

## Example finals answers

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**Disclaimer.** These notes are not guaranteed to be correct or complete, but they are a reasonable guide and they are as correct and complete as possible without a lengthy process of re-checking. I have included quite a lot of example explanatory statements, but have omitted some of the argument and all the diagrams. Where argument is omitted, the phrase ‘Answers without derivation’ appears. This is, in the event, rare. I have included in full explanatory arguments such as singlet-triplet splitting, with reservations as I partially explained in the lecture, and will underline here.

The process of putting together an argument in your own words, without guidance, **IS** the learning process. It cannot be avoided. Therefore my argument should be examined after you have tried **hard** to make your own complete statement, not before. By giving you the opportunity to use my ‘answer’ as an after-check, which is a positive thing, I have unavoidably made more likely the situation that you will read my statement after only a moderate effort of thought. You may well then feel that you understand my statement, and so be satisfied, and yet after even a day you would be unable to reproduce the argument because you never gave yourself the chance to experience what the issues are for you: i.e. what you might have said but shouldn’t, and you what might easily overlook. This chalice which I am offering you is therefore poisoned: you will be ok if you first take the antidote (=hard mental labour).

**1999. 3.** The spin-orbit interaction is a coupling between the magnetic dipole moment of the electron and the magnetic field it experiences:

$$H = -\boldsymbol{\mu} \cdot \mathbf{B}.$$

Now  $\boldsymbol{\mu} = -g\mu_B\mathbf{s}'$

$$\text{where } g = 2, \quad \mu_B = \frac{e\hbar}{2m}$$

and  $\mathbf{s}'$  is dimensionless spin.

$$\text{Hence } \boldsymbol{\mu} = -\frac{e}{m}\mathbf{s}$$

Field:

$$\mathbf{B} = \frac{-\mathbf{v} \wedge \mathbf{E}}{c^2} = \left( \frac{-\mathbf{v} \wedge \mathbf{r}}{c^2} \right) \frac{E}{r} = \left( \frac{\mathbf{r} \wedge \mathbf{p}}{mc^2} \right) \frac{e}{4\pi\epsilon_0 r^3}$$

But

$$\begin{aligned} c^2 &= 1/\epsilon_0\mu_0 \\ \text{and } \mathbf{l} &= \mathbf{r} \wedge \mathbf{p} \end{aligned}$$

So

$$\begin{aligned} -\boldsymbol{\mu} \cdot \mathbf{B} &= \frac{e}{m} \mathbf{s} \cdot \mathbf{l} \left( \frac{\mu_0}{m} \frac{e}{4\pi r^3} \right) \\ &= \frac{\mu_0}{4\pi} \frac{e^2}{m^2} \frac{1}{r^3} \mathbf{l} \cdot \mathbf{s} \end{aligned}$$

When Thomas precession is taken into account, this result is reduced by a factor 1/2:  $\rightarrow$  form given.

Answers without derivation:

$$\langle \mathbf{s} \cdot \mathbf{l} \rangle = \frac{j(j+1) - l(l+1) - s(s+1)}{2} \hbar^2$$

$3p \ ^2P_{3/2}$ :

$$s = 1/2, \quad l = 1, l; \quad j = 3/2$$

$$\begin{aligned} \Delta E &= \frac{(3/2)(5/2) - 2 - 3/4}{27 \times 1(3/2)(2)} \dots \\ &= 4.47 \times 10^{-6} \text{ eV} \end{aligned}$$

$3p \ ^2P_{1/2}$ :

$$s = 1/2, \quad l = 1, l; \quad j = 1/2$$

$$\begin{aligned} \Delta E &= \frac{(1/2)(3/2) - 2 - 3/4}{27} \text{ etc} \\ &= -2 \times (\text{previous result}) \\ &= -8.94 \times 10^{-6} \text{ eV} \end{aligned}$$

$\rightarrow$  diagram

Electromagnetic interactions are insensitive to charge conjugation, therefore exactly the same result is expected for anti-hydrogen.

a) Hydrogen-like sodium:

scaling is  $Z^4$ , hence splitting  $(13.5 \times 10^{-6}) \times 11^4 = 0.197 \text{ eV}$ .

b) muonic sodium: have  $m$  as well as  $Z$  dependence.

Consider  $a_0 m \alpha c = \hbar \Rightarrow a_0 \propto 1/m$

Hence overall, splitting is  $\propto mZ^4$ .

$m_\mu = 207m_e$ ,  
hence splitting =  $207 \times 0.197 = 41$  eV.

