

Chapter 2

Fine Structure

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2.1 Review of hydrogen atom

The hydrogen atom Hamiltonian is by now familiar to you. You have found the bound state spectrum in more than one way and learned about the large degeneracy that exists for all states except the ground state. We will call the hydrogen atom Hamiltonian $H^{(0)}$ and it is given by

$$H^{(0)} = \frac{\mathbf{p}^2}{2m} - \frac{e^2}{r}. \quad (2.1.1)$$

We take this to be the “known” Hamiltonian, meaning that we know its spectrum. This Hamiltonian is supplemented with corrections that can be studied in perturbation theory. That study is the subject of this chapter. We begin, however, with some review and comments.

The mass m in $H^{(0)}$ is the reduced mass of the electron and proton, which we can accurately set equal to the mass of the electron. If one wishes to consider the case of an electron bound to a nucleus with Z protons one lets $e^2 \rightarrow Ze^2$ in $H^{(0)}$. The Bohr radius is the length scale build from \hbar , m , and e^2

$$a_0 \equiv \frac{\hbar^2}{me^2} \sim 53 \text{ pm}. \quad (2.1.2)$$

The energy levels are enumerated using a *principal* quantum number n , an integer that must be greater or equal to one:

$$E_n = -\frac{e^2}{2a_0} \frac{1}{n^2}, \quad n = 1, 2, \dots \quad (2.1.3)$$

Note that $H^{(0)}$ is a non-relativistic Hamiltonian: the speed of light does not enter in it, and the kinetic term is that of Newtonian mechanics. The energy scale relevant to the

bound state spectrum can be better appreciated using the speed of light to consider both the fine structure constant and the rest energy of the electron. The fine structure constant is given by

$$\alpha \equiv \frac{e^2}{\hbar c} \simeq \frac{1}{137}, \quad (2.1.4)$$

and the rest energy of the electron is mc^2 . Then,

$$\frac{e^2}{a_0} = \frac{me^4}{\hbar^2} = \frac{m\alpha^2\hbar^2c^2}{\hbar^2} = \alpha^2 mc^2. \quad (2.1.5)$$

This states that the energy scale of hydrogen bound states is a factor of α^2 smaller than the rest energy of the electron, that is, about 19000 times smaller. We can thus rewrite the possible energies as:

$$E_n = -\frac{1}{2} \alpha^2 mc^2 \frac{1}{n^2}. \quad (2.1.6)$$

The typical momentum in the hydrogen atom is

$$p \simeq \frac{\hbar}{a_0} = \frac{me^2}{\hbar} = \frac{e^2}{\hbar c} mc \rightarrow p \simeq \alpha(mc), \quad (2.1.7)$$

which, written as $p \simeq m(\alpha c)$ says that the typical velocity is $v \simeq \alpha c$, which is low enough that the non-relativistic approximation is fairly accurate. Finally, we note that

$$a_0 = \frac{\hbar^2}{m\alpha\hbar c} = \frac{\hbar}{mc} \frac{1}{\alpha} = \frac{\lambda}{\alpha}, \quad (2.1.8)$$

which says that the Bohr radius is over a hundred times bigger than the (reduced) Compton wavelength of the electron.

The degeneracy of the hydrogen atom spectrum is completely quantified by the relation

$$n = N + \ell + 1. \quad (2.1.9)$$

Here $N \geq 0$ is the degree of a polynomial in r that appears in a wavefunction where the leading dependence on r near the origin is factored out. The quantum number $\ell \geq 0$ is the angular momentum of the state. For each fixed n , you can see that the number ℓ ranges from zero to $n - 1$. And for each fixed ℓ the eigenvalue of L_z is $m\hbar$ with m ranging from $-\ell$ up to ℓ :

$$\begin{array}{ll} n = 1, 2, \dots & \ell = 0, 1, \dots, n - 1 \\ m = -\ell, \dots, \ell & \# \text{ of states with energy } E_n = \sum_{\ell=0}^{n-1} (2\ell + 1) = n^2 \end{array}$$

The states of hydrogen are shown in this energy diagram, which is not drawn to scale,

	<i>S</i> $\ell = 0$	<i>P</i> $\ell = 1$	<i>D</i> $\ell = 2$	<i>F</i> $\ell = 3$
\vdots	\vdots	\vdots	\vdots	\vdots
$n = 4$	████ $N = 3$	████ $N = 2$	████ $N = 1$	████ $N = 0$
$n = 3$	████ $N = 2$	████ $N = 1$	████ $N = 0$	
$n = 2$	████ $N = 1$	████ $N = 0$		
$n = 1$	████ $N = 0$			

The table features the commonly used notation where capital letters are used to denote the various values of the orbital angular momentum ℓ . If we have L denote the generic capital letter for angular momentum we have $L(\ell)$ where

$$L(\ell = 0) = S, \quad L(\ell = 1) = P, \quad L(\ell = 2) = D, \quad L(\ell = 3) = F, \dots \quad (2.1.10)$$

Thus, for example, an *S* state is a state with $\ell = 0$, a *P* state is a state with $\ell = 1$, and a *D* state is a state with $\ell = 2$.

Any hydrogen eigenstate specified by the three quantum numbers n, ℓ, m , because, as it follows from (2.1.9), the value of N is then fixed. The wavefunction takes the form

$$\psi_{n,\ell,m}(\mathbf{x}) = A \left(\frac{r}{a_0} \right)^\ell \cdot \left(\text{Polynomial in } \frac{r}{a_0} \text{ of degree } N \right) \cdot e^{-\frac{r}{na_0}} Y_{\ell,m}(\theta, \phi), \quad (2.1.11)$$

where A is a normalization constant and $N = n - (\ell + 1)$. If you look at the wavefunction, the value of n can be read from the exponential factor. The value of ℓ can be read from the radial prefactor, or from the spherical harmonic. The value of m can be read from the spherical harmonic. For the ground state $n = 1, \ell = 0$ and $m = 0$. The normalized wavefunction is

$$\psi_{1,0,0}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}}. \quad (2.1.12)$$

Comments:

1. There are n^2 degenerate states at any energy level with principal quantum number n . This degeneracy explained by the existence of a conserved quantum Runge-Lenz vector. For a given n the states with various ℓ 's correspond, in the semiclassical picture, to orbits of different eccentricity but the same semi-major axis. The orbit with $\ell = 0$ is the most eccentric one and the orbit with maximum $\ell = n - 1$ is the most circular one.

2. For each fixed value of ℓ , the states have increasing N as we move up in energy. The number N is the number of nodes in the solution of the radial equation, that's why it is the degree of the polynomial in r that features in the wavefunction (2.1.11).
3. The analysis of $H^{(0)}$ so far ignored electron spin. Since the electron is a spin one-half particle there is an extra degeneracy: each of the $H^{(0)}$ eigenstates is really two degenerate states, one with the electron spin up and the other with the electron spin down. These states are degenerate because $H^{(0)}$ has no spin dependence.
4. We will have to supplement $H^{(0)}$ with terms that correspond to corrections that arise from relativity and from the spin of the electron. This will be the main subject of the following analysis. It will determine the *fine-structure* of the hydrogen atom. The corrections will break much of the degeneracy of the spectrum.
5. In order to understand better the spectrum and the properties of the Hydrogen atom one can apply an electric field, leading to the *Stark* effect or a magnetic field, leading to the *Zeeman* effect. These external fields are represented by extra terms in the hydrogen atom Hamiltonian.

