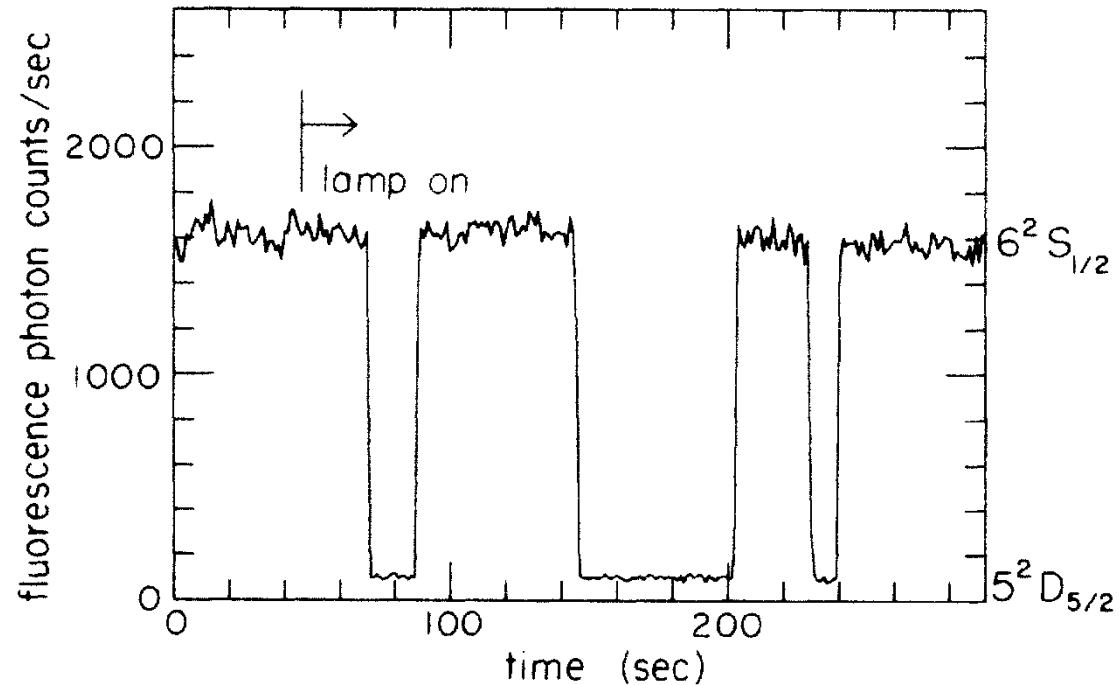


# Advanced Quantum Physics

## Lecture 21



David Ritchie

[www.sp.phy.cam.ac.uk/~dar11/pdf](http://www.sp.phy.cam.ac.uk/~dar11/pdf)

# Section 5: Atoms

5.1 The real hydrogen atom

5.2 Multielectron atoms



5.3 Coupling schemes

5.4 Atomic spectra

5.5 Atoms in a uniform magnetic field

## Coupling Schemes (Lecture 20)

- In a partially filled subshell the angular momenta of electrons can couple in different ways giving different total angular momenta and energies.

- Consider the Hamiltonian:

- $\hat{H}_0$  includes K.E and central field

- $\hat{H}_1$  is the residual Coulomb energy

- $\hat{H}_2$  Spin orbit term

$$\hat{H} \approx \hat{H}_0 + \underbrace{\sum_{i < j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}}_{\hat{H}_1} + \underbrace{\sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i}_{\hat{H}_2}$$

- Two possible scenarios:

- $\hat{H}_1 \gg \hat{H}_2$  - applies for light atoms, consider eigenstates of  $\hat{H}_0 + \hat{H}_1$  and treat  $\hat{H}_2$  as a perturbation – called **LS** or Russell-Saunders coupling

- $\hat{H}_1 \ll \hat{H}_2$  - applies in very heavy atoms or heavily ionised light atoms where electrons move faster and relativistic effects (such as spin-orbit interaction) more important. Scheme called **jj** coupling.

- Both schemes are approximations, real atoms cannot always be represented by either.

# Coupling Schemes: jj coupling

- In this approximation we consider the eigenstates of:

$$\hat{H}_0 + \hat{H}_2 = \hat{H}_0 + \sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i$$

- By rotational invariance they must be eigenstates of  $\hat{\mathbf{J}}^2$  and of  $\hat{\mathbf{J}}_i^2$  for each electron.
- The coupling procedure is to combine  $l$  and  $s$  for each electron to find the allowed values of  $j$ , with energies separated by the spin-orbit interaction. Values of  $j$  for individual electrons are then combined to give values of total  $J$ .
- The effect of the residual Coulomb interaction is to split the  $J$  values for a given set of values of  $j$ . There are no simple rules like Hund's rules...

