Real hydrogen atom

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Willis Eugene Lamb, Jr. (July 12, 1913 – May 15, 2008) was an American physicist who won the Nobel Prize in Physics in 1955 together with Polykarp Kusch "for his discoveries concerning the fine structure of the hydrogen spectrum". Lamb and Kusch were able to precisely determine certain electromagnetic properties of the electron (see Lamb shift). Lamb was a professor at the University of Arizona College of Optical Sciences.

http://en.wikipedia.org/wiki/Willis_Lamb

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1. Bohr model

According to the Bohr model, the energy of the hydrogen-like atom with *Ze* is given by

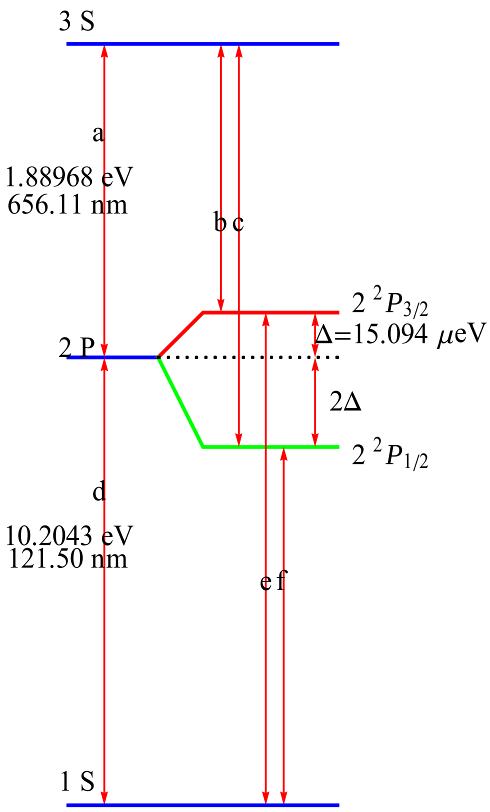
$$E_n = -\frac{Z^2 e^2}{8\pi\varepsilon_0 n^2 a_0} = -Z^2 \frac{E_0}{n^2}$$

where

$$E_0 = \frac{e^2}{8\pi\varepsilon_0 a_0} = \frac{e^2}{8\pi\varepsilon_0 \dfrac{4\pi\varepsilon_0\hbar^2}{me^2}} = \frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2}$$

E_0 =13.60569253 eV

Note that E_n is dependent only on n.
Here we consider the case of hydrogen atom (Z = 1)



(i) Transition ***a*** between n = 2 and n = 3 states

$$E_3 - E_2 = 1.88968 \text{ eV}$$

$$\lambda = \frac{hc}{E_2 - E_1} = 656.112 \text{ nm}$$

(ii) Transition ***d*** between n = 1 and n = 2 states (see a figure below).

$$E_2 - E_1 = 10.2043 \text{ eV}$$

$$\lambda = \frac{hc}{E_2 - E_1} = 121.502 \text{ nm}$$

2. Spin-orbit coupling

$$\Delta E_{SO} = \frac{\xi}{2}(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2) = \frac{\xi\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)]$$
$$= \frac{(Z\alpha)^4}{2n^4} mc^2 \frac{[j(j+1) - l(l+1) - s(s+1)]}{l(l+1)(2l+1)}$$

where α is the fine structure

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} = \frac{1}{137.036} = 7.2973525698 \times 10^{-3}$$

and Z is the atomic number.

(1) The 2p state is split into two states due to the spin-orbit coupling.

$l = 1$ (2p) and spin s = 1/2 $\rightarrow j = 3/2$ and $j = 1/2$

($D_1 \times D_{1/2} = D_{3/2} + D_{1/2}$).

$2\ {}^2P_{3/2}$ ($j = 3/2$, $l = 1$, $s = 1/2$)

$2\ {}^2P_{1/2}$ ($j = 1/2$, $l = 1$, $s = 1/2$)

When Z = 1 and s = 1/2,

$\Delta E_{SO} = \Delta = 1.50942 \times 10^{-5}$ eV for the $2\ {}^2P_{3/2}$ state

$\Delta E_{SO} = -2\Delta = -3.01884 \times 10^{-5}$ eV for the $2\ {}^2P_{1/2}$ state

The energy difference is $3\Delta = 4.52826 \times 10^{-5}$ eV.

