Fine Structure of Hydrogen

According to special relativity, the kinetic energy (*i.e.*, the difference between the total energy and the rest mass energy) of a particle of rest mass m and momentum p is

$$T = \sqrt{p^2\,c^2 + m^2\,c^4} - m\,c^2. \tag{966}$$

In the non-relativistic limit $p \ll m\,c$, we can expand the square-root in the above expression to give

$$T = \frac{p^2}{2\,m}\left[1 - \frac{1}{4}\left(\frac{p}{m\,c}\right)^2 + \mathcal{O}\left(\frac{p}{m\,c}\right)^4\right]. \tag{967}$$

Hence,

$$T \simeq \frac{p^2}{2\,m} - \frac{p^4}{8\,m^3\,c^2}. \tag{968}$$

Of course, we recognize the first term on the right-hand side of this equation as the standard non-relativistic expression for the kinetic energy. The second term is the lowest-order relativistic correction to this energy. Let us consider the effect of this type of correction on the energy levels of a hydrogen atom. So, the unperturbed Hamiltonian is given by Eq. (911), and the perturbing Hamiltonian takes the form

$$H_1 = -\frac{p^4}{8\,m_e^3\,c^2}. \tag{969}$$

Now, according to standard first-order perturbation theory (see Sect. 12.4), the lowest-order relativistic correction to the energy of a hydrogen atom state characterized by the standard quantum numbers n, l, and m is given by

$$\begin{aligned}\Delta E_{nlm} &= \langle n,l,m|H_1|n,l,m\rangle = -\frac{1}{8\,m_e^3\,c^2}\,\langle n,l,m|p^4|n,l,m\rangle\\ &= -\frac{1}{8\,m_e^3\,c^2}\,\langle n,l,m|p^2\,p^2|n,l,m\rangle.\end{aligned} \tag{970}$$

However, Schrödinger's equation for a unperturbed hydrogen atom can be written

$$p^2\,\psi_{n,l,m} = 2\,m_e\,(E_n - V)\,\psi_{n,l,m}, \tag{971}$$

where $V = -e^2/(4\pi\epsilon_0\,r)$. Since p^2 is an Hermitian operator, it follows that

$$\begin{aligned}\Delta E_{nlm} &= -\frac{1}{2\,m_e\,c^2}\,\langle n,l,m|(E_n - V)^2|n,l,m\rangle\\ &= -\frac{1}{2\,m_e\,c^2}\left(E_n^2 - 2\,E_n\,\langle n,l,m|V|n,l,m\rangle + \langle n,l,m|V^2|n,l,m\rangle\right)\\ &= -\frac{1}{2\,m_e\,c^2}\left[E_n^2 + 2\,E_n\left(\frac{e^2}{4\pi\epsilon_0}\right)\left\langle\frac{1}{r}\right\rangle + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle\right].\end{aligned} \tag{972}$$

It follows from Eqs. (695) and (696) that

$$\Delta E_{nlm} = -\frac{1}{2\,m_e\,c^2}\left[E_n^2 + 2\,E_n\left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{1}{n^2\,a_0} + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{1}{(l+1/2)\,n^3\,a_0^2}\right]. \tag{973}$$

Finally, making use of Eqs. (676), (678), and (679), the above expression reduces to

$$\Delta E_{nlm} = E_n\,\frac{\alpha^2}{n^2}\left(\frac{n}{l+1/2} - \frac{3}{4}\right), \tag{974}$$

where

$$\alpha = \frac{e^2}{4\pi\epsilon_0\,\hbar\,c} \simeq \frac{1}{137} \tag{975}$$

is the dimensionless *fine structure constant*.

Note that the above derivation implicitly assumes that p^4 is an Hermitian operator. It turns out that this is not the case for $l = 0$ states. However, somewhat fortuitously, our calculation still gives the correct answer when $l = 0$. Note, also, that we are able to use *non-degenerate* perturbation theory in the above calculation, using the ψ_{nlm} eigenstates, because the perturbing Hamiltonian commutes with both L^2 and L_z. It follows that there is no coupling between states with different l and m quantum numbers. Hence, all coupled states have different n quantum numbers, and therefore have different energies.