## Coupling Schemes: jj coupling (2)

- Example  $-(np)^2$  in the jj coupling scheme – c/w carbon in  $LS$  coupling.
- Each electron has  $j = \frac{1}{2}$  or  $\frac{3}{2}$  - *equivalent* electrons if they have the same value. We require an antisymmetric state – the following are possibilities:

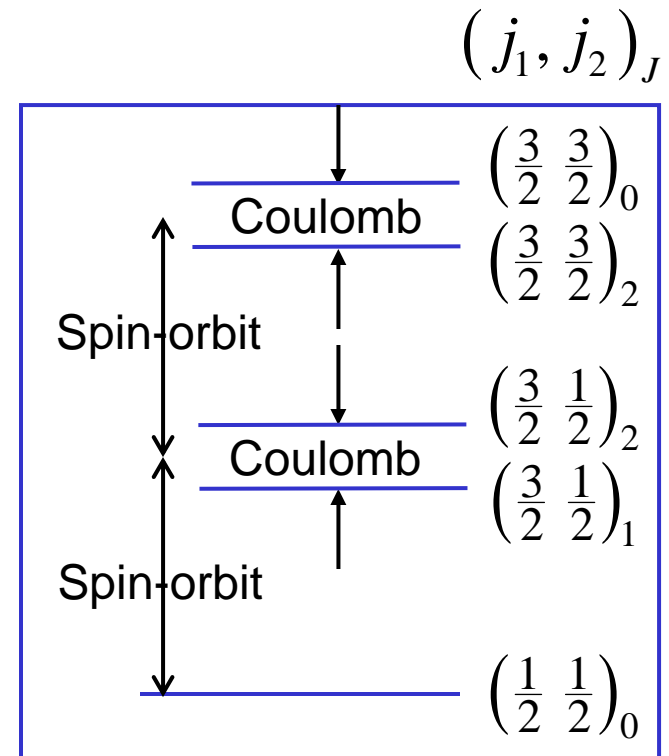
$$j_1 = j_2 = \frac{3}{2} \Rightarrow J = 3, 2, 1, 0 \quad J = 2, 0 \text{ are antisymmetric – different } m_j$$

$$j_1 = j_2 = \frac{1}{2} \Rightarrow J = 1, 0 \quad J = 0 \text{ is antisymmetric – different } m_j$$

- And for *non-equivalent* electrons

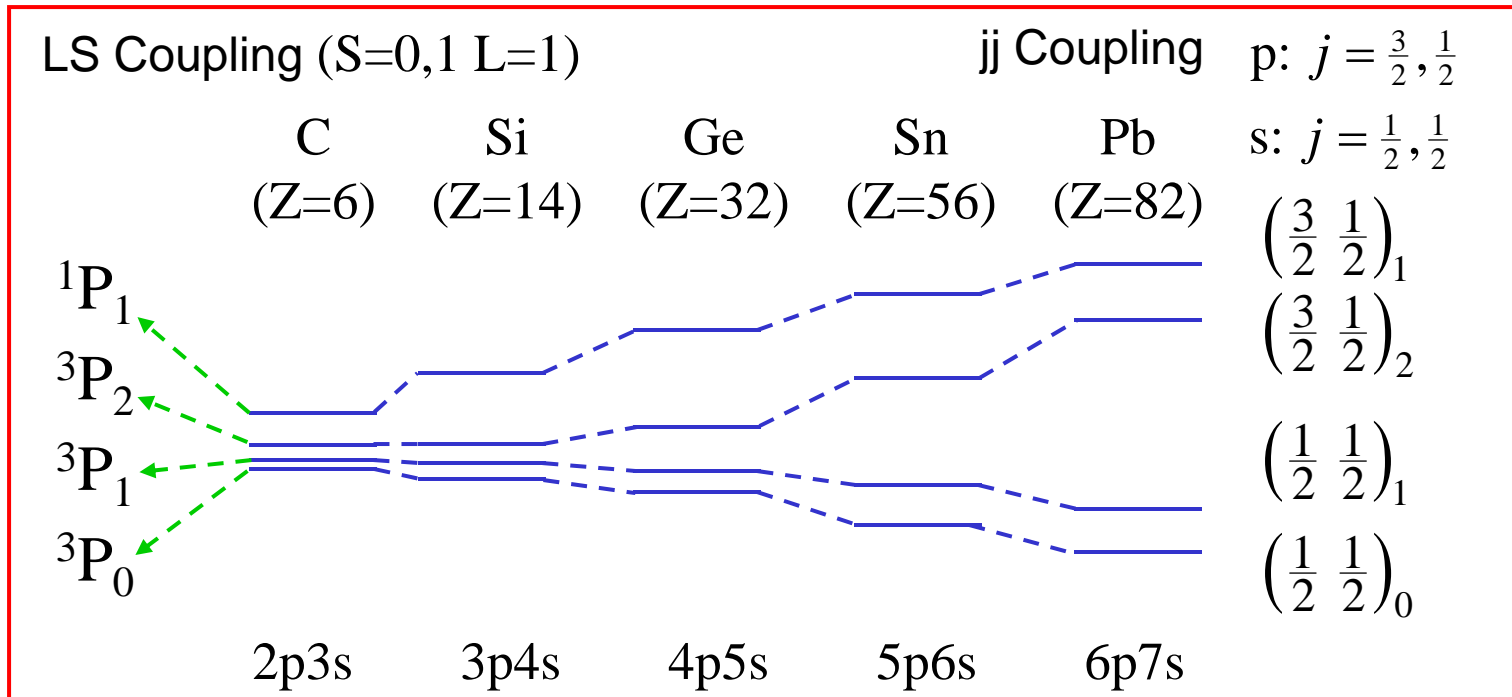
$$j_1 = \frac{3}{2}, j_2 = \frac{1}{2} \Rightarrow J = 2, 1$$

- Both  $LS$  and  $jj$  coupling lead to the same values of  $J$  with same ordering in energy.
- Different pattern of energy levels.
- $LS$  and  $jj$  states must be linear combinations of each other, real physical states are slightly different from either approximation.



