

Fine structure splittingEnergy corrections due to  $H_{1,2,3}$   $\Rightarrow$ 

$$\Delta E_1 = -E_n \frac{(Z\alpha)^2}{n^2} \left[ \frac{3}{4} - \frac{n}{l+\frac{1}{2}} \right]$$

HW!

$$\Delta E_2 = -E_n \frac{(Z\alpha)^2}{2nl(l+\frac{1}{2})(l+1)} \times \begin{cases} l & \text{for } j = l + \frac{1}{2} \\ -l-1 & \text{for } j = l - \frac{1}{2} \end{cases}$$

$$\Delta E_2 = 0 \text{ for } l=0$$

$$\Delta E_3 = -E_n \frac{(Z\alpha)^2}{n} \text{ for } l=0 \text{ and } 0 \text{ for } l \neq 0$$

Total fine-structure correction:

HW!

$$\Delta E = \Delta E_1 + \Delta E_2 + \Delta E_3 = E_n \frac{(Z\alpha)^2}{n^2} \left( \frac{n}{j+\frac{1}{2}} - \frac{3}{4} \right)$$

Total energy:

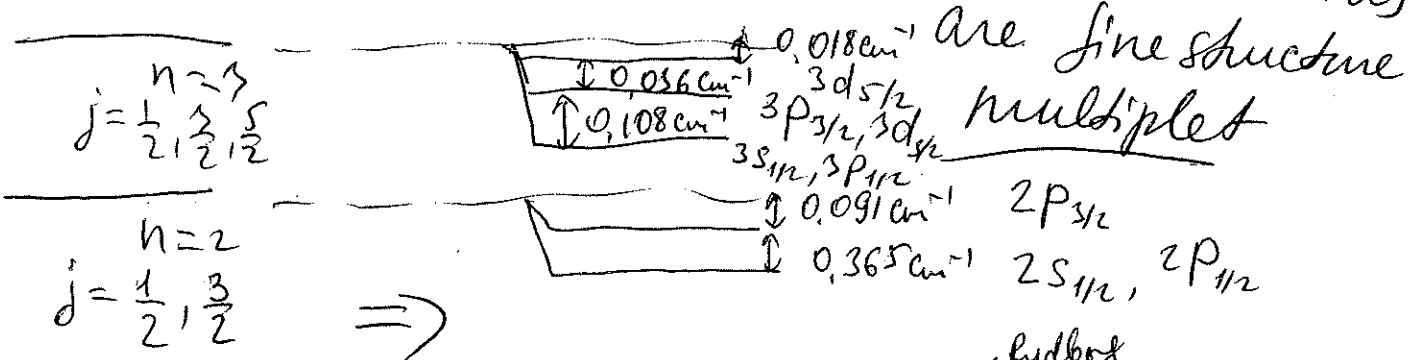
$$E_{nj} = E_n \left[ 1 + \frac{(Z\alpha)^2}{n^2} \left( \frac{n}{j+\frac{1}{2}} - \frac{3}{4} \right) \right] \text{ Note: dependence on } j, \text{ and not on } l!$$

$$= -\frac{E_I Z^2}{n^2}$$

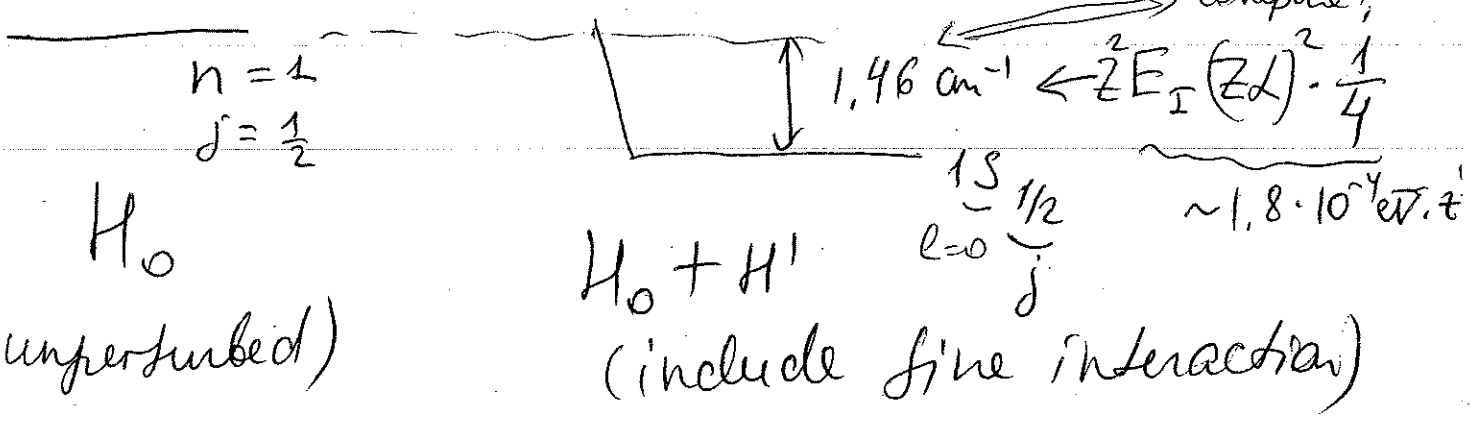
So,  $2n^2$  degeneracy of the  $n^{\text{th}}$  level is partially removed  $\Rightarrow$  for  $n$  fixed  $\Rightarrow l=0, \dots, n-1$

