

For example,

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

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

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

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

• The idea can be generalized to meaning more than one particle at a time.

2-particle cfp.

- Consider the functions

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

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

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

• ~~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 $|l^y \alpha_1 SL\rangle$ according to

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

then the seniority of the state is y .

$$p: \quad \begin{array}{c} 2p \\ y = 1 \end{array}$$

$$p^2: \quad \begin{array}{ccc} 1S & 3P & 1D \\ y = 0 & 2 & 2 \end{array}$$

$$p^3: \quad \begin{array}{ccc} 2P & 2D & 4S \\ y = 1 & 3 & 3 \end{array}$$

$$p^4: \quad \begin{array}{ccc} 1S & 3P & 1D \\ y = 0 & 2 & 2 \end{array}$$

$$p^5: \quad \begin{array}{c} 2P \\ y = 1 \end{array}$$

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

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

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

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

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

For d^x configurations, the set of quantum numbers νSL specifies the states completely. Racah (Phys. Rev. ~~118~~ 76, 1352 (1949)) introduced the seniority operator (see also Judd, "Operator Techniques in Atomic Spectroscopy").

- Racah showed that

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

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

0 otherwise.

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

$$\langle l^x \alpha \nu S L M_S M_L | F | l^{x-1} \alpha' \nu' S' L' M_S' M_L' \rangle$$

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

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

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

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

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			M_L	M_S
1	0	-1	$= \sum m_l$	$= \sum m_s$
$\uparrow\downarrow$	$\uparrow$		2	$1/2$
$\uparrow\downarrow$	$\downarrow$		2	$-1/2$
$\uparrow\downarrow$		$\uparrow$	1	$1/2$
$\uparrow\downarrow$		$\downarrow$	1	$-1/2$
$\uparrow$	$\uparrow\downarrow$		1	$1/2$
$\downarrow$	$\uparrow\downarrow$		1	$-1/2$
	$\uparrow\downarrow$	$\uparrow$	-1	$1/2$
	$\uparrow\downarrow$	$\downarrow$	-1	$-1/2$
$\uparrow$		$\uparrow\downarrow$	-1	$1/2$
$\downarrow$		$\uparrow\downarrow$	-1	$-1/2$
	$\uparrow$	$\uparrow\downarrow$	-2	$1/2$
	$\downarrow$	$\uparrow\downarrow$	-2	$-1/2$
$\uparrow$	$\uparrow$	$\uparrow$	0	$3/2$
$\uparrow$	$\uparrow$	$\downarrow$	0	$1/2$
$\uparrow$	$\downarrow$	$\uparrow$	0	$1/2$
$\downarrow$	$\uparrow$	$\uparrow$	0	$1/2$
$\downarrow$	$\downarrow$	$\uparrow$	0	$-1/2$
$\downarrow$	$\uparrow$	$\downarrow$	0	$-1/2$
$\uparrow$	$\downarrow$	$\downarrow$	0	$-1/2$
$\downarrow$	$\downarrow$	$\downarrow$	0	$-3/2$

Number of states

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

$$\begin{aligned}
 &= \begin{matrix} & 1/2 & -1/2 \\ \begin{matrix} 1 \\ 0 \\ -1 \end{matrix} & \begin{bmatrix} 1 & 1 \\ 1 & 1 \\ 1 & 1 \end{bmatrix} \end{matrix} + \begin{matrix} & 1/2 & -1/2 \\ \begin{matrix} 2 \\ 1 \\ 0 \\ -1 \\ -2 \end{matrix} & \begin{bmatrix} 1 & 1 \\ 1 & 1 \\ 1 & 1 \\ 1 & 1 \\ 1 & 1 \end{bmatrix} \end{matrix} + \begin{matrix} & 3/2 & 1/2 & -1/2 & -3/2 \\ \begin{matrix} 0 \end{matrix} & \begin{bmatrix} 1 & 1 & 1 & 1 \end{bmatrix} \end{matrix} \\
 &= 2P + 2D + 4S
 \end{aligned}$$

