MACROMOLECULES

lecture for physics and biophysics students

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LHS model: Hückel theory with geometry (bond length) optimization (Longuet-Higgins, Salem; 1959)

LHS - modell : π - elektronok ← Hückel
+
σ - elektronok ← 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 : $f_\sigma(r) \Rightarrow E_{\sigma,tot} = \sum_m f_\sigma(r_m)$

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

Egyensúly: (r_m függvényei)

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

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

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

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

COULSON relation

LHS model: Hückel theory with geometry (bond length) optimization (Longuet-Higgins, Salem; 1959)

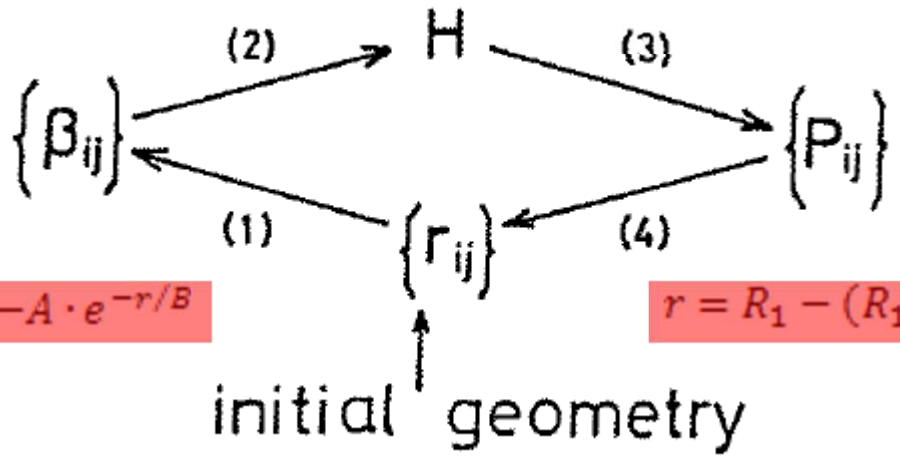
$$H = \sum_i \alpha_i \cdot a_i^+ a_i + \sum_{i<j} \beta_{ij} \cdot (a_j^+ a_i + a_i^+ a_j) + \left(\sum_k f_\sigma(r_k) \right)$$

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

p_m (mobile) bond order:

$$p_m = \frac{1}{2} \sum_i (C_k^{i*} C_l^i + C_l^{i*} C_k^i) \cdot n_i \quad where \quad m:(k,l)$$

$$\varphi^i(r) = \sum_j C_j^i \cdot \vartheta_j(r) \quad \text{MO - LCAO}$$



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

$$r = R_1 - (R_1 - R_2) \cdot p$$ Coulson relation

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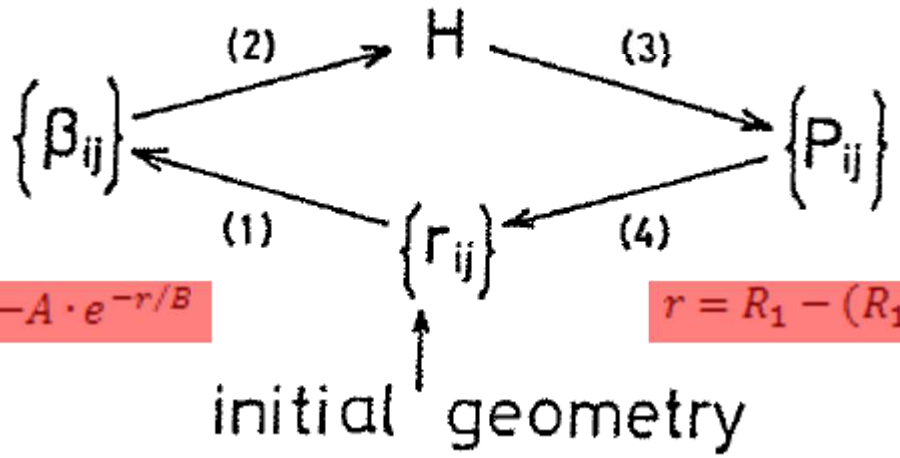