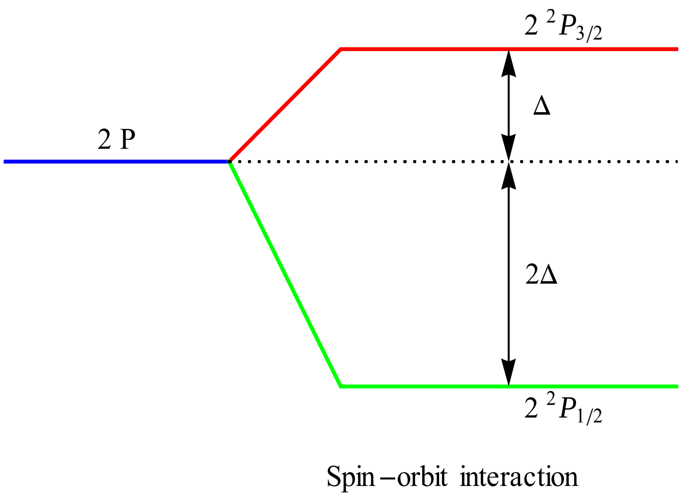


Fig. Splitting of 2 P level into two states ($2\,^2P_{3/2}$ and $2\,^2P_{1/2}$).

The energy level of the 2S state does not change since $L = 0$.

((**Note**)) g-factor for each level.

$$g_J = \frac{3}{2} + \frac{s(s+1) - l(l+1)}{2j(j+1)}$$

For $4\,^2P_{3/2}$ ($j = 3/2$, $l = 1$, $s = 1/2$)

$$g_1 = \frac{3}{2} + \frac{\frac{3}{4} - 1(1+1)}{2\frac{3}{2}\frac{5}{2}} = \frac{4}{3}$$

For $4\,^2P_{1/2}$ ($j = 1/2$, $l = 1$, $s = 1/2$)

$$g_2 = \frac{3}{2} + \frac{\frac{3}{4} - 1(1+1)}{2\frac{1}{2}\frac{3}{2}} = \frac{2}{3}$$

(2) The 3p state is split into two states due to the spin-orbit coupling.

$l = 1$ (3p) and spin s = 1/2 $\rightarrow j = 3/2$ and $j = 1/2$

($D_1 \times D_{1/2} = D_{3/2} + D_{1/2}$).

$3\ ^2P_{3/2}$ $(j = 3/2,\ l = 1,\ s = 1/2)$

$3\ ^2P_{1/2}$ $(j = 1/2,\ l = 1,\ s = 1/2)$

When $Z = 1$ and s = 1/2, we have

$\Delta E_{SO} = \Delta = 4.47236 \times 10^{-6}$ eV for the $3\ ^2P_{3/2}$ state

$\Delta E_{SO} = -2\Delta = -8.94471 \times 10^{-6}$ eV for the $3\ ^2P_{1/2}$ state

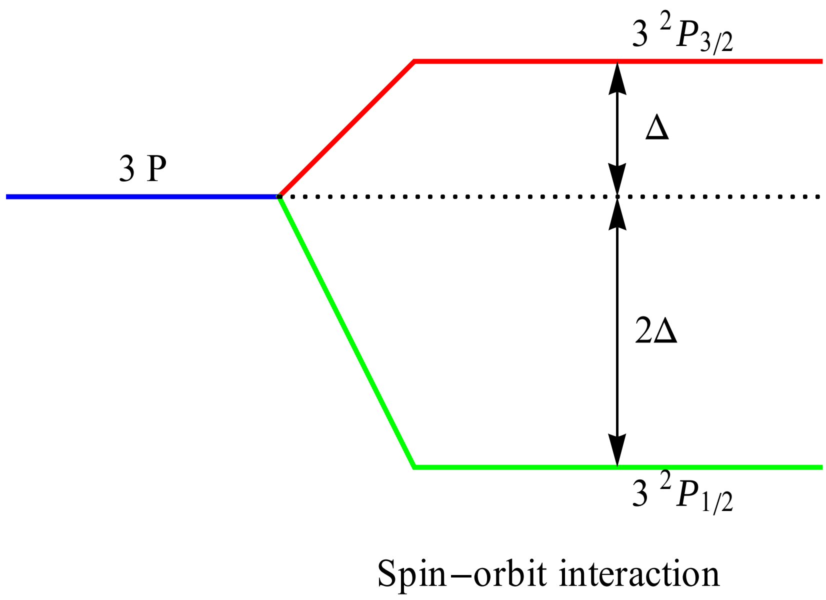


Fig. Splitting of 3 P level into two states ($3\ ^2P_{3/2}$ and $3\ ^2P_{1/2}$)

The energy level of the 3S state does not change since $L = 0$.

