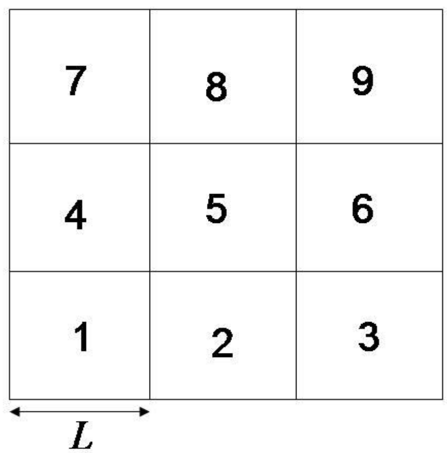
# Quantum Mechanics (3)

Def 3.1

Consider a system with $N$ identical particles. We can always divide the space into many grids, and name them to be 1,2,3,….respectively. Suppose there are $n_1+\Delta n$ particles in grid 1, $n_2$ to $n_2+\Delta n$ particles in grid 2, , $n_3$ to $n_3+\Delta n$ particles in grid 3 and so on, then we say the system belong to a coarse particle distribution of $N(\mathbf{r})$.

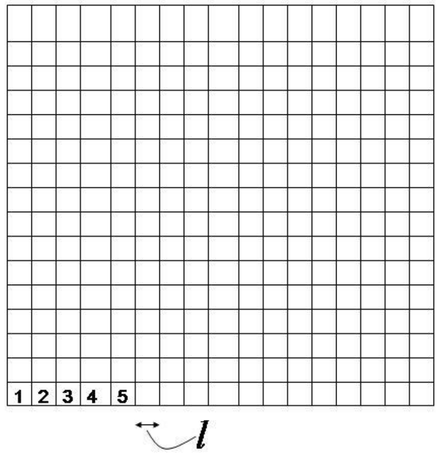



Axiom 3.2

At any instant, the world belong to exactly one definite coarse particles distribution. (For simplicity, we have assumed the world consists of one kind of particles only)

Def 3.3

Consider the same system with $N$ identical particles. We also divide the space into grids, but now each grid has a much smaller side, $l$, such that $l << L$. We also name these grid as 1,2,3,….and so on. Suppose there are $n_1+dn$ particles in grid 1, $n_2$ to $n_2+dn$ particles in grid 2, , $n_3$ to $n_3+dn$ particles in grid 3 and so on, where $dn << \Delta n$, then we say the system belong to a accurate particle distribution $n(\mathbf{r})$.




Lemma 3.4

For every $n(\mathbf{r})$, $\exists N(\mathbf{r})$ such that $n(\mathbf{r}) \in N(\mathbf{r})$.

Axiom 3.5

Although from Axiom 3.2, at every instant, the world belong to a definite $N(\mathbf{r})$, however, we cannot say which accurate particle distribution $n(\mathbf{r})$ in $N(\mathbf{r})$ the world is belonging to.

Axiom 3.6

For every $n(\mathbf{r})$, $\exists\ |n(\mathbf{r})\rangle$in $\mathfrak{F}_N$ or $\mathscr{B}_N$, depends on whether the particles are fermion or boson, (we have assume there are $N$ particles), such that this $n(\mathbf{r})$ is corresponding to.

Axiom 3.7

$$\langle n_i(\mathbf{r}) | n_j(\mathbf{r}) \rangle = \delta_{ij} \qquad \text{…….(3.7.1)}$$

Axiom 3.8

At any instant, $\exists$a wavefunction $|\Psi\rangle \in \mathrm{F}_N$ or $\mathrm{B}_N$, depends on whether the particles are fermion or boson, which correspond to the world.

Axiom 3.9

Suppose at time t, the world belong to $N_t(\mathbf{r})$, then $\exists\ a_{n(r)} \in \mathbb{C}$for $n(\mathbf{r}) \in N_t(\mathbf{r})$ such that the wavefunction at that time can be expressed as

$$|\Psi\rangle = \sum_{n(\mathbf{r}) \in N_t(\mathbf{r})} a_{n(\mathbf{r})} |n(\mathbf{r})\rangle \qquad \text{……(3.9.1)}$$

Axiom 3.10

Suppose at time *t*, the wavefunction of the world is $|\Psi, t\rangle$, and at time *t*+Δ*t*, the wavefunction of the world is $|\Psi, t+\Delta t\rangle$, then $|\Psi, t\rangle$and $|\Psi, t+\Delta t\rangle$are related by

$$|\Psi, t+\Delta t\rangle = e^{-\frac{i}{\hbar}\hat{H}\Delta t}|\Psi, t\rangle \qquad .....(3.10.1)$$

Thm 3.11

$\exists\ b_{n(\mathbf{r})} \in$ Cfor all possible *n*(**r**) such that

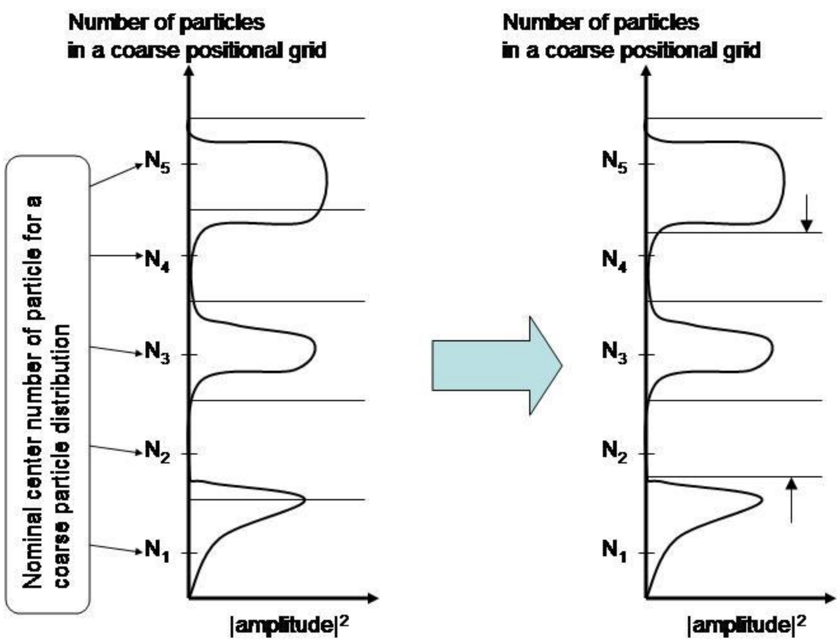
$$|\Psi, t+\Delta t\rangle = \sum_{n(\mathbf{r})} b_{n(\mathbf{r})}|n(\mathbf{r})\rangle \qquad ......(3.11.1)$$

Axiom 3.12

At time *t*+Δ*t*, there is a probability for every *N*(**r**) such that the world will belong to it. The probability for the world to take $N_1$(**r**) is

$$P(\text{world} \in N_1(\mathbf{r})) = \sum_{n(\mathbf{r})\in N_1(\mathbf{r})} |b_{n(\mathbf{r})}|^2 \qquad ......(3.12.1)$$

However, before doing this analysis, number of particles boundaries between adjacent coarse particle distribution in each coarse positional grid (mentioned in Def. 3.1) has to be adjusted such that they do not cut through the non-zeros region of wavefunction amplitude. But on the other hand, these adjustment in boundaries should not lead to a coarse particle distribution grid to concede its own nominal center number of particles, such that each coarse particle distribution will remain exists and retain its identity (although the region it rules over may have expanded or contracted).



