Atoms and Nuclei
PA 322

Lecture 7

Unit 1: Recap
Unit 2: Spectrum of the Helium atom

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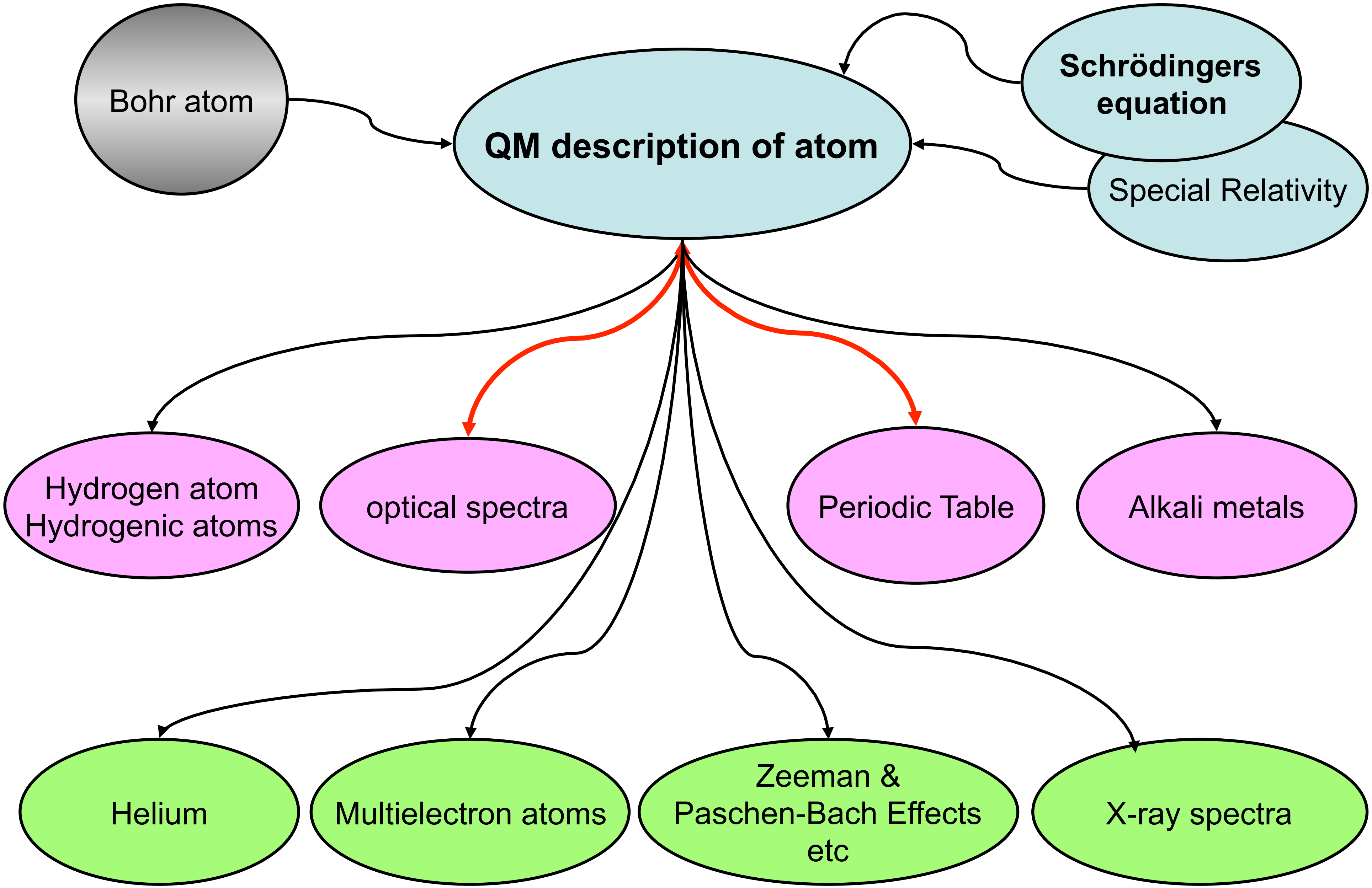
Lecture notes

