Real hydrogen atom

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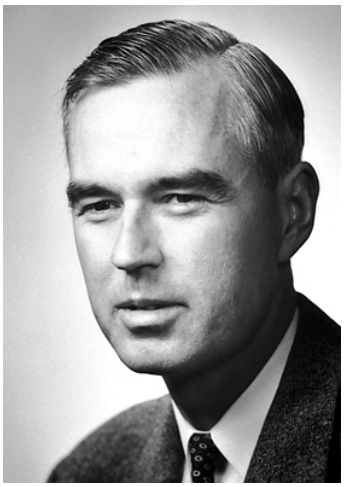
Willis Eugene Lamb, Jr. (July 12, 1913 – May 15, 2008) was an American physicist who won the Nobel Prize in Physics in 1955 together with Polykarp Kusch "for his discoveries concerning the fine structure of the hydrogen spectrum". Lamb and Kusch were able to precisely determine certain electromagnetic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

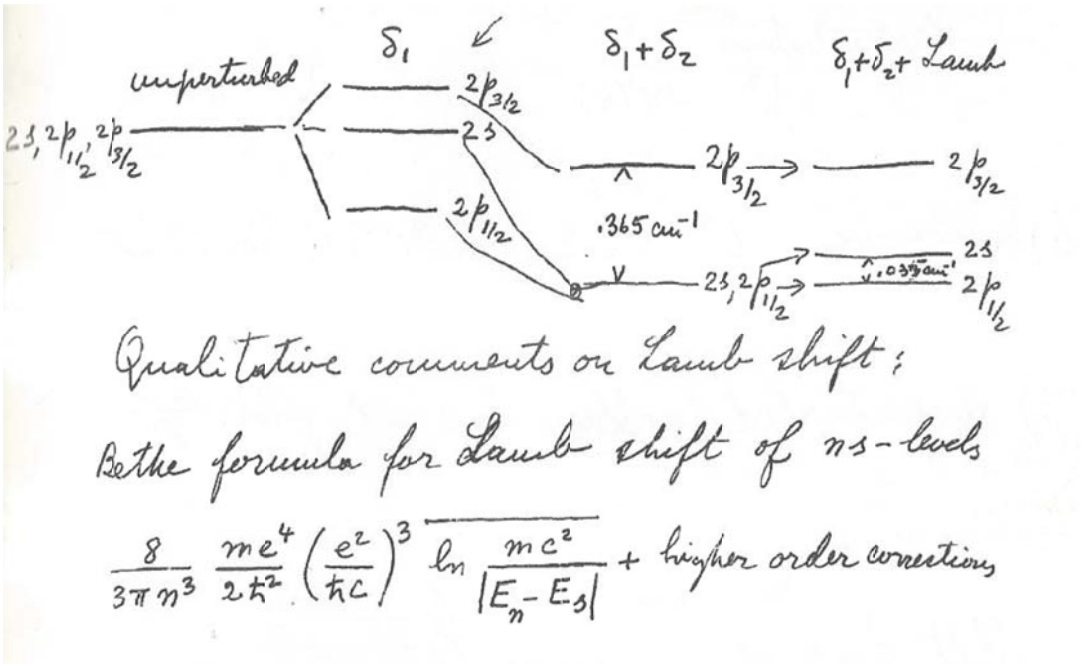


Fig. From the note on quantum mechanics (E. Fermi). p.117.
E. Fermi, *Note on Quantum Mechanics* (The University of Chicago, 1961).

The corrections to the Bohr energy are called the fine structure. They are all relativistic in nature. The energy of the electron in hydrogen can be expressed in terms of the fine structure constant, with the use of the perturbation theory.

To the order of α^2:

$$E_n^{(0)} = -\frac{1}{2} m_e c^2 \frac{\alpha^2}{n^2},$$

To the order of α^4:

$$E_n^{(1)} = E_n^{(0)} \alpha^2 \frac{1}{n}\left(\frac{1}{j+1/2} - \frac{3}{4n}\right) \qquad \text{for } l \neq 0$$

$$E_n^{(1)} == E_n^{(0)} \alpha^2 \frac{1}{n}\left(1 - \frac{3}{4n}\right) \qquad \text{for } l = 0$$

To the order of α^5:

the expression of the frequency for the Lamb shift (the non-relativistic case) (for n = 2), can be expressed as

$$\nu = \frac{\alpha^5 m_e c^3}{12\pi^2 \hbar c} \ln(\frac{1}{8.9\alpha^2}) = 1038.27 \text{ MHz} \approx 1057 \text{ MHz (experimental value).}$$

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1. Bohr model

According to the Bohr model, the electron energy of the hydrogen atom is given by

$$E_n^{(0)} = -\frac{e^2}{2n^2 a_B} = -\frac{E_0}{n^2} = -\frac{1}{2} m_e c^2 \frac{\alpha^2}{n^2},$$

$$\hat{H}_0 |nlm\rangle = (\frac{\hat{\boldsymbol{p}}^2}{2m_e} - \frac{e^2}{|\hat{\boldsymbol{r}}|}) |nlm\rangle = E_n^{(0)} |nlm\rangle,$$

where

$$E_0 = \frac{e^2}{2a_B} = \frac{m_e e^4}{2\hbar^2} = \frac{m_e c^2}{2} \frac{e^4}{\hbar^2 c^2} = \frac{1}{2} m_e c^2 \alpha^2$$

E_0 =13.60569253 eV

and the fine structure constant α is

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137.036} = 7.2973525698 \text{ x } 10^{-3}$$

The Bohr radius is given by

$$a_B = \frac{\hbar^2}{m_e e^2} = 0.5291772109217 \text{ Å}$$

The velocity of the electron in the n-th state:

$$v_n = \frac{e^2}{n\hbar} = \frac{e^2}{\hbar c} \frac{c}{n} = \alpha \frac{c}{n} = \frac{1}{n} \frac{c}{137.036}$$

n: principal quantum number
l: Azimuthal quantum number
m: magnetic quantum number

((**Note**)) **Fine structure constant** $\alpha\,(=\frac{e^2}{\hbar c})$

In physics, the fine-structure constant, also known as Sommerfeld's constant, commonly denoted α (the Greek letter *alpha*), is a fundamental physical constant characterizing the strength of the electromagnetic interaction between elementary charged particles. It is related to the elementary charge (the electromagnetic coupling constant) e, which characterizes the strength of the coupling of an elementary charged particle with the electromagnetic field, by the formula $\alpha\,(=e^2/(\hbar c))$. Being a dimensionless quantity, it has the same numerical value in all systems of units. Arnold Sommerfeld introduced the fine-structure constant in 1916.
https://en.wikipedia.org/wiki/Fine-structure_constant

2. Hydrogen fine structure

The Schrödinger solution gives a very good description of the hydrogen atom. The motion of electrons is treated as a non-relativistic particle. In reality it is not. There are corrections to these values of the energy. From the Dirac's relativistic electron theory, the approximation of the Hamiltonian can be derived as follows.

$$H=\frac{1}{2m_e}\boldsymbol{p}^2-e\phi-\frac{\boldsymbol{p}^4}{8m_e{}^2c^2}+\frac{e\hbar}{4m_e{}^2c^2}\boldsymbol{\sigma}\cdot(\boldsymbol{E}\times\boldsymbol{p})+\frac{e\hbar^2}{8m_e{}^2c^2}\nabla\cdot\boldsymbol{E},$$

where $e>0$.

(i) Third term: relativistic correction

$$\begin{aligned}\sqrt{m_e{}^2c^4+\boldsymbol{p}^2c^2}-m_ec^2&=m_ec^2\sqrt{1+\frac{\boldsymbol{p}^2}{m_e{}^2c^2}}-m_ec^2\\&=m_ec^2[1+\frac{\boldsymbol{p}^2}{2m_e{}^2c^2}-\frac{1}{8}\frac{\boldsymbol{p}^4}{m_e{}^4c^4}+\ldots]-m_ec^2\\&=\frac{\boldsymbol{p}^2}{2m_e}-\frac{1}{8}\frac{\boldsymbol{p}^4}{m_e{}^3c^2}+\ldots\end{aligned}$$

(ii) The fourth term (Thomas correction): spin-orbit interaction

Thomas term = $\frac{e\hbar}{4m_e^2c^2}\boldsymbol{\sigma}\cdot(\boldsymbol{E}\times\boldsymbol{p})$.

For a central potential

$$-e\phi(r)=V(r)=-\frac{e^2}{r}, \qquad \text{or} \qquad \phi(r)=-\frac{1}{e}V(r),$$

where ϕ is the scalar potential, $-e$ is the charge of electron (e>0 here).

$$\boldsymbol{E}=-\nabla\phi=\frac{1}{e}\nabla V(r)=\frac{1}{e}\frac{dV}{dr}\boldsymbol{e}_r=\frac{1}{er}\frac{dV}{dr}\boldsymbol{r},$$

$$\boldsymbol{E}\times\boldsymbol{p}=\frac{1}{er}\frac{dV}{dr}(\boldsymbol{r}\times\boldsymbol{p})=\frac{1}{er}\frac{dV}{dr}\boldsymbol{L},$$

where $\boldsymbol{L}$ is an orbital angular momentum. Then the Thomas term is rewritten as

$$\begin{aligned}\frac{e\hbar}{4m_e^2c^2}\boldsymbol{\sigma}\cdot(\boldsymbol{E}\times\boldsymbol{p}) &= \frac{e\hbar}{4m_e^2c^2}\left(\frac{1}{er}\frac{dV}{dr}\right)\boldsymbol{\sigma}\cdot\boldsymbol{L}\\ &= \frac{1}{2m_e^2c^2}\frac{1}{r}\frac{dV}{dr}\boldsymbol{S}\cdot\boldsymbol{L}\\ &= \frac{e^2}{2m_e^2c^2}\frac{1}{r^3}\boldsymbol{S}\cdot\boldsymbol{L}\end{aligned}$$

(Spin-orbit interaction)

The spin angular momentum is defined by

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

which is an automatic consequence of the Dirac theory.

(iii) The last term is called the Darwin term.

The Darwin term changes the effective potential at the nucleus. It can be interpreted as a smearing out of the electrostatic interaction between the electron and nucleus due to zitterbewegung, or rapid quantum oscillation, of the electron. Sir Charles Galton Darwin (18 December 1887 – 31 December 1962) was an English physicist, the grandson of Charles Darwin.

The Darwin term = $\frac{e\hbar^2}{8m_e{}^2c^2}\nabla\cdot\boldsymbol{E}$

For a hydrogen atom,

$$\nabla\cdot\boldsymbol{E}=\frac{1}{e}\nabla^2V=-e\nabla^2\frac{1}{r}=4\pi e\delta(\boldsymbol{r}).$$

It gives rise to an energy shift (the diagonal matrix element)

$$\int\frac{e^2\hbar^2}{8m_e{}^2c^2}4\pi\delta(\boldsymbol{r})\left|\psi_{nlm}(\boldsymbol{r})\right|^2d\boldsymbol{r}=\int\frac{e^2\hbar^2\pi}{2m_e{}^2c^2}\delta(\boldsymbol{r})\left|\psi_{nlm}(\boldsymbol{r})\right|^2d\boldsymbol{r}$$

which is non-vanishing only for the *s* state.

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3. Relativistic correction

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

$$K=\frac{\boldsymbol{p}^2}{2m_e}-\frac{\boldsymbol{p}^4}{8m_e{}^3c^2}.$$

The first term is the standard non-relativistic expression for kinetic energy. The second term is the lowest-order relativistic correction to this energy. We apply the perturbation theory for this system.

$$\hat{H}=\hat{H}_0+\hat{H}_R=(\frac{\hat{\boldsymbol{p}}^2}{2m_e}-\frac{e^2}{|\hat{\boldsymbol{r}}|})-\frac{\hat{\boldsymbol{p}}^4}{8m_e{}^3c^2}$$

where

$$\hat{H}_0\left|nlm\right\rangle=E_n{}^{(0)}\left|nlm\right\rangle,$$

and

$$\hat{H}_0 = \frac{\hat{\boldsymbol{p}}^2}{2m_e} - \frac{e^2}{|\hat{\boldsymbol{r}}|}, \qquad \hat{H}_R = -\frac{\hat{\boldsymbol{p}}^4}{8m_e{}^3c^2}$$

Noting that

$$\hat{\boldsymbol{p}}^2 = 2m_e(\hat{H}_0 + \frac{e^2}{|\hat{\boldsymbol{r}}|})$$

we calculate the matrix element

$$\begin{aligned}\langle nlm|\hat{\boldsymbol{p}}^4|nlm\rangle &= 4m_e{}^2\langle nlm|(\hat{H}_0 + \frac{e^2}{|\hat{\boldsymbol{r}}|})(\hat{H}_0 + \frac{e^2}{|\hat{\boldsymbol{r}}|})|nlm\rangle \\ &= 4m_e{}^2[\left(E_n{}^{(0)}\right)^2 + 2e^2E_n{}^{(0)}\left\langle\frac{1}{r}\right\rangle_{av} + e^4\left\langle\frac{1}{r^2}\right\rangle_{av}]\end{aligned}$$

((**Comment**))

A. Das, Lectures on Quantum Mechanics 2nd edition (World Scientific, 2003)

As a result, even though the energy levels are degenerate, we can still apply non-degenerate perturbation theory, since the potentially dangerous terms are zero because the numerator vanishes.

