Relativistisk H-atom (Dirac-ligning)

Må skrive Dirac-ligning i kulekoordinater:

$$(E - q\varphi)\psi = \left(c\,\vec{\alpha}\cdot\vec{p} + \beta m c^2\right)\psi$$

Generell Dirac-ligning i elektrostatisk felt.

$$-q\varphi = \frac{Ze^2}{4\pi\varepsilon_0 r} = -V \quad : \text{Kulesymmetrisk potensial}$$

Dirac-ligning for H-atomet

$$\boxed{H\psi = \left(c\,\vec{\alpha}\cdot\vec{p} + V(r) + \beta m c^2\right)\psi = E\psi}$$

Uttrykker $\vec{\alpha}\cdot\vec{p}$ i kulekoordinater

Husk: $(\vec{\alpha}\cdot\vec{A})(\vec{\alpha}\cdot\vec{B}) = \vec{A}\cdot\vec{B} + i\,\vec{\Sigma}\cdot(\vec{A}\times\vec{B})$

$$(\vec{\alpha}\cdot\vec{r})(\vec{\alpha}\cdot\vec{r}) = \vec{r}^2 + i\,\vec{\Sigma}\cdot(\vec{r}\times\vec{r}) = \vec{r}^2$$

$$\frac{(\vec{\alpha}\cdot\vec{r})}{r}\,\frac{(\vec{\alpha}\cdot\vec{r})}{r} = 1 \qquad \boxed{\frac{\vec{\alpha}\cdot\vec{r}}{r} \equiv \alpha_r}$$

Akkurat hva dette er, skal vi se snart.

$$\vec{\alpha}\cdot\vec{p} = 1\,\vec{\alpha}\cdot\vec{p} = \frac{(\vec{\alpha}\cdot\vec{r})^2}{r^2}(\vec{\alpha}\cdot\vec{p})$$

$$= \frac{\vec{\alpha}\cdot\vec{r}}{r^2}\left((\vec{\alpha}\cdot\vec{r})(\vec{\alpha}\cdot\vec{p})\right) \qquad \underline{NB!!}$$

$$= \frac{\vec{\alpha}\cdot\vec{r}}{r^2}\left[\vec{r}\cdot\vec{p} + i\,\vec{\Sigma}\cdot(\vec{r}\times\vec{p})\right]$$

$$\vec{\alpha}\cdot\vec{p} = \frac{\alpha_r}{r}\left(\vec{r}\cdot\vec{p} + i\,\underbrace{\vec{\Sigma}\cdot\vec{L}}_{\text{Spinn-bane kobling}}\right)$$

Se på operatoren $p_r = -i\hbar\,\frac{1}{r}\frac{\partial}{\partial r}(r$ (ikke radialkomp. av $\vec{p}$!)

$$r p_r = -i\hbar\,\frac{\partial}{\partial r}(r$$

$$= -i\hbar\left(r\frac{\partial}{\partial r} + 1\right) = -i\hbar\left\{r\,\underbrace{\frac{\partial x_i}{\partial r}}_{x_i/r}\frac{\partial}{\partial x_i} + 1\right\}$$

$$= -i\hbar\left\{\vec{r}\cdot\vec{\nabla} + 1\right\} = \vec{r}\cdot\vec{p} - i\hbar$$

Altså:

$$\vec{\alpha}\cdot\vec{p} = \frac{\alpha_r}{r}\left(r p_r + i\left(\vec{\Sigma}\cdot\vec{L}+\hbar\right)\right)$$

$$= \alpha_r\left[p_r + \frac{i\left(\vec{\Sigma}\cdot\vec{L}+\hbar\right)}{r}\right]$$

Innfør operatoren:

$$\boxed{K \equiv \underbrace{\beta}_{\text{NB!!//}}\left(\vec{\Sigma}\cdot\vec{L}+\hbar\right)} \Longrightarrow$$

$[H, K] = 0$ (Vis dette). Dermed har H og K felles egenfunksjoner.

