Cvičení kvantovka

19.9.2019

Řešení Sch.R. pro částici v potenciálové jámě : $V(x)=0$

(1) $$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi(x) = E\cdot\Psi(x)$$

vrazíte že řešením je fce:

a) $C\sin(kx) + D\cos(kx) = \Psi(x)$

a najdete E

1. derivace:

$$C\cdot\cos(kx)\cdot k \pm Dk\sin(kx)$$

2. der. $$-Ck^2\sin(kx) - Dk^2\cos(kx)$$

$$+\frac{\hbar^2k^2}{2m}\left(C\sin(kx) + D\cos(kx)\right) = \underline{\underline{E}}\cdot(C\sin\ldots)$$

$$\boxed{E = \frac{\hbar^2k^2}{2m}}$$

↑ tzv. vlastní funkce operátoru energie

↳ levá strana rovnice (1)

co je to k ~~atd.~~ C a D je případ od případu

jáma:

$\Psi(0)=0 \wedge \Psi(L)=0$

$$0 = \underbrace{C\cdot\sin(0)}_{0} + D\underbrace{\cos(0)}_{1}$$

$$\boxed{D=0}$$

$$0 = C\cdot\sin(\underbrace{kL}_{n\cdot\pi}) \qquad k\cdot L = n\cdot\pi$$

$$\boxed{k = \frac{n\cdot\pi}{L}}$$

nebo $C=0$

↳ triviální řešení

stačí brát $n\in N$ ← $n\in\mathbb{Z}$; $n=0$ → řešení částice ~~nem~~

1

záporné n v páru s kladnými
$\Rightarrow n = \{1, 2, 3, \dots\}$ kvantování

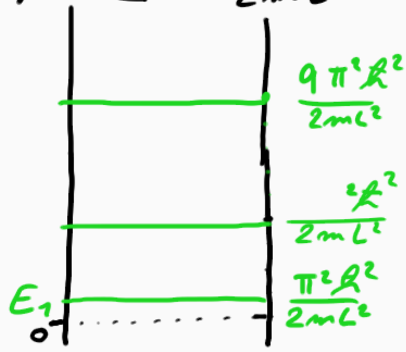
Ot: funkční předpis Ψ když $n = 1, 2$ a 3
a určete E

$$\Psi_1(x) = C \cdot \sin\left(\frac{\pi \cdot x}{L}\right) \rightarrow E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \pi^2}{2mL^2}$$

$$\Psi_2(x) = C \cdot \sin\left(\frac{2\pi x}{L}\right) \rightarrow E = \frac{\hbar^2 4\pi^2}{2mL^2}$$

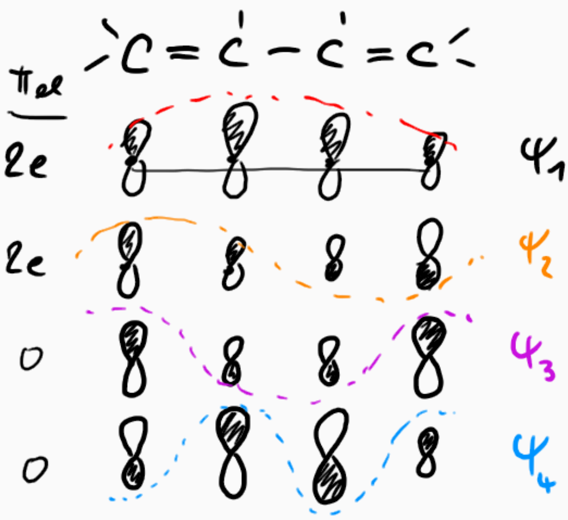
$$\Psi_3(x) = C \cdot \sin\left(\frac{3\pi x}{L}\right) \rightarrow E = \frac{\hbar^2 9\pi^2}{2mL^2}$$

Teď to nakreslit



Ot: aplikujte model částice v jámě na výpočet rozdílu energií HOMO a LUMO v molekule butadienu

exp: $\lambda = 217$ nm



$L = 7$ Å

$m_e = 9{,}1 \cdot 10^{-31}$ kg

$E = E_3 - E_2$ ↗ převést na λ

$$= \frac{\hbar^2 \pi^2}{2mL^2}(9-4)$$

$$= \frac{5\hbar^2\pi^2}{2mL^2} \qquad h = 6{,}63 \cdot 10^{-34}$$

$$= \frac{5 \cdot h^2 \pi^2}{4\pi^2 \cdot 2mL^2}$$

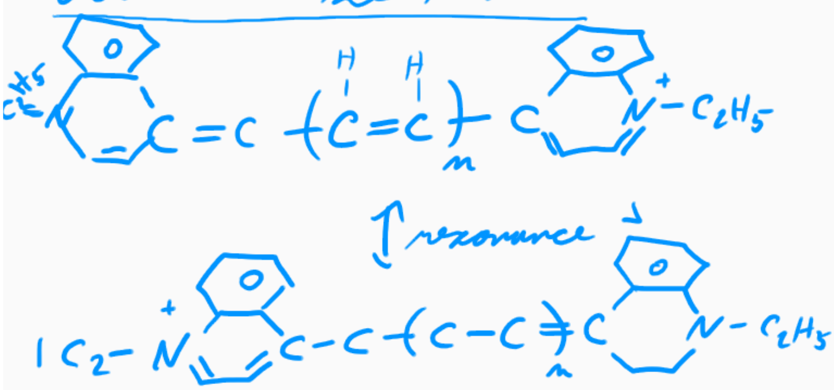
$$= \frac{5h^2}{8mL^2} = 6{,}15 \cdot 10^{-19}$$

$$= 3{,}8 \text{ eV}$$

$$E = h\nu = h\frac{c}{\lambda} \rightarrow \lambda = \frac{hc}{E} = 323{,}2 \text{ nm} \Rightarrow \lambda = 323{,}2 \text{ nm}$$

