Organic materials based photovoltaics

2.   Introduction (9:15-9:45)

2.1. Organic Semiconductors

A Molecular Orbitals (9:55-10:40)

B Electronic Properties (10:55 – 11:40)

C Absorption and Fluorescence (11:55-12:30)

D Exciton Theory, Energy & Electron Transfer (13:30-13:45)

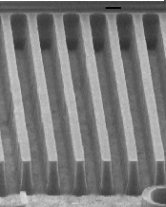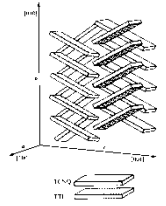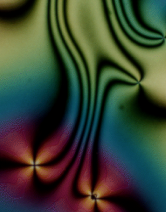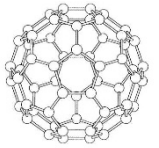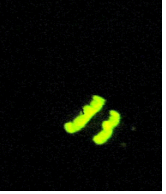**2.2. Organic and Dye Sensitized Solar Cells**

A Organic Solar Cells (14:00-14:55)

B Dye Sensitized Solar Cells (15:10-15:50)

2.3. Hybrid Solar Cells - Perovskites Quantum Dots

A Perovskite Solar Cells (16:05-16:55)

B Quantum Dot Solar Cells (16:55-17:05)

Best Research-Cell Efficiencies

Solar cell efficiency **refers to the portion of energy in the form of sunlight that can be converted via photovoltaics into electricity by the solar cell**.

Price-experience curve for solar modules

Renewable power generation costs (2017)

www.irena.org

Photosynthesis – the principle

With the help of ***light absorbing molecules***, ***light energy*** is converted in ***chemical energy***

$$6\,CO_2 + 12H_2O \xrightarrow{\;h\nu\;} C_6H_{12}O_6 + 6O_2 + 6H_2O$$
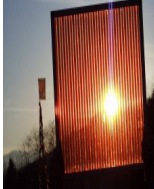
Photosynthetic organisms use ***solar energy*** to ***synthesize carbon compounds*** that cannot be formed without the input of energy

$$CO_2 + H_2O \xrightarrow{\;h\nu\;} CH_2O + O_2 \qquad \Delta G^0 = 478\,kJ/mol\,CO_2$$

Photosynthesis – light reaction

Overall process of photosynthesis is a *redox* chemical reaction

Electrons are removed from water (**oxidation**) and added to CO_2 (**reduction**)

When chlorophyll *absorbs energy* from sunlight, an electron in the chlorophyll *molecule is excited* from a lower to a higher energy state

Electron transport chain:
Chain of molecules that easily accept and donate electrons

e^- CO_2

$h\nu$ CH_2O

O_2 e^-

H_2O

Organic semiconductors ≠ biomaterials

in Chlorophyll b

The electrons in the highlighted region are the ones that gets excited when light is absorbed.

long tail

Chlorophyll a

Organic compounds

- are any chemical compounds that contain **carbon-hydrogen bonds**. Due to carbon's ability to catenate (form chains with other carbon atoms), millions of organic compounds are known

- Generally they are **electrical insulators.**

Copper phthalocyanine

PET

Diketopyrrolopyrrol

Band gap − Optical properties and more...

- ❑ Conductivity: ***charge carriers*** in ***conduction band*** (=«band» of electron orbitals)

- ❑ Inorganic semiconductors: electrons are thermally excited into the valence band

- ❑ How does that now work in organics??

Molecular crystals?

- Electroluminescence in anthrazene single crystals (1963)
- Injected charges

$\approx 1eV$

bandgap

energy

$\propto \beta$

≡ Mc2

energy levels
of the molecule

energy bands of the
organic semicond.

The discovery of conducting polymers 1977

Hideki Shirakawa   Alan G. MacDiarmid   Alan J. Heeger

Nobel prize in chemistry 2000

- Polyacetylene become ***conductive upon doping***

- ***Conjugation creates an orbit*** that allows the charge carriers to move

Conducting polymers

❑ Spray coat or print a cheap material with semiconducting properties?

❑ Synthesize individual soluble building blocks that absorb in the visible domain

❑ Bring these building blocks close together in order to allow charge transfer from one block to the other (this is actually a compromise between cost efficient processing and useful semiconductor properties).

Polyacetylene   Polythiophene   Poly(*p*-phenylene)

Poly(*p*-phenylenevinylene)   Poly-*p*-phenylene-sulphide

Semiconductor properties

❑ Depend on the very nature of the semiconducting materials

❑ Dictated by the interaction between constituting building blocks (atoms or molecules).

❑ Depend on the structure of the material (crystalline, amorphous, disordered)

	Inorganic SC	Organic SC
Absorption (cm^{-1})	10^3-10^4 (Si) 10^4-10^5 (GaAs)	10^5-10^6 (fluorescent dyes) 10^4-10^5 (CT compounds, Triplet emitters)
Charge carrier mobility (cm^2 V^{-1} s^{-1})	c-Si: 1500 (e^-), 450 (h^+) GaAs: 8500 (e^-),400 (h^+) a-Si: 1	c-anthracene:1.6(e^-), 1.2 (h^+) c-fullerene C_{60}:1.1(e^-),1.0 (h^+) amorphous OSC: 10^{-5} to 10^{-3}

OE-A Roadmap for Organic and Printed Electronics Applications 2015

	Existing until 2015	Short term 2016–2018	Medium term 2019–2022	Longer term 2023+
OLED Lighting	Rigid modules for design driven luminaires B2B and B2C	Flexible lighting for design driven applications	Mass-produced flexible lighting	General lighting
Organic Photovoltaics	Consumer electronic chargers, solar lamps, architectual installations	Consumer electronics, mobile power, energy harvesting, specialized BIPV and BAPV	Mobile power, Internet of Everything energy harvesting, building integration, medium size off-grid	Large volume BIPV integration, large and industrial off-grid, grid-connected PV
Flexible and OLED Display	Curved OLED TVs, flexible OLED displays, mobile OLED displays, e-reader, wearables	In-moulded displays, (semi-) transparent bendable display, OLED monitors and TVs	Portable foldable OLED displays, (semi-) transparent rollable display	Stretchable display, rollable OLED TV, rollable consumer electronics
Electronics & Components	Primary batteries, memory for brand protection, ITO-free transparent conductive films and touch sensors	Rechargeable batteries, transparent touch sensors, reflective display elements, flexible & large area ITO-free touch sensors	Multi-cell batteries, wireless readable memory, printed logic chips, bendable ITO-free touch & gesture sensors	Directly printed batteries, smart objects integrating actives and passive devices, fully integrated touch & gesture sensors
Integrated Smart Systems	Garments with integrated sensors, anti-theft/forgery labels, temperature sensor smart labels, printed sensors and test strips	NFC enabled sensor labels, intelligent packaging, integrated systems on garment	Multi-cell batteries, wireless readable memory, printed logic chips, bendable ITO-free touch & gesture sensors	OLED on textile, disposable health monitoring systems, wireless sensors for smart buildings

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Organic materials based photovoltaics, 2. Introduction Nr.14

Printed oLED displays

Organic Photovoltaics (oPV)

FLEXIBLE.
TRANSPARENT.
THIN + LIGHT WEIGHT.
RECYCLABLE.

ORGANIC.

TOMORROW:
ORGANIC
PHOTOVOLTAICS
= OPV

source: Belectric GmbH

Thin film devices with polymer semiconductors:

Printed
Electronics
everywhere

2.1A Molecular Orbitals

HOMO

LUMO

2.1A Molecular Orbitals

Learning goals

❑ What is the *origin of electrical conductivity* in *organic carbon compounds*?

    ❑ What is an *orbital* ? Quantum mechanical description

    ❑ How can you describe the *electronic wavefunction of molecules (molecular orbitals, hybrid orbitals)*

    ❑ *Resonance transfer integral*

Chemical bonds

❑ The formation of *molecules* is build upon *covalent bonds*

❑ The covalent bond involves the *sharing of electron pairs* between atoms, the *balance between attractive & repulsive forces* will lead to bonding

❑ Shared electron pairs provides an effective *qualitative picture* of covalent bonding

❑ For many molecules, the sharing of electrons allows each atom to attain the *equivalent of a full valence shell*, corresponding to a stable electronic configuration

https://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/intro2.htm

What is an orbital and why are they important for organic semiconductors?

