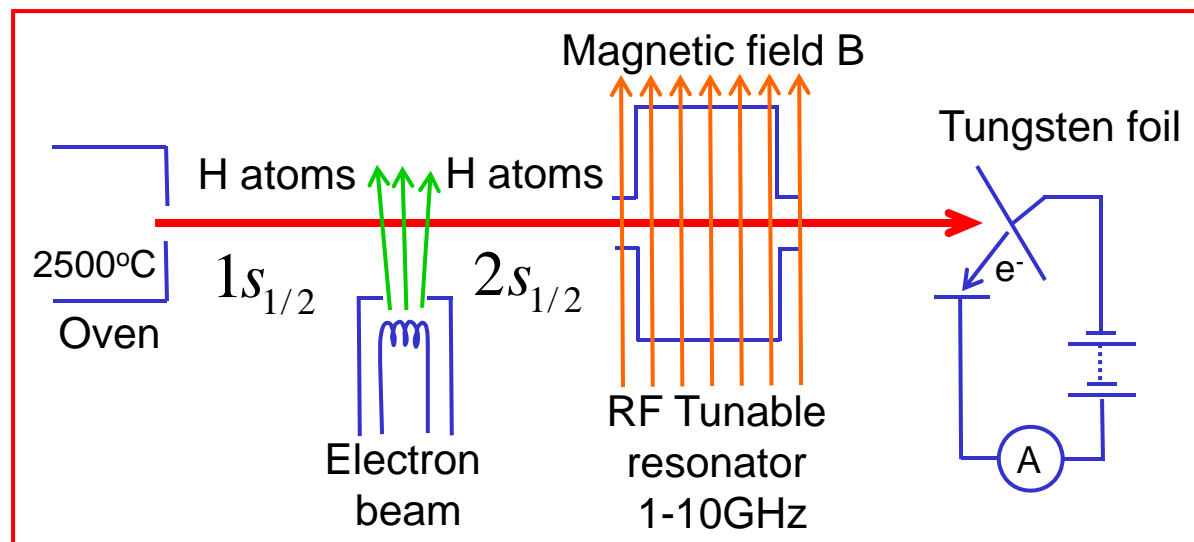


Advanced Quantum Physics

Lecture 19



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Section 5: Atoms



5.1 The real hydrogen atom

5.2 Multielectron atoms

5.3 Coupling schemes

5.4 Atomic spectra

5.5 Atoms in a uniform magnetic field

5.1 The real hydrogen atom – nuclear effects

- The real hydrogen atom is complicated with changes to the energy level structure due to the nucleus:
- *The nuclear mass* is taken into account with a reduced mass, a mixture of isotopes causes different energy levels and separation of spectral lines.
- *The finite nuclear size* most affects the 1s and 2s levels where the electrons get closest to the nucleus. This is a small effect in hydrogen, but significant for larger atoms or muonic atoms - where a muon replaces an electron. In this case the Bohr radius is 200x smaller than normal hence there is a larger nuclear size effect on the energy levels.
- *Nuclear spin magnetic moments* interact with electron orbital and spin magnetic moments generating *hyperfine* structure in the energy levels. This has a much smaller effect than the (electron) spin orbit interaction.
- Electron has a spin magnetic moment : $\mu_e = g_e \mu_B S / \hbar \approx \mu_B = e\hbar / 2m_e$
- Similarly for a proton: $\mu_p = g_p \mu_n I / \hbar \approx 2.793 \mu_n$
(since $\mu_n = e\hbar / 2m_p$, $g_p = 5.5857$, $I = \frac{1}{2} \hbar$)
- Because $m_p = 1836m_e$ we have $\mu_p / \mu_e = 1.53 \times 10^{-3}$.

