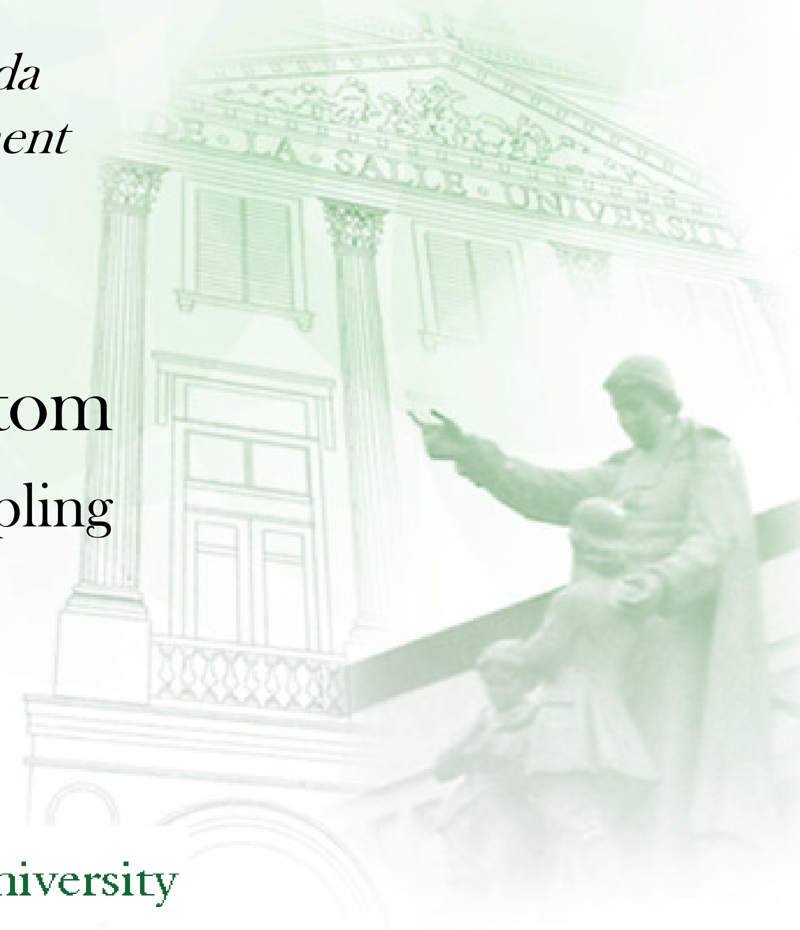
Quantum Mechanics 2

Robert C. Roleda
Physics Department

Hydrogen Atom

Spin-Orbit Coupling



De La Salle University

Magnetic Field

Classically, from the electron's frame of reference inside an atom, the nucleus is circling around it. A charge moving in a circle sets up a magnetic field. At the center of the circle,

$$B = \mu_0 \frac{I}{2r}$$

The current set up by a "circling" proton is

$$I = \frac{e}{T}$$

The period may be derived from the electron's angular momentum, as the orbital period is the same from both the electron's and the proton's frame

$$L = m_e v r = \frac{m_e 2\pi r^2}{T}$$

Thus,

$$B = \mu_0 \frac{e}{2rT} = \mu_0 \frac{e}{m_e 4\pi r^3} L$$

Spin-Orbit Coupling

One glaring omission of Schrödinger's atom is spin. With a spin S, the electron would have a magnetic moment

$$\mu_e = -\frac{e}{m_e} S$$

which will interact with the magnetic field at the electron's location to yield an interaction energy

$$H_I = -\mu_e \cdot B$$

In this case,

$$H_I = \left(\frac{e}{m_e} S\right) \cdot \left(\mu_0 \frac{e}{m_e 4\pi r^3} L\right) = \mu_0 \frac{e^2}{4\pi m_e^2 r^3} S \cdot L$$

Because this involves a dot product between the spin and orbital angular momenta, it is called a spin-orbit coupling.