Let us now discuss two different choices of basis states for the hydrogen atom, both of which include the electron spin properly.

Recall that, in general, for a multiplet of angular momentum j , we have states (j, m_j) , with m_j running from $-j$ to j in integer steps. All states in the multiplet are $\hat{\mathbf{J}}^2$ eigenstates with eigenvalue $\hbar^2 j(j+1)$ and, for each state, $\hbar m_j$ is the eigenvalue of \hat{J}_z .

Because the electron has spin one half, its states are labeled as

$$(s, m_s), \quad \text{with } s = \frac{1}{2}, \quad m_s = \pm \frac{1}{2}. \quad (2.1.13)$$

In the hydrogen atom the angular momentum ℓ can take different values, but the spin of the electron is always one-half. As a result, the label s is often omitted, and we usually only record the value of m_s . For hydrogen basis states we thus have quantum numbers n, ℓ, m_ℓ , and m_s . To avoid confusion, we have added the ℓ subscript to m_ℓ , thus emphasizing that this is the azimuthal quantum number for orbital angular momentum. Since we are not combining the electron spin to its orbital angular momentum, the states form the “uncoupled basis”:

Uncoupled basis quantum numbers: (n, ℓ, m_ℓ, m_s) .

(2.1.14)

The states are completely specified by these quantum numbers. As we let those quantum numbers run over all possible values we obtain an orthonormal basis of states.

It is often useful to use an alternative basis where the states are eigenstates of $\hat{\mathbf{J}}^2$ and \hat{J}_z , where the total angular momentum $\hat{\mathbf{J}}$ is obtained by adding the orbital angular momentum $\hat{\mathbf{L}}$ to the spin angular momentum $\hat{\mathbf{S}}$:

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}. \quad (2.1.15)$$

When we form $\ell \otimes s$ we are tensoring a full ℓ multiplet to an s multiplet (here, of course, $s = 1/2$). All states in $\ell \otimes s$ are eigenstates of $\hat{\mathbf{L}}^2$ and eigenstates of $\hat{\mathbf{S}}^2$, so ℓ and s are good (constant) quantum numbers for all j multiplets that arise in the tensor product. Each j multiplet has states with quantum numbers (j, m_j) .

The coupled basis is one where states are organized into j multiplets. While states are no longer \hat{L}_z nor \hat{S}_z eigenstates they are still $\hat{\mathbf{L}}^2$ eigenstates, thus the ℓ quantum number survives. The coupled basis quantum numbers are therefore

$$\boxed{\text{Coupled basis quantum numbers: } (n, \ell, j, m_j)}. \quad (2.1.16)$$

The (m_ℓ, m_s) quantum numbers of the uncoupled basis have been traded for (j, m_j) quantum numbers and we have kept the n, ℓ quantum numbers. The coupled states are linear combinations of uncoupled states that involve different values of m_ℓ and m_s , those combinations that yield the same value of $m_j = m_\ell + m_s$.

To find the list of coupled basis states we must tensor *each* ℓ multiplet in the hydrogen atom spectrum with the spin doublet $\frac{1}{2}$. The rules of addition of angular momentum imply that we find two j multiplets:

$$\ell \otimes \frac{1}{2} = (j = \ell + \frac{1}{2}) \oplus (j = \ell - \frac{1}{2}). \quad (2.1.17)$$

For $\ell = 0$, we only obtain a $j = 1/2$ multiplet. We use the notation L_j for the coupled multiplets, with $L = S, P, D, F$ for $\ell = 0, 1, 2$, and 3 (see (2.1.10)). The change of basis is summarized by the replacements

$$\ell \otimes \frac{1}{2} \rightarrow L(\ell)_{j=\ell+\frac{1}{2}} \oplus L(\ell)_{j=\ell-\frac{1}{2}} \quad (2.1.18)$$

or more explicitly,

$$\begin{aligned} 0 \otimes \frac{1}{2} &\rightarrow S_{\frac{1}{2}} \\ 1 \otimes \frac{1}{2} &\rightarrow P_{\frac{3}{2}} \oplus P_{\frac{1}{2}} \\ 2 \otimes \frac{1}{2} &\rightarrow D_{\frac{5}{2}} \oplus D_{\frac{3}{2}} \\ 3 \otimes \frac{1}{2} &\rightarrow F_{\frac{7}{2}} \oplus F_{\frac{5}{2}} \end{aligned} \quad (2.1.19)$$

Thus, by the time we combine with electron spin, each $\ell = 0$ state gives one $j = \frac{1}{2}$ multiplet, each $\ell = 1$ state gives $j = \frac{3}{2}$ and $j = \frac{1}{2}$ multiplets, each $\ell = 2$ state gives $j = \frac{5}{2}$ and $j = \frac{3}{2}$ multiplets, and so on. For hydrogen, the principal quantum number is placed ahead to denote the coupled multiplets by

$$\text{Coupled basis notation for multiplets: } \boxed{nL_j} \quad (2.1.20)$$

Using this notation for coupled basis multiplets the diagram of hydrogen atom energy eigenstates becomes:

	S $\ell = 0$	P $\ell = 1$	D $\ell = 2$
\vdots	\vdots	\vdots	\vdots
$n = 4$	$\underline{4S_{\frac{1}{2}}}$	$\underline{\hspace{2cm}}$	
$n = 3$	$\underline{3S_{\frac{1}{2}}}$ (2)	$\underline{3P_{\frac{3}{2}}}$ (6) $\underline{3P_{\frac{1}{2}}}$	$\underline{3D_{\frac{3}{2}}}$ (10) $\underline{3D_{\frac{5}{2}}}$
$n = 2$	$\underline{2S_{\frac{1}{2}}}$ (2)	$\underline{2P_{\frac{3}{2}}}$ (6) $\underline{2P_{\frac{1}{2}}}$	
$n = 1$	$\underline{1S_{\frac{1}{2}}}$ (2)		

The number of states is indicated in parenthesis.

2.2 The Pauli equation

In the hydrogen atom the spin-orbit coupling arises because the electron is moving in the electric field of the proton. Since the electron is moving relative to the frame where we have a static electric field, the electron also sees a magnetic field \mathbf{B} . The spin-orbit coupling is the coupling $-\boldsymbol{\mu} \cdot \mathbf{B}$ of that magnetic field to the magnetic dipole moment $\boldsymbol{\mu}$ of the electron.