$$j = \frac{1}{2}, \frac{3}{2}, \dots, n - \frac{1}{2}$$

$$|l-s| \leq j \leq |l+s| \quad \text{these } n \text{ levels}$$



$R = \frac{E_{1s}}{a_0} = 109737 \text{ cm}^{-1}$   
 Rydberg



Note: difference in energy between  $j = \frac{1}{2}$  and  $j = n - \frac{1}{2}$

$$j = n - \frac{1}{2} \Rightarrow \delta E = \underbrace{|E_n|}_{\frac{Z^2 E_I}{n^2}} (Z\alpha)^2 \frac{n-1}{n^2} = \frac{Z^4 \alpha^2 (n-1)}{2n^4} E_I$$

for any  $n \neq 1$  level  $\Rightarrow$  splitting

As  $n \uparrow \Rightarrow \delta E \downarrow$

$l=0 \Rightarrow$  shift  
 other levels  $\Rightarrow$  splitting

Note:  $Z^4$ -dependence of  $\delta E$ !

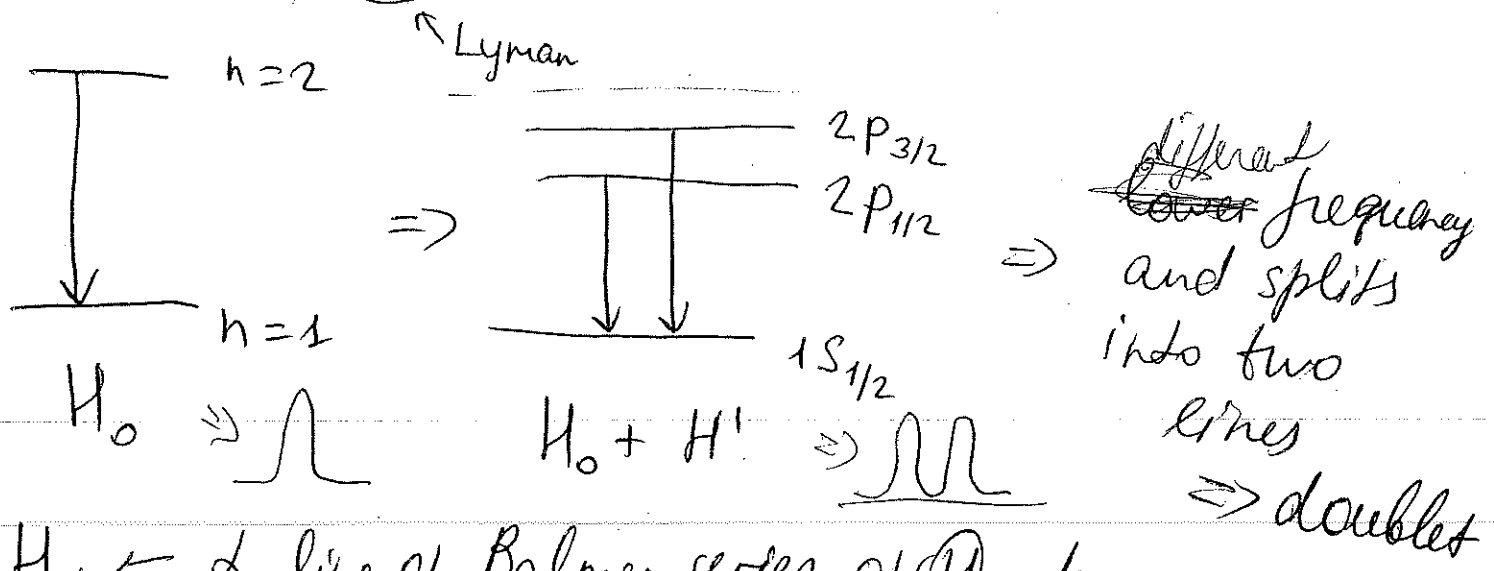
# Fine structure of spectral lines

(3)

