ORBITÁLNÍ MOMENT HYBNOSTI

$$\boxed{\vec{L} = \vec{r} \times \vec{p}} \qquad L_i = \varepsilon_{ijk} x_j p_k$$

$$L_i = \varepsilon_{ijk} x_j \left(-i \frac{\partial}{\partial x_k}\right) = -i\, \varepsilon_{ijk} x_j \frac{\partial}{\partial x_k}$$

$$L_i = \varepsilon_{ijk} x_j (-i) \left(n_k \frac{\partial}{\partial r} + \frac{D_k^n}{r}\right) =$$

$$= -i \varepsilon_{ijk} r n_j \left(n_k \frac{\partial}{\partial r} + \frac{D_k^n}{r}\right) =$$

$$= -i \underbrace{\varepsilon_{ijk}}_{A} r \underbrace{n_j n_k}_{S} \frac{\partial}{\partial r} - i \varepsilon_{ijk} r n_j \frac{D_k^n}{r} =$$

$$\Rightarrow 0$$

$$= -i \varepsilon_{ijk} n_j D_k^n$$

$$[L_i, L_j] = [\varepsilon_{imn} x_m p_n, \varepsilon_{jpq} x_p p_q] =$$

$$= \varepsilon_{imn} \varepsilon_{jpq} \underbrace{[x_m p_n, x_p p_q]}_{} =$$

$$x_m \underbrace{[p_n, x_p p_q]}_{[p_n, x_p] p_q} + \underbrace{[x_m, x_p p_q]}_{x_p [x_m, p_q]} p_n$$

$$\underbrace{[p_n, x_p]}_{-i\delta_{pn}} p_q \qquad x_p \underbrace{[x_m, p_q]}_{i\delta_{mq}}$$

$$= -i x_m p_q \delta_{pn} + i x_p p_n \delta_{mq}$$

$$= -i \varepsilon_{imp} \varepsilon_{jpq} x_m p_q + i \varepsilon_{iqn} \varepsilon_{jpq} x_p p_n$$

$$= -i (\delta_{iq} \delta_{mj} - \delta_{ij} \delta_{mq}) x_m p_q + i (\delta_{ip} \delta_{nj} - \delta_{ij} \delta_{np}) x_p p_n$$

$$= -i x_j p_i + i\delta_{ij} x_m p_m + i x_i p_j - i \delta_{ij} x_n p_n$$

$$= i(x_i p_j - x_j p_i) =$$

$$= i\, \varepsilon_{kij} x_i p_j = \underline{\underline{i L_k}}$$

$$\underline{\underline{[L_i, L^2]}} = [L_i, L_k L_k] = L_k [L_i, L_k] + [L_i, L_k] L_k =$$

$$= i \varepsilon_{ikm} L_k L_m + i \varepsilon_{ikm} L_k L_m =$$

$$= i\, \varepsilon_{ikm} (L_k L_m + L_m L_k) = i \cdot A \cdot S = \underline{\underline{0}}$$

$$L^2 = \ldots = -(\nabla^{\Omega})^2$$

vlastní funkce L^2, L_z: kulové funkce
(spherical harmonics)

$$L^2 |l, m\rangle = l(l+1) |l, m\rangle$$
$$L_z |l, m\rangle = m |l, m\rangle$$

$$\langle \vec{n} | l, m\rangle = Y_{l,m}(\theta, \varphi)$$

Jak vypadají kulové funkce Y_{lm}?

→ nejnižší $Y_{00}(\theta, \varphi)$:

$$L^2 |00\rangle = 0$$
$$L_z |00\rangle = 0$$

⇒ žádná úhlová závislost ⇒ jen konstanta

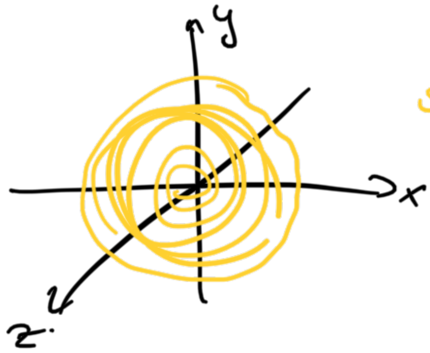
z normalizace:

$$\int |Y_{00}|^2 d\Omega = 1$$

$$|Y_{00}|^2 \int_0^{\pi} \sin\vartheta \, d\vartheta \int_0^{2\pi} d\varphi = |Y_{00}|^2 \cdot 2 \cdot 2\pi = 4\pi |Y_{00}|^2 \doteq 1$$

$$\Rightarrow Y_{00} = \frac{1}{\sqrt{4\pi}}$$

$\Rightarrow$ s-orbital



sféra

a můžeme dostat vyšší p, d, f, ... orbitaly:

