POSTECH 이성익 교수의
양자 세계에 관한 강연
- 12장 -

편집 도우미: POSTECH 학부생 임향택

Chapter 12

The Real Hydrogen Atom

가짜 수소 (Ideal Hydrogen atom)
진짜 수소 (Real Hydrogen atom)

Relativistic effect

Spin orbit effect
Zeeman effect

외부 B-field
$\vec{L}\cdot\vec{B}$ Zeeman effect
$\left(\vec{L}+2\vec{S}\right)\cdot\vec{B}$ anomalous

Zeeman effect

내부 B field
$\vec{L}\cdot\vec{S}$ coupling

$\vec{M}\propto\vec{S}$
$\vec{B}\propto\vec{L}$
1) $\vec{L}\cdot\vec{S}$ coupling
2) $\vec{L}\cdot\vec{I}$ coupling
유명한 21.4cm wave

$$H_0=\frac{p^2}{2\mu}-\frac{ze^2}{r} \quad\rightarrow\quad mc^2+\frac{p^2}{2\mu}-\frac{1}{8}\frac{\left(p^2\right)^2}{m^3c^2}-\frac{ze^2}{r}$$

pf.

1) $H=\frac{p^2}{2m}-\frac{ze^2}{r}$에서 $H=\frac{p^2}{2\mu}-\frac{ze^2}{r}$ pf

2) $H=\frac{p^2}{2\mu}-\frac{ze^2}{r}\rightarrow mc^2+\frac{p^2}{2\mu}-\frac{1}{8}\frac{\left(p^2\right)^2}{m^3c^2}-\frac{ze^2}{r}$

pf. $\frac{p_e^2}{2m}+\frac{p_p^2}{2M}=\frac{1}{2\mu}p^2$임을 증명하자.

electron의 좌표 $\left(x_1,y_1,z_1\right)$

proton의 좌표 $\left(x_2,y_2,z_2\right)$

Let $x = x_1 - x_2$

$$X = \frac{1}{m+M}\left(mx_1 + Mx_2\right)$$

$$\frac{p_e^2}{2m} + \frac{p_p^2}{2M} = -\frac{\hbar^2}{2m}\left[\left(\frac{\partial}{\partial x_1}\right)^2 + \left(\frac{\partial}{\partial y_1}\right)^2 + \left(\frac{\partial}{\partial z_1}\right)^2\right] - \frac{\hbar^2}{2M}\left[\left(\frac{\partial}{\partial x_2}\right)^2 + \left(\frac{\partial}{\partial y_2}\right)^2 + \left(\frac{\partial}{\partial z_2}\right)^2\right]$$

$$\frac{\partial}{\partial x_1} = \frac{\partial}{\partial x}\cdot\frac{\partial x}{\partial x_1} + \frac{\partial}{\partial X}\cdot\frac{\partial X}{\partial x_1} = \frac{\partial}{\partial x} + \frac{m}{m+M}\cdot\frac{\partial}{\partial X}$$

$$\frac{\partial}{\partial x_1} = -\frac{\partial}{\partial x} + \frac{M}{m+M}\cdot\frac{\partial}{\partial X}$$

$$= -\frac{\hbar^2}{2m}\left(\frac{\partial}{\partial x} + \frac{m}{m+M}\cdot\frac{\partial}{\partial X}\right)^2 - \frac{\hbar^2}{2M}\left(-\frac{\partial}{\partial x} + \frac{M}{m+M}\cdot\frac{\partial}{\partial X}\right)^2$$

$$= -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{m}{m+M}\frac{\partial}{\partial x}\frac{\partial}{\partial X} + \left(\frac{m}{m+M}\right)^2\cdot\frac{\partial^2}{\partial X^2}\right] - \frac{\hbar^2}{2M}\left[\frac{\partial^2}{\partial x^2} - \frac{M}{m+M}\frac{\partial}{\partial x}\frac{\partial}{\partial X} + \left(\frac{M}{m+M}\right)^2\frac{\partial^2}{\partial X^2}\right]$$

$$= -\frac{1}{2\mu}\frac{\partial^2}{\partial x^2} + \frac{1}{2(m+M)}\frac{\partial^2}{\partial X^2}$$

