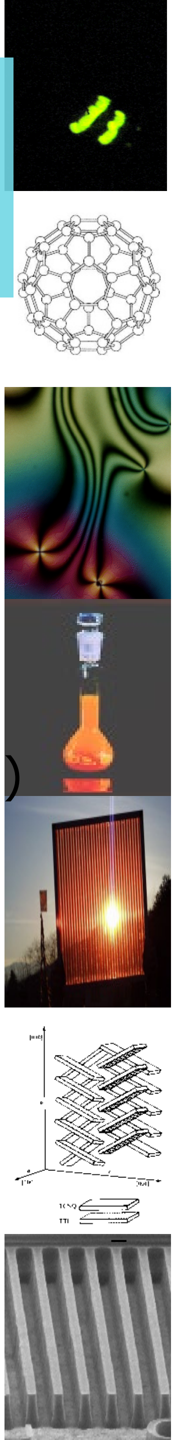
Organic materials based photovoltaics



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

2.1. Organic Semiconductors

A Molecular Orbitals (09:50-10:45)

B Electronic Properties (11:00 – 11:55)

C Absorption and Fluorescence (12:00-12:30)

D Exciton Theory, Energy & Electron Transfer (13:30-14:00)

2.2. Organic and Dye Sensitized Solar Cells

A Organic Solar Cells (14:05-15:00)

B Dye Sensitized Solar Cells (15:15-15:30)

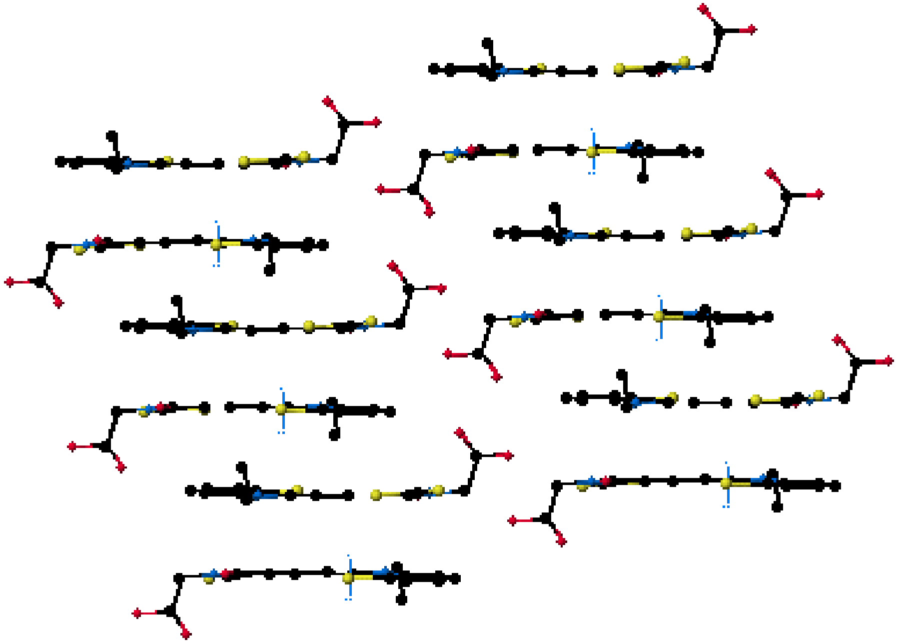
2.3. Hybrid Solar Cells - Perovskites and Quantum Dots

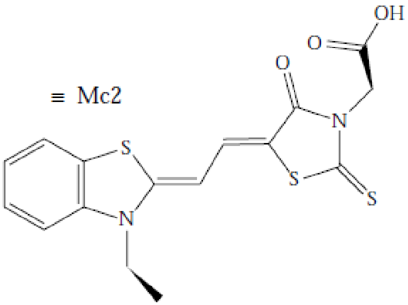
A Perovskite Solar Cells (15:35-16:50)

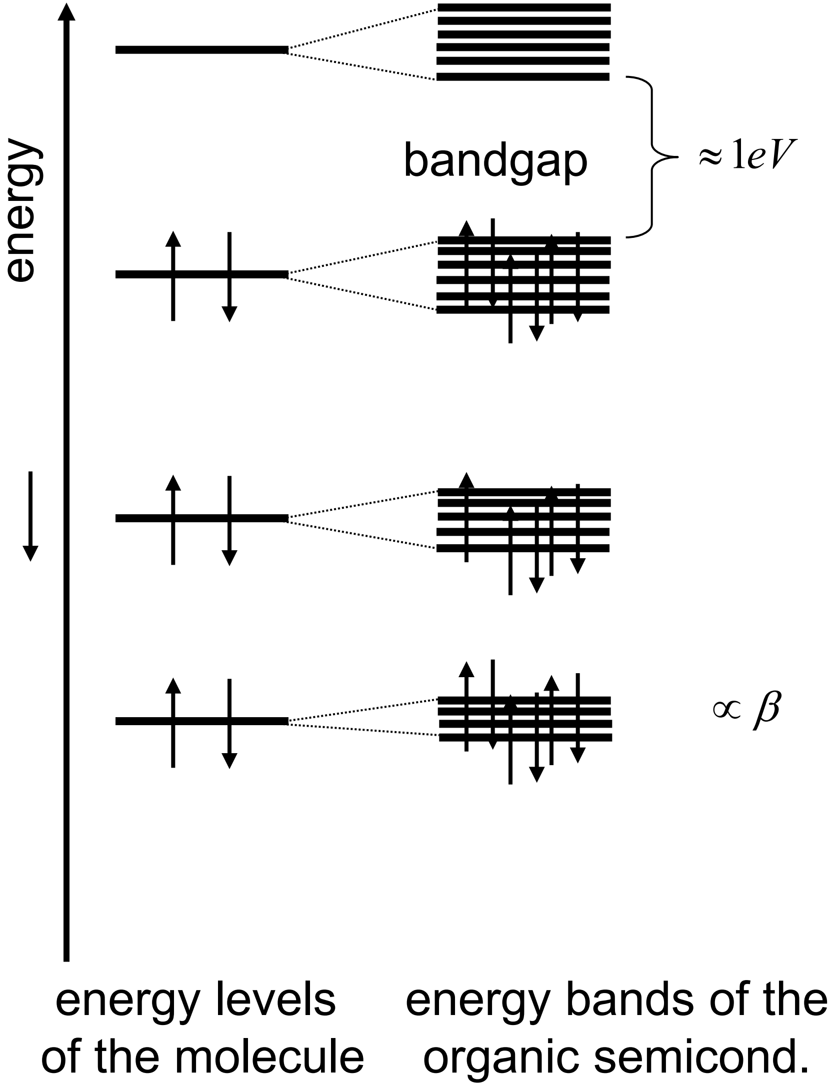
B Quantum Dot Solar Cells (16:55-17:05)

Molecular crystals?

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

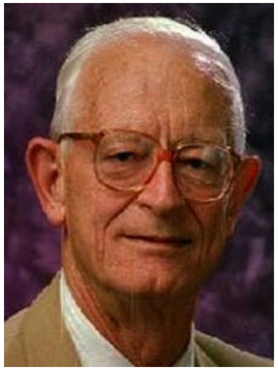




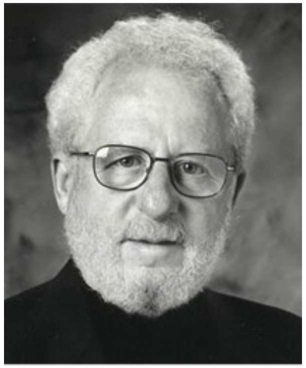


The discovery of conducting polymers 1977

Hideki Shirakawa



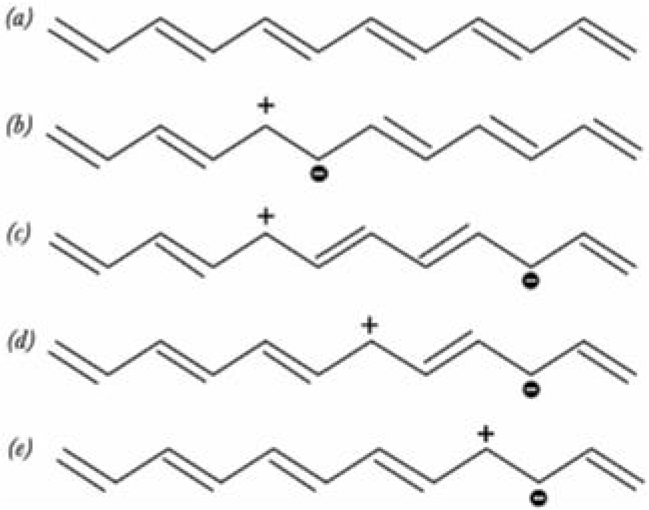
Alan G. MacDiarmid



Alan J. Heeger

Nobel prize in chemistry 2000

- Polyacetylene become ***conductive upon doping***
- ***Conjugation creates an orbit*** that allows the charge carriers to move



Why organic electronics? – it is a new technology, where are the benefits?

- ***Increased Efficiency:*** New technologies often bring with them improved processes and automation capabilities
  - Low cost, mass produce by printing

- ***Enhanced Customer Experience***
  - True for self-emissive pixels in oLEDs: broad color spectrum, fast response time, wider viewing angle, less power

- ***Market Expansion:*** new technologies can open up untapped markets and create new revenue streams
  - Polymer TFTs enable flexible displays

Flexible, printed, organic electronics

- Often used interchangeable

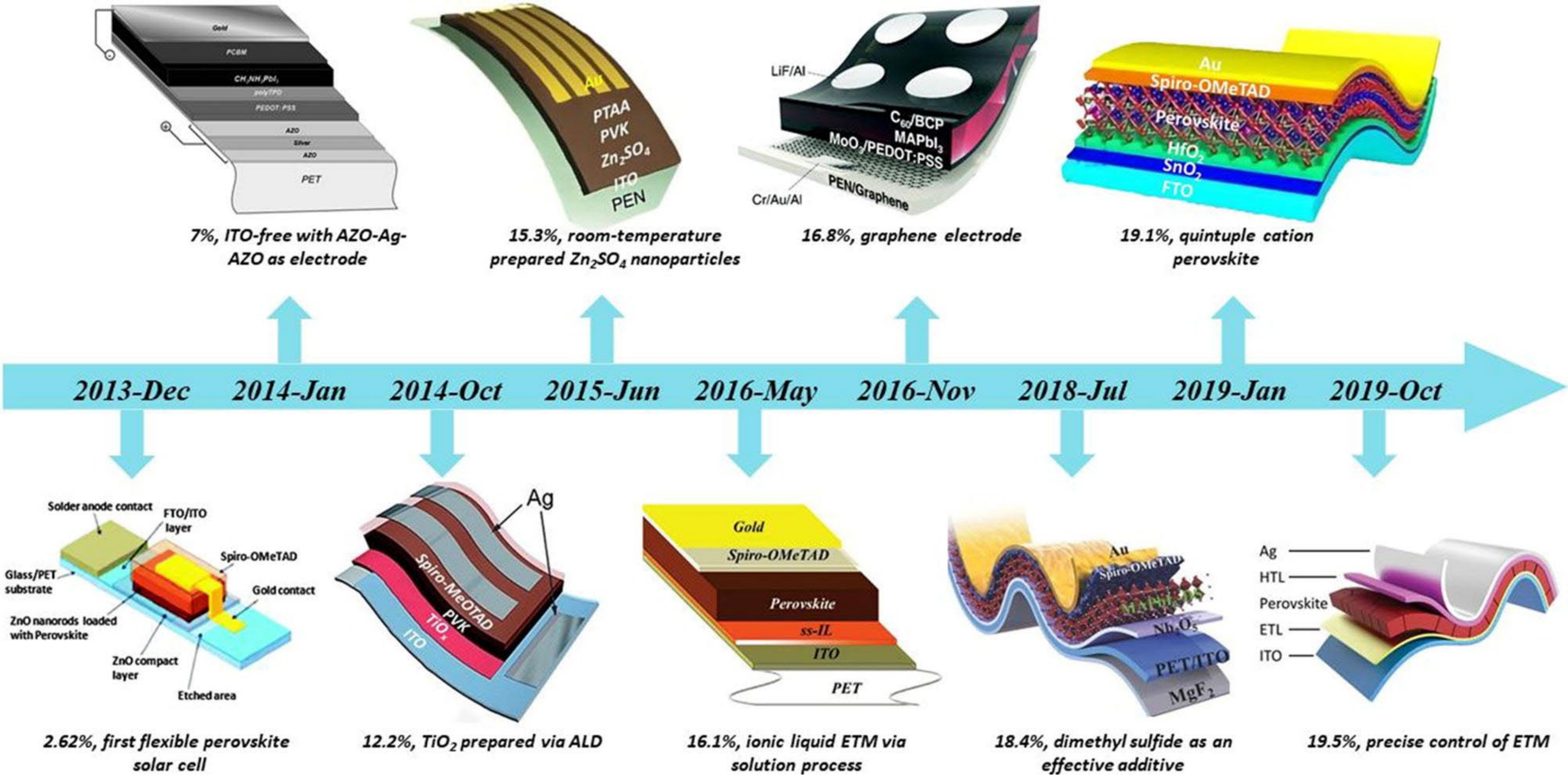
- Strictly spoken:
  - Flexible: does not need to be organic
  - Printed: does not need to be organic

Plastic 12-bit RFID Tag and Read-out System with Screen-Printed Antenna

  - Organic: does not need to be flexible or printed

oLED material evaporated onto ITO glass

Flexible, printed, organic photovoltaics



2013-Dec: 2.62%, first flexible perovskite solar cell

2014-Jan: 7%, ITO-free with AZO-Ag-AZO as electrode

2014-Oct: 12.2%, TiO_2 prepared via ALD

2015-Jun: 15.3%, room-temperature prepared Zn_2SO_4 nanoparticles

2016-May: 16.1%, ionic liquid ETM via solution process

2016-Nov: 16.8%, graphene electrode

2018-Jul: 18.4%, dimethyl sulfide as an effective additive

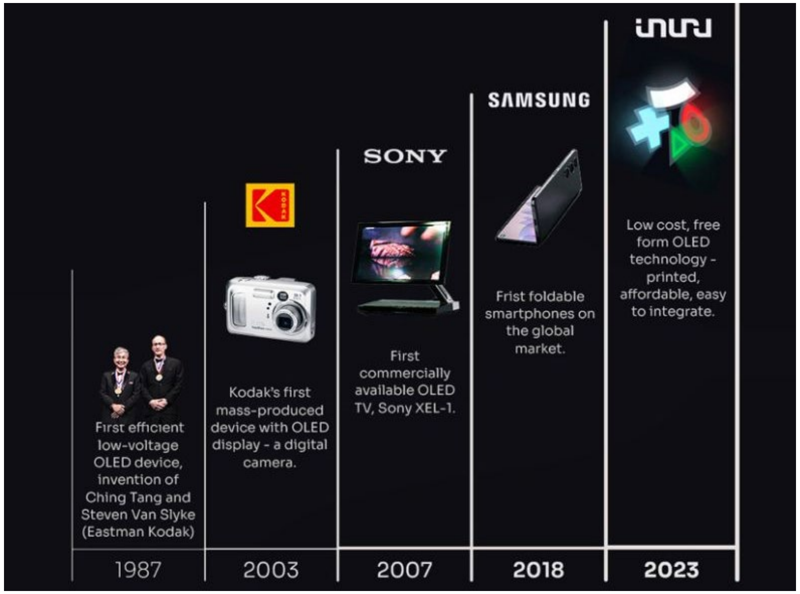
2019-Jan: 19.1%, quintuple cation perovskite

2019-Oct: 19.5%, precise control of ETM

Applications for organic printed electronics

Image source: InnovationLab

Success story oLEDs



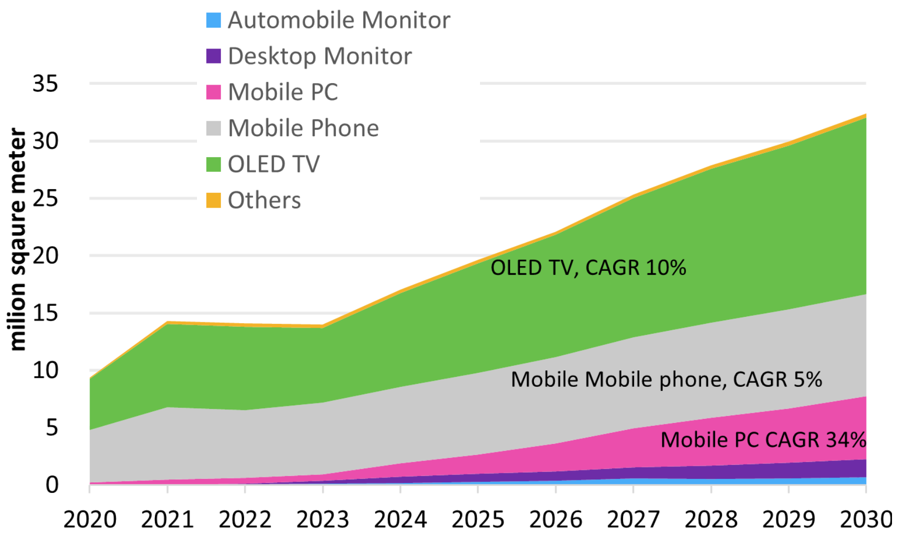
First efficient low-voltage OLED device, invention of Ching Tang and Steven Van Slyke (Eastman Kodak)

Kodak's first mass-produced device with OLED display - a digital camera.

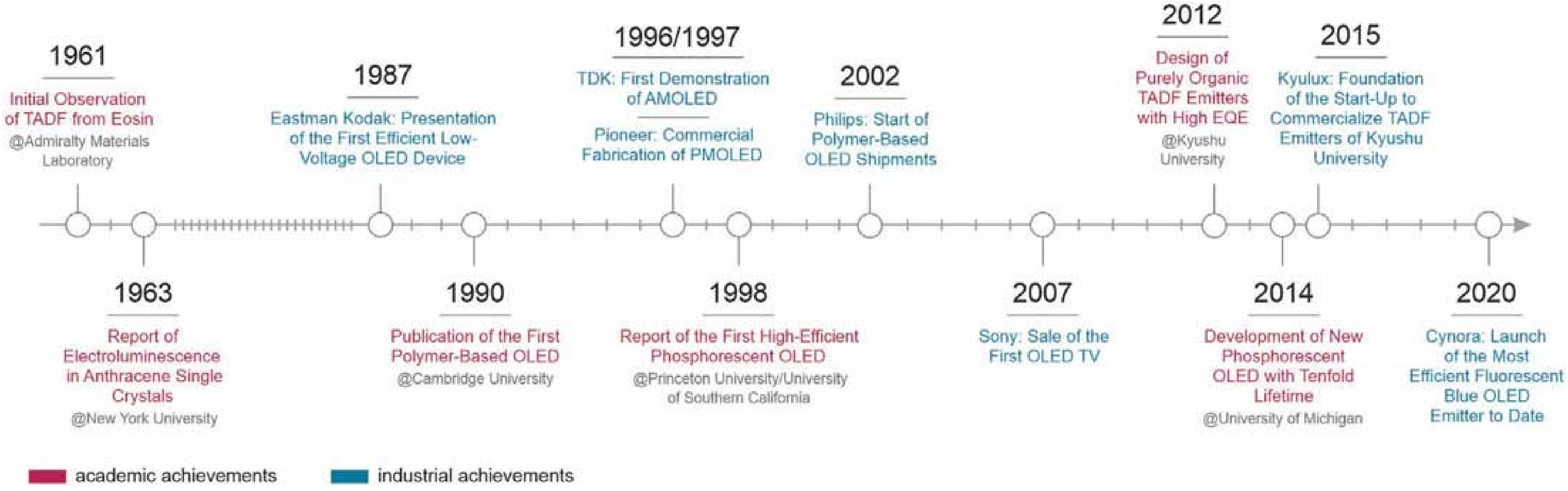
First commercially available OLED TV, Sony XEL-1.

Frist foldable smartphones on the global market.

Low cost, free form OLED technology - printed, affordable, easy to integrate.