The expression can be harmonized with the expressions we have for hydrogen atom energy by noting that

$$c = \frac{1}{\sqrt{\mu_0 \varepsilon_0}}$$

Thomas Precession

Thus

$$H_I = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{m_e^2c^2r^3}S\cdot L$$

The foregoing discussion was made on classical grounds. This is actually off by a factor of 2 accounted for by a kinematic correction to offset the shifting between reference frames, known as the Thomas precession. The correct expression is

$$H_I = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{2m_e^2c^2r^3}S\cdot L$$

The first-order correction to energy due to spin-orbit coupling is

$$E_{n(SO)}^{(1)} = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{2m_e^2c^2}\left\langle nlm_lm_s{}^{(0)}\right|\frac{S\cdot L}{r^3}\left|nlm_lm_s{}^{(0)}\right\rangle$$

Total Angular Momentum

The dot product may be evaluated as follows. Let us take the total angular momentum

$$J = L + S$$

Noting that

$$[L, S] = 0$$

we have

$$J^2 = L^2 + S^2 + 2S \cdot L$$

Hence,

$$S \cdot L = \frac{J^2 - L^2 - S^2}{2}$$

The good quantum numbers in this case are j, m instead of m_l, m_s. Thus, we write

$$\left\langle nlm_l {m_s}^{(0)} \middle| \frac{S \cdot L}{r^3} \middle| nlm_l {m_s}^{(0)} \right\rangle = \langle nl^{(0)} | r^{-3} | nl^{(0)} \rangle \left\langle lsjm^{(0)} \middle| \frac{J^2 - L^2 - S^2}{2} \middle| lsjm^{(0)} \right\rangle$$

$$= \langle r^{-3} \rangle \frac{1}{2} [j(j+1) - l(l+1) - s(s+1)] \hbar^2$$

Radial Part

The radial part can be evaluated using Kramers' relation [Hydrogen 4]

$$\frac{s+1}{n^2}Z^2\langle r^s\rangle - (2s+1)Za_0\langle r^{s-1}\rangle + \frac{s}{4}[(2l+1)^2 - s^2]a_0^2\langle r^{s-2}\rangle = 0$$

In particular, for $s = -1$,

$$a_0\langle r^{-2}\rangle - \frac{1}{4}[(2l+1)^2 - 1]a_0^2\langle r^{-3}\rangle = 0$$

From [Hydrogen 6],

$$\left\langle\frac{1}{r^2}\right\rangle = \frac{2}{(2l+1)n^3a_0^2}$$

Hence,

$$a_0\frac{2}{(2l+1)n^3a_0^2} = \frac{1}{4}[4l^2 + 4l + 1 - 1]a_0^2\langle r^{-3}\rangle$$

and

$$\langle r^{-3}\rangle = \frac{1}{l(l+1)(l+\frac{1}{2})n^3a_0^3}$$

Spin-Orbit Correction

Putting everything together, we then have

$$E_{n(SO)}^{(1)} = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{2m_e^2c^2}\frac{\left[j(j+1)-l(l+1)-\frac{3}{4}\right]\hbar^2}{2l(l+1)(l+\frac{1}{2})n^3a_0^3}$$

$$= \frac{e^2}{4\pi\varepsilon_0}\frac{\hbar^2}{m_ea_0}\frac{1}{4n^3a_0^2}\frac{1}{m_ec^2}\frac{\left[j(j+1)-l(l+1)-\frac{3}{4}\right]}{l(l+1)(l+\frac{1}{2})}$$

$$= \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\frac{1}{4n^4a_0^2}\frac{1}{m_ec^2}\frac{n\left[j(j+1)-l(l+1)-\frac{3}{4}\right]}{l(l+1)(l+\frac{1}{2})}$$

This can be written as

$$E_{n(SO)}^{(1)} = \frac{\left(E_n^{(0)}\right)^2}{m_ec^2}\frac{n\left[j(j+1)-l(l+1)-\frac{3}{4}\right]}{l(l+1)(l+\frac{1}{2})}$$