

## Notes 9: Interaction of atoms and electromagnetic fields

Up to now we have focused on the structure of atoms themselves with little attention on the interaction of atoms with external fields other than brief peaks at the Stark and Zeeman effects. We begin that discussion in earnest here.

We will be particularly interested in the absorption and emission of light by atoms and more generally the coherent interaction of atoms and electromagnetic waves. A detailed treatment of the atom-photon coherence is outside the scope of this course and is mainly the subject of quantum optics. We will make brief a brief foray here.

### Optically active electrons

In hydrogen or hydrogenic atoms (one electron) the effect of absorption and emission is to affect the relative motion of the electron to the nucleus, describable as exciting and de-exciting the electron between ground and excited states. For multielectron atoms, the situation is more complicated. Electrons within a closed shell are tightly bound to the nucleus and are not easily excited. These electrons are said to be "core electrons". The electrons in the last subshell are said to be "optically active" electrons and can be excited

by light. Even then, it is often the case that only one electron of the optically active electrons is excited because multiple excitations are not bound, e.g. helium

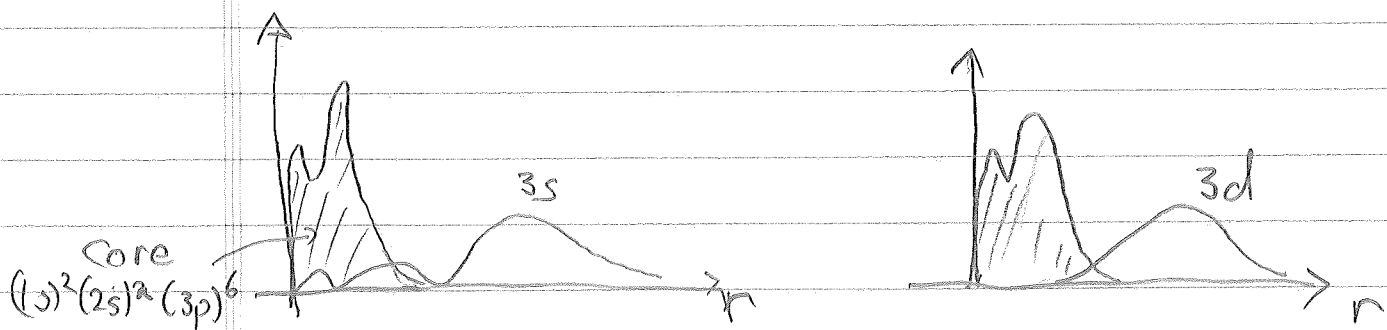
## Alkalies

The simplest atoms for absorption and emission are the Group-I atoms (alkali metals) because they have only one electron in the valence shell. The core electrons are inert and do not get excited.

Config.

H:  $1s$ , Li:  $[He]2s$ , Na:  $[Ne]3s$ , K:  $[Ar]4s$   
Rb:  $[Kr]5s$ , Cs:  $[Xe]6s$ , Fr:  $[Rn]7s$

The excited energy levels of the alkalis are thus very similar to hydrogen, but there are substantial differences because of the penetration of valence electron into the core. This will depend on the angular momentum



The 3s electron penetrates into the core much more than the 3d and thus sees more of the nuclear charge and is more deeply bound.

