Ay126: Solutions to Homework 2

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1A). The electronic configuration of Na I is $1s^2 2s^2 2p^6 3s^1$. Thus the spectroscopic term for the ground state is $^2 S_{1/2}$. The principal series is thus transitions from the ground state to levels where the valence electron is in np states with $n = 3, 4, 5....$

We have the following: ionization potential of $5.139\,\mathrm{eV}$ which corresponds to $\mathcal{I} = 41,423.0\,\mathrm{cm}^{-1}$. The first member of the principal series is $\lambda \approx 5983\,\text{Å}$ or $k_3 = 16,969.3\,\mathrm{cm}^{-1}$.

Let the energy levels (in wave numbers) of the S and P states be given by

$$E_s(n) = -\frac{Z^2 R}{(m - \mu_s)^2} \tag{1}$$

$$E_p(n) = -\frac{Z^2 R}{(n - \mu_p)^2}. \tag{2}$$

For neutral sodium the effective charge experienced by the valence electron is $Z = 1$. We equate $\mathcal{I} = -E_s(3)$ and find $\mu_s = 1.3723$. This is not needed for the problem at hand but useful to relate to μ_p.

The wave numbers of the principal series are given by

$$k_p(n) = \mathcal{I} + E_p(n) \tag{3}$$

where $n = 3$ is the first member of the principal series and $n = 4$ is the second member and so on. Thus we have

$$n - \mu_p = \sqrt{\frac{Z^2 R}{\mathcal{I} - k_p(n)}}. \tag{4}$$

Substituting $k_p(3)$ into this equation we find $\mu_p = 0.8816$. Substituting this into Equation 3 for $n = 4$ we find $k_p(4) = 30,132.8\,\mathrm{cm}^{-1}$ or $\lambda = 3318\,\text{Å}$.

Quantum defect δ(ℓ) for the Alkali metals

Atom	$L=$	0	1		
n=2 Li		0·40	0·04	0·00	~
3 Na		1·35	0·85	0·01	0·00
4 K		2·19	1·71	0·25	0·00
5 Rb		3·13	2·66	1·34	0·01
6 Cs		4·06	3·59	2·46	0·02

$$E_{n,l} = -hcR\frac{1}{n^{*2}} = -hcR\frac{1}{\left[n-\delta(\ell)\right]^2}$$

$$= -13.6\frac{1}{\left[n-\delta(\ell)\right]^2} \ eV$$

Effective principal quantum number n* for the Alkali metals ground states

Level	Li (n_o=2)	Na (n_o=3)	K (n_o=4)	Rb (n_o=5)
$(n_o s)\ ^2S_{1/2}$	1·588	1·626	1·771	1·805
$(n_o p)\ ^2P_{1/2}$	1·966	2·116	2·232	2·280
$(n_o p)\ ^2P_{3/2}$	1·966	2·117	2·235	2·293

Energy level diagram for Sodium showing fine structure and the emission lines

Sodium 'D'-lines
$^2P_{1/2} - {}^2S_{1/2}$
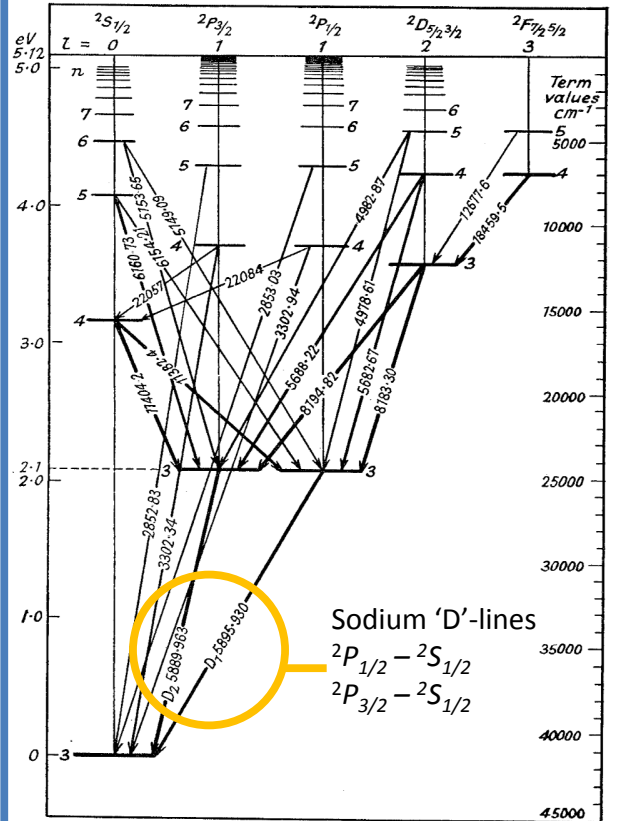$^2P_{3/2} - {}^2S_{1/2}$

Figure 1: The quantum defect and Grotrian diagram for Na I.

