For example,

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

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

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

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

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

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 $|l^x \alpha SL\rangle$ can be formed from a state $|l^\nu \alpha_1 SL\rangle$ according to

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

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		

$$d: \quad {}^2D$$
$$\nu = 1$$

$$d^2: \quad {}^1S \quad {}^3P \quad {}^1D \quad {}^3F \quad {}^1G$$
$$\nu = 0 \quad 2 \quad 2 \quad 2 \quad 2$$

$$d^3: \quad {}^2P \quad {}^4P \quad {}^2D \quad {}^2D \quad {}^2F \quad {}^4F \quad {}^2G \quad {}^2H$$
$$\nu = 3 \quad 3 \quad 1 \quad 3 \quad 3 \quad 3 \quad 3 \quad 3$$

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

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

For d^x configurations, the set of quantum numbers νSL 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

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

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

i.e. for a state $|l^x \alpha \nu S L\rangle$, only those parent states $|l^{x-1} \alpha' \nu' S' L'\rangle$ ~~contribute~~ with $\nu' = \nu \pm 1$ 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 $\Delta\nu = 0, \pm 2$.

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

$$= x \sum_{\alpha_p S_p L_p} \langle S_p L_p, l; S L M_S M_L | f(x) | S_p L_p, l; S' L' M_S' M_L' \rangle$$

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

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

$$\nu_p = \nu \pm 1 = \nu' \pm 1$$

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

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

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

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

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

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

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

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

$M_S =$

$M_L =$	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

$$\# \quad \begin{array}{cc} 1 & 1 \\ 1 & 1 \\ 1 & 1 \\ 1 & 1 \\ 1 & 1 \end{array} = \begin{array}{cc} 1 & 1 \\ 1 & 1 \\ 1 & 1 \\ 1 & 1 \\ 1 & 1 \end{array} + \begin{array}{cc} 1 & 1 \\ 1 & 1 \\ 1 & 1 \end{array} + \begin{array}{cccc} 1 & 1 & 1 & 1 \end{array}$$

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

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

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

$$= \frac{p^2}{2m} - \frac{1}{2m}\frac{e}{c}[\vec{A}\cdot\vec{p} + \vec{p}\cdot\vec{A}] + \mathcal{O}(A^2/c^2) + \mathcal{O}(c^{-3})$$

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

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

$$= \frac{e\hbar}{2mc}\vec{\sigma}\cdot\vec{\mathcal{H}}$$

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

~~[illegible]~~ We can always add $\nabla\phi(r)$ 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

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

μ_B = Bohr magneton.

<u>The Multipole Operators</u>

- 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}).

$\frac{\Delta E}{\hbar} = \omega \quad (\tau^{-1})$ - 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.

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

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

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

$$\therefore \langle\alpha|\underset{\sim}{p}\cdot\nabla f + \nabla f\cdot\underset{\sim}{p}|\beta\rangle$$

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,

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

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

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

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

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

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

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

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

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

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