Konjugált polimerek kvantumkémiai leírása

- Born-Oppenheimer (adiabatikus) közelítés

$$\Psi\left(\{\{\xi\}_{el}, \{R\}_{mc}\right) = \Psi_{el}\left(\{\{\xi\}, \{R\}\right) \times \Psi_{mc}\left(\{R\}\right)$$

- σ - π szeparáció

$$\Psi_{el}\left(\{\{\xi_\pi, \xi_\sigma\}\right) = \Psi_\pi\left(\{\{\xi_\pi\}\right) \times \Psi_\sigma\left(\{\{\xi_\sigma\}\right)$$

További közelítések → „egyszerű" modellek (π)

- Hückel-modell — egyelektron kép, nincs explicit el-el kölcsönhatás

- Hubbard-modell — azonos atomon lévő π elektron párok Cb-taszítását figyelembe veszi

- Pariser-Parr Pople PPP-modell — bármely két atomon lévő π elektron párok Cb-taszítását figyelembe veszi

(Össz-vegyértékelektron módszerek (σ és π!) : szemiempirikus (CNDO, MNDO ....) ab initio, DFT)

HÜCKEL – MODELL

– független elektronok (1 Slater-determináns)

$$\Psi_\pi(\{\xi_\pi\}) = \Psi(\xi_1 \dots \xi_N) = \hat{A}(\psi_1(1) \dots \psi_N(N))$$

($\psi_i = \phi_i(\vec{r}) \cdot \gamma_i(s)$ spin-orbital)

– LCAO–MO

$$\phi_i(\vec{r}) = \sum_j C_j^{(i)} \cdot \chi_j(\vec{r})$$

MO ↑ AO

$$\chi_j(\vec{r}) = \chi_{p_z}(\vec{r} - \vec{r}_j)$$

Másodkvantált formalizmusban:

$$\hat{H} = \sum_{m,n} \sum_s h_{mn} a_{ms}^+ a_{ns} =$$

$$= \sum_m \alpha_m \sum_s a_{ms}^+ a_{ms} + \sum_{m,n}^{\text{első szomszédok}} \beta_{mn} \sum_s a_{ms}^+ a_{ns}$$

i: $i_1 \leftrightarrow i_2$

$$\Rightarrow \hat{H} = \sum_m \alpha_m \sum_s a_{ms}^+ a_{ms} + \sum_i \beta_i \sum_s \left(a_{i_1 s}^+ a_{i_2 s} + a_{i_2 s}^+ a_{i_1 s} \right)$$

atomokra kötésekre

β: rezonancia integrál, hopping –

Spec. azonos atomok

$$\hat{H} = \alpha \sum_{m,s} a_{ms}^+ a_{ms} + \beta \sum_{i,s} \left(a_{i_1 s}^+ a_{i_2 s} + a_{i_2 s}^+ a_{i_1 s} \right)$$

TOPOLÓGIA

HUBBARD – MODELL

$$\hat{H} = \sum_{m n, s} h_{mn} a^{+}_{ms} a_{ns} + \sum_{n} \gamma_{n} \hat{N}_{n\uparrow} \hat{N}_{n\downarrow}$$

$$\left(\hat{N}_{n\sigma} \equiv a^{+}_{n\sigma} a_{n\sigma} \right)$$

Spec. azonos atomok

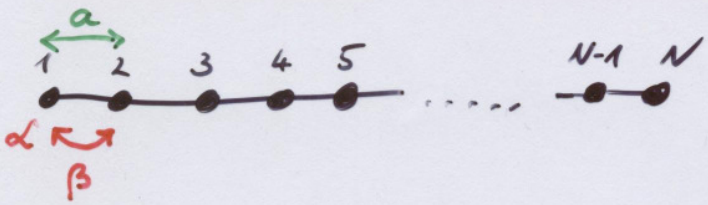
$$\hat{H} = \alpha \sum_{n} \sum_{s} a^{+}_{ns} a_{ns} + \beta \sum_{i} \sum_{s} \left(a^{+}_{i_1 s} a_{i_2 s} + a^{+}_{i_2 s} a_{i_1 s} \right) + U \sum_{n} \hat{N}_{n\uparrow} \hat{N}_{n\downarrow}$$

PPP – modell

$$\hat{H} = \sum_{mn, s} h_{mn} a^{+}_{ms} a_{ns} + \frac{1}{2} \sum_{mn} \sum_{s_1 s_2} \gamma_{mm} \hat{N}_{ms_1} \hat{N}_{ms_2} - \frac{1}{2} \sum_{n} \sum_{s} \gamma_{nn} \hat{N}_{ns}$$

$$\gamma_{mn} = \begin{cases} \dfrac{1}{R_{mn} + 2/(\gamma_{mm} + \gamma_{nn})} & \text{Mataga – Nishimoto} \\ \dfrac{1}{\sqrt{R_{mn}^2 + 4/(\gamma_{mm} + \gamma_{nn})^2}} & \text{Ohno} \end{cases}$$

