

Lecture 15: Spectra of Multielectron Atoms

In Lect. 9 we studied the selection rules for multiple radiation in hydrogenic (single electron) atoms. These were relatively straightforward because

- (i) Only one electron reacts in response to radiation
- (ii) The quantum numbers are exact

For multi-electron atoms the situation is much more complicated because in principle many electrons can participate in radiation, and we can only approximately label the quantum numbers (e.g. Russell-Saunders).

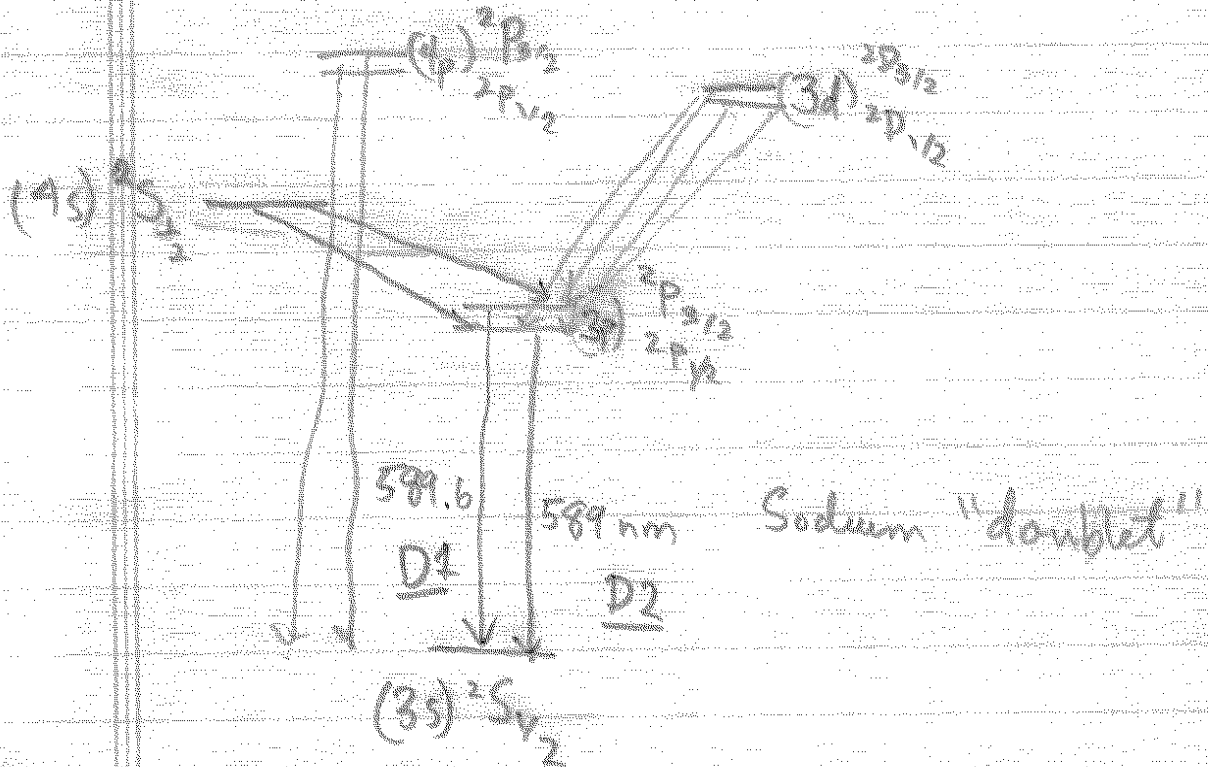
Here we will consider situations of single photon transitions where only one of electrons in a configuration is "optically active" and where L-S coupling is a good approximation. We then seek selection rules. Some of these are only approximate, to the degree that quantum numbers are approximate. In addition, it may be the case that a multiphoton transition could drive an otherwise forbidden transition.

