Lectures 2-3

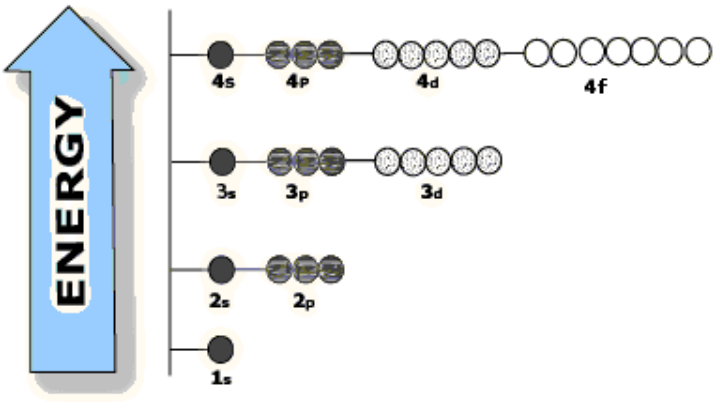
Hydrogen atom. Relativistic corrections of energy terms: relativistic mass correction, Darwin term, and spin-orbit term. Fine structure. Lamb shift. Hyperfine structure.

Energy levels of the hydrogen atom so far:

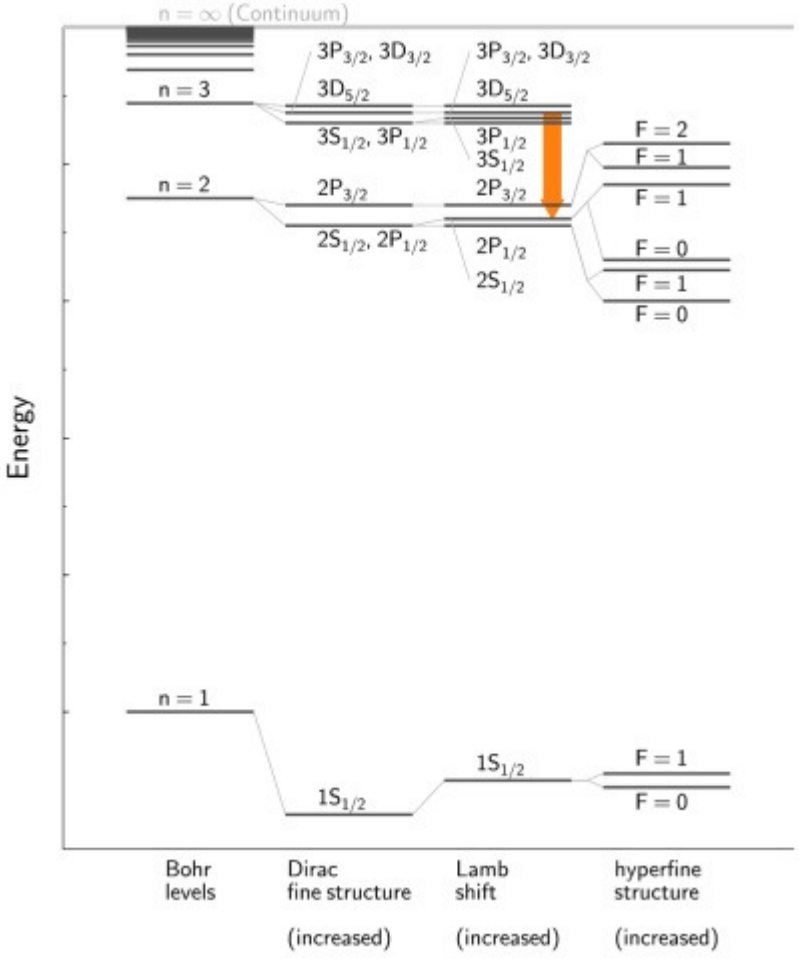
$$E = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \ldots$$

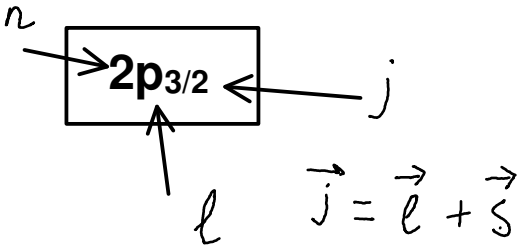
$$E_1 = -13.6\,eV$$

$\ell = 0$	s
$\ell = 1$	p
$\ell = 2$	d
$\ell = 3$	f



Actual energy level scheme (no external fields)