$$K\,\psi_{j\omega}^{m} = \hbar k\,\psi_{j\omega}^{m}$$

$$\boxed{\vec{\Sigma}\cdot\vec{L}+\hbar = \beta K}$$

$$\boxed{\left(c\,\alpha_r\left(p_r + \frac{i\beta K}{r}\right) + V(r) + \beta m c^2\right)\psi = E\psi}$$

Vi trenger å vite hva $\underline{\alpha_r}$ og K gjør med $\underline{\psi}$.

$$\vec{J} = \vec{L}+\vec{S} \Rightarrow J^2 = L^2 + S^2 + 2\vec{L}\cdot\vec{S}$$

$$= L^2 + S^2 + \hbar\,\vec{\Sigma}\cdot\vec{L}\ ; \quad \vec{S} = \frac{\hbar}{2}\vec{\Sigma}$$

$$\vec{\Sigma}\cdot\vec{L} = \frac{1}{\hbar}\left(J^2 - L^2 - S^2\right)$$

$$K = \frac{\beta}{\hbar}\left(J^2 - L^2 - \frac{3}{4}\hbar^2 + \hbar^2\right) = \underline{\frac{\beta}{\hbar}\left(J^2 - L^2 + \frac{\hbar^2}{4}\right)}$$

$$\psi_{j\omega}^{m} = \begin{pmatrix} i\,\frac{G(r)}{r}\,\mathcal{Y}_{jl\frac{1}{2}}^{m} \\ \frac{F(r)}{r}\,\mathcal{Y}_{jl'\frac{1}{2}}^{m} \end{pmatrix} \qquad \begin{aligned} l &= j - \frac{\omega}{2} \\ l' &= j + \frac{\omega}{2} \end{aligned}$$

$\omega = \pm 1$: Egenverdi til paritetsoperatoren!

Ansatz for egenfunksjonen.
Separert spinor i radial-del og spinn-vinkel del $\mathcal{Y}_{jl\frac{1}{2}}^{m}$, $\mathcal{Y}_{jl'\frac{1}{2}}^{m}$

$K\psi_{j\omega}^{m}$ (husk β!!)

$$= \frac{1}{\hbar r}\begin{pmatrix} iG(r)\left(J^2 - L^2 + \frac{\hbar^2}{4}\right)\mathcal{Y}_{jl\frac{1}{2}}^{m} \\ -F(r)\left(J^2 - L^2 + \frac{\hbar^2}{4}\right)\mathcal{Y}_{jl'1/2}^{m} \end{pmatrix}$$

$$= \frac{\hbar^2}{\hbar r}\begin{pmatrix} iG(r)\left(j(j+1) - (j-\frac{\omega}{2})(j-\frac{\omega}{2}+1) + \frac{1}{4}\right)\mathcal{Y}_{jl1/2}^{m} \\ -F(r)\left(j(j+1) - (j+\frac{\omega}{2})(j+\frac{\omega}{2}+1) + \frac{1}{4}\right)\mathcal{Y}_{jl'1/2}^{m} \end{pmatrix}$$

$$= \frac{\hbar}{r}\,\frac{\omega}{2}(2j+1)\begin{pmatrix} iG(r)\,\mathcal{Y}_{jl1/2}^{m} \\ F(r)\,\mathcal{Y}_{jl'1/2}^{m} \end{pmatrix}$$

$$= \hbar\omega(j+1/2)\,\underline{\underline{\psi_{j\omega}^{m}}}$$

Egenfunksjon til K!!

$$K\psi_{j\omega}^{m} = \hbar k\,\psi_{j\omega}^{m}$$

$$k = \omega(j+1/2)$$

$\omega = \pm 1$

$j = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$

Må nå vite hva

$$\vec{\alpha}\cdot\hat{r}\,\psi_{j\omega}^{m}$$

$$\vec{\alpha}\cdot\hat{r} = \begin{pmatrix} 0 & \vec{\sigma}\cdot\hat{r} \\ \vec{\sigma}\cdot\hat{r} & 0 \end{pmatrix}$$

$$\alpha_r\psi = \begin{pmatrix} 0 & \vec{\sigma}\cdot\hat{r} \\ \vec{\sigma}\cdot\hat{r} & 0 \end{pmatrix}\begin{pmatrix} \psi_a \\ \psi_b \end{pmatrix} = \begin{pmatrix} \vec{\sigma}\cdot\hat{r}\,\psi_b \\ \vec{\sigma}\cdot\hat{r}\,\psi_a \end{pmatrix} = \text{konst}\begin{pmatrix} \psi_a \\ \psi_b \end{pmatrix}$$