Alkalies

The Group I elements have only one electron in the valence shell. As such the terms are Hydrogenic: $^2L_{1/2, 3/2}$, the difference with hydrogen being the radial wave function due to the non $1/r$ potential near the core so that lower l have lower energy.

Ex: Sodium $[\overset{Ne}{(2s)^2(2p)^6}] 3s$ ground state
 nl excited state

Excluding hyperfine structure



Dominant electric dipole transition

The energy levels of of alkalis empirically follow a Hydrogen-like formula

$$E_{nl} = -\frac{1}{2} \frac{1}{(n-\mu_{nl})^2} \text{ a.u.}$$

μ_{nl} is known as the "quantum defect".
For the core close to spherically symmetric,
 $\mu_{nl} \cong \alpha(l)$, only depending on l

More general Case: Selection rules for LS coupling

We find selection rules based on symmetries

- Space inversion
- Rotation

The first is parity, the second is angular mom

The multipole ~~operator~~ operators T_q are tensors "under rotation" by same angular momentum. In addition, they are even or odd under parity

E1: Electric Dipole $\vec{d} = \sum_i e \vec{r}_i$

\vec{d} : Vector under \vec{L} and \vec{J}
Odd under parity

$$\Rightarrow \Delta J = 0, \pm 1 \quad (\text{no } J=0 \rightarrow J'=0)$$

$$\Delta L = 0, \pm 1 \quad (\text{no } L=0 \rightarrow L'=0)$$

$$\Delta S = 0$$

$$\Delta M_J = 0, \pm 1 \quad (\text{according to polarization})$$

Note: Parity $\neq (-1)^L$, parity = $\prod_i (-1)^{l_i}$

Opposite parity couples only

For single electron only $\Delta l_i = \pm 1$ $\Pi = (-1)^l$

M1: Magnetic dipole

$\vec{\mu}$: Vector under \vec{S} and \vec{J}
Even under parity

$$\Rightarrow \Delta J = 0, \pm 1 \quad (\text{no } J=0 \rightarrow J'=0)$$

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

Even parity only

with L-S

Since total magnetic moment per electron

$$\vec{\mu} = \mu_B (\vec{L} + 2\vec{S})$$

$$\Rightarrow \text{Summed over all electrons } \vec{\mu} = \mu_B (\vec{L} + 2\vec{S})$$

These M1 transitions involve matrix element

$$\langle \psi_{\text{final}} | \vec{\mu} \cdot \vec{B} | \psi_{\text{initial}} \rangle = \mu_B \langle \psi_f | (\vec{L} + 2\vec{S}) | \psi_i \rangle \cdot \vec{B}$$

$$\text{But } [\hat{L}^2, \hat{L}] = 0 \quad \text{and} \quad [\hat{S}^2, \hat{S}] = 0$$

$$\Rightarrow \Delta S = 0 \quad \Delta L = 0$$

Moreover, when decomposed into single particle orbitals, $\Delta l = 0$, $\Delta m_l = 0, \pm 1$, $\Delta m_s = 0, \pm 1$

But no change in radial motion $\Delta n = 0$

\Rightarrow In pure L-S coupling only transitions within a given configuration of levels with the same L-S

\Rightarrow Between different fine-structure states within a multiplet satisfying $\Delta J = 0, \pm 1$

Note: With hyperfine interaction

$$\vec{\mu} = \vec{L} + 2\vec{S} + g_I \vec{I}$$

Vector under $\vec{F} = \vec{L} + \vec{S} + \vec{I}$

$\Rightarrow \Delta F = 0, \pm 1$ (no $F=0 \rightarrow F'=0$)

Can have transition between different hyperfine levels within the same LSJ

E2: Electric Quadrupole

\hat{Q} Rank 2 tensor under \hat{L} and \hat{J} (rank under \hat{J})

$$\rightarrow \Delta L = 0, \pm 1, \pm 2 \quad (\text{no } 0 \rightarrow 0)$$

$$\Delta J = 0, \pm 1, \pm 2$$

$$\Delta M_J = 0, \pm 1, \pm 2$$

Even parity transitions

For single electron $\Delta l_i = 0, \pm 2$ ($l_i = 0 \rightarrow l'_i = 0$)

