Atomic & Molecular Physics :

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Part - A $\longrightarrow$ Prof. Ashoke Sen

16.01.2013 Book : Brandsen & Joachain (1)
(Physics of Atoms & Molecules)

Convention : $\hbar = c = 1$. (Recover via dimensional analysis)

Gaussian units in Electromagnetism.

$$\vec{\nabla}\cdot\vec{E} = 4\pi\rho \qquad \vec{\nabla}\times\vec{B} = 4\pi\vec{j} + \frac{\partial\vec{E}}{\partial t}$$

$$\vec{\nabla}\times\vec{E} = -\frac{\partial\vec{B}}{\partial t} \qquad \vec{\nabla}\cdot\vec{B} = 0$$

Coulomb's Law $\longrightarrow$ $\dfrac{q_1 q_2}{r^2}\hat{r} = \vec{F}$

Set $\epsilon_0 = \dfrac{1}{4\pi}$ & $\mu_0 = 4\pi$

ϵ_0 $\rightarrow$ vacuum permitivity; μ_0 $\longrightarrow$ vacuum permeability

FOR ANY CONVERSIONS

Plan : (1) Single electron atoms

$\longrightarrow$ application of techniques learned in QM (1 & 2) courses
|| + results

(2) Multi - electron atoms $\longrightarrow$ require new techniques to deal with e-e force.

(3) Molecules

(1)// start . . .

Neutral H - atom (all isotopes)

He^+

Zeroth-order approximation : Treat the nucleus as a point charge Ze of infinite mass and the electron as a non-relativistic particle. (of charge $-e$.)

$$H = p^2/2m - \frac{Ze^2}{r}.$$

$$\hat{H} = -\frac{1}{2m}\nabla^2 - \frac{Ze^2}{r}.$$ Find eigenvalues

$$\hat{H}\psi = E_n\psi.$$ The eigenfunctions can be labelled by $\{n_r \; l \; m_l\}$

$$\psi_{n_r l m_l}(r, \theta, \phi) = f_{n_r l}(r)\, Y_{l m_l}(\theta, \phi)$$

called n in QM 1, 2

n_r takes values $1, 2, 3, \dots$

l takes values $0, 1, 2, 3, \dots$

$$E_{n_r, l} = -\frac{m Z^2 e^4}{\underbrace{(n_r + l)^2}_{n} 2}$$

$$E_n = -\frac{m Z^2 e^4}{2n^2}$$

m_l goes from $-l$ to l in integral steps

$n = 1, 2, \dots$ arbitrary integer

$l = 0, 1, 2, \dots (n-1)$

$$f_{n_r, l}(r) \longrightarrow R_{nl}(r)$$

$$-\frac{1}{2mr^2}\frac{d}{dr}\left(r^2 \frac{dR_{nl}}{dr}\right) + \frac{l(l+1)}{2mr^2} R_{nl} - Ze^2/r \, R_{nl} = -\frac{mZ^2e^4}{2n^2} R_{nl}$$

Calculation of total degeneracy for a given n :

$$\sum_{l=0}^{n-1} (2l+1) = 2\frac{(n-1)n}{2} + n = n^2.$$

Introduce spin $\vec{S}$. $\Rightarrow$ Wavefunction ~~is~~ has additional 2-fold degeneracy $\left(m_s = \pm \frac{1}{2}\right)$

$\Rightarrow$ Total degeneracy $= 2n^2$.

$$|n, l, m_l, s, m_s\rangle \iff R_{nl}(r)\, Y_{lm}(\theta, \phi) \otimes |m_s\rangle$$

$s \longrightarrow$ always $\frac{1}{2}$; $\quad m_s = \pm \frac{1}{2}$

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

$$L^2 |n, l, m_l, s, m_s\rangle = l(l+1)\, |n, l, m_l, s, m_s\rangle$$

<u>choice of basis</u>

$$S^2 |n, l, m_l, s, m_s\rangle = \frac{3}{4} \, |\ldots\rangle$$

$$L_z |\ldots\rangle = m_l \, |\ldots\rangle$$

$$S_z |\ldots\rangle = m_s \, |\ldots\rangle$$

- Choose a different basis

$\vec{J}^2$, J_z eigenbasis $\Rightarrow |n, l, s, j, m_j\rangle$

$$= \sum_{m_l, m_s} C^{\,j\ l\ s}_{\,m_j\ m_l\ m_s} \, |n, l, m_l, s, m_s\rangle$$

$\longrightarrow$ Clebsch-Gordon coefficients

$$\vec{J}^2 |n, l, j, s, m_j\rangle = j(j+1)\, |\ldots\rangle$$

$$J_z |\ldots\rangle = m_j \, |\ldots\rangle$$

(In new basis)

For given n,

$l = 0, 1, 2, \ldots (n-1)$.