Lineáris lánc, azonos atomok és kötések



$N \to \infty$! $N+1 \equiv 1$ periódikus határfeltétel

Bloch-tétel: $\phi(x + l \cdot a) = e^{ik(la)} \phi(x)$

$$\Rightarrow \quad \phi^{(k)}(x) = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} \underbrace{e^{ik \cdot ja}}_{e^{ikx} \cdot e^{-ik(x-ja)}} \chi(x - ja)$$

$$\hat{H} = \begin{pmatrix} \alpha & \beta & 0 & 0 & \cdots \\ \beta & \alpha & \beta & 0 & \\ 0 & \beta & \alpha & \beta & \ddots \\ \vdots & & & & \end{pmatrix} \qquad \underline{\underline{S}} = \begin{pmatrix} 1 & s & & & \\ s & 1 & s & & \\ & s & 1 & s & \\ & & & & \end{pmatrix}$$

$S = \langle \chi_j | \chi_{j+1} \rangle$

$$\underline{\underline{H}}\ \underline{c}^{(k)} = \varepsilon^{(k)}\ \underline{\underline{S}}\ \underline{c}^{(k)} \qquad \left(\varepsilon^{(k)} \underline{\underline{S}}\ \underline{c}^{(k)}\right)$$

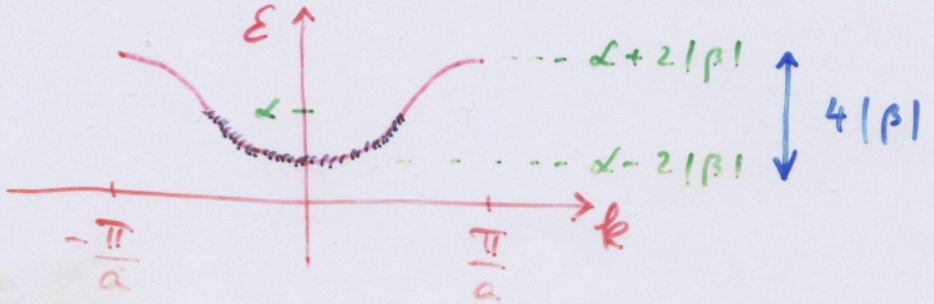
$$\Rightarrow \quad \beta\, c_{j-1}^{(k)} + \alpha\, c_j^{(k)} + \beta\, c_{j+1}^{(k)} = \varepsilon^{(k)} c_j^{(k)} \qquad \left(\varepsilon^{(k)} \{ s c_{j-1} + c_j + s c_{j+1} \}\right)$$

$$\beta e^{-ika} + \alpha + \beta e^{ika} = \varepsilon(k) \qquad s \approx 0$$

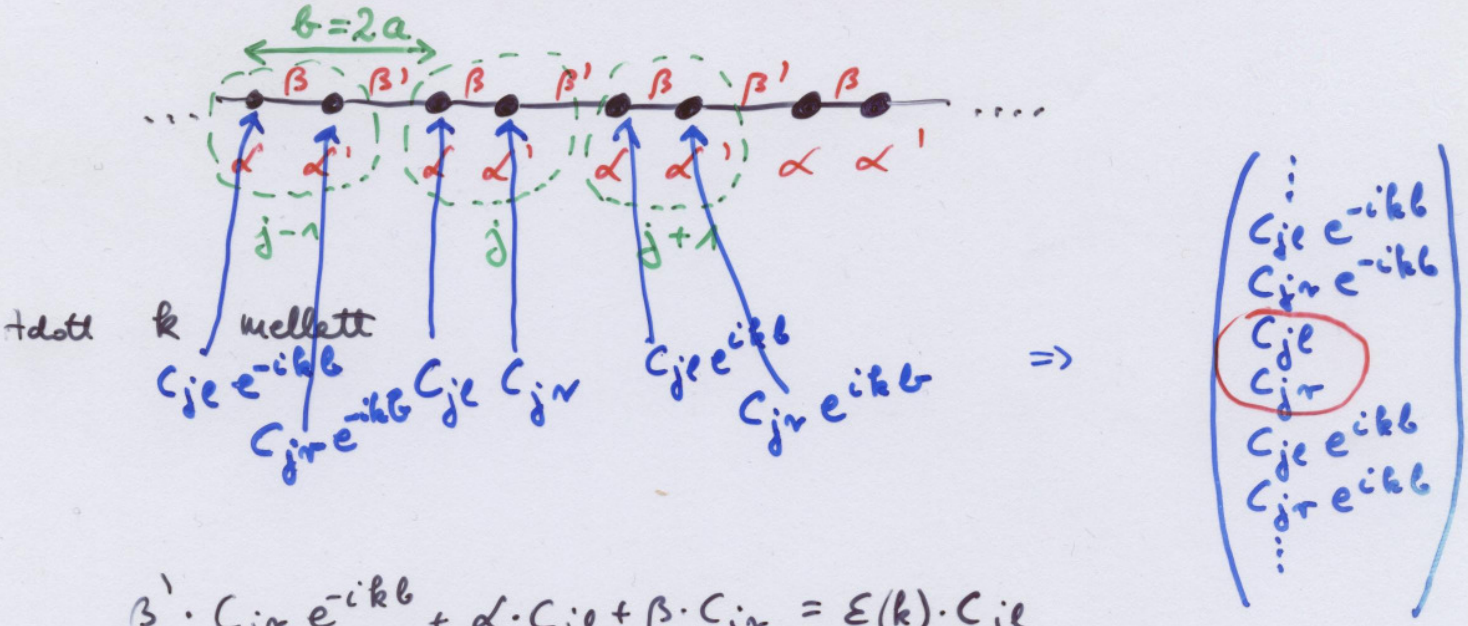
$$\boxed{\alpha + 2\beta \cos ka = \varepsilon(k)} \qquad \left(\frac{\alpha + 2\beta \cos ka}{1 + 2s \cdot \cos ka}\right)$$