26.9.2019

<u>Úloha 1 ze zadání</u>



$E = h \cdot \nu$

$= h \cdot \frac{c}{\lambda}$

$\lambda = \frac{h \cdot c}{E}$

$= (2n+10) l \qquad l = 1{,}39 Å$

počet e^-: $2n+10$

ΔE a λ pro $n = 0, 1, 2, 3$

$E_0 = \frac{h^2 \pi^2 \cdot 0}{2m \cdot (10 l)} = 0$

$E_1 = \frac{h^2 \pi^2 \cdot 1}{2m \cdot 12 l} =$

$\lambda_1 =$

$E_2 =$

$E = \frac{h^2}{2m} \cdots$

↓

co dál?

odvodíme z ψ

$\psi_n = A \cdot \sin\left(\frac{n \pi x}{L}\right)$

$\hat{H} \psi = E \psi$

$-\frac{h^2}{2m} \frac{d^2}{dx^2} \cdot \psi = \ldots$

$\boxed{\frac{h^2 n^2 \pi^2}{2mL^2} = E} \quad \boxed{= \frac{h^2 n^2}{8mL^2}}$

$n = 0 \quad \rightarrow$ p. elektronů : 10

ψ_6
ψ_5

$E_5 = \frac{h^2 \pi^2 \cdot 5^2}{2m L^2}$

$E_6 = \frac{h^2 \pi^2 6^2}{2m L^2}$

$L = 10 l = 13{,}9 \cdot 10^{-10}$

$E_6 - E_5 = \frac{h^2 \pi^2}{2m L^2} \cdot (6^2 - 5^2)$

$\Delta E = 3{,}43 \cdot 10^{-19}$ J

$\lambda = \frac{h \cdot c}{E} = 579{,}5$ nm

$= 5795 Å$

experiment: $5750 Å$ ← blíže než D.Ú.

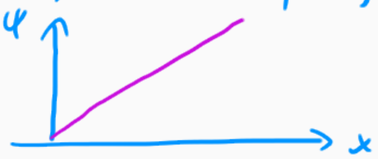
Doma: $n = 3$

③

ze zadání $n \to \pi$ ... délka řetízce

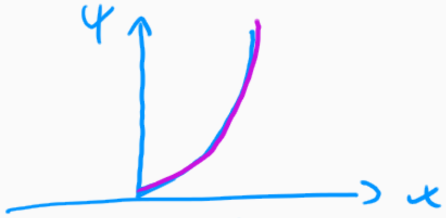
Úloha 2 : Fyzikální přijatelnost vlnové fce

a) $\psi = x$



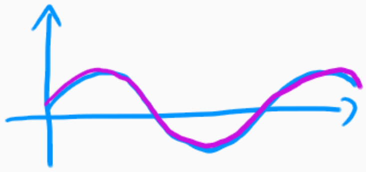
spoj ✓
jednoz ✓
integ. v kvad. ✗

b) $\psi = x^2$



spoj. ✓
jednozn. ✓
integ. v kvadr. ✗

c) $\psi = \sin x$



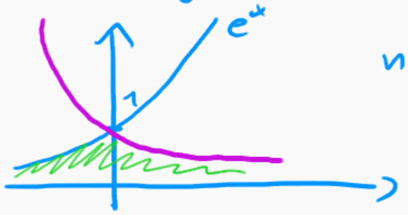
jed. ✓
spoj ✓
integr. v kvad. ✗
↳ ale popisuje volný e^-

d) $\psi = \sin x$ pro $x \in \langle 0, L \rangle$ $\Rightarrow$ Fyzikálně přijatelná ✓

jedn. ✓
spoj ✗ ale pro $L = 2\pi$ už ✓
kv. integ. ✓

proto povolený $\sin\left(\frac{n\pi}{L} \cdot x\right)$

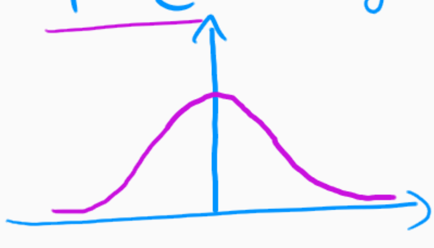
e) $\psi = e^{-x}$



není kv. integ.
ale $e^{-|x|}$ už ano
(základní stav H)

f) $\psi = e^{-x^2}$ ... Gauss

přijatelná
(harmonický oscilátor)



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Úloha 3: Normovací podmínka

$$\psi = A \cdot \sin\left(\frac{n\pi x}{L}\right) \quad a) \int_0^L \psi^2(x)\,dx = P$$

a) $$\int_0^L A^2 \sin^2\left(\frac{n\pi x}{L}\right) dx = \cancel{P} \quad \left| \; a = \frac{n\pi x}{L} \quad \frac{da}{dx} = \frac{n\pi}{L} \quad dx = \frac{da}{\frac{L}{n\pi}} \right|$$

$$= \int_0^L A^2 \cdot \frac{L}{n\cdot\pi} \cdot \sin^2(a) \cdot da = \; \dots ?$$

$$A^2 \left[\frac{x}{2} - \frac{L}{n\pi} \cdot \sin\left(2\,\frac{n\pi x}{L}\right)\right]_0^L = A^2 \cdot \left[\frac{L}{2} - \underbrace{\frac{L}{n\pi} \cdot \sin(2\pi n)}_{0} - 0 + \underbrace{\frac{L}{n\pi} \cdot \sin(0)}_{0}\right]$$

$$= A^2 \cdot \frac{L}{2}$$ norma vlnové fce

b) $$P = 1 = A^2 \frac{L}{2} \rightarrow A = \sqrt{\frac{2}{L}}$$

$$\psi_n = \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{n\pi x}{L}\right)$$ ... v jámě

