6.3 H-atom energy levels with spin-orbit coupling (Z=1)

$$E(n,\ell,s,j) = -\frac{e^2}{2n^2 a_o (4\pi\varepsilon_o)} + hc\alpha^2 R_\infty \frac{1}{2}\left\{\frac{j(j+1)-\ell(\ell+1)-s(s+1)}{n^3\ell\left(\ell+\frac{1}{2}\right)(\ell+1)}\right\}$$

$$= -\frac{e^2}{2n^2 a_o (4\pi\varepsilon_o)} + hc\,\xi_{n,\ell}\frac{1}{2}\left[j(j+1)-\ell(\ell+1)-s(s+1)\right]$$

1s orbital: $n=1\ \ \ell=0\ \ s=\frac{1}{2}\ \ j=\frac{1}{2}$ therefore, no SO coupling since l = 0

$$\therefore E_{1,0,\frac{1}{2},\frac{1}{2},m_j} = -\frac{e^2}{2a_o(4\pi\varepsilon_o)}$$

:2 degenerate states with $m_j = \pm ½$

2s orbital: $n=2 \;\; \ell=0 \;\; s=\frac{1}{2} \;\; j=\frac{1}{2}$ therefore, no SO coupling since l = 0

$$\therefore E_{2,0,\frac{1}{2},\frac{1}{2},m_j} = -\frac{e^2}{8a_o(4\pi\varepsilon_o)}$$:2 degenerate states with $m_j = \pm ½$

2p orbital: $n=2 \;\; \ell=1 \;\; s=\frac{1}{2}$ 1.) $j=\frac{3}{2};\; m_j=\pm\frac{3}{2},\pm\frac{1}{2}$:4 degenerate levels

$$\therefore E_{2,1,\frac{1}{2},\frac{3}{2},m_j} = -\frac{e^2}{8a_o(4\pi\varepsilon_o)} + hc\xi_{2,1}\frac{1}{2}\left[\underbrace{\left(\frac{3}{2}\right)\left(\frac{5}{2}\right)-(1)(2)-\left(\frac{1}{2}\right)\left(\frac{3}{2}\right)}_{=1}\right]$$

$$= -\frac{e^2}{8a_o(4\pi\varepsilon_o)} + \frac{1}{2}hc\xi_{2,1}$$

$$= -\frac{e^2}{8a_o(4\pi\varepsilon_o)} + \frac{1}{2}hc\alpha^2 R_\infty \frac{1}{(8)(1)\left(\frac{3}{2}\right)(2)}$$

$$= -\frac{e^2}{8a_o(4\pi\varepsilon_o)} + \frac{1}{3}\frac{hc}{16}\alpha^2 R_\infty$$

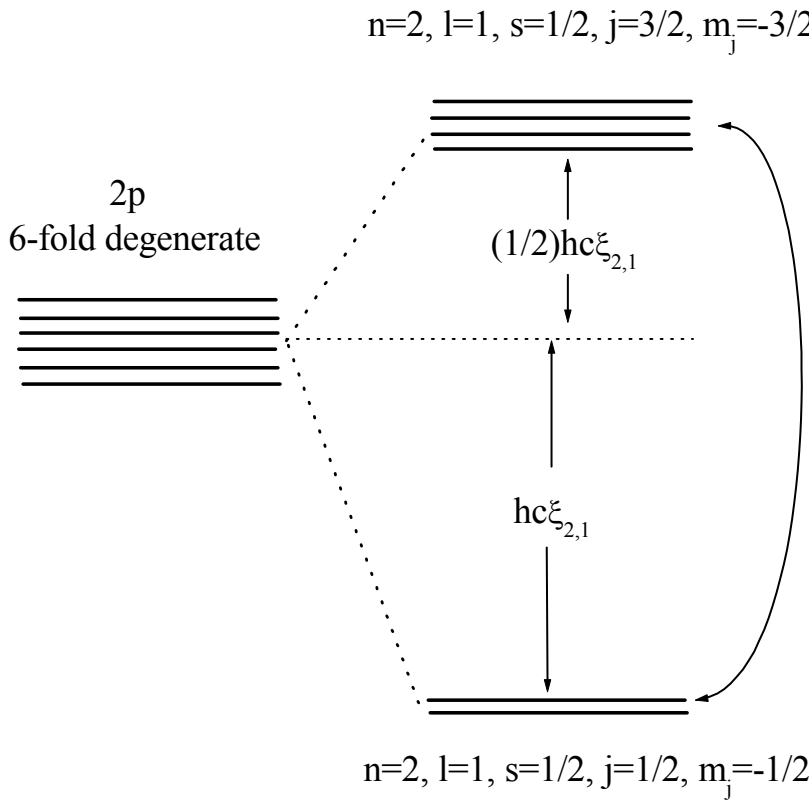
2p orbital: $n=2 \;\; \ell=1 \;\; s=\frac{1}{2}$ 2.) $j=\frac{1}{2};\; m_j=\pm\frac{1}{2}$:2 degenerate levels

