Example finals answers

Prof. Andrew Steane

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1999. 1. The quantum defect δ is a factor introduced to convert the formula for hydrogen energy levels so that it can be used for alkali atoms:

$$E(n, l) = -\frac{E_R}{(n-\delta)^2}$$

This is based on the central field model of the atom, it takes into account the shift in energy due to the fact that the central potential is not $\propto 1/r$.

This is useful because for a given atom the value of δ turns out to be almost independent of n. Therefore one can reconstruct the complete energy levels from only a few numbers.

a) δ decreases as l gets larger because for large l the valance electron is more likely to be far from the core, and in this region the potential is more hydrogen-like. For small l the electron penetrates the core, so is less screened and more tightly bound.

b) Far from the core, the potential is always hydrogen-like, but within the core it gets deeper as the atomic number increases. Therefore δ is larger for heavier alkalis.

Absorption spectrum $\Rightarrow$ transitions from the ground state.

Sodium, 11 electrons $\Rightarrow$ $1s^2\ 2s^2\ 2p^6\ 3s$ $\Rightarrow$ $n = 3$ ground state.

Series limit $\Rightarrow$ ionization energy is 1/241 nm $= 4.149 \times 10^6$ m^{-1}

$$= 0.3781R \text{ (in wavenumber units)}$$

$$\begin{aligned} \text{Hence} \quad 0.3781 &= \frac{1}{(3-\delta_s)^2} \\ \Rightarrow \quad \delta_s &= 1.37 \end{aligned}$$

First doublet is 3s–3p
Wavenumber $1/589.3$ nm $= 1.697 \times 10^6$ m$^{-1} = 0.1546R$.

$$\text{Hence} \quad (0.3781 - 0.1546) = \frac{1}{(3-\delta_p)^2}$$
$$\Rightarrow \quad \delta_p = 0.885$$

2nd doublet is 3s–4p.

$$\frac{1}{(4-\delta_p)^2} = 0.1030$$

$\Rightarrow$ 4p is above ground state by

$$(0.3781 - 0.1030)R$$
$$= 0.275R = 3.018 \times 10^6 \text{ m}^{-1}$$

$$\Rightarrow \quad \text{Wavelength is } 1/\cdots = 331 \text{ nm}$$

Next series is also doublets, so it must be 3p–ns.
Find 4s energy:

$$\frac{1}{(4-1.37)^2} = 0.1446$$

Recall 3p energy is at $(0.3781 - 0.1546) = 0.2235$ Hence 4s is above 3p by

$$\begin{aligned}(0.2235 - 0.1446)R \\ = 0.0789R \; = \; 865849 \text{ m}^{-1}\end{aligned}$$

$$\Rightarrow \quad \text{Wavelength is } 1/\cdots = 1160 \text{ nm}$$

Series limit is given by 3p energy, i.e. $1/0.2235R = 408$ nm.

Spectrograph . . .

The calibration is done by allowing light from a source of known wavelengths to enter the spectrograph and fall on the same film (or CCD) without changing the conditions. A fit to the known line positions will then allow the unknown ones to be determined.

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

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

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

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

and $\mathbf{s}$ is spin operator.

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

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

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

So

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

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

Use 1st order perturbation theory:
energy shift $\Delta E = \langle H \rangle$

Now $\mathbf{j} = \mathbf{l} + \mathbf{s}$
so $\mathbf{j}^2 = \mathbf{l}^2 + \mathbf{s}^2 + 2\mathbf{s} \cdot \mathbf{l}$
Hence

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

So

$$\Delta E = \frac{\mu_0}{4\pi} \frac{e^2 \hbar^2}{2m^2} \, \frac{j(j+1) - l(l+1) - s(s+1)}{2 a_0^3 n^3 l(l+1/2)(l+1)}$$

Now

$$\frac{\mu_0}{4\pi} \frac{e^2 \hbar^2}{2m^2} \, \frac{1}{2a_0^3} = 3.622 \times 10^{-4} \text{ eV}$$

3p $^2P_{3/2}$:
$s = 1/2, \;\; l = 1, l; \; j = 3/2$

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

3p $^2P_{1/2}$:
$s = 1/2, \quad l = 1, l; \; j = 1/2$

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

→ 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 $(13.5 \times 10^{-6} \times 11^4 = 0.197$ eV.

b) muonic sodium: have m as well as Z dependance.

