Applied Spectroscopy

Atomic Spectroscopy II

Multielectron Atoms

Recommended Reading:

Banwell And McCash Chapter 5

The Building-Up (aufbau) Principle

How do the electrons in multi-electron atoms get distributed among the orbitals?

Basic rules:

1) Pauli's principle: no two electrons can have the same set of quantum numbers, i.e. the same values for n, l, m, m_s.

Example: 1s orbital, n = 1, l = 0, m_l = 0: only quantum number that can be different is the m_s which can have the values +1/2 and -1/2. 1s (or ns) orbital can only hold two electrons with opposite spins. 1s orbital the electrons can have the quantum numbers (n = 1, l = 0, m_l = 0, m_s = +1/2) and (n = 1, l = 0, m_l = 0, m_s = -1/2)

Example: a p-orbital, np, l = 1, m_l = -1, 0, +1, and m_s = ±½. so allowed quantum numbers are:

(n, l = 1, m_l = -1, m_s = ±½.)
(n, l = 1, m_l = 0, m_s = ±½.)
(n, l = 1, m_l = +1, m_s = ±½.)

So p-orbital can hold 6 electrons. Three with spin up and three with spin down.

2) Electrons tend to occupy the orbital with the lowest energy available

Orbitals have the following order in energy and fill up in this order:
1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < …. (some exceptions)

When the 1s orbital is full (He, 2 electrons) the next electron will go into the 2s orbital (Li, Be), then the 2p orbitals (B, C, N, O, F, Ne) and so on.

3) Hund's principle: electrons tend to occupy degenerate orbitals singly with their spins parallel. Example: when a $2p_x$ orbital contains an electron the next electron goes into $2p_y$ or $2p_z$ orbital with its spin parallel to the electron in the p_x orbital.

When a set of orbitals of given n and *l* is filled it forms a closed shell . Examples: $1s^2$ orbital in He, the $2s^2$ orbital of Be, the 2p6 orbital of Ne

Atom	1s	2s	2p	3s	configuration
Hydrogen	↑				$1s^1$
Helium	↑↓				$1s^2$ Closed
Lithium	↑↓	↑			$1s^2 2s^1$
Berylium	↑↓	↑↓			$1s^2 2s^2$ Closed
Boron	↑↓	↑↓	↑		$1s^2 2s^2 2p^1$
Carbon	↑↓	↑↓	↑ ↑		$1s^2 2s^2 2p^2$
Nitrogen	↑↓	↑↓	↑ ↑ ↑		$1s^2 2s^2 2p^3$
Oxygen	↑↓	↑↓	↑↓ ↑ ↑		$1s^2 2s^2 2p^4$
Fluorine	↑↓	↑↓	↑↓ ↑↓ ↑		$1s^2 2s^2 2p^5$
Neon	↑↓	↑↓	↑↓ ↑↓ ↑↓		$1s^2 2s^2 2p^6$ Closed
Sodium	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑	$1s^2 2s^2 2p^6 3s^1$
Magnesium	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	$1s^2 2s^2 2p^6 3s^2$ Closed
etc					

Electronic structure of first 12 atoms in the periodic table.

A closed shell orbital makes no contribution to the angular momentum of an atom.

For example consider a filled s orbital, ns^2:
each s electron has $l = 0$, so total orbital angular momentum is

$$L = l_1 + l_2 = 0 + 0 = 0$$

total spin angular momentum is

$$S = s_1 + s_2 = 1/2 + (-1/2) = 0$$

Total angular momentum is $J = L + S = 0$

The Spectrum of Alkali Metals

The alkali metals, Lithium Li, Sodium Na, potassium K, Rubidium Rb, Cesium Cs, occupy column 1 of the periodic table (underneath H).