From Bacher & Goudsmidt the term values are $E_s(3) = 41,449\,\mathrm{cm}^{-1}$, $E_p(3) = 24,483\,\mathrm{cm}^{-1}$ and $E_p(4) = 11,176.9\,\mathrm{cm}^{-1}$. Thus $k_p(4) = 30,270\,\mathrm{cm}^{-1}$, which is agreeable with our finding. See also Figure 1.

1B). The electronic configuration of C is $1s^2 2s^2 2p^2$ and that of CIV is thus $1s^2 2s^1$. Thus the ground state is $^2S_{1/2}$. The principal series will thus have to be from S to P states. The principal series will $1s^2 2s^1\ {}^2S \rightarrow 1s^2 np^1\ {}^2P$. The first member is thus $1s^2 2s^1 \rightarrow 1s^2 2p^1$. This problem is thus the same as the previous one except that $Z = 4$ and the series starts at $n = 2$ instead of 3.

We have $R = 109737.3\,\mathrm{cm}^{-1}$ and equivalently $13.605\,\mathrm{eV}$. The ionization potential from the ground state is $64.4766\,\mathrm{eV}$ which is $\mathcal{I} = 519709.9\,\mathrm{cm}^{-1}$. The first member of the principal series has a wave number, $k_p(2) = 64555.6\,\mathrm{cm}^{-1}$.

The effective charge as seen from the valence electron is $Z = 4$. We equate $\mathcal{I} = -E_s(2)$ and find $\mu_s = 0.1619$. This is not needed for the problem at hand but useful to relate to μ_p. Substituting $k_p(2) = 64,555.6\,\mathrm{cm}^{-1}$ and $n = 2$ we find $\mu_p = 0.03593$.

Substituting μ_p into Equation 3 we find $k_p(3) = 319,863.6\,\mathrm{cm}^{-1}$ or $\lambda = 312.6\,\text{Å}$. [The observed value is $312.43\,\text{Å}$.]

1C). We have four lines with wave numbers: $k = [1.301, 2.471, 2.900, 3.107] \times 10^4\,\mathrm{cm}$. Since these are seen in absorption we can safely assume that the four lines constitute the principal series. Thus the energy of the ground state is the ionization potential, $\mathcal{I}$. The wavenumber of the transitions is given by

$$k_j = \mathcal{I} - \frac{R}{(n' + j)^2} \tag{5}$$

where $j = 0, 1, 2, 3$. Here R is the Rydberg constant and is $109{,}677.8\,\mathrm{cm}^{-1}$. The unknowns are the ionization potential ($\mathcal{I}$) where $n' = n_0 - \mu$; here n_0 is the energy quantum number of the ground state. We have three unknowns and four measurements and so the problem is solvable, in principle.

We have

$$\begin{aligned}
\frac{k_2 - k_1}{R} &= \frac{1}{n'^2} - \frac{1}{(n'+1)^2} = 0.1067 \\
\frac{k_3 - k_1}{R} &= \frac{1}{n'^2} - \frac{1}{(n'+2)^2} = 0.1458 \\
\frac{k_4 - k_1}{R} &= \frac{1}{n'^2} - \frac{1}{(n'+3)^2} = 0.1647,
\end{aligned} \tag{6}$$

This leads to a mean value of $n' = 2.225$. Quantum defects can be larger unity. Thus possible values of n_0 are either 3 or 4. To sort out this ambiguity

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Table 1: Term values for Potassium

Conf.	term	value (cm^{-1})
4s	^2S	35005.58
4p	^2P	22002.77, 21963.06
5s	^2S	13980.28
3d	^2D	13470.26, 13467.52
5p	^2P	10304.39, 10285.70

we need a clue. As can seen from Equation 5

$$\mathcal{I} = \left\langle k_j + \frac{R}{(n' + j)^2} \right\rangle \tag{7}$$

where the angular brackets refer to an average. We find $\mathcal{I} = 0.3205R$ or $35168\,\text{cm}^{-1}$ or 4.36 eV. I looked up the periodic table and found the element to be potassium whose electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$. Thus I infer $n_0 = 4$. The quantum defect is then 1.775. The transitions in question are thus $4s^1 \to np^1$ where $n = 4, 5, ...$

I then looked up Bacher & Goudsmidt's compilation of energy levels (Table 1). The principal first line of the principal series, $4s \to 4p^1$, is consistent with that stated in the problem set. After some sleuthing I found the term value for $5p$ and found the second line to be consistent with that stated in the problem.