We have discussed before, in the context of the Stern-Gerlach experiment, the value of the magnetic dipole moment of the electron. Recall the logic we used. In Gaussian units, the classical magnetic moment of a planar current loop is given by $\boldsymbol{\mu} = \frac{I}{c} \mathbf{a}$, where I is the current and \mathbf{a} is the area vector associated with the loop. From this one quickly derives that for a uniformly rotating particle with charge q and mass m the magnetic moment is

$$\boldsymbol{\mu} = \frac{q}{2mc} \mathbf{L}, \quad (2.2.1)$$

where \mathbf{L} is the angular momentum due to the rotation. For an elementary particle, this motivates the following relation between the spin angular momentum operator $\hat{\mathbf{S}}$ and the magnetic moment

$$\boldsymbol{\mu} = g \frac{q}{2mc} \hat{\mathbf{S}} \quad (2.2.2)$$

where g is a factor that is added to parameterize our ignorance; after all there is no reason why the classically motivated formula for the magnetic dipole should hold in the quantum domain of spin. As it turns out, for an electron one has $g = 2$. Since $q = -e$ for an electron,

we have

$$\boldsymbol{\mu} = 2 \frac{-e}{2m_e c} \hat{\mathbf{S}} = -2 \frac{e\hbar}{2m_e c} \frac{\hat{\mathbf{S}}}{\hbar} = -2 \frac{e\hbar}{2m_e c} \frac{1}{2} \boldsymbol{\sigma} = -\frac{e\hbar}{2m_e c} \boldsymbol{\sigma}. \quad (2.2.3)$$

For numerical applications we note that the *Bohr magneton* μ_B is defined by

$$\mu_B = \frac{e\hbar}{2m_e c} \simeq 9.274 \times 10^{-21} \frac{\text{erg}}{\text{gauss}} = 5.79 \times 10^{-9} \frac{\text{eV}}{\text{gauss}}. \quad (2.2.4)$$

(for SI values use Tesla = 10^4 gauss). The coupling of an electron to an external magnetic field is therefore represented by a Hamiltonian H_B given by

$$H_B = -\boldsymbol{\mu} \cdot \mathbf{B} = \frac{e\hbar}{2m_e c} \boldsymbol{\sigma} \cdot \mathbf{B}. \quad (2.2.5)$$

Our goal now is to show that this coupling, and its associated prediction of $g = 2$, arises naturally from the non-relativistic Pauli equation for an electron.

Consider first the time-independent Schrödinger equation for a free particle:

$$\frac{\hat{\mathbf{p}}^2}{2m} \psi = E \psi. \quad (2.2.6)$$

Since a spin one-half particle has two degrees of freedom, usually assembled into a column vector χ , the expected equation for a free spin one-half particle is

$$\frac{\hat{\mathbf{p}}^2}{2m} \chi = E \chi \quad \text{with} \quad \chi = \begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix}. \quad (2.2.7)$$

One sometimes calls χ a Pauli spinor. Note there's an implicit two-by-two identity matrix $\mathbb{1}_{2 \times 2}$ in the Hamiltonian

$$H = \frac{\hat{\mathbf{p}}^2}{2m} \mathbb{1}_{2 \times 2}. \quad (2.2.8)$$

We can *rewrite* this Hamiltonian using Pauli matrices if we recall the identity

$$(\boldsymbol{\sigma} \cdot \mathbf{a})(\boldsymbol{\sigma} \cdot \mathbf{b}) = \mathbf{a} \cdot \mathbf{b} \mathbb{1}_{2 \times 2} + i \boldsymbol{\sigma} \cdot (\mathbf{a} \times \mathbf{b}), \quad (2.2.9)$$

valid for arbitrary vector operators \mathbf{a} and \mathbf{b} . Taking $\mathbf{a} = \mathbf{b} = \hat{\mathbf{p}}$, with $\hat{\mathbf{p}}$ the momentum operator, and recognizing that $\hat{\mathbf{p}} \times \hat{\mathbf{p}} = \mathbf{0}$, we have

$$(\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}) \cdot (\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}) = \hat{\mathbf{p}}^2 \mathbb{1}_{2 \times 2}. \quad (2.2.10)$$

This means that the Hamiltonian (2.2.8) can be rewritten as

$$H = \frac{1}{2m} (\boldsymbol{\sigma} \cdot \hat{\mathbf{p}})(\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}). \quad (2.2.11)$$

So far, this is all just rewriting with no change in physics. But new things happen when we the particle is charged and we couple it to external electromagnetic fields. The quantum mechanical rule is that this inclusion can be taken care with the replacement

$$\boxed{\hat{\mathbf{p}} \rightarrow \hat{\boldsymbol{\pi}} \equiv \hat{\mathbf{p}} - \frac{q}{c} \mathbf{A}.} \quad (2.2.12)$$

Here q is the charge of the particle and \mathbf{A} is the external vector potential, a function of position that becomes an operator $\mathbf{A}(\hat{\mathbf{x}})$ since position is an operator. In addition, if there is a electromagnetic scalar potential Φ it contributes an additional term $q\Phi(\hat{\mathbf{x}})$ to the Hamiltonian.

With the replacement (2.2.12) applied to the Hamiltonian (2.2.11), and the inclusion of the coupling to the scalar potential, we get the **Pauli Hamiltonian**:

$$\boxed{H_{\text{Pauli}} = \frac{1}{2m} (\boldsymbol{\sigma} \cdot \hat{\boldsymbol{\pi}}) (\boldsymbol{\sigma} \cdot \hat{\boldsymbol{\pi}}) + q\Phi(\hat{\mathbf{x}}).} \quad (2.2.13)$$

This time, using the identity (2.2.9), the second term survives

$$H_{\text{Pauli}} = \frac{1}{2m} [(\hat{\boldsymbol{\pi}} \cdot \hat{\boldsymbol{\pi}})\mathbb{1} + i\boldsymbol{\sigma} \cdot (\hat{\boldsymbol{\pi}} \times \hat{\boldsymbol{\pi}})] + q\Phi(\hat{\mathbf{x}}). \quad (2.2.14)$$

We have $\hat{\boldsymbol{\pi}} \times \hat{\boldsymbol{\pi}} \neq \mathbf{0}$ because the various π_i do not commute. Note that the replacement (2.2.12) applied to the original Hamiltonian (2.2.8) would not have given us the $\hat{\boldsymbol{\pi}} \times \hat{\boldsymbol{\pi}}$ term.

To evaluate that term we use

$$(\hat{\boldsymbol{\pi}} \times \hat{\boldsymbol{\pi}})_k = \epsilon_{ijk} \hat{\pi}_i \hat{\pi}_j = \frac{1}{2} \epsilon_{ijk} [\hat{\pi}_i, \hat{\pi}_j]. \quad (2.2.15)$$

The commutator here is

$$[\pi_i, \pi_j] = \left[p_i - \frac{q}{c} A_i, p_j - \frac{q}{c} A_j \right]. \quad (2.2.16)$$

As usual, the $\hat{\mathbf{p}}$ components can be thought of as derivatives acting on the spatially dependent components of \mathbf{A} . Moreover, the A_i 's being only functions of position, commute among themselves and we have

$$[\pi_i, \pi_j] = -\frac{\hbar q}{i c} (\partial_i A_j - \partial_j A_i) = \frac{i\hbar q}{c} (\partial_i A_j - \partial_j A_i). \quad (2.2.17)$$

Therefore, back in (2.2.16)

$$(\boldsymbol{\pi} \times \boldsymbol{\pi})_k = \frac{1}{2} \epsilon_{ijk} \frac{i\hbar q}{c} (\partial_i A_j - \partial_j A_i) = \frac{i\hbar q}{c} \epsilon_{ijk} \partial_i A_j = \frac{i\hbar q}{c} (\nabla \times \mathbf{A})_k, \quad (2.2.18)$$

leading to the elegant result:

$$\hat{\boldsymbol{\pi}} \times \hat{\boldsymbol{\pi}} = \frac{i\hbar q}{c} \mathbf{B}. \quad (2.2.19)$$

This equation is a bit reminiscent of the equation $\hat{\mathbf{L}} \times \hat{\mathbf{L}} = i\hbar\hat{\mathbf{L}}$, for angular momentum.

