Příklady z přednášky č. 3 C9930

1. $\bar{E}_+$ a $\bar{E}_-$ pro $F = 0{,}1$ a.u. :

$$\bar{E} = -\frac{15}{16} \pm \frac{\sqrt{\frac{9}{64} + F^2 \cdot \frac{2^{17}}{3^{10}}}}{2}$$

$$\bar{E}_- = -\frac{5}{16} - \frac{\sqrt{\frac{9}{64} + 0{,}01 \cdot \frac{2^{17}}{3^{10}}}}{2} \doteq -\frac{5}{16} - 0{,}201756 \doteq$$

$$\doteq \underline{\underline{-0{,}514256 \text{ a.u.}}}$$

$$\bar{E}_+ = -\frac{5}{16} + 0{,}201756 \doteq \underline{\underline{-0{,}110744 \text{ a.u.}}}$$

2. Řešení soustavy homogenních rovnic pro $\bar{E}_-$:

$$c_1(H_{11} - \bar{E}_-) + c_2 H_{12} = 0$$
$$c_1 H_{12} + c_2 (H_{22} - \bar{E}_-) = 0$$

$H_{11} = -\frac{1}{2}$ a.u. $\quad H_{12} = H_{21} = -F \cdot \frac{2^{\frac{15}{2}}}{3^5}$ a.u.

$H_{22} = -\frac{1}{8}$ a.u. $\quad \doteq -0{,}074494$ a.u.

$\bar{E}_- = -0{,}514256$ a.u.

$$c_1\left(-\tfrac{1}{2} + 0{,}514256\right) - 0{,}074494 c_2 = 0$$
$$-0{,}074494 c_1 + c_2\left(-\tfrac{1}{8} + 0{,}514256\right) = 0$$

$$0{,}014256 c_1 - 0{,}074494 c_2 = 0 \implies c_1 = \frac{0{,}074494}{0{,}014256} c_2 = 5{,}2254 c_2$$
$$-0{,}074494 c_1 + 0{,}038926 c_2 = 0$$

Normovací podmínka: $\boxed{c_1^2 + c_2^2 = 1}$

volím kladné znaménko c_2

$$5{,}2254^2 c_2^2 + c_2^2 = 1 \implies c_2 = \sqrt{\frac{1}{1 + 5{,}2254^2}} = 0{,}18796$$

$$c_1 = 5{,}2254 \cdot 0{,}18796 = 0{,}98217$$

VF: $\boxed{\psi = 0{,}982 \cdot 1s + 0{,}188 \cdot 2p_z}$

Řešení pro $\bar{E}_+$:

$$c_1 \cdot \left(-\tfrac{1}{2} + 0{,}110744\right) - 0{,}074494 c_2 = 0$$
$$-0{,}074494 c_1 + c_2\left(-\tfrac{1}{8} + 0{,}110744\right) = 0$$

$$-0{,}389256 c_1 - 0{,}074494 c_2 = 0 \implies c_2 \doteq -5{,}2253 c_1$$
$$-0{,}074494 c_1 - 0{,}014256 c_2 = 0$$

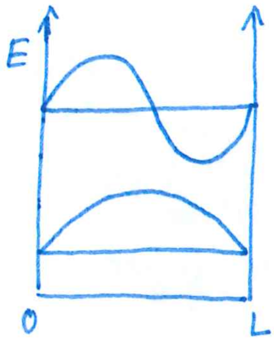
Normovací podmínka $c_1^2 + c_2^2 = 1$

$$c_1 = \sqrt{\frac{1}{c_2^2 + 1}} \doteq 0{,}18796 \implies c_2 = -0{,}98217$$

$$\boxed{\psi' = 0{,}18796 \cdot 1s - 0{,}98217 \cdot 2p_z}$$

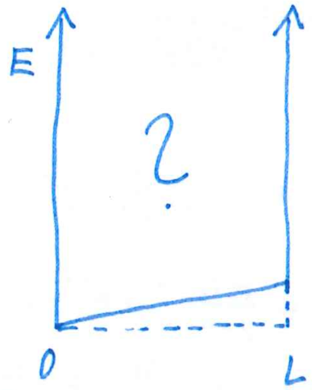
Příklady z cvičení č.3 C9930

7-8.A Problems / 7-2



$$\psi_2 = \sqrt{\frac{2}{L}} \sin \frac{2\pi x}{L} \qquad E_2 = \frac{4h^2}{8mL^2}$$

$$\psi_1 = \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L} \qquad E_1 = \frac{h^2}{8mL^2}$$



Zkušební VF pro základní stav: $\phi = \underbrace{\sqrt{0{,}9}}_{c_1}\,\psi_1 + \underbrace{\sqrt{0{,}1}}_{c_2}\,\psi_2$.