↑ center of mass의 움직임. potential과 무관
constant of motion $\rightarrow$ neglect

$$\left(p_e^2c^2 + m^2c^4\right)^{1/2} + \frac{p_p^2}{2M} = mc^2\left(1 + \frac{p_e^2}{m^2c^2}\right)^{1/2} + \frac{p_p^2}{2M}$$

$$= mc^2\left(1 + \frac{p_e^2}{2m^2c^2} - \frac{1}{8}\frac{p_e^4}{m^4c^4}\right) + \frac{p_p^2}{2M} \qquad \because (1+x)^{1/2} = 1 + \frac{1}{2}x - \frac{1}{8}x^2$$

$$= mc^2 + \frac{p_e^2}{2m} + \frac{p_p^2}{2M} - \frac{1}{8}\frac{p_e^4}{m^3c^2}$$

$$= mc^2 + \frac{p^2}{2\mu} - \frac{p^4}{8m^3c^2}$$

mc^2 : constant

$$H_1 = -\frac{\left(p^2\right)^2}{8m^3c^2}$$

estimate $\dfrac{\langle H_1\rangle}{\langle H_0\rangle}=\dfrac{\dfrac{p^4}{8m^3c^2}}{\dfrac{p^2}{2m}}$

$$\sim\frac{p^2}{m^2c^2}\sim\frac{m^2c^2z^2\alpha^2}{m^2c^2}\sim z^2\alpha^2$$

$p\sim mcz\alpha$

Spin-Orbit Coupling

$-\vec{M}\cdot\vec{B}=\dfrac{e}{mc}\vec{S}\cdot\dfrac{1}{c}\cdot\vec{v}\times\vec{E}$ $\left(\dfrac{1}{c}\cdot\vec{v}\times\vec{E}:electron\right.$이 느끼는 B field$\left.\right)$

$$=\frac{e}{mc^2}\vec{S}\cdot\vec{v}\times\vec{E}$$

$$=\frac{e}{m^2c^2}\vec{S}\cdot\vec{p}\times\vec{E}$$

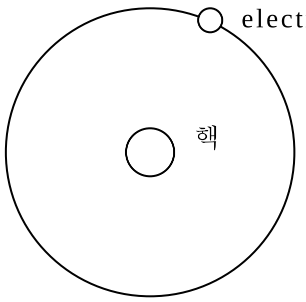
$$=-\frac{e}{m^2c^2r}\vec{S}\cdot(\vec{p}\times\vec{r})\frac{\partial}{\partial r}\phi$$

$$=\frac{e}{m^2c^2}\frac{1}{r}\vec{S}\cdot\vec{L}\frac{\partial}{\partial r}\frac{e}{r}$$

$$=\frac{e}{m^2c^2}\frac{1}{r}\vec{S}\cdot\vec{L}\frac{\partial\phi}{\partial r}$$

$$=-\frac{e}{m^2c^2}\frac{1}{r}e\left(-\frac{1}{r^2}\right)\vec{S}\cdot\vec{L}$$

$$=\frac{e^2}{m^2c^2r^3}\vec{S}\cdot\vec{L}$$



$(-e)\vec{E}=-\nabla(-e\phi:\text{Potential energy})$

$$\vec{E}=-\nabla\phi$$

$$=-\frac{\vec{r}}{r}\frac{\partial\phi}{\partial r}$$

$$\phi=\frac{e}{r}$$

$$H_2=\frac{e}{2m^2c^2}\frac{1}{r}\vec{S}\cdot\vec{L}\frac{\partial\phi}{\partial r}$$

$$H_1=-\frac{1}{8}\frac{(p^2)^2}{m^3c^2}$$

$$=-\frac{1}{2mc^2}\left(\frac{p^2}{2m}\right)^2 \qquad H_0=\frac{p^2}{2m}-\frac{ze^2}{r}$$

$$=-\frac{1}{2mc^2}\left(H_0+\frac{ze^2}{r}\right)\left(H_0+\frac{ze^2}{r}\right)$$

$$\langle \phi_{nlm} | H_1 | \phi_{nlm} \rangle = -\frac{1}{2mc^2} \langle \phi_{nlm} | \left(H_0 + \frac{ze^2}{r} \right) \left(H_0 + \frac{ze^2}{r} \right) | \phi_{nlm} \rangle$$

