s-stavy vodíku a fyzické energie

$$\left[-\frac{1}{2}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+\frac{\ell(\ell+1)}{2r^2}-\frac{1}{r}\right]R_{n\ell}(r)=E_{n_\ell}R_{n\ell}(r)$$

$\ell = 0 \quad \rightarrow$ s-stavy

$$\left[-\frac{1}{2}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)-\frac{1}{r}\right]R(r)=E\,R(r)$$

Schrödingerova rovnice

$$\hat{H}_r|\psi_n\rangle = E_n|\psi_n\rangle$$

$n \in R$

$$\langle\psi_n|\hat{H}_r - E|\psi_n\rangle = 0$$

$$E_n = -\frac{1}{2n^2}$$

$$\int_0^\infty dr\, r^2\, \psi_n(r)\left(-\frac{1}{2}\frac{\partial^2}{\partial r^2}-\frac{1}{r}\frac{\partial}{\partial r}-\frac{1}{r}-E_n\right)\psi_n(r)=0$$

$r = nr'$
$dr = n\,dr'$

$$n\int_0^\infty dr'\, \cancel{n^2}\, r'^2\, \psi_n(nr')\left(-\frac{1}{2\cancel{n^2}}\frac{\partial^2}{\partial r'^2}-\frac{1}{\cancel{n^2}r'}\frac{\partial}{\partial r'}-\frac{n}{\cancel{n^2}r'}+\frac{1}{2\cancel{n^2}}\right)\psi_n(nr')=0$$

$$\hat{p} \equiv \hat{p}_r = -i\left(\frac{\partial}{\partial r}+\frac{1}{r}\right)$$

$$\hat{p}_r^2 = -\left(\frac{\partial}{\partial r}+\frac{1}{r}\right)\left(\frac{\partial}{\partial r}+\frac{1}{r}\right) = -\frac{\partial^2}{\partial r^2}-\frac{1}{r^2}-\frac{1}{r}\frac{\partial}{\partial r}-\underline{\underline{\frac{\partial}{\partial r}\frac{1}{r}}}$$

$$\frac{\partial}{\partial r}\frac{1}{r}\psi(r) =$$
$$= -\frac{1}{r^2}\psi(r)+\frac{1}{r}\frac{\partial}{\partial r}\psi(r)$$

$$= -\frac{\partial^2}{\partial r^2} - \frac{2}{r}\frac{\partial}{\partial r}$$

$$n\int_0^\infty dr'\, r'^2\, \Psi_n(nr') \left(\frac{p_r^2}{2} + \frac{1}{2} - \frac{n}{r'} \right) \Psi_n(nr') = 0$$

$$\int_0^\infty dr'\, r'\, \Psi_n(nr') \left(\frac{r p_r^2}{2} + \frac{r'}{2} - n \right) \Psi_n(nr') = 0$$

$$\chi_n(r') = \Psi_n(nr')$$

$$\boxed{\int_0^\infty dr\, r\, \chi_n(r) \left(\frac{r \hat{p}^2}{2} + \frac{r}{2} - n \right) \chi_n(r) = 0}$$

$$\langle \chi | \hat{T}_3 - n | \chi \rangle = 0$$

1) Nový, ekvivalentní vlastní problém s operátorem

$$\hat{T}_3 = \frac{r\hat{p}^2}{2} + \frac{r}{2}$$

a vlastními hodnotami

$$t_n = n$$

2) Pozor máme jiný skalární součin

3) Nalezneme-li vlastní hodnoty t_n, můžeme poskytnout vlastní energie původního problému

$$E_n = -\frac{1}{2t_n^2}$$

algebraické řešení problému s funkcemi X

Sada operátorů

$$\hat{W}_1 = \hat{r} \qquad [\hat{W}_1, \hat{W}_2] = i\hat{W}_1$$
$$\hat{W}_2 = \hat{r}\hat{p}_r \quad \Rightarrow \quad [\hat{W}_2, \hat{W}_3] = i\hat{W}_3$$
$$\hat{W}_3 = r\hat{p}_r^2 \qquad [\hat{W}_1, \hat{W}_3] = 2i\hat{W}_2$$

