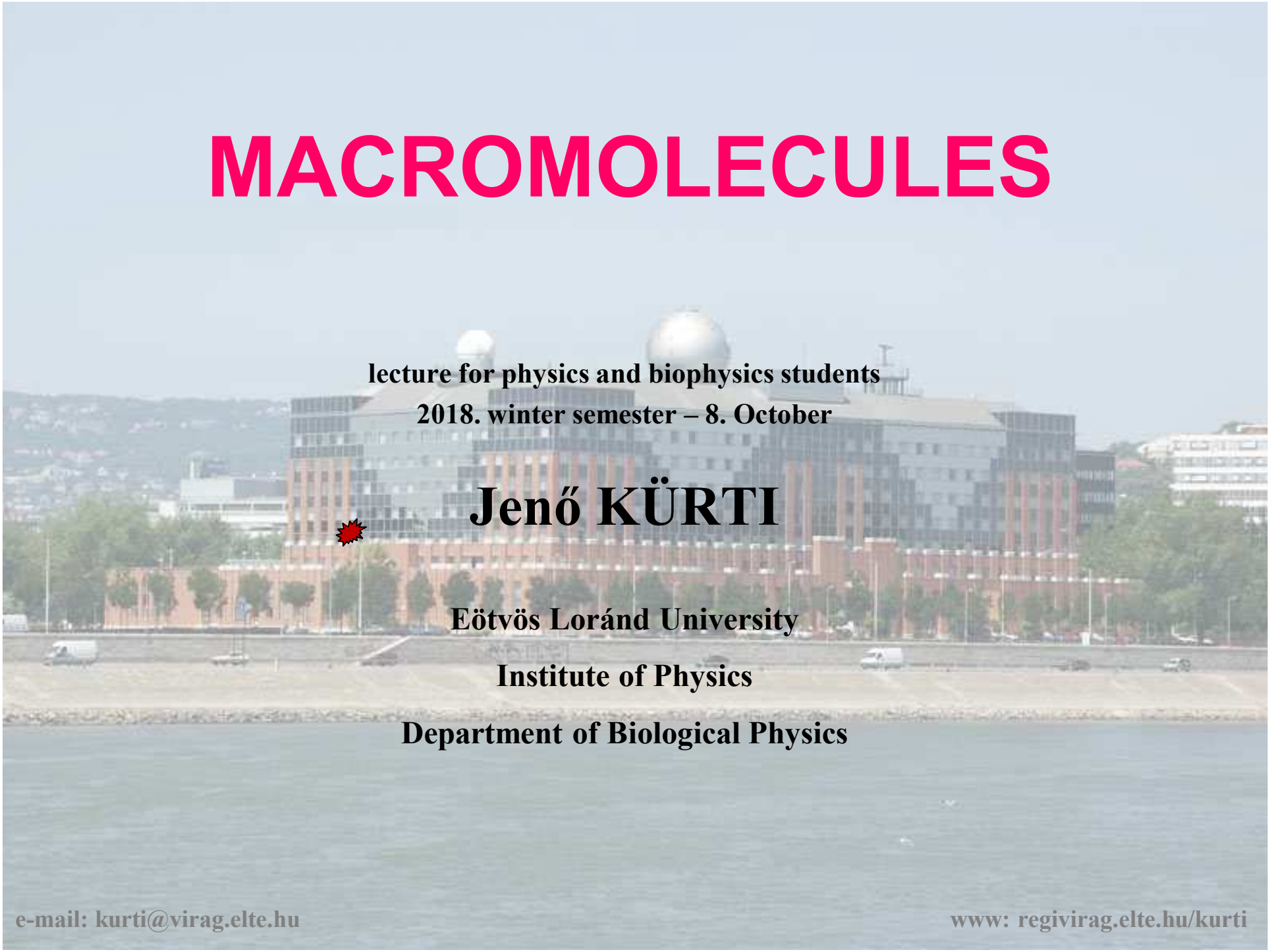
MACROMOLECULES



lecture for physics and biophysics students

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