periódikus határfeltétel: $c_{j+N} \equiv c_j \Rightarrow e^{i \underbrace{kNa}_{2\pi \cdot \text{egész}}} \equiv 1$

$$\Rightarrow \quad k = \frac{2\pi}{a} \cdot \frac{\text{egész}}{N}, \quad N \text{ féle}$$



Lineáris lánc, dimerizálódás



$$\beta' \cdot C_{jr} e^{-ikb} + \alpha \cdot C_{je} + \beta \cdot C_{jr} = \varepsilon(k) \cdot C_{je}$$

$$\beta \cdot C_{je} + \alpha' C_{jr} + \beta' C_{je} e^{ikb} = \varepsilon(k)\, C_{jr}$$

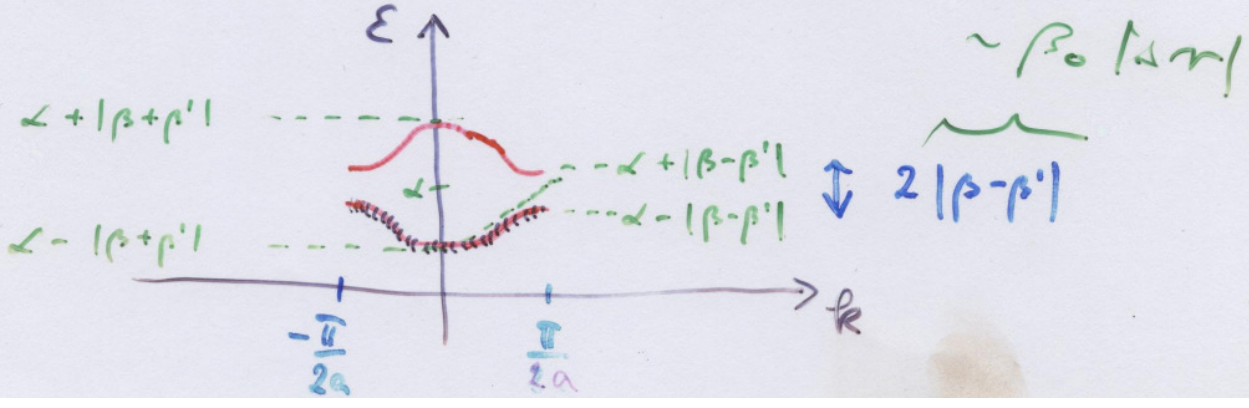
$$\Rightarrow \begin{pmatrix} \alpha & \beta + \beta' e^{-ikb} \\ \beta + \beta' e^{ikb} & \alpha' \end{pmatrix} \begin{pmatrix} C_{je} \\ C_{jr} \end{pmatrix} = \varepsilon(k) \begin{pmatrix} C_{je} \\ C_{jr} \end{pmatrix}$$

$$\Rightarrow \varepsilon(k)^2 - \underbrace{(\alpha+\alpha')}_{\text{Spur } \hat{H}}\varepsilon(k) + \Big[\underbrace{\alpha\alpha' - (\beta+\beta' e^{-ikb})\cdot(\beta+\beta' e^{ikb})}_{\text{det } \hat{H}}\Big] = 0$$

$$z \cdot z^* = |z|^2 = (\beta+\beta'\cos kb)^2 + (\beta' \sin kb)^2$$

$$\Rightarrow \varepsilon^{1,2}(k) = \frac{\alpha+\alpha'}{2} \pm \sqrt{\left(\frac{\alpha-\alpha'}{2}\right)^2 + \beta^2 + \beta'^2 + 2\beta\beta' \cos k \cdot \underbrace{b}_{=2a}}\,!$$