- Verify for degeneracies.

$$j = l - \frac{1}{2} \text{ or } l + \frac{1}{2} \qquad \left(\text{for } l = 0,\ j = \frac{1}{2}\right)$$

For given n, l can take values

$$
\begin{array}{lccccccc}
l = & 0 & 1 & 2 & 3 & \cdots & (n-2) & (n-1) \\
j & \frac{1}{2} & \frac{1}{2}, \frac{3}{2} & \frac{3}{2}\ \frac{5}{2} & & & (n-\frac{5}{2})\ (n-\frac{3}{2}) & (n-\frac{3}{2}),\ (n-\frac{1}{2})
\end{array}
$$

$$\text{Total degeneracy} = 2 \sum_{j=\frac{1}{2}, \frac{3}{2}, \cdots (n-3/2)} (2j+1) \quad + \left(2\left(n-\frac{1}{2}\right)+1\right)$$

Let $j = (k - 1/2)$ where $k = 1, 2, \cdots (n-1)$

$$\Rightarrow \quad 2j+1 = 2k$$

So, total degeneracy $= 2 \sum_{k=1}^{n-1} 2k + 2n$

$$= 4 \frac{(n-1)n}{2} + 2n$$

$$= 2n^2. \quad (\text{matches !})$$

<u>Symbol for l</u>

$l =$	0,	1,	2,	3,	4,	5	
Symbol	s	p	d	f	g	h	— — —

$$|n\, l\, s\, j\, m_j\rangle \longleftrightarrow n\,(\text{symbol of } l)_j$$

($\underline{2j+1}$ fold degenerate)

$$\left|n=1,\ l=0,\ j=\frac{1}{2}\right\rangle \Rightarrow 1s_{1/2}$$

$$\left|n=3,\ l=2,\ j=\frac{5}{2}\right\rangle \Rightarrow 3d_{5/2}$$

$$\{1s_{1/2}\};\ \{2s_{1/2},\ 2p_{1/2},\ 2p_{3/2}\};$$

$$\{3s_{1/2},\ 3p_{1/2},\ 3p_{3/2},\ 3d_{3/2},\ 3d_{5/2}\};$$

— — — .

× Corrections to this formula

① Relativistic effects.

② Nucleus has finite mass & finite size.

① ⇒ start . . .

$|n, l, s, j, m_j\rangle$ (You can't take $\vec{L}$ & $\vec{S}$ as separate conserved charges)

- Result depends on j (correction of levels)

$$\underset{(n,l,j,m_j)}{E} = m\left[\left\{1 + \left(\frac{Ze^2}{n-j-\frac{1}{2} + \left\{(j+\frac{1}{2})^2 - Z^2e^4\right\}^{1/2}}\right)^2\right\}^{-1/2} - 1\right]$$

rest mass

Leading term = 0.

$Z^2e^4 \longrightarrow \boxed{\text{small parameter}}$

$O(Z^4e^8) \longrightarrow$ first correction

Check : $E \cong -\frac{mZ^2e^4}{2n^2}\left[1 + \frac{Z^2e^4}{n^2} \times \left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right) + O(Z^4e^8)\right]$

- Some degeneracies get lifted
- Higher j has higher energy

$2s_{1/2}, 2p_{1/2} \longrightarrow \boxed{\text{degenerate}}$

$3s_{1/2}, 3p_{1/2} \longrightarrow$ "

$3p_{3/2}, 3d_{3/2} \longrightarrow$ " and so on . . .

FINE STRUCTURE SPLITTING

Nucleus

a) Finite mass effect : • Back to non-relativistic electron

(Avoid superposing various corrections)

$$H = -\frac{1}{2M}\vec{\nabla}_N^2 - \frac{1}{2m}\vec{\nabla}_e^2 - \frac{Ze^2}{|\vec{r}_e - \vec{r}_N|}$$

{ Mass of the nucleus }

Introduce

$$\begin{cases} \vec{R} = \dfrac{M\vec{R}_N + m\vec{r}_e}{M+m} \\ \vec{r} = \vec{r}_e - \vec{r}_N \end{cases}$$

Exercise.

$$H = -\frac{1}{2(M+m)}\vec{\nabla}_R^2 - \frac{1}{2\mu}\vec{\nabla}_r^2 - \frac{Ze^2}{r}$$

$$\mu = \frac{Mm}{M+m} = m\Big(1+\underbrace{\frac{m}{M}}_{\text{(small parameter)}}\Big)^{-1}$$

$$\cong m\left(1-\frac{m}{M}\right) + \text{higher order terms}$$

$$E_n = -\frac{\mu Z^2 e^4}{2n^2} = -\frac{Z^2e^4}{2n^2}\, m\left(1+\frac{m}{M}\right)^{-1}$$

