

Chemická struktura B

Elektronová struktura molekul

Lubomír Rulíšek, Martin Srnec

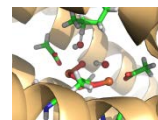
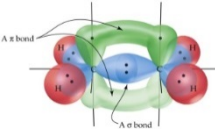
rulisek@uochb.cas.cz; srnec@jh-inst.cas.cz



ÚOCHB AV
ČR
IOCB PRAGUE



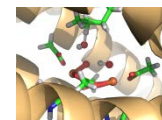
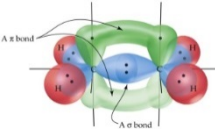
(2016/17: pondělí CH3 8:10–9:40, CH3 9:50–10:35)



Přednáška 3: Shrnutí a obrázky

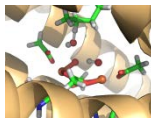
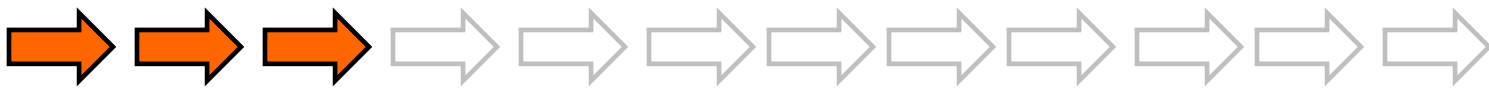
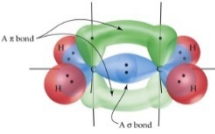
(podrobnější materiál: Atkins, *Molecular Quantum Mechanics*, kapitola 2)

- Obecné vlastnosti a kvalitativní úvahy řešení Schrödingerovy rovnice
- Volná částice
- Bariéra potenciální energie (konečná, nekonečná) - tunelování
- Částice v krabici (jednorozměrné, dvojrozměrné)
- Harmonický oscilátor

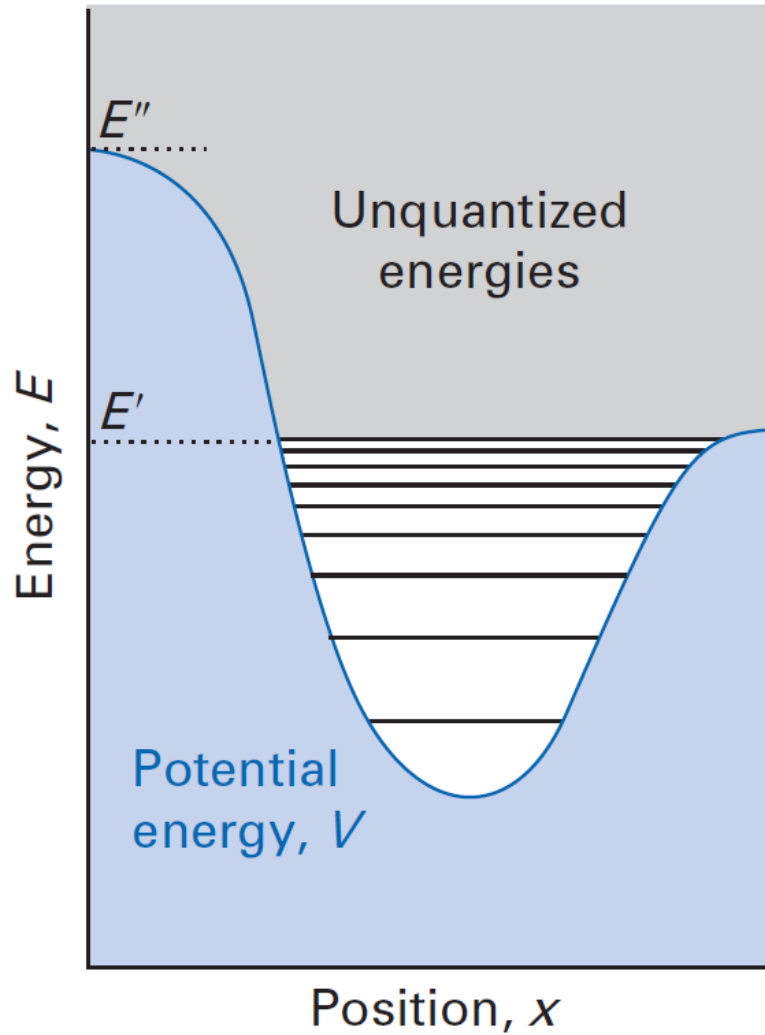


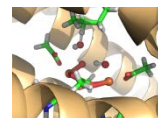
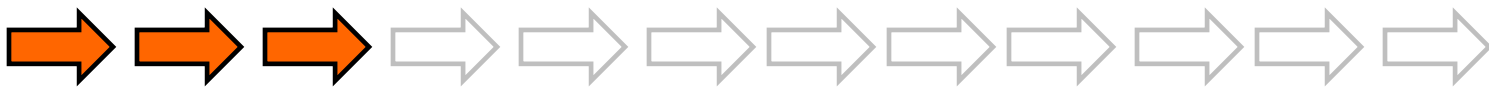
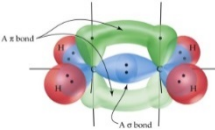
Zakřivení vlnové funkce