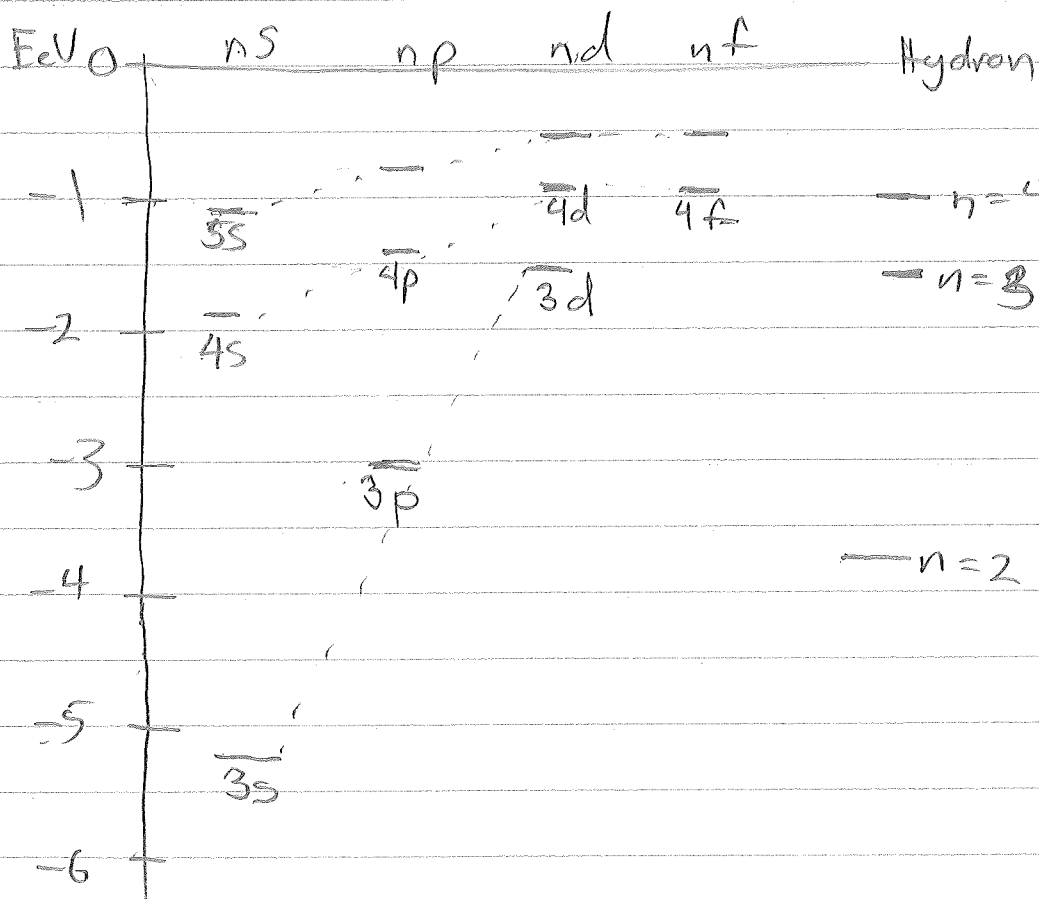
The energy levels are well approximated by a simple modification of the hydrogenic formula. The energy is specified by the valence orbital ( $nl$ )

$$E_{nl} \approx -\frac{1}{2} \frac{1}{(n - \delta_l)^2} \quad \text{in a.u.}$$

denoted  $n^*$

Here  $\delta_l$  is known as the 'quantum defect' reflects the different binding of the states depending on the angular momentum barrier (Note, this is only approximate; the quantum defect also has a small dependence on  $n$ )

For sodium:  $\delta_s \approx 1.35$ ,  $\delta_p \approx 0.86$ ,  $\delta_d \approx 0.01$



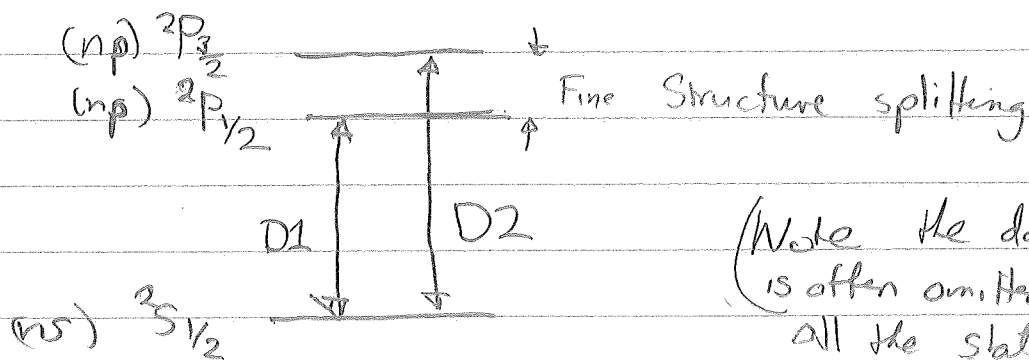
With only one electron in the valence shell, the "term" for this configuration is trivial

$$(nl) \ ^2L_{J=|l \pm \frac{1}{2}|}$$

where  $s_{pm} = \frac{1}{2}$   
so  $2S+1 = 2$

$$L = l, \quad J = |L \pm S| = |l \pm \frac{1}{2}|$$

The important level structure of alkalis for optical excitation involves the first excited state



(Note the doublet label is often omitted since all the states are the same)

The two optically excited spectral lines are historically denoted:

$$D1: \quad n^2S_{1/2} \rightarrow n^2P_{1/2}$$

$$D2: \quad n^2S_{1/2} \rightarrow n^2P_{3/2}$$

(Note the "D" stands for "Doublet")