$s = 1/2$

$\ell = 1$

$j = 1/2, 3/2$

$|\ell - s| \le j \le \ell + s$

Relativistic corrections of energy terms

Proper treatment: solve Dirac equation. However, the corrections are small so we can use our non-relativistic solution and apply first-order perturbation theory.

$$H = H_0 + H' \; ; \quad H_0 \psi_n^0 = E_n^0 \psi_n^0$$

$$H\psi_n = E_n \psi_n \Rightarrow \quad E_n = E_n^0 + E_n^1 + \dots , \qquad E^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle$$

Relativistic effects:

(1) The relativistic dependence of electron mass on its velocity → small decrease in kinetic energy.
(2) Darwin term - smears the effective potential felt by the electron → change in the potential energy.
(3) Spin-orbit term: the interaction of the magnetic moment of the electron [due to electron spin] with the effective magnetic field the electrons see due to orbital motion around the nucleus.

1) Relativistic mass dependence

Nonrelativistic: $E_{nr} = \dfrac{p^2}{2m} + U$

Relativistic: $E = c\sqrt{m_0^2 c^2 + p^2} - m_0 c^2 + U$ ($m_0 c^2$: mass at rest)

For an electron in the hydrogen atom, $v \ll c$ $\qquad \dfrac{p^2}{m_0^2 c^2} \ll 1$

Class exercise: expand the square root (keep 3 terms) and find the expression for H'.

$$\sqrt{1 + \frac{p^2}{m_0^2 c^2}} = 1 + \frac{1}{2}\frac{p^2}{m_0^2 c^2} - \frac{1}{8}\frac{p^4}{m_0^4 c^4} + \dots \Rightarrow$$

$$E = m_0 c^2 \sqrt{1 + \frac{p^2}{m_0^2 c^2}} - m_0 c^2 + U \approx m_0 c^2 \left\{ 1 + \frac{p^2}{2 m_0^2 c^2} - \frac{1}{8}\frac{p^4}{m_0^4 c^4} + \dots \right\}$$

$$- m_0 c^2 + U \approx \underbrace{\frac{p^2}{2m_0} + U}_{E_{nr}} - \frac{1}{8}\frac{p^4}{m_0^3 c^2} \Rightarrow \quad H' = -\frac{1}{8}\frac{p^4}{m_0^3 c^2}$$

Then, $H' = -\frac{p^4}{8 m_0^3 c^2}$ and first-order correction to the energy is given by

$$\Delta E_{r(n)} = \langle \psi_n^0 | H' | \psi_n^0 \rangle = \int \psi_n^{0*} H' \psi_n^0 \, d^3 r$$

$$\boxed{\Delta E_r = -E_{nr} \frac{z^2 \alpha^2}{n} \left(\frac{3}{4n} - \frac{1}{\ell + 1/2} \right)}$$

now energy depends on l

$$\alpha = \frac{e^2}{4\pi\varepsilon_0} \frac{1}{\hbar c} = \frac{1}{137} \leftarrow \text{fine-structure constant}$$

2) Darwin term

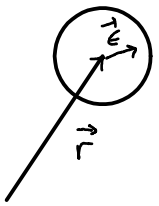
Even in a model where the electron is considered to be a point charge, the momentary position of the electron can not be defined more precisely than within the volume $\lambda_c^3 = \left(\frac{\hbar}{m_e c}\right)^3$

Compton wavelength of the electron

Then, we can not determine the electron position, but only a "fuzzy ball" about the size of λ_c.

To quantify the corresponding correction, we define effective potential that is the average of the potential over the "fuzzy ball".

Electron "fuzzy ball"



$$V_{eff} = \frac{1}{\text{volume}} \int V(\vec{r} + \vec{\epsilon}) \, d^3\epsilon$$

$$V(\vec{r} + \vec{\epsilon}) = V(\vec{r}) + \vec{\epsilon} \nabla V + \sum_{i,j=1}^{3} \frac{1}{2} \epsilon_i \epsilon_j \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_j} V + \ldots$$

$$\int V(\vec{r}) \, d^3\epsilon = V(\vec{r}) \times \text{volume}$$

$$\int \vec{\epsilon} \cdot \nabla V \, d^3\epsilon = \nabla V \cdot \int \vec{\epsilon} \, d^3\epsilon = 0 \quad (\text{spherical symmetry})$$