Proč $\sqrt{0{,}9}$ a $\sqrt{0{,}1}$?

– normovací podmínka $c_1^2 + c_2^2 = 1$
$(\sqrt{0{,}9})^2 + (\sqrt{0{,}1})^2 = 1$ $\Rightarrow$ ϕ je normovaná

Jaká je střední hodnota kinetické energie odpovídající ϕ?

$$\langle T \rangle = \frac{\int \phi^* \hat{T} \phi \, d\tau}{\underbrace{\int \phi^* \phi \, d\tau}_{=1 \text{ (normovaná)}}}$$

$\hat{T} = \hat{H}$ pro částici v nekonečné 1D potenciálové jámě
$\Downarrow$
$\hat{T}\psi_1 = E_1\psi_1 \qquad \hat{T}\psi_2 = E_2\psi_2$

$$\hat{T}(c_1\psi_1 + c_2\psi_2) = c_1 \cdot E_1\psi_1 + c_2 E_2 \psi_2$$

$$\phi \hat{T} \phi = (c_1\psi_1 + c_2\psi_2)(c_1E_1\psi_1 + c_2E_2\psi_2) = c_1^2E_1\psi_1^2 + c_1c_2E_2\psi_1\psi_2 + c_1c_2E_1\psi_1\psi_2 + c_2^2E_2\psi_2^2$$

$$\langle T \rangle = \int \phi \hat{T} \phi \, d\tau = \int (c_1^2E_1\psi_1^2 + c_1c_2E_2\psi_1\psi_2 + c_1c_2E_1\psi_1\psi_2 + c_2^2E_2\psi_2^2)\,d\tau$$

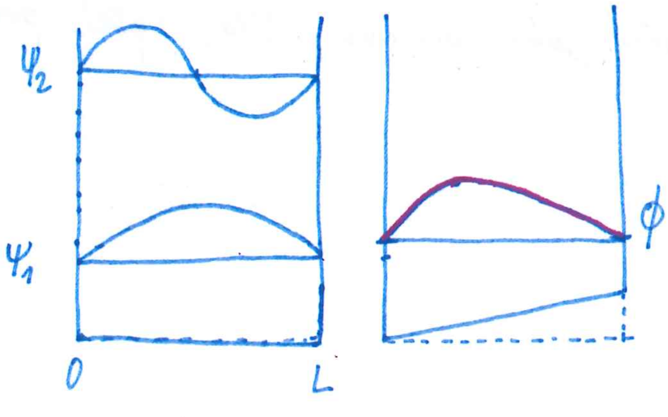
nulové integrály (orthogonální VF)

$$= c_1^2E_1 \underbrace{\int \psi_1^2 d\tau}_{1} + c_2^2E_2 \underbrace{\int \psi_2^2 d\tau}_{1}$$

(ψ_1 a ψ_2 jsou normované)

$$\langle T \rangle = c_1^2E_1 + c_2^2E_2 = 0{,}9 \cdot \frac{h^2}{8mL^2} + 0{,}1 \cdot \frac{4h^2}{8mL^2} = \frac{h^2}{8mL^2}(0{,}9 + 0{,}1 \cdot 4) = \frac{1{,}3\,h^2}{8mL^2}$$

$$\boxed{\langle T \rangle = \frac{1{,}3\,h^2}{8mL^2}}$$



7-2 Nonlinear variation: The Hydrogen Atom

zkušební VF: $\phi = \underbrace{\sqrt{\frac{\alpha^3}{\pi}}}_{N} e^{-\alpha r}$ (v zájmu čitelnosti jsem ξ přeznačila na α)

$$\bar{E} = \frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau} \qquad \int \phi^* \phi \, d\tau = 1 \text{ (} \phi \text{ je normovaná)}$$