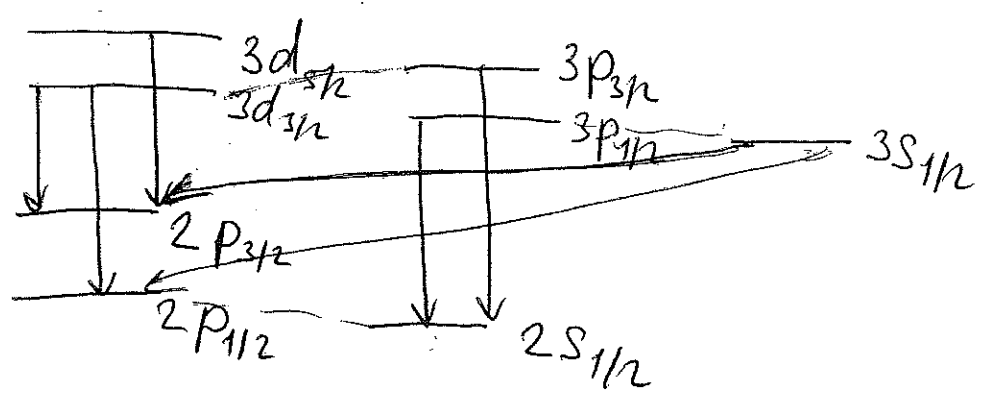
Consider transitions allowed in electric dipole approx.  $\Rightarrow \Delta l = \pm 1 \Rightarrow \Delta j = \pm 1, 0$

$\vec{D} = -e\vec{r}$  (doesn't couple spin)

So, e.g., Ly  $\alpha$  line of H-atom  $\Rightarrow$



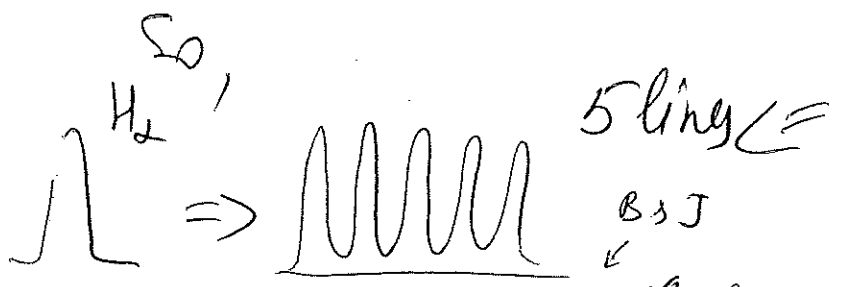
$H_{\alpha} \leftarrow \alpha$ -line of Balmer series of H-atom  $\Rightarrow$   
 $\nearrow$  656.3 nm



7 transitions, but since

$3d_{3/2} \rightarrow 2p_{1/2}$  and  $3P_{3/2} \rightarrow 2S_{1/2}$ , as well as

$3P_{1/2} \rightarrow 2S_{1/2}$  and  $3S_{1/2} \rightarrow 2P_{1/2}$  have same frequencies (in this approx.)



$\nearrow$  see p. 248 for relative intensities

Since  $\delta E \downarrow$  as  $n \uparrow \Rightarrow$  fine structure splitting (4)  
 splitting is mostly due to the lower level splitting  $\Rightarrow$

in Balmer series  $\Rightarrow$  doublets  $\Rightarrow$   $\left. \begin{array}{l} 3d_{3/2} \rightarrow 2p_{1/2} \\ 3s_{1/2} \rightarrow 2p_{1/2} \end{array} \right) \stackrel{= 3p_{3/2} \rightarrow 2s_{1/2}}{\text{①}}$

in Paschen series

e.g. for  $n=3 \rightarrow n=2$

$3s_{1/2} \rightarrow 2p_{1/2}$

$\left. \begin{array}{l} 3p_{1/2} \rightarrow 2s_{1/2} \\ 3d_{5/2} \rightarrow 2p_{3/2} \end{array} \right) \text{②}$

three groups of lines etc.

