



UNIVERSITY OF
CAMBRIDGE

NST Part II Physics
Michaelmas Term 2022
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ADVANCED QUANTUM PHYSICS

Handout 4

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- ▶ The ‘real’ Hydrogen atom
 - ▶ Relativistic corrections
 - ▶ Fine structure (Lamb shift)
 - ▶ Hyperfine structure

The “Real” Hydrogen Atom

- So far, our treatment of the hydrogen atom has been non-relativistic and has neglected the effects of electron and proton spin
 - now move, step by step, towards a more realistic treatment :
- 1) “switch on” electron spin “by hand”, remaining non-relativistic
- 2) add the leading-order relativistic effects predicted by the *Dirac equation* (the relativistic generalisation of the Schrödinger equation)
 - relativistic corrections to kinetic energy
 - spin-orbit coupling
 - the Darwin term

→ **fine structure**
- 3) “switch on” nuclear (proton) spin
 - add the interaction between the proton and electron magnetic dipole moments

→ **hyperfine structure**

The H atom, including electron spin

- If we simply “switch on” the electron spin (staying non-relativistic), the “zeroth-order” Hamiltonian for the hydrogen atom remains as

$$\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m_e} + V(r) ; \quad V(r) = -e\phi(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

- Since H_0 does not contain the electron spin operator S , direct products of the spatial and spin eigenstates,

$$|nlm_\ell sm_s\rangle = |nlm_\ell\rangle \otimes |sm_s\rangle = \begin{cases} |nlm_\ell\rangle |\uparrow\rangle \\ |nlm_\ell\rangle |\downarrow\rangle \end{cases} \quad (s = 1/2)$$

are energy eigenstates

- The energies depend only on the principal quantum number $n = 1, 2, 3, \dots$

$$\hat{H}_0 |nlm_\ell sm_s\rangle = E_n |nlm_\ell sm_s\rangle ; \quad E_n = -\frac{Z^2}{n^2} R_\infty$$

The energy levels are degenerate with respect to the quantum numbers ℓ , m_ℓ and m_s ; the degeneracy of each level is $g = 2n^2$

The H atom, including electron spin (2)

- In spherical polar coordinates, the spatial components take the form

$$|n\ell m_\ell\rangle = R_{n\ell}(r)Y_{\ell,m_\ell}(\theta, \phi) \quad (4.4.1)$$

- The energy eigenstates form an orthonormal set :

$$\begin{aligned}\langle n'\ell'm'_\ell m'_s | n\ell m_\ell m_s \rangle &= \langle n'\ell'm'_\ell | n\ell m_\ell \rangle \langle m'_s | m_s \rangle \\ &= \delta_{n'n} \delta_{\ell'\ell} \delta_{m'_\ell m_\ell} \delta_{m'_s m_s}\end{aligned}$$

where orthogonality in ℓ and m_ℓ arises from the angular component, and orthogonality in n from the radial component (see slide 1.50)

- An alternative set of basis states is provided by the eigenstates $|njm_j\ell s\rangle$ of the total angular momentum operator, $\mathbf{J} = \mathbf{L} + \mathbf{S}$, of the electron :

$$\left. \begin{array}{l} \hat{\mathbf{J}}^2 |njm_j\ell s\rangle = j(j+1)\hbar^2 |njm_j\ell s\rangle \\ \hat{J}_z |njm_j\ell s\rangle = m_j \hbar |njm_j\ell s\rangle \end{array} \right\} \quad \begin{array}{l} \hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}} \\ j = \ell \otimes s = \ell \pm \frac{1}{2} \end{array}$$

$$\langle n'j'm'_j\ell's | njm_j\ell s \rangle = \delta_{n'n} \delta_{j'j} \delta_{m'_j m_j} \delta_{\ell'\ell}$$

The H atom, including electron spin (3)

- Since the energies depend only on n , these are also eigenstates of H_0 :

$$\hat{H}_0|n jm_j \ell s\rangle = E_n|n jm_j \ell s\rangle ; \quad E_n = -\frac{Z^2}{n^2}R_\infty$$

- For example, for the $n = 2$ energy level, with degeneracy $g = 8$, the two alternative sets of basis states are :

$|n \ell m_\ell\rangle |s m_s\rangle$

ℓ	m_ℓ	m_s	g
0	0	$\pm 1/2$	$1 \times 2 = 2$
1	0, ± 1	$\pm 1/2$	$3 \times 2 = 6$

$(s = 1/2)$

“uncoupled”

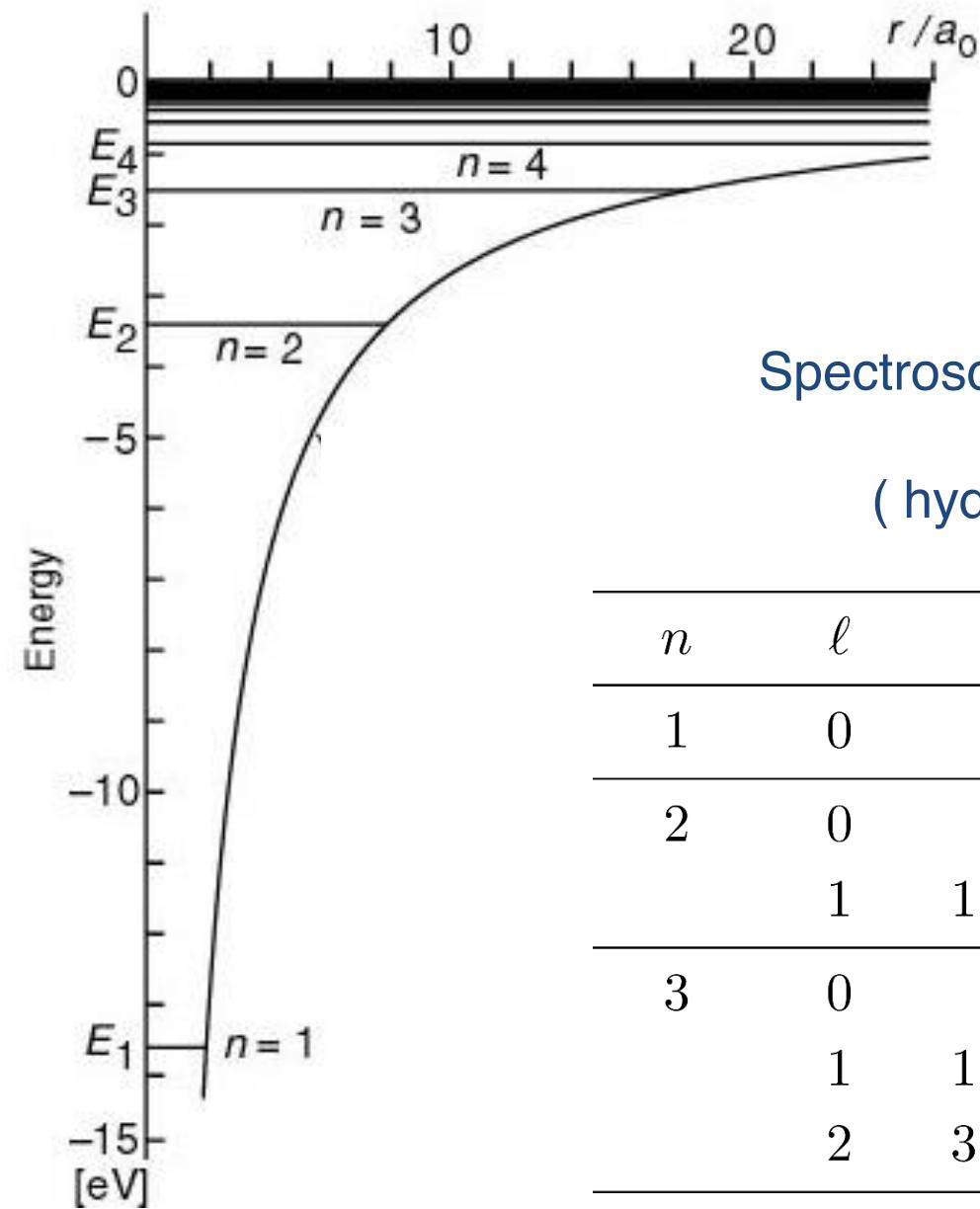
$|n jm_j \ell s\rangle$

ℓ	j	m_j	g
0	$1/2$	$\pm 1/2$	2
1	$1/2$	$\pm 1/2$	2
1	$3/2$	$\pm 3/2, \pm 1/2$	4

“coupled”

- These alternative bases are linear combinations of each other, and we can use whichever is most convenient

The H atom, including electron spin (4)



$$E_n = -\frac{Z^2}{n^2} R_\infty$$

Spectroscopic term notation :

$$n^{2S+1}L_J$$

(hydrogen : $L \equiv \ell$, $S \equiv s$, $J \equiv j$)

n	ℓ	j	subshell	terms
1	0	1/2	1s	1 ² S _{1/2}
2	0	1/2	2s	2 ² S _{1/2}
	1	1/2, 3/2	2p	2 ² P _{1/2} , 2 ² P _{3/2}
3	0	1/2	3s	3 ² S _{1/2}
	1	1/2, 3/2	3p	3 ² P _{1/2} , 3 ² P _{3/2}
	2	3/2, 5/2	3d	3 ² D _{3/2} , 3 ² D _{5/2}

The H atom, including electron spin (5)

- The coupled states expand in terms of the uncoupled states as

$$|n j m_j \ell s\rangle = \sum_{\substack{m_\ell, m_s \\ m_\ell + m_s = m_j}} |n \ell m_\ell s m_s\rangle \underbrace{\langle \ell m_\ell; s m_s | j m_j \rangle}_{(Clebsch-Gordan coefficients)} \quad (4.7.1)$$

where, for $s = 1/2$, the summation contains at most two non-zero terms :

$$m_s = \pm \frac{1}{2}, \quad m_\ell \pm \frac{1}{2} = m_j$$

- For example, for $\ell = 1$ we have $j = 1 \otimes \frac{1}{2} = \frac{3}{2}, \frac{1}{2}$

For $m_j = +3/2$, the only possibility is $j = 3/2$:

$$\underbrace{|n, \frac{3}{2}, +\frac{3}{2}, 1, \frac{1}{2}\rangle}_{|n j m_j \ell s\rangle} = \underbrace{|n, 1, +1\rangle}_{|n \ell m_\ell\rangle} |\uparrow\rangle_{|s m_s\rangle}$$

For $m_j = +1/2$, both $j = 3/2$ and $j = 1/2$ are possible ...

The H atom, including electron spin (6)

- Using the Clebsch-Gordan coefficients from slide 1.73, the coupled states with $m_j = +1/2$ expand (for any n) as

$$j = 3/2 : |n, \frac{3}{2}, +\frac{1}{2}, 1, \frac{1}{2}\rangle = \underbrace{\sqrt{\frac{1}{3}}|n, 1, +1\rangle|\downarrow\rangle}_{|njm_j\ell s\rangle} + \underbrace{\sqrt{\frac{2}{3}}|n, 1, 0\rangle|\uparrow\rangle}_{|n\ell m_\ell\rangle|sm_s\rangle}$$
$$j = 1/2 : |n, \frac{1}{2}, +\frac{1}{2}, 1, \frac{1}{2}\rangle = \underbrace{\sqrt{\frac{2}{3}}|n, 1, +1\rangle|\downarrow\rangle}_{|njm_j\ell s\rangle} - \underbrace{\sqrt{\frac{1}{3}}|n, 1, 0\rangle|\uparrow\rangle}_{|n\ell m_\ell\rangle|sm_s\rangle}$$

- Explicitly, the wavefunctions above for the $m_j = +1/2$ states are

$$j = 3/2 : |n, \frac{3}{2}, +\frac{1}{2}, 1, \frac{1}{2}\rangle = R_{n1}(r) \left[\sqrt{\frac{1}{3}}Y_{11}(\theta, \phi)|\downarrow\rangle + \sqrt{\frac{2}{3}}Y_{10}(\theta, \phi)|\uparrow\rangle \right]$$
$$j = 1/2 : |n, \frac{1}{2}, +\frac{1}{2}, 1, \frac{1}{2}\rangle = R_{n1}(r) \left[\sqrt{\frac{2}{3}}Y_{11}(\theta, \phi)|\downarrow\rangle - \sqrt{\frac{1}{3}}Y_{10}(\theta, \phi)|\uparrow\rangle \right]$$

These are easily seen to be orthogonal to each other

The H atom, including electron spin (7)

- We can gain further insight by considering the commutation properties of the various angular momentum operators ...

The operators \mathbf{L} and \mathbf{S} are independent, and commute with each other :

$$[\hat{\mathbf{L}}, \hat{\mathbf{S}}] = 0 ; \quad [\hat{\mathbf{L}}^2, \hat{\mathbf{S}}^2] = 0$$

The operator product $\mathbf{L} \cdot \mathbf{S}$ therefore commutes with \mathbf{L}^2 and \mathbf{S}^2 :

$$[\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \hat{\mathbf{L}}^2] = \sum_i [\hat{L}_i \hat{S}_i, \hat{\mathbf{L}}^2] = \sum_i \hat{S}_i [\hat{L}_i, \hat{\mathbf{L}}^2] = 0$$

$$[\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \hat{\mathbf{S}}^2] = \sum_i [\hat{L}_i \hat{S}_i, \hat{\mathbf{S}}^2] = \sum_i \hat{L}_i [\hat{S}_i, \hat{\mathbf{S}}^2] = 0$$

- The operator \mathbf{J}^2 expands as

$$\hat{\mathbf{J}}^2 = (\hat{\mathbf{L}} + \hat{\mathbf{S}})^2 = \hat{\mathbf{L}}^2 + \hat{\mathbf{S}}^2 + 2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$$

Therefore \mathbf{J}^2 commutes with \mathbf{L}^2 , \mathbf{S}^2 and $\mathbf{L} \cdot \mathbf{S}$:

$$[\hat{\mathbf{J}}^2, \hat{\mathbf{L}}^2] = [\hat{\mathbf{J}}^2, \hat{\mathbf{S}}^2] = [\hat{\mathbf{J}}^2, \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}] = 0$$

The H atom, including electron spin (8)

- As already noted on slide (1.51), for $\hat{\mathbf{L}} = \hat{\mathbf{r}} \wedge \hat{\mathbf{p}}$, we have

$$[\hat{\mathbf{p}}^2, \hat{\mathbf{L}}] = [\hat{\mathbf{p}}^2, \hat{\mathbf{L}}^2] = 0; \quad [V(r), \hat{\mathbf{L}}] = [V(r), \hat{\mathbf{L}}^2] = 0$$

The same relations clearly hold also for S , and hence also for $J = L + S$:

$$[\hat{\mathbf{p}}^2, \hat{\mathbf{J}}] = [\hat{\mathbf{p}}^2, \hat{\mathbf{J}}^2] = 0; \quad [V(r), \hat{\mathbf{J}}] = [V(r), \hat{\mathbf{J}}^2] = 0$$

The Hamiltonian $\hat{H}_0 = \hat{\mathbf{p}}^2/2m + V(r)$ therefore commutes with all the angular momentum operators L^2, L, S^2, S, J^2, J

→ $\ell, m_\ell, s, m_s, j, m_j$ are all good quantum numbers

- We thus have two mutually commuting sets of operators, each of which must possess its own set of simultaneous eigenstates :

$$\{\hat{H}_0, \hat{\mathbf{L}}^2, \hat{L}_z, \hat{\mathbf{S}}^2, \hat{S}_z\}$$

$$|n\ell m_\ell s m_s\rangle$$

“uncoupled”

$$\{\hat{H}_0, \hat{\mathbf{J}}^2, \hat{J}_z, \hat{\mathbf{L}}^2, \hat{\mathbf{S}}^2\}$$

$$|njm_j\ell s\rangle$$

“coupled”

We are now in a position to include the leading relativistic effects ...

