전자물리특강:
유기반도체의 전자 구조

2007. 9. 12.

Changhee Lee
School of Electrical Engineering and Computer Science
Seoul National Univ.
chlee7@snu.ac.kr

Brief Review of QM

Time dependent Schrodinger equation

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi$$

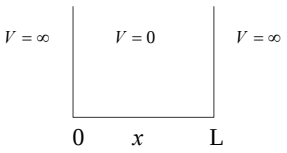
Time independent Schrodinger equation

$$-\frac{\hbar^2}{2m}\nabla^2 x + (V(x,y,z) - E)\psi(x) = 0$$

In spherical coordinates,

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} |\psi(r,\theta,\phi)|^2 r^2 \sin\theta dr d\theta d\phi = 1$$

Particle in a wall



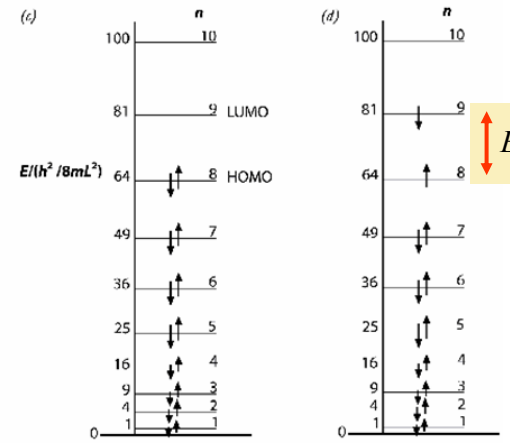
$$-\frac{\hbar}{2m}\frac{d^2\psi}{dx^2} - E\psi = 0 \qquad E = \frac{\hbar^2 k^2}{2m}$$

$$\psi_n = \left(\frac{2}{L}\right)^{1/2} \sin\frac{n\pi x}{L}$$

$$E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

Energy gap – simple quantum mechanics

Polymer: Chain of N atoms separated by a (L=Na)
Electrons from p-orbitals fill the energy levels.



$$E_g \propto \frac{1}{N}$$

Particle in a box.

Energy levels

$$E_n = \frac{h^2 n^2}{8mL^2}$$

HOMO level

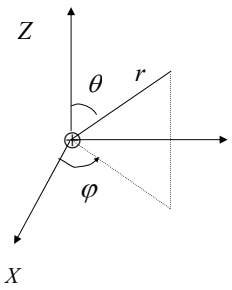
$$E(HOMO) = \frac{h^2}{8m(Na)^2}(N/2)^2$$

LUMO level

$$E(LUMO) = \frac{h^2}{8m(Na)^2}(N/2+1)^2$$

Energy Gap $\Delta E = E(LUMO) - E(HOMO) = \frac{h^2}{8m(Na)^2}(N+1) \approx \frac{h^2}{8ma^2}(\frac{1}{N})$

Atomic orbitals



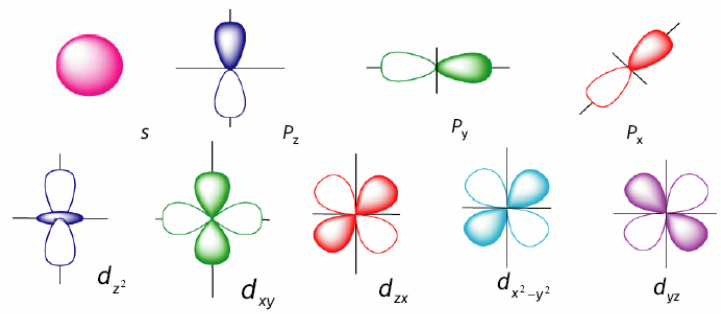
Hydrogen atom

$$\nabla^2\psi + \left(\frac{2m}{\hbar^2}\right)\{E - V(r)\}\psi = 0,\ V(r) = -\frac{q}{r}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\psi + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\psi + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\psi^2} + \frac{2m}{\hbar^2}\left(\frac{q^2}{r} + E\right)\psi = 0$$

