

HYPERFINE SPLITTING AND THE 21 CM LINE OF HYDROGEN

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 6.27.

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We've looked at the relativistic and spin-orbit corrections to the energies in the hydrogen atom and together, these make up the fine structure of the energy levels. There is, however, one other influence on the electron's energy and that is the magnetic moment of the proton. This gives rise to a much smaller correction to the energy and is therefore called hyperfine splitting.

The proton's magnetic moment is given by

$$\boldsymbol{\mu}_p = \frac{g_p e}{2m_p} \mathbf{S}_p \quad (1)$$

where g_p is the g-factor of the proton, and is measured to be 5.59. The magnetic field due to the proton's dipole moment is then given by

$$\mathbf{B}_p = \frac{\mu_0}{4\pi r^3} [3(\boldsymbol{\mu}_p \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}} - \boldsymbol{\mu}_p] + \frac{2}{3} \mu_0 \delta^3(\mathbf{r}) \boldsymbol{\mu}_p \quad (2)$$

The energy of the electron's dipole in this field is then

$$U = -\boldsymbol{\mu}_e \cdot \mathbf{B}_p \quad (3)$$

with the electron's magnetic moment given by

$$\boldsymbol{\mu}_e = -\frac{e}{m_e} \mathbf{S}_e \quad (4)$$

Plugging in the magnetic moments in terms of spin, we get for the hyperfine splitting hamiltonian H'_{hs} :

$$U = H'_{hs} = \frac{\mu_0 e^2 g_p}{8\pi r^3 m_p m_e} [3(\mathbf{S}_p \cdot \hat{\mathbf{r}})(\mathbf{S}_e \cdot \hat{\mathbf{r}}) - \mathbf{S}_p \cdot \mathbf{S}_e] + \frac{\mu_0 e^2 g_p}{3m_p m_e} \delta^3(\mathbf{r}) \mathbf{S}_p \cdot \mathbf{S}_e \quad (5)$$

In order to apply perturbation theory to this hamiltonian, we need to find some operators that commute with H'_{hs} and with the unperturbed hamiltonian. Looking at our analysis of spin-orbit coupling, we can work out the commutators in the same way, except here we replace \mathbf{L} by \mathbf{S}_p . We'll find that

$$[\mathbf{S}_p \cdot \mathbf{S}_e, S_p^2] = [\mathbf{S}_p \cdot \mathbf{S}_e, S_e^2] = [\mathbf{S}_p \cdot \mathbf{S}_e, S^2] = 0 \quad (6)$$

where $\mathbf{S} = \mathbf{S}_p + \mathbf{S}_e$ is the total spin. Thus the correct states to use as eigenstates of S^2 , S_p^2 and S_e^2 .

What about the $(\mathbf{S}_p \cdot \hat{\mathbf{r}})(\mathbf{S}_e \cdot \hat{\mathbf{r}})$ term? In fact, the whole term in square brackets averages out to zero, as we can see by direct calculation. Writing in rectangular coordinates, we have

$$\hat{\mathbf{r}} = \sin \theta \cos \phi \hat{\mathbf{x}} + \sin \theta \sin \phi \hat{\mathbf{y}} + \cos \theta \hat{\mathbf{z}} \quad (7)$$

For two constant vectors \mathbf{a} and \mathbf{b} (that is, independent of spatial coordinates which the spin vectors are), we then have

$$\int_0^\pi \int_0^{2\pi} (\mathbf{a} \cdot \hat{\mathbf{r}})(\mathbf{b} \cdot \hat{\mathbf{r}}) \sin \theta d\phi d\theta = \int_0^\pi \int_0^{2\pi} (a_x \sin \theta \cos \phi + a_y \sin \theta \sin \phi + a_z \cos \theta) \quad (8)$$

$$\times (b_x \sin \theta \cos \phi + b_y \sin \theta \sin \phi + b_z \cos \theta) \sin \theta d\phi d\theta \quad (9)$$

The ϕ integral will be zero for most of the terms in the expansion of this integrand, since

$$\int_0^{2\pi} \cos \phi d\phi = \int_0^{2\pi} \sin \phi d\phi = \int_0^{2\pi} \sin \phi \cos \phi d\phi = 0 \quad (10)$$

The remaining terms are

$$\int_0^\pi \int_0^{2\pi} (a_x b_x \sin^3 \theta \cos^2 \phi + a_y b_y \sin^3 \theta \sin^2 \phi + a_z b_z \sin \theta \cos^2 \theta) d\phi d\theta = \quad (11)$$

$$\frac{4\pi}{3} (a_x b_x + a_y b_y + a_z b_z) = \frac{4\pi}{3} \mathbf{a} \cdot \mathbf{b} \quad (12)$$

Therefore, the average over angular coordinates of the first term in square brackets in 5 is $4\pi \mathbf{S}_p \cdot \mathbf{S}_e$.