Example, Oxygen: $[1s^2 2s^2] 2p^4$

Terms $3P, 1D, 1S$



Including hyperfine

$$\Delta F = 0, \pm 1, \pm 2 \quad (F + F' \geq 2)$$

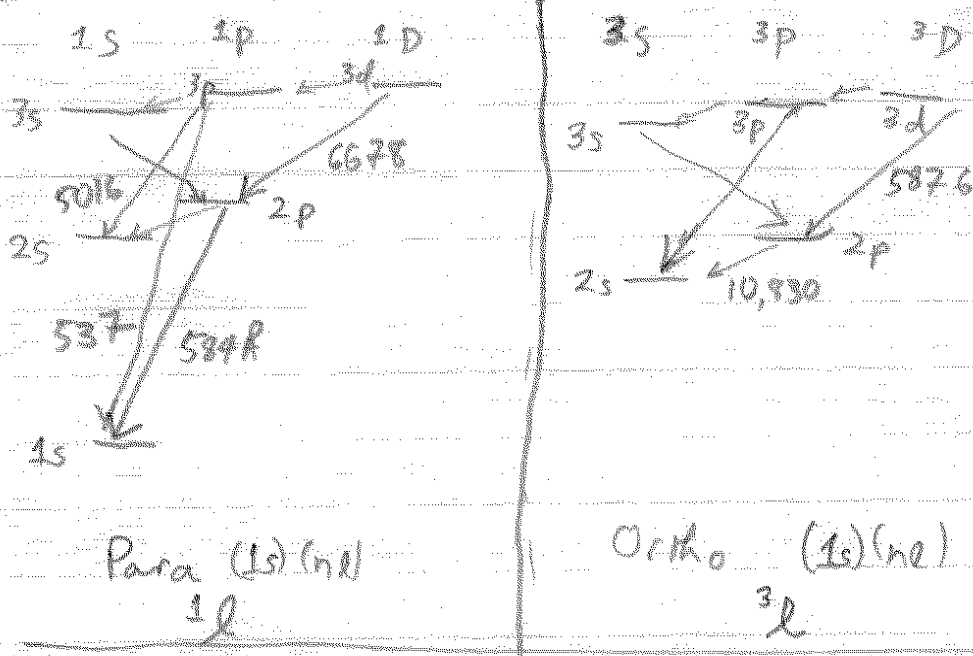
$$\Delta M_F = 0, \pm 2$$

Examples: Helium and Alkaline-Earth atoms

We saw in Lecture 11 that the bound configurations of He are $1s nl$, with $(1s)^2$ the Ground state.

For given config $(1s)nl$, two Terms 3l and 1l except for ground state which is 1s .

To the degree L-S coupling correct, no transitions possible triplet to singlet (ortho to para)



The Fine structure splitting in L-S coupling $H_2 \sim \vec{L} \cdot \vec{S}$, where A depends on l

For He, not very strong: Compton effect

Electron-electron spin interactions $r^{-5} \vec{S}_1 \cdot \vec{S}_2 + 3(r^{-5} \vec{S}_1 \cdot \vec{r})(\vec{S}_2 \cdot \vec{r})$

Cross spin orbit $\vec{L}_1 \cdot \vec{S}_2 \Rightarrow$ Break down of Landé interval rule

Alkaline Earths: (Group II elements)