Relativistic Wave Equations

- The Schrödinger equation is not Lorentz-invariant; it contains a *first-order* time derivative but contains *second-order* spatial derivatives
 - it therefore cannot describe *relativistic* particles
- The natural relativistic generalisation of the Schrödinger equation is obtained by applying the operator replacements

$$\mathbf{p} \rightarrow -i\hbar\nabla ; \quad E \rightarrow i\hbar \frac{\partial}{\partial t}$$

to the relativistic relation

$$E^2 = |\mathbf{p}|^2 c^2 + m^2 c^4$$

- This gives the (Lorentz-invariant) *Klein-Gordon equation* :

$$\boxed{\frac{1}{c^2} \frac{\partial^2 \psi}{\partial t^2} - \nabla^2 \psi + \frac{m^2 c^2}{\hbar^2} \psi = 0}$$

(which was in fact first studied by Schrödinger)

- The Klein-Gordon equation describes relativistic particles of zero spin

Relativistic Wave Equations (2)

- For *spin-half* particles, the appropriate relativistic wave equation was first proposed by Dirac (1928) :

The *Dirac equation* is essentially the square-root of the Klein-Gordon equation, and contains only first-order time and space derivatives

This is covered in detail in Part III; below we give only a brief introduction

- The interpretation of relativistic wave equations such as the Dirac equation is beset by conceptual problems (negative energies and probabilities)
 - these can only be properly resolved by embedding such equations within a quantum field theory (QFT)

We then naturally obtain *antiparticles* as well as particles, and can accommodate the creation and annihilation of particles and antiparticles

- To describe atomic electrons, we need only the *low energy limit* of the Dirac equation for a spin-half particle moving in an external EM field
 - in this limit, these conceptual problems are not an issue

The Dirac Equation

- For a single, free, relativistic spin-half particle, the Dirac equation is

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi ; \quad \boxed{\hat{H} = c\boldsymbol{\alpha} \cdot \hat{\mathbf{p}} + \beta mc^2} \quad (\hat{\mathbf{p}} = -i\hbar\nabla)$$

where $\boldsymbol{\alpha} = (\alpha_x, \alpha_y, \alpha_z)$ and β are constants

- For this to work, the constants $\boldsymbol{\alpha}$ and β cannot be ordinary complex numbers ; they have to be 4×4 complex *matrices* :

$$\alpha_x = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}; \quad \alpha_y = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix}; \quad \alpha_z = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}; \quad \beta = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

The wavefunction $\psi(\mathbf{r},t)$ must then be a four-component object, known as a spinor :

The four degrees of freedom can be interpreted as two *particle*, plus two *antiparticle*, spin states

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix}$$

The Dirac Equation (2)

- An external EM field described by potentials $\mathbf{A}(\mathbf{r},t)$ and $\phi(\mathbf{r},t)$ can be introduced, as before, via the minimal substitution prescription :

$$\mathbf{p} \rightarrow \mathbf{p} - q\mathbf{A} ; \quad E \rightarrow E + q\phi \quad (E = \sqrt{p^2c^2 + m^2c^4})$$

- Keeping only terms up to order v^2/c^2 , the Dirac equation then becomes (after a lengthy calculation, in any gauge)

$$(E' - q\phi)\psi = \left[\frac{1}{2m}(\hat{\mathbf{p}} - q\mathbf{A})^2 - \frac{q}{m}(\hat{\mathbf{S}} \cdot \mathbf{B}) - \frac{\hat{\mathbf{p}}^4}{8m^3c^2} + \frac{q\hbar^2}{8m^2c^2}(\nabla^2\phi) + \frac{q}{2m^2c^2}\hat{\mathbf{S}} \cdot (\nabla\phi \wedge \hat{\mathbf{p}}) \right] \psi \quad (4.14.1)$$

where $\mathbf{B} = \nabla \wedge \mathbf{A}$, and where E' is the relativistic kinetic energy :

$$E' \equiv E - mc^2$$

The Dirac Equation (3)

- The operator S in equation (4.14.1) is

$$\hat{S} = \frac{\hbar}{2} \boldsymbol{\sigma}$$

where $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ contains the 2×2 Pauli spin matrices (slide 1.58) :

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} ; \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} ; \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

In the non-relativistic limit, ψ becomes a two-component spinor; the antiparticle degrees of freedom no longer play a role $\psi = \begin{pmatrix} \psi_a \\ \psi_b \end{pmatrix}$

- The Pauli matrices have the properties

$$[\sigma_i, \sigma_j] = 2i \sum_k \epsilon_{ijk} \sigma_k$$

$$\sigma_i^2 = I ; \quad \boldsymbol{\sigma}^2 = \sigma_x^2 + \sigma_y^2 + \sigma_z^2 = 3I$$

Hence the operator S satisfies the angular momentum commutation relations

$$[\hat{S}_i, \hat{S}_j] = i\hbar \sum_k \epsilon_{ijk} \hat{S}_k$$

The Dirac Equation (4)

- The operator S^2 is

$$\hat{S}^2 = \frac{\hbar^2}{4} \hat{\sigma}^2 = \frac{3}{4} \hbar^2 I = \frac{3}{4} \hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Thus any spinor ψ is an eigenstate of S^2 , with angular momentum $s = 1/2$:

$$\hat{S}^2 \psi = \frac{3}{4} \hbar^2 \psi = s(s+1) \hbar^2 \psi \quad (s = 1/2)$$

- This is true even for a particle at rest, with no *orbital* angular momentum
 - Particles described by the Dirac equation are predicted to possess an *internal* (intrinsic, spin) angular momentum $s = 1/2$
- The right-hand side of equation (4.14.1) includes a term

$$\boxed{\hat{H}_B = -\hat{\mu}_S \cdot \mathbf{B} ; \quad \hat{\mu}_S \equiv \frac{q}{m} \hat{S}} \quad \left(\gamma_S = \frac{q}{m} \right)$$

The Dirac equation thus predicts that spin-half particles have an *internal* (intrinsic) *magnetic moment* (as already introduced “by hand” in slide 3.31)

The Dirac Equation (5)

- In particular, the internal magnetic dipole moment of the electron ($q = -e$) is predicted to be

$$(\hat{\boldsymbol{\mu}}_S)_e = -\frac{e}{m_e} \hat{\mathbf{S}} ; \quad \mu_e = -\mu_B ; \quad g_e = 2$$

At the time (1929) this prediction was a triumph; a g -factor $g_e = 2$ was needed to explain many observed features of atomic spectra

(it only became clear later that $g_e \approx 2.0023$, which needs QED)

- The term $\frac{1}{2m}(\hat{\mathbf{p}} - q\mathbf{A})^2$ in equation (4.14.1) was considered earlier, and was found (slide 3.27) to include a contribution

$$-\frac{q}{2m}(\hat{\mathbf{L}} \cdot \mathbf{B})$$

- Thus, overall, the Dirac Hamiltonian contains both an orbital and a spin magnetic moment interaction :

$$\hat{H}_B = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B} ; \quad \hat{\boldsymbol{\mu}} = \frac{q}{2m}(\hat{\mathbf{L}} + 2\hat{\mathbf{S}})$$

The Dirac equation for the H atom

- We can now compute the leading relativistic effects predicted by the Dirac equation for the hydrogen atom, up to terms of order v^2/c^2 :

For an atomic electron moving in the electric field of an infinitely heavy nucleus of charge Ze , we have

$$\mathbf{A} = 0, \quad \mathbf{B} = 0, \quad q = -e, \quad \phi = \phi(r) = \frac{Ze}{4\pi\epsilon_0 r}$$

- In this case, the low energy (order v^2/c^2) Dirac equation (4.14.1) becomes

$$E'\psi = \left[\frac{\hat{\mathbf{p}}^2}{2m_e} - e\phi(r) - \frac{\hat{\mathbf{p}}^4}{8m_e^3 c^2} - \frac{e\hbar^2}{8m_e^2 c^2} (\nabla^2 \phi) - \frac{e}{2m_e^2 c^2} \hat{\mathbf{S}} \cdot (\nabla \phi \wedge \hat{\mathbf{p}}) \right] \psi$$

- This corresponds to applying a perturbation H' given by

$$\hat{H}' = -\frac{\hat{\mathbf{p}}^4}{8m_e^3 c^2} - \frac{e\hbar^2}{8m_e^2 c^2} (\nabla^2 \phi) - \frac{e}{2m_e^2 c^2} \hat{\mathbf{S}} \cdot (\nabla \phi \wedge \hat{\mathbf{p}})$$

$$(\hat{H}_R)$$

$$(\hat{H}_D)$$

$$(\hat{H}_{SO})$$

(4.18.1)

The Dirac equation for the H atom (2)

- Expanded in powers of momentum, the relativistic total energy of the electron is

$$E = \sqrt{\mathbf{p}^2 c^2 + m_e^2 c^4} = m_e c^2 + \frac{\mathbf{p}^2}{2m_e} - \frac{(\mathbf{p}^2)^2}{8m_e^3 c^2} + \dots$$

Thus the term H_R in equation (4.18.1),

$$\hat{H}_R = -\frac{\hat{\mathbf{p}}^4}{8m_e^3 c^2}$$

can be understood physically as the first-order relativistic correction to the electron energy

- The term H_{SO} in the perturbation H' is

$$\hat{H}_{SO} = -\frac{e}{2m_e^2 c^2} \hat{\mathbf{S}} \cdot (\nabla \phi \wedge \hat{\mathbf{p}})$$

For a central potential $\phi = \phi(r)$, we have

$$\nabla \phi = \frac{1}{r} \frac{d\phi}{dr} \mathbf{r} ; \quad \nabla \phi \wedge \hat{\mathbf{p}} = \frac{1}{r} \frac{d\phi}{dr} (\mathbf{r} \wedge \hat{\mathbf{p}}) = \frac{1}{r} \frac{d\phi}{dr} \hat{\mathbf{L}}$$

The Dirac equation for the H atom (3)

- Hence the perturbation H_{SO} introduces a spin-orbit coupling :

$$\hat{H}_{SO} = \frac{1}{2m_e^2 c^2} \frac{1}{r} \frac{dV(r)}{dr} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$$
$$V(r) = -e\phi(r)$$

In particular, for a hydrogen-like atom :

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} \Rightarrow \hat{H}_{SO} = \frac{1}{2m_e^2 c^2} \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r^3} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$$

- As shown in the PtII E+O course, the physical origin of the spin-orbit term can be understood using a semi-classical approach :
 - As the orbiting electron moves through the electric field $\mathbf{E} = -\nabla\phi$ of the nucleus, it experiences (after a L.T.) a *magnetic* field
 - The interaction $-\mu \cdot \mathbf{B}$ of the electron magnetic dipole moment μ with this apparent magnetic field \mathbf{B} produces the spin-orbit interaction

(The classical derivation is included, for completeness, as an Appendix)

The Dirac equation for the H atom (4)

- In summary, the terms H_R and H_{SO} in equation (4.18.1), emerging from the Dirac equation, could have been anticipated on classical grounds :

H_R : the first-order relativistic correction to the electron energy

H_{SO} : the energy of the magnetic dipole moment of the electron moving through the electric field set up by the proton

However the term H_D in equation (4.18.1), the *Darwin term*, has no classical interpretation; it is purely quantum in origin

- Relative to H_0 , the correction H_R represents a small perturbation :

$$\frac{\langle \hat{H}_R \rangle}{\langle \hat{H}_0 \rangle} \sim \frac{p^4/8m_e^3c^2}{p^2/2m_e} \sim \frac{v^2}{c^2} \sim (Z\alpha)^2 \ll 1 \quad (\alpha \approx 1/137)$$

Hence we can expect that the resulting energy corrections should be small, and that first-order perturbation theory should be reliable

(and similarly for H_{SO} and H_D)

The Dirac equation for the H atom (5)

- The unperturbed energy levels, of energy $E_n = -Z^2 R_\infty / n^2$, are degenerate for all n , with degeneracy $g = 2n^2$;
→ we must use *degenerate* perturbation theory

We need to find, and (potentially) diagonalise, a $2n^2 \times 2n^2$ matrix containing the matrix elements $\hat{H}'_{jk} \equiv \langle n_j^{(0)} | \hat{H}' | n_k^{(0)} \rangle$ for each energy level n

- Together with the QED Lamb shift, the energy corrections will break (some of) the initial degeneracy, causing each energy level (except the ground state) to split into two or more closely spaced levels, giving levels with what is known as **fine structure**
- We now apply degenerate perturbation theory to each of the contributions in equation (4.18.1) in turn, starting with H_R ...

Relativistic Energy Correction

- Since H_R is independent of spin, the best choice of basis for the unperturbed states is likely to be the uncoupled basis $|n\ell m_\ell\rangle|sm_s\rangle$:

$$\langle n\ell' m'_\ell sm'_s | \hat{H}_R | n\ell m_\ell sm_s \rangle = \langle n\ell' m'_\ell | \hat{H}_R | n\ell m_\ell \rangle \delta_{m'_s m_s}$$

- The operator $\hat{\mathbf{p}}^4 = (-i\hbar\nabla)^4$ in H_R is not easy to work with directly; the trick is to express H_R in terms of H_0 :

$$\begin{aligned} \hat{H}_R &= -\frac{1}{2m_e c^2} \left(\frac{\hat{\mathbf{p}}^2}{2m_e} \right)^2 = -\frac{1}{2m_e c^2} (\hat{H}_0 - V)^2 & \left(\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m_e} + V \right) \\ &= -\frac{1}{2m_e c^2} (\hat{H}_0^2 - \hat{H}_0 V - V \hat{H}_0 + V^2) \end{aligned}$$

- The matrix elements of the H_0^2 term are easily evaluated as

$$\langle n\ell' m'_\ell | \hat{H}_0^2 | n\ell m_\ell \rangle = E_n^2 \delta_{\ell' \ell} \delta_{m'_\ell m_\ell}$$

The remaining terms all involve the potential $V(r) = -Ze^2/4\pi\epsilon_0 r \dots$

Relativistic energy correction (2)

- The spatial component of $|nlm_\ell\rangle|sm_s\rangle$ is given by equation (4.4.1) :

$$|nlm_\ell\rangle = R_{nl}(r)Y_{\ell,m_\ell}(\theta, \phi)$$

The matrix elements of any radial function $f(r)$ are given by the integrals

$$\begin{aligned}\langle nl'm'_\ell | f(r) | nlm_\ell \rangle &= \int_0^\infty \int_{-1}^{+1} \int_0^{2\pi} R_{nl'}(r) Y_{\ell',m'_\ell}^*(\theta, \phi) \\ &\quad \times f(r) R_{nl}(r) Y_{\ell,m_\ell}(\theta, \phi) r^2 dr d\theta d\phi\end{aligned}$$

- Since the spherical harmonics $Y_{\ell m}$ are orthonormal functions, we obtain

$$\langle nl'm'_\ell | f(r) | nlm_\ell \rangle = \left[\int_0^\infty r^2 f(r) R_{nl}(r)^2 dr \right] \delta_{\ell'\ell} \delta_{m'_\ell m_\ell}$$

i.e.

$$\langle nl'm'_\ell | f(r) | nlm_\ell \rangle = \langle f(r) \rangle_{nl} \delta_{\ell'\ell} \delta_{m'_\ell m_\ell} \quad (4.24.1)$$

where, for any m_ℓ :

$$\langle f(r) \rangle_{nl} = \left[\int_0^\infty r^2 f(r) R_{nl}(r)^2 dr \right] = \langle nlm_\ell | f(r) | nlm_\ell \rangle$$

Relativistic energy correction (3)

- Thus, in the basis of states $|n\ell m_\ell\rangle$, the matrix elements of $f(r)$ are diagonal in ℓ and m_ℓ , and the expectation values of $f(r)$ depend only on n and ℓ

All these properties, i.e. equation (4.24.1), are a direct consequence of *rotational symmetry* (the *Wigner-Eckart Theorem* : see next handout)

- Applying equation (4.24.1) to $f(r) = V(r)$ and to $f(r) = V(r)^2$ shows that, within each energy level n , the matrix representation of H_R is diagonal :

$$\langle n\ell' m'_\ell s m'_s | \hat{H}_R | n\ell m_\ell s m_s \rangle = \langle \hat{H}_R \rangle_{n\ell} \delta_{\ell'\ell} \delta_{m'_\ell m_\ell} \delta_{m'_s m_s}$$

where (for any m_ℓ) :

$$\langle \hat{H}_R \rangle_{n\ell} = \langle n\ell m_\ell | \hat{H}_R | n\ell m_\ell \rangle$$

Thus the uncoupled states $|n\ell m_\ell\rangle |s m_s\rangle$ can be used directly as zeroth-order states in perturbation theory

(H_R is already diagonal in this basis; no explicit diagonalization is needed)

Relativistic energy correction (4)

- The first-order energy corrections are given by the diagonal elements :

$$(\Delta E)_R = \langle \hat{H}_R \rangle_{n\ell} = -\frac{1}{2m_e c^2} \langle \hat{H}_0^2 - \hat{H}_0 V - V \hat{H}_0 + V^2 \rangle$$

- Using $\langle n\ell m_\ell | \hat{H}_0 = E_n \langle n\ell m_\ell |$, we have, for example,

$$\langle \hat{H}_0 V \rangle = \langle n\ell m_\ell | \hat{H}_0 V | n\ell m_\ell \rangle = E_n \langle V \rangle$$

Hence

$$(\Delta E)_R = -\frac{1}{2m_e c^2} \left[E_n^2 + 2E_n \left(\frac{Ze^2}{4\pi\epsilon_0} \right) \left\langle \frac{1}{r} \right\rangle_{n\ell} + \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle_{n\ell} \right]$$

- The expectation values of $1/r$ and $1/r^2$ can be shown to be given by

$$\left\langle \frac{1}{r} \right\rangle = \langle n\ell m_\ell | \frac{1}{r} | n\ell m_\ell \rangle = \int_0^\infty r R_{n\ell}(r)^2 dr = \frac{Z}{a_0 n^2}$$

$$\left\langle \frac{1}{r^2} \right\rangle = \langle n\ell m_\ell | \frac{1}{r^2} | n\ell m_\ell \rangle = \int_0^\infty R_{n\ell}(r)^2 dr = \frac{Z^2}{a_0^2 n^3 (\ell + 1/2)}$$

Relativistic energy correction (5)

- The energies E_n can be expressed in terms of the fine structure constant :

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137.036} \approx \frac{1}{137}$$

$$E_n = -\frac{Z^2}{n^2} R_\infty ; \quad 2R_\infty = \frac{e^2}{4\pi\epsilon_0 a_0} = \alpha^2 m_e c^2$$

- Combining the various equations above then gives

$$(\Delta E)_R = - \left(\frac{Z}{n} \right)^4 \left(\frac{n}{\ell + 1/2} - \frac{3}{4} \right) \alpha^2 R_\infty$$

Thus, for each energy level n , the perturbation H_R (the relativistic energy correction) lifts the degeneracy between states of different ℓ

e.g. the $n = 3$ level splits into three separate levels ($\ell = 0, 1, 2$)