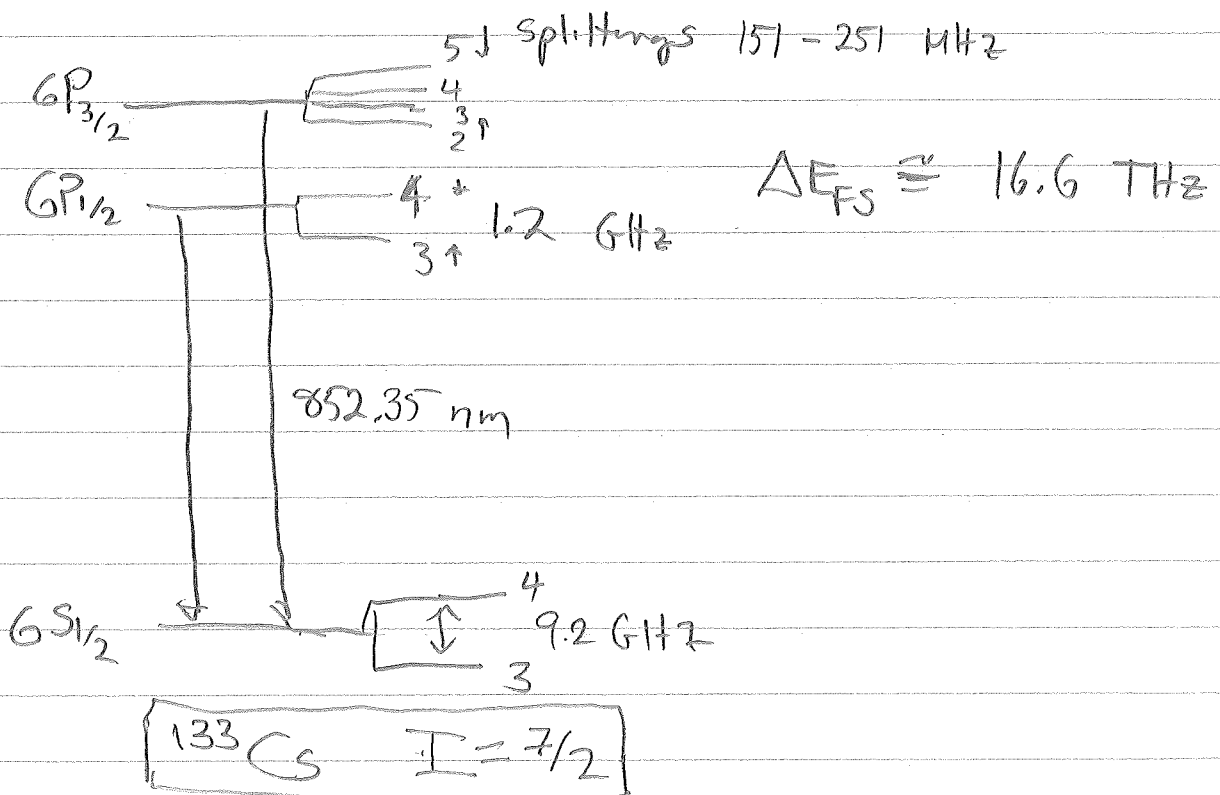
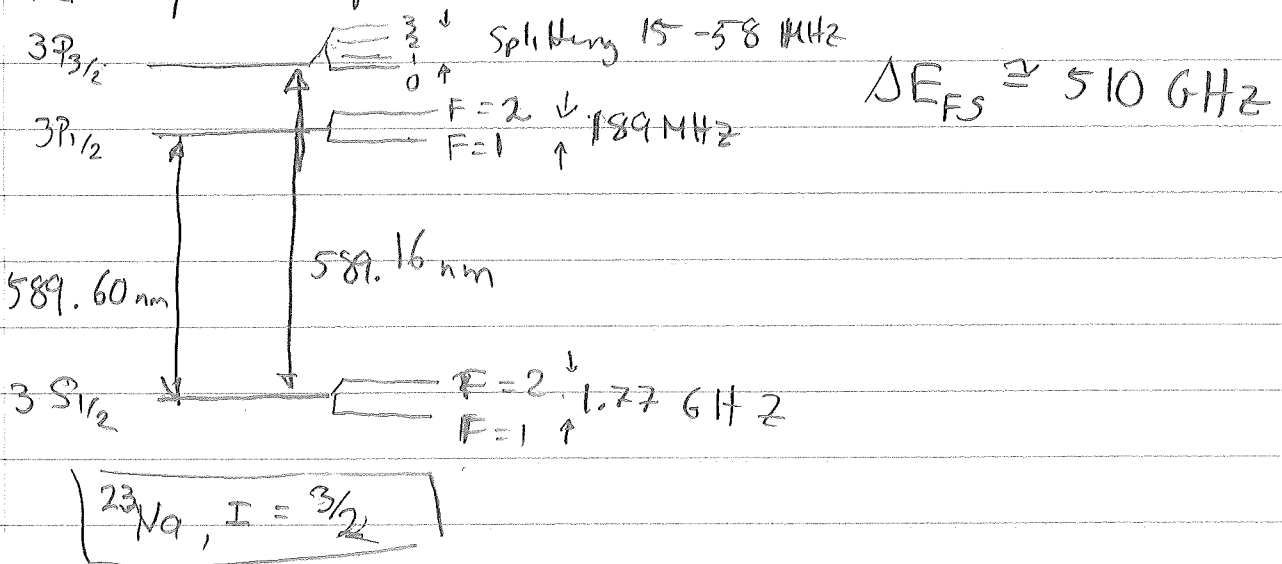
The fine-structure splitting is large and grows rapidly with atomic number  $Z$ . It is well approximated by  $H_{\text{F.S.}} = \frac{\alpha^2}{2} \left\langle \frac{1}{r} \frac{dV_{\text{eff}}(r)}{dr} \right\rangle \vec{l} \cdot \vec{s}$

