Quantum Mechanics 2

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Hydrogen Atom
Hyperfine Structure
Dipole-Dipole Interaction

Protons and electrons have magnetic moments that interact with each other.

\[ \mu_p = \frac{ge}{2m_p} S_p, \quad \mu_e = -\frac{e}{m_e} S_e \]

where the \( g \) – factor is measured to be 5.59.

Classically, a dipole \( \mu \) sets up a magnetic field

\[ B = \frac{1}{c^2 r^3} [3(\mu \cdot \hat{r})\hat{r} - \mu] + \frac{8\pi}{3c^2} \mu \delta(r) \]

The magnetic interaction energy between the electron and proton dipoles is then

\[ H_I = -\frac{1}{c^2 r^3} [3(\mu_p \cdot \hat{r})(\mu_e \cdot \hat{r}) - \mu_p \cdot \mu_e] - \frac{8\pi}{3c^2} \mu_p \cdot \mu_e \delta(r) \]

In terms of spins,

\[ H_I = \frac{ge^2}{2m_pm_e c^2 r^3} [3(S_p \cdot \hat{r})(S_e \cdot \hat{r}) - S_p \cdot S_e] + \frac{4\pi ge^2}{3m_pm_e c^2} S_p \cdot S_e \delta(r) \]

This spin-spin interaction is called the hyperfine interaction.
The first-order correction to the eigenenergy due to hyperfine interaction is

\[ E_{n(hf)}^{(1)} = \frac{ge^2}{2m_pm_ec^2} \left( \frac{3}{r^3} \left( \mathbf{S}_p \cdot \mathbf{\hat{r}} \right) \left( \mathbf{S}_e \cdot \mathbf{\hat{r}} \right) - \mathbf{S}_p \cdot \mathbf{S}_e \right) + \frac{4\pi ge^2}{3m_pm_ec^2} \langle \mathbf{S}_p \cdot \mathbf{S}_e \rangle |\psi(0)|^2 \]

Since this is independent of orbital angular momentum, it is convenient to calculate using \( l = 0, m = 0 \) states.

Now, for the spatial part of the expectation values,

\[ \left\langle \frac{(S_p \cdot \mathbf{\hat{r}})(S_e \cdot \mathbf{\hat{r}})}{r^3} \right\rangle = \left\langle \frac{(S_p \cdot \mathbf{\hat{r}})(S_e \cdot \mathbf{\hat{r}})}{r^5} \right\rangle = \int r^2 dr \frac{1}{r^5} |u_{n00}|^2 \int d\Omega (S_p \cdot \mathbf{\hat{r}})(S_e \cdot \mathbf{\hat{r}}) \]

We first carry out the angular integration

\[ \int d\Omega (S_p \cdot \mathbf{\hat{r}})(S_e \cdot \mathbf{\hat{r}}) = \int d\Omega (xS_{px} + yS_{py} + zS_{pz})(xS_{ex} + yS_{ey} + zS_{ez}) \]

\[ = \int d\Omega \left[ x^2 S_{px}S_{ex} + y^2 S_{py}S_{ey} + z^2 S_{pz}S_{ez} + xy(S_{px}S_{ey} + S_{py}S_{ex}) + yz(S_{py}S_{ez} + S_{pz}S_{ey}) + xz(S_{px}S_{ez} + S_{pz}S_{ex}) \right] \]
Angular Integrations

We have the following angular integrals

\[
\int d\Omega x^2 = r^2 \int_0^\pi \sin^2 \theta \sin \theta \, d\theta \int_0^{2\pi} \cos^2 \varphi \, d\varphi
\]

\[
\int d\Omega y^2 = r^2 \int_0^\pi \sin^2 \theta \sin \theta \, d\theta \int_0^{2\pi} \sin^2 \varphi \, d\varphi
\]

\[
\int d\Omega z^2 = r^2 \int_0^\pi \cos^2 \theta \sin \theta \, d\theta \int_0^{2\pi} d\varphi
\]

\[
\int d\Omega xy = r^2 \int_0^\pi \sin^2 \theta \sin \theta \, d\theta \int_0^{2\pi} \cos \varphi \sin \varphi \, d\varphi
\]