(mild change)

go to rest frame & get rid of it

• Doppler effect

$\left[-\frac{1}{2(M+m)}\vec{\nabla}_R^2\right]$ term

$\leftarrow\cdots$ o $\longrightarrow$

atom   photon

• Isotope detection

(no new degeneracies are lifted)

17.01.2013 ②

Single-electron atom

$|n, l, s=\frac{1}{2}, j, m_j\rangle$

$$\left\{\begin{array}{l} n = 1, 2, 3, 4, \ldots \\ j = \cancel{0, 1, 2, \ldots \left(n-\frac{1}{2}\right)} \quad \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots \left(n-\frac{1}{2}\right) \\ l = \{0, 1\}, \ \{1, 2\}, \ \{2, 3\}, \ \ldots \ (n-1) \end{array}\right.$$

- Relativistic corrections preserve j, m_j quantum numbers

$$l = j + \frac{1}{2} \text{ or } j - \frac{1}{2} \text{ for } j \leq n - \frac{3}{2}$$

$$= j - \frac{1}{2} \text{ for } n - \frac{1}{2}$$

$m \longrightarrow (2j+1)$ values

$$E = -\frac{m Z^2 e^4}{2n^2}\left[1 + \underbrace{\frac{Z^2 e^4}{n^2}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)}_{\text{relativistic correction}} \underbrace{- \frac{m}{M}}_{\text{nuclear mass correction}} + \ldots \right]$$

Degeneracy

For $j \leq n - \frac{3}{2}$, $(2j+1) \times 2$ → Lifted by QED corrections (Lamb Shift)

" $j = n - \frac{1}{2}$, $(2j+1)$

$2s_{1/2}$ is above $2p_{1/2}$

Today : Discuss the effect of finite spin and size of the nucleus.

Nucleus has rotationally invariant Hamiltonian H_N. $\Rightarrow$ existence of nuclear angular momentum as a conserved quantity.

$$[I_k, H_N] = 0 \quad \text{for } k = 1, 2, 3.$$

$$[I_k, I_l] = i\,\epsilon_{klm} I_m$$

(Algebra of I's)

$$\left\{ \begin{aligned} [I_k, L_m] &= 0 \\ [I_k, S_m] &= 0 \end{aligned} \right\}$$

Ground state of H_N

$|I, m_I\rangle$ such that

$$\vec{I}^{\,2} |I, m_I\rangle = I(I+1)\,|I, m_I\rangle$$

$$I_z\,|I, m_I\rangle = m_I\,|I, m_I\rangle$$

$$m_I = -I, -I+1, \cdots, I.$$

- Ignore excited states of the nucleus.

  (Question of energy scales)

- $(2I+1)$ fold degeneracy of ground state.

  $\longrightarrow$ no accidental degeneracies

$\Rightarrow$ Combined state of electron + nucleus

$$|n, l, s = \tfrac{1}{2}, j, m_j\rangle \otimes |I, m_I\rangle$$

TOTAL STATE

<u>Degeneracy</u> : $2(2j+1) \times (2I+1)$

for $j \leq (n - \frac{3}{2})$

(Neglecting Lamb shift)

$(2j+1) \times (2I+1)$ for $j = (n - \frac{1}{2})$.

- In the presence of weak magnetic field, $(\vec{B})$

$$H_N \longrightarrow H_N - \vec{B} \cdot \vec{M}_N$$

$\Rightarrow$ magnetic moment operator of nucleus

- Classical ED $\rightarrow$ Rotating charge distributions carry a magnetic moment.

<u>Claim</u> : For our problem, we can take

$$\vec{M}_N \propto \vec{I}$$

$$\vec{M}_N = g_\ell \, \mu_N \, \vec{I} \longrightarrow \text{[not same as the electron]}$$

g_ℓ : constant of order 1.

$\mu_N = \frac{e}{2M_p}$, $M_p \longrightarrow$ proton mass

- Whether $\langle I, m_I \mid \vec{M}_N \mid I, m_I' \rangle$

$$= g_\ell \, \mu_N \, \langle I, m_I \mid \vec{I} \mid I, m_I' \rangle$$

for all possible m_I, m_I' ?

