Relativistic correction to Hydrogen atom

We start with the SE: $i\hbar \frac{\partial}{\partial t} \Psi = H\Psi$

We can write that operator $i\hbar \frac{\partial}{\partial t}$ extracts the total energy E of the particle from the WF: $i\hbar \frac{\partial}{\partial t} \Psi = E\Psi$

We can write the total energy E in relativistic form:

$$E = \sqrt{c^2 p^2 + m_0^2 c^4}$$

Our purpose isto substitute operators $E = i\hbar \frac{\partial}{\partial t}$ and $\vec{p} = -i\hbar \vec{\nabla}$ and obtain the Schrödinger-like equation with the new Hamiltonian. To do it, we need to get rid of $\sqrt{\ }$ in the expr. for energy.

Approach 1

$$E^2 = c^2 p^2 + m_0^2 c^4$$

$$-\hbar^2 \frac{\partial^2}{\partial t^2} \Psi = \left(-c^2 \hbar^2 \vec{\nabla}^2 + m_0^2 c^4\right) \Psi$$

$$\left(c^2 \hbar^2 \nabla^2 - \hbar^2 \frac{\partial^2}{\partial t^2} - m_0^2 c^4\right) \Psi = 0$$

– Klein-Gordon equation for free particle

A more general form of KG eq. will be to add electromagnetic field:

$$E = i\hbar \frac{\partial}{\partial t} - e\Phi$$

$$\vec{p} = -i\hbar \vec{\nabla} - \frac{e}{c} \vec{A},$$

where Φ and $\vec{A}$ are scalar and vector potentials of EM field:

$$\vec{\mathcal{E}} = -\nabla\Phi - \frac{\partial}{\partial t} \vec{A}$$

$$\vec{B} = \vec{\nabla} \times \vec{A}$$

we obtain:

$$\left[\left(i\hbar \frac{\partial}{\partial t} - e\Phi\right)^2 - c^2 \left(-i\hbar \vec{\nabla} - \frac{e}{c} \vec{A}\right)^2 - m_0^2 c^4\right] \Psi = 0$$

For the case of H atom, we can consider EM potential as static Coulomb interaction of an $\bar{e}$ with the nuclei:

$$\vec{A} \equiv 0, \quad \varphi \equiv -\frac{Ze}{r}$$

Then KG equation becomes:

$$\left[\left(i\hbar\frac{\partial}{\partial t} - e\varphi(\vec{x})\right)^2 + c^2\hbar^2\vec{\nabla}^2 - m_0^2c^4\right]\psi(\vec{x},t) = 0$$

We look for stationary solutions, so $\psi(\vec{x},t) = \psi(\vec{x})e^{-\frac{i}{\hbar}Et}$

Action of the operator $\left(i\hbar\frac{\partial}{\partial t} - e\varphi(x)\right)\psi(\vec{x},t) =$

$$= \psi(\vec{x})\left(E - e\varphi(x)\right)e^{-\frac{i}{\hbar}Et}$$

and $\left(i\hbar\frac{\partial}{\partial t} - e\varphi(x)\right)^2\psi(\vec{x},t) = \psi(\vec{x})\left(E - e\varphi(x)\right)^2 e^{-\frac{i}{\hbar}Et}$

So we can write the stationary KG equation:

$$\left[\left(E - e\varphi(x)\right)^2 + c^2\hbar^2\vec{\nabla}^2 - m_0^2c^4\right]\psi(\vec{x}) = 0$$

or $\left[\vec{\nabla}^2 + \frac{1}{c^2\hbar^2}\left(\left(E + \frac{Ze^2}{r}\right)^2 - m_0^2c^4\right)\right]\psi(\vec{x}) = 0,$

this eq. has analytic solution:

$$E = m_0c^2\left(1 + \frac{Z^2\alpha^2}{\lambda^2}\right)^{-1/2}, \text{ where } \lambda = n + \left[\left(l+\tfrac{1}{2}\right)^2 - Z^2\alpha^2\right]^{1/2} - \left(l+\tfrac{1}{2}\right)$$

Expanding in Taylor series:

$$E \approx m_0c^2\left(1 - \frac{Z^2\alpha^2}{2n^2} \underbrace{- \frac{Z^4\alpha^4}{2n^4}\left(\frac{n}{l+\frac{1}{2}} - \frac{3}{4}\right)}_{\text{relativistic correction}}\right)$$