$$= -\frac{1}{2mc^2} \left[E_n^2 + 2E_n \cdot ze^2 \left\langle \frac{1}{r} \right\rangle_{nlm} + \left(ze^2\right)^2 \cdot \left\langle \frac{1}{r^2} \right\rangle_{nlm} \right]$$

$$= -\frac{1}{2mc^2} \left\{ \left[\frac{mc^2 (z\alpha)^2}{2n^2} \right]^2 + \left[-\frac{2mc^2 (z\alpha)^2}{2n^2} \cdot ze^2 \cdot \left(\frac{z}{a_0 n^2} \right) + \left(ze^2\right)^2 \cdot \frac{z^2}{a_0^2 n^3 \left(l + \frac{1}{2} \right)} \right] \right\}$$

$$= -\frac{1}{2mc^2} (z\alpha)^2 \cdot \left[\frac{(z\alpha)^2}{n^3 \left(l + \frac{1}{2} \right)} - \frac{3(z\alpha)^2}{4n^4} \right]$$

$\langle H_1 \rangle$의 크기

$$= -\frac{1}{2} mc^2 (z\alpha)^2 \left[\frac{(z\alpha)^2}{n^3 \left(l + \frac{1}{2} \right)} - \frac{3(z\alpha)^2}{4n^4} \right]$$

특징 1. l의 함수이다.

2. n이 커지면 작아진다.

3. $(z\alpha)$가 커지면 커진다.

$$H_2 = -\frac{1}{2m^2c^2} \vec{S} \cdot \vec{L} \frac{1}{r} e \cdot \frac{d\phi}{dr} \qquad \phi = \frac{ze}{r}$$

$$= \frac{1}{2m^2c^2} \frac{1}{r} \left(\frac{ze}{r^2} \right) e \vec{S} \cdot \vec{L}$$

$$= \frac{ze^2}{2m^2c^2} \vec{S} \cdot \vec{L} \frac{1}{r^3}$$

크기를 어떻게 계산하나?

$\vec{S} \cdot \vec{L}, L^2, S^2, J^2$은 commute 한다.

더 중요한 사실 $\left[\vec{S} \cdot \vec{L}, J^2 \right] = 0, \left[\vec{S} \cdot \vec{L}, J_z \right] = 0$

eigenvector

$$\psi_{j=l+\frac{1}{2}, m_j = m \pm \frac{1}{2}} \quad \text{or} \quad \psi_{j=l-\frac{1}{2}, m_j = m \pm \frac{1}{2}}$$

$$\vec{S}\cdot\vec{L}\psi_{j=l+\frac{1}{2},m_j=m\pm\frac{1}{2}} = \frac{1}{2}\left(J^2-L^2-S^2\right)\psi_{j=l+\frac{1}{2},m_j=m\pm\frac{1}{2}}$$

$$= \frac{1}{2}\left[\left(l+\frac{1}{2}\right)\left(l+\frac{3}{2}\right)-l\left(l+1\right)-\frac{3}{4}\right]\hbar^2$$

$$= \frac{1}{2}\left[l^2+2l+\frac{3}{4}-l^2-l-\frac{3}{4}\right]\hbar^2$$

$$\therefore \quad = \frac{1}{2}l\hbar^2$$

$$\vec{S}\cdot\vec{L}\psi_{j=l-\frac{1}{2},m_j=m\pm\frac{1}{2}} = \frac{1}{2}\left[\left(l-\frac{1}{2}\right)\left(l+\frac{1}{2}\right)-l\left(l+1\right)-\frac{3}{4}\right]\hbar^2$$

$$= \frac{1}{2}\left[l^2-\frac{1}{4}-l^2-l-\frac{3}{4}\right]\hbar^2$$

$$= \frac{1}{2}\left(-l-1\right)\hbar^2$$

$$\therefore \left\langle \phi_{l\pm\frac{1}{2},m_j\pm\frac{1}{2}} \middle| H_2 \middle| \phi_{l\pm\frac{1}{2},m_j\pm\frac{1}{2}} \right\rangle = \frac{ze^2}{2mc^2}\frac{\hbar^2}{2}\begin{Bmatrix} l \\ -\left(l+1\right)\end{Bmatrix}\int dr\cdot r^2\cdot\left[R_{nl}\left(r\right)\right]^2\cdot\frac{1}{r^3}$$

$$\left\langle \frac{1}{r^3}\right\rangle_{nl} = \frac{z^3}{a_0^3}\frac{1}{n^3 l\left(l+\frac{1}{2}\right)\left(l+1\right)}$$

$$\therefore \Delta E = \frac{1}{4}mc^2\left(z\alpha\right)^4\cdot\frac{\begin{Bmatrix} l \\ -(l+1)\end{Bmatrix}}{n^3 l\left(l+\frac{1}{2}\right)\left(l+1\right)}$$

