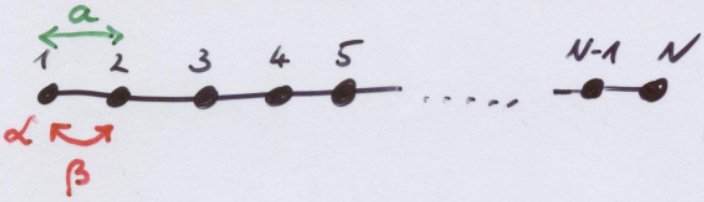
# Lineáris lánc, azonos atomok és kötések




$N \to \infty$ $\qquad \overset{!}{N+1} \equiv 1 \qquad$ periódikus határfeltétel

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

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

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

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

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

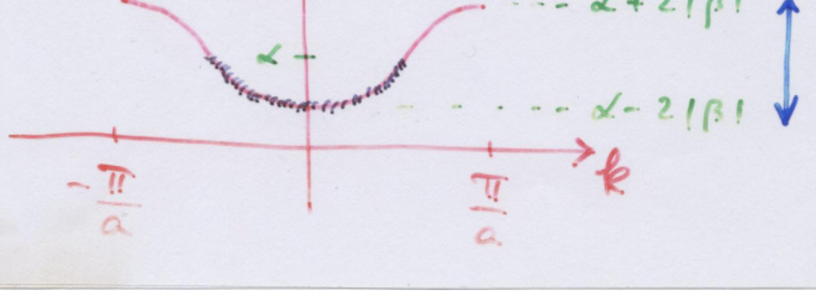
$$\Rightarrow \quad \beta c_{j-1}^{(k)} + \alpha c_j^{(k)} + \beta c_{j+1}^{(k)} = \varepsilon^{(k)} c_j^{(k)} \qquad \left(\varepsilon^{(k)}\{S c_{j-1} + c_j + S c_{j+1}\}\right)$$

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

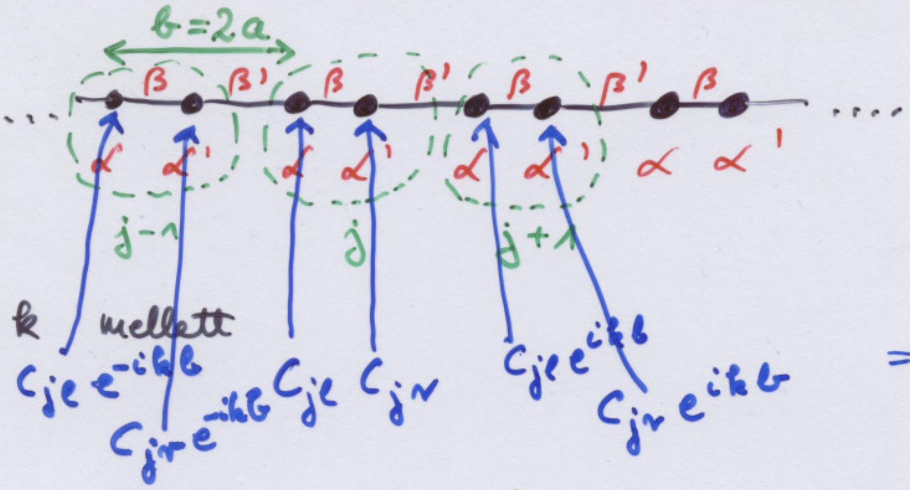
$$\boxed{\alpha + 2\beta \cos ka = \varepsilon(k)} \qquad S \approx 0 \quad \left(\frac{\alpha + 2\beta\cos ka}{1 + 2S\cdot\cos ka}\right)$$

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

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



# lineáris lánc, dimerizálódás




$$\Rightarrow \begin{pmatrix} \vdots \\ c_{jl}e^{-ikb} \\ c_{jr}e^{-ikb} \\ c_{jl} \\ c_{jr} \\ c_{jl}e^{ikb} \\ c_{jr}e^{ikb} \\ \vdots \end{pmatrix}$$