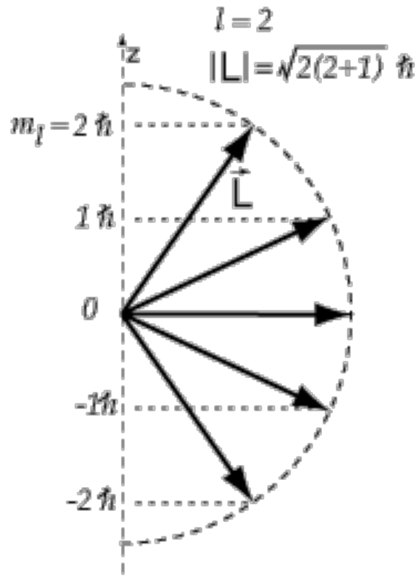
- Available at:

http://www.star.le.ac.uk/~nrt3/322


Bohr atom
QM description of atom
Schrödingers equation
Special Relativity
Hydrogen atom Hydrogenic atoms
optical spectra
Periodic Table
Alkali metals
Helium
Multielectron atoms
Zeeman & Paschen-Bach Effects etc
X-ray spectra

Terminology: Quantum Numbers

Quantum no.	Name	Allowed values for electron	Amplitudes
n	principal	any +ve integer: 1 … ∞	
l	orbital angular momentum	l=0, 1, … n-1	$\lvert\mathbf{l}\rvert = \sqrt{l(l+1)}\hbar$
s	spin	s=1/2	$\lvert\mathbf{s}\rvert = \sqrt{s(s+1)}\hbar$
m_l	orbital magnetic	m_l = -l, … +l (integer steps)	$l_z = m_l\hbar$
m_s	spin magnetic	m_s= ± s = ± 1/2	$s_z = m_s\hbar$
j	total angular momentum	j = | l - s | … (l + s) (integer steps) j = l ±1/2 for single electron	$\lvert\mathbf{j}\rvert = \sqrt{j(j+1)}\hbar$
m_j	total angular momentum projection	m_j= -j, … +j (integer steps)	$j_z = m_j\hbar$



Terminology: shells, subshells etc.

Concept	Related quantum numbers	Notes
shell	n	all levels with same n belong to the same shell
sub-shell	n, l	all levels with the same n, l belong to the same sub-shell

Also

term: configuration with specific (n, l, s) split into levels with different j

Alternative notation for shells

For convenience & brevity, the **shells** are sometimes specified by an upper-case letter

value of n	1	2	3	4	5	6	7
letter code for shell	K	L	M	N	O	P	Q

Use particularly in context of X-ray spectra
(For example one might see expressions like ***K-shell*** *photoelectric absorption edge*...)

Terminology:
notation for subshells

The configuration of the N equivalent electrons in a given sub-shell is usually written as

$\boxed{n\,l^{N}}$ eg $\boxed{3p^{6}}$

where

- n is the principal quantum number (a positive integer, as above)
- l is a letter used to specify the value of the orbital angular momentum quantum number (allowed values $l = 0, 1, ..., n - 1$)

value of l	0	1	2	3	4	5	6	7	8
letter code	s	p	d	f	g	h	i	k	l

The superscript value for N is often omitted if $N = 1$.

Terminology:
notation for *terms*

The combination of quantum numbers for a specific configuration of optically active electron(s) can be written as a *spectroscopic term symbol* :

$\boxed{{}^{2S+1}\mathrm{L}_J}$ e.g. $\boxed{{}^{2}\mathrm{P}_{3/2}}$

where

- S is the spin quantum number & $(2S+1)$ is the spin multiplicity ($=2$ for a single electron $\Rightarrow$ called ‘doublet’)
- L is the letter used to specify the value of the orbital angular momentum quantum number (in upper case)
- J is the total angular momentum quantum number

Important concepts for multi-electron atoms

- Need to work out how spin and orbital angular momenta couple together for multiple optically active electrons. Two approximation schemes are used for different situations:
  - LS coupling: coupling between *combined* orbital and spin angular momenta $\mathbf{L} = \Sigma\, \mathbf{l}_i\, ; \mathbf{S} = \Sigma\, \mathbf{s}_i\, ; \mathbf{J} = \mathbf{L} + \mathbf{S}$ *(vector sums)*
    - strong electron-electron interactions 'break' individual spin-orbit coupling
  - j-j coupling: strong spin-orbit coupling of individual electrons, net combined angular momenta couple $\mathbf{J} = \Sigma\, \mathbf{j}_i$