- Wigner - Eckart Theorem

- We are using vector operator property of both $\vec{M}_N$ and $\vec{I}$.

$$\begin{cases} (M_N)_{(1)} = \frac{1}{\sqrt{2}}\left((M_N)_x + i(M_N)_y\right) \\ (M_N)_{(0)} = (M_N)_z \\ (M_N)_{(-1)} = \frac{1}{\sqrt{2}}\left((M_N)_x - i(M_N)_y\right) \end{cases}$$

$$\begin{cases} I_{(1)} = \frac{1}{\sqrt{2}}\left(I_x + i I_y\right) \\ I_{(0)} = I_{(z)} \\ I_{(-1)} = \frac{1}{\sqrt{2}}\left(I_x - i I_y\right) \end{cases}$$

$$\langle I, m_I \mid (M_N)_{(m)} \mid I, m_I' \rangle = C^{I \;\; 1 \;\; I}_{m_I \;\; m \;\; m_I'} \times \langle I \| M_N \| I \rangle$$

(WE THEOREM)

$$\langle I, m_I \mid I_{(m)} \mid I, m_I' \rangle = C^{I \;\; 1 \;\; I}_{m_I \;\; m \;\; m_I'} \times \langle I \| I \| I \rangle$$

$$\therefore \left\langle I, m_I \middle| \left(M_{(N)}\right)_{(m)} \middle| I, m_I' \right\rangle$$

$$= \underbrace{\frac{\langle I \| M_{(N)} \| I \rangle}{\langle I \| I \| I \rangle}}_{\boxed{g_l \, \mu_N}} \langle I, m_I | I_{(m)} | I, m_I' \rangle$$

(Identify)

Given $\overrightarrow{M}_{(N)}$ $\Rightarrow$ generates a vector potential

$$\vec{A} = - \vec{M}_N \times \vec{\nabla}\left(1/r\right)$$

$$\boxed{\begin{aligned} \vec{B} &= \vec{\nabla} \times \vec{A} \\ \vec{\nabla} \times \vec{B} &= 4\pi \vec{J} \end{aligned}}$$

solve

(for a dipole of moment $\vec{M}_N$)

Non-relativistic limit of Dirac Equation :

$$H = \frac{1}{2m}\left(\vec{p} + e\vec{A}\right)^2 + e A_0 + \frac{e}{2m} \times 2 \, \vec{B} \cdot \vec{S}$$

g-factor of electron

[$e > 0$, electron charge $= -e$]

$$\vec{p} \longrightarrow -i\vec{\nabla}$$

- Use weak field approximation (terms upto $O(\vec{A})$)

(Justification $\longrightarrow$ $1/c$ in Maxwell's equations + $1/M_p$ in $\overrightarrow{M}_N$)

$$\hat{H}\psi = -\frac{1}{2m}\vec{\nabla}^2\psi + e A_0 \psi$$

$$- \frac{ie}{2m}\left(\vec{\nabla}\cdot(\vec{A}\psi) + \vec{A}\cdot\vec{\nabla}\psi\right)$$

$$+ \frac{e}{m}(\vec{\nabla}\times\vec{A})\cdot\vec{S}\psi + O(\vec{A}^2)$$

$\psi \to$ spinor

$$\left(\vec{S} = \frac{\vec{\sigma}}{2}\right)$$

Rewrite $(\vec{\nabla}\cdot\vec{A})\psi + 2\vec{A}\cdot\vec{\nabla}\psi$

$$\therefore \quad H \cong \left[-\frac{1}{2m} \vec{\nabla}^2 + e A_0 \right] - \frac{ie}{2m} \left((\vec{\nabla}\cdot\vec{A}) + 2\vec{A}\cdot\vec{\nabla} \right)$$

$$+ \frac{e}{m} (\vec{\nabla}\times\vec{A}) \cdot \vec{S} .$$

<u>unperturbed Hamiltonian</u>

$$\vec{A} = -\vec{M}_N \times \vec{\nabla}(1/r)$$

$$A_k = -\epsilon_{klm} (M_N)_l \partial_m (1/r)$$

$$\vec{\nabla}\cdot\vec{A} = \partial_k A_k$$

$$= -\epsilon_{klm} (M_N)_l \partial_k \partial_m (1/r) = 0.$$

$\Downarrow$

(doesn't depend on r)

$$H = H_0 \text{ (unperturbed)} + H_1' + H_2'$$

$$-\frac{ie}{m} \vec{A}\cdot\vec{\nabla} \qquad\qquad \frac{e}{m} (\vec{\nabla}\times\vec{A})\cdot\vec{S}$$

$$H_1' = -\frac{ie}{m} \vec{A}\cdot\vec{\nabla}$$

$$= -\frac{ie}{m} A_k \partial_k \qquad \boxed{\text{Check !}}$$

$$= \frac{ie}{m} \underbrace{\epsilon_{klm}}_{\epsilon_{lmk}} (M_N)_l \left(-\frac{x_m}{r^3}\right) \partial_k$$