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

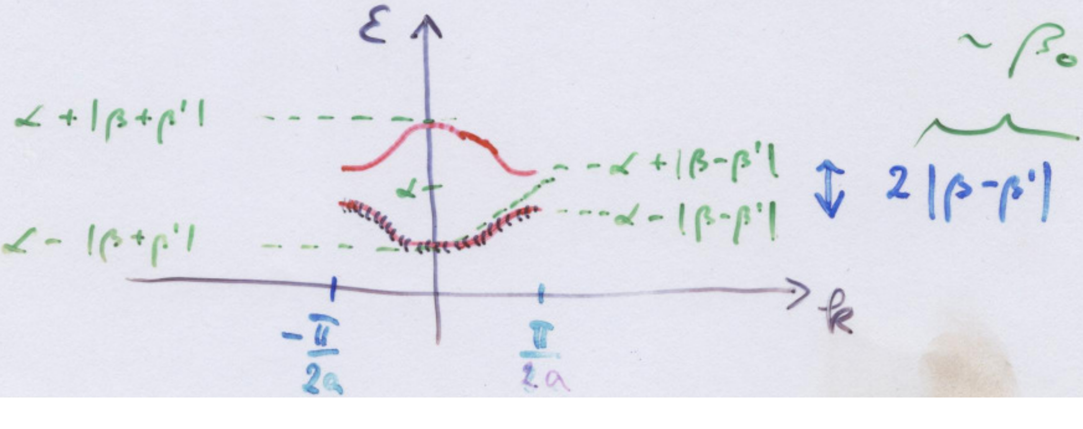
$$\beta \cdot c_{jl} + \alpha' c_{jr} + \beta' c_{jl} e^{ikb} = \varepsilon(k)\, c_{jr}$$

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

$$\Rightarrow \varepsilon(k)^2 - \overset{\text{Spur } \hat{H}}{(\alpha+\alpha')}\, \varepsilon(k) + \overset{\det \hat{H}}{\Big[\alpha\alpha' - \underbrace{(\beta+\beta' e^{-ikb}) \cdot (\beta+\beta' e^{ikb})}_{z \cdot z^* = |z|^2 = (\beta+\beta' \cos kb)^2 + (\beta' \sin kb)^2}\Big]} = 0$$

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

Spec. $\alpha = \alpha'$



LHS-modell : $\pi$-elektronok ← Hückel
+
$\sigma$-elektronok ← $\sigma$-potenciál

$\pi$

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

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

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

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

$$\Rightarrow E_{\pi,tot} = \sum_i \varepsilon_i \cdot n_i = \underbrace{\sum_j \alpha_j q_j}_{\text{(atomok)}} + 2 \underbrace{\sum_m \beta_m p_m}_{\text{(kötések)}}$$ ← 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: $\rightarrow \beta = \beta(r)$ $\qquad \beta(r) = -A \cdot e^{-\frac{r}{B}}$

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

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

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

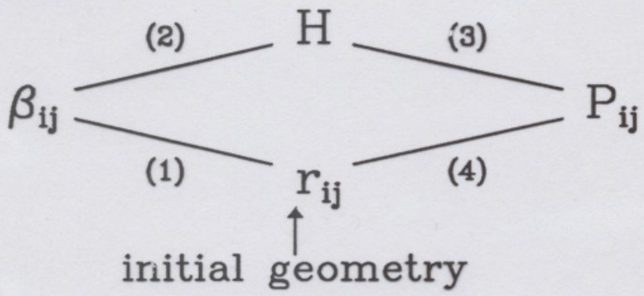
~ SSH

(Longuet-Higgins, Salem)

**– HAMILTONIAN (HUECKEL) :**

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

**– GEOMETRY OPTIMIZATION :**




!!!