Source: Omdia, Dislay long-term demand forecast tracker



1961
Initial Observation of TADF from Eosin
@Admiralty Materials Laboratory

1963
Report of Electroluminescence in Anthracene Single Crystals
@New York University

1987
Eastman Kodak: Presentation of the First Efficient Low-Voltage OLED Device

1990
Publication of the First Polymer-Based OLED
@Cambridge University

1996/1997
TDK: First Demonstration of AMOLED
Pioneer: Commercial Fabrication of PMOLED

1998
Report of the First High-Efficient Phosphorescent OLED
@Princeton University/University of Southern California

2002
Philips: Start of Polymer-Based OLED Shipments

2007
Sony: Sale of the First OLED TV

2012
Design of Purely Organic TADF Emitters with High EQE
@Kyushu University

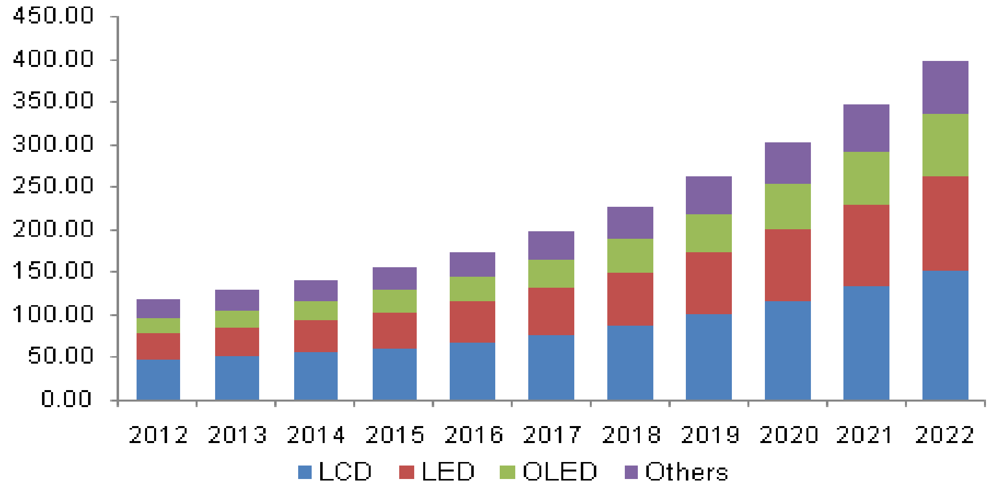
2014
Development of New Phosphorescent OLED with Tenfold Lifetime
@University of Michigan

2015
Kyulux: Foundation of the Start-Up to Commercialize TADF Emitters of Kyushu University

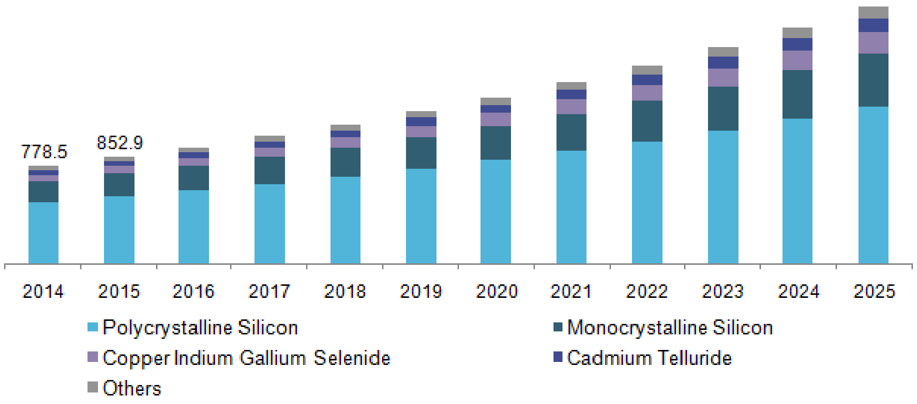
2020
Cynora: Launch of the Most Efficient Fluorescent Blue OLED Emitter to Date

🟥 academic achievements 🟦 industrial achievements

Display and Photovoltaic Market Size by Technology (Mio US $)



- ***Why oLED but no oPV?***
  - "Similar" technology
  - Same discovery time



Global PV Materials Market, 2018
Grand View Market

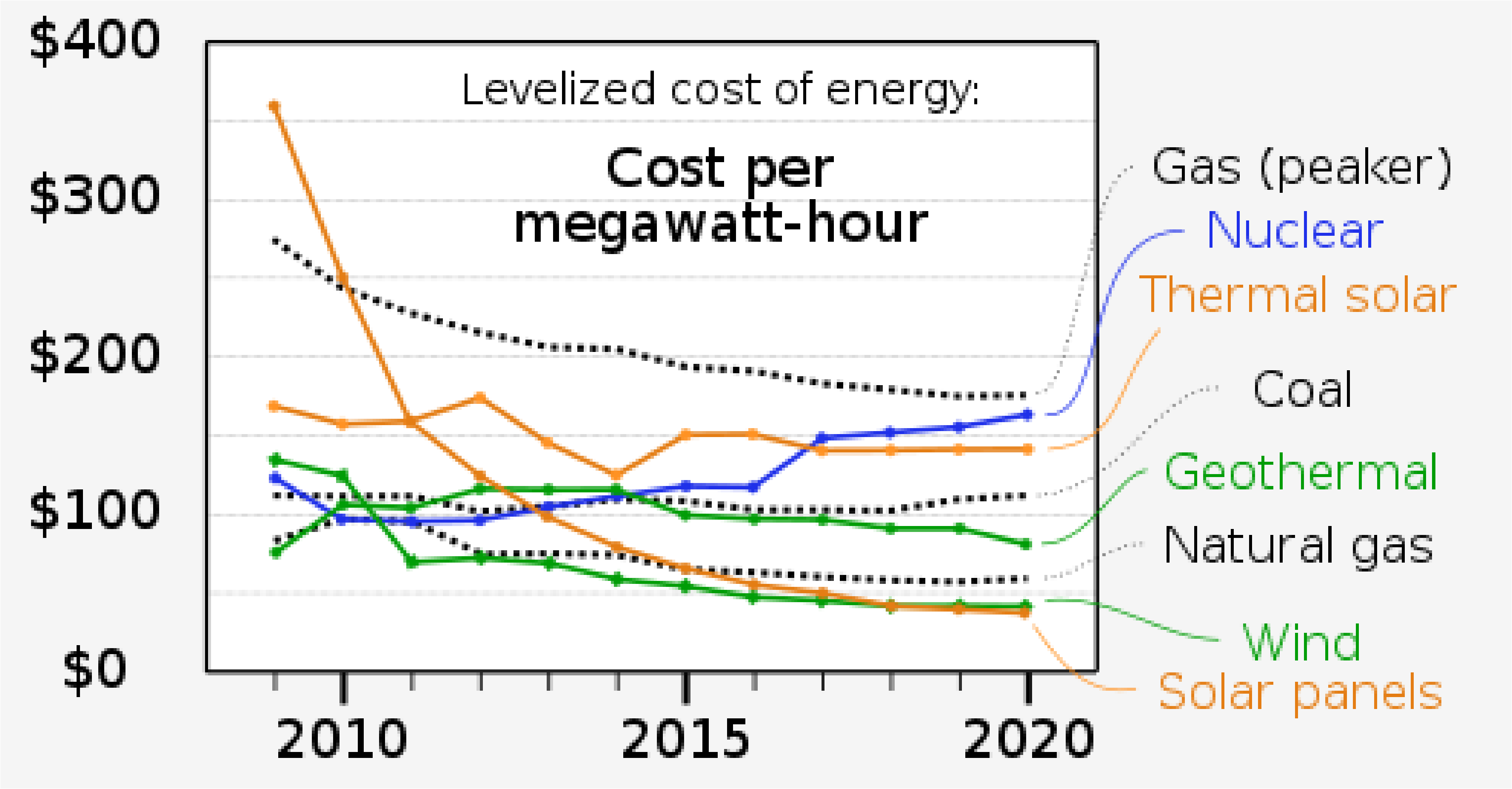
Why oLED and not oPV

- ***Obvious advantages over dominating LCD technology:***
  - Self-emissive pixels in oLEDs: broad color spectrum, fast response time, wider viewing angle, less power, can be made flexible - oPV less efficient, less stable than Si; only potential to be printable

- ***Large companies jumped in:***
  - Efforts to industrialize oPV was mainly done by Start-ups

- ***Price structure:***
  - Displays «can» be more expensive: IHS released its LCD and OLED smartphone display cost model: 5.7" 2560x1440 rigid OLED costs $18.62 to produce, a 5.7" full-display 2880x1440 LCD costs $15.39 to produce (source HIS) – oPV has to compete with the decreasing prices of Si-modules

Cost of energy



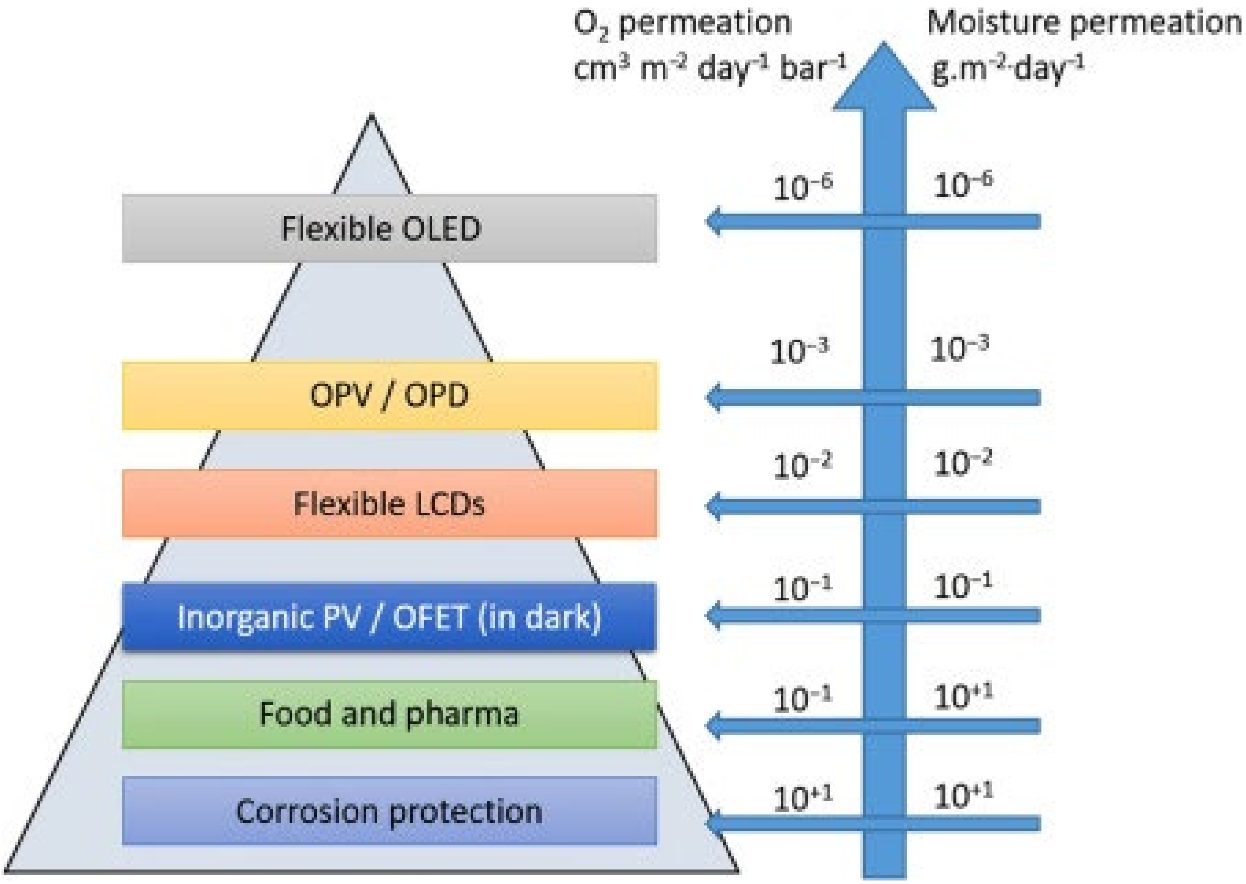
"Lazard's Levelized Cost of Energy Version 14.0" (PDF). Lazard.com. Lazard. 19 October 2020.

Why oLED and not oPV

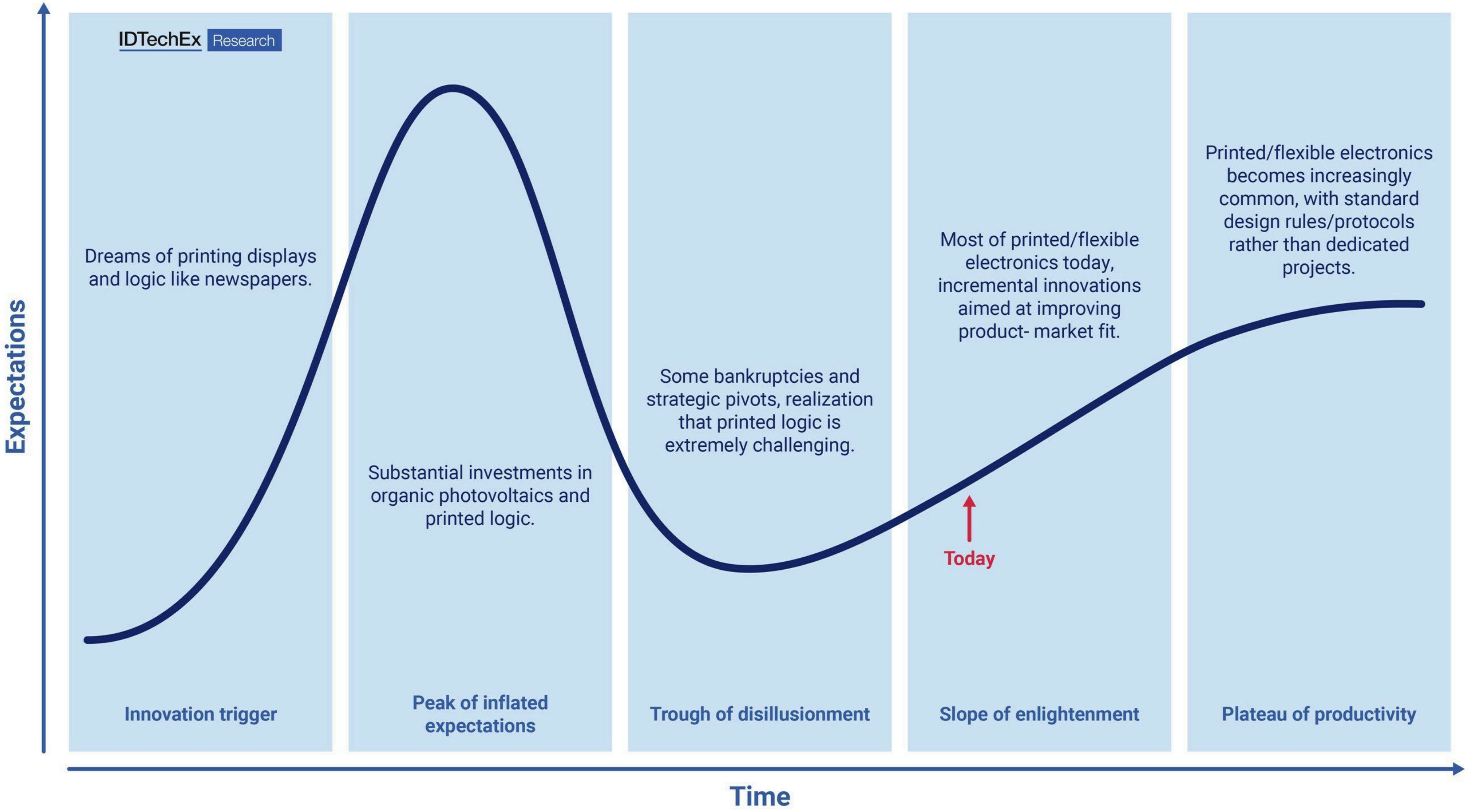
- ***oLED started small:***
  - - oPV needs large area modules, or less attractive niche markets
- ***Large companies jumped in:***
  - Efforts to industrialize oPV was mainly done by Start-ups
- ***Price structure:***
  - Displays «can» be more expensive: IHS released its LCD and OLED smartphone display cost model: 5.7" 2560x1440 rigid OLED costs $18.62 to produce, a 5.7" full-display 2880x1440 LCD costs $15.39 to produce (source HIS) – oPV has to compete with the decreasing prices of Si-modules
- ***Exposure to harsh environmental conditions:***
  - Displays not really exposed

Where oPV can profit from oLED research

- ***Acceptable levels of exposure to water vapour and oxygen is much smaller in oLEDs than in oPV***



Gartner Hype Cycle



Dreams of printing displays and logic like newspapers.

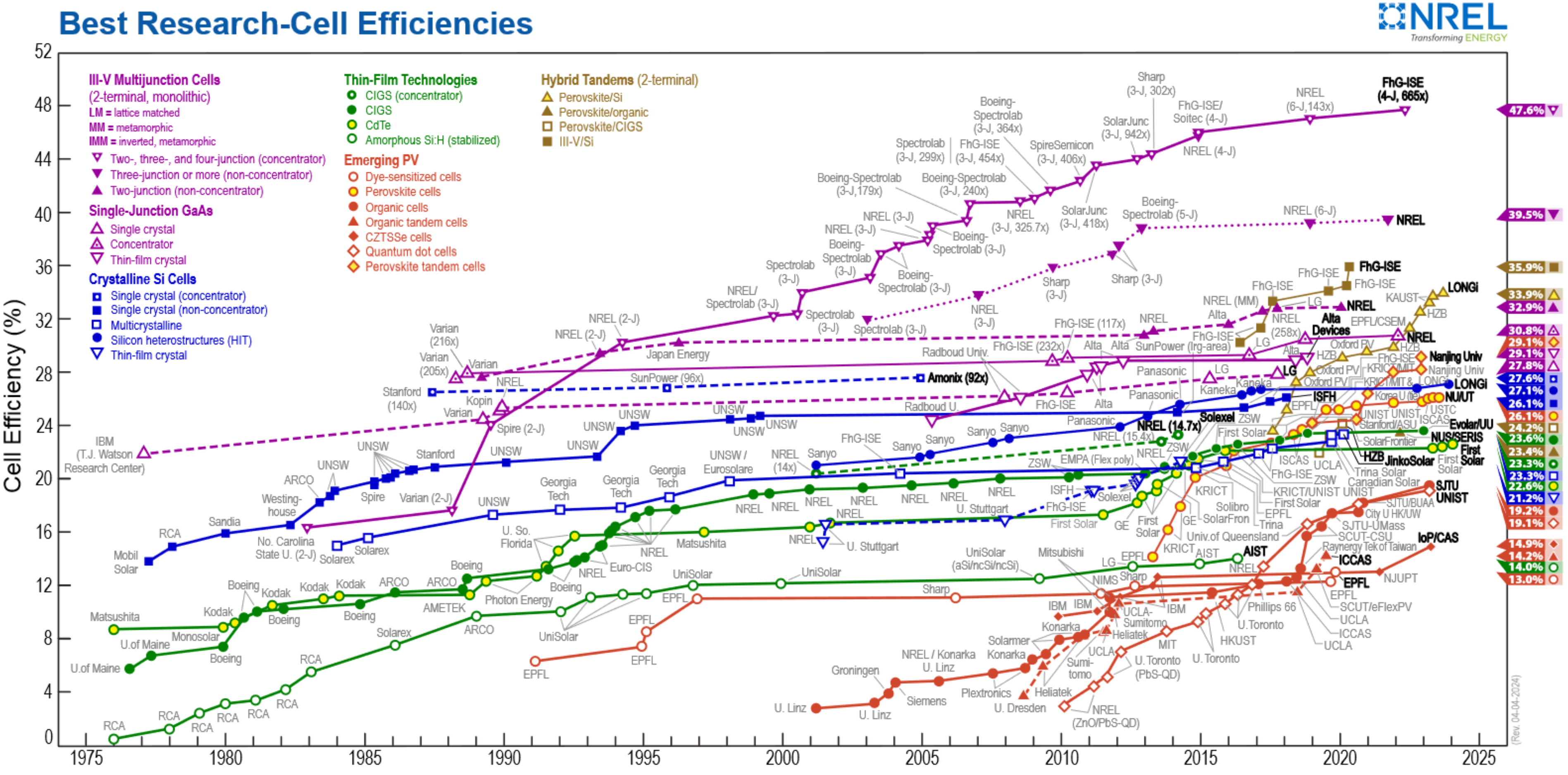
Substantial investments in organic photovoltaics and printed logic.

Some bankruptcies and strategic pivots, realization that printed logic is extremely challenging.

Most of printed/flexible electronics today, incremental innovations aimed at improving product- market fit.

Printed/flexible electronics becomes increasingly common, with standard design rules/protocols rather than dedicated projects.

Best Research-Cell Efficiencies



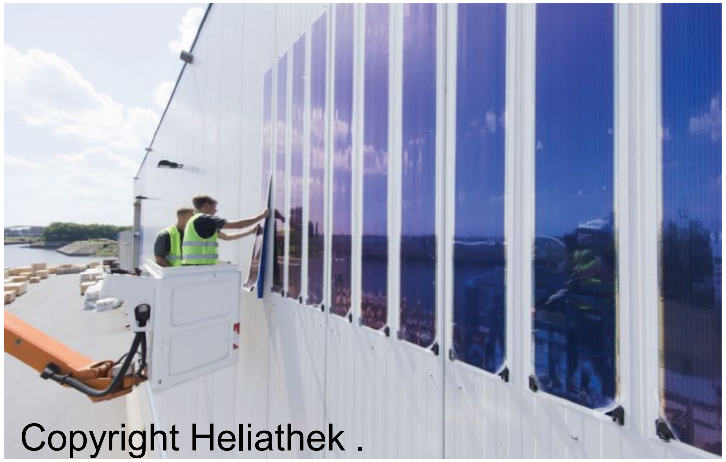
Solar cell efficiency **refers to the portion of energy in the form of sunlight that can be converted via photovoltaics into electricity by the solar cell**.

oPV – the path to commercial success

- Today: ***cannot beat the price*** of silicon photovoltaics, today’s solutions are not yet printed (but evaporated)

- ***Efficiency*** is important, allows to bring $/W down

- Can serve ***niche markets*** (5% of photovoltaics market), light weight building integrated photovoltaics, semitransparency in windows)

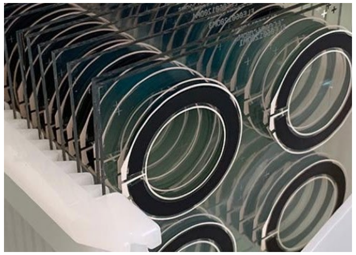


Copyright Heliathek .