$$\therefore E_{2,1,\frac{1}{2},\frac{1}{2},m_j} = -\frac{e^2}{8a_o(4\pi\varepsilon_o)} + hc\xi_{2,1}\frac{1}{2}\left[\underbrace{\left(\frac{1}{2}\right)\left(\frac{3}{2}\right)-(1)(2)-\left(\frac{1}{2}\right)\left(\frac{3}{2}\right)}_{=-2}\right]$$

$$= -\frac{e^2}{8a_o(4\pi\varepsilon_o)} - hc\xi_{2,1}$$

$$= -\frac{e^2}{8a_o(4\pi\varepsilon_o)} - \frac{2}{3}\frac{hc}{16}\alpha^2 R_\infty$$

These 2 degenerate levels are lower in energy by $hc\xi_{2,1}$

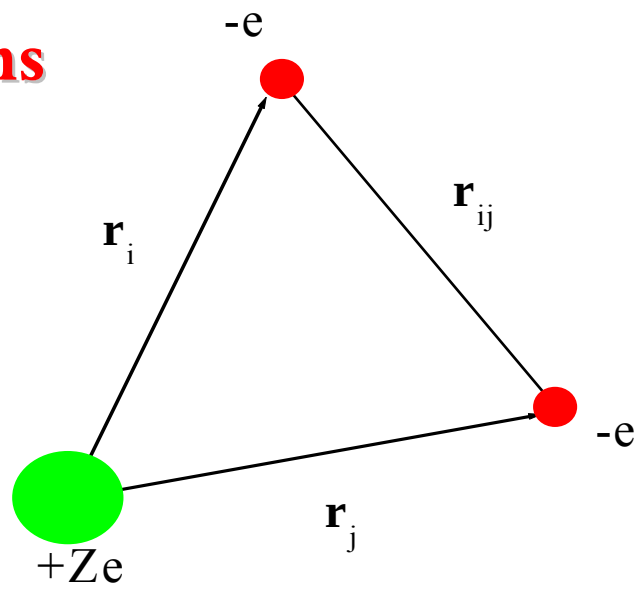


$$\frac{3}{2}hc\xi_{2,1} = \frac{hc}{16}R_\infty\alpha^2 = \left(0.365\,cm^{-1}\right)hc$$

Compare with $\Delta E_{n_2,n_1} = hcR_\infty\left\{\frac{1}{n_1^2} - \frac{1}{n_2^2}\right\} = hc\cdot 0.75R_\infty = \left(82{,}303\ cm^{-1}\right)hc$

Splitting is small (but measurable).

7: Many electron atoms



7.1: The Hamiltonian:

$$\hat{H} = \hat{T} + \hat{V} = \underbrace{-\frac{\hbar^2}{2m_e}\sum_{j=1}^{N}\vec{\nabla}_j^2}_{\text{kinetic energy}} + \underbrace{\sum_{j=1}^{N}\left(-\frac{Ze^2}{r_j}\right)}_{\substack{\text{Coulomb potential energy} \\ \text{nucleus–electron} \\ \text{attractive}}} + \underbrace{\sum_{i>j}^{N}\frac{e^2}{r_{ij}}}_{\substack{\text{Coulomb potential energy} \\ \text{electron–electron} \\ \text{repulsive}}}$$