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r}$$

$$\hat{H} = -\frac{1}{2}\cdot\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} - \frac{1}{r}$$

① $\hat{H}\phi = -\frac{1}{2}\cdot\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}\left(N\cdot e^{-\alpha r}\right) - \frac{N}{r}e^{-\alpha r} = -\frac{N}{2r^2}\frac{d}{dr}r^2(-\alpha)e^{-\alpha r} - \frac{N}{r}e^{-\alpha r} = \frac{\alpha N}{2r^2}\frac{d}{dr}r^2 e^{-\alpha r} - \frac{N}{r}e^{-\alpha r}$

$$= \frac{\alpha N}{2r^2}\left(2re^{-\alpha r} - \alpha r^2 e^{-\alpha r}\right) - \frac{N}{r}e^{-\alpha r} = \frac{\alpha N}{r}e^{-\alpha r} - \frac{\alpha^2 N}{2}e^{-\alpha r} - \frac{N}{r}e^{-\alpha r}$$

$$\hat{H}\phi = N\cdot e^{-\alpha r}\left(\frac{\alpha}{r} - \frac{\alpha^2}{2} - \frac{1}{r}\right) = N\cdot e^{-\alpha r}\left(\frac{\alpha-1}{r} - \frac{\alpha^2}{2}\right)$$

② $\phi\hat{H}\phi = N^2 e^{-2\alpha r}\left(\frac{\alpha-1}{r} - \frac{\alpha^2}{2}\right)$ $\qquad N^2 = \frac{\alpha^3}{\pi}$

③ $\bar{E} = \int \phi\hat{H}\phi \, d\tau = \int_0^\infty\int_0^\pi\int_0^{2\pi} N^2 e^{-2\alpha r}\left(\frac{\alpha-1}{r} - \frac{\alpha^2}{2}\right) r^2 \sin\theta \, d\varphi \, d\theta \, dr = \int_0^\infty N^2 r^2\left(\frac{\alpha-1}{r} - \frac{\alpha^2}{2}\right)e^{-2\alpha r} dr \cdot \overbrace{\int_0^\pi \sin\theta \, d\theta \cdot \int_0^{2\pi} d\varphi}^{2\,\cdot\,2\pi}$

$$\bar{E} = 4\pi\cdot\frac{\alpha^3}{\pi}\int_0^\infty e^{-2\alpha r}\left(r(\alpha-1) - \frac{r^2\alpha^2}{2}\right)dr = 4\alpha^3\left(\int_0^\infty (\alpha-1)\cdot r e^{-2\alpha r} dr - \frac{\alpha^2}{2}\int_0^\infty r^2 e^{-2\alpha r} dr\right)$$

$$\boxed{\text{vzoreček: } \int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}}$$

$$(\alpha-1)\int_0^\infty r\cdot e^{-2\alpha r} dr = (\alpha-1)\cdot\frac{1!}{(2\alpha)^2} = \frac{\alpha-1}{4\alpha^2}$$

$$-\frac{\alpha^2}{2}\int_0^\infty r^2 e^{-2\alpha r} dr = -\frac{\alpha^2}{2}\cdot\frac{2}{8\alpha^3} = -\frac{1}{8\alpha}$$

$$\bar{E} = 4\alpha^3\cdot\left(\frac{\alpha-1}{4\alpha^2} - \frac{1}{8\alpha}\right) = \alpha(\alpha-1) - \frac{\alpha^2}{2} = \alpha^2 - \alpha - \frac{\alpha^2}{2} = \frac{\alpha^2}{2} - \alpha$$

$$\boxed{\bar{E} = \frac{\alpha^2}{2} - \alpha}$$

④ $\frac{d\bar{E}}{d\alpha} = \frac{2\alpha}{2} - 1 \overset{⑤}{=} 0 \Rightarrow \boxed{\alpha = 1}$

⑥ $\bar{E} = \frac{1^2}{2} - 1 = -\frac{1}{2}$ a.u.