Spec. $\alpha = \alpha'$



LHS-modell : π-elektronok + σ-elektronok ← Hückel ← σ-potenciál

π

$$\phi_i(r) = \sum_{j=1}^{N} C_j^{(i)} \cdot \chi_j(r)$$

$$\Rightarrow \varepsilon_i = \langle \phi_i | \hat{H}_\pi | \phi_i \rangle = \sum_j \alpha_j C_j^{(i)*} C_j^{(i)} + \sum_{k>l} \beta_{kl} \left(C_k^{(i)*} C_l^{(i)} + C_l^{(i)*} C_k^{(i)} \right)$$

jelölés: $q_j = \sum_i C_j^{(i)*} C_j^{(i)} \cdot n_i$

$$p_m = \frac{1}{2} \sum_i \left(C_k^{(i)*} C_l^{(i)} + C_l^{(i)*} C_k^{(i)} \right) \cdot n_i$$

$k, l \Rightarrow m$ $\quad n_i = 0, 1$

$$\Rightarrow E_{\pi,tot} = \sum_i \varepsilon_i \cdot n_i = \sum_j \alpha_j q_j + 2 \sum_m \beta_m p_m$$

(atomok) (kötések) ← kötésrend

$$q_j = \frac{\partial E_{\pi,tot}}{\partial \alpha_j} \qquad p_m = \frac{1}{2} \frac{\partial E_{\pi,tot}}{\partial \beta_m}$$

LHS: → $\beta = \beta(r)$ $\qquad \beta(r) = -A \cdot e^{-\frac{r}{B}}$

→ σ-potenciál : $f_\sigma(r) \Rightarrow E_{\sigma,tot} = \sum_m f_\sigma(r_m)$

$$\Rightarrow E_{tot} = E_{\pi,tot}\left(\alpha_1, \dots; \beta_1(r_1) \dots; \{n_i\}\right) + E_{\sigma,tot}\left(\{r_m\}\right)$$

Egyensúly: (r_m függvényei)

$$\frac{\partial E_{tot}}{\partial r_m} = 0 \Rightarrow \frac{d f_m}{d r_m} + \underbrace{\frac{\partial E_{\pi,tot}}{\partial \beta_m}}_{\equiv 2 p_m} \cdot \frac{d \beta_m}{d r_m} = 0 \Rightarrow$$

ha $r = R_1 - (R_1 - R_2) \cdot p$ (co

$$\Updownarrow$$

$$f_\sigma(r) = \frac{2}{R_1 - R_2} \beta(r) (r - R_1 +$$

LHS MODEL

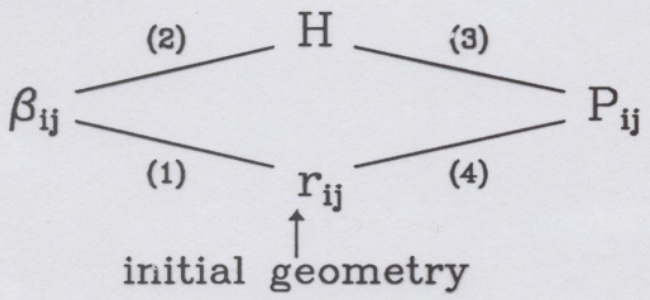
~ SSH

(Longuet-Higgins, Salem)

– HAMILTONIAN (HUECKEL) :

$$H = \sum_i \alpha_i \, a_i^+ a_i + \sum_{i<j} \beta_{ij} \, (a_j^+ a_i + a_i^+ a_j) + \sum_k f_G(r_k) \qquad ...(2)$$

– GEOMETRY OPTIMIZATION :



!!!

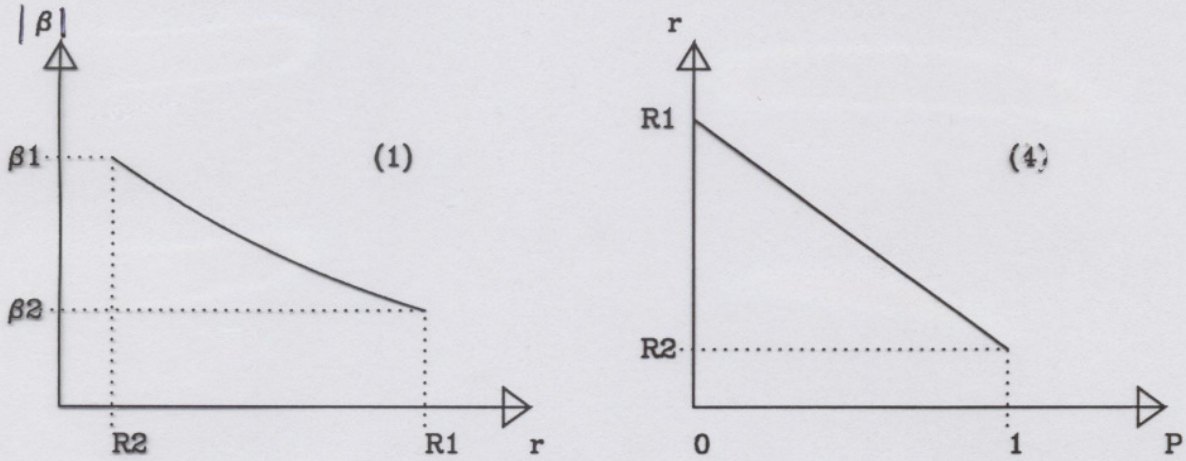
where

Bond order : $P_{ij} = \sum_n N_n (C_{ni}^* C_{nj} + c.c.)/2$ ...(3)

