PH 585 Lecture # 20
AMP

~~[illegible]~~

Interaction of many-electron atoms with EM fields

Need to solve $i\hbar \frac{\partial \Psi(X,t)}{\partial t} = H(t)\Psi(X,t)$

$X = (q_1, q_2, \ldots, q_N) \leftarrow$ N electrons

$$H(t) = \underbrace{\frac{1}{2m}\sum_{i=1}^{N} \vec{p}_i^{\,2} + \underbrace{V}_{= -\sum_{i=1}^{N}\frac{Ze^2}{4\pi\epsilon_0 r_i} + \sum_{i<j=1}^{N}\frac{e^2}{4\pi\epsilon_0 r_{ij}}}}_{= H_0} + \underbrace{\frac{e}{m}\sum_{i=1}^{N}\vec{A}(\vec{r}_i,t)\cdot\vec{p}_i + \frac{e^2}{2m}\sum_{i=1}^{N}\vec{A}^2(\vec{r}_i,t)}_{= H_{int}}$$

$\Downarrow$

all steps same as for hydrogenic atoms

$\Downarrow$

$$W_{ba} = \frac{4\pi^2}{m^2 c}\frac{e^2}{4\pi\epsilon_0}\frac{I(\omega_{ba})}{\omega_{ba}^2}|M_{ba}(\omega_{ba})|^2$$

transition rate for absorption

$$M_{ba} = \sum_{i=1}^{N} \langle \psi_b | e^{i\vec{k}\cdot\vec{r}_i}\hat{\varepsilon}\cdot\vec{\nabla}_{r_i}|\psi_a\rangle$$

Electric dipole approximation: $M_{ba}^D = \sum_{i=1}^{N}\hat{\varepsilon}\cdot\langle\psi_b|\vec{\nabla}_{r_i}|\psi_a\rangle =$

$$= -\frac{m\omega_{ba}}{\hbar}\sum_{i=1}^{N}\vec{\mathcal{E}}\cdot\underbrace{(\vec{r}_i)_{ba}}_{\langle\Psi_b|\vec{r}_i|\Psi_a\rangle} = -N\frac{m\omega_{ba}}{\hbar}\vec{\mathcal{E}}\cdot\vec{r}_{ba} =$$

since e^- are indistinguishable

$$= \frac{m\omega_{ba}}{\hbar e}\vec{\mathcal{E}}\cdot\vec{D}_{ba} \Longrightarrow$$

selection rules

electric dipole moment operator of the atom $\rightarrow$ $\vec{D} = -e\sum_{i=1}^{N}\vec{r}_i = -e\vec{R}$

$$\vec{D}_{ba} = \langle\gamma' J' M_J'|\vec{D}|\gamma J M_J\rangle$$

$$\langle\gamma' J' M_J'|D_q|\gamma J M_J\rangle = \frac{1}{\sqrt{2J+1}}\langle J\,1\,M_J\,q|J' M_J'\rangle\langle\gamma' J'\|\vec{D}\|\gamma J\rangle$$

$M_J + q = M_J'$

$|J-1| \le J' \le J+1$

$Y_{1q} \Leftrightarrow L$

$\vec{J} = \vec{L} + \vec{S}$

1) $\Delta J = 0, \pm 1$ (except for $J=0 \leftrightarrow J'=0$)

2) $\Delta M_J = 0, \pm 1$

3) $|a\rangle$ & $|b\rangle$ must have opposite parity

Laporte's rule

If spin-orbit coupling is weak (L-S coupling regime)

Lecture # 19

work in $|\gamma L S M_L M_S\rangle$ basis

$\Delta L = 0, \pm 1$ (except $L=0 \leftrightarrow L'=0$)

$\Delta S = 0$

$\Delta M_L = 0, \pm 1$

Oscillator strength $\Rightarrow$ $f_{ka} = \frac{2m\omega_{ka}}{3\hbar} \left| \sum_{i=1}^{N} (\vec{r}_i)_{ka} \right|^2$

$$\sum_k f_{ka} = N$$

If expand $e^{i\vec{k}\cdot\vec{r}_i} = 1 + \underbrace{i\vec{k}\cdot\vec{r}_i}_{} + \ldots$

electric quadrupole $\Leftarrow$ $\Rightarrow$ magnetic dipole

$\Downarrow$

$\Rightarrow$ between states $|a\rangle$ & $|b\rangle$ of same parity

Example:

Spectra of the alkalis $\leftarrow$ Li, Na, K, Rb, Cs, Fr

Li: $\underbrace{1s^2}_{^1S_0}\, 2s$ Na: $\underbrace{1s^2 2s^2 2p^6}_{^1S_0} 3s$ K: $\underbrace{1s^2 2s^2 2p^6 3s^2 3p^6}_{^1S_0} 4s$

in a.u.