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
$\uparrow\downarrow$	$\uparrow$			2	$\frac{1}{2}$
$\uparrow\downarrow$			$\uparrow$	1	$\frac{1}{2}$
$\uparrow$	$\uparrow\downarrow$			1	$\frac{1}{2}$
$\uparrow$	$\uparrow$	$\uparrow$		0	$\frac{3}{2}$
$\uparrow$	$\uparrow$	$\downarrow$		0	$\frac{1}{2}$
$\uparrow$	$\downarrow$	$\uparrow$		0	$\frac{1}{2}$
$\downarrow$	$\uparrow$	$\uparrow$		0	$\frac{1}{2}$

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

$M_S =$

	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$
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

$$\begin{aligned}
 & \begin{array}{c} \# \\ \\ \\ \\ \\ \end{array} \begin{array}{c} 1 \ 1 \\ 1 \ 1 \\ 1 \ 1 \\ 1 \ 1 \\ 1 \ 1 \end{array} \\
 & = \begin{array}{c} 1 \ 1 \\ 1 \ 1 \\ 1 \ 1 \\ 1 \ 1 \end{array} + \begin{array}{c} 1 \ 1 \\ 1 \ 1 \\ 1 \ 1 \end{array} + \begin{array}{c} 1 \ 1 \ 1 \ 1 \\ 1 \ 1 \end{array} \\
 & = 2D + 2P + 4S
 \end{aligned}$$

The decomposition is not unique for more complex cases.

What States are Possible?

p^3			M_L	M_S
1	0	-1		
$\uparrow\downarrow$	$\uparrow$		2	$\frac{1}{2}$
$\uparrow\downarrow$	$\downarrow$		2	$-\frac{1}{2}$
$\uparrow\downarrow$		$\uparrow$	1	$\frac{1}{2}$
$\uparrow\downarrow$		$\downarrow$	1	$-\frac{1}{2}$
$\uparrow$	$\uparrow\downarrow$		1	$\frac{1}{2}$
$\downarrow$	$\uparrow\downarrow$		1	$-\frac{1}{2}$
	$\uparrow\downarrow$	$\uparrow$	-1	$\frac{1}{2}$
	$\uparrow\downarrow$	$\downarrow$	-1	$-\frac{1}{2}$
$\uparrow$		$\uparrow\downarrow$	-1	$\frac{1}{2}$
$\downarrow$		$\uparrow\downarrow$	-1	$-\frac{1}{2}$
	$\uparrow$	$\uparrow\downarrow$	-2	$\frac{1}{2}$
	$\downarrow$	$\uparrow\downarrow$	-2	$-\frac{1}{2}$
$\uparrow$	$\uparrow$	$\uparrow$	0	$\frac{3}{2}$
$\uparrow$	$\uparrow$	$\downarrow$	0	$\frac{1}{2}$
$\uparrow$	$\downarrow$	$\uparrow$	0	$\frac{1}{2}$
$\downarrow$	$\uparrow$	$\uparrow$	0	$\frac{1}{2}$
$\downarrow$	$\downarrow$	$\uparrow$	0	$-\frac{1}{2}$
$\downarrow$	$\uparrow$	$\downarrow$	0	$-\frac{1}{2}$
$\uparrow$	$\downarrow$	$\downarrow$	0	$-\frac{1}{2}$
$\downarrow$	$\downarrow$	$\downarrow$	0	$-\frac{3}{2}$

		M_S			
		$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$
$M_L =$	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

$$= 2D + 2P + 4S$$

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

Radiative Transitions

In the absence of external perturbations, the Hamiltonian for an 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 $H = + \frac{(\vec{\sigma} \cdot \vec{\pi})^2}{2m} + V(r)$

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

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

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

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

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

NOTE: 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)

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

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

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

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

$$\vec{\mu} = g_S \vec{S} \left(\frac{e\hbar}{2mc} \right) = \mu_B g_S \vec{S} \quad \left| \begin{array}{l} g_S = 2 \\ g_L = 1 \end{array} \right.$$

μ_B = Bohr magneton.