Nuclear effects (2)

- The magnetic moment and dipolar magnetic field due to a hydrogen nucleus (proton) are given, where $\hat{\mathbf{I}}$ is the nuclear spin operator by:

$$\hat{\mathbf{M}} = \frac{e g_p}{2m_p} \hat{\mathbf{I}}, \quad \mathbf{B} = \frac{\mu_0}{4\pi} \left(\frac{3\mathbf{r}(\mathbf{r} \cdot \hat{\mathbf{M}}) - r^2 \hat{\mathbf{M}}}{r^5} + \frac{8\pi}{3} \hat{\mathbf{M}} \delta(\mathbf{r}) \right)$$

$$g_e \approx 2$$

- The hyperfine perturbation is:

$$\hat{H}_{hf} = \frac{e}{2m_e} (\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) \cdot \mathbf{B} = \frac{e^2 g_p}{4m_e m_p} \frac{1}{4\pi\epsilon_0 c^2} \left(\frac{3\mathbf{r}(\mathbf{r} \cdot \hat{\mathbf{I}}) - r^2 \hat{\mathbf{I}}}{r^5} + \frac{8\pi}{3} \hat{\mathbf{I}} \delta(\mathbf{r}) \right) \cdot (\hat{\mathbf{L}} + 2\hat{\mathbf{S}})$$

$$\mu_0 = \frac{1}{\epsilon_0 c^2}$$

- For the s states we ignore $\hat{\mathbf{L}}$ and evaluate: $\Delta E_{hf} = \int |\psi_{n00}|^2 \hat{H}_{hf} d^3r$
- The first two terms in \hat{H}_{hf} cancel due to symmetry and we have:

$$\Delta E_{hf} = \frac{e^2 g_p}{6m_e m_p} \frac{1}{\epsilon_0 c^2} \langle \hat{\mathbf{I}} \cdot \hat{\mathbf{S}} \rangle \int |\psi_{n00}|^2 \delta(\mathbf{r}) d^3r = \frac{e^2 g_p}{6m_e m_p} \frac{1}{\epsilon_0 c^2} \frac{1}{\pi n^3 a_0^3} \langle \hat{\mathbf{I}} \cdot \hat{\mathbf{S}} \rangle$$

$$\psi_{n00}(0) = \sqrt{\frac{1}{\pi n^3 a_0^3}}$$

$$= \frac{4g_p}{3m_p n^3} \frac{\alpha^4 m_e^2 c^2}{\hbar^2} \langle \hat{\mathbf{I}} \cdot \hat{\mathbf{S}} \rangle$$

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c}, \quad a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}$$

$$\int f(t) \delta(t-a) dt = f(a)$$

Nuclear effects (3)

- The energy splitting due to the hyperfine structure of the s states of Hydrogen ($l = 0$) is;

$$\Delta E_{hf} = \frac{4}{3} g_p \frac{m_e}{m_p} \alpha^4 \frac{m_e c^2}{n^3} \frac{\langle \hat{\mathbf{I}} \cdot \hat{\mathbf{S}} \rangle}{\hbar^2}$$

where $\hat{\mathbf{I}}$ is the nuclear spin operator and $\hat{\mathbf{S}}$ the electron spin operator.

- Since the total angular momentum, $\hat{\mathbf{F}} = \hat{\mathbf{S}} + \hat{\mathbf{I}}$ then $\hat{\mathbf{I}} \cdot \hat{\mathbf{S}} = \frac{1}{2} [\hat{\mathbf{F}}^2 - \hat{\mathbf{I}}^2 - \hat{\mathbf{S}}^2]$

- The 1s state of hydrogen is split into two, corresponding to the two possible values $F = 0, 1$ (since $I = S = \frac{1}{2}$).

- Now $\langle \hat{\mathbf{I}} \cdot \hat{\mathbf{S}} \rangle = \frac{1}{2} \hbar^2 [F(F+1) - S(S+1) - I(I+1)] = -\frac{3}{4} \hbar^2, \frac{1}{4} \hbar^2$ for $F = 0, 1$

- Hence $\Delta E_{hf} = \frac{4}{3} g_p \frac{m_e}{m_p} \alpha^4 \frac{m_e c^2}{n^3}$

Transition between these levels has
 $f = 1420 \text{ MHz}$, $\lambda = 21 \text{ cm}$, $E = 6 \times 10^{-6} \text{ eV}$

- This transition has no change in orbital angular momentum and so cannot easily be excited by radiation.
- $F = 1$ state is excited by collisions, on return to $F = 0$ state atom radiates.
- Has important applications in astronomy for detecting density (1 cm^{-3}), motion and temperature (100K) of hydrogen gas clouds.