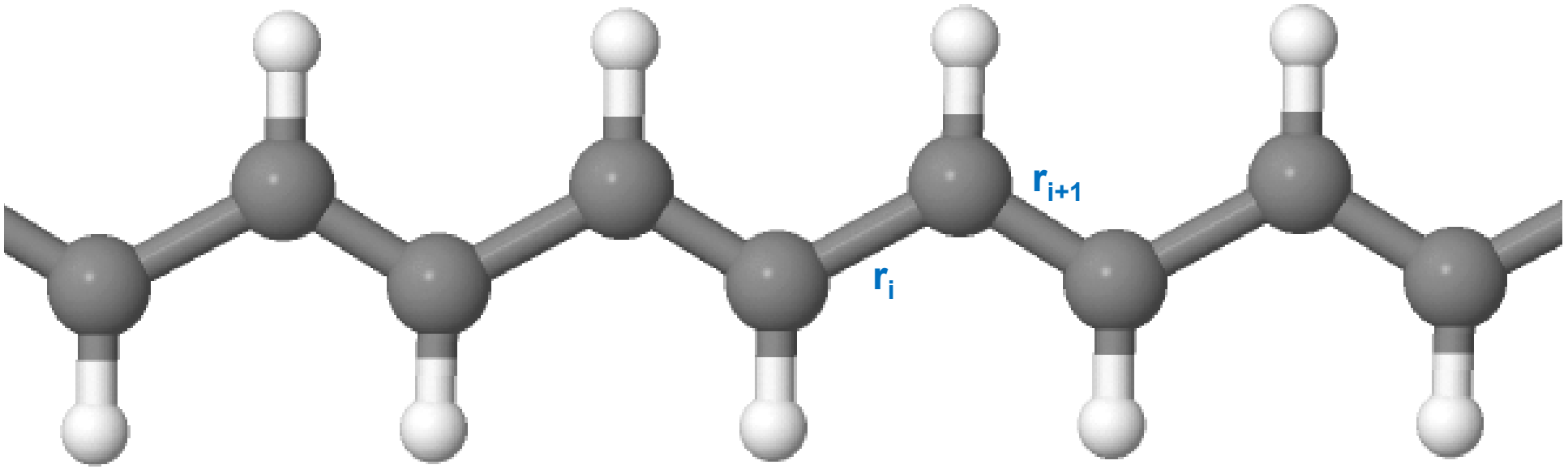
Bond Length Alternation: $BLA_i = |r_{i+1} - r_i|$



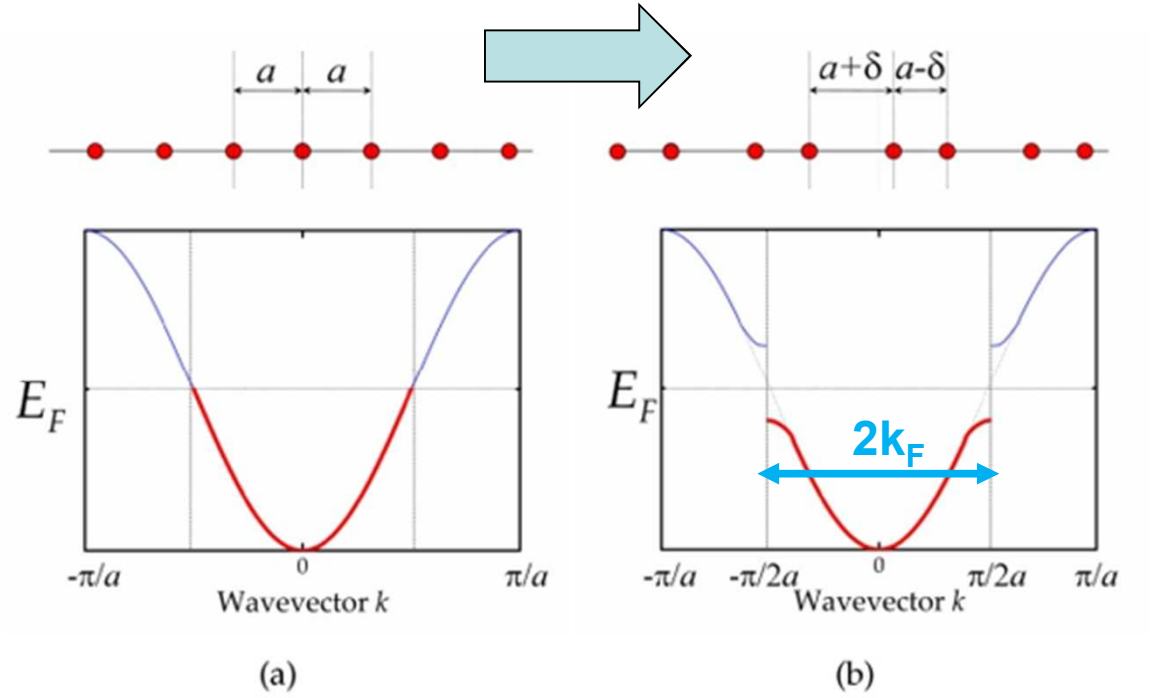
physics student (not well educated): BLA = 0 ☹