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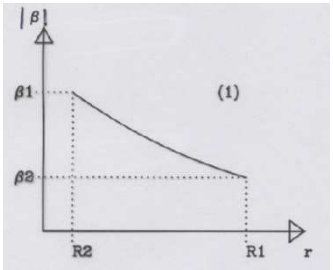
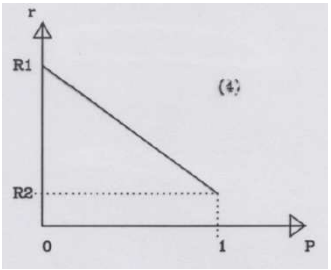
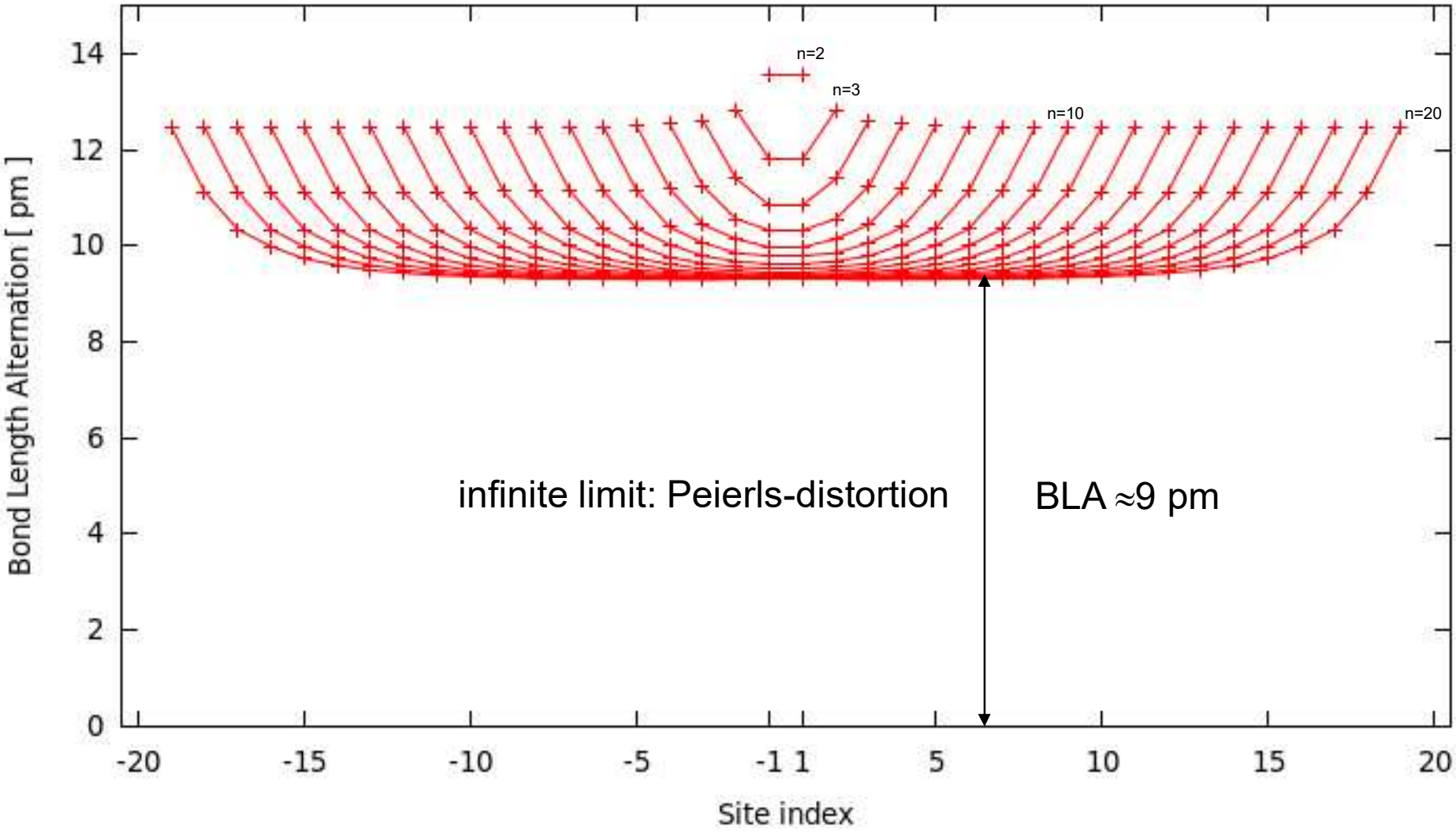




LHS results for BLA along $C_{2n}H_{2n+2}$ chains



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: $\zeta = 1.72$ (Clark et al.)