Axiom 3.13

After the world is found to belong to $N_{t+\Delta t}(\mathbf{r})$ at time $t+\Delta t$, the wavefunction will immediately given by

$$|\Psi\rangle = \frac{\sum_{n(\mathbf{r})\in N_{t+\Delta t}(\mathbf{r})} b_{n(\mathbf{r})}|n(\mathbf{r})\rangle}{\sqrt{\sum_{n(\mathbf{r})\in N_{t+\Delta t}(\mathbf{r})} |b_{n(\mathbf{r})}|^2}} \qquad \text{.....(3.13.1)}$$

And the wavefunction a time $t+2\Delta t$ will again be predicted by (3.10.1).

Def 3.14

Define $\mathrm{H} = \{f: \mathrm{R} \to \mathrm{C}, \int |f(r)|^2 d^3r < +\infty\}$. Define $\mathrm{H}_N = \underbrace{\mathrm{H} \otimes \cdots \otimes \mathrm{H}}_{\text{N times}}$. We will adopt the notation $|\varphi\rangle \equiv \varphi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ for $\forall |\varphi\rangle \in \mathrm{H}_N$, for $\forall N$. Let $|\psi\rangle, |\varphi\rangle \in \mathrm{H}_N$, define

$$\langle\varphi|\psi\rangle = \int \cdots \int \varphi^*(\mathbf{r}_1, \ldots, \mathbf{r}_N)\psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) d^3r_1 \cdots d^3r_N \qquad \text{......(3.14.1)}$$

Def 3.15

Define $\hat{P}^{(N)}_{\{\mathrm{B\ or\ F}\}}: \mathrm{H}_N \to \mathrm{H}_N$ by $\hat{P}^{(N)}_{\{\mathrm{B\ or\ F}\}}|\psi\rangle = \hat{P}^{(N)}_{\{\mathrm{B\ or\ F}\}}\psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \frac{1}{N!}\sum_p \varsigma^p\, \psi(\mathbf{r}_{P_1}, \ldots, \mathbf{r}_{P_N})$, for $\forall |\psi\rangle \in \mathrm{H}_N$, where ζ=+1 for bosons and ζ=-1 for fermions.

Def 3.16

Define $\mathrm{F}_N = \{|\psi\rangle \in \mathrm{H}_N: \exists |\psi'\rangle \in \mathrm{H}_N \text{ such that } \hat{P}^{(N)}_{\mathrm{F}}|\psi'\rangle = |\psi\rangle\}$. Define $\mathrm{B}_N = \{|\psi\rangle \in \mathrm{H}_N: \exists |\psi'\rangle \in \mathrm{H}_N \text{ such that } \hat{P}^{(N)}_{\mathrm{B}}|\psi'\rangle = |\psi\rangle\}$.

Def 3.17

Suppose $|\alpha_i\rangle \in \mathrm{H}$ for $i$=1,…,$N$, and $\langle\alpha_j|\alpha_i\rangle = \delta_{ij}$, define

$$|\alpha_1 \cdots \alpha_N) = |\alpha_1\rangle \otimes \cdots \otimes |\alpha_N\rangle \qquad \text{......(3.17.1)}$$
$$|\alpha_1 \cdots \alpha_N\} = \sqrt{N!}\, \hat{P}^{(N)}_{\{\mathrm{B\ or\ F}\}}|\alpha_1 \cdots \alpha_N) \qquad \text{.......(3.17.2)}$$
$$|\alpha_1 \cdots \alpha_N\rangle = \frac{1}{\sqrt{\prod_\alpha n_\alpha!}}|\alpha_1 \cdots \alpha_N\} \qquad \text{.......(3.17.3)}$$

where there are $n_\alpha$ state among $\alpha_1, \ldots, \alpha_N$ equals α.

Def 3.18

Define $|i\rangle \in \mathrm{H}$ such that

$$i(\mathbf{r}) = \begin{cases} 1/l^3 & \text{if } \mathbf{r} \in \text{ grid } i \\ 0 & \text{if } \mathbf{r} \notin \text{ grid } i \end{cases} \qquad \text{.......(3.18.1)}$$

where the definition of grid *i* should be referred to Def 3.3. Define

$$|n(\mathbf{r})\rangle = \left| \underbrace{1 \cdots 1}_{n_1} \quad \underbrace{2 \cdots 2}_{n_2} \quad \underbrace{3 \cdots 3}_{n_3} \quad \cdots\cdots \right\rangle \qquad \text{.......(3.18.2)}$$

given that $n(\mathbf{r})$ is an accurate particles distribution with $n_1+dn$ particles in grid 1, $n_2$ to $n_2+dn$ particles in grid 2, , $n_3$ to $n_3+dn$ particles in grid 3 and so on.

<u>Def 3.19</u>

Suppose the particles we are talking about are electrons (Recall in Axiom 3.2 we have assumed the world consists of only one kind of particles), also given that the external potential to these electrons are given by $U(\mathbf{r})$, then the Hamiltonian operator $\widehat{H}$appeared in (3.10.1) will be given by

$$\widehat{H} = \sum_{i=1}^{N} \{-\frac{\hbar^2}{2m_e}\nabla^2_{\mathbf{r}_i} + U(\mathbf{r}_i)\} + \frac{e}{8\pi\varepsilon_0}\sum_{\substack{i,j=1 \\ i\neq j}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \qquad \text{.......(3.19.1)}$$

<u>Def 3.20</u>

Let $\mathfrak{X}$ be a complex vector space. $\langle\bullet,\bullet\rangle$: X × X → Fis an inner product on $\mathfrak{X}$ iff

$$\text{(IP1)} \ \ \langle y, x+z\rangle = \langle y,x\rangle + \langle y,z\rangle$$
$$\text{(IP2)} \ \ \langle y, \lambda x\rangle = \lambda\langle x,y\rangle$$
$$\text{(IP3)} \ \ \langle y, x\rangle = \langle x,y\rangle^*$$
$$\text{(IP4)} \ \ \langle x, x\rangle \geq 0 \ \text{ and } \ \langle x,x\rangle = 0 \ \text{ iff } \ x = 0 \ \text{ for } \ x,y,z \in \text{X}$$

Let $\langle\bullet,\bullet\rangle$be an inner product on $\mathfrak{X}$. Then ($\mathfrak{X}$, $\langle\bullet,\bullet\rangle$) is an inner product space.