Integrating the last term gives a result close to full relativistic calculation which yields

$$H' = \frac{1}{8} \left(\frac{\hbar}{mc}\right)^2 \nabla^2 V \qquad \nabla^2 V = -\nabla^2 \frac{ze^2}{4\pi\epsilon_0} \frac{1}{r} = 4\pi\delta(\vec{r}) \frac{ze^2}{4\pi\epsilon_0}$$

since $\nabla^2 \frac{1}{r} = -4\pi\delta(\vec{r})$ $\qquad \nabla = (\vec{\nabla})^2$

$$H_{Darwin} = \frac{\pi\hbar^2}{2m^2c^2}\frac{Ze^2}{4\pi\epsilon_0}\delta(\vec{r}) \qquad (\text{only for } \ell = 0)$$

$$\Delta E = \langle \psi_{n00} | H_{Darwin} | \psi_{n00} \rangle$$

$$= \frac{\pi\hbar^2}{2m^2c^2}\frac{Ze^2}{4\pi\epsilon_0}|\psi_{n00}(0)|^2 \qquad \text{since } Y_{00} = \frac{1}{\sqrt{4\pi}}$$

$$|\psi_{n00}|^2 = \frac{1}{4\pi}|R_{n0}(0)|^2 = \frac{Z^3}{\pi a^3}\frac{1}{n^3}$$

a: Bohr radius

The radial wave functions are non-zero at the origin only for l=0, i.e. 1s, 2s, 3s, etc.

$$\Delta E = -E_n \frac{(Z\alpha)^2}{n}, \quad \ell = 0$$

(3) The spin-orbit interaction

From special relativity, a particle moving in an electric field **E** experiences a magnetic field **B** in its reference frame:

$$\vec{B} = -\frac{1}{c^2}\vec{v}\times\vec{E} + O(v^2/c^2)$$

A simple explanation for hydrogen: in the coordinate system where the electron is at rest at the origin, the nucleus with the positive charge Ze moves in a circle around the electron. This causes a circular current that produces magnetic field at the location of the electron.

$$\vec{E} = \frac{1}{e}\frac{\partial V}{\partial r}\frac{\vec{r}}{r}$$

(factor of e comes in since electron's potential energy equals its charge times the electrostatic potential)

For hydrogen,

$$V = -\frac{e^2 Z}{4\pi\epsilon_0}\frac{1}{r}.$$

$$B = +\frac{1}{c^2}\left(\frac{1}{er}\frac{\partial V}{\partial r}\right)\frac{1}{m_e}\underbrace{\vec{r}\times m_e\vec{v}}_{\vec{\ell}} = \frac{1}{m_e c^2}\left(\frac{1}{er}\frac{\partial V}{\partial r}\right)\vec{\ell}$$

The interaction of the electron's magnetic spin moment with the orbital field gives the following Hamiltonian of the spin-orbit interaction:

$$H = -\mu_s B \,.$$

$$\mu_s = -g_s \frac{\mu_B}{\hbar}\vec{s}$$

$g_s \approx 2$

$$\mu_B = \frac{e\hbar}{2m_e} \leftarrow \text{Bohr magneton}$$

Note that $\mu_\ell = -\frac{\mu_B}{\hbar}\vec{\ell}$

$$H = g_s \frac{1}{2m_e}\frac{1}{m_e c^2}\left(\frac{1}{r}\frac{\partial V}{\partial r}\right)\vec{\ell}\cdot\vec{s}$$

However, the corresponding energy splitting's are twice as large as observed by the experiment. This is due to Thomas precession - a relativistic effect that arises because we are calculating the magnetic field in the frame of reference that is not stationary but rotates as the electron moves about the nucleus, so

$$\boxed{H = \frac{1}{2} g_s \frac{1}{2m_e^2 c^2}\left(\frac{1}{r}\frac{\partial V}{\partial r}\right)\vec{\ell}\cdot\vec{s}}$$

For hydrogen,

$$V = -\frac{e^2 Z}{4\pi\epsilon_0}\frac{1}{r} \Rightarrow \frac{\partial V}{\partial r} = \frac{e^2 Z}{4\pi\epsilon_0}\frac{1}{r^2} \qquad \frac{1}{\epsilon_0} = \mu_0 c^2$$