Then we have the first order correction to the energy eigenvalue

$$\begin{aligned}\langle nlm|\hat{H}_R|nlm\rangle &= -\frac{1}{8m_e{}^3c^2}\langle nlm|\hat{\boldsymbol{p}}^4|nlm\rangle \\ &= -\frac{1}{2m_ec^2}[\left(E_n{}^{(0)}\right)^2 + 2e^2E_n{}^{(0)}\left\langle\frac{1}{r}\right\rangle_{av} + e^4\left\langle\frac{1}{r^2}\right\rangle_{av}]\end{aligned}$$

Here we use

$$\left\langle\frac{1}{r}\right\rangle_{av} = \frac{1}{n^2a_B},$$

$$\left\langle \frac{1}{r^2} \right\rangle_{av} = \frac{1}{n^3 a_B{}^2 (l+\frac{1}{2})}$$

and

$$E_n{}^{(0)} = -\frac{1}{2} m_e c^2 \frac{\alpha^2}{n^2},$$

where

$$a_B = \frac{\hbar^2}{m_e e^2} \quad \text{(Bohr radius)}, \qquad \alpha = \frac{e^2}{\hbar c} \quad \text{(fine structure constant)}.$$

Then we find that

$$\begin{aligned} E_n{}^{(1)} &= \langle nlm | \hat{H}_{rel} | nlm \rangle \\ &= -\frac{1}{2} m_e c^2 \alpha^4 [\frac{1}{n^3 (l+1/2)} - \frac{3}{4n^4}] \\ &= -\frac{m_e c^2 \alpha^4}{2n^3} (\frac{1}{l+1/2} - \frac{3}{4n}) \\ &= -\frac{m_e c^2 \alpha^4}{8n^4} (\frac{4n}{l+1/2} - 3) \\ &= -\frac{\left(E_n{}^{(0)}\right)^2}{2 m_e c^2} (\frac{4n}{l+1/2} - 3) \\ &= \alpha^2 E_n{}^{(0)} \frac{1}{n} (\frac{1}{l+\frac{1}{2}} - \frac{3}{4n}) \end{aligned}$$

where

$$\left(E_n{}^{(0)}\right)^2 = \frac{1}{4} m_e{}^2 c^4 \frac{\alpha^4}{n^4}. \qquad E_n{}^{(0)} = -\frac{1}{2} m_e c^2 \frac{\alpha^2}{n^2}$$

((Calculation of $E_n{}^{(1)}$)) Hydrogen

	$E_n^{(1)}$
1s ($l = 0$)	-7.30456 cm^{-1}
2s ($l = 0$)	-1.18699 cm^{-1}
2p ($l = 1$)	-0.21305 cm^{-1}
3s ($l = 0$)	-0.378755 cm-1
3p ($l = 1$)	-0.0901798 cm-1
3d ($l = 2$)	-0.0324647
4s ($l = 0$)	-0,165494 cm^{-1}
4p ($l = 1$)	-0.0437513 cm^{-1}
4d ($l = 2$)	-0.094027 cm^{-1}
4f ($l = 3$)	-0.00896766 cm^{-1}

((**Note**)) **Commutation relations**

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

We note that

$$[\hat{\boldsymbol{p}}^2, \hat{L}_x] = [\hat{\boldsymbol{p}}^2, \hat{L}_y] = [\hat{\boldsymbol{p}}^2, \hat{L}_z] = 0$$

$$[\hat{\boldsymbol{p}}^2, \hat{\boldsymbol{L}}^2] = 0$$

since the Hamiltonian of free particle $\hat{H}_{free} = \frac{\hat{\boldsymbol{p}}^2}{2m_e}$ is invariant under the rotation of the system, Then we have

$$[\hat{H}_{free}, \hat{L}_x] = [\hat{H}_{free}, \hat{L}_y] = [\hat{H}_{free}, \hat{L}_z] = 0 .$$

$$[\hat{H}_{free}, \hat{\boldsymbol{L}}^2] = 0$$

These relations lead to the commutation relations

$$[\hat{\boldsymbol{p}}^4, \hat{\boldsymbol{L}}^2] = 0, \qquad [\hat{\boldsymbol{p}}^4, \hat{L}_z] = 0$$

since

$$[\hat{\boldsymbol{p}}^4, \hat{\boldsymbol{L}}^2] = \hat{\boldsymbol{p}}^2[\hat{\boldsymbol{p}}^2, \hat{\boldsymbol{L}}^2] + [\hat{\boldsymbol{p}}^2, \hat{\boldsymbol{L}}^2]\hat{\boldsymbol{p}}^2 = 0$$

$$[\hat{\boldsymbol{p}}^4, \hat{L}_z] = \hat{\boldsymbol{p}}^2[\hat{\boldsymbol{p}}^2, \hat{L}_z] + [\hat{\boldsymbol{p}}^2, \hat{L}_z]\hat{\boldsymbol{p}}^2 = 0$$

Thus we have

$$[\hat{H}_R, \hat{\boldsymbol{L}}^2] = 0, \qquad [\hat{H}_R, \hat{L}_z] = 0$$

Since

$$[\hat{H}_0, \hat{\boldsymbol{L}}^2] = 0, \qquad [\hat{H}_0, \hat{L}_z] = 0$$

with

$$\hat{H}_0 = \frac{\hat{\boldsymbol{p}}^2}{2m_e} - \frac{e^2}{|\hat{\boldsymbol{r}}|}$$

We note that

$$[\hat{H}, \hat{\boldsymbol{L}}^2] = 0, \qquad [\hat{H}, \hat{L}_z] = 0$$

but

$$[\hat{H}_R, \hat{H}] \neq 0$$

((**Perturbation theory-non-degenerate case**))

$|\psi\rangle$ is a simultaneous eigenket of $\hat{H}$, $\hat{\boldsymbol{L}}^2$, and $\hat{L}_z$;

$$\hat{H}|\psi\rangle = E|\psi\rangle, \qquad \hat{\boldsymbol{L}}^2|\psi\rangle = \hbar^2 l(l+1)|\psi\rangle, \qquad \hat{L}_z|\psi\rangle = m\hbar|\psi\rangle$$

We apply the perturbation theory for the non-degenerate case;

$$(\hat{H}_0 + \lambda\hat{H}_R)(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + ...) = (E_n^{(0)} + \lambda E_n^{(1)} + ...)(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + ...)$$

with

$$|\psi_n^{(0)}\rangle = |nlm\rangle$$

0-th order

$$\hat{H}_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle$$

λ-th order

$$\hat{H}_R|\psi_n^{(0)}\rangle + \hat{H}_0|\psi_n^{(1)}\rangle = E_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}|\psi_n^{(0)}\rangle$$

Multiplying $\langle\psi_n^{(0)}|$ from the left-side of this equation

$$\langle\psi_n^{(0)}|\hat{H}_R|\psi_n^{(0)}\rangle + \langle\psi_n^{(0)}|\hat{H}_0|\psi_n^{(1)}\rangle = E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}$$

or

$$\begin{aligned} E_n^{(1)} &= \langle\psi_n^{(0)}|\hat{H}_R|\psi_n^{(0)}\rangle \\ &= \langle nlm|\hat{H}_R|nlm\rangle \\ &= E_n^{(0)}[1 + \alpha^2 \frac{1}{n}(\frac{1}{l+\frac{1}{2}} - \frac{3}{4n})] \end{aligned}$$

The energy depends on both *n* and *l*.

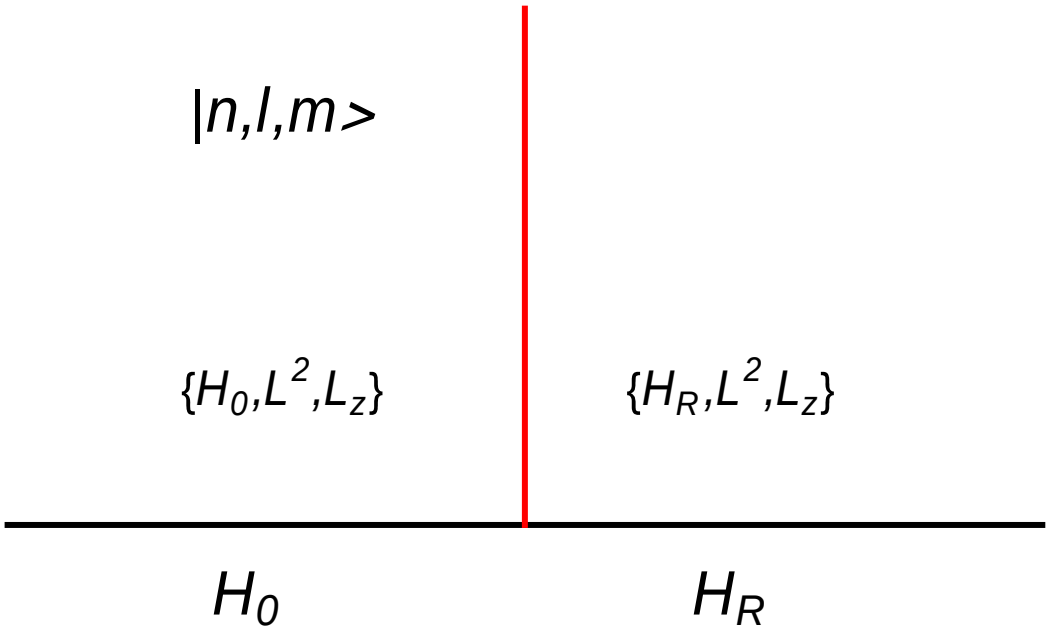

Fig. Effect of perturbation of $\hat{H}_R$. $|nlm\rangle$ is the simultaneous eigenket of $\{\hat{H}_0, \hat{\boldsymbol{L}}^2, \hat{L}_z\}$. We note that $[\hat{H}, \hat{\boldsymbol{L}}^2] = 0$, $[\hat{H}, \hat{L}_z] = 0$, where $\hat{H} = \hat{H}_0 + \hat{H}_R$. Note that. $[\hat{H}_0, \hat{H}_R] \neq 0$. The quantum numbers l and m remain unchanged when $\hat{H}_R$ is added to $\hat{H}_0$. $\hat{H}_R$ is the perturbation. $|nlm\rangle$ is the unperturbed eigenstate.

((**Mathematica**)) Commutation relation
Proof of

$$[\hat{\boldsymbol{p}}^4, \hat{L}_x] = [\hat{\boldsymbol{p}}^4, \hat{L}_y] = [\hat{\boldsymbol{p}}^4, \hat{L}_z] = 0\,, \qquad [\hat{\boldsymbol{p}}^4, \hat{\boldsymbol{L}}^2] = 0\,, \quad [\hat{\boldsymbol{p}}^4, \hat{H}_0] \neq 0$$

```
Clear["Global`"]; ux = {1, 0, 0}; uy = {0, 1, 0}; uz = {0, 0, 1};
r = {x, y, z}; p := (-i ħ Grad[#, {x, y, z}, "Cartesian"] &) // Simplify;
px := (ux.p[#]) &; py := (uy.p[#]) &; pz := (uz.p[#]) &;
L := (-i ħ (Cross[r, Grad[#, {x, y, z}, "Cartesian"]]) &) // Simplify;
Lx := (ux.L[#]) &; Ly := (uy.L[#]) &; Lz := (uz.L[#]) &;
Lsq := (Lx[Lx[#]] + Ly[Ly[#]] + Lz[Lz[#]]) &;
Psq := (px[px[#]] + py[py[#]] + pz[pz[#]]) &; Pf := Psq[Psq[#]] &;
H1 := (1/(2 m) Psq[#] - q^2/(x^2 + y^2 + z^2)^(1/2) #) &;
```

```
Pf[Lz[ψ[x, y, z]]] - Lz[Pf[ψ[x, y, z]]] // Simplify
```

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0
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Pf[Lx[ψ[x, y, z]]] - Lx[Pf[ψ[x, y, z]]] // Simplify
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0
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Pf[Ly[ψ[x, y, z]]] - Ly[Pf[ψ[x, y, z]]] // Simplify
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0
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```
Pf[Lsq[ψ[x, y, z]]] - Lsq[Pf[ψ[x, y, z]]] // Simplify
```