7.2-i: The Angular Momenta: first scheme

$$\vec{L} = \sum_i \vec{\ell}_i$$ = total orbital angular momentum

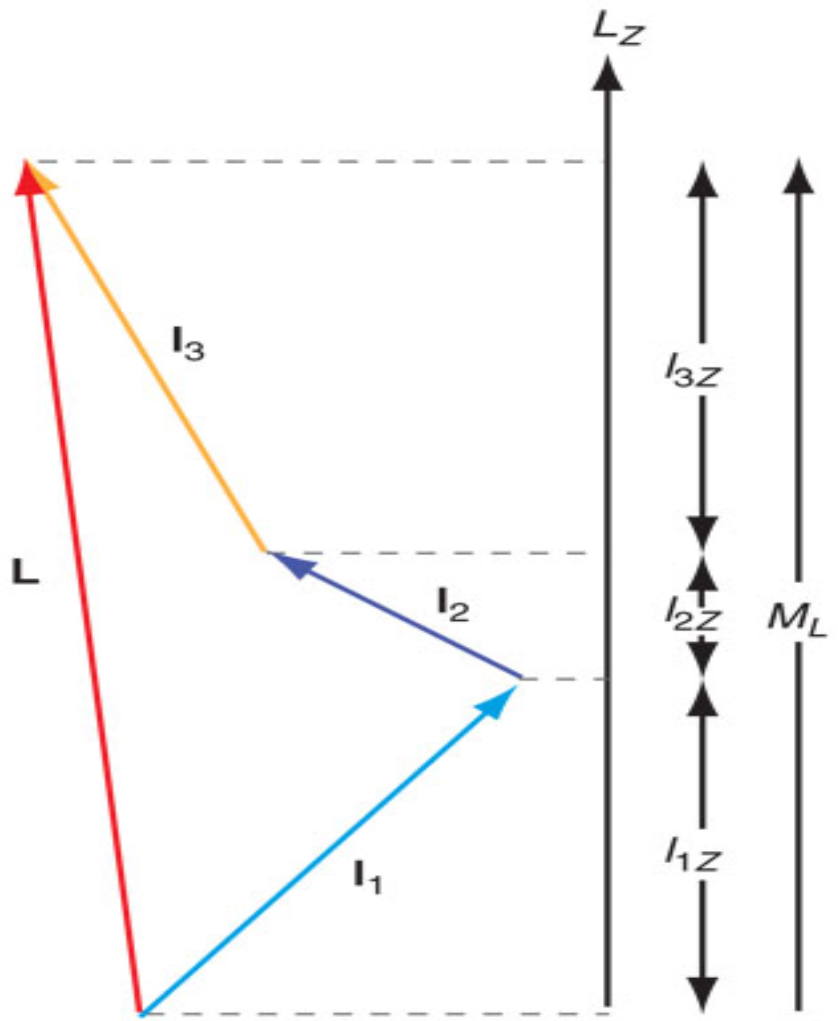
$$\vec{S} = \sum_i \vec{s}_i$$ = total spin angular momentum

$$\vec{J} = \vec{L} + \vec{S} = \sum_i \vec{\ell}_i + \sum_i \vec{s}_i$$ = total angular momentum
= Russell-Saunders or L-S coupling scheme
= good for atom with Z~< 40

$$\vec{L}_z = \sum_i \vec{L}_{iz} = \frac{\hbar}{i} \sum_i \left(x_i \frac{\partial}{\partial y_i} - y_i \frac{\partial}{\partial x_i} \right)$$

$$\vec{S}_z = \sum_i \vec{s}_{iz}$$

3 orbital angular momenta showing how $M_L = \sum_i m_{\ell_i}$



7.2-ii: Angular Momentum: second scheme

$$\vec{j}_i = \vec{\ell}_i + \vec{s}_i$$ for each electron

$$\vec{J} = \sum_i \vec{j}_i$$

= j-j coupling scheme
= important when spin-orbit interactions are large
= important for heavier element Z~>40.

7.3: Commutators: No LS coupling

$\hat{H}, \hat{L}^2, \hat{S}^2, \hat{L}_z, \hat{S}_z, \hat{\Pi}$ form a set of commuting, self-adjoint operators

Operator	*Eigenvalues*
$\hat{H}$	E
$\hat{L}^2$	$L(L+1)\hbar^2$
$\hat{S}^2$	$S(S+1)\hbar^2$
$\hat{L}_z$	$M_L\hbar$
$\hat{S}_z$	$M_S\hbar$
$\hat{\Pi}$	I

The wave functions depend on quantum numbers: E, L,S, M_L, M_S, I $\Rightarrow |E, L, S, M_L, M_S, I>$