$g_s \approx 2$

$$H_{so} = \frac{1}{2m_e^2 c^2}\frac{1}{r}\frac{e^2 Z}{4\pi}\mu_0 c^2 \frac{1}{r^2} = \frac{\mu_0 e^2 Z}{8\pi m_e^2}\frac{1}{r^3}\vec{\ell}\cdot\vec{s}$$

$$E_{so} = \langle \psi_n^0 | H_{so} | \psi_n^0 \rangle = \frac{\mu_0 e^2 Z}{8\pi m^2 e}\left\langle\frac{1}{r^3}\right\rangle\langle\vec{\ell}\cdot\vec{s}\rangle$$

Class exercise: calculate $\langle \vec{\ell} \cdot \vec{s} \rangle$

Hints: $\vec{j} = \vec{\ell} + \vec{s}$ $\qquad j^2 \psi_{n\ell j m_\ell} = \hbar^2 j(j+1) \psi_{n\ell j m_\ell}$

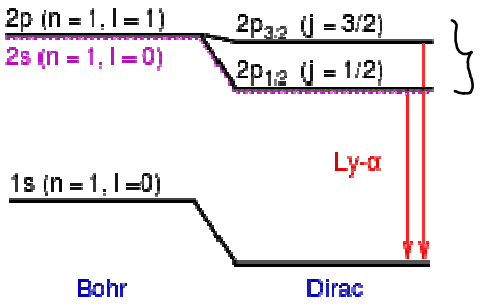
$$j^2 = \ell^2 + s^2 + 2\vec{\ell}\cdot\vec{s} \Rightarrow \vec{\ell}\cdot\vec{s} = \frac{1}{2}\left(j^2 - \ell^2 - s^2\right)$$

$$\left.\begin{aligned} \langle j^2 \rangle &= \hbar^2 j(j+1) \\ \langle \ell^2 \rangle &= \hbar^2 \ell(\ell+1) \\ \langle s^2 \rangle &= \hbar^2 s(s+1) \end{aligned}\right\} \Rightarrow \langle \vec{\ell}\cdot\vec{s} \rangle = \frac{1}{2}\hbar^2\left(j(j+1) - \ell(\ell+1) - s(s+1)\right)$$

$$\Delta E_{n\ell j} = \frac{a}{2}\left(j(j+1) - \ell(\ell+1) - s(s+1)\right) \qquad a = \frac{\mu_0 Z e^2 \hbar^2}{8\pi m_e^2}\left\langle \frac{1}{r^3} \right\rangle$$

$$a = -E_n \frac{Z^2\alpha^2}{n\ell(\ell+\frac{1}{2})(\ell+1)}$$

"Fine-structure" refers to splitting of levels with the same ℓ but different j. For example,



fine structure $\quad \ell = 1, \; s = 1/2 \quad j = \ell \pm 1/2 \Rightarrow j = 1/2,\ 3/2$

If $\ell = 0 \Rightarrow \Delta E = 0$ for this term.

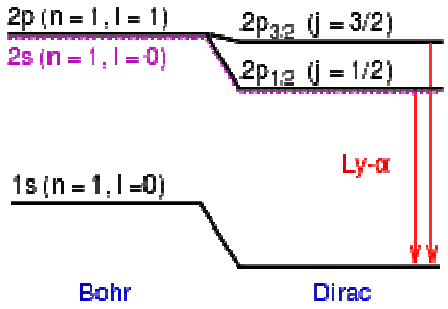
Conclusion: putting all three effects together, we get the following expression for the energy:

$$E_{nj} = E_n\left\{1 + \frac{Z^2\alpha^2}{n}\left(\frac{1}{j+1/2} - \frac{3}{4n}\right)\right\}$$

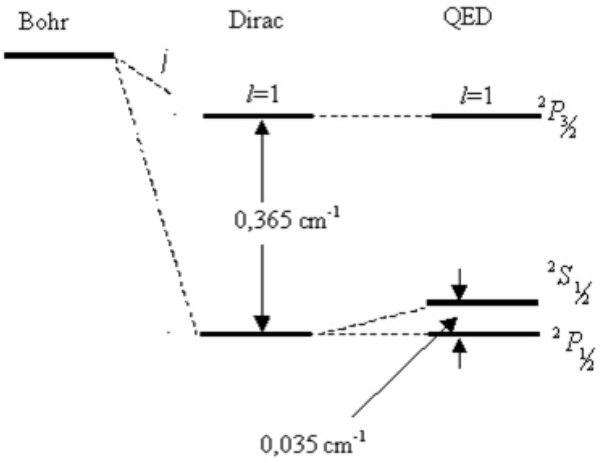
Note that this expression does not depend on ℓ! Then, $2s_{1/2}$ and $2p_{1/2}$ levels of hydrogen still have the same energy.