- Much lower ***carbon footprint*** (5–9 g CO_2 / kWh, a factor of 10 lower than for Silicon photovoltaics)

Perovskite solar cells – the path to success

- Today: ***cannot beat the price*** of silicon photovoltaics
- Still ***issues*** with ***stability, module efficiency, manufacturing***
- ***Niche markets*** (5% of photovoltaics market): in-door applications



http://perovskia.solar.com

- Si-Perovskite tandem cells

www.oxfordpv.com

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

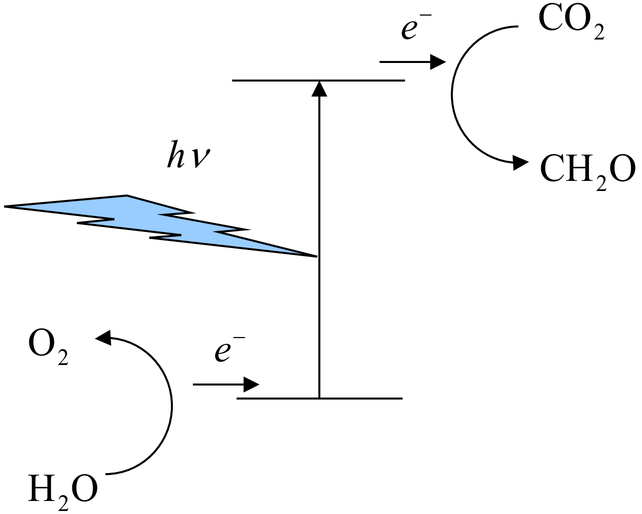
$$CO_2 + H_2O \xrightarrow{h\nu} CH_2O \;+ O_2 \qquad \Delta G^0 = 478\,\text{kJ/mol}\,CO_2$$

Photosynthesis – light reaction

Overall process of photosynthesis is a ***redox*** chemical reaction

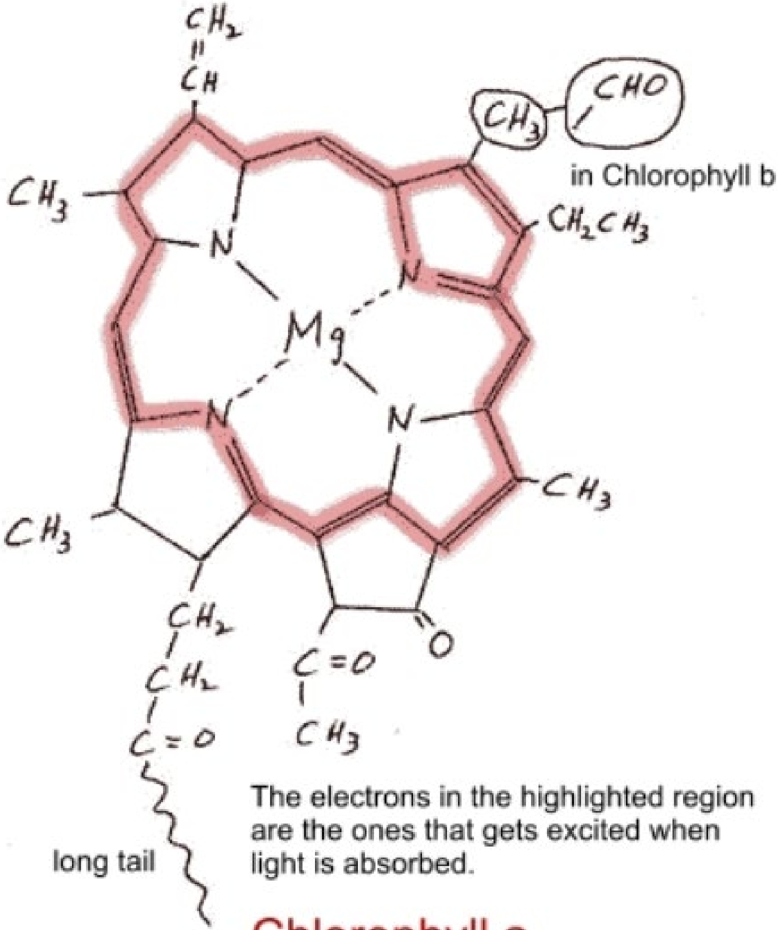
Electrons are removed from water (***oxidation***) and added to CO_2 (***reduction***)

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

Organic semiconductors ≠ biomaterials

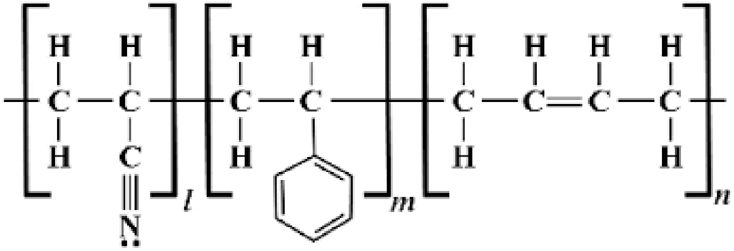


The electrons in the highlighted region are the ones that gets excited when light is absorbed.

Chlorophyll a

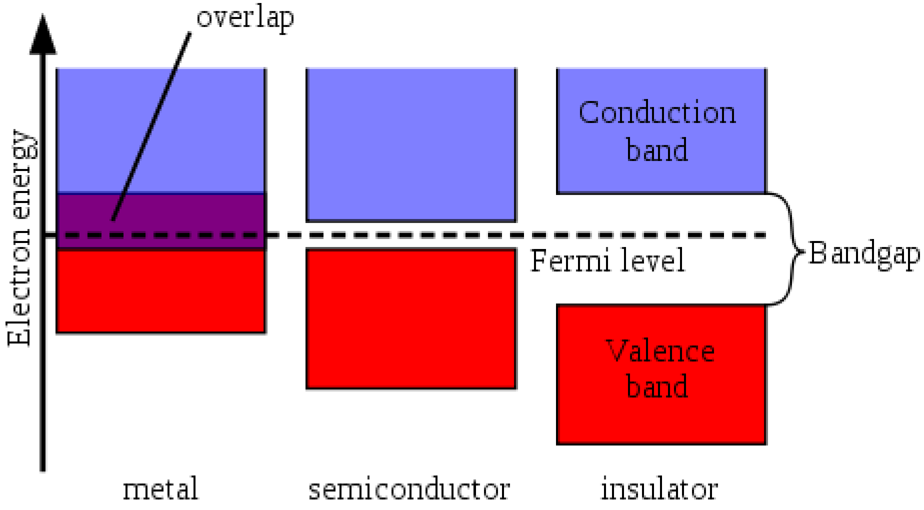
Organic compounds

- 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.***



Acrylonitrile butadiene styrene (ABS)

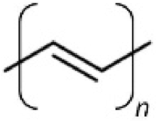
Band gap – Optical properties and more…



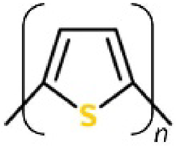
- Metals: ***charge carriers*** in ***conduction band*** (=«band» of electron orbitals)
- Semiconductors: electrons can be thermally excited into the conduction band
- Insulators: Bandgap > 4 eV

Conducting polymers

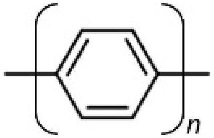
- Synthesize individual soluble building blocks that absorb in the visible domain



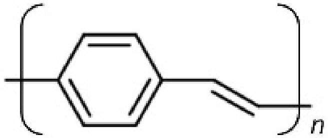
Polyacetylene



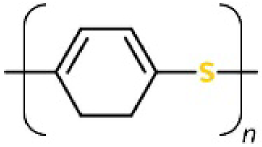
Polythiophene



Poly(*p*-phenylene)



Poly(*p*-phenylenevinylene)



Poly-*p*-phenylene-sulphide

- Solution processable, printable

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}
	Rely on existing materials and doping	Adapt properties by custom synthesizing materials

Summary

- ☐ Organic Photovoltaics is part of the emerging field of printed/organic electronics
- ☐ Difference in properties between inorganic and organic SCs has significant influence on the working principle of organic solar cells.
- ☐ A very specific case are the hybrid Perovskite solar cells

Printed oLED displays

BUSINESS

Japan enters display fray with world's first printed OLED panels

JDI
Japan Display Inc.

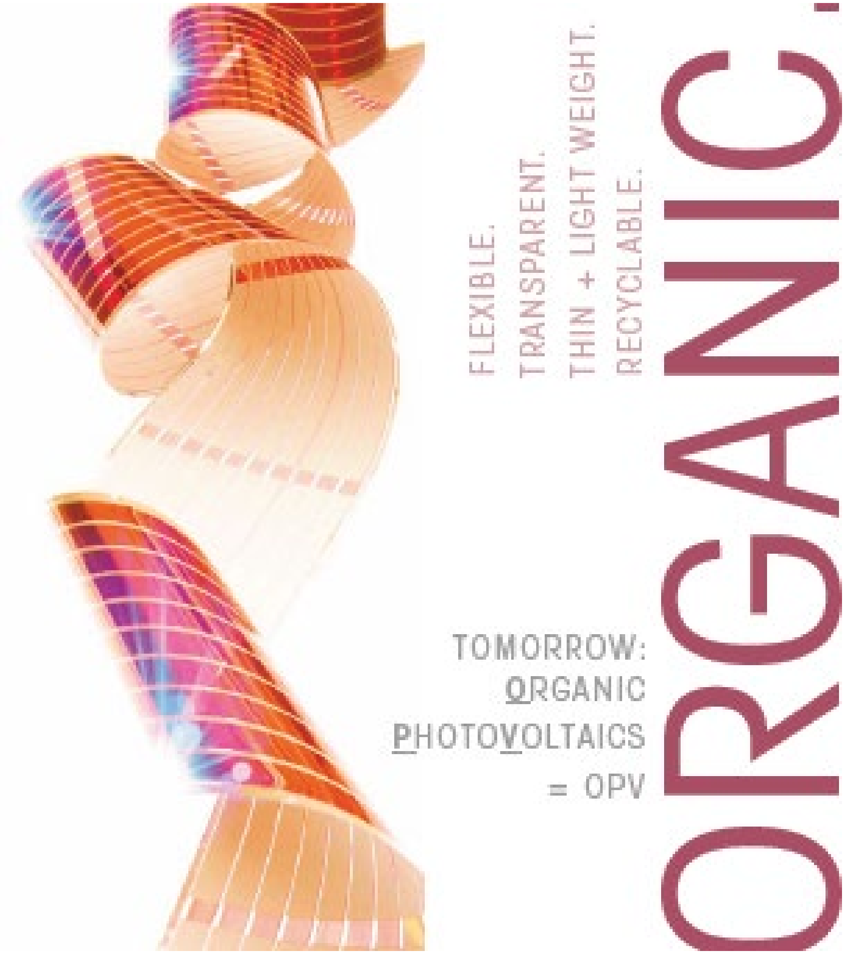
SONY

HITACHI

TOSHIBA

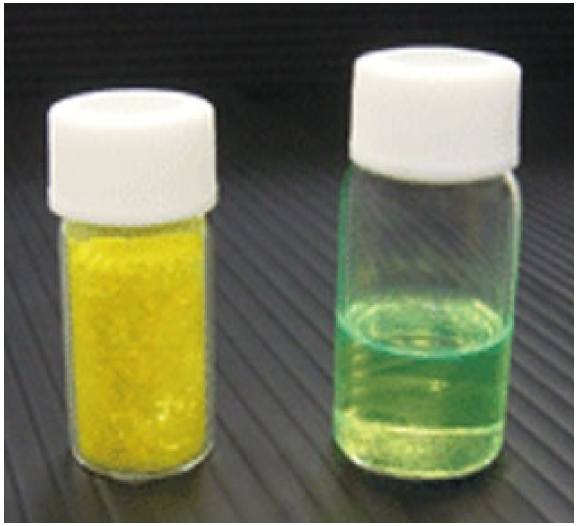
TCL

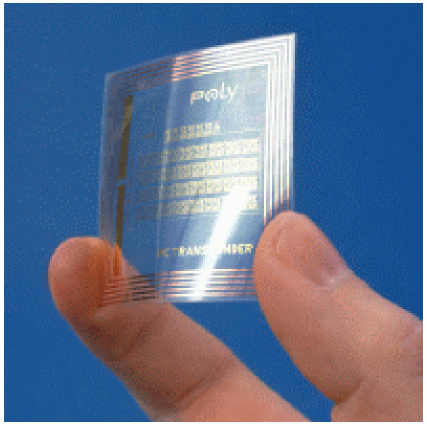
Organic Photovoltaics (oPV)

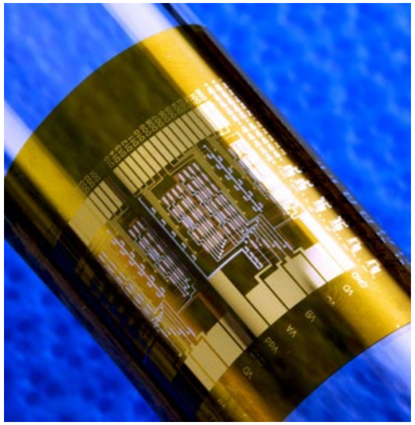


source: Belectric GmbH

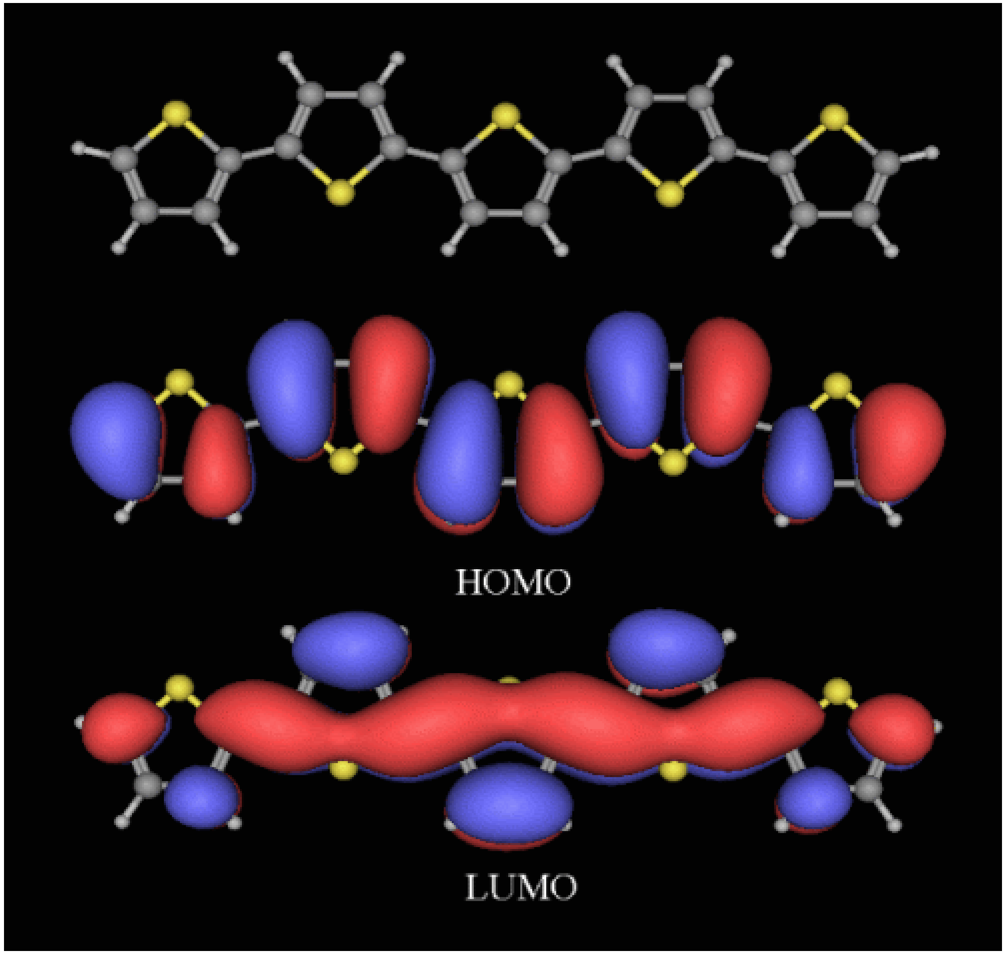
Thin film devices with polymer semiconductors:

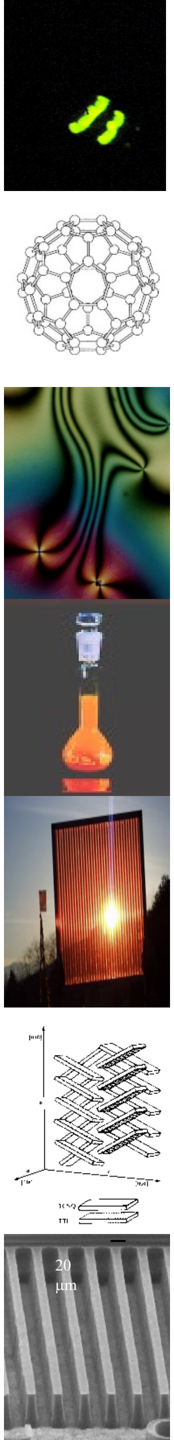






2.1A Molecular Orbitals





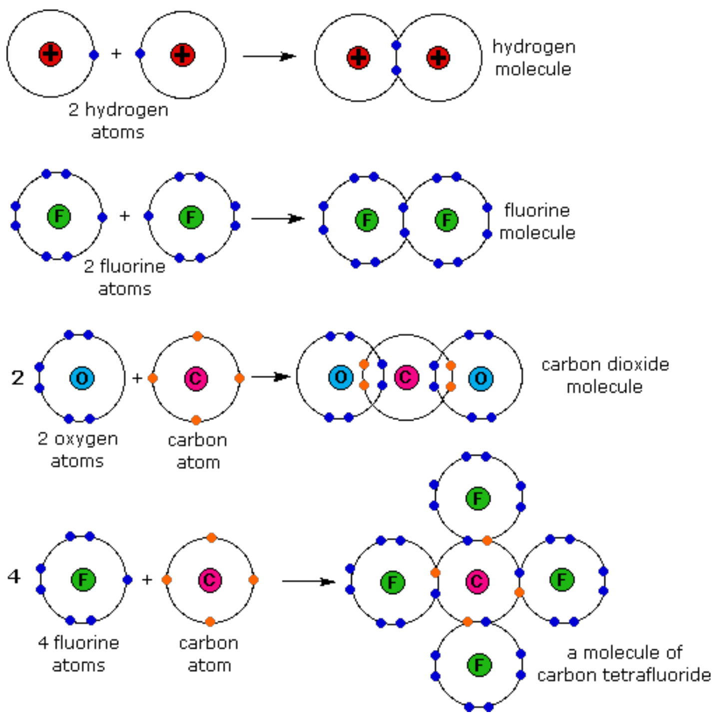
2.1A Molecular Orbitals

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 – Lewis structure

- ❑ 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

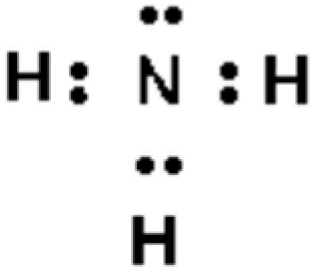


- ❑ Shared electron pairs provides an effective ***qualitative picture*** of covalent bonding
- ❑ For many molecules, the sharing of electrons allows each atom to attain the ***equivalent of a full valence shell***, corresponding to a stable electronic configuration

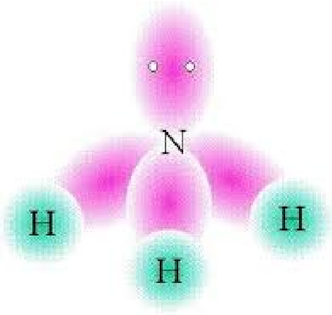
https://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/intro2.htm

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 $\vec{r} = (r_1, r_2, \dots r_N)$ and nuclear positions $\vec{R} = (R_1, R_2, \dots R_M)$:

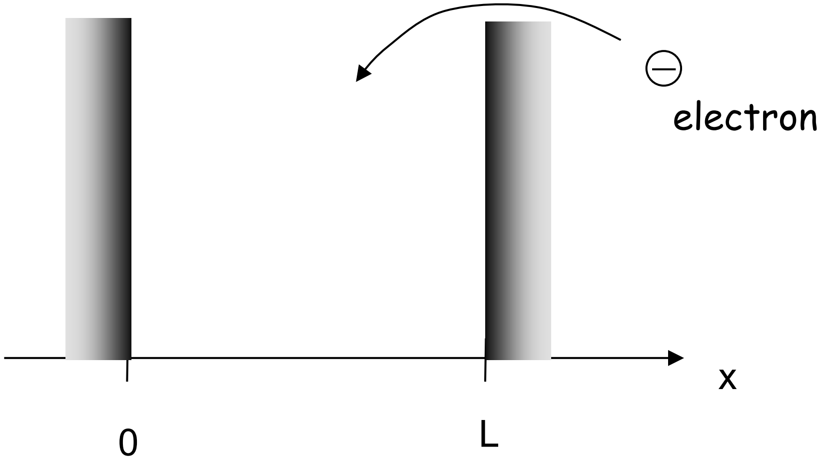
$$\hat{H}\psi(\vec{r}, \vec{R}, t) = i\hbar \frac{d\psi(\vec{r}, \vec{R}, t)}{dt}$$

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

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

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

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



Calculate the energy levels and wavefunctions for one electron:

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

Solutions are standing waves:

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

Boundary conditions (probability to find particle = 0)

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

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

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

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

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

Normalisation of ψ:

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

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

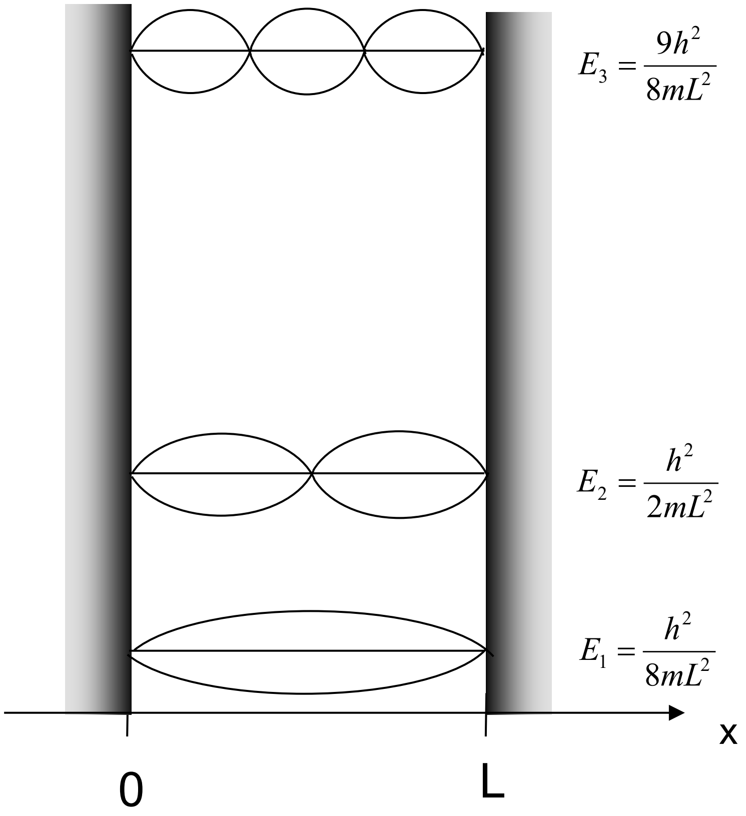
Solutions of the particle in a box problem are standing waves:

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)

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

ψ is the particle wavefunction.

