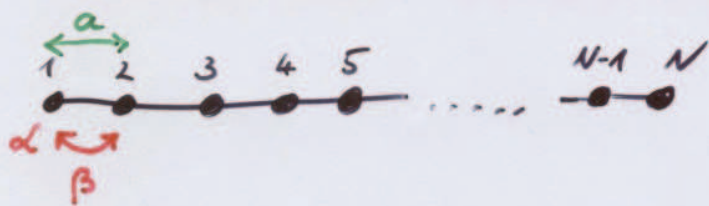


Lineáris lánc, azonos atomok és kötések



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

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

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

$$\hat{H} = \begin{pmatrix} \alpha & \beta & 0 & 0 & \dots \\ \beta & \alpha & \beta & 0 & \dots \\ 0 & \beta & \alpha & \beta & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

$$S = \begin{pmatrix} \chi_j \\ \chi_{j+1} \\ \chi_{j+2} \\ \vdots \end{pmatrix}$$

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

$$(E^{(k)} S) = \underline{C}^{(k)}$$

$$\underline{H} \underline{C}^{(k)} = E^{(k)} \underline{C}^{(k)}$$

$$\Rightarrow \beta C_{j-1}^{(k)} + \alpha C_j^{(k)} + \beta C_{j+1}^{(k)} = E^{(k)} C_j^{(k)}$$

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

$$(E^{(k)} \{S C_{j-1} + C_j + S C_{j+1}\})$$

$$S=0$$

$$\boxed{\alpha + 2\beta \cos ka = E(k)}$$

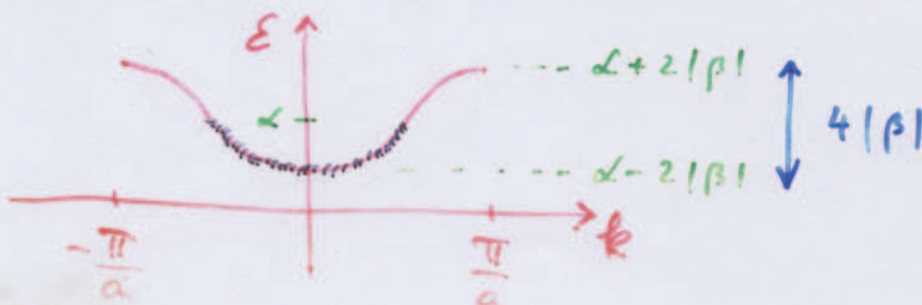
$$\left(\frac{\alpha + 2\beta \cos ka}{1 + 2S \cdot \cos ka} \right)$$

periódikus határfeltétel:

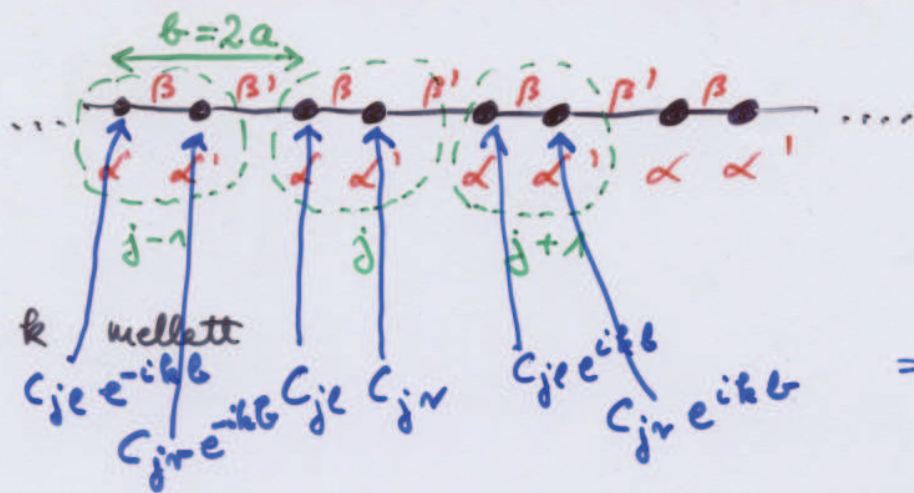
$$C_{j+N} \equiv C_j \Rightarrow e^{i \underbrace{kNa}_{2\pi \cdot \text{egész}}} \equiv 1$$

