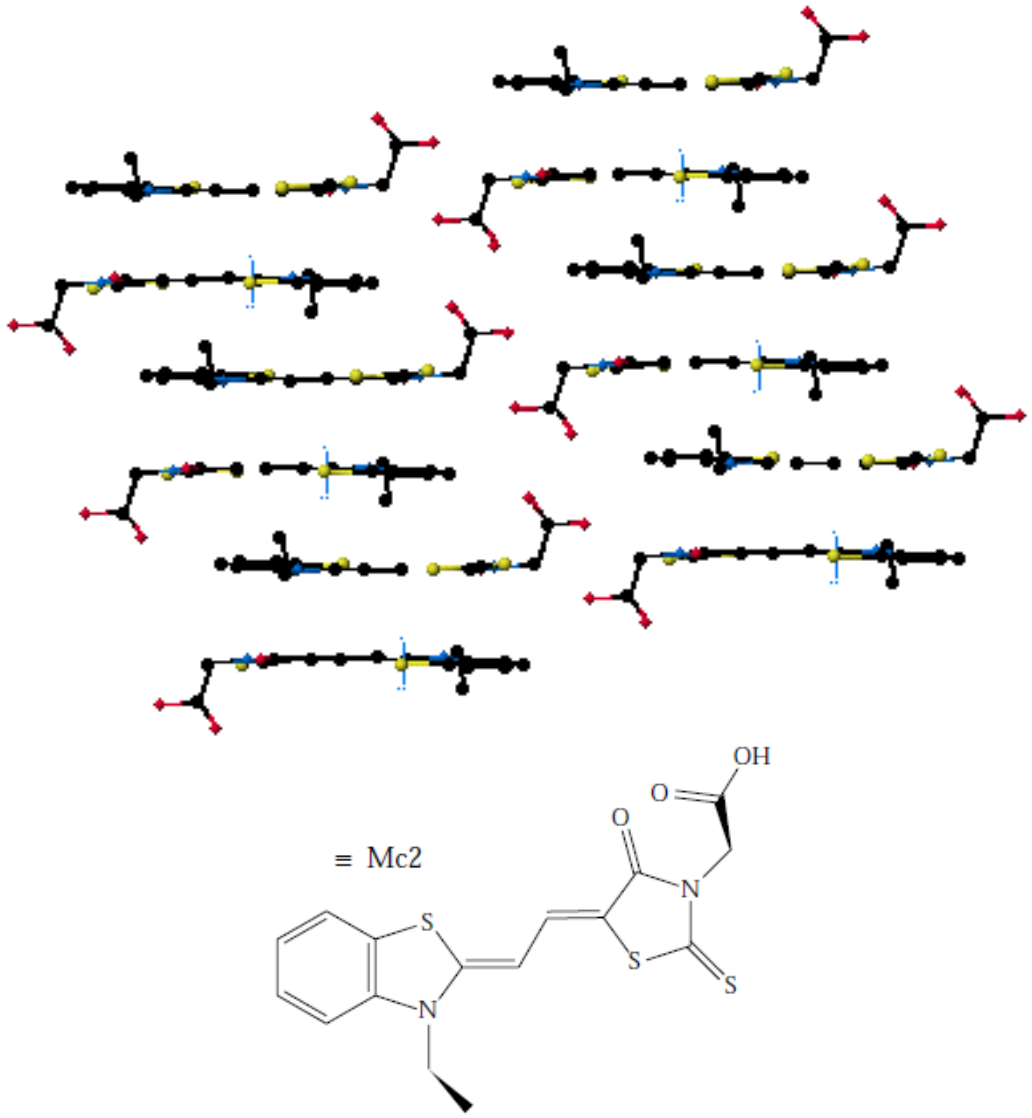
$t_{inorganic}$= 1 - 3 eV
$t_{molecular}$= 0.01- 0.1eV