<u>Def 3.21</u>

$\hat{Q}$: X → Xis hermitian on the inner product space ($\mathfrak{X}$, $\langle\bullet,\bullet\rangle$) iff

$$\langle \hat{Q}x, y\rangle = \langle x, \hat{Q}y\rangle \qquad \text{for } \forall x,y \in \text{X} \qquad \text{......(3.21.1)}$$

<u>Thm 3.22</u>

Let $\hat{Q}$ be hermitian on the inner product space ($\mathfrak{X}$, $\langle\bullet,\bullet\rangle$). Then $\exists\{\varphi_{np}\} \in$ Xwhich are orthonormal and span $\mathfrak{X}$, such that $\exists\{q_n\} \in$ R:

$\hat{Q}\varphi_{np} = q_n\varphi_{np}$ for $\forall n$ and $p = 1,\ldots,N_n$ …..(3.22.1)

Thm 3.22a(Schmidt orthogonalization)

Let $\{\psi_n\}_{n=1}^{N} \in$ Xbe linear independent. Define $\{\varphi_n\}_{n=1}^{N} \in$ Xby the recurring formula:

$$\varphi_n = \{-\sum_{i=1}^{n-1}\frac{\langle\varphi_i,\psi_n\rangle}{\langle\varphi_i,\psi_i\rangle}\varphi_i\} + \psi_n \quad \ldots\ldots(3.22a.1)$$

Then $\langle\varphi_n,\varphi_m\rangle = 0$ for $\forall n, m = 1,\ldots,N$ such that $n \neq m$.

Thm 3.23

Let all assumption in Thm 3.22 still valid. Suppose there exists another operator$\hat{R}$: X $\rightarrow$ Xsuch that $\hat{Q}, \hat{R}$commute. Then it can be proven that

$$\hat{R}\varphi_{np} = \sum_{r=1}^{N_n}\langle\varphi_{nr},\hat{R}\varphi_{np}\rangle\varphi_{nr} \quad \ldots\ldots.(3.23.1)$$

Then, let

$$\hat{R}(\sum_{j=1}^{N_n} a_{njk}\phi_{nj}) = r_{nk}(\sum_{j=1}^{N_n} a_{njk}\phi_{nj}) \Rightarrow \sum_{r,j=1}^{N_n} a_{njk}R_{(nr)(nj)}\phi_{nr} = r_{nk}(\sum_{r=1}^{N_n} a_{nrk}\phi_{nr})$$
$$\Rightarrow \begin{bmatrix} R_{(n1)(n1)} & \cdots & R_{(n1)(nN_n)} \\ \vdots & & \vdots \\ R_{(nN_n)(n1)} & \cdots & R_{(nN_n)(nN_n)} \end{bmatrix}\begin{bmatrix} a_{n1k} \\ \\ a_{nN_nk} \end{bmatrix} = r_{nk}\begin{bmatrix} a_{n1k} \\ \\ a_{nN_nk} \end{bmatrix} \quad \ldots\ldots.(3.23.2)$$

For (3.23.2), we can find $\varphi'_{nk} = \sum_{j=1}^{N_n} a_{njk}\varphi_{nj}$ ……(3.23.3)
for $\forall n, k = 1,\ldots N_n$, where $\varphi'_{nk}$ for $\forall n, k = 1,\ldots,N_n$are orthonormal, and $r_{nk}$ for $\forall n,k$=1,…,$N_n$ such that

$$\begin{cases} \hat{Q}\varphi'_{nk} = q_n\varphi'_{nk} \\ \hat{R}\varphi'_{nk} = r_{nk}\varphi'_{nk} \end{cases} \quad \ldots..(3.23.4a) \text{ and } (3.23.4b)$$

Thm 3.24 (Perturbation theory for the case of no degeneracy)

Suppose $\hat{H}_0\left|E_n^{(0)}\right\rangle = E_n^{(0)}\left|E_n^{(0)}\right\rangle$…..(3.24.1) for $\forall$ n with no degeneracy. We have

$$(\hat{H}_0 + \beta\hat{H}')(\left|E_n^{(0)}\right\rangle + \beta\left|E_n^{(1)}\right\rangle + \cdots) = (E_n^{(0)} + \beta E_n^{(1)} + \cdots)(\left|E_n^{(0)}\right\rangle + \beta\left|E_n^{(1)}\right\rangle + \cdots) \quad \ldots..(3.24.2)$$

We have

$\hat{H}_0\left|E_n^{(1)}\right\rangle + \hat{H}'\left|E_n^{(0)}\right\rangle = E_n^{(0)}\left|E_n^{(1)}\right\rangle + E_n^{(1)}\left|E_n^{(0)}\right\rangle$ ……(3.23.3)

Since $\left|E_n^{(1)}\right\rangle = \sum_m a_{nm}^{(1)}\left|E_m^{(0)}\right\rangle$ ……(3.23.4)

We have

$\sum_m a_{nm}^{(1)} E_m^{(0)}\left|E_m^{(0)}\right\rangle + \hat{H}'\left|E_n^{(0)}\right\rangle = E_n^{(0)}\sum_m a_{nm}^{(1)}\left|E_m^{(0)}\right\rangle +$
$E_n^{(1)}\left|E_n^{(0)}\right\rangle$ ……(3.24.5)

Multiply (3.24.5) by $\left\langle E_n^{(0)}\right|$, we have

$$a_{nn}^{(1)}E_n^{(0)} + \left\langle E_n^{(0)}\middle|\hat{H}'\middle|E_n^{(0)}\right\rangle = E_n^{(0)}a_{nn}^{(1)} + E_n^{(1)}$$

$\Rightarrow E_n^{(1)} = \left\langle E_n^{(0)}\middle|\hat{H}'\middle|E_n^{(0)}\right\rangle$ …….(3.24.6)

Multiply (3.24.5) by $\left\langle E_p^{(0)}\right|, p \neq n$, we have

$a_{np}^{(1)} = \frac{\left\langle E_p^{(0)}\middle|H'\middle|E_n^{(0)}\right\rangle}{E_n^{(0)}-E_p^{(0)}}$ …….(3.24.7)

By some unknown reason, we can set $a_{nn}^{(1)} = 0$, so overally we have

$E_n = \left|E_n^{(0)}\right\rangle + \beta\sum_{\substack{m,\\ m\neq n}}\frac{\Sigma\left|E_m^{(0)}\right\rangle\left\langle E_m^{(0)}\middle|H'\middle|E_n^{(0)}\right\rangle}{E_n^{(0)}-E_m^{(0)}}$ …..(3.24.9)

<u>Thm 3.25 (Perturbation theory for the case of degeneracy)</u>

Suppose $\hat{H}_0\left|E_{ni}^{(0)}\right\rangle = E_n^{(0)}\left|E_{ni}^{(0)}\right\rangle$for $\forall n, i$. …..(3.25.1) We have to define a new set of zeroth order wavevector:

$\left|E_{ni}^{(0)}\right\rangle' = \sum_j a_{nij}^{(0)}\left|E_{nj}^{(0)}\right\rangle$ …….(3.25.2)

Then, with analogue to (3.24.2), we have

$(\hat{H}_0 + \beta\hat{H}')(\left|E_{ni}^{(0)}\right\rangle' + \beta\left|E_{ni}^{(1)}\right\rangle' + \cdots) = (E_n^{(0)} + \beta E_{ni}^{(1)} + \cdots)(\left|E_{ni}^{(0)}\right\rangle' + \beta\left|E_{ni}^{(1)}\right\rangle' + \cdots)$ …(3.25.3)