Nové symetričtější komutační relace

$$\underbrace{\begin{aligned}\hat{T}_1 &= \tfrac{1}{2}(\hat{W}_3 - \hat{W}_1)\\ \hat{T}_2 &= \hat{W}_2\\ \hat{T}_3 &= \tfrac{1}{2}(\hat{W}_3 + \hat{W}_1)\end{aligned}} \quad \Rightarrow \quad \begin{aligned}[\hat{T}_1, \hat{T}_2] &= -i\hat{T}_3\\ [\hat{T}_2, \hat{T}_3] &= i\hat{T}_1\\ [\hat{T}_3, \hat{T}_1] &= i\hat{T}_2\end{aligned}$$

$$\hat{T}_\pm = \hat{T}_1 \pm i\hat{T}_2$$

Harmonický oscilátor

$$[\hat{T}_3, \hat{T}_\pm] = \pm\hat{T}_\pm \longrightarrow \begin{aligned}[\hat{H}, \hat{a}] &= -\hat{a}\\ [\hat{H}, \hat{a}^+] &= \hat{a}^+\end{aligned}$$

$$\hat{T}_3 |n\rangle = n|n\rangle \qquad ; \qquad \chi_n(r) = \langle r|n\rangle$$

$\hat{T}_+|n\rangle$ je také vlastní stav $\hat{T}_3$? ověříme ?

$$\hat{T}_3 \hat{T}_+ |n\rangle = (\hat{T}_+ + \hat{T}_+\hat{T}_3)|n\rangle = \hat{T}_+(1+n)|n\rangle$$

$$T_3 T_+ - T_+ T_3 = \hat{T}_+$$
$$T_3 T_+ = \hat{T}_+ + \hat{T}_+\hat{T}_3$$

$\Downarrow$

$\hat{T}_+$ zdvihá vlastní stav, kvantové číslo n o 1.

$$\hat{T}_3 T_- |n\rangle = (n-1) T_- |n\rangle$$

Pokud existuje základní stav

$$T_- |n_{min}\rangle = 0$$

$$\hat{T}_+ \hat{T}_- |n\rangle = (\hat{T}_1 + i\hat{T}_2)(\hat{T}_1 - i\hat{T}_2)|n\rangle$$
$$= (\hat{T}_1^2 + \hat{T}_2^2 - i[\hat{T}_1, \hat{T}_2])|n\rangle$$
$$= (\underbrace{\hat{T}_1^2 + \hat{T}_2^2}_{\hat{T}_3^2} - \hat{T}_3)|n\rangle$$
$$= (\hat{T}_3^2 - \hat{T}_3)|n\rangle = n(n-1)|n\rangle$$

$$T_+ T_- |n_{min}\rangle = n_{min}(n_{min}-1)|n_{min}\rangle = 0$$

$$\Rightarrow n_{min}(n_{min}-1) = 0$$

$$n_{min} = 0 \longrightarrow E_0 = \frac{1}{-2n_{min}^2} \to -\infty$$

$$n_{min} = 1 \longrightarrow \boxed{E_1 = -\frac{1}{2}}$$

$\longrightarrow$ Energie základního stavu přirozeného podmínku.

$$t_n = 1, 2, 3, \ldots$$

$$E_n = -\frac{1}{2n^2} = -\frac{1}{2}, -\frac{1}{8}, -\frac{1}{18}, \ldots$$

energie s-stavů atomu vodíku.

Vlastní funkce ve sférických souřadnicích

$$\psi_n(nm) \overset{\vee}{=} \chi_n(r)$$

Předpokládejme

$$\int_0^\infty dr\, r\, \chi_n(r)\chi_m(r) = \delta_{nm}$$

$$r = \frac{r'}{n} \Rightarrow dr = \frac{1}{n} dr'$$

$$\frac{1}{n^2}\int_0^\infty dr'\, r'\, \chi_n\left(\frac{r'}{n}\right)\chi_n\left(\frac{r'}{n}\right) = 1$$

$$\int_0^\infty dr'\, r' \left|\frac{\chi_n(r/n)}{n}\right|^2 = \int_0^\infty dr\, r\, \chi_n(r)\chi_n(r)$$

$$\psi_n(r) = K\frac{\chi_n(r/n)}{n}$$

Normujme:

$$\int_0^\infty dr\, r^2 |\psi_n(r)|^2 = \frac{K^2}{n^2}\int_0^\infty dr\, r\chi_n\left(\frac{r}{n}\right) r\chi_n\left(\frac{r}{n}\right)$$

$$r' = \frac{r}{n} \;;\; dr' = \frac{dr}{n}$$

$$= n K^2 \int_0^\infty dr'\, r' \underbrace{\chi_n(r')\, r'\chi_n(r')}$$

Vzpomeneme na $\hat{r} = \hat{W}_1$

$$\hat{T}_1 = \frac{1}{2}(\hat{W}_2 - \hat{W}_1)$$
$$\hat{T}_3 = \frac{1}{2}(\hat{W}_3 + \hat{W}_1)$$
$$\Rightarrow \hat{W}_1 = \hat{T}_3 - \hat{T}_1$$

