PartIV
Electronic Structure of Many-Electron Atoms

9 Periodic Table and One-electronic Level of Atoms

9.1 One-electronic Level Structure of a Hydrogen-like Atom

We begin with obtaining a single-particle structure of a hydrogen-like atom. The Schroedinger equation for the Hamiltonian in our case can be written

$$h = \frac{p^2}{2m} - \frac{\alpha}{r}$$
$$h\psi = E\psi$$
$$\alpha = \frac{Ze^2}{4\pi\epsilon_0}$$

The angular momentum operator:

$$\vec{L} = \vec{r} \times \vec{p}$$
$$L_i = \epsilon_{ijk} r_j p_k$$

can give [173] [174]

$$[\vec{L}, h] = 0$$

Further (obeys the Pauli 's),

$$\vec{M} = \frac{1}{2m}(\vec{p} \times \vec{L} - \vec{L} \times \vec{p}) - \frac{\alpha}{r}\vec{r}$$

[173] We can first write

$$[r_i, p_j]f = r_i p_j f - p_j r_i f = r_i p_j f - (p_j r_i)f - r_i p_j f = +i\hbar\partial_j r_i f = i\hbar\delta_{ij} f \longrightarrow [r_i, p_j] = i\hbar\delta_{ij}$$
$$[p_i, f]g = p_i f g - f p_i g = (p_i f)g + f p_i g - f p_i g = (p_i f)g = -i\hbar(\partial_i f)g \quad \longrightarrow [p_i, f] = -i\hbar(\partial_i f)$$

$$[p_i, r^{-n}] = -i\hbar\partial_i (r_j r_j)^{-n/2} = i\hbar(n/2)(r_j r_j)^{-n/2-1} 2r_i = i\hbar n r^{-n-2} r_i$$

[174]

$$[L_i, p_a] = \epsilon_{ijk}[r_j p_k, p_a] = \epsilon_{ijk}[r_j, p_a]p_k = i\hbar\epsilon_{iak}p_k$$
$$[L_i, p^2] = \epsilon_{iab}[r_a p_b, p_\ell p_\ell] = \epsilon_{iab}(p_\ell[r_a, p_\ell] + [r_a, p_\ell]p_\ell)p_b = 2i\hbar\epsilon_{i\ell b}p_\ell p_b = 0 \ [\vec{L}, \frac{p^2}{2m}] = 0$$

$$[L_i, r^{-1}] = \epsilon_{iab}[r_a p_b, r^{-1}] = \epsilon_{iab} r_a [p_b, r^{-1}] = \epsilon_{iab} r_a i\hbar r^{-3} r_i = 0$$
$$\textit{Likewise}, \quad [L_i, r^{-n}] = 0$$

Thus,

$$[\vec{L}, h] = 0$$

which gives [175]

$$[\vec{M}, h] = 0$$

So, $\vec{L}$ and $\vec{M}$ become the conserved quantities. Further, [176]

$$[M_a, M_b] = -i\hbar\frac{2}{m}h\epsilon_{abc}L_c$$

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$$\begin{aligned}
[(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})_i, p^2] &= \epsilon_{ijk}[p_jL_k - L_jp_k, p_\ell p_\ell] = \epsilon_{ijk}(p_j[L_k,p^2]-[L_j,p^2]p_k) = 0\\
[(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})_i, r^{-1}] &= \epsilon_{ijk}[p_jL_k - L_jp_k, r^{-1}] = \epsilon_{ijk}([p_j,r^{-1}]L_k - L_j[p_k,r^{-1}]) = i\hbar r^{-3}\epsilon_{ijk}(r_jL_k - L_jr_k)\\
&= i\hbar r^{-3}\epsilon_{ijk}(r_j\epsilon_{kab}r_ap_b - \epsilon_{jab}r_ap_br_k)\\
&= i\hbar r^{-3}\{(\delta_{ia}\delta_{jb}-\delta_{ib}\delta_{ja})r_jr_ap_b + (\delta_{ia}\delta_{kb}-\delta_{ib}\delta_{ka})r_ap_br_k)\}\\
&= i\hbar r^{-3}\{(r_jr_ip_j - r_jr_jp_i + r_ip_kr_k - r_kp_ir_k)\\
&= i\hbar r^{-3}\{r_jr_ip_j - r^2p_i + r_ip_kr_k - r_k(r_kp_i + [p_i,r_k])\}\\
&= i\hbar r^{-3}(r_jr_ip_j - 2r^2p_i + r_ip_kr_k + i\hbar r_i)\\
[r^{-1}r_i, p^2] &= -[p^2, r^{-1}r_i] = -r^{-1}[p^2,r_i] - [p^2,r^{-1}]r_i = 2i\hbar r^{-1}p_i - [p^2,r^{-1}]r_i\\
&= 2i\hbar r^{-1}p_i - p_\ell[p_\ell,r^{-1}]r_i - [p_\ell,r^{-1}]p_\ell r_i\\
&= 2i\hbar r^{-1}p_i - i\hbar p_\ell r^{-3}r_\ell r_i - i\hbar r^{-3}r_\ell p_\ell r_i\\
&= 2i\hbar r^{-1}p_i - i\hbar(r^{-3}p_\ell + [p_\ell,r^{-3}])r_\ell r_i - i\hbar r^{-3}r_\ell p_\ell r_i\\
&= 2i\hbar r^{-1}p_i - i\hbar r^{-3}p_\ell r_\ell r_i - i\hbar[p_\ell,r^{-3}]r_\ell r_i - i\hbar r^{-3}r_\ell p_\ell r_i\\
&= i\hbar r^{-3}(2r^2p_i - p_\ell r_\ell r_i - r_\ell p_\ell r_i) - 3(i\hbar)^2r^{-5}r_\ell r_\ell r_i\\
&= i\hbar r^{-3}(2r^2p_i - p_\ell r_\ell r_i - r_\ell p_\ell r_i - 3i\hbar r_i)
\end{aligned}$$

Thus,

$$\begin{aligned}
[M_i, h] &= -\frac{\alpha}{2m}i\hbar r^{-3}(r_jr_ip_j + r_ip_kr_k - p_\ell r_\ell r_i - r_\ell p_\ell r_i - 2i\hbar r_i)\\
&= -\frac{\alpha}{2m}i\hbar r^{-3}(r_\ell r_ip_\ell + r_ip_\ell r_\ell - p_\ell r_\ell r_i - r_\ell p_\ell r_i - 2i\hbar r_i)\\
&= -\frac{\alpha}{2m}i\hbar r^{-3}(r_\ell[r_i,p_\ell] + [r_i,p_\ell r_\ell] - 2i\hbar r_i)\\
&= -\frac{\alpha}{2m}i\hbar r^{-3}(r_i[r_i,p_i] + [r_i,p_i]r_i - 2i\hbar r_i) = 0
\end{aligned}$$

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$$\begin{aligned}
(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})_i &= \epsilon_{ijk}(p_jL_k - L_jp_k) = \epsilon_{ijk}(p_jL_k - p_kL_j - [L_j,p_k])\\
&= \epsilon_{ijk}(p_jL_k - p_kL_j - i\hbar\epsilon_{jkl}p_l) = \epsilon_{ijk}(p_jL_k - p_kL_j) - 2i\hbar\delta_{il}p_l\\
&= \epsilon_{ijk}(p_jL_k - p_kL_j) - 2i\hbar p_i\\
&= \epsilon_{ijk}(p_j\epsilon_{kab} - p_k\epsilon_{jab})r_ap_b - 2i\hbar p_i\\
&= \{(\delta_{ia}\delta_{jb}-\delta_{ib}\delta_{ja})p_j + (\delta_{ia}\delta_{kb}-\delta_{ib}\delta_{ka})p_k\}r_ap_b - 2i\hbar p_i\\
&= p_jr_ip_j - p_jr_jp_i + p_kr_ip_k - p_kr_kp_i - 2i\hbar p_i\\
&= 2p_jr_ip_j - 2p_jr_jp_i - 2i\hbar p_i\\
&= 2p_j(p_jr_i + i\hbar\delta_{ij}) - 2p_j(p_ir_j + i\hbar\delta_{ij}) - 2i\hbar p_i\\
&= 2p^2r_i - 2p_jp_ir_j - 2i\hbar p_i
\end{aligned}$$

In the bound states $E<0$, we can write

$$\tilde{M}_a=\sqrt{-\frac{m}{2E}}M_a$$

Such that we can assume:

$$[\tilde{M}_a,\tilde{M}_b]=i\hbar\epsilon_{abc}L_c$$

$$
\begin{aligned}
&\frac{1}{4}[(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})_a,(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})_b]\\
=&[p^2r_a-p_ip_ar_i-i\hbar p_a,p^2r_b-p_jp_br_j-i\hbar p_b]\\
=&[p^2r_a,p^2r_b-p_jp_br_j-i\hbar p_b]\\
&-[p_ip_ar_i,p^2r_b-p_jp_br_j-i\hbar p_b]\\
&-i\hbar[p_a,p^2r_b-p_jp_br_j-i\hbar p_b]\\
=&[p^2r_a,p^2r_b]-[p^2r_a,p_jp_br_j]-i\hbar[p^2r_a,p_b]\\
&-[p_ip_ar_i,p^2r_b]+[p_ip_ar_i,p_jp_br_j]+i\hbar[p_ip_ar_i,p_b]\\
&-i\hbar[p_a,p^2r_b]+i\hbar[p_a,p_jp_br_j]+(i\hbar)^2[p_a,p_b]\\
=&\{p^2[r_a,p^2]r_b+p^2[p^2,r_b]r_a\}-\{p^2[r_a,p_jp_b]r_j+p_jp_b[p^2,r_j]r_a\}-i\hbar p^2[r_a,p_b]\\
&-\{p_ip_a[r_i,p^2]r_b+p^2[p_ip_a,r_b]r_i\}+\{p_ip_a[r_i,p_jp_b]r_j+p_jp_b[p_ip_a,r_j]r_i\}+i\hbar p_ip_a[r_i,p_b]\\
&-i\hbar p^2[p_a,r_b]+i\hbar p_jp_b[p_a,r_j]\\
=&\{2i\hbar p^2p_ar_b-2i\hbar p^2p_br_a\}-i\hbar\{p^2(\delta_{aj}p_b+\delta_{ab}p_j)r_j-2p_jp_bp_jr_a\}-(i\hbar)^2p^2\delta_{ab}\\
&-\{2i\hbar p_ip_ap_ir_b-i\hbar p^2(\delta_{ib}p_a+\delta_{ab}p_i)r_i\}+i\hbar\{p_ip_a(\delta_{ij}p_b+\delta_{ib}p_j)r_j-p_jp_b(\delta_{ij}p_a+\delta_{aj}p_i)r_i\}+(i\hbar)^2p_ip_a\delta_{ib}\\
&+(i\hbar)^2p^2\delta_{ab}-(i\hbar)^2p_jp_b\delta_{aj}\\
=&\{\overbrace{2i\hbar p^2p_ar_b}^{4}-\overbrace{2i\hbar p^2p_br_a}^{5}\}-i\hbar\{p^2(p_br_a+\overbrace{\delta_{ab}p_jr_j}^{1})-\overbrace{2p_jp_bp_jr_a}^{5}\}-\overbrace{(i\hbar)^2p^2\delta_{ab}}^{2}\\
&-\{\overbrace{2i\hbar p_ip_ap_ir_b}^{4}-i\hbar p^2(p_ar_b+\overbrace{\delta_{ab}p_ir_i}^{1})\}+i\hbar\{\overbrace{p_ip_ap_br_i}^{6}+\overbrace{p_bp_ap_jr_j}^{7}-\overbrace{p_ip_bp_ar_i}^{7}-\overbrace{p_ap_bp_ir_i}^{6}\}+\overbrace{(i\hbar)^2p_bp_a}^{3}\\
&+\overbrace{(i\hbar)^2p^2\delta_{ab}}^{2}-\overbrace{(i\hbar)^2p_ap_b}^{3}\\
=&i\hbar p^2(p_ar_b-p_br_a)=i\hbar p^2(r_bp_a-r_ap_b)=-i\hbar p^2(r_ap_b-r_bp_a)
\end{aligned}
$$

$$
\begin{aligned}
&\frac{1}{2}[(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})_a, r^{-1}r_b] \\
=&[p^2r_a - p_ip_ar_i - i\hbar p_a, r^{-1}r_b] = [p^2r_a, r^{-1}r_b] - [p_ip_ar_i, r^{-1}r_b] - i\hbar[p_a, r^{-1}r_b] \\
=&p_i[p_i, r^{-1}r_b]r_a + [p_i, r^{-1}r_b]p_ir_a - p_i[p_a, r^{-1}r_b]r_i - [p_i, r^{-1}r_b]p_ar_i - i\hbar[p_a, r^{-1}r_b] \\
&\quad([p_\alpha, r^{-1}r_\beta] = r^{-1}[p_\alpha, r_\beta] + [p_\alpha, r^{-1}]r_\beta = -i\hbar r^{-1}\delta_{\alpha\beta} + i\hbar r^{-3}r_\alpha r_\beta) \\
=&i\hbar p_i(-r^{-1}\delta_{ib} + r^{-3}r_ir_b)r_a + i\hbar(-r^{-1}\delta_{ib} + r^{-3}r_ir_b)p_ir_a - i\hbar p_i(-r^{-1}\delta_{ab} + r^{-3}r_ar_b)r_i \\
&- i\hbar(-r^{-1}\delta_{ib} + r^{-3}r_ir_b)p_ar_i - (i\hbar)^2(-r^{-1}\delta_{ab} + r^{-3}r_ar_b) \\
=&i\hbar\{-p_br^{-1}r_a + \overbrace{p_ir^{-3}r_ir_br_a}^{3} - \overbrace{r^{-1}p_br_a}^{2} + \overbrace{r^{-3}r_ir_bp_ir_a}^{1} + \delta_{ab}p_ir^{-1}r_i - \overbrace{p_ir^{-3}r_ar_br_i}^{3} \\
&+ \overbrace{r^{-1}p_ar_b}^{2} - \overbrace{r^{-3}r_ir_bp_ar_i}^{1} + i\hbar r^{-1}\delta_{ab} - i\hbar r^{-3}r_ar_b\} \\
=&i\hbar\{-p_br^{-1}r_a + \overbrace{r^{-1}(p_ar_b - p_br_a)}^{2} + \overbrace{r^{-3}r_ir_b(p_ir_a - p_ar_i)}^{1} + \delta_{ab}p_ir^{-1}r_i + i\hbar r^{-1}\delta_{ab} - i\hbar r^{-3}r_ar_b\} \\
=&i\hbar\{-p_br^{-1}r_a + \overbrace{r^{-1}(r_bp_a - r_ap_b)}^{2} + \overbrace{r^{-3}r_ir_b(r_ap_i - r_ip_a)}^{1} + \delta_{ab}p_ir^{-1}r_i + i\hbar r^{-1}\delta_{ab} - i\hbar r^{-3}r_ar_b\} \\
=&i\hbar\{-p_br^{-1}r_a + r^{-1}(\overbrace{r_bp_a}^{1} - r_ap_b) + r^{-3}r_ir_br_ap_i - \overbrace{r^{-1}r_bp_a}^{1} + \delta_{ab}p_ir^{-1}r_i + i\hbar r^{-1}\delta_{ab} - i\hbar r^{-3}r_ar_b\} \\
=&i\hbar\{-p_br^{-1}r_a - r^{-1}r_ap_b + r^{-3}r_ir_br_ap_i + \delta_{ab}p_ir^{-1}r_i + i\hbar r^{-1}\delta_{ab} - i\hbar r^{-3}r_ar_b\}
\end{aligned}
$$

This gives

$$
\begin{aligned}
&\frac{1}{2}\{[(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})_a, r^{-1}r_b] + [r^{-1}r_a, (\vec{p}\times\vec{L}-\vec{L}\times\vec{p})_b]\} \\
&\quad= i\hbar\{-p_br^{-1}r_a + p_ar^{-1}r_b - r^{-1}(r_ap_b - r_bp_a)\} \\
&\quad= i\hbar\{-r^{-1}p_br_a - [p_b, r^{-1}]r_a + r^{-1}p_ar_b + [p_a, r^{-1}]r_b - r^{-1}(r_ap_b - r_bp_a)\} \\
&\quad= i\hbar\{r^{-1}(-p_br_a + p_ar_b) - r^{-1}(r_ap_b - r_bp_a)\} \\
&\quad= i\hbar\{r^{-1}(-r_ap_b + r_bp_a) - r^{-1}(r_ap_b - r_bp_a)\} \\
&\quad= -2i\hbar r^{-1}(r_ap_b - r_bp_a)
\end{aligned}
$$

Thus,

$$
\begin{aligned}
[M_a, M_b] &= [\frac{1}{2m}(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})_a - \alpha r^{-1}r_a, \frac{1}{2m}(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})_b - \alpha r^{-1}r_b] \\
&= -\frac{1}{m^2}i\hbar p^2(r_ap_b - r_bp_a) + \frac{\alpha}{m}2i\hbar r^{-1}(r_ap_b - r_bp_a) \\
&= -i\hbar\frac{2}{m}\left(\frac{p^2}{2m} - \frac{\alpha}{r}\right)\epsilon_{abc}L_c = -i\hbar\frac{2}{m}h\epsilon_{abc}L_c \\
&\qquad \epsilon_{abc}L_c = \epsilon_{abc}\epsilon_{cij}r_ip_j = (\delta_{ai}\delta_{bj} - \delta_{aj}\delta_{bi})r_ip_j = r_ap_b - r_bp_a
\end{aligned}
$$