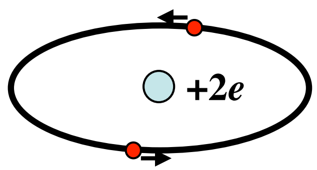
Note, vectors are bold

Note, use of capitals to distinguish **total** from **individual** QNs

  - LS coupling dominates for low Z elements (and for low n orbitals)

Helium

- Basic facts
  - Helium discovered as element late (1868) – first detected in spectrum of Sun (hence name)
  - not isolated as terrestrial element in 1895 – second lightest element
  - optical spectrum difficult to understand:
    - two distinct families of lines (but not two different elements!)



Spectrum of the Helium atom

- Context
  - atoms considered in Unit 1: hydrogen, hydrogenic species, alkali metals
  - all had *single* electron in outer shell
    - outermost electron essentially independent of inner electrons in their closed shells
    - **magnetic moments from orbital and spin angular momenta in closed shells cancel out**
  - but we now know helium has $1\mathrm{s}^2$ configuration, i.e. two (potentially active) electrons in outer shell
    - $\Rightarrow$ more complexity $\Rightarrow$ introduction to multi-electron atoms

Important concepts for helium

- Energy state for electrons in helium:

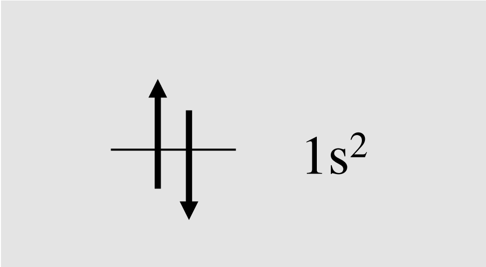
$$E = E(n,l) + E_{\text{so}} + E_{\text{opt.el.}}$$

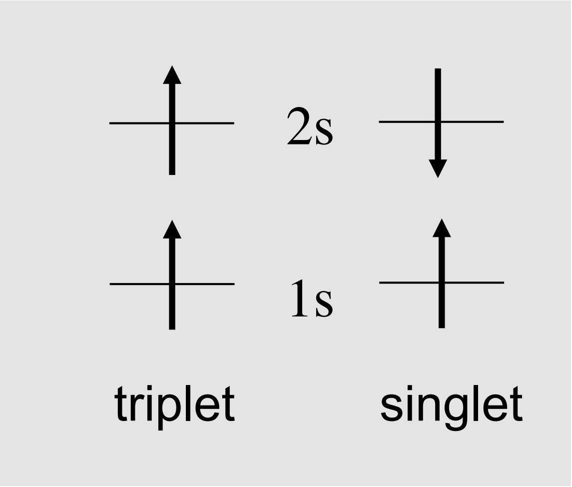
binding to nucleus (Schr. eqn.)	spin-orbit coupling	electron interactions (electrostatic)

- In fact, here we will mainly be concerned with the splitting of energy levels and their relative positioning.

Total spin angular momentum

- *Total* spin angular momentum in helium
  - two electrons in ground state must have m_s= +½ and m_s=- ½ (Pauli Exclusion Principle)
  - in ground configuration spins paired, i.e. anti-parallel and resultant magnetic moment is zero
  - excited states (e.g. 1s2s …) can have spins parallel or anti-parallel
    - parallel spins: triplet states
    - anti-parallel spins: singlet states





Total spin angular momentum
(for helium)

- Must consider total spin angular momentum $\mathbf{S} = \mathbf{s_1} + \mathbf{s_2}$ (vector sum)

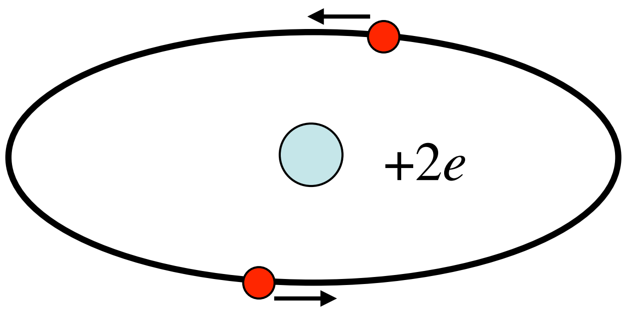
- Related *total* spin angular momentum *quantum number* S:
  - amplitude of spin vector $|\mathbf{S}| = [S(S+1)]^{1/2}\,\hbar$