Back in the Pauli Hamiltonian (2.2.14), leaving identity matrices implicit, and setting $q = -e$, we find

$$\begin{aligned} H_{\text{Pauli}} &= \frac{1}{2m} \left(\hat{\mathbf{p}} + \frac{e}{c} \mathbf{A} \right)^2 + \frac{i}{2m} \frac{i\hbar q}{c} \boldsymbol{\sigma} \cdot \mathbf{B} - e\Phi(\hat{\mathbf{x}}) \\ &= \frac{1}{2m} \left(\hat{\mathbf{p}} + \frac{e}{c} \mathbf{A} \right)^2 + \frac{e\hbar}{2mc} \boldsymbol{\sigma} \cdot \mathbf{B} - e\Phi(\hat{\mathbf{x}}). \end{aligned} \quad (2.2.20)$$

The second term in this expanded Pauli Hamiltonian gives the coupling of the electron spin to the magnetic field and agrees precisely with the expected coupling (2.2.5). We thus see that the Pauli equation predicts the $g = 2$ value in the electron magnetic moment.

2.3 The Dirac equation

While the Pauli equation incorporates correctly the coupling of the electron spin to electromagnetic fields, it is not a relativistic equation. As discovered by Dirac, to include relativity one has to work with matrices and the Pauli spinor must be upgraded to a four-component spinor. The analysis begins with the familiar relation between relativistic energies and momenta

$$E^2 - \mathbf{p}^2 c^2 = m^2 c^4 \quad \rightarrow \quad E = \sqrt{\mathbf{p}^2 c^2 + m^2 c^4} \quad (2.3.1)$$

This suggests that a relativistic Hamiltonian for a free particle could take the form

$$H = \sqrt{\hat{\mathbf{p}}^2 c^2 + m^2 c^4}, \quad (2.3.2)$$

with associated Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = \sqrt{\hat{\mathbf{p}}^2 c^2 + m^2 c^4} \psi. \quad (2.3.3)$$

It is not clear how to treat the square root so, at least for small velocities $p \ll mc$, the Hamiltonian can be expanded:

$$\begin{aligned} H &= mc^2 \sqrt{1 + \frac{\hat{\mathbf{p}}^2}{m^2 c^2}} = mc^2 \left[1 + \frac{\hat{\mathbf{p}}^2}{2m^2 c^2} - \frac{1}{8} \left(\frac{\hat{\mathbf{p}}^2}{m^2 c^2} \right)^2 + \dots \right] \\ &= mc^2 + \frac{\hat{\mathbf{p}}^2}{2m} - \frac{1}{8} \frac{\hat{\mathbf{p}}^4}{m^3 c^2} + \dots \end{aligned} \quad (2.3.4)$$

If we ignore the constant rest mass, the first term is the familiar non-relativistic Hamiltonian, and the next term is the first nontrivial relativistic correction. For small momenta we will treat that term as a perturbation.

More elegantly, Dirac wanted to find a Hamiltonian linear in momenta and without square roots. This would be possible if one could write the relativistic energy as the square of a linear function of the momentum:

$$c^2 \hat{\mathbf{p}}^2 + m^2 c^4 = (c\boldsymbol{\alpha} \cdot \hat{\mathbf{p}} + \beta mc^2)^2 = (c\alpha_1 \hat{p}_1 + c\alpha_2 \hat{p}_2 + c\alpha_3 \hat{p}_3 + \beta mc^2)^2. \quad (2.3.5)$$

Expanding the right-hand side and equating coefficients one finds that the following must hold

$$\begin{aligned}\alpha_1^2 = \alpha_2^2 = \alpha_3^2 = \beta^2 &= 1, \\ \alpha_i \alpha_j + \alpha_j \alpha_i &= \{\alpha_i, \alpha_j\} = 0, \quad i \neq j, \\ \alpha_i \beta + \beta \alpha_i &= \{\alpha_i, \beta\} = 0.\end{aligned}\tag{2.3.6}$$

The relations on the second and third lines imply that α 's and β 's can't be numbers, because they would have to be zero. It turns out that α 's and β 's are four-by-four hermitian matrices:

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} \mathbf{1} & 0 \\ 0 & -\mathbf{1} \end{pmatrix}.\tag{2.3.7}$$

Using (2.3.5), the Dirac Hamiltonian is simply the linear function of momentum that is the square root of $c^2 \hat{\mathbf{p}}^2 + m^2 c^4$. We thus have

$$H_{\text{Dirac}} = c \boldsymbol{\alpha} \cdot \mathbf{p} + \beta m c^2.\tag{2.3.8}$$

The Dirac equation is

$$i \hbar \frac{\partial \Psi}{\partial t} = (c \boldsymbol{\alpha} \cdot \mathbf{p} + \beta m c^2) \Psi,\tag{2.3.9}$$

where Ψ is a Dirac spinor, a four-component column vector that can be thought to be composed by two two-component Pauli spinors χ and η :

$$\Psi = \begin{pmatrix} \chi \\ \eta \end{pmatrix}, \quad \chi = \begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix}, \quad \eta = \begin{pmatrix} \eta_1 \\ \eta_2 \end{pmatrix}.\tag{2.3.10}$$

The coupling to electromagnetic fields is done as before

$$i \hbar \frac{\partial \Psi}{\partial t} = \left[c \boldsymbol{\alpha} \cdot \left(\hat{\mathbf{p}} + \frac{e}{c} \mathbf{A} \right) + \beta m c^2 + V(r) \right] \Psi,\tag{2.3.11}$$

where the coupling of the electron to the scalar potential $\Phi(r)$ is included via

$$V(r) = -e \Phi(r) = -\frac{e^2}{r}.\tag{2.3.12}$$

The great advantage of the Dirac equation (2.3.11) is that the corrections to the hydrogen Hamiltonian $H^{(0)}$ can be derived systematically by finding the appropriate Hamiltonian H that acts on the Pauli spinor χ . The analysis, can be done with $\mathbf{A} = 0$, since the stationary proton creates no vector potential. The result of the analysis shows that

$$H \chi = E \chi,\tag{2.3.13}$$

where:

$$H = \underbrace{\frac{\hat{\mathbf{p}}^2}{2m} + V}_{H^{(0)}} - \underbrace{\frac{\hat{\mathbf{p}}^4}{8m^3 c^2}}_{\delta H_{\text{rel.}}} + \underbrace{\frac{1}{2m^2 c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{S} \cdot \mathbf{L}}_{\delta H_{\text{spin-orbit}}} + \underbrace{\frac{\hbar^2}{8m^2 c^2} \nabla^2 V}_{\delta H_{\text{Darwin}}}.\tag{2.3.14}$$

The first correction is the relativistic energy correction anticipated earlier. The second is the spin-orbit coupling, and the third is the *Darwin* correction, that as we shall see affects only $\ell = 0$ states.

Recall that the energy scale for $H^{(0)}$ eigenstates is $\alpha^2 mc^2$. We will now see that *all the above energy corrections are of order $\alpha^4 mc^2$* thus smaller by a factor of $\alpha^2 \simeq \frac{1}{19000}$ than the zeroth-order energies. This suggests that for the hydrogen atom, the role of the unit-free parameter λ of perturbation theory is taken by the fine structure constant: $\lambda \sim \alpha^2$. Of course, in reality we cannot adjust the value of α^2 nor we can take it to zero.