```
0
```

```
Pf[H1[ψ[x, y, z]]] - H1[Pf[ψ[x, y, z]]] // Simplify
```

$$\frac{1}{\left(x^2+y^2+z^2\right)^{5/2}}$$

$$4\,q^2\,\hbar^4\,\Big(\left(x^2+y^2-2\,z^2\right)\psi^{(0,0,2)}[x,y,z]+z\left(x^2+y^2+z^2\right)\psi^{(0,0,3)}[x,y,z]-$$
$$6\,y\,z\,\psi^{(0,1,1)}[x,y,z]+x^2\,y\,\psi^{(0,1,2)}[x,y,z]+y^3\,\psi^{(0,1,2)}[x,y,z]+$$
$$y\,z^2\,\psi^{(0,1,2)}[x,y,z]+x^2\,\psi^{(0,2,0)}[x,y,z]-2\,y^2\,\psi^{(0,2,0)}[x,y,z]+$$
$$z^2\,\psi^{(0,2,0)}[x,y,z]+x^2\,z\,\psi^{(0,2,1)}[x,y,z]+y^2\,z\,\psi^{(0,2,1)}[x,y,z]+$$
$$z^3\,\psi^{(0,2,1)}[x,y,z]+x^2\,y\,\psi^{(0,3,0)}[x,y,z]+y^3\,\psi^{(0,3,0)}[x,y,z]+$$
$$y\,z^2\,\psi^{(0,3,0)}[x,y,z]-6\,x\,z\,\psi^{(1,0,1)}[x,y,z]+x^3\,\psi^{(1,0,2)}[x,y,z]+$$
$$x\,y^2\,\psi^{(1,0,2)}[x,y,z]+x\,z^2\,\psi^{(1,0,2)}[x,y,z]-6\,x\,y\,\psi^{(1,1,0)}[x,y,z]+$$
$$x^3\,\psi^{(1,2,0)}[x,y,z]+x\,y^2\,\psi^{(1,2,0)}[x,y,z]+x\,z^2\,\psi^{(1,2,0)}[x,y,z]-$$
$$2\,x^2\,\psi^{(2,0,0)}[x,y,z]+y^2\,\psi^{(2,0,0)}[x,y,z]+z^2\,\psi^{(2,0,0)}[x,y,z]+$$
$$x^2\,z\,\psi^{(2,0,1)}[x,y,z]+y^2\,z\,\psi^{(2,0,1)}[x,y,z]+z^3\,\psi^{(2,0,1)}[x,y,z]+$$
$$x^2\,y\,\psi^{(2,1,0)}[x,y,z]+y^3\,\psi^{(2,1,0)}[x,y,z]+y\,z^2\,\psi^{(2,1,0)}[x,y,z]+$$
$$x^3\,\psi^{(3,0,0)}[x,y,z]+x\,y^2\,\psi^{(3,0,0)}[x,y,z]+x\,z^2\,\psi^{(3,0,0)}[x,y,z]\Big)$$

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4. Spin-orbit coupling (see the detail for the section of spin-orbit interaction)

We introduce a new Hamiltonian given by

$$\hat{H}=\hat{H}_0+\hat{H}_{so},$$

The total angular momentum J is the addition of the orbital angular momentum and the spin angular momentum,

$$\hat{\boldsymbol{J}}=\hat{\boldsymbol{L}}+\hat{\boldsymbol{S}},$$

The spin-orbit interaction is defined by

$$\hat{H}_{so}=\xi\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}=\xi\frac{1}{2}(\hat{\boldsymbol{J}}^2-\hat{\boldsymbol{L}}^2-\hat{\boldsymbol{S}}^2).$$

where

$$\hat{\boldsymbol{L}}\times\hat{\boldsymbol{L}}=i\hbar\hat{\boldsymbol{L}},\qquad\qquad\hat{\boldsymbol{S}}\times\hat{\boldsymbol{S}}=i\hbar\hat{\boldsymbol{S}}$$

The unperturbed Hamiltonian $\hat{H}_0$ commutes with all the components of $\hat{\boldsymbol{L}}$ and $\hat{\boldsymbol{S}}$.

$$[\hat{H}_0, \hat{\boldsymbol{L}}^2] = [\hat{H}_0, \hat{L}_z{}^2] = [\hat{H}_0, \hat{L}_z] = 0,$$

$$[\hat{H}_0, \hat{\boldsymbol{S}}^2] = [\hat{H}_0, \hat{S}_z{}^2] = [\hat{H}_0, \hat{S}_z] = 0,$$

and

$$[\hat{H}_0, \hat{J}_z] = [\hat{H}_0, \hat{L}_z + \hat{S}_z] = 0$$

We note that

$$\begin{aligned}[\hat{H}_0, \hat{H}_{so}] &= [\hat{H}_0, \xi\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}] \\ &= [\hat{H}_0, \xi(\hat{L}_x\hat{S}_x + \hat{L}_y\hat{S}_y + \hat{L}_z\hat{S}_z)] \\ &= 0\end{aligned}$$

Then we have

$$[\hat{H}_0, \hat{\boldsymbol{J}}^2 - \hat{\boldsymbol{L}}^2 - \hat{\boldsymbol{S}}^2] = 0$$

or

$$[\hat{H}_0, \hat{\boldsymbol{J}}^2] = 0$$

We also note that

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

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

$$\begin{aligned}[\hat{\boldsymbol{J}}^2, \hat{J}_z] &= [\hat{\boldsymbol{L}}^2 + \hat{\boldsymbol{S}}^2 + 2\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}, \hat{L}_z + \hat{S}_z] \\ &= 2[\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}, \hat{L}_z + \hat{S}_z] = 0 \\ &= -2[\hat{L}_z, \hat{L}_x]\hat{S}_x + 2[\hat{L}_y, \hat{L}_z]\hat{S}_y - 2\hat{L}_x[\hat{S}_z, \hat{S}_x] + 2\hat{L}_y[\hat{S}_y, \hat{S}_z] \\ &= -2i\hbar\hat{L}_y\hat{S}_x + 2i\hbar\hat{L}_x\hat{S}_y - 2i\hbar\hat{L}_x\hat{S}_y + 2i\hbar\hat{L}_y\hat{S}_x \\ &= 0\end{aligned}$$

Thus we conclude that $|\psi\rangle$ is the simultaneous eigenket of the mutually commuting observables $\{\hat{H}_0, \hat{\boldsymbol{L}}^2, \hat{\boldsymbol{S}}^2, \hat{\boldsymbol{J}}^2, \text{and } \hat{J}_z\}$.

$$\hat{H}_0|\psi\rangle = E_n^{(0)}|\psi\rangle$$

$$\hat{\boldsymbol{L}}^2|\psi\rangle = \hbar^2 l(l+1)|\psi\rangle$$

$$\hat{\boldsymbol{S}}^2|\psi\rangle = \hbar^2 s(s+1)|\psi\rangle$$

$$\hat{\boldsymbol{J}}^2|\psi\rangle = \hbar^2 j(j+1)|\psi\rangle$$

$$\hat{J}_z|\psi\rangle = \hbar m|\psi\rangle .$$

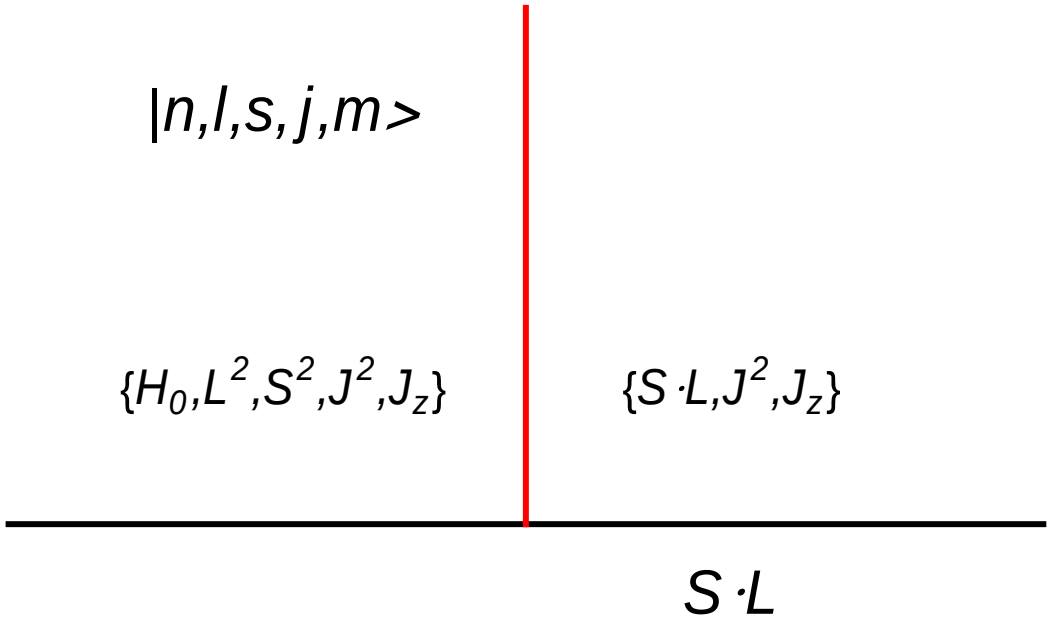


Fig. Perturbation due to the spin-orbit interaction. $|n,l,s,j,m\rangle$ is the simultaneous eigenkets of $\hat{H}_0, \hat{\boldsymbol{L}}^2, \hat{\boldsymbol{S}}^2, \hat{\boldsymbol{J}}^2$, and $\hat{J}_z$ without spin-orbit interaction. When the spin-orbit interaction is switched on, $\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}$ mixes states of same j, m and different m_l and m_s. $[\hat{H}, \hat{\boldsymbol{J}}^2] = 0$. $[\hat{H}, \hat{J}_z] = 0$. $\hat{H}$ is the total Hamiltonian.

The eigenket can be described by

$$|\psi\rangle = |j,m;l,s\rangle$$

Note that the expression of the state can be formulated using the Clebsch-Gordan coefficient (which will be discussed later). The value of j is related to l and s (=1/2) as

$$j = l + s = l + \frac{1}{2}, \qquad j = l - s = l - \frac{1}{2}.$$

When the spin orbit interaction is the perturbation Hamiltonian, we can apply the degenerate theory for the perturbation theory.

$$\begin{aligned}\hat{H}_{so}|j,m;l,s\rangle &= \frac{\xi}{2}(\hat{\boldsymbol{J}}^2 - \hat{\boldsymbol{L}}^2 - \hat{\boldsymbol{S}}^2)|j,m;l,s\rangle \\ &= \frac{\xi\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)|j,m;l,s\rangle \\ &= E_{so}{}^{(1)}|j,m;l,s\rangle\end{aligned}$$

where

$$E_{so}{}^{(1)} = \frac{\xi\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)]$$

with s = 1/2. Here we note that

$$\begin{aligned}\xi &= \frac{e^2}{2m_e{}^2c^2}\left\langle\frac{1}{r^3}\right\rangle_{av} \\ &= \frac{e^2}{2m_e{}^2c^2}\frac{1}{l(l+1/2)(l+1)n^3a_B{}^3} \\ &= \frac{1}{2}m_ec^2\frac{\alpha^4}{\hbar^2}\frac{1}{l(l+1/2)(l+1)n^3}\end{aligned}$$

where

$$\left\langle\frac{1}{r^3}\right\rangle_{av} = \frac{1}{l(l+1/2)(l+1)n^3a_B{}^3}.$$

with

$$a_B = \frac{\hbar^2}{m_e e^2}, \qquad \alpha = \frac{e^2}{\hbar c}$$

Then we have

$$\begin{aligned} E_{so}^{(1)} &= \frac{\xi\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1) \\ &= \frac{1}{4} m_e c^2 \alpha^4 \frac{[j(j+1) - l(l+1) - s(s+1)]}{n^3 l(l+1/2)(l+1)} \\ &= \frac{1}{2} m_e c^2 \frac{\alpha^4}{n^3} \frac{[j(j+1) - l(l+1) - \frac{3}{4}]}{2l(l+1/2)(l+1)} \end{aligned}$$

When $j = l + \frac{1}{2}$

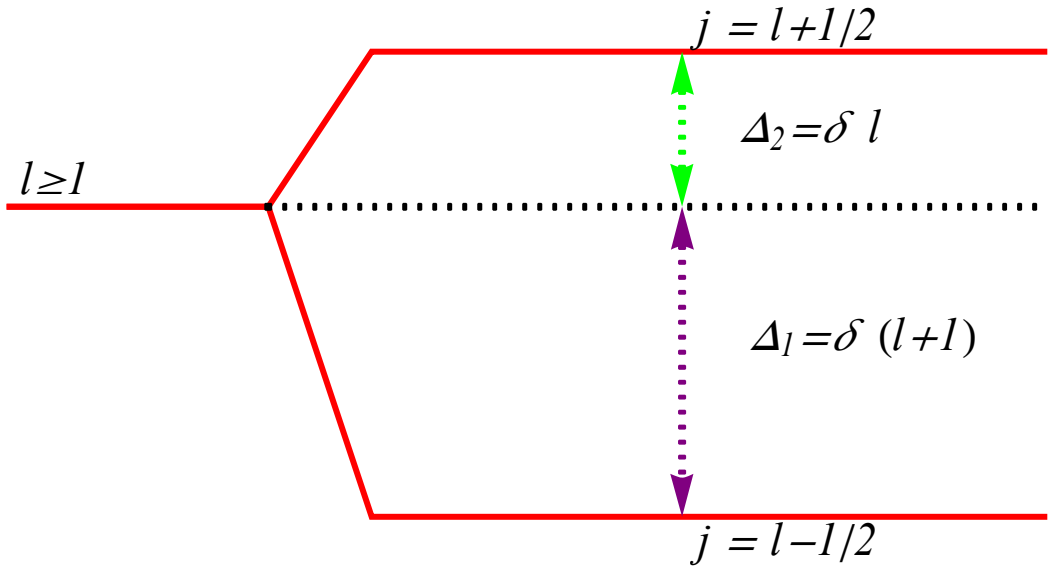
$$\begin{aligned} E_{so}^{(1)} &= \frac{1}{2} m_e c^2 \frac{\alpha^4}{n^3} \frac{l}{2l(l+1/2)(l+1)} \\ &= -\frac{E_n^{(0)}}{2} \alpha^2 \frac{l}{nl(l+1/2)(l+1)} \end{aligned}$$

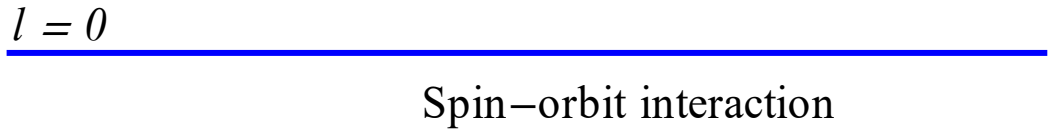
When $j = l - \frac{1}{2}$

$$\begin{aligned} E_{so}^{(1)} &= \frac{1}{2} m_e c^2 \frac{\alpha^4}{n^3} \frac{-(l+1)}{2l(l+1/2)(l+1)} \\ &= \frac{E_n^{(0)}}{2} \alpha^2 \frac{l+1}{nl(l+1/2)(l+1)} \end{aligned}$$

where

$$E_n^{(0)} = -\frac{1}{2} m_e c^2 \frac{\alpha^2}{n^2}.$$





Spin−orbit interaction

4. Darwin term

The additional perturbation of the Darwin term is given by

$$\hat{H}_D = -\frac{1}{8m_e{}^2c^2}[\hat{\boldsymbol{p}}\cdot,[\hat{\boldsymbol{p}},V(|\hat{\boldsymbol{r}}|)]$$

The first-order energy shift due to the Darwin term is

$$
\begin{aligned}
E_D^{(1)} &= \langle n,l,m|\hat{H}_D|n,l,m\rangle \\
&= -\frac{1}{8m_e{}^2c^2}\langle n,l,m|[\hat{\boldsymbol{p}}\cdot,[\hat{\boldsymbol{p}},V(|\hat{\boldsymbol{r}}|)]]|n,l,m\rangle \\
&= -\frac{1}{8m_e{}^2c^2}\int d\boldsymbol{r}\int d\boldsymbol{r}'\langle n,l,m|\boldsymbol{r}\rangle\langle \boldsymbol{r}|[\hat{\boldsymbol{p}}\cdot,[\hat{\boldsymbol{p}},V(|\hat{\boldsymbol{r}}|)]]|\boldsymbol{r}'\rangle\langle \boldsymbol{r}'|n,l,m\rangle \\
&= -\frac{1}{8m_e{}^2c^2}\int d\boldsymbol{r}\psi_{nlm}{}^*(\boldsymbol{r})[\boldsymbol{p}\cdot,[\boldsymbol{p},V(r)]]\psi_{nlm}(\boldsymbol{r}) \\
&= -\frac{1}{8m_e{}^2c^2}\int d\boldsymbol{r}\psi_{nlm}{}^*(\boldsymbol{r})[\boldsymbol{p}\cdot,[\boldsymbol{p},V(r)]]\psi_{nlm}(\boldsymbol{r}) \\
&= -\frac{1}{8m_e{}^2c^2}\int d\boldsymbol{r}\psi_{nlm}{}^*(\boldsymbol{r})[-\hbar^2\psi_{nlm}(\boldsymbol{r})]\nabla^2V(\boldsymbol{r}) \\
&= \frac{\hbar^2}{8m_e{}^2c^2}\int d\boldsymbol{r}|\psi_{nlm}(\boldsymbol{r})|^2\nabla^2V(\boldsymbol{r})
\end{aligned}
$$

The potential energy is given by the Coulomb energy

$$V(\boldsymbol{r}) = -\frac{e^2}{r}.$$

Noting that

$$\nabla^2\frac{1}{r} = -4\pi\delta(\boldsymbol{r}),$$

we get

$$
\begin{aligned}
E_D{}^{(1)} &= \frac{-\hbar^2e^2}{8m_e{}^2c^2}\int d\boldsymbol{r}|\psi_{nlm}(\boldsymbol{r})|^2\nabla^2(\frac{1}{r}) \\
&= \frac{\pi\hbar^2e^2}{2m_e{}^2c^2}\int d\boldsymbol{r}|\psi_{nlm}(\boldsymbol{r})|^2\delta(\boldsymbol{r}) \\
&= \frac{\pi\hbar^2e^2}{2m_e{}^2c^2}|\psi_{nlm}(\boldsymbol{r}=0)|^2
\end{aligned}
$$

We note that only $l = 0$ states are nonzero of the wave function at the origin. This implies that the Darwin term contributes only for the *s* states.

$$
\begin{aligned}
E_D^{(1)} &= \langle n,0,0|\hat{H}_D|n,0,0\rangle \\
&= \frac{\pi\hbar^2 e^2}{2m_e{}^2c^2}\left|\psi_{n00}(\boldsymbol{r}=0)\right|^2 \\
&= \frac{\pi\hbar^2 e^2}{2m_e{}^2c^2}\left|R_{n0}(r=0)\right|^2\left|Y_0^0(\theta,\phi)\right|^2 \\
&= \frac{\hbar^2 e^2}{8m_e{}^2c^2}\frac{4}{n^3 a_B{}^3} \\
&= \frac{m_e c^2}{2n^3}\alpha^4
\end{aligned}
$$

where

$$
Y_0^0(\theta,\phi) = \frac{1}{2\sqrt{\pi}},
$$

$$
\left|R_{n0}(r=0)\right|^2 = \frac{4}{n^3 a_B^3},
$$

and

$$
a_B = \frac{\hbar^2}{m_e e^2}. \qquad\qquad \alpha = \frac{e^2}{\hbar c}
$$

((**Mathematica**)) Proof

The proof of the formula by using the Mathematica.

$$
\{[p_x,[p_x,V(\boldsymbol{r})]+[p_y,[p_y,V(\boldsymbol{r})]+[p_z,[p_z,V(\boldsymbol{r})]\}\psi(\boldsymbol{r}) = -\hbar^2\psi(\boldsymbol{r})\nabla^2 V(\boldsymbol{r})
$$

where

$$
p_x = \frac{\hbar}{i}\frac{\partial}{\partial x}, \qquad p_y = \frac{\hbar}{i}\frac{\partial}{\partial y}, \qquad p_z = \frac{\hbar}{i}\frac{\partial}{\partial z},
$$

In the following mathematica, we use the unit of $\hbar = 1$.