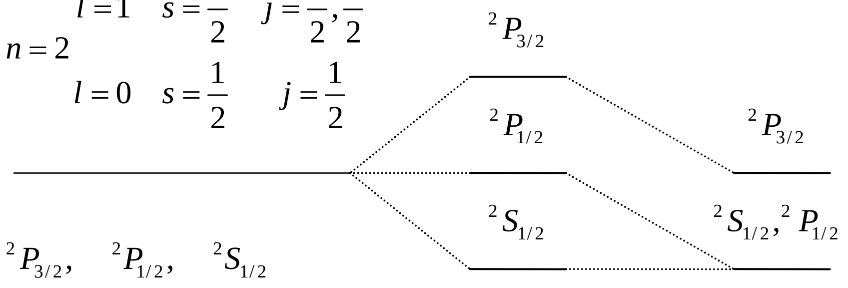
참고: H_2 때문에 생겨난 ΔE는 Spin-orbit coupling

1) l, j만의 함수이다.

2) l이 커지면 작아진다.
3) $z\alpha$가 커지면 커진다.

수소 $n=2$ state

$$n=2 \quad \begin{matrix} l=1 & s=\frac{1}{2} & j=\frac{3}{2},\frac{1}{2} \\ l=0 & s=\frac{1}{2} & j=\frac{1}{2} \end{matrix}$$



ΔE due to H_1 and H_2

$$\Delta E = \Delta E_1 + \Delta E_2 \qquad (1\text{:relativistic, } 2\text{: spin-orbit})$$

$$= -\frac{1}{2}mc^2(z\alpha)^4 \cdot \left[\frac{1}{n^3\left(l+\frac{1}{2}\right)} - \frac{3}{4n^4}\right] + \frac{1}{4}mc^2(z\alpha)^4 \cdot \frac{\begin{matrix} l \\ -(l+1) \end{matrix}}{n^3\left(l+\frac{1}{2}\right)(l+1)}$$

$j=l-\frac{1}{2}$ 경우와 $j=l+\frac{1}{2}$인 경우

$$\Delta E = -\frac{1}{2}mc^2 \cdot (z\alpha)^4 \cdot \frac{1}{n^3}\left[\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right]$$

j가 같으면 같다.

Relativistic Dirac equation $\rightarrow$ $l=0$에서는 맞는다.

Anomalous Zeeman Effect

$\vec{L}\cdot\vec{S}$ coupling에 Zeeman effect가 섞여 있다.

$$H_0 = \frac{p^2}{2\mu} - \frac{ze^2}{r} + \frac{1}{2m^2c^2}\frac{ze^2}{r^3}\vec{L}\cdot\vec{S}$$

Perturbation:

$$H_1 = \frac{e}{2mc}\left(\vec{L}+2\vec{S}\right)\cdot\vec{B}$$

$\vec{L}\cdot\vec{S}$ coupling과 relativistic effect는

$|j, j_z\rangle$가 eigen state였다.

또한 j가 같으면 에너지 eigenvalue가 같았다.

$$\vec{M} = -\frac{eg}{2mc}\vec{S}$$

$$\left\langle \phi_{j,m_j,l} \middle| \frac{eB}{2mc}\left(L_z + 2S_z\right) \middle| \phi_{j,m_j,l} \right\rangle = \left\langle \phi_{j,m_j,l} \middle| \frac{eB}{2mc}\left(J_z + S_z\right) \middle| \phi_{j,m_j,l} \right\rangle$$

$$= \frac{eB}{2mc}\left(\hbar m_j\right) + \frac{eB}{2mc}\left\langle \phi_{j,m_j,l} \middle| S_z \middle| \phi_{j,m_j,l} \right\rangle$$