chemistry student (average) : BLA = $R_1 - R_2 \approx 21$ pm 😐

physics student (well educated): $0 \leq BLA \approx 9 \text{ pm} \leq R_1 - R_2$ ☺

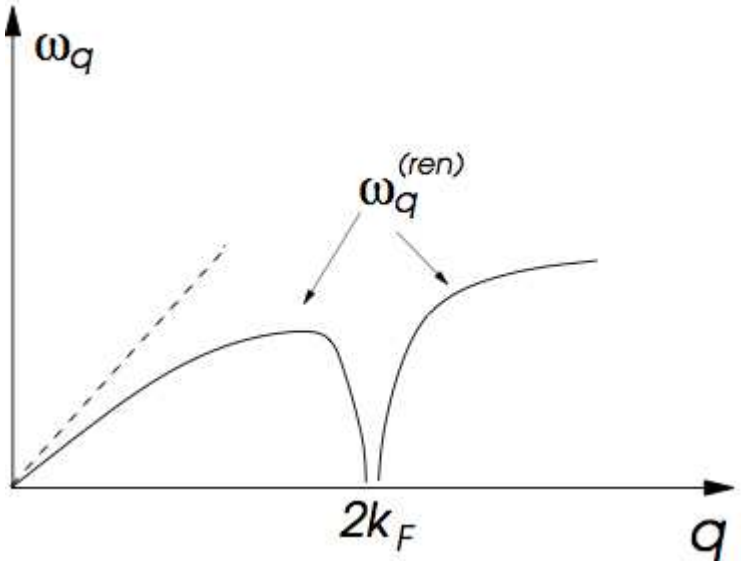
↓

Peierls-distortion



Peierls-instabilitás

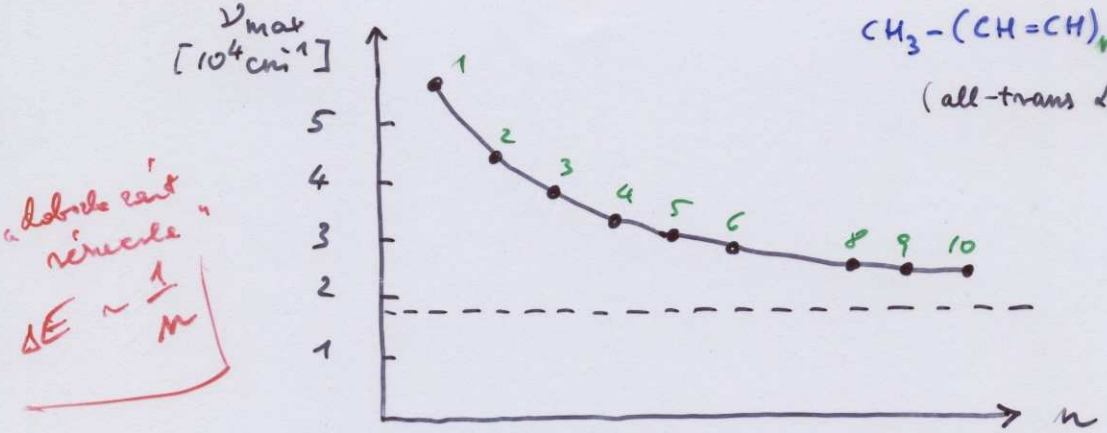
(https://www.utwente.nl/tnw/pin/onderzoek/physical_properties_of_low-dimensional_systems/physical_properties_of_low-dimensional_systems-8.png)



Kohn anomália (http://www.itp.phys.ethz.ch/education/fs14/sst/slides/Peierls.pdf)

Mit mondanak a kísérletek?

i) gap



$CH_3-(CH=CH)_n-CH_3$

(all-trans α,ω dimethylpo

„dobozba zárt részecske"