The probability amplitude. $|\psi(x)|^2 dx$ is the probability of finding the particle between x and x+dx



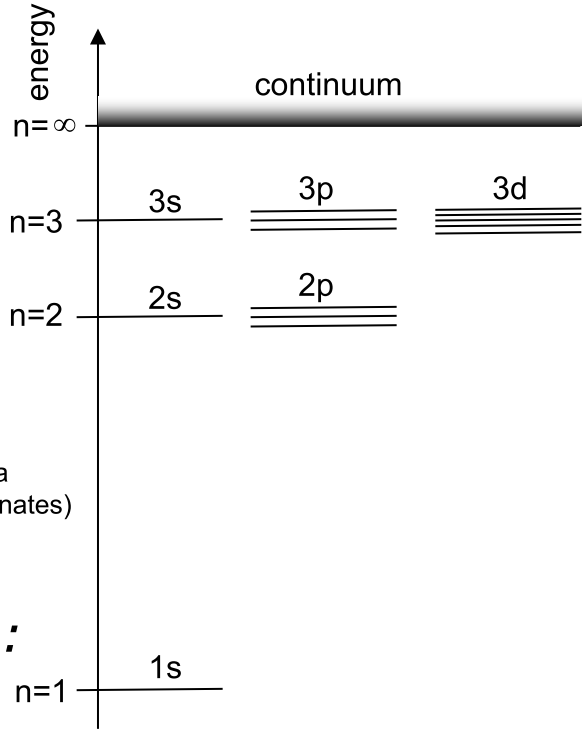
H-atom orbitals

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:*

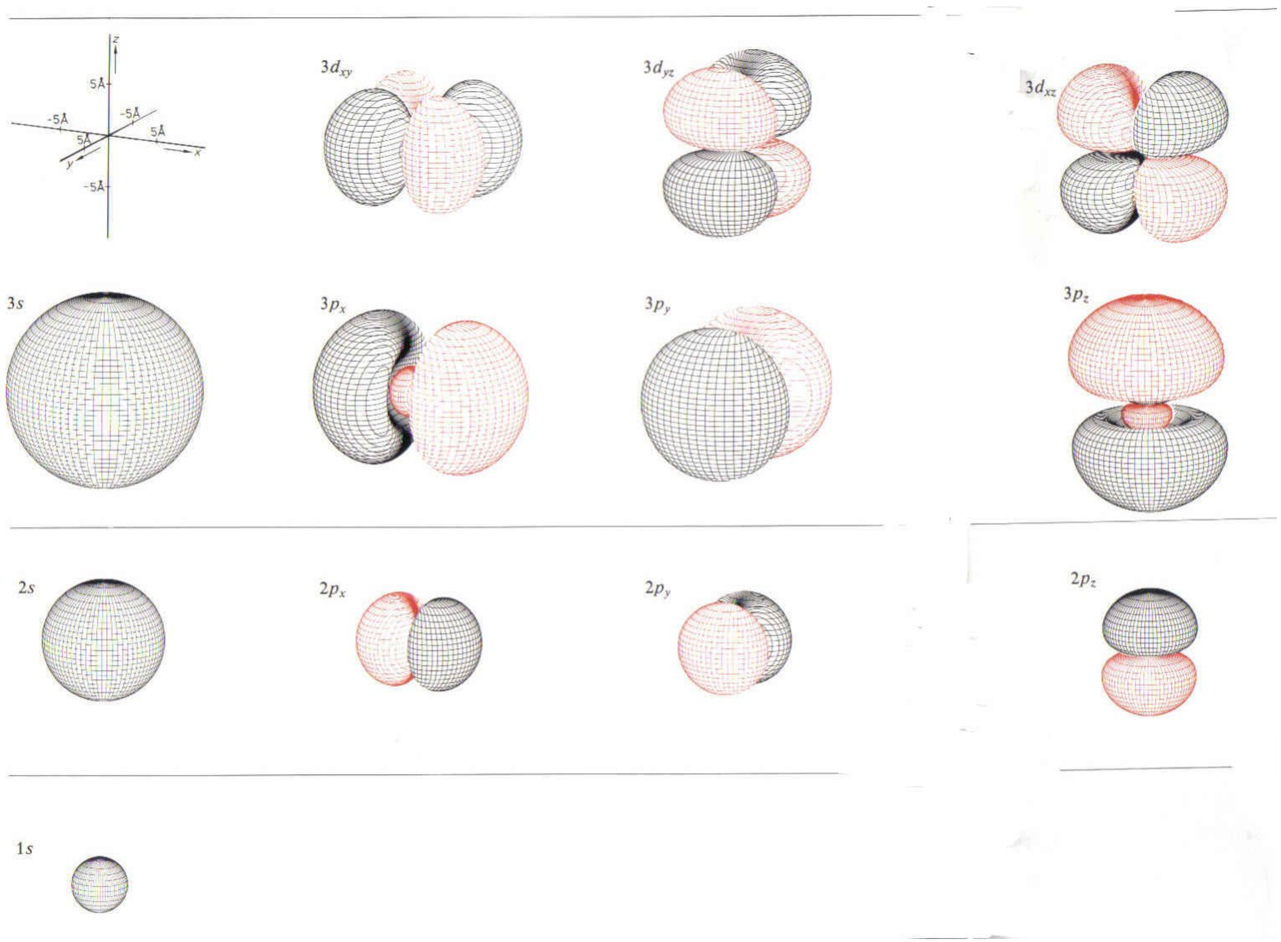
n = 1, 2, 3, … principal quantum

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 orbital here is defined as the volume where the probability of finding the electron is 90%



Molecular orbital theory

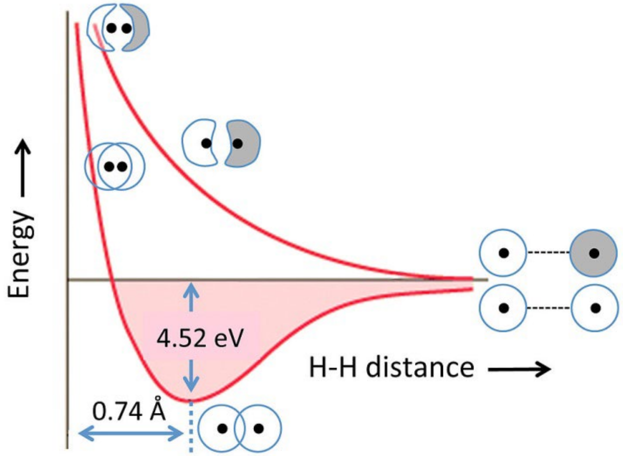
- ☐ Only for the H-atom an analytical solution for the orbitals can be found
- ☐ Neglect interactions between electrons = reduce a many-electron problem to many one-electron problems
- ☐ Molecular orbital theory revolutionized the study of chemical bonding by approximating the states of bonded electrons—the molecular orbitals—as linear combinations of atomic orbitals (LCAO):

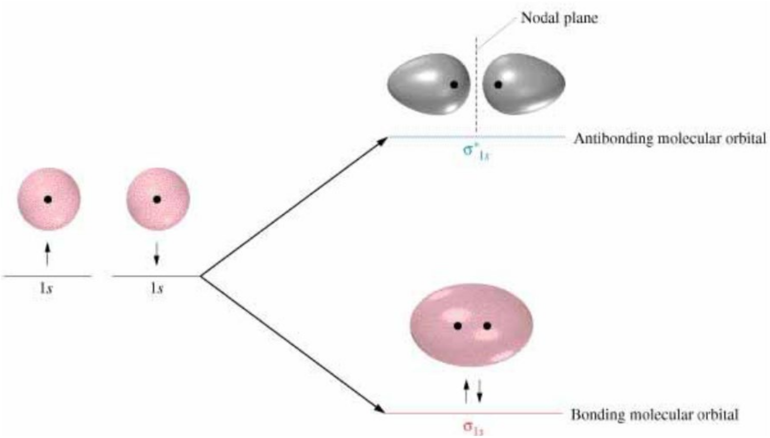
$$\psi_j \approx \prod_i c_{ij}\varphi_i$$

φ_i := atomic 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***.





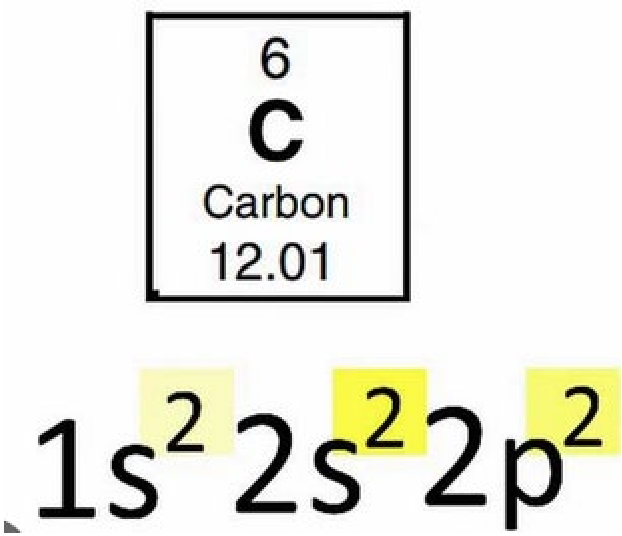
- Molecular orbitals are obtained by combining the atomic orbitals

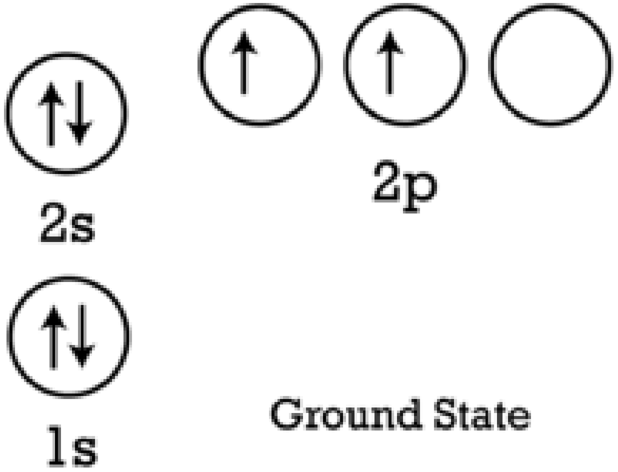
- In the hydrogen molecule you can construct in-phase and out-of-phase combinations of H 1s orbitals

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

Molecular orbitals of the second energy level

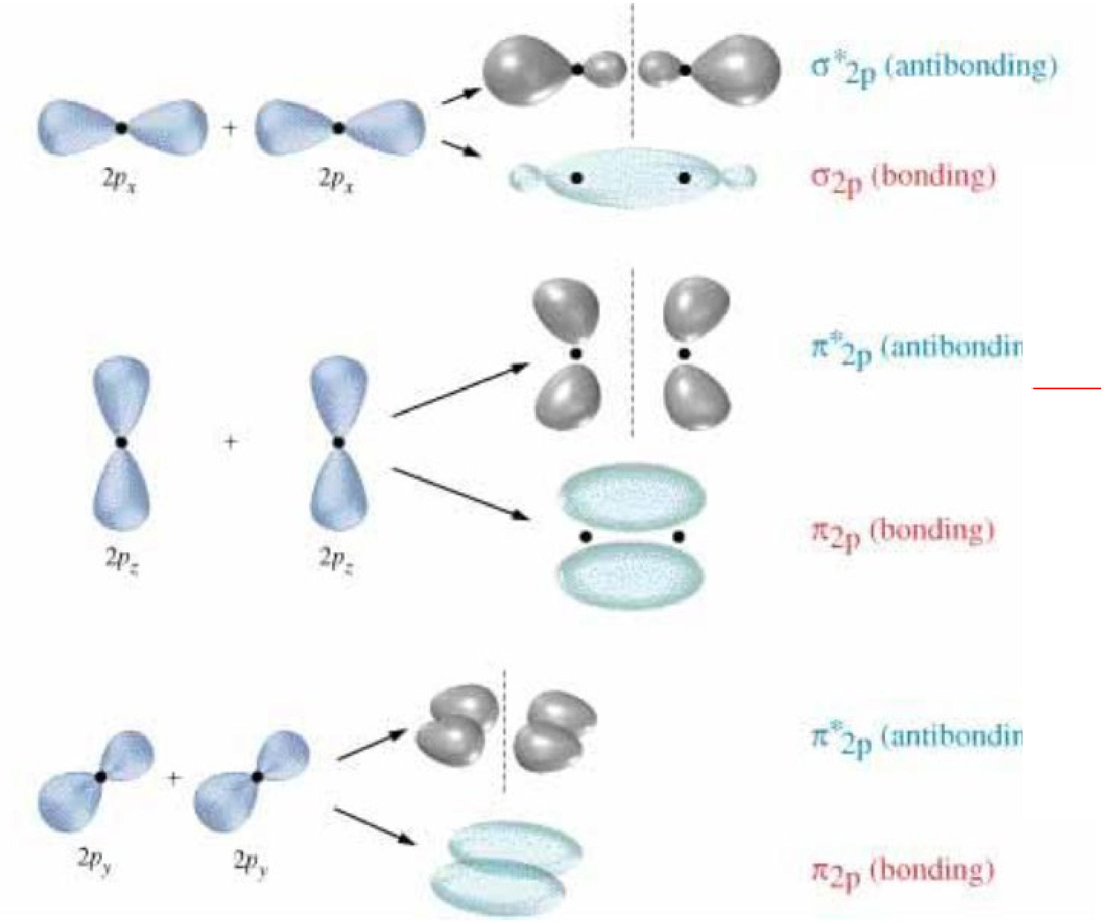
- These are the ones of interest when looking at organic molecules

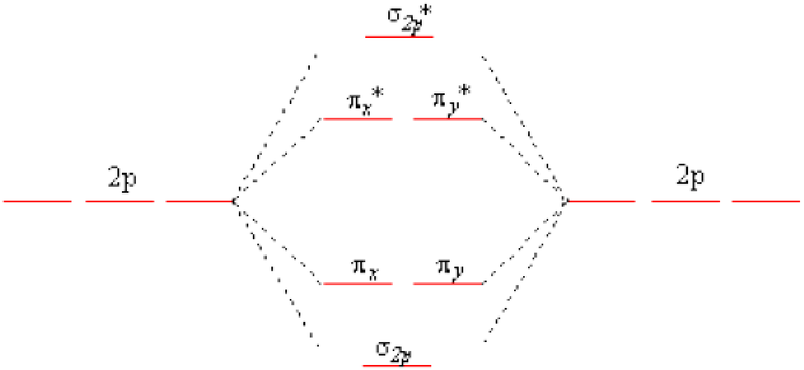




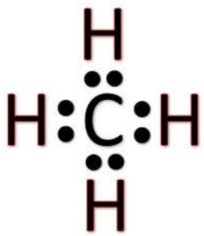
Molecular orbitals of the second energy level

- Pi (π) bonds are weaker and are due to lateral overlap between p (or d) orbitals

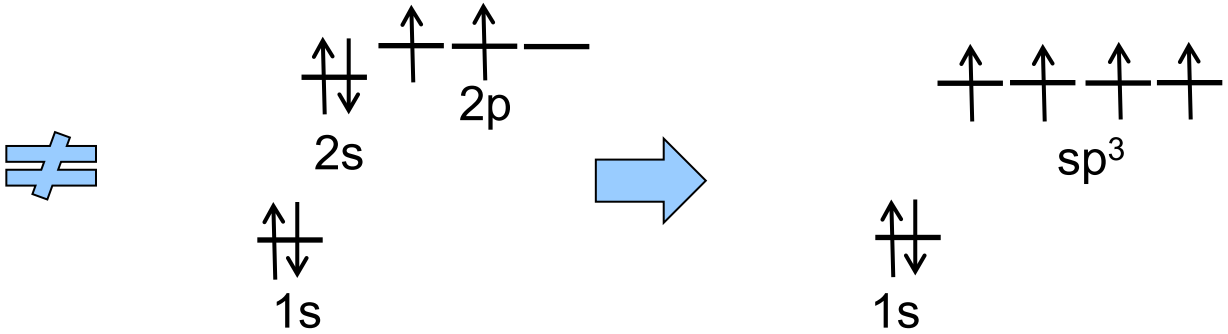


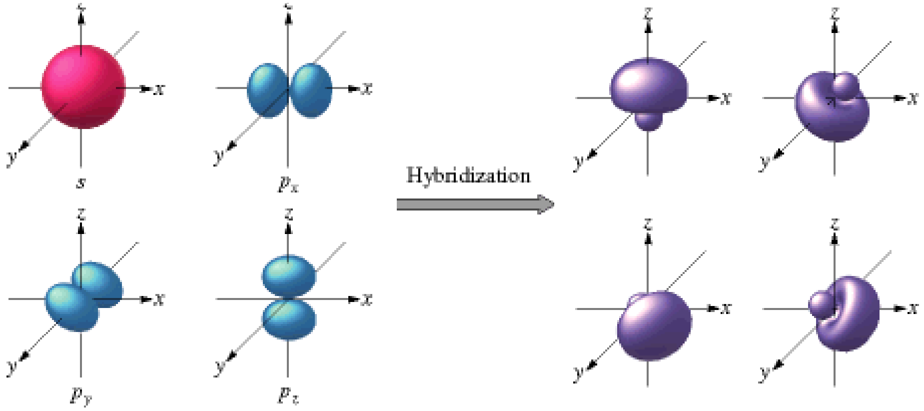


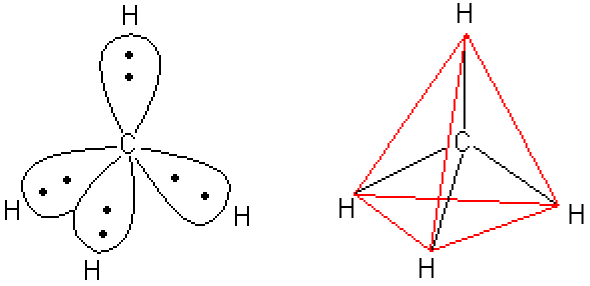
Building molecules from atoms – sp³ hybridization

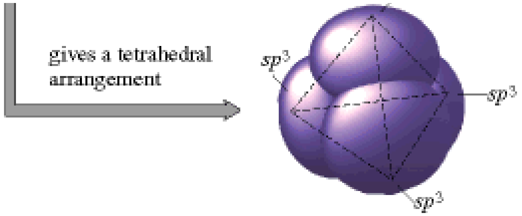


Methane

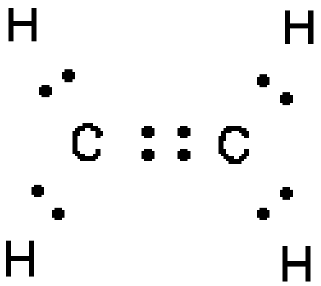




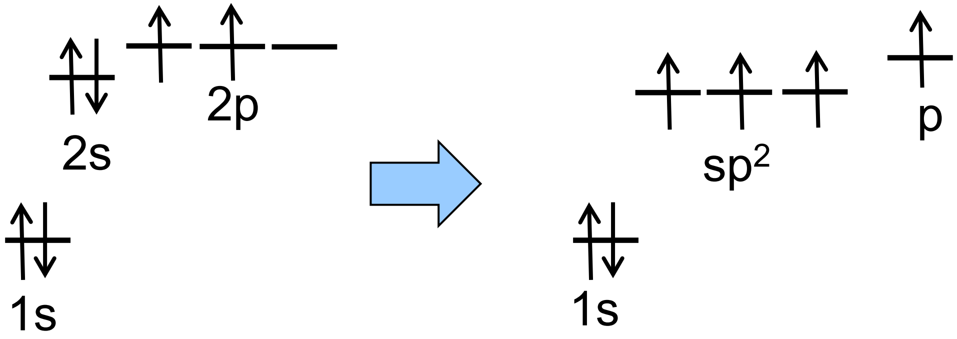


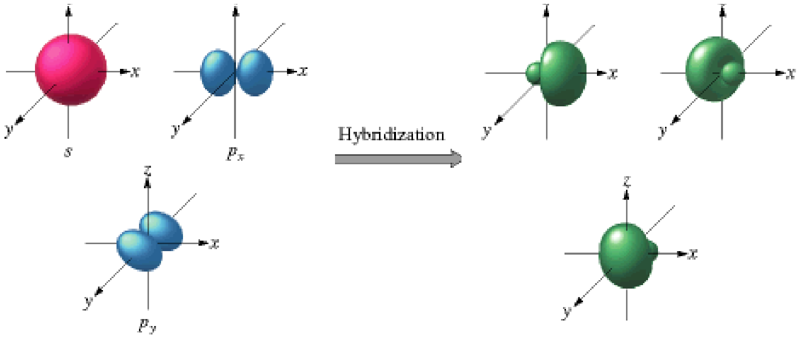


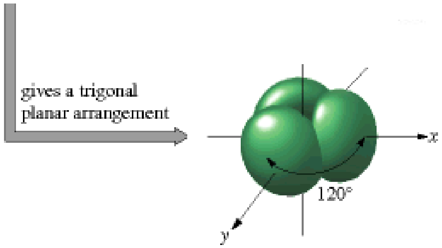
Building molecules from atoms – sp^2 hybridization