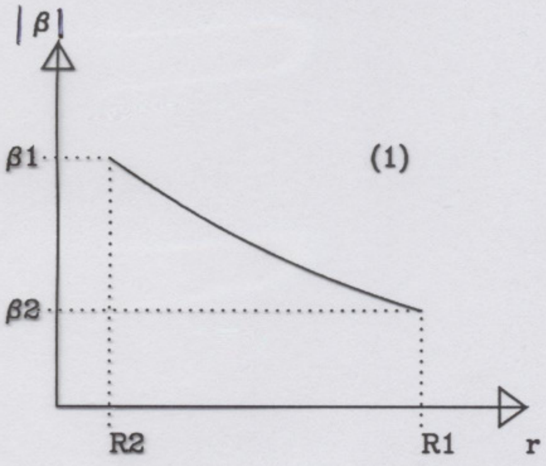
where

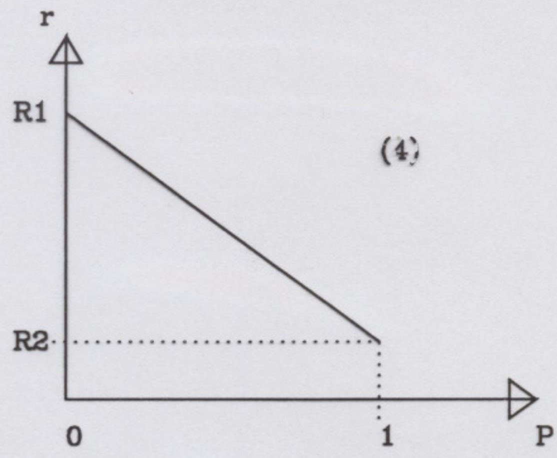
Bond order : $P_{ij} = \sum_n N_n \left( C_{ni}^{*} C_{nj} + \text{c.c.} \right)/2$ ...(3)

($N_n$: 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)

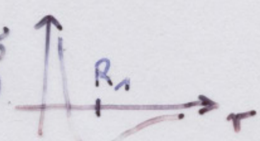



**Some results for conjugated polymers without heteroatoms:**

| | gap (eV) | bondlength alternation (A) |
|---|---|---|
| polyacetylene | 1.56 | 1.36 / 1.45 |
| polyparaphenylene | 3.39 | 1.50 – 1.40 / 1.40 |
| (solitons, polarons, bipolarons etc.) | | |

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



# 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 : $\xi = 1.72$ (Hehre et al.)

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

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

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

| X | $N_\pi$ | $\alpha/\beta_0$ | A(eV) | B(Å) | $R_1$(Å) | $R_2$(Å) | $\beta_1$(eV) | $\beta_2$(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