$\phi_{j,l+\frac{1}{2},l}$

total angular momentum : $l+\frac{1}{2}$

z component : $m+\frac{1}{2}$

$m+\frac{1}{2}$은 $l+\frac{1}{2}$과 $-\left(l+\frac{1}{2}\right)$ 사이에 있다.

$$\phi_{j,l+\frac{1}{2},l} = \sqrt{\frac{l+m+1}{2l+1}}Y_{l,m}\chi_+ + \sqrt{\frac{l-m}{2l+1}}Y_{l,m+1}\chi_-$$

$$\phi_{j,l-\frac{1}{2},l} = \sqrt{\frac{l-m}{2l+1}}Y_{l,m}\chi_+ - \sqrt{\frac{l+m+1}{2l+1}}Y_{l,m+1}\chi_-$$

$$\therefore \left\langle \phi_{j,l+\frac{1}{2},l} \middle| S_z \middle| \phi_{j,l+\frac{1}{2},l} \right\rangle$$

$$= \left\langle \sqrt{\frac{l+m+1}{2l+1}}Y_{l,m}\chi_+ + \sqrt{\frac{l-m}{2l+1}}Y_{l,m+1}\chi_- \middle| S_z \middle| \sqrt{\frac{l+m+1}{2l+1}}Y_{l,m}\chi_+ + \sqrt{\frac{l-m}{2l+1}}Y_{l,m+1}\chi_- \right\rangle$$

$$= \frac{l+m+1}{2l+1}\cdot\frac{\hbar}{2} - \frac{l-m}{2l+1}\cdot\frac{\hbar}{2}$$

$$= \frac{2m+1}{2l+1}\cdot\frac{\hbar}{2}$$

$$= \frac{\hbar m_j}{2l+1}$$

같은 방법으로

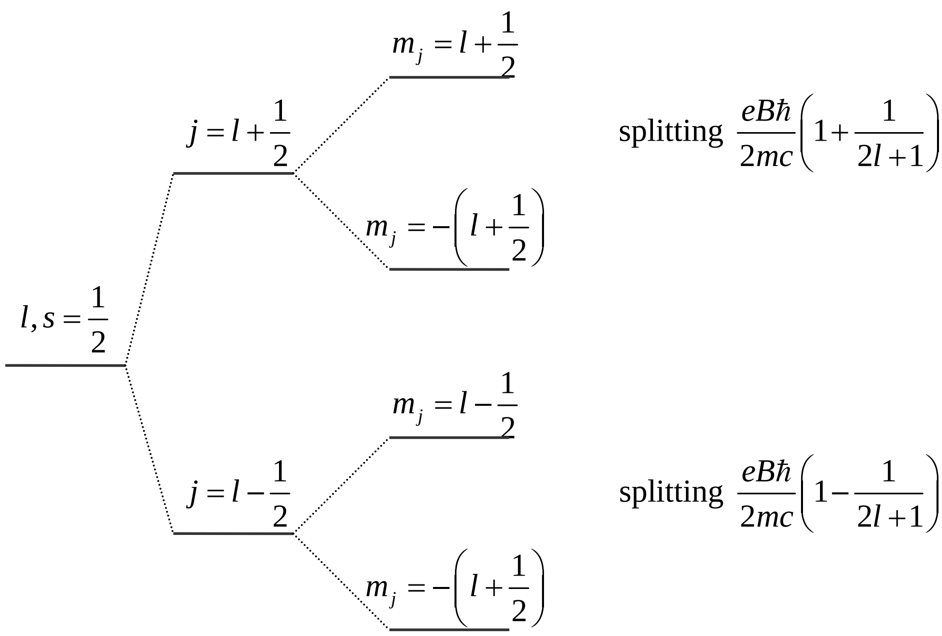
$$\left\langle \phi_{j,l+\frac{1}{2},l} \middle| S_z \middle| \phi_{j,l+\frac{1}{2},l} \right\rangle = \frac{\hbar}{2}\cdot\frac{l-m}{2l+1} - \frac{\hbar}{2}\cdot\frac{l+m+1}{2l+1}$$

$$= -\frac{\hbar}{2}\cdot\frac{2m+1}{2l+1}$$

$$= -\frac{\hbar m_j}{2l+1}$$

$$\therefore \begin{aligned} \Delta E &= \frac{eB}{2mc}\left(\hbar m_j\right) + \frac{eB}{2mc}\left(\pm\frac{\hbar m_j}{2l+1}\right) \\ &= \frac{eB\hbar m_j}{2mc}\left(1 \pm \frac{1}{2l+1}\right) \qquad \text{where } j = l \pm \frac{1}{2} \end{aligned}$$