$\alpha_r^2 = 1 \Rightarrow$ Egenverdi til $\alpha_r = \pm 1$; <u>konst $= -1$</u>

Nå setter vi opp Dirac-ligningen:

$$\left(c\,\alpha_r\left(p_r + i\beta\frac{K}{r}\right) + V(r) + \beta mc^2 - E\right)\begin{pmatrix}\psi_a\\ \psi_b\end{pmatrix} = 0$$

$$\begin{pmatrix} V(r) - E + mc^2 & c\,\sigma_r\left(p_r - \frac{iK}{r}\right) \\ c\,\sigma_r\left(p_r + \frac{iK}{r}\right) & V(r) - E - mc^2 \end{pmatrix}\begin{pmatrix}\psi_a\\ \psi_b\end{pmatrix} = 0$$

NB!! Her har vi brukt: i) $c\,\alpha_r\, p_r = c\begin{pmatrix}0 & \sigma_r p_r\\ \sigma_r p_r & 0\end{pmatrix}$

ii) $c\,\alpha_r\, i\beta\,\frac{K}{r}$

$$\left.\begin{aligned} &= ci\begin{pmatrix}0 & \sigma_r\\ \sigma_r & 0\end{pmatrix}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\frac{K}{r} \\ &= ci\begin{pmatrix}0 & -\sigma_r\\ \sigma_r & 0\end{pmatrix}\frac{K}{r}\end{aligned}\right\} \text{Litt subtilt!!}$$

$$= \underline{\begin{pmatrix}0 & -ic\sigma_r\frac{K}{r}\\ ic\sigma_r\frac{K}{r} & 0\end{pmatrix}}$$

Fortegnsskiftet!

Altså: Koblede 2x2 ligninger for store og små komponenter:

$$(V + mc^2 - E)\psi_a + c\,\sigma_r\left(p_r - \frac{i\hbar k}{r}\right)\psi_b = 0$$

$$(V - mc^2 - E)\psi_b + c\,\sigma_r\left(p_r + \frac{i\hbar k}{r}\right)\psi_a = 0$$

Dette ombyttet er essensielt for å kunne stryke vinkeldelen

$$\left\{\begin{aligned}\sigma_r\psi_b &= -\psi_a\\ \sigma_r\psi_a &= -\psi_b\end{aligned}\right\}$$

Ikke helt rett.

Har brukt at $\underline{\underline{\alpha_r\psi = -\psi}}$

$$\boxed{\begin{aligned}(V + mc^2 - E)\,\frac{iG(r)}{r} - c\left(p_r - \frac{i\hbar k}{r}\right)\frac{F(r)}{r} &= 0\\ (V - mc^2 - E)\,\frac{F(r)}{r} - c\left(p_r + \frac{i\hbar k}{r}\right) i\,\frac{G(r)}{r} &= 0\end{aligned}}$$

Nå blir det klart for hvorfor vi definerte radialfunksjonene ~~[illegible]~~ som $iG(r)/r$, $F(r)/r$. Det forenkler ligningene betraktelig!

$$p_r = -i\hbar \frac{1}{r}\frac{\partial}{\partial r} r$$

$$p_r\left(\frac{F}{r}\right) = -i\hbar \frac{1}{r}\frac{\partial F}{\partial r}$$

$$p_r\left(\frac{G}{r}\right) = -i\hbar \frac{1}{r}\frac{\partial G}{\partial r}$$

$$\left(V + mc^2 - E\right) i\frac{G}{r} + \frac{i\hbar c}{r}\left(\frac{\partial}{\partial r} + \frac{k}{r}\right)F = 0$$

$$\left(V - mc^2 - E\right)\frac{F}{r} + \frac{ii\hbar c}{r}\left(\frac{\partial}{\partial r} - \frac{k}{r}\right)G = 0$$