- In case of 2 electrons in helium possibilities are
  - $s_1 = s_2 = 1/2 \Rightarrow S = 0$ or $S = 1$

- total spin angular momentum has $2S+1$ quantised components characterised by quantum number $m_S = -S, \ldots +S$
  - for $S = 0$ single component $(2S+1=1)$ hence *singlet* state
  - for $S = 1$ three components $(2S+1=3)$ hence *triplet* state

Energy difference between singlet and triplet states

- Singlet and triplet states have different energies because the electrons in these states have different spatial distributions
  - crudely speaking triplet states have *lower* energies because electrons are "more separated": lower probability of being in close proximity (recall electrostatic repulsion $\propto 1/r^2$)
  - full QM treatment in terms of *Coulomb* and *exchange* integrals provides this result



Transitions in helium

- Consider transitions involving just one electron

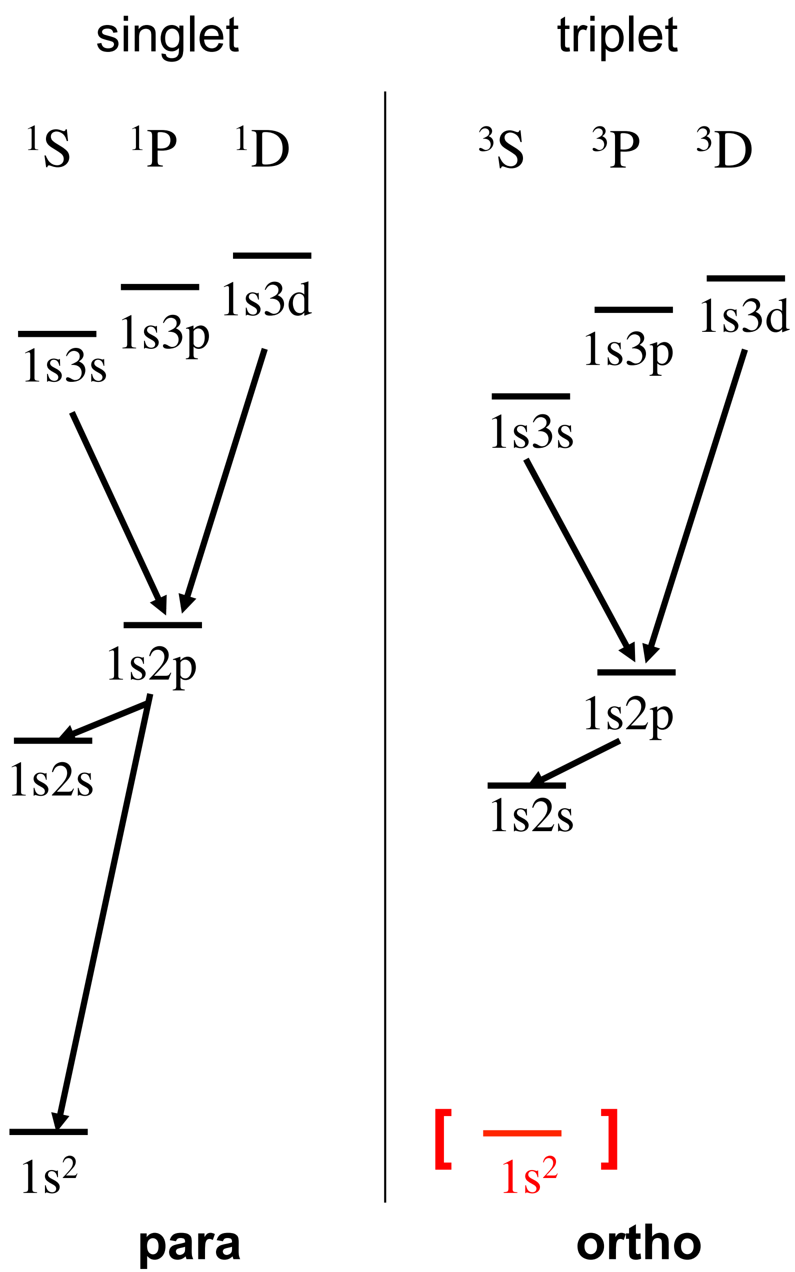
- Absorption (usually from ground state): $1snl \leftarrow 1\mathrm{s}^2$ (e.g. $1\mathrm{s}\ 2\mathrm{p} \leftarrow 1\mathrm{s}^2$)
- Emission: $nl\ n'l' \rightarrow nl\ n''l''$ (i.e. between arbitrary excited states)