The spin-orbit interaction (1)

- In Lecture 11 we calculated this effect with the Dirac equation, here we take a semiclassical approach.
- As the electron moves through the electric field of the nucleus in its rest frame it experiences a magnetic field. The orientation of the electron's magnetic moment w.r.t this field generates a term in the Hamiltonian:
- With a central field determined by the electrostatic potential $\phi(r)$ the electric field is:

$$\mathbf{E} = -\nabla \phi(r) = -\mathbf{r} \frac{1}{r} \frac{d\phi}{dr}$$

- Magnetic field seen by electron at velocity \mathbf{v} is $\mathbf{B} = -\mathbf{v} \times \mathbf{E}/c^2$, magnetic moment due to the electron spin is $\hat{\boldsymbol{\mu}}_s = -g_e e \hat{\mathbf{S}}/2m_e$ with $g_e \approx 2$.
- Hence given that $\mathbf{E} = -\nabla \phi$ and $\hat{\mathbf{L}} = -\hat{\mathbf{p}} \times \mathbf{r}$ the interaction energy is:

$$-\hat{\boldsymbol{\mu}}_s \cdot \mathbf{B} = -\frac{e}{m_e} \hat{\mathbf{S}} \cdot (\mathbf{v} \times \mathbf{E})/c^2 = \frac{e}{m_e^2 c^2} \hat{\mathbf{S}} \cdot \left(\hat{\mathbf{p}} \times \mathbf{r} \frac{1}{r} \frac{d\phi}{dr} \right) = -\frac{e}{m_e^2 c^2} \frac{1}{r} \frac{d\phi}{dr} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$$

- This is exactly twice the *correct* result from the Dirac equation – change of frame must be treated relativistically – an effect called *Thomas precession*.

The spin-orbit interaction (2)

- To estimate the spin-orbit interaction in hydrogen from the last slide:

$$-\boldsymbol{\mu}_s \cdot \mathbf{B} = -\frac{e}{m_e^2 c^2} \frac{1}{r} \frac{d\phi}{dr} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \quad \text{and assuming} \quad \frac{d\phi}{dr} = \frac{e}{4\pi\epsilon_0 r^2}$$

with $r \sim a_0$ and $L \sim \hbar$ we get energy $\sim \alpha^4 m_e c^2 \approx 10^{-4} \text{ eV}$

- The operator $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ is evaluated using $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ and hence:

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

- So the eigenstates of $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ are eigenstates of $\hat{\mathbf{J}}^2$ with eigenvalues:

$$\langle jls | \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} | jls \rangle = \frac{1}{2}[j(j+1) - l(l+1) - s(s+1)]\hbar^2$$

- So for given l and s the states of different j have different energies.
- The energy splitting $\sim \alpha^4 m_e c^2$ is small compared to the spacing of the hydrogen energy levels $\sim \alpha^2 m_e c^2$ - given $\alpha \approx \frac{1}{137}$ and is known as *fine structure*.
- The spin-orbit splitting becomes larger in heavier atoms with larger nuclear charge.

Relativistic effects (1)

- From the Dirac equation in the non-relativistic limit retaining the terms contributing energies of order $\alpha^4 m_e c^2$ we get:

$$\hat{H} \approx \underbrace{\frac{\hat{p}^2}{2m_e} + V(r)}_{\hat{H}_0} - \underbrace{\frac{\hat{p}^4}{8m_e^3 c^2}}_{\hat{H}_1} + \underbrace{\frac{1}{2m_e^2 c^2 r} \frac{dV}{dr} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}}_{\hat{H}_2} + \underbrace{\frac{\pi \hbar^2}{2m_e^2 c^2} \frac{e^2}{4\pi \epsilon_0} \delta(\mathbf{r})}_{\hat{H}_3}$$

Where $V(r) = -e^2 / 4\pi\epsilon_0 r$

- \hat{H}_1 is a relativistic correction to the kinetic energy

$$(p^2 c^2 + m_e^2 c^4)^{\frac{1}{2}} - m_e c^2 \approx m_e c^2 \left[1 + \frac{p^2 c^2}{2m_e^2 c^4} - \frac{1}{8} \left(\frac{p^2 c^2}{m_e^2 c^4} \right)^2 \dots \right] - m_e c^2 = \frac{p^2}{2m_e} - \frac{p^4}{8m_e^3 c^2} \dots$$

- \hat{H}_2 is the spin-orbit interaction: agrees with the semiclassical result given earlier apart from a factor of 2 due to *Thomas precession*.
- \hat{H}_3 is the *Darwin term* – it has no easy classical interpretation, acts only at the origin and hence only affects the energy of the s states.
- In hydrogenic atoms these terms are of similar size, in multielectron atoms

spin-orbit effects dominate.

