Hydrogen atom in a weak external field

① Our goal will be to find the shift in energies of a hydrogen atom in the presence of a weak external (electric and magnetic) field.

$$E_n^{(0)} = -\frac{\mu Z^2 e^4}{2\hbar^2}\frac{1}{n^2}.$$

$$H_0 = \frac{p^2}{2\mu} - \frac{Ze^2}{r}$$

$$E_{nlm} = E_n^{(0)} + \delta E_{nlm}$$

$$H = H_0 + \delta H$$

② $$H_0 |n,l,m\rangle = E_n^{(0)} |n,l,m\rangle$$

$$E_n^{(0)} = -\frac{\mu Z^2 e^4}{2\hbar^2}\frac{1}{n^2}$$

$$= -\frac{1}{2}(\mu c^2)\left(\frac{e^2}{\hbar c}\right)^2 \frac{Z^2}{n^2}$$

$$= -(13.6\,eV)\frac{Z^2}{n^2}$$

$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137.036}$

fine structure constant.

$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$

$= \frac{1}{m_1}$ $m_1 << m_2$

$\mu c^2 = 0.511$ MeV (for electron)

(3) The Hamiltonian for a hydrogen atom in an electromagnetic field (given by $\vec{A}$ and ϕ) is

$$H = \frac{1}{2\mu}\left(\vec{P} - \frac{e}{c}\vec{A}\right)^2 - \frac{Ze^2}{r} + e\phi$$

where

$$\vec{B} = \vec{\nabla} \times \vec{A}$$

$$\vec{\mathcal{E}} = -\vec{\nabla}\phi - \underbrace{\frac{1}{c}\frac{\partial \vec{A}}{\partial t}}_{\text{absent for static fields.}}$$

$\vec{A}$ – vector potential (not to be confused with axial vector.)

ϕ – scalar potential

$\vec{B}$ – magnetic field

$\vec{\mathcal{E}}$ – electric field.

(4) For uniform $\vec{\mathcal{E}}$ and $\vec{B}$ (in space and time) we have.

$$\phi = -\vec{\mathcal{E}}\cdot\vec{r} \quad \text{and} \quad \vec{A} = \frac{1}{2}\vec{B}\times\vec{r}.$$

This is easily verified:

Note: $\vec{\mathcal{E}}$ and $\vec{B}$ are classical quantities and thus are not operators.

$$\begin{aligned}
-\vec{\nabla}\phi &= \vec{\nabla}\,\vec{\mathcal{E}}\cdot\vec{r} \\
&= (\vec{\nabla}\,\vec{r})\cdot\vec{\mathcal{E}} \\
&= \vec{\mathbb{1}}\cdot\vec{\mathcal{E}} \\
&= \vec{\mathcal{E}}
\end{aligned}$$

$$\begin{aligned}
\vec{\nabla}\times\vec{A} &= \frac{1}{2}\,\vec{\nabla}\times(\vec{B}\times\vec{r}) \\
&= \frac{1}{2}\left[\vec{B}\,(\vec{\nabla}\cdot\vec{r}) - (\vec{B}\cdot\vec{\nabla})\,\vec{r}\right] \\
&= \frac{1}{2}\left[3\vec{B} - \vec{B}\right] \\
&= \vec{B}
\end{aligned}$$

5 Using 4 in 3 we have.

$$H = \frac{1}{2\mu}\left(\vec{P} - \frac{e}{2c}\vec{B}\times\vec{r}\right)^2 - \frac{Ze^2}{r} - e\,\vec{\mathcal{E}}\cdot\vec{r}$$

$$= H_0 - \frac{e}{4\mu c}\left(\vec{P}\cdot\vec{B}\times\vec{r} + \vec{B}\times\vec{r}\cdot\vec{P}\right) + \frac{1}{2\mu}\left(\frac{e}{2c}\right)^2 (\vec{B}\times\vec{r})\cdot(\vec{B}\times\vec{r}) - e\,\vec{\mathcal{E}}\cdot\vec{r}$$

Keeping only leading contributions we have

$$H = H_0 - \frac{e}{4\mu c}\left(\vec{P}\cdot\vec{B}\times\vec{r} + \vec{B}\times\vec{r}\cdot\vec{P}\right) - e\,\vec{\mathcal{E}}\cdot\vec{r}$$