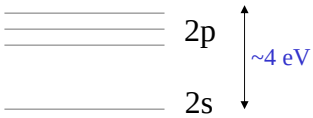
$$\psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi)$$

atomic orbitals



Carbon and Hybridization

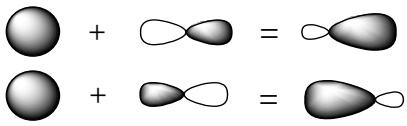
Electronic Configuration of carbon: $C=1s^2 2s^2 2p^2$



Covalent bonding energy for the s orbital:
3~4 eV per bond

⟹ hybridization: sp, sp^2 , sp^3

"In carbon, three possible hybridizations occur: sp, sp^2 , and sp^3 ; other group IV elements such as Si, Ge exhibit primarily sp^3 hybridization. Carbon differs from Si and Ge insofar as carbon does not have inner atomic orbitals except for the spherical 1s orbitals, and the absence of nearby inner orbitals facilitates hybridizations involving only valence s and p orbitals for carbon."
Ref. R. Saito *et al.* "Physical Properties of Carbon Nanotubes" (Imperial College Press, 1998, Singapore) p.5.



$$\varphi_1 = \frac{1}{\sqrt{2}}(\phi_s + \phi_{p_x})$$

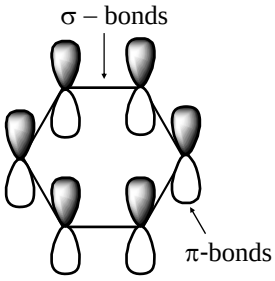
$$\varphi_2 = \frac{1}{\sqrt{2}}(\phi_s - \phi_{p_x})$$

Orthonormality : $\langle \varphi_1 | \varphi_1 \rangle = 1,\ \langle \varphi_2 | \varphi_2 \rangle = 1, \langle \varphi_1 | \varphi_2 \rangle = 0,\ \langle \varphi_2 | \varphi_1 \rangle = 0$

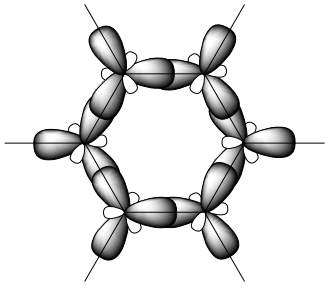
sp hybridization

Electronic Configuration of Benzene

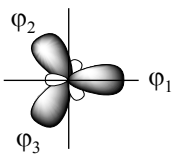
Benzene: sp^2 (σ bonds) + p_z (π bonds)



Backbone
σ-bonds



sp^2 (σ bonds)



$$\varphi_1 = \frac{1}{\sqrt{3}}(\phi_s + \sqrt{2}\,\phi_{p_x})$$

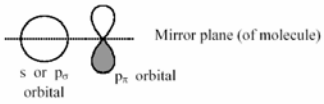
$$\varphi_2 = \frac{1}{\sqrt{3}}(\phi_s - \frac{1}{\sqrt{2}}\phi_{p_x} + \frac{\sqrt{3}}{2}\phi_{p_y})$$

$$\varphi_3 = \frac{1}{\sqrt{3}}(\phi_s - \frac{1}{\sqrt{2}}\phi_{p_x} - \frac{\sqrt{3}}{2}\phi_{p_y})$$

Huckel Molecular Orbital Theory

Basic Assumption

1. The atomic orbitals contributing to the π-bonding are of a different symmetry to the atomic orbitals contributing to the σ-bonding and may be treated independently.
2. Coulomb integrals for all the carbon atoms are assumed to be identical.
3. All resonance integrals between directly-bonded atoms are assumed to be the same; whilst those between atoms that are not directly bonded are neglected.
4. All overlap integrals representing the overlap of atomic orbitals centered on different atoms are neglected.