## Coupling Schemes: jj coupling (3)

- This idealised form of jj coupling not seen in neutral atoms (even Pb  $(6p)^2$ )
- May be seen in highly ionized atoms – Cr  $^{18+}$ , with same configuration  $(2p)^2$  as Carbon but because of large unscreened nuclear charge, electrons move faster, are more relativistic – enhancing spin orbit coupling.
- Classic example of transition of LS to jj coupling seen in C-Si-Ge-Sn-Pb excited states  $(2p)(3s)\dots\dots(6p)(7s)$ .
- Here electrons not in same shell so Coulomb effect reduced w.r.t spin-orbit.



## 5.4 Atomic spectra

- Spectra due to electronic transitions via emission or absorption of a photon.
- *Emission spectra* – atoms are excited thermally or by an electric discharge, discrete spectral lines are observed in the light emitted.
- *Absorption spectra* – illuminate atoms with broadband source and observe dark absorption lines in the transmitted light. Atoms thus excited emit photons in all directions – *Fluorescence radiation*.
- Both processes involve the excitation of single electron from the ground state to a higher level. This may just involve a change of angular momentum coupling while retaining the same electronic configuration.
- Other types of process are possible – x-ray emission occurs where an electron is removed from the inner shell of a heavy atom & electrons cascade to fill the hole emitting high energy photons.
- Theory outlined in section 4 of course on transitions.
- In electric dipole transition – rate of transition  $\propto \left| \langle \psi_k | \hat{\mathbf{d}} | \psi_j \rangle \right|^2$ .
- Rate of spontaneous transitions  $\propto \omega^3$
- Matrix elements used to derive selection rules.

## Atomic spectra (2)

- In section 4 we only considered a single electron but the principles can be generalised, giving selection rules as follows:

(1) Parity must change (2)  $\Delta J = \pm 1, 0$  But not  $0 \rightarrow 0$  (3)  $\Delta M_J = \pm 1, 0$

- Atomic states are eigenstates of parity and  $J$  - rules are absolutely valid in the electric-dipole *approximation* (but other processes may also occur).

- In the case of ideal LS coupling additional rules apply:

(1)  $\Delta S = 0$  &  $\Delta M_S = 0$  (2)  $\Delta L = \pm 1, 0$  not  $0 \rightarrow 0$

(3)  $\Delta M_L = \pm 1, 0$  (4)  $\Delta \ell_i = \pm 1$  if only electron  $i$  is involved.

- In LS coupling since dipole operator does not operate on spin part of wavefunction, states are eigenstates of  $S$  implying the rules for  $\Delta S, \Delta M_S$ .

- This combined with absolute rules for  $J$  imply the rules for  $L$  and  $M_L$ .

- The rule for  $\Delta \ell_i$  comes from the parity change rule – the parity of an atom is a product of the parities of the separate electron wavefunctions:  $(-1)^{\ell_i}$

- Since LS coupling is an approximation rules do not always hold.

# Single electron atoms

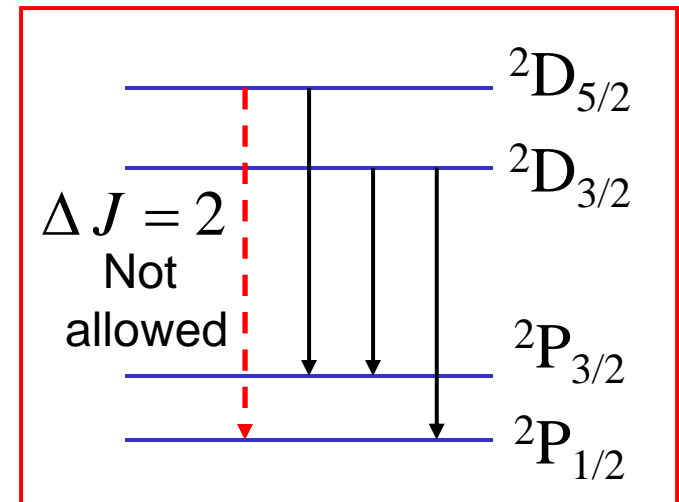
• Atoms with a ground state of one electron in s level outside closed shells.  
 Example: Sodium with a configuration  $(3s)^1$ .

(1) Ground state term  $^2S_{1/2}$ . For excited states  $J = L \pm \frac{1}{2}$  which are singlet s states for  $L=0$  and doublets for  $L=1,2,\dots$

(2) Parity is given by  $(-1)^{\ell_i}$ , the allowed transitions change  $\ell$  by  $\pm 1$  ( $s \leftrightarrow p$ ,  $p \leftrightarrow d$  etc). Bigger changes in  $\ell$  are not allowed by the  $\Delta J$  rule.