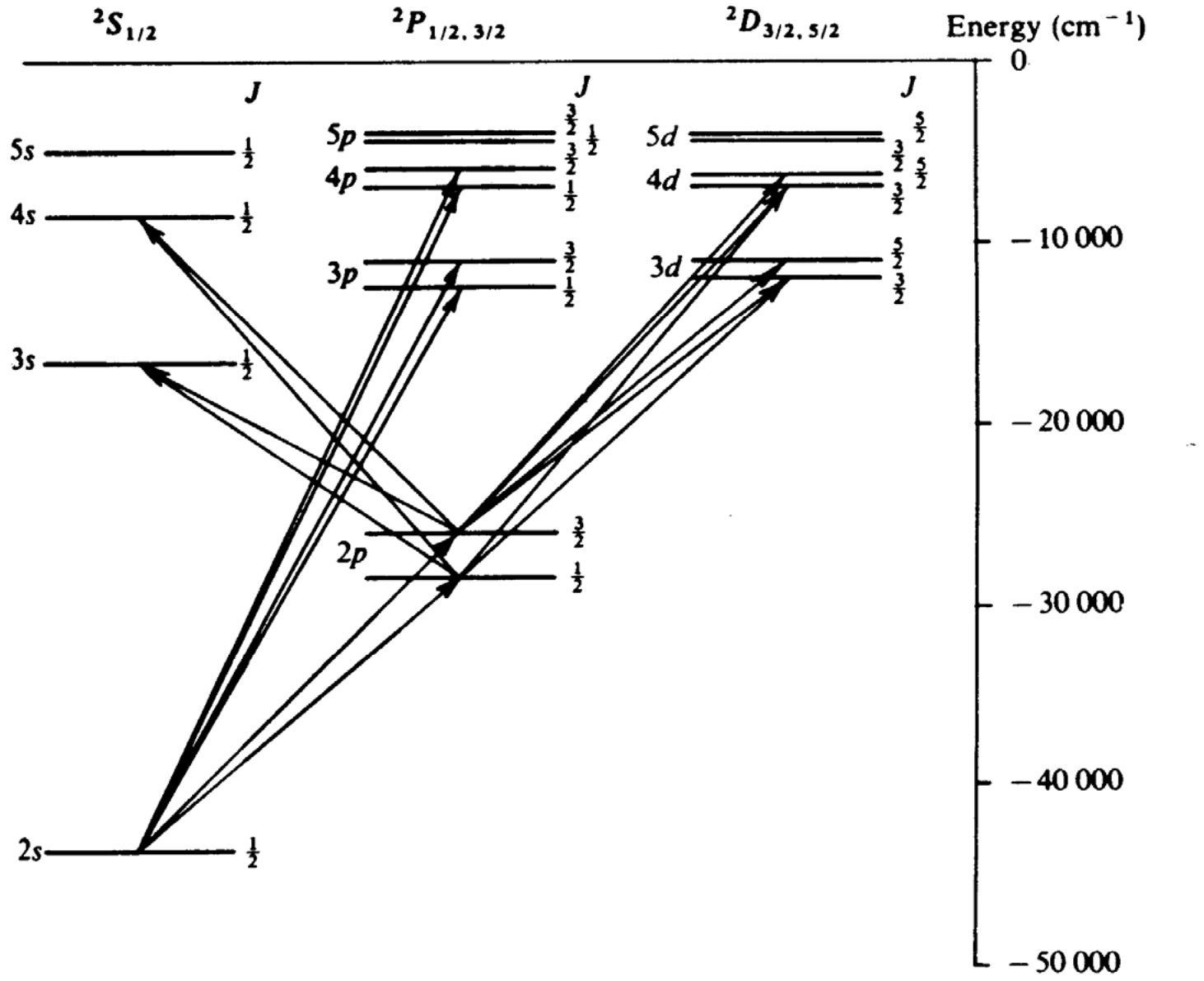
All have a closed inner core and a single outer s- electron

Li:	$1s^2 2s^1$	$[He]\ 2s^1$
Na:	$1s^2 2s^2 2p^6 3s^1$	$[Ne]\ 3s^1$
K:	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	$[Ar]\ 4s^1$