\[
\int d\Omega yz = r^2 \int_0^\pi \sin \theta \cos \theta \sin \theta \, d\theta \int_0^{2\pi} \sin \varphi \, d\varphi
\]

\[
\int d\Omega xz = r^2 \int_0^\pi \sin \theta \cos \theta \sin \theta \, d\theta \int_0^{2\pi} \cos \varphi \, d\varphi
\]
Now,
\[ \int_{0}^{2\pi} \cos \varphi \, d\varphi = \sin 2\pi - \sin 0 = 0 \]
Thus,
\[ \int d\Omega \, xz = r^2 \int_{0}^{\pi} \sin \theta \cos \theta \sin \theta \, d\theta \int_{0}^{2\pi} \cos \varphi \, d\varphi = 0 \]
Likewise
\[ \int_{0}^{2\pi} \sin \varphi \, d\varphi = -\cos 2\pi + \cos 0 = 1 - 1 = 0 \]
Thus,
\[ \int d\Omega \, yz = r^2 \int_{0}^{\pi} \sin \theta \cos \theta \sin \theta \, d\theta \int_{0}^{2\pi} \sin \varphi \, d\varphi = 0 \]
Noting that
\[ \int_0^{2\pi} \cos \varphi \sin \varphi \, d\varphi = -\int_0^{2\pi} \cos \varphi \, d(\cos \varphi) = -\frac{\cos^2 2\pi}{2} + \frac{\cos^2 0}{2} = -\frac{1}{2} + \frac{1}{2} = 0 \]

We have
\[ \int d\Omega \, x y = r^2 \int_0^\pi \sin^2 \theta \sin \theta \, d\theta \int_0^{2\pi} \cos \varphi \sin \varphi \, d\varphi = 0 \]

On the other hand,
\[ \int_0^{2\pi} \cos^2 \varphi \, d\varphi = \frac{1}{2} \int_0^{2\pi} (\cos 2\varphi + 1) \, d\varphi = \frac{1}{4} (\sin 4\pi - \sin 0) + \frac{2\pi}{2} - 0 = \pi \]
\[ \int_0^{2\pi} \sin^2 \varphi \, d\varphi = \frac{1}{2} \int_0^{2\pi} (1 - \cos 2\varphi) \, d\varphi = \frac{2\pi}{2} - 0 - \frac{1}{4} (\sin 4\pi - \sin 0) = \pi \]
\[ \int_0^\pi \sin^2 \theta \sin \theta \, d\theta = -\int_0^\pi (1 - \cos^2 \theta) \, d(\cos \theta) = -(\cos \pi - \cos 0) + \frac{\cos^3 \pi}{3} - \frac{\cos^3 0}{3} = \frac{4\pi}{3} \]
\[ = -(-1 - 1) - \frac{1}{3} - \frac{1}{3} = \frac{4}{3} \]
Angular Integrations

Thus,
\[ \int d\Omega x^2 = r^2 \int_0^\pi \sin^2\theta \sin \theta \, d\theta \int_0^{2\pi} \cos^2\varphi \, d\varphi = \frac{4}{3} \pi r^2 \]
\[ \int d\Omega y^2 = r^2 \int_0^\pi \sin^2\theta \sin \theta \, d\theta \int_0^{2\pi} \sin^2\varphi \, d\varphi = \frac{4}{3} \pi r^2 \]

And finally,
\[ \int_0^\pi \cos^2\theta \sin \theta \, d\theta = -\int_0^\pi \cos^2\theta \, d(\cos \theta) = -\frac{\cos^3\pi}{3} + \frac{\cos^30}{3} = \frac{2}{3} \]

gives
\[ \int d\Omega z^2 = r^2 \int_0^\pi \cos^2\theta \sin \theta \, d\theta \int_0^{2\pi} \, d\varphi = \frac{4}{3} \pi r^2 \]
Spatial Integrations