Nå har vi fått separert ut radialdelene!

$$\Rightarrow \boxed{\begin{aligned} &\left(\frac{\partial}{\partial r} + \frac{k}{r}\right)F + \left(\frac{V}{\hbar c} + \frac{mc}{\hbar} - \frac{E}{\hbar c}\right)G = 0 \\ &\left(\frac{\partial}{\partial r} - \frac{k}{r}\right)G - \left(\frac{V}{\hbar c} - \frac{mc}{\hbar} - \frac{E}{\hbar c}\right)F = 0 \end{aligned}}$$

Forenkle disse ligningene ved å innføre:

$$\left.\begin{aligned} \varkappa &= \frac{1}{\hbar c}\sqrt{(mc^2)^2 - E^2} \\ \alpha &= \frac{e^2}{4\pi\varepsilon_0 \hbar c} \\ \frac{V(r)}{\hbar c} &= -\frac{Z\alpha}{r} \end{aligned}\right\}$$

Tilsvarende parametrisering hadde vi også i Klein-Gordon ligningen!!

$$\nu = \sqrt{\frac{mc^2 - E}{mc^2 + E}} = \frac{mc^2 - E}{\hbar c \varkappa} = \frac{\hbar c \varkappa}{mc^2 + E}$$

$$\varkappa\nu = \frac{mc}{\hbar} - \frac{E}{\hbar c}$$

$$\frac{\varkappa}{\nu} = \frac{mc}{\hbar} + \frac{E}{\hbar c}$$

$$\left(\frac{\partial}{\partial r} + \frac{k}{r}\right)F + \left(\varkappa\nu - \frac{Z\alpha}{r}\right)G = 0$$

$$\left(\frac{\partial}{\partial r} - \frac{k}{r}\right)G + \left(\frac{\varkappa}{\nu} + \frac{\alpha}{r}\right)F = 0$$

$$\varkappa r = \rho \quad (\text{Samme som i K-G!})$$

$$\boxed{\begin{aligned}&\left(\frac{\partial}{\partial\rho} + \frac{k}{\rho}\right)F + \left(\nu - \frac{Z\alpha}{\rho}\right)G = 0\\ &\left(\frac{\partial}{\partial\rho} - \frac{k}{\rho}\right)G + \left(\frac{1}{\nu} + \frac{Z\alpha}{\rho}\right)F = 0\end{aligned}}$$

Asymptotisk: $\rho \to \infty$

$$\left.\begin{aligned}\frac{\partial F}{\partial\rho} &= -\nu G\\ \frac{\partial G}{\partial\rho} &= -F\end{aligned}\right\} \qquad \begin{aligned}\frac{\partial^2 F}{\partial\rho^2} &= -\nu\frac{\partial G}{\partial\rho} = F\\ \frac{\partial^2 G}{\partial\rho^2} &= G\end{aligned}$$

$$\left.\begin{aligned}F &\sim e^{-\rho}\\ G &\sim e^{-\rho}\end{aligned}\right\} \text{ Asymptotisk form.}$$

Setter opp Ansatz for løsning:

$$G = e^{-\rho} \rho^{s} \sum_{\mu} a_{\mu} \rho^{\mu} = e^{-\rho} g$$

$$F = e^{-\rho} \rho^{s} \sum_{\mu} b_{\mu} \rho^{\mu} = e^{-\rho} f$$

$$\frac{\partial F}{\partial \rho} = -e^{-\rho} f + e^{-\rho} f'$$

$$\frac{\partial G}{\partial \rho} = -e^{-\rho} g + e^{-\rho} g'$$

$$\frac{k}{\rho} f + (-f + f') + \left(\nu - \frac{Z\alpha}{\rho}\right) g = 0$$

$$\left(-g + g' - \frac{k}{\rho} g\right) + \left(\frac{1}{\nu} + \frac{Z\alpha}{\rho}\right) f = 0$$

$$\boxed{\begin{aligned} f' - f + \frac{k}{\rho} f &= \left(-\nu + \frac{Z\alpha}{\rho}\right) g \\ g' - g - \frac{k}{\rho} g &= \left(-\frac{1}{\nu} - \frac{Z\alpha}{\rho}\right) f \end{aligned}}$$