(N_n: 0,1, or 2 – occupation number of the *n*th MO)

Coulson's relation : $r_{ij} = R1 - (R1-R2)*P_{ij}$ ...(4)

Resonance integral : $\beta_{ij} = -A*\exp(-r_{ij}/B)$ ...(1)

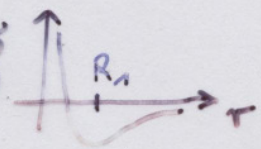


Some results for conjugated polymers without heteroatoms:

	gap (eV)	bondlength alternation (Å)
polyacetylene	1.50	1.36 / 1.45
polyparaphenylene	3.39	1.50 – 1.40 / 1.40

(solitons, polarons, bipolarons etc.)

$f_G(r) = 2\beta(r)(r - R_1 + B)/(R_1 - R_2)$



LHS - parameters for C and S

$$\beta(r) = -A \cdot e^{-\frac{r}{B}}$$

$k=\beta_</\beta_>$	1.2	1.3	1.34	1.35	1.36	1.4	1.5
$P_<$	0.8074	0.8314	0.8409	0.8433	0.8457	0.8553	0.8792
$P_>$	0.4539	0.4206	0.4073	0.4040	0.4006	0.3873	0.3540
• $r_<$(A)	1.3704	1.3654	1.3634	1.3629	1.3624	1.3604	1.3554
• $r_>$(A)	1.4447	1.4517	1.4544	1.4552	1.4559	1.4587	1.4657
$B=(r_<-r_>)/\ln k$	0.4072	0.3288	0.3112	0.3074	0.3040	0.2921	0.2720
$\Delta/W=(k-1)/(k+1)$	0.0909	0.1304	0.1453	0.1489	0.1525	0.1667	0.2000

standardized p-orbital exponent for C: $\zeta = 1.72$ (Hehre et al.)

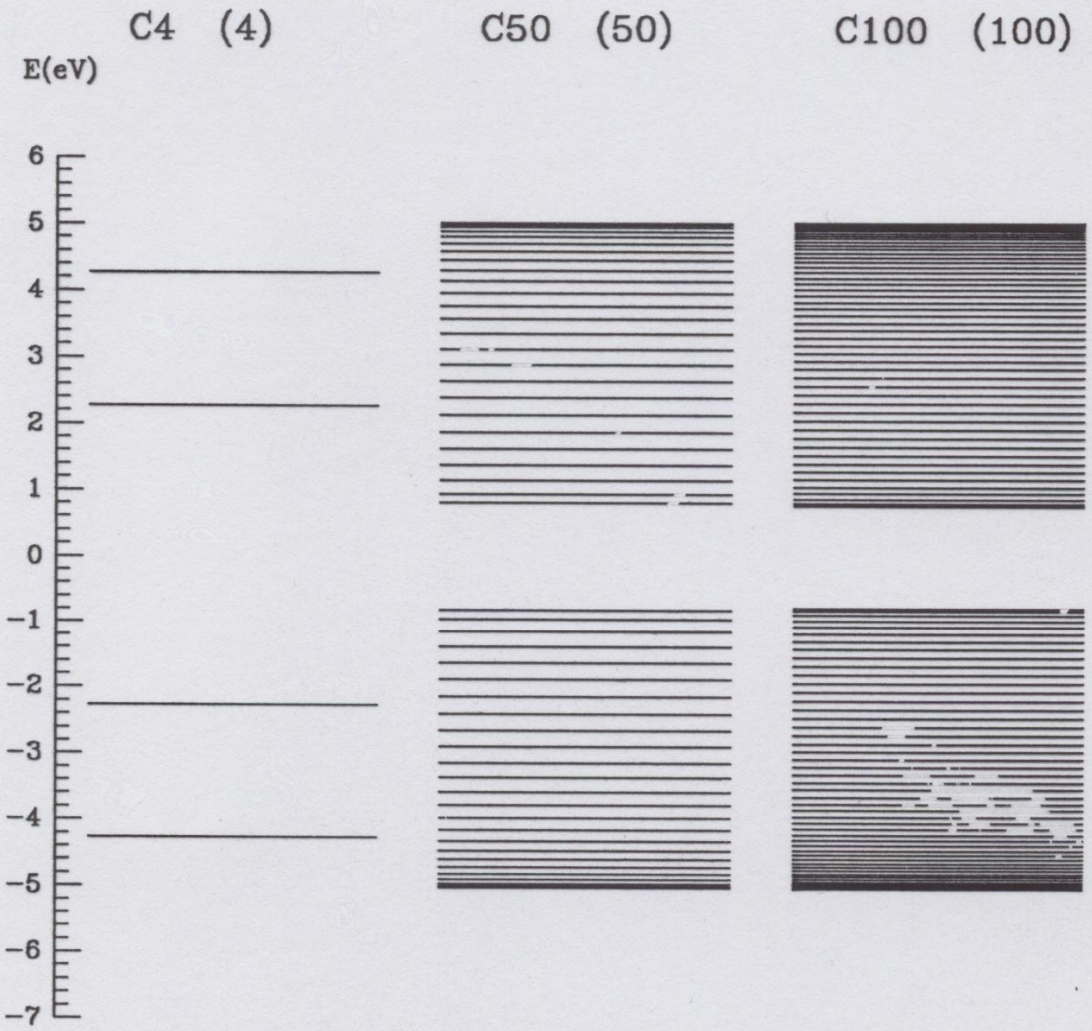
$\Rightarrow B_\zeta = \frac{a_0}{\zeta} = \frac{0.529}{\zeta} = 0.3076$