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

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

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

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 is smaller than that in the ion.

2000. 2. The term describes the interaction between the magnetic dipole moment of the nucleus and the magnetic field created by the electrons at the nucleus:

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

where
dipole moment $\boldsymbol{\mu} \propto \mathbf{I}$ the spin of the nucleus

magnetic field $B \propto \mathbf{J}$ the total angular momentum of the electrons.

Both the motion and the spin of the electrons give rise to B fields proportional to $\mathbf{l}$ and $\mathbf{s}$. However, internal interactions amongst the electrons cause these to precess about $\mathbf{J}$ (since $\mathbf{J}$ is a constant of the motion) and hence all components of B average to zero except those along $\mathbf{J}$.

Hence overall the form is (const) $\times \mathbf{I} \cdot \mathbf{J}$

1st order perturbation theory: energy shift $\Delta E = \langle H \rangle = A \langle \mathbf{I} \cdot \mathbf{J} \rangle$

Let $\mathbf{F} = \mathbf{I} + \mathbf{J}$

$$\begin{aligned} \mathbf{F}^2 &= (\mathbf{I} + \mathbf{J})^2 = \mathbf{I}^2 + \mathbf{J}^2 + 2\mathbf{I} \cdot \mathbf{J} \\ \Rightarrow \quad \mathbf{I} \cdot \mathbf{J} &= \frac{(\mathbf{F}^2 - \mathbf{I}^2 - \mathbf{J}^2)}{2} \\ \Rightarrow \quad \Delta E_F &= \frac{A}{2} \left(F(F+1) - I(I+1) - J(J+1) \right) \end{aligned}$$

since states are eigenstates of F^2, I^2 and J^2 (before the perturbation acts).

Hence separation between one level and the next is

$$\Delta E_{F,F-1} = \Delta E_F - \Delta E_{F-1}$$

$$
\begin{aligned}
&= \frac{A}{2}\left[(F(F+1) - I(I+1) - J(J+1))\right. \\
&\qquad \left.-((F-1)(F) - I(I+1) - J(J+1))\right] \\
&= \frac{A}{2}\left[F^2 + F - F^2 + F\right] \\
&= AF
\end{aligned}
$$

$$
\Rightarrow \quad \frac{\Delta E_{F,F-1}}{\Delta E_{F-1,F-2}} = \frac{AF}{A(F-1)} = \frac{F}{F-1}
$$

The structure is dominated by the 4d^3 5s ^5P term because the valence electron is in an s state (while the other term is p). Its wavefunction therefore is non-zero at the nucleus, and the magnetic dipole of this electron produces an especially large magnetic field there ("Fermi contact interaction").

Ignore the upper level splitting. Then the 5 transitions imply 5 energy levels in lower state.
$\Rightarrow$ either $I = 2$ or $J = 2$ (in order to get 5 values of F).

We have ^5P so $S = 2, \quad L = 1 \;\Rightarrow\; J = 1,\ 2,$ or 3.

Notice the atomic weight 93 is odd $\Rightarrow$ I is half-integer.

$$\Rightarrow \quad \text{must be } J = 2, \qquad \text{and } F \text{ is half-integer}$$

Must be $I > 2$, so 5/2 or 7/2 or 9/2, $\cdots$

Examine interval rule:

$$\begin{aligned} \frac{F}{F-1} &= r \\ \Rightarrow \quad F &= r(F-1) \\ \Rightarrow \quad F(1-r) &= -r \\ \Rightarrow \quad F &= \frac{r}{r-1} \end{aligned}$$

Diagram → gaps 42.0, 35.6, 29.1, 22.7

r	r/(r-1)
$42/35.6 = 1.18$	6.56
$35.6/29.1 = 1.22$	5.48
$29.1/22.7 = 1.28$	4.55

This looks like $F = 6.5, 5.5, 4.5$
(and so the other two values are $3.5, 2.5$)

Therefore nuclear spin $I = 4.5 = 9/2$.

To observe hyperfine structure, the emission lines from a discharge lamp can be examined using a line filter in combination with a Fabry-Perot etalon.

$\cdots$ diagram

The detector is in the focal plane of the lens. Each hyperfine component gives its own set of interference fringes. The hyperfine splittings can be measured by comparing them to the free spectral range of the etalon.