*Last part is off the 2nd year syllabus*

*For neutral atom, the observed result is intermediate between hydrogen and the hydrogen-like ion. It is more than for hydrogen, because when the electron penetrates the core it experiences a greater electric field. It is less than for the ion, because the nuclear charge is nevertheless somewhat screened, so the electric field, and hence the magnetic field, is smaller than that in the ion.*

**1999. 2.** *Last part only:*

1s2s in helium: levels are  $^3S_1$  and  $^1S_0$ , i.e.

$n_1 = 1, l_1 = 0, n_2 = 2, l_2 = 0,$

$S = 1, L = 0, J = 1$

and  $S = 0, L = 0, J = 0$

The energy difference is caused by the Coulomb repulsion of the electrons. The state of the two electrons must be antisymmetric w.r.t. exchange of the labels, since they are fermions. The solutions can be written as a product of spatial and spin parts, so there are two possibilities:

either  $\psi_S(\text{spatial}) \times \chi_A(\text{spin})$

or  $\psi_A(\text{spatial}) \times \chi_S(\text{spin})$

where S,A signifies symmetric, antisymmetric

Now, the mean distance between the electrons is smaller in  $\psi_S(\text{spatial})$  so this state has more energy from Coulomb repulsion. This is the singlet ( $S = 0$ ) state, since the singlet spin state is antisymmetric.

why metastable:

1s2s  $^3S_1$  has only the ground state  $1s^2 \ ^1S_0$  below it. It cannot decay because of parity rule ( $\Delta l = \pm 1$ ) and selection rules on  $L$  ( $L = 0 \not\leftrightarrow L = 0$ ) and  $S$  ( $\Delta S = 0$ ).

1s2s  $^1S_0$  cannot decay to the ground state because of parity and selection rules on  $L$  and  $J$  ( $J = 0 \not\leftrightarrow J = 0$ )

It cannot decay to 1s2s  $^3S_1$  because of parity and selection rules on  $L$  and  $S$ .

**2000. 4.**

Physical origin of terms: ...

Approximations:

- (1) neglect relativistic corrections, including spin-orbit effect
- (2) neglect nuclear effects (finite volume, magnetic dipole moment of the nucleus)
- (3) neglect motion of nucleus (i.e. assume heavy nucleus)

Electrons are identical fermions, and therefore their joint state must have the property

$$\psi(1, 2) = -\psi(2, 1)$$

i.e. it merely changes sign when the labels are exchanged (Exchange Principle).

Any state whose spatial part is  $\psi_{a,b} = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)$  does not have this property and so is not possible.

The state of the electrons can have the form

$$\begin{array}{l} \text{either } \psi_S(\text{spatial}) \times \chi_A(\text{spin}) \\ \text{or } \psi_A(\text{spatial}) \times \chi_S(\text{spin}) \end{array}$$

(both of these are antisymmetric overall).

$\chi_A$  is the singlet spin state ( $S = 0$ ).

$\chi_S$  is the triplet group of spin states ( $S = 1$ ).

The  $1s^2$  configuration has both electrons in the same spatial state, so its spatial part must be symmetric w.r.t. exchange:

$$\psi_{\text{spatial}} = \phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)$$

Therefore it must be a singlet:  $^1S_0$ .

The  $1s2s$  configuration has two possibilities:

$$\begin{aligned} \psi_S &= \frac{1}{\sqrt{2}} (\psi_{a,b} + \psi_{b,a}) \\ \psi_A &= \frac{1}{\sqrt{2}} (\psi_{a,b} - \psi_{b,a}) \end{aligned}$$

The first must be the singlet, the second the triplet.

The first has more energy because the electrons are on average closer together in  $\psi_S$  so have more energy from their Coulomb repulsion.

→ diagram

Answers without derivation:

to ionize  $\text{He}^+$  requires  $2^2 E_R = 54.4 \text{ eV}$ .

to ionize  $\text{O}^{7+}$  requires  $8^2 E_R = 870 \text{ eV}$ .

explanation in terms of screening. To make it quantitative, use the measured results to deduce  $Z_{\text{eff}} = Z - \sigma$ . Get  $\sigma = 0.64$  for He,  $\sigma = 0.62$  for  $\text{O}^{6+}$ .

So both results are consistent with partial screening by a single electron.

**2000. 3.** Electric dipole selection rules:

1. total angular momentum:  
 $J = 0 \not\leftrightarrow J = 0$   
 $M_J = 0 \not\leftrightarrow M_J = 0$  when  $\Delta J = 0$   
 $\Delta J = 0, \pm 1$   
 $\Delta M_J = 0, \pm 1$
2. parity must change  
 $\Rightarrow \Delta l = \pm 1$
3. [Configuration: only one electron jumps *this rule not required at 2nd year level*]
4. when  $L$  and  $S$  are good quantum numbers:  
 $\Delta S = 0,$   
 $[\Delta L = 0, \pm 1$  and  $L = 0 \not\leftrightarrow L = 0$  *this rule, though correct, is not needed in hydrogen and helium and it can be missed out at 2nd year level*]

Justification:

In electric dipole radiation, the photon carries 1 unit of angular momentum, and angular momentum is conserved. This explains the selection rules on  $J$  and  $M_J$ .