❑ ***Lewis structures*** are diagrams that show the bonding between atoms of a molecule, as well as the lone pairs of electrons that may exist in the molecule

❑ An ***orbital*** is a ***one electron wavefunction*** that describes the probability to find the electron at a certain location.

❑ The use of orbitals therefore is a good approximation to describe the electronic structure of a complex multi-electron system.

Lewis structure

sp^3 hybrid orbital

Quantum mechanical description

Time–dependent many–body Schrödinger equation with electrons at positions $\vec{r} = (r_1, r_2, \ldots r_N)$ and nuclear positions $\vec{R} = (R_1, R_2, \ldots R_M)$:

$$\widehat{H}\psi(\vec{r}, \vec{R}, t) = i\hbar \, \frac{d\psi(\vec{r}, \vec{R}, t)}{dt}$$

Time independent Hamiltonian $\widehat{H}$ (stationary states):

$$\psi(\vec{r}, \vec{R}, t) = \psi(\vec{r}, \vec{R})e^{-iEt/\hbar} \qquad\qquad \widehat{H}\psi(\vec{r}, \vec{R}) = E\,\psi(\vec{r}, \vec{R})$$

Electronic wavefunctions only: $\widehat{H}\psi^{el}(\vec{r}) = E\,\psi^{el}(\vec{r})$

The particle in a box - a simple model of an atom

electron

Boundary conditions (probability to find particle = 0)

$$\psi(0) = 0 \rightarrow 0 = A + B \rightarrow B = -A$$

$$\Rightarrow \psi(x) = Ae^{ikx} - Ae^{-ikx} = A2i \sin kx = A'\sin kx$$

$$\psi(L) = 0 \quad \rightarrow \quad A'\sin(kL) = 0 \quad \rightarrow \quad k = n\frac{\pi}{L} \text{with} \quad n = 1,2,3...$$

Calculate the energy levels and wavefunctions for one electron:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x)$$

$$\Rightarrow E = \frac{\hbar^2 \pi^2 n^2}{2mL^2} = \frac{h^2 n^2}{8mL^2} \rightarrow n = 1,2,3...$$

$$\Rightarrow \psi = A'\sin\left(\frac{n\pi}{L}x\right) \qquad \text{with} \qquad A' = \sqrt{\frac{2}{L}}$$

Solutions are standing waves:

$$\psi(x) = Ae^{ikx} + B^{-ikx}$$

Normalisation of ψ:

$$1 = \int_0^L \psi * \psi = A'^2 \int_0^L \sin^2 kx dx = A'^2 \underbrace{\int_0^L \sin^2\left(\frac{n\pi}{L}x\right)dx}_{\frac{1}{2}L} = A'^2 \frac{L}{2}$$

$$\Rightarrow A' = \sqrt{\frac{2}{L}}$$

Solutions of the particle in a box problem are standing waves:

Respecting the Pauli principle ("if two electrons, or in general Fermions, occupy the same electron orbital, they must have different spin states", i.e. up and down, respectively)

$$\Rightarrow \psi = A' \sin\left(\frac{n\pi}{L} x\right) \quad \text{with} \quad A' = \sqrt{\frac{2}{L}}$$

ψ is the particle wavefunction.

The probability amplitude. $|\psi(x)|^2 dx$

is the probability of finding the

particle between x and x+dx

$$E_3 = \frac{9h^2}{8mL^2}$$

$$E_2 = \frac{h^2}{2mL^2}$$

$$E_1 = \frac{h^2}{8mL^2}$$

0   L   x

H-atom orbitals

exact analytical solution can be developed by solving:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z)-\frac{e^2}{4\pi\varepsilon\varepsilon_0\sqrt{x^2+y^2+z^2}}\psi(x,y,z)=E\psi(x,y,z)$$

This problem is solved using polar coordinates.

$$E_n=-\frac{13.6\,eV}{n^2}$$

The hydrogen atom wavefunctions are given by:

$$\psi_{n,l,m}(r,\theta,\phi)=R_{n,l}(r)\cdot Y_l^m(\theta,\phi)$$

(Legendre polynomials as a function of spherical coordinates)

Meaning of the different quantum numbers *n, l, m:*
n = 1, 2, 3, …   principal quantum
l = 0, 1, 2, 3, …, *n*-1   azimuthal quantum number
m = *l*, *l* -1, *l* -2, ,0,…. – *l*   magnetic quantum number

H-atom orbitals

The <u>orbital</u> here is defined as the volume where the probability of finding the electron is 90%

Many electron atoms – atomic orbital concept

❑ Only for the H-atom an analytical solution for the orbitals can be found

❑ Neglect interactions between electrons = reduce a many-electron problem to many one-electron problems

$$\psi \approx \prod_i \varphi_i (\vec{r}_i)$$

φ_i **:= atomic or molecular o r b i t a l s**

❑ I treat every electron as if it would be a hydrogen atom (with adapted nuclear charge & some averaged influence of other electrons)

❑ From hydrogen wavefunctions of the same energy, *any linear combination* of those functions will also be an *Eigenfunction* of the hydrogen atom.

❑ These new orbitals are called *hybrid orbitals*.

Building molecules from atoms – hydrogen molecule

❑ *Apply the concept of orbitals* (which was the key to the understanding of the electronic structure of atoms) *to molecules*.

❑ Molecular orbitals are obtained by combining the atomic orbitals

❑ In the hydrogen molecule you can construct in-phase and out-of-phase combinations of H 1s orbitals

❑ Leading to bonding (σ) or antibonding (σ*) orbitals

Molecular orbitals of the second energy level

❑ These are the ones of interest when looking at organic molecules
❑ Pi (π) bonds are weaker and are due to lateral overlap between p (or d) orbitals

Building molecules from atoms – sp³ hybridization

Methane

Hybridization

gives a tetrahedral
arrangement

Organic

Building molecules from atoms – sp² hybridization

Ethylene

sp² Hybridorbital

nicht-hybridisiertes p-Orbital

Hybridization

gives a trigonal
planar arrangement

Building molecules from atoms – sp hybridization

H:C:::C:H

Ethyne / Acetelyne
Linear chain

The construction of delocalized π-orbitals

❑ Schrödinger equation cannot be solved: problem: electron repulsion terms

❑ Molecular orbital methods: use one-electron wavefunctions (molecular orbitals) to describe multi-electron systems (similar to approximate wavefunction composed of a linear combination of atomic orbitals (**LCAO**)).

$$\phi = c_1\varphi_1 + c_2\varphi_2 + c_3\varphi_3 + c_4\varphi_4 + ...$$

❑ Variational method: find the paramters c_i such that the ground state energy is as low as possible.

The Hückel MO model

❑ Successfully applied to *large conjugated systems*, especially those containing chains of carbon atoms with alternating single and double bonds.

❑ Within the Hückel approximation, the covalent bonding in these hydrocarbons can be separated into two independent "frameworks": the σ-bonding framework and the π-bonding framework.