Relative intensities  $\Rightarrow$  ~~Relative intensities~~

~~Relative intensities~~ Consider a specific example

~~shouldn't depend on n~~  
~~take  $m_l = m_s$~~   
~~and  $l = 0, 1, 2$~~

Compare line intensities for

$np_{3/2} \rightarrow n's_{1/2}$  and  $np_{1/2} \rightarrow n's_{1/2}$

transitions.

$-j < m_j < j$

Need  $\Rightarrow |n l m_l m_s\rangle \Leftrightarrow |n l j m_j\rangle$

Recall:

$\underbrace{\pm \frac{1}{2}}_{m_s}$

$\underbrace{l \pm \frac{1}{2}}_{m_j}$

$$| \underbrace{l \pm \frac{1}{2}}_j, m_j \rangle = \frac{1}{\sqrt{2l+1}} \left( \pm \sqrt{l \pm m_j + \frac{1}{2}} | \underbrace{l, m_j - \frac{1}{2}}_{m_l}, \underbrace{\frac{1}{2}}_{m_s} \rangle \right)$$

Sakurai p. 215

$$+ \sqrt{l+1} \sqrt{m_j + \frac{1}{2}} \left| l, \underbrace{m_j + \frac{1}{2}}_{m_l}, \underbrace{-\frac{1}{2}}_{m_s} \right\rangle$$

Then  $\Rightarrow$  need  $|\vec{r}_{ba}|^2 = \left| \langle n'l'm'_l m'_s | \vec{r} | nlm \rangle \right|^2$   
 $\sum_{m'_l, m'_s} A_{l m'_l m'_s} |n'l'm'_l m'_s\rangle$

Then, calculate all possible  $\langle n'l'm'_l m'_s | \vec{r} | nlm \rangle$   
 The rest is similar to Problem #2 of Homework 4

$$\frac{I_{P_{3/2} \rightarrow S_{1/2}}}{I_{P_{1/2} \rightarrow S_{1/2}}} = \frac{\hbar \omega_{3/2 \rightarrow 1/2}}{\hbar \omega_{1/2 \rightarrow 1/2}} \frac{W_{3/2 \rightarrow 1/2}^D}{W_{1/2 \rightarrow 1/2}^D} = \frac{\omega_{3/2 \rightarrow 1/2}^4}{\omega_{1/2 \rightarrow 1/2}^4} \frac{|\Gamma_{3/2 \rightarrow 1/2}^M|^2}{|\Gamma_{1/2 \rightarrow 1/2}^M|^2} \Rightarrow \frac{2m}{3\hbar} \omega_{1/2 \rightarrow 1/2} |\Gamma_{1/2 \rightarrow 1/2}^M|^2 = |f_{1/2 \rightarrow 1/2}|$$

$$W_{1/2 \rightarrow 1/2}^D = \frac{2\hbar^2}{mc^2} \omega_{1/2 \rightarrow 1/2}^2 |f_{1/2 \rightarrow 1/2}|$$

For  $s_p$  transitions:  $\frac{I(S_{1/2} \rightarrow P_{3/2})}{I(S_{1/2} \rightarrow P_{1/2})} = \frac{2}{1}$

pd transition:  $\frac{I(P_{3/2} \rightarrow d_{5/2})}{I(P_{3/2} \rightarrow d_{3/2})} = \frac{9}{1}$   
 see p. 248 for more

# The Lamb shift

(6)

Dirac theory  $\Rightarrow E_{n,j} \Rightarrow$  so, e.g.,  $2S_{1/2}$  and  $2P_{1/2}$

Experiment:  $0.03 \text{ cm}^{-1}$

Houston (1937)

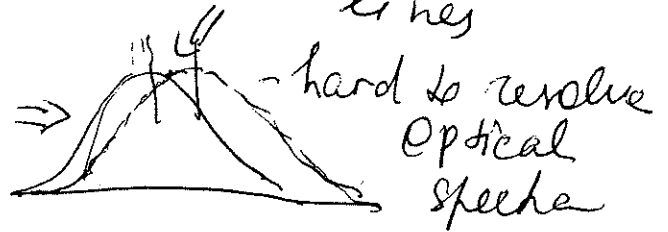
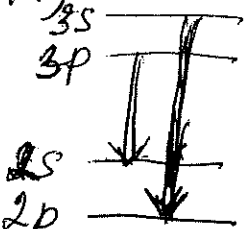
Williams (1938)