6
$$\left(\vec{P}\cdot\vec{B}\times\vec{r}\right)_i = p_i\,\epsilon_{ijk}\,B_j\,r_k$$
$$= \epsilon_{ijk}\,B_j\,p_i\,r_k$$
$$= \epsilon_{ijk}\,B_j\,(r_k\,p_i - \underbrace{i\hbar\,\delta_{ki}}_{=0})$$
$$= \epsilon_{ijk}\,B_j\,r_k\,p_i$$
$$= \vec{B}\cdot\vec{r}\times\vec{P}$$

$[r_k, p_i] = i\hbar\,\delta_{ik}$

$$\vec{P}\cdot\vec{B}\times\vec{r} + \vec{B}\times\vec{r}\cdot\vec{P} = \vec{B}\cdot\vec{r}\times\vec{P} + \vec{B}\cdot(\vec{r}\times\vec{P})$$
$$= 2\,\vec{B}\cdot\vec{L}$$

$\vec{L} = \vec{r}\times\vec{P}$

7 Using 6 in 5 we have.

$$H = H_0 \underbrace{- \frac{e}{2\mu c}\vec{B}\cdot\vec{L} - e\,\vec{\mathcal{E}}\cdot\vec{r}}_{\delta H}$$

8 We are interested in the energy shift δE_{nlm} due to the perturbation in the Hamiltonian, δH.

Consider

$$H(\lambda)\,|\underbrace{E,r}_{}\,;\lambda\rangle = E(\lambda)\,|E,r;\lambda\rangle$$

eigenstates of energy with labels r. eg: n,l,m.

λ is any parameter dependence of energy. eg: z, $\vec{B}$, $\vec{E}$, e, etc.

9 Taking the derivative with respect to λ

$$\left(\frac{\partial H}{\partial \lambda} - \frac{\partial E}{\partial \lambda}\right)|E,r;\lambda\rangle + \left(H(\lambda) - E(\lambda)\right)\frac{\partial}{\partial \lambda}|E,r;\lambda\rangle = 0$$

$$\langle E,r';\lambda|\left(\frac{\partial H}{\partial \lambda} - \frac{\partial E}{\partial \lambda}\right)|E,r;\lambda\rangle + \langle E,r';\lambda|\left(\underbrace{H(\lambda)}_{E(\lambda)} - E(\lambda)\right)\frac{\partial}{\partial \lambda}|E,r;\lambda\rangle = 0$$

$$\langle E,r';\lambda|\,\frac{\partial H}{\partial \lambda}\,|E,r;\lambda\rangle = \frac{\partial E}{\partial \lambda}\,\langle E,r';\lambda|E,r;\lambda\rangle$$

$$\langle E,r';\lambda|\,\delta H\,|E,r;\lambda\rangle = \delta E\;\delta(r,r')$$

10 Notice that the basis, r, which is degenerate w.r.t. H_0, and that diagonalizes the matrix of δH simplifies the work. We will see that the basis $|n;m_1,m_2\rangle$ is more suitable over $|n,l,m\rangle$ for this purpose.

(11) The energy eigenstates of hydrogen atom are

$$|n, l, m\rangle$$

which are closely related to

$$|n; m_1, m_2\rangle = |n; j_1, m_1\rangle_{1} \, |n; j_2, m_2\rangle_{2} ,$$

which are constructed using $\vec{L}$ and $\vec{A}$. Thus our goal will be achieved if we can express δH in terms of $\vec{L}$ and $\vec{A}$. In particular, we shall show that δ can be expressed in terms of $\vec{A}$ upto a total time derivative.

(12) Let us point out here that a total time derivative does not contribute to the energy shifts.

Consider

$$\langle E, r'; \lambda | \frac{dF}{dt} | E, r; \lambda\rangle = \langle E, r'; \lambda | \frac{1}{i\hbar} [F, H] \, | E, r; \lambda\rangle$$

$$= \frac{1}{i\hbar} \langle E, r'; \lambda | (F \underset{E}{\underset{\downarrow}{H}} - \underset{E}{\underset{\downarrow}{H}} F) | E, r; \lambda\rangle$$

$$= 0 .$$

13 Virial theorem

$$\frac{d}{dt}(\vec{r}\cdot\vec{p}) = \frac{d\vec{r}}{dt}\cdot\vec{p} + \vec{r}\cdot\frac{d\vec{p}}{dt}$$