Example: ethylene

(a) C_2H_4 σ-bonded framework (b) C_2H_4 π bonding

❑ Describe as linear combination of the 2pz orbitals:

$$\psi_{orbital} = c_A \psi_{pz}(A) + c_B \psi_{pz}(B)$$

❑ Minimize E with respect to c_A and c_B:

$$E = \frac{\int \psi_{orbital} H \psi_{orbital} dx}{\int \psi_{orbital}^2 dx} \qquad \rightarrow \frac{\partial E}{\partial c_A} = 0 \quad , \quad \frac{\partial E}{\partial c_B} = 0$$

❑ Let us first calculate:

$$\int \psi_{orbital}^2 dx = \int c_A^2 \psi_{pz}^2(A) dx + \int c_B^2 \psi_{pz}^2(B) dx + 2 c_A c_B \underbrace{\int \psi_{pz}(A) \psi_{pz}(B) dx}_{S}$$

$$= c_A^2 \underbrace{\int |\psi_{pz}(A)|^2 dx}_{=1} + c_B^2 \underbrace{\int |\psi_{pz}(B)|^2 dx}_{=1} + 2 c_A c_B \cdot S$$

S…overlap integral

$$\int \psi_{\text{orbital}} H \, \psi_{\text{orbital}} \, dx = \int \left(c_A \psi_{pz}(A) + c_B \, \psi_{pz}(B) \right) H \left(c_A \psi_{pz}(A) + c_B \psi_{pz}(B) \right) dx$$

$$= c_A{}^2 \underbrace{\int \psi_{pz}(A) H \psi_{pz}(A) dx}_{\alpha} + c_B{}^2 \underbrace{\int \psi_{pz}(B) H \psi_{pz}(B) dx}_{\alpha} + 2 c_A c_B \underbrace{\int \psi_{pz}(A) H \psi_{pz}(B) dx}_{\beta}$$

A: **Coulomb integral < 0;** account for the interactions between the nuclei, the electrons, and the nuclei and electrons, more precise: interaction of the electrons around one nuclei with the other proton.

B: **Resonance (exchange) integral < 0**; of qm origin; no simple physical interpretation, but it can be shown to arise entirely due to the anti-symmetry requirements;

probability   A $\longleftrightarrow$ B

$$E = \frac{\overbrace{\alpha \, (c_A{}^2 + c_B{}^2) + 2 c_A c_B \, \beta}^{f}}{\underbrace{c_A{}^2 + c_B{}^2 + 2 \, c_A c_B \cdot S}_{g}}$$

$$\left(\frac{f}{g} \right)' = \frac{1}{g^2} \left[f'g - fg' \right]$$

$$\frac{\partial E}{\partial c_A} = 0 \rightarrow \frac{1}{g^2}\left[(2\alpha\, c_A + 2\beta\, c_B)g - f(2\, c_A + 2c_B \cdot S)\right] = 0$$

$$2\alpha\, c_A + 2c_B\beta - \underbrace{\frac{f}{g}}_{=E}(2c_A + 2c_B \cdot S) = 0$$

$$\rightarrow c_A(\alpha - E) + c_B(\beta - ES) = 0$$

and in analogy

$$\frac{\partial E}{\partial c_B} = 0 \rightarrow c_A(\beta - ES) + c_B(\alpha - E) = 0$$

(3)

(3) is a linear homogeneous system of equations with unknown c_A and c_B. The solution consists of setting the secular determinant equal to zero.

$$Det\begin{bmatrix} (\alpha - E) & (\beta - ES) \\ (\beta - ES) & (\alpha - E) \end{bmatrix} = 0$$

❑ This can be solved, but is a bit tedious. We would like to make an additional approximation (small orbital overlap S):

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

❑ solving for E:

$$(\alpha - E)^2 - \beta^2 = 0 \rightarrow \alpha^2 - 2\alpha E + E^2 - \beta^2 = 0 \qquad\qquad E^2 - 2\alpha E + \alpha^2 - \beta^2 = 0$$

$$E\pm = \frac{2\alpha \pm \sqrt{4\alpha^2 - 4(\alpha^2 - \beta^2)}}{2} = \alpha \pm \beta$$

$\alpha - \beta$

α

2β

$\alpha + \beta$

α

antibonding orbital with energy E-

bonding orbital with energy E+

β can be estimated from spectroscopic data

❑ Finding the coefficients c_A, c_B (and hence the wavefunctions), For $E = E_+$:

$$\begin{bmatrix} (\alpha - E+) & \beta \\ \beta & (\alpha - E+) \end{bmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

$$(\alpha - E_+) c_1 + \beta c_2 = 0 \quad \text{with} \quad E_+ = \alpha + \beta$$

$$- \beta c_1 + \beta c_2 = 0 \qquad \rightarrow c_1 = c_2$$

$$\rightarrow \psi_+ = c_1 \left(\psi_{pz}(A) + \psi_{pz}(B) \right) = \frac{1}{\sqrt{2}} \left(\psi_{pz}(A) + \psi_{pz}(B) \right)$$

from $\int (\psi_+)^2 dx = c_1^2 \left[\underbrace{\int \psi_{pz}(A)^2}_{=1} + \underbrace{\int \psi_{pz}(B)^2}_{=1} + \underbrace{\int \psi_{pz}(A) \psi_{pz}(B)}_{=0} \right] = c_1^2 \cdot 2 = 1 \quad \Rightarrow c_1 = \sqrt{\frac{1}{2}}$

In the same way one obtains for $E = E_-$

$$\psi_- = \frac{1}{\sqrt{2}} \left(\psi_{pz}(A) - \psi_{pz}(B) \right)$$

0.707   -0.707

1 node π^* ———— LUMO

0.707   0.707

0 nodes π ⇅   HOMO

The infinite conjugated chain: polyacetylene I

$$Det \begin{bmatrix} \alpha - E & \beta_{AB} - ES_{AB} & \beta_{AC} - ES_{AC} & ... & ... \\ \beta_{BA} - ES_{BA} & \alpha - E & \beta_{BC} - ES_{BC} & ... & ... \\ \beta_{CA} - ES_{CA} & \beta_{CB} - ES_{CA} & \alpha - E & ... & ... \\ ... & ... & ... & ... & ... \\ ... & ... & ... & ... & ... \end{bmatrix} = 0$$

❑ *Hückel approximations:*

- All overlap integrals are set to zero S=0

- All resonance integrals between non-neighbors are zero

- All resonance integrals between direct neighbors are set to β

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

The infinite conjugated chain: polyacetylene II

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

$$\psi_k = \sum_{n=1}^{N} a_n^k \psi_{2p_z}(n) \qquad a_n^k = \sqrt{\frac{2}{N+1}} \sin\left(\frac{\pi k n}{N+1}\right)$$

unfilled

α

4β

filled

where $\psi_{2p_z}(n)$ are the C2p_z orbitals at site *n*.

Theory predicts *trans*-PA to be a metal

To summarize: both particle in a box and Hückel predict no band gap when n gets very large

https://www.oe.phy.cam.ac.uk

The infinite conjugated chain: polyacetylene III

❑ *Intramolecular conductivity*

❑ *The construction of delocalized π-orbitals*

Within the conjugated structure, π-orbitals are delocalized. This delocalization forms the basis of the molecular conductivtiy of carbon compounds.

But: delocalized π-orbitals *allow for mobile charges*, to make them *conductive*, also *charge carriers* are needed.

Subject of next lecture

The infinite conjugated chain: polyacetylene

❑ *Why is Polyacetylene a semi-conductor and not a metal?*

$$Det\begin{bmatrix} \alpha - E & \beta_1 & 0 & 0 & \cdots & \beta_2 \\ \beta_1 & \alpha - E & \beta_2 & 0 & \cdots & 0 \\ 0 & \beta_2 & \alpha - E & \beta_1 & \cdots & 0 \\ 0 & 0 & \beta_1 & \alpha - E & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \beta_2 & 0 & 0 & 0 & \cdots & \alpha - E \end{bmatrix} = 0$$

$$E_k = \propto \pm \left[\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 cos\left(\frac{2k\pi}{2N+1}\right) \right]^{\frac{1}{2}}$$
$$k = 0, \pm 1, \pm 2, \ldots . \pm N$$

Dimerisation (Peierls distortion) opens up a gap with

$$E_g = 2 \, |\beta_1 - \beta_2|$$

2.1A Molecular Orbitals

Learning outcome

❑ How are molecules held together (molecular bonds)
  - Covalent bonds

❑ What is an ***orbital*** ? Quantum mechanical description
  - *An orbital is a one electron wavefunction that describes the probability to find the electron at a certain location*
  - *Particle in a box*
  - *Hydrogen orbitals*

❑ How can you describe the ***electronic wavefunction of molecules***
  - *Hybrid orbitals, sp^3, sp^2, sp hybridization*
  - *Hückel molecular orbital theory: coupling of atomic orbitals, band splitting via resonance (exchange) interaction*

❑ Origin of ***electrical conductivity*** in ***organic carbon compounds***:
  - *sp^2 hybridization in carbon and graphite*

2.1A Molecular Orbitals

Learning outcome

❑ Infinite ***conjugated polymers (intramolecular conductivity)***:

- *Conjugated polymers: delocalized system of π-electrons runs along the polymer backbone*

- *Bond length alternation opens up a band-gap (semiconductor)*

2.1B Electronic properties of organic semiconductors

Learning goals

❑ From *delocalized π-orbitals* to *conductivity*

    ❑ *Definitions: mobility and conductivity*

    ❑ *Where do charges come from? Intrinsic / extrinsic* semiconductors

    ❑ *Conduction mechanism* in organic semiconductors: is it really band transport?

