

Zeeman effect and hyperfine splitting

This note¹ deals with two applications of stationary perturbation theory to hydrogen. The first application is to hydrogen in a magnetic field, known as the Zeeman effect, and the second is the hydrogen hyperfine splitting, which is a consequence of the interaction between the proton spin and the electron spin.

Zeeman effect

When a hydrogen atom is placed in a magnetic field its Hamiltonian becomes

$$H = \frac{\vec{P}^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} + H_{so} + H_{rel} + H_D + H_z,$$

where the fine-structure corrections H_{so} , H_{rel} and H_D are the spin-orbit, relativistic and Darwin terms respectively. The last term is the Zeeman term which arises from putting the atom inside a magnetic field:

$$H_z \equiv -(\vec{\mu}_l + \vec{\mu}_s) \cdot \vec{B},$$

where the orbital and spin magnetic moments are

$$\vec{\mu}_l = -\frac{e}{2m}\vec{L}, \quad \vec{\mu}_s = -g\frac{e}{2m}\vec{S}.$$

Taking the $\vec{B}$ -field to lie along the z-axis and setting $g = 2$, the Zeeman term becomes

$$H_z = \frac{e}{2m}B(L_z + 2S_z) = \frac{e}{2m}B(J_z + S_z),$$

where we have used $\vec{J} = \vec{L} + \vec{S}$.

Weak field Zeeman effect

In a very weak field we take the unperturbed Hamiltonian to be $H^0 = \frac{\vec{P}^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} + H_{so} + H_{rel} + H_D$ with unperturbed energies

$$E_n^0 = \frac{E_1}{n^2} \left[1 + \frac{\alpha^2}{n^2} \left(\frac{n}{j+1/2} - \frac{3}{4} \right) \right]$$

and the unperturbed energy eigenstates are $|nljm_j\rangle$. The unperturbed energies only depends on n , j , so different values of l and m_j are degenerate, thus we need to use degenerate perturbation theory. In order to calculate the first order energy correction to an energy level with quantum numbers n and j in degenerate perturbation theory, we need to calculate the matrix elements $\langle nl'jm'_j|H_z|nljm_j\rangle$. Inserting the Zeeman term we get

$$\begin{aligned} \langle nl'jm'_j|H_z|nljm_j\rangle &= \frac{eB}{2m} \langle nl'jm'_j|(J_z + S_z)|nljm_j\rangle \\ &= \frac{eB}{2m} (\hbar m_j + \langle nl'jm'_j|S_z|nljm_j\rangle) \end{aligned}$$

¹Adapted from Griffiths "Introduction to quantum mechanics", Cambridge Univ. Press.

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where we have used $J_z|nljm_j\rangle = \hbar m_j|nljm_j\rangle$. The calculation of the last term can be done by expressing the states $|nljm_j\rangle$ in terms of eigenstates of S_z . Generally such an eigenstate of j and m_j can be written in terms of the $|n, l, m\rangle$ and electron spin states as

$$|nljm_j\rangle = \alpha_j|n, l, m_j + \frac{1}{2}\rangle \otimes |\downarrow\rangle + \beta_j|n, l, m_j - \frac{1}{2}\rangle \otimes |\uparrow\rangle$$

Now applying the operator $J^2 = L^2 + S^2 + 2\vec{L} \cdot \vec{S}$ to both sides of this expression and using the orthogonality condition on the states we find that

$$\alpha_{j=l+1/2} = \sqrt{\frac{l + \frac{1}{2} - m_j}{2l + 1}}, \quad \beta_{j=l+1/2} = \sqrt{\frac{l + \frac{1}{2} + m_j}{2l + 1}},$$

and

$$\alpha_{j=l-1/2} = \sqrt{\frac{l + \frac{1}{2} + m_j}{2l + 1}}, \quad \beta_{j=l-1/2} = -\sqrt{\frac{l + \frac{1}{2} - m_j}{2l + 1}}.$$