So we have

$$\hat{H}_0\left|E_{ni}^{(1)}\right\rangle' + \hat{H}'\left|E_{ni}^{(0)}\right\rangle' = E_n^{(0)}\left|E_{ni}^{(1)}\right\rangle' + E_{ni}^{(1)}\left|E_{ni}^{(0)}\right\rangle' \quad .....(3.25.4)$$

As we have

$$\left|E_{ni}^{(1)}\right\rangle' = \sum_{mj} a_{nimj}^{(1)} \left|E_{mj}^{(0)}\right\rangle \quad .....(3.25.6)$$

substitute into (3.25.4):

$\sum_{mj} a_{nimj}^{(1)} E_m^{(0)}\left|E_{mj}^{(0)}\right\rangle + \hat{H}'\sum_j a_{nij}^{(0)} \left|E_{nj}^{(0)}\right\rangle = E_n^{(0)} \sum_{mj} a_{nimj}^{(1)} \left|E_{mj}^{(0)}\right\rangle + E_{ni}^{(1)} \sum_j a_{nij}^{(0)} \left|E_{nj}^{(0)}\right\rangle$ ….(3.25.7)

Multiply (3.25.7) by $\left\langle E_{nk}^{(0)}\right|$, we have

$$a_{nink}^{(1)} E_n^{(0)} + \sum_j a_{nij}^{(0)} \left\langle E_{nk}^{(0)}\middle|\hat{H}'\middle|E_{nj}^{(0)}\right\rangle = E_n^{(0)} a_{nink}^{(1)} + E_{ni}^{(1)} a_{nik}^{(0)}$$

Define $H'_{(nk)(nj)} = \left\langle E_{nk}^{(0)}\middle|\hat{H}'\middle|E_{nj}^{(0)}\right\rangle$, we have

$$\sum_j H'_{(nk)(nj)} a_{nij}^{(0)} = E_{ni}^{(1)} a_{nik}^{(0)} \quad ......(3.25.8)$$

As this can be done for all *k*, we have

$$\begin{bmatrix} H'_{(n1)(n1)} & \cdots & H'_{(n1)(nN_n)} \\ \vdots & & \vdots \\ H'_{(nN_n)(n1)} & \cdots & H'_{(nN_n)(nN_n)} \end{bmatrix} \begin{bmatrix} a_{ni1}^{(0)} \\ \vdots \\ a_{niN_n} \end{bmatrix} = E_{ni}^{(1)} \begin{bmatrix} a_{ni1}^{(0)} \\ \vdots \\ a_{niN_n} \end{bmatrix} \quad .......(3.25.9)$$

where $E_n^{(0)}$ is $N_n$ fold degenerate. From (3.25.9), we can solve for $E_{ni}^{(1)}$ for $i$=1,…,$N_n$ and $\begin{bmatrix} a_{ni1}^{(0)} \\ \vdots \\ a_{niN_n}^{(0)} \end{bmatrix}$ for for $i$=1,…,$N_n$. So overally, we have

$$E_{ni} = E_n^{(0)} + \beta E_{ni}^{(1)} + \cdots \quad .......(3.25.10)$$

and

$$|E_{ni}\rangle' = \left|E_{ni}^{(0)}\right\rangle' + \cdots = \sum_{j=1}^{N_n} a_{nij}^{(0)}\left|E_{nj}^{(0)}\right\rangle + \cdots \qquad \ldots\ldots(3.25.11)$$

<u>Thm 3.26 (Time dependent perturbation theory)</u>

Let the Hamiltonian $\hat{H} = \hat{H}_0 + \beta\hat{H}'$ ……(3.26.1), where $\hat{H}_0$ is time independent. Suppose time independent $|E_{ni}\rangle$ for all *n*, *i* form a complete orthonormal basis for the Hilbert space, such that each of them satisfies

$$\hat{H}_0|E_{ni}\rangle = E_n|E_{ni}\rangle \qquad \ldots\ldots.(3.26.2)$$

Then any wavefunction with time evolution can be expressed as

$$|\Psi\rangle = \sum_{n,j} c_{nj}(t)e^{-\frac{iE_n}{\hbar}t}\left|E_{nj}\right\rangle \qquad \ldots\ldots(3.26.3)$$

Let $c_{nj}(t)$ can be given by

$$c_{nj}(t) = c_{nj}^{(0)}(t) + \beta c_{nj}^{(1)}(t) + \beta^2 c_{nj}^{(2)}(t) + \cdots \qquad \ldots..(3.26.4)$$

By substituting (3.26.1), (3.26.3) & (3.26.4) into the time-dependent Schrödinger equation, and using the relation (3.26.2), and by supposing at time $t$=0,

$$|\Psi\rangle = |E_{lk}\rangle \qquad \ldots..(3.26.5)$$

we can then derive that

$$\begin{cases} c_{nj}^{(0)}(t) = \delta_{nl}\delta_{jk} \\ c_{nj}^{(\alpha)}(0) = 0 \quad \text{for } \alpha = 1,2,3,\ldots \\ \dot{c}_{nj}^{(1)}(t) = \frac{1}{i\hbar}e^{i\omega_{nl}t}H'_{(nj)(lk)} \end{cases} \qquad \ldots..(3.26.6)$$

for all *n*,*j*, where

$$\omega_{nl} = \frac{1}{\hbar}(E_n - E_l) \qquad \ldots\ldots.(3.26.7)$$

$$H'_{(nj)(lk)} = \left\langle E_{nj}\middle|\hat{H}'\middle|E_{lk}\right\rangle \qquad \ldots\ldots.(3.26.8)$$

<u>Thm 3.27</u>

$\hat{L} = \hat{L}_x\mathbf{e}_x + \hat{L}_y\mathbf{e}_y + \hat{L}_z\mathbf{e}_z$ is an operator for angular momenta if $\hat{L}_x, \hat{L}_y, \hat{L}_z$ satisfies the following algebra

$$\begin{cases}[\hat{L}_x,\hat{L}_y]=i\hbar\hat{L}_z\\ [\hat{L}_y,\hat{L}_z]=i\hbar\hat{L}_x\\ [\hat{L}_z,\hat{L}_x]=i\hbar\hat{L}_y\end{cases}$$ …..(3.27.1a), (b) and (c)