$$\frac{d\vec{r}}{dt} = \frac{\vec{p}}{\mu}$$

$$= \frac{\vec{p}}{\mu}\cdot\vec{p} + \vec{r}\cdot\frac{(-Ze^2\vec{r})}{r^3}$$

$$\frac{d\vec{p}}{dt} = -\frac{Ze^2\vec{r}}{r^3}$$

$$= 2\frac{p^2}{2\mu} - \frac{Ze^2}{r}$$

$$= 2H_0 + \frac{Ze^2}{r}$$

Similarly,

$$\frac{d}{dt}(\vec{p}\cdot\vec{r}) = 2H_0 + \frac{Ze^2}{r}$$

14 Thus.

$$\frac{1}{2}\frac{d}{dt}(\vec{r}\cdot\vec{p} + \vec{p}\cdot\vec{r}) = 2H_0 + \frac{Ze^2}{r}$$

$$\frac{d\vec{r}}{dt} = \frac{\vec{p}}{\mu}.$$

$$\frac{\mu}{2}\frac{d}{dt}\left(\vec{r}\cdot\frac{d\vec{r}}{dt} + \frac{d\vec{r}}{dt}\cdot\vec{r}\right) = 2H_0 + \frac{Ze^2}{r}$$

$$\frac{\mu}{2}\frac{d}{dt}\frac{d}{dt}r^2 = 2H_0 + \frac{Ze^2}{r}$$

$$\frac{d^2}{dt^2}\left(\frac{1}{2}\mu r^2\right) = 2H_0 + \frac{Ze^2}{r}$$

15 Multiply by operator $\vec{r}$:

$$2\vec{r}H_0 = -Ze^2\frac{\vec{r}}{r} + \vec{r}\frac{d^2}{dt^2}\left(\frac{1}{2}\mu r^2\right)$$

(16)

$$2\vec{r}H_0 = -Ze^2\frac{\vec{r}}{r} - \frac{d\vec{r}}{dt}\left(\frac{d}{dt}\frac{1}{2}\mu r^2\right) + \frac{d}{dt}\left(\vec{r}\frac{d}{dt}\frac{1}{2}\mu r^2\right)$$

$$= -Ze^2\frac{\vec{r}}{r} - \vec{p}\left(\frac{d}{dt}\frac{1}{2}r^2\right) + \frac{d}{dt}\left(\vec{r}\,\frac{1}{2}(\vec{r}\cdot\vec{p}+\vec{p}\cdot\vec{r})\right) \qquad \text{(using (14) and } \frac{d\vec{r}}{dt} = \frac{\vec{p}}{\mu}\text{)}$$

$$= -Ze^2\frac{\vec{r}}{r} + \frac{d\vec{p}}{dt}\frac{1}{2}r^2 - \frac{d}{dt}\left(\vec{p}\,\frac{1}{2}r^2\right)$$
$$+ \frac{d}{dt}\left(\frac{1}{2}\vec{r}\,(\vec{r}\cdot\vec{p}+\vec{p}\cdot\vec{r})\right)$$

$$= -Ze^2\frac{\vec{r}}{r} - \frac{Ze^2\vec{r}}{r^3}\frac{1}{2}r^2 + \frac{d}{dt}\left[\vec{r}\,\frac{1}{2}(\vec{r}\cdot\vec{p}+\vec{p}\cdot\vec{r}) - \frac{1}{2}\vec{p}r^2\right]$$

$$= -\frac{3}{2}Ze^2\frac{\vec{r}}{r} + \frac{d}{dt}\left[\vec{r}\,\frac{1}{2}(\vec{r}\cdot\vec{p}+\vec{p}\cdot\vec{r}) - \frac{1}{2}\vec{p}r^2\right]$$