Approach 2 : Dirac equation

$$E = \sqrt{c^2 p^2 + m_0^2 c^4}$$

The $\sqrt{\ }$ can be calculated if $c^2 p^2 + m_0^2 c^4 = (\overset{?}{\ldots})^2$

$$\downarrow$$

$$c\vec{\alpha}\cdot\vec{p} + \beta m_0 c^2 =$$

$$= c\alpha_1 p_1 + c\alpha_2 p_2 + c\alpha_3 p_3 + \beta m_0 c^2$$

We want that

$$\left.\begin{array}{ll} & \alpha_1^2 = \alpha_2^2 = \alpha_3^2 = \beta^2 = 1 \\ i \neq j & \alpha_i\alpha_j + \alpha_j\alpha_i = 0 \\ \forall i & \alpha_i\beta + \beta\alpha_i = 0 \end{array}\right\}$$ conditions for coefficients.

It can fulfill if $\vec{\alpha}$ and β are 4x4 matrices:

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix},$$ and

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\sigma_y = \cancel{\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$ are Pauli matrices.

So we have $\left[c\vec{\alpha}\cdot\vec{p} + \beta m_0 c^2\right]\Psi = E\Psi$,

and $\Psi = \begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{bmatrix}$ is a 4-vector.

We can write Dirac equation as a system of two equations:

(1) $$\left(E - m_0 c^2\right)\begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix} = c\vec{\sigma}\cdot\vec{p}\begin{pmatrix} \Psi_3 \\ \Psi_4 \end{pmatrix}$$

(2) $$\left(E + m_0 c^2\right)\begin{pmatrix} \Psi_3 \\ \Psi_4 \end{pmatrix} = c\vec{\sigma}\cdot\vec{p}\begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix}$$

We define

$\Psi_+ = \begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix}$ - solutions with $E > 0$

$\Psi_- = \begin{pmatrix} \Psi_3 \\ \Psi_4 \end{pmatrix}$ - " - $E < 0$

Let us express $\Psi_- = \dfrac{c\vec{\sigma}\cdot\vec{p}}{E + m_0 c^2}\Psi_+$ from (2),

than from (1) we get

$$\left(E - m_0 c^2\right)\Psi_+ = c\vec{\sigma}\cdot\vec{p}\left[\frac{1}{E + m_0 c^2}\right]c\vec{\sigma}\cdot\vec{p}\,\Psi_+$$

Let us add EM field: ~~E~~ $E = E - e\varphi(\vec{x},t)$

$$\vec{p} = -i\hbar\vec{\nabla} - \frac{e}{c}\vec{A}(\vec{x},t)$$

The Dirac equation becomes:

$$\left(E - e\varphi - m_0c^2\right)\psi_+ = c\vec{\sigma}\cdot\vec{p}\left[\frac{1}{E - e\varphi + m_0c^2}\right]c\vec{\sigma}\cdot\vec{p}\,\psi_+$$

$E = E_S + m_0c^2$, where E_S – is non-relativistic SE.

The term $\frac{1}{E - e\varphi + m_0c^2} = \frac{1}{E_S - e\varphi + 2m_0c^2} =$

$$= \frac{1}{2m_0c^2}\left(\frac{1}{1 + \frac{E_S - e\varphi}{2m_0c^2}}\right) = \frac{1}{2m_0c^2}\left(1 + \frac{E_S - e\varphi}{2m_0c^2}\right)^{-1}$$

We expand in series:

$$\approx \frac{1}{2m_0c^2}\left(1 - \frac{E_S - e\varphi}{2m_0c^2}\right) = \frac{1}{2m_0c^2} - \frac{E_S - e\varphi}{4m_0^2c^4}$$

We can write:

$$E_S\psi_+ = \Bigg[\underbrace{\frac{p^2}{2m_0}}_{\text{because } (c\vec{\sigma}\cdot\vec{p})^2 = c^2} + e\varphi + \underbrace{c\vec{\sigma}\cdot\vec{p}\,\frac{E_S - e\varphi}{2m_0c^2}\,c\vec{\sigma}\cdot\vec{p}}_{\text{relativistic terms.}}\Bigg]\psi_+$$

non-relativistic part

Relativistic mass correction

Darwin term

$$c\vec{\sigma}\cdot\vec{p}\,\frac{E_S - e\varphi}{2m_0c^2}\,c\vec{\sigma}\cdot\vec{p} = -\frac{e\hbar^2}{2m_0c}\vec{\sigma}\cdot\vec{\nabla}\times\vec{A} - \frac{\vec{p}^{\,4}}{8m_0^3c^2} + \frac{e\hbar^2}{8m_0^2c^2}\vec{\nabla}^2\varphi - \frac{e\hbar}{4m_0^2c^2}\vec{\sigma}\cdot\vec{\nabla}\varphi\times\vec{p}$$

interaction of $\vec{e}$ with magnetic field

Spin-orbit

Problem 1

Proof that $\langle \psi_i | \frac{-\vec{p}^4}{8 m_0^3 c^2} | \psi_i \rangle$ is equivalent to the relativistic correction in the KG equation