Relativistic effects (2)

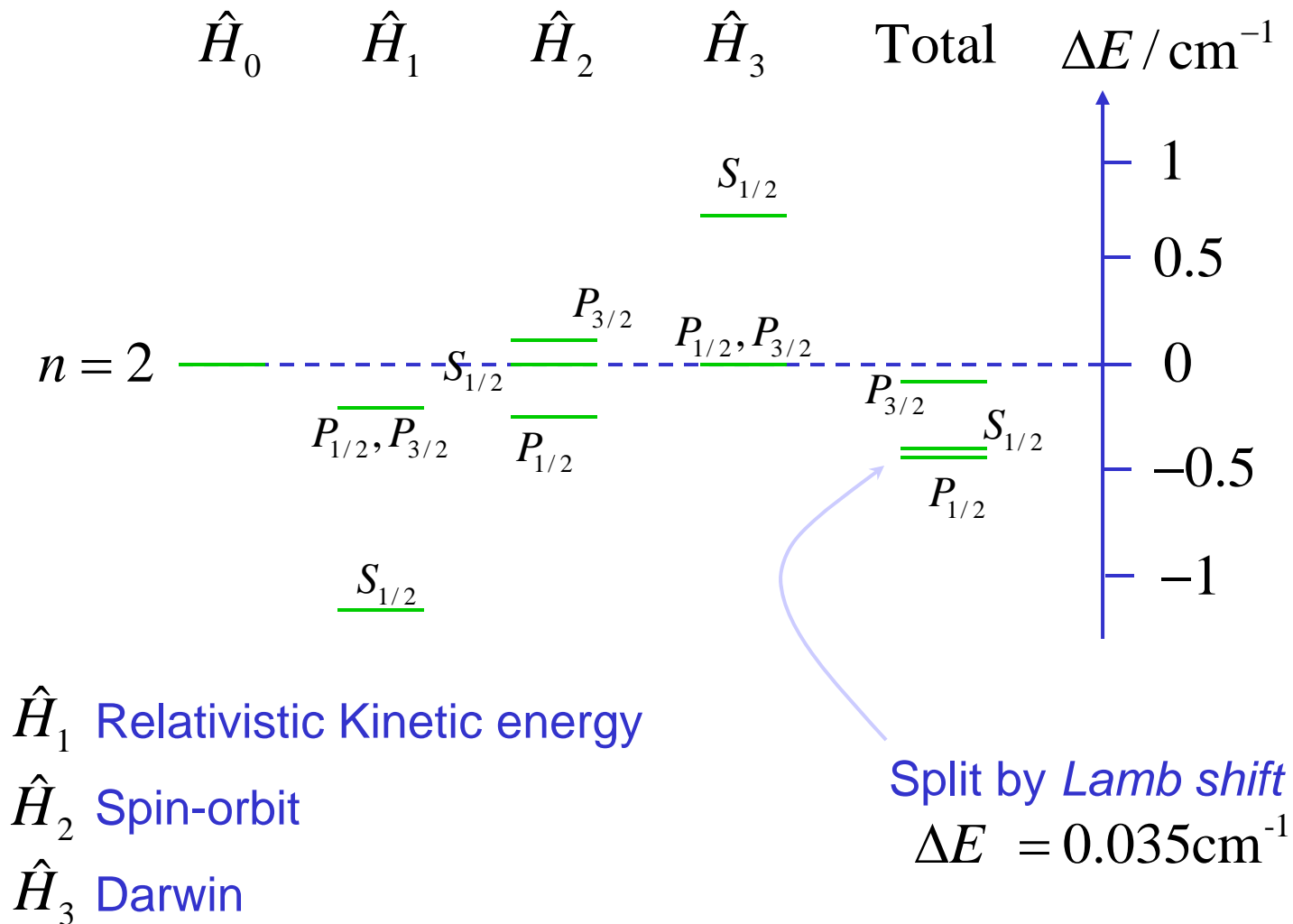
- A solution of the Dirac equation (Lecture 11) for a Coulomb potential gives the following result for the allowed energy levels:

$$E_{nj} = E_{nj}^D - m_e c^2 = E_n^{(0)} \left[1 + \frac{(Z\alpha)^2}{2n^2} \left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) + \dots \right]$$

$$E_n^{(0)} = \frac{1}{2} m_e c^2 \frac{(Z\alpha)^2}{n^2}, \quad \left[\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137} \right]$$

- The leading term of this equation for the energy levels agrees with the result from the Schrodinger equation.
- Note that the energy levels depend only on n and j and not l hence the $2s_{1/2}$ and $2p_{1/2}$ states are still degenerate, while the $2p_{3/2}$ state has a different energy

The real hydrogen atom – effect of corrections



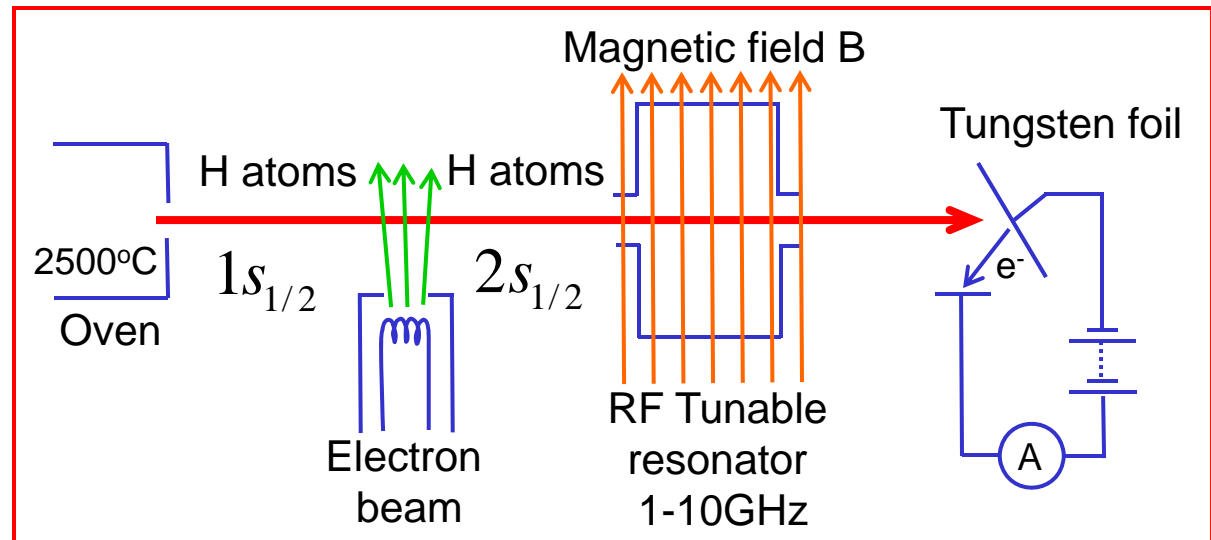
Note: $1 \text{ cm}^{-1} \equiv 1.23 \times 10^{-4} \text{ eV}$

The Lamb shift (1)

- Between 1947 and 1952 Lamb and Retherford conducted a series of experiments showing that the Dirac theory did not completely describe the hydrogen atom.

- H_2 molecules split into atoms in oven.

- A few atoms in $1s_{1/2}$ ground state excited to metastable $2s_{1/2}$ state by electron bombardment



- Atoms pass through tuneable resonator to tungsten foil detector where $2s_{1/2}$ atoms give up excitation energy & release electrons from the metal surface.

- Electron current is used as a measurement of the arrival of $2s_{1/2}$ atoms.

- If the RF resonator is tuned correctly some atoms are excited into the $2p_{1/2}$ state and then emit light returning to the ground state.