(3) Transitions are all doublets. All doublets starting or ending on a given p state have the same energy or frequency spacing. Transition  $3s \leftrightarrow 3p$  give sodium 'D' lines at 589nm wavelength.

(4)  $p \leftrightarrow d$  Transitions involve two doublets  $^2P_{1/2,3/2}$  and  $^2D_{3/2,5/2}$ . But  $^2P_{1/2} \leftrightarrow ^2D_{5/2}$  is forbidden by the  $\Delta J$  rule so the transition is a triplet. The spin-orbit interaction falls with increasing  $\ell$  and  $n$  due to increased screening so  $^2D_{3/2,5/2}$  splitting is often not resolved.

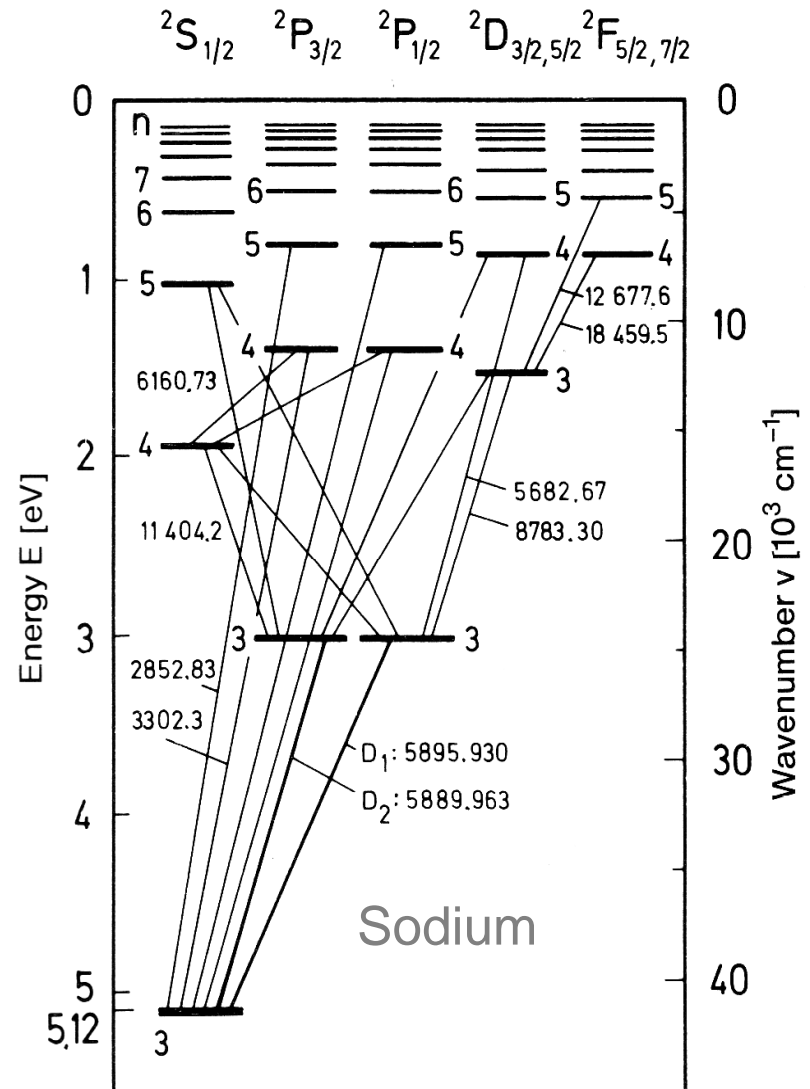


## Single electron atoms (2)

(5) As  $n$  increases the nuclear charge is more effectively screened and the energy levels approach those for H (from below). For electrons with higher  $\ell$  this happens sooner- they are further from the nucleus.

(6) In absorption atoms start in the ground state – only  $3s \leftrightarrow np$  lines are seen. In emission atoms are excited into all levels and many more lines are seen.

- These comments also apply to H except (2s,2p) and (3s, 3p, 3d) are degenerate.
- Hence 2s is metastable with no allowed electric dipole transition to 1s level.
- However 2s can decay by two photons or collisions - a strong electric field is present which mixes 2s & 2p states due to Stark effect so 2p can readily decay to 1s.