We use perturbation theory:

$$E_i^{(1)} = \langle \psi_i | \frac{-\vec{p}^4}{8 m_0^3 c^2} | \psi_i \rangle = -\frac{1}{8 m_0^3 c^2} \langle \psi_i | \vec{p}^2 \cdot \vec{p}^2 | \psi_i \rangle$$

$$H^0 |\psi_i\rangle = E_i |\psi_i\rangle$$

$$\left(\frac{p^2}{2m_0} + V\right) |\psi_i\rangle = E_i |\psi_i\rangle$$

$$p^2 |\psi_i\rangle = 2m_0 (E_i - V) |\psi_i\rangle$$

Thus we can write

$$E_i^{(1)} = -\frac{1}{8 m_0^3 c^2} \langle \psi_i | (2m_0)^2 (E_i - V)^2 | \psi_i \rangle =$$

$$= -\frac{1}{2 m_0 c^2} \left(E_i^2 - 2E_i \langle \psi_i | V | \psi_i \rangle + \langle \psi_i | V^2 | \psi_i \rangle \right)$$

For Hydrogen atom: $V(r) = \frac{-Ze}{r}$

$$\langle \psi_i | V | \psi_i \rangle = \frac{-Ze}{a n^2}$$

$$\langle \psi_i | \frac{1}{r^2} | \psi_i \rangle = \cancel{\frac{1}{an}} \frac{1}{(l + \frac{1}{2}) n^3 a^2}$$

Combining everything, we get:

$$E_i^{(1)} = -\alpha^2 E_n \frac{Z^2}{n^2} \left(\frac{n}{l + \frac{1}{2}} - \frac{3}{4} \right)$$

Darwin correction:

$$\hat{D} = \frac{e\hbar^2}{8m_0^2c^2}\nabla^2\Phi,$$ for Coulomb potential we have

$$\Phi = -\frac{Ze}{r}$$

$$\hat{D} = \frac{\pi\hbar^2 Ze^2}{2m_0^2c^2}\delta^3(\vec{r})$$

$$\langle\hat{D}\rangle = \frac{\hbar^2}{8m_0^2c^2}4\pi\left(Ze^2\right)|\psi(0)|^2$$

$$\psi(0) = 0 \text{ for } l>0$$

$$\psi(0) = \frac{1}{\sqrt{4\pi}}2\left(\frac{Z}{na_0}\right)^{3/2} \text{ for } l=0$$

$$\langle\hat{D}\rangle = \frac{2n}{m_0c^2}E_n^2,$$ so the Darwin term affects only the s orbitals.

Spin-orbit term:

$$-\frac{e\hbar}{4m_0^2c^2}\vec{\sigma}\cdot\nabla\Phi\times\vec{p}$$ for Coulomb potential

$$-\Phi = -\frac{Ze_0}{r}$$

$$\nabla\Phi = -\frac{Ze_0}{r^3}\vec{r}$$

$$\frac{e}{2m_0^2c^2}\underbrace{\frac{\hbar}{2}\vec{\sigma}}_{\vec{S}}\cdot\frac{Ze\vec{r}}{r^3}\times p = \frac{Ze^2}{2m_0^2c^2r^3}\vec{S}\cdot\vec{L},$$ Because $\vec{r}\times\vec{p} = \vec{L}$

The spin orbit interaction $=0$ for s states because $\vec{L}=0$.

In other cases we need to find correction proportional $\sim\langle\psi|\vec{S}\cdot\vec{L}|\psi\rangle$.

Spin orbit coupling:

We work with the Hamitonian in the form:

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{x})}_{H_0} + \underbrace{\frac{ze^2}{2m^2c^2r^3}\vec{S}\cdot\vec{L}}_{\Delta H}$$

We know the eigenstates and energies of the Hamiltonian $\hat{H}_0$.
In principle, we can use perturbation theory to find E of $\hat{H}$.