Lamb & Retherford (1947) } - decisive

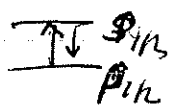
see PRB 72, 241 (1947)

$\Rightarrow$  same energy

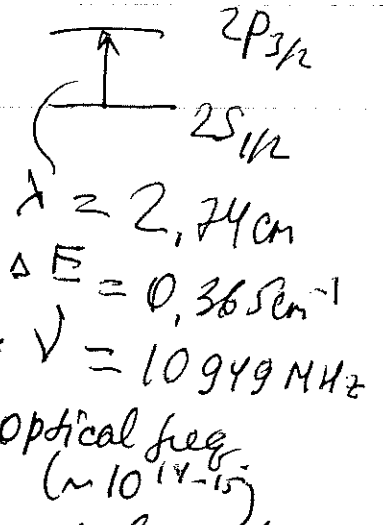
$\rightarrow$  hard to measure due to Doppler broadening of lines



use  $\leftarrow$  microwave  $\leftarrow$  to directly probe  $\leftarrow$  radio frequencies



Ex.:



Recall Doppler broadening:

$$(\omega_1 - \omega_0)^2 = \frac{2k_B T}{Mc^2} \omega_0^2 \ln 2$$

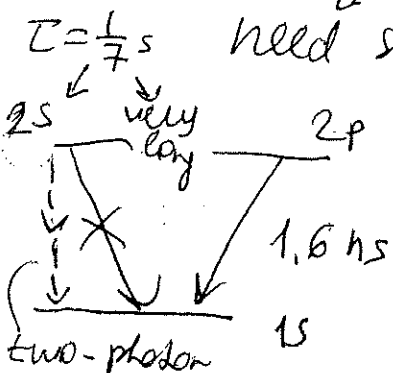
$\approx 10^{10} \text{ Hz} \ll \nu = 10949 \text{ MHz} \Rightarrow \ll \text{optical freq. } (\sim 10^{14-15})$