(17)

$$\vec{r}\times\vec{L} = \vec{r}\times(\vec{r}\times\vec{p})$$
$$= \vec{r}\,(\vec{r}\cdot\vec{p}) - r^2\vec{p}$$
$$= \vec{r}\,(\vec{r}\cdot\vec{p}) - r_j(p_i r_j + i\hbar\delta_{ij})$$
$$= \vec{r}\,(\vec{r}\cdot\vec{p}) - (p_i r_j + i\hbar\delta_{ji})\,r_j - i\hbar\vec{r}$$
$$= \vec{r}\,(\vec{r}\cdot\vec{p}) - \vec{p}r^2 - 2i\hbar\vec{r}$$

$$\vec{L}\times\vec{r} = (\vec{r}\times\vec{p})\times\vec{r}$$
$$= r_j\,p_i\,r_j - \vec{r}\,(\vec{p}\cdot\vec{r})$$
$$= (p_i r_j + i\hbar\delta_{ij})\,r_j - \vec{r}\,(\vec{p}\cdot\vec{r})$$
$$= -\vec{r}\,(\vec{p}\cdot\vec{r}) + \vec{p}r^2 + i\hbar\vec{r}$$

$$\frac{1}{2}(\vec{r}\times\vec{L} - \vec{L}\times\vec{r}) = \vec{r}\,\frac{1}{2}(\vec{r}\cdot\vec{p}+\vec{p}\cdot\vec{r}) - \vec{p}r^2 - \frac{3}{2}i\hbar\vec{r}$$

(18) Using (17) in (16)

$$2\vec{r}\,H_0 = -\frac{3}{2} Ze^2 \frac{\vec{r}}{r} + \frac{d}{dt}\left[\frac{1}{2}(\vec{r}\times\vec{L} - \vec{L}\times\vec{r}) + \frac{3}{2} i\hbar\,\vec{r}\right]$$

(19) Remember

$$\vec{A} = \frac{\vec{r}}{r} - \frac{1}{\mu Ze^2}\frac{1}{2}(\vec{p}\times\vec{L} - \vec{L}\times\vec{p}) \qquad \frac{d\vec{r}}{dt} = \frac{\vec{p}}{\mu}.$$

$$= \frac{\vec{r}}{r} - \frac{1}{2Ze^2}\left(\frac{d\vec{r}}{dt}\times\vec{L} - \vec{L}\times\frac{d\vec{r}}{dt}\right)$$

$$= \frac{\vec{r}}{r} - \frac{1}{2Ze^2}\frac{d}{dt}(\vec{r}\times\vec{L} - \vec{L}\times\vec{r}) \qquad \because \frac{d\vec{L}}{dt} = 0$$

(20) Using (19) in (18)

$$2\vec{r}\,H_0 = -\frac{3}{2} Ze^2\left[\vec{A} + \frac{1}{2Ze^2}\frac{d}{dt}(\vec{r}\times\vec{L} - \vec{L}\times\vec{r})\right] + \frac{d}{dt}\left[\frac{1}{2}(\vec{r}\times\vec{L} - \vec{L}\times\vec{r}) + \frac{3}{2} i\hbar\,\vec{r}\right]$$

$$= -\frac{3}{2} Ze^2 A^2 - \frac{3}{4}\frac{d}{dt}(\vec{r}\times\vec{L} - \vec{L}\times\vec{r}) + \frac{d}{dt}\left[\frac{1}{2}(\vec{r}\times\vec{L} - \vec{L}\times\vec{r}) + \frac{3}{2} i\hbar\,\vec{r}\right]$$

$$= -\frac{3}{2} Ze^2 \vec{A} + \frac{d}{dt}\left[-\frac{1}{4}(\vec{r}\times\vec{L} - \vec{L}\times\vec{r}) + \frac{3}{2} i\hbar\,\vec{r}\right]$$

$$\vec{r}\,H_0 = -\frac{3}{4} Ze^2 \vec{A} - \frac{1}{4}\frac{d}{dt}\left[\frac{1}{2}(\vec{r}\times\vec{L} - \vec{L}\times\vec{r}) - 3 i\hbar\,\vec{r}\right]$$

(21) Using (20) in (7) we have

$$\delta H = -\frac{e}{2\mu c}\vec{B}\cdot\vec{L} - e\,\vec{\mathcal{E}}\cdot\vec{r}$$

$$\rightarrow -\frac{e}{2\mu c}\vec{B}\cdot\vec{L} - e\,\vec{\mathcal{E}}\cdot\frac{3}{4}\frac{Ze^2}{(-H_0)}\vec{A}$$