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

First order correction:

$$E_n^{(1)} = \langle n^{(0)} | \Delta H | n^{(0)} \rangle = \frac{ze^2}{2m^2c^2} \langle n^{(0)} | \frac{1}{r^3} \vec{S}\cdot\vec{L} | n^{(0)} \rangle$$

Problem is to act by operator $\vec{S}\cdot\vec{L}$ on uperturbed states $|n^{(0)}\rangle$

What the operator $\vec{S}\cdot\vec{L}$ means?

$$\vec{S}\cdot\vec{L} = \hat{S}_1 \otimes \hat{L}_1 + \hat{S}_2 \otimes \hat{L}_2 + \hat{S}_3 \otimes \hat{L}_3 = \sum_i \hat{S}_i \otimes \hat{L}_i$$

We can use the summation of angular momenta:

$$\vec{J} = \vec{L} + \vec{S} \equiv \vec{L} \otimes \mathbb{1} + \mathbb{1} \otimes \vec{S}$$

$$\vec{J}^2 = \sum_i J_i \cdot J_i = \vec{L}^2 \otimes \mathbb{1} + \mathbb{1} \otimes \vec{S}^2 + 2 \underbrace{\sum_i \hat{S}_i \otimes \hat{L}_i}_{\vec{S}\cdot\vec{L}}$$

$$\vec{S}\cdot\vec{L} = \frac{1}{2}\left(\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right)$$

It can be shown that

$$[\hat{\vec{L}}^2, \hat{L}_i] = 0 \qquad [\hat{L}_i, \hat{S}_i] = 0$$

$$[\hat{J}^2, \hat{L}^2] = 0 \qquad [\hat{S}^2, \hat{S}_i] = 0 \qquad [\vec{L}^2, \hat{S}_i] = 0$$

$$[\hat{J}^2, \hat{S}^2] = 0 \qquad [\vec{S}^2, \hat{L}_i] = 0$$

Hydrogen atom:

Commuting observables: $\{H, L^2, L_z\}$, for $\hat{H}_0$

which we can expand to add $\{S^2, S_z\}$

What is the set of comm. observables for

$\hat{H} = \hat{H}_0 + \underbrace{\Delta\hat{H}}_{\sim \vec{S}\cdot\vec{L}}$? $\{H, L^2, S^2, J^2, J_z\}$,

but L_z and S_z do not commute with H anymore.

The original state $|l\, m\rangle$ and $|S, m_s\rangle$ form new basis by tensor product: $|l, m\rangle \otimes |S, m_s\rangle$.

Consider the case $n=2$ $l=1$ (2p orbital of H):

We have

$$\begin{matrix} |1,1\rangle & & |\frac{1}{2}, \frac{1}{2}\rangle \\ |1,0\rangle & \otimes & \\ |1,-1\rangle & - & |\frac{1}{2}, -\frac{1}{2}\rangle \\ \text{(3 states)} & & \text{(2 states)} \end{matrix}$$

and will obtain in total 6 new states

Let us classify the states according to $\hat{J}_z = \hat{L}_z + \hat{S}_z$:

$+\frac{3}{2}$: $|1,1\rangle \otimes |\frac{1}{2}, \frac{1}{2}\rangle$

$+\frac{1}{2}$: $|1,0\rangle \otimes |\frac{1}{2}, \frac{1}{2}\rangle$, $|1,1\rangle \otimes |\frac{1}{2}, -\frac{1}{2}\rangle$

$-\frac{1}{2}$: $|1,0\rangle \otimes |\frac{1}{2}, -\frac{1}{2}\rangle$, $|1,-1\rangle \otimes |\frac{1}{2}, \frac{1}{2}\rangle$

$-\frac{3}{2}$: $|1,-1\rangle \otimes |\frac{1}{2}, -\frac{1}{2}\rangle$

We need to form states which are eigenstates of $\hat{J}^2$

We showed that for $l=1, s=\frac{1}{2}$, we can form $J_z = \{+\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}\}$

Thus we obtain possible $J = \{\frac{3}{2}, \frac{1}{2}\}$

$$\underset{\substack{\uparrow \\ \text{4 states} \\ \{+\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}\}}}{\frac{3}{2}} \qquad \underset{\substack{\uparrow \\ \text{2 states} \\ \{+\frac{1}{2}, -\frac{1}{2}\}}}{\frac{1}{2}}$$

Now we form the full set:

(1) $|J=\frac{3}{2}, m=\frac{3}{2}\rangle = |1,1\rangle \otimes |\frac{1}{2},\frac{1}{2}\rangle$ - only one state satisfies this condition.