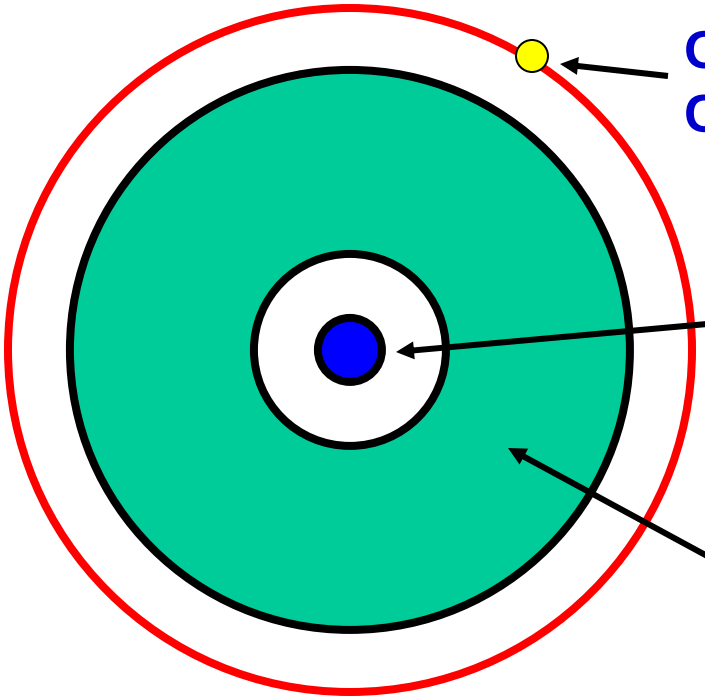
Superficially all resemble the hydrogen atom. To a first approximation we can ignore the angular momentum of the closed shell core and deal with the spin and orbital momentum of the outer electron.

By analogy with the hydrogen atom, we expect the p, d, f, ... levels to be split into doublets because of the coupling between l and s.

Example: Spectrum of Lithium



Energy Levels of Alkali atoms



Outer ns^1 electron
Charge = -e

Nucleus:
Charge = +Ze

Closed Shell of core electrons.
Charge = -(Z-1)e

The (Z-1) core electrons screen the outer s-electron from the Z positive charges in the nucleus.

At large distances from the nucleus the s-electron experiences a potential

$$V(r) = -\frac{e^2}{4\pi\varepsilon_o r} \quad \text{large } r$$

Close to the nucleus the electron sees the full potential

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_o r} \quad \text{small } r$$

This potential is always greater than the corresponding potential for the hydrogen atom $\Rightarrow$ stronger Coulomb attraction $\Rightarrow$ energy levels in alkali halides lie at lower energies than the corresponding energy level in hydrogen, e.g. energy of 2p level in Li < energy of 2p in H, etc.

We can write the potential as

$$V(r) = -\frac{Z_{eff}\, e^2}{4\pi\varepsilon_o r} \quad \text{all } r$$

Where Z_{eff} is the effective nuclear charge seen by the outer s-electron, which will depend on the quantum numbers n and l $\Rightarrow$ each orbital will have a different value of $Z_{eff.}$

$$Z_{eff} = Z - \sigma(n, l)$$

where $\sigma(n, l)$ is the screening parameter. Then, by analogy with the hydrogen atom

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

This model works well for x-ray spectra $\Rightarrow$ transitions involving inner shell electrons. This approach is logical and is analogous with the derivation of the energy levels in H. ...

… historically the spectra of the alkali metals were explained using a formula very similar to that used by Balmer to explain the spectrum of hydrogen

$$E_{n,l} = -hcR\frac{1}{[n-\delta_l]^2} = -hcR\frac{1}{n^{*2}}$$

where $n^* = (n - \delta_l)$ is the **principal quantum number** and δ_l is called the **quantum defect**. Note that n* is not necessarily an integer!

From this expression we can then calculate the wavenumber of transitions in the alkali metals

$$\Delta\varepsilon = \frac{E_2 - E_1}{hc} = \left(\varepsilon_{n_2} - \varepsilon_{n_1}\right) cm^{-1}$$

$$\tilde{\nu} = R\left(\frac{1}{[n_1 - \delta_1(l)]^2} - \frac{1}{[n_2 - \delta_2(l)]^2}\right) cm^{-1}$$

The quantum defects are determined by measurement from the spectra of the alkali metals.

Quantum Defect

Table of experimentally determined quantum defects in Alkali Metals

		s	p	d	f
		$l = 0$	$l = 1$	$l = 2$	$l = 3$
Li	$2s^1$	0.40	0.04	0.00	0.00
Na	$3s^1$	1.35	0.85	0.01	0.00
K	$4s^1$	2.19	1.71	0.25	0.00
Rb	$5s^1$	3.13	2.66	1.34	0.01
Cs	$6s^1$	4.06	3.59	2.46	0.02

Examples:

The Cs 6s electron has an effective principal quantum number

$$n^* = n - \delta(s) = (6 - 4.06) = 1.94$$

Cs 6d electron has an effective principal quantum number

$$n^* = n - \delta(d) = (6 - 2.46) = 3.54$$

K 4p electron has an effective principal quantum number

$$n^* = n - \delta(p) = (4 - 1.71) = 2.29$$

Using this table of quantum defects we can then calculate the energy levels and then work out the energies of transitions in these metals.