The parity must change because the electric dipole operator  $\sum_i -e\mathbf{r}_i$  has odd parity, so only connects even parity states to odd parity ones, and vice versa.

$1s^2 2p \ ^2P_{1/2} - 1s^2 3d \ ^2D_{5/2}$  disallowed ( $\Delta J = 2$ )

$1s^2 2s2p \ ^1P_1 - 1s^2 2p3p \ ^1P_1$  allowed  
 (comment:  $2s \rightarrow 3p$ )

$1s^2 2s^2 \ ^1S_0 - 1s^2 2p^2 \ ^3P_1$  disallowed:  
 2 electrons changed, no parity change,  $\Delta S = 1$

alkali  $\Rightarrow S = 1/2$ .

4 " $\sigma^+/\sigma^-$ " lines and 2 " $\pi$ " lines  
 hence (diagram)  $J_1 = 1/2, J_2 = 3/2$   
 (we are told  $J_2 > J_1$ )

$L_1 = 0$  or  $1$ .

$L_2 = 1$  or  $2$ .

Selection rules: as above, and  
 the  $\pi$  lines are  $\Delta M = 0$ ,  
 the  $\sigma^+/\sigma^-$  lines are  $\Delta M = \pm 1$ .

$$\begin{aligned} \Delta E &= -\langle \boldsymbol{\mu} \cdot \mathbf{B} \rangle \\ &= g_J \mu_B B M_J \end{aligned}$$

where Bohr magneton  $\mu_B = e\hbar/2m_e$ .

Different  $L_1, L_2$  will give different  $g_J$  hence different splittings and associated Zeeman spectrum.

$L_2 = 2$  and we know  $L_1 = 0$  or  $1$ . Hence, to obey  $\Delta L$  selection rule, must have  $L_1 = 1$ .

$$\begin{aligned} S = 1/2, L = 2, J = 3/2 \Rightarrow g_2 &= \frac{3 \times 15/4 + 3/4 - 6}{2 \times 15/4} \\ &= \frac{3 \times 15 + 3 - 24}{30} \\ &= 4/5 \end{aligned}$$

$$\begin{aligned} S = 1/2, L = 1, J = 1/2 \Rightarrow g_1 &= \frac{3 \times 3/4 + 3/4 - 2}{2 \times 3/4} \\ &= \frac{1}{3/2} \\ &= 2/3 \end{aligned}$$

→ diagram.

$M_{J2}$	$M_{J1}$	relative position $(g_2 M_{J2} - g_1 M_{J1})$
$\frac{3}{2}$	$\frac{1}{2}$	$\frac{3}{2} \cdot \frac{4}{5} - \frac{1}{2} \cdot \frac{2}{3} = \frac{6}{5} - \frac{1}{3} \simeq 0.867$
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2} \cdot \left(\frac{4}{5} - \frac{2}{3}\right) = \frac{2}{3} - \frac{1}{3} \simeq 0.067$
$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2} \cdot \left(-\frac{4}{5} - \frac{2}{3}\right) = -\frac{2}{5} - \frac{1}{3} \simeq -0.73$
$\frac{1}{2}$	$-\frac{1}{2}$	
$-\frac{1}{2}$	$-\frac{1}{2}$	negative of the above
$-\frac{3}{2}$	$-\frac{1}{2}$	

**OR:** For convenience, use

$$\begin{aligned} g_J \mu_B B M &= (15g_J) \mu_B B (2M)/30, \\ \text{and } 15g_2 &= 12, \\ 15g_1 &= 10. \end{aligned}$$

$2M_{J_2}$	$2M_{J_1}$	relative position	
3	1	$3 \times 12 - 1 \times 10 = 26$	
1	1	$(12 - 10) \times 1 = 2$	
-1	1	$(-12 - 10) = -22$	
1	-1		
-1	-1	negative of the above	
-3	-1		→ diagram

**2002. 2.** The quantum numbers  $L, S, J, M_J$  are associated with the angular momentum operators for the electrons in the atom:

$$\hat{\mathbf{L}} = \sum_i \hat{\mathbf{l}}_i = \text{total orbital angular momentum}$$

$$\hat{\mathbf{S}} = \sum_i \hat{\mathbf{s}}_i = \text{total spin angular momentum}$$

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}} = \text{total angular momentum}$$

$$\hat{J}_z = \text{z-component of } \hat{\mathbf{J}}$$

The eigenvalues of  $\hat{L}^2$ ,  $\hat{S}^2$ ,  $\hat{J}^2$ , and  $\hat{J}_z$  are  $L(L+1)\hbar^2$ ,  $S(S+1)\hbar^2$ ,  $J(J+1)\hbar^2$  and  $M_J\hbar$  respectively.