We see then that

\[ \int d\Omega (S_p \cdot \hat{r})(S_e \cdot \hat{r}) = \frac{4}{3} \pi r^2 [S_{px}S_{ex} + S_{py}S_{ey} + S_{pz}S_{ez}] = \frac{4}{3} \pi r^2 (S_p \cdot S_e) \]

On the other hand,

\[ \int d\Omega (S_p \cdot S_e) = 4\pi (S_p \cdot S_e) \]

Thus,

\[ \left( \frac{3(S_p \cdot \hat{r})(S_e \cdot \hat{r}) - S_p \cdot S_e}{r^3} \right) = \int r^2 dr \frac{1}{r^3} |u_{n00}|^2 \left[ 3 \left( \frac{4\pi}{3} \right) (S_p \cdot S_e) - 4\pi (S_p \cdot S_e) \right] = 0 \]
The remainder

\[ \frac{4\pi g e^2}{3m_p m_e c^2} \langle S_p \cdot S_e \rangle |u(0)|^2 \]

can be evaluated as follows. For \( l = 0 \)

\[ u_{n00}(r, \theta, \varphi) = \left( \frac{2}{na_0} \right)^{3/2} \sqrt{\frac{1}{2n^2}} L_{n-1}^1 \left( \frac{2r}{na_0} \right) e^{-r/na_0} Y_{00}(\theta, \varphi) \]

Since

\[ L^k_s(0) = \frac{(s + k)!}{s! k!} \]

we have

\[ |u(0)|^2 = \left( \frac{2}{na_0} \right)^3 \left( \frac{1}{2n^2} \right) \left( \frac{n!}{1! (n - 1)!} \right)^2 \left( \frac{1}{4\pi} \right) = \left( \frac{1}{na_0} \right)^3 \frac{1}{\pi} \]
The inner product on the spin part can be evaluated if we introduce the total spin 
\[ S = S_p + S_e \]

Then
\[ S_p \cdot S_e = \frac{1}{2} (S^2 - S_p^2 - S_e^2) \]

and
\[ E_{n(hf)}^{(1)} = \frac{4\pi ge^2}{3m_p m_e c^2} \langle S_p \cdot S_e \rangle |u(0)|^2 = \frac{4\pi ge^2 \hbar^2}{3m_p m_e c^2} \frac{s(s + 1) - \frac{3}{4} - \frac{3}{4}}{2} \left( \frac{1}{na_0} \right)^3 \frac{1}{\pi} \]

The hyperfine correction to the Hydrogen energy is then
\[ E_{n(hf)}^{(1)} = \frac{2ge^2 \hbar^2}{3m_p m_e c^2} \left( \frac{1}{na_0} \right)^3 [s(s + 1) - \frac{3}{2}] \]
The hyperfine energy may be cast in terms of the fine-structure constant 

\[ \alpha = \frac{e^2}{4\pi \varepsilon_0 \hbar c} \]

as

\[ E^{(1)}_{n(hf)} = -E^{(0)}_n \frac{4g m_e}{3n m_p} \alpha^2 [s(s + 1) - \frac{3}{2}] \]

showing that the hyperfine energy is a factor \( m_e \alpha^2 / m_p \) smaller than the Bohr energy.

Now, for

\[ S = S_p + S_e \]

Since both electron and proton spins are \( \frac{1}{2} \),

\[ S = \begin{cases} 0 \\ 1 \end{cases} \]
and

\[ s(s + 1) - \frac{3}{2} = \begin{pmatrix} \frac{1}{2} \\ -\frac{3}{2} \end{pmatrix} \]

showing that the spin-spin coupling breaks the spin degeneracy. The energy gap between the two states is

\[ \Delta E^{(1)}_{n(hf)} = E^{(0)}_n \frac{8g m_e}{3n m_p} \alpha^2 \]

For the ground state, the radiation frequency emitted in a transition between the two levels is 1420 MHz, or a wavelength of 21 cm.

The 21-cm wave plays an important role in radio astronomy. The universe is bathed with this 21-cm radiation and the analysis of its intensity allows astronomers to study the density distribution of neutral hydrogen in interstellar space, as well as the motion and temperature of the gas containing the hydrogen.