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

, N ftlen



lineáris lánc, dimerizálódás



Adott k mellett

$$\begin{aligned}
 & C_{je} e^{-ikb} \\
 & C_{jr} e^{-ikb} \\
 & C_{je} \\
 & C_{jr} \\
 & C_{je} e^{ikb} \\
 & C_{jr} e^{ikb}
 \end{aligned}
 \Rightarrow$$

$$\begin{pmatrix}
 \vdots \\
 C_{je} e^{-ikb} \\
 C_{jr} e^{-ikb} \\
 C_{je} \\
 C_{jr} \\
 C_{je} e^{ikb} \\
 C_{jr} e^{ikb} \\
 \vdots
 \end{pmatrix}$$

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

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

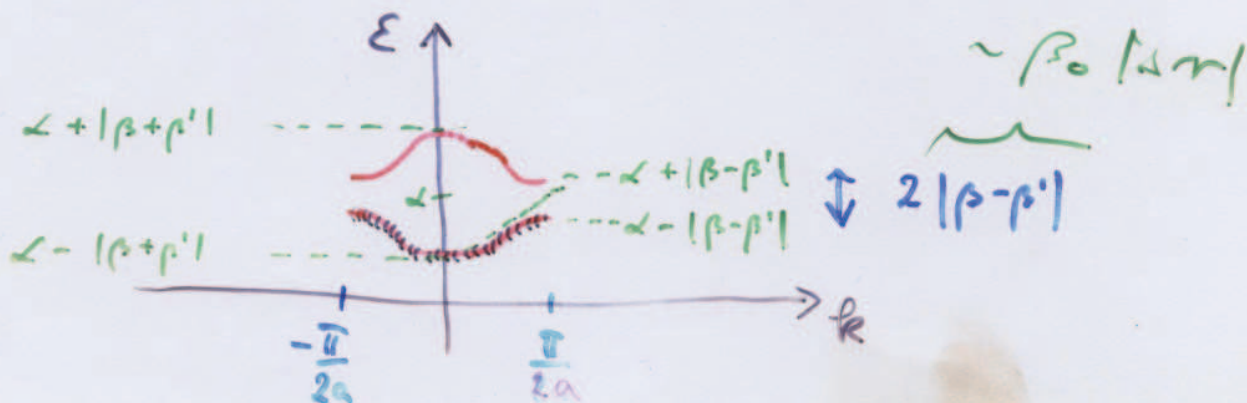
$$\Rightarrow \begin{pmatrix} \alpha & \beta + \beta' e^{-ikb} \\ \beta + \beta' e^{ikb} & \alpha' \end{pmatrix} \begin{pmatrix} C_{je} \\ C_{jr} \end{pmatrix} = \epsilon(k) \begin{pmatrix} C_{je} \\ C_{jr} \end{pmatrix}$$

$$\Rightarrow \epsilon(k)^2 - (\alpha + \alpha') \epsilon(k) + [\alpha \alpha' - (\beta + \beta' e^{-ikb}) \cdot (\beta + \beta' e^{ikb})] = 0$$

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

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

Spec. $\alpha = \alpha'$



LHS - modell : $\begin{matrix} \rightarrow \pi\text{-elektronok} \\ \downarrow \sigma\text{-elektronok} \end{matrix}$ \leftarrow Hückel \leftarrow σ -potencial

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

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

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

$p_m = \frac{1}{2} \sum_i \left(C_k^{(i)*} C_l^{(i)} + C_l^{(i)*} C_k^{(i)} \right) \cdot n_i$
 $k, l \Rightarrow m$ $n_i = 0, 1$