2. The noble elements are characterized by full shells, e.g., the electron configuration of Ar is $1s^2 2s^2 2p^6 3s^2 3p^6$. Two electrons are present in each orbital of a given subshell, and by the Pauli exclusion principle, the electrons must be antiparallel such that $S = 0$. This gives a spin multiplicity of $g_S = 2S + 1 = 1$ for all noble elements with completely filled electron shells.

For half-filled subshells, each electron is in an orbital that is unoccupied by another electron, since it will experience less Coulomb repulsion than a filled orbital, and thus corresponds to a lower energy state (i.e. Hund's rules). Let us assume that three occupied orbitals are $2p_x$, $2p_y$, and $2p_z$. This implies

$\rho_{2p} = \Psi_{2px}^2 + \Psi_{2py}^2 + \Psi_{2pz}^2 = (x^2 + y^2 + z^2) \times \text{some function of r} = \text{some other function of r},$

which is equivalent to spherical symmetry. The total orbital angular momentum is zero, $L = 0$, as is the case for an s-orbital. This is true of all

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half-filled shells (p^3, d^7, f^7), and the same is true for all filled shells. This implies that half-filled and filled shells correspond to S terms.

Another way to think of subshells is in terms of the z-components of angular momentum, e.g., $2p_{-1}$, $2p_0$, $2p_1$. The z-components cancel for half-filled (and filled) shells, and since this is the only component that is observable, we can conclude that orbital angular momentum is zero.

Thus, for filled shells, the spectroscopic term will be $^1S_0$, since $S = 0$ and $L = 0 \implies J = 0$. For half-filled shells, the value s of S and J correspond to the specific atom (e.g. $^4S_{3/2}$ for Nitrogen, $2p^3$, where $S = 3/2$ according to Hund's rules), however, it will always be an S term.

In general, when considering total spin and orbital angular momentum, it is only necessary to consider valence electrons outside of closed shells.

3. For Titanium, $Z = 22$, therefore its electron configuration is $1s^2 2s^2 2p^6 3p^2 3p^6 4s^2 3d^2$. Thus, the d^2 electrons will determine our spectroscopic terms.

The maximum orbital angular momentum quantum number that one of the electrons can have is $m_l = 2$, since $0 \le l < n$ and $m_l = -l \ldots 0 \ldots l$, so we have $m_l = \pm 2, \pm 1, 0$. Each electron must have $m_s = \pm 1/2$. Thus, there are $5 \times 2 = 10$ possible states for a single electron. For the combination of both electrons, there are $10 \times 10 = 100$ total states, however 10 of these states involve identical states of the electrons, and so are excluded, leaving 90 remaining states. Due to the indistinguishability of electrons, there are only $90/2 = 45$ unique combinations of the pair of electrons, and so we must account for these 45 states.

Given that $m_{l,max} = 2$, we know that $M_L = 4, 3, 2, 1, 0$, which corresponds to G, F, D, P, and S spectroscopic terms. Let us start by assuming that both electrons have $m_l = 2$, such that $M_L = 4$ and $M_S = 0$ (the spins must be antiparallel, otherwise the states of the electrons would be identical). Since $g_s = 2M_S + 1 = 1$, $M_L = 4$, and $M_J = \mid M_L + M_S \mid \cdots \mid M_L - M_S \mid = 4$, we have the term $^1G_4$. This accounts for the multiplicity $g = (2M_L + 1)(2M_S + 1) = 9$ of the 45 states.

Let us now consider the case that $m_l = 1$ for both electrons, so $M_L = 2$, $M_S = 0$, $M_J = 2$, and $g = 5$. This corresponds to the term $^1D_2$. If both electrons have $m_l = 0$, then $M_L = 0$, $M_S = 0$, and $M_J = 0$, which corresponds to a singlet, $^1S_0$. 30 states remaining.

We know that there must be $F(M_L = 3)$ and $P(M_L = 1)$ states that we have not yet accounted for. The only way to obtain $M_L = 3$ from the two electrons is to have $m_l = 1$ and $m_l = 2$. Since the m_l quantum numbers are not identical, we can have $m_s = \pm 1/2$, such that $M_S = 1$. So $M_J = 4, 3, 2,$

$g = 21$, and our spectroscopic terms are $^3F_{2,3,4}$. 9 states remaining.