```
Clear["Global`"];

SetCoordinates[Cartesian[x, y, z]];

ux = {1, 0, 0}; uy = {0, 1, 0}; uz = {0, 0, 1};

Px := (-i) ux.Grad[#] & // Simplify;

Py := (-i) uy.Grad[#] & // Simplify;

Pz := (-i) uz.Grad[#] & // Simplify;

f1 = Px[Px[V[x, y, z] ψ[x, y, z]]] - Px[V[x, y, z] Px[ψ[x, y, z]]] +
   Py[Py[V[x, y, z] ψ[x, y, z]]] - Py[V[x, y, z] Py[ψ[x, y, z]]] +
   Pz[Pz[V[x, y, z] ψ[x, y, z]]] - Pz[V[x, y, z] Pz[ψ[x, y, z]]] -
   (Px[V[x, y, z] Px[ψ[x, y, z]]] - V[x, y, z] Px[Px[ψ[x, y, z]]] +
     Py[V[x, y, z] Py[ψ[x, y, z]]] - V[x, y, z] Py[Py[ψ[x, y, z]]] +
     Pz[V[x, y, z] Pz[ψ[x, y, z]]] - V[x, y, z] Pz[Pz[ψ[x, y, z]]]) //
  FullSimplify
```

$$-\psi[x, y, z]\left(V^{(0,0,2)}[x, y, z] + V^{(0,2,0)}[x, y, z] + V^{(2,0,0)}[x, y, z]\right)$$

5. Summary

The sum of the relativistic correction, the spin coupling for $l \neq 0$ is given by

$$\begin{aligned}
E_n^{(1)} &= E_{rel}^{(1)} + E_{so}^{(1)} \\
&= -\frac{\alpha^4}{2n^3} m_e c^2 \left(\frac{1}{l+1/2} - \frac{3}{4n}\right) \\
&\quad + \frac{\alpha^4}{4n^3} m_e c^2 \frac{[j(j+1) - l(l+1) - \frac{3}{4}]}{l(l+1/2)(l+1)} \\
&= \frac{1}{2} m_e c^2 \frac{\alpha^4}{n^3} \left[-\frac{1}{l+1/2} + \frac{3}{4n} + \frac{j(j+1) - l(l+1) - \frac{3}{4}}{2l(l+1)(l+1/2)}\right] \\
&= \frac{1}{2} m_e c^2 \frac{\alpha^4}{n^3} \left[-\frac{1}{j+1/2} + \frac{3}{4n}\right] \\
&= E_n^{(0)} \alpha^2 \frac{1}{n} \left(\frac{1}{j+1/2} - \frac{3}{4n}\right)
\end{aligned}$$

where

$$j = l \pm \frac{1}{2}$$

This result is intriguing in the sense that although both the spin-orbit interaction and the relativistic corrections individually remove the *l*-degeneracy in the hydrogen levels, when they are combined the total shift depends only on the quantum number *j*.

For $l = 0$, the spin-orbit contribution is zero and instead of it, Darwin term is added to $E_n^{(1)}$,

$$\begin{aligned} E_n^{(1)} &= E_{rel}^{(1)} + E_D^{(1)} \\ &= -\frac{1}{2} m_e c^2 \frac{\alpha^4}{n^3}\left(2 - \frac{3}{4n}\right) + \frac{1}{2} m_e c^2 \frac{\alpha^4}{n^3} \\ &= -\frac{1}{2} m_e c^2 \frac{\alpha^4}{n^3}\left(1 - \frac{3}{4n}\right) \\ &= E_n^{(0)} \alpha^2 \frac{1}{n}\left(1 - \frac{3}{4n}\right) \end{aligned}$$

6. Numerical calculation

(a) $n = 2$

$l = 1$, $m_l = 1, 0, -1$

$s = 1/2$ $m_s = 1/2, -1/2$

We note that

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

Then we have

$j = 3/2$ ($m = 3/2, 1/2, -1/2, -3/2$), $2^2P_{3/2}$

$j = 1/2$ ($m = 1/2, -1/2$), $2^2P_{1/2}$

(b) $n = 2$

$l = 0$, $m_l = 0$

$s = 1/2$ $m_s = 1/2, -1/2$

We note that

$$D_0 \times D_{1/2} = D_{1/2}$$

Then we have

$j = 1/2$ ($m = 1/2, -1/2$), $2^2S_{1/2}$

We apply the above formula to the $n = 2$ levels of hydrogen.

$$E(2^2P_{3/2}) = \alpha^2 E_2^{(0)}(-\frac{3}{4}\frac{1}{4} + \frac{1}{2}\frac{1}{2}) = \frac{1}{16}\alpha^2 E_2^{(0)}$$

$$E(2^2P_{1/2}) = \alpha^2 E_2^{(0)}(-\frac{3}{4}\frac{1}{4} + \frac{1}{2}1) = \frac{5}{16}\alpha^2 E_2^{(0)}$$

$$E(2^2S_{1/2}) = \alpha^2 E_2^{(0)}(-\frac{3}{4}\frac{1}{4} + 1) = \frac{13}{16}\alpha^2 E_2^{(0)}$$

When the Darwin term for $l = 0$ is taken into account,

$$E(2^2P_{1/2}) = \alpha^2 E_2^{(0)}(-\frac{3}{4}\frac{1}{4} + \frac{1}{2}1) = \frac{5}{16}\alpha^2 E_2^{(0)}$$

The energy levels for the $n = 2$ (one electron) are as follows.

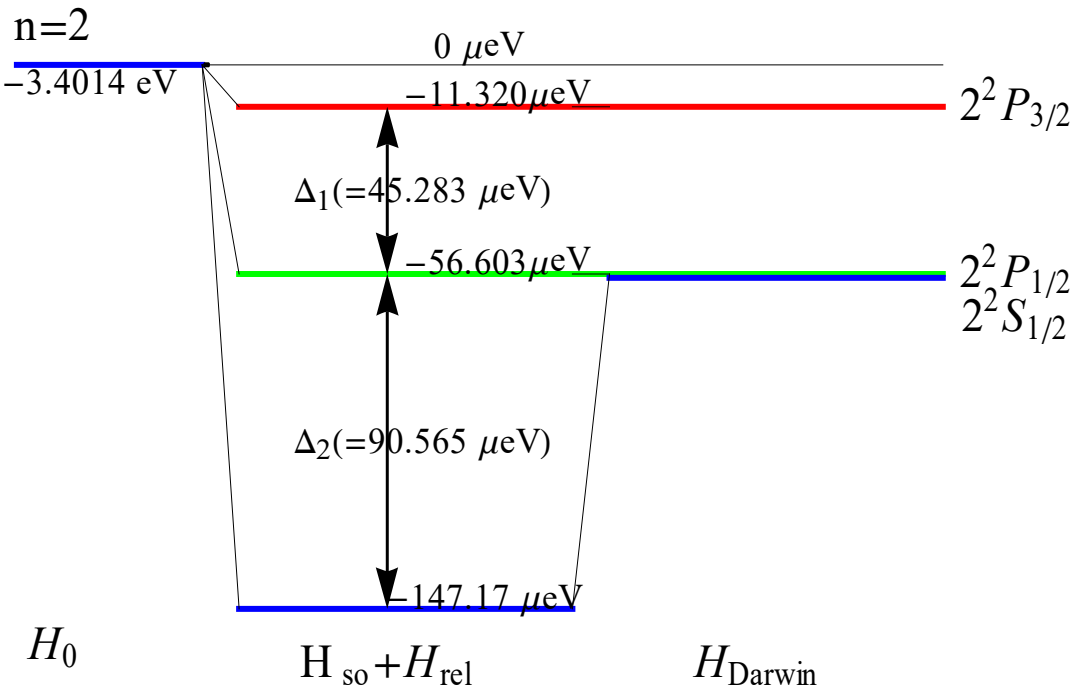


Fig. Hydrogen fine structure in the $n = 2$ level.

---

7. Exact solution from Dirac relativistic theory

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

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

Note that the energy depends only on n and j.

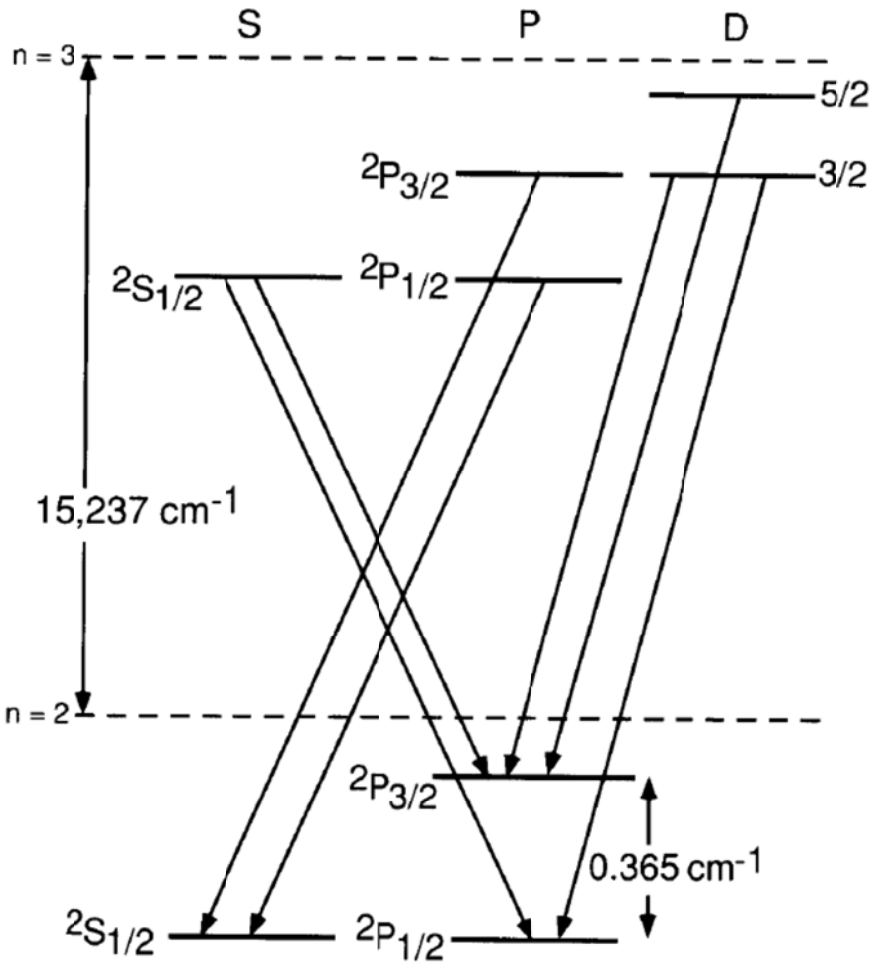


Fig. Energy levels of the hydrogen atom according to the Dirac theory showing the component transition of H_α line. Note that each energy level depends only on the quantum numbers n and j.

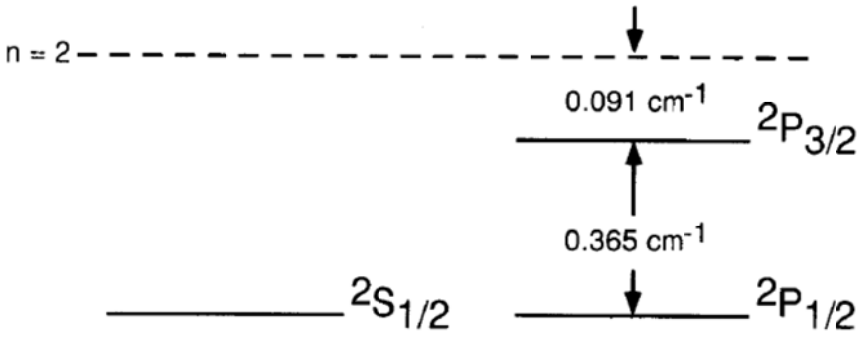


Fig. Fine structure of $n = 2$ levels of hydrogen atom according to the Dirac theory. The dotted line indicates the position of the $n = 2$ level according to the Bohr theory.

((**Series expansion**))

$$\begin{aligned}\Delta E(n,j) &= E(n,j) - E_n^{(0)} \\ &= -\frac{m_e c^2}{2}\frac{\alpha^4}{n^3}\left(\frac{1}{j+1/2} - \frac{3}{4n}\right) + \ldots\ldots \\ &= E_n^{(0)}\frac{\alpha^2}{n}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)\end{aligned}$$

((**Numerical values**))

n	j	$\Delta E(n,j)$ [μeV]
1	1/2	-181.135
2	1/2	-56.6048
2	3/2	-11.3207
3	1/2	-20.1261
3	3/2	-6.70853
3	5/2	-2.23616
4	1/2	-9.19826
4	3/2	-3.53779
4	5/2	-1.65099
4	7/2	-0.707533
5	1/2	-4.92689
5	3/2	-2.02867
5	5/2	-1.06263
5	7/2	-0.579613
5	9/2	-0.289824

((**Mathematica**))