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

(atomok) (közös)

$$q_j = \frac{\partial E_{\pi, \text{tot}}}{\partial \alpha_j}$$

$$p_m = \frac{1}{2} \frac{\partial E_{\pi, \text{tot}}}{\partial \beta_m}$$

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

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

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

Egyenlet:

$$\frac{\partial E_{\text{tot}}}{\partial r_m} = 0 \Rightarrow \frac{d f_m}{d r_m} + \frac{\partial E_{\pi, \text{tot}}}{\partial \beta_m} \cdot \frac{d \beta_m}{d r_m} = 0 \Rightarrow$$

$\frac{\partial E_{\pi, \text{tot}}}{\partial \beta_m} \equiv 2 p_m$

La $r = R_1 - (R_1 - R_2) \cdot p$ (Cs)

\Downarrow

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

LHS MODEL

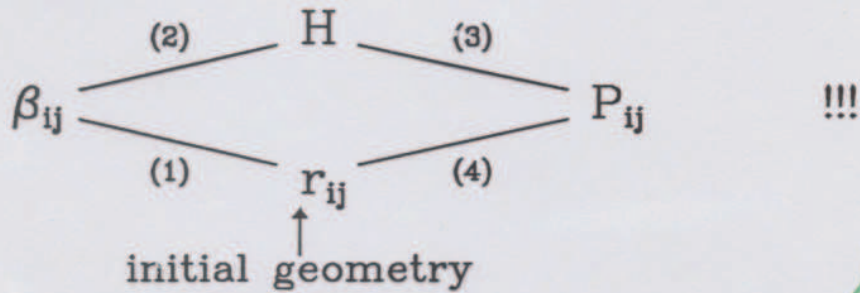
~ SSH

(Donquet - Higgins, Salem)

- HAMILTONIAN (HUECKEL) :

$$H = \sum_i \alpha_i a_i^\dagger a_i + \sum_{i < j} \beta_{ij} (a_j^\dagger a_i + a_i^\dagger a_j) + \sum_k f(r_k) \quad \dots(2)$$

- GEOMETRY OPTIMIZATION :



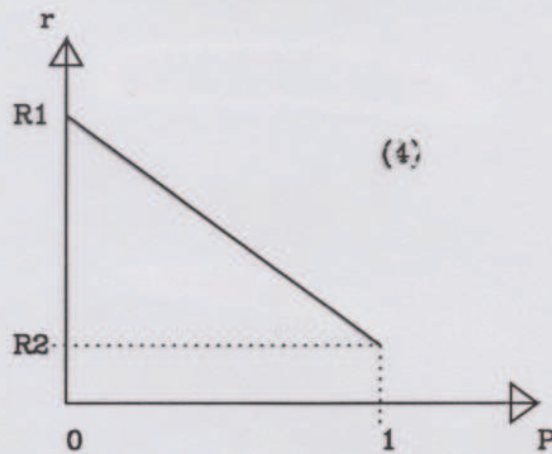
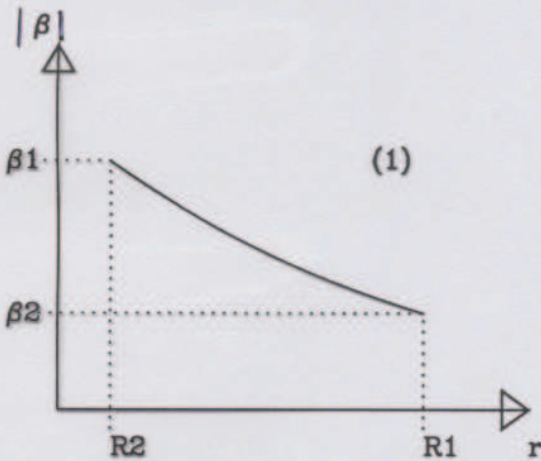
where