Dosazením parametru $\alpha = 1$ do ϕ získáme vlnovou funkci identickou s 1s atomu H $\Rightarrow$ jako energii taky dostaneme energii orbitalu 1s

Naše zkušební VF byla ve stejném tvaru, jaký má orbital 1s, proto nám jako minimum $E(\alpha)$ vyšel právě orbital 1s.

7-8.A Problems 17-5

Máme zkušební VF $\phi = e^{-\alpha r^2}$ pro ZS atomu H. Jaká je nejnižší možná energie vlnové funkce v tomto tvaru $(E = f(\alpha))$?

$$\bar{E} = \frac{\int \phi \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau}$$

ϕ není normovaná!

$$\int \phi^* \phi \, d\tau = \int e^{-2\alpha r^2} d\tau = \int_0^\infty \int_0^\pi \int_0^{2\pi} e^{-2\alpha r^2} r^2 \sin\theta \, d\varphi \, d\theta \, dr = \int_0^\infty r^2 e^{-2\alpha r^2} dr \cdot \int_0^\pi \sin\theta \, d\theta \cdot \int_0^{2\pi} d\varphi$$

$$\int_0^{2\pi} d\varphi = [\varphi]_0^{2\pi} = 2\pi \qquad \int_0^\pi \sin\theta \, d\theta = [-\cos\theta]_0^\pi = -(-1)+1 = 2$$

Vzoreček
$$\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4}\sqrt{\frac{\pi}{a^3}}$$

$$\int \phi \phi \, d\tau = 4\pi \cdot \int_0^\infty r^2 e^{-2\alpha r^2} dr = 4\pi \cdot \frac{1}{4}\sqrt{\frac{\pi}{8\alpha^3}} = \sqrt{\frac{\pi^3}{8\alpha^3}}$$

$$\bar{E} = \sqrt{\frac{8\alpha^3}{\pi^3}} \cdot \int \phi \hat{H} \phi \, d\tau \qquad \hat{H} = -\frac{1}{2} \cdot \frac{1}{r^2}\frac{d}{dr} r^2 \frac{d}{dr} - \frac{1}{r}$$

$$\hat{H}\phi = -\frac{1}{2} \cdot \frac{1}{r^2}\frac{d}{dr} r^2 \frac{d}{dr} e^{-\alpha r^2} - \frac{e^{-\alpha r^2}}{r} = -\frac{1}{2r^2}\frac{d}{dr} r^2 \cdot (-2\alpha) r e^{-\alpha r^2} - \frac{e^{-\alpha r^2}}{r}$$

$$= \frac{\alpha}{r^2}\frac{d}{dr} r^3 e^{-\alpha r^2} - \frac{e^{-\alpha r^2}}{r} = \frac{\alpha}{r^2}\left(3r^2 e^{-\alpha r^2} - 2\alpha r^4 e^{-\alpha r^2}\right) - \frac{e^{-\alpha r^2}}{r}$$

$$= 3\alpha e^{-\alpha r^2} - 2\alpha^2 r^2 e^{-\alpha r^2} - \frac{e^{-\alpha r^2}}{r}$$

Vzorečky
$$\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4}\sqrt{\frac{\pi}{a^3}}$$
$$\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdots (2n-1)}{2^{n+1}}\sqrt{\frac{\pi}{a^{2n+1}}}$$
$$\int_0^\infty x \cdot e^{-ax^2} dx = \frac{1}{2a}$$

$$\phi \hat{H} \phi = e^{-\alpha r^2} \cdot \hat{H}\phi = 3\alpha e^{-2\alpha r^2} - 2\alpha^2 r^2 e^{-2\alpha r^2} - \frac{1}{r} e^{-2\alpha r^2}$$

$$\int \phi \hat{H} \phi \, d\tau = \int_0^\infty \int_0^\pi \int_0^{2\pi} \left(3\alpha e^{-2\alpha r^2} - 2\alpha^2 r^2 e^{-2\alpha r^2} - \frac{1}{r} e^{-2\alpha r^2}\right) r^2 \sin\theta \, d\varphi \, d\theta \, dr$$