- The energy splitting is small, the scale being set by

$$\alpha^2 R_\infty \approx (13.6 \text{ eV})/(137)^2 = 7.2 \times 10^{-4} \text{ eV}$$

Spin-Orbit Correction

- To compute the spin-orbit contribution to the energy correction, we need to evaluate the matrix elements of the operator

$$\hat{H}_{\text{SO}} = \xi(r) \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} , \quad \xi(r) \equiv \frac{1}{2m_e^2 c^2} \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r^3} \propto \frac{1}{r^3}$$

- In this case, the trick is to notice that the operator product $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ can be written entirely in terms of squares of angular momentum operators :

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2} (\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2) \qquad \qquad \hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$$

- The coupled basis states $|n j m_j \ell s\rangle$ are simultaneous eigenstates of the operators $\hat{\mathbf{J}}^2$, $\hat{\mathbf{L}}^2$ and $\hat{\mathbf{S}}^2$:

$$\hat{\mathbf{J}}^2 |n j m_j \ell s\rangle = j(j+1)\hbar^2 |n j m_j \ell s\rangle$$

$$\hat{\mathbf{L}}^2 |n j m_j \ell s\rangle = \ell(\ell+1)\hbar^2 |n j m_j \ell s\rangle \qquad \qquad (s = 1/2)$$

$$\hat{\mathbf{S}}^2 |n j m_j \ell s\rangle = s(s+1)\hbar^2 |n j m_j \ell s\rangle$$

Spin-orbit correction (2)

- They are therefore eigenstates also of the operator $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$:

$$\begin{aligned}\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} |n j m_j \ell s\rangle &= \frac{1}{2} (\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2) |n j m_j \ell s\rangle \\ &= \frac{1}{2} [j(j+1) - \ell(\ell+1) - s(s+1)] \hbar^2 |n j m_j \ell s\rangle\end{aligned}$$

- Hence, in the coupled basis, the matrix elements of H_{SO} are given by

$$\begin{aligned}\langle n j' m'_j \ell' s | \xi(r) \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} | n j m_j \ell s \rangle \\ = \frac{1}{2} [j(j+1) - \ell(\ell+1) - s(s+1)] \hbar^2 \langle n j' m'_j \ell' s | \xi(r) | n j m_j \ell s \rangle\end{aligned}$$

- Since $\xi(r)$ does not depend on angle or spin variables, we have, similarly to equation (4.24.1),

$$\langle n j' m'_j \ell' s | \xi(r) | n j m_j \ell s \rangle = \langle \xi(r) \rangle_{n\ell} \delta_{j'j} \delta_{m'_j m_j} \delta_{\ell' \ell}$$

where the expectation values of $\xi(r)$ are given by

$$\langle \xi(r) \rangle_{n\ell} = \int_0^\infty r^2 \xi(r) R_{n\ell}(r)^2 dr$$

Spin-orbit correction (3)

- Hence, in the coupled basis, within each energy level n , the matrix representation of H_{SO} is diagonal :

$$\begin{aligned} & \langle n j' m'_j \ell' s | \xi(r) \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} | n j m_j \ell s \rangle \\ &= \frac{1}{2} [j(j+1) - \ell(\ell+1) - s(s+1)] \hbar^2 \langle \xi(r) \rangle_{n\ell} \delta_{j'j} \delta_{m'_j m_j} \delta_{\ell' \ell} \end{aligned}$$

The coupled states can therefore be used directly as the zeroth-order states in perturbation theory (no explicit diagonalization is needed)

- The first-order energy corrections due to H_{SO} are given by the diagonal matrix elements (i.e. by the expectation values of H_{SO}) :

$$\begin{aligned} (\Delta E)_{SO} &= \langle n j m_j \ell s | \xi(r) \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} | n j m_j \ell s \rangle \\ &= \frac{1}{2} [j(j+1) - \ell(\ell+1) - s(s+1)] \hbar^2 \langle \xi(r) \rangle_{n\ell} \end{aligned}$$

- For an S-state ($\ell = 0, s = 1/2, j = 1/2$), the factor [...] in brackets on the right-hand side vanishes :

$$(\Delta E)_{SO} = 0 \quad (\ell = 0)$$

Spin-orbit correction (4)

- We have $\xi(r) \sim 1/r^3$; for states with $\ell > 0$, the radial expectation value $\langle 1/r^3 \rangle$ can be shown to be given by

$$\left\langle \frac{1}{r^3} \right\rangle = \int_0^\infty \frac{1}{r} R_{n\ell}(r)^2 dr = \frac{Z^3}{a_0^3 n^3} \frac{1}{\ell(\ell + 1/2)(\ell + 1)}$$

- Hence, for $\ell > 0$, the spin-orbit energy correction is

$$(\Delta E)_{SO} = \frac{1}{2m_e^2 c^2} \frac{Ze^2}{4\pi\epsilon_0} \frac{Z^3}{a_0^3 n^3} \left[\frac{j(j+1) - \ell(\ell+1) - s(s+1)}{2\ell(\ell+1/2)(\ell+1)} \right] \hbar^2$$

- Since $s = 1/2$, there are only two possibilities :

$$j(j+1) - \ell(\ell+1) - s(s+1) = \begin{cases} \ell & (j = \ell + 1/2) \\ -(\ell+1) & (j = \ell - 1/2) \end{cases}$$

- The spin-orbit correction for $\ell > 0$ can thus be written more compactly as

$$(\Delta E)_{SO} = \pm \frac{1}{2} \left(\frac{Z}{n} \right)^4 \frac{n}{(j+1/2)} \frac{1}{(\ell+1/2)} \alpha^2 R_\infty \quad (j = \ell \pm 1/2)$$

Spin-orbit correction (5)

- The spin-orbit energy correction depends on n , j and ℓ ;
Therefore, for each energy level n , the spin-orbit interaction lifts the degeneracy with respect to both j and ℓ
e.g. H_{SO} alone would split the $n = 3$ level into five separate levels :
 $(\ell, j) = (0, 1/2), (1, 1/2), (1, 3/2), (2, 3/2), (2, 5/2)$
- Before moving on to consider the Darwin term, H_D , it will prove useful to obtain some commutation relations involving the spin-orbit and angular momentum operators ...

Spin-orbit commutation relations

- The commutator of $\mathbf{L} \cdot \mathbf{S}$ with L_z contains the contributions

$$[\hat{L}_x \hat{S}_x, \hat{L}_z] = \hat{S}_x [\hat{L}_x, \hat{L}_z] = -i\hbar \hat{L}_y \hat{S}_x$$

$$[\hat{L}_y \hat{S}_y, \hat{L}_z] = \hat{S}_y [\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x \hat{S}_y$$

$$[\hat{L}_z \hat{S}_z, \hat{L}_z] = \hat{S}_z [\hat{L}_z, \hat{L}_z] = 0$$

Summing the three equations above then gives

$$[\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \hat{L}_z] = i\hbar (\hat{L}_x \hat{S}_y - \hat{L}_y \hat{S}_x)$$

- Interchanging \mathbf{L} and \mathbf{S} then immediately gives also

$$[\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \hat{S}_z] = i\hbar (\hat{S}_x \hat{L}_y - \hat{S}_y \hat{L}_x) = -[\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \hat{L}_z]$$

For $J_z = L_z + S_z$, we therefore have

$$[\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \hat{J}_z] = 0$$

- Thus $\mathbf{L} \cdot \mathbf{S}$ commutes with all operators in the coupled set $\{J^2, J_z, \mathbf{L}^2, \mathbf{S}^2\}$, but not with all operators in the uncoupled set $\{\mathbf{L}^2, L_z, \mathbf{S}^2, S_z\}$, because

$$[\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \hat{L}_z] \neq 0 ; \quad [\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \hat{S}_z] \neq 0$$

Spin-orbit commutation relations (2)

- The choice of z axis is arbitrary; the same results must therefore hold also for the x and y components, giving overall

$$[\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \hat{\mathbf{L}}] \neq 0 ; \quad [\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \hat{\mathbf{S}}] \neq 0 ; \quad [\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \hat{\mathbf{J}}] = 0$$

- The spin-orbit operator H_{SO} includes the radial function $\xi(r)$:

$$\hat{H}_{\text{SO}} = \xi(r) \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$$

The operator $\xi(r)$ commutes with “everything” (see slide 1.31) :

$$[\xi(r), \hat{L}_z] = [\xi(r), \hat{\mathbf{L}}^2] = [\xi(r), \hat{S}_z] = [\xi(r), \hat{\mathbf{S}}^2] = [\xi(r), \hat{J}_z] = [\xi(r), \hat{\mathbf{J}}^2] = 0$$

Hence $\xi(r) \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ commutes with all operators in the coupled set, $\{\hat{\mathbf{J}}^2, J_z, \hat{\mathbf{L}}^2, \hat{\mathbf{S}}^2\}$, but not with all operators in the uncoupled set $\{\hat{\mathbf{L}}^2, L_z, \hat{\mathbf{S}}^2, S_z\}$, because

$$[\hat{H}_{\text{SO}}, \hat{L}_z] \neq 0 ; \quad [\hat{H}_{\text{SO}}, \hat{S}_z] \neq 0$$

This result will prove useful later (spin-orbit coupling)

Darwin Term

- Finally, we consider the remaining contribution to H' (slide 4.18), the *Darwin term*, H_D :

$$\hat{H}_D = -\frac{e\hbar^2}{8m_e^2c^2}(\nabla^2\phi)$$

$$\phi(r) = \frac{Ze}{4\pi\epsilon_0 r}$$

The brackets above are needed to distinguish $(\nabla^2\phi)\psi$ from $\nabla^2(\phi\psi)$

- The first-order correction to the energy for a state $|\psi\rangle$ is

$$(\Delta E)_D = \langle\psi|\hat{H}_D|\psi\rangle = -\frac{e\hbar^2}{8m_e^2c^2}\langle\psi|(\nabla^2\phi)|\psi\rangle$$

- For a $1/r$ potential, $\nabla^2\phi$ vanishes everywhere except at the origin, where it diverges :

$$\nabla^2(1/r) = -4\pi\delta^{(3)}(\mathbf{r})$$

Hence the matrix element above is

$$\langle\psi|(\nabla^2\phi)|\psi\rangle = \frac{Ze}{4\pi\epsilon_0} \left\langle \psi \left| \left(\nabla^2 \frac{1}{r} \right) \right| \psi \right\rangle = -\frac{Ze}{\epsilon_0} \langle\psi|\delta^{(3)}(\mathbf{r})|\psi\rangle = -\frac{Ze}{\epsilon_0} |\psi(0)|^2$$

Darwin term (2)

- Only S-states $|n00\rangle$ (with $\ell = 0$) have a wave-function which is non-zero at the origin (see slide 1.47) :

$$|\psi_{n00}(0)|^2 = \frac{Z^3}{\pi n^3 a_0^3}$$

- Hence the energy shift due to the Darwin term is non-zero only for $\ell = 0$:

$$(\Delta E)_D = \begin{cases} \frac{Z^4 \alpha^2}{n^3} R_\infty & (\ell = 0) \\ 0 & (\ell > 0) \end{cases}$$

[Sir Charles Robert Galton Darwin](#)

Hydrogen Atom Fine Structure

- In summary, for all three perturbations (H_R , H_{SO} , H_D), the scale of the energy corrections is set by

$$\frac{\alpha^2 R_\infty}{n^3} = \frac{7.25 \times 10^{-4}}{n^3} \text{ eV} = \frac{175}{n^3} \text{ GHz} \quad \left\{ \begin{array}{l} \alpha \approx 1/137 \\ R_\infty \approx 13.6 \text{ eV} \end{array} \right.$$

- In units of $Z^4 \alpha^2 R_\infty / 4n^3$, the energy corrections are

$$(\Delta E)_R = \frac{3}{n} - \frac{4}{\ell + 1/2} ; \quad (\Delta E)_D = \begin{cases} 4 & (\ell = 0) \\ 0 & (\ell > 0) \end{cases}$$

$$(\Delta E)_{SO} = \begin{cases} \pm \frac{2}{(j + 1/2)(\ell + 1/2)} & (\ell > 0, j = \ell \pm 1/2) \\ 0 & (\ell = 0) \end{cases}$$

- The total energy correction, $(\Delta E)_{FS} = (\Delta E)_R + (\Delta E)_{SO} + (\Delta E)_D$, would at first sight seem to depend on all three quantum numbers n, ℓ, j ...

Hydrogen atom fine structure (2)

- In fact, summing the three energy corrections on the previous slide results in a total correction which depends on n and j , but *does not depend on ℓ* :

$$(\Delta E)_{\text{FS}} = (\Delta E)_{\text{R}} + (\Delta E)_{\text{SO}} + (\Delta E)_{\text{D}}$$

$$(\Delta E)_{\text{FS}} = \frac{Z^4}{4n^3} \left(\frac{3}{n} - \frac{4}{j + 1/2} \right) \alpha^2 R_\infty$$

- The n 'th energy level splits into n separate energy levels, one for each j
e.g. the $n = 3$ level splits into 3 levels ($j = 1/2, 3/2, 5/2$)

States with the same j but different ℓ remain degenerate in energy

e.g. for $n = 3$:
$$\begin{cases} j = 1/2 : 3S_{1/2} (\ell = 0) \text{ and } 3P_{1/2} (\ell = 1) \text{ stay degenerate} \\ j = 3/2 : 3P_{3/2} (\ell = 1) \text{ and } 3D_{3/2} (\ell = 2) \text{ stay degenerate} \end{cases}$$

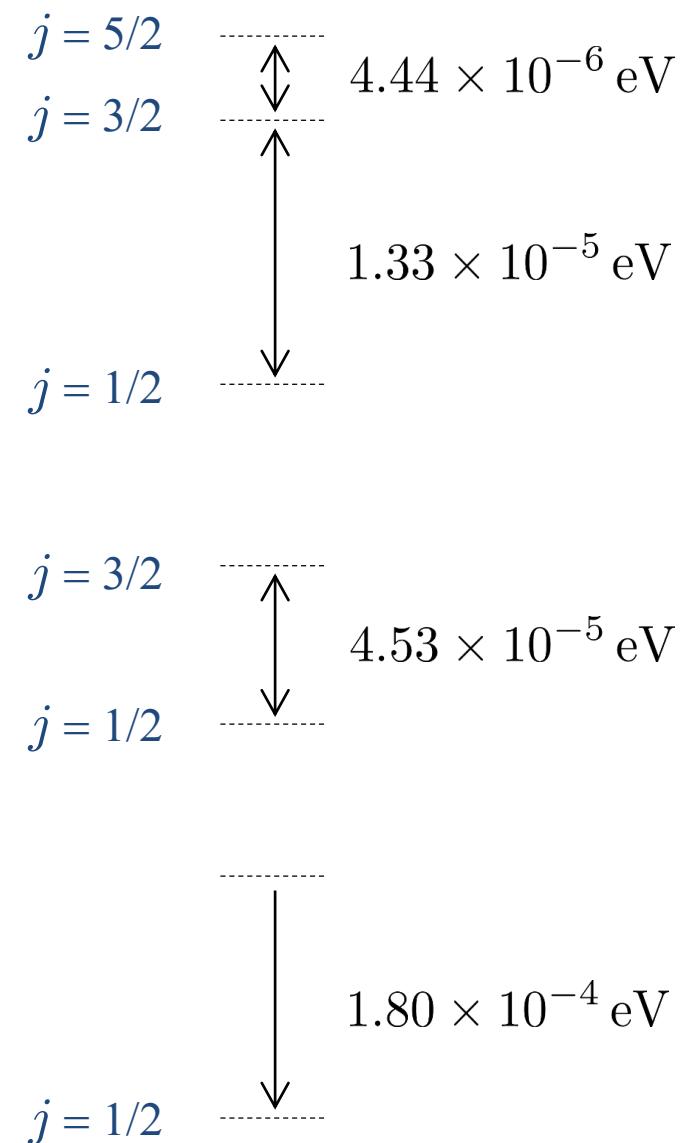
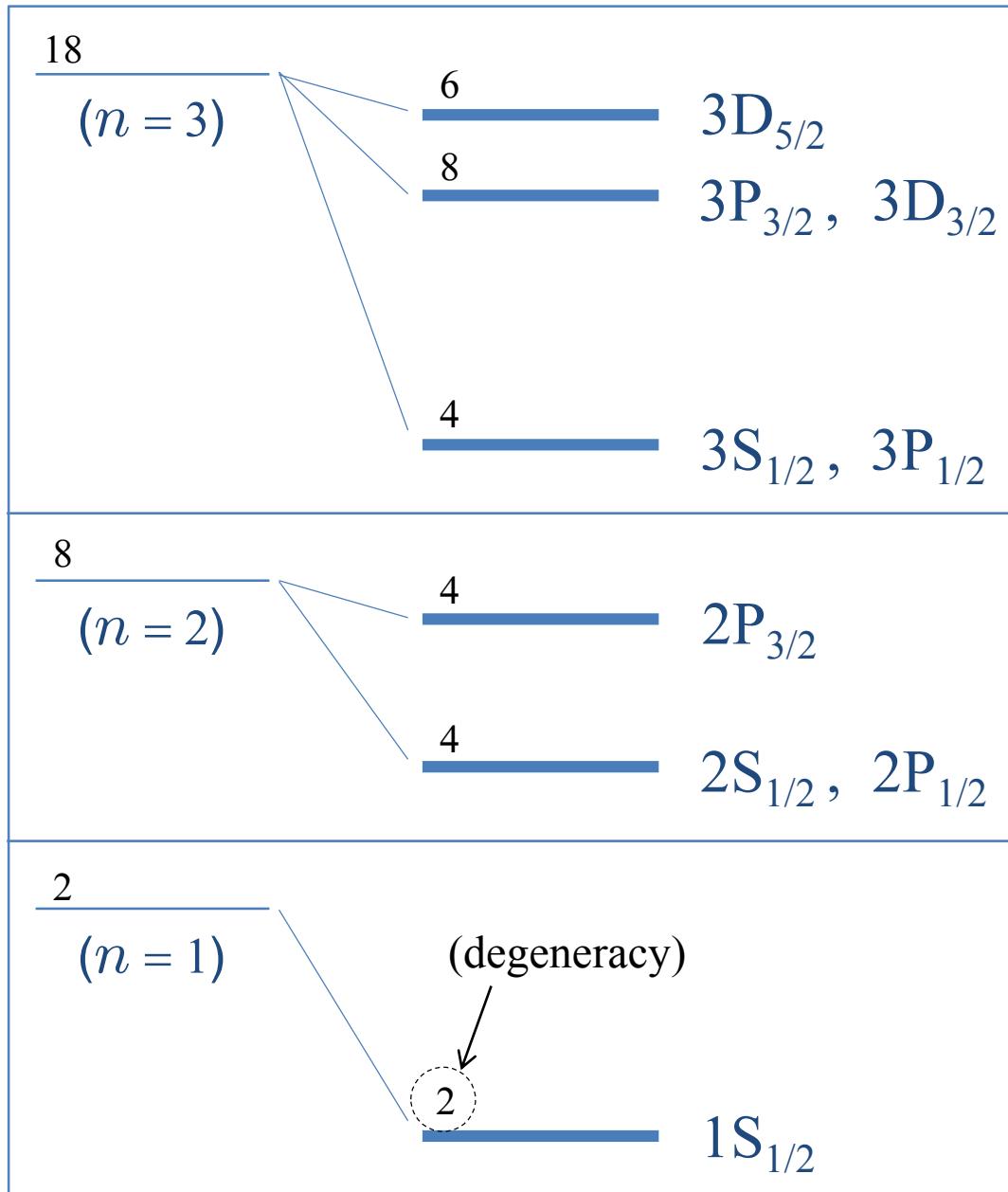
- For each n , the net effect is to *lower* the eigenstate energies (slightly), by an amount depending only on j ...