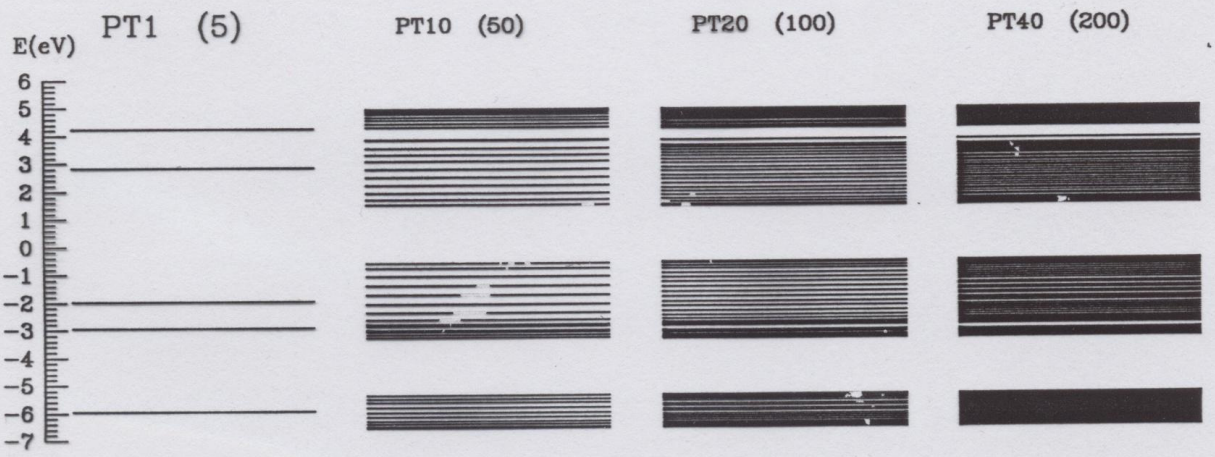
$(CH)_x$: $E_g = 1.5\,eV \Rightarrow A = 243.5\,eV$

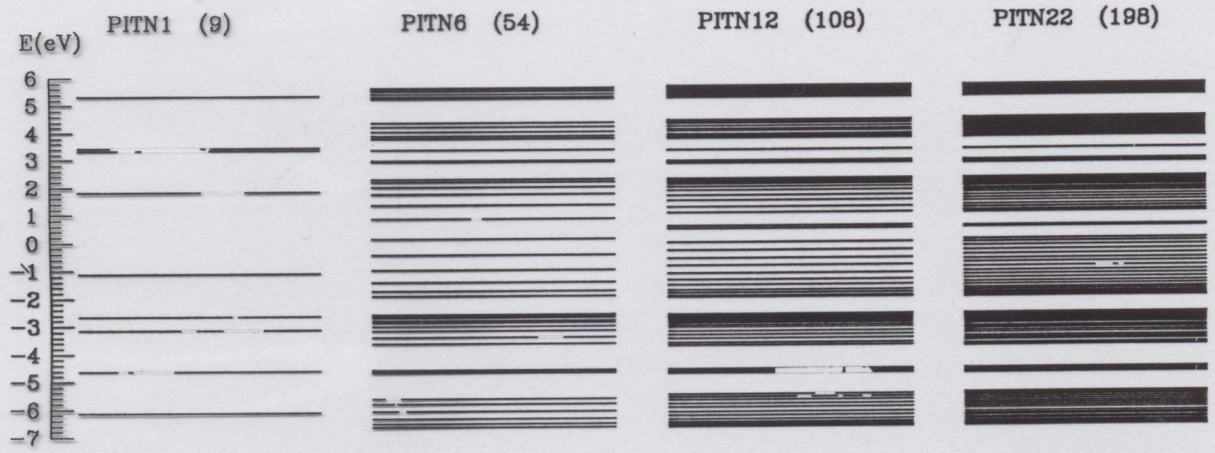
Table 1: Parameters used in the LHS calculations. N_π is the number of π-electrons per atom. β_0 is the resonance integral for the bond in benzene (r = 1.4 Å). $\beta_0 = -2.564\,eV$