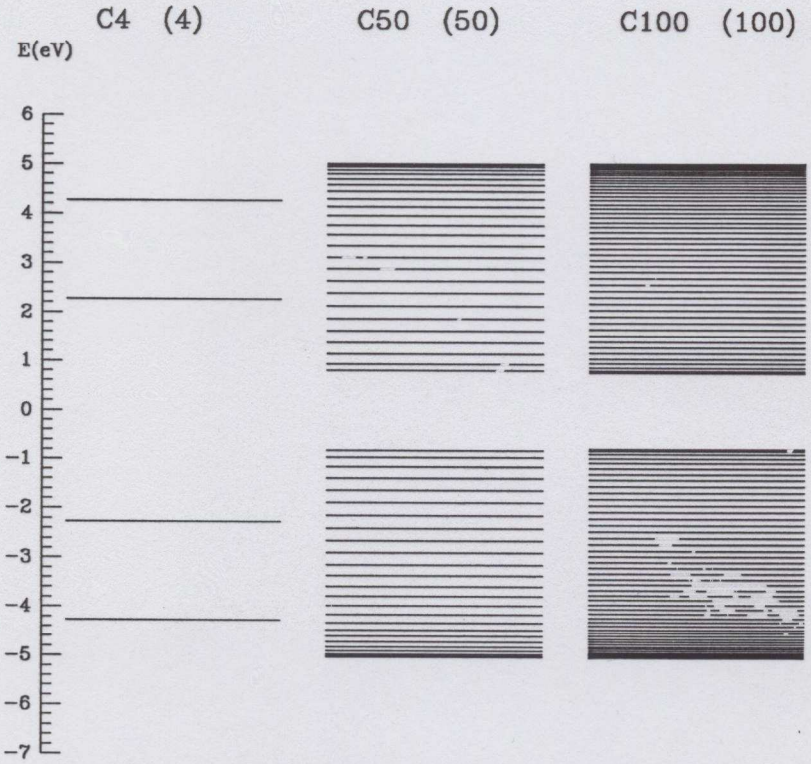
$\Rightarrow B_\zeta = \frac{a_0}{\zeta} = \frac{0.529}{\zeta} = 0.3076$

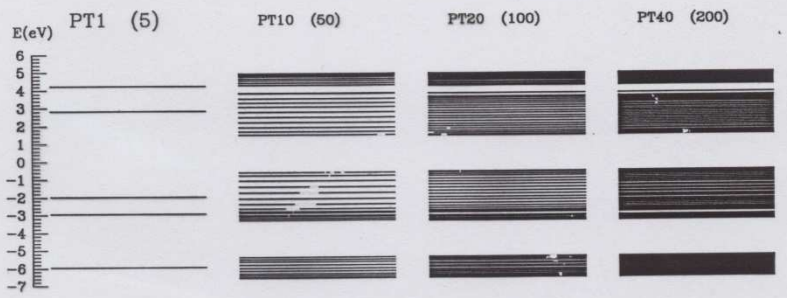
$(CH)_x$: $E_g = 1.5\,eV \Rightarrow A = 243.5\,eV$

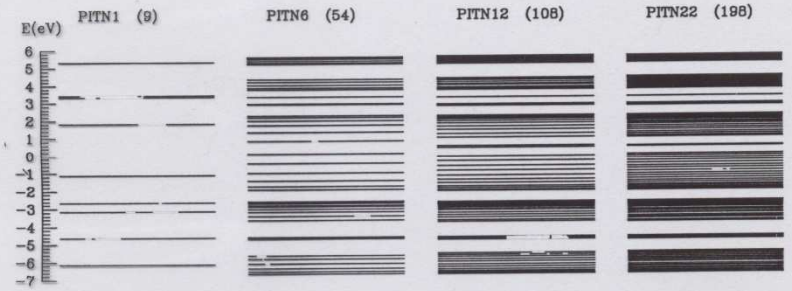
Table 1: Parameters used in the LHS calculations. N_π is the number of π-electrons per atom. β_0 is the resonance integral for the bond in benzene (r = 1.4 Å). $\beta_0 = -2.564$ eV