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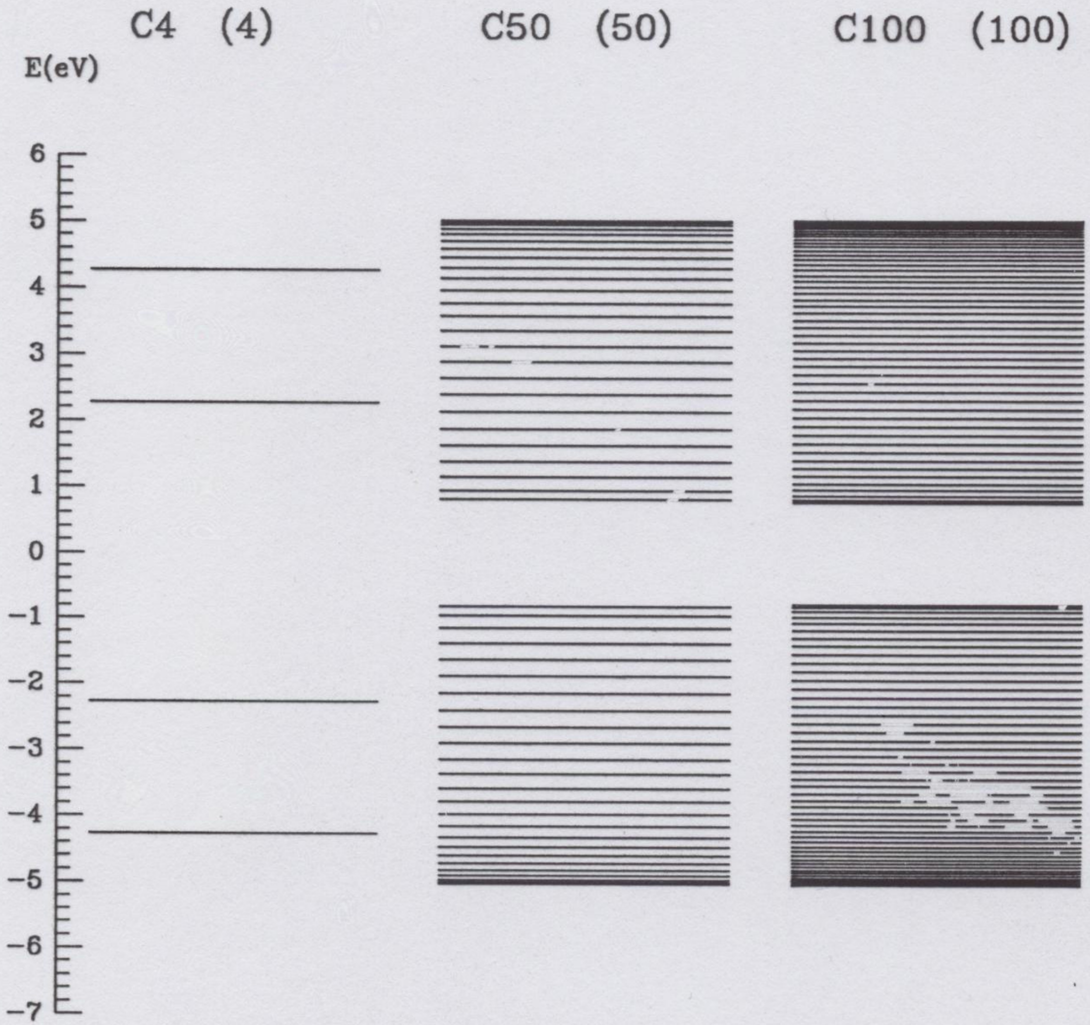
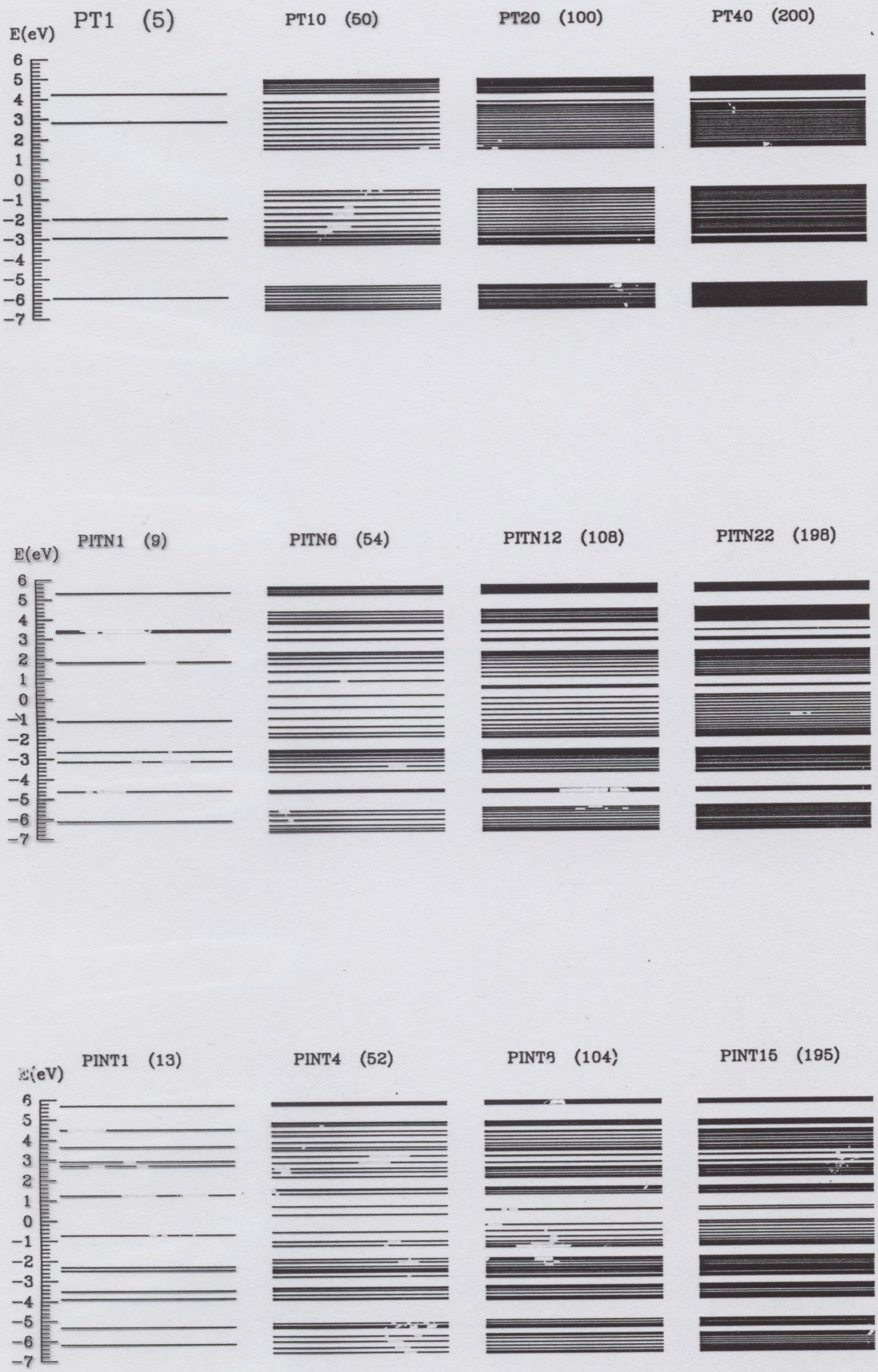