The average over angular coordinates of the second term in square brackets in 5 is then

$$\int_0^\pi \int_0^{2\pi} \mathbf{S}_p \cdot \mathbf{S}_e \sin\theta d\phi d\theta = 4\pi \mathbf{S}_p \cdot \mathbf{S}_e \quad (13)$$

again, since $\mathbf{S}_p \cdot \mathbf{S}_e$ does not depend on spatial coordinates. Subtracting this from the first term, we get zero for the average of the square bracket. As we pointed out in the post on the magnetic field of a dipole, the first term in 2 really applies only for $r > 0$ and the delta function at $r = 0$. Although this is mathematically very dodgy, it is used as the justification for being able to do the angular integrals and get zero and then claim that the radial integral gives something finite so the product is zero.

In any case, it is only the delta function term that contributes to the energy correction $E_{hs1} = \langle n\ell s s_p s_e | H'_{hs} | n\ell s s_p s_e \rangle$. To calculate it, we can write

$$S^2 = (\mathbf{S}_p + \mathbf{S}_e)^2 = S_p^2 + S_e^2 + 2\mathbf{S}_p \cdot \mathbf{S}_e \quad (14)$$

$$\mathbf{S}_p \cdot \mathbf{S}_e = \frac{1}{2} (S^2 - S_p^2 - S_e^2) \quad (15)$$

For the proton and electron the spin is $\frac{1}{2}$ so $\langle S_p^2 \rangle = \langle S_e^2 \rangle = \frac{1}{2} \times \frac{3}{2} = \frac{3}{4}$. The total spin can be either 1 or 0 so

$$\langle \mathbf{S}_p \cdot \mathbf{S}_e \rangle = \frac{\hbar^2}{2} \left(\langle S^2 \rangle - \frac{3}{2} \right) = \begin{cases} +\frac{\hbar^2}{4} & (s = 1) \\ -\frac{3\hbar^2}{4} & (s = 0) \end{cases} \quad (16)$$

The energy corrections are then

$$E_{hs1} = \frac{\mu_0 e^2 g_p}{3m_p m_e} \langle \delta^3(\mathbf{r}) \rangle \langle \mathbf{S}_p \cdot \mathbf{S}_e \rangle \quad (17)$$

The average $\langle \delta^3(\mathbf{r}) \rangle$ is just $|\psi(0)|^2$ for whatever wave function we're considering. The ground state of hydrogen is $\psi_{100} = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$ so $|\psi(0)|^2 = \frac{1}{\pi a^3}$. For this state, the two hyperfine levels are then

$$E_{hs1} = \begin{cases} \frac{1}{4} \frac{\mu_0 e^2 g_p \hbar^2}{3\pi a^3 m_p m_e} & (s = 1) \\ -\frac{3}{4} \frac{\mu_0 e^2 g_p \hbar^2}{3\pi a^3 m_p m_e} & (s = 0) \end{cases} \quad (18)$$

The energy difference between these two levels is then

$$\Delta E_{hs1} = \frac{\mu_0 e^2 g_p \hbar^2}{3\pi a^3 m_p m_e} \quad (19)$$

This can be converted to the form in Griffiths by multiplying top and bottom by the Bohr radius $a = 4\pi\epsilon_0 \hbar^2 / m_e e^2$:

$$\Delta E_{hs1} = \frac{4\epsilon_0\mu_0 g_p \hbar^4}{3a^4 m_p m_e^2} \quad (20)$$

Finally, we use the relation $\epsilon_0\mu_0 = 1/c^2$ to get

$$\Delta E_{hs1} = \frac{4g_p \hbar^4}{3a^4 m_p m_e^2 c^2} \quad (21)$$

Plugging in the numbers, we get

$$\Delta E_{hs1} = 5.88 \times 10^{-6} \text{ eV} \quad (22)$$

From the Planck formula relating energy and frequency

$$\nu = \frac{\Delta E_{hs1}}{h} = 1.42 \times 10^9 \quad (23)$$

which corresponds to a wavelength of 21 cm. This 21 cm line of hydrogen is of great use in astronomy, as it tends to penetrate a lot of interstellar dust allowing us to see objects with radio telescopes that are otherwise invisible.

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