	$E < V$	$E > V$
$\psi > 0$		
$\psi < 0$		

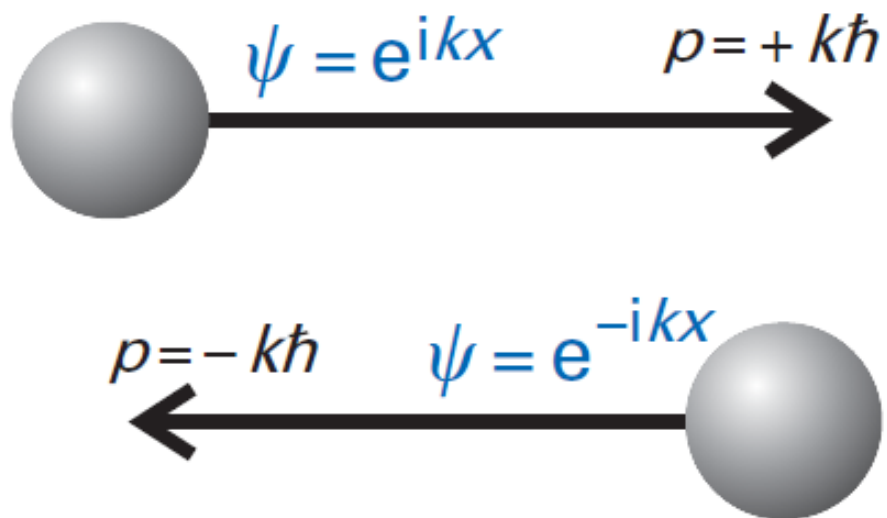


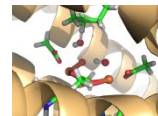
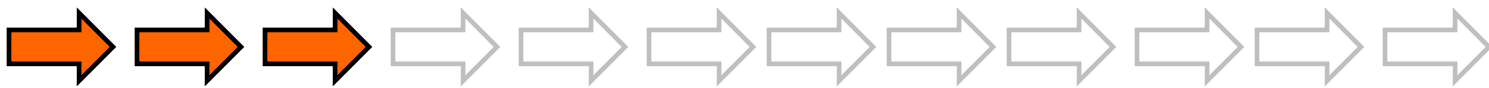
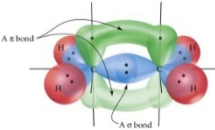
„Ohraničující“ potenciál = kvantování energie



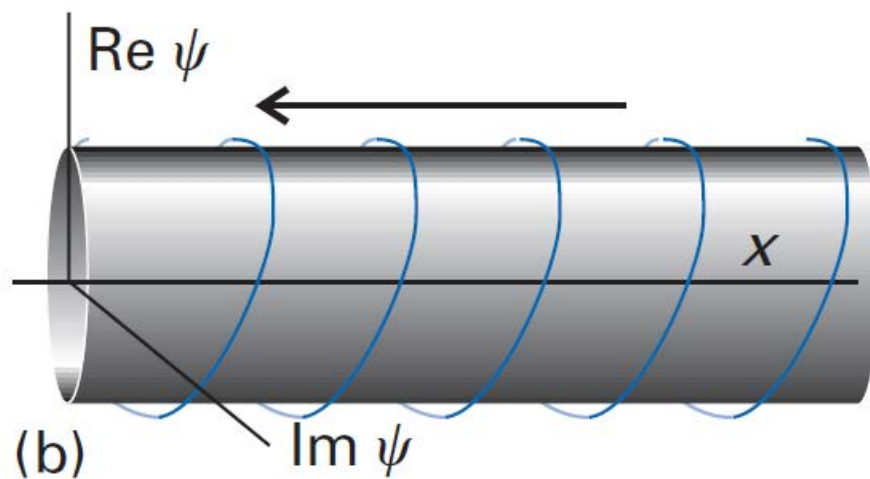
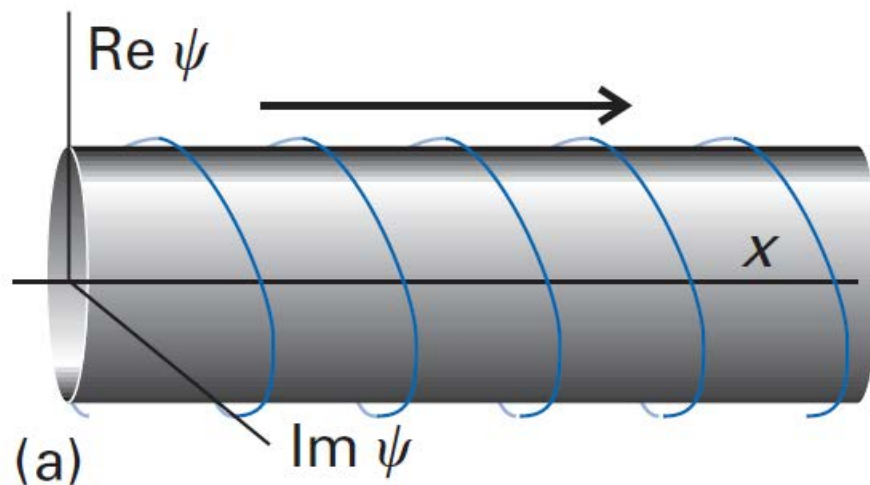