The wave functions are orthonormal so

$$<E,L,S,M_L,M_S,I\,|\,E',L',S',M_L',M_S',I'>=\delta_{EE}\delta_{LL'}\delta_{SS'}\delta_{M_LM_L'}\delta_{M_SM_S'}\delta_{II'}$$

and

$$\hat{L}_+\,|\,E,L,S,M_L.M_S,I>=\sqrt{(L+M_L+1)(L-M_L)}\hbar\,|\,E,L,S,(M_L+1),M_S,I>$$

$$\hat{L}_-\,|\,E,L,S,M_L.M_S,I>=\sqrt{(L-M_L+1)(L+M_L)}\hbar\,|\,E,L,S,(M_L-1),M_S,I>$$

$$\hat{S}_+\,|\,E,L,S,M_L.M_S,I>=\sqrt{(S+M_S+1)(S-M_S)}\hbar\,|\,E,L,S,M_L,(M_S+1),I>$$

$$\hat{S}_-\,|\,E,L,S,M_L.M_S,I>=\sqrt{(S-M_S+1)(S+M_S)}\hbar\,|\,E,L,S,M_L,(M_S-1),I>$$

7.4: Eigenvalues, No LS coupling

a.) L = integer ≥ 0

$$\ell_1, \ell_2 \Rightarrow L' = \ell_1 + \ell_2, \ell_1 + \ell_2 - 1, \ldots, |\ell_1 - \ell_2| \geq 0$$

$$L', \ell_3 \Rightarrow L = L' + \ell_3, L' + \ell_3 - 1, \ldots |L' - \ell_3|, \ \textit{etc.}$$

$$M_L = -L, \_ L+1, \ldots L-1, L$$

b.) S = integer of half-integer ≥ 0

$$N = 2 : s_1, s_2 \Rightarrow S = 1, 0$$

$$N = 3 : s_1, s_2, s_3 \Rightarrow S = \frac{3}{2}, \frac{1}{2} (\times 2)$$

$$N = 4 : s_1, s_2, s_3, s_4 \Rightarrow S = 2, 1 (\times 3), 0 (\times 2)$$

Therefore if the number of electrons N is even S = integer ≥ 0, and if the number of electrons N is odd S =half- integer ≥ 0

c.) E = E(L,S,I): (2L+1) fold-degenerate in M_L and (2S+1) fold-degenerate in M_S

7.5: Selection Rules: No LS coupling, electric-dipole induced,

$$\Delta L = 0, \pm 1 \qquad \Delta \ell = \pm 1$$

$$\Delta M_L = 0, \pm 1 \qquad \Delta m_\ell = 0, \pm 1$$

$$\Delta S = 0 \qquad \Delta s = 0$$

$$\Delta M_S = 0 \qquad \Delta m_s = 0$$

$$\Delta I \neq 0 \qquad \Delta I \neq 0$$

Compare with those for H-like (one electron) systems:

$\Delta \ell \neq 0$ for H-atom since $I = (-1)^\ell$ and therefore parity forbids this.

In multielectron systems $I \neq (-1)^L$ and so this restriction on L is gone.

Here parity is determined by an algebraic sum as: $I = (-1)^{\sum_j \ell_j}$

However, both states in transition cannot have L = 0, M_L =0

7.6: Commutators with LS coupling (Russell-Saunders)

$\hat{H}, \hat{L}^2, \hat{S}^2, \hat{J}^2, \hat{J}_z, \hat{\Pi}$ form a set of commuting, self-adjoint operators

Operator	*Eigenvalue* *s*
$\hat{H}$	E
$\hat{L}^2$	$L(L+1)\hbar^2$
$\hat{S}^2$	$S(S+1)\hbar^2$
$\hat{J}^2$	$J(J+1)\hbar^2$
$\hat{J}_z$	$M_J\hbar$
$\hat{\Pi}$	I

The wave functions depend on quantum numbers: E, L,S, J, M_J, I

$$\Rightarrow | E, L, S, J, M_J, I >$$

The wave functions are orthonormal so

$$<E,L,S,J,M_J,I\,|\,E',L',S',J',M_J',I'>=\delta_{EE'}\delta_{LL'}\delta_{SS'}\delta_{JJ'}\delta_{M_JM_J'}\delta_{II'}$$

7.7: Eigenvalues, with LS coupling

L = integer ≥ 0
S = integer ≥ 0 for an even number of electrons
S = half-integer ≥ 0 for an odd number of electrons

$$J = L+S, L+S-1, \ldots, |L-S|$$

= integer ≥ 0 if S is an integer
= half-integer ≥ 0 if S is a half-integer

$$M_J = -J, -J+1, \ldots, J-1, J$$

7.8: Selection rules with LS coupling

$$\Delta J = 0, \pm 1$$

$$\Delta M_J = 0, \pm 1$$

$$\Delta L = 0, \pm 1$$

$$\Delta S = 0$$

$$\Delta I \neq 0$$

But J = 0 → J' = 0 is forbidden.