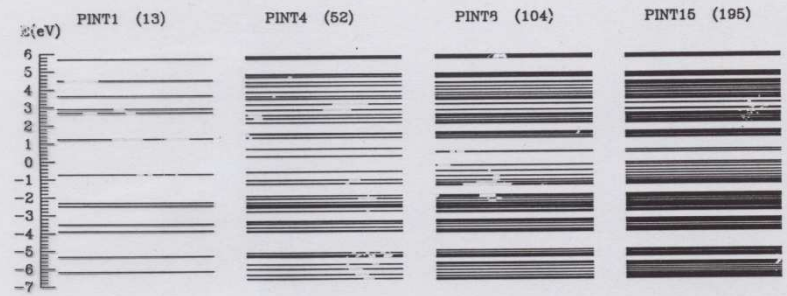
X	N_π	α/β_0	A(eV)	B(Å)	R_1(Å)	R_2(Å)	β_1(eV)	β_2(eV)
C	1	0.0	243.5	0.3075	1.54	1.33	-1.626	-3.220
-S-	2	1.5	1938.1	0.2580	1.82	1.71	-1.674	-2.564

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


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)
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7


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

Su – Schrieffer – Heeger modell

„tight binding"

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

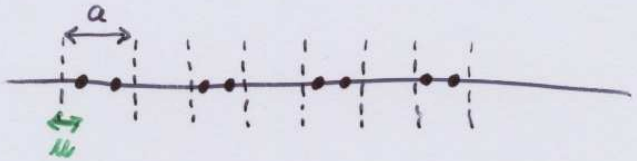
$$H_\pi = -\sum_{n,s}\left[t_0 - \alpha(u_{n+1}-u_n)\right]\cdot\left[a^+_{n+1,s}a_{n,s} + a^+_{n,s}a_{n+1,s}\right]$$

$\beta_{n,n+1}$; β_0; el-ph wech. $\sim \frac{\partial\beta}{\partial t}$

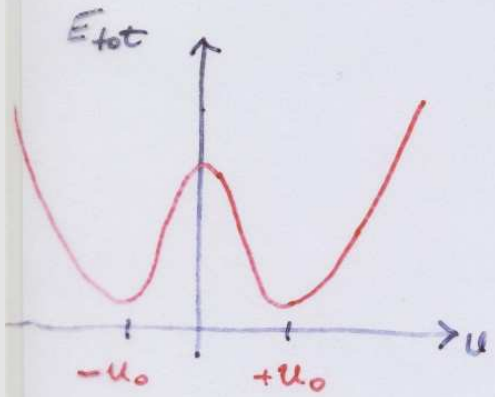
$$H_\sigma = \frac{1}{2}K\sum_n (u_{n+1}-u_n)^2$$

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

$u_n = (-1)^n u$



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



π

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

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

also $\quad \lambda = \frac{2\alpha^2}{Kt_0\pi}$

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

$$I(k) \sim \int_0^{\pi/2} \frac{\sin^2 x \, dx}{\sqrt{1 - k^2 \sin^2 x}} \quad ; \quad k^2 = 1 - \left(\frac{\Delta\beta}{\beta}\right)^2$$