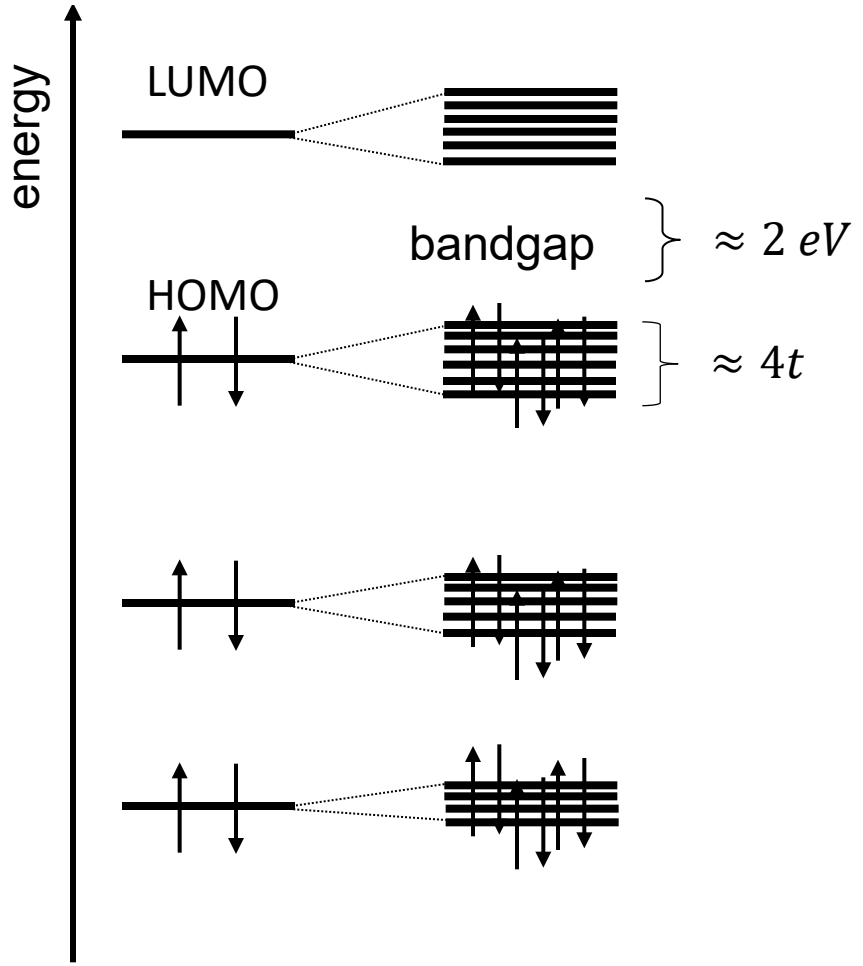
Crystalline Silicon – the diamond structure





Molecular crystals



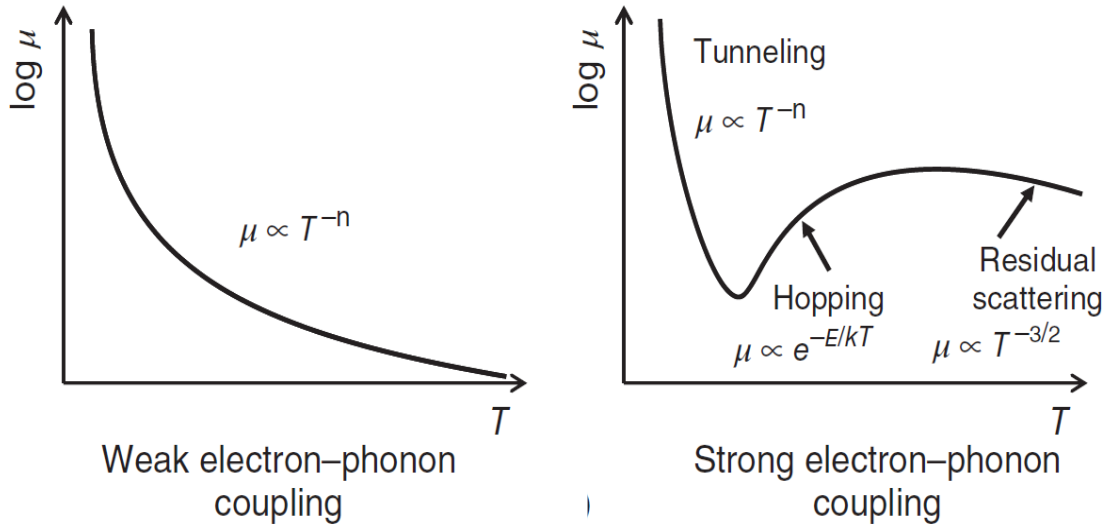


energy levels of the molecule

energy bands of the organic semiconductor

Band transport and Hopping transport

Band transport is effective when the electronic coupling *t* is larger than any other energy terms due to static or dynamic disorder. In this case the mobility of charge carriers increases with decreasing temperature as is the case in a metal (see left figure below). If disorder becomes larger than the electronic coupling between molecular sites, then various regimes are observed, notably a thermally activated hopping regime, which applies to most amorphous films used in organic optoelectronics (right figure below).