For the relativistic correction, recalling that $p \simeq \alpha mc$, we indeed have

$$\delta H_{\text{rel.}} = -\frac{\mathbf{p}^4}{8m^3c^2} \sim -\alpha^4 mc^2. \quad (2.3.15)$$

For spin-orbit we first rewrite the term, using

$$\frac{1}{r} \frac{dV}{dr} = \frac{1}{r} \frac{d}{dr} \left(-\frac{e^2}{r} \right) = \frac{e^2}{r^3}, \quad (2.3.16)$$

so that

$$\delta H_{\text{spin-orbit}} = \frac{e^2}{2m^2c^2} \frac{1}{r^3} \mathbf{S} \cdot \mathbf{L}. \quad (2.3.17)$$

For an estimate we set $\mathbf{S} \cdot \mathbf{L} \sim \hbar^2$, $r \sim a_0$, and recall that $a_0 = \frac{\hbar}{mc} \frac{1}{\alpha}$:

$$\delta H_{\text{spin-orbit}} \sim \frac{e^2}{m^2c^2} \frac{\hbar^2}{a_0^3} = \frac{\alpha \hbar c}{m^2c^2} \frac{\hbar^2}{a_0^3} = \alpha \left(\frac{\hbar}{mca_0} \right)^3 mc^2 = \alpha^4 mc^2. \quad (2.3.18)$$

We can evaluate the Darwin term using $V = -e^2/r$:

$$\delta H_{\text{Darwin}} = -\frac{e^2\hbar^2}{8m^2c^2} \nabla^2 \left(\frac{1}{r} \right) = \frac{e^2\hbar^2}{8m^2c^2} (-4\pi\delta(\mathbf{r})) = \frac{\pi}{2} \frac{e^2\hbar^2}{m^2c^2} \delta(\mathbf{r}). \quad (2.3.19)$$

To estimate this correction note that, due to the δ function the the integral in the expectation value will introduce a factor $|\psi(\mathbf{0})|^2 \sim a_0^{-3}$. We will therefore have

$$\delta H_{\text{Darwin}} \sim \frac{e^2\hbar^2}{m^2c^2a_0^3} \sim \alpha^4 mc^2, \quad (2.3.20)$$

as this is exactly the same combination of constants that we had for spin orbit above.

2.4 Fine structure of hydrogen

The fine structure of hydrogen is the spectrum of the atom once one takes into account the corrections indicated in (2.3.14). After the partial simplifications considered above we have

$$H = \underbrace{\frac{\hat{\mathbf{p}}^2}{2m} + V}_{H^{(0)}} - \underbrace{\frac{\hat{\mathbf{p}}^4}{8m^3c^2}}_{\delta H_{\text{rel.}}} + \underbrace{\frac{e^2}{2m^2c^2} \frac{\mathbf{S} \cdot \mathbf{L}}{r^3}}_{\delta H_{\text{spin-orbit}}} + \underbrace{\frac{\pi}{2} \frac{e^2\hbar^2}{m^2c^2} \delta(\mathbf{r})}_{\delta H_{\text{Darwin}}}. \quad (2.4.21)$$

We will study each of these terms separately and then combine our results to give the fine structure of hydrogen. There are further smaller corrections that we will not examine here, such as hyperfine splitting and Lamb effect.

2.4.1 Darwin correction

Let us now evaluate the Darwin correction. Since this interaction has a delta function at the origin, the first order correction to the energy vanishes unless the wavefunction is non-zero at the origin. This can only happen for nS states. There is no need to use the apparatus of degenerate perturbation theory. Indeed, for fixed n there are two orthogonal $\ell = 0$ states, one with electron spin up and one with electron spin down. While these states are degenerate, the Darwin perturbation commutes with spin and is therefore diagonal in the two-dimensional subspace. There is no need to include the spin in the calculation and we have

$$E_{n00,\text{Darwin}}^{(1)} = \langle \psi_{n00} | \delta H_{\text{Darwin}} | \psi_{n00} \rangle = \frac{\pi e^2 \hbar^2}{2 m^2 c^2} |\psi_{n00}(\mathbf{0})|^2. \quad (2.4.22)$$

As is shown in the homework, the radial equation can be used to determine the value of the nS wavefunctions at the origin. You will find that

$$|\psi_{n00}(0)|^2 = \frac{1}{\pi n^3 a_0^3}. \quad (2.4.23)$$

As a result

$$E_{n00,\text{Darwin}}^{(1)} = \frac{e^2 \hbar^2}{2 m^2 c^2} \frac{1}{a_0^3 n^3} = \alpha^4 (mc^2) \frac{1}{2n^3}. \quad (2.4.24)$$

This completes the evaluation of the Darwin correction

The Darwin term in the Hamiltonian arises from the elimination of one of the two two-component spinors in the Dirac equation. As we will show now such a correction would arise from a nonlocal correction to the potential energy term. It is as if the electron had grown from point-like to a ball with radius of order its Compton wavelength $\frac{\hbar}{m_e c}$. The potential energy due to the field of the proton must then be calculated by integrating the varying electric potential over the charge distribution of the electron. While a simple estimate of this nonlocal potential energy does reproduce the Darwin correction rather closely, one must not reach the conclusion that the electron is no longer a point particle. Still the fact remains that in a relativistic treatment of an electron, its Compton wavelength is relevant and is physically the shortest distance an electron can be localized.

The potential energy $V(\mathbf{r})$ of the electron, as a point particle, is the product of the electron charge $(-e)$ times the electric potential $\Phi(\mathbf{r})$ created by the proton:

$$V(\mathbf{r}) = (-e)\Phi(\mathbf{r}) = (-e) \frac{e}{r}. \quad (2.4.25)$$

Let us call $\tilde{V}(\mathbf{r})$ the potential energy when the electron is a charge distribution centered at a point \mathbf{r} with $|\mathbf{r}| = r$ (see Figure 2.1). This energy is obtained by integration over the

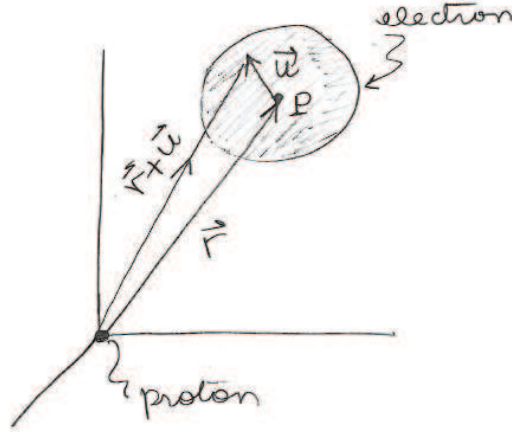


Figure 2.1: A Darwin type correction to the energy arises if the electron charge is smeared over a region of size comparable to its Compton wavelength. Here the center of the spherically symmetric electron cloud is at P and the proton is at the origin. The vector \mathbf{u} is radial relative to the center of the electron.