$\Delta\beta \to 0 \Rightarrow k^2 \to 1 \Rightarrow$

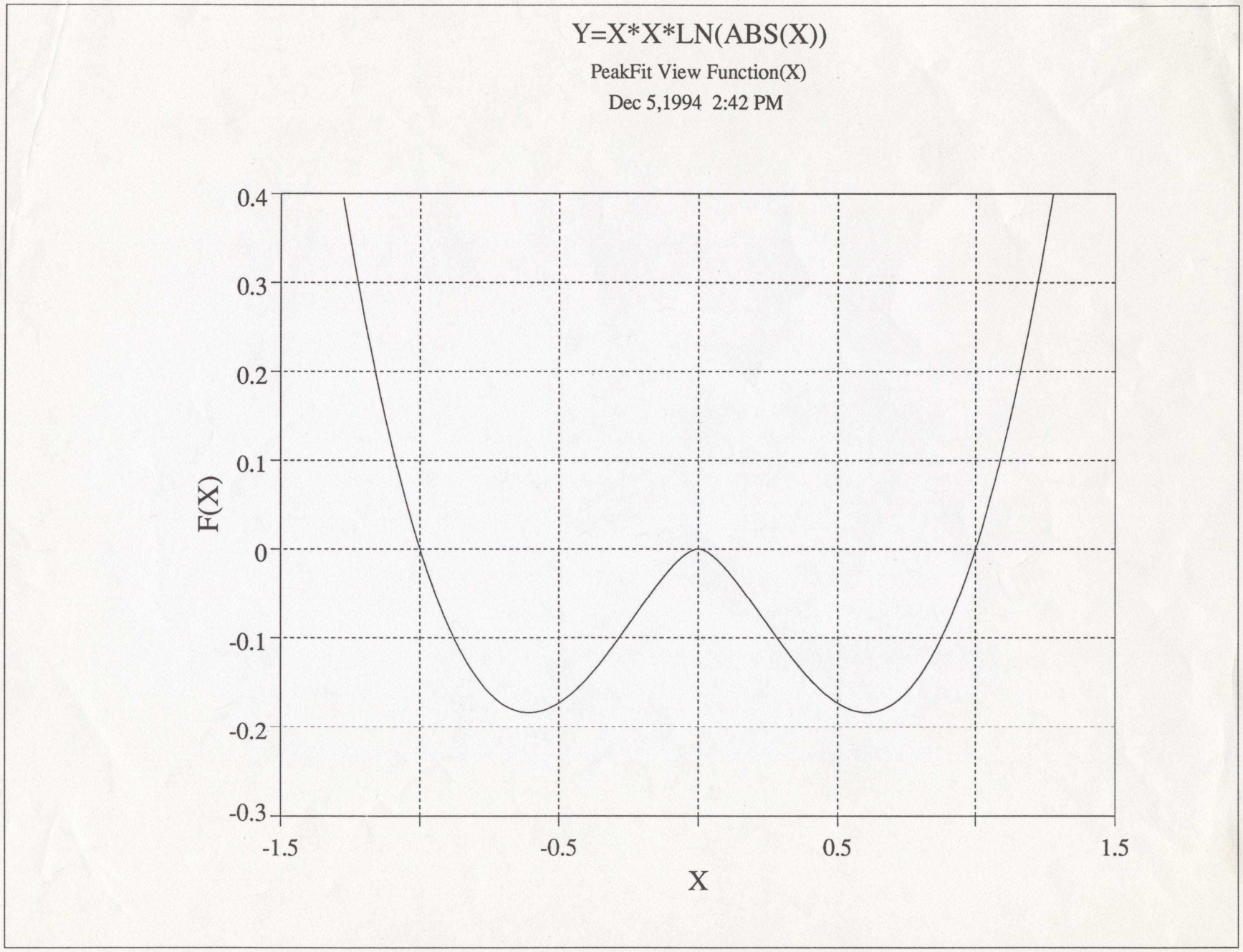
$\Rightarrow I(k) \to \infty$

$\pi/2$ kürzt $\quad x = \frac{\pi}{2} - y \Rightarrow \sin^2 x = 1 - y^2$

$$\Rightarrow I \propto \int_0^{\text{„ewig“}} dy \, \frac{1}{\sqrt{1 - k^2(1-y^2)}} = \dots$$

$$\int \frac{dz}{\sqrt{z^2 + a^2}} = \operatorname{arsh} \frac{z}{a} \ln\left(z + \sqrt{z^2 + a^2}\right) + C$$

$\Rightarrow$ $M_0 \sim \Delta\beta_0 \sim e^{-\frac{1}{\text{„el-ph c}}}$


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