It will be convenient to cover the whole span of 129 m^{-1} comfortably within a free spectral range of the etalon.

$$\begin{aligned} \frac{1}{2nd} &= 200\ \mathrm{m}^{-1} \\ \Rightarrow \quad \text{plate separation} \quad d &\sim \frac{1}{400} = 2.5\ \mathrm{mm} \end{aligned}$$

This is a reasonable value.

1999. 2.

The LS coupling scheme is a model of atomic structure based on a hierarchy of interactions:

$$H_{\text{central field}} \gg H_{\text{residual electrostatic}} \gg H_{\text{spin}-\text{orbit}}.$$

In the central field approximation each electron has a well-defined orbital angular momentum $\mathbf{l}$ and spin $\mathbf{s}$. The residual electrostatic interaction then couples the $\mathbf{l}$. Their total

$$\mathbf{L} = \sum_i \mathbf{l}_i$$

is well-defined and so is the total spin

$$\mathbf{S} = \sum_i \mathbf{s}_i$$

while the individual $\mathbf{l}$ and $\mathbf{s}$ precess about $\mathbf{L}$ and $\mathbf{S}$.

The spin-orbit interaction then couples $\mathbf{L}$ and $\mathbf{S}$ so that they precess slowly about their resultant $\mathbf{J} = \mathbf{L} + \mathbf{S}$.

The scheme is appropriate when the spin-orbit interaction is small compared to the other electrostatic interactions.

Z=12 so $1s^2$ $2s^2$ $2p^6$ $3s^2$ ground state.
Hence expect 3s3p, 3s4s, 3s3d.
We are told 3s4s below 3s3d.
Triplet for given configuration typically below the singlet.

→ diagram

Evidence: (1) the fine structure splitting in the 3s3p ^3P term is small compared to the separation of the triplet from the singlet of each configuration.

(2) the 3s3p $^3P_{0,1,2}$ levels follow the Landé interval rule closely

1999. 2. Last part: “The 1s2s configuration in helium is split into two levels, separated by 6422 cm^{-1}. Assign quantum numbers to these levels, and explain what gives rise to the difference in energy. Why are both these levels metastable?”

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 ψ_S(spatial) × χ_A(spin)
or ψ_A(spatial) × χ_S(spin)

where S,A signifies symmetric, antisymmetric

Now, the mean distance between the electrons is smaller in ψ_S(spat
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: $\cdots$

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

(both of these are antisymmetric overall).

χ_A is the singlet spin state ($S = 0$).
χ_S is the triplet group of spin states ($S = 1$).

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

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

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

The 1s2s configuration has two possibilities:

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

To ensure overall antisymmetry, the spin state must be such that the first is the singlet, the second is the triplet.

The first (ψ_S) has more energy because the electrons are on average closer together in ψ_S compared to ψ_A, so have more energy from their Coulomb repulsion.

→ diagram

Helium: $Z = 2$
Oxygen: $Z = 8$ (since O^{6+} is helium-like)

$$\text{Hydrogen-like ion has energy levels } E = \frac{-Z^2 E_R}{n^2}$$

So to ionize He^+ requires $2^2 E_R = 54.4$ eV.
So to ionize O^{7+} requires $8^2 E_R = 870$ eV.

We can understand the results by using the idea of screening. Each electron in the helium-like system experiences a net electric field from the combination of the nucleus and the other electron. Therefore to ionize the helium (-like) system requires less energy than to ionize the hydrogen-like ion.

The screening effect can be estimated by adjusting the nuclear charge to $Z - \sigma$.

$$(2 - \sigma)^2 E_R = 25 \text{ eV}$$

gives $\sigma = 0.64$ for He.

$$(8 - \sigma)^2 E_R = 740 \text{ eV}$$

gives $\sigma = 0.62$ for 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
   $\Rightarrow \quad \Delta l = \pm 1$
3. Configuration: only one electron jumps
4. when L and S are good quantum numbers:
   $\Delta S = 0,$
   $\Delta L = 0, \pm 1$ and $L = 0 \not\leftrightarrow L = 0$

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 $\Sigma_i -e\mathbf{r}$ 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 $\longrightarrow$ 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 "σ^+/σ^-" lines and 2 "π" 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 π lines are $\Delta M = 0$,
the σ^+/σ^- 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 ΔL selection rule, must have $L_1 = 1$.

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

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

$\longrightarrow$ diagram.

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

OR: For convenience, use

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

$2M_{J2}$	$2M_{J1}$	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

1998. 3.