Electric dipole selection rules: as above.

Justification:

In electric dipole radiation, the photon carries 1 unit of angular momentum, and angular momentum is conserved. This explains the selection rules on  $J$  and  $M_J$ .

The parity must change because the electric dipole operator  $\sum_i -e\mathbf{r}_i$  has odd parity, so only connects even parity states to odd parity ones, and vice versa.

The spherical harmonics  $Y_{lm}$  have parity  $-1^l$ , hence the parity rule together with the angular momentum change by at most 1, implies  $\delta l = \pm 1$ .

The electric dipole operator does not act in spin space, so  $\Delta S = 0$ .

Its effect on  $L$  is limited by the same angular momentum conservation considerations as for  $J$ .

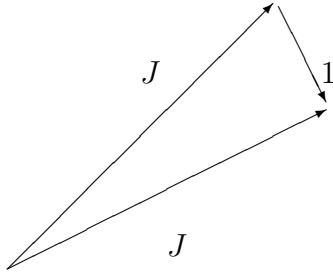
*Comment: the single-electron jump rule is usually included under 'LS coupling' rules. However, strictly speaking an atom could have configuration mixing (i.e. non-central field) but still a very small spin-orbit effect, and hence have very well-defined  $L$  and  $S$  even though the configurations are not well-defined. This means it can be described by LS coupling very well, and yet disobey the single-electron jump rule. This fine distinction is 4th-year material; a part A finals examiner will therefore not insist on the inclusion of this rule here. However, for good measure, I mention it anyway.*

The electric dipole matrix element is a sum of terms, each involving the operator  $\mathbf{r}_i$  of a single electron:

$$\sum_i \langle \psi_2 | -e\mathbf{r}_i | \psi_1 \rangle.$$

In the central field approximation the electrons move independently, so have product wavefunctions  $\psi$ . If more than 1 electron jumps, each term in the matrix element will be a product of a non-zero part and a zero part owing to the orthogonality of the single-electron wavefunctions.

If  $J$  does not change, the only way to add 1 unit of angular momentum from the photon, and still get the same  $J$ , is if the direction of the vector  $\mathbf{J}$  changes:



This implies either its  $z$  component must change, hence  $\Delta M_J = \pm 1$ , or it is rotated in the  $x-y$  plane ( $\Delta M_J = 0$ ). However, for  $M_J = 0$  there is no  $\phi$ -dependence ( $e^{im\phi}$ ) in the wavefunction, so the latter case is not in fact a change in the state, so does not change the angular momentum direction, so is ruled out.

$g_J$  characterises the coupling between the magnetic dipole of the atom and the applied magnetic field. The energy shift (in 1st order perturbation theory) of a state  $M_J$  in level  $J$  is

$$\Delta E = \langle -\boldsymbol{\mu} \cdot \mathbf{B} \rangle = g_J \mu_B B M_J$$

where  $\mu_B$  is the Bohr magneton.

Problem given: use information and selection rules, and count the lines in the Zeeman pattern  $\rightarrow$  deduce  $J_1 = J_2 = 2$ : (no other values work).

It remains to find  $L_1$ .

$$g_2 = \frac{3 \times 6 + 2 - 6}{2 \times 6} = \frac{14}{12} = 7/6$$

$$g_1 = \frac{20 - L(L + 1)}{12},$$

Try  $L = 1$ :  $g_1 = 18/12 = 3/2 = 9/6$

$g_2 = 7/6, \quad g_1 = 9/6:$



$M_{J2}$	$M_{J1}$	relative position
2	2	$(7 - 9) \times 2 = -4$
1	2	$(7 \times 1 - 9 \times 2) = -11$
2	1	$(7 \times 2 - 9) = 5$
1	1	-2
0	1	-9
1	0	7
etc.		(symmetric pattern)

Wrong pattern. Quickly rule out  $L_1 = 2$  (gives same  $g_J$  so lines at zero).  
Hence must be  $L_1 = 3$

(Check:  $g_1 = (20 - 12)/12 = 4/6$ )

$M_{J2}$	$M_{J1}$	relative position	
2	2	$(7 - 4) \times 2 = 6$	
1	2	$(7 \times 1 - 4 \times 2) = -1$	
2	1	$(7 \times 2 - 4) = 10$	
1	1	3	
0	1	-4	
1	0	7	→ correct. )

(Spectrometer apparatus: see practical course.