$a_0 = \frac{\hbar^2}{\mu e^2}$

Compton wavelength $\leftarrow \lambda_0 = \frac{\hbar}{\mu c}$

$\alpha = \frac{\lambda_0}{a_0} = \frac{e^2}{\hbar c} = \frac{1}{137.036}$

(22) $$\frac{Ze^2}{-H_0} = Ze^2\,\frac{2\hbar^2}{\mu Z^2 e^4}\,n^2.$$

$$= \frac{2n^2}{Z}a_0$$

(23) $$\delta H \rightarrow -e\,\vec{\mathcal{E}}\cdot\frac{3}{4}\frac{2n^2}{Z}a_0\vec{A} - \frac{e}{2\mu c}\vec{B}\cdot\vec{L}$$

$$\rightarrow -e\frac{3}{2}\frac{na_0}{\hbar Z}\,\vec{\mathcal{E}}\cdot\hbar n\vec{A} - \frac{e}{2}\frac{\hbar}{\mu c}\vec{B}\cdot\vec{L}\frac{1}{\hbar}.$$

$$\rightarrow -e\frac{3}{2}\frac{na_0}{\hbar Z}\,\vec{\mathcal{E}}\cdot\hbar n\vec{A} - \frac{e}{2}\frac{\lambda_0}{\hbar}\vec{B}\cdot\vec{L}$$

$$\rightarrow -e\frac{3}{2}\frac{na_0}{\hbar Z}\left[\vec{\mathcal{E}}\cdot\hbar n\vec{A} + \frac{Z}{3n}\frac{\lambda_0}{a_0}\vec{B}\cdot\vec{L}\right]$$

$$\rightarrow -e\frac{3}{2}\frac{na_0}{\hbar Z}\left[\vec{\mathcal{E}}\cdot\hbar n\vec{A} + \frac{Z\alpha}{3n}\vec{B}\cdot\vec{L}\right]$$

(24) Since $\alpha \sim \frac{1}{137}$, for small Z the Zeeman effect is smaller.

25 $$\vec{L} = \vec{J}^{(1)} + \vec{J}^{(2)}$$

$$\hbar n \vec{A} = \vec{J}^{(1)} - \vec{J}^{(2)}$$

26 $$\delta H \to -e \frac{3}{2} \frac{n a_0}{\hbar Z} \left[\vec{\mathcal{E}} \cdot \left(\vec{J}^{(1)} - \vec{J}^{(2)} \right) + \frac{Z\alpha}{3n} \vec{B} \cdot \left(\vec{J}^{(1)} + \vec{J}^{(2)} \right) \right]$$

$$\to -e \frac{3}{2} \frac{n a_0}{\hbar Z} \left[\left(\vec{\mathcal{E}} + \frac{Z\alpha}{3n} \vec{B} \right) \cdot \vec{J}^{(1)} - \left(\vec{\mathcal{E}} - \frac{Z\alpha}{3n} \vec{B} \right) \cdot \vec{J}^{(2)} \right]$$

$$\to -e \frac{3 n a_0}{2Z} \left(\vec{\mathcal{E}} + \frac{Z\alpha}{3n} \vec{B} \right) \cdot \frac{1}{\hbar} \vec{J}^{(1)} + e \frac{3 n a_0}{2Z} \left(\vec{\mathcal{E}} - \frac{Z\alpha}{3n} \vec{B} \right) \cdot \frac{1}{\hbar} \vec{J}^{(2)}$$

27 If $\vec{\mathcal{E}} = 0$, we project $\vec{J}^{(1)}$ and $\vec{J}^{(2)}$ along $\vec{B}$.

$$\langle \delta H \rangle = -\frac{e}{2\mu c} |\vec{B}| \hbar m \qquad m = m_1 + m_2 .$$

$$E_{nm} = E_n^{(0)} + \delta E_{nm}$$

$$= E_n^{(0)} - \frac{\hbar e}{2\mu c} B m .$$

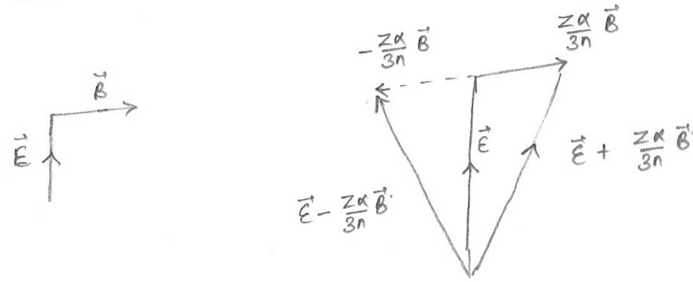
28 If $\vec{B} = 0$, we project $\vec{J}^{(1)}$ and $\vec{J}^{(2)}$ along $\vec{\mathcal{E}}$.