Ethylene





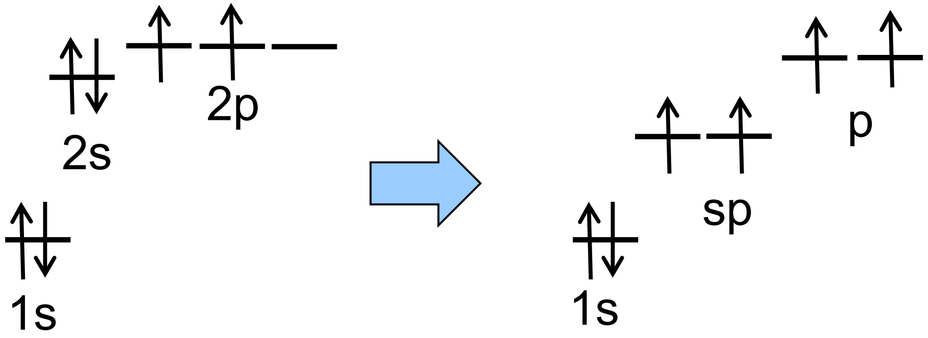


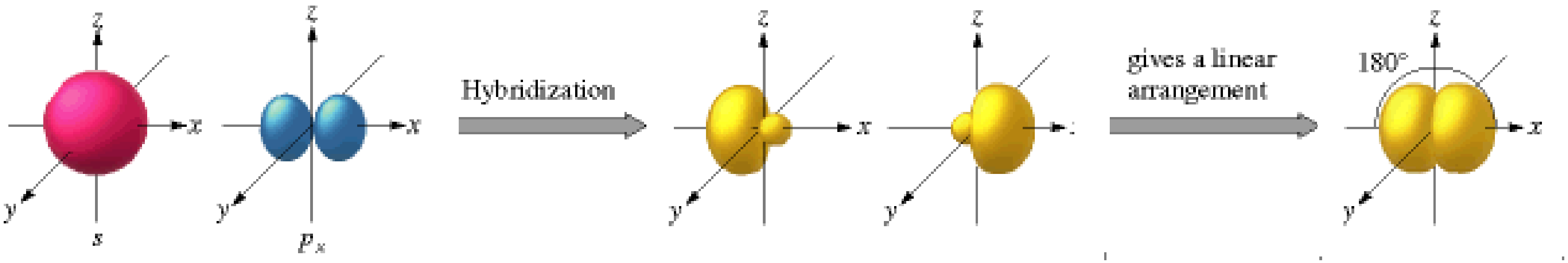
Adobe Stock

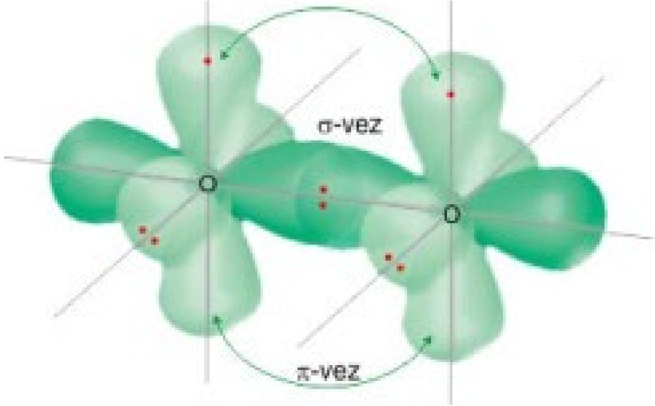
Building molecules from atoms – sp hybridization

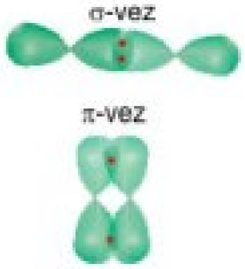
H:C:::C:H

Ethyne / Acetelyne
Linear chain







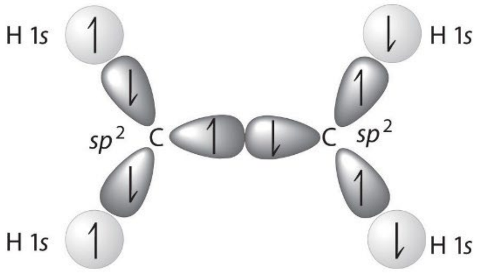


The Hückel MO model

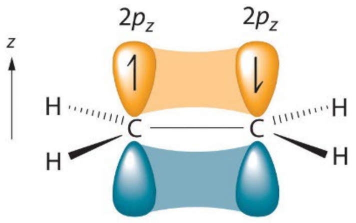
- Successfully applied to ***large conjugated systems***, especially those containing chains of carbon atoms with alternating single and double bonds.

- 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.

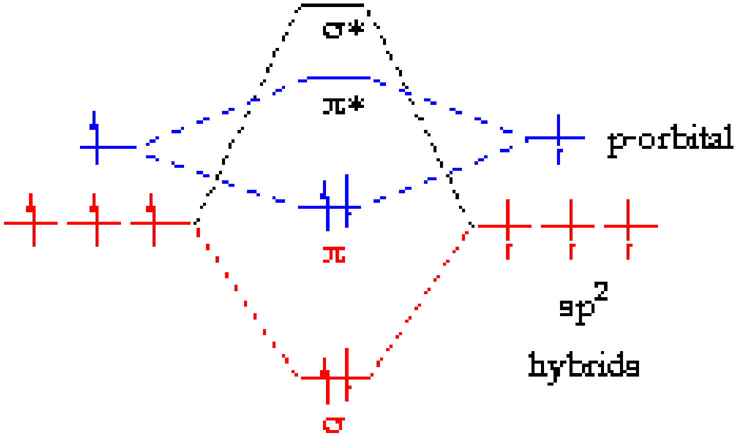
Example: ethylene



(a) C_2H_4 σ-bonded framework



(b) C_2H_4 π bonding



- Describe the wavefunction as linear combination of atomic orbitals (**LCAO**), so these are the two 2p$_z$ orbitals:

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

- Minimize E with respect to c_A and c_B:

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

- Let us first calculate:

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

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

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 ⟷ B

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

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

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

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

$$\left.\begin{array}{l} \rightarrow c_A(\alpha - E) + c_B(\beta - ES) = 0 \\ \\ \text{and in analogy} \\ \dfrac{\partial E}{\partial c_B} = 0 \rightarrow c_A(\beta - ES) + c_B(\alpha - E) = 0 \end{array}\right\} \quad (3)$$

(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.

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

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

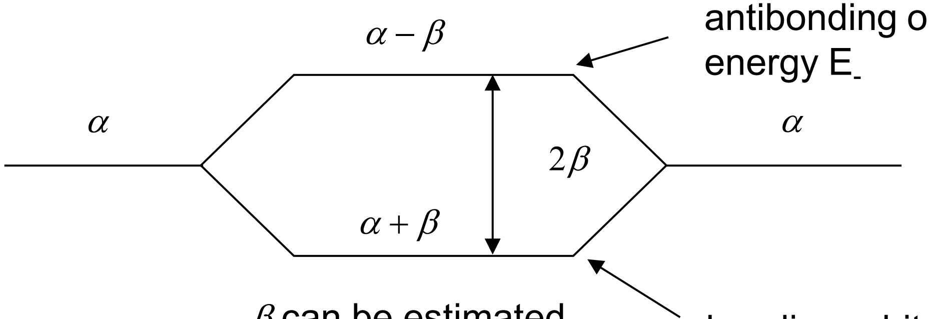
$$Det\begin{bmatrix}(\alpha - \mathrm{E}) & \beta \\ \beta & (\alpha - \mathrm{E})\end{bmatrix} = 0$$

- solving for E:

$$(\alpha - \mathrm{E})^2 - \beta^2 = 0 \rightarrow \alpha^2 - 2\alpha\mathrm{E} + \mathrm{E}^2 - \beta^2 = 0$$

$$E^2 - 2\alpha\mathrm{E} + \alpha^2 - \beta^2 = 0$$

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



antibonding orbital with energy E_-

bonding orbital with energy E_+

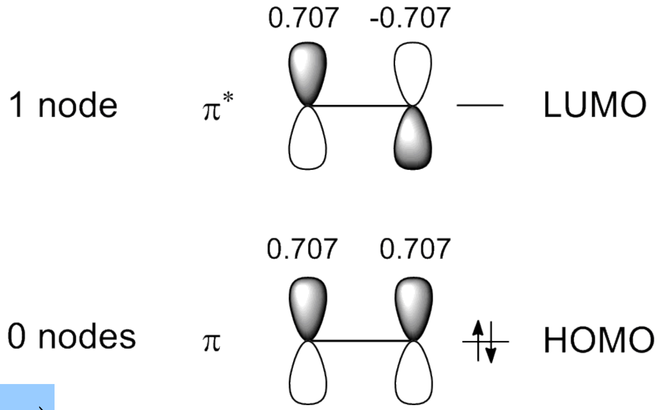
β can be estimated from spectroscopic data

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

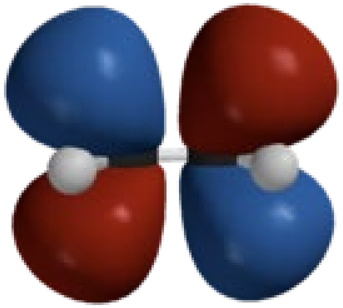
$$\begin{bmatrix} (\alpha - \mathrm{E}+) & \beta \\ \beta & (\alpha - \mathrm{E}+) \end{bmatrix} \begin{pmatrix} \mathrm{c}_1 \\ \mathrm{c}_2 \end{pmatrix} = 0$$

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

$$-\beta \mathrm{c}_1 + \beta \mathrm{c}_2 = 0 \qquad \rightarrow \mathrm{c}_1 = \mathrm{c}_2$$



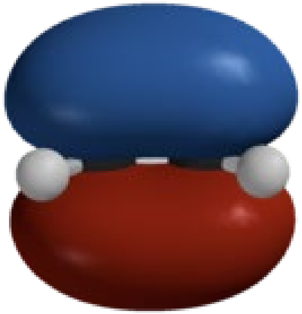
$$\rightarrow \psi_+ = \mathrm{c}_1 \left(\psi_{pz}(\mathrm{A}) + \psi_{pz}(\mathrm{B})\right) = \frac{1}{\sqrt{2}} \left(\psi_{pz}(\mathrm{A}) + \psi_{pz}(\mathrm{B})\right)$$



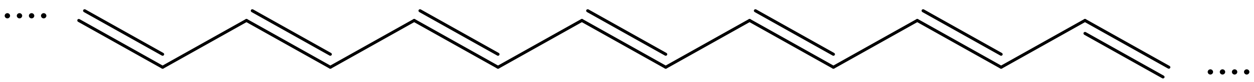
from $$\int (\psi_+)^2 dx = \mathrm{c}_1^{\,2} \left[\underbrace{\int \psi_{pz}(A)^2}_{=1} + \underbrace{\int \psi_{pz}(B)^2}_{=1} + \underbrace{\int \psi_{pz}(\mathrm{A}) \psi_{pz}(B)}_{=0} \right] = c_1^2 \cdot 2 = 1 \quad \Rightarrow c_1 = \sqrt{\frac{1}{2}}$$

In the same way one obtains for E = E_-

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



The infinite conjugated chain: polyacetylene I



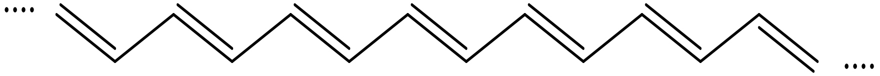
$$
Det\begin{bmatrix}
\alpha - E & \beta_{AB} - ES_{AB} & \beta_{AC} - ES_{AC} & \dots & \dots \\
\beta_{BA} - ES_{BA} & \alpha - E & \beta_{BC} - ES_{BC} & \dots & \dots \\
\beta_{CA} - ES_{CA} & \beta_{CB} - ES_{CA} & \alpha - E & \dots & \dots \\
\dots & \dots & \dots & \dots & \dots \\
\dots & \dots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

❑ 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

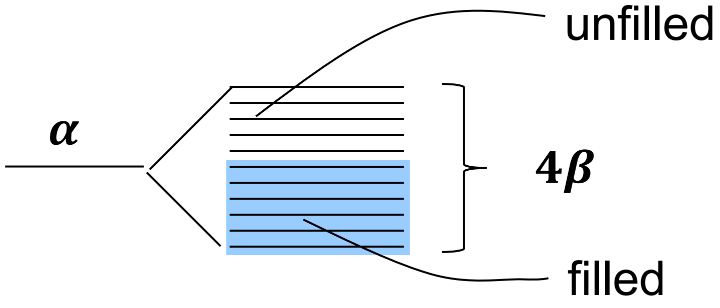
$$
Det\begin{bmatrix}
\alpha - E & \beta & 0 & 0 & \dots \\
\beta & \alpha - E & \beta & 0 & \dots \\
0 & \beta & \alpha - E & \beta & \dots \\
0 & 0 & \beta & \alpha - E & \dots \\
\dots & \dots & \dots & \dots & \dots
\end{bmatrix} = 0
$$

The infinite conjugated chain: polyacetylene II



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

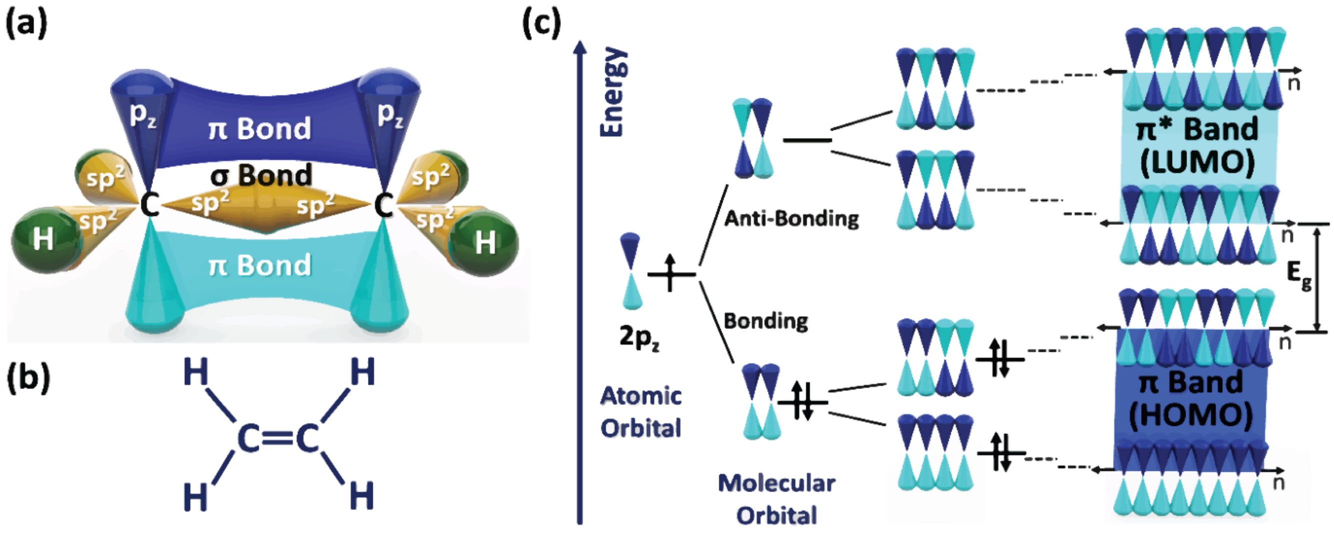
$$\psi_k = \sum_{n=1}^{N} a_n^k \psi_{2p_z}(n) \qquad a_n^k = \sqrt{\frac{2}{N+1}} \sin\left(\frac{\pi k n}{N+1}\right)$$



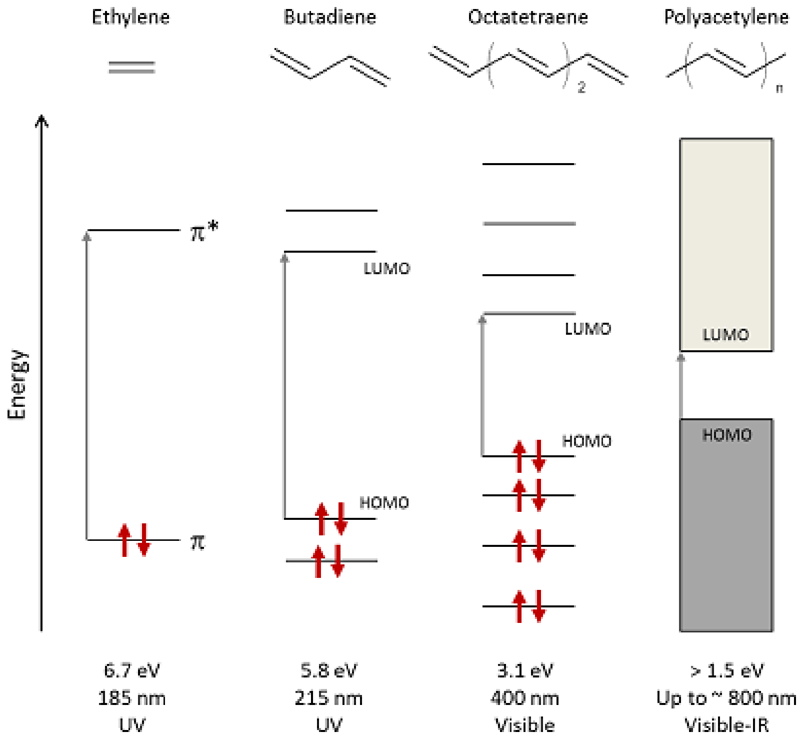
where $\psi_{2p_z}(n)$ are the C2p_z orbitals at site *n*.

Theory predicts *trans*-PA to be a metal

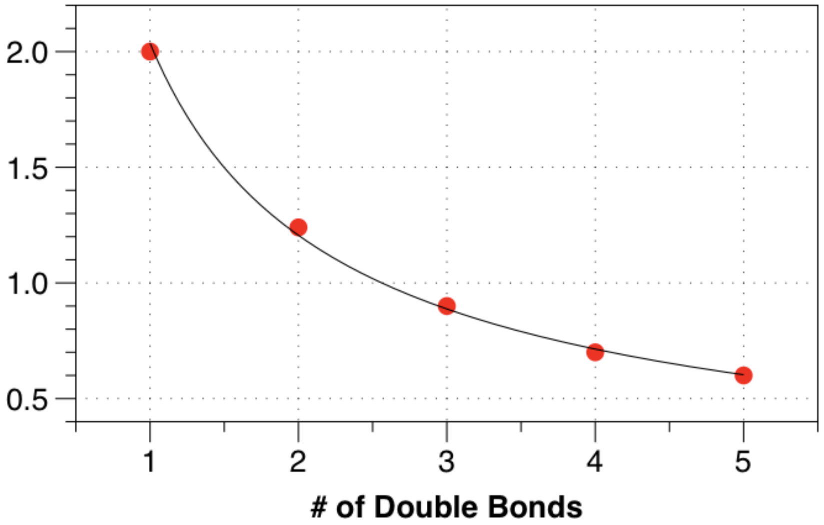
Hückel predicts no band gap when n gets very large:



The infinite conjugated chain: polyacetylene III



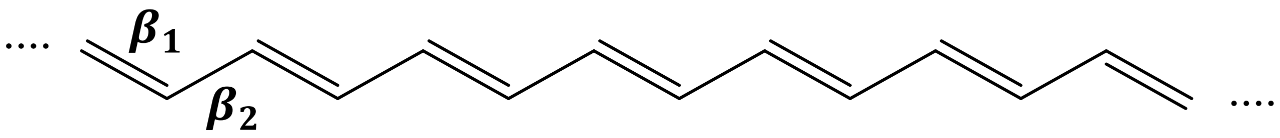
https://www.oe.phy.cam.ac.uk



Hückel predicts no band gap when n gets very large:

The infinite conjugated chain: polyacetylene

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



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

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

$$
k = 0, \pm 1, \pm 2, \dots\dots \pm N
$$

Dimerisation (Peierls distortion) opens up a gap with

$$
\boldsymbol{E_g = 2\,|\beta_1 - \beta_2|}
$$

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***
  - *Molecular 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 – 2 main questions:***
  - ☐ ***Where do charges come from? Intrinsic / extrinsic*** semiconductors – ***doping*** of organic semiconductors
  - ☐ ***Conduction mechanism*** in organic semiconductors: is it really band transport?