```
E1[n_, j_] := me c^2 (((1 + (α/(n - (j + 1/2) + Sqrt[(j + 1/2)^2 - α^2]))^2)^(-1/2)) - 1);

Series[E1[n, j], {α, 0, 6}] // Simplify[#, j > 0] &
```

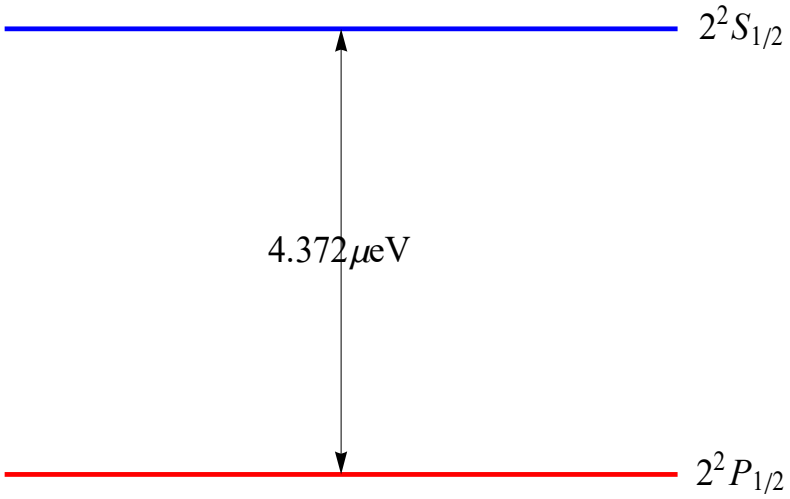
$$-\frac{(c^2\,me)\,\alpha^2}{2\,n^2}+\frac{c^2\,me\,(3+6\,j-8\,n)\,\alpha^4}{8\,(1+2\,j)\,n^4}+\frac{c^2\,me\,\left(-5\,(1+2\,j)^2\,(3+6\,j-8\,n)+32\,(1+2\,j)^2\,n-24\,n^2\,(3+6\,j+2\,n)\right)\alpha^6}{48\,(1+2\,j)^3\,n^6}+O[\alpha]^7$$

8. The Lamb Shift

The **Lamb shift**, named after Willis Lamb (1913–2008), is a small difference in energy between two energy levels $^2S_{1/2}$ and $^2P_{1/2}$ (in term symbol notation) of the hydrogen atom in quantum electrodynamics (QED). According to Dirac, the $^2S_{1/2}$ and $^2P_{1/2}$ orbitals should have the same energies. However, the interaction between the electron and the vacuum causes a tiny energy shift on $^2S_{1/2}$. Lamb and Robert Retherford measured this shift in 1947, and this measurement provided the stimulus for renormalization theory to handle the divergences. It was the harbinger of modern quantum electrodynamics developed by Julian Schwinger, Richard Feynman, and Shin-ichiro Tomonaga. Lamb won the Nobel Prize in Physics in 1955 for his discoveries related to the Lamb shift.

Theoretical and experimental values of the Lamb shift in MHz.

Theoretical	1057.70 ± 0.15 MHz
Experimental	1057.77 ± 0.10 MHz



4.372 μeV
1057.14 MHz
0.0352626 cm^{-1}

((**Experiment**)) Zeeman effect

Landé *g*-factor:

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

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

$$E_1(m_1) = E_1^{(0)} + m_1 g_1 \mu_B B$$

where

$E_1^{(0)}$ = -11.320 μeV

$$g_1 = \frac{4}{3}, \qquad m_1 = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$$

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

$$E_2(m_2) = E_2^{(0)} + m_2 g_2 \mu_B B$$

where

$$E_2^{(0)} = \text{-}56.603\ \mu\text{eV}$$

$$g_2 = 2, \qquad m_2 = \frac{1}{2}, -\frac{1}{2}$$

For $2\ ^2P_{1/2}$

$$E_3(m_3) = E_3^{(0)} + m_3 g_3 \mu_B B$$

where

$$E_3^{(0)} = \text{-}56.603 - 4.372\ \mu\text{eV}$$

$$g_3 = \frac{2}{3}, \qquad m_3 = \frac{1}{2}, -\frac{1}{2}$$

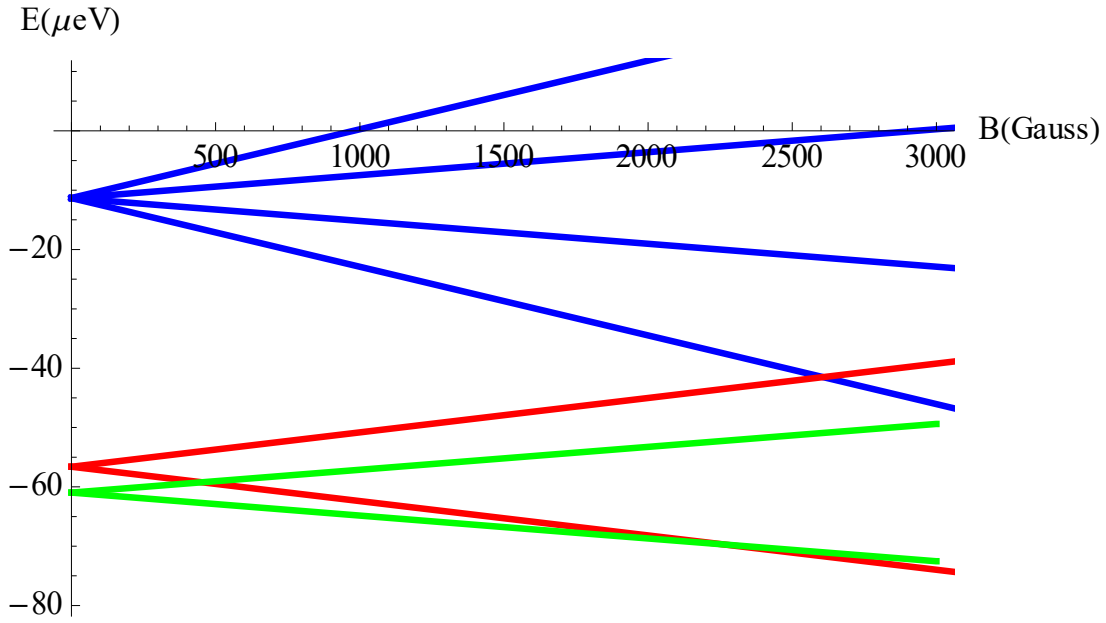


Fig. The Zeeman effect. The energy levels of $^2P_{3/2}$ (blue), $^2S_{1/2}$ (red) and $^2P_{1/2}$ (green). The Lamb shift is taken into account.

((**Experimental results**))
W. Lamb, Novel lecture (1955).

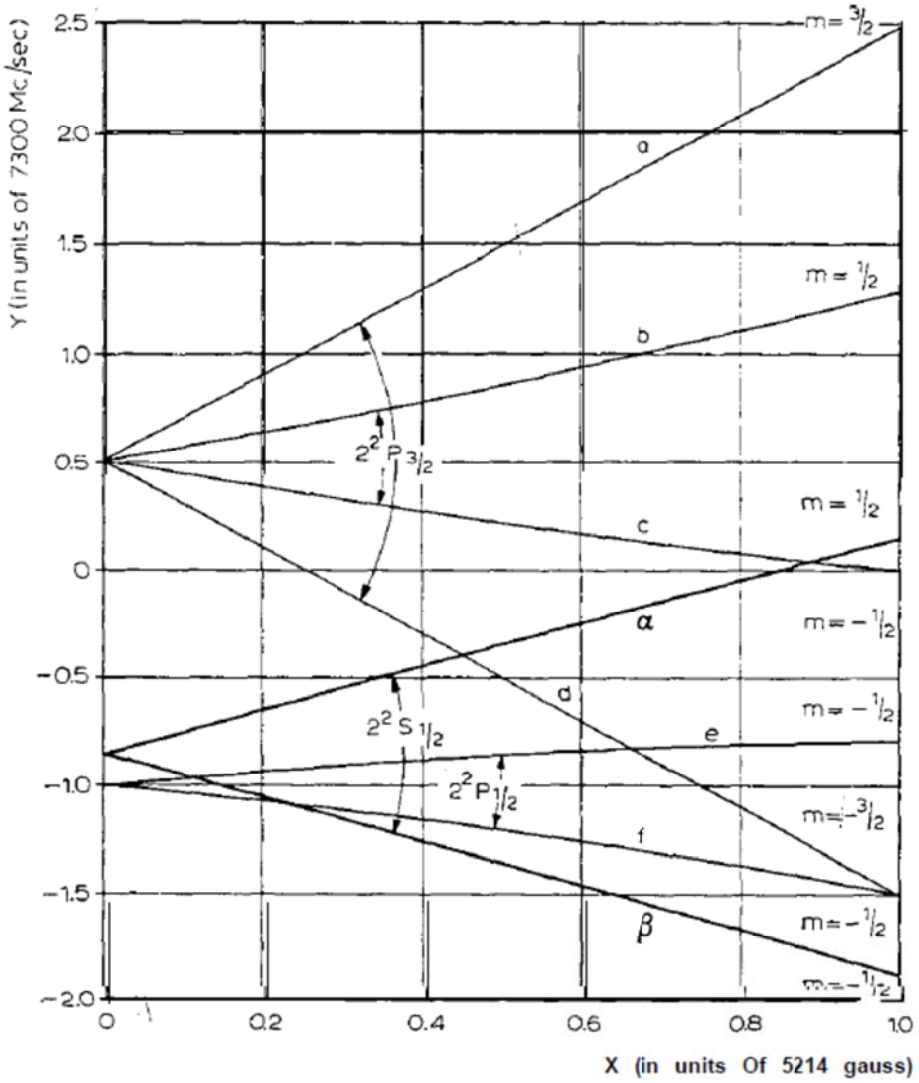
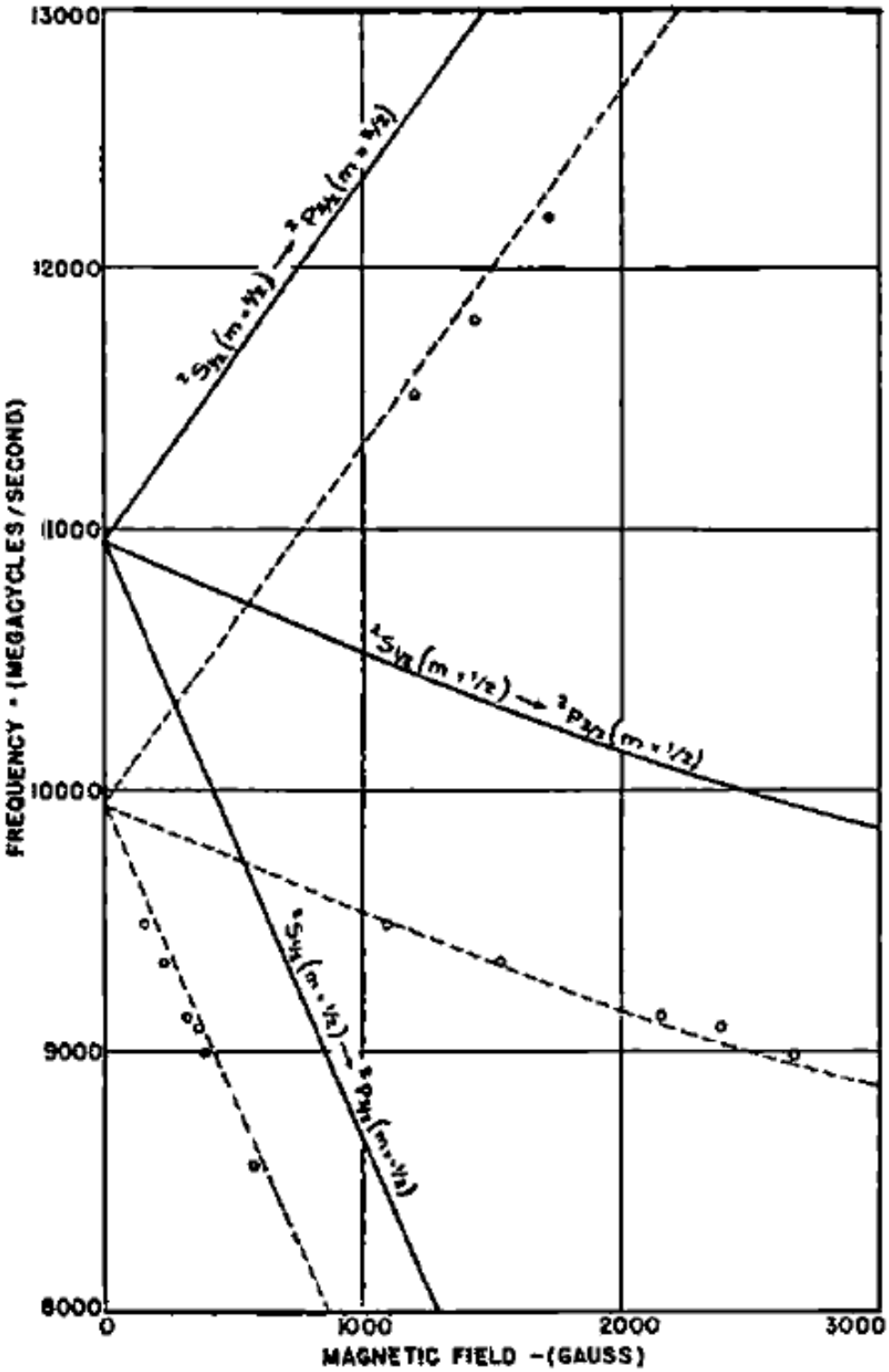

Y (in units of 7300 Mc/sec)
X (in units Of 5214 gauss)
m = 3/2
m = 1/2
m = 1/2
m = −1/2
m = −1/2
m = −3/2
m = −1/2
m = −1/2
a
b
c
d
e
f
α
β
2² P 3/2
2² S 1/2
2² P 1/2
2.5
2.0
1.5
1.0
0.5
0
−0.5
−1.0
−1.5
−2.0
0
0.2
0.4
0.6
0.8
1.0

Fig.



9. Stark effect in Lamb shift

Problem 5-13 (Sakurai and Napolitano)

Sakurai 5-13

Compute the Stark effect for the 2 $S_{1/2}$ and 2 $P_{1/2}$ levels of hydrogen for an electric field ε sufficiently weak that $e\varepsilon a_0$ is small compared to the fine structure, but take the Lamb shift (δ (= 1,057 MHz) into account (that is, ignore 2 $P_{3/2}$ in this calculation). Show that $e\varepsilon a_0 << \delta$, the energy shifts are quadratic in ε, whereas for $e\varepsilon a_0 >> \delta$, they are linear in ε. (The radial integral you need is $\langle 2s|r|2p\rangle = 3\sqrt{3}a_0$) Briefly discuss the consequences (if any) of time reversal for this problem. This problem is from Gottfried 1966, Problem 7-3.

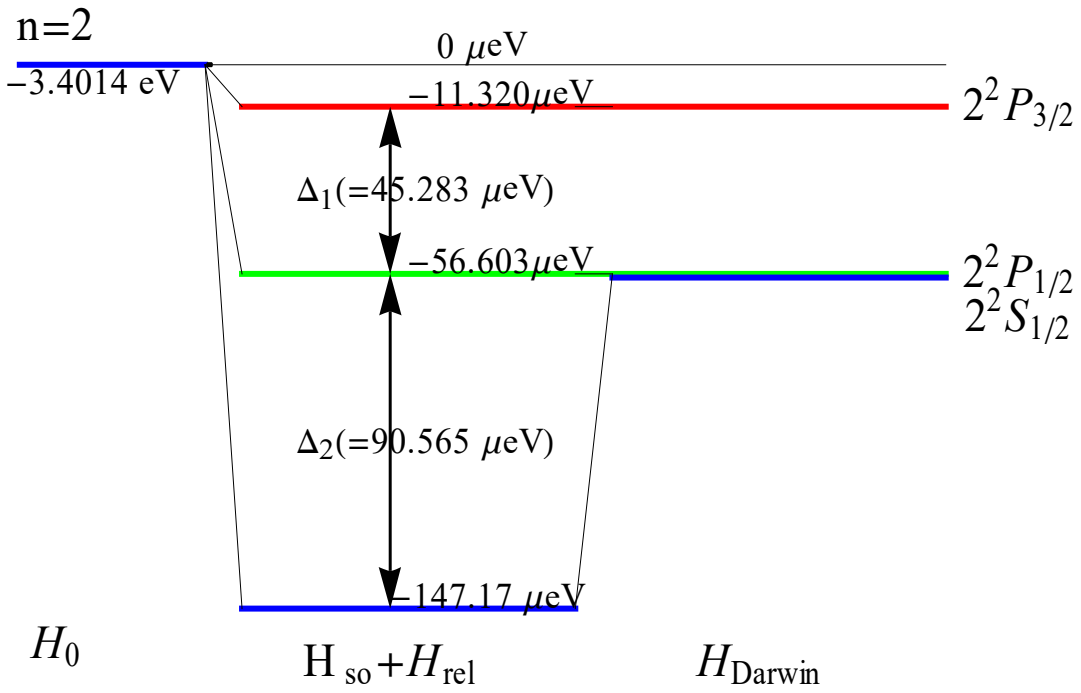


Fig. Energy level of real hydrogen atom. There is a small energy difference between between 2 $^2S_{1/2}$ and 2 $^2P_{1/2}$ (Lamb shift). In Dirac relativistic electron theory of hydrogen, the energy level depends only on the value of j.

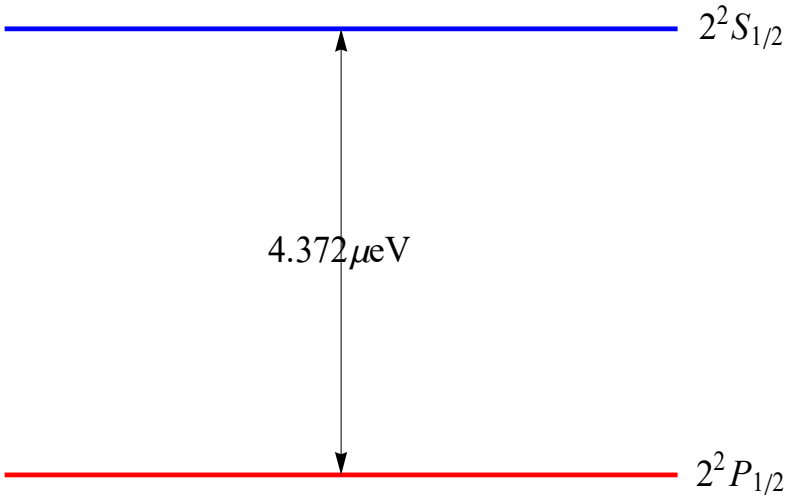


Fig. Lamb shift. There is an energy difference between $2\ ^2S_{1/2}$ and $2\ ^2P_{1/2}$.

Lamb shift: the energy level of $2S_{1/2}$ (doubly degenerate states) is higher than that of $2P_{1/2}$ (doubly degenerate) by δ (= 4.372 x 10^{-6} eV = 1057 MHz).

The perturbation (Stark effect)

$$\hat{H}_1 = e\mathcal{E}\hat{z}$$

where $e>0$. This Hamiltonian is invariant under the time reversal.

We now consider the state with $n = 2$.

$n = 2$ state (4 states degenerate)
$l = 1$ ($m = \pm 1, 0$): p-state
$l = 0$ ($m = 0$): s-state.

$$\langle nl'm'|e\hat{z}|nlm\rangle = \iiint r^2 dr \sin\theta d\theta d\phi R_{nl'}(r) Y_{l'}^{m'}(\theta,\phi) er\cos\theta R_{nl}(r) Y_{l'}^{m}(\theta,\phi)$$

Addition of spin and orbital angular momentum

(i)

$l = 1$, $s = 1/2$

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

$2P_{3/2}$

$j = 3/2$
$m = 3/2,\ 1/2,\ -1/2,$ and $-3/2$

$2P_{1/2}$

$j = 1/2$
$m = 1/2,\ -1/2$

We use the Clebsch-Gordan co-efficient;

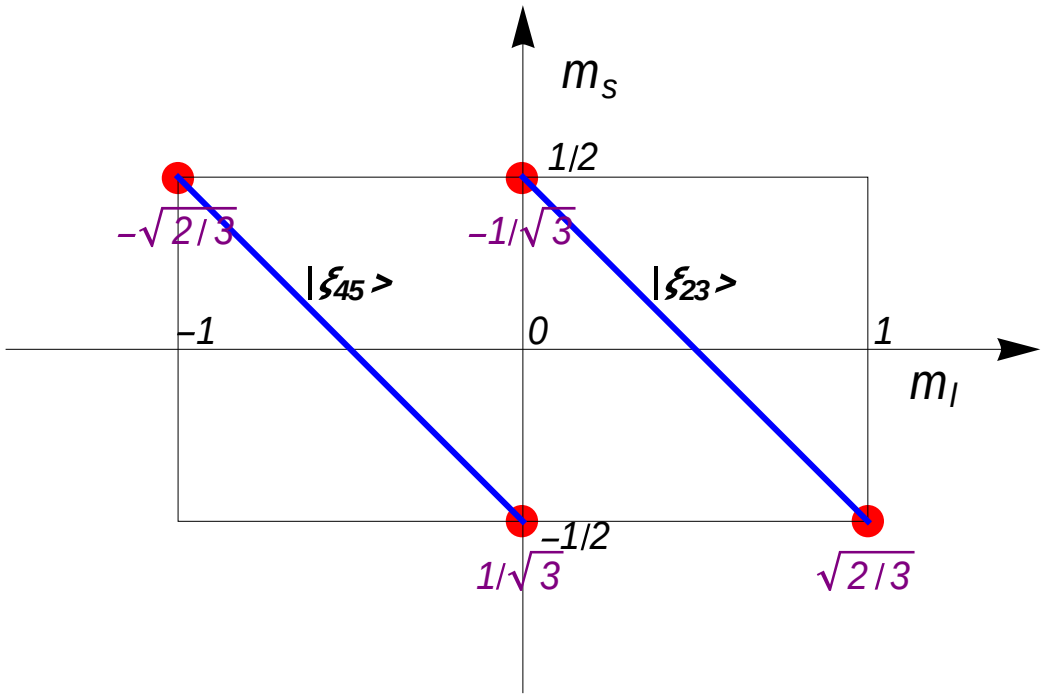


Fig. Clebsch-Gordan co-efficient. $j = \frac{1}{2}.\ l = 1.\ s = \frac{1}{2}.$

$$\left| j = \frac{1}{2}, m = \frac{1}{2} \right\rangle = |\varsigma_{23}\rangle = -\sqrt{\frac{1}{3}} |l = 1, m_l = 0\rangle \otimes |+z\rangle + \sqrt{\frac{2}{3}} |l = 1, m_l = 1\rangle \otimes |-z\rangle$$