Charge carrier mobilities μ at room temperature cm^2/Vs

organic semiconductors			*inorganic semiconductors*		
crystalline			*crystalline*		
Anthracene	1.6 (e^-)	1.2 (h^+)	Si	1500 (e^-)	450 (h^+)
Pyrene	0.7 (e^-)	0.7 (h^+)	Ge	3900 (e^-)	1900 (h^+)
b-phthalocyanine	1.1(e^-)	1.4 (h^+)	GaAs	8500 (e^-)	400 (h^+)
Fullerene C_{60}	1.1(e^-)	1.0 (h^+)	InAs	80000 (e^-)	1250 (h^+)
amorphous			*amorphous*		
10^{-5} to 10^{-3} at high fields (1MV/cm)			Si ≈ 1		

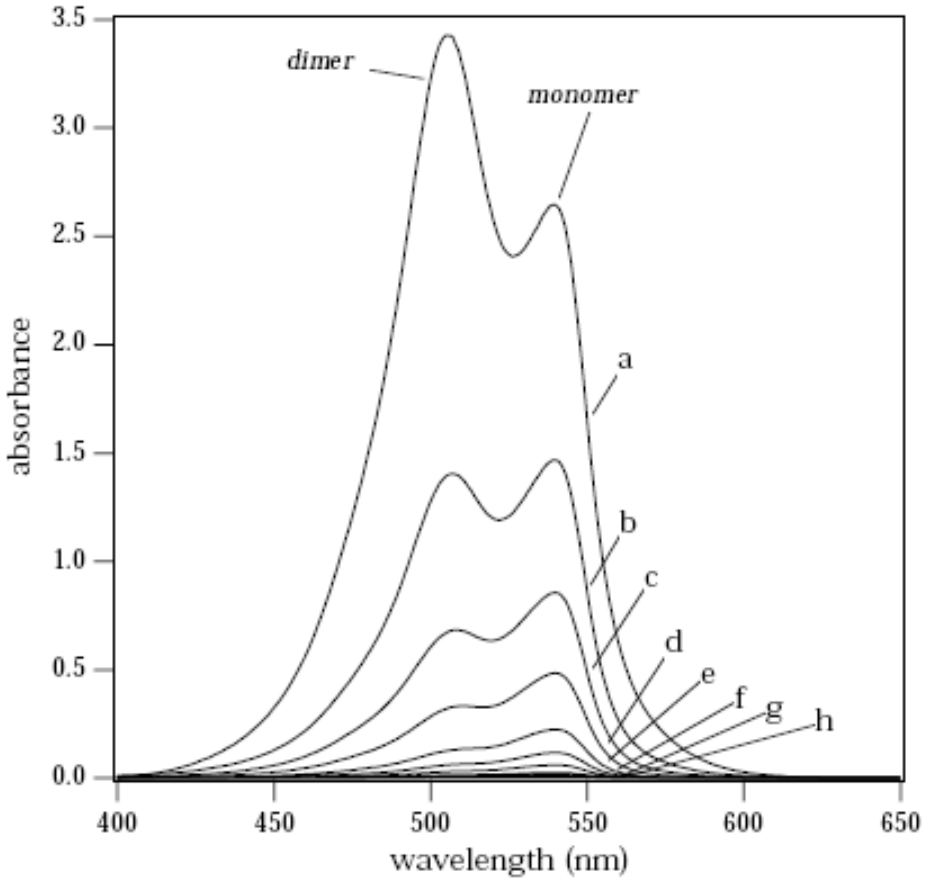
Relation between mobility and electronic coupling (transfer integral *t*):