$$= \int_0^\infty \left(3\alpha r^2 e^{-2\alpha r^2} - 2\alpha^2 r^4 e^{-2\alpha r^2} - r \cdot e^{-2\alpha r^2}\right) dr \cdot \underbrace{\int_0^\pi \sin\theta \, d\theta}_{=2\pi} \cdot \underbrace{\int_0^{2\pi} d\varphi}_{=2}$$

$$= 4\pi \cdot \left(3\alpha \int_0^\infty r^2 e^{-2\alpha r^2} dr - 2\alpha^2 \int_0^\infty r^4 e^{-2\alpha r^2} dr - \int_0^\infty r \cdot e^{-2\alpha r^2} dr\right)$$

$$= 4\pi \cdot \left(\frac{3\alpha}{4}\sqrt{\frac{\pi}{8\alpha^3}} - 2\alpha^2 \cdot \frac{3}{8}\sqrt{\frac{\pi}{32\alpha^5}} - \frac{1}{4\alpha}\right) = 3\alpha\sqrt{\frac{\pi^3}{8\alpha^3}} - 3\alpha^2\sqrt{\frac{\pi^3}{\alpha^5 \cdot 32}} - \frac{\pi}{\alpha}$$

$$\bar{E} = \sqrt{\frac{8\alpha^3}{\pi^3}} \cdot \left(3\alpha\sqrt{\frac{\pi^3}{8\alpha^3}} - 3\alpha^2\sqrt{\frac{\pi^3}{\alpha^5 \cdot 32}} - \frac{\pi}{\alpha}\right) = 3\alpha - 3\alpha^2 \sqrt{\frac{8\alpha^3}{32\alpha^5}} - \sqrt{\frac{8\alpha}{\pi}} = 3\alpha - 3\alpha^2 \cdot \sqrt{\frac{1}{4\alpha^2}} - \sqrt{\frac{8\alpha}{\pi}}$$

$$= 3\alpha - \frac{3\alpha^2}{2\alpha} - \sqrt{\frac{8\alpha}{\pi}} = 3\alpha - \frac{3}{2}\alpha - \sqrt{\frac{8\alpha}{\pi}} = \frac{3}{2}\alpha - \sqrt{\frac{8\alpha}{\pi}}$$

$$\boxed{\bar{E} = \frac{3}{2}\alpha - \sqrt{\frac{8\alpha}{\pi}}}$$

Hledáme minimum $\bar{E}(\alpha)$: $\bar{E} = \frac{3}{2}\alpha - \sqrt{\frac{8}{\pi}}\,\alpha^{\frac{1}{2}}$

$$\frac{d\bar{E}}{d\alpha} = \frac{3}{2} - \frac{1}{2}\sqrt{\frac{8}{\pi}}\,\alpha^{-\frac{1}{2}} = 0$$

$$\frac{3}{2} = \sqrt{\frac{2}{\pi}} \cdot \frac{1}{\sqrt{\alpha}}$$

$$\sqrt{\alpha} = \frac{2}{3}\sqrt{\frac{2}{\pi}}$$

$$\alpha = \frac{4 \cdot 2}{9\pi} = \frac{8}{9\pi} \qquad \boxed{\alpha = \frac{8}{9\pi}}$$

$$\bar{E} = \frac{3}{2} \cdot \frac{8}{9\pi} - \sqrt{\frac{8}{\pi}}\sqrt{\frac{8}{9\pi}} = \frac{24}{18\pi} - \sqrt{\frac{64}{9\pi^2}} = \frac{4}{3\pi} - \frac{8}{3\pi} = -\frac{4}{3\pi} \text{ a.u.}$$

$$\boxed{\bar{E} \doteq -0{,}4244 \text{ a.u.}} \qquad E_{1s} = -\frac{1}{2} \text{ a.u.}$$

VF ve tvaru $\phi = e^{-\alpha r^2}$ pro atom H může mít minimální energii $\bar{E} = -0{,}4244$ a.u., což je vyšší energie než E_{1s} (základní stav pro atom H). To je v souladu s variačním principem.

$$\boxed{\phi = \sqrt{\frac{8\alpha^3}{\pi^3}} \cdot e^{-\frac{8r^2}{9\pi}}}$$