Example: the 3p $\rightarrow$ 3s transition in Na, (strong yellow line)

First find the quantum defects for the 3p and 3s states

$\delta(s) = 1.35$ and $\delta(p) = 0.85$

Then

$$E_{3p} = -hcR_{Na}\frac{1}{[3-0.85]^2} \qquad E_{3s} = -hcR_{Na}\frac{1}{[3-1.35]^2}$$

From which

$$\tilde{\nu} = \frac{E_{3s}-E_{3p}}{hc} = R_{Na}\left(\frac{1}{[3-1.35]^2}-\frac{1}{[3-0.85]^2}\right)\text{cm}^{-1} = 1.6964\,\text{cm}^{-1}$$

Where we have used

$$R_{Na} = \frac{\mu_{Na}}{m_e}R\infty = \frac{M_{Na}m_e}{m_e\left(M_{Na}+m_e\right)}R_\infty$$

We can also calculate the ionization potentials as follows

$$I_P = hcR\left[\frac{1}{[n-\delta(l)]^2}-\frac{1}{\infty}\right]$$

Example: For Na n = 3 and $\delta(s) = 1.35$

$$I_P(3s) = hcR_{Na}\left[\frac{1}{[3-1.35]^2} - \frac{1}{\infty}\right] = 5.14eV$$

In a similar manner the ionization potentials for the outer s-electrons in the other Alkali metals are:

	Li	Na	K	Rb	Cs
I_p (ev)	5.39	5.14	4.34	4.18	3.89

Note that this is the ionization potential from the ground state. It is also possible to calculate the ionization potentials for excited states, for example, the ionization potential for the (excited) 5p state in K would be

$$I_P(5p) = hcR_K\left[\frac{1}{[5-1.71]^2} - \frac{1}{\infty}\right]$$

Term Symbols for Alkalis

Since we are dealing with a single outer s-electron, these should be the same as those for Hydrogen

Ground state has a single s-electron $ns^1 \Rightarrow l = 0, s = 1/2 \Rightarrow {}^2S_{1/2}$

Excited states are:

n's $\Rightarrow l = 0,\ s = 1/2,\ j = 1/2 \Rightarrow {}^2S_{1/2}$

n'p $\Rightarrow l = 1,\ s = 1/2,\ j = 1/2, 3/2 \Rightarrow {}^2P_{1/2}, {}^2P_{3/2}$

n'd $\Rightarrow l = 2,\ s = 1/2,\ j = 3/2, 5/2 \Rightarrow {}^2D_{3/2}, {}^2D_{5/2}$

and so on

Absorption Spectroscopy:

Pass light through alkali vapour and measure amount of absorption at each wavelength. At room (or low temp) all atoms will be in the ${}^2S_{1/2}$ ground state.

From selection rules, only $n_0s \rightarrow np$ transitions allowed, where n_0 = principal quantum number of ground state electron, ($n_0 = 2$ for Li, $n_0 = 3$ for Na etc.)

$\Rightarrow$ only one series of lines seen in absorption spectra of alkalis

For example, in Li the following absorptions can take place:

$2s \rightarrow 2p,\ 3p,\ 4p, \ldots$

terms involved are $n_0{}^2S_{1/2} \rightarrow n^2P_{1/2},\ n^2P_{3/2}$

each line will be a doublet due to the fine structure. This is called the **Principal Series.**