Don't forget to filter out other spectral lines.)

### 2000. 1.

Apparatus: X-ray tube + crystal spectrograph (entrance slit, crystal of known structure and spacing, photographic film)

Each wavelength scatters off the crystal at a different angle (Bragg scattering).

Describe main features ... for you to do. Mention Bremsstrahlung, cut-off, characteristic lines in series (and explain).

L-shell absorption edge: raise electron from  $n = 2$  to first empty state.

Potassium:  $Z = 19$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s$ ,

i.e.  $n = 4$

Rubidium:  $Z = 37$ :

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s$ , i.e.  $n = 5$

The energy change in the absorption can be written

$$E = E_R \left[ \frac{(Z - \sigma_L)^2}{2^2} - \frac{(Z - \sigma')^2}{n^2} \right]$$

Solve for  $\sigma_L$ :

$$\begin{aligned} \frac{(Z - \sigma_L)^2}{4} &= \frac{E}{E_R} + \frac{\sim 1}{n^2} \\ \Rightarrow (Z - \sigma_L) &= 2\sqrt{E/E_R + \sim 1/n^2} \\ \Rightarrow \sigma_L &= Z - 2\sqrt{E/E_R + \sim 1/n^2} \end{aligned}$$

potassium	rubidium
Z=19	Z=37
n=4	n=5
E=294 eV	E=1840 eV

$$\begin{aligned} \Rightarrow \sigma_L &= 9.7 & \Rightarrow \sigma_L &= 13.7 \\ Z_{\text{eff}} &= 9.3 & Z_{\text{eff}} &= 23 \end{aligned}$$

Comments:

The nuclear charge is screened by the atomic electrons. We should expect contributions:

$$\begin{aligned} \sigma_L &\simeq 2 && \text{from } n = 1 \text{ electrons} \\ &+ \sim 8/2 && \text{from } n = 2 \text{ electrons} \\ &+ && \text{contribution from electrons in higher} \\ &&& \text{shells, especially those in s states.} \end{aligned}$$

For rubidium there are a further 27 electrons, compared with 9 for potassium, so expect larger  $\sigma_L$  as observed.

( Could mention external screening.)

$K_\alpha$  emission line is at

$$E = E_R \left[ \frac{(Z - \sigma_K)^2}{1^2} - \frac{(Z - \sigma_L)^2}{n^2} \right]$$

with  $\sigma_K \simeq 2$  to 10, and  $\sigma_L \simeq 6$  to 20, both increasing slightly with  $Z$ .

The wavelengths vary smoothly with  $Z$  because  $\sigma_K$  and  $\sigma_L$  don't change dramatically as  $Z$  increases. With each new period in the periodic table a new s-state is introduced, which causes a slightly larger than normal increase in  $\sigma_K$  and  $\sigma_L$ , but this is still a small effect compared to  $(Z - \sigma_K)^2$ .

Rubidium: observe  $K_\alpha$  at 13.4 keV.  $\rightarrow$  deduce  $\sigma_K = 3.5$ .

Potassium: guess  $\sigma_K \simeq 2$   
 $\Rightarrow K_\alpha$  energy is  $E \simeq 3600$  eV.

We can be confident that  $\sigma_L < 3.5$  since potassium has fewer electrons than rubidium. Therefore  $E < 4110$  eV.

(Also, it is very likely that  $\sigma_L > 1$  so a lower bound is  $E > 2970$  eV.)

### 2002. 3.

Electron screening:

Each electron in a multi-electron atom experiences a net electric field from the nucleus and the other electrons. The charge distribution of the electrons is approximately spherically symmetric, especially for the inner shells, so, using Gauss' theorem, the net electric field at radius  $r$  is the same as that due to a point charge at the origin of charge  $Z - \sigma$ , where  $\sigma$  quantifies the degree to which the negative electron charge thus 'screens' the positive nuclear charge.

The absence of one electron can be regarded as a single 'hole' moving in this field. Hence we propose the formula for the energy levels:

$$E_{n,l} = \frac{hcR(Z - \sigma_{n,l})^2}{n^2}$$

(positive because the hole has positive charge).

From the form of the wavefunctions, we should expect  $\sigma_{n,l}$  to decrease with  $n$  and  $l$ .

Spectrometer: as before.

Reasoned estimate: in order to observe the complete X-ray line spectrum, it must be possible to eject a  $K$  shell electron from the atom. The required energy is  $E = hcR(34 - \sigma_{1,0})^2$ .