$$\hat{T}_+ = \hat{T}_1 + i\hat{T}_2$$
$$\hat{T}_- = \hat{T}_1 - i\hat{T}_2 \quad \Rightarrow \quad \hat{T}_1 = \frac{1}{2}\left(\hat{T}_+ - \hat{T}_-\right)$$

$$\hat{W} \equiv \hat{r} = \hat{T}_3 - \frac{1}{2}\left(\hat{T}_+ + \hat{T}_-\right)$$

$$r\chi_n = \left(\hat{T}_3 - \frac{1}{2}\left(\hat{T}_+ + \hat{T}_-\right)\right)\chi_n$$

$$\int_0^\infty dr\, r^2\, |\psi_n(r)|^2 = nk^2 \int_0^\infty dr\, r\, \chi_n(r)\left(\hat{T}_3 - \frac{1}{2}\left(\hat{T}_+ + \hat{T}_-\right)\right)\chi_n(r)$$

$$= nk^2 \langle n| \left[\hat{T}_3 - \frac{1}{2}\left(\hat{T}_+ + \hat{T}_-\right)\right] |n\rangle$$

$$= nk^2 \Big(\langle n|\hat{T}_3|n\rangle - \frac{1}{2}(n+1)\langle n|n+1\rangle - \frac{1}{2}(n-1)\langle n|n-1\rangle \Big)$$

$$= n^2k^2 = 1 \quad \Rightarrow \quad \boxed{k = \frac{1}{n}}$$

$$\boxed{\psi_n(r) = \frac{1}{n^2}\chi_n(r/n)}$$

<u>základní stav atomu vodíku</u>

$$\hat{T}_-\chi_1(r) = 0$$

$$\left(\hat{T}_1 - i\hat{T}_2\right)\chi_1(r) = 0$$

$$\left(\frac{1}{2}\left(\hat{W}_3 - \hat{W}_1\right) - i\hat{W}_2\right)\chi_1(r) = 0$$

$$\left(\frac{1}{2}\hat{r}\hat{p}_r^2 - \frac{1}{2}r - i r\hat{p}_r\right)\chi_1(r) = 0$$

$$\hat{p}_r^2 = -\frac{\partial^2}{\partial r^2} - \frac{2}{r}\frac{\partial}{\partial r}$$

$$r\hat{p}_r^2 = -r\frac{\partial^2}{\partial r^2} - 2\frac{\partial}{\partial r}$$

$$\frac{r}{2}\hat{p}_r^2 = -\frac{r}{2}\frac{\partial^2}{\partial r^2} - \frac{\partial}{\partial r}$$

$$\left(-\frac{r}{2}\frac{\partial^2}{\partial r^2} - \frac{\partial}{\partial r} - \frac{1}{2}r - r\left(\frac{\partial}{\partial r} + \frac{1}{r}\right)\right)\chi_1(r) = 0$$

$$\boxed{\chi_1(r) = a e^{-r}}$$

$$\frac{\partial^2}{\partial r^2} a e^{-r} = a e^{-r}$$

$$\frac{\partial}{\partial r} a e^{-r} = -a e^{-r}$$

$$\cancel{-\frac{ra}{2}e^{-r}} \cancel{+ a e^{-r}} \cancel{- \frac{ra}{2}e^{-r}} \cancel{+ a r e^{-r}} \cancel{- a e^{-r}} = 0$$

Nalezneme normalizaci:

$$a^2\int_0^\infty dr\, \underset{u}{r}\, \underset{v'}{e^{-2r}} = a^2\left[r\left(-\frac{1}{2}\right)e^{-2r}\right]_0^\infty - a^2\int_0^\infty dr\left(-\frac{1}{2}\right)e^{-2r}$$

$$= \frac{a^2}{2}\int_0^\infty dr\, e^{-2r} = \frac{a^2}{2}\left[\left(-\frac{1}{2}\right)e^{-2r}\right]_0^\infty$$

$$= \frac{a^2}{4} \stackrel{!}{=} 1 \implies \boxed{a = 2}$$

$$\boxed{\chi_1(r) = 2 e^{-r}}$$

$$\boxed{\psi_1(r) = 2e^{-r}}$$ ← Radiální funkce základního stavu atomu vodíku.