Now we write [177]

$$\vec{L}\cdot\vec{M}=\vec{M}\cdot\vec{L}=0$$
$$\vec{L}\cdot\tilde{\vec{M}}=\tilde{\vec{M}}\cdot\vec{L}=0$$

Further we can write [178]

$$[M_i,L_j]=\epsilon_{ijk}M_k$$
$$[\tilde{M}_i,L_j]=\epsilon_{ijk}\tilde{M}_k$$

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$$\begin{aligned}
\vec{M}\cdot\vec{L}&=\frac{1}{2m}(\vec{p}\times\vec{L}-\vec{L}\times\vec{p})_iL_i-\alpha r^{-1}r_iL_i\\
&=\frac{1}{m}(p^2r_i-p_jp_ir_j-i\hbar p_i)\epsilon_{iab}r_ap_b-\alpha r^{-1}r_i\epsilon_{iab}r_ap_b\\
&=-\frac{1}{m}\epsilon_{iab}(p_jp_ir_jr_ap_b+i\hbar p_ir_ap_b)\\
&=-\frac{1}{m}\epsilon_{iab}\{p_jp_i(p_br_jr_a+[r_jr_a,p_b])+i\hbar p_i(p_br_a+[r_a,p_b])\}\\
&=-\frac{1}{m}\epsilon_{iab}\{p_jp_i[r_jr_a,p_b]+i\hbar p_i[r_a,p_b]\}\\
&=-\frac{1}{m}\epsilon_{iab}\{p_jp_i(\delta_{ja}p_b+\delta_{ab}r_a)+(i\hbar)^2p_i\delta_{ab}\}=0\\
\vec{L}\cdot\vec{M}&=(\vec{M}\cdot\vec{L})^\dagger=0
\end{aligned}$$

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$$\begin{aligned}
[M_i,L_j]&=\frac{2}{m}\epsilon_{jab}[p^2r_i-p_jp_ir_j-i\hbar p_i,r_ap_b]-\alpha\epsilon_{jab}[r^{-1}r_i,r_ap_b]\\
&=\frac{2}{m}\epsilon_{jab}\{[p^2,r_a]p_br_i+p^2r_a[r_i,p_b]\\
&\quad-[p_jp_i,r_a]p_br_j-p_jp_ir_a[r_j,p_b]\\
&\quad-i\hbar[p_i,r_a]p_b\}\\
&\quad-\alpha\epsilon_{jab}r_a\{r^{-1}[r_i,p_b]+[r^{-1},p_b]r_i\}\\
&=\frac{2i\hbar}{m}\epsilon_{jab}\{-2p_ap_br_i+p^2r_a\delta_{ib}\\
&\quad+(\delta_{ja}p_i+\delta_{ia}p_j)p_br_j-p_jp_ir_a\delta_{jb}\\
&\quad+i\hbar\delta_{ia}p_b\}\\
&\quad-\alpha\epsilon_{jab}r_a\{r^{-1}\delta_{ib}-r^{-3}r_br_i\}\\
&=\frac{2i\hbar}{m}\{\epsilon_{jai}p^2r_a\\
&\quad+\epsilon_{jib}p_jp_br_j\\
&\quad+\epsilon_{jib}i\hbar p_b\}\\
&\quad-\alpha\epsilon_{jai}r_ar^{-1}\\
&=i\hbar\epsilon_{ija}\{\frac{2}{m}(p^2r_a-p_jp_ar_j-i\hbar p_a)-\alpha r^{-1}r_a\}=\epsilon_{ija}M_a
\end{aligned}$$

Calculate for M^2, we obtain [179]

[179]

$$
\begin{aligned}
M^2 =&\{\frac{1}{2m}\epsilon_{iab}(p_aL_b - L_ap_b) - \alpha r^{-1}r_i\}\{\frac{1}{2m}\epsilon_{icd}(p_cL_d - L_cp_d) - \alpha r^{-1}r_i\}\\
=&\frac{1}{4m^2}(\delta_{ac}\delta_{bd} - \delta_{ad}\delta_{bc})(p_aL_b - L_ap_b)(p_cL_d - L_cp_d)\\
&- \frac{\alpha}{2m}\epsilon_{iab}\{(p_aL_b - L_ap_b)r^{-1}r_i + r^{-1}r_i(p_aL_b - L_ap_b)\} + \alpha^2\\
=&\frac{1}{4m^2}\{(p_aL_b - L_ap_b)(p_aL_b - L_ap_b) - (p_aL_b - L_ap_b)(p_bL_a - L_bp_a)\}\\
&- \frac{\alpha}{2m}\epsilon_{iab}\{(p_aL_b - L_ap_b)r^{-1}r_i + r^{-1}r_i(p_aL_b - L_ap_b)\} + \alpha^2
\end{aligned}
$$

First,

$$
\begin{aligned}
&(p_aL_b - L_ap_b)(p_aL_b - L_ap_b) - (p_aL_b - L_ap_b)(p_bL_a - L_bp_a)\\
=&(p_aL_b - L_ap_b)(p_aL_b - L_ap_b - p_bL_a + L_bp_a)\\
=&(p_aL_b - p_bL_a - [L_a, p_b])(p_aL_b - p_bL_a - [L_a, p_b] - p_bL_a + p_aL_b + [L_b, p_a])\\
=&(p_aL_b - p_bL_a - i\hbar\epsilon_{abc}p_c)(p_aL_b - p_bL_a - i\hbar\epsilon_{abc}p_c - p_bL_a + p_aL_b + i\hbar\epsilon_{bac}p_c)\\
=&2(p_aL_b - p_bL_a - i\hbar\epsilon_{abc}p_c)(p_aL_b - p_bL_a - i\hbar\epsilon_{abd}p_d)\\
=&2\Big\{p_aL_b(p_aL_b - p_bL_a - i\hbar\epsilon_{abd}p_d)\\
&- p_bL_a(p_aL_b - p_bL_a - i\hbar\epsilon_{abd}p_d)\\
&- i\hbar\epsilon_{abc}p_c(p_aL_b - p_bL_a - i\hbar\epsilon_{abd}p_d)\Big\}\\
=&2\Big\{p_aL_bp_aL_b - p_aL_bp_bL_a - i\hbar\epsilon_{abd}p_aL_bp_d\\
&- p_bL_ap_aL_b + p_bL_ap_bL_a + i\hbar\epsilon_{abd}p_bL_ap_d\\
&- i\hbar\epsilon_{abc}p_cp_aL_b + i\hbar\epsilon_{abc}p_cp_bL_a - \hbar^2\epsilon_{abd}\epsilon_{abc}p_cp_d\Big\}\\
=&2\Big\{p_a(p_aL_b + [L_b, p_a])L_b - p_ap_bL_bL_a - i\hbar\epsilon_{abd}p_a(p_dL_b + [L_b, p_d])\\
&- p_bp_aL_aL_b + p_b(p_bL_a + [L_a, p_b])L_a + i\hbar\epsilon_{abd}p_b(p_dL_a + [L_a, p_d])\\
&- \hbar^2 2p^2\Big\}\\
=&2\Big\{p^2L^2 - p_ap_bL_bL_a + \hbar^2\epsilon_{abd}\epsilon_{bdc}p_ap_c\\
&+ p_bp_aL_aL_b + p^2L^2 - \hbar^2\epsilon_{abd}\epsilon_{adc}p_bp_c - 2\hbar^2p^2\Big\}\\
=&2\Big\{2p^2L^2 - p_ap_bL_bL_a + \hbar^2 2\delta_{ac}p_ap_c\\
&+ p_bp_aL_aL_b + \hbar^2 2\delta_{bc}p_bp_c - 2\hbar^2p^2\Big\}\\
=&4p^2L^2 + 4\hbar^2p^2 + 2p_ap_b(L_aL_b - L_bL_a) = 4p^2(L^2 + \hbar^2)
\end{aligned}
$$

$$M^2 = \frac{2}{m}h(L^2+\hbar^2)+\alpha^2$$

In the next step:

$$\begin{aligned}
\epsilon_{iab}\{(p_aL_b - L_ap_b)r^{-1}r_i &= \epsilon_{iab}\{p_ar^{-1}L_br_i - L_a(r^{-1}p_b + [p_b,r^{-1}])r_i\}\\
&= \epsilon_{iab}\{(r^{-1}p_a + [p_a,r^{-1}])L_br_i - r^{-1}L_ap_br_i - i\hbar L_ar^{-3}r_br_i\}\\
&= \epsilon_{iab}\{(r^{-1}p_a + i\hbar r^{-3}r_a)L_br_i - r^{-1}L_ap_br_i\}\\
&= \epsilon_{iab}\{r^{-1}p_aL_br_i + i\hbar r^{-3}(L_br_a + i\hbar\epsilon_{baj}r_j)r_i - r^{-1}L_ap_br_i\}\\
&= \epsilon_{iab}\{r^{-1}p_aL_br_i + i\hbar r^{-3}i\hbar\epsilon_{baj}r_jr_i - r^{-1}L_ap_br_i\}\\
&\qquad [r_i,L_j] = \epsilon_{jab}[r_i,r_ap_b] = \epsilon_{jab}r_a[r_i,p_b] = i\hbar\epsilon_{jab}r_a\delta_{ib} = i\hbar\epsilon_{ija}r_a\\
&= r^{-1}\epsilon_{iab}(p_aL_b - L_ap_b)r_i + 2\hbar^2r^{-1}
\end{aligned}$$

By adding the two above, we obtain

$$\begin{aligned}
M^2 =& \frac{p^2}{m^2}(L^2+\hbar^2)\\
&-\frac{\alpha}{2m}r^{-1}\{\epsilon_{iab}\Big(r_i(p_aL_b - L_ap_b) + (p_aL_b - L_ap_b)r_i\Big) + 2\hbar^2\} + \alpha^2
\end{aligned}$$

While we know

$$\begin{aligned}
\epsilon_{iab}\{r_i(p_aL_b - L_ap_b) + (p_aL_b - L_ap_b)r_i\} &= \epsilon_{iab}\{r_ip_aL_b - r_iL_ap_b + p_aL_br_i - L_ap_br_i\}\\
&= \epsilon_{iab}\{r_ip_aL_b - r_i(p_bL_a + [L_a,p_b]) + (L_bp_a + [p_a,L_b])r_i - L_ap_br_i\}\\
&= \epsilon_{iab}\{r_ip_aL_b - r_ip_bL_a - i\hbar r_i\epsilon_{abc}p_c + L_bp_ar_i + i\hbar\epsilon_{abc}p_cr_i - L_ap_br_i\}\\
&= \epsilon_{iab}\{r_ip_aL_b - r_ip_bL_a + L_bp_ar_i - L_ap_br_i\}\\
&= \epsilon_{iab}\{r_ip_aL_b - r_ap_iL_b + L_bp_ar_i - L_bp_ir_a\}\\
&= \epsilon_{iab}(r_ip_a - r_ap_i)L_b + L_b\epsilon_{iab}(p_ar_i - p_ir_a)\\
&= \epsilon_{iab}(r_ip_a - r_ap_i)L_b + L_b\epsilon_{iab}(r_ip_a - r_ap_i) = 2L^2
\end{aligned}$$

We can obtain

$$\begin{aligned}
M^2 &= \frac{p^2}{m^2}(L^2+\hbar^2) - \frac{\alpha}{m}\frac{2}{r}(L^2+\hbar^2)+\alpha^2\\
&= \frac{2}{m}h(L^2+\hbar^2)+\alpha^2
\end{aligned}$$

For the bound states energy $E < 0$, we can write [180]

$$0 = \frac{2E}{m}((L \pm \tilde{M})^2 + \hbar^2) + \alpha^2$$

At the same time, we know that

$$\vec{I} = \frac{1}{2}(\vec{L} + \vec{\tilde{M}})$$
$$\vec{J} = \frac{1}{2}(\vec{L} - \vec{\tilde{M}})$$

and [181]

$$[I_i, I_j] = i\hbar\epsilon_{ijk} I_k$$
$$[J_i, J_j] = i\hbar\epsilon_{ijk} J_k$$

satisfy the commutation relations for the angular momentum thereby, independent of each other: [182]

$$[I_i, J_j] = 0$$

---

[180]

$$-\frac{2E}{m}\tilde{M}^2 = \frac{2E}{m}(L^2 + \hbar^2) + \alpha^2$$
$$0 = \frac{2E}{m}(L^2 + \tilde{M}^2 + \hbar^2) + \alpha^2$$
$$= \frac{2E}{m}((L \pm \tilde{M})^2 + \hbar^2) + \alpha^2$$

[181]

$$[I_i, I_j] = \frac{1}{4}\Big([\tilde{M}_i, \tilde{M}_j] + [\tilde{M}_i, L_j] + [L_i, \tilde{M}_j] + [L_i, L_j]\Big)$$
$$= \frac{i\hbar}{4}\epsilon_{ijk}(\tilde{L}_k + \tilde{M}_k + \tilde{M}_k + L_k) = \epsilon_{ijk} I_k$$

$$[J_i, J_j] = \frac{1}{4}\Big([\tilde{M}_i, \tilde{M}_j] - [\tilde{M}_i, L_j] - [L_i, \tilde{M}_j] + [L_i, L_j]\Big)$$
$$= \frac{i\hbar}{4}\epsilon_{ijk}(\tilde{L}_k - \tilde{M}_k - \tilde{M}_k + L_k) = \epsilon_{ijk} J_k$$

[182]

$$[I_i, J_j] = \frac{1}{4}[L_i + \tilde{M}_i, L_j - \tilde{M}_j]$$
$$= \frac{1}{4}([L_i, L_j] - [L_i, \tilde{M}_j] + [\tilde{M}_i, L_j] - [\tilde{M}_i, \tilde{M}_j])$$
$$= i\hbar\epsilon_{ijk}(L_k - \tilde{M}_k + \tilde{M}_k - L_k) = 0$$

Using the half-odd integers i and j, we can express

$$\begin{aligned} I^2 =& \hbar^2 i(i+1) \\ J^2 =& \hbar^2 j(j+1) \end{aligned}$$

and given $\vec{L}\cdot\tilde{M}=0$, we let n be the integers and further write [183]

$$E = -\frac{m\alpha^2}{2\hbar^2}\frac{1}{n^2}$$

Since the degeneration $\vec{I} = \vec{L} + \tilde{\vec{M}}$ is given, the possible L for $i = \frac{n-1}{2}$ can be found in

$$0, 1, \cdots, \frac{n-1}{2}$$

The total degeneration therefore can be expressed as

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

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$$i = j = \frac{n-1}{2}$$

Thus we write

$$\begin{aligned} 0 =& \frac{2E}{m}(4I^2+\hbar^2)+\alpha^2 \\ =& \frac{2E\hbar^2}{m}(4i(i+1)+1)+\alpha^2 \\ =& \frac{2E\hbar^2}{m}((n-1)(n+1)+1)+\alpha^2 = \frac{2E\hbar^2}{m}n^2+\alpha^2 \\ E =& -\frac{m\alpha^2}{2\hbar^2}\frac{1}{n^2} \end{aligned}$$

9.2 The Hamiltonian in Many-electron Atoms

We consider the following second quantization formalism as the Hamiltonian in many-electron atoms of having the nucleus at the origin with the charge $+Ze$:

$$\begin{aligned}
H &= H_0 + H_{int} \\
H_0 &= \int d\tau\, \psi^\dagger(\tau) h(\tau) \psi^\dagger(\tau) \\
&= \sum_\sigma \int d\vec{r}\, \psi^\dagger_\sigma(\vec{r}) \Big(-\frac{\hbar^2 \vec{\nabla}^2}{2m} - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r} \Big) \psi_\sigma(\vec{r}) \\
H_{int} &= \frac{1}{2}\int d\tau \int d\tau' \psi^\dagger(\tau)\psi^\dagger(\tau') g(|\tau-\tau'|)\psi(\tau')\psi(\tau) \\
&= \frac{1}{4\pi\epsilon_0}\frac{e^2}{2}\int d\vec{r}\int d\vec{r}'\ \sum_\sigma \sum_{\sigma'} \psi^\dagger_\sigma(\vec{r})\psi^\dagger_{\sigma'}(\vec{r}')\frac{1}{|\vec{r}-\vec{r}'|}\psi_{\sigma'}(\vec{r}')\psi_\sigma(\vec{r}) \\
\int d\tau &= \int d^3r \sum_\sigma
\end{aligned}$$

The second quantized operator:

$$\psi(\tau) = \psi_\sigma(\vec{r}), \quad \tau = (\vec{r}, \sigma)$$

which forms

$$\phi_{\alpha\mu}(\tau) = \phi_\alpha(\vec{r})\chi_\mu(\sigma)$$

,a complete set of normalized spin-orbital function for the bound states in central force field, and which can be further defined as in the followings:

$$\begin{aligned}
\psi(\tau) &= \psi_\sigma(\vec{r}) = \sum_{\alpha,\mu} \phi_\alpha(\vec{r})\chi_\mu(\sigma) c_{\alpha\mu} \\
\{c^\dagger_{\alpha\mu}, c_{\alpha'\mu'}\} &= \delta_{\alpha\alpha'}\delta_{\mu\mu'}, \{c_{\alpha,\mu}, c_{\alpha'\mu'}\} = 0, \\
\alpha : nlm &= \{1\mathrm{s},\ 2\mathrm{s},\ 2\mathrm{p}_{\mathrm{m}=1}\cdots\} \\
\Big(-\frac{\hbar^2\vec{\nabla}^2}{2m} - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r} \Big)\phi_{nlm}(\vec{r}) &= \epsilon_{nlm}\phi_{nlm}(\vec{r}) \\
\vec{\ell}^{\,2}\phi_{nlm}(\vec{r}) &= \hbar^2 l(l+1)\phi_{nlm}(\vec{r}) \\
\ell_z\phi_{nlm}(\vec{r}) &= \hbar m \phi_{nlm}(\vec{r}) \\
\vec{\ell} &= \vec{r}\times\frac{\hbar}{i}\vec{\nabla} \\
s_z\chi_{\uparrow\downarrow}(\sigma) &= \pm\frac{1}{2}\hbar\chi_{\uparrow\downarrow}(\sigma) \\
\vec{s}^{\,2}\chi_{\uparrow\downarrow}(\sigma) &= \frac{1}{2}(\frac{1}{2}+1)\hbar^2\chi_{\uparrow\downarrow}(\sigma)
\end{aligned}$$