    ❑ *Thermodynamics of electron transfer, Marcus theory*

    ❑ *Electrical contact* to devices

Conduction in molecular solids

❑ ***Mobility*** μ***:*** when a charged particle in a gas or liquid is acted upon by a uniform electric field, it will be accelerated until it reaches a ***constant drift velocity v$_d$***.

❑ A semiconducting material can be best assessed by its ***conductivity*** σ. It is defined as the ratio of the density of the current J to the electric field E. n is the **charge carrier density** (m^{-3}).

❑ For ***conductivity*** we thus need to look at the product of mobility and charge carrier density

$$v_d = \mu E$$
$$J = nev_d$$

$$J = ne\mu E$$
$$J = \sigma E$$

$$\boldsymbol{\sigma = ne\mu}$$

Intrinsic semiconductors

❑ also called an undoped semiconductor or i-type semiconductor, is a pure semiconductor without any significant dopant species present

$$n_{\text{int}\,r} = N_{eff}\,e^{-\Delta E_{gap}/2kT}$$

n_{intr} is the intrinsic charge density, N_{eff} is the density of states.

Silicon:
N_c =2.82 10^{19} cm^{-3}, N_v =1.83 10^{19} cm^{-3}
E_g =1.1eV
μ =1000 cm^2 V^{-1} s^{-1}
σ =10^{-6} Ω^{-1}cm^{-1}

Organic semiconductors:
N_0 =10^{21} cm^{-3}
E_g =2.0 eV
μ =1 cm^2 V^{-1} s^{-1}
σ =10^{-12} Ω^{-1}cm^{-1}

N_c and N_v are the density of states of the conduction and valence band, respectively, E_g is the band gap and N_0 is the molecular density.

❑ The ***conductivity of intrinsic semiconductors*** is purely due to ***thermal excitation of carriers*** from the valence band to the conduction band.

Extrinsic semiconductors

❑ An extrinsic semiconductor is one that has been ***doped***; during manufacture of the semiconductor crystal a trace element or chemical called a doping agent has been incorporated chemically into the crystal

n-Dotierung   p-Dotierung

❑ Most organic semiconductors lack intrinsic charge carriers
❑ Organic semiconductors get their ***conductivity from extrinsic factors***:

- ▪ Dopants
- ▪ Photosensitization
- ▪ Injection

2 Questions to ask:

❑ How can you dope organic semiconductors?
❑ How are charges transported in organic semiconductors? Band transport?

❑ In most organic materials, the HOMO is around −5 to−6 eV below the vacuum level. A *p-type dopant* therefore has to act as a very *strong electron acceptor*. Similarly, *n-type dopants* had to have a *HOMO level near −2.5 to −3.5 eV*

Doping of polymers

□ Either partial oxidation with electron acceptors (i.e. anions, p-doping) or partial reduction with electron donors (i.e. cations, n-doping).

□ Charged defects, such as polarons, bipolarons and solitons, are introduced into the polymer structure as a result of the doping process.

□ A polaron is a quasiparticle composed of a charge and its accompanying polarization field

□ These defects then play the role of charge carriers. This is analogous to the p and n doping of Si

RSC Adv.,2015, 5,1161

POLY-
ACETYLENE
$\sigma_{max} > 2 \times 10^4$ S cm^{-1}

POLY-
THIOPHENE
$\sigma_{max} = 2000$ S cm^{-1}

DOPED

UNDOPED

POLY-
PYRROLE
$\sigma_{max} = 500$ S cm^{-1}

Poly-(dioxythiophene) doped with polystyrenesulfonate or PEDOT:PSS

Doped conjugated polymers and doped molecular crystals can span a *whole range of conductivities*

Pentacene doped with iodine

Band-like carrier transport in organic single crystals of high purity

❑ Carrier **mobility** strongly depends on the resonance integral β.

For a face-centered cubic lattice of side a it can be shown that:

$$\mu = \frac{2 \cdot \beta \cdot a^2 \cdot e \cdot \tau_C}{\hbar^2}$$

Where β is the transfer integral, a is a lattice distance and τ_C is the time between two collisions.

Using β=100 meV, *a*= 5Å, τ_C=10^{-13}s, we obtain a mobility of 3.5 cm^2/(Vs) above which band transport can be expected.

❑ β in organics is is about one order of magnitude lower than in inorganics

Warta, W., Karl, N., Phys. Rev. B, 32 (2), 1172, 1985.

Band transport and Hopping transport

❑ Band transport is effective when ***the electronic coupling*** β is larger than any other energy terms due static or dynamic disorder.

❑ T-dependence of mobility due to increased scattering at acoustic phonons, impurities and electron interactions.

❑ If ***coupling to molecular vibrations*** (called local phonon coupling, not to be mixed up with lattice vibrations) becomes comparable to electronic coupling, then the band model is inappropriate

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

Band transport and *Hopping transport*

❑ 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.

❑ Organics can be molecular crystals, molecular glasses, polymeric glasses, all will give different transport mechanisms, dominated by either ***electronic coupling, inter- and intra molecular vibrations, static inter- and intramolecular disorder***

Weak electron–phonon coupling

$\mu \propto T^{-n}$

Strong electron–phonon coupling

Tunneling
$\mu \propto T^{-n}$

Hopping
$\mu \propto e^{-E/kT}$

Residual scattering
$\mu \propto T^{-3/2}$

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

Thermodynamics of electron transfer

❑ **Marcus' theory** of electron transfer most famous

❑ Describes the rates of electron transfer between weakly coupled donor and acceptor states when the potential energy depends on a nuclear coordinate.

❑ This reaction is mediated by a nuclear coordinate q. This does not need to be, and generally isn't, a simple vibrational coordinate, but includes e.g. the molecules of the surrounding

Thermodynamics of electron transfer

It is assumed that the free energy or potential of mean force for the initial and final state is well represented by two parabolas.

Overall free energy change ΔG_0 for an electron transfer reaction is determined from the redox potentials of the reactants.

Rate of transfer determined by collision frequency ν_n and barrier $\Delta G^\ddagger$:

$$k_r = \nu_n e^{-\Delta G^\ddagger / RT}$$

$\Delta G^\ddagger$ can be calculated to be $\Delta G^{\#} = \dfrac{(\Delta G_0 + \lambda)^2}{4\lambda}$ from the definition of the reorganization energy (λ), which is the energy to be dissipated on the acceptor surface if the electron is transferred at d_D.

Charge carrier mobilities μ at room temperature for organic and inorganic semiconductors (in cm^2/Vs)

$$J = nev_{drift} = ne\mu E$$

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 $\approx$ 1		

M. Pope, C. E. Swenberg, "Electronic Processes in Organic Crystals and Polymers", Oxford Universtiy Press, 1999
S. M. Sze «Physics of semiconductors», Wiley, New York, 1981

Basic Aspects of Electrical Currents in a Device

❑ Either limited by the efficiency of charge injection:

Injection limited current

❑ or by the ability of the device to transport the charges:

Space charge limited current (SCLC)

Contacting organic opto-electronic devices

Contacts are chosen to provide barrier-free injection of charge carriers into
the device. This implies that the Fermi energy of the contact has to be
aligned to relevant molecular orbital, i.e. to the LUMO if electrons are
injected or to the HOMO, if holes are injected.

Due to the large bandgap of organic semiconductors, specific contacts allow
the injection of one type of charge carriers (e.g. electrons into the LUMO)
and block injection of the other charge carrier type (e.g. holes into the
HOMO).