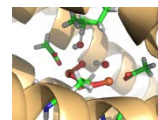
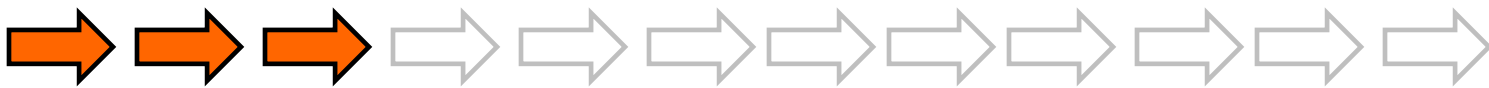
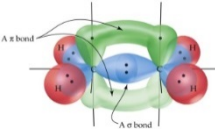
Volná částice – dvě složky vlnové funkce



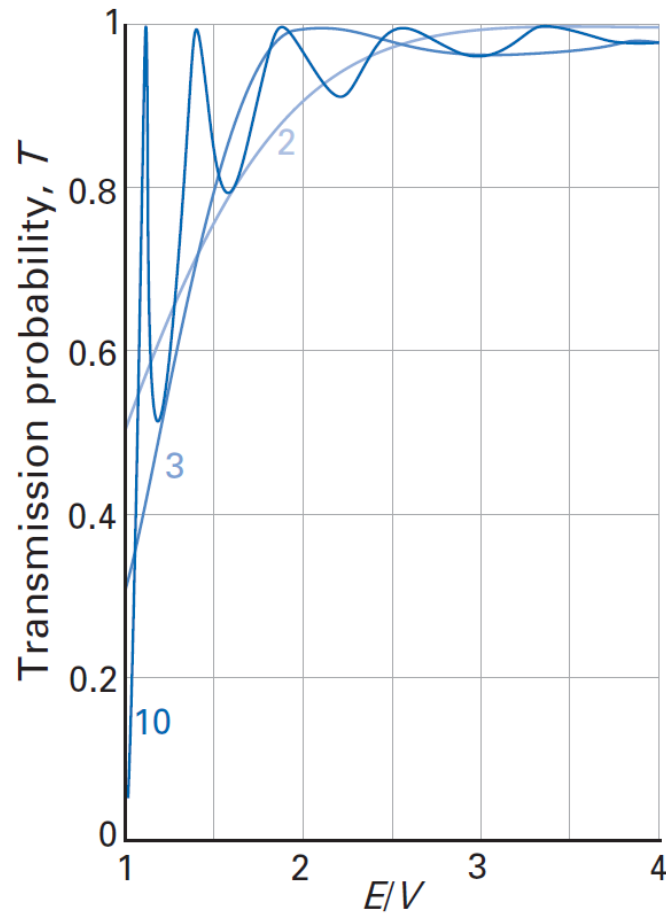
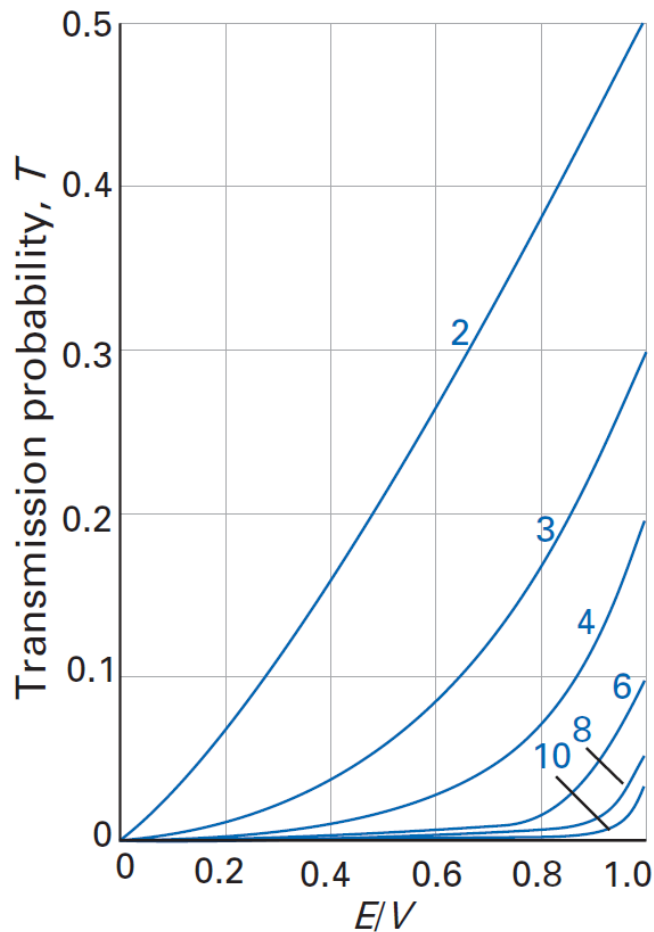


Volná částice – dvě složky vlnové funkce



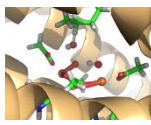
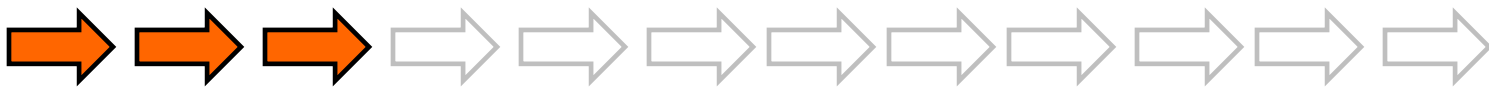
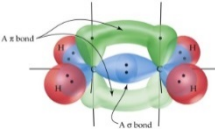