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3. Effect of the spin-orbit coupling on the hydrogen spectra

Transition a

$$\lambda = \frac{hc}{E_3 - E_2} = 656.112 \text{ nm}$$

Transition b

$$\lambda = \frac{hc}{E_3 - (E_2 + \Delta E_{SO}(n = 2, l = 1, j = 3/2)} = 656.117 \text{ nm}$$

Transition c

$$\lambda = \frac{hc}{E_3 - (E_2 + \Delta E_{SO}(n = 2, l = 1, j = 1/2)} = 656.102 \text{ nm}$$

Transition e

$$\lambda = \frac{hc}{-E_1 + (E_2 + \Delta E_{SO}(n = 2, l = 1, j = 3/2)} = 121.502 \text{ nm}$$

Transition f

$$\lambda = \frac{hc}{-E_1 + (E_2 + \Delta E_{SO}(n = 2, l = 1, j = 1/2)} = 121.503 \text{ nm}$$

4. Relativistic correction

According to special relativity, the kinetic energy of an electron of mass *m* and velocity *v* is:

$$T = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2}$$

The first term is the standard non-relativistic expression for kinetic energy. The second term is the lowest-order relativistic correction to this energy. Using perturbation theory, it can be show that

$$\Delta E_{rel} = -\frac{E_n{}^2}{2mc^2}\left(\frac{4n}{l+\frac{1}{2}} - 3\right) = -\frac{E_0{}^2 Z^4}{2mc^2 n^4}\left(\frac{4n}{l+\frac{1}{2}} - 3\right)$$
$$= -\frac{Z^4\alpha^4}{n^3} mc^2 \left(\frac{1}{2l+1} - \frac{3}{8n}\right)$$

where

$$E_n = -Z^2\frac{E_0}{n^2} = -Z^2\frac{mc^2}{2n^2}\alpha^2$$

with

$$E_0 = \frac{e^2}{8\pi\varepsilon_0 a_0} = \frac{e^2}{8\pi\varepsilon_0 \frac{4\pi\varepsilon_0\hbar^2}{me^2}} = \frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2} = \frac{1}{2}mc^2\alpha^2$$

The sum of the relativistic correction and the spin coupling is given by

$$\begin{aligned}
\Delta E &= \Delta E_{rel}(n,l) + \Delta E_{SO} \\
&= -\frac{(Z\alpha)^4}{n^3} mc^2\left(\frac{1}{2l+1} - \frac{3}{8n}\right) \\
&\quad + \frac{(Z\alpha)^4}{2n^3} mc^2 \frac{[j(j+1) - l(l+1) - s(s+1)]}{l(l+1)(2l+1)} \\
&= \frac{(Z\alpha)^4}{n^3} mc^2 \left\{-\left(\frac{1}{2l+1} - \frac{3}{8n}\right) + \frac{j(j+1) - l(l+1) - s(s+1)}{2l(l+1)(2l+1)}\right\}
\end{aligned}$$

When $s = 1/2$, and $j = l \pm 1/2$, we have

$$\boxed{\Delta E = V(n,j) = -\frac{(Z\alpha)^4}{2n^3} mc^2\left(\frac{2}{2j+1} - \frac{3}{4n}\right)}$$

which depends only on n and j, but not on l.

For $2\ {}^2P_{3/2}$

$V(n=2, j=3/2) =$-1.13206 x 10^{-5} eV

For 2 $^2P_{1/2}$ and 2 $^2S_{1/2}$

$V(n=2, j=1/2) =$ -5.66032 x 10^{-5} eV

Then we have the energy difference

$V(n=2, j=3/2) - V(n=2, j=1/2) =$ 4.52826 x10^{-5} eV

which is the same as 4*Δ* for the 2 $^2P_{3/2}$ state the 2 $^2P_{1/2}$ state (spin-orbit coupling).