Homopolar «electron-only» device

Homopolar «hole-only» device

Bipolar device (e.g. for OLEDs

Band bending

From: Z. Zhang, J.T. Yates: Band Bending in Semiconductors, Chem. Rev 2012, 112, 5520

Measuring conductivity

$$R = V / I$$

$$I = JA = JWd = \sigma \frac{V}{L} Wd = V / R$$

$$\sigma = \frac{L}{RWd} \left[\frac{1}{\Omega m} \right]$$

$$\rho = \frac{1}{\sigma} = \frac{WRd}{L} \left[\Omega m \right]$$

Why use a 4-point probe?
Voltage drop only depends
on R_{S2}

Space charge limited current

The semiconductor is assumed to be undoped, diffusion currents are neglected, current density *J* for one type of charge carriers (holes or electrons but not both together):

Charge in device:
$$q = CV = \varepsilon_r \varepsilon_0 \frac{V}{L}$$

Maximum current through device: $j = \dfrac{q}{\tau_{trav}}$ $\Longrightarrow$ $j = \mu \varepsilon \varepsilon_0 \cdot \dfrac{V^2}{L^3}$

Travel time :
$$\tau_{trav} = \frac{L}{\mu E} = \frac{L^2}{\mu V}$$

Mott and Gurney (1948) performed a proper calculation:

$$j = \frac{9}{8} \mu \varepsilon \varepsilon_0 \cdot \frac{V^2}{L^3}$$

where ε is the dielectric constant, *V* is the applied voltage and *L* is the thickness of the molecular solid sandwiched between two electrodes. *E* is the electric field

Other methods to determine mobility

❑ Time-of-flight

❑ Current transient methods (CELIV)

❑ Transistor mobility measurement (OFET)

❑ Transient Stark spectroscopy

❑ Electron spin resonance measurement (ESR)

2.1B Electronic properties of organic semiconductors

Learning outcome

❑ *Conduction mechanism* in organic semiconductors
  ▪ *Band like* transport is possible, but only in the "weak electron-phonon coupling regime". The general case is a *hopping* mechanism. In polymers band like transport along the chain, hoping between chains.

❑ *Intrinsic / extrinsic* semiconductors
  ▪ Organic intrinsic semiconductors are more or less *insulators*, conduction by *doping, injection or excitation*

❑ *Thermodynamics of electron transfer, Marcus theory*
  ▪ Describes a transfer rate mediated by a nuclear coordinate

❑ *Contacts* to devices
  ▪ Space charge and injection limited currents

2.1C Absorption and fluorescence

Learning goals

❑ Mathematical frame work of optical transitions

❑ Selection rules

❑ Relate absorption to molecular properties

❑ Relaxation mechanisms of optically excited molecules

Optical transitions

- ❑ The electric component of the radiation (the optical field E_{opt}) interacts with the charges of the molecule.

- ❑ In first approximation, the interaction is between the optical field E_{opt} and the electric dipole moment μ of the molecule.

$$\vec{\mu} = e\vec{r}$$

- ❑ Molecular dipole moments are usually given in Debye (D), where $1D = 3.336 \cdot 10^{-30}$ Cm.

- ❑ The problem can only be solved with quantum mechanics: time dependent perturbation theory, adding the radiation field to the unperturbed Hamiltonian:.

$$\hat{H}_{total} = \hat{H}_0 + \hat{H}' \quad \text{where} \quad \hat{H}' = \vec{\mu} \cdot \vec{E}_{photon}$$

❑ We only look at a two-level system , the ground state with wavefunction ψ_0 (and corresponding energy E_0) and the excited state with wavefunction ψ_1 (and corresponding energy E_1)

❑ Conditions for the absorption of a photon:

1) $$h\nu = E_1 - E_0$$

2) $$\mu_{1,0} = \left\langle \psi_1 \middle| \vec{\mu}_{10} \middle| \psi_0 \right\rangle \neq 0 \quad \text{where} \quad \mu_{1,0} \text{ is the transition dipolemoment.}$$

❑ Note: this a non-diagonal element of the Dipol operator, for which there is no classical analogon. This is not the difference in dipolmoment between the ground state and the excited state.

❑ The ***transition dipole moment*** tells you how well a molecule can couple to electromagnetic radiation , and in that sense it tells how strong a molecule absorbs light.

❑ The ***transition probability P*** is proportional to the square of the transition dipole moment μ^2 and the energy density of the radiation field E^2:

$$P \propto \left| \mu_{1,0} \right|^2 \cdot \left| E \right|^2$$

❑ **_Born–Oppenheimer (BO) approximation:_** the motion of atomic nuclei and electrons in a molecule can be treated separately

$$\psi = N \cdot E = N\varphi S$$

where φ is the electronic spatial wavefunction, S is the spin wavefunction and N is the nuclear wavefunction.

$$\mu_{1,0} = \langle \psi_1 | \vec{\mu} | \psi_0 \rangle = \langle N_0 | N_1 \rangle \langle \varphi_1 | \vec{\mu} | \varphi_0 \rangle \langle S_0 | S_1 \rangle$$

❑ A **_transition_** is said to be **_forbidden,_** if any of the above terms is zero.

   Analyse

   a) overlap and symmetry of **_spatial wavefunction_**

   b) **_nuclear wavefunction_** (vibrational / rotational) with respect to overlap

   c) **_spin wavefunction_** with respect to spin conservation

a) Symmetry allowed transitions

So, instead of looking if $\langle \varphi_1 | \vec{\mu} | \varphi_0 \rangle = \int \varphi_1 \overrightarrow{(r)} \mu \varphi_0 \overrightarrow{(r)} \, d^3 r$ is non-zero

Look at the symmetry of $m_{10} \overrightarrow{(r)} = \varphi_1 \overrightarrow{(r)} \mu \varphi_0 \overrightarrow{(r)}$

The integral is zero, if $m_{10} \overrightarrow{(-r)} = -m_{10} \overrightarrow{(r)}$ (odd symmetry)

The integral is non-zero if $m_{10} \overrightarrow{(-r)} = m_{10} \overrightarrow{(r)}$ (even symmetry)

a) Symmetry allowed transitions (cont.)

❑ In reality more complicated, *Group theory* can be applied to determine if the integral vanishes or not, group theory can not determine the precise value of the integral.

❑ Molecule: formaldehyde

❑ Point group C2v:
  - Identity
  - Two-fold rotation around C_2
  - Two planes of symmetry crossing the C_2 axis.

C_{2v}	I	C_2	σ(xy)	σ'(yz)
A1	1	1	1	1
A2	1	1	-1	-1
B1	1	-1	1	-1
B2	1	-1	-1	1

❑ Mulliken Symbols: used to identify irreducible representations of groups

a) Symmetry allowed transitions (cont.)

☐, n and π^* orbitals

unhybridized 2p orbitals of carbon and oxygen

Formaldehyd

$H-\underset{\underset{H}{|}}{C}=O$

1e- H: 1s

6e- C: $1s^2 2s^2 2p_x 2p_y$ → $1s^2(2sp^2)^3 2p_z^1$

8e- O: $1s^2 2s^2 2p_y^2 2p_x^2$ → $1s^2(2sp^2)^5 2p_z^1$ $H(1s)-C(2sp^2)$
σ bond

overlap of sp^2 hybridized orbitals of carbon and oxygen leads to σ bond

π^*

n

π

$\pi - \pi^*$ $n - \pi^*$

excited   ground states   excited

σ bond $2p_z(C) + 2p_z(O) \begin{smallmatrix} \pi^* \\ \pi \end{smallmatrix}$

π bond formed by overlap of 2p orbitals of carbon and oxygen

nd

Carey, Organic Chemistry, 1987

a) Symmetry allowed transitions (cont.)

C$_{2v}$	I	C$_2$	σ(xy)	σ'(yz)
A1	1	1	1	1
A2	1	1	-1	-1
B1	1	-1	1	-1
B2	1	-1	-1	1

Orbitals:

- **π-orbital:** antisymmetric with respect to rotation; symmetric with respect to σ(xy), and antisymmetric with respect σ'(yz): **b1**

- **π*-orbital:** antisymmetric with respect to rotation; symmetric with respect to σ(xy), and antisymmmertic with respect σ'(yz): **b1**

- **n-orbital:** antisymmetric with respect to rotation; antisymmetric with respect to σ(xy), and symmmertic with respect σ'(yz): **b2**

a) Symmetry allowed transitions (cont.)

