PH 585
AMO

Lecture # 10

Interaction of one-electron atom with external electric & magnetic fields

1) Static electric fields $-\vec{D}\cdot\vec{E}$ ($\vec{D} = -e\vec{r}$) ← ch. 6 in B&J

Linear Stark effect $\Rightarrow H' = e\mathcal{E}z$ in $H = H_0 + H'$, with $\mathcal{E}$ the electric field and $H_0 = -\frac{\hbar^2}{2m}\vec{\nabla}^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$

Clearly,

$$\Delta E^{(1)}_{1S} = \langle 100|e\mathcal{E}z|100\rangle = 0$$

← $\mathcal{E}$ doesn't change energy of 1S in the 1st-order approx.

Recall QM:

$n=2$ state $\Rightarrow$ $2n^2$-degenerate

Since H' doesn't couple spin states, can consider 4-fold degenerate $\Rightarrow$

need $\langle \Psi_{2l'm'}|H'|\Psi_{2lm}\rangle$ ← 4x4 matrix

200
210
21±1

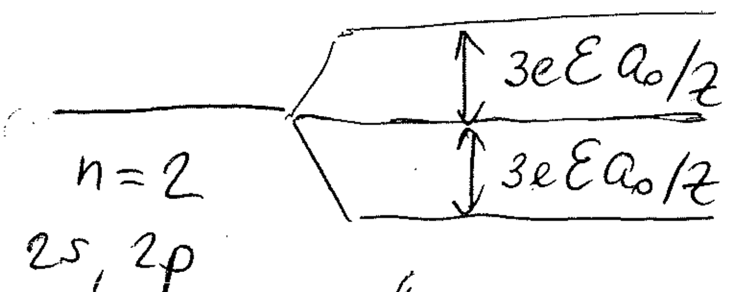
Then, diagonalize the matrix and find energy corrections $\Rightarrow$

$$\Delta E^{(1)} = \pm 3e\mathcal{E}\frac{a_0}{Z}$$

$$\Delta E^{(1)}_{2\text{-deg}} = 0$$

$$\delta\tilde{\nu} = \pm\frac{3ea_0}{hc}\frac{\mathcal{E}}{Z} \doteq \pm 12.8\frac{\mathcal{E}}{Z}\cdot 10^{-7}\,\text{cm}^{-1}$$

$\Delta W = \hbar/\tau$ $\quad 10^{-7}\,eV \quad$ $hc\tilde{\nu} = E$



$\frac{1}{\sqrt{2}}(\psi_{200} - \psi_{210}) \quad (m=0)$

$\psi_{21,\pm1} \quad (m=\pm1)$

$\frac{1}{\sqrt{2}}(\psi_{200} + \psi_{210}) \quad (m=0)$

$\Downarrow$

Depending on $\mathcal{E}$ and Z could be smaller or larger than, e.g., fine structure splitting $\Rightarrow$ if larger, treat H'_{fine} as a perturbation to $H_0 + H'$; if smaller $\rightarrow$ treat H' as a perturbation to $H_0 + H'_{fine}$.

Compare: for $n=2 \Rightarrow \tilde{\nu}_{fine} \sim 0.4\,cm^{-1}$
(H)-atom

Lecture #10

Stark: $\sim 25\,\mathcal{E} \cdot 10^{-7}\,cm^{-1} \simeq 0.4\,cm^{-1}$

$Z=1 \quad \frac{12.8 \cdot 2}{Z}$

$\Downarrow$

at $\mathcal{E} \sim 1.6 \cdot 10^{5}\,\frac{V}{cm}$

splitting comparable to fine structure

Note: Dielectric strength of air is $\sim 3 \cdot 10^{6}\,\frac{V}{m} \Rightarrow 3 \cdot 10^{4}\,\frac{V}{cm}$