Hydrogen Fine Structure : $n = 1, 2, 3$

$$(\Delta E)_{\text{FS}} = (\Delta E)_{\text{R}} + (\Delta E)_{\text{SO}} + (\Delta E)_{\text{D}}$$

			units of $(\alpha^2 R_\infty / 4n^3)$			GHz	
			$(\Delta E)_{\text{R}}$	$(\Delta E)_{\text{SO}}$	$(\Delta E)_{\text{D}}$	$(\Delta E)_{\text{FS}}$	
$n = 1$	$\ell = 0, j = 1/2$	$1S_{1/2}$	-5	0	+4	-1	-43.7
$n = 2$	$\ell = 0, j = 1/2$	$2S_{1/2}$	$-13/2$	0	+4	$-5/2$	-13.7
	$\ell = 1, j = 1/2$	$2P_{1/2}$	$-7/6$	$-4/3$	0	$-5/2$	-13.7
	$\ell = 1, j = 3/2$	$2P_{3/2}$	$-7/6$	$+2/3$	0	$-1/2$	-2.7
$n = 3$	$\ell = 0, j = 1/2$	$3S_{1/2}$	-7	0	+4	-3	-4.9
	$\ell = 1, j = 1/2$	$3P_{1/2}$	$-5/3$	$-4/3$	0	-3	-4.9
	$\ell = 1, j = 3/2$	$3P_{3/2}$	$-5/3$	$+2/3$	0	-1	-1.6
	$\ell = 2, j = 3/2$	$3D_{3/2}$	$-3/5$	$-4/10$	0	-1	-1.6
	$\ell = 2, j = 5/2$	$3D_{5/2}$	$-3/5$	$+4/15$	0	$-1/3$	-0.5

Hydrogen Fine Structure : $n = 1, 2, 3$



The Lamb Shift

- The Dirac equation predicts that states with the same j but different ℓ remain degenerate in energy :

$$2S_{1/2} = 2P_{1/2}, \quad 3S_{1/2} = 3P_{1/2}, \quad 3P_{3/2} = 3D_{3/2}, \quad \dots$$

- But, at the Shelter Island Conference (1947), Willis Lamb presented experimental evidence that the $2S_{1/2}$ and $2P_{1/2}$ levels are not degenerate :

→ the Lamb shift : $\Delta\nu(2S_{1/2} - 2P_{1/2}) \approx 1000 \text{ MHz}$

W. Lamb & E. Rutherford, Phys. Rev. 72 (1947) 241

- On the train home, Hans Bethe obtained $\Delta\nu \sim 1040 \text{ MHz}$ using a “back of the envelope” “QED-inspired” calculation H. Bethe, Phys. Rev. 72 (1947) 339

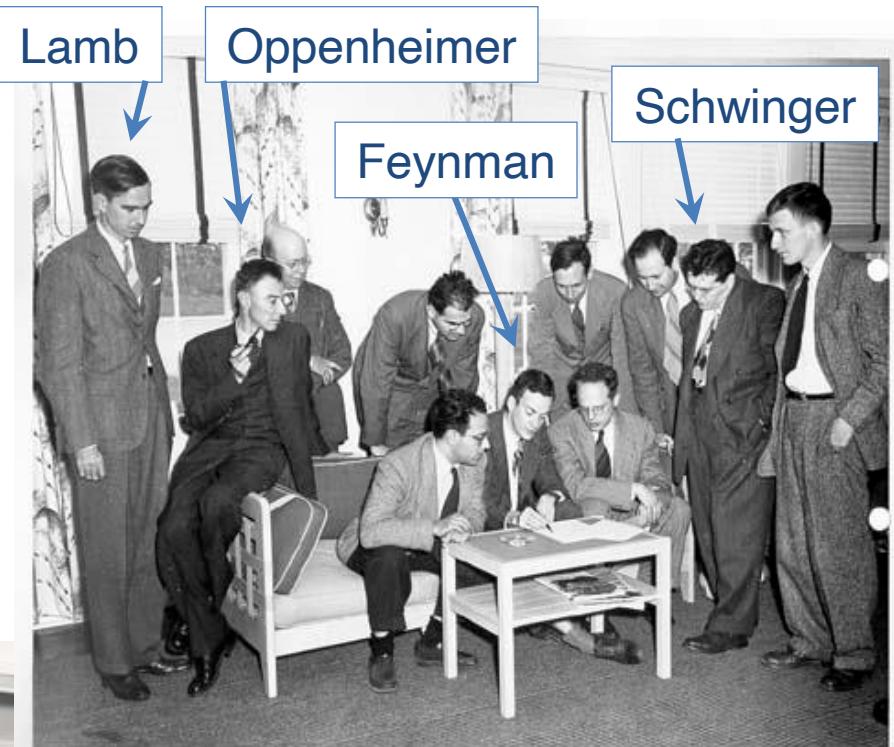
→ a key step in establishing QED as the correct approach to quantising the electromagnetic field F. Dyson, Physics Today 58 (Oct. 2005), p48

- Also, Rabi presented the first evidence that g_e is not precisely $g_e = 2$
→ this can also only be understood using QED

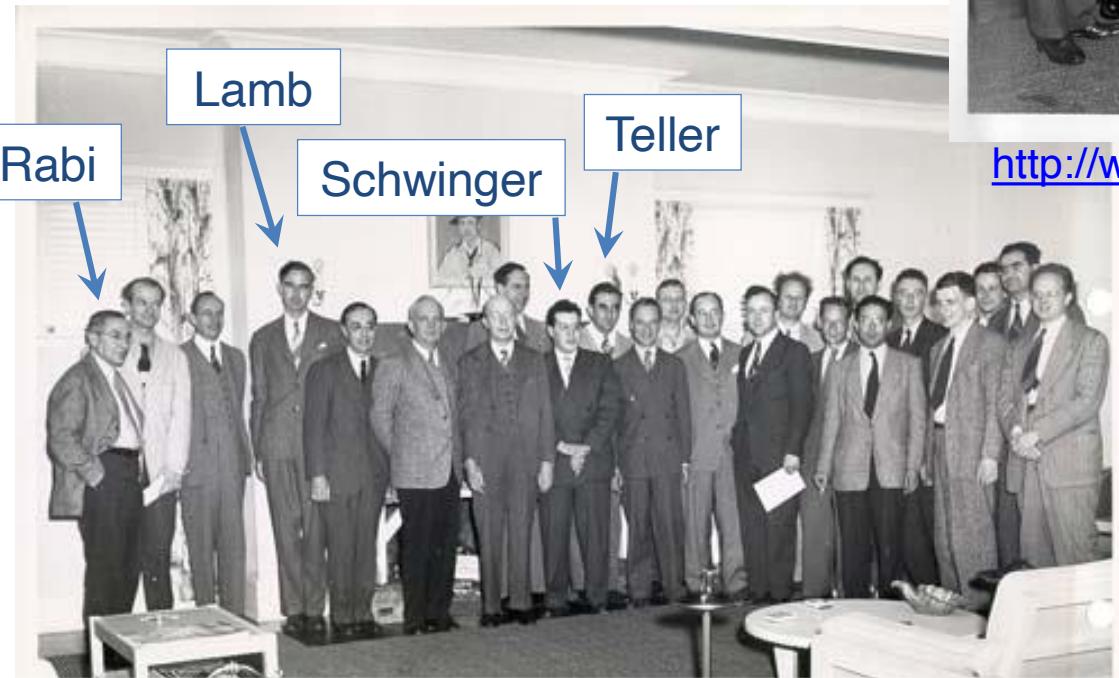
The Ram's Head Inn, Shelter Island (Long Island, NY)

“There have been many conferences in the world since, but I’ve never felt any to be as important as this.”

R. P. Feynman (1966)



<http://www.nas.edu/history/sic/sicgroup2.html>



<http://www.nas.edu/history/sic/sicgroup1.html>

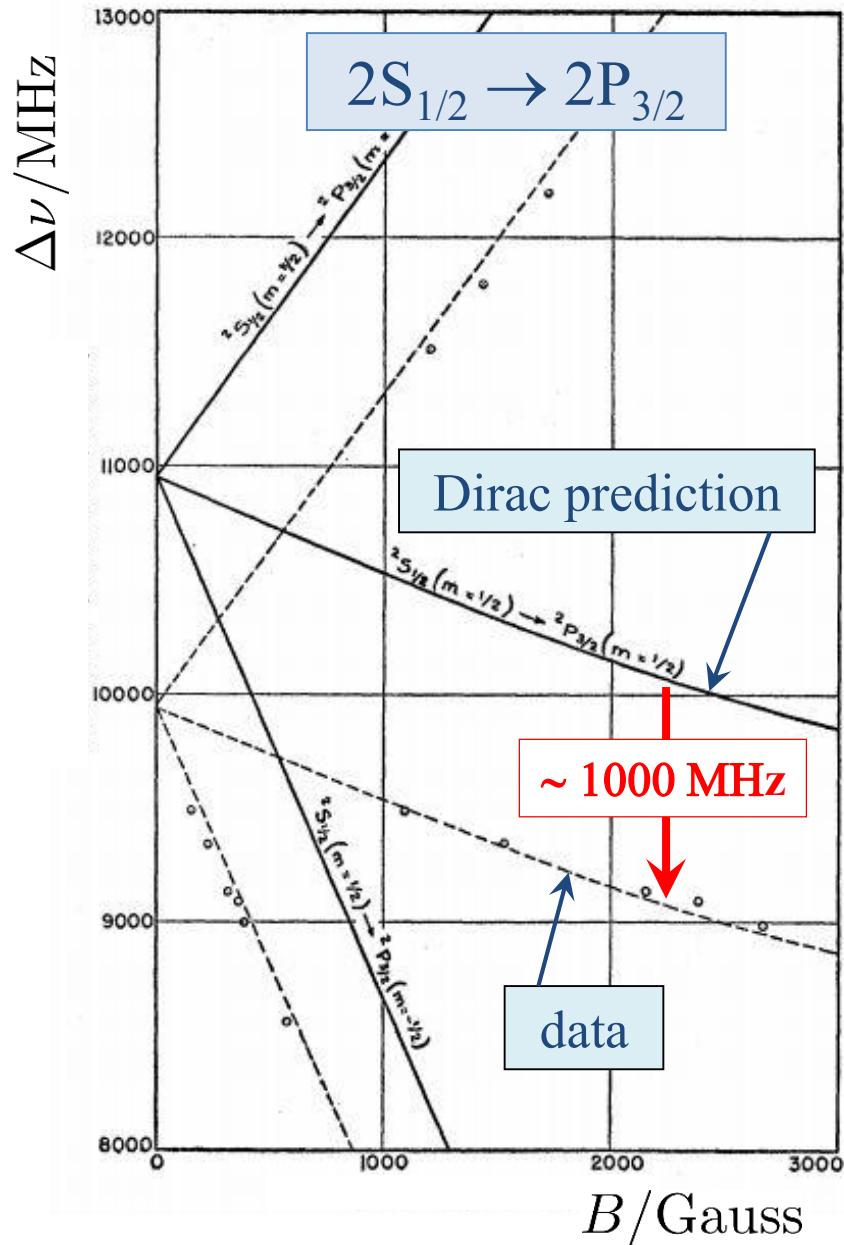
The Lamb shift : initial observation

- Lamb and Rutherford used a beam of hydrogen atoms excited to the metastable $2S_{1/2}$ state (see later)
- $2S_{1/2} \rightarrow 2P_{3/2}$ and $2S_{1/2} \rightarrow 2P_{1/2}$ transitions were induced by microwave radiation, in the presence of an external magnetic field
(the *Zeeman effect* – see later)
- For $2S_{1/2} \rightarrow 2P_{3/2}$ (see figure) the transition frequencies were found to be systematically smaller than the Dirac prediction by

$$\Delta\nu \sim 1000 \text{ MHz}$$

(the *Lamb shift*)

$$(\Delta\nu/\nu \sim 10\%)$$



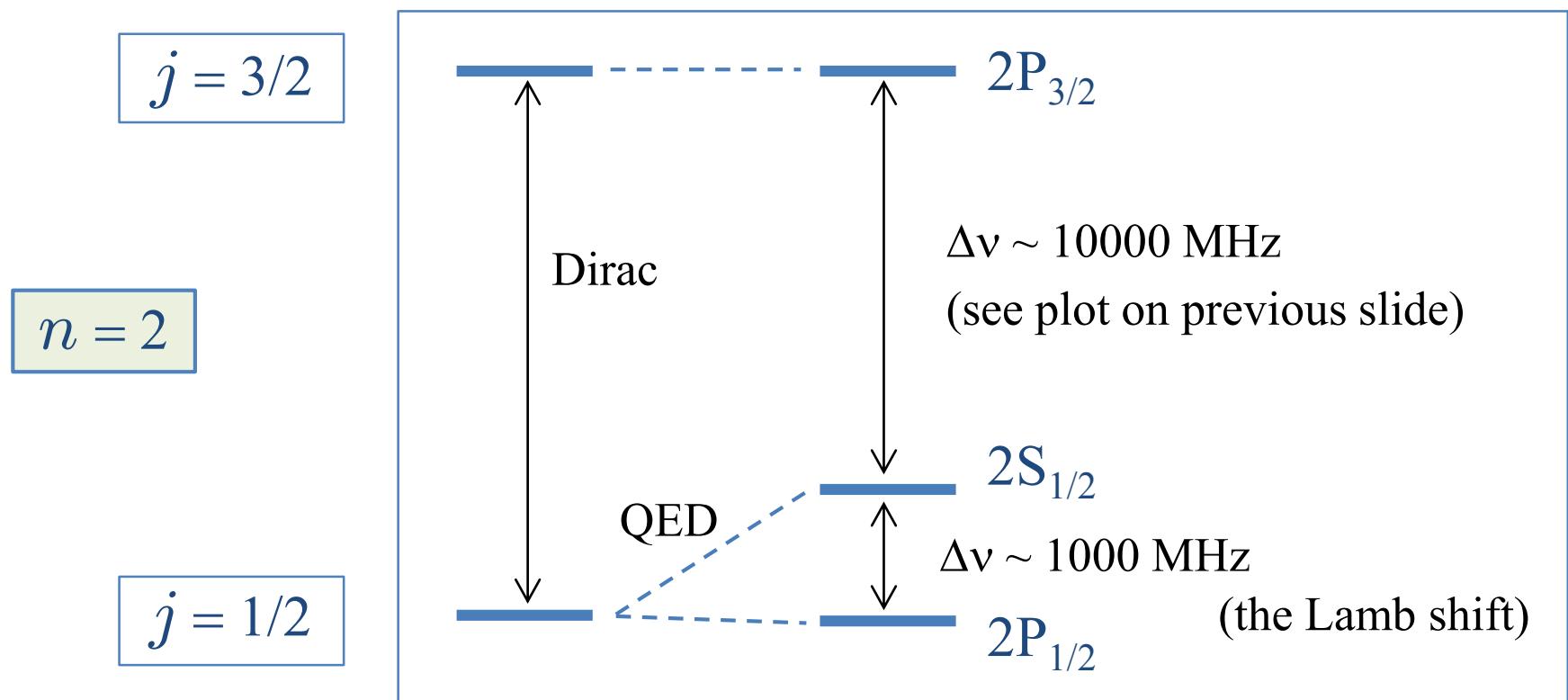
The Lamb shift : QED

- Agreement between theory and experiment is restored by QED :

QED corrections break the degeneracy in ℓ

(for fixed j)

In particular, the QED correction $\Delta E_{(QED)}$ is much larger for S-states ($\ell = 0$) than for non-S states ($\ell > 0$)



The Lamb shift : QED (2)

+8173 MHz $1S_{1/2}$

$n = 1$

Dirac
QED

+8 MHz $2P_{3/2}$

$n = 2$

$2S_{1/2}$
 $2P_{1/2}$

9911 MHz



+1045 MHz



-13 MHz

Dirac
QED

$3D_{5/2}$

$n = 3$

1078 MHz



$3P_{3/2}$
 $3D_{3/2}$



2930 MHz



315 MHz

$3S_{1/2}$
 $3P_{1/2}$

Dirac
QED

The Lamb shift : more recent observations

- The advent of tuneable dye lasers allowed the Doppler broadening of spectral lines to be eliminated

(Doppler $\Delta\nu \sim 6$ GHz for H at room temp.)