Ethylene C_2H_4 $\quad \psi = C_1\phi_1 + C_2\phi_2$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \qquad H_{ij} = \int \phi_i^* \hat{H} \phi_i d\upsilon \qquad S_{ij} = \int \phi_i^* \phi_j d\upsilon$$

Assume $S_{ij} = \delta_{ij}$, $H_{ii} = \alpha$, $H_{ij} = \beta$ (neighbori ng atoms)

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

$$E = \alpha \pm \beta \quad (+ : \text{bonding}, \; - : \text{antibondin g})$$

Example: Ethylene Molecules

Ethylene C_2H_4

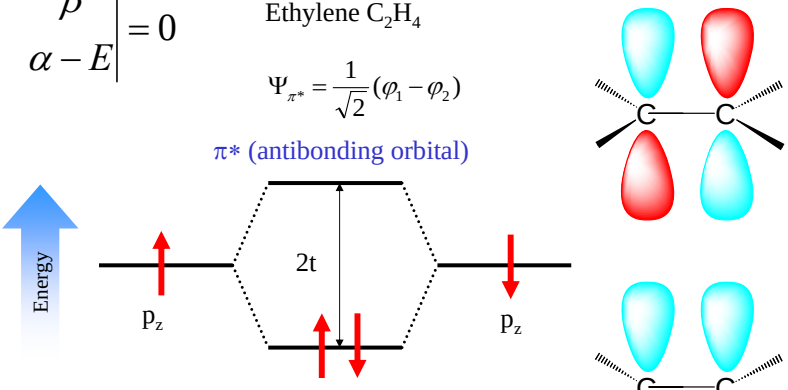
$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

$$E = \alpha \pm \beta \quad (+ : \text{bonding}, - : \text{antibonding})$$

Ethylene C_2H_4

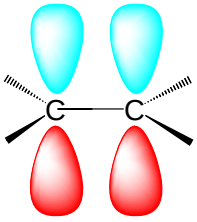
$$\Psi_{\pi^*} = \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_2)$$

π* (antibonding orbital)



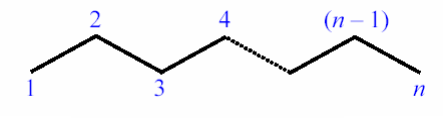
π (bonding orbital)

$$\Psi_{\pi} = \frac{1}{\sqrt{2}}(\varphi_1 + \varphi_2)$$

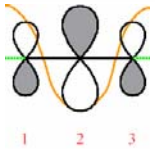


Example: Linear Conjugated Hydrocarbons

General Solution (n-atom chain ; e.g. $C_nH_{(n+2)}$ conjugated polyenes)



$$c_s \propto \sin\left(\frac{\pi k s}{n+1}\right)$$



	1	2	3			n
1	x	1	0	0	…	0
2	1	x	1			
3	0	1	x			
	0					
					x	1
n	0	…	…	…	1	x

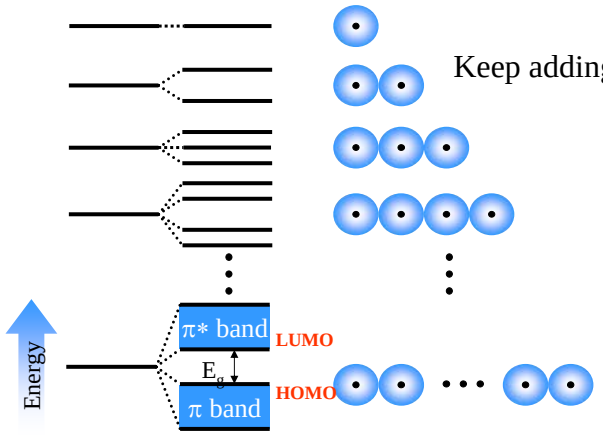
$= 0$

n - total number of atoms in the conjugated chain
s - atom number (i.e. 1, 2, …., n)
k - quantum number, identifying the MO (= 1, 2, …., n)