$\Rightarrow$ díky $[L^2, n_j] = 2(n_j - D_j^n)$

$$[L^2, n_j]|0,0\rangle = 2(n_j - D_j^n)|0,0\rangle$$

$$(L^2 n_j - n_j \underbrace{L^2)|0,0\rangle}_{=0} = 2(n_j - \underbrace{D_j^n)|0,0\rangle}_{=0}$$

$$L^2 \, n_j|0,0\rangle = 1(1+1) \, n_j|0,0\rangle$$

úhlová fce s $l=1$ $\Leftrightarrow$ p-orbital

$j = x, y, z \Rightarrow p_x, p_y, p_z$

a podobně další:

$$[L^2, n_j] n_z Y_{00} = 2(n_j - D_j^n) n_z Y_{00}$$

$$(L^2 n_j - n_j \underbrace{L^2) n_z Y_{00}}_{\Rightarrow 2} = 2(n_j - \underbrace{D_j^n) n_z}_{= n_z D_j^n + \delta_{zj} - n_z n_j} Y_{00}$$

$$D_j^n Y_{00} \Rightarrow 0$$

$$L^2 n_j n_z Y_{00} - 2 n_j n_z Y_{00} = [2 n_j n_z - 2(\delta_{zj} - n_z n_j)] Y_{00}$$

$$L^2 n_j n_k Y_{00} = (6 n_j n_k - 2\delta_{kj}) Y_{00}$$

$$L^2 \left(n_j n_k - \tfrac{1}{3}\delta_{jk}\right) Y_{00} = 6\left(n_j n_k - \tfrac{1}{3}\delta_{kj}\right) Y_{00}$$

$2(2+1)$ d-orbitaly $(l=2)$

atd.

ale! chemické orbitaly (reálné LK Y_{lm})

! nejsou vl. funkcemi L_z

$\Rightarrow$ vl. fce L_z (tj. Y_{lm}) najdeme pomocí $[L_i, n_j] = i\varepsilon_{ijk} n_k$

$[L_i, n_j] = i\varepsilon_{ijk} n_k$

$\underline{[L_z, n_z] = 0}$

$\underline{[L_z, n_\pm]} = [L_z, n_x \pm i n_y] = i n_y \pm i(-i n_x) =$

$= \pm(n_x \pm i n_y) = \underline{\pm n_\pm}$

$[L_z, n_z] Y_{00} = 0$

$L_z n_z Y_{00} = 0$

$[L_z, n_\pm] Y_{00} = \pm n_\pm Y_{00}$

$(L_z n_\pm - n_\pm L_z) Y_{00} = \pm n_\pm Y_{00}$

$\Rightarrow 0$

$L_z (n_\pm Y_{00}) = \pm (n_\pm Y_{00})$

$Y_{10} \sim n_z Y_{00}$

$Y_{1,\pm 1} \sim n_\pm Y_{00}$

(až na normalizaci)

$\int d\Omega\, |Y_{lm}|^2 = 1$

$$\Rightarrow Y_{10} = \sqrt{\frac{3}{4\pi}}\, n_z = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$Y_{1,\pm 1} = (\pm)\sqrt{\frac{3}{8\pi}} \sin\theta\, e^{\pm i\varphi}$$