Pravděpodobnost průchodu pravoúhlnou bariérou

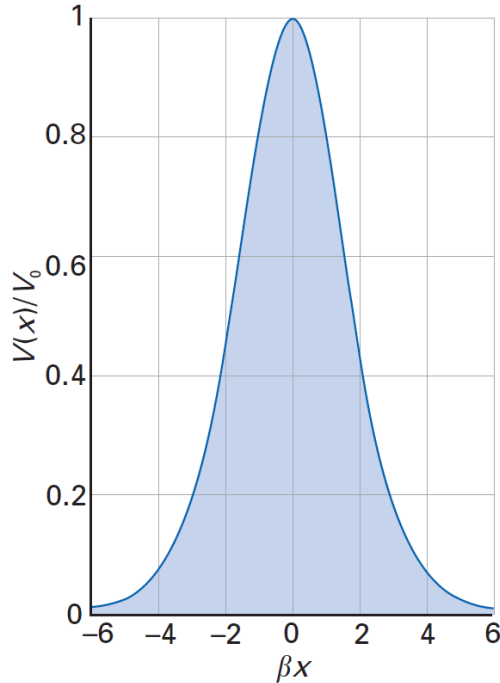


Křivky odpovídají hodnotám

$$L(2mV)^{1/2} / \hbar$$

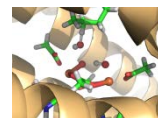
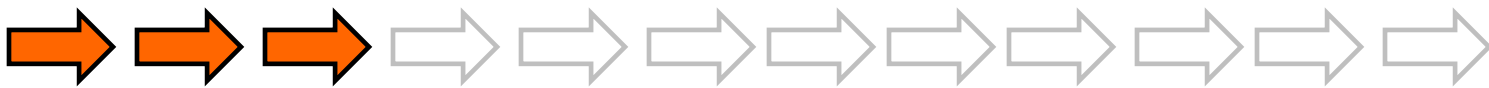
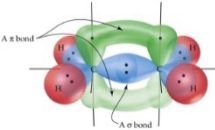


* Eckartova bariéra potenciální energie

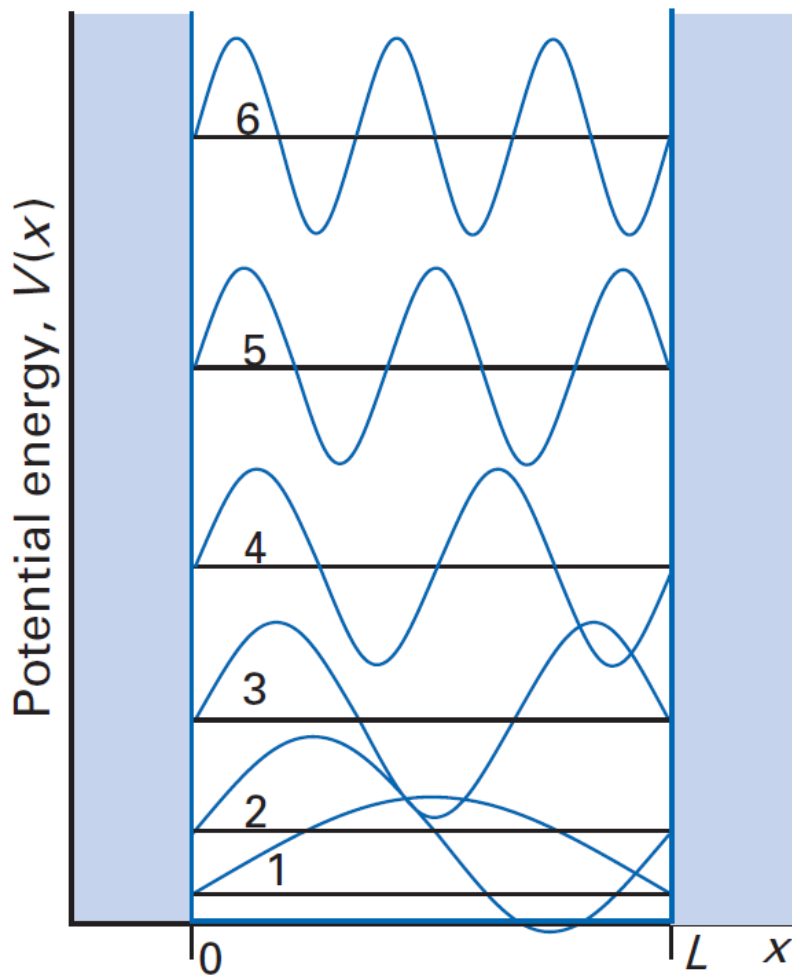


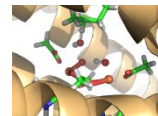
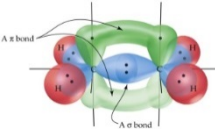
$$V(x) = \frac{4V_0 e^{\beta x}}{(1 + e^{\beta x})^2}$$

$$T = \frac{\cosh\left\{4\pi(2mE)^{1/2}/\hbar\beta\right\} - 1}{\cosh\left\{4\pi(2mE)^{1/2}/\hbar\beta\right\} + \cosh\left\{2\pi\left[8mV_0 - (\hbar\beta/2)^2\right]^{1/2}/\hbar\beta\right\}}$$