Now, by using the fact that both the angular momentum and the spin being conserved, we can express by spectroscopy notation:

$$s(l=0),\ p(l=1),\ d(l=2),\ f(l=3),\ g(l=4),\ h(l=5),\cdots$$

9.3 Periodic Law of the Elements and the Shielding Effect

If the interaction between electrons can be ignored while the electrons move independently then, the ground state of N-electron system can be obtained by packing the particles of up to two for each level of the eigenstate of H_0 in the lower to the higher energy order. Let us summarize the single-particle eigenenergy ϵ_{nlm} of H_0:

- Let n be the principal quantum number, be the orbital angular momentum quantum number, and m be the magnetic angular momentum quantum number.
- We define $n = 1, 2, 3, \cdots$, which can be also expressed as $\ell = 0, 1, 2, \cdots, n$ or $\ell = 0(s)$, $\ell = 1(p)$, $\ell = 2(d)$, and $\ell = 3(f)$.
- The energy degenerates for the magnetic angular momentum quantum number. (Spherical-symmetric potential)

$$\epsilon_{nlm} = \epsilon_{nlm'}$$

- The energy also degenerates for the orbital angular momentum quantum number. (Peculiarity of Coulomb force)

$$\epsilon_{nlm} = \epsilon_{nl'm}$$

- The smaller the principal quantum number n, the lower the energy becomes.

$$\begin{aligned} \epsilon_{nlm} \ < \ & \epsilon_{n'lm}, \quad n < n', \\ & (1s) < (2s) < (3s) < \cdots \\ & (2p) < (3p) < (4p) < \cdots \\ & (3d) < (4d) < \cdots \end{aligned}$$

In considering the interaction among electrons, the center of the nucleus is known to have relatively large electron density, and which gives a stronger shielding against the central force generated by the nucleus thereby, the interaction energy

is considered to be low. There is a greater probability for the existence of interaction at periphery of atomic nucleus when there is smaller angular momentum. Such effects may in fact provide us a clue for solving the degeneration problem of the orbital angular momentum for a pure Coulomb force. Given these facts, it is clear that the ground states of the elements in the small to large electron number order are given by the electron configurations described in the following.

$$
\begin{aligned}
H^1 &\quad (1s)^1 \\
He^2 &\quad (1s)^2 \\
Li^3 &\quad (He)(2s)^1 \\
Be^4 &\quad (He)(2s)^2 \\
B^5 &\quad (He)(2s)^2(2p)^1 \\
C^6 &\quad (He)(2s)^2(2p)^2 \\
N^7 &\quad (He)(2s)^2(2p)^3 \\
O^8 &\quad (He)(2s)^2(2p)^4 \\
F^9 &\quad (He)(2s)^2(2p)^5 \\
Ne^{10} &\quad (He)(2s)^2(2p)^6 \\
Na^{11} &\quad (Ne)(3s) \\
Mg^{12} &\quad (Ne)(3s)^2 \\
Al^{13} &\quad (Ne)(3s)^2(3p)^1 \\
Si^{14} &\quad (Ne)(3s)^2(3p)^2 \\
P^{15} &\quad (Ne)(3s)^2(3p)^3 \\
S^{16} &\quad (Ne)(3s)^2(3p)^4 \\
Cl^{17} &\quad (Ne)(3s)^2(3p)^5 \\
Ar^{18} &\quad (Ne)(3s)^2(3p)^6
\end{aligned}
$$

Up until this point, we all understand the above with considering the Coulomb force. Now, we only consider the Coulomb force to just pack the electron in $3d$; however, now we should further consider the shielding effect we have discussed before, which makes $(4s)$ energetically lower than $3d$:

$$
\begin{aligned}
K^{19} &\quad (Ar)(4s)^1 \\
Ca^{20} &\quad (Ar)(4s)^2
\end{aligned}
$$

Therefore, the electron is filled first in $(4s)$. After for a while, the electrons go into $(3d)$, which are called the transition metals. The electron in such elements found

at the farthest from the nucleus possesses some common properties that $(4s)^2$ has, hence the two shares the similar chemical properties.

$$
\begin{aligned}
Sc^{21} \quad & (Ar)(3d)^1(4s)^2 \\
Ti^{22} \quad & (Ar)(3d)^2(4s)^2 \\
V^{23} \quad & (Ar)(3d)^3(4s)^2 \\
Cr^{24} \quad & (Ar)(3d)^5(4s)^1 \quad (\ exception) \\
Mn^{25} \quad & (Ar)(3d)^5(4s)^2 \\
Fe^{26} \quad & (Ar)(3d)^6(4s)^2 \\
Co^{27} \quad & (Ar)(3d)^7(4s)^2 \\
Ni^{28} \quad & (Ar)(3d)^8(4s)^2 \\
Cu^{29} \quad & (Ar)(3d)^{10}(4s)^1 \quad (\ exception) \\
Zn^{30} \quad & (Ar)(3d)^{10}(4s)^2 \\
\vdots \quad &
\end{aligned}
$$

10 Electron Configurations and Multiplet Structures

10.1 Multiplet Terms and Perturbation Theory

In the previous section, we generalized to understand the effects of many-electron via the shielding effect. Now, we take a look at the Coulomb interaction with a perspective of the perturbation theory. Before we start, it is important to note that the Hamiltonian including the interaction takes the total orbital angular momentum as well as the total spin as the conserved quantity. We will study this in a second quantization form. Generally, in the second quantization, the total orbital angular momentum operator and the spin operator is given as

$$\begin{aligned} \vec{L} &= \int d^3r \sum_{\sigma} \psi^\dagger_\sigma(\vec{r})\ \vec{\ell}(\vec{r})\psi_\sigma(\vec{r}) \\ \vec{S} &= \int d^3r \sum_{\sigma,\sigma'} \psi^\dagger_\sigma(\vec{r})\vec{s}_{\sigma\sigma'}\psi_{\sigma'}(\vec{r}) \end{aligned}$$

More precisely, the operators above can be expressed by using a specific representation:

$$\begin{aligned} \vec{\ell}(\vec{r}) &= -i\hbar\vec{r}\times\vec{\nabla} \\ \vec{s} &= \frac{\hbar}{2}[\vec{\sigma}]_{\sigma\sigma'} \end{aligned}$$

Here $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ can be understood as the matrix representations called Pauli matrices in the following: [184]

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix},\quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix},\quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

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$$\sigma_\alpha^2 = I,\ \sigma_\alpha\sigma_\beta = -\sigma_\beta\sigma_\alpha\ (\alpha\neq\beta),\ \sigma_x\sigma_y = i\sigma_z, \cdots$$

The above satisfies the commutation relations for the angular momentum: [185]

$$
\begin{aligned}
[L_i, L_j] &= i\hbar\epsilon_{ijk}L_k \\
[S_i, S_j] &= i\hbar\epsilon_{ijk}S_k
\end{aligned}
$$

[185] For example,

$$
\begin{aligned}
L_xL_y &= \int d^3r \int d^3r' \sum_\sigma \sum_\tau \psi^\dagger_\sigma(\vec{r})(-i\hbar\vec{r}\times\vec{\nabla}_r)_x\psi_\sigma(\vec{r})\psi^\dagger_\tau(\vec{r}')_y(-i\hbar\vec{r}'\times\vec{\nabla}_{r'})\psi_\tau(\vec{r}') \\
&= \int d^3r \int d^3r' \sum_\sigma \sum_\tau \psi^\dagger_\sigma(\vec{r})(-i\hbar\vec{r}\times\vec{\nabla}_r)_x\{-\psi^\dagger_\tau(\vec{r}')\psi_\sigma(\vec{r}) + \delta(\vec{r}-\vec{r}')\delta_{\sigma\tau}\}(-i\hbar\vec{r}'\times\vec{\nabla}_{r'})_y\psi_\tau(\vec{r}') \\
&= \int d^3r \int d^3r' \sum_\sigma \sum_\tau \psi^\dagger_\sigma(\vec{r})\psi^\dagger_\tau(\vec{r}')(-i\hbar\vec{r}\times\vec{\nabla}_r)_x(-i\hbar\vec{r}'\times\vec{\nabla}_{r'})_y\psi_\tau(\vec{r}')\psi_\sigma(\vec{r}) \\
&\quad + \int d^3r \sum_\sigma \psi^\dagger_\sigma(\vec{r})(-i\hbar\vec{r}\times\vec{\nabla}_r)_x(-i\hbar\vec{r}'\times\vec{\nabla}_r)_y\psi_\sigma(\vec{r})
\end{aligned}
$$

Thus,

$$
\begin{aligned}
[L_x, L_y] &= \int d^3r \sum_\sigma \psi^\dagger_\sigma(\vec{r})[(-i\hbar\vec{r}\times\vec{\nabla}_r)_x, (-i\hbar\vec{r}'\times\vec{\nabla}_r)_y]\psi_\sigma(\vec{r}) \\
&= i\hbar\int d^3r \sum_\sigma \psi^\dagger_\sigma(\vec{r})(-i\hbar\vec{r}\times\vec{\nabla}_r)_z\psi_\sigma(\vec{r}) \\
&= i\hbar L_z
\end{aligned}
$$

To give an example for the spin operator:

$$
\begin{aligned}
S_xS_y &= \int d^3r \int d^3r' \sum_{\sigma\sigma'} \sum_{\tau\tau'} \psi^\dagger_\sigma(\vec{r})\frac{\hbar}{2}[\sigma^x]_{\sigma\sigma'}\psi_\sigma(\vec{r})\psi^\dagger_\tau(\vec{r}')_y\frac{\hbar}{2}[\sigma^y]_{\tau\tau'}\psi_\tau(\vec{r}') \\
&= \frac{\hbar^2}{4}\int d^3r \int d^3r' \sum_{\sigma\sigma'} \sum_{\tau\tau'} \psi^\dagger_\sigma(\vec{r})\frac{\hbar}{2}[\sigma^x]_{\sigma\sigma'}\{-\psi^\dagger_\tau(\vec{r}')\psi_{\sigma'}(\vec{r}) + \delta(\vec{r}-\vec{r}')\delta_{\sigma'\tau}\}[\sigma^y]_{\tau\tau'}\psi_{\tau'}(\vec{r}') \\
&= \frac{\hbar^2}{4}\int d^3r \int d^3r' \sum_{\sigma\sigma'} \sum_{\tau\tau'} \psi^\dagger_\sigma(\vec{r})\psi^\dagger_\tau(\vec{r}')[\sigma^x]_{\sigma\sigma'}[\sigma^y]_{\tau\tau'}\psi_{\tau'}(\vec{r}')\psi_{\sigma'}(\vec{r}) \\
&+ \frac{\hbar^2}{4}\int d^3r \sum_{\sigma\tau'} \psi^\dagger_\sigma(\vec{r})[\sigma^x\sigma^y]_{\sigma\tau'}\psi_{\tau'}(\vec{r})
\end{aligned}
$$

Thus,

$$
\begin{aligned}
[S_x, S_y] &= i\hbar\int d^3r \sum_{\sigma\sigma'} \psi^\dagger_\sigma(\vec{r})\frac{\hbar}{2}[\sigma^z]_{\sigma\sigma'}\psi_{\sigma'}(\vec{r}) \\
&= i\hbar S_z
\end{aligned}
$$

$\vec{L}$ and $\vec{S}$ commute with Hamiltonians that include interaction. [186] [187] [188] [189] [190]

[186]For

$$[H_0, \vec{L}] = 0$$

, we understand from the following that it obeys:

$$\begin{aligned}
H_0 L_\alpha &= -(\frac{\hbar^2}{2m}) \int d^3r \int d^3r' \sum_\sigma \sum_{\sigma'} \psi^\dagger_\sigma(\vec{r}) \vec{\nabla}_r{}^2 \psi_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}') \ell^{r'}_\alpha \psi_{\sigma'}(\vec{r}') \\
&= -(\frac{\hbar^2}{2m}) \int d^3r \int d^3r' \sum_\sigma \sum_{\sigma'} \psi^\dagger_\sigma(\vec{r}) \vec{\nabla}_r{}^2 (-\psi^\dagger_{\sigma'}(\vec{r}') \psi_\sigma(\vec{r}) + \delta(\vec{r}\vec{r}')\delta_{\sigma\sigma'}) \ell^{r'}_\alpha \psi_{\sigma'}(\vec{r}') \\
&= -(\frac{\hbar^2}{2m}) \int d^3r \int d^3r' \sum_\sigma \sum_{\sigma'} \psi^\dagger_{\sigma'}(\vec{r}') \psi^\dagger_\sigma(\vec{r}) \vec{\nabla}_r{}^2 \psi_\sigma(\vec{r}) \ell^{r'}_\alpha \psi_{\sigma'}(\vec{r}') \\
&\quad -(\frac{\hbar^2}{2m}) \int d^3r \sum_\sigma \psi^\dagger_{\sigma'}(\vec{r}) \vec{\nabla}_r{}^2 \left[\ell^r_\alpha \psi_{\sigma'}(\vec{r})\right] \\
\\
L_\alpha H_0 &= -(\frac{\hbar^2}{2m}) \int d^3r \int d^3r' \sum_\sigma \sum_{\sigma'} \psi^\dagger_{\sigma'}(\vec{r}') \ell^{r'}_\alpha \psi_{\sigma'}(\vec{r}') \psi^\dagger_\sigma(\vec{r}) \vec{\nabla}_r{}^2 \psi_\sigma(\vec{r}) \\
&= -(\frac{\hbar^2}{2m}) \int d^3r \int d^3r' \sum_\sigma \sum_{\sigma'} \psi^\dagger_{\sigma'}(\vec{r}') \ell^{r'}_\alpha (-\psi^\dagger_\sigma(\vec{r}) \psi_{\sigma'}(\vec{r}') + \delta(\vec{r}\vec{r}')\delta_{\sigma\sigma'}) \vec{\nabla}_r{}^2 \psi_\sigma(\vec{r}) \\
&= -(\frac{\hbar^2}{2m}) \int d^3r \int d^3r' \sum_\sigma \sum_{\sigma'} (-) \psi^\dagger_{\sigma'}(\vec{r}') \psi^\dagger_\sigma(\vec{r}) \ell^{r'}_\alpha \psi_{\sigma'}(\vec{r}') \vec{\nabla}_r{}^2 \psi_\sigma(\vec{r}) \\
&\quad -(\frac{\hbar^2}{2m}) \int d^3r' \sum_{\sigma'} \psi^\dagger_{\sigma'}(\vec{r}') \ell^{r'}_\alpha \vec{\nabla}_{r'}{}^2 \psi_\sigma(\vec{r}')
\end{aligned}$$

[187]Next, we consider the interaction term. First we have

$$\begin{aligned}
(\frac{e^2}{2})^{-1} H_{int} L_\alpha &= \int d^3r d^3r' d^3r'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}') g(\vec{r}-\vec{r}') \psi_{\sigma'}(\vec{r}') \psi_\sigma(\vec{r}) \psi^\dagger_{\sigma''}(\vec{r}'') \ell^{r''}_\alpha \psi_{\sigma''}(\vec{r}'') \\
&= \int d^3r d^3r' d^3r'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}') g(\vec{r}-\vec{r}') \psi_{\sigma'}(\vec{r}') \Big(-\psi^\dagger_{\sigma''}(\vec{r}'') \psi_\sigma(\vec{r}) + \delta(\vec{r}-\vec{r}'')\delta_{\sigma\sigma''} \Big) \ell^{r''}_\alpha \psi_{\sigma''}(\vec{r}'') \\
&= \int d^3r d^3r' d^3r'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}') g(\vec{r}-\vec{r}') (-) \psi_{\sigma'}(\vec{r}') \psi^\dagger_{\sigma''}(\vec{r}'') \psi_\sigma(\vec{r}) \ell^{r''}_\alpha \psi_{\sigma''}(\vec{r}'') \\
&\quad + \int d^3r d^3r' \sum_\sigma \sum_{\sigma'} \psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}') g(\vec{r}-\vec{r}') \psi_{\sigma'}(\vec{r}') \ell^r_\alpha \psi_\sigma(\vec{r}) \\
&= \int d^3r d^3r' d^3r'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}') g(\vec{r}-\vec{r}') \Big(\psi^\dagger_{\sigma''}(\vec{r}'') \psi_{\sigma'}(\vec{r}') - \delta(\vec{r}'-\vec{r}'')\delta_{\sigma'\sigma''} \Big) \psi_\sigma(\vec{r}) \ell^{r''}_\alpha \psi_{\sigma''}(\vec{r}'') \\
&\quad + \int d^3r d^3r' \sum_\sigma \sum_{\sigma'} \psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}') g(\vec{r}-\vec{r}') \psi_{\sigma'}(\vec{r}') \ell^r_\alpha \psi_\sigma(\vec{r}) \\
&= \int d^3r d^3r' d^3r'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec{r}'') \psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}') g(\vec{r}-\vec{r}') \psi_{\sigma'}(\vec{r}') \psi_\sigma(\vec{r}) \ell^{r''}_\alpha \psi_{\sigma''}(\vec{r}'') \\
&\quad - \int d^3r d^3r' \sum_{\sigma\sigma'} \psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}') g(\vec{r}-\vec{r}') \psi_\sigma(\vec{r}) \ell^{r'}_\alpha \psi_{\sigma'}(\vec{r}') \\
&\quad + \int d^3r d^3r' \sum_\sigma \sum_{\sigma'} \psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}') g(\vec{r}-\vec{r}') \psi_{\sigma'}(\vec{r}') \ell^r_\alpha \psi_\sigma(\vec{r})
\end{aligned}$$