3. 10. 2019

D.ú. z minula

$n = 3$ ... $$\Delta E = \frac{[(6+n)^2 - (5+n)^2] \cdot h^2}{8 m L^2}$$

homo a lumo

ΔE

⑤

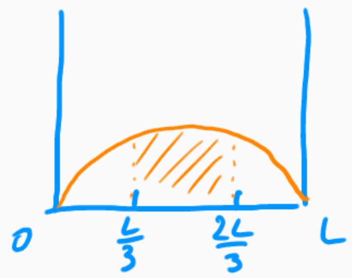
1. úloha

normovaná potenc. jáma

$$\psi_1 = \sqrt{\frac{2}{L}}\, \sin \frac{\pi x}{L}$$

$$\psi_2 = \sqrt{\frac{2}{L}}\, \sin \frac{2\pi x}{L}$$

$$\psi_3 = \sqrt{\frac{2}{L}}\, \sin \frac{3\pi x}{L}$$



Hledáme pravděpodobnost nalezení částice v intervalu $\langle \frac{L}{3}; \frac{2L}{3} \rangle$

$$P_1 = \int_{\frac{L}{3}}^{\frac{2L}{3}} \psi_1^2 \, dx$$

pomoc: $\int \sin^2 bx \, dx = \frac{x}{2} - \frac{1}{4b} \sin(2bx)$

$$= \int \frac{2}{L} \sin^2\left(\frac{\pi x}{L}\right) dx = \frac{2}{L} \int \sin^2\left(\frac{\pi x}{L}\right) dx$$

$$= \frac{2}{L} \left[\frac{x}{2} - \frac{1 \cdot L}{4\pi} \cdot \sin\left(\frac{2\pi}{L} \cdot x\right)\right]_{\frac{L}{3}}^{\frac{2L}{3}}$$

$$= \frac{2}{L} \cdot \left(\frac{L}{3} - \frac{L}{4\pi} \cdot \underbrace{\sin\left(\frac{4}{3}\pi\right)}_{-\frac{\sqrt{3}}{2}} - \frac{L}{6} + \underbrace{\frac{L}{4\pi} \cdot \sin\left(\frac{2\pi}{3}\right)}_{\frac{\sqrt{3}}{2}}\right)$$

$$= \frac{2}{L} \cdot \left(\frac{L}{3} + \frac{L\sqrt{3}}{8\pi} - \frac{L}{6} + \frac{L\sqrt{3}}{8\pi}\right)$$

$$= 2 \cdot \left(\frac{1}{3} - \frac{1}{6} + \frac{\sqrt{3}}{4\pi}\right) = \underline{\frac{1}{3} + \frac{\sqrt{3}}{2\pi}}$$

$$\doteq (0{,}61) = \underline{\underline{0{,}609}}$$

→ pravděpodobnost je cca 60%

⇒ výrazná preference středu

teď pro ψ_2

6

$$P_2 = \int_{\frac{L}{3}}^{\frac{2L}{3}} \frac{2}{L} \cdot \sin^2\left(\frac{2\pi}{L} \cdot x\right) dx$$

$$= \frac{2}{L} \int \sin^2\left(\frac{2\pi}{L} \cdot x\right) dx = \frac{2}{L} \cdot \left[\frac{x}{2} - \frac{L}{8\pi} \cdot \sin\left(\frac{4\pi}{L} \cdot x\right)\right]_{\frac{L}{3}}^{\frac{2L}{3}}$$

$$= \frac{2}{L} \cdot \left[\frac{L}{3} - \frac{L}{8\pi} \cdot \underbrace{\sin\left(\frac{8\pi}{3}\right)}_{\frac{\sqrt{3}}{2}} - \frac{L}{6} + \frac{L}{8\pi} \cdot \underbrace{\sin\left(\frac{4\pi}{3}\right)}_{-\frac{\sqrt{3}}{2}}\right]$$

$$= 2 \cdot \left[\frac{1}{6} - \frac{\cancel{L}\sqrt{3}}{16\pi} - \frac{\cancel{L}\sqrt{3}}{16\pi}\right]$$

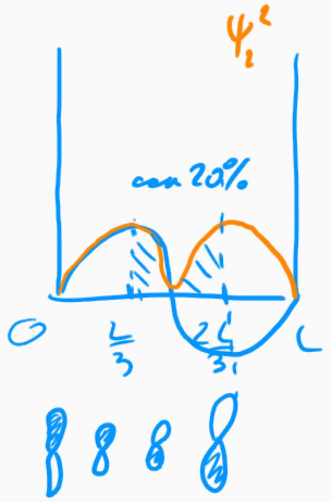
$$= \frac{1}{3} - \frac{\sqrt{3}}{4\pi} \doteq \underline{\underline{0{,}1955}}$$