It can be proved for any angular momentum operator $\hat{L}_1,\hat{L}_2$, let $\hat{L}=\hat{L}_1+\hat{L}_2$, then $\hat{L}^2$commute with the operator $(\hat{L}_1^2\mathbf{e}_1+\hat{L}_2^2\mathbf{e}_2+\hat{L}_z\mathbf{e}_3)$. Let $|l_1,l_2,m_1,m_2\rangle$be the orthonormal eigenvector to $(\hat{L}_1^2\mathbf{e}_1+\hat{L}_2^2\mathbf{e}_2+\hat{L}_z\mathbf{e}_3)$ and span the Hilbert space $\mathcal{H}$, with eigenvalues $l_1(l_1+1)\hbar^2\mathbf{e}_1+l_2(l_2+1)\hbar^2\mathbf{e}_2+(m_1+m_2)\hbar\mathbf{e}_3$respectively, then by Thm 3.23, we can derive that ∃

$$|l_1,l_2,l,m\rangle=\sum_{m_1+m_2=m}|l_1,l_2,m_1,m_2\rangle(l_1,l_2,m_1,m_2|l_1,l_2,l,m) \quad …..(3.27.2)$$

for $l=max\{|m|,|l_1-l_2|\},\ldots,l_1+l_2$. The multiplicity=no. of possible value of $l$ for a fixed $l_1$, $l_2$=2 $min\{l_1,l_2\}+1$ …….(3.27.2a)

$$\hat{L}^2|l_1,l_2,l,m\rangle=l(l+1)\hbar^2|l_1,l_2,l,m\rangle \quad …….(3.27.3)$$

and

$$(\hat{L}_1^2\mathbf{e}_1+\hat{L}_2^2\mathbf{e}_2+\hat{L}_z\mathbf{e}_3)|l_1,l_2,l,m\rangle=l_1(l_1+1)\hbar^2\mathbf{e}_1+l_2(l_2+1)\hbar^2\mathbf{e}_2+m\hbar\mathbf{e}_3|l_1,l_2,l,m\rangle \quad ….(3.27.4)$$

Thm 3.28

$f(u)=\frac{sin^2 u}{u^2}$is small whenever u is not near to zero, and

$$\int_{-\infty}^{+\infty}\frac{sin^2 u}{u^2}du=\pi \quad ……..(3.28.1)$$

Thm 3.29 (Fermi's golden rule)

Suppose everything in Thm 3.26 still valid. Suppose the $H'_{(nj)(lk)}$in (3.26.6) is time independent, then by making use of (3.28.1), we can prove that

$$|c_{nj}^{(1)}(t)|^2=\frac{2\pi}{\hbar}|H'_{(nj)(lk)}|^2\delta(E_n-E_l)t \quad ……(3.29.1)$$

Suppose now the $H'_{(nj)(lk)}$can be given by $H'_{(nj)(lk)}=H''_{(nj)(lk)}\,sin\,\omega\,t$or $H'_{(nj)(lk)}=H''_{(nj)(lk)}\,cos\,\omega\,t$, where $H''_{(nj)(lk)}$is time independent, then , by making use of (3.28.1), we can prove that

$$|c_{nj}^{(1)}(t)|^2=\frac{2\pi}{\hbar}|H''_{(nj)(lk)}|^2\{\delta(E_n-E_l+\frac{\omega}{\hbar})+\delta(E_n-E_l-\frac{\omega}{\hbar})\}t \quad ……(3.29.2)$$

Thm 3.30

Let $\mathfrak{X}$ be a Hilbert Space, $\hat{L}_x, \hat{L}_y, \hat{L}_z$ be hermitian operator in $\mathfrak{X}$ such that

$$\begin{cases} [\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z \\ [\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x \\ [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y \end{cases} \quad \text{.......(3.30.1)}$$

Define $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$. Let $\exists$A $\subseteq$ R$^2$, $\{|\alpha,\beta\rangle \in$ X: $(\alpha,\beta) \in$ A$\}$ such that $\hat{L}^2|\alpha,\beta\rangle = \alpha|\alpha,\beta\rangle$ and $\hat{L}_z|\alpha,\beta\rangle = \beta|\alpha,\beta\rangle$ for $\forall(\alpha,\beta) \in$ A, and $\{|\alpha,\beta\rangle \in$ X: $(\alpha,\beta) \in$ A$\}$ span $\mathfrak{X}$. Then we have A $\subseteq \{(\alpha,\beta): \alpha = \frac{N}{2}(\frac{N}{2}+1)\hbar^2$ for $N = 0,1,2,\ldots$ and $\beta = -\frac{N}{2},\ldots,\frac{N}{2}\}$.

Thm 3.31

Suppose in Thm 3.30, we are restricted in the space $\{|\alpha,\beta\rangle \in$ X: $\alpha = \frac{1}{2}(\frac{1}{2}+1)\hbar^2\}$, then $\hat{L}_x, \hat{L}_y, \hat{L}_z$ can be represented by the matrices:

$$[\hat{L}_x] = \frac{\hbar}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \text{.....(3.31.1a)} \qquad [\hat{L}_y] = \frac{\hbar}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad \text{....(3.31.1b)}$$

$$[\hat{L}_z] = \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad \text{......(3.31.1c)}$$

Suppose in Thm 3.30, we are restricted in the space $\{|\alpha,\beta\rangle \in$ X: $\alpha = 1(1+1)\hbar^2\}$, then $\hat{L}_x, \hat{L}_y, \hat{L}_z$ can be represented by the matrices:

$$[\hat{L}_x] = \frac{\hbar}{\sqrt{2}}\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \quad \text{.....(3.31.2a)} \qquad [\hat{L}_y] = \frac{\hbar}{\sqrt{2}}\begin{bmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{bmatrix} \quad \text{....(3.31.2b)}$$

$$[\hat{L}_z] = \hbar\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad \text{......(3.31.2c)}$$

Thm 3.32 (Rotational Field Approximation)

Consider the following differential equation

$$\dot{c}(t) = f_1(c(t),t)e^{i\omega_1 t} + f_2(c(t),t)e^{i\omega_2 t} \quad \text{........(*)}$$

Suppose $\omega_2 >> \omega_1$. Suppose we solve (*) for $t = n\Delta t$, $n$=0,1,2,…by the recurring formula

$$c((n+1)\Delta t) = c(n\Delta t) + \dot{c}(n\Delta t)\Delta t \quad \text{.......(\#)}$$

such that $\Delta t$is comparable to $T_2$ ($\frac{2\pi}{T_2}=\omega_2$), but $\Delta t$is not exactly equal to $T_2$. Then we will find that the term $e^{i\omega_2 t}$oscillates very fast and on average it makes no contribution to $\dot{c}(n\Delta t)$ in expression (*), then (*) can be approximated as

$$\dot{c}(t) \approx f_1(c(t),t)e^{i\omega_1 t} \qquad \text{.......(\&)}$$

This is the rotational field approximation.

Thm 3.33 (Central Field Approx.)

