Hyperfine structure

Summary:

(0) The $1s$ state of the hydrogen atom is four-fold degenerate corresponding to the spin states of the proton and the electron. This degeneracy is partially lifted by the hyperfine interaction.

(1) The interaction Hamiltonian between the electron and proton magnetic moment is given by

$$H_{hf} = \frac{\mu_0 g_p g_e e^2}{16\pi m_e m_p}\left[\frac{3(\vec{s}_p\cdot\hat{r})(\vec{s}\cdot\hat{r})}{r^3} - \frac{\vec{s}_p\cdot\vec{s}}{r^3} + \frac{8\pi}{3}\delta(\vec{r})\,\vec{s}_p\cdot\vec{s}\right] . \tag{1}$$

The delta function term requires care.

(2) We need to evaluate $\langle n=1,\ell=0,m_\ell=0,m_s,M_s|H_{hf}|n=1,\ell=0,m_\ell=0,m_s,M_s\rangle$ where m_s is the z-component of the electron spin and M_s that of the proton. It is conventional to evaluate the average over the spatial degrees of freedom (integrate over d^3r) and write the Hamiltonian as an operator in spin space

$$H_{hf} = \frac{\lambda_{hf}}{\hbar^2}\,\vec{s}_p\cdot\vec{s}_e .$$

In any spherically symmetric state the angular average over the first two terms in Equation (1) vanishes and only the delta function term contributes. We obtain

$$\lambda_{hf} \approx \frac{2\pi}{3}\,g_p g_e\,\frac{q^2}{m_e m_p c^2}\,|\psi(0)|^2$$

and $\psi(0)$ is the value of the electronic wave function at the nucleus.

(3) The eigenvalues of H_{hf} are trivially calculated using $\vec{j} = \vec{s}_p + \vec{s}$. The singlet has an energy $-3\lambda_{hf}/4$ and the triplet an energy of $\lambda_{hf}/4$ and the separation is λ_{hf} is given by $5.86\times10^{-6}\,eV$. The energy difference between these states corresponds to the famous $21\,cm$ line ($1420\,Mc$) useful in astrophysical applications.

This is one of the most precisely measured frequencies and is

$$1420,\ 405,\ 751.766\,7 \pm 0.0009\,Hz\,.$$

Gory details

We derive the interaction between the magnetic moment of the proton and the electron in hydrogen. We restrict our attention to $\ell = 0$ states.

The classical vector potential due to $\vec{\mu}$ is given by (See Griffiths or Jackson)

$$\vec{A} = \frac{\mu_0}{4\pi} \frac{\vec{\mu} \times \vec{r}}{r^3} .$$

This can be written as

$$\vec{A} = -\frac{\mu_0}{4\pi} \vec{\mu} \times \vec{\nabla} \left(\frac{1}{r} \right)$$

and the magnetic field due to this vector potential is

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

We use

$$\vec{\nabla} \times (\vec{C} \times \vec{D}) = (\vec{D} \cdot \vec{\nabla})\vec{C} - (\vec{C} \cdot \vec{\nabla})\vec{D} + \vec{C}(\vec{\nabla} \cdot \vec{D}) - \vec{D}(\vec{\nabla} \cdot \vec{C})$$

and let $\vec{C} = \vec{\mu}$ and $\vec{D} = \vec{\nabla}(1/r)$ to obtain

$$\vec{B} = -\frac{\mu_0}{4\pi} \left[(\vec{\mu} \cdot \vec{\nabla})\vec{\nabla} \left(\frac{1}{r} \right) + \vec{\mu}\, \nabla^2 \left(\frac{1}{r} \right) \right] .$$

We write this as

$$B_i = -\frac{\mu_0}{4\pi} \left[-\mu_j \frac{\partial}{\partial x_j} \frac{\partial}{\partial x_i} \left(\frac{1}{r} \right) - 4\pi\, \mu_i\, \delta(\vec{r}) \right] .$$

We now note the identity

$$\frac{\partial}{\partial x_j} \frac{\partial}{\partial x_i} \left(\frac{1}{r} \right) = \frac{3x_i x_j - r^2 \delta_{ij}}{r^5} - \frac{4\pi}{3} \delta_{ij}\, \delta(\vec{r}) .$$

Where did the last term come from? When we set $i = j$ and sum over i we obtain $\nabla^2(1/r)$ which must equal $-4\pi\delta(\vec{r})$. Thus we obtain

$$\vec{B} = -\frac{\mu_0}{4\pi} \left[\frac{\vec{\mu}}{r^3} - \frac{3\vec{\mu} \cdot \hat{r}\, \hat{r}}{r^3} - \frac{8\pi}{3} \mu \delta^3(\vec{r}) \right] .$$

Now we set $\vec{\mu} = \vec{\mu}_N$ the nuclear magnetic moment and the energy is given by $-\mu_e \cdot \vec{B}$. This yields

$$\frac{\mu_0}{4\pi}\left[\frac{\vec{\mu}_N \cdot \vec{\mu}_e}{r^3} - \frac{3\vec{\mu}_N \cdot \vec{r}\,\vec{\mu}_e \cdot \vec{r}}{r^5}\right] - \frac{2}{3}\mu_0 \vec{\mu}_e \cdot \vec{\mu}_N \delta^3(\vec{r})\,.$$