$$= \frac{e}{mr^3} (M_N)_l L_l \qquad \underbrace{(-i\partial_k)}_{p_k}$$

$$= \frac{e}{mr^3} \vec{M}_N \cdot \vec{L}$$

$$= \frac{e}{mr^3} g_l \mu_N (\vec{I}\cdot\vec{L})$$

$\left\{ \begin{array}{l} \text{nuclear spin} \longleftrightarrow \text{orbital} \\ \text{angular momentum of } \bar{e} \end{array} \right\}$

$$\mathcal{H}_2' = \frac{e}{m}\left(\vec{\nabla}\times\vec{A}\right)\cdot\vec{S}$$

$$= -\frac{e}{m}\,\vec{\nabla}\times\left(\vec{M}_N \times \vec{\nabla}(1/r)\right)\cdot\vec{S}$$

$$= -\frac{e}{m}\,\epsilon_{klm}\, S_k\, \partial_l \left(\vec{M}_N \times \vec{\nabla}(1/r)\right)_m$$

$$\Downarrow$$

$$\epsilon_{mnp}\,(M_N)_n\,\partial_p(1/r)$$

$$= -\frac{e}{m}\,\epsilon_{klm}\,\epsilon_{mnp}\, S_k\,\partial_l\partial_p(1/r)\,(M_N)_n$$

$$= -\frac{e}{m}\left(\delta_{kn}\delta_{lp} - \delta_{kp}\delta_{ln}\right) S_k (M_N)_n\, \partial_l\partial_p(1/r)$$

$$= -\frac{e}{m}\,\vec{S}\cdot\vec{M}_N\,\vec{\nabla}^2(1/r) + \frac{e}{m}\,S_k (M_N)_l\, \partial_l\partial_k(1/r)$$

$$-4\pi\,\delta^3(\vec{r})$$

$$C\,\delta_{lk}\,\delta^{(3)}(\vec{r}) + \left(-\frac{\delta_{lk}}{r^3} + \frac{3x_l x_k}{r^5}\right)$$

- Set $l=k$ and sum over l.

$$\Rightarrow \left\{\begin{array}{l} 3C = -4\pi \\ C = -\dfrac{4\pi}{3} \end{array}\right\}$$

$$\mathcal{H}_2' = \frac{e}{m}\,4\pi\,\delta^3(\vec{r})\,\vec{S}\cdot\vec{M}_N + \frac{e}{m}\left(-\frac{4\pi}{3}\right)\delta^3(\vec{r})\,\vec{S}\cdot\vec{M}_N$$

$$+ \frac{e}{mr^3}\left(-\vec{S}\cdot\vec{M}_N + \frac{3}{r^2}\,\vec{S}\cdot\vec{r}\;\vec{M}_N\cdot\vec{r}\right)$$

Remember $\mathcal{H}_1' = \dfrac{e}{mr^3}\, g_l\, \mu_N\, \vec{I}\cdot\vec{L}$

($\vec{L}$ & $\vec{S}$ respond differently)

$$\Delta \mathcal{H} = \mathcal{H}_1' + \mathcal{H}_2'$$

$$= \frac{e}{m}\left(\frac{8\pi}{3}\right) \delta^3(\vec{r})\, g_I \mu_N\, \vec{I}\cdot\vec{S} \; +$$

$$\frac{e}{m r^3}\, g_I \mu_N\, \vec{I}\cdot\left(\vec{L} - \vec{S} + \frac{3}{r^2}\vec{r}\,(\vec{S}\cdot\vec{r})\right)$$

- Do first order perturbation theory with this.

Degeneracy $\longrightarrow$ $\begin{cases} 2(2j+1)(2I+1) & \text{for } j \leq n - 3/2 \\ (2j+1)(2I+1) & \text{for } j = \left(n - \frac{1}{2}\right) \end{cases}$

- Degenerate Perturbation Theory

Define $\vec{F} = \vec{I} + \vec{J}$

- Choose eigenstates of $\vec{F}^2, (\vec{F})_z$ (as basis)

$$\left| n, l, \cancel{g}\, s = \frac{1}{2}, j, \cancel{g}\, I, F, m_F \right\rangle$$

$$\vec{F}^2 \left| \cdots \right\rangle = F(F+1) \left| \cdots \right\rangle$$

$$F_z \left| \cdots \right\rangle = F_z \left| \cdots \right\rangle$$

$$= \sum_{m_I, m_j} C^{F\; I\; j}_{m_F\; m_I\; m_j} \left| n, l, s = \frac{1}{2}, j, m_j \right\rangle \otimes \left| I, m_I \right\rangle$$

- Different F's & (m_F's $\cancel{}$ don't mix) (✓)
- l's still mix (2 × 2 matrix)
- Parity $\longrightarrow$ $\vec{L}$ is already diagonalized.