RUNGEHO-LENZŮV VEKTOR

$$\frac{d\vec{p}}{dt} = \vec{F} = -\nabla V(r)$$ centrální síla působící na částici

zde $V(r) = -\frac{Z}{r} \xrightarrow{Z=1} -\frac{1}{r}$

coulombický potenciál

$$-\nabla V(r) \Rightarrow -\frac{\partial}{\partial x_i}\left(-\frac{1}{r}\right) = \frac{\partial}{\partial x_i}\left(\frac{1}{r}\right)$$

$$r = (x_j x_j)^{1/2}$$

$$= \frac{\partial (x_j x_j)^{-1/2}}{\partial x_i} =$$

$$= -\frac{1}{2}(x_j x_j)^{-3/2}(\delta_{ij} x_j + x_j \delta_{ij}) =$$

$$= -(x_j x_j)^{-3/2} x_i =$$

$$= -n_i \frac{1}{r^2}$$

$$-\nabla V(r) = -\frac{\vec{x}}{r^3}$$

$$\frac{d\vec{p}}{dt} = \frac{-\vec{x}}{r^3}$$

$$\vec{L} \times \frac{d\vec{p}}{dt} = -\frac{1}{r^3}\vec{L} \times \vec{r}$$

$$(\vec{L} \times \vec{r})_i = \varepsilon_{ijk}\varepsilon_{jlm} x_l p_m x_k =$$

$$= (\delta_{kl}\delta_{im} - \delta_{km}\delta_{il}) x_l p_m x_k =$$

$$= x_k p_i x_k - x_i p_k x_k = \qquad [x_i, p_k] = i$$

$$= x_k (x_k p_i - i\delta_{ik}) - x_i (x_k p_k - i) =$$

$$= x_k x_k p_i - x_i x_k p_k =$$

$$= r^2 \frac{d}{dt}(r n_i) - r^2 n_i n_k \frac{d}{dt}(r n_k) =$$

$$= r^2 \left(n_i \frac{\partial r}{\partial t} + r \frac{\partial n_i}{\partial t}\right) - r^2 n_i n_k \left(\frac{\partial r}{\partial t} n_k + r \frac{\partial n_k}{\partial t}\right)$$

$$= r^3 \frac{\partial n_i}{\partial t} - r^3 n_i \underbrace{n_k \frac{\partial n_k}{\partial t}}_{=0}$$

$$= r^3 \frac{\partial n_i}{\partial t}$$

$$\vec{L} \times \frac{d\vec{p}}{dt} = \frac{d}{dt}(\vec{L} \times \vec{p}) \qquad \text{protože } \frac{d\vec{L}}{dt} = 0$$

integrál pohybu

$$\Rightarrow \frac{d}{dt}(\vec{L} \times \vec{p}) = -\frac{d\vec{n}}{dt}$$

$$\frac{d}{dt}\underbrace{(\vec{L} \times \vec{p} + \vec{n})} = 0 \qquad \Rightarrow \text{integrál pohybu}$$

$$\boxed{\begin{array}{c}\text{Rungeho-Lenzeův vektor} \\ \vec{X} = \vec{L} \times \vec{p} + z\vec{n}\end{array}}$$

$\Rightarrow$ význam RL vektoru:

- $$\vec{L} \cdot \vec{X} = \vec{L} \cdot (\vec{L} \times \vec{p}) + z \underbrace{\vec{L} \cdot \vec{n}} = 0 + 0 = 0$$

$$(\vec{r} \times \vec{p}) \cdot \vec{n} =$$
$$= (r\vec{n} \times \vec{p}) \cdot \vec{n} = 0$$

$\Rightarrow \vec{L}$ a $\vec{X}$ jsou na sebe kolmé

$\Rightarrow \vec{L}$ kolmý k rovině oběhu tělesa $\Rightarrow$

$\vec{X}$ leží v rovině oběhu tělesa

- $\vec{r}\cdot\vec{X} = \vec{r}\cdot(\vec{L}\times\vec{p}) + Z\vec{r}\cdot\vec{n} =$