Estimate  $\sigma_{1,0} \simeq 2$ , since only 1 other  $K$ -shell electron and the other electrons do not contribute greatly to  $\sigma_{1,0}$ . In any case the  $E$  estimate is not sensitive to this.

Thus  $E \simeq 13.6 \times (32)^2 \simeq 14$  keV.

Spectrum:

The high energies are of order of  $E$ , so are in the  $K$  series.

The fine structure decreases with  $n$ .

$\sigma_{n,l}$  decreases with  $l$ .

→ diagram.

Notice

$$\begin{aligned} 1.492 - 1.486 &= 0.006 \\ 12.496 - 12.490 &= 0.006 \end{aligned}$$

Using diagram, this must be the splitting of 3p.

$Z = 34$  so  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 \mathbf{4p^4}$ , i.e.  $n = 4$

The transition at 12.652 keV is to 4p, but this means the hole is in the outer shell, i.e. the atom is

just ionized, i.e. energy=0.  
 $\Rightarrow$  energy of 1s is 12.652 keV.  
 Other energies

$$\begin{aligned}
 12.652 - 11.182 &= 1.47 \\
 12.652 - 11.222 &= 1.43 \\
 12.652 - 12.490 &= 0.162 \\
 12.652 - 12.496 &= 0.156 \\
 0.162 + 1.486 &= 1.648 \quad (= 0.156 + 1.492)
 \end{aligned}$$

Approximations: central field model of the ion (hence  $n, l$ ). Ignore the fact that the ion might be left in an excited state of the valence electrons (small energies, of order eV).

Deducing  $\sigma_{n,l}$ :

We now know the energies, so use

$$E = E_R(Z - \sigma)^2/n^2$$

$$\Rightarrow Z - \sigma = n\sqrt{E/E_R} \Rightarrow \sigma = Z - n\sqrt{E/E_R}$$

There is an ambiguity in the question. I assume the  $\sigma$  for levels of low  $n$  and  $l$  are required.  
 Hence

$n$	$l$	$j$	$\sigma_{n,l}$
1	0	1/2	3.50
2	0	1/2	12.0
2	1	1/2	13.2
2	1	3/2	13.5

(The levels of least energy are 4s, 4p and the excited states of valence electron, all these have  $\sigma \simeq 33$ ).

Comments:  $\sigma_{1,0}$  is small, because when the hole is in the ground state the mean radius of the orbit is small, so is not well screened from the nuclear charge.  $\sigma_{2,1} > \sigma_{2,0}$  because  $l$  states have larger mean radius than  $s$  states. There are 2 electrons in a full K shell, and 8 in a full L shell. The values  $\sim 3.5$  and  $\sim 12$  or  $13$  are therefore roughly of the expected size, being larger owing to all the other electrons in higher shells.

Note the fine structure splitting of  $3p$ : this is from spin-orbit effect, so not well modelled by a 'screening' argument which is based on central field approximation.

## 1998. 2.

Rate equations for population:

$$\frac{dN_2}{dt} = -A_{21}N_2 + B_{12}\rho N_1 - B_{21}\rho N_2$$

$A_{21}$  = rate coefficient for spontaneous emission

$B_{12}$  = rate coefficient for absorption

$B_{21}$  = rate coefficient for stimulated emission

Consider a gas of atoms in thermal equilibrium with thermal radiation at temperature  $T$ :

$$\begin{aligned} \rho &= \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/k_B T} - 1} \\ \frac{dN_2}{dt} &= 0 \quad (\text{thermal equil} \Rightarrow \text{steady state}) \\ \Rightarrow N_2(A_{21} + B_{21}\rho) &= B_{12}\rho N_1 \\ \Rightarrow \frac{N_2}{N_1} &= \frac{B_{12}\rho}{A_{21} + B_{21}\rho} \\ \text{But } \frac{N_2}{N_1} &= \frac{g_2}{g_1} e^{-h\nu/k_B T} \quad \text{Boltzman distribution} \\ \Rightarrow \frac{g_2}{g_1} e^{-h\nu/k_B T} &= \frac{B_{12}/B_{21}}{\frac{A_{21}}{B_{21}\rho} + 1} \\ &= \frac{B_{12}/B_{21}}{\frac{A_{21}}{B_{21}} \frac{c^3}{8\pi h\nu^3} (e^{h\nu/k_B T} - 1) + 1} \end{aligned}$$

True for all  $T$

$$\Rightarrow \frac{A_{21}}{B_{21}} \frac{c^3}{8\pi h\nu^3} = 1, \quad \frac{g_2}{g_1} = \frac{B_{12}}{B_{21}}.$$

$$\begin{aligned} \Rightarrow g_2 B_{21} &= g_1 B_{12}, \quad A_{21} = \frac{8\pi h\nu^3}{c^3} B_{21} \\ \Rightarrow g_2 A_{21} &= \frac{8\pi h\nu^3}{c^3} g_1 B_{12}. \end{aligned}$$