[188]While we can write

$$
\begin{aligned}
(\frac{e^2}{2})^{-1}L_\alpha H_{int} &= \int d^3r\, d^3r'd^3r'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec{r}'')\ell^{r''}_\alpha \psi_{\sigma''}(\vec{r}'')\psi^\dagger_\sigma(\vec{r})\psi^\dagger_{\sigma'}(\vec{r}')g(\vec{r}-\vec{r}')\psi_{\sigma'}(\vec{r}')\psi_\sigma(\vec{r}) \\
&= \int d^3r\, d^3r'd^3r'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec{r}'')\ell^{r''}_\alpha \Big(-\psi^\dagger_\sigma(\vec{r})\psi_{\sigma''}(\vec{r}'') + \delta(\vec{r}-\vec{r}'')\delta_{\sigma\sigma''}\Big)\psi^\dagger_{\sigma'}(\vec{r}')g(\vec{r}-\vec{r}')\psi_{\sigma'}(\vec{r}')\psi_\sigma \\
&= \int d^3r\, d^3r'd^3r'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec{r}'')(-)\psi^\dagger_\sigma(\vec{r})\ell^{r''}_\alpha \psi_{\sigma''}(\vec{r}'')\psi^\dagger_{\sigma'}(\vec{r}')g(\vec{r}-\vec{r}')\psi_{\sigma'}(\vec{r}')\psi_\sigma(\vec{r}) \\
&\quad + \int d^3r'd^3r'' \sum_{\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec{r}'')\ell^{r''}_\alpha \Big(\psi^\dagger_{\sigma'}(\vec{r}')g(\vec{r}''-\vec{r}')\psi_{\sigma'}(\vec{r}')\psi_{\sigma''}(\vec{r}'')\Big) \\
&= \int d^3r\, d^3r'd^3r'' \sum_{\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec{r}'')\psi^\dagger_\sigma(\vec{r})\ell^{r''}_\alpha \Big(\psi^\dagger_{\sigma'}(\vec{r}')\psi_{\sigma''}(\vec{r}'') - \delta(\vec{r}'-\vec{r}'')\delta_{\sigma'\sigma''}\Big)g(\vec{r}-\vec{r}')\psi_{\sigma'}(\vec{r}')\psi_\sigma(\vec{r} \\
&\quad + \int d^3r'd^3r'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec{r}'')\ell^{r''}_\alpha \Big(\psi^\dagger_{\sigma'}(\vec{r}')g(\vec{r}''-\vec{r}')\psi_{\sigma'}(\vec{r}')\psi_{\sigma''}(\vec{r}'')\Big) \\
&= \int d^3r\, d^3r'd^3r'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec{r}'')\psi^\dagger_\sigma(\vec{r})\psi^\dagger_{\sigma'}(\vec{r}')\ell^{r''}_\alpha \psi_{\sigma''}(\vec{r}'')g(\vec{r}-\vec{r}')\psi_{\sigma'}(\vec{r}')\psi_\sigma(\vec{r}) \\
&\quad - \int d^3r\, d^3r'' \sum_{\sigma\sigma''} \psi^\dagger_{\sigma''}(\vec{r}'')\psi^\dagger_\sigma(\vec{r})\ell^{r''}_\alpha \Big(g(\vec{r}-\vec{r}'')\psi_{\sigma'}(\vec{r}'')\psi_\sigma(\vec{r})\Big) \\
&\quad + \int d^3r'd^3r'' \sum_{\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec{r}'')\ell^{r''}_\alpha \Big(\psi^\dagger_{\sigma'}(\vec{r}')g(\vec{r}''-\vec{r}')\psi_{\sigma'}(\vec{r}')\psi_{\sigma''}(\vec{r}'')\Big) \\
&= \int d^3r\, d^3r'd^3r'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec{r}'')\psi^\dagger_\sigma(\vec{r})\psi^\dagger_{\sigma'}(\vec{r}')g(\vec{r}-\vec{r}')\psi_{\sigma'}(\vec{r}')\psi_\sigma(\vec{r})\ell^{r''}_\alpha \psi_{\sigma''}(\vec{r}'') \\
&\quad + \int d^3r\, d^3r'' \sum_{\sigma\sigma''} \psi^\dagger_{\sigma''}(\vec{r}'')\psi^\dagger_\sigma(\vec{r})g(\vec{r}-\vec{r}'')\psi_\sigma(\vec{r})\ell^{r''}_\alpha \psi_{\sigma'}(\vec{r}'') \\
&\qquad + \int d^3r\, d^3r'' \sum_{\sigma\sigma''} \psi^\dagger_{\sigma''}(\vec{r}'')\psi^\dagger_\sigma(\vec{r})\Big(\ell^{r''}_\alpha g(\vec{r}-\vec{r}'')\Big)\psi_\sigma(\vec{r})\psi_{\sigma'}(\vec{r}'') \\
&\quad + \int d^3r'd^3r'' \sum_{\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec{r}'')\psi^\dagger_{\sigma'}(\vec{r}')g(\vec{r}''-\vec{r}')\psi_{\sigma'}(\vec{r}')\ell^{r''}_\alpha \psi_{\sigma''}(\vec{r}'') \\
&\qquad + \int d^3r'd^3r'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec{r}'')\psi^\dagger_{\sigma'}(\vec{r}')\Big(\ell^{r''}_\alpha g(\vec{r}''-\vec{r}')\Big)\psi_{\sigma'}(\vec{r}')\psi_{\sigma''}(\vec{r}'')
\end{aligned}
$$

Therefore,

$$
\begin{aligned}
(\frac{e^2}{2})^{-1}[H_{int}, L_\alpha] &= \int d^3r\, d^3r'' \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma''}(\vec{r}'')\psi^\dagger_{\sigma'}(\vec{r}')\Big(\Big(\ell^{r'}_\alpha + \ell^{r''}_\alpha\Big)g(\vec{r}''-\vec{r}')\Big)\psi_{\sigma'}(\vec{r}')\psi_{\sigma''}(\vec{r}'') \\
&= 0
\end{aligned}
$$

We used the fact that the angular momentum is the first order differential operator. Physically, the interaction is the internal force of the two body force such that the angular momentum is conserved.

[189] As for the spin we can write

$$
\begin{aligned}
H_0 S_\alpha &= \int d^3r\, d^3r'\, \sum_{\sigma\sigma'\sigma''} \psi^\dagger_\sigma(\vec{r}) h(r) \psi_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}\,') [s_\alpha]_{\sigma'\sigma''} \psi_{\sigma''}(\vec{r}\,') \\
&= \int d^3r\, d^3r'\, \sum_{\sigma\sigma'\sigma''} \psi^\dagger_\sigma(\vec{r}) h(r) \Big(-\psi^\dagger_{\sigma'}(\vec{r}\,') \psi_\sigma(\vec{r}) + \delta(\vec{r}-\vec{r}\,')\delta_{\sigma\sigma'} \Big) [s_\alpha]_{\sigma'\sigma''} \psi_{\sigma''}(\vec{r}\,') \\
&= \int d^3r\, d^3r'\, \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma'}(\vec{r}\,') \psi^\dagger_\sigma(\vec{r}) h(r) [s_\alpha]_{\sigma'\sigma''} \psi_\sigma(\vec{r}) \psi_{\sigma''}(\vec{r}\,') \\
&\quad + \int d^3r \sum_{\sigma\sigma''} \psi^\dagger_\sigma(\vec{r}) h(r) [s_\alpha]_{\sigma\sigma''} \psi_{\sigma''}(\vec{r}) \\
S_\alpha H_0 &= \int d^3r\, d^3r'\, \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma'}(\vec{r}\,') [s_\alpha]_{\sigma'\sigma''} \psi_{\sigma''}(\vec{r}\,') \psi^\dagger_\sigma(\vec{r}) h(r) \psi_\sigma(\vec{r}) \\
&= \int d^3r\, d^3r'\, \sum_{\sigma\sigma'\sigma''} \psi^\dagger_{\sigma'}(\vec{r}\,') [s_\alpha]_{\sigma'\sigma''} \Big(-\psi^\dagger_\sigma(\vec{r}) \psi_{\sigma''}(\vec{r}\,') + \delta(\vec{r}-\vec{r}\,')\delta_{\sigma\sigma''} \Big) h(r) \psi_\sigma(\vec{r}) \\
&= \int d^3r\, d^3r'\, \sum_{\sigma\sigma'\sigma''} \psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}\,') [s_\alpha]_{\sigma'\sigma''} h(r) \psi_{\sigma''}(\vec{r}\,') \psi_\sigma(\vec{r}) \\
&\quad + \int d^3r\, d^3r' \sum_{\sigma\sigma'} \psi^\dagger_{\sigma'}(\vec{r}) [s_\alpha]_{\sigma'\sigma} h(r) \psi_\sigma(\vec{r})
\end{aligned}
$$

Thus,

$$[S_\alpha H_0] = 0$$

[190]

$$
\begin{aligned}
[H_{int}, S_\alpha] &= \frac{1}{2} \int d^3r\, d^3r'\, g(|\vec{r}-\vec{r}\,'|) \int d^3r'' \sum_{\sigma\sigma'\sigma''\sigma'''} [\psi^\dagger_\sigma(\vec{r}) \psi^\dagger_{\sigma'}(\vec{r}\,') \psi_{\sigma'}(\vec{r}\,') \psi_\sigma(\vec{r}), \psi^\dagger_{\sigma''}(\vec{r}\,'') [s_\alpha]_{\sigma''\sigma'''} \psi_{\sigma'''}(\vec{r}\,'')] \\
&= \frac{1}{2} \int d(1) \int d(2) g(1,2) \int d(3) \int d(4) [\psi^\dagger(1)\psi^\dagger(2)\psi(2)\psi(1), \psi^\dagger(3)[s]_{34}\psi(4)]
\end{aligned}
$$

Here we have

$$
\begin{aligned}
[\psi^\dagger(1)\psi^\dagger(2)\psi(2)\psi(1), \psi^\dagger(3)[s]_{34}\psi(4)] &= \psi^\dagger(1)\psi^\dagger(2)[\psi(2)\psi(1), \psi^\dagger(3)[s]_{34}\psi(4)] \\
&\quad + [\psi^\dagger(1)\psi^\dagger(2), \psi^\dagger(3)[s]_{34}\psi(4)]\psi(2)\psi(1) \\
&= \psi^\dagger(1)\psi^\dagger(2)[\psi(2)\psi(1), \psi^\dagger(3)][s]_{34}\psi(4) \\
&\quad + \psi^\dagger(3)[s]_{34}[\psi^\dagger(1)\psi^\dagger(2), \psi(4)]\psi(2)\psi(1)
\end{aligned}
$$

$$
\begin{aligned}
[\psi(2)\psi(1),\psi^\dagger(3)] &= \psi(2)\psi(1)\psi^\dagger(3) - \psi^\dagger(3)\psi(2)\psi(1)\\
&= \psi(2)(-\psi^\dagger(3)\psi(1) + \delta(31)) - \psi^\dagger(3)\psi(2)\psi(1)\\
&= \delta(31)\psi(2) - \delta(32)\psi(1)\\
[\psi^\dagger(1)\psi^\dagger(2),\psi(3)] &= -\delta(31)\psi^\dagger(2) + \delta(32)\psi^\dagger(1)\\
[\psi^\dagger(1)\psi^\dagger(2),\psi(4)] &= -\delta(41)\psi^\dagger(2) + \delta(42)\psi^\dagger(1)
\end{aligned}
$$

Thus,

$$
\begin{aligned}
[H_{int},S_\alpha] &= \frac{1}{2}\int d(1)\int d(2)g(1,2)\int d(4)\psi^\dagger(1)\psi^\dagger(2)(\psi(2)[s]_{14}\psi(4) - \psi(1)[s]_{24}\psi(4))\\
&+ \frac{1}{2}\int d(1)\int d(2)g(1,2)\int d(3)(-\psi^\dagger(3)[s]_{31}\psi^\dagger(2)\psi(2)\psi(1) + \psi^\dagger(3)[s]_{32}\psi^\dagger(1)\psi(2)\psi(1))\\
&= \frac{1}{2}\int d(1)\int d(2)g(1,2)\int d(3)\psi^\dagger(1)\psi^\dagger(2)(\psi(2)[s]_{13}\psi(3) - \psi(1)[s]_{23}\psi(3))\\
&+ \frac{1}{2}\int d(1)\int d(2)g(1,2)\int d(3)(-\psi^\dagger(3)[s]_{31}\psi^\dagger(2)\psi(2)\psi(1) + \psi^\dagger(3)[s]_{32}\psi^\dagger(1)\psi(2)\psi(1))\\
&= \frac{1}{2}\int d(1)\int d(2)g(1,2)\int d(3)\\
&\times \{\psi^\dagger(2)\psi(2)\psi^\dagger(1)[s]_{13}\psi(3) + \psi^\dagger(1)\psi(1)\psi^\dagger(2)[s]_{23}\psi(3)\\
&- \psi^\dagger(2)\psi(2)\psi^\dagger(3)[s]_{31}\psi(1) - \psi^\dagger(1)\psi(1)\psi^\dagger(3)[s]_{32}\psi(2)\} = 0
\end{aligned}
$$

In this way, we may have

$$
\begin{aligned}
[H_{int}, L_\alpha] =& \frac{1}{2}\int d(1)d(2)d(3)[\psi^\dagger(1)\psi^\dagger(2)g(12)\psi(2)\psi(1), \psi^\dagger(3)\ell_\alpha(3)\psi(3)] \\
=& \frac{1}{2}\int d(1)d(2)d(3) \\
& \times \{\psi^\dagger(3)\ell_\alpha(3)[\psi^\dagger(1)\psi^\dagger(2)g(12)\psi(2)\psi(1), \psi(3)] + [\psi^\dagger(1)\psi^\dagger(2)g(12)\psi(2)\psi(1), \psi^\dagger(3)]\ell_\alpha(3)\psi(3)\} \\
=& \frac{1}{2}\int d(1)d(2)d(3) \\
& \times \{\psi^\dagger(3)\ell_\alpha(3)[\psi^\dagger(1)\psi^\dagger(2), \psi(3)]g(12)\psi(2)\psi(1) + \psi^\dagger(1)\psi^\dagger(2)g(12)[\psi(2)\psi(1), \psi^\dagger(3)]\ell_\alpha(3)\psi(3)\} \\
=& \frac{1}{2}\int d(1)d(2)d(3) \\
& \times \{\psi^\dagger(3)\ell_\alpha(3)(-\delta(31)\psi^\dagger(2) + \delta(32)\psi^\dagger(1))g(12)\psi(2)\psi(1) \\
& \quad + \psi^\dagger(1)\psi^\dagger(2)g(12)(\delta(31)\psi(2) - \delta(32)\psi(1))\ell_\alpha(3)\psi(3)\} \\
=& \frac{1}{2}\int d(1)d(2) \\
& \times \{\Big(- \psi^\dagger(1)\ell_\alpha(1)\psi^\dagger(2) + \psi^\dagger(2)\ell_\alpha(2)\psi^\dagger(1)\Big)g(12)\psi(2)\psi(1) \\
& \quad + \psi^\dagger(1)\psi^\dagger(2)g(12)\Big(\psi(2)\ell_\alpha(1)\psi(1) - \psi(1)\ell_\alpha(2)\psi(2)\Big)\} \\
=& \frac{1}{2}\int d(1)d(2) \\
& \times \{-\psi^\dagger(1)\psi^\dagger(2)\ell_\alpha(1)g(12)\psi(2)\psi(1) - \psi^\dagger(1)\psi^\dagger(2)\ell_\alpha(2)g(12)\psi(2)\psi(1) \\
& \quad + \psi^\dagger(1)\psi^\dagger(2)g(12)\ell_\alpha(1)\psi(2)\psi(1) + \psi^\dagger(1)\psi^\dagger(2)g(12)\ell_\alpha(2)\psi(2)\psi(1)\} \\
=& -\frac{1}{2}\int d(1)d(2)\{\psi^\dagger(1)\psi^\dagger(2)\Big(\ell_\alpha(1)g(12)\Big)\psi(2)\psi(1) + \psi^\dagger(1)\psi^\dagger(2)\Big(\ell_\alpha(2)g(12)\Big)\psi(2)\psi(1)\} \\
=& -\frac{1}{2}\int d(1)d(2)\{\psi^\dagger(1)\psi^\dagger(2)\Big((\ell_\alpha(1) + \ell_\alpha(2))g(12)\Big)\psi(2)\psi(1)\} = 0
\end{aligned}
$$