electron distribution. Using the vector \mathbf{u} to define position relative to the center P of the electron, and letting $\rho(\mathbf{u})$ denote the position dependent charge density, we have

$$\tilde{V}(\mathbf{r}) = \int_{\text{electron}} d^3\mathbf{u} \rho(\mathbf{u}) \Phi(\mathbf{r} + \mathbf{u}), \quad (2.4.26)$$

where, as shown in the Figure, $\mathbf{r} + \mathbf{u}$ is the position of the integration point, measured relative to the proton at the origin. It is convenient to write the charge density in terms of a normalized function ρ_0 :

$$\rho(\mathbf{u}) = -e \rho_0(\mathbf{u}) \quad \rightarrow \quad \int_{\text{electron}} d^3\mathbf{u} \rho_0(\mathbf{u}) = 1, \quad (2.4.27)$$

which guarantees that the integral of ρ over the electron is indeed $(-e)$. Recalling that $-e\Phi(\mathbf{r} + \mathbf{u}) = V(\mathbf{r} + \mathbf{u})$ we now rewrite (2.4.26) as

$$\tilde{V}(\mathbf{r}) = \int_{\text{electron}} d^3\mathbf{u} \rho_0(\mathbf{u}) V(\mathbf{r} + \mathbf{u}). \quad (2.4.28)$$

This equation has a clear interpretation: the potential energy is obtained as a weighted integral of potential due to the proton over the extended electron. If the electron charge would be perfectly localized, $\rho_0(\mathbf{u}) = \delta(\mathbf{u})$ and $\tilde{V}(\mathbf{r})$ would just be equal to $V(\mathbf{r})$. We will assume that the distribution of charge is spherically symmetric, so that

$$\rho_0(\mathbf{u}) = \rho_0(u). \quad (2.4.29)$$

To evaluate (2.4.31), we first do a Taylor expansion of the potential that enters the integral about the point $\mathbf{u} = 0$:

$$V(\mathbf{r} + \mathbf{u}) = V(\mathbf{r}) + \sum_i \partial_i V \Big|_{\mathbf{r}} u_i + \frac{1}{2} \sum_{i,j} \partial_i \partial_j V \Big|_{\mathbf{r}} u_i u_j + \dots \quad (2.4.30)$$

All derivatives here are evaluated at the center of the electron. Plugging back into the integral (2.4.31) and dropping the subscript ‘electron’ we have

$$\tilde{V}(\mathbf{r}) = \int d^3\mathbf{u} \rho_0(\mathbf{u}) \left(V(\mathbf{r}) + \sum_i \partial_i V \Big|_{\mathbf{r}} u_i + \frac{1}{2} \sum_{i,j} \partial_i \partial_j V \Big|_{\mathbf{r}} u_i u_j + \dots \right). \quad (2.4.31)$$

All \mathbf{r} dependent functions can be taken out of the integrals. Recalling that the integral of ρ_0 over volume is one, we get

$$\tilde{V}(\mathbf{r}) = V(\mathbf{r}) + \sum_i \partial_i V \Big|_{\mathbf{r}} \int d^3\mathbf{u} \rho_0(\mathbf{u}) \rho_i + \frac{1}{2} \sum_{i,j} \partial_i \partial_j V \Big|_{\mathbf{r}} \int d^3\mathbf{u} \rho_0(\mathbf{u}) u_i u_j + \dots \quad (2.4.32)$$

Due to spherical symmetry the first integral vanishes and the second takes the form

$$\int d^3\mathbf{u} \rho_0(\mathbf{u}) u_i u_j = \frac{1}{3} \delta_{ij} \int d^3\mathbf{u} \rho_0(\mathbf{u}) u^2. \quad (2.4.33)$$

Indeed the integral must vanish for $i \neq j$ and must take equal values for $i = j = 1, 2, 3$. Since $u^2 = u_1^2 + u_2^2 + u_3^2$, the result follows. Using this we get

$$\begin{aligned} \tilde{V}(\mathbf{r}) &= V(\mathbf{r}) + \frac{1}{2} \sum_i \partial_i \partial_i V \Big|_{\mathbf{r}} \frac{1}{3} \int d^3\mathbf{u} \rho_0(\mathbf{u}) u^2 + \dots \\ &= V(\mathbf{r}) + \frac{1}{6} \nabla^2 V \int d^3\mathbf{u} \rho_0(\mathbf{u}) u^2 + \dots \end{aligned} \quad (2.4.34)$$

The second term represents the correction δV to the potential energy:

$$\delta V = \frac{1}{6} \nabla^2 V \int d^3\mathbf{u} \rho_0(\mathbf{u}) u^2. \quad (2.4.35)$$

To get an estimate, let us assume that the charge is distributed uniformly over a sphere of radius u_0 . This means that $\rho_0(\mathbf{u})$ is a constant for $u < u_0$

$$\rho_0(\mathbf{u}) = \frac{3}{4\pi u_0^3} \begin{cases} 1, & u < u_0, \\ 0, & u > u_0. \end{cases} \quad (2.4.36)$$

The integral one must evaluate then gives

$$\int d^3\mathbf{u} \rho_0(\mathbf{u}) u^2 = \int_0^{u_0} \frac{4\pi u^2 du u^2}{\frac{4\pi}{3} u_0^3} = \frac{3}{u_0^3} \int_0^{u_0} u^4 du = \frac{3}{5} u_0^2. \quad (2.4.37)$$

Therefore,

$$\delta V = \frac{1}{10} u_0^2 \nabla^2 V. \quad (2.4.38)$$

If we choose the radius u_0 of the charge distribution to be the Compton wavelength $\frac{\hbar}{mc}$ of the electron we get,

$$\delta V = \frac{\hbar^2}{10 m^2 c^2} \nabla^2 V. \quad (2.4.39)$$

Comparing with (2.3.14) we see that, up to a small correction ($\frac{1}{8}$ as opposed to $\frac{1}{10}$), this is the Darwin energy shift. The agreement is surprisingly good for what is, admittedly, a heuristic argument.

2.4.2 Relativistic correction

We now turn to the relativistic correction. The energy shifts of the hydrogen states can be analyzed among the degenerate states with principal quantum number n . We write tentatively for the corrections

$$E_{n,\ell m_\ell m_s;\text{rel}}^{(1)} = -\frac{1}{8m^3 c^2} \langle \psi_{n\ell m_\ell m_s} | \mathbf{p}^2 \mathbf{p}^2 | \psi_{n\ell m_\ell} \rangle. \quad (2.4.40)$$

We can use this formula because the uncoupled basis of states at fixed n is good: the perturbation is diagonal in this basis. This is checked using Remark 3 in section 1.2.2. This is clear because the perturbing operator $\mathbf{p}^2 \mathbf{p}^2$ commutes with \mathbf{L}^2 , with L_z , and with S_z . The first operator guarantees that the matrix for the perturbation is diagonal in ℓ , the second guarantees that the perturbation is diagonal in m_ℓ , and the third guarantees, rather trivially, that the perturbation is diagonal in m_s .