and

$$\left|j=\frac{1}{2},m=-\frac{1}{2}\right\rangle=\left|\varsigma_{45}\right\rangle=-\sqrt{\frac{2}{3}}\left|l=1,m_l=-1\right\rangle\otimes\left|+z\right\rangle+\sqrt{\frac{1}{3}}\left|l=1,m_l=0\right\rangle\otimes\left|-z\right\rangle$$

or

$$\left|2P_{1/2};m=1/2\right\rangle=-\sqrt{\frac{1}{3}}\left|n=2,l=1,m=0\right\rangle\otimes\left|+z\right\rangle+\sqrt{\frac{2}{3}}\left|n=2,l=1,m=1\right\rangle\otimes\left|-z\right\rangle$$

$$\left|2P_{1/2},m=-1/2\right\rangle=-\sqrt{\frac{2}{3}}\left|n=2,l=1,m=-1\right\rangle\otimes\left|+z\right\rangle+\sqrt{\frac{1}{3}}\left|n=2,l=1,m=0\right\rangle\otimes\left|-z\right\rangle$$

(ii)

$l = 0$, $s = 1/2$

$$D_0\times D_{1/2}=D_{1/2}$$

$2S_{1/2}$

$j = 1/2$
$m = 1/2, -1/2$

Then we have

$$\left|2S_{1/2},m=1/2\right\rangle=\left|n=2,l=0,m=0\right\rangle\otimes\left|+z\right\rangle$$

$$\left|2S_{1/2},m=-1/2\right\rangle=\left|n=2,l=0,m=0\right\rangle\otimes\left|-z\right\rangle$$

We calculate the matrix elements of the perturbation.

$$\left\langle 2S_{1/2},m=-1/2\left|\hat{z}\right|2S_{1/2},m=-1/2\right\rangle=0$$

$$\left\langle 2S_{1/2},m=1/2\left|\hat{z}\right|2S_{1/2},m=-1/2\right\rangle=0$$

$$\left\langle 2P_{1/2}, m=-1/2 \middle| \hat{z} \middle| 2S_{1/2}, m=-1/2 \right\rangle$$
$$= \sqrt{\frac{1}{3}} \left\langle n=2, l=1, m=0 \middle| \hat{z} \middle| n=2, l=0, m=0 \right\rangle = \alpha$$

$$\left\langle 2P_{1/2}, m=1/2 \middle| \hat{z} \middle| 2S_{1/2}, m=-1/2 \right\rangle$$
$$= \sqrt{\frac{2}{3}} \left\langle n=2, l=1, m=1 \middle| \hat{z} \middle| n=2, l=0, m=0 \right\rangle = 0$$

$$\left\langle 2S_{1/2}, m=-1/2 \middle| \hat{z} \middle| 2S_{1/2}, m=1/2 \right\rangle = 0$$

$$\left\langle 2S_{1/2}, m=1/2 \middle| \hat{z} \middle| 2S_{1/2}, m=1/2 \right\rangle = 0$$

$$\left\langle 2P_{1/2}, m=-1/2 \middle| \hat{z} \middle| 2S_{1/2}, m=1/2 \right\rangle$$
$$= -\sqrt{\frac{2}{3}} \left\langle n=2, l=1, m=-1 \middle| \hat{z} \middle| n=2, l=0, m=0 \right\rangle$$
$$= 0$$

$$\left\langle 2P_{1/2}, m=1/2 \middle| \hat{z} \middle| 2S_{1/2}, m=1/2 \right\rangle$$
$$= -\sqrt{\frac{1}{3}} \left\langle n=2, l=1, m=0 \middle| \hat{z} \middle| n=2, l=0, m=0 \right\rangle$$
$$= \beta$$

Note that the operator $\hat{z}$ is Hermitian. Then we have the matrix of $\hat{H}_1 (= e\varepsilon\hat{z})$ and Lamb shift ($\hat{H}_\delta$).

	$\left\|2P_{1/2}, m=1/2\right\rangle$	$\left\|2P_{1/2}, m=-1/2\right\rangle$	$\left\|2S_{1/2}, m=1/2\right\rangle$	$\left\|2S_{1/2}, m=-1/2\right\rangle$
$\left\langle 2P_{1/2}, m=1/2\right\|$	0	0	$e\varepsilon\beta = \sqrt{3}e\varepsilon a_0$	0
$\left\langle 2P_{1/2}, m=-1/2\right\|$	0	0	0	$e\varepsilon\alpha = -\sqrt{3}e\varepsilon a_0$
$\left\langle 2S_{1/2}, m=1/2\right\|$	$e\varepsilon\beta = \sqrt{3}e\varepsilon a_0$	0	δ	0
$\left\langle 2S_{1/2}, m=-1/2\right\|$	0	$e\varepsilon\alpha = -\sqrt{3}e\varepsilon a_0$	0	δ

where δ is the Lamb shift energy

$$\langle n=2,l=1,m=0|\hat{z}|n=2,l=0,m=0\rangle=-3a_0$$

$$\alpha=\sqrt{\frac{1}{3}}\langle n=2,l=1,m=0|\hat{z}|n=2,l=0,m=0\rangle=-\sqrt{3}a_0$$

$$\beta=-\sqrt{\frac{1}{3}}\langle n=2,l=1,m=0|\hat{z}|n=2,l=0,m=0\rangle=\sqrt{3}a_0$$

The eigenvalue problem

We use the Mathematica

Energy eigenvalue and eigenket with $p=\sqrt{3}e\mathcal{E}a_0$

$$E_1=\frac{\delta}{2}-\frac{\sqrt{4p^2+\delta^2}}{2}$$

$$|\psi_1\rangle=\frac{1}{\sqrt{2+\frac{\delta(\delta+\sqrt{4p^2+\delta^2}}{2p^2}}}[\frac{\delta+\sqrt{4p^2+\delta^2}}{2p}|2P_{1/2},m=-1/2\rangle+|2S_{1/2},m=-1/2\rangle]$$

$$E_2=\frac{\delta}{2}+\frac{\sqrt{4p^2+\delta^2}}{2}$$

$$|\psi_2\rangle=\frac{1}{\sqrt{2+\frac{\delta(\delta+\sqrt{4p^2+\delta^2}}{2p^2}}}[-\frac{\delta+\sqrt{4p^2+\delta^2}}{2p}|2P_{1/2},m=1/2\rangle+|2S_{1/2},m=1/2\rangle]$$

$$E_3=\frac{\delta}{2}+\frac{\sqrt{4p^2+\delta^2}}{2}$$

$$|\psi_3\rangle=\frac{1}{\sqrt{2+\frac{\delta(\delta-\sqrt{4p^2+\delta^2}}{2p^2}}}[\frac{\delta-\sqrt{4p^2+\delta^2}}{2p}|2P_{1/2},m=-1/2\rangle+|2S_{1/2},m=-1/2\rangle]$$

$$E_4 = \frac{\delta}{2} + \frac{\sqrt{4p^2 + \delta^2}}{2}$$

$$|\psi_3\rangle = \frac{1}{\sqrt{2 + \frac{\delta(\delta - \sqrt{4p^2 + \delta^2}}{2p^2}}}[\frac{-\delta + \sqrt{4p^2 + \delta^2}}{2p}|2P_{1/2}, m = 1/2\rangle + |2S_{1/2}, m = 1/2\rangle]$$

The energy levels (E_1=E_2, E_3=E_4) are degenerate. The perturbation (Stark effect) $\hat{H}_1 = e\varepsilon\hat{z}$ is invariant under the time reversal. Since j = 1/2, each level are still doubly degenerate (Kramers doublet).

In the limit of $\delta >> p$

$$E_1 = E_2 = -\frac{p^2}{\delta} + \frac{p^4}{\delta^3}$$
$$E_3 = E_4 = \delta + \frac{p^2}{\delta} - \frac{p^4}{\delta^3}$$

The change of energy is quadratic in ε.

In the limit of $\delta << p$

$$E_1 = E_2 = \frac{\delta}{2} - p + \frac{\delta^2}{8p} + \frac{\delta^4}{128p^3}$$
$$E_3 = E_4 = \frac{\delta}{2} + p + \frac{\delta^2}{8p} - \frac{\delta^4}{128p^3}$$

The change of energy is linear in ε.

((**Mathematica**))