$$E = \alpha + 2\beta\cos\left(\frac{\pi k}{n+1}\right)$$

$$(\alpha + 2\beta) \le E \le (\alpha - 2\beta)$$

Macromolecules (polymers) and solid: Formation of bands

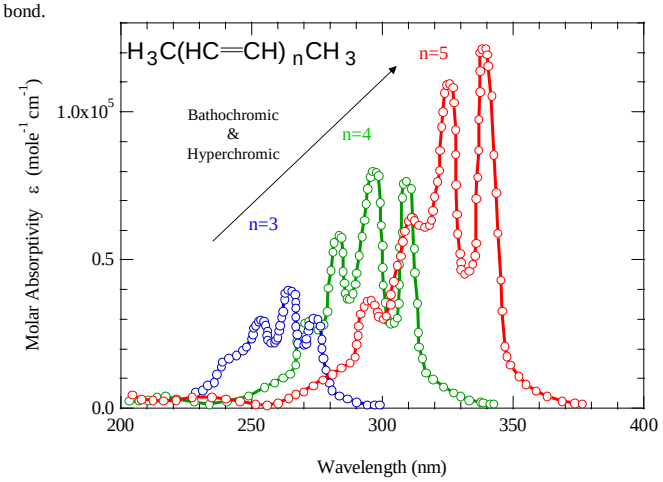


- The average energy separation between MOs decrease as n increases → Formation of bands.
- The HOMO-LUMO separation, ΔE = EHOMO – ELUMO, decreases as n increases.
- Energetically favored electron excitation is from the HOMO to the LUMO
- The interchain transfer integral (t) expresses the ease of charge transfer between two interacting chains.
- The larger the HOMO (LUMO) band-width (the magnitude of transfer integral), the higher the hole (electron) mobility.

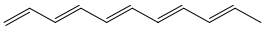
Absorption spectra of polyenes: Dependence of conjugation

Extending conjugation results in bathochromic and hyperchromic shifts in absorption.

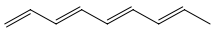
The dimethylpolyene spectra show that each additional double bond in the conjugated π-electron system shifts the absorption maximum about 30 nm to longer wavelengths. Also, the molar absorptivity (ε) roughly doubles with each new conjugated double bond.



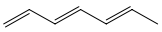
n=5
5 double bonds, 10 π electrons



n=4
4 double bonds, 8 π electrons



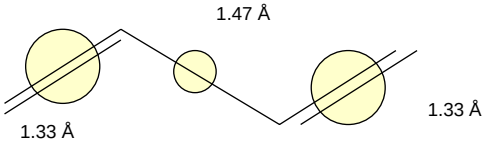
n=3
3 double bonds, 6 π electrons



Ref. D. L. Pavia, G. M. Lampman, G. S. Kriz, Introduction to Spectroscopy, 2nd ed. (Saunders College Publishing, 1996), p.289

Electron-Phonon coupling

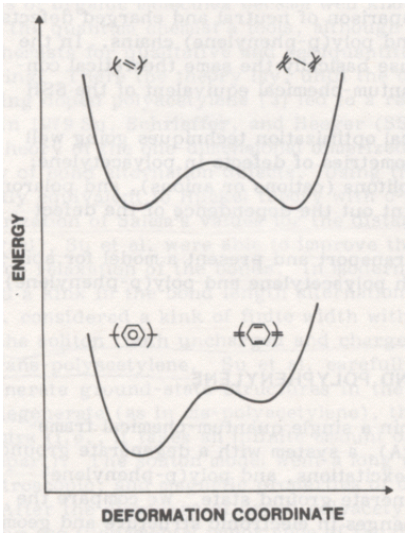
• Strong electron-phonon coupling:
p-electron bond densities directly determine the geometric structure,
e.g., butadiene, C_4H_6.



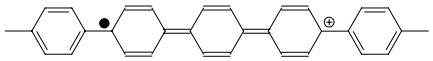
- Vibronic progressions in optical absorption and photoluminescence spectra
- Stokes shift between optical absorption and emission.
- Polaron formation

* Charge transfer or low energy charge-excitations (via doping or photoexcitation) strongly affects the π-electron bond densities → geometric structure.