If  $\omega_0 \downarrow \Rightarrow \omega_1 - \omega_0 \downarrow$

$\Rightarrow$  reduced broadening at lower frequencies

But: since  $W_{ab}^S \sim \nu^3$

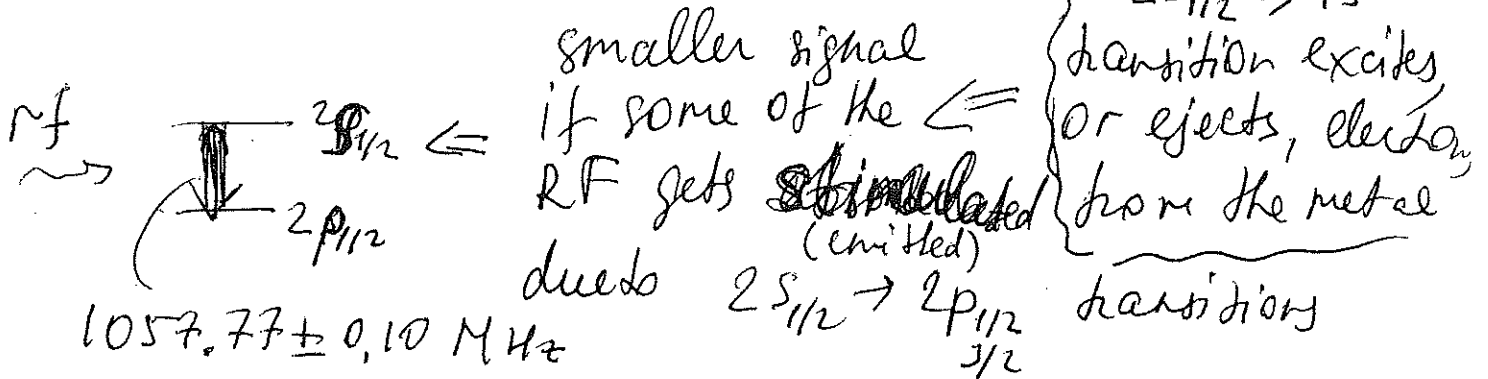
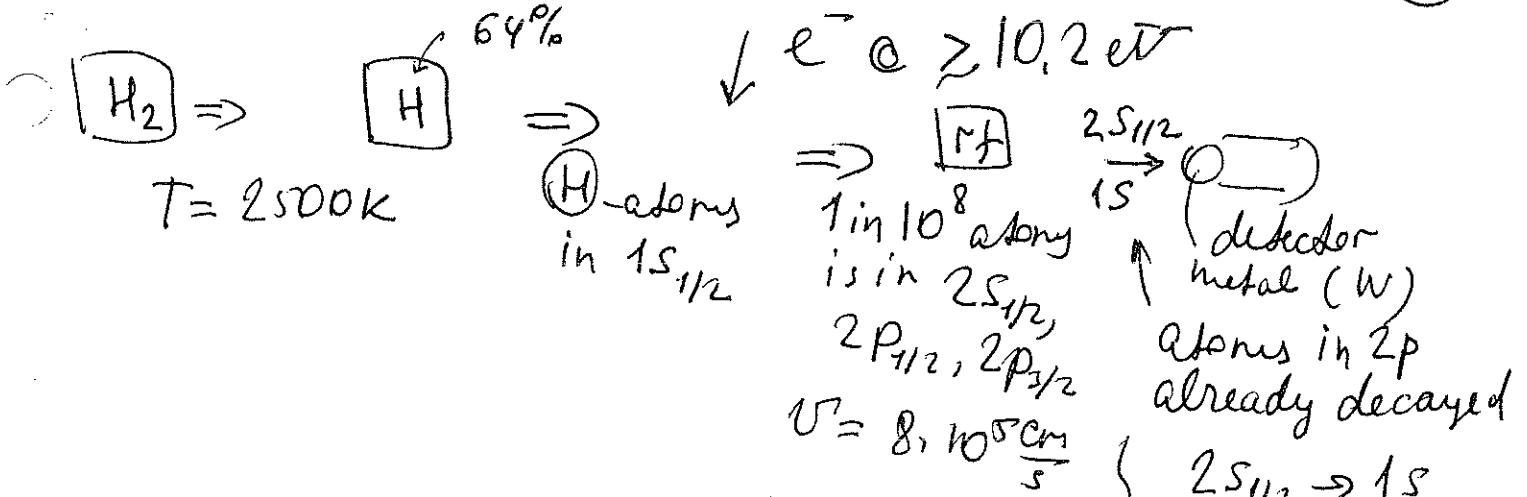
$\Rightarrow$  small transition rates  $\uparrow$  need stimulated emission and unequal population of levels



$\Rightarrow \tau_{2S} \gg \tau_{2P}$   
metastable level

Lamb & Retherford  $\Rightarrow$

$$E_{n=2} - E_{n=1} \quad (7)$$

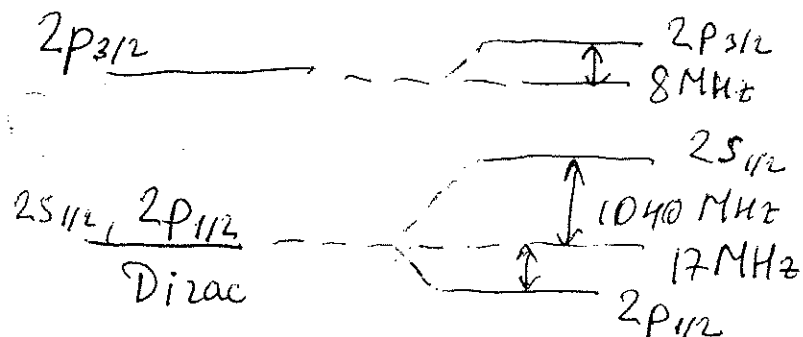


How to include this into Dirac theory?  $\Rightarrow$

"radiative corrections"  $\rightarrow$  QED  $\rightarrow$  take into account interaction of the electron with the quantized EM field

$$H_{EM} = \hbar \omega \sum_k (a_k^\dagger a_k + \frac{1}{2})$$

rapid oscillat. motion  $\Leftarrow$  act on  $e^-$   $\Leftarrow$  fluctuations of this field even in vacuum  $\Leftarrow$  zero-point oscillation even at zero field  
 acts stronger on s-states (recall Darwin term!)



In 1972  $\Rightarrow$  measured optically using Doppler-free spectroscopy of  $H_\alpha$  line.

B.5.15.2