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

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

$$\text{Coulson's relation : } r_{ij} = R_1 - (R_1 - R_2) P_{ij} \quad \dots(4)$$

$$\text{Resonance integral : } \beta_{ij} = -A \exp(-r_{ij}/B) \quad \dots(1)$$



Some results for conjugated polymers without heteroatoms:

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

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

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
$r_{<}(\text{Å})$	1.3704	1.3654	1.3634	1.3629	1.3624	1.3604	1.3554
$r_{>}(\text{Å})$	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: $\zeta = 1.72$ (Helme et al.)

$$\Rightarrow B_{\zeta} = \frac{a_0}{\zeta} = \frac{0.529}{1.72} = 0.3076$$

$$(CH)_x : !E_g = 1.5 \text{ eV} \Rightarrow \underline{A} = 243.5 \text{ eV}$$

Table 1: Parameters used in the LHS calculations. N_r is the number of π -electrons per atom. B_0 is the resonance integral for the bond in benzene ($r = 1.4 \text{ Å}$).

$$\beta_0 = -2.564 \text{ eV}$$

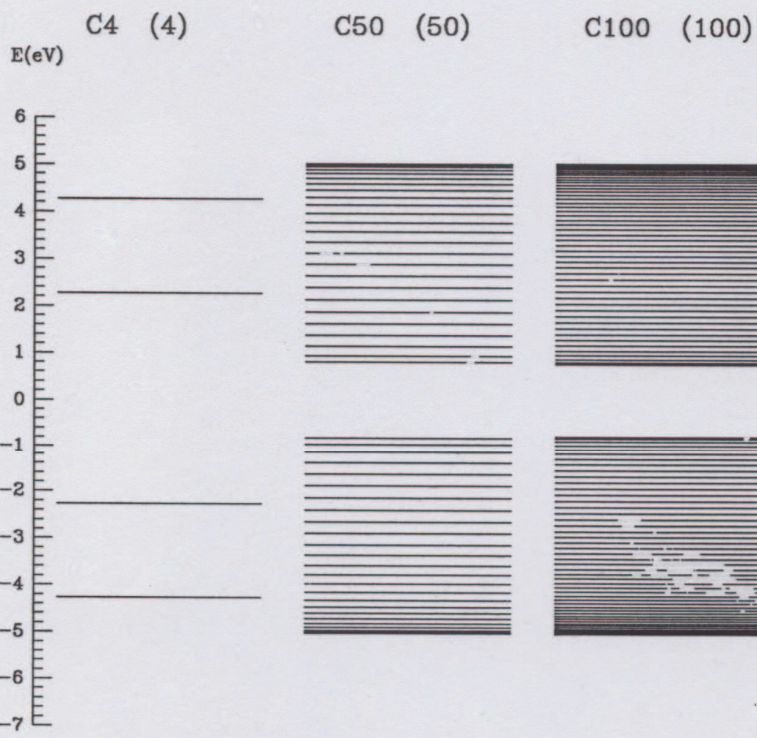
X	N_r	α/B_0	A (eV)	B (Å)	R_1 (Å)	R_2 (Å)	B_1 (eV)	B_2 (eV)
C	1	0.0	243.5	0.3075	1.54	1.33	-1.626	-3.220
-S-	2	1.5	1938.1	0.2580	1.82	1.71	-1.674	-2.564