In the notation ^1L and ^3L, the superscript indicates the value of $2S + 1$ where S is the total spin of the atom—in these examples $S = 0$ and $S = 1$. The letter L indicates the orbital angular momentum in spectroscopic notation: the letters S,P,D ... signify L=1,2,3 ...

1s2s gives terms ^1S and ^3S.
1s2p gives terms ^1P and ^3P.

⟶ diagram

Similarities: use screening concept, Z_{eff} = approx 1 but slightly larger, especially for low n and l

Differences:

1. in helium energy depends on l as well as n (net potential is not simply $1/r$).
2. in helium each configuration has two terms (singlet and triplet) with a splitting owing to the electrostatic repulsion between the electrons.

To estimate: first obtain Z_{eff} for 1s2p

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

$$\begin{aligned} \hat{\mathbf{L}} = \sum_i \hat{\mathbf{l}}_i &= \text{total orbital angular momentum} \\ \hat{\mathbf{S}} = \sum_i \hat{\mathbf{s}}_i &= \text{total spin angular momentum} \\ \hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}} &= \text{total angular momentum} \\ \hat{J}_z &= \text{z-component of } \hat{\mathbf{J}} \end{aligned}$$

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:

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
   $\Rightarrow \quad \Delta l = \pm 1$
3. Configuration: only one electron jumps
4. when L and S are good quantum numbers:
   $\Delta S = 0,$
   $\Delta L = 0, \pm 1$ and $L = 0 \not\leftrightarrow L = 0$

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 $\Sigma_i -e\mathbf{r}$ 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 $\Delta S = 0$.

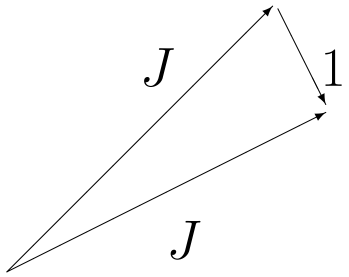
Its effect on L is limited by the same angular momentum conservation considerations as for J.

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 ψ. 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 ϕ-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 μ_B is the Bohr magneton.

Problem given: let 2 be upper level, 1 be lower.
We have $S_2 = 1$, $L_2 = 2$, hence $J_2 = 1, 2$ or 3.
To satisfy selection rules, must have $S_1 = 1$, $L_1 = 1, 2$ or 3, $J_1 =$ integer.
12 components in the Zeeman spectrum suggests maybe $J_1 = 3/2$?
But already ruled this out. Try $J_1 = J_2 = 2$: gives correct number. No other value works $\Rightarrow \quad J_1 = J_2 = 2.$

It remains to find L_1.

$$\begin{aligned} g_2 &= \frac{3 \times 6 + 2 - 6}{2 \times 6} = \frac{14}{12} = 7/6 \\ g_1 &= \frac{20 - L(L+1)}{12}, \end{aligned}$$

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

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

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).

Spectrum: the continuous background is Bremsstrahlung, produced by rapid deceleration of the electrons as they hit and enter the anode. The cut-off is when the all the energy is given to a single photon, at $hf = hc/\lambda = eV$ where V is the potential difference between cathode and anode.

The sharp emission lines are characteristic of the element of which the anode is made. A fast incoming electron knocks an atomic electron out of an inner shell of the atom. The X rays are produced when other electrons in higher shells of the atom “fall down” to fill the hole. The lines come in series, associated with the lower level of the set of transitions.

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 σ_L:

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

$$\Rightarrow \quad \sigma_L \;=\; Z - 2\sqrt{E/E_R + \sim 1/n^2}$$

potassium	rubidium
Z=19	Z=37
n=4	n= 5
E=294 eV	E=1840 eV
$\Rightarrow \quad \sigma_L = 9.7$	$\Rightarrow \quad \sigma_L = 13.7$
$Z_{\text{eff}} = 9.3$	$Z_{\text{eff}} = 23$

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

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

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

(Could mention external screening.)

K_α 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 σ_K and σ_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 σ_K and σ_L, but this is still a small effect compared to $(Z - \sigma_K)^2$.