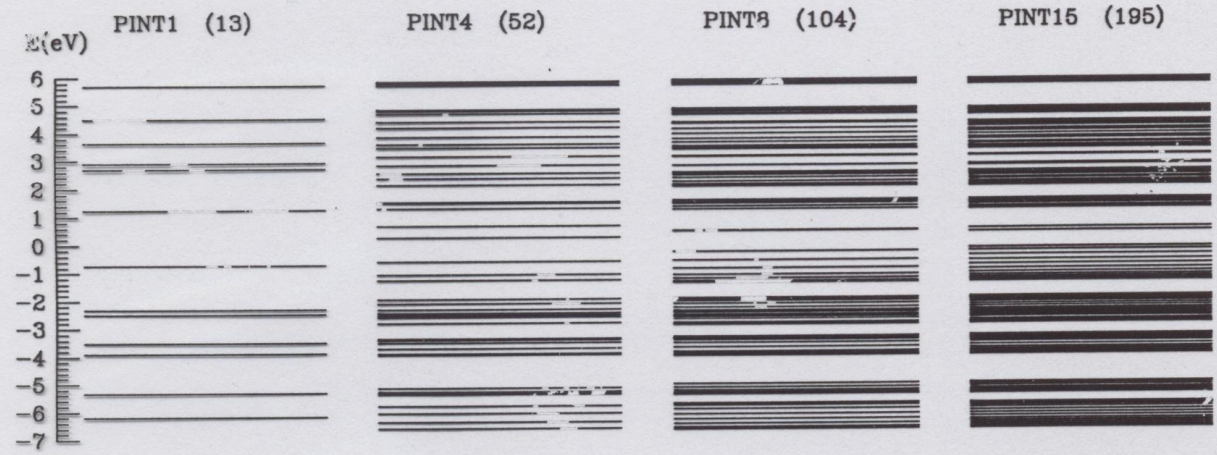
X	N_π	α/β_0	A(eV)	B(Å)	R_1(Å)	R_2(Å)	β_1(eV)	β_2(eV)
C	1	0.0	243.5	0.3075	1.54	1.33	-1.626	-3.220
-S-	2	1.5	1938.1	0.2580	1.82	1.71	-1.674	-2.564

Streitwieser — from Slater exponents — standard values — Streitwieser


C4 (4)
C50 (50)
C100 (100)
E(eV)
6
5
4
3
2
1
0
−1
−2
−3
−4
−5
−6
−7


PT1 (5)
PT10 (50)
PT20 (100)
PT40 (200)
E(eV)
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7


PITN1 (9)
PITN6 (54)
PITN12 (108)
PITN22 (198)
E(eV)
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7


PINT1 (13)
PINT4 (52)
PINT8 (104)
PINT15 (195)
E(eV)
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7

Su – Schrieffer – Heeger modell

„tight binding"

$$H_{SSH} = H_\pi + H_\sigma + H_{kin}$$

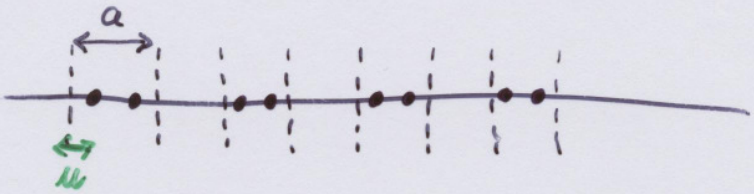
$$H_\pi = -\sum_{n,s} \underbrace{\left[t_0 - \alpha(u_{n+1} - u_n)\right]}_{\beta_{n,n+1}} \cdot \left[a^+_{n+1,s}\, a_{n,s} + a^+_{n,s}\, a_{n+1,s}\right]$$

β_0 ; el-ph coupl. $\sim \frac{\partial \beta}{\partial r}$

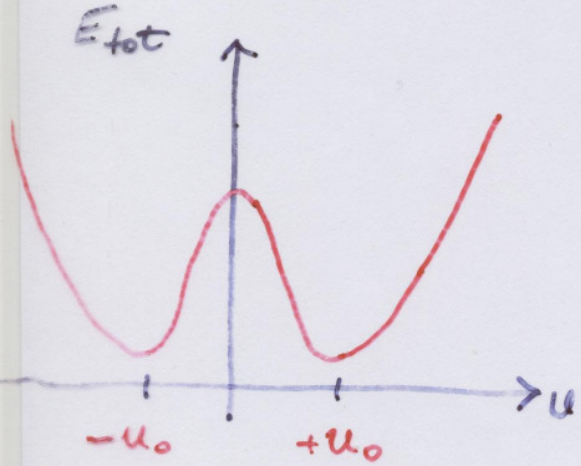
$$H_\sigma = \frac{1}{2} K \sum_n (u_{n+1} - u_n)^2$$

$$H_{kin} = \frac{1}{2} M \sum_n \dot{u}_n^2$$

$u_n = (-1)^n u$



$\dot{u}_n \equiv 0 \quad \Rightarrow \quad \left.\frac{dE_{tot}}{du}\right|_{u_0} = 0 \qquad u_0 \neq 0\,!$