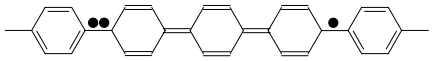
Quasiparticles in Conjugated Polymers



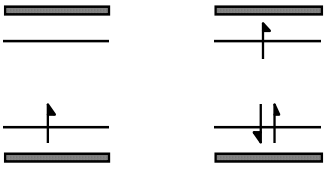
Potential Energy of Conjugated Polymers



Positive polaron



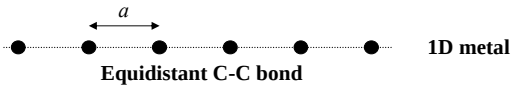
Negative polaron

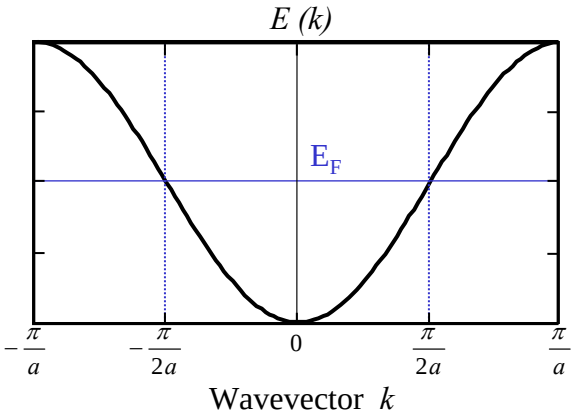


Positive polaron

Negative polaron

1D infinite chain of carbons

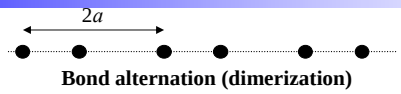


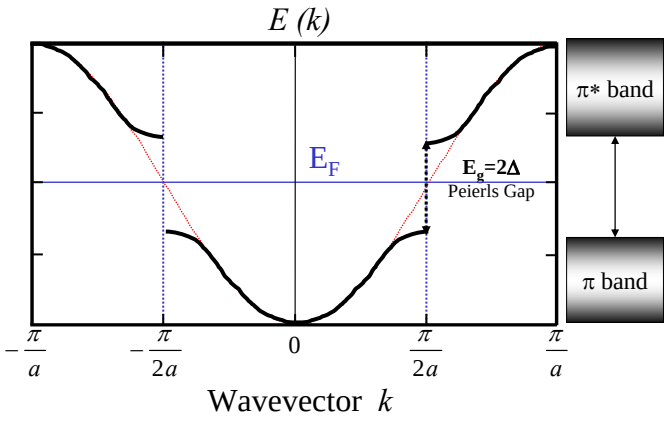


Tight-binding approximation: $E = E_{pz} - \beta - 2t \cos ka$

Peierls instability →Energy Band gap

Sir Rudolf E. Peierls
1907-1995





R.E. Peierls *Quantum Theory of Solids* (Oxford University, London Chap.5(1955).

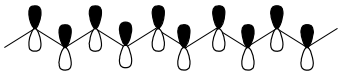
Polyacetylene: SSH Hamiltonian

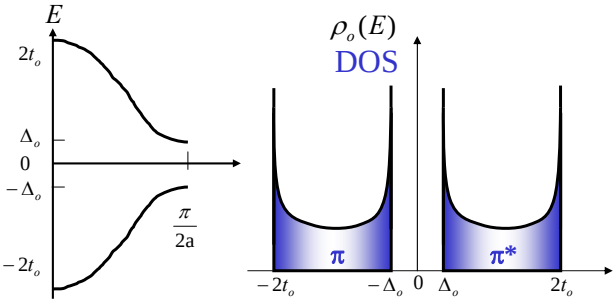
$$H = H_{kinetic} + H_{elastic} + H_{electronic}$$

$$= \frac{M}{2}\sum \dot{u}_n^{\,2} + \frac{K}{2}\sum_n (u_n - u_{n+1})^2 - \sum_{n,s}[t_0 + \alpha(u_n - u_{n+1})](c^+_{n+1,s}c_{n,s} + c^+_{n,s}c_{n+1,s})$$