C4 (4)
C50 (50)
C100 (100)
E(eV)
6
5
4
3
2
1
0
−1
−2
−3
−4
−5
−6
−7



E(eV)
PT1 (5)
PT10 (50)
PT20 (100)
PT40 (200)
6
5
4
3
2
1
0
−1
−2
−3
−4
−5
−6
−7
E(eV)
PITN1 (9)
PITN6 (54)
PITN12 (108)
PITN22 (198)
E(eV)
PINT1 (13)
PINT4 (52)
PINT8 (104)
PINT15 (195)

# Su – Schrieffer – Heeger modell

„tight binding"

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

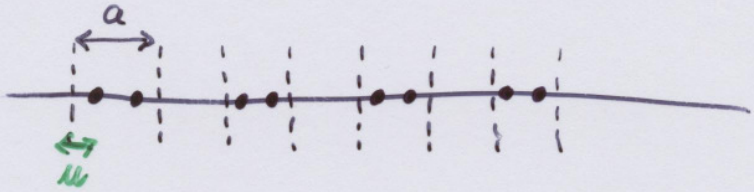
$$H_{\pi} = -\sum_{n,s} \overbrace{\left[t_0 - \alpha(u_{n+1} - u_n)\right]}^{\beta_{n,n+1}} \cdot \left[a^{+}_{n+1,s}\, a_{n s} + a^{+}_{n,s}\, a_{n+1,s}\right]$$

$\beta_0$    el-ph csat. $\sim \frac{\partial \beta}{\partial r}$

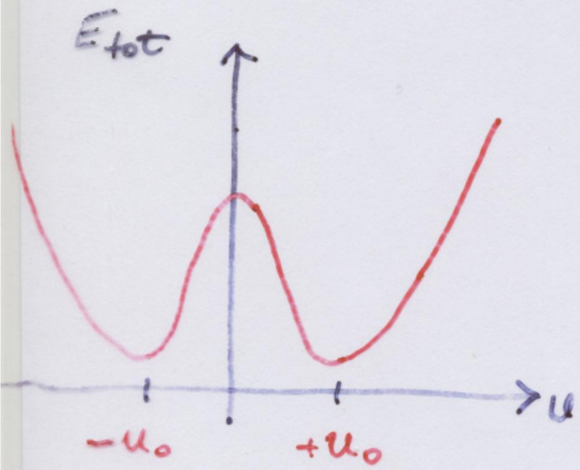
$$H_{\sigma} = \frac{1}{2} K \sum_n (u_{n+1} - u_n)^2$$