$= \vec{L}\cdot(\vec{p}\times\vec{r}) + Zr\,\vec{n}\cdot\vec{n} =$

$= -L^2 + Zr$

↳ zvolíme souřadnou soustava

→ xy rovina běhu $(\vec{L} \parallel \vec{z})$

→ zvolíme x ve směru $\vec{X}$

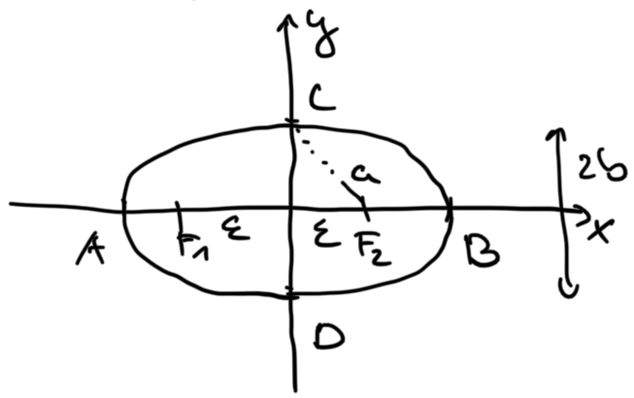
polární souřadnice: $x = r\cos\varphi$

$y = r\sin\varphi$

$\Rightarrow \vec{r}\cdot\vec{X} = -L^2 + Zr$

$rX\cos\varphi = Zr - L^2$

pozn.: elipsa $\left(\frac{x}{a}\right)^2 + \left(\frac{y}{b}\right)^2 = 1$ → výstřednost $\varepsilon^2 = a^2 - b^2$



→ posun počátku souřadnic do ohniska $x \to x - \varepsilon$
+ polární souřadnice:

$$\left(\frac{x}{a}\right)^2 + \left(\frac{y}{b}\right)^2 = 1 \quad x \to x - \varepsilon$$

$$\left(\frac{x-\varepsilon}{a}\right)^2 + \left(\frac{y}{b}\right)^2 = 1$$

$$b^2(r\cos\varphi - \varepsilon)^2 + a^2(r\sin\varphi)^2 = a^2b^2$$

$$b^2(r^2\cos^2\varphi - 2r\varepsilon\cos\varphi + \varepsilon^2) + a^2r^2\sin^2\varphi = a^2b^2$$

$$a^2r^2(1-\cos^2\varphi)$$

$$r^2\cos^2\varphi\,(b^2-a^2) - 2r\varepsilon\cos\varphi\, b^2 + b^2(\cancel{a^2} - b^2 - \cancel{a^2}) + a^2r^2 = 0$$

$$r^2\cos^2\varphi\,\varepsilon^2 + 2r\varepsilon\cos\varphi\, b^2 + b^4 = (ar)^2$$

$$(r\varepsilon\cos\varphi + b^2)^2 = (ar)^2$$

$$r\varepsilon\cos\varphi = ar - b^2 \quad \text{elipsa}$$

vs. $r X \cos\varphi = Zr - L^2$ R-L

$\Rightarrow$ velikost RL vektoru rovna výstřednosti elipsy s hl. osou $a = Z$ a $b = L$

RL míří z centra elipsy do jednoho z ohnisek

$\Rightarrow \frac{d\vec{X}}{dt} = 0 \Rightarrow$ klasický pohyb v Coulombově poli se děje po elipse a tato elipsa zachovává v čase svůj tvar a orientaci (tj. nestáčí se ani se nijak nedeformuje)

– 1. Keplerův zákon

v QM RL antisym. $\boxed{\hat{\vec{X}} = \frac{1}{2}(\hat{\vec{L}} \times \hat{\vec{p}} - \hat{\vec{p}} \times \hat{\vec{L}}) + Z\hat{\vec{n}}}$

$\Rightarrow$ hermitovský operátor

$$\vec{X} = \frac{1}{2}(\hat{\vec{L}} \times \hat{\vec{p}} - \hat{\vec{p}} \times \hat{\vec{L}}) + Z\hat{\vec{n}}$$

$$X_i = \frac{1}{2}(\varepsilon_{ijk}L_jp_k - \varepsilon_{ijk}p_jL_k) + Zn_i$$

$$\varepsilon_{ijk}L_jp_k = \varepsilon_{ijk}\varepsilon_{jmn}x_mp_np_k =$$

$$- (\delta_{kp}\delta_{iq} - \delta_{ip}\delta_{kq}) x_p p_q p_k =$$

$$= x_k p_i p_k - x_i p_k p_k$$

$$= x_k p_k p_i - x_i p^2$$

$$\varepsilon_{ijk} p_j L_k = \varepsilon_{ijk} p_j \varepsilon_{kpq} x_p p_q$$

$$= (\delta_{ip}\delta_{jq} - \delta_{iq}\delta_{jp}) p_j x_p p_q =$$

$$= p_j x_i p_j - p_j x_j p_i$$

$$= (x_i p_j - i\delta_{ij}) p_j - (x_j p_j - i\delta_{jj}) p_i$$

$$= \frac{1}{2}\left(x_k p_k p_i - x_i p^2 - x_i p^2 + i\delta_{ij} p_j + x_j p_j p_i - 3i p_i \right) + 2n_i$$