- Selection rules: Δn = *any*; $\Delta l = \pm 1$; $\boxed{\Delta S = 0}$

  $\Rightarrow$ *transitions between singlet and triplet states are forbidden*

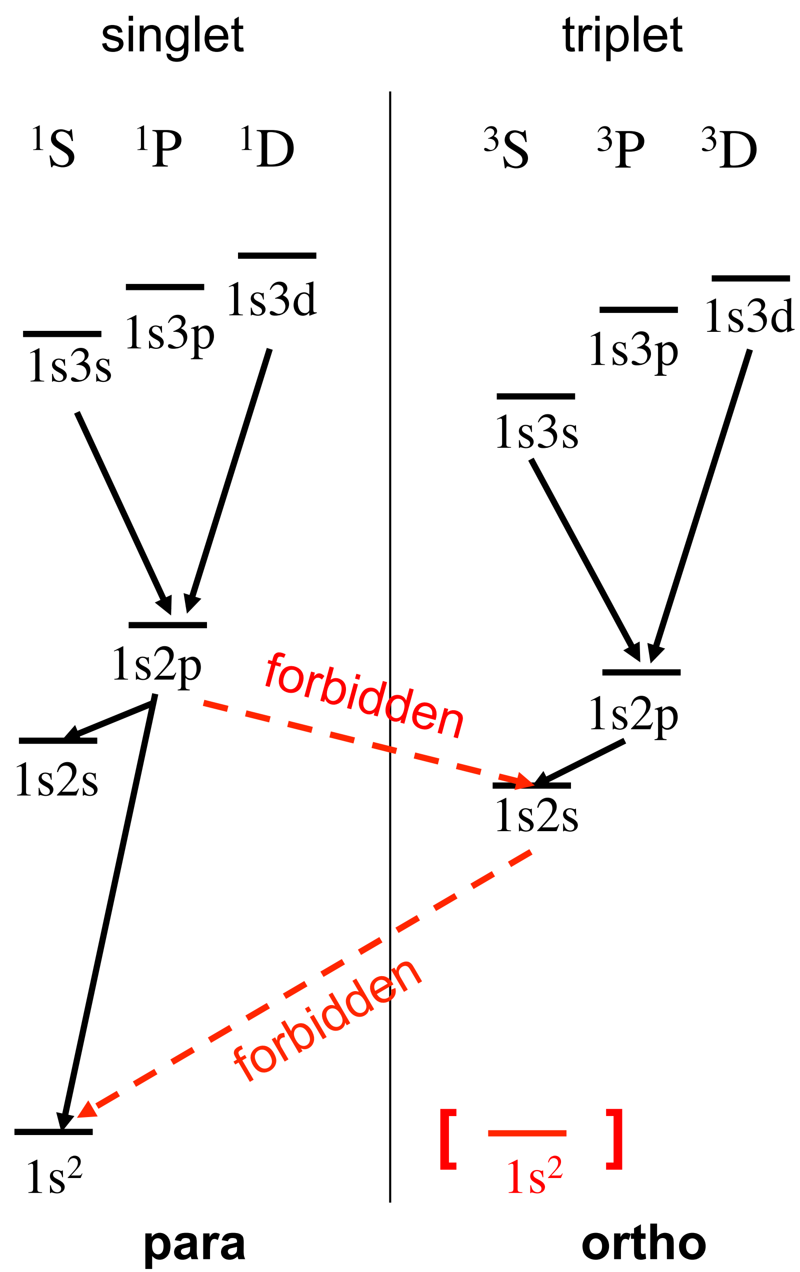
- Implications:
  - **absorption lines** are all between **singlet states** (as ground state is singlet state)
  - **emission lines** (e.g. from discharge tube which populates various excited states): two distinct sets of lines corresponding to
    - singlet $\leftrightarrow$singlet states
    - triplet $\leftrightarrow$ triplet states