Ground state: $\pi^2 n^2 \pi^{*0}$

n-π^* excited state: $\pi^2 n^1 \pi^{*1}$

π-π^* excited state: $\pi^1 n^2 \pi^{*1}$

involved in binding
the hydrogens

σ^*

π^*

p_x

sp^2 sp^2 sp^2 n p_x p_y

sp sp

π

σ

lone pairs not
involved in bonding

carbon   **oxygen**

Ground state: $(b_1 \times b_1) \times (b_2 \times b_2) = a_1$
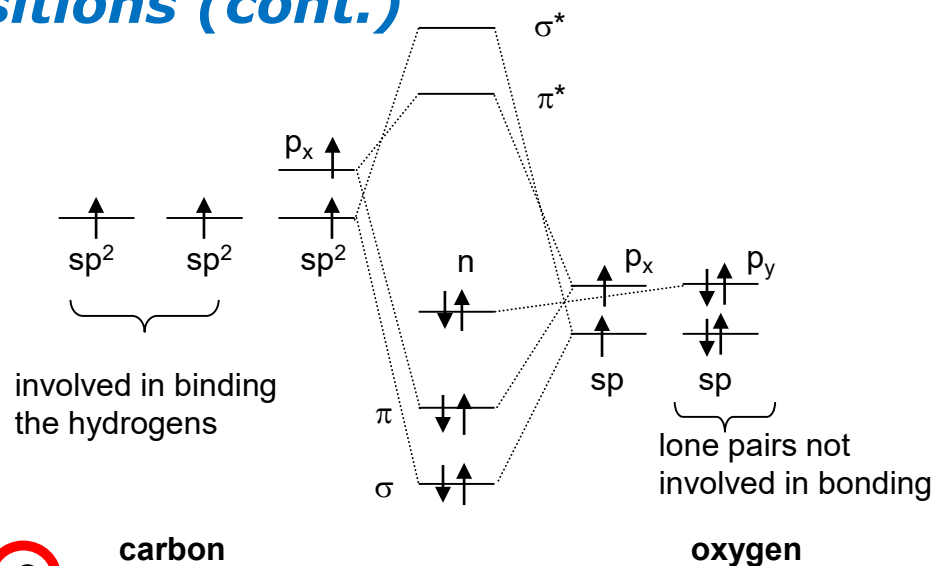
n-π^* excited state: $(b_1 \times b_1) \times b_2 \times b_1 = a_2$

π-π^* excited state: $(b_1 \times (b_2 \times b_2) \times b_1 = a_1$

The *symmetry of the occupied orbitals* must be *conserved*
during the transition

➡ The π–π^* **transition is allowed**, while the **n-π^* transition is forbidden** by symmetry

Vibronic fine structure

□ Transitions also show a ***vibrational structure***, originates from the ***nuclear wavefunction***

□ Not described by the Born-Oppenheimer approximation: the dipol operator was not acting on the nuclear wave function

b) Vibronically allowed transitions - the Franck-Condon principle

Electronic transitions occur rapidly compared to nuclear motion (0.1 to 1 fs vs 10 -1000 fs), the nuclei remains essentially "frozen" in the ground state during the transition.

Franck-Condon:

The better the vibronic overlap, the larger will be the nuclear overlap integral $\langle N_1 | N_0 \rangle$ and the more probable will be the transition.

Franck-Condon factor: probability of transition: $\langle N_1 | N_2 \rangle^2$

Or: the more compatible the wavefunctions of ground and excited state are, the more likely the transition

$$N_0 \sim e^{-k \cdot Q^2/2}$$

$$E_{vib} = \hbar\omega(v + 1/2)$$

c) Spin selection rule

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).

In the **excited state**, much more states are possible:

Spin multiplicity M is the number of possible orientations
$M = 2S + 1$

This spin state is antisymmetric and is called singlet.

c) Spin selection rule

In the **excited state**, spins take one of **4 possible spin states**, namely 1 singlet state and 3 triplet states.

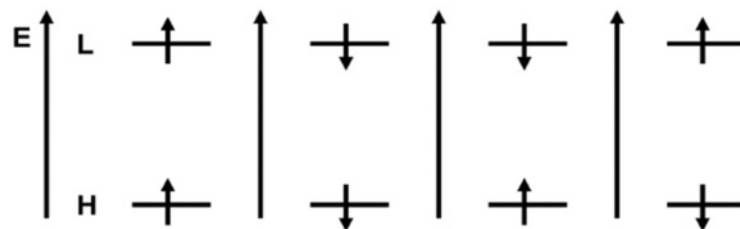Triplet state manifold is (triply) degenerate, which means that it contains three equally-valid linearly-independent eigenstates. Any one of them can be chosen, or any suitable linear combination of them. For any optical transition, the following spin selection rule holds:

$$\Delta S = 0$$

$$\frac{1}{\sqrt{2}} \uparrow\downarrow - \downarrow\uparrow$$

Singlet State S = 0

$$\frac{1}{\sqrt{2}} \uparrow\downarrow + \downarrow\uparrow$$

Triplet State S = 1

Absorption and the oscillator strength

Beer-Lambert law:

the quantity of light absorbed by a substance dissolved in a fully transmitting solvent is directly proportional to the concentration of the substance c and the path length l of the light through the solution (α is the absorption coefficient, ε is the molar extinction coefficient in l mol^{-1}cm^{-1}, c is the concentration mol l^{-1} and l is the distance in cm over which light is absorbed).

$$T = \frac{I}{I_0} = 10^{-\alpha l} = 10^{-\varepsilon c l}$$

From here: the **decadic absorbance A**, which is widely used in the field of photochemistry and molecular materials science:

$$A = -\log\left(\frac{I}{I_0}\right) = \varepsilon c l$$

Absorption and the oscillator strength

Connecting macroscopic and microscopic properties
The extinction coefficient can be expressed in microscopic terms introducing the cross section σ, i.e., the target area that a molecule presents to the incoming photon. If this area is struck, the photon is absorbed.

$$\sigma = \frac{10^3}{N_A} \ln 10 \cdot \varepsilon$$

molecule with
cross section σ

length *l*

$$A_{band} = \int_{band} \varepsilon(\bar{v}) d\bar{v}$$

where $\bar{v} = \frac{1}{\lambda}$ is the wavenumber in cm^{-1}

The **oscillator strength** is a measure of the strength of an electric dipole transition:

$$f_{1.0} = \left[\frac{4\varepsilon_0 m_e c^2 \ln(10)}{N_A e^2} \right] A_{band}$$

The collection of fundamental constants has a value of 4.310·10^{-9} mol dm^{-3}cm^2.

From theory we get a connection between the oscillator strength f_{10} and the transition dipole moment:

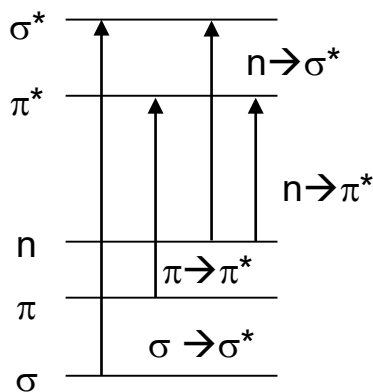$$f_{10} = \left[\frac{8\pi^2 m_e c}{3e^2 h}\right] \bar{v}_{10}|\bar{\mu}_{10}|^2$$

where $\bar{v}_{10}$ is the wavenumber of the transition, which we will take to be $\bar{v}_{max}$ (the wavenumber at maximum absorption). The collection of physical constants has the value $4.226 \cdot 10^{52}$ $C^{-2}m^{-2}cm$, or $4.702 \cdot 10^{-7}$ $D^{-2}cm$. Thus

$$f_{10} = 4.702 \cdot 10^{-7} \bar{v}_{10}|\bar{\mu}_{10}|^2$$

Types of transition

❑ In organic molecules we are concerned mostly with orbitals originating from the overlap of atomic s and p orbitals or their hybrids.