$\Delta E \sim \frac{1}{n}$

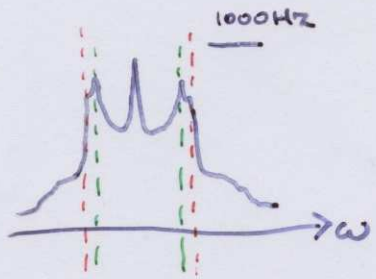
Konjugált polimerekben $E_g \approx 1{,}5-4$ eV

H_2C =CH - CH

ii) alternálás

$(CH)_x$ ^{13}C NMR (Yannoni, Clark)

Előállításnál: keverő $H-{}^{13}C\equiv{}^{13}C-H$ is!



Felhasadás dipól-dipól kh. miatt

$\Rightarrow$ $r_1 = 1{,}44$ Å

$r_2 = 1{,}36$ Å

Konjugált polimerek kvantumkémiai leírása

- Born-Oppenheimer (adiabatikus) közelítés

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

- 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

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

MO, AO

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

Másodkvantált formalizmusban:

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

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

első szomszédok

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 hopping integral

Spec. azonos atomok

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

TOPOLÓGIA

HUBBARD – MODELL

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

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

Spec. azonos atomok

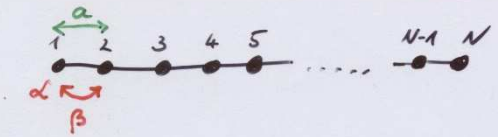
$$\hat{H} = \alpha \sum_{n} \sum_{s} a^{+}_{ns} a_{ns} + \beta \sum_{i} \sum_{s} \left(a^{+}_{i_1 s} a_{i_2 s} + a^{+}_{i_2 s} a_{i_1 s} \right) + U \sum_{n} \hat{N}_{n\uparrow} \hat{N}_{n\downarrow}$$

PPP – modell

$$\hat{H} = \sum_{mn, s} h_{mn} a^{+}_{ms} a_{ns} + \frac{1}{2} \sum_{mn} \sum_{s_1 s_2} \gamma_{mn} \hat{N}_{ms_1} \hat{N}_{ns_2} - \frac{1}{2} \sum_{n} \sum_{s} \gamma_{nn} \hat{N}_{ns}$$

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

Lineáris lánc, azonos atomok és kötések



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

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

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

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

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

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

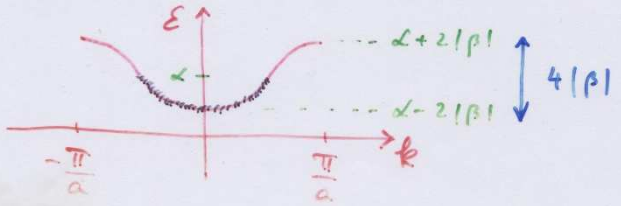
$$\Rightarrow \quad \beta\, c_{j-1}^{(k)} + \alpha\, c_j^{(k)} + \beta\, c_{j+1}^{(k)} = \varepsilon^{(k)} c_j^{(k)} \qquad \left(\varepsilon^{(k)} S c_{j-1} + c_j + S c_{j+1}\right)$$

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

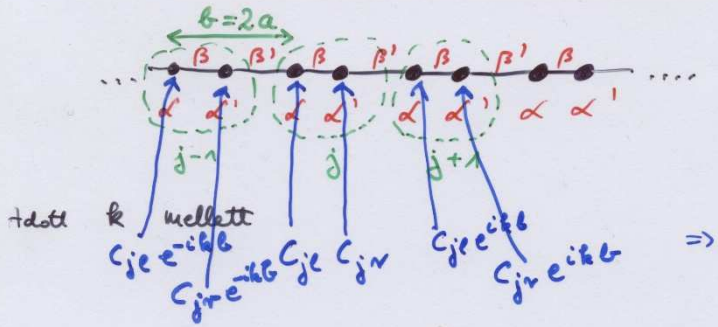
$$\boxed{\alpha + 2\beta \cos ka = \varepsilon(k)} \qquad \left(\frac{\alpha + 2\beta \cos ka}{1 + 2S \cdot \cos ka}\right) \quad S \approx 0$$

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

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



lineáris lánc, linearizálódás



$\Rightarrow$

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

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

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

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

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

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

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

Spec. $\alpha = \alpha'$