Inserting this expressions we find, which is valid for both cases $j = l \pm 1/2$, that

$$\begin{aligned} \langle nl'jm'_j|S_z|nljm_j\rangle &= \left(\langle n, l', m'_j + \frac{1}{2}| \otimes \langle \downarrow| \alpha^* + \langle n, l', m'_j - \frac{1}{2}| \otimes \langle \uparrow| \beta^* \right) \\ &\quad \frac{\hbar}{2} \left(-\alpha|n, l, m_j + \frac{1}{2}\rangle \otimes |\downarrow\rangle + \beta|n, l, m_j - \frac{1}{2}\rangle \otimes |\uparrow\rangle \right) \\ &= \frac{\hbar}{2} (|\beta|^2 - |\alpha|^2) \delta_{ll'} \delta_{m_j m'_j} \\ &= \hbar \left(|\beta|^2 - \frac{1}{2} \right) \delta_{ll'} \delta_{m_j m'_j} \end{aligned}$$

where we have used $|\alpha|^2 + |\beta|^2 = 1$. We see that the matrix is diagonal, and so the states $|nljm_j\rangle$ are good states, and so we can just read off the energy corrections as the diagonal elements. The modulus square of the β coefficients are

$$|\beta|^2 = \begin{cases} \frac{l + \frac{1}{2} + m_j}{2l + 1} = \frac{1}{2} + \frac{m_j}{2l + 1}, & j = l + \frac{1}{2} \\ \frac{l + \frac{1}{2} - m_j}{2l + 1} = \frac{1}{2} - \frac{m_j}{2l + 1}, & j = l - \frac{1}{2} \end{cases}$$

and we thus find that the energy corrections are

$$E_z^1 = \frac{eB\hbar}{2m} \left(m_j \pm \frac{m_j}{2l + 1} \right) = \frac{e\hbar}{2m} B \left(1 \pm \frac{1}{2l + 1} \right) m_j = \mu_B B \left(1 \pm \frac{1}{2l + 1} \right) m_j$$

where the $\pm$ refers to $j = l \pm \frac{1}{2}$ and $m_j = \{-j, -j + 1, \dots, j - 1, j\}$ and $\mu_B \equiv \frac{e\hbar}{2m} \approx 5.8 \cdot 10^{-5} \text{eV/T}$ is the Bohr magneton, The factor $(1 \pm \frac{1}{2l+1})$ is often referred to as the Lande g-factor for $j = |l \pm 1/2|$. This result is valid in the weak-field regime where the energy change due to the magnetic field is smaller than the fine-structure splittings which are of the order $-E_1\alpha^2$. This means that

$$\mu_B B \ll -E_1\alpha^2$$

implying that the magnetic field $B \ll 12T$ for the weak-field regime to hold.

Strong field Zeeman effect

In the opposite limit, when the magnetic field is very strong, as in for instance certain astrophysical settings, we can neglect the fine-structure terms and take as unperturbed Hamiltonian the Coulomb Hamiltonian

$$H = \frac{\vec{P}^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} + H_z.$$

In this case the unperturbed eigenstates are $|nlmm_s\rangle$, and all unperturbed energy levels are degenerate since the energies only depends on n . Using first order degenerate perturbation theory, we must calculate the perturbation matrix

$$\begin{aligned} \langle nl'm'm'_s | H_z | nlmm_s \rangle &= \frac{e}{2m} B \langle nl'm'm'_s | (L_z + 2S_z) | nlmm_s \rangle \\ &= \frac{e\hbar}{2m} B (m + 2m_s) \delta_{l'l} \delta_{m'm} \delta_{m'_s, m_s}. \end{aligned}$$

The matrix is diagonal, so the states $|nlmm_s\rangle$ are good states that diagonalize the perturbation. We can therefore read off the energy corrections in the strong-field regime as

$$E_z^1 = \frac{e\hbar}{2m} B (m + 2m_s) = \mu_B B (m + 2m_s).$$

This is known as the Paschen-Back effect.