Now, an electron in a hydrogen atom experiences an electric field

$$\mathbf{E} = \frac{e\,\mathbf{r}}{4\pi\epsilon_0\, r^3} \tag{976}$$

due to the charge on the nucleus. However, according to electromagnetic theory, a non-relativistic particle moving in a electric field $\mathbf{E}$ with velocity $\mathbf{v}$ also experiences an effective magnetic field

$$\mathbf{B} = -\frac{\mathbf{v}\times\mathbf{E}}{c^2}. \tag{977}$$

Recall, that an electron possesses a magnetic moment [see Eqs. (759) and (760)]

$$\boldsymbol{\mu} = -\frac{e}{m_e}\,\mathbf{S} \tag{978}$$

due to its spin angular momentum, $\mathbf{S}$. We, therefore, expect an additional contribution to the Hamiltonian of a hydrogen atom of the form [see Eq. (761)]

$$\begin{aligned} H_1 &= -\boldsymbol{\mu}\cdot\mathbf{B} \\ &= -\frac{e^2}{4\pi\epsilon_0\, m_e\, c^2\, r^3}\,\mathbf{v}\times\mathbf{r}\cdot\mathbf{S} \\ &= \frac{e^2}{4\pi\epsilon_0\, m_e^2\, c^2\, r^3}\,\mathbf{L}\cdot\mathbf{S}, \end{aligned} \tag{979}$$

where $\mathbf{L} = m_e\,\mathbf{r}\times\mathbf{v}$ is the electron's orbital angular momentum. This effect is known as *spin-orbit coupling*. It turns out that the above expression is too large, by a factor 2, due to an obscure relativistic effect known as *Thomas precession*. Hence, the true spin-orbit correction to the Hamiltonian is

$$H_1 = \frac{e^2}{8\pi\,\epsilon_0\, m_e^2\, c^2\, r^3}\,\mathbf{L}\cdot\mathbf{S}. \tag{980}$$

Let us now apply perturbation theory to the hydrogen atom, using the above expression as the perturbing Hamiltonian.

Now

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \tag{981}$$

is the total angular momentum of the system. Hence,

$$J^2 = L^2 + S^2 + 2\,\mathbf{L}\cdot\mathbf{S}, \tag{982}$$

giving

$$\mathbf{L}\cdot\mathbf{S} = \frac{1}{2}\,(J^2 - L^2 - S^2). \tag{983}$$

Recall, from Sect. 11.2, that whilst J^2 commutes with both L^2 and S^2, it does not commute with either L_z or S_z. It follows that the perturbing Hamiltonian (980) also commutes with both L^2 and S^2, but does not commute with either L_z or S_z. Hence, the simultaneous eigenstates of the unperturbed Hamiltonian (911) and the perturbing Hamiltonian (980) are the same as the simultaneous eigenstates of L^2, S^2, and J^2 discussed in Sect. 11.3. It is important to know this since, according to Sect. 12.6, we can only safely apply perturbation theory to the simultaneous eigenstates of the unperturbed and perturbing Hamiltonians.

Adopting the notation introduced in Sect. 11.3, let $\psi^{(2)}_{l,s;j,m_j}$ be a simultaneous eigenstate of L^2, S^2, J^2, and J_z corresponding to the eigenvalues

$$L^2\,\psi^{(2)}_{l,s;j,m_j} = l\,(l+1)\,\hbar^2\,\psi^{(2)}_{l,s;j,m_j}, \tag{984}$$

$$S^2\,\psi^{(2)}_{l,s;j,m_j} = s\,(s+1)\,\hbar^2\,\psi^{(2)}_{l,s;j,m_j}, \tag{985}$$

$$J^2\,\psi^{(2)}_{l,s;j,m_j} = j\,(j+1)\,\hbar^2\,\psi^{(2)}_{l,s;j,m_j}, \tag{986}$$

$$J_z\,\psi^{(2)}_{l,s,j,m_j} = m_j\,\hbar\,\psi^{(2)}_{l,s,j,m_j}. \tag{987}$$

According to standard first-order perturbation theory, the energy-shift induced in such a state by spin-orbit coupling is given by

$$\begin{aligned}\Delta E_{l,1/2,j,m_j} &= \langle l,1/2;j,m_j|H_1|l,1/2;j,m_j\rangle\\ &= \frac{e^2}{16\pi\,\epsilon_0\,m_e^2\,c^2}\left\langle 1,1/2;j,m_j\left|\frac{J^2-L^2-S^2}{r^3}\right|l,1/2;j,m_j\right\rangle\\ &= \frac{e^2\,\hbar^2}{16\pi\,\epsilon_0\,m_e^2\,c^2}\,[j\,(j+1)-l\,(l+1)-3/4]\,\left\langle\frac{1}{r^3}\right\rangle.\end{aligned} \tag{988}$$