```
(*Sakurai 5-13
   p=√3 e ∈ a0
*)

M = {{0, 0, p, 0}, {0, 0, 0, -p}, {p, 0, δ, 0}, {0, -p, 0, δ}};
M // MatrixForm
```

$$\begin{pmatrix} 0 & 0 & p & 0 \\ 0 & 0 & 0 & -p \\ p & 0 & \delta & 0 \\ 0 & -p & 0 & \delta \end{pmatrix}$$

```
eq1 = Eigensystem[M] // Simplify
```

$$\left\{\left\{\frac{1}{2}\left(\delta-\sqrt{4\,p^2+\delta^2}\right),\ \frac{1}{2}\left(\delta-\sqrt{4\,p^2+\delta^2}\right),\right.\right.$$
$$\left.\left.\frac{1}{2}\left(\delta+\sqrt{4\,p^2+\delta^2}\right),\ \frac{1}{2}\left(\delta+\sqrt{4\,p^2+\delta^2}\right)\right\},$$
$$\left\{\left\{0,\ \frac{\delta+\sqrt{4\,p^2+\delta^2}}{2\,p},\ 0,\ 1\right\},\ \left\{-\frac{\delta+\sqrt{4\,p^2+\delta^2}}{2\,p},\ 0,\ 1,\ 0\right\},\right.$$
$$\left.\left\{0,\ \frac{\delta-\sqrt{4\,p^2+\delta^2}}{2\,p},\ 0,\ 1\right\},\ \left\{\frac{-\delta+\sqrt{4\,p^2+\delta^2}}{2\,p},\ 0,\ 1,\ 0\right\}\right\}\right\}$$

```
(*Normalization*)

E1 = eq1[[1, 1]];

E2 = eq1[[1, 3]]
```

$$\frac{1}{2}\left(\delta + \sqrt{4\,p^2 + \delta^2}\right)$$

```
Simplify[Series[E1, {p, 0, 5}], δ > 0]
```

$$-\frac{p^2}{\delta} + \frac{p^4}{\delta^3} + O[p]^6$$

```
Simplify[Series[E2, {p, 0, 5}], δ > 0]
```

$$\delta + \frac{p^2}{\delta} - \frac{p^4}{\delta^3} + O[p]^6$$

```
Simplify[Series[E1, {δ, 0, 5}], p > 0]
```

$$-p + \frac{\delta}{2} - \frac{\delta^2}{8\,p} + \frac{\delta^4}{128\,p^3} + O[\delta]^6$$

```
Simplify[Series[E2, {δ, 0, 5}], p > 0]
```

$$p + \frac{\delta}{2} + \frac{\delta^2}{8\,p} - \frac{\delta^4}{128\,p^3} + O[\delta]^6$$

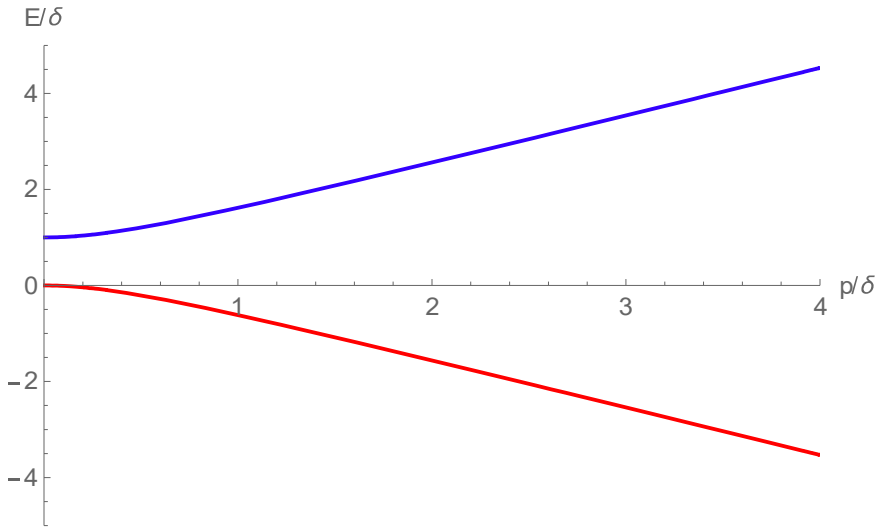
```
E11 = E1 /. δ → 1
```

$$\frac{1}{2}\left(1 - \sqrt{1 + 4\,p^2}\right)$$