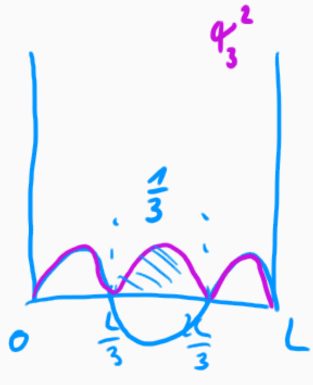
$$P_3 = \int_{\frac{L}{3}}^{\frac{2L}{3}} \frac{2}{L} \cdot \sin^2\left(\frac{3\pi}{L} x\right) dx = \frac{2}{L} \cdot \left[\frac{x}{2} - \frac{4L}{3\pi} \cdot \sin\left(\frac{6\pi}{L} x\right)\right]_{\frac{L}{3}}^{\frac{2L}{3}}$$

$$= \frac{2}{L}\left[\frac{L}{3} - \underbrace{\frac{4L}{3\pi} \cdot \sin(4\pi)}_{0} - \frac{L}{6} + \underbrace{\frac{4L}{3\pi} \cdot \sin(2\pi)}_{0}\right]$$

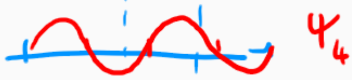
$$= \frac{2}{\cancel{L}} \cdot \frac{\cancel{L}}{6} = \underline{\frac{1}{3}}$$

~ 1 grafu





pro $n = 4$



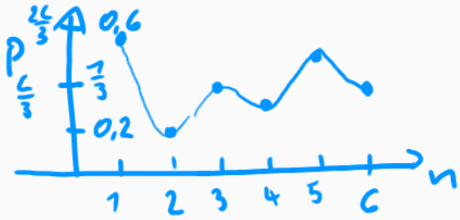
$P_5 \in (33 \div 60)$ $\quad P_6 = \frac{1}{3}$

↳ kolísání

$20\% < P_4 < 33\%$

2. úloha: ukažte že ψ_1 a ψ_2 / ψ_1 a ψ_3 jsou ortogonální (není D.Ú.)

Zobrazení pravděpodobnosti



10. 10. 2019

1) Určete nejpravděpodobnější vzdálenost e^- od jádra pro H v zákl. st.

$$\psi^2(x,y,z) \leftarrow R^2(r)\cdot 4\pi\cancel{r^2} = \text{RDF} = R^2\cdot r^2$$

radiální distr. fce

$$\swarrow R(r)\cdot Y(\theta,\varphi)$$

$$R(r) = \frac{2}{\sqrt{a_0^3}}\cdot e^{-\frac{r}{a_0}}$$

hledáme extrém:

$$\frac{d}{dr}\left(\left(\frac{2}{\sqrt{a_0^3}}\right)^2 e^{-\frac{2r}{a_0}}\cdot \cancel{4\pi} r^2\right) = 0$$

$$\frac{4\cdot\cancel{4\pi}}{a_0^3}\cdot\frac{d}{dr}\left(e^{-\frac{2r}{a_0}}\cdot r^2\right) = 0 = \frac{\overset{4}{\cancel{16\pi}}}{a_0^3}\cdot ☆ = \frac{4}{a_0^3}\cdot e^{-\frac{2r}{a_0}}\cdot\left(2r-\frac{2r^2}{a_0}\right)$$

☆: $(a\cdot b)' = a'\cdot b + a\cdot b'$

$$e^{-\frac{2r}{a_0}}\cdot\left(-\frac{2}{a_0}\right)\cdot r^2 + e^{-\frac{2r}{a_0}}\cdot 2\cdot r$$

$$e^{-\frac{2r}{a_0}}\cdot\left(-\frac{2r^2}{a_0}+2r\right)$$

cv. 8

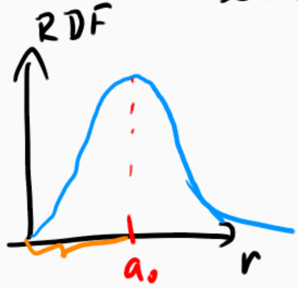
$$0 = \frac{8}{a_0^3} \cdot e^{-\frac{2r}{a_0}} \cdot \left(r - \frac{r^2}{a_0}\right)$$

$$\Rightarrow \left(r - \frac{r^2}{a_0}\right) = 0 \qquad /\cdot -a_0 \quad /:r$$

$$-a_0 + r = 0$$

$$\underline{\underline{r = a_0}}$$

Příklad 2:
Určete pravděpodobnost, že elektron bude ve vzdálenosti od jádra $\leq a_0$



$$\int_0^{a_0} R^2(r) \cdot r^2 \, dr =$$

$$= \int_0^{a_0} \frac{4}{a_0^3} \cdot e^{-\frac{2r}{a_0}} \cdot r^2 \, dr = \left| \begin{matrix} u = r^2 & v' = e^{-\frac{2r}{a_0}} \\ u' = 2r & v = e^{-\frac{2r}{a_0}} \cdot \frac{-a_0}{2} \end{matrix} \right|$$

$\int u'v = uv - \int uv'$

$$= \frac{4}{a_0^3}\left[-\frac{r^2 a_0}{2} \cdot e^{-\frac{2r}{a_0}} + \int_0^{a_0} +a_0 \cdot r \cdot e^{-\frac{2r}{a_0}} \, dr\right]$$

$$\left| \begin{matrix} u = r & v' = e^{-\frac{2r}{a_0}} \\ u' = 1 & v = e^{-\frac{2r}{a_0}} \cdot \frac{-a_0}{2} \end{matrix} \right| = \frac{4}{a_0^2}\left[-\frac{r^2}{2} \cdot e^{-\frac{2r}{a_0}} + \cancel{a_0} \cdot (☼)\right]$$

$$☼ = \int_0^{a_0} r \cdot e^{-\frac{2r}{a_0}} \, dr$$

$$= -\frac{r a_0}{2} \cdot e^{-\frac{2r}{a_0}} - \int_0^{a_0} \frac{-a_0}{2} \cdot e^{-\frac{2r}{a_0}} \, dr$$