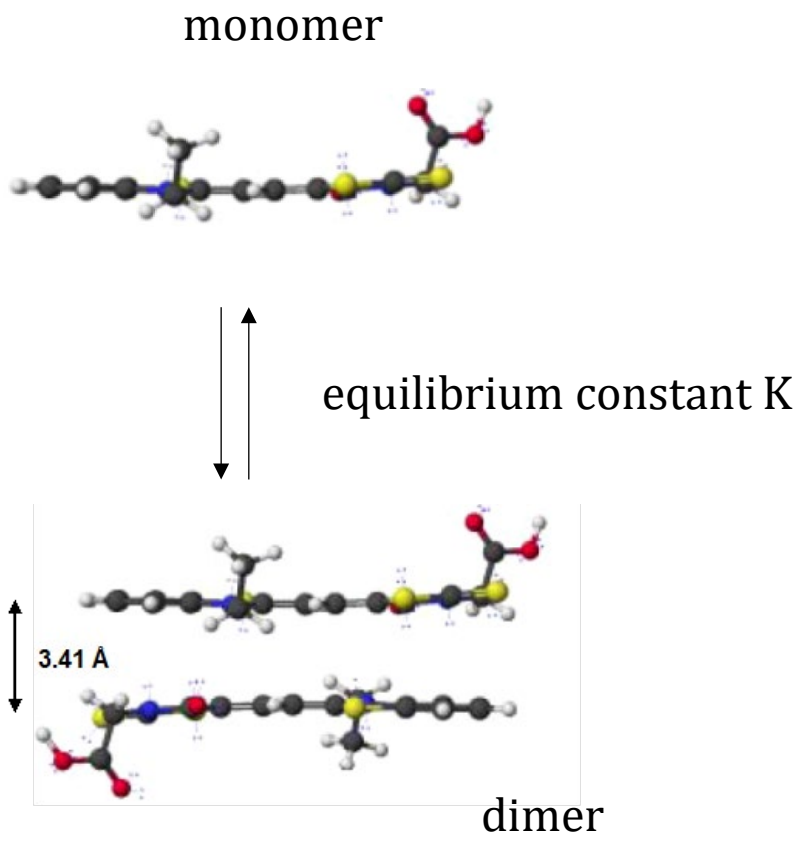
Strong electron coupling case: $\mu \sim t$

Weak electron coupling case: $\mu \sim t^2$

A. Köhler and H. Bässler Electronic Processes in Organic Semiconductors, Wiley-VCH, Weinheim, 2015.

7.4 Molecular exciton theory –transfer of energy





Absorption spectrum of a merocyanine dye in water for different concentrations. a: $5 \cdot 10^{-4}$ M, b: $2 \cdot 10^{-4}$ M, c: $1 \cdot 10^{-4}$ M, d: $5 \cdot 10^{-5}$ M, e: $2 \cdot 10^{-5}$ M, f: $1 \cdot 10^{-6}$ M , g: $5 \cdot 10^{-6}$ M, h: $2 \cdot 10^{-6}$ M.

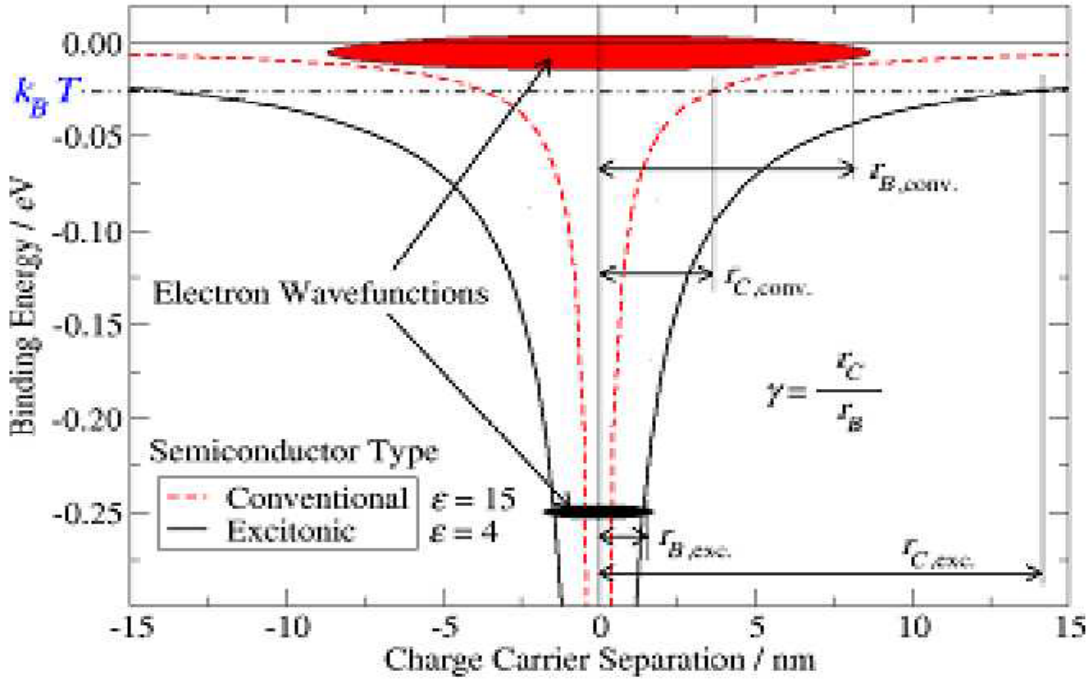
F. Nüesch et al., Chemical Physics 193 (1995) 1-17