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$$[H,\vec{L}]=0,\quad [H,\vec{S}]=0,\quad [\vec{L},\vec{S}]=0$$

Each energy eigenstate can be given as a set of simultaneous eigenstates of $\vec{S}^2$, S_z, $\vec{L}^2$, and $\vec{L}_z$. Among which, the degeneration of energy can be observed for those having different $S_z=M_S$ and $L_z=M_L$. While among the levels with different $\vec{S}^2=S(S+1)$ and $\vec{L}^2=L(L+1)$, there is no matrix element for the Hamiltonian thus, the energy can be considered separately. [192]

To be more specific, when electric configuration $\{(n\ell)^{n_\ell}\}$ $(1\le n_\ell\le 2(2\ell+1)$ is

[191]Let us have

$$\begin{aligned}
\mathcal{A}&=\int d(1)\psi^\dagger(1)A(1)\psi(1),\quad \mathcal{B}=\int d(2)\psi^\dagger(2)B(2)\psi(2)\quad then,\\
[\mathcal{A},\mathcal{B}]&=\int d(1)\int d(2)[\psi^\dagger(1)A(1)\psi(1),\psi^\dagger(2)B(2)\psi(2)]\\
&=\int d(1)\int d(2)\Big(\psi^\dagger(1)A(1)[\psi(1),\psi^\dagger(2)B(2)\psi(2)]+[\psi^\dagger(1)A(1),\psi^\dagger(2)B(2)\psi(2)]\psi(1)\\
\psi^\dagger(1)A(1)[\psi(1),\psi^\dagger(2)B(2)\psi(2)]&=\psi^\dagger(1)A(1)\{\psi(1)\psi^\dagger(2)B(2)\psi(2)-\psi^\dagger(2)B(2)\psi(2)\psi(1)\}\\
&=\psi^\dagger(1)A(1)\{\psi(1)\psi^\dagger(2)B(2)\psi(2)+\psi^\dagger(2)B(2)\psi(1)\psi(2)\}\\
&=\psi^\dagger(1)A(1)\{\psi(1)\psi^\dagger(2)B(2)\psi(2)+(-\psi(1)\psi^\dagger(2)+\delta(12))B(2)\psi(2)\}\\
&=\psi^\dagger(1)A(1)B(2)\psi(2)\delta(12)\\
[\psi^\dagger(1)A(1),\psi^\dagger(2)B(2)\psi(2)]\psi(1)&=\{\psi^\dagger(1)A(1)\psi^\dagger(2)B(2)\psi(2)-\psi^\dagger(2)B(2)\psi(2)\psi^\dagger(1)A(1)\}\psi(1)\\
&=\{\psi^\dagger(1)A(1)\psi^\dagger(2)B(2)\psi(2)-\psi^\dagger(2)B(2)(-\psi^\dagger(1)\psi(2)+\delta(12))A(1)\}\psi(1)\\
&=\psi^\dagger(1)\psi^\dagger(2)A(1)B(2)\psi(2)\psi(1)-\psi^\dagger(2)\psi^\dagger(1)B(2)A(1)\psi(1)\psi(2)-\psi^\dagger(2)B(2)A(1)\psi(\\
[\mathcal{A},\mathcal{B}]&=\int d(1)\psi^\dagger(1)[A,B]\psi(1)
\end{aligned}$$

[192]When the Hermitian operator $\mathcal{O}$ is commutable with the conserved quantity; i.e., commutable with Hamiltonian, the matrix element of the Hamiltonian becomes zero among the states with different eigenvalues of $\mathcal{O}$:

$$\begin{aligned}
[H,\mathcal{O}] &= H\mathcal{O}-\mathcal{O}H=0\\
\mathcal{O}|1\rangle &= o_1|1\rangle\\
\mathcal{O}|2\rangle &= o_2|2\rangle\\
o_1 &\neq o_2
\end{aligned}$$

Here,

$$\begin{aligned}
0 &= \langle o_1[H,\mathcal{O}]|o_2\rangle\\
&= \langle o_1 H\mathcal{O}-\mathcal{O}H|o_2\rangle\\
&= (o_1-o_2)\langle o_1|H|o_2\rangle
\end{aligned}$$

Given $o_1\neq o_2$, we can write

$$\langle o_1|H|o_2\rangle=0$$

given, the interaction terms are not made merely by the summation of the spins such that each spin can possibly hold different energies. Under no interaction, the levels which have been degenerating may begin splitting at each value of the total spin. These are called multiplet terms. We will investigate the multiplet with a few examples after some preparation steps in the followings.

10.2 Angular Momentum Operator, Spin-orbital Function, and Second Quantization

Let us first make some preparation before we demonstrate a concrete example of calculations. We use a particular spin-orbital function to rewrite the angular momentum operator and the spin operator. [193]

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$$
\begin{aligned}
\ell_\pm \phi_{\ell m} &= \hbar\sqrt{(\ell \mp m)(\ell \pm m + 1)}\phi_{\ell m\pm 1} \\
\ell_z \phi_{\ell m} &= \hbar m \phi_{\ell m} \\
s_+|\downarrow\rangle &= \hbar|\uparrow\rangle \\
s_-|\uparrow\rangle &= \hbar|\downarrow\rangle \\
s_z|\uparrow\rangle &= \frac{1}{2}\hbar|\uparrow\rangle \\
s_z|\downarrow\rangle &= -\frac{1}{2}\hbar|\downarrow\rangle
\end{aligned}
$$

$$
\begin{aligned}
L_z &= \int d^3r \sum_\sigma \psi_\sigma(\vec{r})\ell_z\psi_\sigma(\vec{r}) \\
&= \sum_{\mu\mu'} \chi^*_\mu(\sigma)\chi_{\mu'}(\sigma)\int d^3r \sum_{jj'} \phi^*_j(\vec{r})\ell_z\phi_{j'}(\vec{r})c^\dagger_{j\mu}c_{j'\mu'} \\
&= \sum_{nlm} \hbar m c^\dagger_{nlm\mu}c_{nlm\mu}
\end{aligned}
$$

and so on.

$$
\begin{aligned}
L_z &= \sum_{nlm\mu} \hbar m c^\dagger_{nlm\mu} c_{nlm\mu} \\
L_\pm &= L_x \pm i L_y \\
&= \sum_{nlm\mu} \hbar \sqrt{(l \mp m)(l \pm m + 1)} c^\dagger_{nlm\pm 1\mu} c_{nlm\mu} \\
S_z &= \sum_{nlm} \frac{1}{2} \hbar (c^\dagger_{nlm\uparrow} c_{nlm\uparrow} - c^\dagger_{nlm\downarrow} c_{nlm\downarrow}) \\
S_+ &= \sum_{nlm} \hbar c^\dagger_{nlm\uparrow} c_{nlm\downarrow} \\
S_- &= \sum_{nlm} \hbar c^\dagger_{nlm\downarrow} c_{nlm\uparrow}
\end{aligned}
$$

The operator is expressed as

$$
\psi_\sigma(\vec{r}) = \sum_{\alpha\mu} \phi_\alpha(\vec{r}) \chi_\mu(\sigma) c_{\alpha,\mu}, \quad \alpha = (nlm)
$$

While one body term of the Hamiltonian can be written as

$$
H_0 = \sum_{nlm,\mu} \epsilon_{nlm} c^\dagger_{nlm,\mu} c_{nlm,\mu}
$$

The interaction term can be written as [194]

$$H_{int} = \sum_{n_1,l_1;n_2,l_2;n_3,l_3;n_4,l_4} I(n_1,l_1;n_2,l_2;n_3,l_3;n_4,l_4) \sum_{\ell,m} \sum$$

$$\begin{array}{ll} m_1,m_2,m_3,m_4 & \\ m_1+m=m_4 & \sum_{\mu_1,\mu_2} c^\ell(l_1m_1,l_4m_4)c^\ell(l_2m_2,l_3m_3) \\ m_3+m=m_2 & \\ & \times c^\dagger_{\alpha_1,\mu_1} c^\dagger_{\alpha_2,\mu_2} c_{\alpha_3,\mu_2} c_{\alpha_4,\mu_1} \end{array}$$

$$\mathrm{c}^\ell(lm,l'm') = \sqrt{\tfrac{4\pi}{2\ell+1}} \int d\Omega\, Y^*_{lm}(\Omega) Y_{\ell,m-m'}(\Omega) Y_{l,m,}(\Omega) : real$$

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$$\begin{aligned}
H_{int} &= \sum_{\sigma\sigma'} \int d\vec{r}\, d\vec{r}\,'\, \psi_\sigma(\vec{r})^\dagger \psi_{\sigma'}(\vec{r}\,')^\dagger \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}\,' - \vec{r}|} \psi_{\sigma'}(\vec{r}\,') \psi_\sigma(\vec{r}) \\
&= \sum_{\sigma\sigma'} \int d\vec{r}\, d\vec{r}\,' \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}\,' - \vec{r}|} \sum_{\alpha_1,\alpha_2,\alpha_3,\alpha_4} \phi^*_{\alpha_1}(\vec{r}) \phi^*_{\alpha_2}(\vec{r}\,') \phi_{\alpha_3}(\vec{r}\,') \phi_{\alpha_4}(\vec{r}) \\
&\qquad \times \sum_{\mu_1,\mu_2,\mu_3,\mu_4} \chi^*_{\mu_1}(\sigma) \chi^*_{\mu_2}(\sigma') \chi_{\mu_3}(\sigma') \chi_{\mu_4}(\sigma) c^\dagger_{\alpha_1,\mu_1} c^\dagger_{\alpha_2,\mu_2} c_{\alpha_3,\mu_3} c_{\alpha_4,\mu_4} \\
&= \int d\vec{r}\, d\vec{r}\,' \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}\,' - \vec{r}|} \sum_{\alpha_1,\alpha_2,\alpha_3,\alpha_4} \phi^*_{\alpha_1}(\vec{r}) \phi^*_{\alpha_2}(\vec{r}\,') \phi_{\alpha_3}(\vec{r}\,') \phi_{\alpha_4}(\vec{r}) \sum_{\mu_1,\mu_2} c^\dagger_{\alpha_1,\mu_1} c^\dagger_{\alpha_2,\mu_2} c_{\alpha_3,\mu_2} c_{\alpha_4,\mu_1} \\
&= \sum_{\alpha_1,\alpha_2,\alpha_3,\alpha_4} \int dr\, dr\,' \int d\Omega \int d\Omega' \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}\,' - \vec{r}|} R^*_{n_1 l_1}(r) R^*_{n_2 l_2}(r\,') R_{n_3 l_3}(r\,') R_{n_4 l_4}(r) \\
&\qquad \times Y^*_{l_1 m_1}(\Omega) Y^*_{l_2 m_2}(\Omega\,') Y_{l_3 m_3}(\Omega\,') Y_{l_4 m_4}(\Omega) \sum_{\mu_1,\mu_2} c^\dagger_{\alpha_1,\mu_1} c^\dagger_{\alpha_2,\mu_2} c_{\alpha_3,\mu_2} c_{\alpha_4,\mu_1} \\
&= \frac{e^2}{4\pi\epsilon_0} \sum_{\alpha_1,\alpha_2,\alpha_3,\alpha_4} \sum_{\ell m} \frac{4\pi}{2\ell+1} \int dr\, R^*_{n_1 l_1}(r) R_{n_4 l_4}(r) \int dr\,' R^*_{n_2 l_2}(r\,') R_{n_3 l_3}(r\,') \cdot \frac{r^\ell_<}{r^{\ell+1}_>} \\
&\qquad \times \int d\Omega Y^*_{l_1 m_1}(\Omega) Y^*_{\ell m}(\Omega) Y_{l_4 m_4}(\Omega) \int d\Omega'\, Y^*_{l_2 m_2}(\Omega\,') Y_{\ell m}(\Omega') Y_{l_3 m_3}(\Omega\,') \\
&\qquad\qquad \times \sum_{\mu_1,\mu_2} c^\dagger_{\alpha_1,\mu_1} c^\dagger_{\alpha_2,\mu_2} c_{\alpha_3,\mu_2} c_{\alpha_4,\mu_1} \\
&= \sum_{n_1,l_1;n_2,l_2;n_3,l_3;n_4,l_4} I(n_1,l_1;n_2,l_2;n_3,l_3;n_4,l_4) \sum_{\ell,m} \sum_{\substack{m_1,\,m_2,\,m_3,\,m_4 \\ m_1+m=m_4 \\ m_3+m=m_2}} \sum_{\mu_1,\mu_2} c^\ell(l_1m_1,l_4m_4) c^\ell(l_2m_2,l_3m_3) \\
&\qquad \times c^\dagger_{\alpha_1,\mu_1} c^\dagger_{\alpha_2,\mu_2} c_{\alpha_3,\mu_2} c_{\alpha_4,\mu_1} \\
c^\ell(lm,l'm') &= \sqrt{\frac{4\pi}{2\ell+1}} \int d\Omega\, Y^*_{lm}(\Omega) Y_{\ell,m-m'}(\Omega) Y_{l,m,}(\Omega) : real
\end{aligned}$$

10.3 Some Concrete Examples of Multiplet Terms and the Method of Trace

10.3.1 $(1s)(2s)$

In this case, there are possibly four different degeneration states for the non-perturbation:

$$\begin{aligned}
|(1s)^{\uparrow}(2s)^{\uparrow}\rangle &= c^{\dagger}_{1s\uparrow}c^{\dagger}_{2s\uparrow}|0\rangle \\
|(1s)^{\uparrow}(2s)^{\downarrow}\rangle &= c^{\dagger}_{1s\uparrow}c^{\dagger}_{2s\downarrow}|0\rangle \\
|(1s)^{\downarrow}(2s)^{\uparrow}\rangle &= c^{\dagger}_{1s\downarrow}c^{\dagger}_{2s\uparrow}|0\rangle \\
|(1s)^{\downarrow}(2s)^{\downarrow}\rangle &= c^{\dagger}_{1s\downarrow}c^{\dagger}_{2s\downarrow}|0\rangle
\end{aligned}$$

We use the above as basis for calculating the degenerate perturbation theory. To make diagonalization of 4×4 Hamiltonian matrices, the conservation of the spin and angular momentum, which we discussed in the last subsection, should be considered. Here, we use $\hbar = 1$ in the calculations. The linear combination of the four states above can give the eigenstate for the total spin. To demonstrate this, let us first confirm that $S_+|(1s)^{\uparrow}(2s)^{\uparrow}\rangle = 0$ and $S_z|(1s)^{\uparrow}(2s)^{\uparrow}\rangle = (\frac{1}{2} + \frac{1}{2})\ |(1s)^{\uparrow}(2s)^{\uparrow}\rangle$ [195]

are the eigenstates of $S = 1$ and $M_S = 1$:

$$\begin{aligned}
\vec{S}^2|(1s)^{\uparrow}(2s)^{\uparrow}\rangle &= 1(1+1)|(1s)^{\uparrow}(2s)^{\uparrow}\rangle \\
S_z|(1s)^{\uparrow}(2s)^{\uparrow}\rangle &= 1 \cdot |(1s)^{\uparrow}(2s)^{\uparrow}\rangle
\end{aligned}$$

In other form, the above can be written as

$$|S = 1, M_S = 1\rangle = |(1s)^{\uparrow}(2s)^{\uparrow}\rangle$$

Likewise, we can write

$$\begin{aligned}
\vec{S}^2|(1s)^{\downarrow}(2s)^{\downarrow}\rangle &= 1(1+1)|(1s)^{\downarrow}(2s)^{\downarrow}\rangle \\
S_z|(1s)^{\downarrow}(2s)^{\downarrow}\rangle &= -1 \cdot |(1s)^{\downarrow}(2s)^{\downarrow}\rangle
\end{aligned}$$

The above indicates that $|(1s)^{\downarrow}(2s)^{\downarrow}\rangle$ being the eigenstate of $S = 1$ and $M_S = -1$:

$$|S = 1, M_S = -1\rangle = |(1s)^{\downarrow}(2s)^{\downarrow}\rangle$$

The states for $M_S = 0$ can be obtained by linear combination of $|(1s)^{\uparrow}(2s)^{\downarrow}\rangle$ and $|(1s)^{\downarrow}(2s)^{\uparrow}\rangle$, and among which the state for $S = 1$ is proportional to [196]

[195] Demonstrate this.
[196] Demonstrate this.

$$\begin{aligned} S_-|(1s)^\uparrow(2s)^\uparrow\rangle &= (c^\dagger_{1s\downarrow}c_{1s\uparrow} + c^\dagger_{1s\downarrow}c_{1s\uparrow} + \cdots)|(1s)^\uparrow(2s)^\uparrow\rangle \\ &= |(1s)^\uparrow(2s)^\downarrow\rangle + |(1s)^\downarrow(2s)^\uparrow\rangle \end{aligned}$$

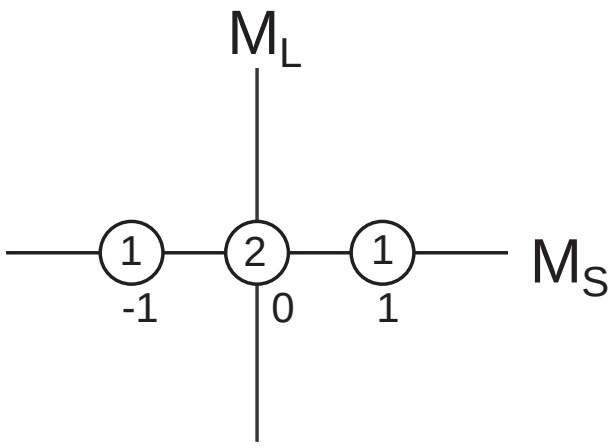
Consider the normalization we have

$$\begin{aligned} |S=1, M_S=0\rangle &= \frac{1}{\sqrt{2}}\big(|(1s)^\uparrow(2s)^\downarrow\rangle + |(1s)^\downarrow(2s)^\uparrow\rangle\big) \\ &= \frac{1}{\sqrt{2}}(c^\dagger_{1s\uparrow}c^\dagger_{2s\uparrow} + c^\dagger_{1s\uparrow}c^\dagger_{2s\downarrow})|0\rangle \end{aligned}$$

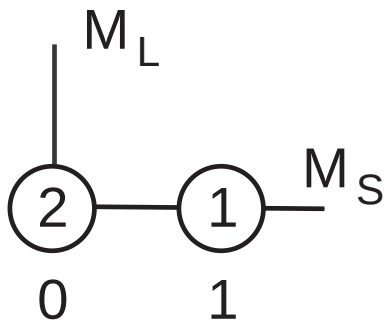
The rest of the states we know from general theory of angular momentum for $S=0$ can be written as an orthogonal form of the above:

$$\begin{aligned} |S=0, M_S=0\rangle &= \frac{1}{\sqrt{2}}\big(|(1s)^\uparrow(2s)^\downarrow\rangle - |(1s)^\downarrow(2s)^\uparrow\rangle\big) \\ &= \frac{1}{\sqrt{2}}(c^\dagger_{1s\uparrow}c^\dagger_{2s\downarrow} - c^\dagger_{1s\downarrow}c^\dagger_{2s\uparrow})|0\rangle \end{aligned}$$

We obtained the eigenstates without conducting diagonalization of the Hamiltonian matrices. This, in fact is one of the important features of the conserved quantity. We can easily understand how this may take place by the figures below that describe the dimension of the basis using the orbital angular momentum M_L and the spin angular momentum M_S:



Abbreviate the negative parts, we have



In general, the state for the total angular momentum L and the total spin S is expressed as ${}^{2S+1}L$ ($S(L=0)$, $P(L=1)$, $D(L=2)$, $F(L=3)$). The triplet degeneration state for $S=1$, for example, we have ${}^3S$ while for $S=0$ we have ${}^1S$.