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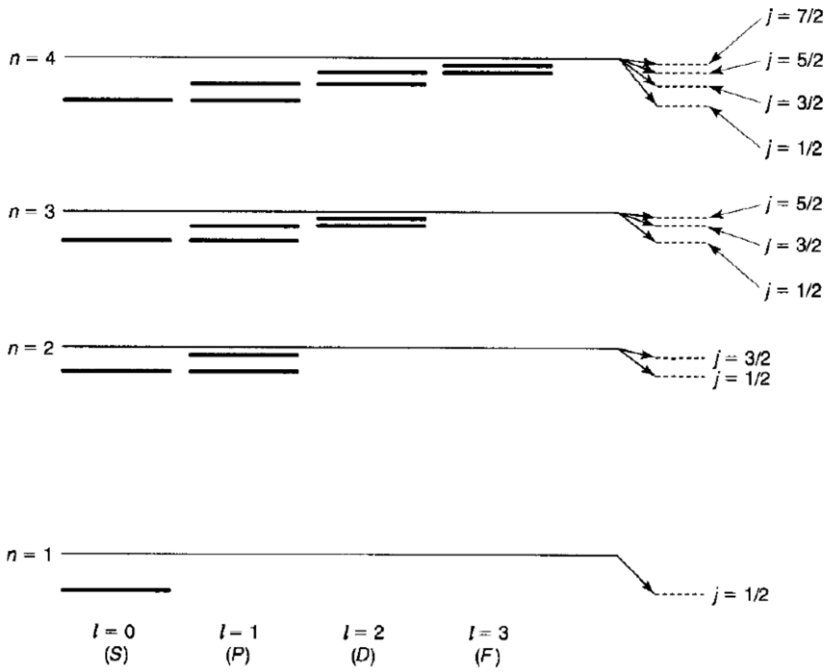
6. Exact solution from Dirac

The exact fine-structure formula for hydrogen (obtained from the Dirac equation without recourse to the perturbation theory) is

$$E(n, j) = mc^2\{[1 + (\frac{\alpha}{n - (j+2) + \sqrt{(j+\frac{1}{2})^2 - \alpha^2}})^2]^{-1/2} - 1\}\,.$$

Note that the energy depends only on *n* and *j*.



((Series expansion))

$$E(n,j) = -\frac{mc^2}{2n^2}\alpha^2 + \frac{mc^2}{8n^4}\alpha^4(3 - \frac{8n}{1+2j}) + ...$$

((Numerical values))

n	j	E(n,j) [eV]
1	1/2	-13.6059
2	1/2	-3.40148
2	3/2	-3.40143
3	1/2	-1.51176
3	3/2	-1.51175
3	5/2	-1.51175
4	1/2	-0.850365
4	3/2	-0.850359
4	5/2	-0.850357
4	7/2	-0.850356

5	1/2	-0.544233
5	3/2	-0.544230
5	5/2	-0.544229
5	7/2	-0.544228
5	9/2	-0.544228

((**Mathematica**))

$$\mathtt{E1}[n\_,\ j\_] := \mathrm{me}\, c^2 \left(\left(1+\left(\frac{\alpha}{n-(j+1/2)+\sqrt{\left(j+\frac{1}{2}\right)^2-\alpha^2}}\right)^2\right)^{-1/2}-1\right);$$

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Series[E1[n, j], {α, 0, 6}] // Simplify[#, j > 0] &
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$$-\frac{(c^2\,\mathrm{me})\,\alpha^2}{2\,n^2}+\frac{c^2\,\mathrm{me}\,(3+6\,j-8\,n)\,\alpha^4}{8\,(1+2\,j)\,n^4}+$$
$$\frac{c^2\,\mathrm{me}\,\left(-5\,(1+2\,j)^2\,(3+6\,j-8\,n)+32\,(1+2\,j)^2\,n-24\,n^2\,(3+6\,j+2\,n)\right)\,\alpha^6}{48\,(1+2\,j)^3\,n^6}+O[\alpha]^7$$

7. Lamb shift

Spectral lines give information on nucleus. Main effects are isotope shift and hyperfine structure.

According to Schrödinger and Dirac theory, states with same n and j but different l are degenerate. However, Lamb and Retherford showed in 1947 that 2 $^2S_{1/2}$ and 2 $^2P_{1/2}$ of H-atom are not degenerate.

Experiment proved that even states with the same total angular momentum *j* are energetically different.

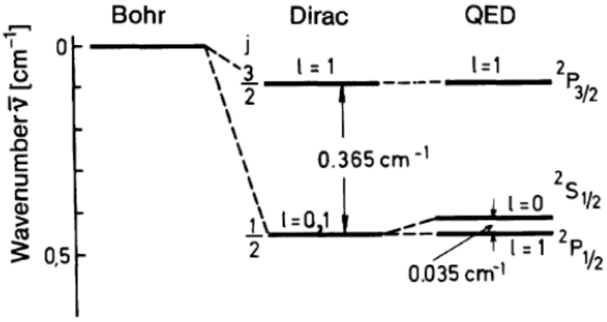

Fig. 12.21. The Lamb shift: fine structure of the $n = 2$ level in the H atom according to *Bohr*, *Dirac* and quantum electrodynamics taking into account the Lamb shift. The j degeneracy is lifted