ΔH is parity symmetric

18.01.2013

Basis

of single electron + nuclear ground state

$$|n, l, s = \tfrac{1}{2}, j, F, I, m_F\rangle = \sum_{m_j, m_I} C^{F\ I\ j}_{m_F\ m_I\ m_j} |n, l, s = \tfrac{1}{2}, j, m_j\rangle \otimes |I, m_I\rangle$$

For nuclear ground state, I is a fixed number.

$$\Delta H = \frac{8\pi}{3}\frac{e}{m} g_l \mu_N \vec{I}\cdot\vec{S}\ \delta^3(\vec{r}) + \frac{e}{m r^3} g_l \mu_N \vec{I}\cdot\vec{G} \longrightarrow \vec{G} = \vec{L} - \vec{S} + \frac{3\vec{r}(\vec{S}\cdot\vec{r})}{r^2}$$

(total perturbation)

- Implement first order perturbation theory.

$$\langle n, l, s = \tfrac{1}{2}, j, m_j | \otimes \langle I, m_I| \ \Delta H \ |n, l, s = \tfrac{1}{2}, j, m_j'\rangle \otimes |I, m_I'\rangle$$

- For $\delta^3(\vec{r})$ term, only $l = 0$ will contribute ($\psi \sim r^l$ near $r = 0$)
- Concentrate on 2nd perturbation term.

$$\langle n, l, s = \tfrac{1}{2}, j, m_j | \frac{G_k}{r^3} |n, l, s = \tfrac{1}{2}, j, m_j'\rangle$$

$\longrightarrow$ Analyze using WE Theorem

Compare with $\langle n, l, s = \tfrac{1}{2}, j, m_j | J_k | n, l, s = \tfrac{1}{2}, j, m_j'\rangle$

The ratio is independent of m_j, m_j' and k.

So, $\left\langle n, l, s=\frac{1}{2}, j, m_j \right| \frac{G_k}{r^3} \left| n, l, s=\frac{1}{2}, j, m_j' \right\rangle$

$= K \left\langle n, l, s=\frac{1}{2}, j, m_j \right| J_k \left| n, l, s=\frac{1}{2}, j, m_j' \right\rangle$

depends on

$[l, j, n, G]$ $\left\{ G_k \rightarrow \text{components of a vector operator} \right\}$

So, $\left\langle n, l, s=\frac{1}{2}, j, I, F, m_F \right| \vec{I}\cdot\vec{G}/r^3 \left| n, l, s=\frac{1}{2}, j, I, F, m_F \right\rangle$

$= K \left\langle n, l, s=\frac{1}{2}, j, I, F, m_F \right| \vec{I}\cdot\vec{J} \left| n, l, s=\frac{1}{2}, j, I, F, m_F \right\rangle$

$\frac{1}{2}\left[(\vec{I}+\vec{J})^2 - \vec{I}^2 - \vec{J}^2\right]$

$= \frac{1}{2}\left[\vec{F}^2 - \vec{I}^2 - \vec{J}^2\right]$

- Magic of symmetry

eigenstate with eigenvalue $\frac{1}{2}\left[F(F+1) - I(I+1) - J(J+1)\right]$

- Calculation of K

Start with

$\left\langle n, l, s=\frac{1}{2}, j, m_j \right| \frac{(\vec{G})_k(\vec{J})_k}{r^3} \left| n, l, s=\frac{1}{2}, j, m_j \right\rangle$

introduce $|s\rangle\langle s|$

$= \sum_s \left\langle n, l, s=\frac{1}{2}, j, m_j \right| \frac{G_k}{r^3} \left| s \right\rangle \times$

$\left\langle s \right| J_k \left| n, l, s=\frac{1}{2}, j, m_j \right\rangle$

$\underbrace{\left| n, l, s=\frac{1}{2}, j, m_j' \right\rangle}$ very constrained (only m_j can change)

$= \cancel{\sum_{m_j}} K \sum_{m_j'} \left\langle n, l, s=\frac{1}{2}, j, m_j \right| J_k \left| n, l, s=\frac{1}{2}, j, m_j' \right\rangle$

$\left\langle n, l, s=\frac{1}{2}, j, m_j' \right| J_k \left| n, l, s=\frac{1}{2}, j, m_j \right\rangle$

$$= K\ J(J+1) \qquad (!)$$

$$\therefore\ K = \frac{1}{J(J+1)} \left\langle n, l, s=\tfrac{1}{2}, j, m_j \left| \frac{G_k J_k}{r^3} \right| n, l, s=\tfrac{1}{2}, j, m_j \right\rangle$$