$$= -\frac{a_0}{2}\left[r \cdot e^{-\frac{2r}{a_0}} + \cancel{2} e^{-\frac{2r}{a_0}} \cdot \frac{+a_0}{2}\right]$$

$$=$$

$$= \frac{4}{a_0^2} \cdot \left[-\frac{r^2}{2} \cdot e^{-\frac{2r}{a_0}} - \frac{a_0 r}{2} \cdot e^{-\frac{2r}{a_0}} - \frac{a_0^2}{4} \cdot e^{-\frac{2r}{a_0}}\right]$$

$$= \frac{4}{a_0^2} \cdot \left[e^{-\frac{2r}{a_0}} \cdot \left(-\frac{r^2}{2} - \frac{a_0 r}{2} - \frac{a_0^2}{4}\right)\right]$$

cv. 9

$$= \frac{4}{a_0^2} \cdot \left[-e^{-2} \cdot \underbrace{\left(\frac{a_0^2}{2} + \frac{a_0^2}{2} + \frac{a_0^2}{4} \right)}_{\frac{2+2+1}{4} \} \frac{5}{4} a_0^2} + \underbrace{e^{0}}_{1} \cdot \frac{a_0^2}{4} \right]$$

$$= \cancel{\frac{4}{a_0^2}} \cdot \left[-e^{-2} \cdot \frac{5}{\cancel{4}} \cancel{a_0^2} + \frac{\cancel{a_0^2}}{\cancel{4}} \right]$$

$$= \underline{-5e^{-2} + 1} = \underline{\underline{0{,}32}} \checkmark$$

obecně:

$$\frac{4}{a_0^3} \cdot \left[-e^{-\frac{2r}{a_0}} \cdot \left(\frac{a_0 r^2}{2} + \frac{a_0 r}{2} + \frac{a_0^3}{4} \right) \right]_{\text{dolní mez}}^{\text{horní mez}}$$

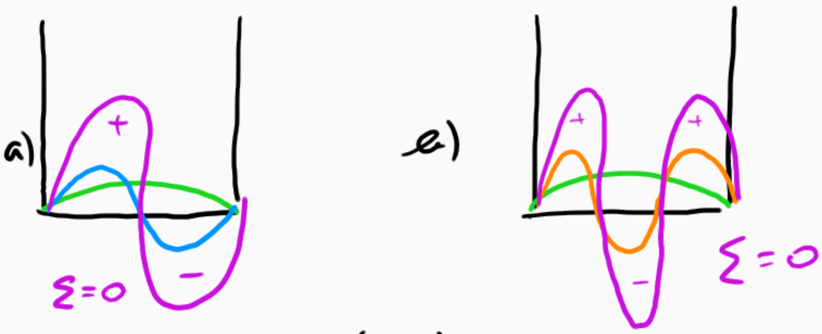
dopis za 17. 10.

Ukažte že násl. ψ pro částici v jámě jsou ortogonální $\longrightarrow \int \psi_1^* \cdot \psi_2 \, dx = 0$

a) ψ_1 a ψ_2

b) ψ_1 a ψ_3

graficky: ψ_1 ψ_2 ψ_3 součin



číselně: $\psi_1 = \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{\pi x}{L}\right)$

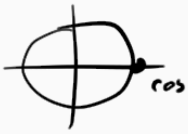
$\psi_3 = \sqrt{\frac{2}{L}} \sin\left(\frac{3\pi}{L} \cdot x\right)$

pomůcka $\sin\alpha \cdot \sin\beta = \frac{1}{2}\left[\cos(\alpha - \beta) - \cos(\alpha + \beta)\right]$

cv 10

$$\psi_{1\times3} = \int_0^L \sqrt{\frac{2}{L}}\cdot\sin\left(\frac{\pi}{L}\cdot x\right)\cdot\sqrt{\frac{2}{L}}\cdot\sin\left(\frac{3\pi}{L}\cdot x\right)\,dx$$

$$= \frac{2}{L}\cdot\int_0^L \frac{1}{2}\cdot\left[\underbrace{\cos\left(-\frac{2\pi}{L}\cdot x\right)}_{1} - \underbrace{\cos\left(\frac{4\pi}{L}\cdot x\right)}_{1}\right]dx$$

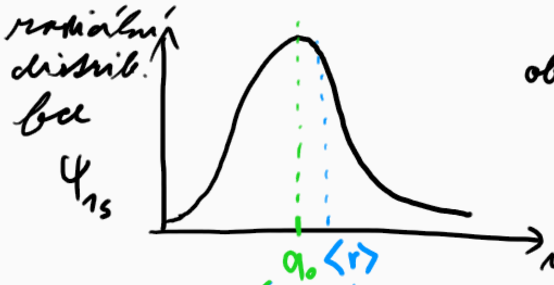


$$= \frac{2}{L}\cdot\int_0^L \frac{1}{2}\cdot 0\,dx = \underline{\underline{0}}$$

je to ortogonální

vždy 2 fce které odpovídají různým vlastním hodnotám (různé E) jsou ortogonální

Atom vodíku



↳ střední hodnota

↳ průměrná hodnota

nejpravděpodobnější mp (most probable)

obecně $\langle\hat{A}\rangle = \int \psi^* \hat{A}\,\psi\,d\tau$

Určete $\langle r\rangle$ pro základní stav vodíku

když: $\langle r\rangle = \int \psi_{1s}^* \cdot r\cdot\psi_{1s}\,d\tau$ ... $d\tau = r^2\cdot\sin\theta\,dr\,d\varphi\,d\theta$