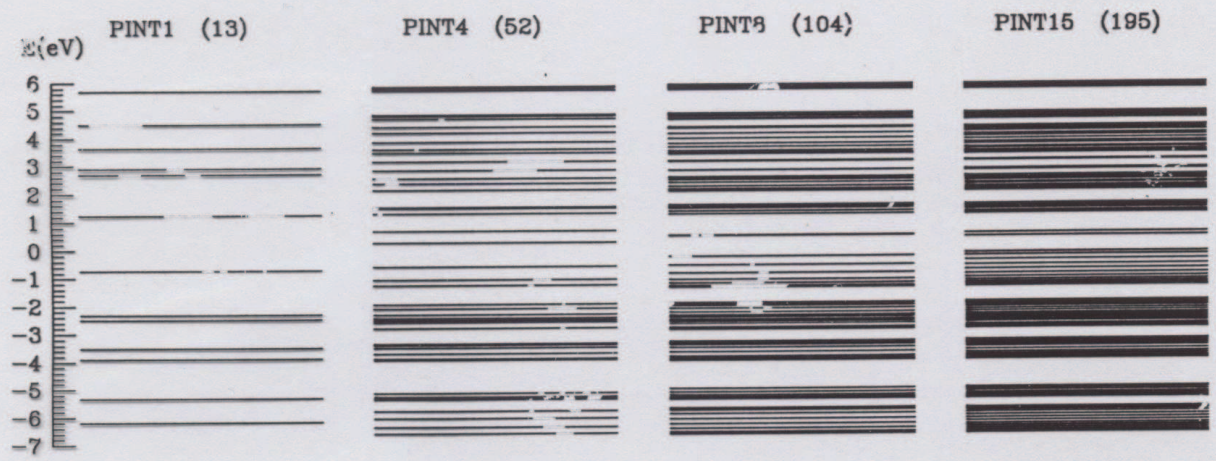
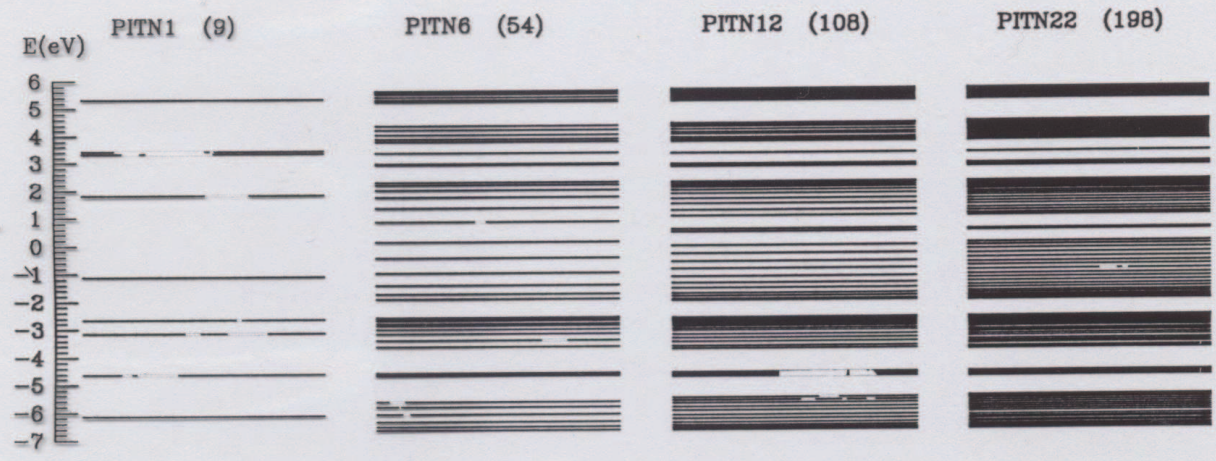
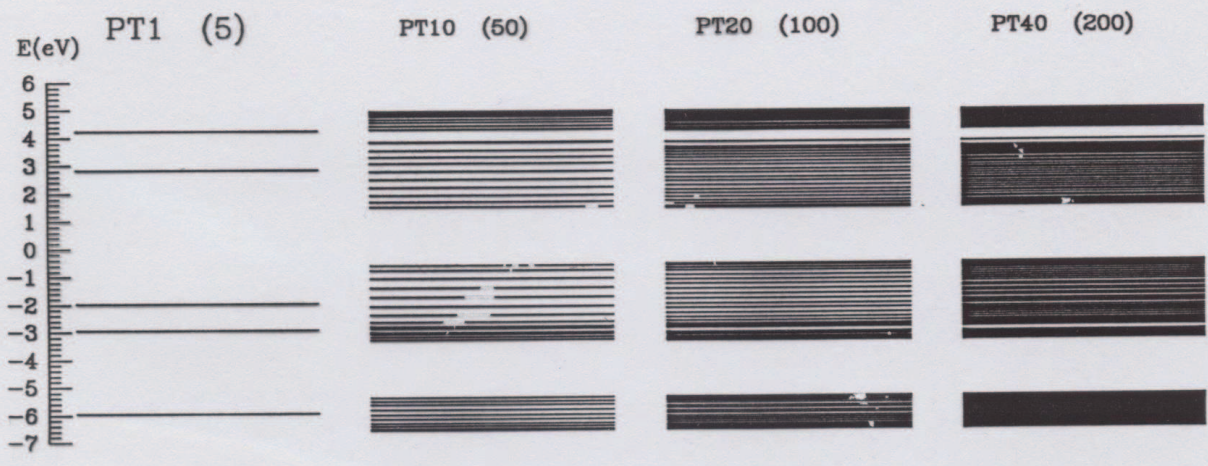
Strukturierer