$$\Rightarrow \Delta E_{\text{F.S.}} \approx \frac{Z_{\text{in}}^2 Z_{\text{out}}^2}{(n^*)^2 l(l+1)} \frac{\alpha^2}{2} \quad \text{in 9.4}$$

In addition, there is substantial hyperfine structure due to nuclear spin magnetic momentum.

$$E_{\text{HFS}} \approx \frac{\alpha^2}{2} \left( \frac{m}{I} \right) \frac{Z_{\text{in}} Z_{\text{out}}^2}{(n^*)^3} \left\{ \frac{F(F+1) - I(I+1) - J(J+1)}{J(J+1)(2L+1)} \right\}$$

Example Spectra:



## Interaction of atoms and electromagnetic fields

To study absorption and emission and other E-M interactions we begin with the fundamental Hamiltonian for interaction of charges and fields

minimal  
coupling  
Hamiltonian

$$\left\{ \begin{aligned} H = & \sum_i \frac{1}{2m_i} \left| \vec{p}_i - \frac{q_i}{c} \vec{A}(\vec{r}_i, t) \right|^2 + V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \\ & + \sum_i q_i \Phi(\vec{r}_i, t) - \sum_i \vec{\mu}_i^{\text{spin}} \cdot \vec{B}(\vec{r}_i, t) \end{aligned} \right.$$

Here  $(\Phi, \vec{A})$  are the scalar and vector potentials of the applied E-M fields and  $V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$  is the interaction potential energy between the charges  $\sum_i \frac{q_i q_j}{|\vec{r}_i - \vec{r}_j|}$

$$\vec{\mu}_i^{\text{spin}} = \begin{cases} -2\mu_B \vec{S}_i & \text{for electrons} \\ g_I \mu_N \vec{I} & \text{for the nucleus} \end{cases}$$

Here I have chosen the "Coulomb Gauge"  $\vec{\nabla} \cdot \vec{A} = 0$   
so  $\vec{A}(\vec{r}, t)$  is the potential associated with E-M radiation  $\vec{E}_{\text{rad}} = -\frac{1}{c} \frac{\partial \vec{A}}{\partial t}$   
 $\vec{B}_{\text{rad}} = \vec{\nabla} \times \vec{A}$

and  $\Phi(\vec{r}, t)$  is the electrostatic potential (eg. due to charged plates)

## Multipole expansion

In classical physics we know that the absorption and emission of electromagnetic radiation by charges is dominated by low order multipole moments when the wavelength of the radiation is much larger than the extent of the distribution. Here this means  $\lambda \gg a_0 \leftarrow$  Bohr radius.

The same holds true in quantum physics. The transition rates are dominated by the lowest nonvanishing multipole moments when  $\lambda \gg a_0$ . It is then convenient to reexpress the Hamiltonian in a form conducive to a multipole expansion. To do so we perform a Gauge transformation implemented by the unitary transformation

$$\hat{U} = e^{-\frac{i}{\hbar c} \sum_i q_i \chi(\vec{r}_i, t)}$$

$$\text{Then } H \Rightarrow \hat{U}^\dagger H \hat{U} - \frac{\hbar}{i} \frac{\partial \hat{U}^\dagger}{\partial t} \hat{U}$$

$$\begin{aligned} \text{and } \vec{A}(\vec{r}, t) &\Rightarrow \vec{A} + \vec{\nabla} \chi \\ \Phi(\vec{r}, t) &\Rightarrow \Phi - \frac{1}{c} \frac{\partial \chi}{\partial t} \end{aligned} \left. \vphantom{\begin{aligned} \vec{A}(\vec{r}, t) \\ \Phi(\vec{r}, t) \end{aligned}} \right\} \begin{array}{l} \text{Gauge} \\ \text{transformation} \end{array}$$