Localized vs delocalized excitons in semiconductors

Due to the low dielectric constant in organic semiconductors (ε = 3-4) holes and electrons are not screened as much as in inorganic semiconductors (ε = 10-15). Also the electronic wavefunctions are localized as compared to those in inorganic semiconductors.

These conditions lead to high binding energy for excitons in organic semiconducotrs of about 0.4 eV, which means that excitons can not thermally be separated into free charge carriers. This contrasts with inorganic semiconductors, where excitons can be thermally split into free charge carriers at room temperature.
A large enough driving force (at least as high as the exciton binding energy) is therefore required for charge separation in organic semiconductors (strong electric field, heterointerface).

While delocalized **Wannier-Mott excitons** can be treated similar to a hydrogen atom to understand their optical properties, for **localized Frenkel excitons** in organic semiconductors and silver halides, a different treatment is required.



Adapted from Brian A. Gregg et al., Journal of Applied Physics, 93 (2003) 3605

Energy transfer processes

Energy transfer (ET) is an extremely important process in organic semiconductor devices with huge implications photochemistry, optoelectronics, biochemistry and sensorics. It can be viewed as follows:

$A^* + B \overset{ET}{\Rightarrow} A + B^*$ *A* and *B* designate the ground states of the molecules, A^* and B^* stand for the excited states.

The different processes may be classified according to:

- Radiative energy transfer in which the emitted photon from A^* is reabsorbed by B:
  This process requires that the emission spectrum of A^* overlaps with the absorption spectrum of B
.
- Nonradiative energy transfer in which a specific interaction between A^* and *B* is required. Two types of interaction may be identified which are termed Coulombic and electron-exchange energy transfer.

Coulombic energy transfer is dominated by “long-range” dipole-dipole interactions which cause perturbations of the electronic systems. It is also called **Förster Resonance Energy Transfer** (FRET) and has a range of 1-10 nm.

Electron exchange energy transfer, also called **Dexter Energy Transfer**, requires much closer contact between A^* and *B* since it involves an electron transfer mechanism. The typical range is 3-10 Å.

Molecular excitons

The formation of new absorption bands induced by intermolecular energy transfer interaction was considered by A. S. Davydov in 1948. Here we will treat the problem in a simpler way such as developed by Mc Rae and Kasha in 1964. The essential assumption of the theory is energy resonance:

$$A^* + B \overset{ET}{\Leftrightarrow} A + B^*$$

The solution of finding the excited state energies when energy resonance is present is to write the excited state wavefunction as a linear combination of excited state wavefunctions where each term incorporates an excited state of one of the molecules in the solid. For a dimer (two molecules) this would give:

$$\Phi_E = r \cdot \tilde{\psi}_A \psi_B + s \cdot \psi_A \tilde{\psi}_B$$

where ψ_A and ψ_B are the ground state wavefunctions of A and B, and $\tilde{\psi}_A$ and $\tilde{\psi}_B$ correspond to the excited states.