```
E21 = E2 /. δ → 1
```

$$\frac{1}{2}\left(1 + \sqrt{1 + 4\,p^2}\right)$$

```
Plot[Evaluate[{E11, E21}], {p, 0, 4},
 PlotRange → {{0, 4}, {-5, 5}}, PlotStyle → {Hue[0], Hue[0.7]},
 Prolog → AbsoluteThickness[1.5], AxesLabel → {"p/δ", "E/δ"}]
```



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APPENDIX-A

Relativistic correction for Na ($Z = 11$)

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

$$K = \frac{\boldsymbol{p}^2}{2m_e} - \frac{\boldsymbol{p}^4}{8m_e{}^3c^2} .$$

The first term is the standard non-relativistic expression for kinetic energy. The second term is the lowest-order relativistic correction to this energy. We apply the perturbation theory for this system.

$$\hat{H} = \hat{H}_0 + \hat{H}_{rel} = (\frac{\hat{\boldsymbol{p}}^2}{2m_e} - \frac{Ze^2}{|\hat{\boldsymbol{r}}|}) - \frac{\hat{\boldsymbol{p}}^4}{8m_e{}^3c^2}$$

where

$$\hat{H}_0 |nlm\rangle = E_n{}^{(0)} |nlm\rangle$$

and

$$\hat{H}_0 = \frac{\hat{\boldsymbol{p}}^2}{2m_e} - \frac{Ze^2}{|\hat{\boldsymbol{r}}|} , \qquad \hat{H}_{rel} = -\frac{\hat{\boldsymbol{p}}^4}{8m_e{}^3c^2}$$

Noting that

$$\hat{\boldsymbol{p}}^2 = 2m_e(\hat{H}_0 + \frac{Ze^2}{|\hat{\boldsymbol{r}}|})$$

we calculate the matrix element

$$\langle nlm|\hat{\boldsymbol{p}}^4|nlm\rangle = 4m_e{}^2\langle nlm|(\hat{H}_0 + \frac{Ze^2}{|\hat{\boldsymbol{r}}|})(\hat{H}_0 + \frac{Ze^2}{|\hat{\boldsymbol{r}}|})|nlm\rangle$$

$$= 4m_e{}^2[\left(E_n{}^{(0)}\right)^2 + 2Ze^2E_n{}^{(0)}\left\langle\frac{1}{r}\right\rangle_{av} + Z^2e^4\left\langle\frac{1}{r^2}\right\rangle_{av}]$$

Then we have the first order correction to the energy eigenvalue

$$\langle nlm|\hat{H}_{rel}|nlm\rangle = -\frac{1}{8m_e{}^3c^2}\langle nlm|\hat{\boldsymbol{p}}^4|nlm\rangle$$
$$= -\frac{1}{2m_ec^2}[\left(E_n{}^{(0)}\right)^2 + 2Ze^2E_n{}^{(0)}\left\langle\frac{1}{r}\right\rangle_{av} + Z^2e^4\left\langle\frac{1}{r^2}\right\rangle_{av}]$$

Here we use

$$\left\langle\frac{1}{r}\right\rangle_{av} = \frac{Z}{n^2a_B},$$

$$\left\langle\frac{1}{r^2}\right\rangle_{av} = \frac{Z^2}{n^3a_B{}^2(l+\frac{1}{2})}$$

and

$$E_n{}^{(0)} = -\frac{1}{2}m_ec^2\frac{Z^2\alpha^2}{n^2}$$

where

$$a_B = \frac{\hbar^2}{m_ee^2} \quad \text{(Bohr radius),} \qquad \alpha = \frac{e^2}{\hbar c} \quad \text{(fine structure constant)}$$

Then we find that

$$E_{rel}{}^{(1)} = E_{rel}(n,l) = -\frac{\left(E_n{}^{(0)}\right)^2}{2m_ec^2}(\frac{4n}{l+1/2}-3)$$

We calculate the wavelength of emitted light between the states of $n = 3$, $l = 1$ and $n = 3$, $l = 0$ for Na (Z = 11);

$$\lambda = \frac{hc}{E_{rel}(3,1) - E_{rel}(3,0)} = 23668.5 \text{ Å} = 4 \text{ x } 5890 \text{ Å}.$$

APPENDIX-B

B-1 Lamb's report

The Lamb Shift and the Magnetic Moment of the Electron

(S.S. Schweber, QED and the men who made it: Dyson, Feynman , Schwinger, and Tomonaga, Chapter 5, p.206).

Molecular hydrogen is thermally dissociation in a tungsten oven, and a jet of atoms emerges from a slit to be cross-bombarded by an electron stream. About one part in a hundred million of the atoms is thereby excited to the metastable $2^2S_{1/2}$ state. The metastable atoms (with small recoil deflection) move on out of the bombardment region and are detected by the process of electron ejection from a metal target. The electron current is measured with an FP-54 electrometer tube and a sensitive galvanometer. If the beam of metastable atoms is subjected to any perturbing fields which may cause a transition to any of the 2^2P states, the atom will decay while moving through a very small distance. As a result, the beam current will decrease, since the detector does not respond to atoms in the ground state. Transitions may be induced by radiofrequency radiation for which $h\nu$ corresponds to the energy difference between one of the Zeeman components of $2^2S_{1/2}$ and any component of either $2^2P_{1/2}$ or $2^2P_{3/2}$. Such measurements provide a precise method for the location of $2^2S_{1/2}$ state relative to the P states, as well as the distance between the later states.

We have observed an electrometer current of the order of 10^{-14} A which must be ascribed to metastable hydrogen atoms. We have also observed the decrease in the beam of metastable atoms caused by microwaves in the wave length range 2.4 to 18.5 cm in various magnetic fields. The results indicate clearly that, contrary to theory but in essential agreement with Pasternack's hypothesis, the $2^2S_{1/2}$ state is higher than $2^2P_{1/2}$ by about 1000 MHz (0.033 cm^{-1}).
[October 1946 to March 1948].

B-2 Beth's calculation

(S.S. Schweber, QED and the men who made it: Dyson, Feynman , Schwinger, and Tomonaga, Chapter 5, p.231).

The actual calculation of the nonrelativistic Lamb shift was made on a train ride from New York to Schenectady. Bethe had stayed in New York after the Shelter Island Conference to visit his mother, and had gone on to Schenectady to consult for General Electric. The calculation is

straightforward (Beth 1947). The self-energy of an electron in a quantum state m, due to its interaction with the radiation field, is

$$W = \frac{8}{3\pi}\left(\frac{e^2}{\hbar c}\right)^3 Ry \frac{Z^4}{n^3} \ln \frac{K}{< E_n - E_m >_{ave}}$$

where Ry is the Rydberg energy $\alpha^2 \frac{1}{2} mc^2$, $\alpha = \frac{e^2}{\hbar c}$. This is the expression that Bethe had obtained on his arrival at Schenectady. He was not quite confident of its accuracy, because he was not quite sure of the correctness of a factor of $\sqrt{2}$ in his expansion of the radiation operators in terms of creation and annihilation operators. This he checked on Monday morning in Heitler's book. He also got Miss Steward and Dr. Stehn from GE to evaluate numerically $< E_n - E_m >_{ave}$ for the 2s state. It was found to be 17.8 Ry, "an amazingly high value. Inserting this into the above equation Bethe found W_{2s} = 1040 MHz, "in excellent agreement with the observed value of 1000 MHz" (Bethe, 1947).

((**Note**))
The expression of the frequency for the Lamb shift (the non-relativistic case) (for n = 2), can be expressed as

$$\nu = \frac{\alpha^5 m_e c^3}{12\pi^2 \hbar c} \ln\left(\frac{1}{8.9\alpha^2}\right) = 1038.27 \text{ MHz.}$$

http://quantummechanics.ucsd.edu/ph130a/130_notes/node476.html

((**Mathematica**))

```
Clear["Global`*"];

rule1 = {c → 2.99792 × 10^10,
    ħ → 1.054571628 10^-27,
    me → 9.10938215 10^-28,
    α → 7.2973525376 × 10^-3, MHz → 10^6};

(α^5 me c^3 / (12 π^2 ħ c) Log[1 / (8.9 α^2)]) / MHz /. rule1 //
 N

1038.27
```

B-3 Feynman's Nobel Lecture:

R.P. Feynman, Nobel Lecture, December 11, 1965

The development of the space-time view of quantum electrodynamics.

Then Lamb did his experiment, measuring the separation of the $2^2S_{1/2}$ and $2^2P_{1/2}$ levels of hydrogen, finding it to be about 1000 megacycles of frequency difference. Professor Bethe, with whom I was then associated at Cornell, is a man who has this characteristic: If there's a good experimental number you've got to figure it out from theory. So, he forced the quantum electrodynamics of the day to give him an answer to the separation of these two levels. He pointed out that the self-energy of an electron itself is infinite, so that the calculated energy of a bound electron should also come out infinite. But, when you calculated the separation of the two energy levels in terms of the corrected mass instead of the old mass, it would turn out, he thought, that the theory would give convergent finite answers. He made an estimate of the splitting that way and found out that it was still divergent, but he guessed that was probably due to the fact that he used an un-relativistic theory of the matter. Assuming it would be convergent if relativistically treated, he estimated he would get about a thousand megacycles for the Lamb-shift, and thus, made the most important discovery in the history of the theory of quantum electrodynamics. He worked this out on the train from Ithaca, New York to Schenectady and telephoned me excitedly from Schenectady.

APPENDIX-C

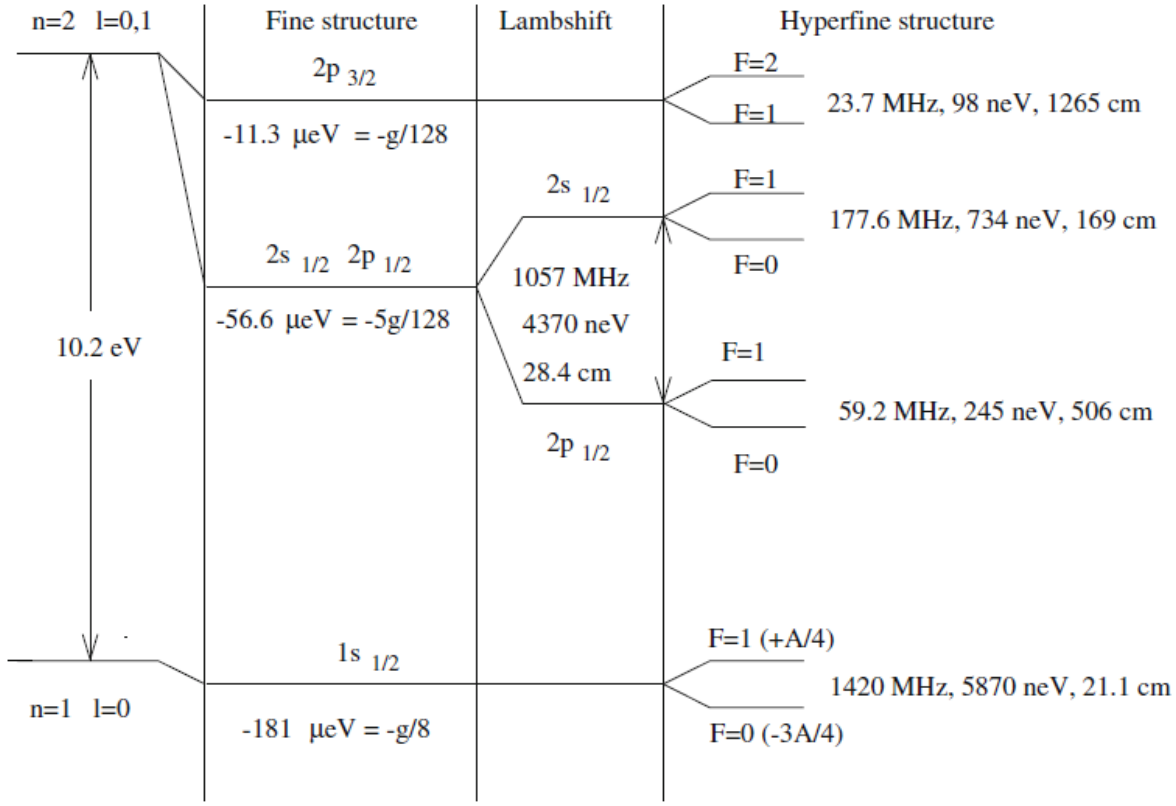

Fig. Fine and hyperfine structure of the hydrogen atom. Abbreviations: $g = mc^2\alpha^4$ =1.45 x 10^{-3} eV, A = 1,420 MHz. The finite size of the nucleus is not taken into account. Scales are not preserved. [J. Pade, Quantum Mechanics for Pedestrians 2: Applications and Extensions (Springer, 2014)]. The lamb shift is 1057 MHz.