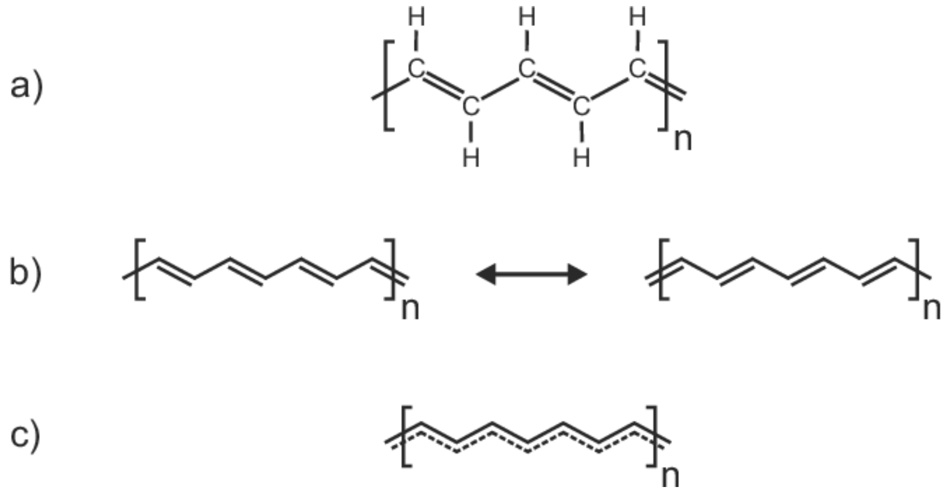
Thermodynamics of electron transfer, Marcus theory

- ☐ ***Definitions: mobility and conductivity***

- ☐ ***Electrical contact*** to devices

The infinite conjugated chain: polyacetylene III

❑ *Intramolecular conductivity*



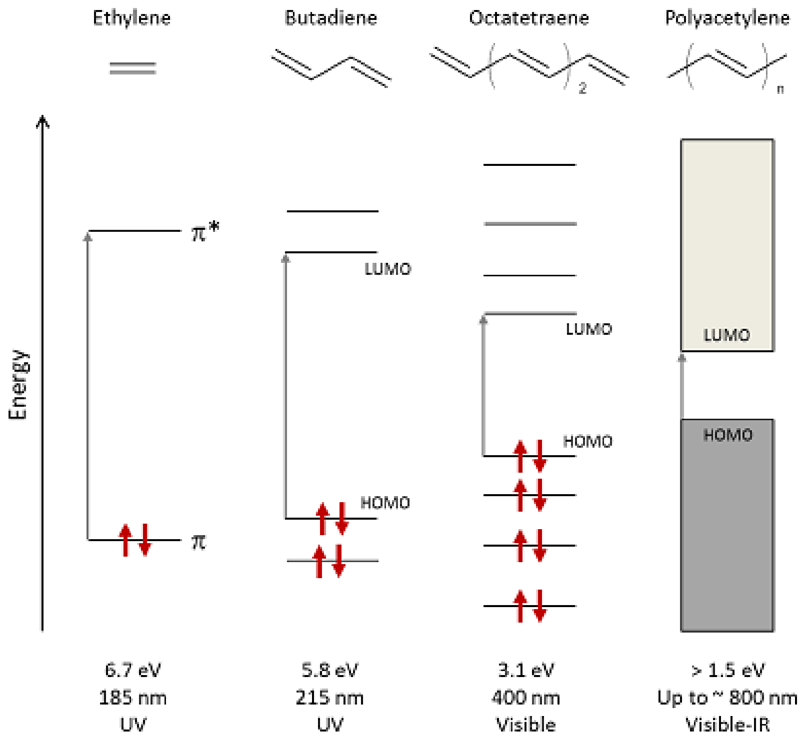
❑ *The construction of delocalized π-orbitals*

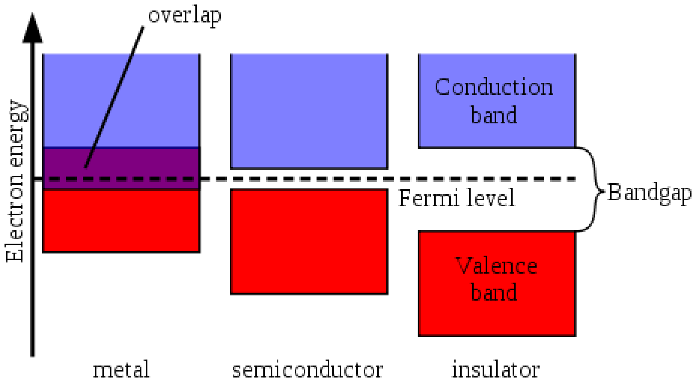
Within the conjugated structure, π-orbitals are delocalized. This delocalization forms the basis of the molecular conductivtiy of carbon compounds. ***Electrons are*** not confinded to a specific atom or bond, but ***shared across multiple atoms***.

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

Intrinsic semiconductors

- We have seen before, because of the Peierls distortion, the infinite conjugated chain has a band gap





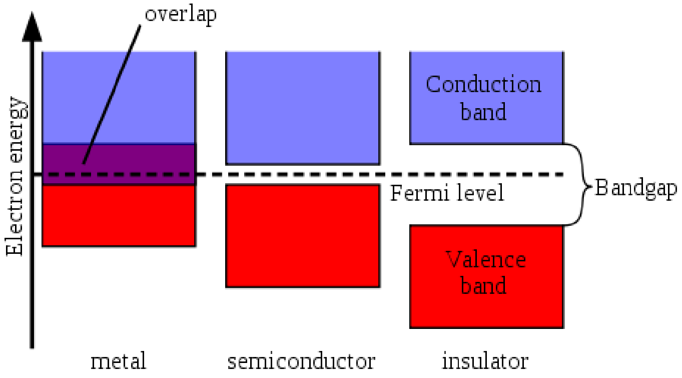
- A chemist’s terminology: LUMO and HOMO level

- A physicist’s terminology: Conduction band and Valence band

Intrinsic semiconductors

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

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



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

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

Silicon:
$N_c = 2.82\ 10^{19}\ \mathrm{cm}^{-3}$, $N_v = 1.83\ 10^{19}\ \mathrm{cm}^{-3}$
$E_g = 1.1\mathrm{eV}$
$\mu = 1000\ \mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$
$\sigma = 10^{-6}\ \Omega^{-1}\mathrm{cm}^{-1}$

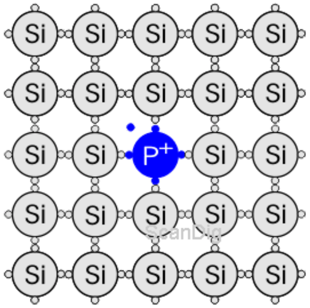
Organic semiconductors:
$N_0 = 10^{21}\ \mathrm{cm}^{-3}$
$E_g = 2.0\ \mathrm{eV}$
$\mu = 1\ \mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$
$\sigma = 10^{-12}\ \Omega^{-1}\mathrm{cm}^{-1}$

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.

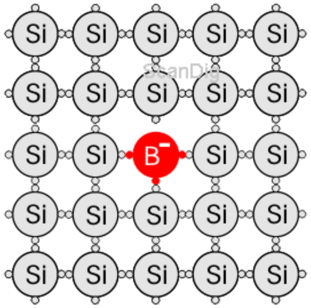
- While the delocalized π-electron system provides the inherent ***pathway for charge movement***, the ***significant energy barrier*** of the band gap effectively confines these electrons in their ***ground state***

Extrinsic semiconductors

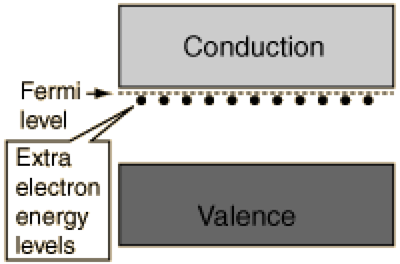
- ❑ An extrinsic semiconductor is one that has been ***doped***
- ❑ In conventional inorganic semiconductors: a trace element or chemical called a doping agent is incorporated chemically into the crystal



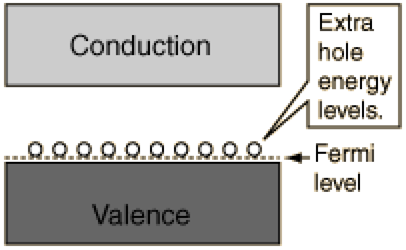
n-Dotierung



p-Dotierung



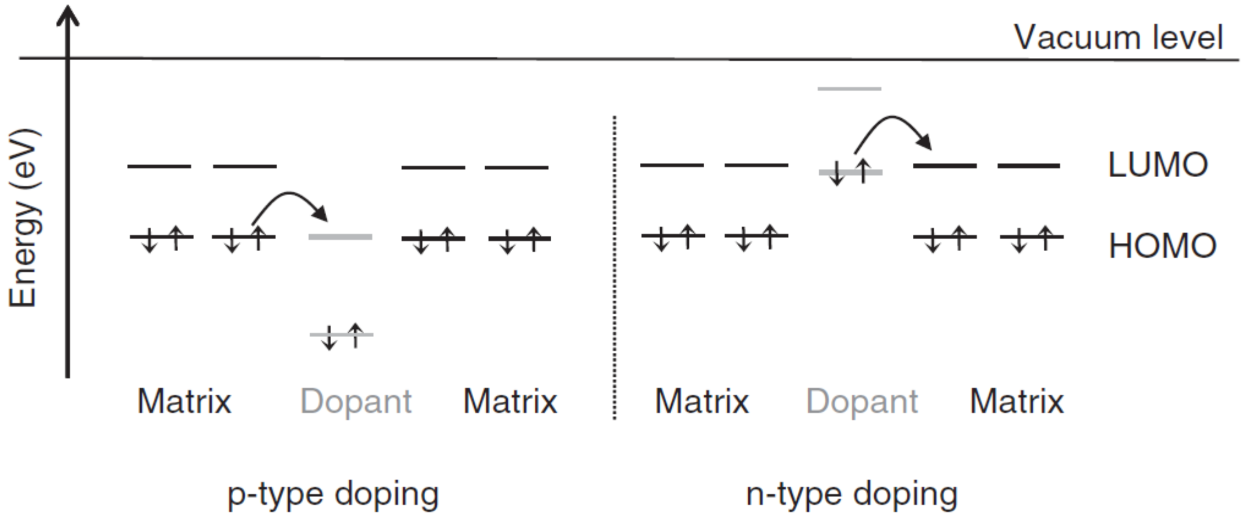
N-Type



P-Type

- ❑ In conjugated polymers primarily by a partial ***redox (reduction-oxidation) process***. This involves the direct transfer of electrons to or from the polymer backbone, which in turn generates mobile, delocalized charges on the polymer chain
- ❑ Organic semiconductors get their ***conductivity from extrinsic factors***:
  - ▪ Dopants
  - ▪ Photosensitization
  - ▪ Injection

Doping of organic semiconductors:



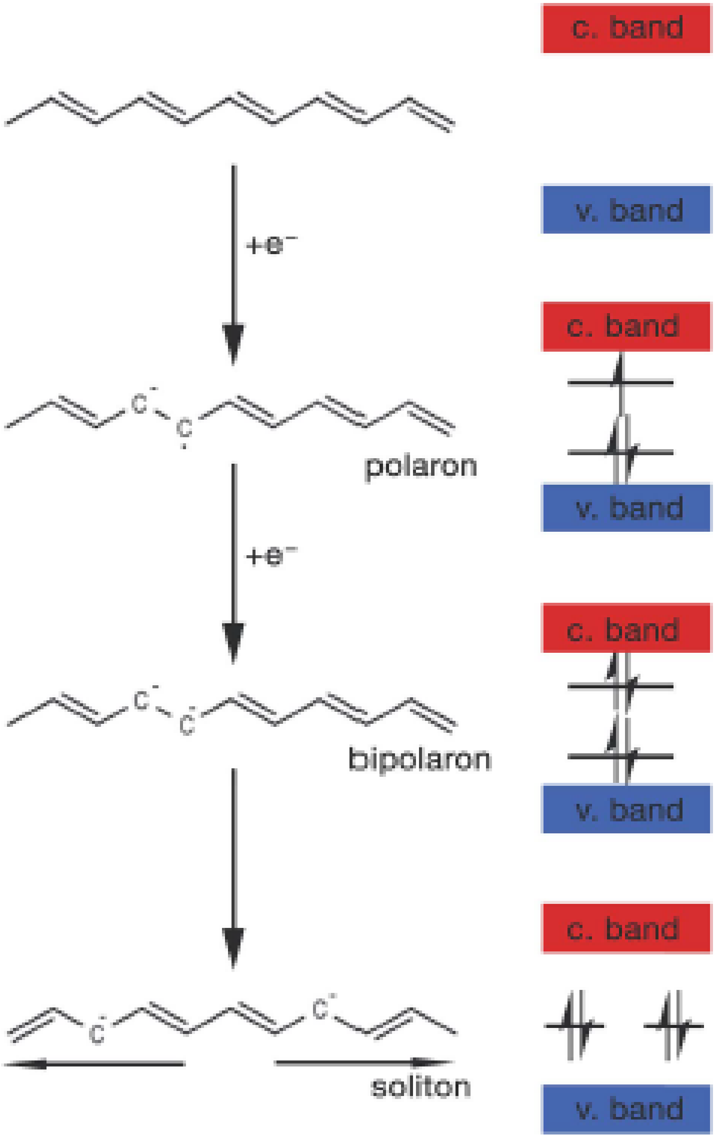
- In p-type doping, an electron is removed from the HOMO of the polymer chain and transferred to the LUMO of the dopant species. That leaves behind a positive charge ("hole") within the polymer backbone. This process is an electro-oxidation.
- In n-type doping, electrons are transferred from the HOMO of the dopant species to the LUMO of the polymer chain. This injection of electrons significantly increases the electron density within the polymer backbone. This corresponds to an electro-reduction process.

Doping of organic semiconductors:

- 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***.
- ***Chemical doping*** can be achieved through various methods involving ***exposure to oxidizing agents***. Common techniques include vapor-phase or gaseous doping, where polymers are exposed to gaseous dopant compounds such as bromine, iodine, chlorine, or arsenic pentafluoride (AsF_5) in a controlled environment. Alternatively, solution doping involves immersing the solid polymer into a solvent containing dissolved dopant ions.
- Similarly, ***n-type dopants*** had to have a ***HOMO level near −2.5 to −3.5 eV***
- While strong electron donors are necessary for efficient doping (implying a low activation energy for electron transfer), these powerful reducing agents are often inherently unstable when exposed to ambient air

Charge carriers in doped polymers

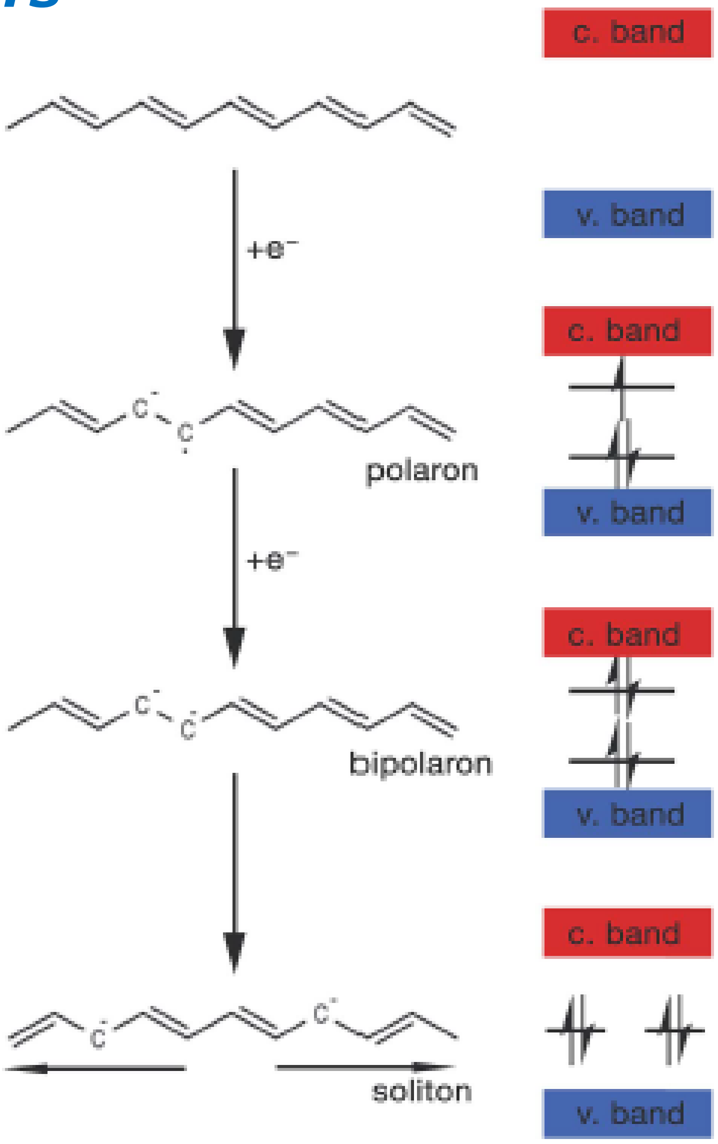
- ☐ What are actually the ***charge carriers?***
- ☐ Different from the inorganics, it is ***NOT free electrons or holes*** as in a rigid crystalline lattice
- ☐ But: the ***charge*** is intrinsically ***coupled*** with a localized ***structural distortion*** or rearrangement of the polymer backbone
- ☐ The specific type of charge carrier that forms—whether a ***polaron, bipolaron, or soliton***—is determined by the inherent electronic structure of the polymer's ground state (categorized as degenerate or non-degenerate systems) and the extent or level of doping applied



RSC Adv.,2015, 5,1161

Charge carriers in doped polymers

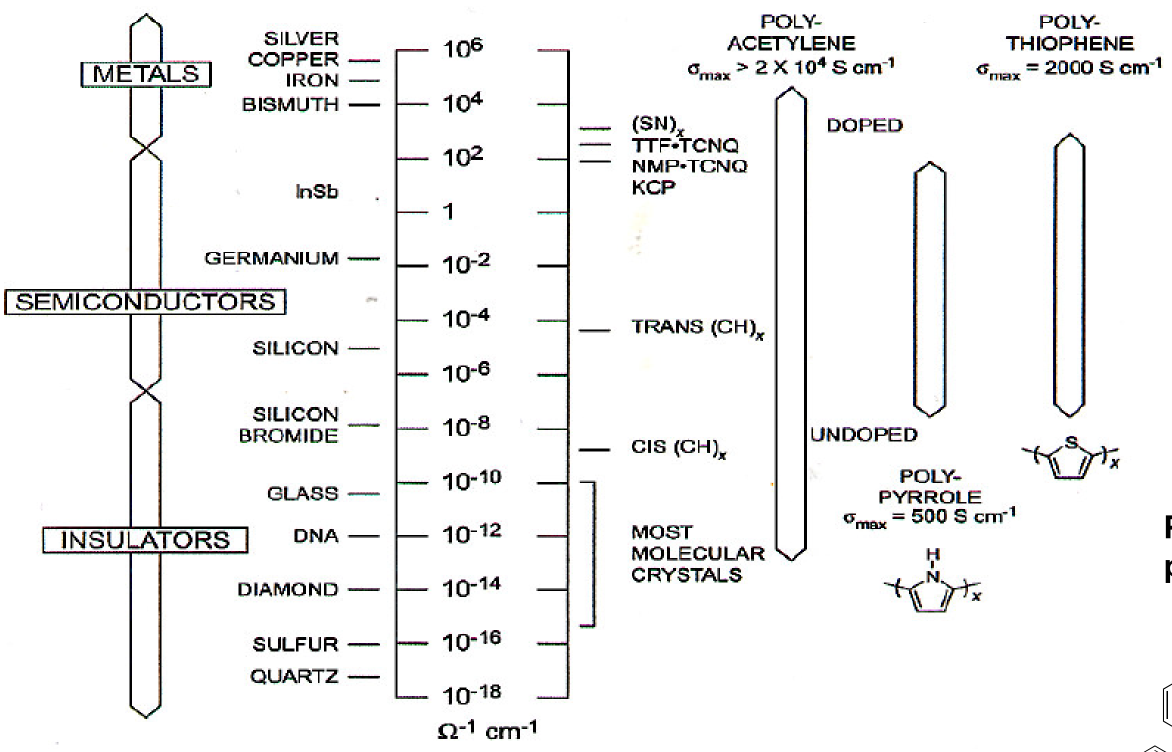
- **Polarons:** either by oxidation or reduction; in the traditional band picture, two distinct states are depicted as moving into the band gap: one that is half-filled (occupied by the unpaired electron)
- **Bipolarons:** formed upon further oxidation or reduction of a polaron; two intragap states are moving further into the band gap. "Bipolaronic bands" can significantly reduce the effective energy gap for charge transport.
- **Solitons:** distinct type of charge carrier primarily observed in degenerate ground-state conjugated polymer systems.

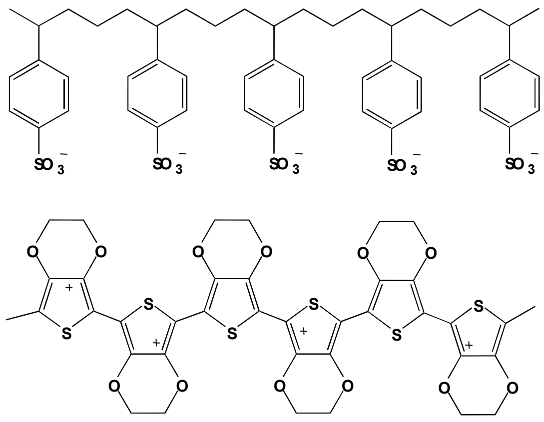


RSC Adv.,2015, 5,1161

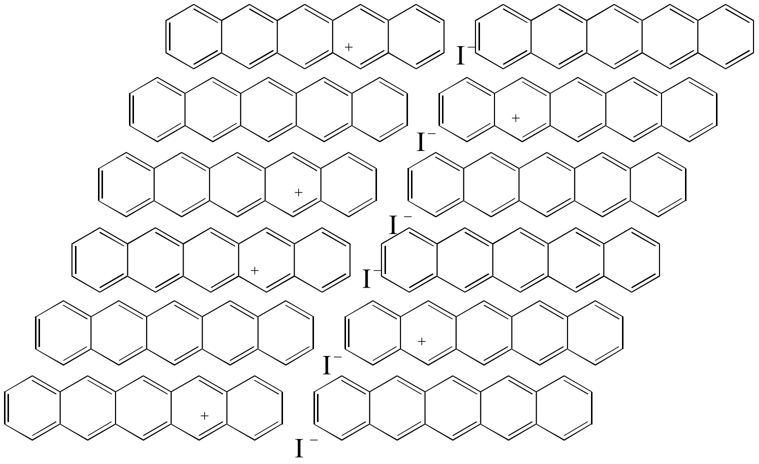
Summary of charge carriers in doped polymers

Carrier Type	Net Charge	Spin (for charged species)	Formation Mechanism	Associated Structural Change	Effect on Band Gap (Intragap States/Bands)	Typical Polymer Systems
Polaron	±1	1/2	Initial doping (1 electron removed/added)	Local aromatic-to-quinoidal deformation (moderate)	Creates 1 or 2 localized states within the gap	Polythiophene (PT), Polypyrrole (PPy)
Bipolaron	±2	0	Further doping (2 electrons removed/added)	Local aromatic-to-quinoidal deformation (pronounced/extended)	Forms 2 narrow bipolaronic bands within the gap	PT, PPy
Soliton	±1	0	Doping in degenerate systems (1 electron removed/added at domain wall)	Boundary between degenerate structures	Forms a soliton band at mid-gap	Polyacetylene (PA)





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



Pentacene doped with iodine

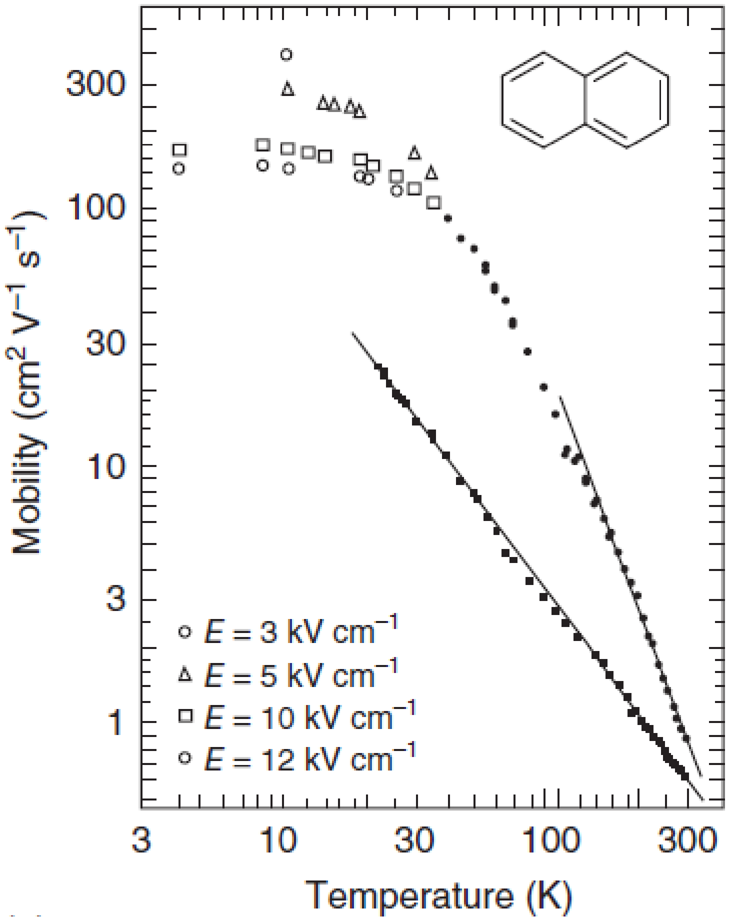
Doped conjugated polymers and doped molecular crystals can span a ***whole range of conductivities***

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

- In band like carrier transport, mobility has the following T dependence due to increased scattering at acoustic phonons, impurities and electron interactions:

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

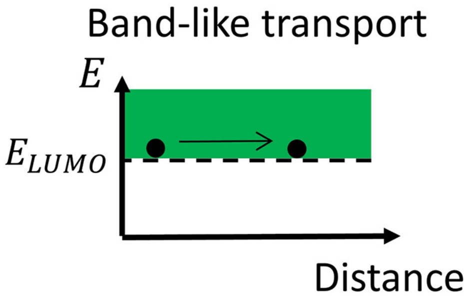
- But: the exception in organic semiconductors

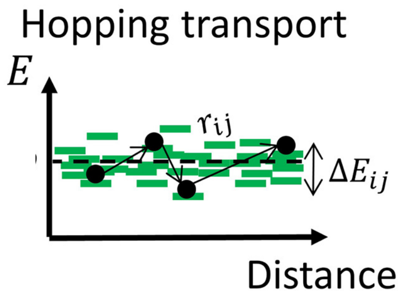


Warta, W., Karl, N., Phys. Rev. B, 32 (2), 1172, 1985.