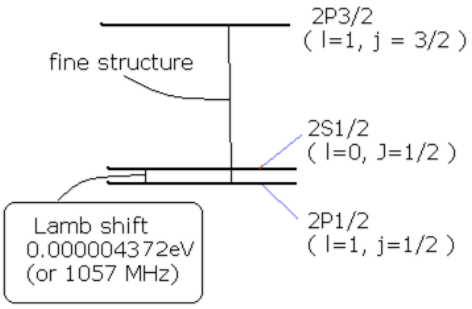
Lamb shift

Prediction of the relativistic (Dirac equation) theory for hydrogen energy levels:



The solution of the relativistic Dirac equation for hydrogen gives the same energies of the states with different l but the same j, such as $2s_{1/2}$ and $2p_{1/2}$ levels in hydrogen. However, this contradicts experimental observations which show a small difference between the energy levels of these states. Willis Lamb and Robert Retherford were the first to measure this shift in 1947 [see W. E. Lamb and R.C. Retherford, Physical Review 72, 241 (1947).] This observation was of paramount significance and led to the development of quantum electrodynamics (QED) - quantum field theory that describes electromagnetic interactions.

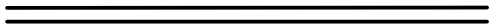




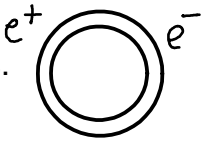
In quantum electrodynamics, so-called "radiative corrections" to the Dirac theory are obtained by taking into account interactions of electrons with the quantized electromagnetic field.

In QED, a quantized radiation field in the lowest-energy state of NOT the one with ZERO electromagnetic fields, but there exist zero-point oscillations. [*Note: remember for example that the lowest energy (or zero-point energy) of the harmonic oscillator is not zero but* $h\nu/2$.] Then, there are non-zero electromagnetic fields that are present even in the absence of any external radiation due to the fields associated with zero-point energy. Such fields are referred to as "vacuum" fluctuations since they are present even in the "vacuum", i.e. absence of observable photons. The process where atomic electron emits and then absorbs a photon of energy $\hbar\omega$ during time $\Delta t < \hbar/\Delta E$ does not violate the energy conservation law because of the uncertainty relation $\Delta E \Delta t \geq \hbar$.

Feynman diagrams for Lamb shift:

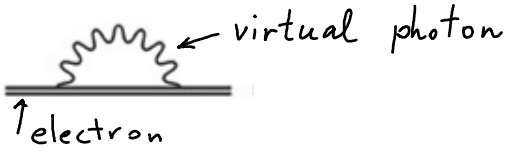
Element #1: Double line represents bound electrons 

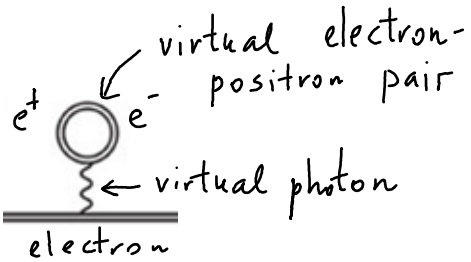
Element #2: Wavy line represents a virtual photon 

Element #3: Double circle represent virtual electron-positron pairs. 

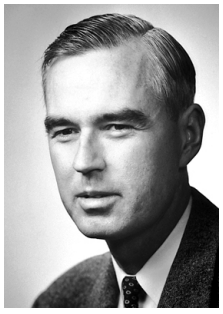
There are two dominant QED contributions that cause the Lamb shift: **self-energy and vacuum polarization.**

The electron self-energy QED correction is due to emission and absorption of virtual photons. This leads to smearing of the electron ("fuzzy electron ball" effect again - remember the Darwin term).

The corresponding Feynman diagrams is 

The Feynman diagram for **vacuum polarization** QED term is 

There is a "cloud" of the electron-positron pairs confined to a localized region around the electron of order the Compton wavelength. It get polarized by the Coulomb field from the nucleus [i.e. virtual electrons get attracted and virtual positrons are repelled by the nucleus] which binds the s electron more tightly. This correction is very small in hydrogen. This effect becomes important in highly-charged ions and muonic hydrogen as muon is 200 times heavier than electron and, therefore, more tightly bound.