The energy for ${}^3S$: [197]

$$\begin{aligned} E({}^3S) &= \langle {}^3S|H|{}^3S\rangle = \langle (1s)^\uparrow(2s)^\uparrow|H|(1s)^\uparrow(2s)^\uparrow\rangle \\ &= I(1s) + I(2s) + J(1s,2s) - K(1s,2s) \end{aligned}$$

While the energy for ${}^1S$ be [198]

$$\begin{aligned} E({}^1S) &= \langle {}^1S|H|{}^1S\rangle = I(1s) + I(2s) + J(1s,2s) + K(1s,2s) \\ |{}^1S\rangle &= \frac{1}{\sqrt{2}}(\ |(1s)^\uparrow(2s)^\downarrow\rangle - |(1s)^\downarrow(2s)^\uparrow\rangle\ ) \end{aligned}$$

In the above, we directly obtained the energy for ${}^1S$. We now reconsider the above from different view. The Hamiltonian matrices are diagonalized by unitary transformation of the basis as we have demonstrated, and the traces of matrices are known to be invariables. The z-component of the angular momentum M is the conserved quantity so that the diagonalization procedures can be taken by each M since there is no matrix element found among the blocks that have different Ms. Hence, the trace is same for the before and after diagonalization. In our

[197] Using the degeneration, we have $|(1s)^\uparrow(2s)^\uparrow\rangle$ for ${}^3S$.

[198]

$$\begin{aligned} \psi_{\sigma'}(\vec{r}\,')\psi_\sigma(\vec{r})|(1s)^\uparrow(2s)^\downarrow\rangle &= (-1)\Big(\varphi_{1s}(\vec{r}\,')|\uparrow\rangle_{\sigma'}\varphi_{2s}(\vec{r})|\downarrow\rangle_\sigma - \varphi_{2s}(\vec{r}\,')|\downarrow\rangle_{\sigma'}\varphi_{1s}(\vec{r})|\uparrow\rangle_\sigma\Big)|0\rangle \\ \psi_{\sigma'}(\vec{r}\,')\psi_\sigma(\vec{r})|(1s)^\downarrow(2s)^\uparrow\rangle &= (-1)\Big(\varphi_{1s}(\vec{r}\,')|\downarrow\rangle_{\sigma'}\varphi_{2s}(\vec{r})|\uparrow\rangle_\sigma - \varphi_{2s}(\vec{r}\,')|\uparrow\rangle_{\sigma'}\varphi_{1s}(\vec{r})|\downarrow\rangle_\sigma\Big)|0\rangle \end{aligned}$$

Thus,

$$\langle {}^1S|H_{int}|{}^1S\rangle = \frac{1}{2}(2J(1s,2s) - 2K(1s,2s) + 4K(1s,2s)) = J(1s,2s) + K(1s,2s)$$

present case, for example, the block of $M=0$ is the 2×2 matrix having the basis $(1s)^{\uparrow}(2s)^{\downarrow}$ and $(1s)^{\downarrow}(2s)^{\uparrow}$. After we make diagonalization for them, [consider the multiplet terms which will be given by this block] we have ${}^1S$ and ${}^3S$. So, we can write

$$\langle (1s)^{\uparrow}(2s)^{\downarrow}|H|(1s)^{\uparrow}(2s)^{\downarrow}\rangle + \langle (1s)^{\downarrow}(2s)^{\uparrow}|H|(1s)^{\downarrow}(2s)^{\uparrow}\rangle = \langle {}^1S|H|{}^1S\rangle + \langle {}^3S|H|{}^3S\rangle$$

Thus,

$$\begin{aligned} E({}^1S) + E({}^3S) &= E((1s)^{\uparrow},(2s)^{\downarrow}) + E((1s)^{\downarrow},(2s)^{\uparrow}) \\ &= 2(I(1s)+I(2s)+J(1s,2s)) \end{aligned}$$

For the block of $M=1$ we have

$$\begin{aligned} E({}^3S) &= E((1s)^{\uparrow},(2s)^{\uparrow}) \\ &= I(1s)+I(2s)+J(1s,2s)-K(1s,2s) \end{aligned}$$

Hence, we obtain

$$E({}^1S) = I(1s)+I(2s)+J(1s,2s)+K(1s,2s)$$

We call the above,<u>the method of trace</u>. Further, we determine the wavefunction for the coordinates ' representation:

$$\begin{aligned} \Psi_{{}^3S,M_S=1}(\vec{r}_1,\vec{r}_2) &= \langle r_1,r_2;\sigma_1,\sigma_2|{}^3S\rangle \\ &= \frac{1}{\sqrt{2!}}\begin{vmatrix} \varphi_{1s}(\vec{r}_1)\chi_{\uparrow}(\sigma_1) & \varphi_{1s}(\vec{r}_2)\chi_{\uparrow}(\sigma_2) \\ \varphi_{2s}(\vec{r}_1)\chi_{\uparrow}(\sigma_1) & \varphi_{2s}(\vec{r}_2)\chi_{\uparrow}(\sigma_2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}}\begin{vmatrix} \varphi_{1s}(\vec{r}_1) & \varphi_{1s}(\vec{r}_2) \\ \varphi_{2s}(\vec{r}_1) & \varphi_{2s}(\vec{r}_2) \end{vmatrix}\chi_{\uparrow}(\sigma_1)\chi_{\uparrow}(\sigma_2) \\ &= \frac{1}{\sqrt{2}}\Big(\varphi_{1s}(\vec{r}_1)\varphi_{2s}(\vec{r}_2)-\varphi_{2s}(\vec{r}_1)\varphi_{1s}(\vec{r}_2)\Big)\chi_{\uparrow}(\sigma_1)\chi_{\uparrow}(\sigma_2) \\ &= \frac{1}{\sqrt{2}}\big(\varphi_{1s}\varphi_{2s}-\varphi_{2s}\varphi_{1s}\big)\chi_{\uparrow}\chi_{\uparrow} \end{aligned}$$

In the same way we can write

$$\begin{aligned} \Psi_{{}^3S,M_S=-1}(\vec{r}_1,\vec{r}_2) &= \frac{1}{\sqrt{2}}\Big(\varphi_{1s}(\vec{r}_1)\varphi_{2s}(\vec{r}_2)-\varphi_{2s}(\vec{r}_1)\varphi_{1s}(\vec{r}_2)\Big)\chi_{\downarrow}(\sigma_1)\chi_{\downarrow}(\sigma_2) \\ &= \frac{1}{\sqrt{2}}\big(\varphi_{1s}\varphi_{2s}-\varphi_{2s}\varphi_{1s}\big)\chi_{\downarrow}\chi_{\downarrow} \end{aligned}$$

The wavefunction for ${}^3S$ and $M_S = 0$ that are left out can be written as [199]

$$\begin{aligned}\Psi_{{}^3S,M_S=0}(\vec{r}_1,\vec{r}_2) &= \frac{1}{\sqrt{2}}\Big(\varphi_{1s}(\vec{r}_1)\varphi_{2s}(\vec{r}_2)-\varphi_{2s}(\vec{r}_1)\varphi_{1s}(\vec{r}_2)\Big)\frac{\chi_\uparrow(\sigma_1)\chi_\downarrow(\sigma_2)+\chi_\downarrow(\sigma_1)\chi_\uparrow(\sigma_2)}{\sqrt{2}}\\ &= \frac{1}{\sqrt{2}}\Big(\varphi_{1s}\varphi_{2s}-\varphi_{2s}\varphi_{1s}\Big)\frac{\chi_\uparrow\chi_\downarrow+\chi_\downarrow\chi_\uparrow}{\sqrt{2}}\end{aligned}$$

Apparently, the functions which belong to ${}^3S$ are antisymmetric to the switching of the particles $\vec{r}_1\sigma_1 \leftrightarrow \vec{r}_2\sigma_2$; however, we should note that the space component for the functions, the antisymmetric spin component, has symmetric property.

For ${}^1S$, the function can be obtained as

$$\begin{aligned}\Psi_{{}^1S,M_S=0}(\vec{r}_1,\vec{r}_2) &= \frac{1}{\sqrt{2}}\Big(\varphi_{1s}(\vec{r}_1)\varphi_{2s}(\vec{r}_2)+\varphi_{2s}(\vec{r}_1)\varphi_{1s}(\vec{r}_2)\Big)\frac{\chi_\uparrow(\sigma_1)\chi_\downarrow(\sigma_2)-\chi_\downarrow(\sigma_1)\chi_\uparrow(\sigma_2)}{\sqrt{2}}\\ &= \frac{1}{\sqrt{2}}\Big(\varphi_{1s}\varphi_{2s}+\varphi_{2s}\varphi_{1s}\Big)\frac{\chi_\uparrow\chi_\downarrow-\chi_\downarrow\chi_\uparrow}{\sqrt{2}}\end{aligned}$$

The space component is symmetric while the spin component is antisymmetric for the above. The difference observed in the space components of the wavefunction creates the energy gap in physical terms.

10.3.2 $(1s)(1s)$

In this case, only one state is applicable to the non-perturbation state:

$$|(1s)^\uparrow(1s)^\downarrow\rangle = c^\dagger_{1s\uparrow}c^\dagger_{2s\downarrow}|0\rangle$$

where $M_S = 0$ is only valid. It is obvious that $S = 0$ therefore, ${}^1S$ is the only state we obtain.

10.3.3 $(1s)(2s)(3s)$

In this case, we can consider $2^3 = 8$ degenerate states for the non-perturbation. To make a list of the states in terms of M_S, we have:

[199]

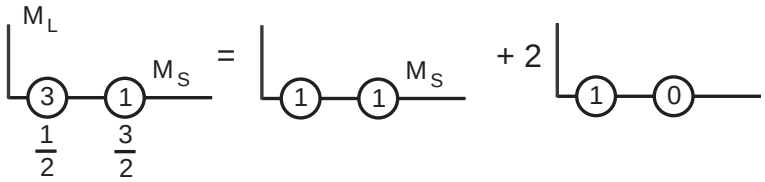
$$\begin{aligned}\langle r_1,r_2;\sigma_1,\sigma_2|(1s)^\uparrow(2s)^\downarrow\rangle &= \frac{1}{\sqrt{2!}}\begin{vmatrix}\varphi_{1s}(\vec{r}_1)\chi_\uparrow(\sigma_1) & \varphi_{1s}(\vec{r}_2)\chi_\uparrow(\sigma_2)\\ \varphi_{2s}(\vec{r}_1)\chi_\downarrow(\sigma_1) & \varphi_{2s}(\vec{r}_2)\chi_\downarrow(\sigma_2)\end{vmatrix}\\ &= \frac{1}{\sqrt{2}}\big(\varphi_{1s}(\vec{r}_1)\varphi_{2s}(\vec{r}_2)\chi_\uparrow(\sigma_1)\chi_\downarrow(\sigma_2)-\varphi_{2s}(\vec{r}_1)\varphi_{1s}(\vec{r}_2)\chi_\downarrow(\sigma_1)\chi_\uparrow(\sigma_2)\big)\end{aligned}$$

$$\langle r_1,r_2;\sigma_1,\sigma_2|(1s)^\downarrow(2s)^\uparrow\rangle = \frac{1}{\sqrt{2}}\big(\varphi_{1s}(\vec{r}_1)\varphi_{2s}(\vec{r}_2)\chi_\downarrow(\sigma_1)\chi_\uparrow(\sigma_2)-\varphi_{2s}(\vec{r}_1)\varphi_{1s}(\vec{r}_2)\chi_\uparrow(\sigma_1)\chi_\downarrow(\sigma_2)\big)$$

m_{1s}	m_{2s}	m_{3s}	M_S
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$
$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$
$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$
$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$
$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$
$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$

Therefore,

M_S	Number of states
$\frac{3}{2}$	1
$\frac{1}{2}$	3



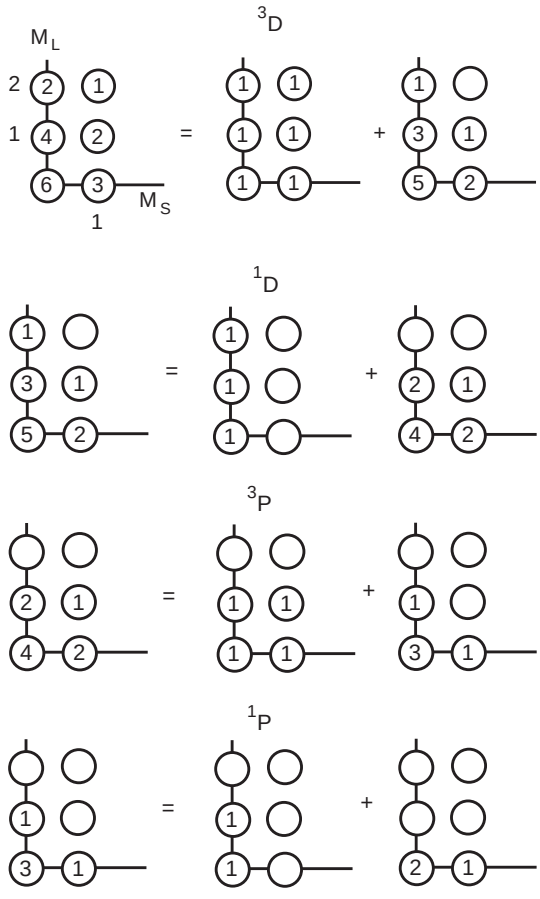
In short, we are having one ${}^4S$ and two ${}^2S$.