Disse brukes til å skaffe rek.-formler for a_{μ}, b_{μ}.

$$\boxed{\begin{aligned} &\text{I} \quad (s+\mu+k)\, b_{\mu} - b_{\mu-1} = -\nu\, a_{\mu-1} + Z\alpha\, a_{\mu} \\ &\text{II} \quad (s+\mu-k)\, a_{\mu} - a_{\mu-1} = -\frac{1}{\nu} b_{\mu-1} - Z\alpha\, b_{\mu} \end{aligned}}$$

I + ν II: ~~Mange~~ $a_{\mu-1}$, $b_{\mu-1}$ koeff. kansellere!

$$(s+\mu+k)\,b_\mu - b_{\mu-1}$$

$$+\ \nu\,(s+\mu-k)\,a_\mu - \nu\,a_{\mu-1}$$

$$= -\nu\,a_{\mu-1} + Z\alpha\,a_\mu - b_{\mu-1} - Z\alpha\nu\,b_\mu$$

(xxx) $$(s+\mu+k+Z\alpha\nu)\,b_\mu = \left[Z\alpha - \nu(s+\mu-k)\right]a_\mu$$

b_μ uttrykkes ved a_μ, slik at

b_μ, $b_{\mu-1}$ kan elimineres i (II)

Da får vi:

$$(s+\mu-k)\,a_\mu - a_{\mu-1}$$

$$= \frac{1}{\nu}\,\frac{\left(\nu(s+\mu-1-k) - Z\alpha\right)}{s+\mu-1+k+Z\alpha\nu}\,a_{\mu-1}$$

$$+\ Z\alpha\,\frac{\left(\nu(s+\mu-k) - Z\alpha\right)}{s+\mu+k+Z\alpha\nu}\,a_\mu$$

$$\boxed{\frac{a_\mu}{a_{\mu-1}} = \frac{1 + \frac{1}{\nu}\,\frac{\nu(s+\mu-1-k)-Z\alpha}{s+\mu-1+k+Z\alpha}}{s+\mu-k - Z\alpha\left(\frac{\nu(s+\mu-k)-Z\alpha}{s+\mu+k+Z\alpha\nu}\right)}}$$ Helt sentralt resultat!!

Dette forholdet når $\mu \to \infty$:

$$\frac{a_\mu}{a_{\mu-1}} = \frac{1+\frac{\nu\cancel{\mu}}{\nu}}{\mu} = \frac{2}{\mu} \Rightarrow g \sim e^{2\rho}$$

Tilsvarende: $f \sim e^{2\rho}$

$$G = e^{-\rho} \cdot g$$

$$F = e^{-\rho} f$$

Skal G, F være normerbare:

Rekken for g, f må terminere!

Det må finnes en $\mu = \mu_0$ s.a.:

$$a_{\mu_0+1} = 0$$

$$a_{\mu_0} \neq 0$$

<u>NB!!</u> Da vil vi også ha

$$b_{\mu_0+1} = 0$$

$$b_{\mu_0} \neq 0$$

fordi $b_\mu \sim a_\mu$ iflg. (xxx)

hvis:

$$s + \mu + 1 + k + Z\alpha\nu \neq 0$$

$\mu = 0$

$$(s+k)\, b_0 = Z\alpha\, a_0$$
$$(s-k)\, a_0 = -Z\alpha\, b_0$$

Innsatt i (I) og (II)

$$(s+k)\, b_0 = -\frac{Z^2\alpha^2}{s-k}\, b_0$$

$$(s^2 - k^2 + Z^2\alpha^2)\, b_0 = 0$$

$$s = \pm\sqrt{k^2 - Z^2\alpha^2}$$

Må velge + -tegn for å få integrerbar singularitet i $|\psi|^2$ i origo!