Band transport and Hopping transport

- The inherent structural and energetic disorder in conjugated polymers is a defining characteristic. Such disorder arises from variations in molecular conformations, localized molecular environments, and the random arrangement of molecules within the material. This disorder creates a landscape of localized states and traps that impede free carrier movement.





- Charge carriers cannot propagate freely as they would in a band-like transport mechanism. Instead, they must "hop" from one localized state to another

Polymer International, Volume: 2019, 68, 4, 620-636, DOI: (10.1002/pi.5768)

Band transport and Hopping transport

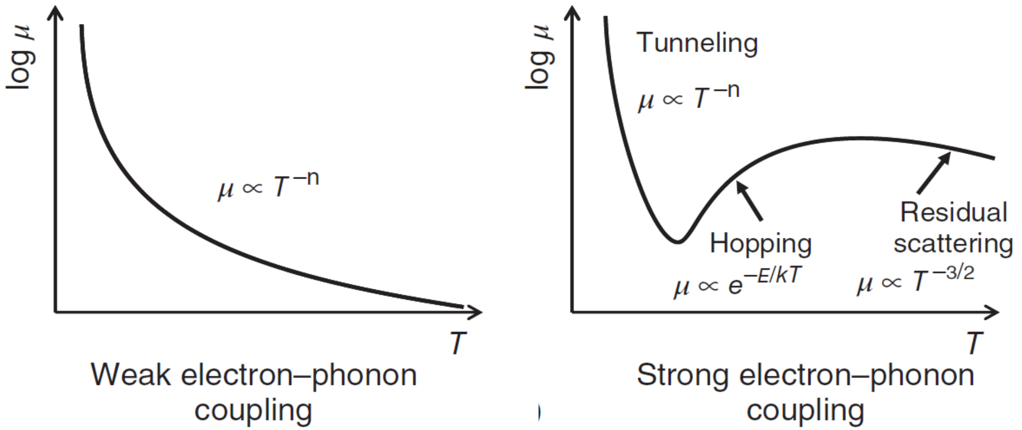
- ❑ Band transport is effective when ***the electronic coupling*** β is larger than any other energy term due static or dynamic disorder.

- ❑ The resonance integral β ***determines the strength of electronic coupling between the molecules*** (remember from lecture 2.1A)

- ❑ **Interchain and Intrachain Hopping:** Charge transport in polymeric systems is a complex process involving movement both along individual polymer chains (intrachain hopping) and between adjacent polymer chains (interchain hopping). The overall macroscopic ***conductivity*** of the material is a ***cumulative result of these two distinct hopping pathways***. The electronic coupling and reorganization energy, which are critical parameters governing hopping rates, can differ significantly for intrachain versus interchain hops.

Band transport and Hopping transport II

- Also, 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***



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

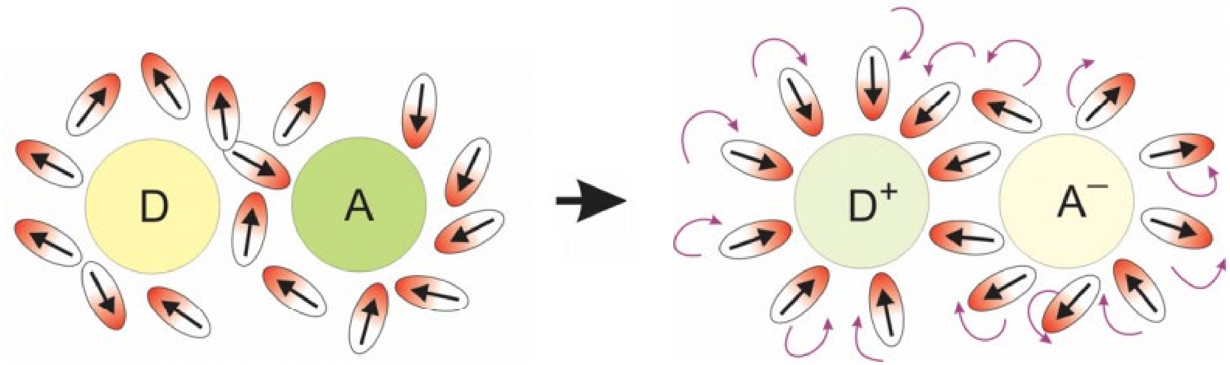
- Hopping rates are strongly dependent on temperature. This relationship typically follows an ***Arrhenius-type behavior***, where mobility (μ) is proportional to exp($-E_a/k_BT$), with Ea being the activation energy, kB the Boltzmann constant, and T the absolute temperature.

Thermodynamics of electron transfer

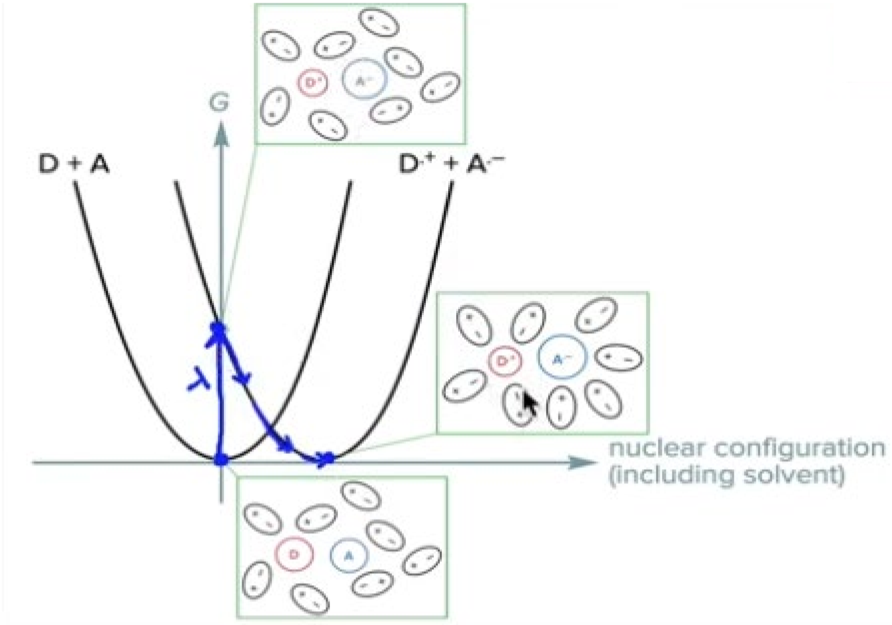
- ☐ Carriers can ***jump to nearby states*** with different energies, a process that typically requires the ***absorption of phonons*** (lattice vibrations) to provide the necessary activation energy.

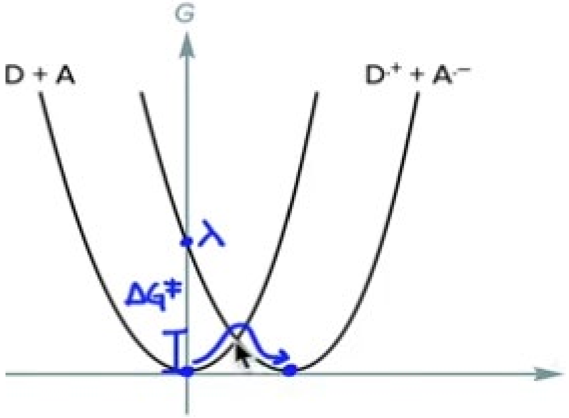
- ☐ Marcus' theory of electron transfer was originally developed to describe electron transfer processes in solution, but the framework is well suited to describe a hopping process

- ☐ The idea: two thing will happen: changes in the molecule (size, bondlength, …) and changes in the environment (dipoles of the solvent molecules will "screen" the charges)



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.

Different ways to get form "A" to "B":

- Invest the so-called reorganization energy (λ) to get onto the $D^+ + A^-$ branch before relaxing to the new position (Libby).
- Solvent molecules can rearrange in synch with electron transfer, lowering the energy barrier:

$$k_r = \nu_n e^{-\Delta G^\ddagger/RT} \qquad \Delta G^\# = \frac{\lambda}{4}$$

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

$$\left.\begin{array}{l}\left.\begin{array}{l} v_d = \mu E \\[2ex] J = nev_d \end{array}\right\} \; J = ne\mu E \\[4ex] \qquad\qquad\qquad\; J = \sigma E \end{array}\right\} \; \boldsymbol{\sigma = ne\mu}$$

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 ≈ 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

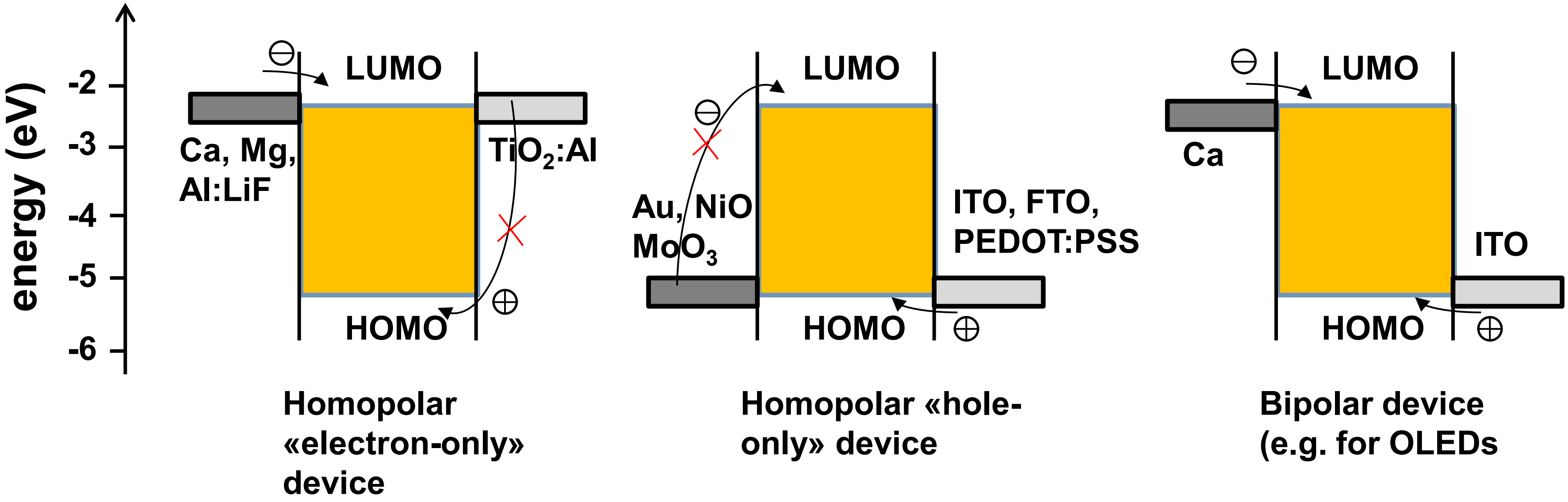
- ☐ or by the ability of the device to transport the charges:

  Space charge limited current (SCLC)

Contacting organic opto-electronic devices

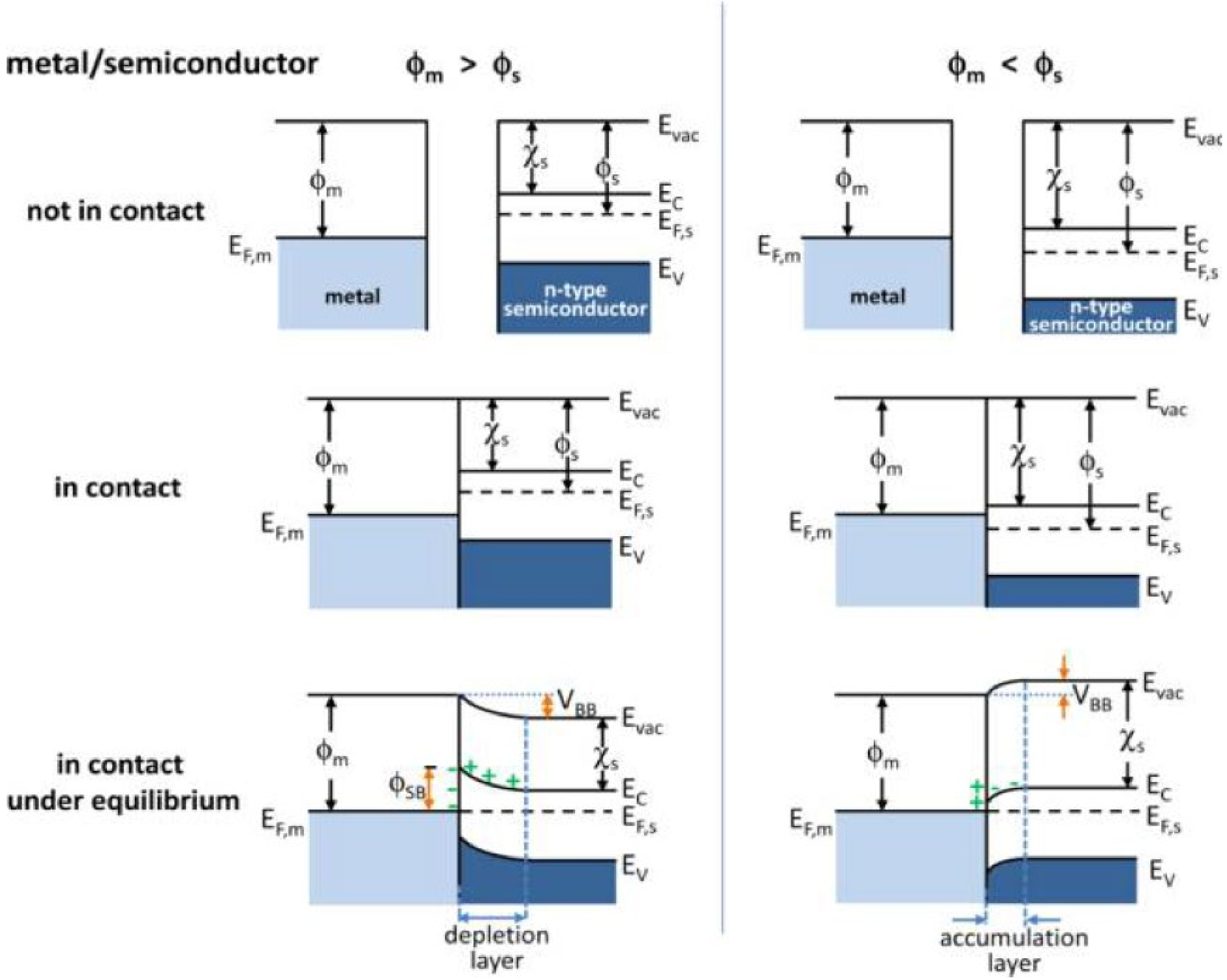
Contacts are chosen to provide barrier-free injection of charge carriers into the device. This implies that the Fermi energy of the contact has to be aligned to relevant molecular orbital, i.e. to the LUMO if electrons are injected or to the HOMO, if holes are injected.

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).



Band bending

Subject of an excercise



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

Space charge limited current

Subject of an excercise

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: $j = \frac{q}{\tau_{trav}} \Longrightarrow j = \mu \varepsilon \varepsilon_0 \cdot \frac{V^2}{L^3}$

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
  - The ***delocalized π-electron system*** provides the inherent ***pathway for charge movement***, but the significant energy barrier of the band gap effectively confines these electrons in their ground state. This means that the potential for conductivity is intrinsic to their structure, but it remains "locked" or "inactive" without an external stimulus.

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

2.1B Electronic properties of organic semiconductors

Learning outcome

- ***Charge carriers*** are not free electrons or holes as in a rigid crystalline lattice, but rather complex "nonlinear local excitations" ***(polarons, bipolarons, solitons)***
- ***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

☐ ***Thermodynamics of electron transfer, Marcus theory***

- Describes a transfer rate mediated by a nuclear coordinate

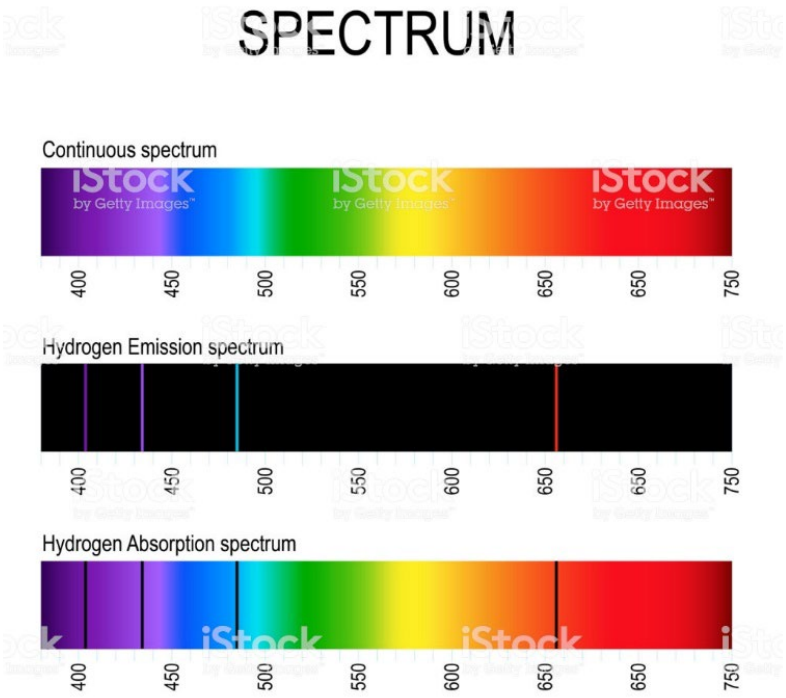
☐ ***Contacts*** to devices

- 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) $$\mu_{1,0} = \langle \psi_1 | \vec{\mu}_{10} | \psi_0 \rangle \neq 0$$ where $\mu_{1,0}$ 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.