$\boxed{\text{scalar operator}}$

$$\vec{G} = \vec{L} - \vec{S} + 3\vec{r}\,(\vec{S}\cdot\vec{r})\,/r^2$$

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

$$\vec{G}\cdot\vec{J} = \vec{L}^2 - \vec{S}^2 + \frac{3}{r^2}(\vec{r}\cdot\vec{S})^2$$

$$\boxed{\vec{S} = \frac{\vec{\sigma}}{2}} \qquad \vec{r}\cdot\vec{S} = \frac{1}{2}\vec{r}\cdot\vec{\sigma}$$

$$\therefore\ (\vec{r}\cdot\vec{S})^2 = \frac{1}{4}(\vec{r}\cdot\vec{\sigma})^2 = \frac{r^2}{4}$$

So, $\vec{G}\cdot\vec{J} = \vec{L}^2$

$$\left(\because\ \vec{S}^2 = \frac{3}{4}\mathbb{1}\right)$$

$\therefore$ This term vanishes for $l = 0$.

For $l \neq 0$,

$$K = \frac{l(l+1)}{J(J+1)} \left\langle n, l, s, j, m_j \left| \frac{1}{r^3} \right| n, l, s, j, m_j \right\rangle$$

$$\frac{\int d^3r\ {}^1/_{r^3}\, |R_{nl}(r)|^2}{\int d^3r\ |R_{nl}(r)|^2} = \frac{\int_0^\infty {}^1/_r\, |R_{nl}(r)|^2\, dr}{\int_0^\infty r^2\, |R_{nl}(r)|^2\, dr}$$

$$\boxed{\frac{(Ze^2 m)^3}{n^3\, l(l+1)\left(l+\frac{1}{2}\right)}} \qquad \underline{\text{Use } R_{nl}(r)}$$

$$\left\langle \frac{1}{r^k} \right\rangle \sim (Ze^2 m)^k .$$ $\quad r_0 \sim \frac{1}{m Z e^2}$

$$K = \frac{(Ze^2 m)^3}{n^3 \, j(j+1)\left(l+\frac{1}{2}\right)} .$$

$$\Delta E = \frac{e}{2m} g_l \, \mu_N \left\{ F(F+1) - I(I+1) - j(j+1) \right\}$$
$$\times \frac{Z^3 e^6 m^3}{j(j+1)\left(l+\frac{1}{2}\right) n^3} \quad \text{for } l \neq 0 .$$

Here
$$\mu_N = \frac{e}{2M_p} = \text{nuclear magneton} .$$

<u>Now, the $l = 0$ case</u>

$$\Delta E = \frac{8\pi}{3} \frac{e}{m} g_l \mu_N \left\langle \vec{I} \cdot \vec{S} \, \delta^3(\vec{r}) \right\rangle$$

between the same states as in previous case

$$\vec{J} = \vec{L} + \vec{S}$$
$$= \vec{S} \quad (\text{for } \vec{L} = 0)$$

$$\vec{I} \cdot \vec{J} = \frac{1}{2}\left(\vec{F}^2 - \vec{I}^2 - \vec{J}^2\right)$$
$$= \frac{1}{2}\left(F(F+1) - I(I+1) - j(j+1) \right)$$

$\langle \delta^3(\vec{r}) \rangle \longrightarrow$ spherically symmetric.

$\longrightarrow$ Hermitian operator

$$= \frac{\int d^3 r \; \delta^3(\vec{r}) \; |R_{nl}(r)|^2}{\int d^3 r \; |R_{nl}(r)|^2}$$

$$\overset{(l=0)}{=} \frac{|R_{nl}(0)|^2}{4\pi \int_0^\infty r^2 \, |R_{nl}(r)|^2 \, dr} = \frac{Z^3 e^6 m^3}{\pi n^3}$$

(easily evaluated!)

Finally

$$\Delta E = \frac{8\cancel{\pi}}{3} \frac{e}{m} g_\ell \mu_N \frac{1}{2} \left\{ F(F+1) - I(I+1) - j(j+1) \right\} \times \frac{Z^3 e^6 m^3}{\cancel{\pi} n^3} \quad (\text{for } l = 0)$$

Compare with $l \neq 0$ answer. (it agrees if we put $l = 0$!)

$$\Delta E_{total} = \frac{\cancel{e^2} m^2}{4 M_p} g_\ell Z^3 e^8 \left\{ F(F+1) - I(I+1) - j(j+1) \right\} \div \left[j(j+1)(\ell + \tfrac{1}{2}) n^3 \right]$$

m/M_p

- Comparison with relativistic correction -

$$- \frac{m Z^4 e^8}{4 n^4} \left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \quad (\text{LARGE !})$$

$\rightarrow$ very small.