Consider an atom of atomic no. $Z$ and with $N$ electrons. The Hamiltonian will be given by

$$\hat{H} = \sum_{i=1}^{N}\{-\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{4\pi\varepsilon_o r_i}\} + \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\frac{e^2}{4\pi\varepsilon_o|\mathbf{r}_i-\mathbf{r}_j|} \qquad \text{........(3.33.1)}$$

We propose that we can find a $V(r)$ such that the effect of $\hat{H}'$ will be much smaller than $\hat{H}_0$and $\hat{H}'$ can be treated by the perturbation method, where

$$\hat{H}_0 = \sum_{i=1}^{N}\{-\frac{\hbar^2}{2m}\nabla_i^2 + V(r_i)\} \qquad \text{........(3.33.2)}$$

$$\hat{H}' = \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\frac{e^2}{4\pi\varepsilon_o|\mathbf{r}_i-\mathbf{r}_j|} + \sum_{i=1}^{N}\{-\frac{Ze^2}{4\pi\varepsilon_o r_i} - V(r_i)\} \qquad \text{........(3.33.3)}$$

and $\hat{H} = \hat{H}_0 + \hat{H}'$ .........(3.33.4)

Thm 3.34

Every electron in the atom in Thm 3.33 will experience a B field. Suppose the ith electron experience a B field equals to $\mathbf{B}_i$, then this electron will possess an energy equals

$$W_i = -\frac{1}{2}\boldsymbol{\mu}_{i,s}\cdot\mathbf{B}_i \qquad \text{.......(3.34.1)}$$

where $\boldsymbol{\mu}_{i,s}$is the magnetic moment of the ith electron arises due to its spin. It can be proved that (by relativistic quantum mechanics)

$$\boldsymbol{\mu}_{i,s} = -\frac{e}{m}\mathbf{s}_i \qquad \text{.......(3.34.2)}$$

Then the factor ½ in (3.34.1) arises from a relativistic effect named “Thomas’ precession”. From (2.25.5a)

$\mathbf{B}_i = \frac{1}{c^2}\mathbf{E}_i \times \mathbf{u}_i = \frac{1}{c^2}\mathbf{E}_i \times \frac{\mathbf{p}_i}{m}$ …….(3.34.3)

$\mathbf{E}_i$ can be found form Thm 3.33

$$\mathbf{E}_i = -\nabla_i\{\sum_{j=1}^{N\sum} V(r_j) + H^{?}$$

But recall that in Thm 3.33, $H^{?}$ is negligible when comparing with $\sum_{j=1}^{N} V(r_j)$. ∴

$\mathbf{E}_i = -\nabla_i\{\sum_{j=1}^{N} V(r_j)\} = -\frac{\partial V(r_i)}{\partial r_i}\frac{\mathbf{r}_i}{r_i}$ ……..(3.34.4)

Substitute (3.34.4) into (3.34.3),

$B_i = \frac{1}{mc^2}(-\frac{\partial V(r_i)}{\partial r_i}\frac{\mathbf{r}_i}{r_i}) \times \mathbf{p}_i = -\frac{1}{mc^2 r_i}\frac{\partial V(r_i)}{\partial r_i}\mathbf{L}_i$ ……(3.34.5)

$\Rightarrow W_i = -\frac{e}{2m^2c^2r_i}\frac{\partial V(r_i)}{\partial r_i}\mathbf{s}_i \cdot \mathbf{L}_i = f(r_i)\mathbf{s}_i \cdot \mathbf{L}_i$ ……(3.34.6)

∴The Hamiltonian $\widehat{H}$in (3.33.4) should be modified to

$\widehat{H} = \widehat{H}_0 + \widehat{H}' + \widehat{H}_{\text{SO}}$ …….(3.34.7)

where

$\widehat{H}_{\text{SO}} = \sum_{i=1}^{N} W_i$ …….(3.34.8)

<u>Thm 3.35</u>

Let $u_{nlm_lm_s} = R_{nl}(r)Y_{lm_l}(\vartheta,\varphi)\underline{\chi}_{m_s}$ ……(3.35.1)

be the orthonormal eignefunctions to the eigenvalues equation

$$[-\frac{\hbar^2}{2m}\nabla^2 + V(r)]u = Eu$$

with eigenvalues $E_{nl}$, i.e.

$[-\frac{\hbar^2}{2m}\nabla^2 + V(r)]u_{nlm_lm_s} = E_{nl}u_{nlm_lm_s}$ …….(3.35.2)

Let $u_1, \ldots., u_N$be as described in (3.35.1) with eigenvalues $E_1, \ldots, E_N$respectively, then we have

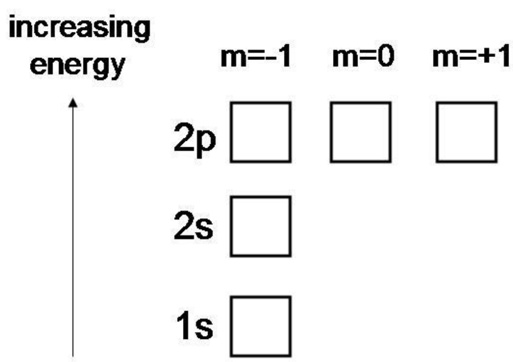
$\widehat{H}_0|u_1,\ldots,u_N\rangle = E_{1,\ldots,N}|u_1,\ldots,u_N\rangle$ ………(3.35.3)

where $E_{1,\ldots N} = \sum_{i=1}^{N} E_i$ ……..(3.35.4)

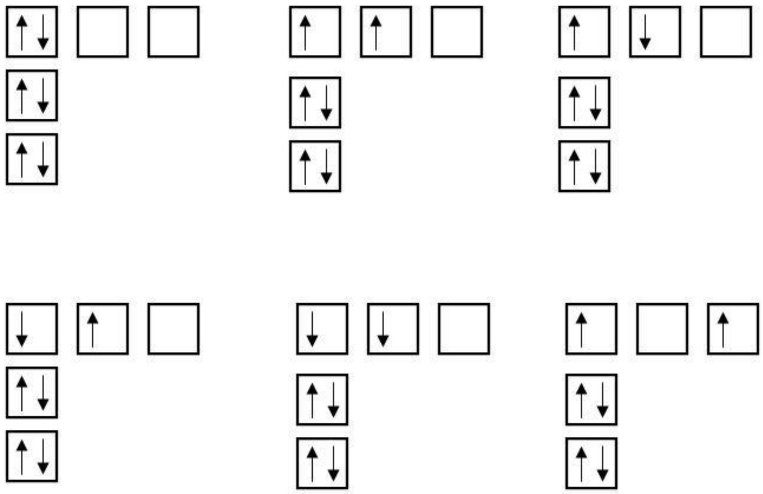
$|u_1,\ldots,u_N\rangle$ is given by (3.17.3).

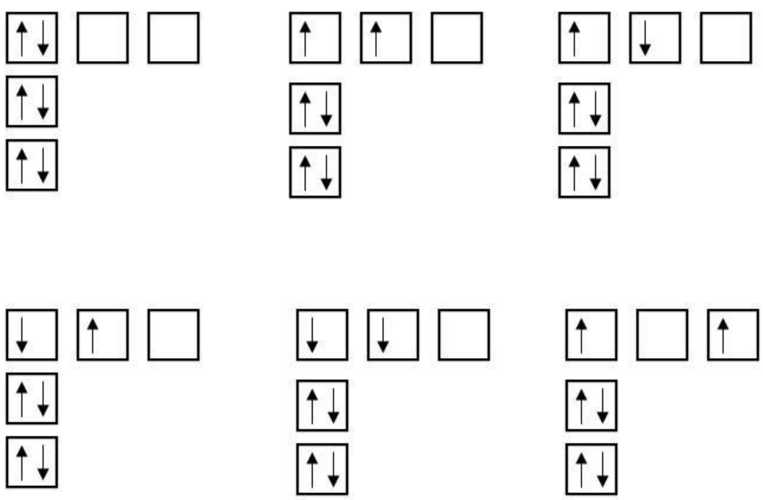
Thm 3.36

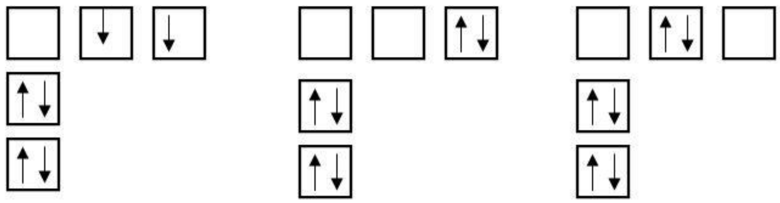
After we have found eigenfunction & eigenvalues to $\widehat{H}_0$in (3.34.7) in Thm 3.35, we are now going to apply perturbation theory to $\widehat{H}'$and $\widehat{H}_{SO}$in (3.34.7). Suppose the atom we are considering is carbon. Since (3.35.2), the eigenvalue depend on only *n* & *l*, but $m_l$ & $m_s$, then we can picturize the states as