pro $\psi_{1s} = \frac{1}{(\pi a_0^3)^{\frac{1}{2}}}\cdot e^{-\frac{r}{a_0}}$

$$\langle r\rangle = \int_0^\infty\int_0^{2\pi}\int_0^{\pi} \frac{1}{(\pi a_0^3)^{\frac{1}{2}}}\cdot e^{-\frac{r}{a_0}}\cdot r\cdot\frac{1}{(\pi a_0^3)^{\frac{1}{2}}}\cdot e^{-\frac{r}{a_0}}\cdot r^2\cdot\sin\theta\,dr\,d\varphi\,d\theta$$

cv. 11

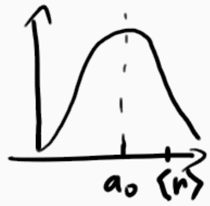
$$\boxed{\int_0^\infty x^n \cdot e^{-qx}\, dx = \frac{n!}{q^{n+1}}}$$

$$\langle r\rangle = \frac{1}{\pi a_0^3}\iiint r^3 \cdot e^{-\frac{2r}{a_0}} \cdot \sin\theta \; dr\, d\varphi\, d\theta$$

$$= \frac{2\cancel{\pi}}{\cancel{\pi}\cdot a_0^3} \cdot \underbrace{\int_0^\infty r^3 \cdot e^{-\frac{2}{a_0}\cdot r}\, dr}_{\left[\frac{3!}{\left(-\frac{2}{a_0}\right)^4}\right]_0^\infty} \cdot \underbrace{\int_0^\pi \sin\theta\, d\theta}_{\left[-\cos\theta\right]_0^\pi}$$

$$= \frac{2}{\cancel{a_0^3}} \cdot \frac{6\cdot a_0^{\cancel{4}}}{16} \cdot \left[\underbrace{-\cos(\pi)}_{1} + \underbrace{\cos(0)}_{1}\right]$$

$$= \frac{4a_0 \cdot 6}{16} = \frac{6}{4}a_0 = \underline{\underline{\frac{3}{2}a_0}}$$



D.ú. $\langle r\rangle$ pro $2p_z$ orbital vodíku $(Z=1)$

$$\psi_{2p_0} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{2a_0}\right)^{\frac{5}{2}} \cdot r \cdot e^{-\frac{r}{2a_0}} \cos\theta$$

$$\langle r\rangle = \iiint \frac{1}{\pi}\left(\frac{1}{2a_0}\right)^5 \cdot r^2 \cdot e^{-\frac{\cancel{2}r}{\cancel{2}a_0}} \cdot \cos^2\theta \cdot r \cdot r^2 \cdot \sin\theta\; dr\, d\varphi\, d\theta$$

$$= \frac{2\cancel{\pi}}{\cancel{\pi}(2a_0)^5}\underbrace{\int_0^\infty r^5 \cdot e^{-\frac{r}{a_0}}\, dr}_{\frac{5!}{\left(-\frac{1}{a_0}\right)^6}} \cdot \underbrace{\int_0^\pi \cos^2\theta \cdot \sin\theta\, d\theta}_{\left(\frac{e^{i\theta}+e^{-i\theta}}{2}\right)^2 \cdot \left(\frac{e^{i\theta}-e^{-i\theta}}{2i}\right)}$$

$$= \dots = \frac{1}{4}\cdot\left[\sin(3\theta) - \sin\theta\right]$$

$$= \frac{2\cdot 5!\cdot a_0^{\cancel{6}}}{2^5\, \cancel{a_0^5}} \cdot \frac{1}{4}\int_0^\pi \sin(3\theta) - \sin\theta\; d\theta$$

$$= \frac{5!}{2^4}a_0 \cdot \frac{1}{4}\left[\frac{1}{3}\left[-\cos(3\theta)\right]_0^\pi - \left[-\cos\theta\right]_0^\pi\right]$$

$$= \frac{5!\, a_0}{2^6}\cdot\left[\frac{1}{3}(1+1) - (1+1)\right] = \frac{5\cdot\cancel{4}\cdot\cancel{3}\cdot\cancel{2}\cdot a_0}{2^{\cancel{6}}}\cdot\left(-\frac{\cancel{4}}{\cancel{3}}\right)$$

? $= -\frac{5}{2}a_0$ ... divné < 0

cv. 12

24.10.2019

výsledek domácího úkolu:

$$\int_0^\pi \cos^2\theta \cdot \sin\theta \, d\theta \qquad \left| \; \left(\cos^3\theta\right)' = 3\cdot\cos^2\theta\cdot(-\sin\theta) \right|$$

$$= -\frac{1}{3}\left[\cos^3\theta\right]_0^\pi = -\frac{1}{3}\left[-1-1\right] = \frac{2}{3}$$

dopočítat doma:

$$\langle r\rangle = \frac{\cancel{2}\cancel{\pi}}{\cancel{\pi}\,\cancel{2}^5\cdot \cancel{a_0^3}} \cdot \frac{5\cdot \cancel{4}\cdot\cancel{3}\cdot\cancel{2}\cdot a_0^{\cancel{4}}}{1}\cdot\frac{\cancel{2}}{\cancel{3}} = 5\cdot a_0$$