ΔE_{total} ~ hyperfine splitting

Relativistic ~ fine structure splitting

$\rightarrow$ Lifts essentially <u>all</u> degeneracies.
(depends on ℓ, F, j)

- Higher multipoles $\longrightarrow$ negligible

$$\left\langle \frac{(r_N)^k}{r^k} \right\rangle \sim (Ze^2 m)^k \, (r_N)^k$$

$$\boxed{r_e \sim \frac{1}{m Z e^2}} = a_0 \qquad \boxed{r_N \sim 1/M_p}$$

[Nuclear quadrupole moment vanishes.]

$e^2 = 1/137$ $\longleftrightarrow$ $m/M_p \sim 1/2000$

- Electric dipole moments ? (OF NUCLEUS)

Suppose, we have a charge distribution $\rho(\vec{r}\,')$

Electric potential (Multipole Expansion)

$$-A_0 = \phi = \int d^3 r' \, \frac{\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}$$

$$\xrightarrow{\text{large } r} \int d^3 r' \, \rho(\vec{r}\,') \left\{ 1/r + \frac{\vec{r}\cdot\vec{r}\,'}{r^3} + \frac{3}{2r^5}\left((\vec{r}\cdot\vec{r}\,')^2 - \frac{1}{3}\left(r^2 \vec{r}\,'^2\right)\right) + \cdots \right\}$$

$$= \underbrace{\frac{1}{r}\int d^3 r' \, \rho(\vec{r}\,')}_{\text{MONOPOLE}} + \underbrace{\frac{\vec{r}}{r^3}\cdot \int d^3 r' \, \rho(\vec{r}\,')\,\vec{r}\,'}_{\text{DIPOLE}}$$

$$+ \underbrace{\frac{1}{r^5}\, r_i r_j \, \frac{3}{2} \int d^3 r' \, \rho(\vec{r}\,') \left(r_i' r_j' - \frac{1}{3} r'^2 \delta_{ij}\right)}_{\text{QUADRUPOLE}} + \cdots$$

$$\begin{cases} \vec{D} = \int d^3 r' \, \rho(\vec{r}\,')\,\vec{r}\,' \\ \overleftrightarrow{Q}_{ij} = \frac{3}{2}\int d^3 r' \, \rho(\vec{r}\,') \left(r_i' r_j' - \frac{1}{3} r'^2 \delta_{ij}\right) \end{cases}$$

$\rightarrow$ $\boxed{\text{operators in QM}}$

$\langle N | \vec{D} | N \rangle = 0$??

$N \downarrow$ nuclear ground state

$\langle I, m_I | \vec{D} | I, m_I \rangle \stackrel{?}{=} 0$.

- Each state is an eigenstate of parity operator.

$P : \vec{r} \longrightarrow -\vec{r}$

(parity operator) $\quad P | I, m_I \rangle = \epsilon \, | I, m_I \rangle$

$\epsilon = \pm 1$

$$\langle \,|\vec{D}|\, \rangle = \langle \,|P\vec{D}P|\, \rangle$$

$$\vec{D} \longrightarrow -\vec{D} \quad \text{under parity}$$

$$= -\langle \,|\vec{D}|\, \rangle = 0.$$

- Parity is a good symmetry (of strong & e.m. interactions)
- Q_{ij} is traceless.

<u>Nuclear quadrupole moment correction</u>

$$\Delta E = -e \left\langle n, l, s, j, F, m_F \right| Q_{ij} \cdot \frac{r_i r_j - r^2/3\,\delta_{ij}}{r^5} \left| n, l, s, j, F, m_F \right\rangle$$

(First order perturbation theory)

$$\boxed{\frac{1}{2}(I_i I_j + I_j I_i) - \frac{1}{3}\vec{I}^2 \delta_{ij}} \quad I = 2 \text{ operator}$$

(traceless, symmetric, spin 2)

$$Q_{ij} = C \left\{ \frac{1}{2}(I_i I_j + I_j I_i) - \frac{1}{3}\vec{I}^2 \delta_{ij} \right\}$$

$$= c \frac{e}{M_p^2} \left\{ - \quad - - - - \right\}$$

<u>no. of order 1</u>

(dimensionless)

1st homework problem

- <u>Calculate ΔE</u>

— x — x — x — x — x — x — x —

<u>23. 01. 2013</u>

P. T. O.