For example,

$$|p^3\ {}^2D\rangle = \frac{1}{\sqrt{2}}\left[\,|p^2({}^3P), p;\ {}^2D\rangle - |p^2({}^1D), p;\ {}^2D\rangle\,\right]$$

$$|p^3\ {}^2P\rangle = \frac{1}{18}\left\{2|p^2({}^1S), p;\ {}^2P\rangle - 3|p^2({}^3P), p;\ {}^2P\rangle - \sqrt{5}\,|p^2({}^1D), p;\ {}^2P\rangle\right]$$

$$|p^3\ {}^4S\rangle = |p^2(\underline{{}^3P}), p;\ {}^4S\rangle$$

Each term by itself is not antisym., but the linear combinations are antisym.

- The idea can be generalized to removing more than one particle at a time.

2-particle cfp.
- Consider the functions

$$|\,l^{x-2}(\alpha_1 S_1 L_1), l^2(S_2 L_2); SL\rangle \quad \text{.. not antisym.}$$

The state $|l^x \alpha SL\rangle$ is then

$$|l^x \alpha SL\rangle = \sum_{\substack{\alpha_1 S_1 L_1 \\ S_2 L_2}} |\,l^{x-2}(\alpha_1 S_1 L_1), l^2(S_2 L_2); SL\rangle \times \langle l^{x-2}(\alpha_1 S_1 L_1)\, l^2(S_2 L_2) SL |\} l^x \alpha SL\rangle$$

~~.. It is interesting that the above reduction is not always possible.~~

Seniority Quantum No.

- A new quantum no. ν = seniority emerges if we restrict ourselves to $S_2 = 0, L_2 = 0$. Then $S_1 = S$, $L_1 = L$ and

$$|\, l^{x} \alpha S L \rangle = \sum_{\alpha_1} |\, l^{x-2}(\alpha_1 S L), l^{2}({}^1S); S L \rangle$$
$$\times \langle l^{x-2}(\alpha_1 S L), l^{2}({}^1S); S L |\} l^{x} \alpha S L \rangle$$

The above is possible for some states, but not all. It is often not possible to form a state with quantum numbers SL out of the configuration l^{x-2}.

- Definition: if a state $|\, l^{x} \alpha S L \rangle$ can be formed from a state $|\, l^{\nu} \alpha_1 S L \rangle$ according to

$$|\, l^{x} \alpha S L \rangle = \sum_{\alpha_1} |\, l^{\nu}(\alpha_1 S L)\, l^{x-\nu}({}^1S); S L \rangle$$
$$\times \langle l^{\nu}(\alpha_1 S L)\, l^{x-\nu}({}^1S); S L |\} l^{x} \alpha S L \rangle$$

then the seniority of the state is ν.

p: ${}^2P$
$\nu = 1$

p^2: ${}^1S$ ${}^3P$ ${}^1D$
$\nu =$ 0 2 2

p^3: ${}^2P$ ${}^2D$ ${}^4S$
$\nu =$ 1 3 3

p^4: ${}^1S$ ${}^3P$ ${}^1D$
$\nu =$ 0 2 2

p^5 ${}^2P$
$\nu = 1$

d: ^2D
$v = 1$

d^2: ^1S ^3P ^1D ^3F ^1G
$v = 0$ 2 2 2 2

d^3: ^2P ^4P ^2D ^2D ^2F ^4F ^2G ^2H
$v = 3$ 3 1 3 3 3 3 3

$$|d^3\ ^2D_1\rangle = \frac{1}{\sqrt{60}}\Big[4|d^2(^1S_0), d\ ^2D\rangle - 3|d^2(^3P), d\ ^2D\rangle - \sqrt{5}|d^2(^1D), d\ ^2D\rangle - \sqrt{21}|d^2(^3F), d\ ^2D\rangle - 3|d^2(^1G), d\ ^2D\rangle \Big]$$

$$|d^3\ ^2D_3\rangle = \frac{1}{\sqrt{140}}\Big[-7|d^2(^3P), d\ ^2D\rangle + \sqrt{45}|d^2(^1D), d\ ^2D\rangle + \sqrt{21}|d^2(^3F), d\ ^2D\rangle - 5|d^2(^1G), d\ ^2D\rangle \Big]$$

For d^x configurations, the set of quantum numbers vSL specifies the states completely. Racah (Phys. Rev. 76, 1352 (1949)) introduced the seniority operator (see also Judd, "Operator Techniques in Atomic Spectroscopy".)