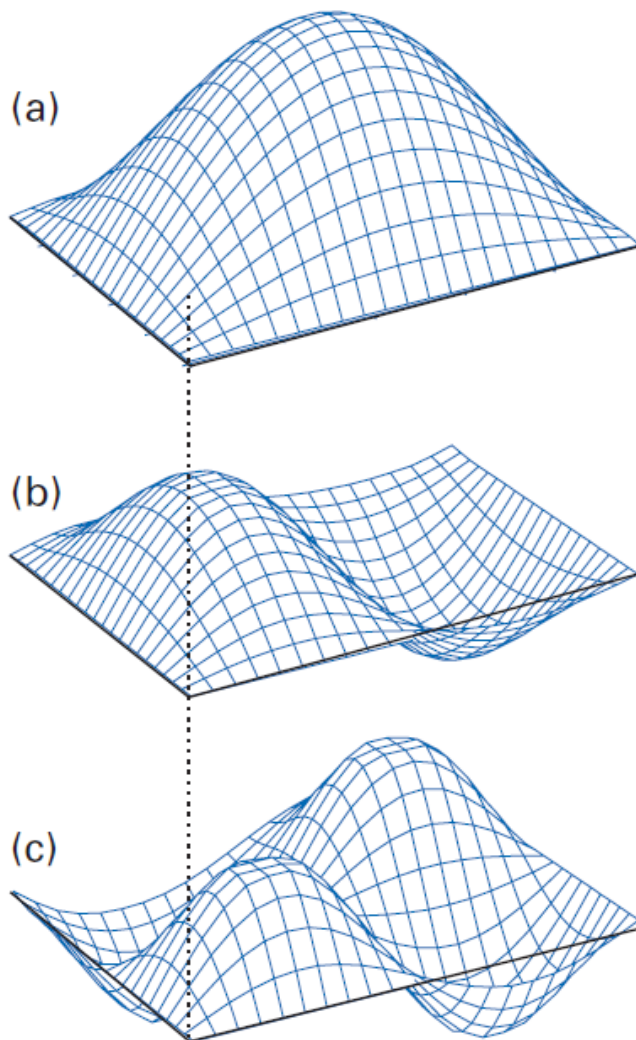


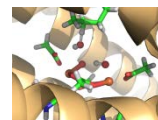
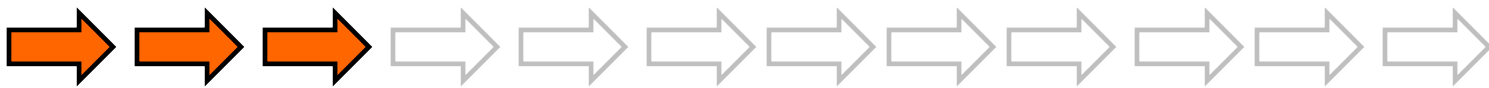
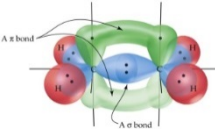
Částice v krabici – prvních 6 hladin energie a vlnových funkcí