Willis Eugene Lamb

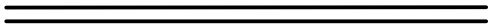
The Nobel Prize in Physics 1955 was divided equally between Willis Eugene Lamb "*for his discoveries concerning the fine structure of the hydrogen spectrum*" and Polykarp Kusch "for his precision determination of the magnetic moment of the electron".

For the second-order Lamb shift, virtual photons and electron–positron pairs interact with themselves and each other to generate two loops.

Class exercise: draw 10 second-order Lamb shift diagrams.

Rules: there can be no more than two virtual photon lines and no more than two virtual electron-positron pair loops in a second-order diagram.

Feynman diagrams for Lamb shift:

Element #1: Double line represents bound electrons 

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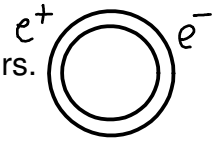
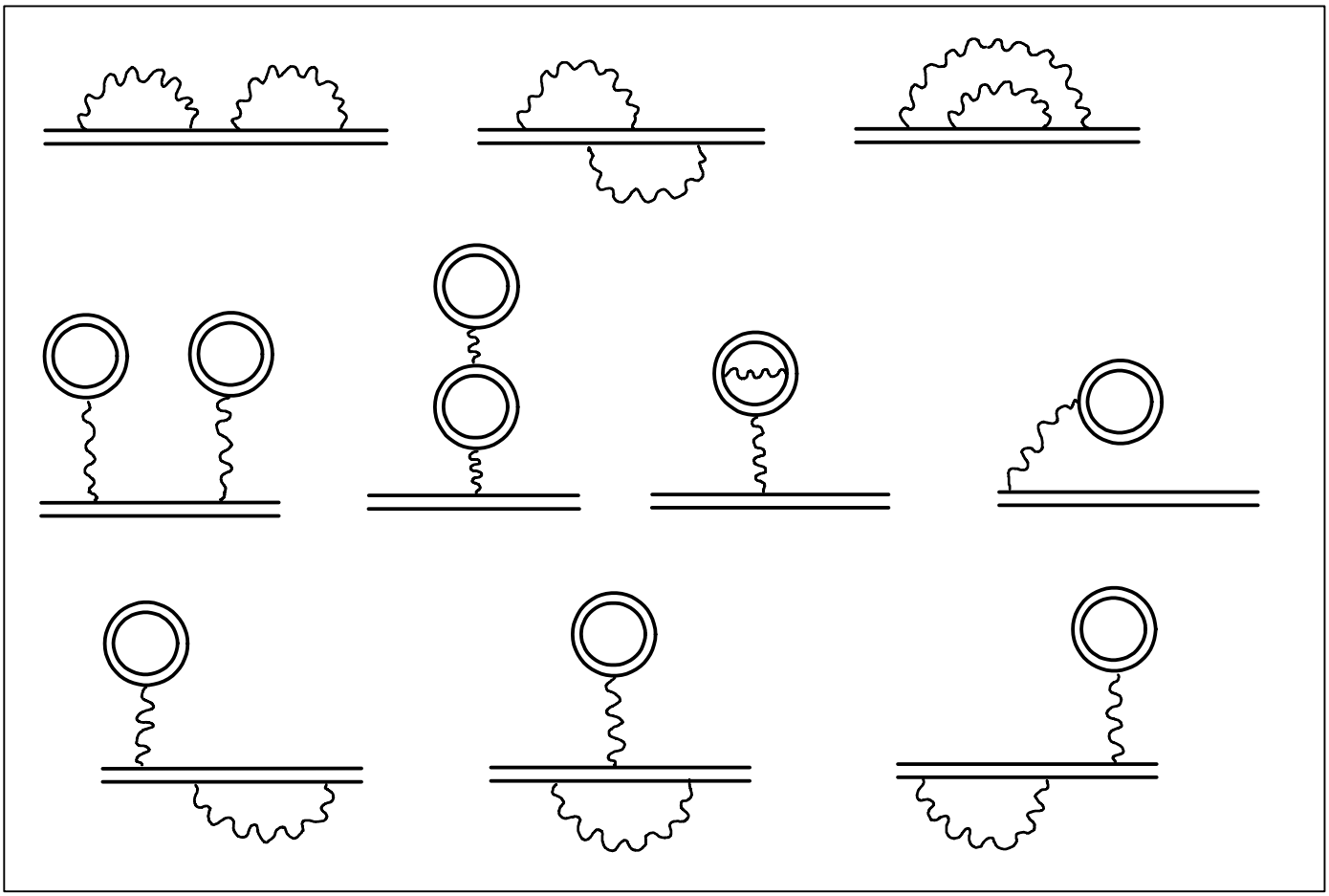
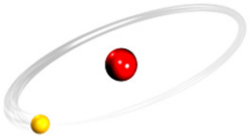
Element #3: Double circle represents virtual electron-positron pairs. 