- Racah showed that

$$\langle l^{x-1}(\alpha' v' S' L'), l; SL | \} l^x \alpha v S L \rangle$$

$$= \begin{cases} \left[\dfrac{(4l+4-x-v)v}{2x(2l+2-v)} \right]^{1/2} \langle l^{v'}(\alpha' v' S' L'), l; SL | \} l^v \alpha v S L \rangle & v' = v-1 \\[2ex] \left[\dfrac{(x-v)(v+2)}{2x} \right]^{1/2} \langle l^{v'}(\alpha' v' S' L'), l; SL | \} l^{v+x} \alpha v S L \rangle & v' = v+1 \\[2ex] 0 \quad \text{otherwise.} \end{cases}$$

ie. for a state $|l^x \alpha v S L\rangle$, only those parent states $|l^{x-1} \alpha' v' S' L'\rangle$ ~~can contribute~~ with $v' = v \pm 1$ can contribute in the fractional parentage expansion.

Seniority Selection Rule

The matrix element of a sum of one-electron operators $F = \sum_i f(i)$ vanishes unless the initial and final states have common parent states. This can only happen if $\Delta v = 0, \pm 2$.

$$\langle l^x \alpha v S L M_S M_L | F | l^x \alpha' v' S' L' M_S' M_L' \rangle$$

$$= x \sum_{\alpha_p S_p L_p} \langle S_p L_p, l; S L M_S M_L | \overset{\vec{r}_x}{F(x)} | S_p L_p, l; S' L' M_S' M_L' \rangle$$

$$\times \langle l^x \alpha^* v^* S L \{ | l^{x-1} (\alpha_p v_p S_p L_p), l; S L \rangle$$

$$\times \langle l^{x-1} (\alpha_p v_p S_p L_p), l; S' L' | \} l^x \alpha' v' S' L' \rangle$$

$$v_p = v \pm 1 = v' \pm 1$$

For a two-electron operator such as $V = \sum_{i>j} 1/r_{ij}$,

$$\Delta v = 0, \pm 2, \pm 4.$$

What LS Terms are Possible?

e.g. p^3.

m_ℓ: 1	0	−1	$M_L = \sum m_\ell$	$M_S = \sum m_s$
↑↓	↑		2	1/2
↑↓	↓		2	−1/2
↑↓		↑	1	1/2
↑↓		↓	1	−1/2
↑	↑↓		1	1/2
↓	↑↓		1	−1/2
	↑↓	↑	−1	1/2
	↑↓	↓	−1	−1/2
↑		↑↓	−1	1/2
↓		↑↓	−1	−1/2
	↑	↑↓	−2	1/2
	↓	↑↓	−2	−1/2
↑	↑	↑	0	3/2
↑	↑	↓	0	1/2
↑	↓	↑	0	1/2
↓	↑	↑	0	1/2
↓	↓	↑	0	−1/2
↓	↑	↓	0	−1/2
↑	↓	↓	0	−1/2
↓	↓	↓	0	−3/2

Number of states

$$M_S =$$

$$M_L = \begin{array}{c|cccc} & 3/2 & 1/2 & -1/2 & -3/2 \\ \hline 2 & 0 & 1 & 1 & 0 \\ 1 & 0 & 2 & 2 & 0 \\ 0 & 1 & 3 & 3 & 1 \\ -1 & 0 & 2 & 2 & 0 \\ -2 & 0 & 1 & 1 & 0 \end{array}$$