Here, we have made use of the fact that $s=1/2$ for an electron. It follows from Eq. (697) that

$$\Delta E_{l,1/2;j,m_j} = \frac{e^2\,\hbar^2}{16\pi\,\epsilon_0\,m_e^2\,c^2\,a_0^3}\left[\frac{j\,(j+1)-l\,(l+1)-3/4}{l\,(l+1/2)\,(l+1)\,n^3}\right], \tag{989}$$

where n is the radial quantum number. Finally, making use of Eqs. (676), (678), and (679), the above expression reduces to

$$\Delta E_{l,1/2;j,m_j} = E_n\,\frac{\alpha^2}{n^2}\left[\frac{n\,\{3/4+l\,(l+1)-j\,(j+1)\}}{2\,l\,(l+1/2)\,(l+1)}\right], \tag{990}$$

where α is the fine structure constant. A comparison of this expression with Eq. (974) reveals that the energy-shift due to spin-orbit coupling is of the same order of magnitude as that due to the lowest-order relativistic correction to the Hamiltonian. We can add these two corrections together (making use of the fact that $j=l\pm1/2$ for a hydrogen atom--see Sect. 11.3) to obtain a net energy-shift of

$$\Delta E_{l,1/2;j,m_j} = E_n\,\frac{\alpha^2}{n^2}\left(\frac{n}{j+1/2}-\frac{3}{4}\right). \tag{991}$$

This modification of the energy levels of a hydrogen atom due to a combination of relativity and spin-orbit coupling is known as *fine structure*.

Now, it is conventional to refer to the energy eigenstates of a hydrogen atom which are also simultaneous eigenstates of J^2 as nL_j states, where n is the radial quantum number, $L=(S,P,D,F,\cdots)$ as $l=(0,1,2,3,\cdots)$, and j is the total angular momentum quantum number. Let us examine the effect of the fine structure energy-shift (991) on these eigenstates for $n=1,2$ and 3.

For $n=1$, in the absence of fine structure, there are two degenerate $1S_{1/2}$ states. According to Eq. (991), the fine structure induced energy-shifts of these two states are the same. Hence, fine structure does not break the degeneracy of the two $1S_{1/2}$ states of hydrogen.

For $n=2$, in the absence of fine structure, there are two $2S_{1/2}$ states, two $2P_{1/2}$ states, and four $2P_{3/2}$ states, all of which are degenerate. According to Eq. (991), the fine structure induced energy-shifts of the $2S_{1/2}$ and $2P_{1/2}$ states are the same as one another, but are different from the induced energy-shift of the $2P_{3/2}$ states. Hence, fine structure does not break the degeneracy of the $2S_{1/2}$ and $2P_{1/2}$ states of hydrogen, but does break the degeneracy of these states relative to the $2P_{3/2}$ states.

For $n=3$, in the absence of fine structure, there are two $3S_{1/2}$ states, two $3P_{1/2}$ states, four $3P_{3/2}$ states, four $3D_{3/2}$ states, and six $3D_{5/2}$ states, all of which are degenerate. According to Eq. (991), fine structure breaks these states into three groups: the $3S_{1/2}$ and $3P_{1/2}$ states, the $3P_{3/2}$ and $3D_{3/2}$ states, and the $3D_{5/2}$ states.

The effect of the fine structure energy-shift on the $n=1$, 2, and 3 energy states of a hydrogen atom is illustrated in Fig. 23.

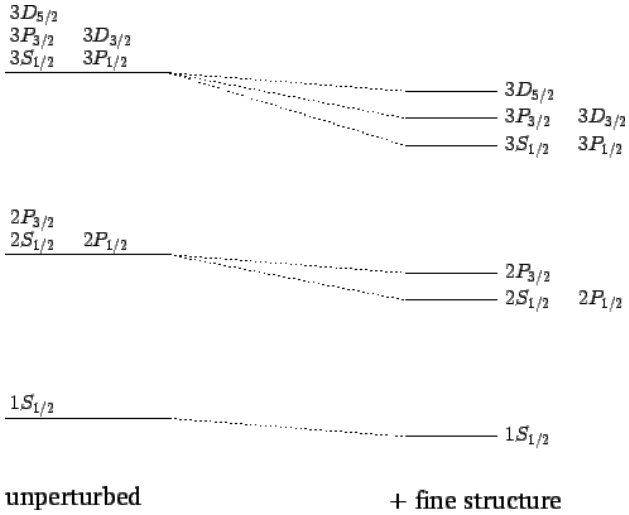

Figure 23: *Effect of the fine structure energy-shift on the* $n = 1, 2$ *and 3 states of a hydrogen atom. Not to scale.*

Note, finally, that although expression (990) does not have a well-defined value for $l = 0$, when added to expression (974) it, somewhat fortuitously, gives rise to an expression (991) which is both well-defined and correct when $l = 0$.

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