# Quantum Mechanics 2

*Robert C. Roleda*
*Physics Department*

## Hydrogen Atom

### Hyperfine Structure

De La Salle University

# Dipole-Dipole Interaction

Protons and electrons have magnetic moments that interacts 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

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

In terms of spins,

$$H_I = \frac{ge^2}{2m_p m_e c^2 r^3}\left[3\left(S_p \cdot \hat{r}\right)(S_e \cdot \hat{r}) - S_p \cdot S_e\right] + \frac{4\pi g e^2}{3m_p m_e c^2} S_p \cdot S_e\, \delta(r)$$

This spin-spin interaction is called the hyperfine interaction.

# Spatial Integrations

The first-order correction to the eigenenergy due to hyperfine interaction is

$$E_{n(hf)}^{(1)} = \frac{ge^2}{2m_p m_e c^2}\left\langle \frac{3(S_p\cdot\hat{r})(S_e\cdot\hat{r}) - S_p\cdot S_e}{r^3}\right\rangle + \frac{4\pi g e^2}{3m_p m_e c^2}\,\langle S_p\cdot S_e\rangle |u(0)|^2$$

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,

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

We first carry out the angular integration

$$\int d\Omega (S_p\cdot\vec{r})(S_e\cdot\vec{r}) = \int d\Omega (xS_{px} + yS_{py} + zS_{pz})(xS_{ex} + yS_{ey} + zS_{ez})$$

$$= \int d\Omega [x^2 S_{px}S_{ex} + y^2 S_{py}S_{ey} + z^2 S_{pz}S_{ez} + xy(S_{px}S_{ey} + S_{py}S_{ex})$$

$$+ yz(S_{py}S_{ez} + S_{pz}S_{ey}) + xz(S_{px}S_{ez} + S_{pz}S_{ex})]$$

# Angular Integrations

We have the following angular integrals

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

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

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

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

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

$$\int d\Omega\, xz = r^2 \int_0^{\pi} \sin\theta \cos\theta \sin\theta \;\, d\theta \int_0^{2\pi} \cos\varphi \, d\varphi$$

# Angular Integrations

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,

$$\int d\Omega \, yz = r^2 \int_0^{\pi} \sin\theta \cos\theta \sin\theta \;\; d\theta \int_0^{2\pi} \sin\varphi \, d\varphi \; = 0$$

# Angular Integrations

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

$$\int d\Omega \, xy = r^2 \int_0^{\pi} \sin^2\theta \sin\theta \; d\theta \int_0^{2\pi} \cos\varphi \sin\varphi \; d\varphi = 0$$

On the other hand,

$$\int_0^{2\pi} \cos^2\varphi \; d\varphi = \frac{1}{2}\int_0^{2\pi} (\cos 2\varphi + 1) \; d\varphi = \frac{1}{4}(\sin 4\pi - \sin 0) + \frac{2\pi}{2} - 0 = \pi$$

$$\int_0^{2\pi} \sin^2\varphi \; d\varphi = \frac{1}{2}\int_0^{2\pi} (1 - \cos 2\varphi) \; d\varphi = \frac{2\pi}{2} - 0 - \frac{1}{4}(\sin 4\pi - \sin 0) = \pi$$

$$\int_0^{\pi} \sin^2\theta \sin\theta \; d\theta = -\int_0^{\pi} (1 - \cos^2\theta) \, d\,(\cos\theta) = -(\cos\pi - \cos 0) + \frac{\cos^3\pi}{3} - \frac{\cos^3 0}{3}$$

$$= -(-1 - 1) - \frac{1}{3} - \frac{1}{3} = \frac{4}{3}$$

# 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,

$$\int_0^{\pi} \cos^2\theta \sin\theta \;\, d\theta = -\int_0^{\pi} \cos^2\theta \, d\,(\cos\theta) = -\frac{\cos^3\pi}{3} + \frac{\cos^3 0}{3} = \frac{2}{3}$$

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

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

On the other hand,

$$\int d\Omega(S_p \cdot S_e) = 4\pi\,(S_p \cdot S_e)$$

Thus,

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

# Wave Function at the center

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

$$L_s^k(0) = \frac{(s+k)!}{s!\,k!}$$

we have

$$|u(0)|^2 = \left(\frac{2}{na_0}\right)^3\left(\frac{1}{2n^2}\right)\left(\frac{n!}{1!\;(n-1)!}\right)^2\left(\frac{1}{4\pi}\right) = \left(\frac{1}{na_0}\right)^3\frac{1}{\pi}$$

# Hyperfine Correction

The inner product on the spin part can be evaluated if we introduce the total spin

$$S = S_p + S_e$$

Then

$$S_p \cdot S_e = \frac{1}{2}\left(S^2 - S_p^2 - S_e^2\right)$$

and

$$E_{n(hf)}^{(1)} = \frac{4\pi g e^2}{3 m_p m_e c^2} \langle S_p \cdot S_e \rangle |u(0)|^2 = \frac{4\pi g e^2 \hbar^2}{3 m_p m_e c^2} \frac{\left[s(s+1) - \frac{3}{4} - \frac{3}{4}\right]}{2} \left(\frac{1}{n a_0}\right)^3 \frac{1}{\pi}$$

The hyperfine correction to the Hydrogen energy is then

$$E_{n(hf)}^{(1)} = \frac{2 g e^2 \hbar^2}{3 m_p m_e c^2} \left(\frac{1}{n a_0}\right)^3 \left[s(s+1) - \frac{3}{2}\right]$$

# Hyperfine Correction

The hyperfine energy may be cast in terms of the fine-structure constant

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

as

$$E_{n(hf)}^{(1)} = -E_n^{(0)}\frac{4g}{3n}\frac{m_e}{m_p}\alpha^2\left[s(s+1) - \tfrac{3}{2}\right]$$

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 ½,

$$S = \begin{cases} 0 \\ 1 \end{cases}$$

# Hyperfine Correction

and

$$s(s+1) - \frac{3}{2} = \begin{cases} \frac{1}{2} \\ -\frac{3}{2} \end{cases}$$

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

$$\Delta E_{n(hf)}^{(1)} = E_n^{(0)} \frac{8g}{3n} \frac{m_e}{m_p} \alpha^2$$

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.