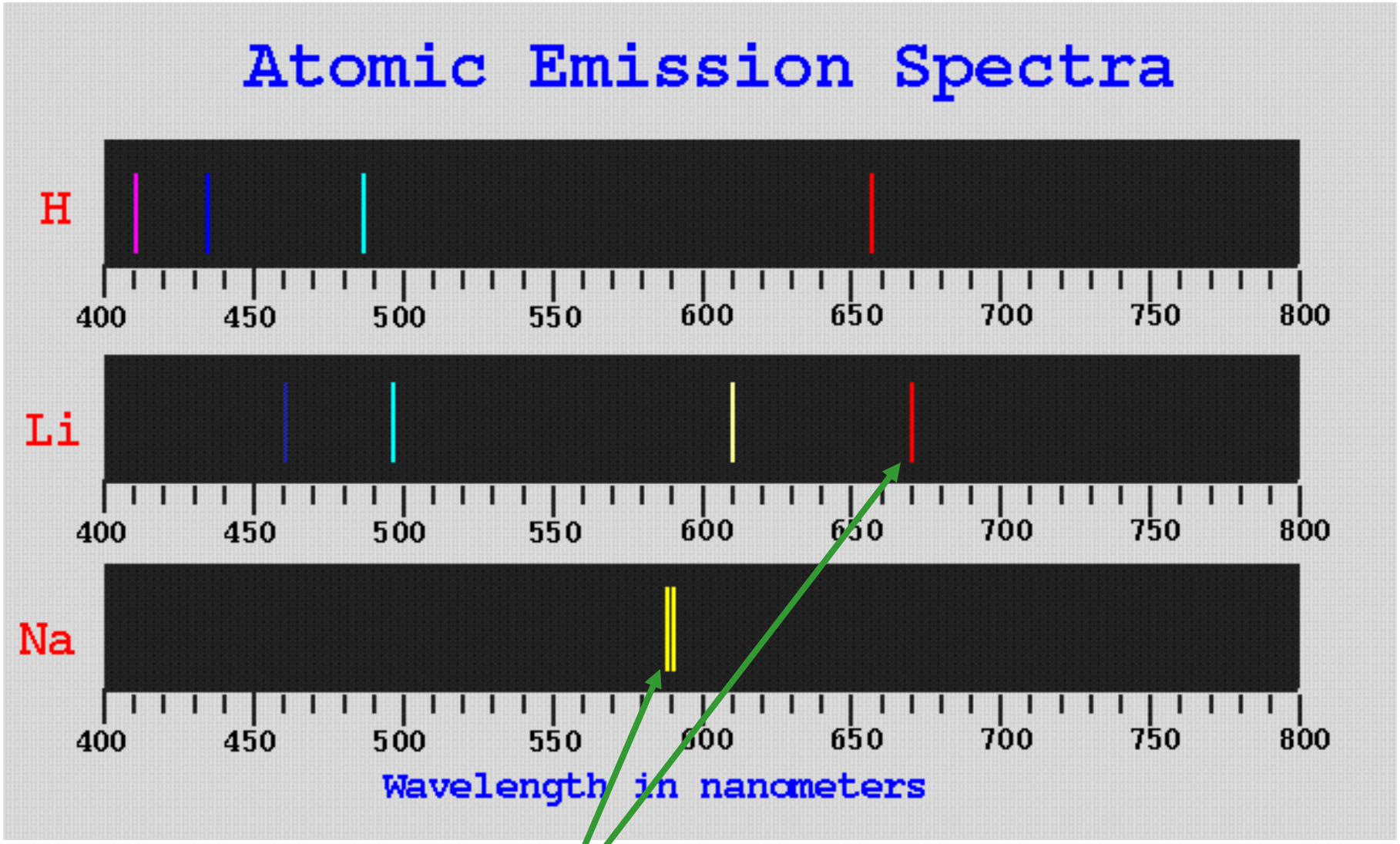
Emission Spectroscopy

Excite alkali vapour by heating it or by passing an electrical discharge through it. Atoms will emit as they decay back to the ground state. The **principal series** is also seen in emission as the excited np electrons return to the n_0s ground state. The strongest emission line always corresponds to the $n_0p \rightarrow n_0s$ transition this is called <u>the resonance line</u>.

For example, in Na the $3p \rightarrow 3s$ transition gives rise to a doublet at 589.0 and 589.6 nm, this transition gives Na street lights their characteristic yellow color.

Table of Resonance Line wavenumbers and wavelengths:

Atom	n_0	cm^{-1}	nm
Li	2	14904	670.0
Na	3	16956	589.0
		16973	589.6
K	4	12985	769.9
		13043	766.5


Atomic Emission Spectra
H
Li
Na
400
450
500
550
600
650
700
750
800
Wavelength in nanometers
Resonance Lines

Other transition lines are also observed in emission spectra of the alkalis, including:

Sharp Series

$ns \rightarrow n_0p$

terms involved are $n^2S_{1/2} \rightarrow n_0{}^2P_{1/2},\ n_0{}^2P_{3/2}$

Diffuse Series

$nd \rightarrow n_0p$

terms involved are $n^2D_{3/2} \rightarrow n_0{}^2P_{1/2},\ n_0{}^2P_{3/2}$

$n^2D_{5/2} \rightarrow n_0{}^2P_{3/2}$

Fundamental Series

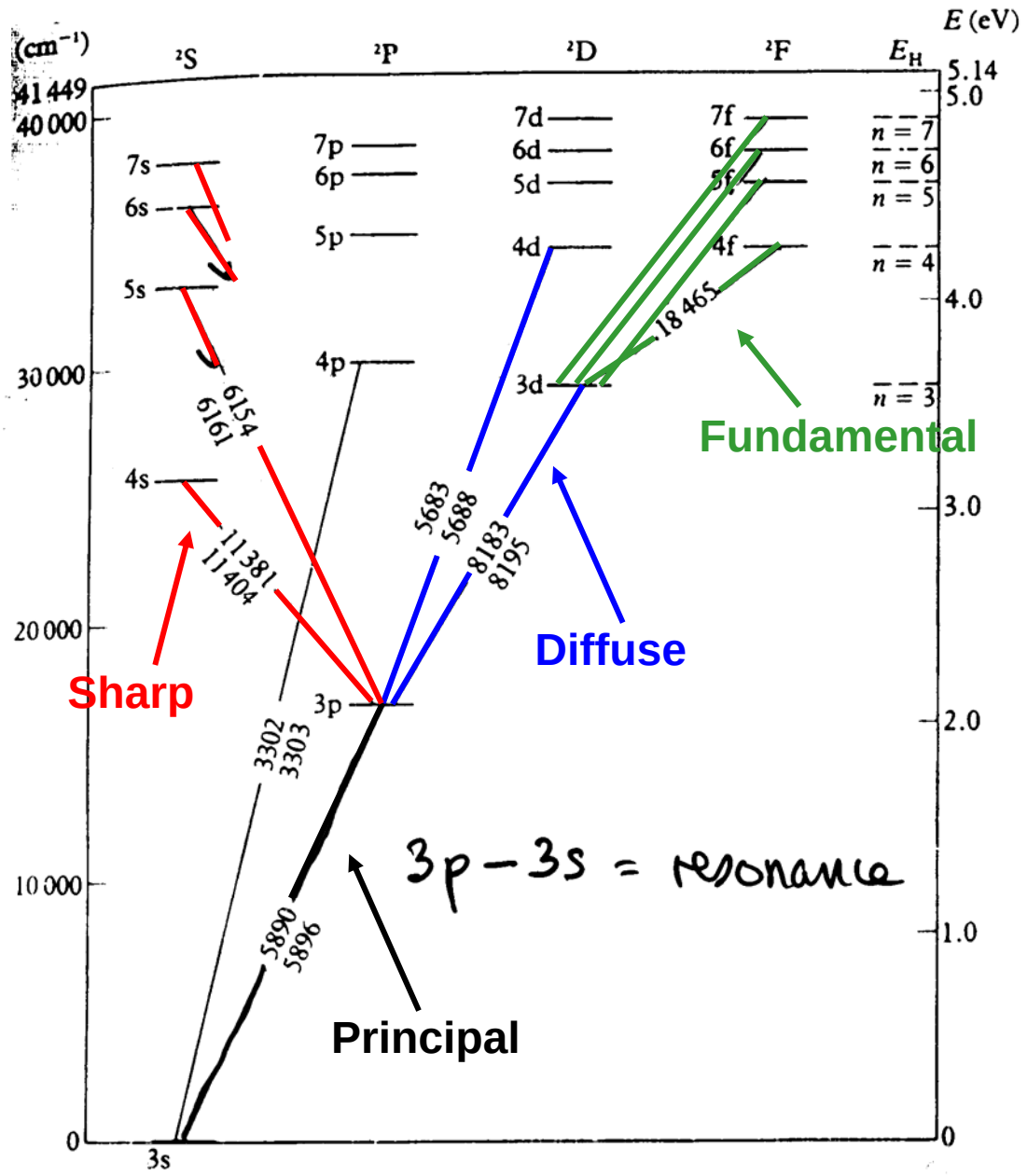
$nf \rightarrow n_0d$

terms involved are $n^2F_{5/2} \rightarrow n_0{}^2D_{3/2},\ n_0{}^2D_{5/2}$

$n^2F_{7/2} \rightarrow n_0{}^2D_{5/2}$

Sodium Energy Levels and Emission Lines

Note that fine structure is not shown in this diagram, so splitting of the p, d, f levels due to l-s coupling is not shown



Lithium Energy Levels and Emission Lines