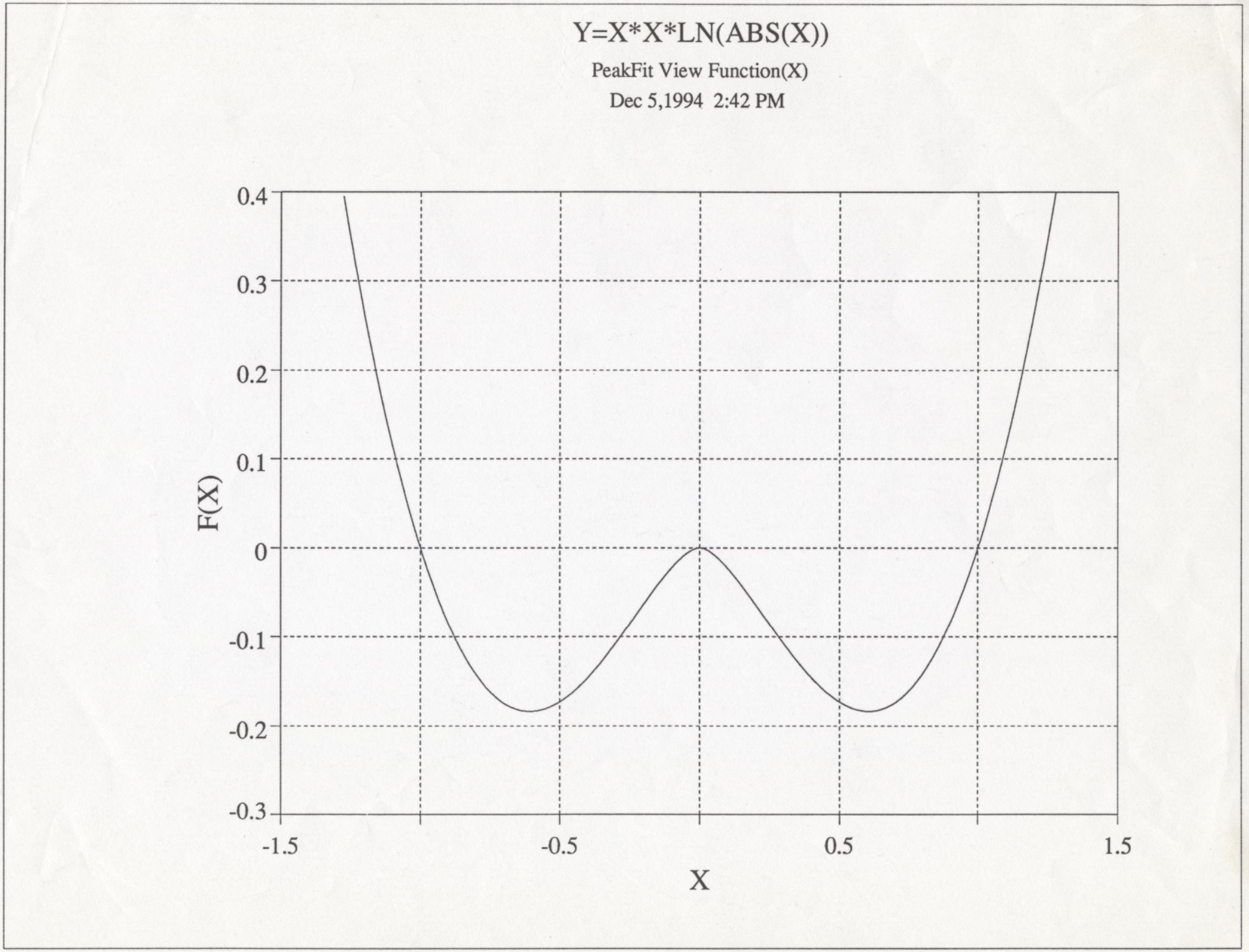
$$\frac{1}{N} \cdot E_{tot}(u) = A + B \cdot u^2 \ln\left(\frac{u}{a}\right) + \frac{1}{2} K u^2$$

π

$$u_0 = \pm \frac{2t_0}{\alpha} e^{-\left(1 + \frac{1}{2\lambda}\right)}$$

ahol $\quad \lambda = \frac{2\alpha^2}{K t_0 \pi}$

$$E_g = 8\alpha \cdot u_0$$


Y=X*X*LN(ABS(X))
PeakFit View Function(X)
Dec 5,1994 2:42 PM
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
F(X)
-1.5
-0.5
0.5
1.5
X