The result of this model is that the excited state energy of the dimer $\tilde{E}$ is split up into two exciton levels $\tilde{E}_J$:

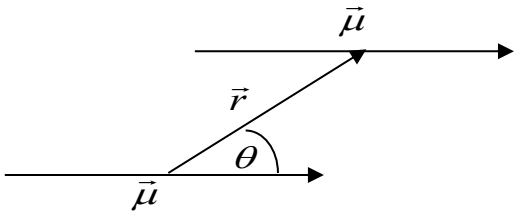
$$\tilde{E}_J = \tilde{E} \pm J$$

where J is the exciton coupling energy and can be as high as 200 meV.

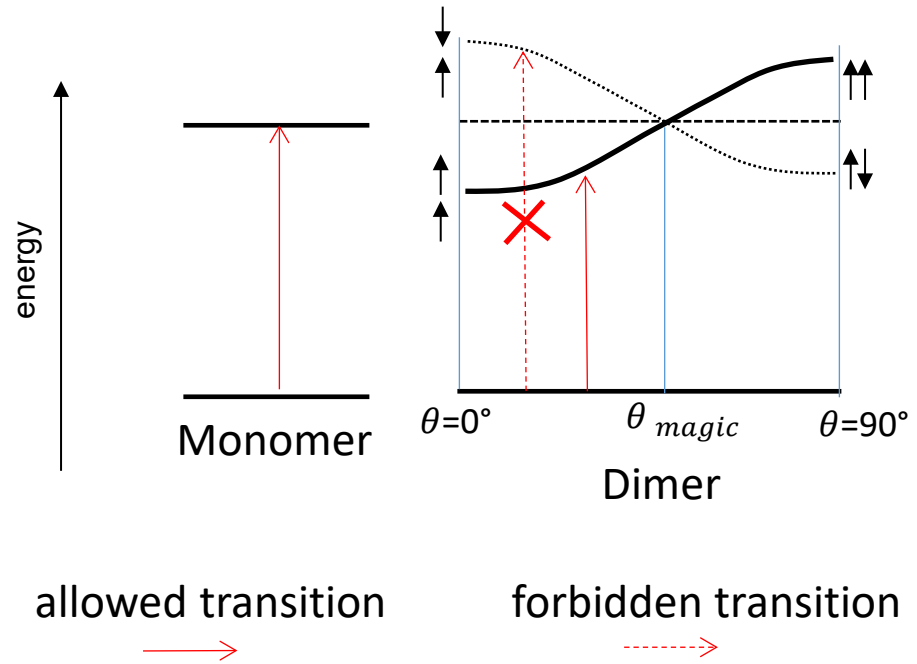
In the point dipole approximation, J is given by: $$J = \frac{1}{4\pi\varepsilon\varepsilon_0}\left[\frac{\vec{\mu}_A \cdot \vec{\mu}_B}{r^3} - \frac{3(\vec{\mu}_A \cdot \vec{r}) \cdot (\vec{\mu}_B \cdot \vec{r})}{r^5}\right]$$

where $\vec{\mu}_A = \int \psi_A e\vec{r}\tilde{\psi}_A$ and $\vec{\mu}_B = \int \psi_B e\vec{r}\tilde{\psi}_B$ are the transition dipole moments of *A* and *B*, respectively.
In the case of parallel transition dipole moments of identical molecules, a simple expression for J can be obtained:

$$J = \frac{\vec{\mu}^2}{4\pi\varepsilon\varepsilon_0 r^3}[1 - 3 \cdot \cos^2\theta]$$