Vyzkoušet normování!

$$\int_0^\infty dr\, r^2\, 4e^{-2r} \equiv 1$$

Vyšší stavy (excitované)

$$\chi_2(r) \approx \hat{T}_+ \chi_1(r)$$ … jak je to s normováním

$$T_-|n\rangle = A_n|n-1\rangle$$

$$T_+|n\rangle = B_n|n+1\rangle$$

$$(\hat{T}_-)^+ = \hat{T}_+$$

$$\langle n|\hat{T}_+\hat{T}_-|n\rangle =$$

$$\langle n|n(n-1)|n\rangle = n(n-1) = |A_n|^2$$

$$T_-|n\rangle = \sqrt{n(n-1)}\,|n-1\rangle$$

$$T_+\sqrt{n(n-1)}\,|n-1\rangle = n(n-1)|n\rangle$$

$$T_+|n-1\rangle = \sqrt{n(n-1)}\,|n\rangle$$

$$T_+|n\rangle = \sqrt{n(n+1)}\,|n+1\rangle$$

$$\boxed{|n+1\rangle = \frac{T_+}{\sqrt{(n+1)n}}\,|n\rangle}$$

$$\chi_2(r) = \frac{T_+}{\sqrt{2}}\chi_1(r)$$

$$\hat{T}_+ = \hat{T}_1 + i\hat{T}_2 = \frac{1}{2}(\hat{W}_3 - \hat{W}_1) + i\hat{W}_2$$

$$= \frac{1}{2}(\hat{r}\hat{p}_r - \hat{r}) + i\hat{r}\hat{p}_r$$

$$\hat{T}_+ = -\frac{1}{2}r\frac{\partial^2}{\partial r^2} - (1-r)\frac{\partial}{\partial r} + 1 - \frac{1}{2}r$$

$$\chi_1(r) = \langle r|1s\rangle = 2e^{-r}$$

$$s \to l=0$$

$$\frac{\hat{T}_+}{\sqrt{2}}2e^{-r} = \chi_2(r) = \frac{4(1-r)e^{-r}}{\sqrt{2}}$$

$$\psi_2(r) = \frac{1}{4}\chi_2(r/2) = \frac{1}{\sqrt{2}}\left(1-\frac{r}{2}\right)e^{-\frac{r}{2}}$$

Lze ověřit, že

$$\langle 2s|2s\rangle = \int_0^\infty dr\, r^2\,\frac{1}{2}\left(1-\frac{r}{2}\right)^2 e^{-r} = 1$$

Stavy typu s atomu vodíku

$$\psi_{1s}(r,\vartheta,\varphi) = \underbrace{R_{1s}(r)}_{\psi_1(r)}\, Y_{00}(\vartheta,\varphi)$$

$Y_{\ell m}$ ← je konstanta

$$A^2\int_0^{2\pi} d\varphi \int_0^{\pi} d\vartheta \sin\vartheta = 1 \Rightarrow A = \frac{1}{\sqrt{4\pi}}$$

$$\boxed{\psi_{1s}(r,\vartheta,\varphi) = \frac{1}{\sqrt{4\pi}}\, 2\, e^{-r}}$$

Obecné řešení vyžaduje složitější radiální funkci

$$R_{n\ell}(r)$$

$$-\frac{1}{2}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\ell(\ell+1)}{r^2} - \frac{1}{r}\right)R_{n\ell}(r) = E R_{n\ell}(r)$$

algebraické řešení

$\ell = 0 \Rightarrow 0$

$$\hat{T}_3 = \frac{r\hat{p}_r^2}{2} + \frac{\ell(\ell+1)}{2r} + \frac{\hat{r}}{2}$$

Pozměníme operátor $\hat{W}_3 \rightarrow \hat{W}_3 = \hat{r}\hat{p}_r + \frac{\ell(\ell+1)}{r}$

Obdržíme komutační relace pro $\hat{T}_1$, $\hat{T}_2$ a $\hat{T}_3$

$$\hat{T}^2 = \hat{T}_3^2 - \hat{T}_1^2 - \hat{T}_2^2 = l(l+1)$$

↑ přirozeně je to 0

$$\hat{T}^2 |n,l\rangle = l(l+1)\,|n,l\rangle$$

$$\hat{T}_3 |n,l\rangle = n\,|n,l\rangle$$

obdobně jako u momentu hybnosti

⇙

$$n_{min} = l+1$$

Návrat k původnímu problému

$$E_n = -\frac{1}{2n^2} \qquad n = l+1+n_r$$

$$n_r = 0, 1, 2, \dots$$

$$\chi_{nl}(r) \rightarrow \boxed{R_{nl}(r) = \frac{1}{n^2}\chi_{nl}\left(\frac{r}{n}\right)}$$

$$\boxed{\chi_{l+1,l}(r) = \frac{2}{\sqrt{(2l+1)!}}(2r)^l e^{-r}}$$

$$\hat{r} = \hat{T}_3 - \hat{T}_1 = \hat{T}_3 - \frac{1}{2}\left(\hat{T}_+ + \hat{T}_-\right)$$

$$\boxed{r\,\chi_{nl}(r) = \left(\hat{T}_3 - \frac{1}{2}\left(\hat{T}_+ + \hat{T}_-\right)\right)\chi_{nl}(r)}$$