$$\delta E_{n, m_1, m_2} = -e \frac{3 n a_0}{2Z} |\vec{\mathcal{E}}| (m_1 - m_2)$$

(29) In general, $\vec{J}^{(1)}$ and $\vec{J}^{(2)}$ needs to be projected along combinations of $\vec{E}$ and $\vec{B}$, and the degeneracy is completely remove except for the case when $\vec{E} \perp^{r} \vec{B}$.

$$\delta E_{n,m_1,m_2} = -e\,\frac{3na_0}{2Z}\left|\vec{E} + \frac{Z\alpha}{3n}\vec{B}\right| m_1 + e\,\frac{3na_0}{2Z}\left|\vec{E} - \frac{Z\alpha}{3n}\vec{B}\right| m_2$$

(30) For the case when $\vec{E} \perp^{r} \vec{B}$ we have.

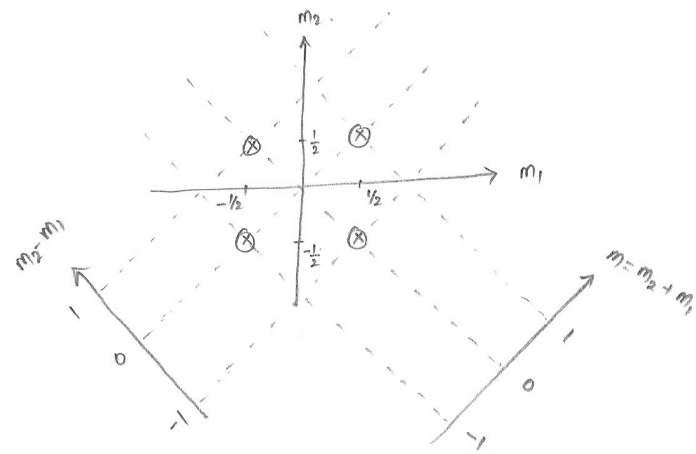


$$\left|\vec{E} + \frac{Z\alpha}{3n}\vec{B}\right| = \left|\vec{E} - \frac{Z\alpha}{3n}\vec{B}\right|.$$

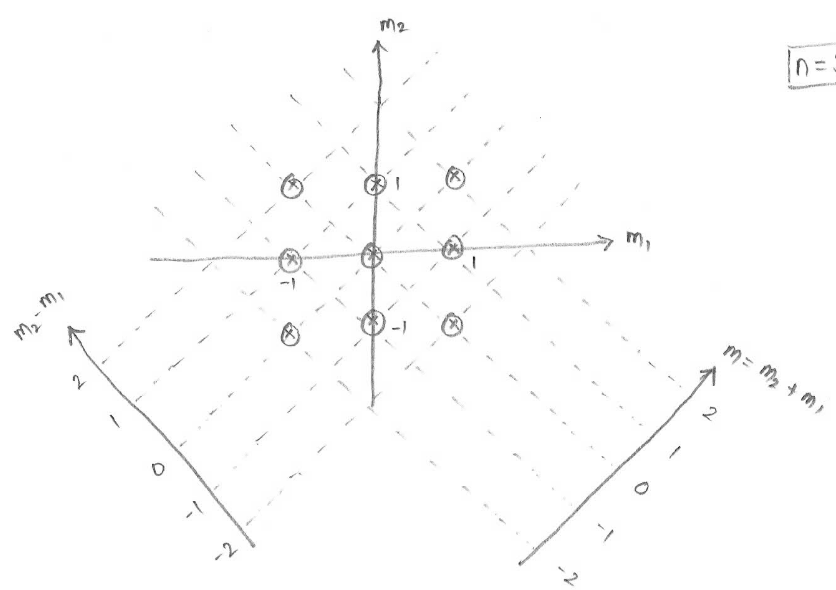
Further, in this particular case.

$$\delta E_{n,m_1,m_2} = -e\,\frac{3na_0}{2Z}\left|\vec{E} + \frac{Z\alpha}{3n}\vec{B}\right|(m_1 - m_2).$$

(31) The states in $|n; m_1, m_2\rangle$ basis can be visualized in the following way



$\boxed{n=2}$ $j_1 = j_2 = \frac{1}{2}$



$\boxed{n=3}$ $j_1 = j_2 = 1$