Consider $\vec{s}_p$ and $\vec{s}$ where $\vec{s}_p$ is the spin operator of the proton and $\vec{s}$ that of the electron. The proton has a magnetic moment given by $\vec{\mu}_p = g_p\,[e/(2m_p)]\,\vec{s}_p$ where $g_p \approx 2\times 2.79$ which reflects the constituent quark structure of the proton. The electron magnetic moment is given as usual by $-g_e\,[e/(2m_e)]\,\vec{s}$. The first-order correction is given by the expectation value of the Hamiltonian which is given by (obtained by substituting the expressions for the moments in terms of the spin operators)

$$H_{hf} = \frac{\mu_0 g_p g_e e^2}{16\pi m_e m_p}\left[\frac{3(\vec{s}_p \cdot \vec{r})(\vec{s} \cdot \vec{r})}{r^5} - \frac{\vec{s}_p \cdot \vec{s}}{r^3} + \frac{8\pi}{3}\delta(\vec{r})\,\vec{s}_p \cdot \vec{s}\right]\,. \tag{2}$$

The effective hyperfine Hamiltonian can be obtained by taking the expectation value of this in the ground state, partially, i.e., with respect to the coordinate space wave function only and leave the rest as an operator in spin space. So we need to evaluate

$$\int d^3r\,\psi_{10}(\vec{r})\,H_{hf}\,\psi_{10}(\vec{r})\quad .$$

As shown in class the terms which do not involve the delta-function vanish. The key result is

$$\int d\Omega\,(\vec{a}\cdot\hat{r})\,(\vec{b}\cdot\hat{r}) = \frac{4\pi}{3}\,\vec{a}\cdot\vec{b}\,.$$

This is easily verified by noting the integral is a scalar that is linear in $\vec{a}$ and $\vec{b}$ and is therefore, proportional to $\vec{a}\cdot\vec{b}$. The constant of proportionality is evaluated by choosing $\vec{a} = \vec{b} = \hat{z}$. So if one performs the angular integral first we have

$$\int d\Omega\,3(\vec{s}_p\cdot\hat{r})\,(\vec{s}\cdot\hat{r}) = 4\pi\,\vec{s}_p\cdot\vec{s} = \int d\Omega\,\vec{s}_p\cdot\vec{s}.$$

The delta function term yields $(8\pi/3)\,|\psi_{10}(0)|^2$ apart from the constants outside the square bracket in Equation (2) and the operator part $\vec{s}_p\cdot\vec{s}$. Note that $\psi(0)$ is the value of the electronic wave function at the nucleus.This leads to the Hamiltonian after some rearrangements

$$H_{hf} = \frac{\lambda_{hf}}{\hbar^2}\,\vec{s}_p\cdot\vec{s} \tag{3}$$

where

$$\lambda_{hf} \approx \frac{2\pi}{3}\,g_p g_e\,\frac{q^2\hbar^2}{m_e m_p c^2}\,|\psi(0)|^2\,.$$

We have used $\mu_0\epsilon_0 = 1/c^2$ and write $q^2 = e^2/(4\pi\epsilon_0)$. It is easy to write this using $\psi(0)$ for the $1s$ state as $\lambda_{fs} = \frac{4}{3}\, g_e g_p \,\frac{m_e}{m_p}\, \alpha^2\, \frac{q^2}{2a_0}$. Why is this form instructive?

This expression yields $1420 MHz$ for the frequency split as is easily verified.

This is one of the most precisely measured frequencies as specified earlier. To obtain agreement with this kind of accuracy one must include very accurate values for the proton magnetic moment, QED corrections to the electron g factor and also the magnetic and charge form factors of the proton, the so-called Zemach corrections. Currently attempts are underway to measure this in an anti-hydrogen atom to test various fundamental issues such as CPT violation.

The hyperfine splitting has been measured in many alkalis carefully.

Comments about the delta function term

It is worth recalling the result (you should actually derive this result!) that if one has a uniformly magnetized sphere then the field $\vec{B}$ outside is that of a dipole of moment $\vec{\mu} = \frac{4\pi a^3}{3}\,\vec{M}$ where $\vec{M}$ is the magnetization defined to be the magnetic moment per unit volume. Inside the sphere the field $\vec{B}$ is a constant given by

$$\vec{B} = \frac{\mu_0}{2\pi}\,\frac{\vec{\mu}}{a^3}.$$

Therefore, if one takes the ideal dipole limit of $a \to 0$ with a fixed magnetic dipole moment this contribution diverges. However, when integrated over the volume of the sphere it yields a constant contribution independent of a:

$$\frac{\mu_0}{2\pi}\,\frac{\vec{\mu}}{a^3}\,\frac{4\pi a^3}{3} = \frac{2\mu_0}{3}\,\vec{\mu}$$

and this contribution is captured by the δ-function term given earlier:

$$\frac{2\mu_0}{3}\,\vec{\mu}\,\delta(\vec{r})\,.$$