Jinak:

$$\int_0^\pi \cos^2\theta\cdot\sin\theta\, d\theta \qquad \begin{aligned} e^{i\theta} &= \cos\theta + i\sin\theta \\ e^{-i\theta} &= \cos\theta - i\sin\theta \end{aligned}$$

$$\left(\frac{e^{i\theta}+e^{-i\theta}}{2}\right)^2\cdot\left(\frac{e^{i\theta}-e^{-i\theta}}{2i}\right) = \left(\frac{e^{i2\theta}}{4} + \frac{\cancel{2}\, e^{\overbrace{i\theta-i\theta}^{0}}}{2\cdot\cancel{2}} + \frac{e^{-2i\theta}}{4}\right)\cdot\left(\frac{e^{i\theta}}{2i}-\frac{e^{-i\theta}}{2i}\right) =$$

$$\frac{e^{i\theta(2+1)}}{8i}^{\,3} - \frac{e^{i\theta(2-1)}}{8i}^{\,1} + \frac{e^{i\theta}}{4i}^{\,1} - \frac{e^{-i\theta}}{4i}^{\,-1} + \frac{e^{i\theta(-2+1)}}{8i}^{\,-1} - \frac{e^{i\theta(-2-1)}}{8i}^{\,-3} =$$

$$\frac{1}{4}\sin(3\theta) + e^{i\theta}\underbrace{\left(-\frac{1}{8i}+\frac{1}{4i}\right)}_{\frac{-1+2}{8i}=\frac{1}{8i}} + e^{-i\theta}\underbrace{\left(-\frac{1}{4i}+\frac{1}{8i}\right)}_{\frac{-2+1}{8i}=\frac{-1}{8i}} =$$

$$\frac{1}{4}\sin(3\theta) + \frac{1}{4}\sin\theta \rightarrow \int_0^\pi$$

$$\frac{1}{4}\int_0^\pi \sin(3\theta)\,d\theta = \left| \begin{aligned} a &= 3\theta \\ d\theta &= \frac{da}{3}\end{aligned}\right|$$

$$= \frac{1}{4}\int\frac{1}{3}\sin a\, da = \frac{1}{12}\left[\cos a\right]$$

$$= \frac{1}{12}\left[-\cos(3\theta)\right]_0^\pi = \frac{1}{12}(1+1) = \frac{1}{6}$$

$$\frac{1}{4}\int_0^\pi \sin\theta\, d\theta = \frac{1}{4}\left[-\cos\theta\right]_0^\pi$$

$$= \frac{1}{4}(1+1) = \frac{1}{2}$$

$$\int_0^\pi \frac{1}{4}\sin(3\theta) + \frac{1}{4}\sin\theta\; d\theta =$$

$$= \frac{1}{6}+\frac{1}{2} = \frac{1+3}{6} = \frac{4}{6}$$

$$= \frac{3}{2}$$

cv. 13

Rozvinte determinant pro vln. fci $_3Li$: $\uparrow$ 2s, $\uparrow\downarrow$ 1s

$$\Psi_{1,2,3} = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1) & 1s(2) & 1s(3) \\ 1\bar{s}(1) & 1\bar{s}(2) & 1\bar{s}(3) \\ 2s(1) & 2s(2) & 2s(3) \end{vmatrix}$$

s ... spin α
$\bar{s}$ ... spin β

$1s(1)$ $1s(2)$ $1s(3)$
$1\bar{s}(1)$ $1\bar{s}(2)$ $1\bar{s}(3)$

$\frac{1}{\sqrt{n!}}$
↳ počet e⁻

$$= \frac{1}{\sqrt{6}} \cdot \Big[1s(1)\,1\bar{s}(2)\,2s(3) + 1s(2)\,1\bar{s}(3)\,2s(1) + 1s(3)\,1\bar{s}(1)\,2s(2) - \big(1s(1)\,1\bar{s}(3)\,2s(2) + 1s(2)\,1\bar{s}(1)\,2s(3) + 1s(3)\,1\bar{s}(2)\,2s(1)\big) \Big]$$

stejně vyjádřete $\Psi_{2,1,3}$

$$\frac{1}{\sqrt{6}} \begin{vmatrix} 1s(2) & 1s(1) & 1s(3) \\ 1\bar{s}(2) & 1\bar{s}(1) & 1\bar{s}(3) \\ 2s(2) & 2s(1) & 2s(3) \end{vmatrix}$$

$1s(2)$ $1s(1)$ $1s(3)$
$1\bar{s}(2)$ $1\bar{s}(1)$ $1\bar{s}(3)$

$$= \frac{1}{\sqrt{6}} \Big[1s(2)\,1\bar{s}(1)\,2s(3) + 1s(3)\,1\bar{s}(2)\,2s(1) + 1s(1)\,1\bar{s}(3)\,2s(2) - 1s(3)\,1\bar{s}(1)\,2s(2) - 1s(1)\,1\bar{s}(2)\,2s(3) - 1s(2)\,1\bar{s}(3)\,2s(1) \Big]$$

$$\Psi_{1,2,3} = -\Psi_{2,1,3}$$

vlnová fce je antisymetrická vůči výměně prostorových a spinových souřadnic 2 elektronů

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úloha3 : ionŧ H_2^+ MO-LCAO

$$c_A(H_{AA}-ES_{AA})+c_B(H_{AB}-ES_{AB})=0$$
$$c_A(H_{BA}-ES_{BA})+c_B(H_{BB}-ES_{BB})=0$$

Vypočítejte možné hod. E, když $S_{AA}=S_{BB}=1$
$H_{AB}=H_{BA}$
$H_{AA}=H_{BB}=H$
$S_{AB}=S_{BA}$

