The Fine Structure of Hydrogenic Atoms

*** MKS (SI) units: let $k_0 \equiv 1/4\pi\epsilon_0$ ***

$$a_0 \approx \frac{\hbar}{m_e e^2} = \frac{\hbar}{m_e c\,\alpha}$$

$$\alpha = e^2/\hbar c$$

1 Relativistic kinetic energy correction

Consider the following central-potential Hamiltonian, accounting for a relativistic electron and a non-relativistic proton:

$$\begin{aligned}
\widehat{H} &= \widehat{K}_e + \widehat{K}_p + V(\widehat{r}\,) \\
&= \sqrt{\widehat{p_e^2}\,c^2 + (m_e c^2)^2} - m_e c^2 + \frac{\widehat{p_p^2}}{2m_p} + V(\widehat{r}\,) \\
&= m_e c^2 \left[\sqrt{1 + \left(\frac{\widehat{p_e}}{m_e c}\right)^2} - 1\right] + \frac{\widehat{p_p^2}}{2m_p} + V(\widehat{r}\,) \\
&\approx \left[\frac{\widehat{p_e^2}}{2m_e} - \frac{\widehat{p_e^4}}{8m_e^3 c^2} + \mathcal{O}(3)\right] + \frac{\widehat{p_p^2}}{2m_p} + V(\widehat{r}\,)
\end{aligned} \tag{1}$$

where

$$V(\widehat{r}\,) = -k_0\, Z e^2\, \widehat{r^{-1}}$$

is the Coulomb potential. (Note the operator form of r^{-1}.) Equation 1 can be written in terms of an unperturbed Hamiltonian $\widehat{H}_0$ and a kinetic-energy perturbation $\widehat{H}_1^{kin}$ as follows:

$$\widehat{H} = \widehat{H}_0 + \widehat{H}_1^{kin}, \tag{2}$$

with

$$\widehat{H}_0 \equiv \frac{\widehat{p_e^2}}{2m_e} + \frac{\widehat{p_p^2}}{2m_p} + V(\widehat{r}) = \frac{\widehat{p^2}}{2\mu} + V(\widehat{r}) \tag{3}$$

$$\widehat{H}_1^{kin} \equiv -\frac{\widehat{p_e^4}}{8m_e^3c^2}. \tag{4}$$

The last expression on the right of Eq. 3 is the center-of-mass representation, with $\widehat{p}$ the total momentum and μ the reduced mass. (Because of the electron's smaller mass, its kinetic energy may be assumed to dominate i.e. $\widehat{p^2}/2\mu \approx \widehat{p_e^2}/2m_e$.) The EVPs for the unperturbed and perturbed Hamiltonians are, respectively,

$$\widehat{H}_0 \left|nlm\right\rangle = E_n^{(0)} \left|nlm\right\rangle \quad \leftarrow \text{known}$$

$$\widehat{H} \left|\psi_{nlm}\right\rangle = E_n \left|\psi_{nlm}\right\rangle \quad \leftarrow \text{unknown.}$$

For simplicity, $|nlm^0\rangle \equiv |nlm\rangle$. The unperturbed energies can be treated non-relativistically since

$$|E_n^{(0)}| = \left|\langle nlm|\widehat{H}_0|nlm\rangle\right| = \left|\langle nlm|\frac{\widehat{p^2}}{2\mu}|nlm\rangle\right| \approx \frac{m_e c^2 Z^2\alpha^2}{2n^2} \ll m_e c^2.$$

The perturbed eigenkets and eigenvalues are sought as power series in a perturbation parameter $\lambda \in [0,1]$:

$$\left|\psi_{nlm}\right\rangle = \left|nlm\right\rangle + \sum_{j=1}^{\infty} \lambda^j \left|nlm^j\right\rangle \tag{5}$$

$$E_n = E_n^{(0)} + \sum_{j=1}^{\infty} \lambda^j K_n^{(j)}. \tag{6}$$

The sum on the RHS of Eq. 6 involves the various orders of the relativistic kinetic energy shifts. The perturbation $\widehat{H}_1^{kin}$ is rotationally invariant because $[\widehat{H}_1^{kin}, \widehat{\mathbf{L}}] = 0$. Therefore, it is already diagonal in the (degenerate) subspace of the $|nlm\rangle$ states. Because of this, the energy shifts can be found by *non-degenerate* perturbation theory. The first-order correction to the n-th energy level is

$$\begin{aligned}
K_n^{(1)} &= -\langle nlm|\frac{\widehat{p_e^4}}{8m_e^3c^2}|nlm\rangle \\
&= -\frac{1}{2m_e c^2}\left\langle nlm\right| \left(\frac{\widehat{p_e^2}}{2m_e}\right)^2 \left|nlm\right\rangle \\
&\approx -\frac{1}{2m_e c^2}\left\langle nlm\right| \left(\widehat{H}_0 + k_0\, Ze^2\, \widehat{r^{-1}}\right)^2 \left|nlm\right\rangle \\
&= -\frac{1}{2m_e c^2}\left[(E_n^{(0)})^2 + 2Ze^2E_n^{(0)}\left\langle r^{-1}\right\rangle_{nlm} + Z^2e^4\left\langle r^{-2}\right\rangle_{nlm}\right].
\end{aligned} \tag{7}$$