Lastly, the P term ($m_l = 0$, $m_l = 1$). Similarly, we find that $M_L = 1$, $M_S = 1$, $M_J = 2, 1, 0$, and $g = 9$. This corresponds to the term $^3P_{0,1,2}$. All states have been accounted for.

Extra point: Let us consider Hund's rules, which dictate the ordering of the energy levels of the atom:

1. The state with the maximum spin multiplicity $g_s = 2S + 1$ has the lowest energy for a given electron configuration. Orbitals of a subshell are each occupied singly with electrons of parallel spin before double occupation occurs, due to repulsive Coulomb forces, which result in a higher energy state.

2. For states with the same spin multiplicity g_s, the state with the largest value of L has the lowest energy, since this corresponds to electrons orbiting in the same direction (reduced repulsion).

3. The lowest J-level has the lowest energy for less than half-filled sub-shells, whereas for more than half-filled subshells, the highest $J - level$ corresponds to the lowest energy.

   The first rule states that either ^3P or ^3F is the lowest energy state of the atom (the ground state). To distinguish between the two states, we invoke the second rule, which indicates that ^3F is the ground state term since $L = 3 > L = 1$. Thus, the predicted order of the terms by Hund's rules is

$$^3F_{2,3,4}, {}^3P_{0,1,2}, {}^1G_4, {}^1D_2, {}^1S_0.$$

   This is likely not the actual ordering of the energy levels. However, Hund's rules can reliably predict the ground state, which is $^3F_2$.

4. For a survey of fine structure lines from the literature, see Table 2.

5. The total fine-structure perturbation to the Bohr energy level is given by

$$\Delta E(n, j) = E_n \left(\frac{Z_{eff}\alpha}{n} \right)^2 \left(\frac{n}{j + 1/2} - \frac{3}{4} \right)$$

   where E_n is the unperturbed energy level, n is the principal quantum number, j is the total angular momentum quantum number, Z is the effective nuclear charge, and α is the fine structure constant.

Atom/ion	λ (μm)	k (cm^{-1})	Terms	Telescope	Object
C II	158	63.3	$^2P_{3/2} \rightarrow\, ^2P_{1/2}$	Herschel	ULIRG
O I	145	69.0	$^3P_0 \rightarrow\, ^3P_1$	Herschel	ULIRG
O I	63	159	$^3P_1 \rightarrow\, ^3P_2$	Herschel	ULIRG
O III	52	192	$^3P_2 \rightarrow\, ^3P_1$	Herschel	ULIRG
N II	122	82.0	$^3P_2 \rightarrow\, ^3P_1$	Herschel	ULIRG
N III	57	175	$^2P_{1/2} \rightarrow\, ^2P_{1/2}$	Herschel	ULIRG
Fe II	26	385	$^6D_{7/2} \rightarrow\, ^6D_{9/2}$	ISO-SWS	AGB
Fe II	35.4	282	$^6D_{5/2} \rightarrow\, ^6D_{7/2}$	ISO-SWS	AGB
Si II	35	286	$^2P_{1/2} \rightarrow\, ^3P_{3/2}$	ISO-SWS	AGB/SFR
Ne II	12.8	781	$^2P_{1/2} \rightarrow\, ^3P_{3/2}$	Spitzer IRS	SFR
Ne II	15.6	641	$^3P_1 \rightarrow\, ^3P_2$	Spitzer IRS	SFR

Table 2: An example of fine structure lines from the literature

We will consider the example of C II ($Z = 6$) with the electron configuration $[He]2s^2 2p^1$. An approximation to the effective nuclear charge due to shielding is $Z_{eff} = 2$, since the chemical species is singly ionized and we are considering the outer valence electron. We use an ionization table and find that the ionization energy $I = 24.4$ eV for C II. We are concerned with transitions relative to $n = 2$, the energy level that corresponds to the ground state of the valence electron, so in this case $E_n = I$.

Thus, we have a wavelength

$$\lambda = hc/(\Delta E(j = 1/2) - \Delta E(j = 3/2)) \approx 195 \ \mu\text{m}$$

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where h is Planck's constant and c is the speed of light. This is off compared to the observed wavelength at 158 μm, which is expected, since the Bohr model is not a good approximation to non-hydrogenic atoms.