To evaluate the matrix element we use the Hermiticity of \mathbf{p}^2 to move one of the factors into the bra

$$E_{n,\ell m_\ell m_s;\text{rel}}^{(1)} = -\frac{1}{8m^3 c^2} \langle \mathbf{p}^2 \psi_{n\ell m} | \mathbf{p}^2 \psi_{n\ell m} \rangle, \quad (2.4.41)$$

where in the right-hand side we evaluated the trivial expectation value for the spin degrees of freedom. To simplify the evaluation we use the Schrödinger equation, which tells us that

$$\left(\frac{\mathbf{p}^2}{2m} + V \right) \psi_{n\ell m} = E_n^{(0)} \psi_{n\ell m} \quad \rightarrow \quad \mathbf{p}^2 \psi_{n\ell m} = 2m(E_n^{(0)} - V) \psi_{n\ell m}. \quad (2.4.42)$$

Using this both for the bra and the ket:

$$E_{n,\ell m_\ell m_s;\text{rel}}^{(1)} = -\frac{1}{2mc^2} \left\langle (E_n^{(0)} - V) \psi_{n\ell m} \left| (E_n^{(0)} - V) \psi_{n\ell m} \right. \right\rangle. \quad (2.4.43)$$

The operator $E_n^{(0)} - V$ is also Hermitian and can be moved from the bra to the ket, giving

$$\begin{aligned} E_{n,\ell m_\ell m_s;\text{rel}}^{(1)} &= -\frac{1}{2mc^2} \left\langle \psi_{n\ell m} \left| \left((E_n^{(0)})^2 - 2VE_n^{(0)} + V^2 \right) \right| \psi_{n\ell m} \right\rangle \\ &= -\frac{1}{2mc^2} \left[(E_n^{(0)})^2 - 2E_n \langle V \rangle_{n\ell m} + \langle V^2 \rangle_{n\ell m} \right]. \end{aligned} \quad (2.4.44)$$

The problem has been reduced to the computation of the expectation value of $V(r)$ and $V^2(r)$ in the $\psi_{n\ell m}$ state. The expectation value of $V(r)$ is obtained from the virial theorem that states that $\langle V \rangle = 2E_n^{(0)}$. For $V^2(r)$ we have

$$\langle V^2 \rangle = e^4 \left\langle \frac{1}{r^2} \right\rangle = e^4 \frac{1}{a_0^2 n^3 (\ell + \frac{1}{2})} = \left(\frac{e^2}{2a_0} \frac{1}{n^2} \right)^2 \frac{4n}{\ell + \frac{1}{2}} = (E_n^{(0)})^2 \cdot \frac{4n}{\ell + \frac{1}{2}}. \quad (2.4.45)$$

Back into (2.4.44) we find

$$E_{n,\ell m_\ell m_s;\text{rel}}^{(1)} = -\frac{(E_n^{(0)})^2}{2mc^2} \left[\frac{4n}{\ell + \frac{1}{2}} - 3 \right] = -\frac{1}{8} \alpha^4 \frac{(mc^2)}{n^4} \left[\frac{4n}{\ell + \frac{1}{2}} - 3 \right]. \quad (2.4.46)$$

The complete degeneracy of ℓ multiplets for a given n has been broken. That degeneracy of $H^{(0)}$ was explained by the conserved Runge-Lenz vector. It is clear that the relativistic correction has broken that symmetry.

We have computed the above correction using the uncoupled basis

$$E_{n,\ell m_\ell m_s;\text{rel}}^{(1)} = \langle n\ell m m_s | \delta H_{\text{rel}} | n\ell m m_s \rangle = f(n, \ell). \quad (2.4.47)$$

Here we added the extra equality to emphasize that the matrix elements depend only on n and ℓ . We have already seen that in the full degenerate subspace with principal quantum number n the matrix for δH_{rel} is diagonal in the uncoupled basis. But now we see that in each degenerate subspace of fixed n and ℓ , δH_{rel} is in fact a multiple of the *identity* matrix, since the matrix elements are independent of m and m_s (the L_z and S_z) eigenvalues. A matrix equal to a multiple of the identity is invariant under any orthonormal change of basis. For any $\ell \otimes \frac{1}{2}$ multiplet, the resulting j multiplets provide an alternative orthonormal basis. The invariance of a matrix proportional to the identity implies that

$$E_{n\ell j m_j;\text{rel}}^{(1)} = \langle n\ell j m_j | \delta H_{\text{rel}} | n\ell j m_j \rangle = f(n, \ell). \quad (2.4.48)$$

with the same function $f(n, \ell)$ as in (2.4.47), and the perturbation is diagonal in this coupled basis too. This is clear anyway because the perturbation commutes with \mathbf{L}^2 , \mathbf{J}^2 and J_z and any two degenerate states in the coupled basis differ either in ℓ , j or j_z .

The preservation of the matrix elements can also be argued more explicitly. Indeed, any state in the coupled basis is a superposition of orthonormal uncoupled basis states with constant coefficients c_i :

$$|n\ell j m_j\rangle = \sum_i c_i |n\ell m_\ell^i m_s^i\rangle, \quad \text{with} \quad \sum_i |c_i|^2 = 1, \quad (2.4.49)$$

because the state on the left-hand side must also have unit norm. Therefore, using the

diagonal nature of the matrix elements in the uncoupled basis we get, as claimed

$$\begin{aligned}
\langle n\ell jm_j | \delta H_{\text{rel}} | n\ell jm_j \rangle &= \sum_{i,k} c_i^* c_k \langle n\ell m_\ell^i m_s^i | \delta H_{\text{rel}} | n\ell m_\ell^k m_s^k \rangle \\
&= \sum_i |c_i|^2 \langle n\ell m_\ell^i m_s^i | \delta H_{\text{rel}} | n\ell m_\ell^i m_s^i \rangle \\
&= \sum_i |c_i|^2 f(n, \ell) = f(n, \ell).
\end{aligned} \tag{2.4.50}$$

2.4.3 Spin orbit coupling

The spin-orbit contribution to the Hamiltonian is

$$\delta H_{\text{spin-orbit}} = \frac{e^2}{2m^2 c^2} \frac{1}{r^3} \mathbf{S} \cdot \mathbf{L}. \tag{2.4.51}$$

Note that $\delta H_{\text{spin-orbit}}$ commutes with \mathbf{L}^2 because \mathbf{L}^2 commutes with any \hat{L}_i and any \hat{S}_i . Moreover, $\delta H_{\text{spin-orbit}}$ commutes with \mathbf{J}^2 and with J_z since, in fact, $[\hat{J}_i, \mathbf{S} \cdot \mathbf{L}] = 0$ for any i ; $\mathbf{S} \cdot \mathbf{L}$ is a scalar operator for \mathbf{J} . It follows that $\delta H_{\text{spin-orbit}}$ is diagonal in the level n degenerate subspace in the coupled basis $|n\ell jm_j\rangle$. In fact, as we will see, the matrix elements are m -independent. This is a nontrivial consequence of $\delta H_{\text{spin-orbit}}$ being a scalar under \mathbf{J} . To compute the matrix elements we recall that $\mathbf{J} = \mathbf{S} + \mathbf{L}$ and

$$\begin{aligned}
E_{n\ell jm_j; \text{spin-orbit}}^{(1)} &= \frac{e^2}{2m^2 c^2} \langle n\ell jm_j | \frac{1}{r^3} \mathbf{S} \cdot \mathbf{L} | n\ell jm_j \rangle \\
&= \frac{e^2}{2m^2 c^2} \frac{\hbar^2}{2} [j(j+1) - \ell(\ell+1) - \frac{3}{4}] \langle n\ell jm_j | \frac{1}{r^3} | n\ell jm_j \rangle.
\end{aligned} \tag{2.4.52}$$