$$= \begin{array}{c|cc} & 1/2 & -1/2 \\ \hline 1 & 1 & 1 \\ 0 & 1 & 1 \\ -1 & 1 & 1 \end{array} + \begin{array}{c|cc} & 1/2 & -1/2 \\ \hline 2 & 1 & 1 \\ 1 & 1 & 1 \\ 0 & 1 & 1 \\ -1 & 1 & 1 \\ -2 & 1 & 1 \end{array} + \begin{array}{c|cccc} & 3/2 & 1/2 & -1/2 & -3/2 \\ \hline 0 & 1 & 1 & 1 & 1 \end{array}$$

$$= \; {}^2P \; + \; {}^2D \; + \; {}^4S$$

The states ${}^4P$, ${}^4D$, ${}^2S$, ${}^4F$, ${}^2F$ are excluded by the Pauli principle.

What states are possible?

p^3

1	0	-1	M_L	M_S
↑↓	↑		2	1/2
↑↓		↑	1	1/2
↑	↑↓		1	1/2
↑	↑	↑	0	3/2
↑	↑	↓	0	1/2
↑	↓	↑	0	1/2
↓	↑	↑	0	1/2

$M_L \geq 0$,
$M_S \geq 0$.

	$M_S =$ 3/2	1/2	-1/2	-3/2
$M_L =$ 2	0	1	1	0
1	0	2	2	0
0	1	3	3	1
-1	0	2	2	0
-2	0	1	1	0

$$\# \quad \begin{matrix} | & | \\ | & | \\ | & | \\ | & | \\ | & | \end{matrix} = \begin{matrix} | & | \\ | & | \\ | & | \\ | & | \\ | & | \end{matrix} + \begin{matrix} | & | \\ | & | \\ | & | \end{matrix} + \begin{matrix} | & | & | & | \end{matrix}$$

$$= {}^2D + {}^2P + {}^4S$$

- The decomposition is not unique for more complex cases.

What States are Possible?

p^3

1	0	-1	M_L	M_S
↑↓	↑		2	1/2
↑↓	↓		2	-1/2
↑↓		↑	1	1/2
↑↓		↓	1	-1/2
↑	↑↓		1	1/2
↓	↑↓		1	-1/2
	↑↓	↑	-1	1/2
	↑↓	↓	-1	-1/2
↑		↑↓	-1	1/2
↓		↑↓	-1	-1/2
	↑	↑↓	-2	1/2
	↓	↑↓	-2	-1/2
↑	↑	↑	0	3/2
↑	↑	↓	0	1/2
↑	↓	↑	0	1/2
↓	↑	↑	0	1/2
↓	↓	↑	0	-1/2
↓	↑	↓	0	-1/2
↑	↓	↓	0	-1/2
↓	↓	↓	0	-3/2

M_S =

M_L =	3/2	1/2	-1/2	-3/2
2	0	1	1	0
1	0	2	2	0
0	1	3	3	1
-1	0	2	2	0
-2	0	1	1	0

$= {}^2D + {}^2P + {}^4S$.

- Can also be done by using the group properties of symmetric ~~rotation~~ permutation group (see Mizushima, Sect. 8-9).

Radiative Transitions

In the absence of external perturbations, the Hamiltonian for ~~one~~ one-electron atom is

$$H = + \frac{p^2}{2m} + V(r)$$
$$= + \frac{(\vec{\sigma}\cdot\vec{p})^2}{2m} + V(r)$$

since $(\vec{\sigma}\cdot\vec{A})(\vec{\sigma}\cdot\vec{B}) = \vec{A}\cdot\vec{B} + i\,\vec{\sigma}\cdot\vec{A}\times\vec{B}$.

In the presence of an electromagnetic field, the canonical momentum is $\vec{\pi} = \vec{p} - \frac{e}{c}\vec{A}$, where $\vec{A}$ = vector potential.