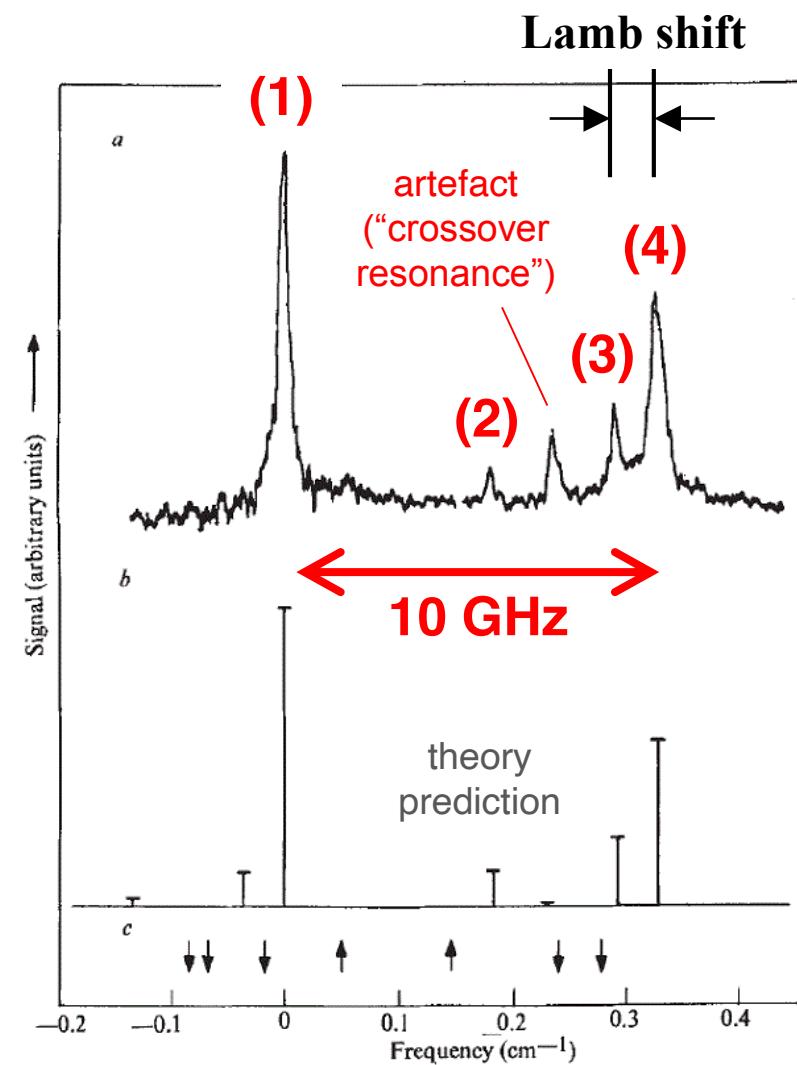
- fine structure and the Lamb shift could then be resolved *optically*

First shown for the Balmer (H_α) line of hydrogen : $(n = 2) \rightarrow (n = 3)$

- The peaks seen are :

$$\begin{array}{ll} (1) : 2P_{3/2} \rightarrow 3D_{3/2} & (3) : 2S_{1/2} \rightarrow 3P_{3/2} \\ (2) : 2S_{1/2} \rightarrow 3P_{1/2} & (4) : 2P_{1/2} \rightarrow 3D_{3/2} \end{array}$$

The (3)-(4) peak separation is dominated by the $n = 2$ Lamb shift (1058 MHz); the $n = 3$ separation is tiny in comparison (5.5 MHz)



The Lamb shift : QED (3)

- For the “classic” Lamb shift ($n = 2$), the latest QED prediction agrees with the most recent experimental measurement to better than 1 part in 10^5 :

$$\text{QED} : \quad \Delta E = 1057.83412(26) \text{ MHz} \quad (0.25 \times 10^{-6})$$

$$\text{Expt.} : \quad \Delta E = 1057.8298(32) \text{ MHz} \quad (3 \times 10^{-6})$$

[N. Bezginov et al., Science 365 \(2019\) 1007](#)

[V. Yerokhin et al., arXiv:1809.00462 \(2018\)](#)

- Roughly speaking, the Lamb shift arises in QED for the same reason as the electron magnetic moment is not exactly $g_e = 2$ (see slide 3.41)
 - the electron is not simply a pointlike particle, but is continually emitting and absorbing virtual photons ...
- Why did it take until ~1950 to develop an accepted and usable quantum theory of the electromagnetic field (i.e. QED) ?
(the basic ideas were already in place as early as 1929)

The Lamb shift : QED

- Perturbation theory for QED (and for other relativistic QFTs) is beset by the problem of *infinities* and *divergences* of various types

Methods to overcome these infinities in QED were pioneered by Dyson, Feynman, Schwinger and Tomonaga :

“... As one of the inventors [of QED] I remember that we thought of QED in 1949 as a temporary and jerry-built structure, with mathematical inconsistencies and renormalized infinities swept under the rug. We did not expect it to last more than 10 years ...”

F. Dyson, as quoted in : [G. Gabrielse & D. Hanneke, CERN Courier \(Oct. 2006\), p35](#)

The entire contents of a recommendation letter from R.H. Fowler to H. Bethe (1946) :

“I’d like to recommend enthusiastically that you take Freeman Dyson as a graduate student in physics. He has not studied much physics but I can say this: Although he is only 19 years old, he is, in my opinion, the best mathematician in England”

[I. Estermann, Am. J. Phys. 43 \(1975\) 661](#)

Hyperfine Structure

- The term hyperfine collectively denotes any effect due to the atomic nucleus, except those due solely to its electric charge or finite mass
 - includes effects due to the finite nuclear size, spin, magnetic dipole moment, electric quadrupole moment, ...
- The most important hyperfine effects are due to the magnetic dipole moment associated with the nuclear spin, I , which for hydrogen is

$$(\hat{\mu}_S)_p = g_p \frac{\mu_N}{\hbar} \hat{\mathbf{I}} \quad (g_p = 5.586)$$

- The proton magnetic dipole moment $(\mu_S)_p$ sets up a magnetic field \mathbf{B}_p . The atomic electron magnetic dipole moment $(\mu_S)_e$ located within the proton's magnetic field \mathbf{B}_p gives rise to a hyperfine interaction

$$\hat{H}_{hf} = -(\hat{\mu}_S)_e \cdot \mathbf{B}_p = \frac{\mu_B}{\hbar} (\hat{\mathbf{L}} + g_e \hat{\mathbf{S}}) \cdot \mathbf{B}_p \quad (4.49.1)$$
$$(g_e \approx 2.0023)$$

Hyperfine structure (2)

- Classically, a magnetic moment \mathbf{M} generates a magnetic field given by

$$\mathbf{A} = -\frac{\mu_0}{4\pi} \mathbf{M} \wedge \nabla(1/r)$$
$$\mathbf{B} = \nabla \wedge \mathbf{A} = \frac{\mu_0}{4\pi} \left[\frac{3\mathbf{r}(\mathbf{r} \cdot \mathbf{M}) - r^2 \mathbf{M}}{r^5} + \frac{8\pi}{3} \mathbf{M} \delta^{(3)}(\mathbf{r}) \right] \quad (4.50.1)$$

- Substituting equation (4.50.1) into (4.49.1), with the vector \mathbf{M} replaced by the proton magnetic dipole operator $(\boldsymbol{\mu}_S)_p$, then gives

$$\hat{H}_{\text{hf}} = g_p \frac{\mu_B \mu_N}{\hbar^2} (\hat{\mathbf{L}} + g_e \hat{\mathbf{S}}) \cdot \frac{\mu_0}{4\pi} \left[\frac{3\mathbf{r}(\mathbf{r} \cdot \hat{\mathbf{I}}) - r^2 \hat{\mathbf{I}}}{r^5} + \frac{8\pi}{3} \hat{\mathbf{I}} \delta^{(3)}(\mathbf{r}) \right]$$

- We can again use (first-order) perturbation theory to estimate the energy corrections

Hyperfine structure : S states

- For an S-state, with $\ell = 0$, the first-order energy correction due to this hyperfine interaction is

$$(\Delta E)_{\ell=0} = \langle n00 | \hat{H}_{\text{hf}} | n00 \rangle = \int \psi_{n00}^*(\mathbf{r}) \hat{H}_{\text{hf}} \psi_{n00}(\mathbf{r}) d^3\mathbf{r}$$

In this case, there is no contribution from the electron's orbital angular momentum, \mathbf{L} , since

$$\langle n00 | \hat{\mathbf{L}} = 0$$

Also the $3\mathbf{r}(\mathbf{r} \cdot \mathbf{I})$ and $-r^2\mathbf{I}$ terms cancel due to symmetry :

$$\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \frac{1}{3} \langle r^2 \rangle$$

- Hence, for S-states, only the spin S and the δ -function terms contribute :

$$(\Delta E)_{\ell=0} = g_e g_p \frac{\mu_B \mu_N}{\hbar^2} \frac{\mu_0}{4\pi} \langle \hat{\mathbf{S}} \cdot \hat{\mathbf{I}} \rangle \frac{8\pi}{3} |\psi_{n00}(0)|^2$$

This is an interaction between the electron and proton magnetic dipoles :

$$(\hat{\boldsymbol{\mu}}_S)_e \cdot (\hat{\boldsymbol{\mu}}_S)_p = \left(g_e \frac{\mu_B}{\hbar} \hat{\mathbf{S}} \right) \cdot \left(g_p \frac{\mu_N}{\hbar} \hat{\mathbf{I}} \right)$$

Hyperfine structure : S states (2)

-- Using $|\psi_{n00}(0)|^2 = \frac{Z^3}{\pi n^3 a_0^3}$ then gives

$$(\Delta E)_{\ell=0} = g_e g_p \frac{2}{3m_p} \frac{Z^3}{n^3} \frac{\alpha^4 m_e^2 c^2}{\hbar^2} \langle \hat{\mathbf{S}} \cdot \hat{\mathbf{I}} \rangle$$

-- The total angular momentum of the hydrogen atom is

$$\hat{\mathbf{F}} = \hat{\mathbf{L}} + \hat{\mathbf{S}} + \hat{\mathbf{I}}$$

Squaring this relation gives

$$\langle \hat{\mathbf{F}}^2 \rangle = \langle \hat{\mathbf{L}}^2 \rangle + \langle \hat{\mathbf{S}}^2 \rangle + \langle \hat{\mathbf{I}}^2 \rangle + 2\langle \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \rangle + 2\langle \hat{\mathbf{L}} \cdot \hat{\mathbf{I}} \rangle + 2\langle \hat{\mathbf{S}} \cdot \hat{\mathbf{I}} \rangle$$

-- In an S-state, with $\ell = 0$, we have $\hat{\mathbf{L}}|n00\rangle = 0$, and hence

$$\langle \hat{\mathbf{L}}^2 \rangle = \langle \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \rangle = \langle \hat{\mathbf{L}} \cdot \hat{\mathbf{I}} \rangle = 0$$

Hence, for $\ell = 0$,

$$\langle \hat{\mathbf{F}}^2 \rangle = \langle \hat{\mathbf{S}}^2 \rangle + \langle \hat{\mathbf{I}}^2 \rangle + 2\langle \hat{\mathbf{S}} \cdot \hat{\mathbf{I}} \rangle$$

(so effectively, for $\ell = 0$, we can just use $\hat{\mathbf{F}} = \hat{\mathbf{S}} + \hat{\mathbf{I}}$)

Hyperfine structure : S states (3)

- The expectation value $\langle \mathbf{S} \cdot \mathbf{I} \rangle$ can now be evaluated using

$$\begin{aligned}\langle \hat{\mathbf{S}} \cdot \hat{\mathbf{I}} \rangle &= \frac{1}{2} [\langle \hat{\mathbf{F}}^2 \rangle - \langle \hat{\mathbf{S}}^2 \rangle - \langle \hat{\mathbf{I}}^2 \rangle] \\ &= \frac{1}{2} [F(F+1) - s(s+1) - I(I+1)] \hbar^2 \quad (s = 1/2)\end{aligned}$$

- For hydrogen atom S-states, with

$$s = 1/2, \quad I = 1/2; \quad F = s \otimes I = 0, 1$$

this gives

$$\langle \hat{\mathbf{S}} \cdot \hat{\mathbf{I}} \rangle = \begin{cases} -(3/4)\hbar^2 & (F = 0) \\ +(1/4)\hbar^2 & (F = 1) \end{cases}$$

- Hence, for hydrogen S-states, first-order perturbation theory predicts

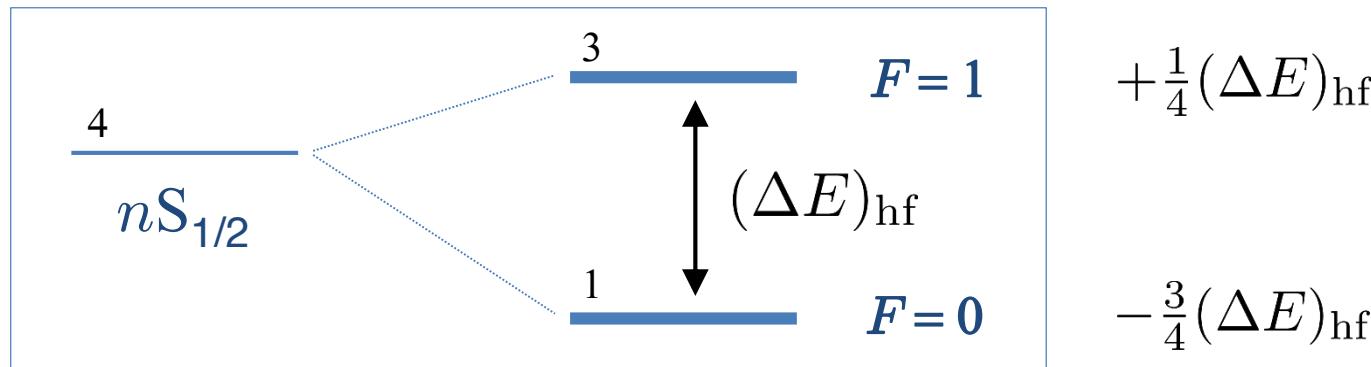
$$\Delta E = \begin{cases} -(3/4)(\Delta E)_{\text{hf}} & (F = 0) \\ +(1/4)(\Delta E)_{\text{hf}} & (F = 1) \end{cases}$$

$$(\Delta E)_{\text{hf}} = \frac{4g_e g_p}{3} \frac{Z^3}{n^3} \frac{m_e}{m_p} \alpha^2 R_\infty$$

where $(\Delta E)_{\text{hf}}$ is the *hyperfine splitting*

Hyperfine structure : S states (4)

- The hyperfine interaction splits each S-state into two separate levels :



(note that the degeneracy of the zeroth-order states is now $g = 4n^2$)

- Relative to fine structure, hyperfine splitting is suppressed by an extra factor of $m_e / m_p \sim 1/2000$
- For the hydrogen atom ground state ($n = 1$), the hyperfine splitting is

$$(\Delta E)_{\text{hf}} \approx 5.87 \times 10^{-6} \text{ eV} ; \quad \Delta\nu = 1420.4 \text{ MHz} ; \quad \lambda = 21.1 \text{ cm}$$