$$= x_k p_k p_i - x_i p^2 - i p_i + 2n_i$$

$$\Rightarrow \boxed{\vec{X} = -\vec{x}\, p^2 + (\vec{x}\cdot\vec{p} - i)\vec{p} + 2\vec{n}}$$

$$X_i = -x_i p^2 + (x_k p_k - i) p_i + 2n_i$$

$$p_i = -i\left(n_i \frac{\partial}{\partial r} + \frac{D_i^n}{r}\right)$$

$$p^2 = -\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{L^2}{r^2}\right)$$

$$- \quad -x_i p^2 = -r n_i (-1)\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{L^2}{r^2}\right) =$$

$$= r n_i \frac{\partial^2}{\partial r^2} + 2n_i \frac{\partial}{\partial r} - n_i \frac{L^2}{r}$$

$$x_k p_k p_i = r n_k (-i)\left(n_k \frac{\partial}{\partial r} + \frac{D_k^n}{r}\right)(-i)\left(n_i \frac{\partial}{\partial r} + \frac{D_i^n}{r}\right) =$$

$$= -r n_k n_k \frac{\partial}{\partial r}\left(n_i \frac{\partial}{\partial r} + \frac{D_i^n}{r}\right) + \underbrace{n_k D_k}_{=0} \cdot (\cdots)$$

$$= -r n_i \frac{\partial^2}{\partial r^2} - r D_i^n \left(-\frac{1}{r^2} + \frac{1}{r}\frac{\partial}{\partial r}\right)$$

$$= -rn_i\frac{\partial^2}{\partial r^2} - D_i^{n}\frac{\partial}{\partial r} + \frac{D_i^n}{r}$$

$$-ip_i = -n_i\frac{\partial}{\partial r} - \frac{D_i^n}{r}$$

$$+2n_i$$

$$= \underline{rn_i\frac{\partial^2}{\partial r^2}} + 2n_i\frac{\partial}{\partial r} - n_i\frac{L^2}{r} - \underline{rn_i\frac{\partial^2}{\partial r^2}} - D_i^n\frac{\partial}{\partial r} + \frac{D_i^n}{r} - n_i\frac{\partial}{\partial r} - \frac{D_i^n}{r}$$

$$= n_i\frac{\partial}{\partial r} - n_i\frac{L^2}{r} - D_i^n\frac{\partial}{\partial r} + 2n_i$$

$$\Rightarrow \boxed{\vec{X} = \vec{n}\left(\frac{\partial}{\partial r} - \frac{L^2}{r} + 2\right) - D_i^{(n)}\frac{\partial}{\partial r}}$$

integrál pohybu $\Leftrightarrow [X_i, H] = 0$

$$H = \frac{p^2}{2} - \frac{2}{r} \xrightarrow[Z=1]{\text{vodík}} \frac{p^2}{2} - \frac{1}{r}$$

$$\underline{\underline{[p_i, H]}} = \left[p_i, \frac{p^2}{2} - \frac{1}{r}\right] = -\left[p_i, \frac{1}{r}\right] =$$

$$= -\left[(-i)\left(n_i\frac{\partial}{\partial r} + \frac{D_i^n}{r}\right), \frac{1}{r}\right] =$$

$$= +in_i\left[\frac{\partial}{\partial r}, \frac{1}{r}\right] =$$

$$= +in_i\left[\frac{\partial}{\partial r}\left(\frac{1}{r}\,\text{"}f\text{"}\right) - \frac{1}{r}\frac{\partial}{\partial r}\text{"}f\text{"}\right] =$$

$$= in_i\left(-\frac{1}{r^2}\text{"}f\text{"} + \frac{1}{r}\frac{\partial}{\partial r}\text{"}f\text{"} - \frac{1}{r}\frac{\partial}{\partial r}\text{"}f\text{"}\right) =$$