→ lineárně závislé rce
⇒ determinant = 0

$$\begin{array}{cc} c_A & c_B \\ \left| \begin{matrix} H_{AA}-E\cdot S_{AA} & H_{AB}-S_{AB}\cdot E \\ H_{BA}-E\,S_{BA} & H_{BB}-E\cdot S_{BB} \end{matrix} \right| = 0 \end{array}$$

$$(H-E)\cdot(H-E)-(H_{AB}-S_{AB}E)^2=0$$

$$H^2-2HE+E^2-H_{AB}^2+2HS_{AB}E-S_{AB}^2E^2=0$$

$$E^2\cdot\underbrace{(1-S_{AB}^2)}_{a}+E\cdot\underbrace{(-2H+2HS_{AB})}_{b}+\underbrace{(H^2-H_{AB}^2)}_{c}=0$$

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31.10.2019

minule ze soustavy rovnic

$$(H_{AA}-E)^2-(H_{AB}-E\cdot S_{AB})^2=0 \qquad \left[a^2-b^2=(a+b)\cdot(a-b)\right]$$

$$\underbrace{(H_{AA}-E+H_{AB}-ES_{AB})}_{E_1}\cdot\underbrace{(H_{AA}-E-H_{AB}+ES_{AB})}_{E_2}=0$$

E_1: $E\cdot(-1-S_{AB})+H_{AA}+H_{AB}=0$

$$\boxed{E_1=\frac{H_{AA}+H_{AB}}{1+S_{AB}}}$$

E_2: $H_{AA}-H_{AB}+E(-1+S_{AB})=0$

$$\boxed{E_2=\frac{H_{AA}-H_{AB}}{1-S_{AB}}}$$

v papírech

\+ co do znamení

teď dosazení:

$$c_A(H_{AA}-E)+c_B(H_{AB}-ES_{AB})=0$$

(1) $$c_A\cdot\left(H_{AA}-\frac{H_{AA}+H_{AB}}{1+S_{AB}}\right)+c_B\left(H_{AB}-S_{AB}\cdot\frac{H_{AA}+H_{AB}}{1+S_{AB}}\right)=0$$

$$c_A\cdot\frac{\cancel{H_{AA}}+H_{AA}S_{AB}-\cancel{H_{AA}}-H_{AB}}{1+S_{AB}}+c_B\frac{\cancel{H_{AB}}+H_{AB}S_{AB}-H_{AA}\cdot S_{AB}-\cancel{H_{AB}}\cdot S_{AB}}{1+S_{AB}}=0 \quad /\cdot(1+$$

$$\cancel{c_AH_{AA}S_{AB}-c_AH_{AB}+c_BH_{AB}S_{AB}-c_B\cdot H_{AA}=0}$$

$$c_A(\cancel{H_{AA}}+H_{AA}S_{AB}-\cancel{H_{AA}}-H_{AB})+c_B(H_{AB}+\cancel{H_{AB}S_{AB}}-H_{AA}S_{AB}-\cancel{H_{AB}S_{AB}})=0$$

$$H_{AA}S_{AB}\cdot\underbrace{(c_A-c_B)}+H_{AB}\underbrace{(-c_A+c_B)}=0$$

$$\boxed{c_A=c_B}$$

(2) $$c_A\cdot\left(H_{AA}\frac{-H_{AA}+H_{AB}}{1-S_{AB}}\right)+c_B\left(H_{AB}\frac{-S_{AB}H_{AA}+S_{AB}H_{AB}}{1-S_{AB}}\right)=0$$

$$c_A(\cancel{H_{AA}}-H_{AA}S_{AB}-\cancel{H_{AA}}+H_{AB})+c_B(H_{AB}-\cancel{H_{AB}S_{AB}}-S_{AB}H_{AA}+\cancel{S_{AB}H_{AB}})=0$$

$$H_{AA}S_{AB}\cdot(-c_A-c_B)+H_{AB}(c_A+c_B)=0$$

$$(c_A+c_B)\cdot(H_{AB}-H_{AA}S_{AB})=0 \qquad \boxed{c_A=-c_B}$$

cv. 16

velikost c_A a c_B = ?

pro $E_{\oplus} \dots E_1$ $\overset{c_A = c_B}{\dots}$ z normovací podmínky

$$1 = \int (c_A 1s_A + c_A 1s_B)^* \cdot (c_A 1s_A + c_A 1s_B)\, d\tau =$$

$$= \int c_A^2 1s_A^2 + 2c_A^2 1s_A 1s_B + c_A^2 1s_B^2 \, d\tau =$$

$$= c_A^2 \underbrace{\int 1s_A^2 d\tau}_{1} + 2c_A^2 \underbrace{\int 1s_A 1s_B \, d\tau}_{S_{AB}} + c_A^2 \underbrace{\int 1s_B^2 d\tau}_{1} =$$

1 . . . . AO . . . pro
vždycky 1
už normované
↳ musíme si je tak
už připravit

$$= 2c_A^2 + 2c_A^2 S_{AB} = 2c_A^2(1 + S_{AB}) = 1$$

$$\rightarrow c_A^2 = \frac{1}{2(1+S_{AB})} \rightarrow c_A = \frac{1}{\sqrt{2(1+S_{AB})}}$$

D.ú.: nalézt z $E_- \dots E_2$ c_A nebo c_B

$$1 = \int (c_A 1s_A - c_A 1s_B)^* \cdot (c_A 1s_A - c_A 1s_B)\, d\tau$$

$$= \int c_A^2 1s_A^2 - 2c_A^2 1s_A 1s_B + c_A^2 1s_B^2 \, d\tau$$

$$= c_A^2 \cdot 1 - 2c_A^2 S_{AB} + c_A^2 \cdot 1 = 1$$

$$c_A^2 \cdot (2 - 2S_{AB}) = 1$$

$$c_A = \frac{1}{\sqrt{2(1-S_{AB})}}$$

cv. 17