# Helium and Alkali earths

- Two electrons in s level, He:  $(1s)^2$   
 Be:  $(2s)^2$  Mg:  $(3s)^2$  Ca  $(4s)^2$

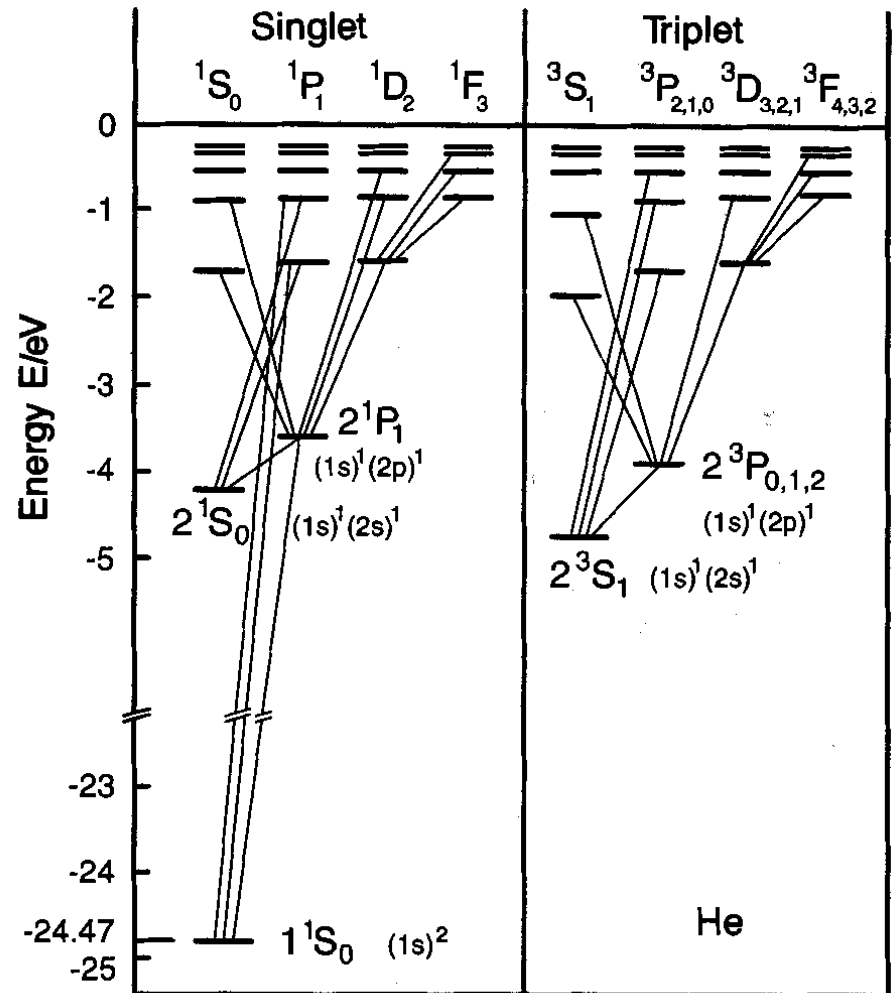
(1) For He ground state:  $^1S_0$ . Excited states  $(1s)(nl)$  have  $S=0$  or  $S=1$  with  $S=1$  lying lowest in energy (Hund 1).

(2) LS coupling a good approximation  $\Delta S = 0$  selection rule implies that  $S=0$  and  $S=1$  states form independent systems for spectroscopy.

(3) Lines in  $S=0$  system all singlets, observed in emission. Those starting from ground state seen in absorption.

(4) Lines in  $S=1$  system are all multiplets – observed in emission only.

Transitions  $^3S_1 \leftrightarrow ^3P_{2,1,0}$  are observed as triplets spaced according to the Landé interval rule. Transitions  $^3P_{2,1,0} \leftrightarrow ^3D_{3,2,1}$  are observed as sextuplets – an application of  $\Delta J = \pm 1, 0$ .