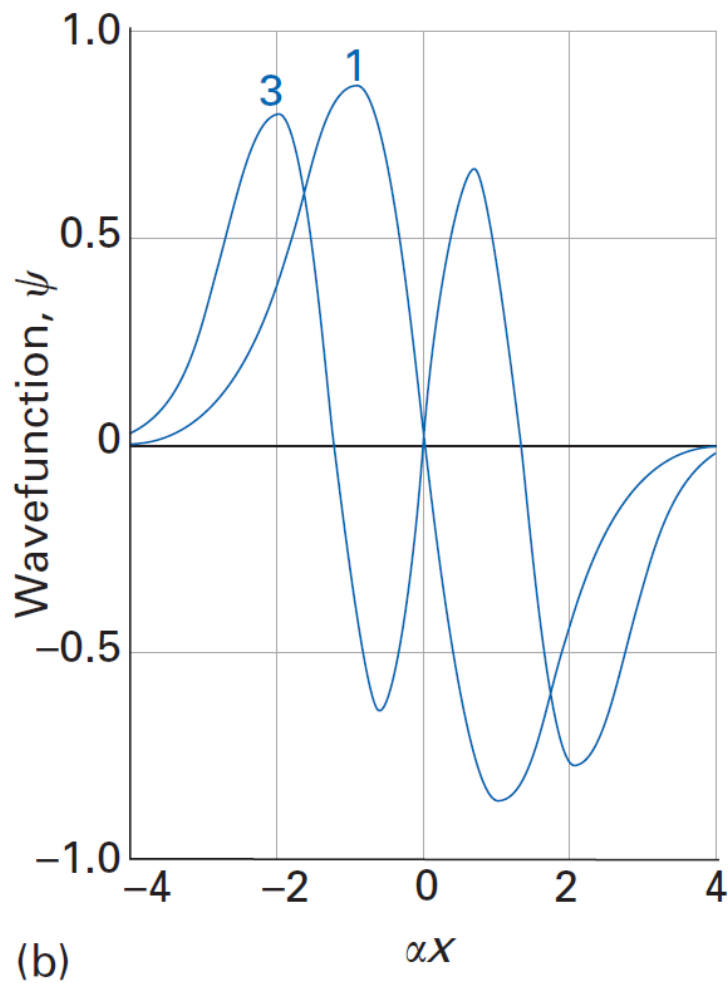
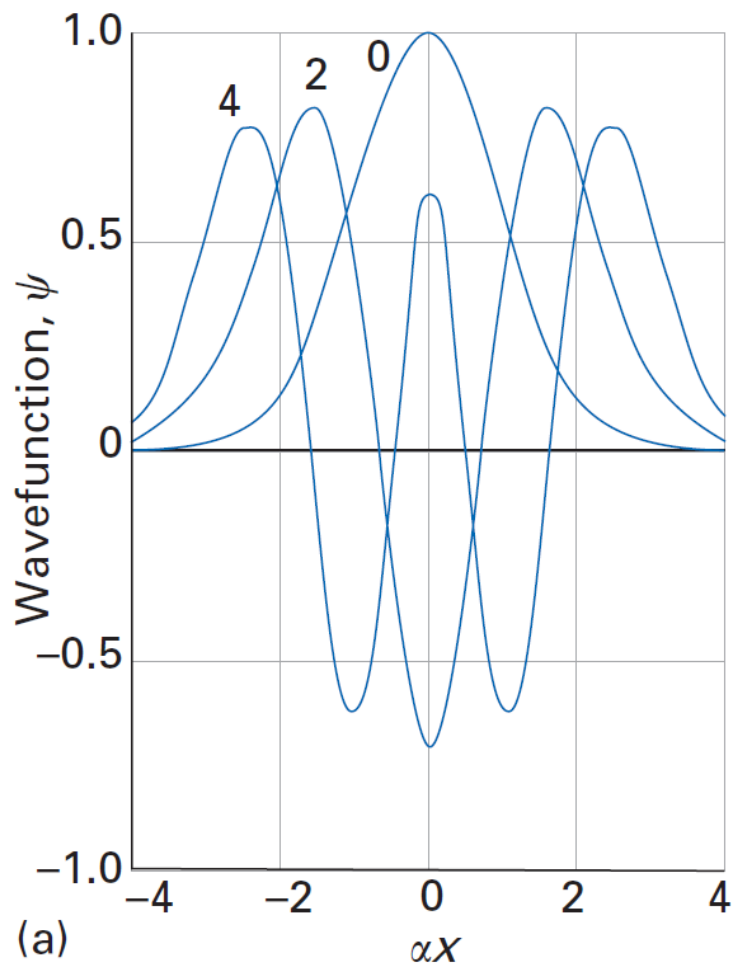


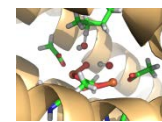
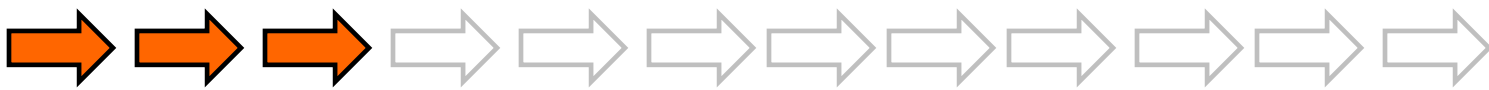
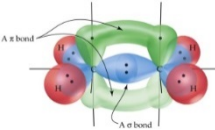
Částice ve 2D krabici, vlnové funkce pro $|1,1\rangle$; $|2,1\rangle$; $|2,2\rangle$