The position-operator expectation values of Eq. 7 are

$$\left\langle \frac{1}{r} \right\rangle_{nlm} := \langle nlm| \widehat{r^{-1}} |nlm\rangle = \frac{Z}{a_0 n^2} \quad \Rightarrow \quad Ze^2 \left\langle \frac{1}{r} \right\rangle_{nlm} = -2E_n^{(0)},$$

$$\left\langle \frac{1}{r^2} \right\rangle_{nlm} := \langle nlm| \widehat{r^{-2}} |nlm\rangle = \frac{Z^2}{a_0 n^3 (l+1/2)} \quad \Rightarrow \quad Z^2 e^4 \left\langle \frac{1}{r^2} \right\rangle_{nlm} = \frac{4\, n (E_n^{(0)})^2}{l+1/2}.$$

The first-order energy shift induced by relativistic corrections to the kinetic energy (Eq. 7) becomes

$$\begin{aligned} K_n^{(1)} \equiv K_{n,l}^{(1)} &= -\frac{(E_n^{(0)})^2}{2m_e c^2} \left(-3 + \frac{4n}{l+1/2} \right) \\ &= -\frac{m_e c^2}{2} (Z\alpha)^4 \left[-\frac{3}{4n^4} + \frac{1}{n^3 \, (l+1/2)} \right]. \end{aligned} \tag{8}$$

2 Spin-orbit coupling

In its rest frame, the electron experiences the magnetic field generated by the nucleus of charge $+Ze$ moving with velocity $-\boldsymbol{v}$. Conceptually, one can estimate this magnetic field by a cavalier version of the Biot-Savart Law,

$$\boldsymbol{B} = \frac{\mu_0}{4\pi} \left(\frac{-Ze\, \boldsymbol{v} \times \boldsymbol{r}}{r^3} \right) = \frac{\mu_0}{4\pi} \frac{Ze}{m_e \, r^3} \boldsymbol{L},$$

where $\boldsymbol{L}$ is the orbital angular momentum of the electron. A more physically sound derivation considers the electron moving with velocity $\boldsymbol{v}$ in the electric field of the nucleus, $\boldsymbol{E} = -\nabla\phi(r)$:

$$\boldsymbol{B} = -\frac{\boldsymbol{v} \times \boldsymbol{E}}{c^2} = -\frac{\boldsymbol{v} \times (-\nabla\phi)}{c^2} = \frac{\boldsymbol{v} \times \boldsymbol{r}}{c^2 \, r} \left(\frac{d\phi}{dr} \right) = \frac{-\boldsymbol{L}}{m_e c^2 \, r} \left(\frac{d\phi}{dr} \right) = k_0 \frac{Ze}{m_e c^2} \frac{\boldsymbol{L}}{r^3},$$

where the electric potential due the nucleus is $\phi(r) = k_0 \, Ze/r$. The interaction of this magnetic field with the electron's intrinsic magnetic moment $\boldsymbol{\mu}_e = -(e/m_e)\boldsymbol{S}$ is modeled via the spin-orbit Hamiltonian

$$\widehat{H}_{LS} = -\widehat{\boldsymbol{\mu}}_e \cdot \widehat{\boldsymbol{B}} = k_0 \frac{Ze^2}{2m_e^2 c^2} \frac{\widehat{\boldsymbol{S}} \cdot \widehat{\boldsymbol{L}}}{\widehat{r}^{\,3}}, \tag{9}$$

where $c = (\mu_0 \epsilon_0)^{-1/2}$ is the speed of light in vacuum; the factor 2 in the denominator of Eq. 9 accounts for *Thomas precession*, a relativistic effect.

We can now use degenerate perturbation theory to obtain the energy shifts arising from the spin-orbit effects on hydrogenic atoms. The perturbed Hamiltonian that is to be diagonalized is

$$\widehat{H} = \widehat{H}_0 + \widehat{H}_{LS} = \frac{\widehat{p^2}}{2\mu} - k_0 \, Ze^2 \, \widehat{r^{-1}} + k_0 \frac{Ze^2}{2m_e^2 c^2} \frac{\widehat{\boldsymbol{S}} \cdot \widehat{\boldsymbol{L}}}{\widehat{r}^{\,3}}. \tag{10}$$