Like Helium valence subshell $(ns)^2$

$n=2$ Be

$n=3$ Mg

$n=4$ Ca

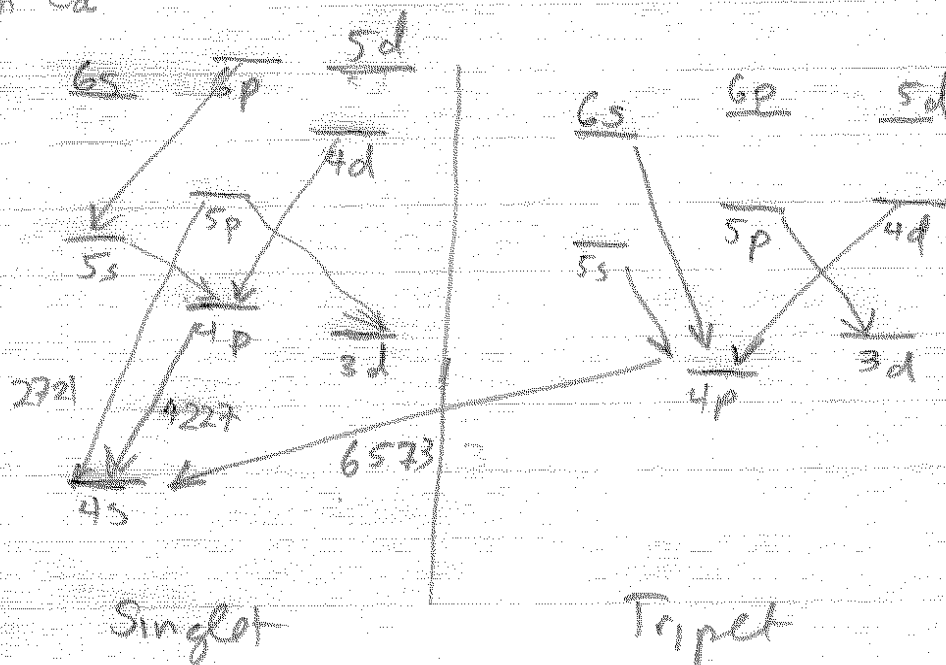
$n=5$ Sr

Differences: Stronger spin-orbit coupling

⇒ Singlet-Triplet mixing

⇒ "Intercombination line"

Energy level diagram for Ca for one optically excited electron in Ca

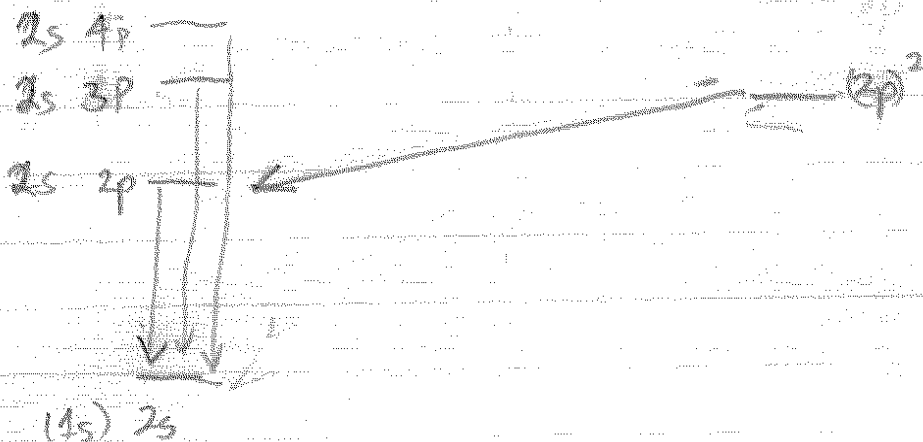


Intercombination line at 6573 \AA

Other differences: doubly excited configurations bound
 \Rightarrow Displaced series

Example: Be $(1s)^2(2s np) \rightarrow (1s)(2s)^2$ (single excited)

Displaced series $(1s)(2p ns) \rightarrow (1s)^2(2p)^2$



$(1s)^2(2s nl)$
 Singlet

$(1s)(2p nl)$
 Singlet

Example: Optical Clock: Ca $[3p^5](nl)nl'$ $\rightarrow Kr$