Grotrian diagram for helium



Examples of allowed transitions

Grotrian diagram for helium



Examples of forbidden transitions

Spin-orbit coupling (revisited) for helium (L-S coupling)

- *Orbital angular momenta* of electrons coupled *as for spin angular momenta*
- Total orbital angular momentum $\mathbf{L} = \mathbf{l_1} + \mathbf{l_2}$ (vector sum)
- For helium with one electron in $1s$ subshell:
  - $\mathbf{l_1} = 0$ and thus $\mathbf{L} = \mathbf{l_2}$
  - *only excited electron can (potentially) contribute to total angular momentum*
- Spin-orbit coupling in helium involves coupling of *total* spin angular momentum with *total* spin angular momentum, ie. $\mathbf{S}$ with $\mathbf{L}$
  - for singlet states with $S = 0$ – no spin-orbit coupling
  - for triplet states coupling to produce total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$

Vector sums revisited

- How do we combine the *quantum numbers* where the corresponding *vectors* are combined in a vector sum?
  - eg. sum of orbital angular momenta

$$\mathbf{L} = \mathbf{l_1} + \mathbf{l_2}$$

- **Rule** is that the corresponding *quantum number* L can take values

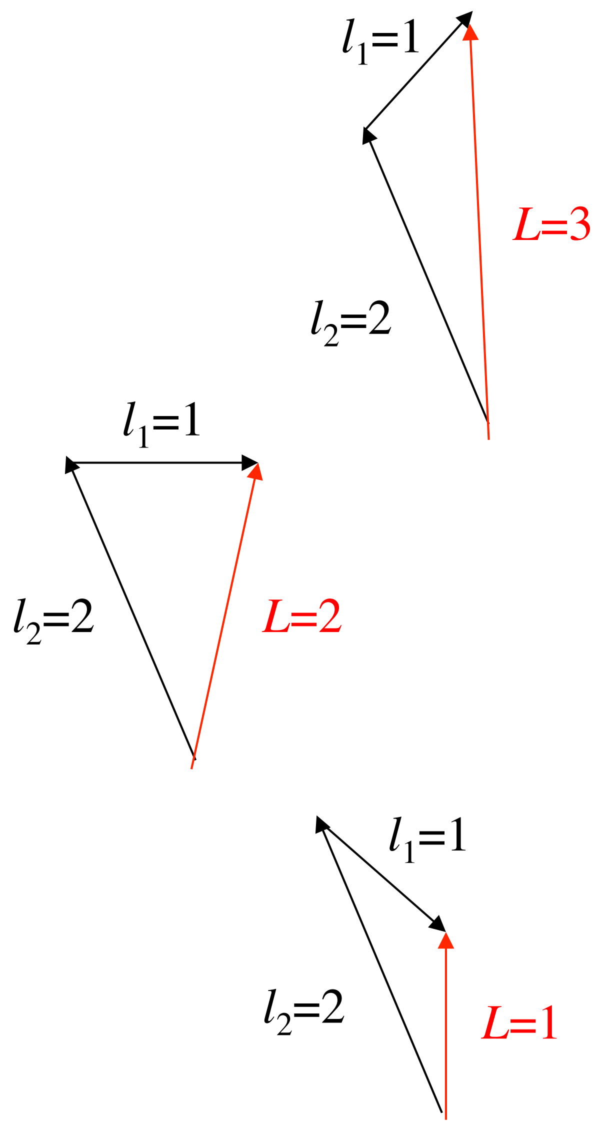
$$L = l_1 + l_2 \;\ldots\ldots\; |l_1 - l_2|$$

- For example consider case where *quantum numbers* are $l_1 = 1$ and $l_2 = 2$
  - in this case the rule gives $L = 3, 2, 1$
- *Rule applies to any quantised vector sum combination*