Hyperfine splitting

We now move on to a very weak intrinsic effect in the absence of a magnetic field. Both the proton and the electron are spin-1/2 particles with associated magnetic moments

$$\vec{\mu}_p = \frac{g_p e}{2m_p} \vec{S}_p, \quad \vec{\mu}_e = -\frac{g_e e}{2m_e} \vec{S}_e,$$

where subscript p refers to the proton, and e to the electron. The gyromagnetic ratio for the proton is $g_p \approx 5.59$ and $g_e \approx 2$ for the electron. In the hydrogen atom there is therefore also a dipole magnetic force between these two magnetic moments. The dipole-dipole interaction is

$$\begin{aligned} H_{hf} &= -\frac{\mu_0}{4\pi r^3} [3(\vec{\mu}_p \cdot \hat{r})(\vec{\mu}_e \cdot \hat{r}) - \vec{\mu}_p \cdot \vec{\mu}_e] - 2\frac{\mu_0}{3} \vec{\mu}_p \cdot \vec{\mu}_e \delta^3(\vec{r}) \\ &= \frac{\mu_0 g_p g_e e^2}{16\pi m_p m_e} \left[\frac{3(\vec{S}_p \cdot \hat{r})(\vec{S}_e \cdot \hat{r}) - \vec{S}_p \cdot \vec{S}_e}{r^3} \right] + \frac{2\mu_0 g_p g_e e^2}{4 \cdot 3 m_p m_e} \vec{S}_p \cdot \vec{S}_e \delta^3(\vec{r}) \end{aligned}$$

Let us consider spherically symmetric $l = 0$ and $m = 0$ states $|n00\rangle$. These states have no fine-structure splitting, and for these the dipole-dipole interaction also simplifies considerably. This can be seen by writing down the expectation value of H_{hf} in $l = 0, m = 0$ states

$$\begin{aligned} \langle n00 | \frac{3(\vec{S}_p \cdot \hat{r})(\vec{S}_e \cdot \hat{r})}{r^3} | n00 \rangle &= 3 \int d^3r \psi_{n00}^*(r) \frac{(\vec{S}_p \cdot \hat{r})(\vec{S}_e \cdot \hat{r})}{r^3} \psi_{n00}(r) \\ &= 3 \int dx dy dz \psi_{n00}^*(r) \frac{(S_p^x x + S_p^y y + S_p^z z)(S_e^x x + S_e^y y + S_e^z z)}{r^5} \psi_{n00}(r) \end{aligned}$$

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where we have changed integration variables to cartesian coordinates where $r \equiv \sqrt{x^2 + y^2 + z^2}$. Multiplying out the parentheses we get cross-terms like for instance

$$S_p^x S_e^y \int dxdydz \psi_{n00}^*(r) \frac{xy}{r^5} \psi_{n00}(r)$$

These cross terms vanish because the $\psi_{n00}(r)$ function is spherically symmetric while xy is antisymmetric under $x \rightarrow -x$ (it is also antisymmetric when $y \rightarrow -y$), and so when integrating over all space, the integral vanishes. The only non-vanishing terms are

$$\langle l=0 | 3 \frac{(\vec{S}_p \cdot \hat{r})(\vec{S}_e \cdot \hat{r})}{r^3} | l=0 \rangle = 3 \int dxdydz \psi_{n00}^*(r) \frac{(S_p^x S_e^x x^2 + S_p^y S_e^y y^2 + S_p^z S_e^z z^2)}{r^5} \psi_{n00}(r)$$

Now for a general spherically symmetric function $f(r)$, the following is true

$$\int d^3r x^2 f(r) = \int d^3r y^2 f(r) = \int d^3r z^2 f(r) = \frac{1}{3} \int d^3r r^2 f(r)$$

since $r^2 = x^2 + y^2 + z^2$, and therefore

$$\langle n00 | \frac{3(\vec{S}_p \cdot \hat{r})(\vec{S}_e \cdot \hat{r})}{r^3} | n00 \rangle = \vec{S}_p \cdot \vec{S}_e 3 \frac{1}{3} \int d^3r \psi_{n00}^*(r) \frac{1}{r^3} \psi_{n00}(r)$$

and so

$$\langle n00 | \frac{3(\vec{S}_p \cdot \hat{r})(\vec{S}_e \cdot \hat{r})}{r^3} - \vec{S}_p \cdot \vec{S}_e | n00 \rangle = 0.$$