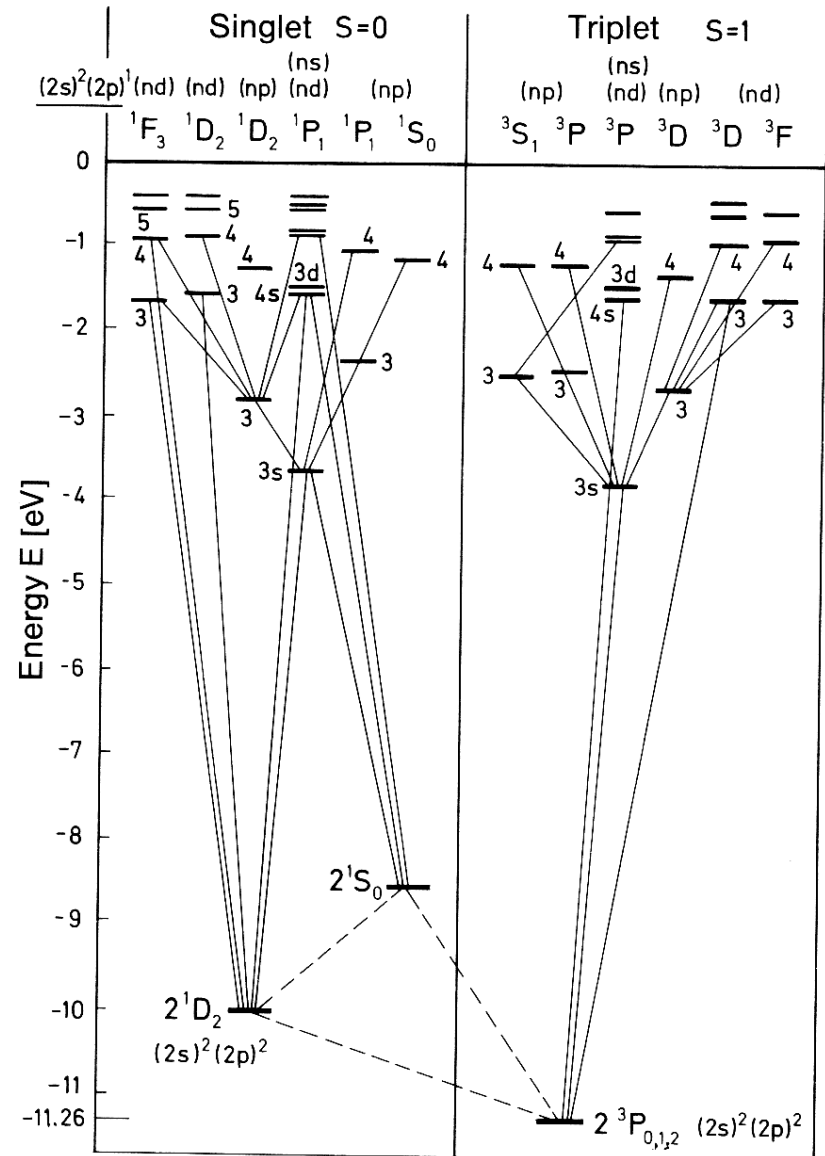


## Helium and Alkali earths (2)

- Alkali earths follow the same principles, for Calcium the triplet  $4p$  state is the lowest triplet state and thus metastable. Faint emission from the transition  $^3P_1 \rightarrow ^1S_0$  ground state is observed violating the  $\Delta S = 0$  rule. LS coupling is not so good in this case!
- A more extreme case is the Mercury ground state  $(6s)^2(5d)^{10}$ . Excited states involving the promotion of electrons to a higher level can be treated like the alkali earths. In this case the 'forbidden'  $^3P_1 \rightarrow ^1S_0$  transition is a prominent feature of the emission spectrum and LS coupling is not a good approximation at all.

# Multielectron atoms - Carbon

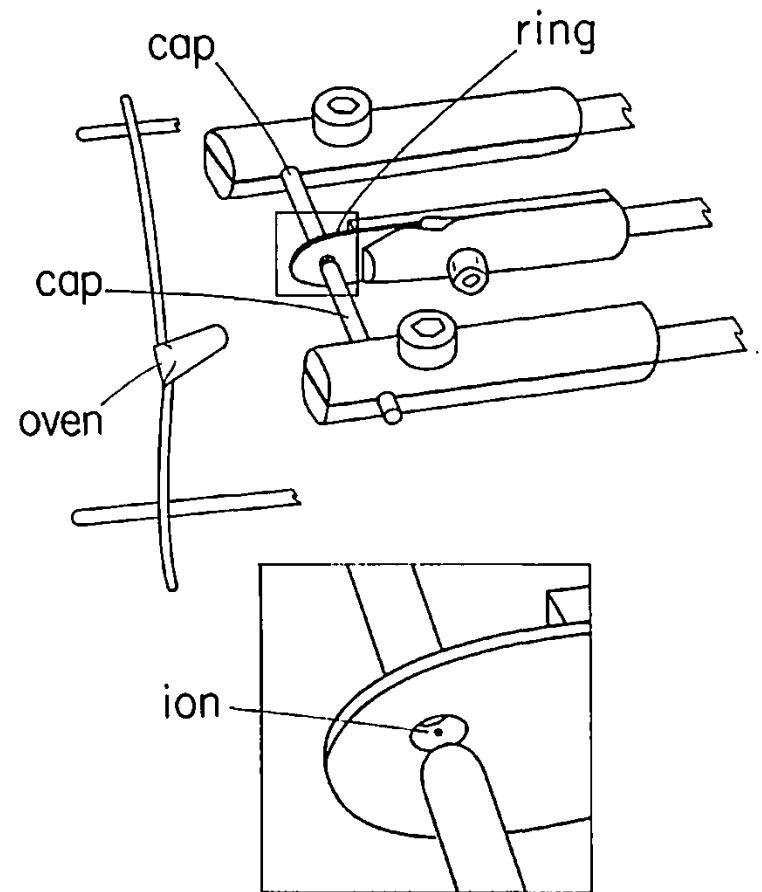
- Similar principles can be applied
- Carbon has a ground state  $(2s)^2(2p)^2$  with terms  $^3P_{2,1,0}$   $^1D_2$   $^1S_0$ .
- Excited states  $(2s)^2(2p)^1(nl)^1$  can be separated into singlets and triplets, excitations of the form  $(2s)^1(2p)^3$  are also seen.