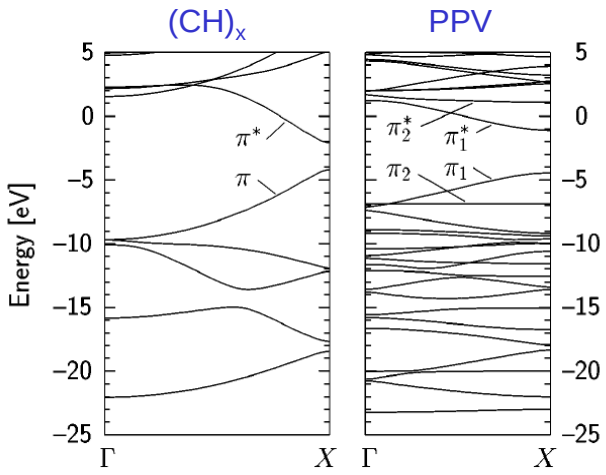
$$\text{Peierls gap}: 2\Delta = 16t_o \ \exp[-(1+\frac{1}{2\lambda})], \text{ where } \lambda = \frac{2\alpha^2}{\pi t_o K}.$$

$(CH)_x$: $E_g \propto 1.7$ eV





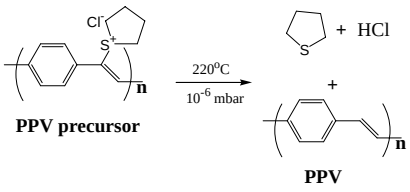
Polyacetylene & PPV: Band structure



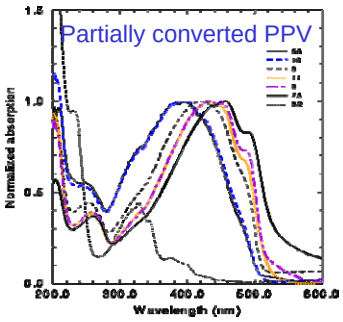
M. Rohlfing and S. G. Louie, *Phys. Rev. Lett.* **82**, 1959 (1999)

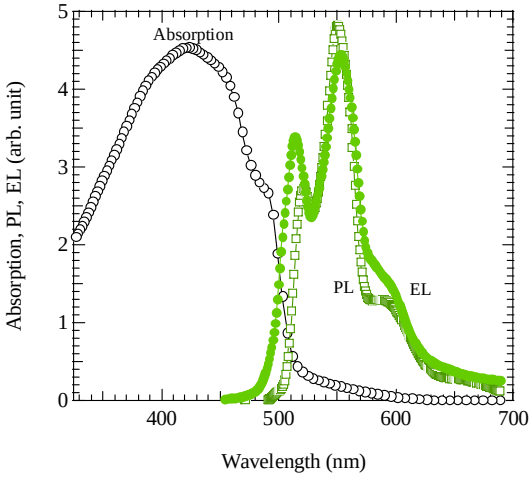
Absorption and PL Spectra of Polymer: PPV