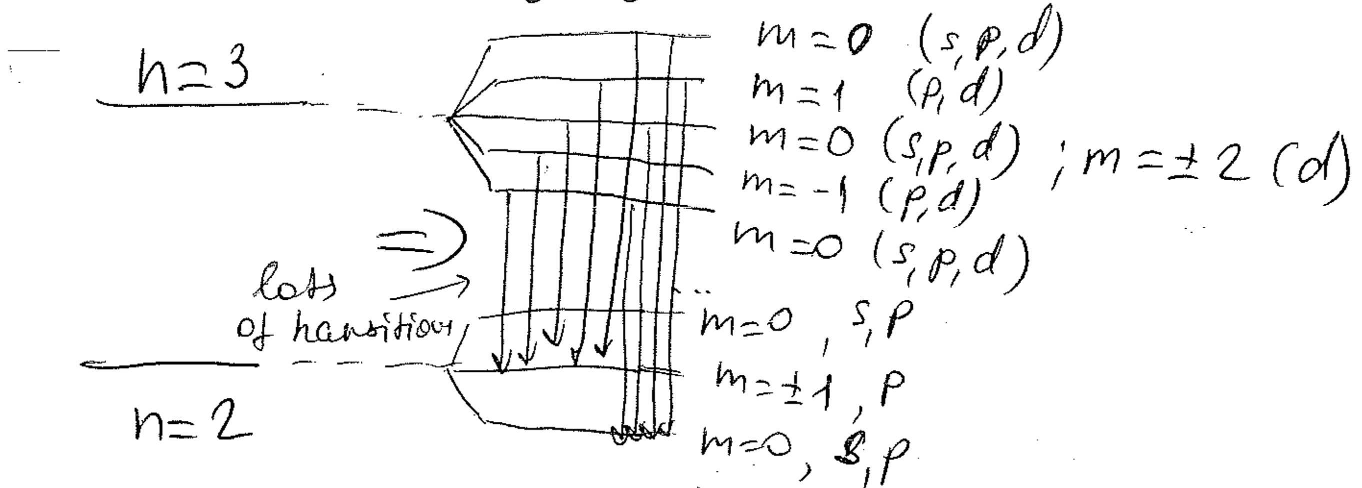
Note: $\tilde{\nu}_{fine} \sim Z^4$

$\tilde{\nu}_{Stark} \sim \frac{1}{Z}$

$2^5 = 32$

So, if $Z=2 \Rightarrow$ need $\mathcal{E} \sim Z^5\,\mathcal{E}_{(H)}$ to get comparable effects

Consider strong fields and H_α-line



H_0 $\qquad\qquad$ $H_0 + \underbrace{H'}_{e\mathcal{E}z}$

Selection rules (electric dipole approx.): $\Delta l = \pm 1$

$\Delta m = \underset{\substack{\uparrow \\ \pi\text{-transitions}}}{0}, \underset{\substack{\nwarrow \\ \sigma\text{-transitions}}}{\pm 1}$

<u>Note;</u> l is not a good quantum number anymore, since states with different l's are mixed! $\Rightarrow$ e.g. $\frac{1}{\sqrt{2}}(\psi_{2s} \pm \psi_{2p0})$

<u>Recall;</u>
$$\left.\begin{array}{l} 2p \to 1s \Rightarrow \tau = 1.6\,ns \\ 2s \to 1s \Rightarrow \tau = \frac{1}{7}\,s \end{array}\right\} \text{if } \mathcal{E} = 0$$

Now, if $\mathcal{E} \neq 0 \Rightarrow 2s$ is mixed with unstable $2p_0$

consider time evolution of $\underset{\text{superpositional state}}{\psi(\vec{r}, t)} \overset{\mathcal{E}\neq 0}{=} C_1 \psi e^{-\frac{i}{\hbar}Et} +$

$+ C_2 \psi_2 e^{-\frac{i}{\hbar}E' t}$ (4)

$$= \frac{1}{\sqrt{2}}\left[\psi_1(\vec{r})\underbrace{e^{-\frac{i}{\hbar}(3e\mathcal{E}a_0)t}}_{\cos()-i\sin()} + \psi_2(\vec{r})\underbrace{e^{\frac{i}{\hbar}(3e\mathcal{E}a_0)t}}_{\cos()+i\sin()}\right] e^{-\frac{i}{\hbar}E_{n=2}t} =$$

$$E = E_{n=2} - 3e\mathcal{E}a_0$$

$$E' = E_{n=2} + 3e\mathcal{E}a_0$$

and $\psi(\vec{r}, t=0) = \psi_{2s}(\vec{r})$

$$t=0 \Rightarrow \frac{1}{\sqrt{2}}(\psi_1(\vec{r}) + \psi_2(\vec{r})) = \psi_{2s}$$

$$= \left(\psi_{2s} \cos\frac{3e\mathcal{E}a_0}{\hbar}t + i\,\psi_{2p0} \sin\frac{3e\mathcal{E}a_0}{\hbar}t\right) e^{-\frac{i}{\hbar}E_{n=2}t}$$

$$\psi_{2p0} = \frac{1}{\sqrt{2}}(\psi_2 - \psi_1)$$

$\Downarrow$

So, the atom oscillates between 2s and 2p0 with a period $T = \frac{\pi\hbar}{3e\mathcal{E}a_0}$