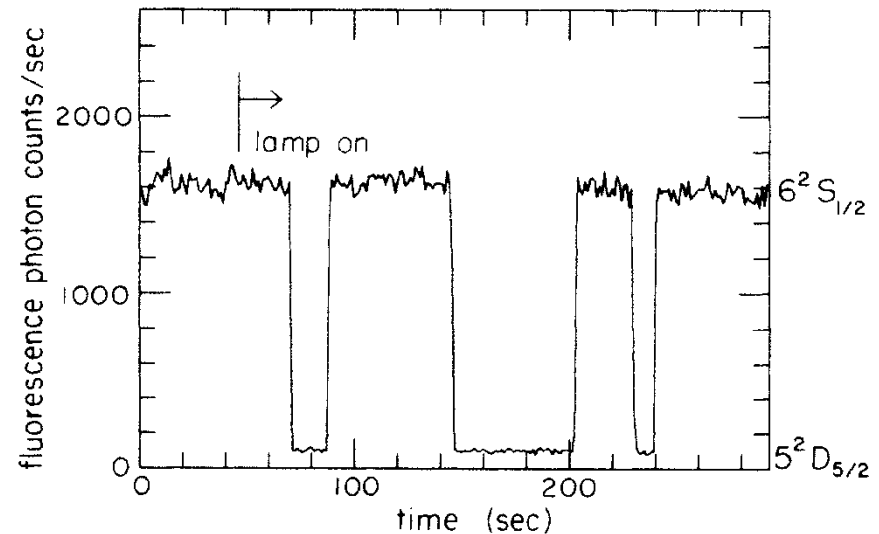
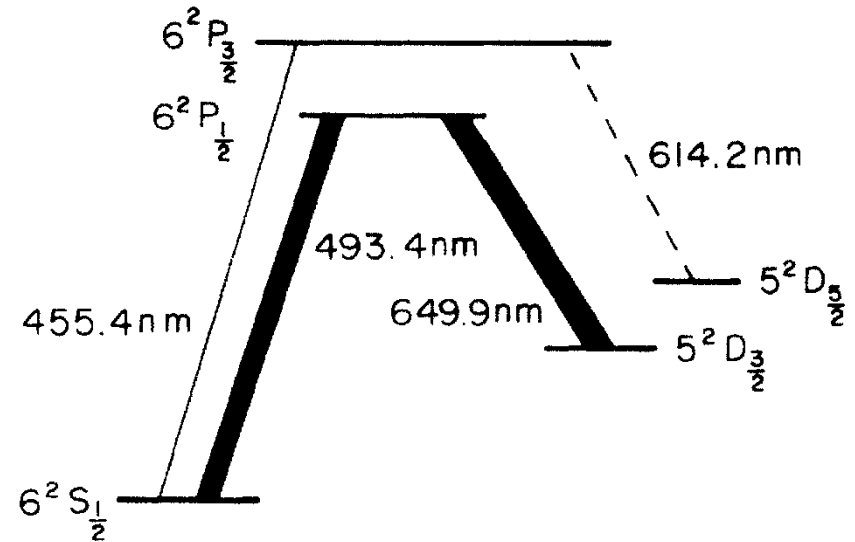
# The observation of quantum jumps in a single ion

- All of the experimental results on atomic transitions described so far rely on transitions taking place in a large number of atoms.
- The use of ion traps has allowed transitions to be observed in single atoms.
- The ion trap is situated in an ultra high vacuum chamber with a pressure of less than  $10^{-10}$ mbar.
- Barium atoms are evaporated from an oven, pass through the trap and are ionised by an electron beam.
- The  $Ba^+$  ions are trapped by voltages on the electrodes – in this way a single ion can be localised to a region  $<1\mu\text{m}$  in diameter.
- The position of the ion can be observed by exciting it with a laser beam and recording the resulting emission.



## Quantum jumps in a single ion (2)

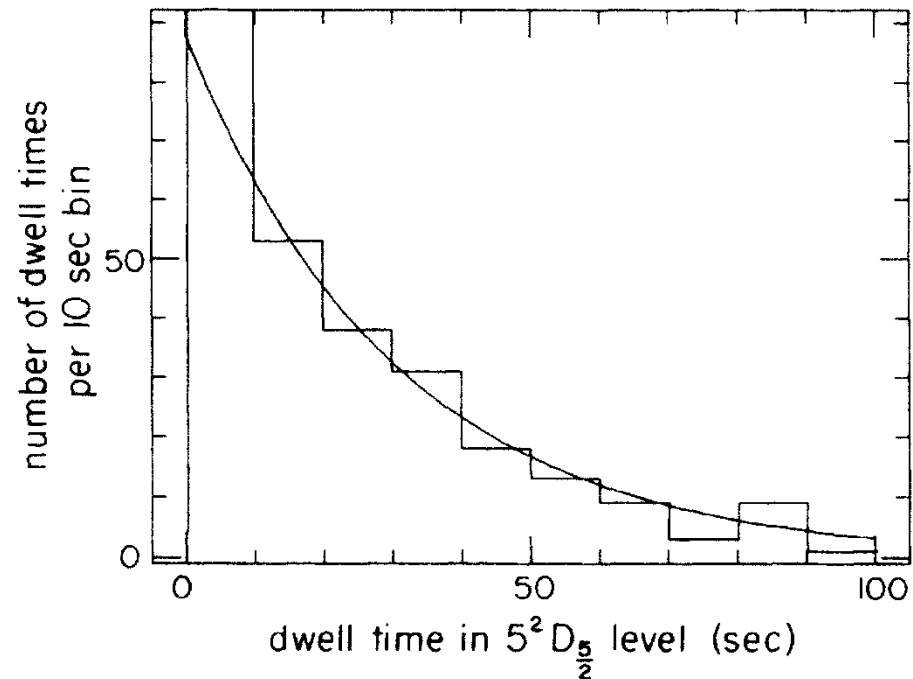
- Energy level structure of Ba<sup>+</sup> ion :
- The  $6^2S_{1/2} \leftrightarrow 6^2P_{1/2}$  &  $5^2D_{3/2} \leftrightarrow 6^2P_{1/2}$  transitions are driven by tuned lasers.
- The radiation emitted at 493.4nm, due to the  $6^2S_{1/2} \leftrightarrow 6^2P_{1/2}$  transition is measured.
- A low level of illumination at 455.4nm is applied to the system.
- On occasions the ion undergoes the transition  $6^2S_{1/2} \rightarrow 6^2P_{3/2} \rightarrow 5^2D_{5/2}$  and the measured radiation drops to zero
- Transitions  $5^2D_{5/2} \rightarrow 6^2S_{1/2}$  are forbidden by electric dipole selection rules -  $5^2D_{5/2}$  is a *metastable* state and has a lifetime of 10s of seconds before returning to  $6^2S_{1/2}$  and being excited again.