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

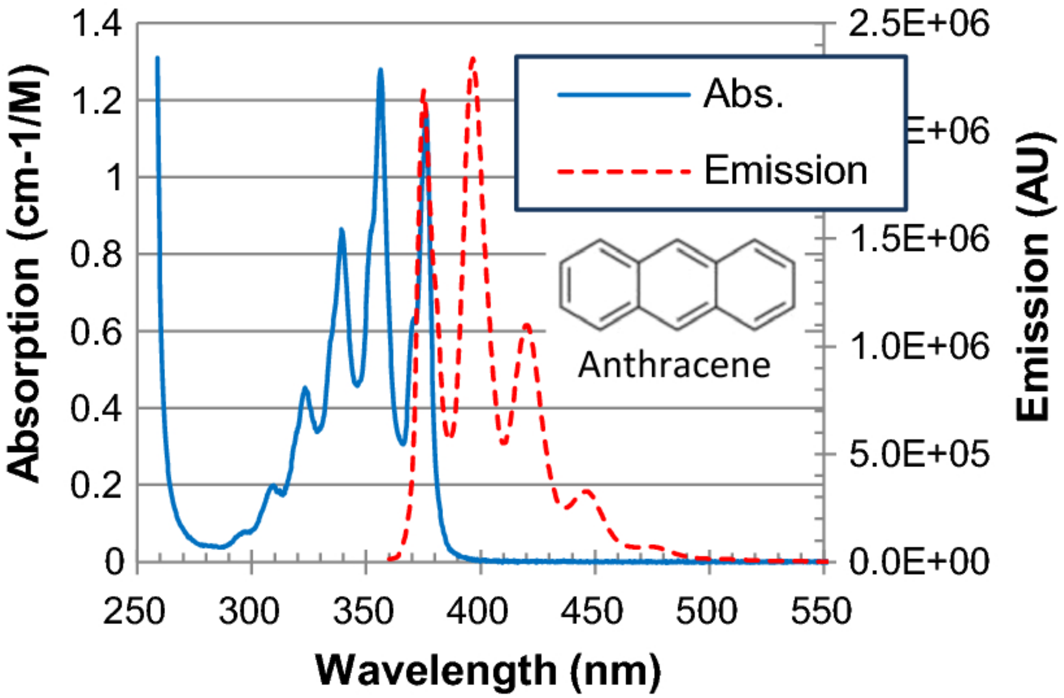
- ☐ A ***transition*** is said to be ***forbidden,*** if any of the above terms is zero.

  a) overlap and symmetry of ***spatial wavefunction***
  => ***answers by Group theory***

  b) ***nuclear wavefunction*** (vibrational / rotational) with respect to overlap

  c) ***spin wavefunction*** with respect to spin conservation
  => ***spin conservation***

Vibronic fine structure



Environmental Earth Sciences
77, 374 (2018)

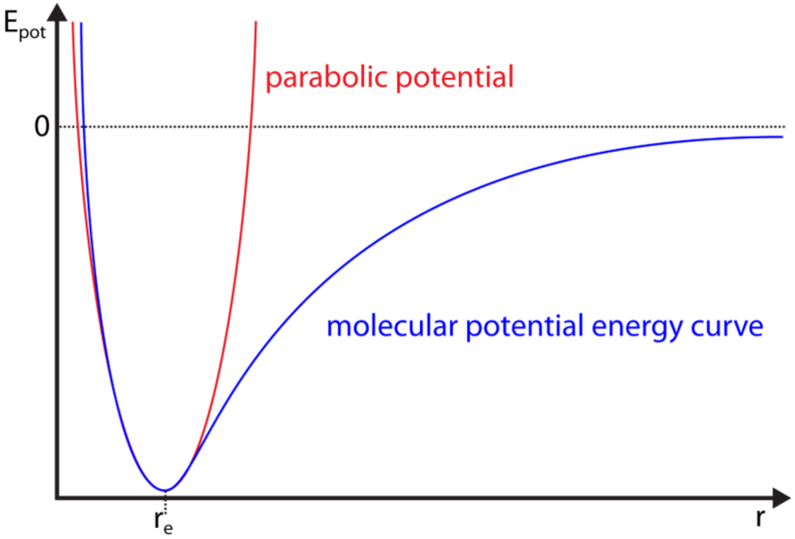
- Transitions also show a ***vibrational structure,*** originates from the ***nuclear wavefunction***
- Not described by the Born-Oppenheimer approximation: the dipol operator was not acting on the nuclear wave function

b) Diatomic molecule

- ☐ The relative motion of two nuclei can therefore be described in terms of the motion of a fictious particle of reduced mass μ moving in a central potential.

- ☐ The energy of a vibration is quantized

- ☐ For small pertubations, a parabolic potential can be used. This potential energy is associated with the force that binds the two atoms together.

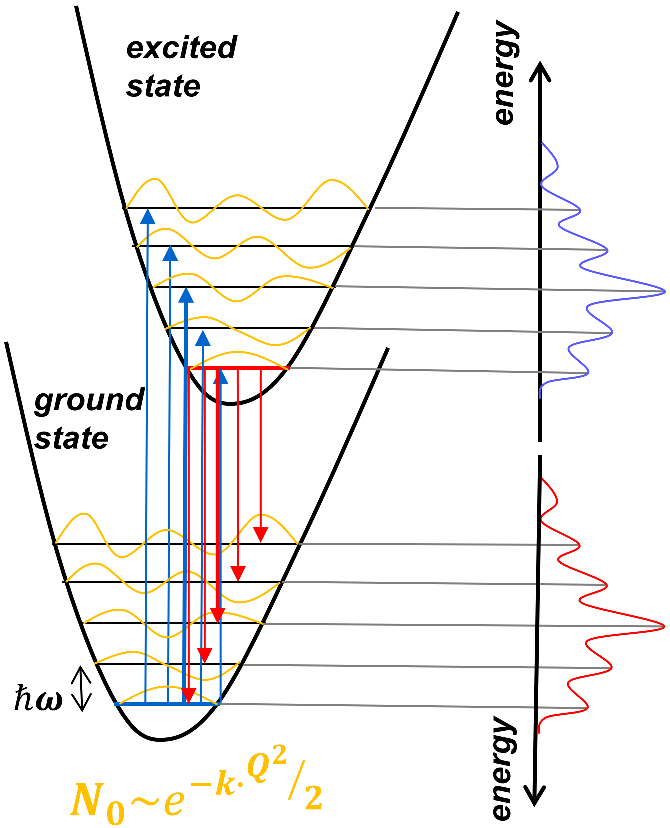


Solving the Schrödinger equation yields the eigenenergies of the vibrational motion of the two nuclei

$$E_{vib} = \hbar\omega(\nu + {}^{1}/_{2})$$

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.



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

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

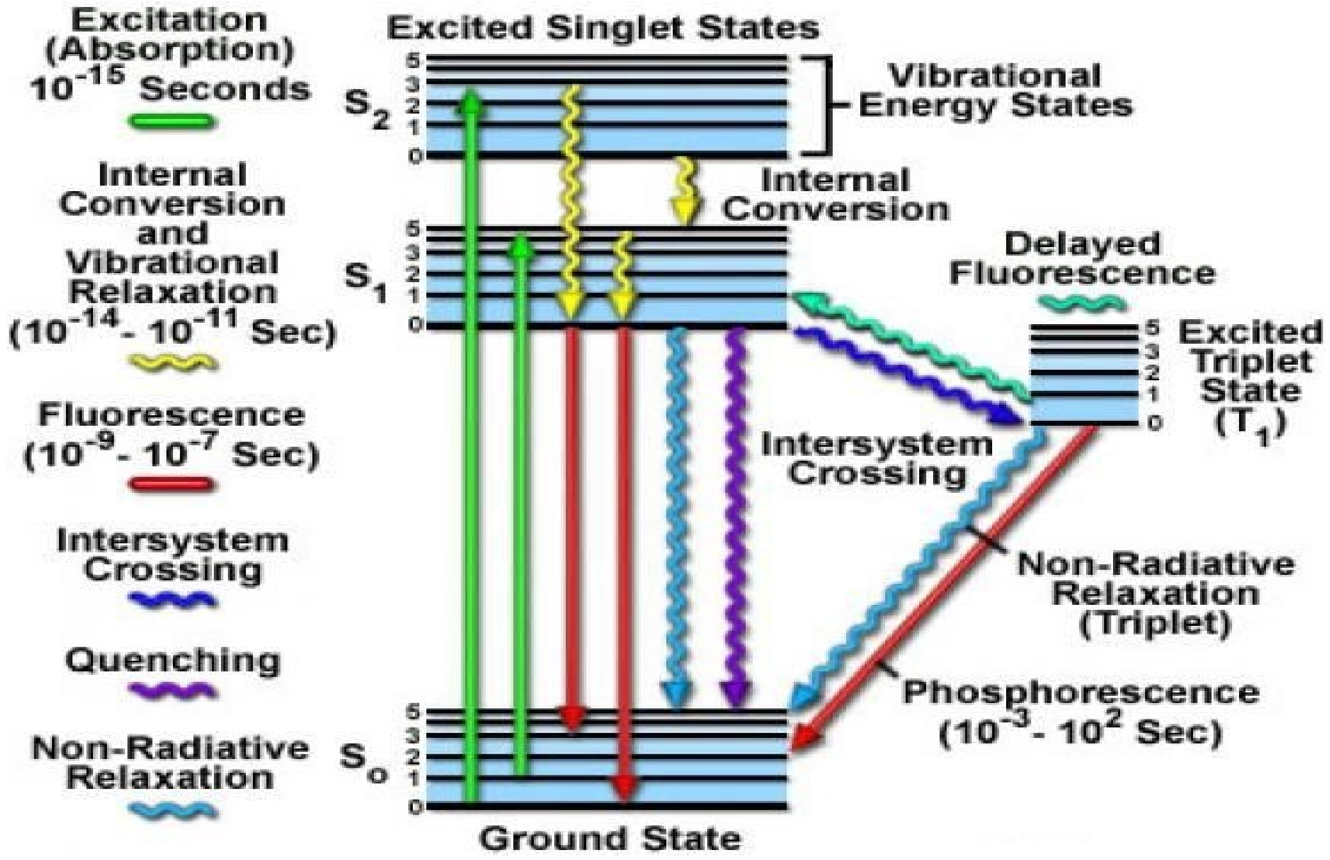
What we are looking for: how do the vibrational features influcene the transition probability $\langle N_1 | N_0 \rangle^2$

Franck-Condon:

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

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

Relaxation of electronically excited molecules



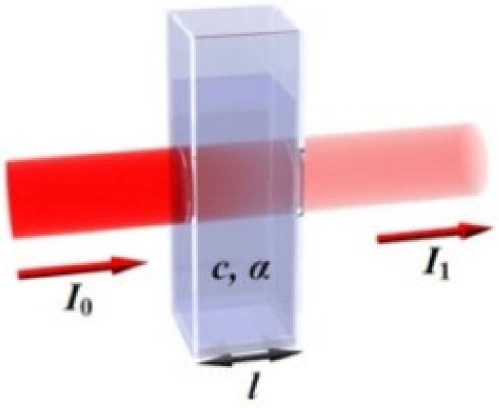
1. Radiative processes (fluorescence, phosphorescence)

2. Non-radiative processes (vibrational relaxation)

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

Jablonski diagram, summarizing intramolecular processes.

Absorption and the oscillator strength



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

***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).

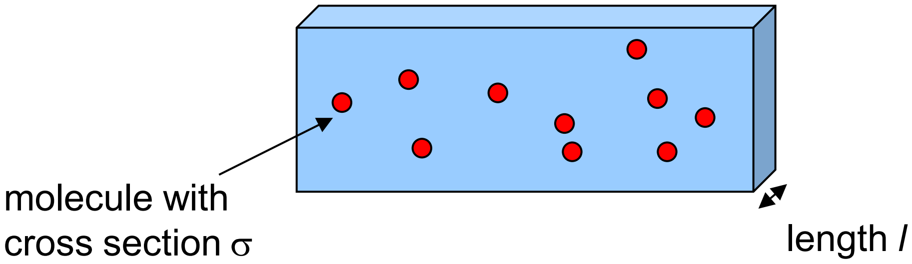
From here: the ***decadic absorbance A***, which is widely used in the field of photochemistry and molecular materials science:

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

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.

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



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

where $\bar{\nu} = \frac{1}{\lambda}$ 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 $4.310 \cdot 10^{-9}$ mol $dm^{-3}cm^2$.

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

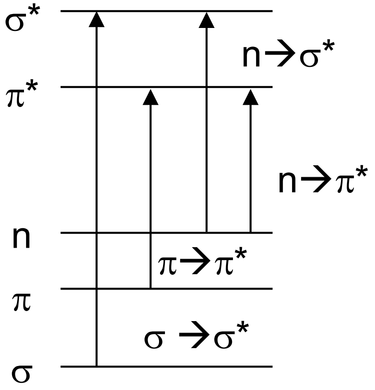
$$f_{10} = \left[\frac{8\pi^2 m_e c}{3e^2 h}\right] \bar{\nu}_{10} |\bar{\mu}_{10}|^2$$

where $\boldsymbol{\bar{\nu}_{10}}$ is the wavenumber of the transition, which we will take to be $\bar{\nu}_{max}$ (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

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

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***.



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

3.1C 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

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

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

2.1D Energy transfer processes

Learning goals:

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

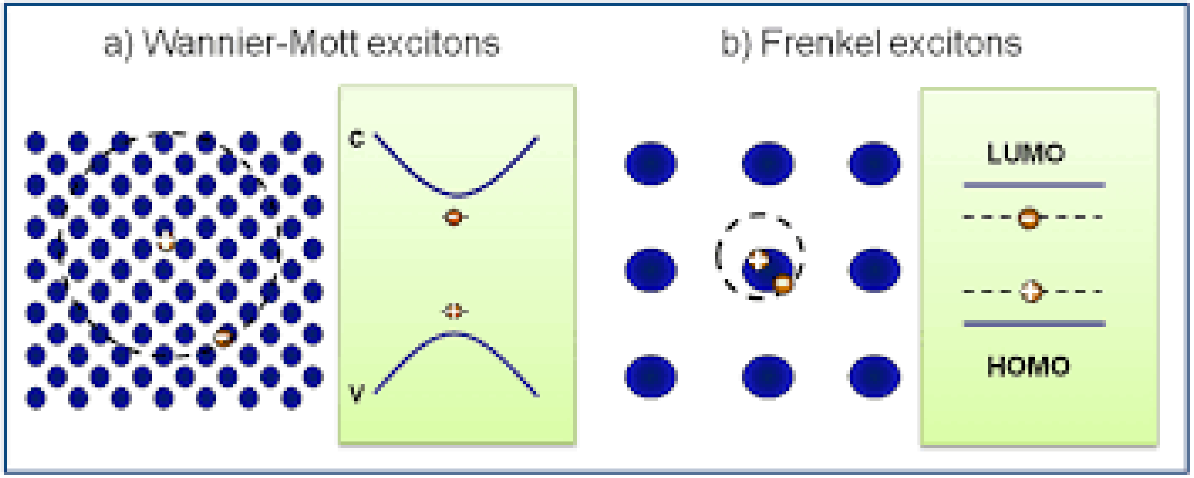
- The ***electron*** in the conduction band is then effectively ***attracted*** to this ***localized hole***

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?

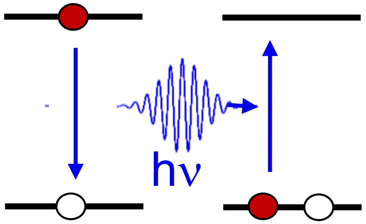
$$A^* + \mathbf{B} \rightarrow \mathbf{A} + B^*$$

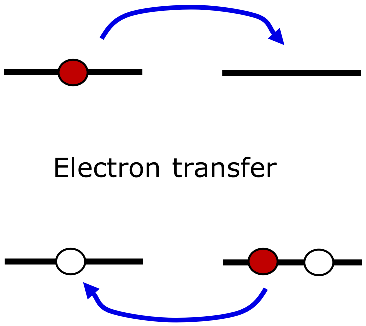
Exciton diffusion

The exciton is regarded as an elementary excitation of condensed matter that can transport energy without transporting net electric charge.

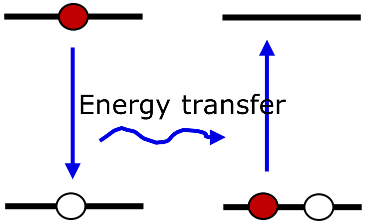
Different mechanisms possible:

Radiative Energy Transfer Nonradiative Energy Transfer





Dexter theory



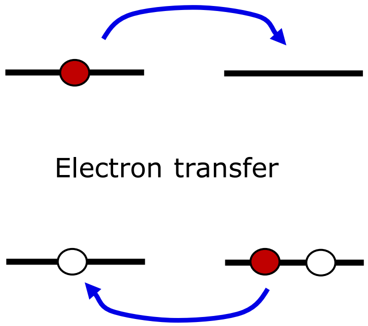
Föster Resonance Energy Transfer (FRET)

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.



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:

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

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

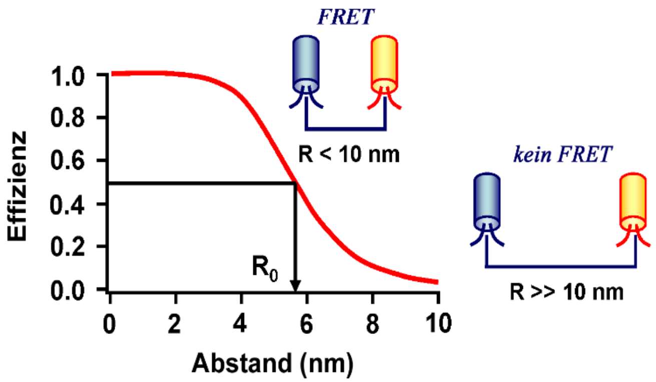
$$\frac{d}{dt}P_n = \frac{0.529\,\kappa^2}{n^4 N_A r^6 \tau_{f,A}} \int_0^\infty F_A(\bar{\nu})\,\varepsilon_B(\bar{\nu})\,\frac{d\bar{\nu}}{\bar{\nu}^4} \quad \text{with} \quad \kappa = cos\theta_{AB} - 3cos\theta_A\, cos\theta_B$$

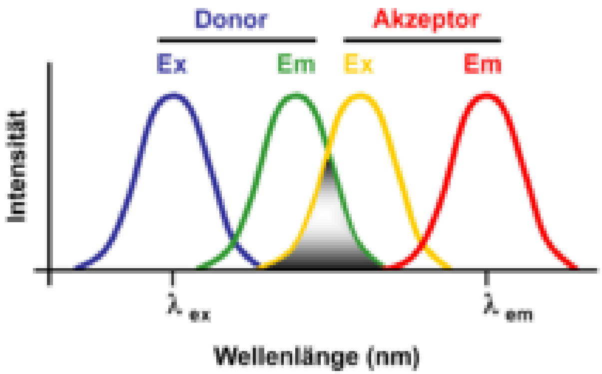
where θ_{AB} is the angle between the transition dipole moment vectors $\vec{\mu}_A$ and $\vec{\mu}_B$, and θ_A and θ_B are the angles between $\vec{\mu}_A$ and $\vec{\mu}_B$ and the internuclear M-Q axis, respectively. Furthermore, n is the solvent refractive index, N_A is Avogadro’s constant and $\tau_{f,A}$ 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:

$$r_0{}^6 = \frac{0.529\,\kappa^2}{n^4 N_A} \int_0^\infty F_A(\bar{\nu})\,\varepsilon_B(\bar{\nu})\,\frac{d\bar{\nu}}{\bar{\nu}^4}$$

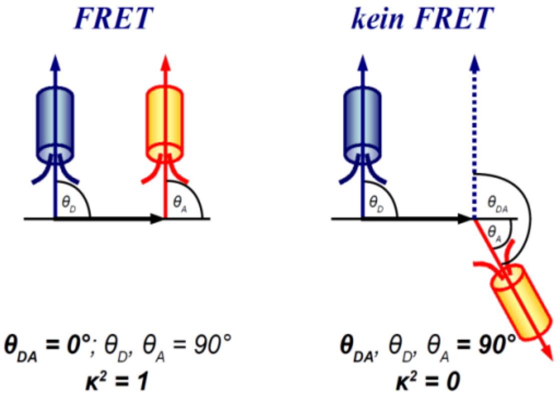
Long-range Coulombic energy transfer (Förster resonance energy transfer – FRET)





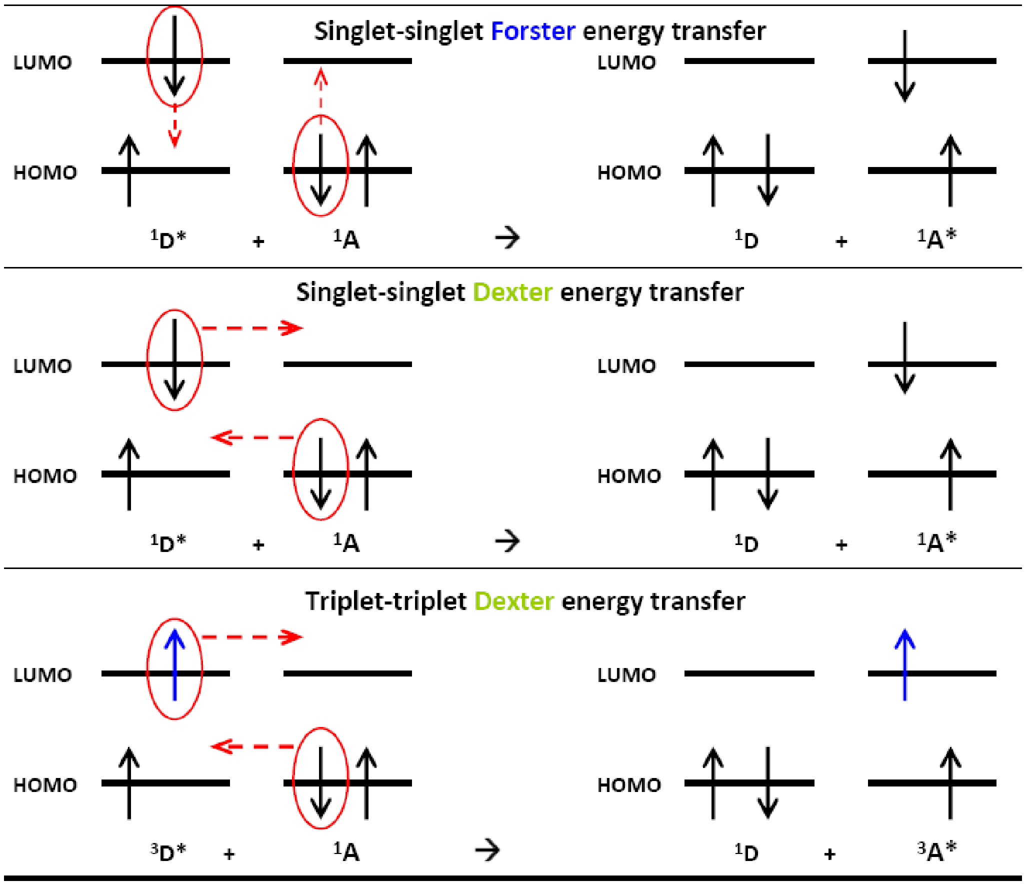
- The FRET efficiency depends on the ***separation distance r*** with an inverse 6th power law due to the dipole-dipole coupling mechanism.

- 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.

Diffusion of Triplet states



$\bar{\rho}_n$

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

3.1D Energy transfer processes

Learning outcome

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

- ☐ How is ***energy transfered*** from one molecule to the other?
  - Via exciton diffusion: radiative, Dexter, Föster