Then $$H = +\frac{(\vec{\sigma}\cdot\vec{\pi})^2}{2m} + V(r)$$

$$= \frac{\pi^2}{2m} + \frac{i}{2m}\vec{\sigma}\cdot\vec{\pi}\times\vec{\pi} + V(r)$$
$$= \frac{p^2}{2m} - \frac{1}{2m}\frac{e}{c}[\vec{A}\cdot\vec{p} + \vec{p}\cdot\vec{A}] + O(A^2/c^2) + O(c^{-3})$$

$$- \frac{ei}{2mc}\vec{\sigma}\cdot(\vec{p}\times\vec{A} + \vec{A}\times\vec{p}) + V(r)$$

$$\frac{e}{2mc}i\,\vec{\sigma}\cdot(\vec{p}\times\vec{A} + \vec{A}\times\vec{p}) = \frac{e\hbar}{2mc}\vec{\sigma}\cdot\vec{\nabla}\times\vec{A}$$
$$= \frac{e\hbar}{2mc}\vec{\sigma}\cdot\vec{\mathcal{H}}$$

$\vec{\mathcal{H}}$ = magnetic field.

~~[illegible]~~ We can always add $\nabla\phi(\underline{r})$ to $\vec{A}$ without physical consequences (gauge transform.) such that $\nabla\cdot\vec{A} = 0$ (Coulomb gauge or radiation gauge)

Then $H_{int} = -\frac{e}{2mc}\left[2\vec{A}\cdot\vec{p} + \hbar\vec{\sigma}\cdot\vec{\mathcal{H}} \right]$

The above applies to an electron. For an arbitrary particle, such as a nucleon,

$$H_{int} = -\frac{e}{2mc}\left[2g_L\vec{A}\cdot\vec{p} + \hbar g_s \vec{S}\cdot\vec{\mathcal{H}} \right]$$

g_s = spin g-factor such that the intrinsic magnetic moment is

$$\vec{\mu} = g_s\vec{S}\left(\frac{e\hbar}{2mc}\right) = \mu_B g_s \vec{S} \qquad \Big| \; \begin{matrix} g_s = 2 \\ g_L = 1 \end{matrix}$$

μ_B = Bohr magneton.

The Multipole Operators

- We know insert into the above the multipole expansion for the vector potential $\vec{A}_q$ describing a circularly polarized plane wave.

$\vec{A}_q(\vec{k},\vec{r}) = \vec{e}_q e^{i\vec{k}\cdot\vec{r}}$ ← definite direction $\hat{k}$ and polarization q.

$$= -\frac{1}{\sqrt{2}} \sum_{LM} \left(q A^m_{LM}(\vec{r}) + A^e_{LM}(r) \right) \mathcal{D}^L_{Mq}(R)$$

definite angular momentum + parity.

R = rotation taking z-axis to direction $\hat{k}$

$$\sqrt{L(L+1)}\ \vec{A}^m_{LM} = i^L(2L+1) j_L(kr) \vec{L}\, C_{LM}$$

and $A^e_{LM} = \frac{1}{k}\nabla\times A^m_{LM}$.

The above normalization corresponds to a flux of $(ck/2\hbar)$ photons/sec along direction $\hat{k}$.

Recall that

$$\underset{\sim}{A}_{LM} = \frac{1}{ik} \nabla \phi_{LM}$$

$$\underset{\sim}{A}^{e}_{LM} = \frac{1}{k\sqrt{L(L+1)}} \nabla \times \underset{\sim}{L}\, \phi_{LM}$$

$$A^{m}_{LM} = \frac{1}{\sqrt{L(L+1)}} \underset{\sim}{L}\, \phi_{LM}$$

$$\phi_{LM} = i^{L}(2L+1) j_{L}(kr) C_{LM}(\theta, \phi)$$

In the long wave length approx.

$$j_L(kr) \simeq (kr)^L/(2L+1)!!$$

It can be shown that

$$\nabla \times L(r^L C_{LM}) = i(L+1)\nabla(r^L C_{LM})$$

$$\therefore \underset{\sim}{A}^{e}_{LM} = \frac{1}{k\sqrt{L(L+1)}} \nabla \times \underset{\sim}{L}\left(\frac{i^L(2L+1)(kr)^L}{(2L+1)!!} C_{LM}\right)$$

$$= \frac{i}{k}\sqrt{\frac{L+1}{L}}\, \frac{(2L+1)}{(2L+1)!!} \nabla\left[(ikr)^L C_{LM}\right]$$

and $$H^{e}_{int} = -\frac{e}{2mc}\left\{\underset{\sim}{p}\cdot\underset{\sim}{A}^{e} + \underset{\sim}{A}^{e}\cdot\underset{\sim}{p}\right]$$

k = wave no. of emitted radiation (a_0^{-1}).