A gauge transformation is a unitary transformation in quantum mechanics

Power-Zienau-Wooley:

The multiple expansion follows from the gauge choice

$$\chi(\vec{r}, t) = -\vec{r} \cdot \vec{A}(\vec{r}, t)$$

$$\Rightarrow \frac{1}{c} \frac{\partial \chi}{\partial t} = \vec{r} \cdot \left( -\frac{1}{c} \frac{\partial \vec{A}}{\partial t} \right) = \vec{r} \cdot \vec{E}(\vec{r}, t)$$

$$\vec{\nabla} \chi = -\left( \vec{A} + \underbrace{\vec{r} \times (\vec{\nabla} \times \vec{A})}_{\vec{B}} + \underbrace{(\vec{r} \cdot \vec{\nabla}) \vec{A}}_{=0, \vec{A} \cdot \vec{\nabla} \vec{A} = 0} \right)$$

Plugging this back into the Hamiltonian after some algebra

$$H \Rightarrow \sum_i \left( \frac{\vec{p}_i^2}{2m_i} + \sum_{j \neq i} \frac{q_i q_j}{|\vec{r}_i - \vec{r}_j|} \right) + \sum_i q_i \phi(\vec{r}_i, t) \\ - \int d^3r \vec{P}(\vec{r}) \cdot \vec{E}(\vec{r}, t) - \int d^3r \vec{M}(\vec{r}) \cdot \vec{B}(\vec{r}, t) \\ - \underbrace{\vec{\mu}_N \cdot \vec{B}(\vec{r}, t)}_{\text{nuclear spin interaction}} + \text{diamagnetic corrections}$$

$$\text{Here } \vec{P}(\vec{r}) = \sum_i q_i \vec{r}_i \delta^{(3)}(\vec{r} - \vec{r}_i) = \\ = \text{electric polarization density}$$

$$\vec{M}(\vec{r}) = \sum_i -\mu_B (\vec{L}_i + 2\vec{S}_i) \delta^{(3)}(\vec{r} - \vec{r}_i) \\ = \text{Magnetization density of electrons}$$



The Hamiltonian thus is

$$\hat{H} = \hat{H}_{\text{Atom}} + \hat{H}_{\text{int}}$$

$$\hat{H}_{\text{Atom}} = \sum_i \left( \frac{\vec{p}_i}{2m_e} + \sum_{j \neq i} \frac{q_i q_j}{|\vec{r}_i - \vec{r}_j|} \right)$$

$$\begin{aligned} \hat{H}_{\text{int}} = & \sum_i q_i \Phi(\vec{r}_i, t) - \int d^3r \vec{P}(\vec{r}) \cdot \vec{E}(\vec{r}, t) \\ & - \int d^3r \vec{M}(\vec{r}) \cdot \vec{B}(\vec{r}, t) - \vec{\mu}_N \cdot \vec{B}(\vec{r}, t) \end{aligned}$$

Making the multipole expansion:

$$\hat{H}_{\text{int}} \approx Q \Phi(\vec{R}, t) - \vec{d} \cdot \vec{E}(\vec{R}, t) - \vec{\mu} \cdot \vec{B}(\vec{R}, t)$$

$$+ \frac{1}{2} \sum_{\alpha\beta} Q_{\alpha\beta} \left. \frac{\partial E_\beta}{\partial x_\alpha} \right|_{\vec{R}} + \dots$$

Monopole:  $Q = \sum_i q_i$

electric dipole:  $\vec{d} = \int d^3r \vec{P}(\vec{r}) = \sum_i q_i \vec{r}_i$

magnetic dipole:  $\vec{\mu} = \sum_i -\mu_B (\vec{L}_i + 2\vec{S}_i) + \mu_N g_N \vec{I}$

electric quadrupole:  $Q_{\alpha\beta} = \sum_i q_i (r_i^\alpha r_i^\beta - \frac{1}{3} |\vec{r}_i|^2 \delta_{\alpha\beta})$

$\vec{R}$  = center of charge  $\approx$  Nuclear coordinate

We see the following:

- If we have an ion with  $Q \neq 0$  we can act on the center-of-mass of ion with an external potential (ion trap)
- The first order interaction that affects the internal degrees of freedom ( $\vec{r}_e$ ) in the electric dipole interaction
- Higher order corrections are magnetic dipole and electric quadrupole.