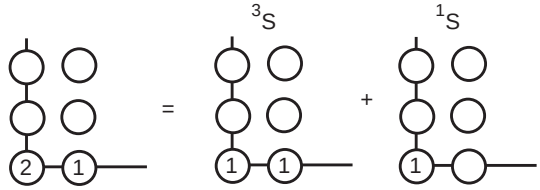
10.3.4 $(2p)(3p)$

In this case, we can think of $(2 \times 3)^2 = 36$ degenerate states for the non-perturbation. To make a list of the possible basis states using M_S and M_L, we have:

M_S	M_L	$(2p_{\ell_z})^{\uparrow,\downarrow}(3p_{\ell_z})^{\uparrow,\downarrow}$
1	2	$(2p_1)^{\uparrow}(3p_1)^{\uparrow}$
0	2	$(2p_1)^{\uparrow}(3p_1)^{\downarrow}$, $(2p_1)^{\downarrow}(3p_1)^{\uparrow}$
-1	2	$(2p_1)^{\downarrow}(3p_1)^{\downarrow}$
1	1	$(2p_1)^{\uparrow}(3p_0)^{\uparrow}$, $(2p_0)^{\uparrow}(3p_1)^{\uparrow}$
0	1	$(2p_1)^{\uparrow}(3p_0)^{\downarrow}$, $(2p_1)^{\downarrow}(3p_0)^{\uparrow}$, $(2p_0)^{\uparrow}(3p_1)^{\downarrow}$ $(2p_0)^{\downarrow}(3p_1)^{\uparrow}$
-1	1	$(2p_1)^{\downarrow}(3p_0)^{\downarrow}$, $(2p_0)^{\downarrow}(3p_1)^{\downarrow}$
1	0	$(2p_1)^{\uparrow}(3p_{-1})^{\uparrow}$, $(2p_0)^{\uparrow}(3p_0)^{\uparrow}$, $(2p_{-1})^{\uparrow}(3p_1)^{\uparrow}$
0	0	$(2p_1)^{\uparrow}(3p_{-1})^{\downarrow}$, $(2p_0)^{\uparrow}(3p_0)^{\downarrow}$, $(2p_{-1})^{\uparrow}(3p_1)^{\downarrow}$, $(2p_1)^{\downarrow}(3p_{-1})^{\uparrow}$, $(2p_0)^{\downarrow}(3p_0)^{\uparrow}$, $(2p_{-1})^{\downarrow}(3p_1)^{\uparrow}$
-1	0	$(2p_1)^{\downarrow}(3p_{-1})^{\downarrow}$, $(2p_0)^{\downarrow}(3p_0)^{\downarrow}$, $(2p_{-1})^{\downarrow}(3p_1)^{\downarrow}$
1	-1	$(2p_{-1})^{\uparrow}(3p_0)^{\uparrow}$, $(2p_0)^{\uparrow}(3p_{-1})^{\uparrow}$
0	-1	$(2p_{-1})^{\uparrow}(3p_0)^{\downarrow}$, $(2p_{-1})^{\downarrow}(3p_0)^{\uparrow}$, $(2p_0)^{\uparrow}(3p_{-1})^{\downarrow}$ $(2p_0)^{\downarrow}(3p_{-1})^{\uparrow}$
-1	-1	$(2p_{-1})^{\downarrow}(3p_0)^{\downarrow}$, $(2p_0)^{\downarrow}(3p_{-1})^{\downarrow}$
1	-2	$(2p_{-1})^{\uparrow}(3p_{-1})^{\uparrow}$
0	-2	$(2p_{-1})^{\uparrow}(3p_{-1})^{\downarrow}$, $(2p_{-1})^{\downarrow}(3p_{-1})^{\uparrow}$
-1	-2	$(2p_{-1})^{\downarrow}(3p_{-1})^{\downarrow}$

Therefore,





In other words ${}^3D$, ${}^1D$, ${}^3P$, ${}^1P$, ${}^3S$, ${}^1S$ are given as multiplet terms.

According to the method of trace, the energy can be expressed as following forms as we are given $E(\alpha,\beta)=\langle\alpha|H|\beta\rangle$ and ${}^3D=E({}^3D)$:

$$
\begin{aligned}
{}^3D&=\langle(2p_1)^\uparrow(3p_1)^\uparrow|H|(2p_1)^\uparrow(3p_1)^\uparrow\rangle = E((2p_1)^\uparrow(3p_1)^\uparrow) \quad (M_S=1,M_L=2)\\
&=I(2p_1)+I(3p_1)+J(2p_1,3p_1)-K(2p_1,3p_1)\\
{}^1D+{}^3D&=E((2p_1)^\uparrow(3p_1)^\downarrow)+E((2p_1)^\downarrow(3p_1)^\uparrow) \quad (M_S=0,M_L=2)\\
&=2I(2p_1)+2I(3p_1)+2J(2p_1,3p_1)\\
{}^3P \quad +{}^3D&=E((2p_1)^\uparrow(3p_0)^\uparrow)+E((2p_0)^\uparrow(3p_1)^\uparrow) \quad (M_S=1,M_L=1)\\
&=I(2p_1)+I(3p_0)+I(2p_0)+I(3p_1)\\
&\quad +J(2p_1,3p_0)-K(2p_1,3p_0)+J(2p_0,3p_1)-K(2p_0,3p_1)\\
{}^3S \quad +{}^3P \quad +{}^3D&=E((2p_1)^\uparrow(3p_{-1})^\uparrow)+E((2p_0)^\uparrow(3p_0)^\uparrow)+E((2p_{-1})^\uparrow(3p_1)^\uparrow) \quad (M_S=1,M_L=\\
&=I(2p_1)+I(3p_{-1})+I(2p_0)+I(3p_0)+I(2p_{-1})+I(3p_1)\\
&\quad +J(2p_1,3p_{-1}))-K(2p_1,3p_{-1})+J(2p_0,3p_0)-K(2p_0,3p_0)\\
&\quad +J(2p_{-1},3p_1)-K(2p_{-1},3p_1)\\
{}^1P+{}^3P+{}^1D+{}^3D&=E((2p_1)^\uparrow(3p_0)^\downarrow)+E((2p_1)^\downarrow(3p_0)^\uparrow)\\
&\quad +E((2p_0)^\uparrow(3p_1)^\downarrow)+E((2p_0)^\downarrow(3p_1)^\uparrow) \quad (M_S=0,M_L=1)\\
&=I(2p_1)+I(3p_0)+I(2p_1)+I(3p_0)+I(2p_0)+I(3p_1)+I(2p_0)+I(3p_1)\\
&\quad +J(2p_1,3p_0)+J(2p_1,3p_0)+J(2p_0,3p_1)+J(2p_0,3p_1)\\
{}^1S+{}^3S+{}^1P+{}^3P+{}^1D+{}^3D&=E((2p_1)^\uparrow(3p_{-1})^\downarrow)+E((2p_0)^\uparrow(3p_0)^\downarrow)+E((2p_{-1})^\uparrow(3p_1)^\downarrow)+E((2p_1)^\downarrow(3p_{-1})\\
&\quad +E((2p_0)^\downarrow(3p_0)^\uparrow)+E((2p_{-1})^\downarrow(3p_1)^\uparrow) \quad (M_S=0,M_L=0)\\
&\quad =2I(2p_1)+2I(3p_{-1})+2I(2p_0)+2I(3p_0)+2I(3p_1)+2I(2p_{-1})\\
&\quad +J((2p_1,3p_{-1})+J(2p_0,3p_0))+J(2p_{-1},3p_1)+J(2p_1,3p_{-1})+\\
&\quad +J(2p_0,3p_0)+J(2p_{-1},3p_1)
\end{aligned}
$$

Recast the above to have

$$\begin{pmatrix} 1 & & & & & \\ 1 & 1 & & & & \\ 1 & & 1 & & & \\ 1 & 1 & 1 & 1 & & \\ 1 & & 1 & & 1 & \\ 1 & 1 & 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} {}^3D \\ {}^1D \\ {}^3P \\ {}^1P \\ {}^3S \\ {}^1S \end{pmatrix} = \begin{pmatrix} * \\ * \\ * \\ * \\ * \\ * \end{pmatrix}$$

The equation has a solution because the left side of the matrix has 1.

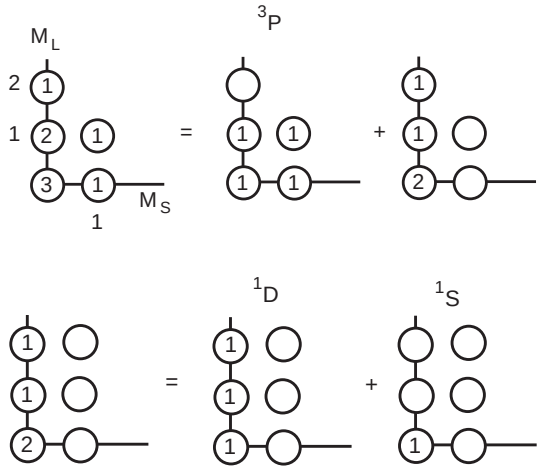
10.3.5 $(2p)^2$

There are ${}_6C_2 = 15$ degenerate states for the non-perturbation. We make a list of possible states to be the basis by using M_S and M_L:

M_S	M_L	$(2p_{\ell_z})^{\uparrow,\downarrow}$
0	2	$(2p_1)^\uparrow(2p_1)^\downarrow$
1	1	$(2p_1)^\uparrow(2p_0)^\uparrow$
0	1	$(2p_1)^\uparrow(2p_0)^\downarrow$
1	0	$(2p_1)^\uparrow(2p_{-1})^\uparrow$
0	0	$(2p_1)^\uparrow(2p_{-1})^\downarrow$
0	1	$(2p_1)^\downarrow(2p_0)^\uparrow$
−1	1	$(2p_1)^\downarrow(2p_0)^\downarrow$
0	0	$(2p_1)^\downarrow(2p_{-1})^\uparrow$
−1	0	$(2p_1)^\downarrow(2p_{-1})^\downarrow$
0	0	$(2p_0)^\uparrow(2p_0)^\downarrow$
1	−1	$(2p_0)^\uparrow(2p_{-1})^\uparrow$
0	−1	$(2p_0)^\uparrow(2p_{-1})^\downarrow$
0	−1	$(2p_0)^\downarrow(2p_{-1})^\uparrow$
−1	−1	$(2p_0)^\downarrow(2p_{-1})^\downarrow$
0	−2	$(2p_{-1})^\uparrow(2p_{-1})^\downarrow$

M_S	M_L	状態数
0	2	1
0	1	2
0	0	3
0	−1	2
0	−2	1
1	1	1
1	0	1
1	−1	1
−1	1	1
−1	0	1
−1	−1	1

Therefore,



In other words, ${}^3P$, ${}^1D$, and ${}^1S$ are given as the multiplet terms.

In determining the energy by using the method of trace,

$$
\begin{aligned}
{}^1D \quad &= E((2p_1)^{\uparrow}(2p_1)^{\downarrow}) \quad (M_S=0, M_L=2) \\
&= 2I(2p_1) + J(2p_1, 2p_1) \\
{}^3P &= E(2p_1)^{\uparrow}, (2p_0)^{\uparrow}) \quad (M_S=1, M_L=1) \\
&= I(2p_1) + I(2p_0) + J(2p_1, 2p_0) - K(2p_1, 2p_0) \\
{}^1S+{}^1D+{}^3P &= E((2p_1)^{\uparrow}(2p_{-1})^{\downarrow}) + E((2p_1)^{\downarrow}(2p_{-1})^{\uparrow}) + E((2p_0)^{\uparrow}(2p_0)^{\downarrow}) \quad (M_S=0, M_L=0) \\
&= 2I(2p_1) + 2I(2p_0) + 2I(2p_{-1}) + 2J(2p_1, 2p_{-1}) + J(2p_0, 2p_0)
\end{aligned}
$$

can give the energy. To provide with other multiplet examples and their results,

10.3.6 pd

$$^3F,^3D,^3P,^1F,^1D,^1P$$

10.3.7 pds

$$^4F,^4D,^4P,2(^2F),2(^2D),2(^2P)$$

10.4 Electron-hole Transformation and the Multiplet $(nl)^x$

10.4.1 Multiplet $(nl)^x$

For the multiplets which fill the electrons of the particular orbits, we can obtain the following results:

- $p^1 : {}^2P$
- $p^2 : {}^3P,^1D,^1S$
- $p^3 : {}^4S,^2D,^2P$
- $p^4 : {}^3P,^1D,^1S$
- $p^5 : {}^2P$
- $d^1 : {}^2D$
- $d^2 : {}^3F,^3P,^1G,^1D,^1S$
- $d^3 : {}^4F,^4P,^2H,^2G,^2F,2(^2D),^2P$
- $d^4 : {}^5D,^3H,^3G,2(^3F),^3D,2(^3P),^1I,2(^1G),^1F,2(^1D),2(^1S)$
- $d^5 : {}^6S,^4G,^4F,^4D,^4P,^2I,^2H,2(^2G),2(^2F),3(^2D),^2P,^2S$
- $d^6 : {}^5D,^3H,^3G,2(^3F),^3D,2(^3P),^1I,2(^1G),^1F,2(^1D),2(^1S)$
- $d^7 : {}^4F,^4P,^2H,^2G,^2F,2(^2D),^2P$
- $d^8 : {}^3F,^3P,^1G,^1D,^1S$
- $d^9 : {}^2D$

The above indicates that $(nl)^x$ and $(nl)^{2(2l+1)-x}$ are given by the same multiplet term due to the electron-hole symmetry. In the following, we will investigate this characteristic.

10.4.2 Electron-hole Transformation

When we limit the electron configuration to the particular (nl), the angular momentum and the spin operator can be

$$
\begin{aligned}
L_z &= \sum_m \sum_\mu \hbar m c^\dagger_{m\mu} c_{m\mu} \\
L_\pm &= \sum_m \sum_\mu \hbar \sqrt{(l \mp m)(l \pm m + 1)} c^\dagger_{m\pm 1\mu} c_{m\mu} \\
S_z &= \frac{1}{2}\hbar \sum_m (c^\dagger_{m\uparrow} c_{m\uparrow} - c^\dagger_{m\downarrow} c_{m\downarrow}) \\
S_+ &= \hbar \sum_m c^\dagger_{m\uparrow} c_{m\downarrow} \\
S_- &= \hbar \sum_m c^\dagger_{m\downarrow} c_{m\uparrow}
\end{aligned}
$$

Let us define

$$
U = \prod_m \prod_\mu (c_{m\mu} + c^\dagger_{m\mu})
$$

then U and

$$
U^\dagger U = U U^\dagger = 1
$$

are the unitary operator. [200] Now we write

$$
\begin{aligned}
\vec{L}' &= U \vec{L} U^\dagger, \\
\vec{S}' &= U \vec{S} U^\dagger
\end{aligned}
$$

which giving

$$
\begin{aligned}
L'_z &= -L_z, \quad L'_\pm = -L_\mp \\
S'_z &= -S_z, \quad S'_\pm = -S_\mp
\end{aligned}
$$

therefore, [201]

$$
\begin{aligned}
\vec{L'}^2 &= \frac{1}{2}(L'_+ L'_- + L'_- L'_+) + L'^2_z = \vec{L}^2 \\
\vec{S'}^2 &= \vec{S}^2
\end{aligned}
$$

200

$$
(c + c^\dagger)(c^\dagger + c) = c c^\dagger + c^\dagger c = 1
$$

201

$$
\begin{aligned}
(c + c^\dagger) c (c + c^\dagger) &= c^\dagger c c^\dagger = c^\dagger \\
(c + c^\dagger) c^\dagger (c + c^\dagger) &= c
\end{aligned}
$$

So, for the arbitrary multiplet $|G\rangle$, we can write

$$\vec{L}^2|G\rangle = \hbar L(L+1)|G\rangle$$
$$\vec{S}^2|G\rangle = \hbar S(S+1)|G\rangle$$

This gives

$$Uc_{m\mu}U^\dagger = c^\dagger_{m\mu}$$
$$Uc^\dagger_{m\mu}U^\dagger = c_{m\mu}$$

Thus,

$$\begin{aligned}
L'_z &= \sum_m \sum_\mu \hbar m c_{m\mu} c^\dagger_{m\mu} \\
&= \sum_m \sum_\mu \hbar m (1 - c^\dagger_{m\mu} c_{m\mu}) = -L_z \\
L'_\pm &= \sum_m \sum_\mu \hbar \sqrt{(l \mp m)(l \pm m + 1)} c_{m\pm 1\mu} c^\dagger_{m\mu} \\
&= -\sum_m \sum_\mu \hbar \sqrt{(l \mp m)(l \pm m + 1)} c^\dagger_{m\mu} c_{m\pm 1\mu} \\
L'_+ &= -\sum_m \sum_\mu \hbar \sqrt{(l - m)(l + m + 1)} c^\dagger_{m\mu} c_{m+1\mu} \\
&= -\sum_{m'} \sum_\mu \hbar \sqrt{(l - m' + 1)(l + m')} c^\dagger_{m'-1\mu} c_{m'\mu}, \quad m' = m + 1 \\
&= -L_- \\
L'_- &= -\sum_m \sum_\mu \hbar \sqrt{(l + m)(l - m + 1)} c^\dagger_{m\mu} c_{m-1\mu} \\
&= -\sum_{m'} \sum_\mu \hbar \sqrt{(l + m' + 1)(l - m')} c^\dagger_{m'+1\mu} c_{m'\mu}, \quad m' = m - 1 \\
&= -L_+ \\
S'_z &= \frac{1}{2}\hbar \sum_m (c_{m\uparrow} c^\dagger_{m\uparrow} - c_{m\downarrow} c^\dagger_{m\downarrow}) = -S_z \\
S'_+ &= \hbar \sum_m c_{m\downarrow} c^\dagger_{m\uparrow} = -S_- \\
S'_- &= \hbar \sum_m c_{m\uparrow} c^\dagger_{m\downarrow} = -S_+
\end{aligned}$$

So that we can write in the form: [202]

$$\vec{L'}^2|G'\rangle = \hbar L(L+1)|G'\rangle$$
$$\vec{S'}^2|G'\rangle = \hbar S(S+1)|G'\rangle$$
$$|G'\rangle = U|G'\rangle$$

As we can readily confirm: [203]

$$|G\rangle \in (nl)^x \leftrightarrow |G'\rangle \in (nl)^{2(2l+1)-x}$$

Therefore, generally speaking, $(nl)^x$ and $(nl)^{2(2l+1)-x}$ may give the same multiplet term.

10.5 Hund 's Rule

Although we can determine the multiplets that are given in the way described in the last few subsections, further calculations (integrations) are required to determine the energy states for such multiplets. In considering the states which contributes to the lowest energy level, an experiential rule called the Hund 's rule can be applied.

> *Hund 's Rule:* Among all multiplets that are given by an electron configuration, the spin with the greatest level may possess the lowest energy. When there are more than one maximum multiplicity spins then, the one with the greatest orbital angular momentum among them has the lowest energy level. In the case where there are more than one maximum multiplicities of the greatest orbital angular momentum then, the spin which has the greatest orbital angular momentum L has the lowest energy level.