$\frac{\Delta E}{\hbar} = \omega$ (τ^{-1}) - frequency

$\frac{\omega}{k} = c$ (velocity of light)

$k = \frac{\omega}{c} \simeq \frac{1}{137}$.

5) The radiative transition probability between states $|\alpha\rangle$ and $\langle\beta|$ is proportional to square of matrix element

$$\langle\alpha|H^e_{int}|\beta\rangle \propto \langle\alpha|\frac{\nabla}{i}\cdot\frac{\nabla}{m}f + \nabla f\cdot\frac{\nabla}{i}|\beta\rangle$$

$$= +\langle\beta|\nabla f\cdot\frac{\nabla}{i}|\alpha\rangle^* + \langle\alpha|\nabla f\cdot\frac{\nabla}{i}|\beta\rangle$$

integrate by parts.

$$= \frac{1}{i}\left[-\langle\beta|f\nabla^2|\alpha\rangle^* + \langle\alpha|f\nabla^2|\beta\rangle\right]$$

$$f = r^L C_{LM}.$$

But $\left[-\frac{\hbar^2}{2m}\nabla^2 + V - E_\beta\right]|\beta\rangle = 0.$

$$\therefore \langle\alpha|p\cdot\nabla f + \nabla f\cdot p|\beta\rangle$$

velocity form

$$= \frac{1}{i}(E_\beta - E_\alpha)\left(\frac{2m}{\hbar^2}\right)\langle\alpha|f|\beta\rangle$$

$$= \frac{1}{i}\omega_{\beta\alpha}\left(\frac{2m}{\hbar}\right)\langle\alpha|f|\beta\rangle$$

length form.

$$\omega_{\beta\alpha} = \frac{E_\beta - E_\alpha}{\hbar}.$$

For electric dipole transitions,

$$\underset{\sim}{A} = \hat{e}_q e^{i\underset{\sim}{k}\cdot r} \simeq \hat{e}_q$$

$$\langle\alpha|H^e_{int}|\beta\rangle = -\frac{e}{2mc}\langle\alpha|2\hat{e}_q\cdot\underset{\sim}{p}|\beta\rangle$$

$$H\hat{e}\cdot\underset{\sim}{r} - \hat{e}\cdot\underset{\sim}{r}H = -\frac{\hbar^2}{2m}\left[\nabla^2\hat{e}\cdot r - \hat{e}\cdot r\nabla^2\right]$$

$$= -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\hat{e}\cdot\underset{\sim}{r}}{dr}\right) + 2\nabla(\hat{e}\cdot\underset{\sim}{r})\cdot\nabla\right]$$

$$H\,\hat{e}\cdot\underset{\sim}{r} - \hat{e}\cdot\underset{\sim}{r}\,H = -\frac{\hbar^2}{m}\,\hat{e}\cdot\nabla$$

$$= -\frac{\hbar i}{m}\,\hat{e}\cdot\underset{\sim}{p}$$

$$\therefore \langle\alpha|H^e_{int}|\beta\rangle = -\frac{e}{mc}\langle\alpha|\hat{e}\cdot\underset{\sim}{p}|\beta\rangle$$

$$= \frac{e}{mc}\cdot\frac{m}{\hbar i}\langle\alpha|H\,\hat{e}\cdot\underset{\sim}{r} - \hat{e}\cdot\underset{\sim}{r}\,H|\beta\rangle$$

$$= \frac{e}{c}\,\frac{1}{\hbar i}\,(E_\alpha - E_\beta)\langle\alpha|\hat{e}\cdot\underset{\sim}{r}|\beta\rangle$$

$$= \frac{e}{ic}\,\omega_{\alpha\beta}\langle\alpha|\hat{e}\cdot\underset{\sim}{r}|\beta\rangle$$