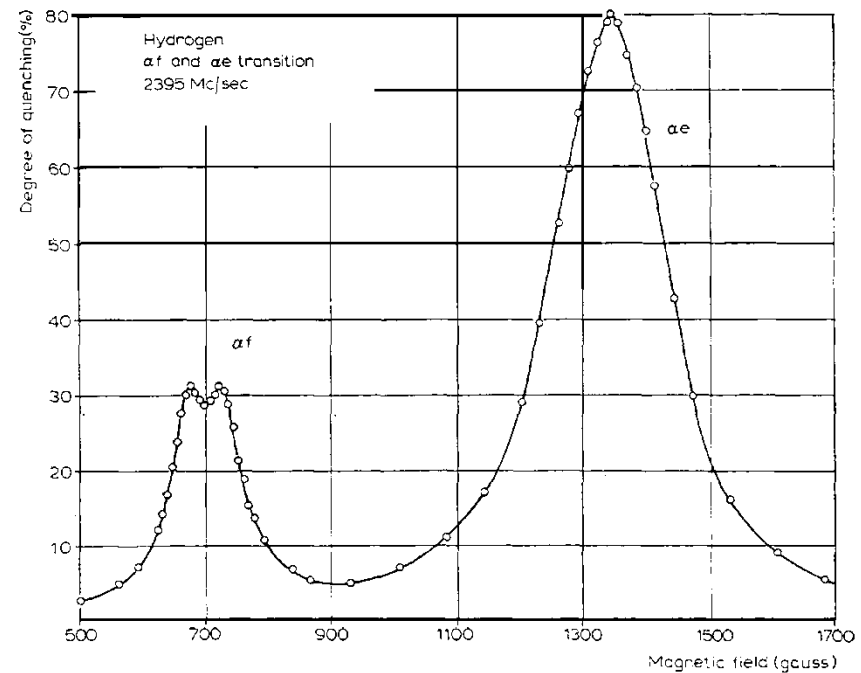
- When absorption of this type take place the measured electron current decreases.

Lamb and Retherford Phys Rev **72**, 241 (1947)

The Lamb shift (2)

- When a magnetic field is applied the energy levels are changed due to the Zeeman effect.

- As the magnetic field is varied with the RF fixed $2s \rightarrow 2p \rightarrow 1s$ transitions take place with a maximum reduction in detector current at a particular field – at this point the *degree of quenching* is at its maximum – see figure.



- Using this data the differences between energy levels were measured as a function of magnetic field and the energy differences between states at zero field was determined.

- A difference between the $2s_{1/2}$ and $2p_{1/2}$ states of 0.033cm^{-1} at zero field was measured - about 10% of the fine structure splitting.

- Note that hyperfine structure is visible on the left hand peak.

- Lamb won the Nobel prize in 1955 – his lecture is on the web site.