Rubidium: observe K_α at 13.4 keV.

$$\begin{aligned} (Z-\sigma_K)^2 &= E/E_R + (Z-\sigma_L)^2/4 \\ \Rightarrow \quad \sigma_K &= Z - \sqrt{E/E_R + (Z-\sigma_L)^2/4} \\ &= 37 - \sqrt{\frac{13400}{13.6} + \frac{(37-13.7)^2}{4}} \\ &= 3.5 \end{aligned}$$

Potassium: guess $\sigma_K \simeq 2$
$\Rightarrow$ K_α 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 σ 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 $1\mathrm{s}^2\ 2\mathrm{s}^2\ 2\mathrm{p}^6\ 3\mathrm{s}^2\ 3\mathrm{p}^6\ 3\mathrm{d}^{10}\ 4\mathrm{s}^2\ \mathbf{4p}^4$, 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.

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

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

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

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

There is an ambiguity in the question. I assume the σ 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:

$$\begin{aligned} \rho &= \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/k_BT}-1} \\ \frac{dN_2}{dt} &= 0 \quad \text{(thermal equil} \;\Rightarrow\; \text{steady state)} \end{aligned}$$

$$\begin{aligned} \Rightarrow \quad N_2(A_{21} + B_{21}\rho) &= B_{12}\rho N_1 \\ \Rightarrow \quad \frac{N_2}{N_1} &= \frac{B_{12}\rho}{A_{21} + B_{21}\rho}. \\ \text{But} \qquad \frac{N_2}{N_1} &= \frac{g_2}{g_1} e^{-h\nu/k_BT} \quad \text{Boltzman distribution} \\ \Rightarrow \quad \frac{g_2}{g_1} e^{-h\nu/k_BT} &= \frac{B_{12}/B_{21}}{\frac{A_{21}}{B_{21}}\frac{1}{\rho} + 1} \\ &= \frac{B_{12}/B_{21}}{\frac{A_{21}}{B_{21}}\frac{c^3}{8\pi h\nu^3}(e^{h\nu/k_BT} - 1) + 1} \end{aligned}$$

True for all T

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

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

---

diagram $\cdots$

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

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

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

$$\begin{aligned}
\Rightarrow \quad \frac{N_3}{N_2} &= \frac{S_3}{A_{32}} \cdot \frac{A_{21}}{S_2 + S_3} = \frac{S_3}{S_2 + S_3} \frac{A_{21}}{A_{32}}, \\
N_3 - N_2 &= \frac{S_3}{A_{32}} - \frac{S_2 + S_3}{A_{21}} = \frac{A_{21}S_3 - A_{32}(S_2 + S_3)}{A_{32}A_{21}}.
\end{aligned}$$

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

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

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 $3 \to 2$. This is how a laser works.

diagram $\cdots$

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

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

$$\begin{aligned}
\text{add:} \qquad 0 &= S_3 + S_2 - N_2A_{21} \\
\Rightarrow \quad N_2 &= \frac{S_2 + S_3}{A_{21}}.
\end{aligned}$$

$$\Rightarrow \quad N_3 = \frac{S_3 + B_{23}\rho\left(\frac{S_2+S_3}{A_{21}}\right)}{A_{32} + B_{32}\rho}.$$

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

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

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

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

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

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

Flux per δf is $\Phi = 10^{14}\ \mathrm{m}^{-2}\ \mathrm{s}^{-1}\ \mathrm{Hz}^{-1}$

Suppose flux passes through area A for time t :

ΦAt photons Hz^{-1}

$\Rightarrow$ $\Phi Ath\nu$ energy Hz^{-1}

This energy fills a volume ctA

$$\Rightarrow \ \rho = \frac{\Phi Athv}{ctA} \qquad (\text{energy Hz}^{-1}/\text{volume})$$

$$
\begin{aligned}
&= \frac{\Phi h\nu}{c} \\
&= 1.326 \times 10^{-13} \quad \mathrm{Jm}^{-3}\ \mathrm{Hz}^{-1}
\end{aligned}
$$

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

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 δv_z given approximately by

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

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

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 τ. Therefore an emitted wave must decay exponentially. Fourier analysing this, we find a Lorenztian 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 Lorenztian distribution of frequency components. If τ is the mean time between collisions then the FWHM is

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

Potassium: Doppler: find FWHM:

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

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

Collision broadening:
mean time t between collisions:

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

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

$$\begin{aligned} PV = RT \;\Rightarrow \quad P &= \frac{NRT}{VN} = nk_BT \\ \Rightarrow \quad n &= \frac{5 \times 10^4}{k_B \times 300} = 1.21 \times 10^{25}\ \text{m}^{-3} \end{aligned}$$

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

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