$$l_1 = 1\ ;\ l_2 = 2$$

$$L = l_1 + l_2\ \ldots\ |l_1 - l_2|$$

$$\Rightarrow L = 3,\ 2,\ 1$$



length of vector **q**

$$|\mathbf{q}| \propto \sqrt{q(q+1)}$$

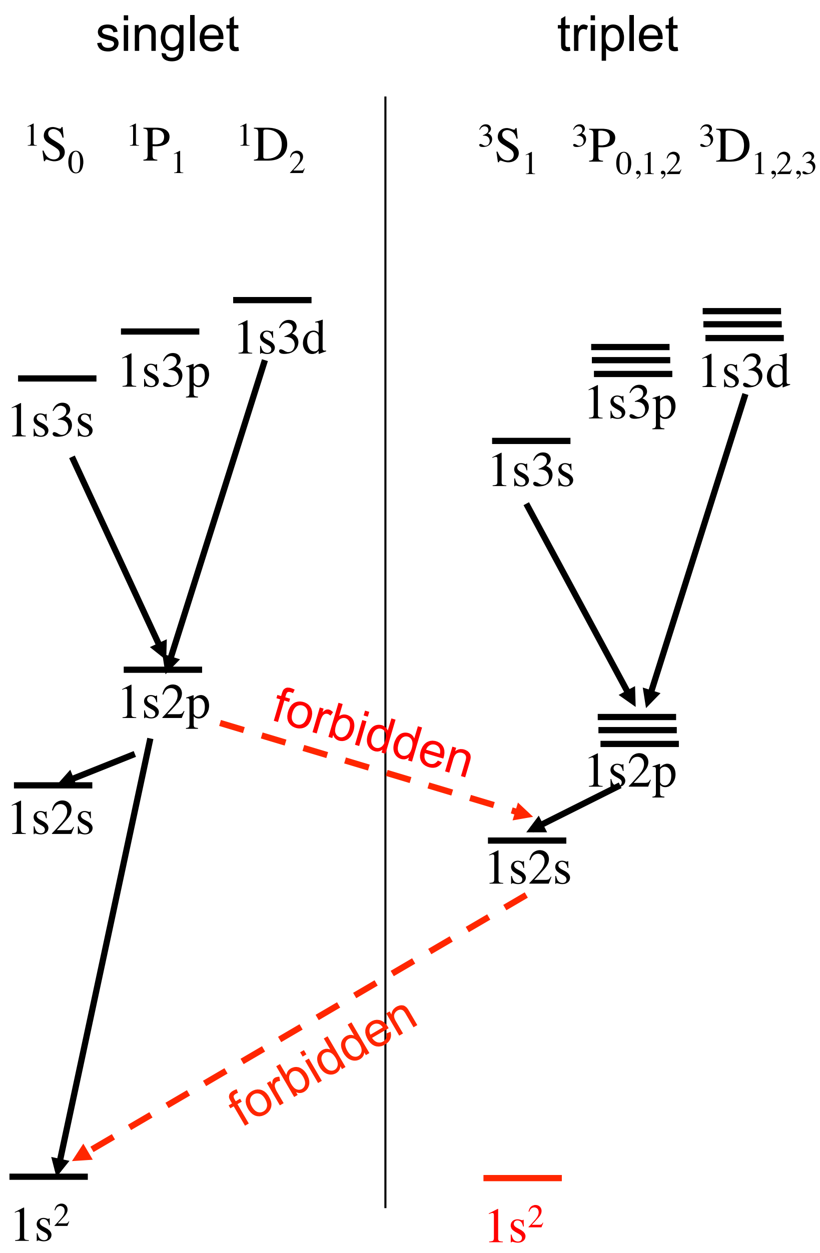
Spin-orbit coupling (revisited) for helium

- For triplet states ($S = 1$) possible values of quantum number J are
  $J = L+1, L, L-1$ [cf. $J = L + S, L + S-1, \ldots \; |L - S|$]
  and each J state is $(2J+1)$-fold degenerate according to value of m_J (total angular momentum projection quantum number)

- Example: 1snp states
  - $L = 1$ (l_1=0 l_2=1)
  - $J = 2, 1, 0$
  - Term symbols: $\boxed{^3P_2, {}^3P_1, {}^3P_0}$
- Example: 1snd states
  - $L = 2$ (l_1=0 l_2=2)
  - $J = 3, 2, 1$
  - Term symbols: $\boxed{^3D_3, {}^3D_2, {}^3D_1}$

- $E_{so} = \frac{1}{2} A\,[J(J+1)-L(L+1)-S(S+1)]\hbar c$ (cf. earlier version, but with much smaller constant)