$$\underline{\underline{= -in_i\frac{1}{r^2}}}$$

$$\underline{\underline{[L_i, H]}} = \left[L_i, \frac{1}{2}\left(p_r^2 + \frac{L^2}{r^2}\right) - \frac{1}{r}\right] =$$

$$= \left[L_i, \frac{L^2}{2r^2}\right] = \underline{\underline{0}}$$

$$[n_i, H] = \left[n_i, \frac{1}{2}\left(p_r^2 + \frac{L^2}{r^2}\right) - \frac{1}{r}\right] =$$

$$= \left[n_i, \frac{1}{2}\frac{L^2}{r^2}\right] =$$

$$= \frac{1}{2r^2}\left[n_i, L^2\right] =$$

$$= \frac{1}{r^2}\left(D_i^{n} - n_i\right)$$

$$[p_j L_k, H] = p_j [L_k, H] + [p_j, H] L_k =$$

$$= p_j \cdot 0 + \left(-i n_j \frac{1}{r^2}\right) L_k =$$

$$= -i n_j L_k \frac{1}{r^2}$$

$$[L_j p_k, H] = L_j [p_k, H] + [L_j, H] p_k =$$

$$= L_j \left(-i n_k \frac{1}{r^2}\right) + 0 \cdot p_k =$$

$$= -i L_j n_k \frac{1}{r^2}$$

$$[X_i, H] = \left[\frac{1}{2}\left(\varepsilon_{ijk} L_j p_k - \varepsilon_{ijk} p_j L_k\right) + n_i, H\right] =$$

$$= \frac{1}{2}\varepsilon_{ijk}[L_j p_k, H] - \frac{1}{2}\varepsilon_{ijk}[p_j L_k, H] + [n_i, H] =$$

$$= \frac{1}{2}\varepsilon_{ijk}\left(-i L_j n_k \frac{1}{r^2}\right) - \frac{1}{2}\varepsilon_{ijk}\left(-i n_j L_k \frac{1}{r^2}\right) +$$

$$+ \frac{1}{r^2}\left(D_i^{(n)} - n_i\right) =$$

$$= \frac{-i}{2r^2}\varepsilon_{ijk}(-i)\varepsilon_{jpq} n_p D_q^{(n)} n_k + \frac{i}{2r^2}\varepsilon_{ijk} n_j (-i)\varepsilon_{kpq} n_p D_q^{n}$$

$$+ \frac{1}{r^2}\left(D_i^{n} - n_i\right) =$$

$$= \frac{1}{2r^2}(\delta_{kp}\delta_{iq} - \delta_{ip}\delta_{kq})\, n_p \nabla_q n_k +$$

$$+ \frac{1}{2r^2}(\delta_{pi}\delta_{qj} - \delta_{pj}\delta_{qi})\, n_j n_p \nabla_q^{(n)} +$$

$$+ \frac{1}{r^2}(\nabla_i^{(n)} - n_i) =$$

$$= + \frac{1}{2r^2}\Big[-n_k \nabla_i^{(n)} n_k + n_i \overset{\to 2}{\nabla_k n_k} + \overset{\to 0}{n_j n_i \nabla_j^{(n)}} - \overset{\to 1}{n_j n_j} \nabla_i^{(n)} + 2(\nabla_i^{(n)} - n_i)\Big] =$$

$$= \frac{1}{2r^2}\Big[-n_k (n_k \nabla_i^{(n)} + \delta_{ik} - n_i n_k) + 2n_i - \nabla_i^{(n)} + 2(\nabla_i^{(n)} - n_i)\Big] =$$

$$= \frac{1}{2r^2}\Big[-\nabla_i^{(n)} - n_i + n_i + \nabla_i^{(n)}\Big] = 0$$

$$\langle n', l', m' | [X_i, H] | n, l, m \rangle = 0$$

$$\langle n', l', m' | (X_i H - H X_i) | n, l, m \rangle = 0$$

$$-\frac{1}{2n'^2} \qquad\qquad -\frac{1}{2n^2}$$

$$\langle n', l', m' | X_i | n, l, m \rangle \left(+ \frac{1}{2n'^2} - \frac{1}{2n^2} \right) = 0$$

$\Rightarrow$ pro $n' \neq n$ musí být $\langle n', l', m' | X_i | n, l, m \rangle = 0$

$\Rightarrow$ RL vektor nemíchá stavy s různým n