❑ These can be classified as σ and π bonding orbitals and σ* and π* antibonding orbitals, as well as nonbonding orbitals n.

❑ Most organic molecules are closed-shell molecules in which the highest occupied molecular orbital *(HOMO) are σ, π or n orbitals*. On excitation, an electron may be promoted into the lowest unoccupied molecular orbital *(LUMO),* which is usually an *σ* or *π* orbital*.

σ* ────────

π* ────────   n→σ*

n ────────   n→π*

π ────────   π→π*

σ ────────   σ →σ*

π →π*: alkenes, alkynes and aromatic molecules

n →π*: compounds with carbonyl, thiocarbonyl, nitro, azo and imine goups

n →σ*: amines, alcohols and haloalkanes

σ →σ*: alkanes

Relaxation of electronically excited molecules

1. Radiative processes (fluorescence, phosphorescence)

2. Non-radiative processes (vibrational relaxation)

3. Quenching processes, which are bi-or multimolecular relaxation processes

Jablonski diagram, summarizing the first two intramolecular processes.

2.1C Absorption and fluorescence

Learning outcome

❑ Mathematical framework of optical transitions
- The transition probability P is proportional to the square of the ***transition dipole moment*** μ^2 and the energy density of the radiation field E^2

❑ Selection rules
- Born-Oppenheimer approximation
- Symmetry, vibrationally and spin allowed/forbidden transitions

❑ Relate absorption to molecular properties
- Beer-Lambert law, oscillator strength

❑ Relaxation mechanisms of optically excited molecules
- Jablonski diagram, visualizes radiative & non-radiative mechanisms

2.1D Energy transfer processes
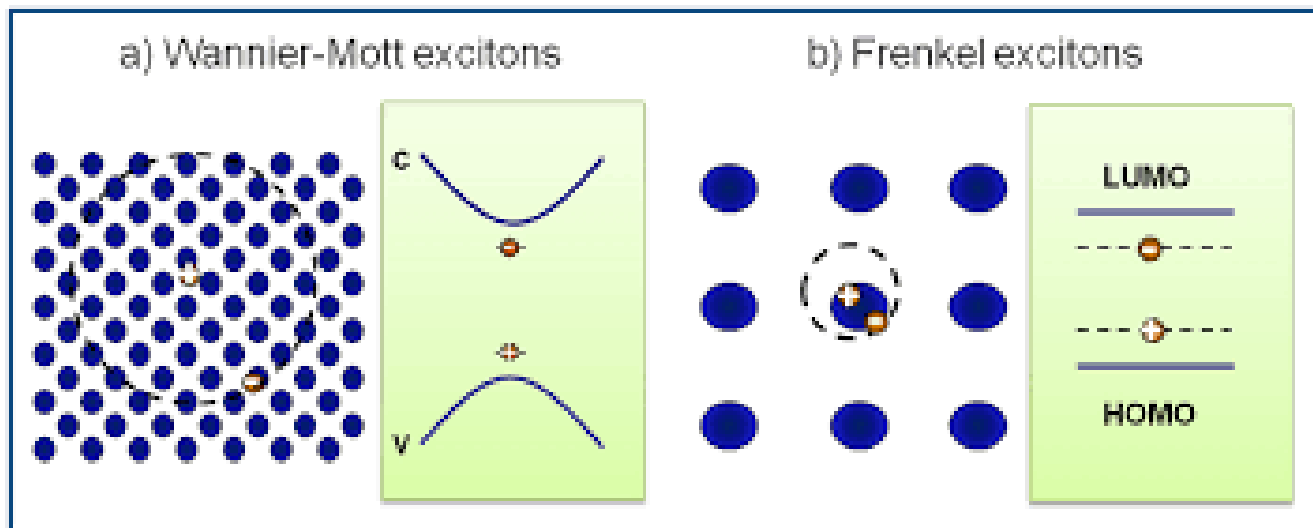
Learning goals:

❑ *Energy (not charge) transfer processes* in organic materials

   ❑ Concept of *excitons*

   ❑ *Excitonic coupling* and *delocalization* of excitons

Excitons

❑ An exciton is a ***bound state of an electron and a hole*** which are attracted to each other by the electrostatic Coulomb force. It is an electrically neutral quasiparticle that exists in insulators, semiconductors and some liquids.

❑ An exciton can form when a ***material absorbs a photon of higher energy than its bandgap***. This excites an electron from the valence band into the conduction band. In turn, this leaves behind a positively charged electron hole (an abstraction for the location from which an electron was moved).

❑ The ***electron*** in the conduction band is then effectively ***attracted*** to this ***localized hole***
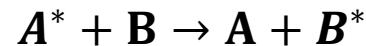
Exciton binding energy

❑ Due to the ***low dielectric constant in organic semiconductors*** (rel. permittivity ε = 3-4) holes and electrons are not screened as much as in inorganic semiconductors (ε = 10-15).

❑ High ***binding energy*** for excitons in organic semiconductos of about 0.5 eV, which means that excitons can not be thermally separated into free charge carriers at room temperature.

❑ A large enough driving force (at least as high as the exciton binding energy) is therefore required.

Photoinduced energy transfer and electron transfer

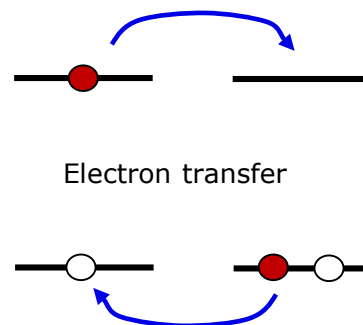How is *energy transferred* from one molecule to the other? It is the underlying mechanism for *exciton diffusion*

$$A^* + B \rightarrow A + B^*$$
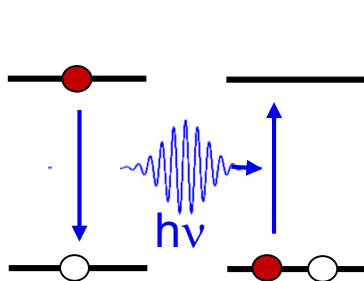
The exciton is regarded as an elementary excitation of condensed matter that can transport energy without transporting net electric charge.

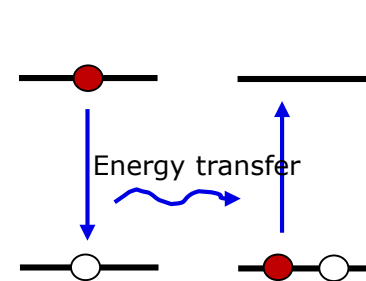Different mechanisms possible:

Radiative Energy Transfer   Nonradiative Energy Transfer
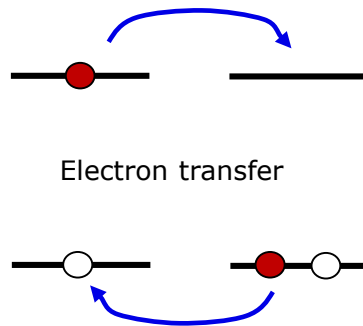

hν   Electron transfer   Energy transfer

Dexter theory   Föster Resonance Energy Transfer (FRET)

Short range electron-exchange energy transfer (Dexter energy transfer)

❑ Dexter energy transfer is a process that the donor and the acceptor *exchange their electron*. In other words, the exchanged electrons should *occupy the orbital of the other party*.

❑ That also implies that the *excited donor and ground-state acceptor should be close enough* (decreases exponentially with distance, typically 10 Angstroms).

❑ Also, the *energies involved must be the same*, means overlap of emission spectra of D and absorption spectra of A.

Electron transfer

Short range electron-exchange energy transfer (Dexter energy transfer)

❑ In 1953 Dexter expressed a ***weak coupling exchange-transfer rate*** constant in terms of Z^2:

$$\frac{d}{dt}P_n = \frac{2\pi}{\hbar}Z^2 \int_0^\infty F_A(\overline{v})\, \varepsilon_B(\overline{v})d\overline{v} \quad \text{with} \quad Z^2 \propto e^{-2r/l}$$

Where *r* is the distance between donor and acceptor molecules and *l* is the van der Waals radius of the donor-acceptor pair (sum of the van der Waals radii of donor and acceptor molecules). The exponential decay of *Z* comes from the fact that *Z* depends on the intermolecular orbital overlap and that molecular wavefunctions decline exponentially at large *r*.