For *excited* S-states ($n > 1$), the hyperfine splitting is even smaller :

$$(\Delta E)_{\text{hf}} \propto 1/n^3$$

Hyperfine structure : the 21cm line

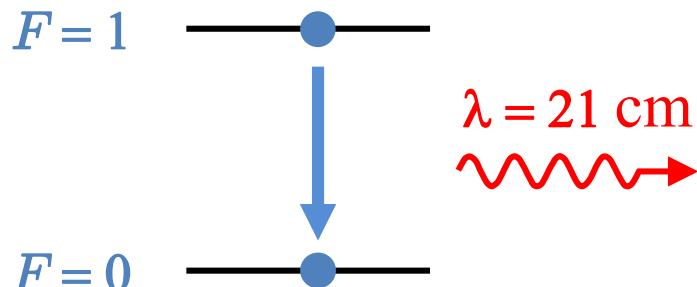
- The hydrogen 21cm line is of great importance in astronomy for detecting the density, motion and temperature of hydrogen gas clouds
- The (very small) hyperfine energy splitting, $\Delta E \approx 5.87 \times 10^{-6}$ eV , is equivalent to a temperature of only

$$(\Delta E)_{\text{hf}} = k_B T ; \quad T \approx 0.07 \text{ K}$$

Even for temperatures as low as that of the cosmic microwave background (CMB), $T = 2.73$ K, the upper ($F = 1$) level is substantially occupied :

$$N(\text{upper}) : N(\text{lower}) \approx 3 : 1 \quad (\text{from } g = 2F + 1)$$

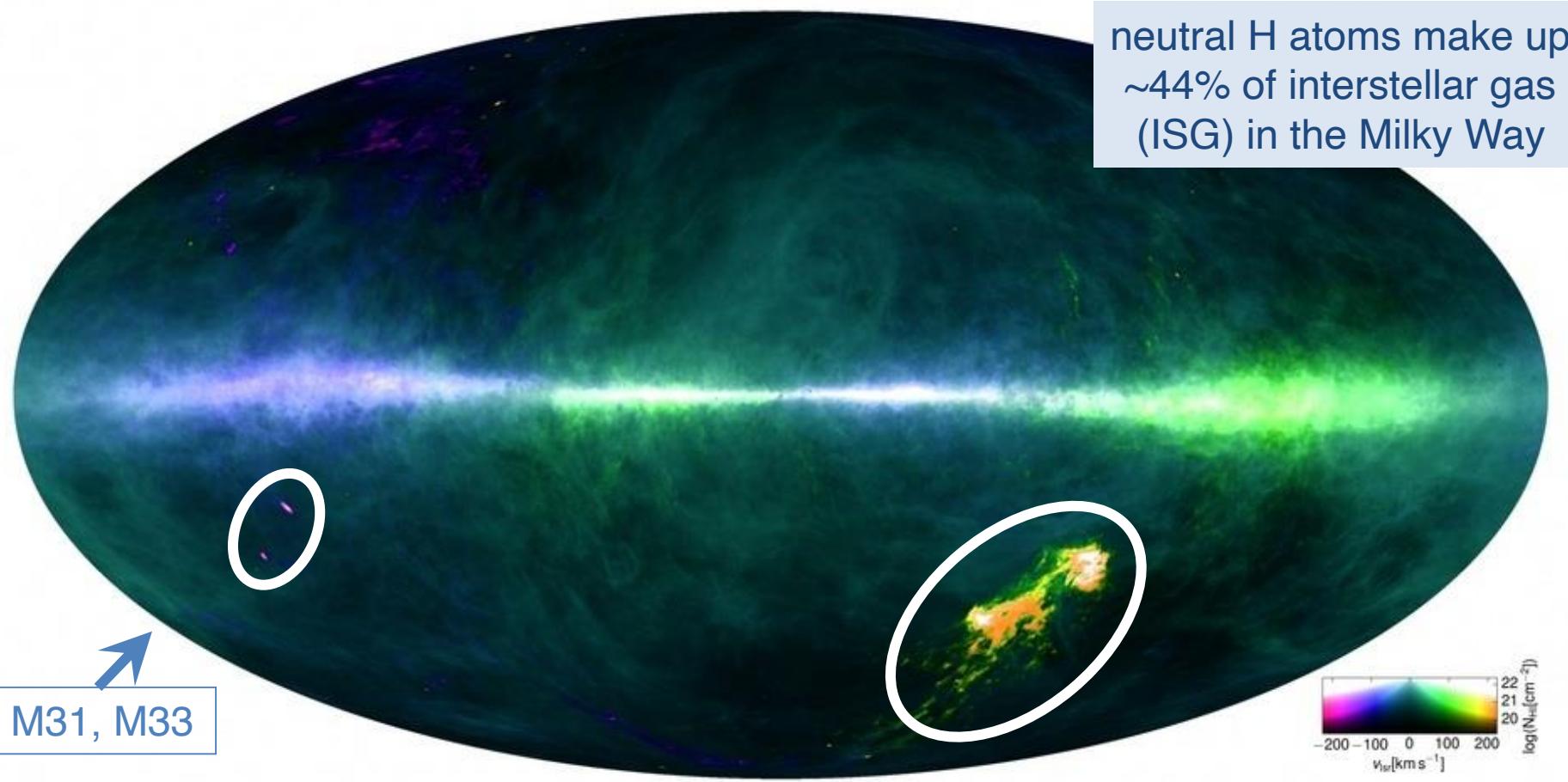
- Spontaneous decay of the upper level gives emission of a 21cm photon :



The emission rate is extremely low :
~ 1 photon per H atom per 120 Myr
But there is a lot of neutral hydrogen out there ...

Hyperfine structure : the 21cm line (2)

- A recent (2016) all-sky survey of neutral atomic hydrogen :



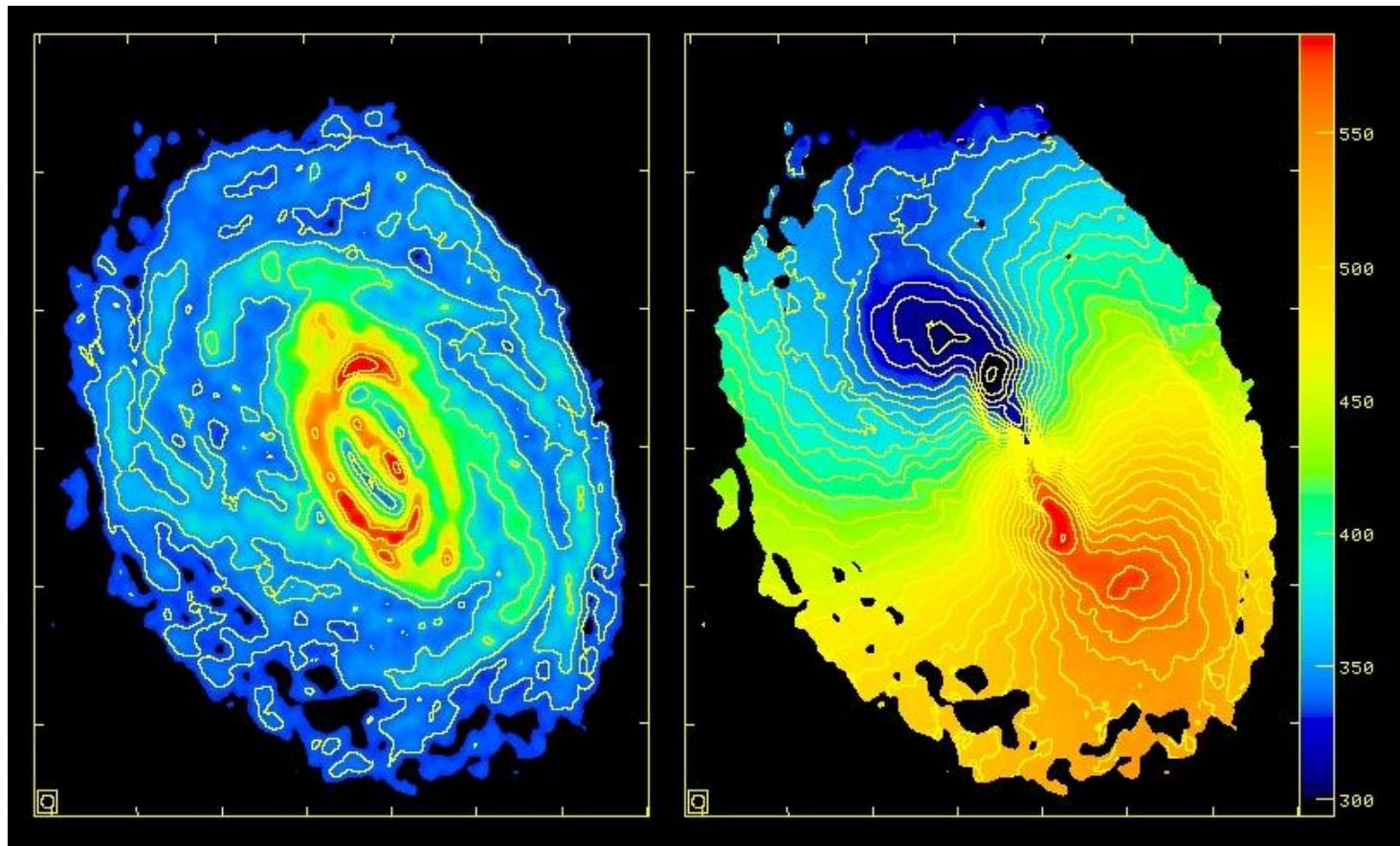
Hyperfine structure : the 21cm line (3)

- An external galaxy (Circinus) rather than the whole sky :

K. L. Jones et al., MNRAS 302 (1999) 649

Intensity

Velocity (km/s)

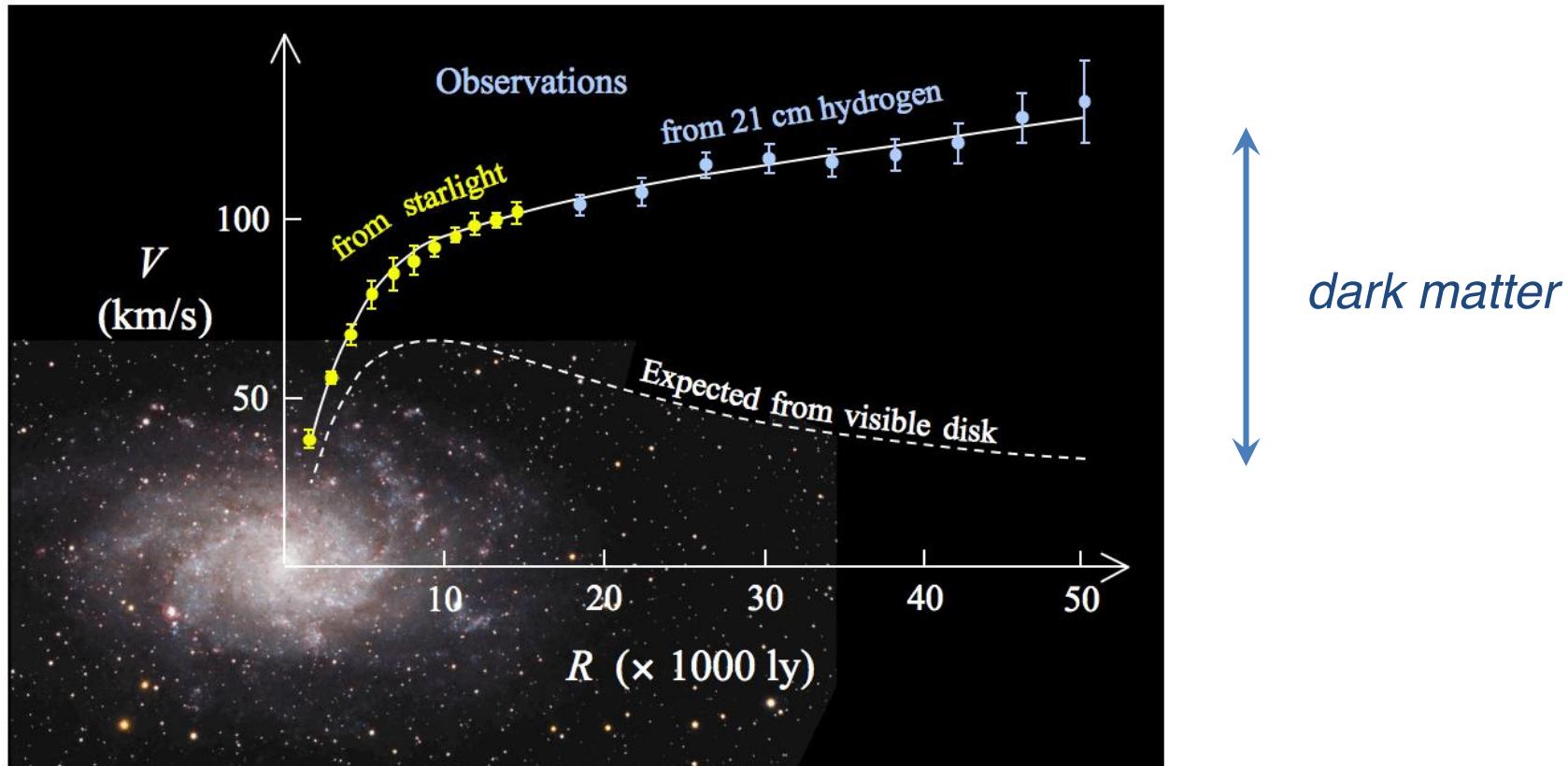


<http://www.atnf.csiro.au/outreach/images/astronomical/circinus.html>

Hyperfine structure : the 21cm line (4)

- Example of a rotation curve for a particular galaxy (M33) :

[E. Corbelli & P. Salucci, MNRAS 311 \(2000\) 441](#)



http://commons.wikimedia.org/wiki/File:M33_rotation_curve_HI.gif (Stefania deluca)

- Visible matter alone cannot explain the large rotational velocities seen at large radius; a spherical halo of dark matter is also needed

Hyperfine structure : the 21cm line (5)

- Neutral hydrogen is also important on a cosmological scale, and for mapping the early history of the Universe

In particular, the 21cm line will be crucial in exploring the “*Epoch of Reionisation*” (EoR), the poorly known era between 0.1-1 billion years (redshift $30 > z > 6$) after the Big Bang

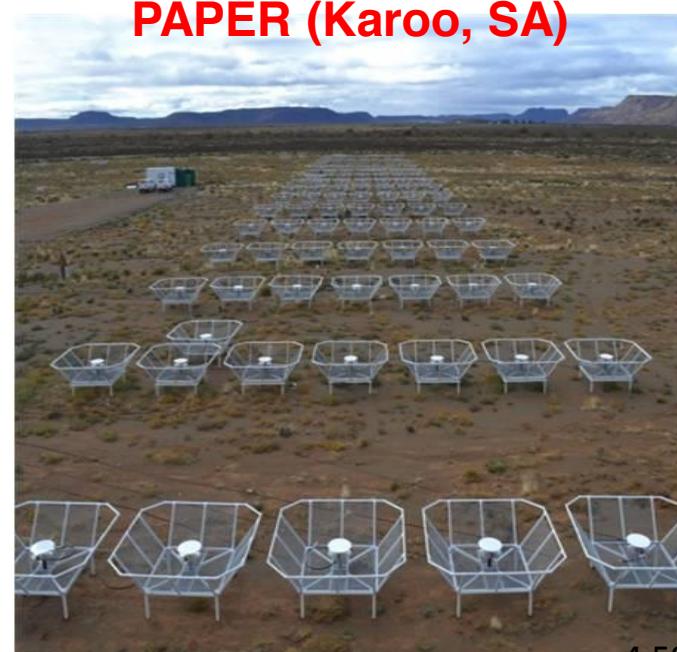
- The 21cm (1420 MHz) EoR emission reaches us redshifted to radio frequencies in the range 50-250 MHz

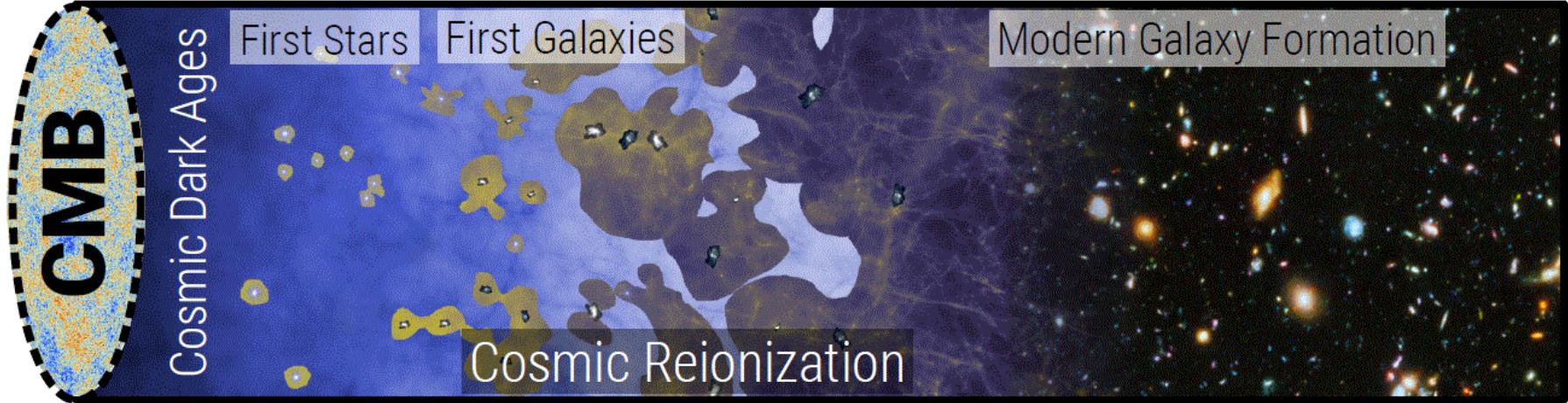
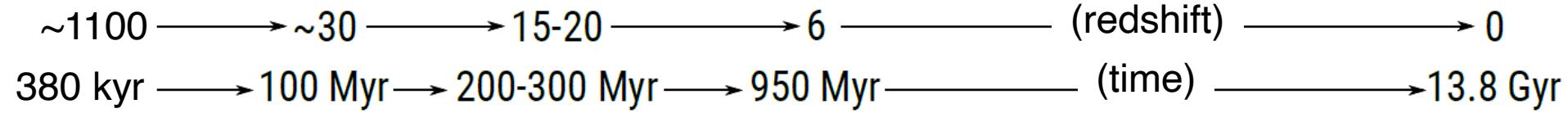
Major experiments are under construction aimed at detecting, and eventually imaging, this radio emission :