from Slater exponents

standard values

Strukturierer





Su-Schrieffer-Heeger modell "tight binding"

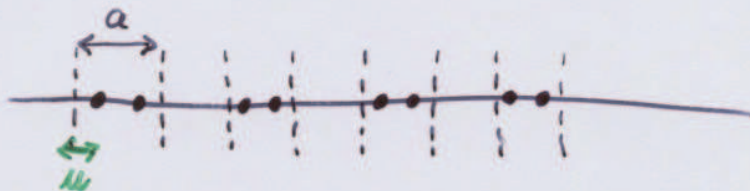
$$H_{SSH} = H_T + H_G + H_{kin}$$

$$H_T = - \sum_{n,s} \left[\underbrace{t_0}_{\beta_0} - \underbrace{d(\mu_{n+1} - \mu_n)}_{\text{d-ph. crt.}} \right] \cdot \left[a_{n+1,s}^+ a_{n,s} + a_{n,s}^+ a_{n+1,s} \right] \sim \frac{\partial \beta}{\partial t}$$

$$H_G = \frac{1}{2} K \sum_n (\mu_{n+1} - \mu_n)^2$$

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

$$\mu_n = (-1)^n u$$



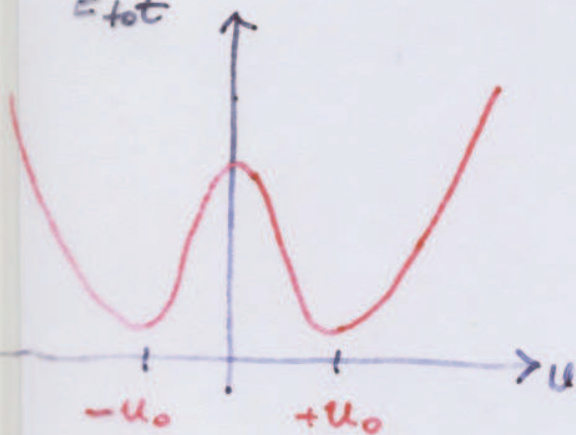
$$\dot{\mu}_n \equiv 0 \Rightarrow$$

\Rightarrow

$$\left. \frac{dE_{tot}}{du} \right|_{u_0} = 0$$

$$u_0 \neq 0!$$

E_{tot}



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

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

$$\text{ahol} \quad \lambda = \frac{2d^2}{Kt_0\pi}$$

$$E_g = 8d \cdot u_0$$

$$Y=X*X*LN(ABS(X))$$

PeakFit View Function(X)

Dec 5,1994 2:42 PM