When we fill in these boxes, we can see that the energy level $E_{1,\ldots,N}$in (3.53.3) in fact has a 15 fold degeneracies:





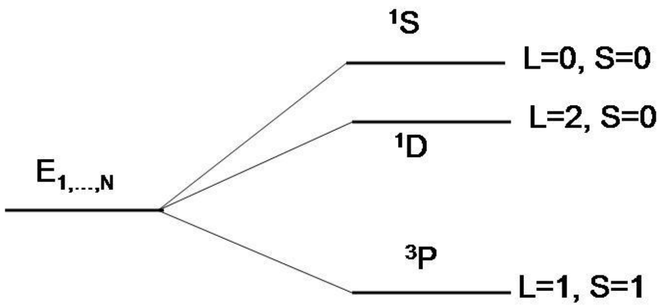


∴When we treat $\widehat{H}'$&$\widehat{H}_{\mathrm{SO}}$by perturbation method, we have to apply degenerated perturbation theory. Firstly, we will assume the effect $\widehat{H}'$is much greater than $\widehat{H}_{\mathrm{SO}}$, so we will firstly apply perturbation theory to $\widehat{H}'$, then $\widehat{H}_{\mathrm{SO}}$. This approximation is called “L-S coupling”.

When we apply degenerated perturbation theory to $\widehat{H}'$, we will find that the original $E_{1,\dots,N}$state will split into 3 different energies, such that their corresponding eignevalues are eigenvectors to the operator **L** & **S**, where

$\mathbf{L} = \sum_{i=1}^{N} \mathbf{L}_i$ ……(3.36.1)
$\mathbf{S} = \sum_{i=1}^{N} \mathbf{S}_i$ …….(3.36.2)

(In our case of carbon, $N$=6) The 3 different energies & their corresponding eigenvalues to **L** and **S** are shown below:




(Refer to Albert Messiah "Quantum Mechanics Vol II" Ch. XVII, §10)

Note that the energy levels above contains the following eigenvectors:

$$1S: |0,0,0,0\rangle$$
$$2D: |2,0,\text{-}2,0\rangle, |2,0,\text{-}1,0\rangle, |2,0,0,0\rangle, |2,0,1,0\rangle, |2,0,2,0\rangle$$
$$3P: |1,1,-1,-1\rangle, |1,1,-1,0\rangle, |1,1,-1,1\rangle, |1,1,0,-1\rangle,$$
$$|1,1,0,0\rangle, |1,1,0,1\rangle, |1,1,1,-1\rangle, |1,1,1,0\rangle, \left|\underbrace{1}_{L},\underbrace{1}_{S},\underbrace{1}_{M_L},\underbrace{1}_{M_S}\right\rangle$$

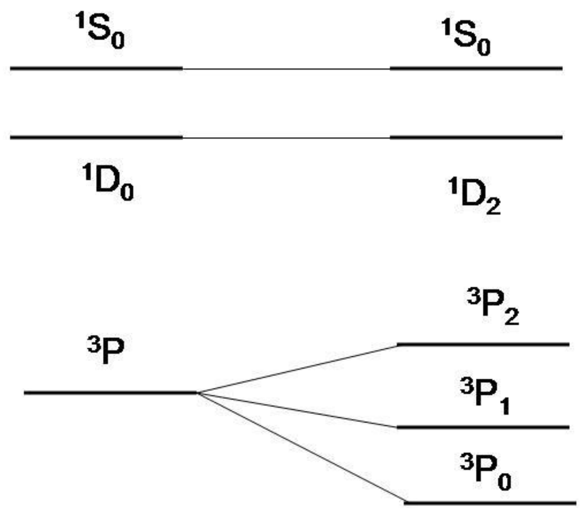
We can see that totally there are 15 eigenvectors, which is consistent with our previous result that $E_{1,\dots,N}$ is 15 fold degenerated.

Now, we are going to apply non-degenerate perturbation theory to the $^1$S state, and degenerate perturbation theory to $^1$D and $^3$P state. From the two perturbation theory Thm 3.24 and Thm 3.25, we know that we have to evaluate the matrix element $\langle L,S,M_L,M_S|\hat{H}_{SO}|L,S,M_L',M_S'\rangle$. From Ch XVI § 11 of "Quantum Mechanics Vol II" written by Albert Messiah, we can prove that there exist a $A$, which is a function of radial coordinates, i.e. $A = A(r_1,\dots,r_N)$, such that

$$\langle L,S,M_L,M_S|\hat{H}_{SO}\big|L,S,M_L^{'},M_S^{'}\big\rangle = \langle L,S,M_L,M_S|A\mathbf{L}\cdot\mathbf{S}\big|L,S,M_L^{'},M_S^{'}\big\rangle$$

for $\forall M_L, M_S, M_L^{'}, M_S^{'}$ ……..(3.36.3)

Then, by making use of $\mathbf{L}\cdot\mathbf{S} = \frac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2)$, the energy level before will be further splitted as




$^1S_0 : |0,0,0,0\rangle$

$^1D_2 : |2,0,2,-2\rangle, |2,0,2,-1\rangle, |2,0,2,0\rangle, |2,0,2,1\rangle, |2,0,2,2\rangle$

$^3P_2 : |1,1,2,-2\rangle, |1,1,2,-1\rangle, |1,1,2,0\rangle, |1,1,2,1\rangle, |1,1,2,1\rangle$

$^3P_1 : |1,1,1,-1\rangle, |1,1,1,0\rangle, |1,1,1,1\rangle$

$^3P_0 : \left|\underbrace{1}_{L},\underbrace{1}_{S},\underbrace{0}_{J},\underbrace{0}_{M_J}\right\rangle$

<u>Thm 3.37</u>

In Thm 3.36, we assume that the effect of $\hat{H}'$ is much bigger than $\hat{H}_{SO}$. Now, let us assume the effect of $\hat{H}_{SO}$ is much bigger $\hat{H}'$ instead. Then we will do the problem in the following way. Firstly, we solve the eigenvalue equation:

$$[-\frac{\hbar^2}{2m}\nabla^2 + V(r) + f(r)\mathbf{L}\cdot\mathbf{S}]u = Eu \qquad \text{........(3.37.1)}$$