General representation of anomalous Zeeman effect



l, s coupling + relativistic effect

if $l = 0$이면

$$\phi_{j=\frac{1}{2}, j_z=\frac{1}{2}, l=0} = Y_{0,0}\chi_+$$

or

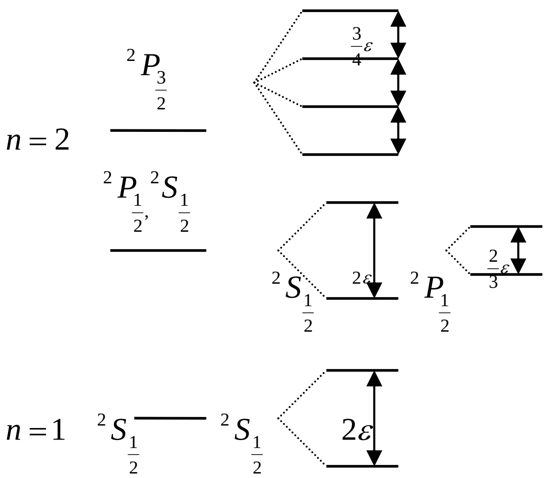
$$\phi_{j=\frac{1}{2}, j_z=-\frac{1}{2}, l=0} = Y_{0,0}\chi_-$$

$$\therefore \left\langle Y_{00}\chi_+ \middle| 2S_z \middle| Y_{00}\chi_+ \right\rangle = 2\cdot\frac{1}{2}\hbar$$

$$\left\langle Y_{00}\chi_- \middle| 2S_z \middle| Y_{00}\chi_- \right\rangle = -\frac{2}{2}\hbar$$

$$\therefore \begin{aligned} \Delta E &= \frac{eB}{2mc}\cdot\frac{2}{2}\hbar + \frac{eB}{2mc}\cdot\frac{2}{2}\hbar \\ &= \frac{2eB}{2mc}\hbar \end{aligned}$$

fine structure

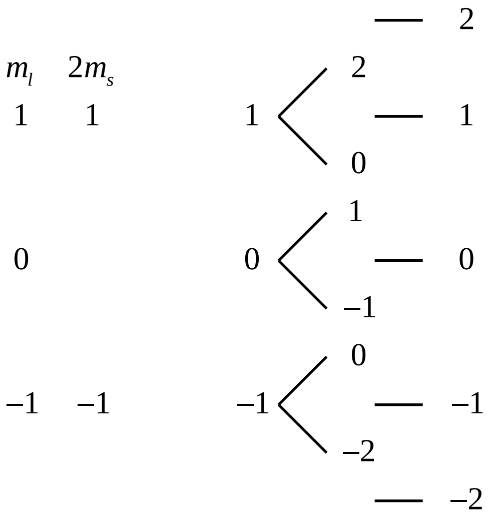


l, s coupling + relativistic effect   anomalous zeeman effect   selection rule $(\Delta l = 1, \Delta m = \pm 1, 0)$

외부 자기장이 매우 크면

$$\frac{eB\hbar}{2mc}(m_l + 2m_s)$$

예. $l = 1, s = \frac{1}{2}$ five level



Famous 21.4cm

1. 수소의 양
2. motion and temperature that contains hydrogen gas

태양계 : hydrogen atom의 density $1cm^{-3}$

온도 $100K$

어디에서 나오나

핵의 magnetic moment와 $S=\frac{1}{2}$인 electron의 spin과의 interaction

Hyperfine structure

$\vec{M}=\frac{zeg_N}{2M_N c}\vec{I}$ g_N : gyromagnetic ratio

핵에 의한 magnetic field

$$\vec{A}(\vec{r})=-\frac{1}{4\pi}\left(\vec{M}\times\nabla\right)\frac{1}{r}$$

$$\begin{aligned}\vec{B}&=\nabla\times\vec{A}\\&=-\frac{1}{4\pi}\left[\nabla\times\left(\vec{M}\times\nabla\frac{1}{r}\right)\right]\\&=-\frac{1}{4\pi}\vec{M}\nabla^2\frac{1}{r}+\frac{1}{4\pi}\nabla\left(\vec{M}\cdot\nabla\right)\frac{1}{r}\end{aligned}$$