The eigenstates of $\widehat{H}_0$ must now include the electronic spin, i.e. $|nlm\rangle \otimes |\frac{1}{2}, \pm\frac{1}{2}\rangle$; the unperturbed wave functions are now $\psi_{nlm}(r,\theta,\phi)|\frac{1}{2}, \pm\frac{1}{2}\rangle$. We can diagonalize $\widehat{H}$ the straightforward—albeit laborious—way. Alternatively, we can look for a set commuting observables in which *both* $\widehat{H}_0$ and $\widehat{H}_{LS}$ are diagonal. (This is equivalent to finding the right decomposition of the unperturbed states in their degenerate subspace.) Such a set is easy to spot: $\{\widehat{L}^2, \widehat{S}^2, \widehat{J}^2, \widehat{J}_z\}$, whose simultaneous eigenkets are $|n\,l\,j\,m_j\rangle$ (we omit the spin states $|\frac{1}{2}, \pm\frac{1}{2}\rangle$ since they are independent of the other quantum numbers). Here, $\widehat{\boldsymbol{J}} = \widehat{\boldsymbol{L}} + \widehat{\boldsymbol{S}}$ is the total angular momentum. The spin-orbit coupling in $\widehat{H}_{LS}$ is then

$$\widehat{\boldsymbol{S}} \cdot \widehat{\boldsymbol{L}} = \frac{1}{2}(\widehat{\boldsymbol{J}}^{\,2} - \widehat{\boldsymbol{L}}^{\,2} - \widehat{\boldsymbol{S}}^{\,2}),$$

whose matrix elements in the $\{|n\,l\,j\,m_j\rangle\}$ basis are

$$\langle \boldsymbol{S} \cdot \boldsymbol{L} \rangle_{n\,l\,j\,m_j} = \frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - \frac{3}{4} \right].$$

The total angular momentum number takes the values $j = l \pm 1/2$, for fixed l. Therefore,

$$\langle \boldsymbol{S} \cdot \boldsymbol{L} \rangle_{n\,l\,j\,m_j} = \frac{\hbar^2}{2} \times \begin{cases} l\,, \text{ for } j = l + 1/2 \\ -l-1\,, \text{ for } j = l - 1/2. \end{cases}$$

The remaining matrix elements of $\widehat{H}_{LS}$ to be calculated are those of $\widehat{r^{-3}}$. These are

$$\left\langle \frac{1}{r^3} \right\rangle_{n\,l\,j\,m_j} = \frac{1}{a_0^3}\,\frac{Z^3}{n^3\,l\,(l+1)\,(l+1/2)}. \quad \textit{(Prove it!)}$$

Consequently, in the $\{|n\,l\,j\,m_j\rangle\}$ basis, the first-order correction matrix elements are

$$E_{LS}^{(1)} = \frac{m_e c^2}{4}(Z\alpha)^4 \frac{1}{n^3\,l\,(l+1)\,(l+1/2)} \times \begin{cases} l\,, \text{ for } j = l + 1/2 \\ -l-1\,, \text{ for } j = l - 1/2. \end{cases} \tag{11}$$

3 Other contributions: the Darwin and Lamb shifts

The "Darwin term" affects the $l = 0$ (S) states. It is related to the effect of the rapidly oscillating S-state wavefunction that alters the electric potential at the nucleus. Its expression is

$$\begin{aligned} E_{\text{Darwin}} &= k_0\, 4\pi\, \frac{\hbar^2}{8m_e^2c^2}\,(Ze^2)\,|\psi_{n00}(0)|^2 \\ &= k_0\,\frac{\hbar^2}{2m_e^2c^2}\,\frac{Z^4e^2}{n^3a_0^3} = k_0\,\frac{\hbar^3}{2m_e^2c}\,\frac{Z^4\alpha}{n^3a_0^3} = k_0\,\frac{\hbar^3}{2m_e^2c}\,\frac{Z^4\alpha}{n^3\hbar^3}\,m_e^3\,c^3\,\alpha^3 \\ &= k_0\,\frac{m_ec^2}{2}\,(Z\alpha)^4\,\frac{1}{n^3}, \end{aligned}$$

where

$$\psi_{n00}(0) = R_{n0}(0)\, Y_{00}(\theta, \phi) = 2 \left(\frac{Z}{n\, a_0} \right)^{3/2} \frac{1}{\sqrt{4\pi}}.$$

The Lamb shift is a minute energy correction arising from the self-interaction of the electron with its own electromagmetic field. It results in raising the ${}^2S_{1/2}$ state above the ${}^2P_{1/2}$ state by a tiny amount. Its order of magnitude is $E_{\text{Lamb}} \sim m_e c^2 (Z\alpha)^4\, \alpha \log \alpha$.

Thus, the fine structure of hydrogenic atoms is, to first order,

$$\begin{aligned} E_n &= E_n^{(0)} + K_{n,l}^{(1)} + E_{LS}^{(1)} + E_{\text{Darwin}} + E_{\text{Lamb}} \\ &= E_n^{(0)} + \frac{m_e c^2}{4} (Z\alpha)^4 \left[-\frac{3}{4n} + \frac{1}{j + 1/2} \right] + E_{\text{Darwin}} + E_{\text{Lamb}}, \end{aligned} \tag{12}$$

valid for both $l = j \pm 1/2$ and $l = 0$.