202

$$U\vec{L}^2U^\dagger U|G\rangle = \hbar L(L+1)U|G\rangle$$
$$U\vec{S}^2U^\dagger U|G\rangle = \hbar S(S+1)U|G\rangle$$

[203] In the case for d^x, if we have

$$|t\rangle = c^\dagger_{1\uparrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}|0\rangle$$

then we can write

$$|t'\rangle = U|t\rangle = c^\dagger_{-2\uparrow}c^\dagger_{-2\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{-1\downarrow}c^\dagger_{0\uparrow}c^\dagger_{0\downarrow}c^\dagger_{2\uparrow}|0\rangle$$

Yet it is considered as an experiential rule, the Hund 's rule has been widely accepted. As we have discussed earlier, in the physical terms, the spin function indeed holds symmetric property in electron replacement for the spins with maximum multiplicity while the space part of the wavefunction is antisymmetric based on the Pauli 's principle. In other words, the wavefunction becomes zero when arbitrary two electron coordinates are the same, and from which we may assume that the Coulomb interaction energy among electrons can be obtained. For the orbital angular momenta of the same spin, the greater the momentum, the less chances are for the electrons to come close to each other since they move at farther distance away because of the centrifugal force. For the last part of the rule that relates to L, there is a small Coulomb repulsion and the low probability for the electrons of greater m value to come close to each other in filling out the parallel spin.

10.6 Spin-orbit Interaction

In considering the electrons in an atom with large atomic number, the relativistic correction will be required. The most important term can be the spin-orbit interaction. By following the procedures we demonstrated in our earlier discussions, the term written below can be added after the second quantization: [204]

[204]

$$
\begin{aligned}
H_{SO} &= C\int d^3r \sum_{\sigma\sigma'} \psi^\dagger_\sigma(\vec{r})\frac{1}{r}\frac{\partial V}{\partial r}\vec{s}_{\sigma\sigma'}\cdot\vec{\ell}\,\psi_{\sigma'}(\vec{r}),\quad C=\frac{\hbar}{4m^2c^2}\\
&= C\sum_{nl}\sum_{n'l'}\int dr\, r^2\phi^*_{nl}(r)\frac{1}{r}\frac{\partial V}{\partial r}\phi_{n'l'}(r) \longrightarrow \xi(nl,n'l')\\
&\times\sum_{\sigma\sigma'}\sum_{\mu\mu'}\chi^*_\mu(\sigma)\vec{s}_{\sigma\sigma'}\chi_{\mu'}(\sigma)\cdot\int d\Omega Y^*_{lm}(\Omega)\,\vec{\ell}\,Y_{l'm'}(\Omega)c^\dagger_{nlm\mu}c_{n'l'm'\mu'}\\
&= \sum_{nn'l}\xi(nl,n'l)\sum_m\\
&\times\Bigg[\frac{1}{2}\Bigg\{\langle\chi_\uparrow|s_+|\chi_\downarrow\rangle\int d\Omega Y^*_{lm-1}(\Omega)\,\ell_-\,Y_{lm}(\Omega)c^\dagger_{nlm-1\uparrow}c_{n'lm\downarrow}\\
&\qquad+\langle\chi_\downarrow|s_-|\chi_\uparrow\rangle\int d\Omega Y^*_{lm+1}(\Omega)\,\ell_-\,Y_{lm}(\Omega)c^\dagger_{nlm-1\uparrow}c_{n'lm\downarrow}\Bigg\}\\
&\qquad+\sum_\mu\langle\chi_\mu|s_z|\chi_\mu\rangle\int d\Omega Y^*_{lm}(\Omega)\,\ell_z\,Y_{lm}(\Omega)c^\dagger_{nlm\mu}c_{n'lm\mu}\Bigg]\\
&= \sum_{nn'l}\xi(nl,n'l)\sum_m\frac{\hbar^2}{2}\Bigg\{\sqrt{(l+m)(l-m+1)}c^\dagger_{nlm-1\uparrow}c_{n'lm\downarrow}+\sqrt{(l-m)(l+m+1)}c^\dagger_{nlm+1\uparrow}c_{n'lm\downarrow}\\
&\qquad+m(c^\dagger_{nlm\uparrow}c_{n'lm\uparrow}-c^\dagger_{nlm\downarrow}c_{n'lm\downarrow})\Bigg\}
\end{aligned}
$$

$$
\begin{aligned}
H_{SO} &= C\int d^3r \sum_{\sigma\sigma'} \psi^\dagger_\sigma(\vec{r})\frac{1}{r}\frac{\partial V}{\partial r}\vec{s}_{\sigma\sigma'}\cdot\vec{\ell}\,\psi_{\sigma'}(\vec{r}), \quad C=\frac{\hbar}{4m^2c^2} \\
&= C\sum_{nl}\sum_{n'l'}\int dr\, r^2\phi^*_{nl}(r)\frac{1}{r}\frac{\partial V}{\partial r}\phi_{n'l'}(r) \longrightarrow \xi(nl,n'l') \\
&\times \sum_{\sigma\sigma'}\sum_{\mu\mu'}\chi^*_\mu(\sigma)\vec{s}_{\sigma\sigma'}\chi_{\mu'}(\sigma)\cdot\int d\Omega Y^*_{lm}(\Omega)\,\vec{\ell}\,Y_{l'm'}(\Omega)c^\dagger_{nlm\mu}c_{n'l'm'\mu'} \\
&= \sum_{nn'l}\xi(nl,n'l)\sum_m\sum_{\mu\mu'}\langle Y_{lm}\chi_\mu|\,(\vec{s}\cdot\vec{\ell})\,|Y_{lm'}\chi_{\mu'}\rangle\, c^\dagger_{nlm\mu}c_{n'lm'\mu'}
\end{aligned}
$$

As far as the effect of the term described above is concerned with only to the discussion of the multiplet; i.e., the eigenstate of L and S, an effective addition of the term to the Hamiltonian is known to be able to bring such discussion:

$$H^{eff}_{SO} = A\vec{S}\cdot\vec{L}$$

Having confirmed with the fact above, we can easily understand that the application of the term no longer allows to conserve the spin and the orbital angular momentum; however,

$$
\begin{aligned}
H^{eff}_{SO} &= A\frac{1}{2}(\vec{J}^2-\vec{S}^2-\vec{L}^2) \\
\vec{J} &= \vec{S}+\vec{L}
\end{aligned}
$$

which indicates that the composition of the spin and the orbital angular momentum $\vec{J}$ is in fact the conserved quantity:

$$
\begin{aligned}
\vec{J}^2 &= J(J+1) \\
J &= |L-S|, |L-S|+1, \cdots, L+S
\end{aligned}
$$

Therefore, the degenerating levels other than ${}^1S$ in the multiplet, which we discussed in the last subsection, are considered to further split due to the spin-orbit interaction. The structure of further splitting of the multiplet is called the *fine structure*. This fine structure can be given by

$$E^J_{SO} = A\frac{1}{2}\big[J(J+1)-L(L+1)-S(S+1)\big]$$

The interval among the levels,

$$\Delta E^J_{SO} = E^J_{SO} - E^{J-1}_{SO} = AJ$$

is proportional to J within one multiplet term. This is known as the *Lande 's interval rule.* [205]

Equivalence of H_{SO} and H_{SO}^{eff}

Let us first define:

$$\begin{aligned} H_{am} =& \int d\tau\, \psi^\dagger(\tau)\xi(r)s_a\ell_m\psi(\tau), \quad a,m = x,y,z \\ H_{SO} =& H_{xx} + H_{yy} + H_{zz} \end{aligned}$$

According to $[s_a, s_b] = i\hbar\epsilon_{abc}s_c$, we can write

$$[S_a, H_{bm}] = \int d\tau\, \psi^\dagger(\tau)\xi(r)[s_a, s_b]\ell_m\psi(\tau) = i\hbar\epsilon_{abc}H_{cm}$$

for $\vec{S} = \int d\tau\psi(\tau)\vec{s}\psi(\tau)$

This yields $H_{\pm m} = H_{xm} \pm iH_{ym}$ so that

$$(H_{xm}, H_{ym}, H_{zm})$$

becomes the irreducible vector operator for S. In the same manner,

$$(H_{ax}, H_{ay}, H_{az})$$

becomes the irreducible vector operator for L.

Now, suppose

$$(T_x, T_y, T_z)$$

satisfies

$$[J_\alpha, T_\beta] = i\hbar\epsilon_{\alpha\beta\gamma}T_\gamma$$

for an angular momentum operator $\vec{J}$. In such case,

$$(T_x, T_y, T_z)$$

[205] We first considered the multiplet splitting caused by the Coulomb interaction before we consider the fine structures given by the spin-orbit interaction. This we call the R-S coupling. Intrinsically, for the atoms with larger atomic numbers, only the J becomes the conserved quantity. The direct treatment of the levels organized by J is called the J-J coupling.

is regarded as irreducible vector operator of J. [206]

The commutation relations for non-zero can be:

$$\begin{aligned}[J_z, T_\pm] &= \pm\hbar T_\pm \\ [J_+, T_-] &= 2\hbar T_z \\ [J_-, T_+] &= -2\hbar T_z\end{aligned}$$

For the eigenfunction $|jm\rangle$ of J^2 and J_z, it is written as

$$\begin{aligned}\langle jm|[J_z, T_\pm]|jm'\rangle &= \pm\,\hbar\langle jm|T_\pm|jm'\rangle \\ &= \hbar(m-m')\langle jm|T_\pm|jm'\rangle\end{aligned}$$

So that we can write

$$\langle jm|T_\pm|jm'\rangle \neq 0, \qquad m - m' = \pm 1$$

Moreover,

$$\begin{aligned}J_+|jm\rangle &= \hbar\sqrt{(j-m)(j+m+1)}|jm+1\rangle \\ J_-|jm\rangle &= \hbar\sqrt{(j+m)(j-m+1)}|jm-1\rangle\end{aligned}$$

gives

$$\begin{aligned}0 &= \langle jm|[J_-, T_-]|jm'\rangle \\ &= \hbar\sqrt{(j-m)(j+m+1)}\langle jm+1|T_-|jm'\rangle - \hbar\sqrt{(j+m')(j-m'+1)}\langle jm|T_-|jm'-1\rangle\end{aligned}$$

On the one hand, we have $m' = m + 2$ so, we can write in the form:

$$\begin{aligned}\sqrt{(j-m)(j+m+1)}\langle jm+1|T_-|jm+2\rangle &= \sqrt{(j+m+2)(j-m-1)}\langle jm|T_-|jm+1\rangle \\ \frac{\langle jm+1|T_-|jm+2\rangle}{\sqrt{(j+m+2)(j-m-1)}} &= \frac{\langle jm|T_-|jm+1\rangle}{\sqrt{(j+m+1)(j-m)}} = independent of \mathrm{m}\end{aligned}$$

[206]

$$\begin{aligned}[J_a, T_a] &= 0 \\ [J_z, T_x] &= i\hbar T_y \\ [J_z, T_y] &= -i\hbar T_x \text{ より} \\ [J_z, T_\pm] &= \pm\hbar T_\pm \\ [J_+, T_+] &= (i[J_x, T_y] + i[J_y, T_x]) = 0 \\ [J_+, T_-] &= (-i[J_x, T_y] + i[J_y, T_x]) = 2\hbar T_z \\ [J_-, T_+] &= (i[J_x, T_y] - i[J_y, T_x]) = -2\hbar T_z \\ [J_-, T_-] &= (-i[J_x, T_y] - i[J_y, T_x]) = 0\end{aligned}$$

Now,

$$\langle jm|J_-|jm+1\rangle = \sqrt{(j-m)(j+m+1)}\hbar$$

gives

$$\langle jm|T_-|jm+1\rangle = c_-\langle jm|J_-|jm+1\rangle$$

Thus, we can write as

$$0 = \langle jm|[J_+, T_+]|jm'\rangle$$
$$= \hbar\sqrt{(j+m)(j-m+1)}\langle jm-1|T_+|jm'\rangle - \hbar\sqrt{(j-m')(j+m'+1)}\langle jm|T_+|jm'+1\rangle$$

For $m' = m-2$, on the other hand, we can write as

$$\sqrt{(j+m)(j-m+1)}\langle jm-1|T_+|jm-2\rangle = \sqrt{(j-m+2)(j+m-1)}\langle jm|T_+|jm-1\rangle$$
$$\frac{\langle jm-1|T_+|jm-2\rangle}{\sqrt{(j-m+2)(j+m-1)}} = \frac{\langle jm|T_+|jm-1\rangle}{\sqrt{(j+m)(j-m+1)}} = independent of m$$

Now,

$$\langle jm|J_+|jm-1\rangle = \sqrt{(j-m+1)(j+m)}\hbar$$

gives

$$\langle jm|T_+|jm-1\rangle = c_+\langle jm|J_+|jm-1\rangle$$

and gives

$$0 = \langle jm|[J_z, T_z]|jm'\rangle = \hbar(m-m')\langle jm|T_z|jm'\rangle$$
$$\langle jm|T_z|jm'\rangle \neq 0, \quad m = m'$$

Further, we can write

$$\begin{aligned}
0 =& \langle jm|[J_+, T_-]|jm\rangle = 2\hbar\langle jm|T_z|jm\rangle \\
=& \hbar\sqrt{(j+m)(j-m+1)}\langle jm-1|T_-|jm\rangle - \hbar\sqrt{(j-m)(j+m+1)}\langle jm|T_-|jm+1\rangle \\
=& c_-\hbar\sqrt{(j+m)(j-m+1)}\langle jm-1|J_-|jm\rangle - \hbar\sqrt{(j-m)(j+m+1)}\langle jm|J_-|jm+1\rangle \\
=& c_- 2\hbar\langle jm|J_z|jm\rangle
\end{aligned}$$

This gives

$$\langle jm|T_z|jm\rangle = c_-\langle jm|J_z|jm\rangle$$

Finally,

$$\begin{aligned}0 =&\langle jm|[J_-, T_+]|jm\rangle = -2\hbar\langle jm|T_z|jm\rangle \\ =&\hbar\sqrt{(j-m)(j+m+1)}\langle jm+1|T_+|jm\rangle - \hbar\sqrt{(j+m)(j-m+1)}\langle jm|T_+|jm-1\rangle \\ =&c_+\hbar\sqrt{(j-m)(j+m+1)}\langle jm+1|J_+|jm\rangle - \hbar\sqrt{(j+m)(j-m+1)}\langle jm|J_+|jm-1\rangle \\ =&c_+ 2\hbar\langle jm|J_z|jm\rangle\end{aligned}$$

which is yielding

$$\langle jm|T_z|jm\rangle = c_+\langle jm|J_z|jm\rangle$$

That is

$$c_- = c_+$$

Thus, we can define the reduction of the matrix element $\langle j||T||j\rangle$ which does not depend on m or

$$\begin{aligned}\langle jm|\vec{T}|jm'\rangle =& c\langle jm|\vec{J}|jm'\rangle \\ c \equiv& \frac{\langle j||T||j\rangle}{\sqrt{j(j+1)(2j+1)}}\end{aligned}$$

We can rewrite the above as

$$\begin{aligned}\langle LSM_LM_S|H_{SO}|LSM_LM_S\rangle =& c\langle LSM_LM_S|\vec{L}\cdot\vec{S}|LSM_LM_S\rangle \\ c =& \frac{\langle LS||H_{SO}||LS\rangle}{\sqrt{L(L+1)(2L+1)S(S+1)(2S+1)}}\end{aligned}$$

To provide a concrete example of the above, let us suppose d^n where $(n \leq 5)$, the ground state should have the maximum multiplicity spin according to the Hund ' s rule:

$$^S L, \quad S = \frac{n}{2}$$

This also gives the greatest value for the orbital angular momentum:

$$L = 3n - (1 + 2 + \cdots + n) = 3n - \frac{n(n+1)}{2} = \frac{5n - n^2}{2} = \frac{(5-n)n}{2}$$

The states for $M_S = S$ and $M_L = L$:

$$|M_S = S, M_L = L\rangle = c^\dagger_{3-1\uparrow}c^\dagger_{3-2\uparrow}\cdots c^\dagger_{3-n\uparrow}|0\rangle$$

The above is used to calculate both sides of the equation:

$$\begin{aligned}\zeta_d\hbar^2\frac{1}{2}L =& cSL\\ c =& \hbar^2\frac{\zeta_d}{2S}\\ \zeta_d =& \int dr\, r^2|\phi_{nl=2}(r)|^2 > 0\end{aligned}$$

Under $n \geq 6$, we may write

$$\begin{aligned}S =& \frac{10-n}{2}\\ L =& -\{3(10-n) - (1+2+\cdots+(10-n)\}\\ =& -3(10-n) + \frac{(10-n)(11-n)}{2} = \frac{(10-n)(n-5)}{2}\end{aligned}$$

The state can be determined as

$$|M_S = S, M_L = L\rangle = c^\dagger_{2\uparrow}c^\dagger_{1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{-2\uparrow}c^\dagger_{3-1\downarrow}c^\dagger_{3-2\downarrow}\cdots c^\dagger_{3-(n-5)\downarrow}|0\rangle$$

with which we calculate the both sides of the equation:

$$\zeta_d\hbar^2(-)\frac{1}{2}(2+1+\cdots+(3-(n-5))) = \zeta_d\hbar^2(-)\frac{(10-n)(n-5)}{2} = cSLThus,$$
$$c = -\hbar^2\frac{\zeta_d}{2S}$$

Where $c > 0$, $d^{1,2,3,4,5}$ is considered to be in the normal position while $d^{6,7,8,9}$ is considered to be in the inverse position under $c < 0$. We have $c = 0$ for d^0 and d^{10}.