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

! $u_n = (-1)^n u$




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

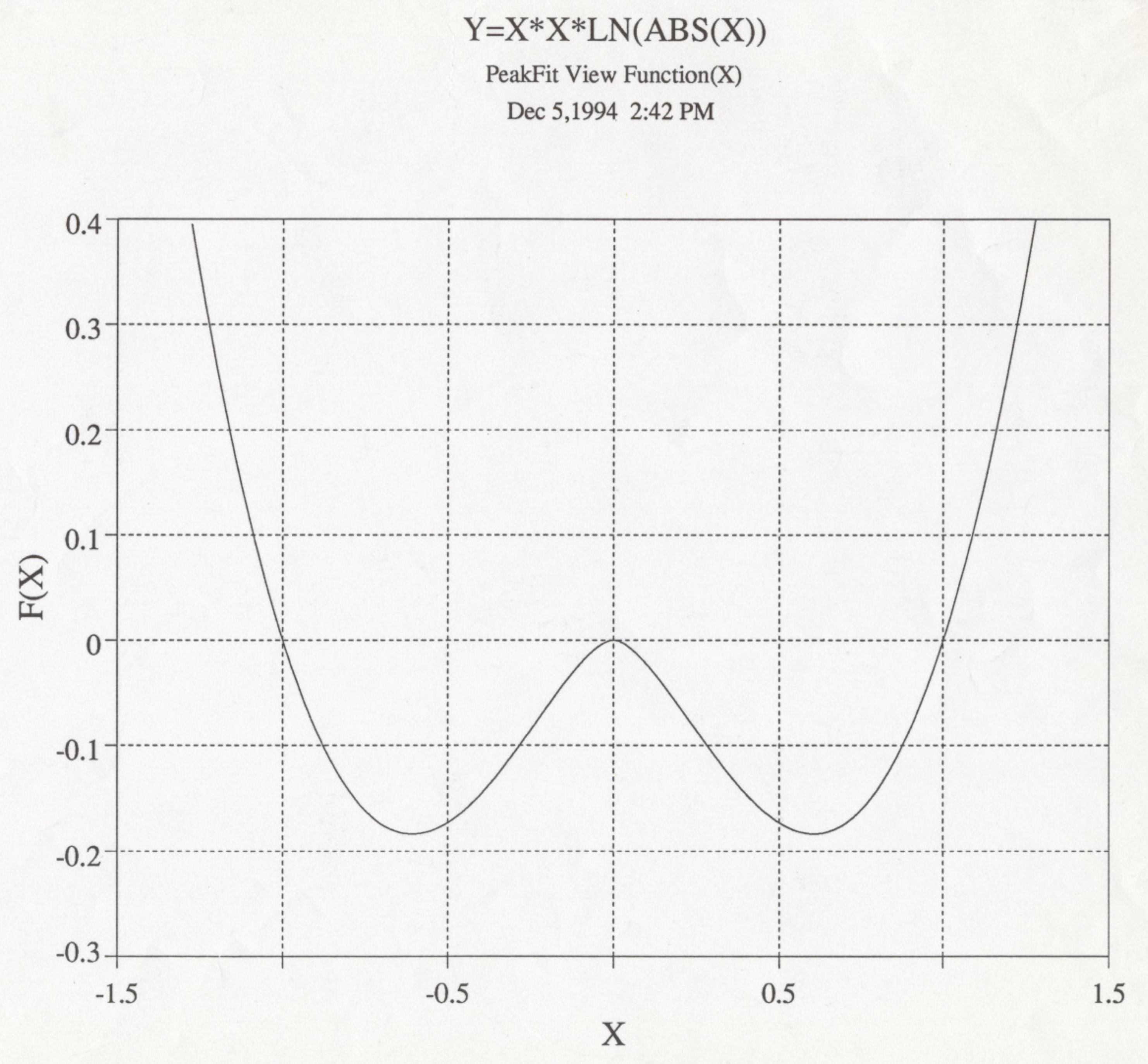



$$\frac{1}{N} \cdot E_{tot}(u) = A + \overbrace{B \cdot u^2 \ln\left(\frac{u}{a}\right)}^{\pi} + \frac{1}{2} K u^2$$

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

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

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


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