Quantum electrodynamics

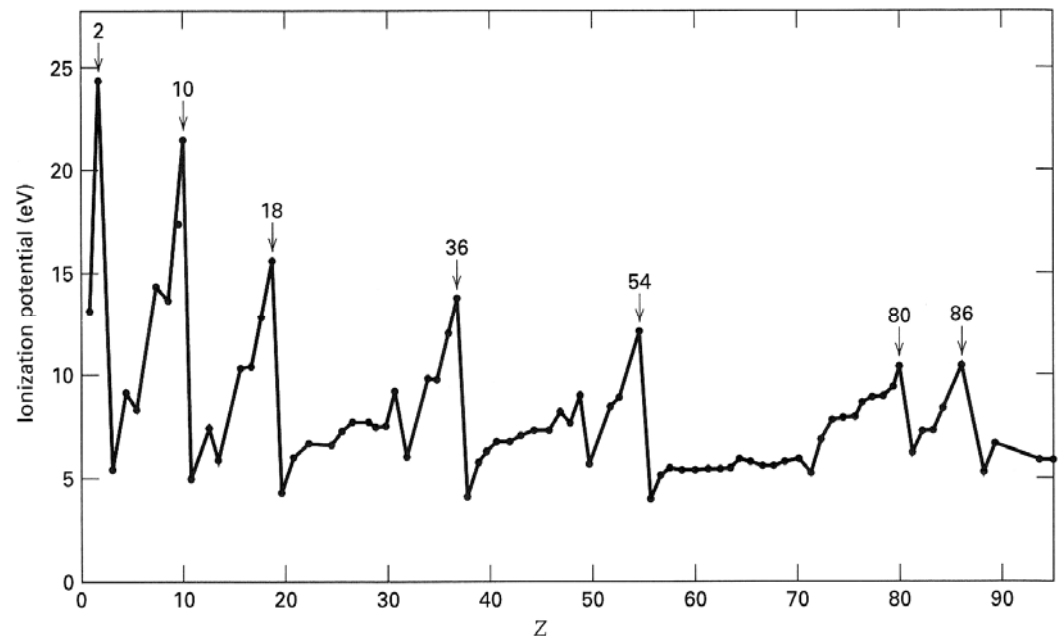
- According to the Dirac equation the $2s_{\frac{1}{2}}$ and $2p_{\frac{1}{2}}$ levels are degenerate
- The experiments of Lamb and Retherford contradicted this showing a small shift – around 10% of fine structure. Known as the *Lamb shift*.
- This work was presented at a conference on Shelter Island in June 1947.
- On his way home from the conference Hans Bethe started to formulate a theory* to explain this data by the interaction of the electron with the radiation field. This theory was published in August 1947 and was within 4% of the experimental results.
- The explanation is due to quantization of the electromagnetic field – the interaction of the electron with the vacuum field causes the position of the electron to fluctuate which leads to a change in the energy as a result of the spatial variation of the potential.
- The measurement of the Lamb shift directly stimulated the development of the theory of quantum electrodynamics – probably the most accurate theory in physics.

*H A Bethe Phys Rev 72, 339 (1947)

5.2 Multielectron atoms

- Fill hydrogen like energy levels from the bottom using the exclusion principle.
- The energy level degeneracy is $2(2l+1)$
- Compare the model with ionization energy data.
- We expect glitches in the ionization energy at closure of a level – but the model doesn't give the observed Z values!
- The model neglects electron-electron repulsion.
- Ionization energy variation with Z is flatter than expected - the outermost electrons are screened from the nucleus.
- For He we showed that screening is important!

n	l	Degeneracy	Total
1	0	2	2
2	0,1	2+6	10
3	0,1,2	2+6+10	28
4	0,1,2,3	2+6+10+14	60



Multielectron atoms (2)

- There is an important connection between electron-electron repulsion and the symmetry of a wavefunction – it must be antisymmetric overall.

- Consider He with two electrons in the ground state - where both electrons are in the 1s level with opposite spins and total spin $S = 0$.

- This corresponds to a wavefunction: $\Psi = \underbrace{\psi_{1s}(r_1)\psi_{1s}(r_2)}_{\substack{\text{spatial wavefunction} \\ \text{symmetric}}} \cdot \underbrace{\frac{1}{\sqrt{2}}[\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2]}_{\substack{\text{spin wavefunction} \\ \text{antisymmetric}}}$

- Overall wavefunction antisymmetric

- For excited state - one electron in 1s the other in 2s, two possibilities:

$$\Psi_S = \frac{1}{\sqrt{2}}[\psi_{1s}(r_1)\psi_{2s}(r_2) + \psi_{2s}(r_1)\psi_{1s}(r_2)] \cdot \frac{1}{\sqrt{2}}[\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2]$$

$S = 0$ Singlet state

$$\Psi_T = \frac{1}{\sqrt{2}}[\psi_{1s}(r_1)\psi_{2s}(r_2) - \psi_{2s}(r_1)\psi_{1s}(r_2)] \cdot \begin{cases} [\uparrow_1\uparrow_2] & M_S = 1 \\ \frac{1}{\sqrt{2}}[\uparrow_1\downarrow_2 + \downarrow_1\uparrow_2] & M_S = 0 \\ [\downarrow_1\downarrow_2] & M_S = -1 \end{cases}$$

$S = 1$ Triplet state

- In triplet state $\Psi_T = 0$ when $r_1 = r_2$ hence electrons tend to be further apart reducing the Coulomb energy for $S = 1$ compared to $S = 0$.