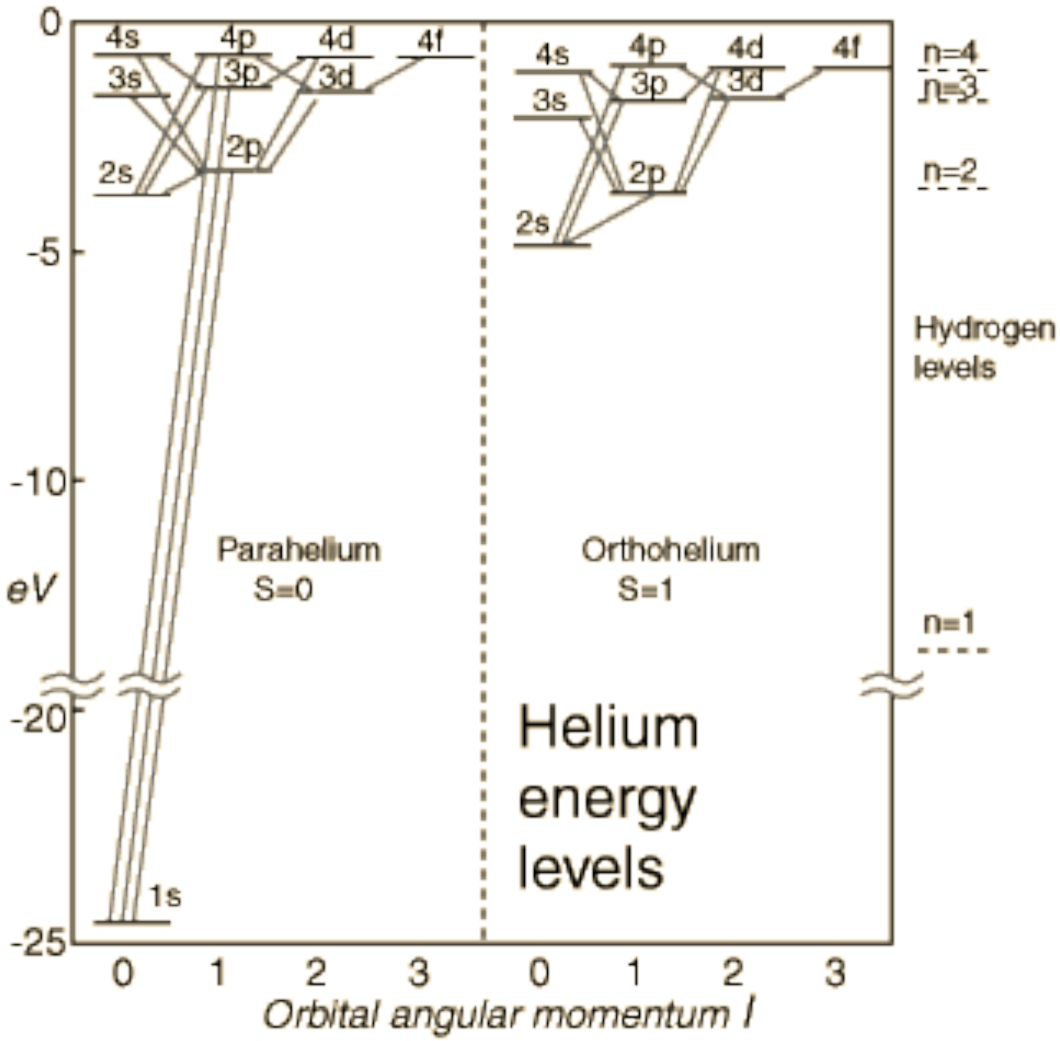
Grotrian diagram for helium (full treatment)



selection rules

$\Delta J = 0, \pm 1$ (not $0 \rightarrow 0$)

$\Delta S = 0$; $\Delta L = \pm 1$


0
-5
-10
-20
-25
eV
4s
3s
2s
1s
4p
3p
2p
4d
3d
4f
Parahelium
S=0
4s
3s
2s
4p
3p
2p
4d
3d
4f
Orthohelium
S=1
n=4
n=3
n=2
n=1
Hydrogen
levels
0
1
2
3
0
1
2
3
Orbital angular momentum l
Helium
energy
levels

Reading

- Helium atom
  - *Softley* Chapter 4: mostly sections 4.1-4.3

- Previous concepts
  - spin-orbit coupling
    - previous lectures
    - *Softley* Section 2.10