→ REACH / PAPER+HERA / SKA

(Cavendish Astrophysics, Cambridge Kavli, and the IoA are involved in all)

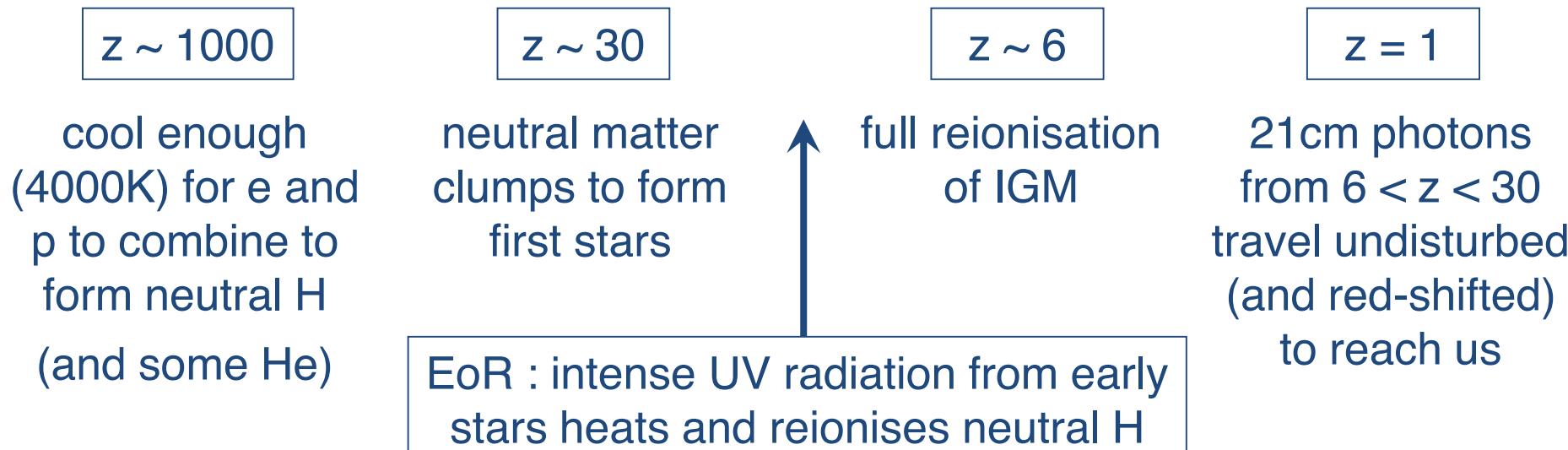
<https://www.astro.phy.cam.ac.uk/research/research-projects>





Reionization stages | Pre-overlap Overlap Post-overlap Highly ionized

[J.H. Wise, arXiv:1907.06653 \(2019\)](https://arxiv.org/abs/1907.06653)



Hyperfine structure : Non-S (P, D, F, \dots) states

- Calculations of the hyperfine corrections for non-S states, with $\ell > 0$, are more involved than for $\ell = 0$; we only briefly summarise the results

The non-S states are also split into two separate levels by hyperfine interactions :

e.g. for $\ell = 1$:
$$\begin{cases} j = 1/2, & I = 1/2 \Rightarrow F = j \otimes I = 0, 1 \\ j = 3/2, & I = 1/2 \Rightarrow F = j \otimes I = 1, 2 \end{cases}$$

The predicted first-order energy shifts turn out to be

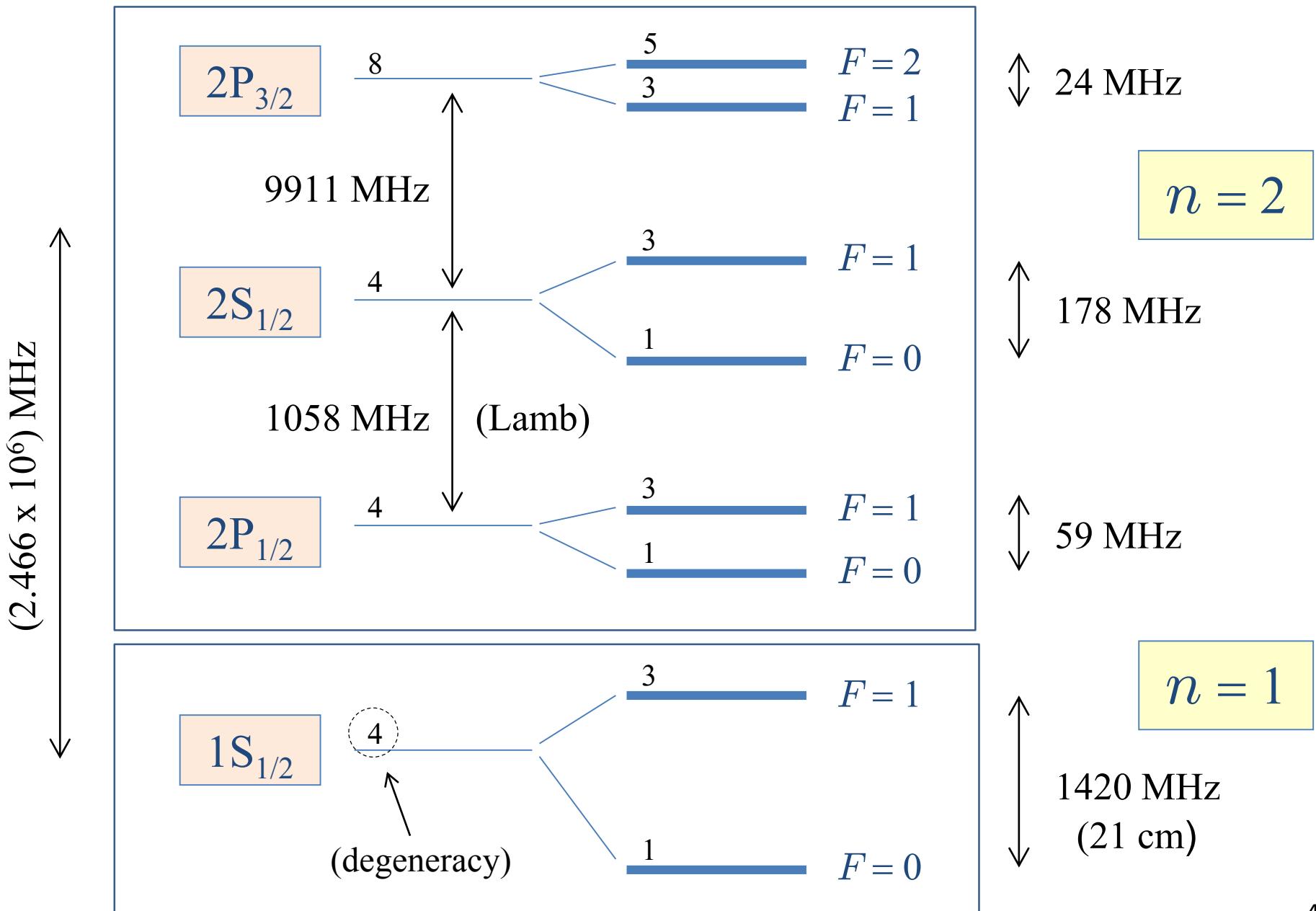
$$(\Delta E)_{\text{hf}} = \frac{g_e g_p}{4} \frac{Z^3}{n^3} \frac{m_e}{m_p} \alpha^2 R_\infty \left[\frac{F(F+1) - j(j+1) - 3/4}{j(j+1)(\ell + 1/2)} \right]$$

- The $\ell > 0$ hyperfine splittings are similar, but smaller, than for $\ell = 0$:

e.g. for $n = 2, \ell = 1$:
$$\begin{cases} (\Delta E)_{\text{hf}} \approx 2.5 \times 10^{-7} \text{ eV} & (2P_{1/2}) \\ (\Delta E)_{\text{hf}} \approx 9.8 \times 10^{-8} \text{ eV} & (2P_{3/2}) \end{cases}$$

while for $\ell = 0$: $(\Delta E)_{\text{hf}} \approx 7.5 \times 10^{-7} \text{ eV} \quad (2S_{1/2})$

Hydrogen Hyperfine Structure : $n = 1, 2$

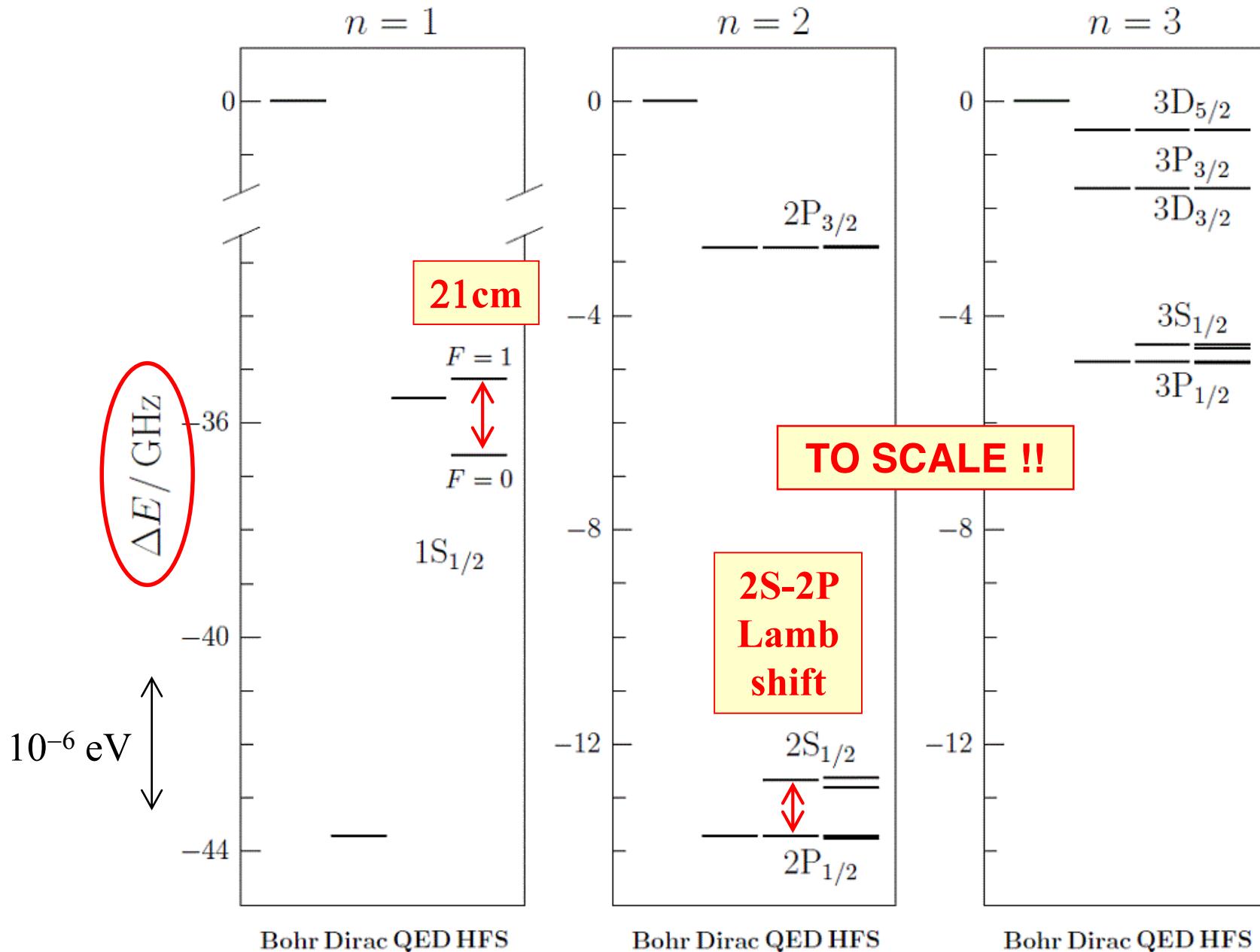


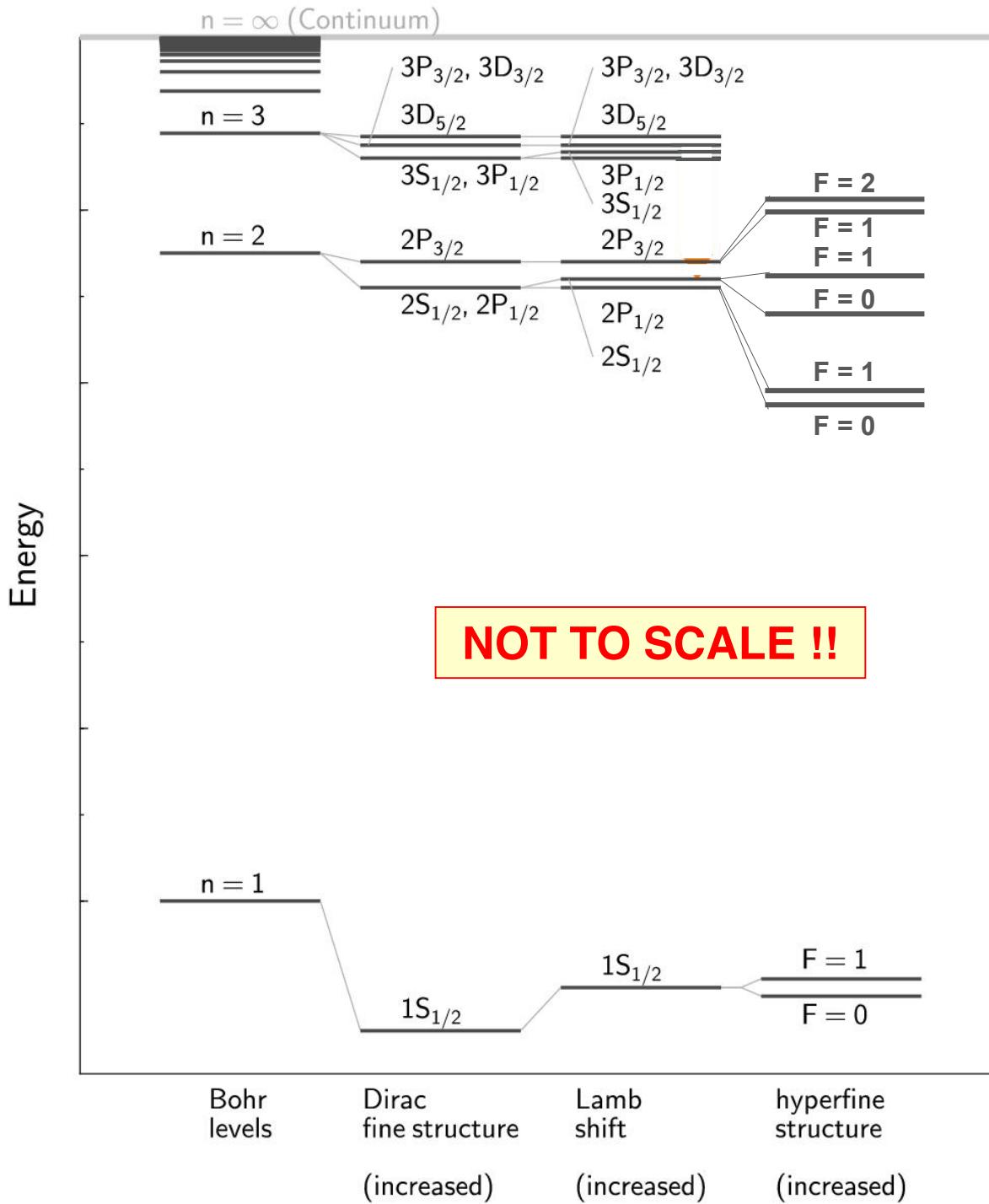
Hydrogen Fine and Hyperfine Structure : $n = 1,2,3$

$$(\Delta E)_{\text{FS}} = (\Delta E)_{\text{R}} + (\Delta E)_{\text{SO}} + (\Delta E)_{\text{D}}$$

			$\Delta E / \text{MHz}$			
			$(\Delta E)_{\text{FS}}$	$(\Delta E)_{\text{QED}}$	F	$(\Delta E)_{\text{HFS}}$
$n = 1$	$\ell = 0, j = 1/2$	$1S_{1/2}$	-43700	+8172	0,1	1420
$n = 2$	$\ell = 0, j = 1/2$	$2S_{1/2}$	-13700	+1040	0,1	178
	$\ell = 1, j = 1/2$	$2P_{1/2}$	-13700	-17	0,1	59
	$\ell = 1, j = 3/2$	$2P_{3/2}$	-2730	+8	1,2	24
$n = 3$	$\ell = 0, j = 1/2$	$3S_{1/2}$	-4860	+309	0,1	53
	$\ell = 1, j = 1/2$	$3P_{1/2}$	-4860	-6	0,1	18
	$\ell = 1, j = 3/2$	$3P_{3/2}$	-1620	+5	1,2	7
	$\ell = 2, j = 3/2$	$3D_{3/2}$	-1620	-1	1,2	4
	$\ell = 2, j = 5/2$	$3D_{5/2}$	-540	+1	2,3	3