The Multipole Operators

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

$$\vec{A}_g(\vec{k}, \vec{r}) = \vec{e}_g e^{i\vec{k} \cdot \vec{r}} \leftarrow \begin{array}{l} \text{definite direction } \vec{k} \text{ and} \\ \text{polarization } g. \end{array}$$

$$= - \frac{1}{\sqrt{2}} \sum_{LM} \left(g A_{LM}^m(\vec{r}) + A_{LM}^e(r) \right) D_{Mg}^L(R)$$

definite angular momentum
+ parity

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

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

$$\text{and } A_{LM}^e = \frac{1}{k} \nabla \times A_{LM}^m.$$

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

Recall that

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

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

$$A_{LM}^m = \frac{1}{\sqrt{L(L+1)}} \underline{L} \phi_{LM}$$

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

In the long wave length approx.

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

It can be shown that

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

$$\begin{aligned} \therefore \underline{A}_{LM}^e &= \frac{1}{k \sqrt{L(L+1)}} \nabla \times \underline{L} \left(\frac{i^L (2L+1) (kr)^L}{(2L+1)!!} C_{LM} \right) \\ &= \frac{i}{k} \sqrt{\frac{L+1}{L}} \frac{(2L+1)}{(2L+1)!!} \nabla \left[(ikr)^L C_{LM} \right] \end{aligned}$$

$$\text{and } H_{int}^e = -\frac{e}{2mc} \left[\underline{\vec{p}} \cdot \underline{\vec{A}}^e + \underline{\vec{A}}^e \cdot \underline{\vec{p}} \right]$$

k = wave no. of emitted radiation (ao^{-1}).
 $\frac{AE}{h} = \omega$ (ao^{-1}) - frequency

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

$$k = \frac{\omega}{c} \approx \frac{1}{137}$$

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

$$\langle \alpha | H_{int}^e | \beta \rangle \propto \langle \alpha | \frac{\nabla \cdot \nabla}{i} F + \nabla F \cdot \frac{\nabla}{i} | \beta \rangle$$

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

integrate by parts.

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

$$F = r^2 C_{LM}$$

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

$$\therefore \langle \alpha | \underline{p} \cdot \nabla F + \nabla F \cdot \underline{p} | \beta \rangle$$

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,

$$\underline{A} = \hat{e}_q e^{i \underline{k} \cdot \underline{r}} \approx \hat{e}_q$$

$$\langle \alpha | H_{int}^e | \beta \rangle = -\frac{e}{2mc} \langle \alpha | 2 \hat{e}_q \cdot \underline{p} | \beta \rangle$$

$$\underline{H}_{int} - \hat{e}_q \cdot \underline{r} H = -\frac{\hbar^2}{2m} \left[\nabla^2 \hat{e}_q \cdot \underline{r} - \hat{e}_q \cdot \nabla^2 \underline{r} \right]$$

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

$$\begin{aligned}
 H \hat{e} \cdot \underline{r} - \hat{e} \cdot \underline{r} H &= -\frac{\hbar^2}{m} \hat{e} \cdot \nabla \\
 &= -\frac{\hbar}{m} i \hat{e} \cdot \underline{p}
 \end{aligned}$$

$$\therefore \langle \alpha | H_{int}^e | \beta \rangle = -\frac{e}{mc} \langle \alpha | \hat{e} \cdot \underline{p} | \beta \rangle$$

$$= \frac{e}{mc} \frac{m}{\hbar^2 i} \langle \alpha | H \hat{e} \cdot \underline{r} - \hat{e} \cdot \underline{r} H | \beta \rangle$$

$$= \frac{e}{c} \frac{1}{\hbar^2 i} (E_\alpha - E_\beta) \langle \alpha | \hat{e} \cdot \underline{r} | \beta \rangle$$

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