$$\begin{aligned}H_1&=-\vec{M}_e\cdot\vec{B}\\&=\frac{e}{mc}\vec{S}\cdot\vec{B}\\&=\frac{e}{mc}\vec{S}\cdot\left[-\frac{\vec{M}}{4\pi}\nabla^2\frac{1}{r}+\frac{1}{4\pi}\nabla\left(\vec{M}\cdot\nabla\right)\frac{1}{r}\right]\text{ where }\vec{M}=\frac{zeg_N}{2M_N c}\vec{I}\\&=\frac{e}{mc}\cdot\frac{zeg_N}{2M_N c}\vec{S}\cdot\left[-\frac{\vec{I}}{4\pi}\nabla^2\frac{1}{r}+\frac{1}{4\pi}\nabla\left(\vec{M}\cdot\nabla\right)\frac{1}{r}\right]\\&=\frac{e}{mc}\cdot\frac{zeg_N}{2M_N c}\left(-\frac{1}{4\pi}\right)\left(-\frac{2}{3}\right)\vec{S}\cdot\vec{I}\int d^3r\left|\phi(\vec{r})\right|^2\cdot\nabla^2\frac{1}{r}\end{aligned}$$

where $\nabla^2\frac{1}{r}=-4\pi\delta(r)$

$$\because\left(\vec{S}\cdot\nabla\right)\left(\vec{I}\cdot\nabla\right)\frac{1}{r}=\frac{1}{3}\vec{S}\cdot\vec{I}\left(\nabla^2\frac{1}{r}\right)$$

$$\text{pf. }\int d^3r\phi^*(r)\left(\vec{S}\cdot\nabla\right)\left(\vec{I}\cdot\nabla\right)\frac{1}{r}\phi(r)=S_iI_k\int d^3r\left|\phi(r)\right|^2\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_k}\left(\frac{1}{r}\right)$$

$$=\frac{1}{3}\vec{S}\cdot\vec{I}\int d^3r\left|\phi(r)\right|^2\nabla^2\frac{1}{r}$$

$i=k$만 남고 $\frac{\partial^2}{\partial x^2}=\frac{1}{3}\frac{\partial^2}{\partial r^2}$ $\because$ Isotropic하다.

For $\phi(\vec{r}) = \phi_{n00}(\vec{r})$ S state

$$H_1 = -\frac{ze^2 g_N}{12\pi m M_N c^2} \cdot (-4\pi) \left|\phi_{n00}(0)\right|^2$$

$$= \frac{g_N}{3} \cdot \frac{m}{M_N} (z\alpha)^2 mc^2 \cdot \frac{\vec{S} \cdot \vec{I}}{\hbar^2} \left(\frac{\hbar}{mc}\right)^3 \left|R_{n0}(0)\right|^2$$

$$\left|R_{n0}(0)\right|^2 = \frac{4}{n^3}\left(\frac{z\alpha mc}{\hbar}\right)^3$$

$$\vec{F} = \vec{S} + \vec{I}$$

$$\frac{\vec{S} \cdot \vec{I}}{\hbar^2} = \frac{F^2 - S^2 - I^2}{2\hbar^2} = \frac{1}{2}\left[F(F+1) - \frac{3}{4} - I(I+1)\right]$$

$F = I + \frac{1}{2}$ 이면

$$\left(I + \frac{1}{2}\right)\left(I + \frac{3}{2}\right) - \frac{3}{4} - I(I+1) = I^2 + 2I + \frac{3}{4} - \frac{3}{4} - I^2 - I$$

$$= I$$

$F = I - \frac{1}{2}$ 이면

$$\left(I - \frac{1}{2}\right)\left(I + \frac{1}{2}\right) - \frac{3}{4} - I(I+1) = I^2 - \frac{1}{4} - \frac{3}{4} - I^2 - I$$

$$= -(I+1)$$

$$\Delta E = \frac{4}{3}(5.56) \cdot \frac{1}{1840} \cdot \frac{1}{(137)^4} \cdot mc^2$$

$\lambda = 21.4\text{cm}$ or 1420MHz