Multielectron atoms (3)

- Using perturbation theory we can calculate energy shift due to e-e repulsion.

$$\hat{H}' = \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \quad \text{for} \quad \Psi = \frac{1}{\sqrt{2}} [\psi_1(r_1)\psi_2(r_2) \pm \psi_2(r_1)\psi_1(r_2)]$$

- Noting that $|\mathbf{r}_1 - \mathbf{r}_2|$ is symmetric under particle exchange we obtain:

$$\Delta E = \int |\psi_1(r_1)|^2 |\psi_2(r_2)|^2 \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

$$\pm \int \psi_1^*(r_1)\psi_1(r_2)\psi_2(r_1)\psi_2^*(r_2) \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

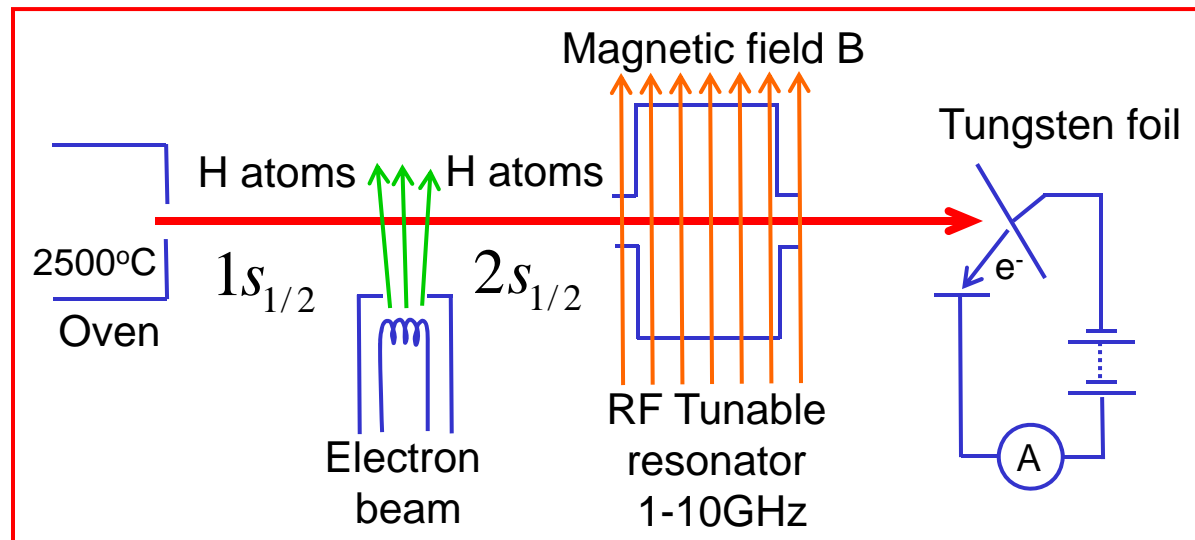
- The second term with opposite signs for Ψ_S and Ψ_T gives rise to the different energy between the states, known as the *exchange interaction*.

$$\int |\psi_1(r_1)|^2 |\psi_2(r_2)|^2 \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2 = \int |\psi_1(r_2)|^2 |\psi_2(r_1)|^2 \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

Lecture 19 - Summary

- The real hydrogen atom:
- Effects on energy level structure due to the spin of the nucleus, leading to hyperfine structure (energy level splitting $\sim 5 \times 10^{-6}$ eV).
- The spin-orbit interaction from a semi-classical perspective, giving twice the (correct) result obtained from the Dirac equation (splitting $\sim 5 \times 10^{-5}$ eV).
- The effect of the relativistic kinetic energy and Darwin terms in the Hamiltonian (splitting $\sim 10^{-4}$ eV).
- The experimental observation of the Lamb shift – giving a small energy splitting ($\sim 5 \times 10^{-6}$ eV) between the $S_{1/2}$ and $P_{1/2}$ energy levels – explained by interaction of electrons with vacuum fluctuations of the E/M field.
- Multielectron atoms – a hydrogen-like model, neglecting electron-electron repulsion is inconsistent with measurements of the ionization energies of the elements - to be continued.....

Lecture 19



The End!!

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