$$E_{nl} = -\frac{1}{2} \frac{\tilde{Z}^2}{\boxed{n - \alpha(l)}^2}$$

$n - \alpha(l) = n^*$; $\alpha(l)$: quantum defect ($\alpha(l) \downarrow$ as $l \uparrow$)

$\Leftarrow$ spherically symmetric core + 1 s-electron moving in central effective potential $V(r)$

$\tilde{Z} = Z - N + 1$

$\uparrow$ net charge of the nucleus and core electrons

$\Rightarrow$ neutral atoms: $\tilde{Z} = 1$

Absorption spectra $\Rightarrow$ $\nu = R \left[\frac{1}{n^{*2}_{n_0 s}} - \frac{1}{n^{*2}_{np}} \right]$

R: Rydberg const

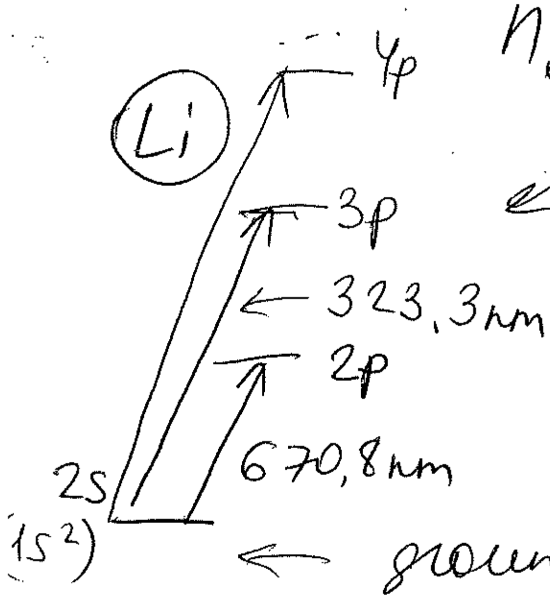
$n_0 s$: ground state of valence e^-

e.g. $n_0 = 2$ for Li, $n_0 = 3$ for Na

Excited states: valence e^- $\Rightarrow$ transition to higher states

$n_0 s \rightarrow np \Leftarrow$ principal series.

(Li)



$\leftarrow$ ground state

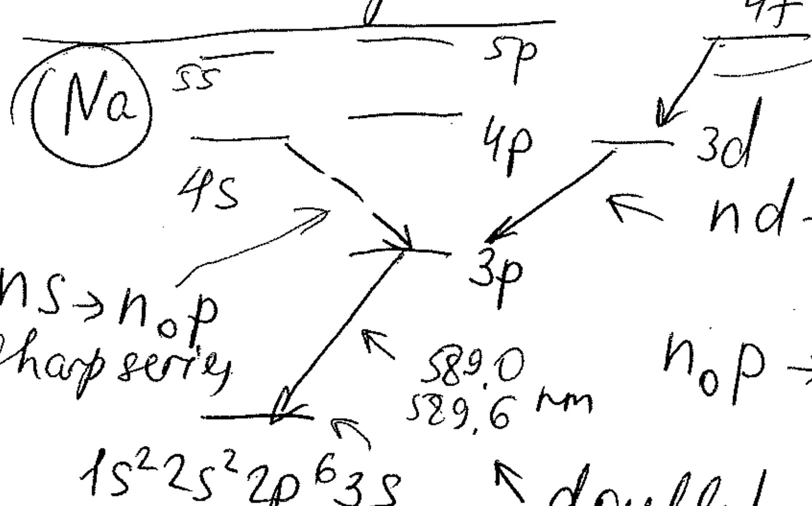
Emission Spectra

fundamental series

$nf \rightarrow n_0 d$

diffuse series

(Na)



$nd \rightarrow n_0 p$

$ns \rightarrow n_0 p$
sharp series

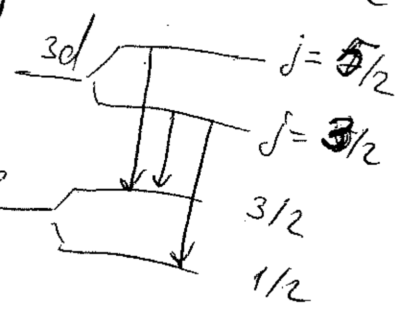
$n_0 p \rightarrow n_0 s \Rightarrow$ resonance line — the shortest line

doublet
due to fine structure of 3p

Principal
& sharp $\Rightarrow$ doublets

$j = l \pm \frac{1}{2} \Rightarrow \Delta E = \frac{\lambda_{nl}}{2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right]$

diffuse
& fundamental $\Rightarrow$ triplets



$\Delta j = 0, \pm 1$