Phys Rev Lett **56**, 2797 (1986)

## Quantum jumps in a single ion (3)

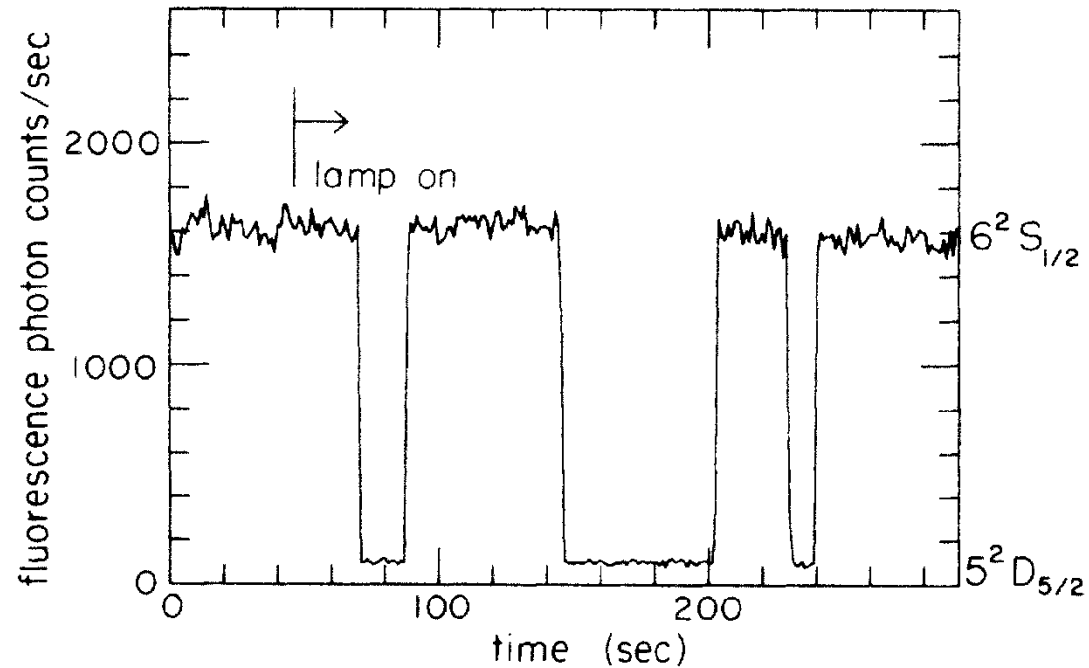
- By using this technique we can observe electronic transitions in a single Ba<sup>+</sup> ion.
- We can measure the dwell time in the metastable  $5^2D_{5/2}$  state.
- To the right is plotted a histogram of times that the system is in the 'dark' state corresponding to the metastable state.
- From the data a figure for the mean lifetime of the metastable state of  $\tau = 30 \pm 3\text{s}$  is calculated.
- From this time the spontaneous emission coefficient,  $A = 1/\tau$ , for this transition can be calculated – normally very difficult to measure for states with a long lifetime.



## Lecture 21 - Summary

- Coupling schemes (continued)
- $jj$  coupling - applies to large atoms where spin-orbit coupling is more important than the Coulomb energy between pairs of electrons.
- $l$  and  $s$  are coupled for individual electrons to give each a value of  $j$ . These values of  $j$  are combined to give an overall value of  $J$ .
- The transition from  $LS$  to  $jj$  coupling - small atoms to large atoms.
- Atomic spectra – emission and absorption, selection rules.
- Spectra for single electron atoms, two electron atoms and multi-electron atoms.
- The observation of quantum jumps in a single ion – a measurement of the lifetime of the  $5^2D_{5/2}$  metastable state in a  $Ba^+$  ion gives a value of 30s.

# Lecture 21



**The End!!**

([www.sp.phy.cam.ac.uk/~dar11/pdf](http://www.sp.phy.cam.ac.uk/~dar11/pdf))