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diagram ...

$$\begin{aligned} \frac{dN_3}{dt} &= S_3 - A_{32}N_3 \\ \frac{dN_2}{dt} &= S_2 + A_{32}N_3 - A_{21}N_2 \\ \frac{dN_1}{dt} &= A_{21}N_2 - X \end{aligned}$$

$$\text{st. state: } S_3 = A_{32}N_3 \quad \Rightarrow N_3 = S_3/A_{32}.$$

$$N_2 = \frac{S_2 + A_{32}N_3}{A_{21}} = \frac{S_2 + S_3}{A_{21}}.$$

$$\Rightarrow \frac{N_3}{N_2} = \frac{S_3}{A_{32}} \cdot \frac{A_{21}}{S_2 + S_3} = \frac{S_3}{S_2 + S_3} \frac{A_{21}}{A_{32}},$$

$$N_3 - N_2 = \frac{S_3}{A_{32}} - \frac{S_2 + S_3}{A_{21}} = \frac{A_{21}S_3 - A_{32}(S_2 + S_3)}{A_{32}A_{21}}.$$

$$\text{So } \frac{N_3}{N_2} > 1 \quad \text{when} \quad \frac{S_3}{S_2 + S_3} \frac{A_{21}}{A_{32}} > 1$$

$$\Rightarrow \frac{S_2}{S_3} < \frac{A_{21}}{A_{32}} - 1$$

If  $N_3 > N_2$  get population inversion. In this case the stimulated emission exceeds the absorption, so we get gain, i.e. coherent amplification of the light, on the transition  $3 \rightarrow 2$ . This is how a laser works.

diagram ...

$$\begin{aligned} \frac{dN_3}{dt} &= S_3 - A_{32}N_3 + B_{23}\rho N_2 - B_{32}\rho N_3 \\ \frac{dN_2}{dt} &= S_2 + A_{32}N_3 - A_{21}N_2 - B_{23}\rho N_2 + B_{32}\rho N_3 \\ \frac{dN_1}{dt} &= A_{21}N_2 - X \end{aligned}$$

$$\begin{aligned} \text{st. state: } 0 &= S_3 - A_{32}N_3 + B_{23}\rho N_2 - B_{32}\rho N_3 \\ 0 &= S_2 + A_{32}N_3 - A_{21}N_2 - B_{23}\rho N_2 + B_{32}\rho N_3 \end{aligned}$$

$$\begin{aligned} \text{add: } 0 &= S_3 + S_2 - N_2 A_{21} \\ \Rightarrow N_2 &= \frac{S_2 + S_3}{A_{21}} \\ \Rightarrow N_3 &= \frac{S_3 + B_{23}\rho \left( \frac{S_2 + S_3}{A_{21}} \right)}{A_{32} + B_{32}\rho} \\ \Rightarrow N_3 - N_2 &= \frac{S_3 + B_{23}\rho \left( \frac{S_2 + S_3}{A_{21}} \right)}{A_{32} + B_{32}\rho} - \frac{S_2 + S_3}{A_{21}} \\ &= \frac{S_3 A_{21} + B_{23}\rho (S_2 + S_3) - (A_{32} + B_{32}\rho)(S_2 + S_3)}{A_{21}(A_{32} + B_{32}\rho)} \end{aligned}$$

$$\text{Now } g_2 = g_3 \Rightarrow B_{23} = B_{32}$$

$$\Rightarrow N_3 - N_2 = \frac{S_3 A_{21} - A_{32}(S_2 + S_3)}{A_{21}(A_{32} + B_{32}\rho)}$$

$$\text{So factor } \frac{(N_3 - N_2)(\text{with rho})}{(N_3 - N_2)(\text{without rho})} = \frac{A_{32}}{A_{32} + B_{32}\rho}$$

$$\text{Evaluate: } \frac{1}{1 + \frac{B_{32}}{A_{32}}\rho}$$

$$\frac{B_{32}}{A_{32}} = \frac{c^3}{8\pi h\nu^3} = 7.49 \times 10^{12} \text{ m}^3/\text{Js}.$$

Flux per  $\delta f$  is  $\Phi = 10^{14} \text{ m}^{-2} \text{ s}^{-1} \text{ Hz}^{-1}$

Suppose flux passes through area  $A$  for time  $t$  :

$$\begin{aligned} & \Phi A t \quad \text{photons Hz}^{-1} \\ \Rightarrow & \Phi A t h \nu \quad \text{energy Hz}^{-1} \end{aligned}$$