Hydrogen : Summary of Fine and Hyperfine structure





Each hyperfine level has degeneracy $g = 2F + 1$

For an *isolated* atom, this degeneracy (w.r.t. m_F) cannot be broken
(rotational symmetry)

For an isolated atom, the energy levels cannot be split further

The degeneracy can only be lifted by putting the atom into an external **E** or **B** field, for example
(thereby breaking the rotational symmetry)

Hyperfine structure : theory vs experiment

- The 21cm hyperfine splitting can be measured very precisely :

$$(\Delta E)_{\text{HFS}}(1S) = 1420.405751768(1) \text{ MHz} \quad (7 \times 10^{-13})$$

[S. G. Karshenboim, Phys. Rep. 422 \(2005\) 1](#)

The QED prediction agrees with data, but is *much* less precise :

$$(\Delta E)_{\text{HFS}}(1S) = 1420.3993(16) \text{ MHz} \quad (1.1 \times 10^{-6})$$

[M. I. Eides et al., Phys. Rep. 342 \(2001\) 63](#)

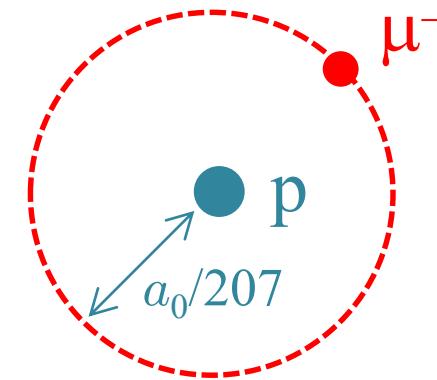
- The error on the QED prediction is dominated by our limited knowledge of the size of the proton, so in practice, things are turned around :
 - the precise spectroscopic measurements are used to determine the radius r_p of the proton
- In passing, we note the extremely precise measurement of the separation between the $n = 1$ and $n = 2$ levels of hydrogen :

$$\Delta E(2S_{1/2} - 1S_{1/2}) = 2466061413.187035(10) \text{ MHz} \quad (4.2 \times 10^{-15})$$

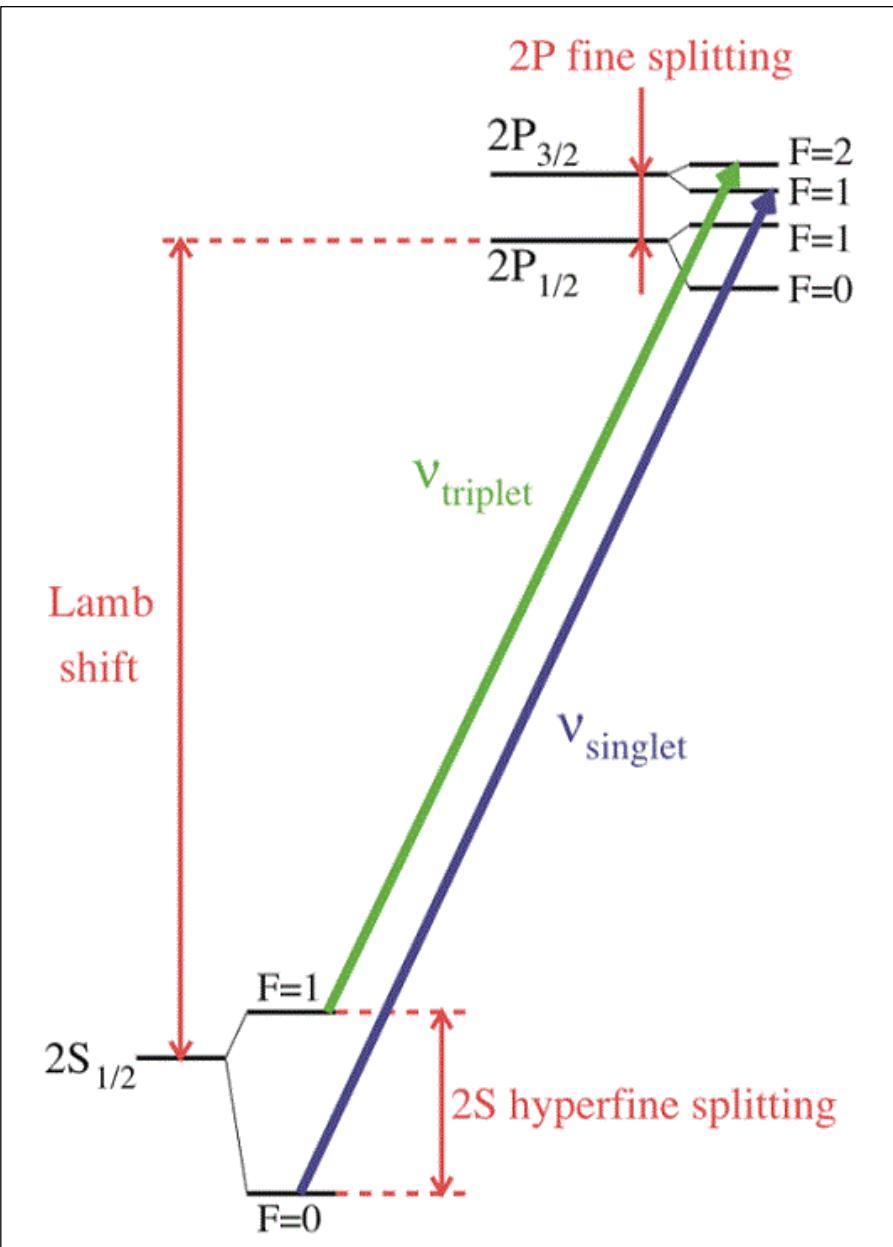
[C. G. Parthey et al., Phys. Rev. Lett. 107 \(2011\) 203001](#)

Muonic hydrogen : the proton radius

- The proton radius can be inferred much more accurately from *muonic* hydrogen ($\mu^- p$) than from ordinary hydrogen ($e^- p$) :
 - the muon is 207 times heavier than the electron
 - atomic wavefunctions scale in radius as $1/m$
$$(a_0 = 4\pi\epsilon_0\hbar^2/e^2m_e)$$
 - hence the wavefunction penetrates the proton much more for a muon than for an electron
- The QED Lamb shift is proportional to m^3
 - the Lamb shift is enhanced by a factor $(207)^3$ in muonic hydrogen
- The 2S-2P Lamb shift in muonic hydrogen has recently been measured with a precision ~ 20 ppm
 - these measurements currently provide the most precise available determination of the proton radius r_p



Muonic hydrogen : precision measurements



$$(\mu^- p) : n = 2$$

$$\nu_{\text{triplet}} = 49881.88(76) \text{ GHz}$$

$$\nu_{\text{singlet}} = 54611.16(1.05) \text{ GHz}$$

[R. Pohl et al., Nature 466 \(2010\) 213](#)

[A. Antognini et al., Science 339 \(2013\) 417](#)

$$\mu^- p : (\Delta\nu)_{\mu p}^{\text{Lamb}} \sim 50000 \text{ GHz}$$

$$e^- p : (\Delta\nu)_{ep}^{\text{Lamb}} \sim 1 \text{ GHz}$$

The $\mu^- p$ measurements determine the proton radius as

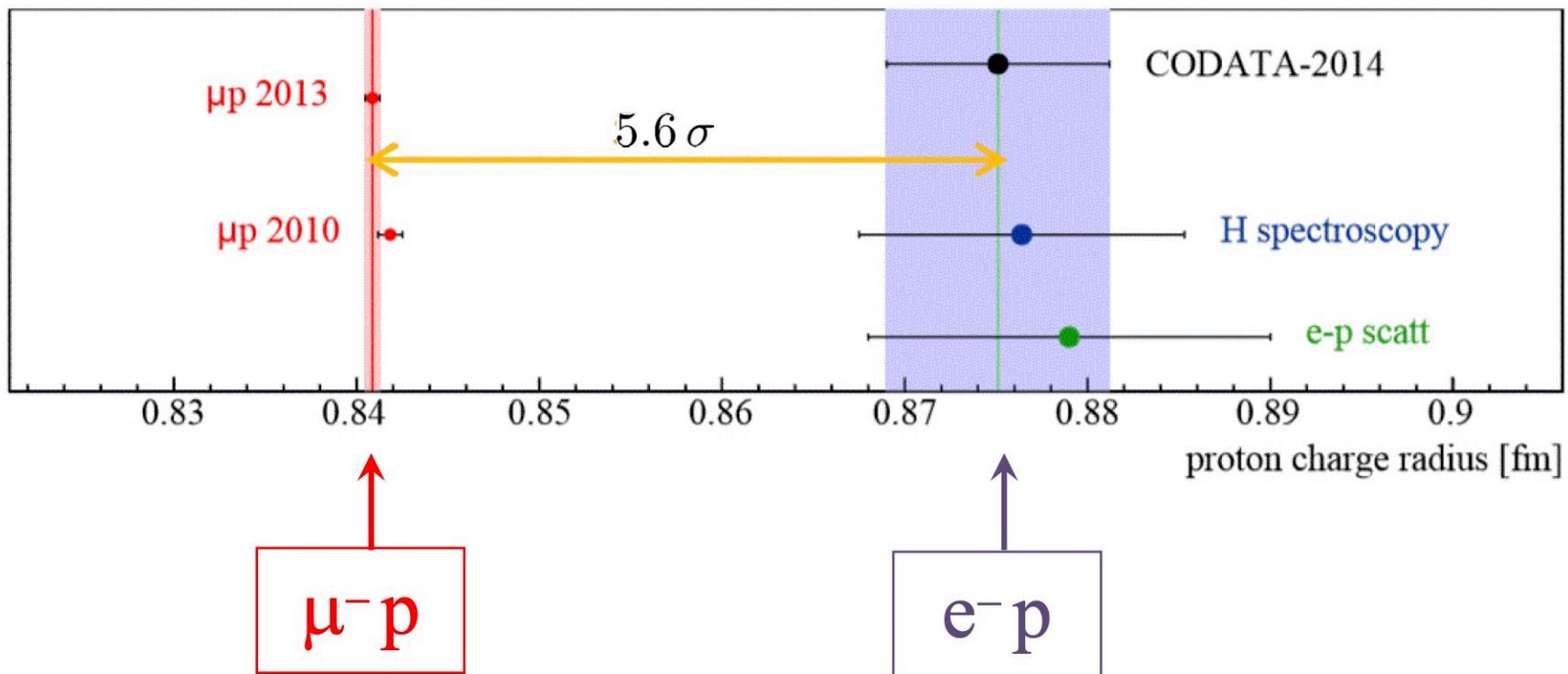
$$r_p = 0.84087(39) \text{ fm}$$

$$(1 \text{ fm} \equiv 10^{-15} \text{ m})$$

The proton radius puzzle

The value of r_p obtained from muonic hydrogen was significantly lower than other, less precise, determinations from e-p spectroscopy and scattering

[J. J. Krauth et al., arXiv:1706.00696 \(2017\)](https://arxiv.org/abs/1706.00696)



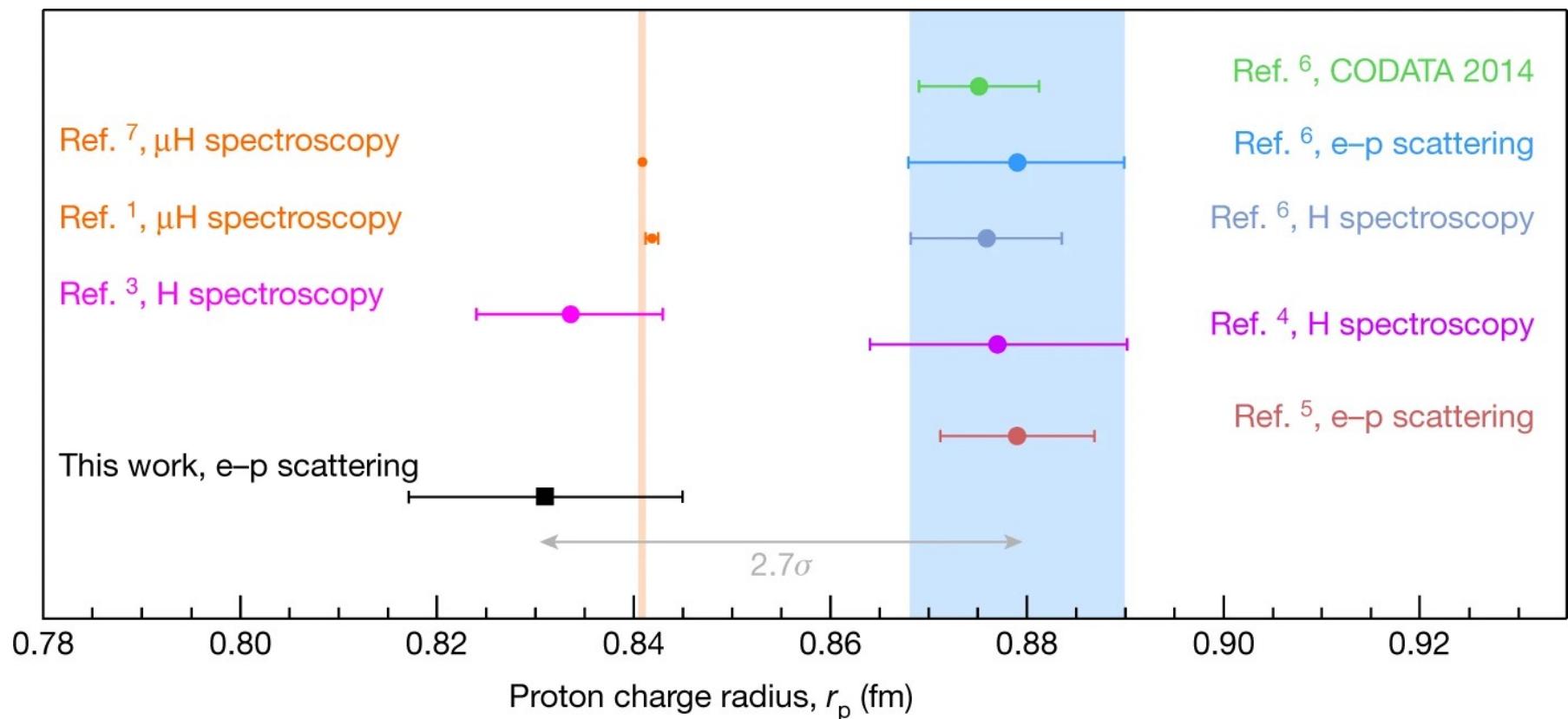
- Known as the “proton radius puzzle”

The proton radius puzzle (2)

Recent new measurements show
a much more consistent picture!

[W. Xiong et al, Nature 575 \(2019\) 147](#)

[N. Bezginov et al, Science 365 \(2019\) 6457](#)



A recent reanalysis of old experimental data, also points to a value in agreement
with the new measurements

[Y.H Lin et al, PRL 128 \(2022\) 052002](#)

Appendix : Classical Spin-Orbit

- The spin-orbit interaction term of slide 4.20, arising in quantum physics from the Dirac equation, can be anticipated also on classical grounds :
- As it orbits within the atom, the atomic electron moves through the electric field $\mathbf{E} = -\nabla\phi$ set up by the nucleus

In the electron rest frame, following a Lorentz transformation of this electric field, the electron experiences a *magnetic* field \mathbf{B} given, in the low energy limit $\gamma \approx 1$, by (see the PtII E+O course)

$$\mathbf{B} = -\frac{1}{c^2} \mathbf{v} \wedge \mathbf{E} = -\frac{1}{c^2} \mathbf{v} \wedge (-\nabla\phi)$$

- For an isotropic electric potential $\phi = \phi(r)$, this is

$$\mathbf{B} = \frac{1}{c^2} \mathbf{v} \wedge \left(\frac{1}{r} \frac{d\phi}{dr} \mathbf{r} \right) = \frac{1}{m_e c^2} \left(\frac{1}{r} \frac{d\phi}{dr} \right) \mathbf{L}$$

where \mathbf{L} is the orbital angular momentum of the electron :

$$\mathbf{L} = \mathbf{r} \wedge \mathbf{p} ; \quad \mathbf{p} = m_e \mathbf{v}$$

Appendix : Classical spin-orbit (2)

- The interaction energy of the electron's magnetic dipole moment with this magnetic field is (converting \mathbf{L} to a quantum operator),

$$-(\hat{\boldsymbol{\mu}}_S)_e \cdot \mathbf{B} = g_e \frac{e}{2m_e} \hat{\mathbf{S}} \cdot \frac{1}{m_e c^2} \left(\frac{1}{r} \frac{d\phi}{dr} \right) \hat{\mathbf{L}} = \frac{e}{m_e^2 c^2} \left(\frac{1}{r} \frac{d\phi}{dr} \right) \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$$

$(g_e = 2)$

- For a hydrogen-like atom, with potential

$$V(r) = -e\phi(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

this interaction energy is

$$\hat{H}_{SO} = \frac{1}{2m_e^2 c^2} \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r^3} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$$

- Apart from an extra factor of 2, this is the same as the term H_{SO} obtained from the Dirac equation
 - (the factor of 2 can be accounted for if the rotational motion of the instantaneous rest frame is also taken into account: *Thomas precession*)