If $\mathcal{E} = 10^7 \frac{V}{m}$ ($10^5 \frac{V}{cm}$) $\Rightarrow T = 1.3 \cdot 10^{-12}\,s \ll 1.6\,ns$ ($2p \to 1s$)

$\Downarrow$

so, on average, population in 2s $\approx$ population in 2p0 during $2p \to 1s$ transition time $\Rightarrow$ can make $2s \to 1s$ happen

Quadratic Stark effect

For example, $\underbrace{\langle 1s | e\mathcal{E}z | 1s\rangle}_{= E_{1s}^{(1)}} = 0 \Rightarrow$ consider higher perturbation order

$$E_{1s}^{(2)} = e^2\mathcal{E}^2 \sum_{n\neq 1, l, m} \frac{|\langle \psi_{nlm} | z | \psi_{100}\rangle|^2}{E_1 - E_n} =$$

$$= -e^2\mathcal{E}^2 \sum_{n\neq 1, l, m} \frac{|\langle \psi_{nlm} | z | \psi_{100}\rangle|^2}{E_n - E_1} > -e^2\mathcal{E}^2 \frac{1}{E_2 - E_1} \cdot$$

$$E_n - E_1 \geq E_2 - E_1$$

$$\underbrace{\sum_{n\neq 1, l, m} |\langle \psi_{nlm} | z | \psi_{100}\rangle|^2}_{= \sum_{nlm}, \; \Leftarrow \langle \psi_{100} | z | \psi_{100}\rangle = 0}$$

$$\sum_{nlm} |\langle \psi_{nlm} | z | \psi_{100}\rangle|^2 = \sum_{nlm} \langle \psi_{100} | z \underbrace{| \psi_{nlm}\rangle \cdot \langle \psi_{nlm} |}_{= I} z | \psi_{100}\rangle = \langle \psi_{100} | z^2 | \psi_{100}\rangle =$$

$$= \frac{a_0^2}{Z^2} \Rightarrow E_{1s}^{(2)} > -\frac{e^2\mathcal{E}^2}{\frac{3}{4} E_I^2 Z_1^2} \frac{a_0^2}{Z_1^2} = -\frac{8}{3}(4\pi\varepsilon_0) \cdot \frac{a_0^3}{Z_1^4}\mathcal{E}^2$$

$$E_2 - E_1 = -E_I^2 Z_1^2 \left[\frac{1}{4} - 1\right] = \frac{3}{4} E_I^2 Z_1^2$$

(6)

Exact evaluation: $E_{1s}^{(2)} = -2.25\,(4\pi\varepsilon_0)\,\frac{a_0^3}{Z^4}\,\mathcal{E}^2$

very small!

at $\mathcal{E} = 10^8 \frac{V}{m} \Rightarrow \tilde{\nu} = 0.02\,cm^{-1}$ (H)-atom

$10^6 \frac{V}{cm}$

Introduce dipole moment

$\vec{D} = \alpha \vec{\mathcal{E}} = -\frac{\partial E_{1s}^{(2)}}{\partial \mathcal{E}}$

static dipole polarisability of atom in 1s

$$\alpha = 2e^2 \sum_{n\neq 1, l, m} \frac{|\langle \psi_{nlm} | z | \psi_{100} \rangle|^2}{E_n - E_1}$$

have used this already in Rayleigh scattering

Note: selection rules: $\Delta l = \pm 1$, $\Delta m = 0$ $\Rightarrow$ $\sum$ over p-states with $m = 0$

$E_{1s}^{(2)} = -\frac{1}{2}\alpha \mathcal{E}^2 \Rightarrow$

$$\alpha = 4{,}5 \cdot (4\pi\varepsilon_0)\,\frac{a_0^3}{Z^4}$$

Note: if $\mathcal{E}$ is very strong $\Rightarrow$ can induce ionisation $\Rightarrow$ e.g. need $\geq 6 \cdot 10^{10} \frac{V}{m}$ to ionize (H)-atom from ground state, but only $\sim 7 \cdot 10^4 \frac{V}{m}$ if the atom is in $n = 30$ state

$\mathcal{E}_{critical} \sim \frac{1}{n^4}$