This energy fills a volume  $ctA$

$$\begin{aligned} \Rightarrow \rho &= \frac{\Phi A t h \nu}{c t A} \quad (\text{energy Hz}^{-1}/\text{volume}) \\ &= \frac{\Phi h \nu}{c} \\ &= 1.326 \times 10^{-13} \text{ Jm}^{-3} \text{ Hz}^{-1} \end{aligned}$$

$$\begin{aligned} \Rightarrow \text{Factor} &= \frac{1}{1 + 7.49 \times 10^{12} \times 1.326 \times 10^{-13}} \\ &= 0.50 \end{aligned}$$

## 2000. 5.

(a) Each atom in the gas has a velocity. The light observed along a given direction  $z$  has its frequency  $f$  Doppler-shifted by

$$\Delta f = f \frac{v_z}{c},$$

$v_z$  = component of velocity along the line of sight. The distribution of velocities is Gaussian (from kinetic theory), with a standard deviation  $\delta v_z$  given approximately by

$$\frac{1}{2} M (\delta v)^2 \simeq \frac{1}{2} k_B T, \quad M = \text{mass of atom}$$

$$\Rightarrow \text{width} \simeq 2\delta v_z \simeq 2\sqrt{k_B T/M}$$

Hence the shape of the spectral line is Gaussian, and line width

$$\Delta f \simeq \frac{f}{c} 2\sqrt{k_B T/M}$$

(Typical number could be 100's of MHz, optical transition at room temperature)

(b) Natural decay of a energy level gives it a finite lifetime  $\tau$ . Therefore an emitted wave must decay exponentially. Fourier analysing this, we find a Lorentzian distribution of frequency components, with full width at half maximum such that  $\Delta\omega = 1/\tau$ , so

$$\Delta f = \frac{1}{2\pi\tau}$$

(c) Collisions between atoms interrupt the phase of the emitted wave. Fourier analysis of such a wave again gives a Lorentzian distribution of frequency components. If  $\tau$  is the mean time between collisions then the FWHM is

$$\Delta f = \frac{1}{2\pi\tau}$$

Potassium: Doppler: find FWHM:

$$\begin{aligned} e^{-(1/2)Mv^2/k_B T} &= \frac{1}{2} \\ \Rightarrow \frac{(1/2)Mv^2}{k_B T} &= \ln 2 \\ \Rightarrow v &= \sqrt{2 \ln 2 k_B T / M} \\ \Rightarrow \Delta v_{\text{FWHM}} &= 2\sqrt{2 \ln 2 k_B T / M} \\ \Rightarrow \frac{\Delta \tilde{\nu}_{\text{FWHM}}}{\tilde{\nu}} &= \frac{\Delta v}{c} \\ &= \frac{2\sqrt{2 \ln 2 \times 1.38 \times 10^{-23} \times 300/39 \times 1.66e-27}}{3 \times 10^8} \\ &= 1.99 \times 10^{-6}. \end{aligned}$$

$$\begin{aligned} \text{Decay rate} &= 1/\tau = 3.7 \times 10^7 \text{ s}^{-1} \\ \Rightarrow \text{natural lifetime broadening } \Delta f &= \frac{1}{2\pi} 3.7 \times 10^7 = 5.89 \text{ MHz} \\ f &= c/(766 \text{ nm}) = 3.914 \times 10^{14} \text{ s}^{-1} \\ \Rightarrow \frac{\Delta \tilde{\nu}_{\text{FWHM}}}{\tilde{\nu}} = \frac{\Delta f}{f} &= 1.50 \times 10^{-8}. \end{aligned}$$

Collision broadening:

mean time  $t$  between collisions:

$$\begin{aligned} vt\sigma n &= 1 \\ \Rightarrow t &= \frac{1}{v\sigma n} \end{aligned}$$

$$\sigma \simeq \pi \times (\text{atomic diameter})^2 \simeq \pi(10^{-10})^2 = 3 \times 10^{-20} \text{ m}^2$$



$$PV = RT \Rightarrow P = \frac{NRT}{VN} = nk_B T$$
$$\Rightarrow n = \frac{5 \times 10^4}{k_B \times 300} = 1.21 \times 10^{25} \text{ m}^{-3}$$

$$v \simeq \sqrt{k_B T / M} = 253 \text{ ms}^{-1}$$

$$\Rightarrow t \simeq 3 \text{ ns}$$
$$\Rightarrow \Delta f = \frac{1}{2\pi t} \simeq 53 \text{ MHz}$$
$$\Rightarrow \frac{\Delta \tilde{\nu}}{\tilde{\nu}} = 1.4 \times 10^{-7}$$