Precursor route to poly(p-phenylenevinylene), PPV

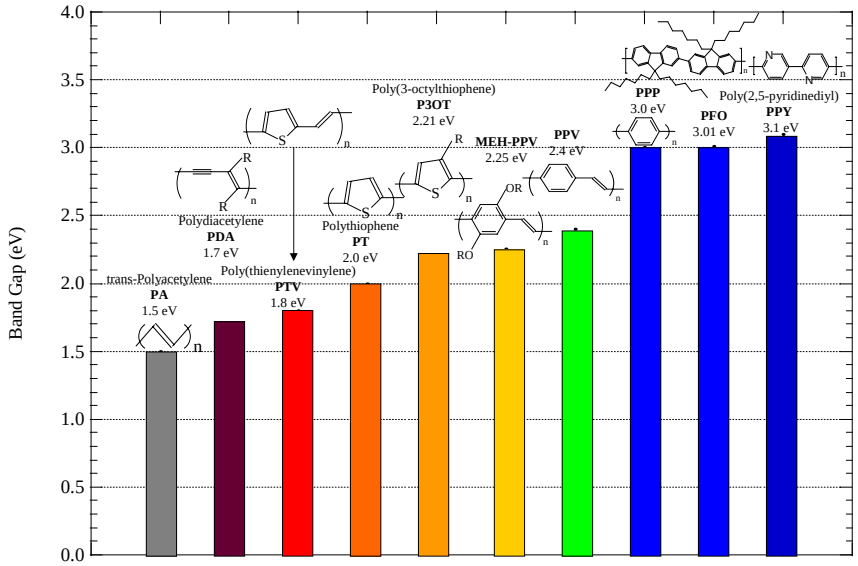


PPV precursor **PPV**





π- π* Energy Gap of Conjugated Polymers



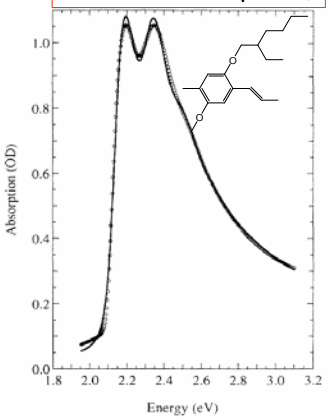
Ref. N. C. Greenham and R. H. Friend, Solid State Physics **49**, 1 (1995) p.13; A. Monkman et al., Phys. Rev. Lett. **6**, 1358 (2001)

DOS and Absorption

Density of States (DOS):

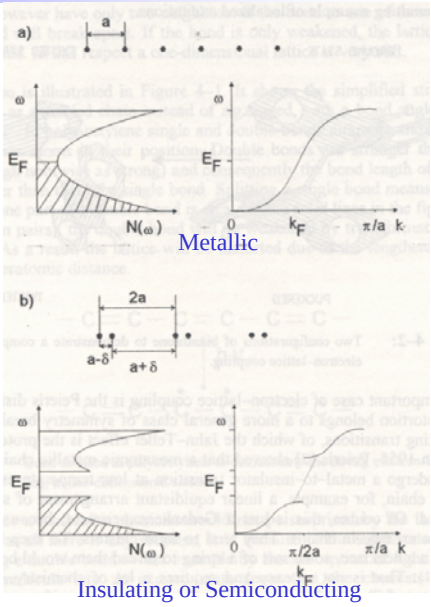
Square-root singularity in 1-d.

$$D(E) = \frac{dN(E)}{dE} \propto \frac{1}{\sqrt{E - E_g}}$$



poly[2-methoxy-5-(2'-ethyl-hexyloxy)-l,4-phenylene vinylene] MEH-PPV

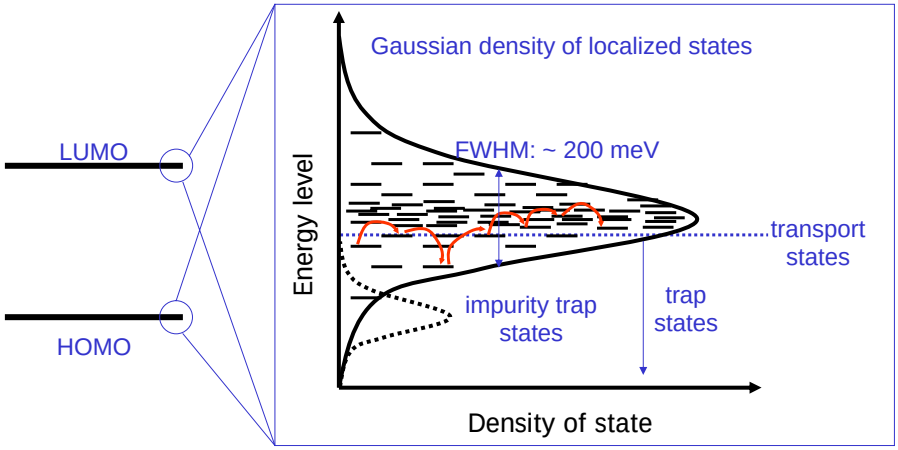
T. W. Hagler et al., Phys. Rev. B 51, 14199 (1995)



Narrow band width and hopping transport

• **Weak van der Waals interaction between molecules**

→ Each molecule keep its molecular levels independent of surrounding matrix in solid



Traps: Localized states below transport states