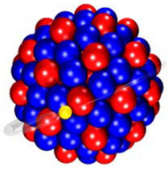
The QED effects are enhanced in ions with high-nuclear charge, for example in H-like or Li-like U. [U with 91 or 89 electrons removed and only 1 or 3 electrons left like in H or Li] since QED effects scale as Z^4 . [Remember that nonrelativistic energy scales as Z^2.]

IONS: atoms with one or more electrons removed

Hydrogen
Z=1, 1 electron
Electron binding energy 13.6 eV



Hydrogen-like U^{91+}
Z=92, stll only 1 electron
Electron binding energy **132 000 eV**

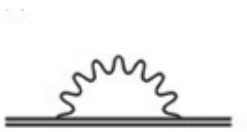


Measurements of Lamb shift in such highly-charged ions [i.e. ions with lots of stripped electrons] allow to test QED predictions and study higher-order QED effects.

Experimental tests of second-order QED effects in H-like U^{91+}

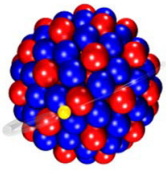
Energy scale (from Thomas Stöhlker, GSI-Darmstadt)

H-like U^{91+} Z=92 E_b=132 000 eV

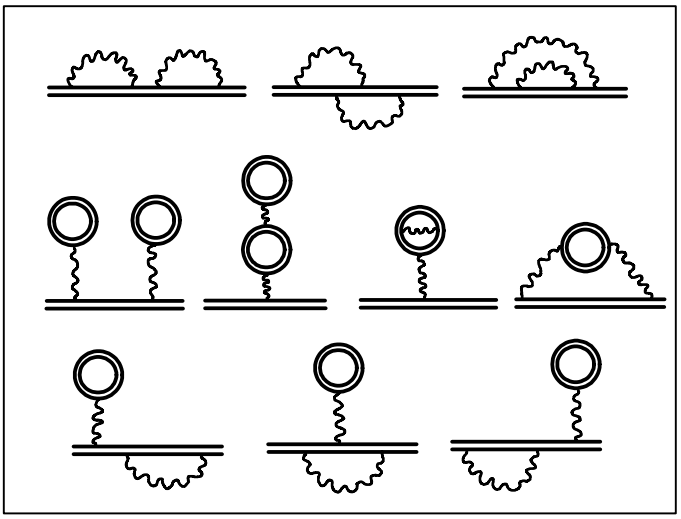


Self-energy
355 eV
0.26%

Vacuum
polarization
- 89 eV



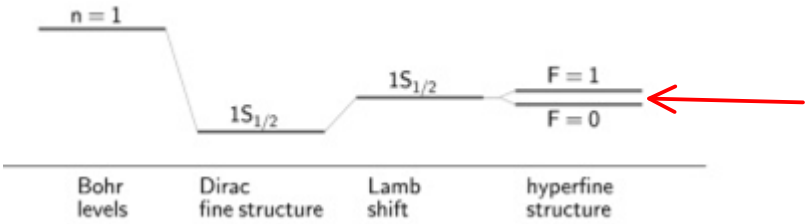
Nuclear size
effects
199 eV



Total for all second-order effects ~1eV

See https://www.llnl.gov/str/May06/pdfs/05_06.4.pdf for article on experiments in Livermore National Laboratory on testing QED in Li-like U ion.

Hyperfine structure



All levels of hydrogen, including fine structure components, are split into two more components.

So far, we ignored the spin of the hydrogen nucleus (i.e. proton), which is I=1/2. Additional splitting of the atomic energy levels appear because of the interaction of the nuclear moments with the electromagnetic fields of the electrons. The level splitting caused by this interaction is even smaller than the fine structure, so it is called hyperfine structure. Hyperfine states that are split from the ground state make particularly good qubits for quantum information due to their long lifetimes. The hyperfine splitting of the ground state of Cs is used to define a second.