$$\boxed{s = \sqrt{k^2 - Z^2\alpha^2}}$$

Husk: $\rho \to 0$: $\frac{G(\rho)}{\rho}, \frac{F(\rho)}{\rho} \sim \rho^{s-1}$

$$\frac{a_{\mu_0+1}}{a_{\mu_0}} = 0 \Rightarrow$$

$$1 + \frac{1}{\nu}\,\frac{\left(\nu(s+\mu_0-k) - Z\alpha\right)}{\left(s+\mu_0+k+Z\alpha\nu\right)} = 0$$

$$\nu\,(s+\mu_0+k+Z\alpha\nu) = -\nu\,(s+\mu_0-k) + Z\alpha$$

$$2\nu\,(s+\mu_0) = Z\alpha\,(1-\nu^2)$$

Ledd med k kansellere

$$\boxed{2\,(s+\mu_0) = Z\alpha\left(\frac{1}{\nu} - \nu\right)}$$

Betingelse for å få terminert rekken :: her ligger kvantiseringsbetingelsen for energier. Husk at vi hadde

$$\nu = \sqrt{\frac{mc^2-E}{mc^2+E}} = \frac{mc^2-E}{\hbar c \varkappa}$$

$$2\,(s+\mu_0) = Z\alpha\left(\sqrt{\frac{mc^2+E}{mc^2-E}} - \sqrt{\frac{mc^2-E}{mc^2+E}}\right)$$

$$= Z\alpha\,\frac{\left[mc^2+E-(mc^2-E)\right]}{\sqrt{(mc^2)^2-E^2}}$$

$$s+\mu_0 = \frac{Z\alpha E}{\sqrt{(mc^2)^2-E^2}}$$

$$(s+\mu_0)^2 = \frac{(Z\alpha)^2E^2}{(mc^2)^2-E^2} \Rightarrow (mc^2)^2 - E^2 = \frac{(Z\alpha)^2}{(s+\mu_0)^2}E^2$$

$$E = \pm\, mc^2 \Big/ \sqrt{1+\frac{Z^2\alpha^2}{(s+\mu_0)^2}}$$

$$E = \pm \frac{mc^2}{\sqrt{1 + \frac{Z^2\alpha^2}{(s+\mu_0)^2}}}$$

$$s = \sqrt{k^2 - Z^2\alpha^2}$$

Sammenlign med Balmer-serien!

$$E = \pm mc^2 \mp \frac{Z^2\alpha^2 mc^2}{2(\mu_0 + |k|)^2}$$

$$n = \mu_0 + |k| = 1, 2, 3, 4 \ldots$$

$$\mu_0 = n - |k| \quad ; \quad k = \omega(j + 1/2)$$

Heltall = heltall − heltall

$$k^2 = (j + 1/2)^2$$

$$E = \pm \frac{mc^2}{\sqrt{1 + \frac{Z^2\alpha^2}{\left(\underbrace{n - (j+\frac{1}{2})}_{\mu_0} + \underbrace{\sqrt{(j+\frac{1}{2})^2 - Z^2\alpha^2}}_{s}\right)^2}}}$$

Dette spekteret har nøyaktig samme form som KG-spekteret for sentral symm. pot, nur $j \to l = 0, 1, 2, 3 \ldots$

$\vec{L}^2\psi = \hbar^2 l(l+1)\psi$

$\vec{J}^2\psi = \hbar^2 j(j+1)\psi$

$\vec{J} = \vec{L} + \vec{S}$

Forskjellen mellom KG og Dirac ligger i $\vec{J}^2 = \vec{L}^2 + \vec{S}^2 + 2\vec{L}\cdot\vec{S}$, siden spekteret er spin-degenerert i ligger, ligger forskjellen i $\vec{L}\cdot\vec{S}$, dvs spin-bane koblingen. (Hush Thomas-Darwin korreksjon). Dette er en annen ting å se at TD-leddet må være spin-bane kobling

Endelig!!

Legg merke til "katastrofen" som skjer:

$$j + \frac{1}{2} = Z\alpha \quad \therefore \quad \underline{Z = 1/\alpha} = \underline{137}$$

Største atom funnet hittil: $Z = 115$ (vår 2004)

Komplekst spektrum.

Vakuum-fluktuasjonene går off the scale!!