Let their solutions to be $u_{nljm_j}$, with eigenvalue $E_{nlj}$, where

$$\hat{J}^2 u_{nljm_j} = j(j+1)\hbar^2 u_{nljm_j} \qquad \text{........(3.37.2)}$$

$$\hat{J}_z u_{nljm_j} = m_j \hbar u_{nljm_j} \qquad \text{........(3.37.3)}$$

$$\hat{L}^2 u_{nljm_j} = l(l+1)\hbar^2 u_{nljm_j} \qquad \text{........(3.37.4)}$$

$[-\frac{\hbar^2}{2m}\nabla^2 + V(r) + f(r)\mathbf{L}\cdot\mathbf{S}]u_{nljm_j} = E_{nlj}u_{nljm_j}$ ……..(3.37.5)

Let $u_1,\ldots,u_N$ be the $u_{nljm_j}$ with eigenvalues $E_1, \ldots, E_N$, then we have

$(\widehat{H}_0 + \widehat{H}_{SO})|u_1,\ldots,u_N\rangle = E_{1,\ldots,N}|u_1,\ldots,u_N\rangle$ ……..(3.37.6)

where $E_{1,\ldots,N} = \sum_{i=1}^{N} E_i$ ……..(3.37.7)

Then we can apply perturbation theory to treat the term $\widehat{H}'$ left.

Thm 3.50

Suppose $\hat{L}_x, \hat{L}_y, \hat{L}_z, \hat{L}^2$ are the angular momentum operator mentioned in Thm 3.27. Suppose $\varphi$ is an eigenfunction to $\hat{L}^2$ & $\hat{L}_z$ with eigenvalues $\alpha$ and $\beta$ respectively. Define

$\hat{L}_+ = \hat{L}_x + i\hat{L}_y$ ……(3.50.1)
$\hat{L}_- = \hat{L}_x - i\hat{L}_y$ …….(3.50.2)

Then by making use of the commutation relations in (3.27.1a) to (3.27.1c), we can prove that

$\hat{L}^2(\hat{L}_+\varphi) = \alpha(\hat{L}_+\varphi)$ …….(3.50.3)
$\hat{L}^2(\hat{L}_-\varphi) = \alpha(\hat{L}_-\varphi)$ ……..(3.50.4)
$\hat{L}_z(\hat{L}_+\varphi) = (\beta + \hbar)(\hat{L}_+\varphi)$ …….(3.50.5)
$\hat{L}_z(\hat{L}_-\varphi) = (\beta - \hbar)(\hat{L}_-\varphi)$ ……..(3.50.6)

Def 3.51

Let $\widehat{Q}: X \to X$ be an operator in the inner product space (X,⟨•,•⟩) $\widehat{Q}^+: X \to X$ is the adjoint operation of $\widehat{Q}$ iff

$\langle \hat{Q}f, g\rangle = \langle f, \hat{Q}^+ g\rangle$ for $\forall f, g \in X$ ……(3.51.1)

Thm 3.52

Let $\hat{L}_x, \hat{L}_y, \hat{L}_z, \hat{L}^2$ be as mentioned in Thm 3.50. Let $\varphi$ be an eigenfunction to to $\hat{L}^2$ & $\hat{L}_z$ with eigenvalues $\alpha$ and $\beta$ respectively. Since from (IP4) of Def 3.20,

$\langle \hat{L}_+\varphi, \hat{L}_+\varphi \rangle \geq 0$ …….(3.52.1)

$\Rightarrow \langle \varphi, \hat{L}_+^+ \hat{L}_+\varphi \rangle \geq 0$

Since $\hat{L}_+ = \hat{L}_x + i\hat{L}_y$, $\hat{L}_+^+ = \hat{L}_x^+ - i\hat{L}_y^+$. As $\hat{L}_x$ and $\hat{L}_y$ are self adjoint,

$\Rightarrow \hat{L}_+^+ = \hat{L}_x - i\hat{L}_y = \hat{L}_- \Rightarrow \langle \varphi, \hat{L}_-\hat{L}_+\varphi \rangle \geq 0$ …..(3.52.2) and (3.52.3)

It can be proven from (3.27.1) that

$\hat{L}_-\hat{L}_+ = \hat{L} - \hat{L}_z^2 - \hbar\hat{L}_z$ …….(3.52.4)

$\therefore \alpha - \beta^2 - \hbar\beta \geq 0 \Rightarrow \alpha \geq \beta^2 + \hbar\beta$ …….(3.52.5)

By $\langle \hat{L}_-\phi, \hat{L}_-\phi \rangle \geq 0$ and using similar procedure, we can prove that

$\alpha \geq \beta^2 - \hbar\beta$ …….(3.52.6)

Thm 3.53

Let $\hat{L}_x, \hat{L}_y, \hat{L}_z, \hat{L}^2$ be as mentioned in Thm 3.50. Let $\varphi$ be an eigenfunction to to $\hat{L}^2$ & $\hat{L}_z$ with eigenvalues $\alpha$ and $\beta$ respectively. Since z-component angular momentum $\beta + n\hbar$ and $\beta - n\hbar$ must satisfies the relation (3.52.5) and (3.52.6), we can assert that there exist $n_1$, $n_2$ such that

$\hat{L}_+^{n_1}\varphi \neq 0$ but $\hat{L}_+^{n_1+1}\varphi = 0$ …….(3.53.1)

Also that

$\hat{L}_-^{n_2}\varphi \neq 0$ but $\hat{L}_-^{n_2-1}\varphi = 0$ …….(3.53.2)

Write

$\beta_1 = \beta + n_1\hbar$ ……(3.53.3a)

$\beta_2 = \beta - n_2\hbar$ ……(3.53.3b)

From (3.53.1), we have

$$\hat{L}_-\hat{L}_+(\hat{L}_+^n\varphi) = (\hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z)(\hat{L}_+^n\varphi) = (\alpha - \beta_1^2 - \hbar\beta_1)(\hat{L}_+^n\varphi) = 0$$

$\Rightarrow \alpha = \beta_1(\beta_1 + \hbar)$ ………(3.53.4)

From (3.53.2), similarly, we have

$\alpha = \beta_2(\beta_2 - \hbar)$ ……..(3.53.5)

From (3.53.4), (3.53.5), we can easily prove that

$\beta_1 = -\beta_2$ …….(3.53.6)

Since

$\beta_1 - \beta_2 = (n_1 + n_2)\hbar$ ……..(3.53.7)

$\Rightarrow \beta_1 = \frac{(n_1+n_2)\hbar}{2} = -\beta_2$ ………(3.53.8)

and $\alpha = \frac{(n_1+n_2)}{2}[\frac{(n_1+n_2)}{2} + 1]\hbar^2$ ……..(3.53.9)

∴We have the conclusion that if $\alpha$and $\beta$are allowed eigenvalue to $\hat{L}^2$and $\hat{L}_z$respectively, then there must exist two integer $N, n'$, such that

$n' \leq N$ …….(3.53.10)

$\alpha = \frac{N}{2}(\frac{N}{2} + 1)\hbar^2$ ……..(3.53.11)

$\beta = (\frac{N}{2} - n')\hbar$ ……..(3.53.12)