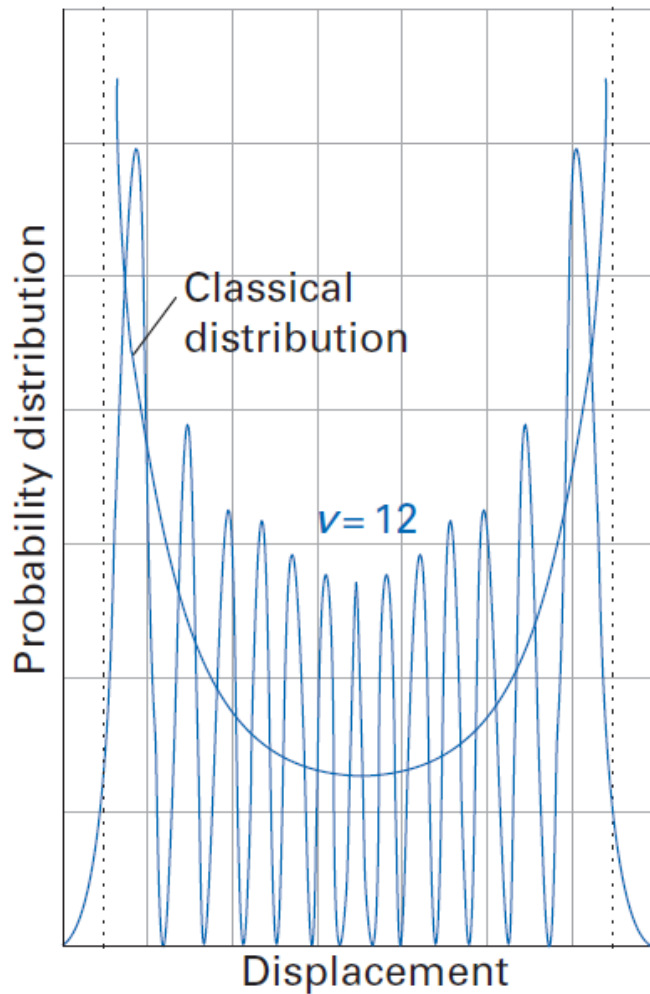


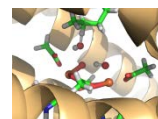
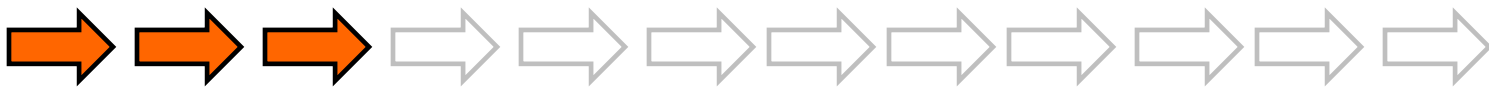
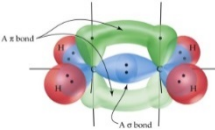
Harmonický oscilátor – vlnové funkce





Porovnání klasického a kvantového HO





Spektra lineárních konjugovaných molekul

- Chem. Phys. **189** (1994) 335 (DOI: 10.1016/0301-0104(94)00243-6)

- J. Chem. Educ. **74** (1997) 1317 (DOI: 10.1021/ed074p1317)

$\text{H}-(\text{C}\equiv\text{C})_n-\text{H}^+$, příprava výbojem v $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H}/\text{He}$, selekce kvadrupólovým filtrem, akumulace v Ne matrici při 5 K

- model 1D krabice, $E_n = n^2 h^2 / (8md^2)$, počet elektronů N

- podle Pauliho principu je obsazeno $[N/2]$ hladin, box má délku $d \sim N$,

dlouhovlnný okraj spektra odpovídá přechodu $[N/2] + 1 \leftarrow [N/2]$

s vlnovou délkou $\lambda = 8mcd^2 / (h(2[N/2] + 1)) \sim N$ (pro velká N)

P. Freivogel et al. / Chemical Physics 189 (1994) 335–341

337

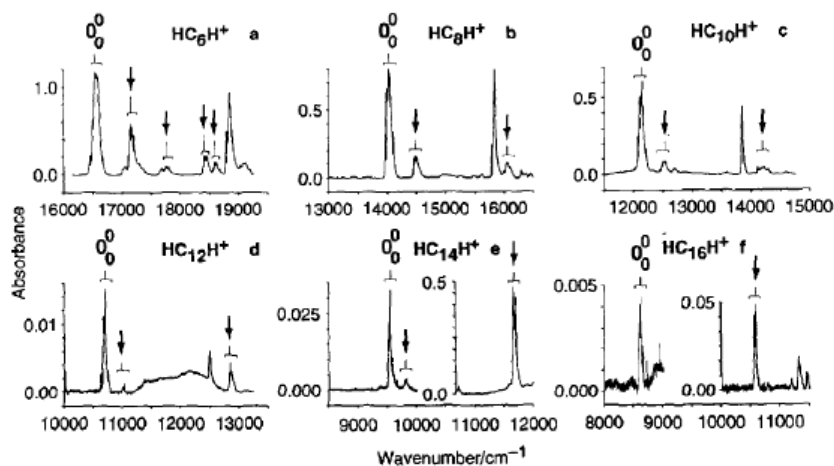


Fig. 2. The $A^2\Pi \leftarrow X^2\Pi$ transitions of the linear polyene cations: $\text{H}-(\text{C}\equiv\text{C})_n-\text{H}^+$ with $n=3-8$. The absorption spectra were recorded after a mass selected beam of ions was deposited concomitantly with neon gas to form a 5 K matrix. The location of the band origins is marked, and the arrows indicate vibrational progressions of the ions in the excited electronic state.