Long-range Coulombic energy transfer (Förster resonance energy transfer – FRET)

❑ Förster (1948) demonstrated that rate constant for weak coupling ***dipole-dipole energy transfer*** from M* to Q is given by the expression
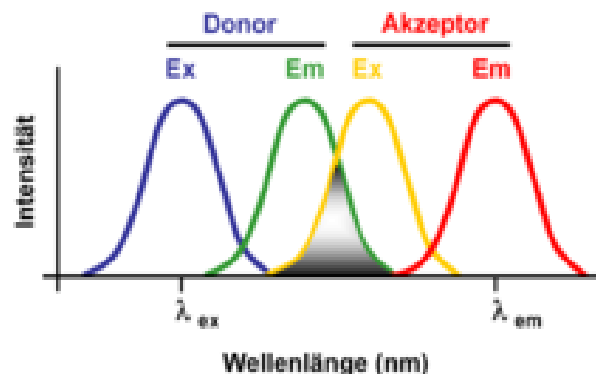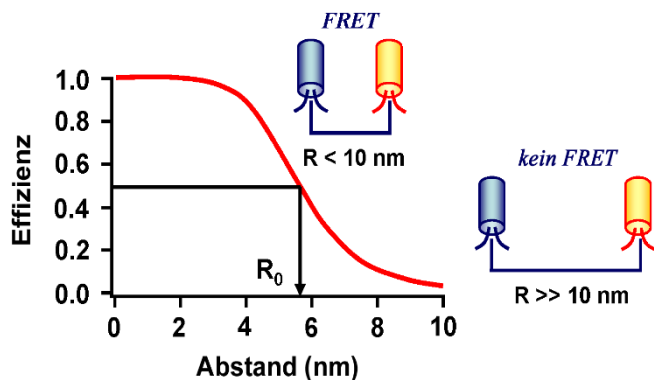
$$\frac{d}{dt}P_n = \frac{0.529\,\kappa^2}{n^4 N_A r^6 \tau_{f,A}} \int_0^\infty F_A(\bar{v})\,\varepsilon_B(\bar{v})\frac{d\bar{v}}{\bar{v}^4} \ \text{ with } \ \kappa = cos\theta_{AB} - 3cos\theta_A\,cos\theta_B$$

where θ_{AB} is the angle between the transition dipole moment vectors $\vec{\mu}_A$ and $\vec{\mu}_B$, and θ_A and θ_B are the angles between $\vec{\mu}_A$ and $\vec{\mu}_B$ and the internuclear M-Q axis, respectively. Furthermore, *n* is the solvent refractive index, N_A is Avogadro's constant and $\tau_{f,A}$ is the radiative lifetime of A* and the numeric value of 0.529 has the units cm^4 L^{-1}.

❑ Defining a ***critical transfer distance r_o*** as the D-A separation at which $\frac{d}{dt}P_n = \frac{1}{\tau_A}$, where τ_A is the actual donor excited state lifetime in the absence of A, we obtain:
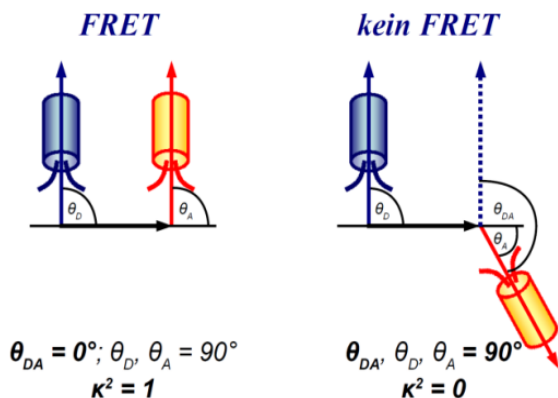
$$r_0{}^6 = \frac{0.529\,\kappa^2}{n^4 N_A} \int_0^\infty F_A(\bar{v})\,\varepsilon_B(\bar{v})\frac{d\bar{v}}{\bar{v}^4}$$

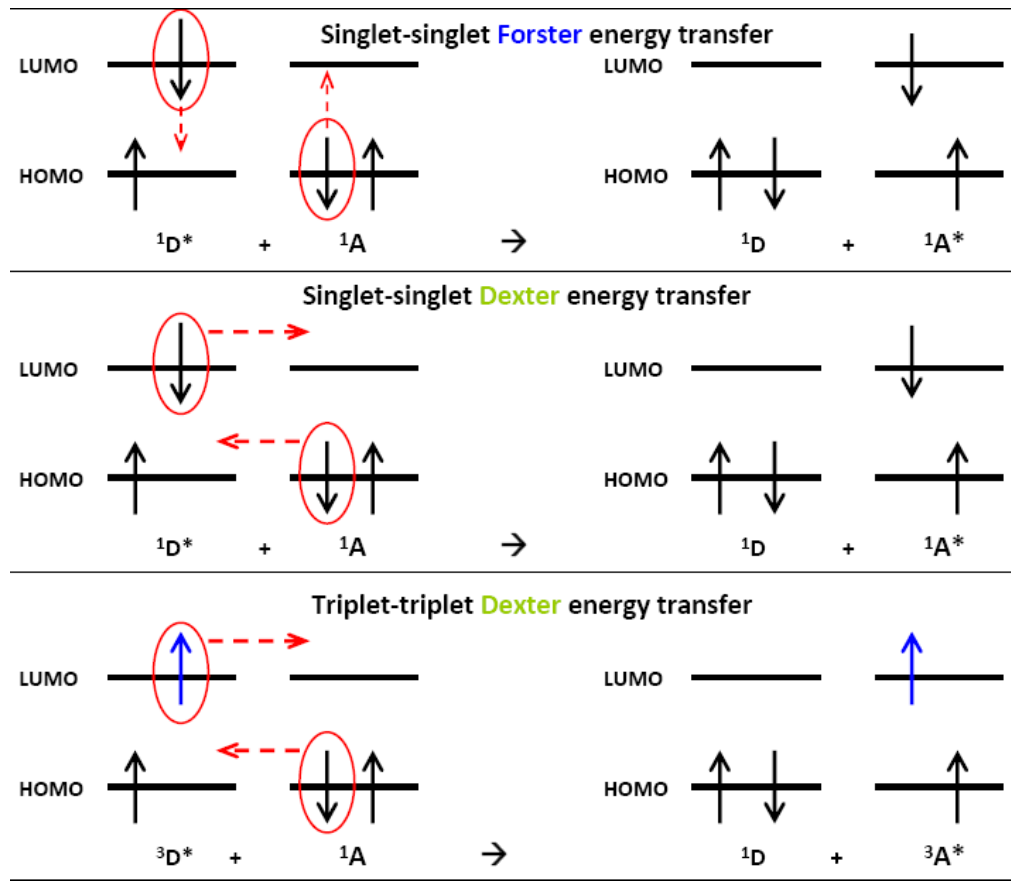# Long-range Coulombic energy transfer (Förster resonance energy transfer – FRET)

- ❑ The FRET efficiency depends on the *separation distance r* with an inverse 6th power law due to the dipole-dipole coupling mechanism.

- ❑ The *spectral overlap* of the donor emission spectrum and the acceptor absorption spectrum.

- ❑ The *relative orientation* of the donor emission dipole moment and the acceptor absorption dipole moment.

$\theta_{DA} = 0°; \theta_D, \theta_A = 90°$
$\kappa^2 = 1$

$\theta_{DA}, \theta_D, \theta_A = 90°$
$\kappa^2 = 0$

Diffusion of Triplet states

❑ Diffusion of ***triplet excitons*** in organic semiconductors occurs via short range Dexter energy transfer.

2.1D Energy transfer processes

Learning outcome

❑ How is **energy transfered** from one molecule to the other
   ▪ Radiative, Dexter, Föster

❑ Concept of **excitons**
   ▪ Bound state of an electron and a hole, Wannier-Mott and Frenkel excitons