The hyperfine interaction in general form is given by

$$H_{hf} = \sum_k T_k \cdot N_k$$

Rank k spherical tensor operator acting on the electronic degrees of freedom

Rank k spherical tensor operator acting on the nuclear degrees of freedom

k=0 just the Coulomb part
k=1 magnetic-dipole interaction (odd) - considered below
k=2 electric-quadrupole interaction (even)
...

Here, we consider magnetic-dipole hyperfine interaction, i.e. the interaction of the nuclear magnetic moment μ_N with the magnetic field produced by the electrons at the nucleus, k=1, and the Hamiltonian is given by:

$$H_{hf} = -\mu_N B_{int}$$

$$\mu_N = \gamma_N I = g_N \frac{\mu_N}{\hbar} I$$

μ_N: nuclear magneton, $\mu_N = \frac{e}{2m_p}\hbar$

I: nucler spin

g_N: nuclear g-factor

$$H_{hf} = -\mu_N B_{int} = -|\mu_N| B_j \cos(\angle \vec{J}, \vec{I})$$

Magnetic field produced at the location of the nucleus by the orbital motion of the electron and the magnetic moment μ_S due to electron spin

$\vec{J} = \vec{l} + \vec{s}$ total angular momentum of electrons

$\vec{I}$ nuclear spin

We now define total angular momentum (nucleus + electrons) $\vec{F} = \vec{J} + \vec{I}$

Example: hydrogen ground state J=1/2, I=1/2 (proton) F=0,1, so two levels (see picture on previous page)

and introduce a magnetic-dipole hyperfine constant A: $A = \dfrac{-g_N \mu_N B_j}{\sqrt{j(j+1)}}$

Class exercise: derive the expression for the energy shift of atomic level due to magnetic-dipole hyperfine interaction. Express your result in terms of I, J, F, and A.
Hint: remember the derivation of the spin-orbit interaction.

$$F^2 = J^2 + I^2 + 2\,\underline{J \cdot I}$$

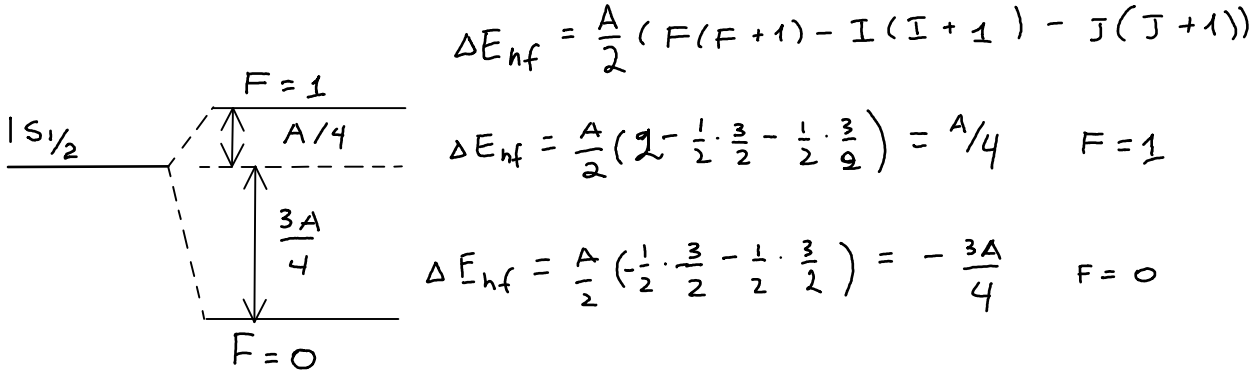
$$J \cdot I = |J||I| \cos(\angle J, I)$$

$$\cos(\angle J, I) = \frac{1}{2|J||I|}\left(F^2 - I^2 - J^2\right)$$

$$\langle H_{hf} \rangle = \frac{\hbar^2 \left(F(F+1) - I(I+1) - J(J+1)\right)}{2\hbar^2 \sqrt{I(I+1)}\sqrt{J(J+1)}}$$

$$|\vec{I}| = \sqrt{I(I+1)}\,\hbar \quad \Rightarrow \quad |\mu_N| = g_N \frac{\mu_N}{\hbar} \sqrt{I(I+1)}\,\hbar$$

$$\boxed{\Delta E_{hf} = \frac{A}{2}\left(F(F+1) - I(I+1) - J(J+1)\right)}$$



Final summary: H energy level structure