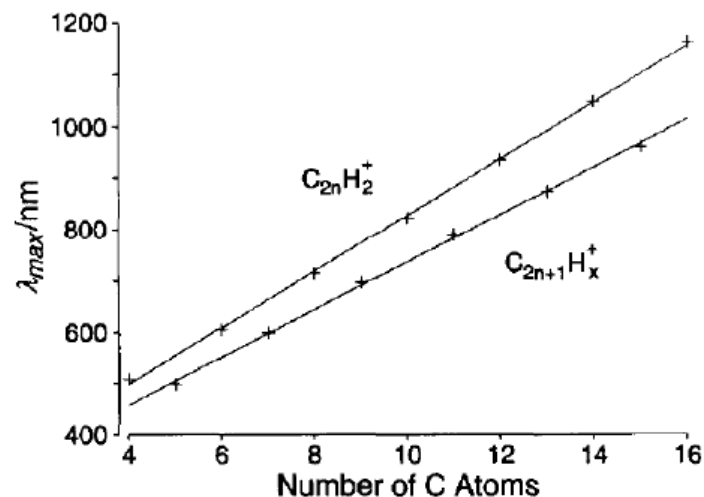
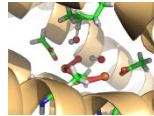
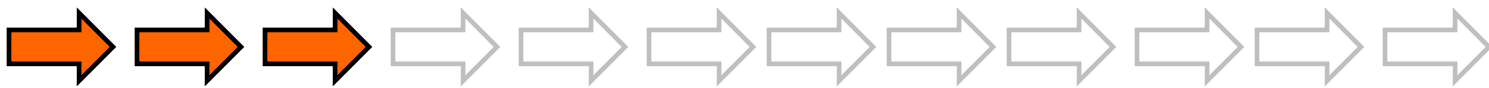
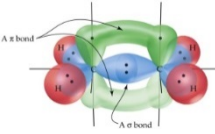
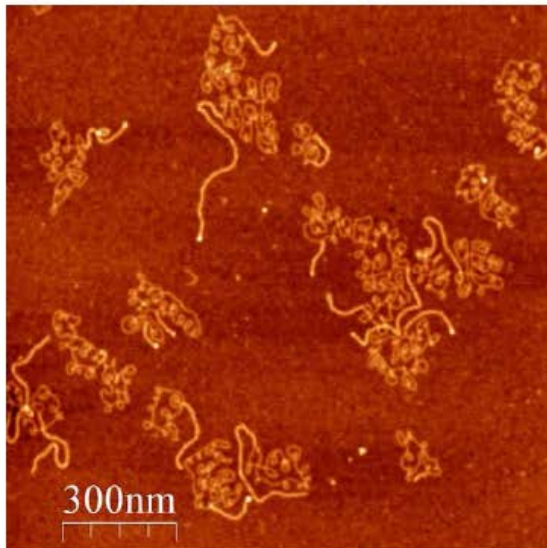
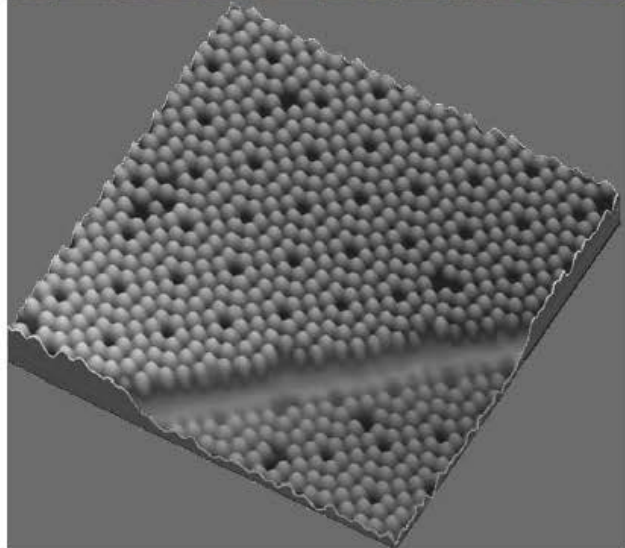
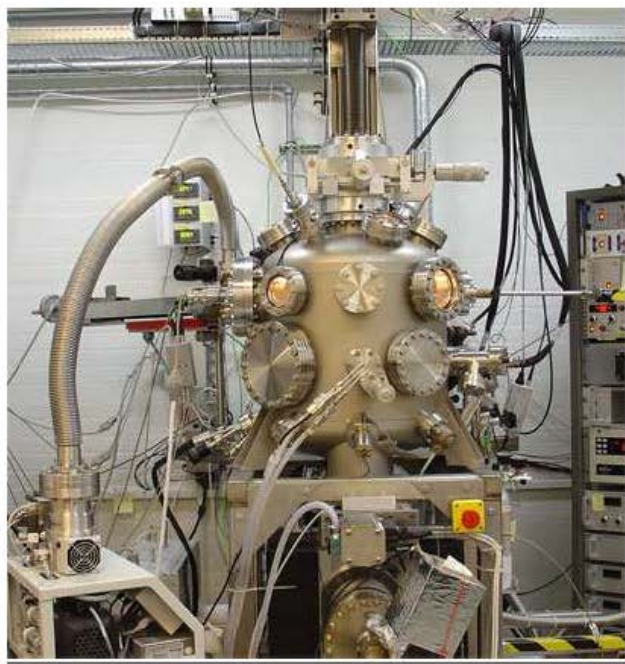
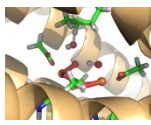
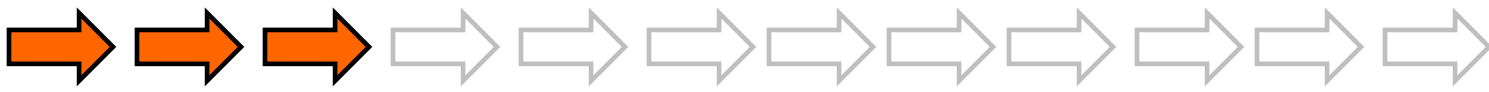
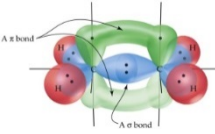


Fig. 4. The wavelength maxima λ of the 0_0^0 transitions from Fig. 2 and Fig. 3 plotted against the number of carbon atoms k of the absorbing species.



STM a AFM





STM, elektron v jámě z Fe na Cu (111)

- Nature **369** (1994) 464 (DOI: 10.1038/369464a0)