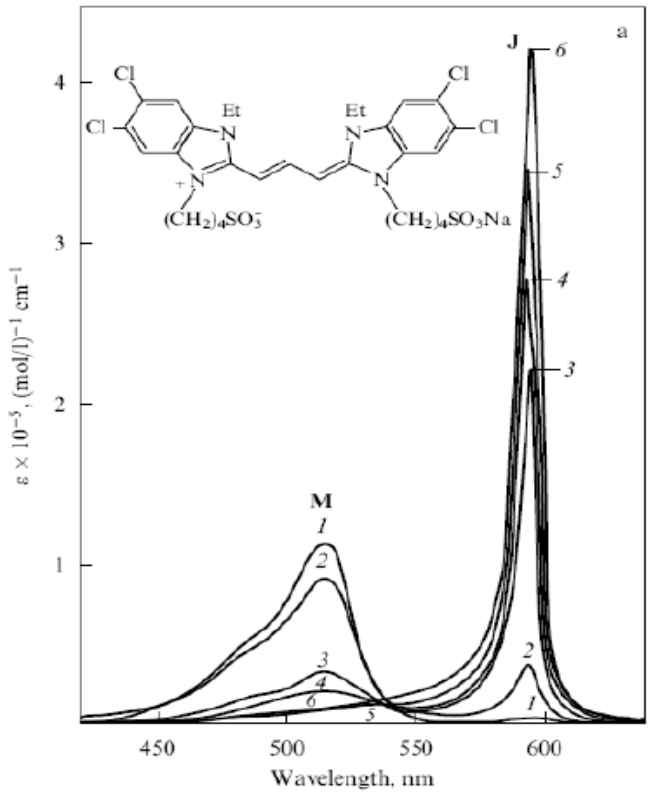


The exciton energy is varying as a function of slipping angle θ. Only one branch corresponds to an optically allowed transition (full black line), while the other branch relates to forbidden transitions (dotted black line). The splitting between the two branches corresponds to $2|J|$. Note that when the absorption wavelength is shifted towards smaller wavelength (hypsochromic shift), we are talking about H-dimers or H-aggregates, while the term J-dimer or J-aggregate applies when the shift is towards longer wavelengths



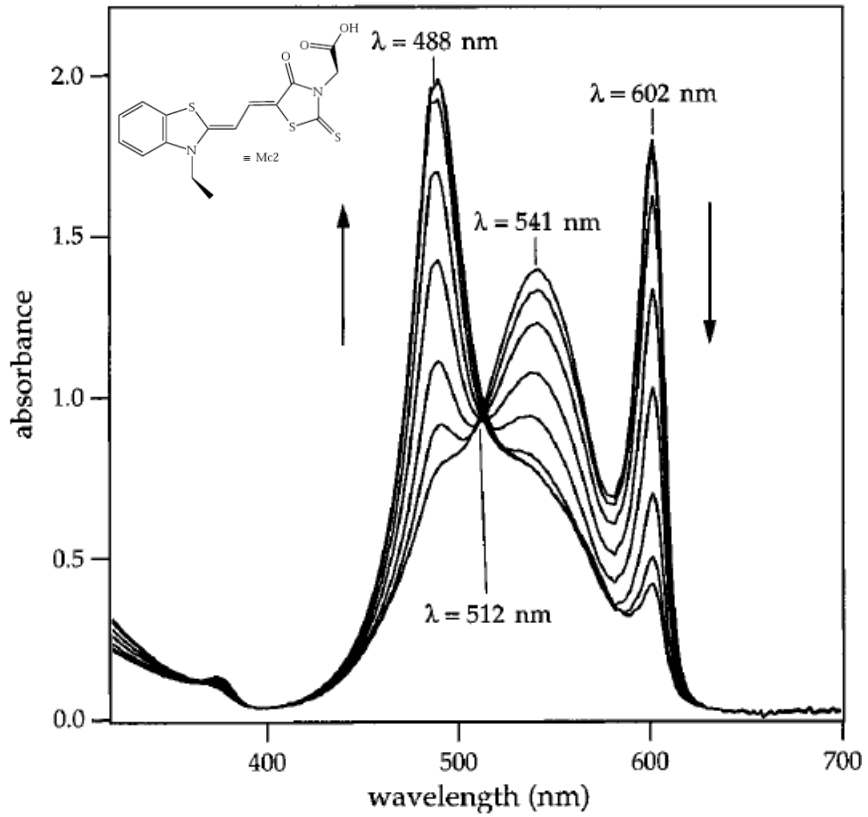
Examples of J- and H-aggregates

Concentration dependence of a Cyanine dye absorption in aqueous NaOH solution.



A.H. Herz, Photogr. Sci. Eng., Vol. 18, No. 323, p. 667, 1974

Merocyanine H- and J- aggregates in a porous TiO_2 film as a function of relative humidity



F. Nüesch et al., J. Am. Chem. Soc., Vol. 118, No. 23, 1996