Same is for

$$|J=\frac{3}{2}, m=-\frac{3}{2}\rangle = |1,-1\rangle \otimes |\frac{1}{2},-\frac{1}{2}\rangle$$

for $|J=\frac{3}{2}, m=\frac{1}{2}\rangle$ it should be a linear combination of

$$|1,0\rangle \otimes |\tfrac{1}{2},\tfrac{1}{2}\rangle \text{ and } |1,1\rangle \otimes |\tfrac{1}{2},-\tfrac{1}{2}\rangle$$

We can obtain the coefficients by using raising and lowering operators:

$$J_\pm |J\, m\rangle = \hbar\sqrt{J(J+1) - m(m\pm 1)}\, |J, m\pm 1\rangle$$

Applying ~~$J_- |J=\frac{3}{2}, m=\frac{3}{2}\rangle$ ... $|J=\frac{3}{2}, m=\frac{1}{2}\rangle$~~

$$J_- |J=\tfrac{3}{2}, m=\tfrac{3}{2}\rangle = \hbar\sqrt{\tfrac{3}{2}\left(\tfrac{5}{2}\right) - \tfrac{3}{2}\left(\tfrac{1}{2}\right)}\, |J=\tfrac{3}{2}, m=\tfrac{1}{2}\rangle = \hbar\sqrt{3}\, |\tfrac{3}{2},\tfrac{1}{2}\rangle$$

We apply it now for the RHS of (1), so

$$J_- |1,1\rangle \otimes |\tfrac{1}{2},\tfrac{1}{2}\rangle = (L_- + S_-)\, |1,1\rangle \otimes |\tfrac{1}{2},\tfrac{1}{2}\rangle =$$

$$= \hbar\sqrt{2}\, |1,0\rangle \otimes |\tfrac{1}{2},\tfrac{1}{2}\rangle + \hbar\, |1,1\rangle \otimes |\tfrac{1}{2},-\tfrac{1}{2}\rangle$$

Finally we get

$$|J=\tfrac{3}{2}, m=\tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{3}}\, |1,0\rangle \otimes |\tfrac{1}{2},\tfrac{1}{2}\rangle + \frac{1}{\sqrt{3}}\, |1,1\rangle \otimes |\tfrac{1}{2},-\tfrac{1}{2}\rangle$$

Similarly, we get

$$|\tfrac{3}{2},-\tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{3}}\,|1,0\rangle \otimes |\tfrac{1}{2},-\tfrac{1}{2}\rangle + \frac{1}{\sqrt{3}}\,|1,-1\rangle \otimes |\tfrac{1}{2},\tfrac{1}{2}\rangle$$

and

$J=\frac{1}{2}$

$$|\tfrac{1}{2},\tfrac{1}{2}\rangle = -\frac{1}{\sqrt{3}}\,|1,0\rangle \otimes |\tfrac{1}{2},\tfrac{1}{2}\rangle + \sqrt{\tfrac{2}{3}}\,|1,1\rangle \otimes |\tfrac{1}{2},-\tfrac{1}{2}\rangle$$

$$|\tfrac{1}{2},-\tfrac{1}{2}\rangle = \frac{1}{\sqrt{3}}\,|1,0\rangle \otimes |\tfrac{1}{2},-\tfrac{1}{2}\rangle + \sqrt{\tfrac{2}{3}}\,|1,-1\rangle \otimes |\tfrac{1}{2},\tfrac{1}{2}\rangle$$

More generally:

$$|n l s j m_j\rangle = \sum_{m_l, m_s} \underbrace{\langle l s m_l m_s | j m_j\rangle}_{\text{Clebsch-Gordan coefficients.}} |n l s m_l m_s\rangle$$

Finally, we have

$$\langle \vec{L}\cdot\vec{S}\rangle = \langle \tfrac{1}{2}(J^2 - L^2 - S^2)\rangle = \frac{\hbar}{2}\left(J(J+1) - l(l+1) - s(s+1)\right)$$

Which is for the case of $l=1$, $s=\frac{1}{2}$ is

$$= \frac{\hbar}{2}\left(J(J+1) - 2 - \frac{3}{4}\right) = \frac{\hbar}{2}\left(J(J+1) - \frac{7}{4}\right)$$