Thus for $l=0$ states the only surviving term in H_{hf} is the delta-function term $\delta^3(\vec{r}) \vec{S}_p \cdot \vec{S}_e$. Let us now further specialize to the ground state $n=1$. Taking into account also the spin states of the proton and the electron our degenerate state space is $|100\rangle \otimes |m_{sp}\rangle \otimes |m_{se}\rangle$, where m_{sp} and m_{se} takes values $\pm 1/2$. The scalar product form of the interaction $\vec{S}_p \cdot \vec{S}_e$ dictates that the good states are the eigenstates $|S_{tot}, M_{tot}\rangle$ of the total spin squared operator $\vec{S}_{tot}^2$ and S_{tot}^z where $\vec{S}_{tot} \equiv \vec{S}_p + \vec{S}_e$, i.e. the familiar spin- triplet and singlet states. The first order perturbation matrix is therefore diagonal, and its diagonal values are

$$\begin{aligned} & \langle 100 | \delta^3(\vec{r}) | 100 \rangle \langle S_{tot}, M_{tot} | \vec{S}_p \cdot \vec{S}_e | S_{tot}, M_{tot} \rangle \\ &= \frac{2\mu_0 g_p g_e e^2}{4 \cdot 3m_p m_e} \int d^3r \psi_{100}^*(r) \delta^3(\vec{r}) \psi_{100}(r) \langle S_{tot}, M_{tot} | \frac{1}{2} (\vec{S}_{tot}^2 - \vec{S}_p^2 - \vec{S}_e^2) | S_{tot}, M_{tot} \rangle \\ &= \frac{2\mu_0 g_p g_e e^2}{4 \cdot 3m_p m_e} |\psi_{100}(0)|^2 \langle S_{tot}, M_{tot} | \frac{1}{2} (\vec{S}_{tot}^2 - \vec{S}_p^2 - \vec{S}_e^2) | S_{tot}, M_{tot} \rangle \\ &= \frac{2\mu_0 g_p g_e e^2}{4 \cdot 3m_p m_e} \frac{1}{\pi a_0^3} \hbar^2 \frac{1}{2} \left(S_{tot}(S_{tot} + 1) - \frac{3}{4} - \frac{3}{4} \right) \\ &= \frac{2g_p g_e}{3m_p} \underbrace{\frac{\mu_0 \epsilon_0}{1/c^2}}_{-2E_1} \underbrace{\frac{4\pi \epsilon_0 a_0}{m_e a_0^2}}_{-2E_1} \frac{\hbar^2}{2} \left(S_{tot}(S_{tot} + 1) - \frac{3}{4} - \frac{3}{4} \right) \\ &= \frac{8}{3} \frac{g_p g_e}{m_p/m_e} E_1 \underbrace{\frac{E_1}{m_e c^2}}_{-\alpha^2/2} \frac{1}{2} \left(S_{tot}(S_{tot} + 1) - \frac{3}{2} \right) \end{aligned}$$

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The two possible values for S_{tot} are 0 and 1 as the electron and protons are spin-1/2 particles. Thus the energy level splits into two distinct energy levels with energies

$$E_{hf}^1 = -E_1 \frac{4}{3} g_p g_e \frac{\alpha^2}{m_p/m_e} \begin{cases} 1/4, & S_{tot} = 1 \\ -3/4, & S_{tot} = 0 \end{cases}$$

Their difference is

$$\Delta E_{hf} = -E_1 \frac{4}{3} g_p g_e \frac{\alpha^2}{m_p/m_e} = 5.88 \cdot 10^{-6} eV$$

Although these corrections are of the same order in α (α^2) as the fine-structure splitting, the ratio of the proton mass to the electron mass in the denominator (~ 2000) makes this splitting even smaller than the fine structure, justifying the name hyperfine splitting. Converting this energy difference to a frequency, one obtains

$$\Delta E_{hf} = h\nu, \quad \nu = 1420 \text{ MHz},$$

which corresponds to a wavelength $\lambda = 21\text{cm}$. One can also convert the energy splitting to a temperature (divide by Boltzmann's constant) and one gets 0.068K. The background temperature in the universe is about 2.7K, thus both hyperfine levels of hydrogen will be populated everywhere in the universe. When spontaneous de-excitations of the upper level happens, the hydrogen atoms will send out radiation with a wavelength 21cm. Looking for 21cm radiation with radiotelescopes has in fact been used with great success to map out the occurrence of hydrogen in our galaxy. This is an example of how science is interconnected in quite surprising ways: Knowing the (hyper)finest details in the spectrum of hydrogen is needed for the very big: Mapping our galaxy.