We need the expectation value of $1/r^3$ in these states. It is known that

$$\langle n\ell m_\ell | \frac{1}{r^3} | n\ell m_\ell \rangle = \frac{1}{n^3 a_0^3 \ell (\ell + \frac{1}{2}) (\ell + 1)}. \tag{2.4.53}$$

Because of the m_ℓ independence of this expectation value (and its obvious m_s independence) the operator $1/r^3$ is a multiple of the identity matrix in each $\ell \otimes \frac{1}{2}$ multiplet. It follows that it is the same multiple of the identity in the coupled basis description. Therefore

$$\langle n\ell jm_j | \frac{1}{r^3} | n\ell jm_j \rangle = \frac{1}{n^3 a_0^3 \ell (\ell + \frac{1}{2}) (\ell + 1)}. \tag{2.4.54}$$

Using this in (2.4.52)

$$E_{n\ell jm_j; \text{spin-orbit}}^{(1)} = \frac{e^2 \hbar^2}{4m^2 c^2} \frac{[j(j+1) - \ell(\ell+1) - \frac{3}{4}]}{n^3 a_0^3 \ell (\ell + \frac{1}{2}) (\ell + 1)}. \tag{2.4.55}$$

Working out the constants in terms of $E_n^{(0)}$ and rest energies we get

$$E_{n\ell jm_j; \text{spin-orbit}}^{(1)} = \frac{(E_n^{(0)})^2}{mc^2} \frac{n [j(j+1) - \ell(\ell+1) - \frac{3}{4}]}{\ell(\ell + \frac{1}{2})(\ell+1)}, \quad \ell \neq 0. \quad (2.4.56)$$

Since \mathbf{L} vanishes identically acting on any $\ell = 0$ state, it is physically reasonable, as we will do, to assume that the spin-orbit correction vanishes for $\ell = 0$ states. On the other hand the limit of the above formula as $\ell \rightarrow 0$, while somewhat ambiguous, is nonzero. We set $j = \ell + \frac{1}{2}$ (the other possibility $j = \ell - \frac{1}{2}$ does not apply for $\ell = 0$) and then take the limit as $\ell \rightarrow 0$. Indeed,

$$\begin{aligned} E_{n\ell jm_j; \text{spin-orbit}}^{(1)} \Big|_{j=\ell+\frac{1}{2}} &= \frac{(E_n^{(0)})^2}{mc^2} \frac{n [(\ell + \frac{1}{2})(\ell + \frac{3}{2}) - \ell(\ell+1) - \frac{3}{4}]}{\ell(\ell + \frac{1}{2})(\ell+1)} \\ &= \frac{(E_n^{(0)})^2}{mc^2} \frac{n}{(\ell + \frac{1}{2})(\ell+1)}, \end{aligned} \quad (2.4.57)$$

and now taking the limit:

$$\lim_{\ell \rightarrow 0} E_{n\ell jm_j; \text{spin-orbit}}^{(1)} \Big|_{j=\ell+\frac{1}{2}} = \frac{(E_n^{(0)})^2}{mc^2} (2n) = \alpha^4 mc^2 \frac{1}{2n^3}. \quad (2.4.58)$$

We see that this limit is in fact identical to the Darwin shift (2.4.24) of the nS states. This is a bit surprising and will play a technical role below.

2.4.4 Combining results

For $\ell \neq 0$ states we can add the energy shifts from spin-orbit and from the relativistic correction, both of them expressed as expectation values in the coupled basis. The result, therefore will give the shifts of the coupled states. Collecting our results (2.4.46) and (2.4.56) we have

$$\begin{aligned} &\langle n\ell jm_j | \delta H_{\text{rel}} + \delta H_{\text{spin-orbit}} | n\ell jm_j \rangle \\ &= \frac{(E_n^{(0)})^2}{2mc^2} \left\{ 3 - \frac{4n}{(\ell + \frac{1}{2})} + \frac{2n [j(j+1) - \ell(\ell+1) - \frac{3}{4}]}{\ell(\ell + \frac{1}{2})(\ell+1)} \right\} \\ &= \frac{(E_n^{(0)})^2}{2mc^2} \left\{ 3 + 2n \left[\frac{j(j+1) - 3\ell(\ell+1) - \frac{3}{4}}{\ell(\ell + \frac{1}{2})(\ell+1)} \right] \right\}. \end{aligned} \quad (2.4.59)$$

These are the fine structure energy shifts for all states in the spectrum of hydrogen. The states in a coupled multiplet are characterized by ℓ , j and m_j and each multiplet as a whole is shifted according to the above formula. The degeneracy within the multiplet is unbroken because the formula has no m_j dependence. This formula, as written, hides some additional degeneracies. We uncover those next.

In the above formula there are two cases to consider for any *fixed* value of j : the multiplet can have $\ell = j - \frac{1}{2}$ or the multiplet can have $\ell = j + \frac{1}{2}$. We will now see something rather surprising. In both of these cases the shift is the same, meaning that the shift is in fact ℓ independent! It just depends on j . Call $f(j, \ell)$ the term in brackets above

$$f(j, \ell) \equiv \frac{j(j+1) - 3\ell(\ell+1) - \frac{3}{4}}{\ell(\ell + \frac{1}{2})(\ell+1)}. \quad (2.4.60)$$

The evaluation of this expression in both cases gives the same result:

$$\begin{aligned} f(j, \ell) \Big|_{\ell=j-\frac{1}{2}} &= \frac{j(j+1) - 3(j-\frac{1}{2})(j+\frac{1}{2}) - \frac{3}{4}}{(j-\frac{1}{2})j(j+\frac{1}{2})} = \frac{-2j^2 + j}{j(j-\frac{1}{2})(j+\frac{1}{2})} = -\frac{2}{(j+\frac{1}{2})}, \\ f(j, \ell) \Big|_{\ell=j+\frac{1}{2}} &= \frac{j(j+1) - 3(j+\frac{1}{2})(j+\frac{3}{2}) - \frac{3}{4}}{(j+\frac{1}{2})(j+1)(j+\frac{3}{2})} = \frac{2j^2 - 5j - 3}{(j+\frac{1}{2})(j+1)(j+\frac{3}{2})} = -\frac{2}{(j+\frac{1}{2})}. \end{aligned} \quad (2.4.61)$$

We can therefore replace in (2.4.59) the result of our evaluation, which we label as fine structure (fs) shifts:

$$E_{n\ell j, m_j; \text{fs}}^{(1)} = -\frac{(E_n^{(0)})^2}{2mc^2} \left[\frac{4n}{j+\frac{1}{2}} - 3 \right] = -\alpha^4 (mc^2) \frac{1}{2n^4} \left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4} \right]. \quad (2.4.62)$$

More briefly we can write

$$\boxed{E_{n\ell j, m_j; \text{fine}}^{(1)} = -\alpha^4 mc^2 \cdot S_{n,j}, \quad \text{with} \quad S_{n,j} \equiv \frac{1}{2n^4} \left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4} \right].} \quad (2.4.63)$$

Let us consider a few remarks:

1. The dependence on j and absence of dependence on ℓ in the energy shifts could be anticipated from the Dirac equation. The rotation generator that commutes with the Dirac Hamiltonian is $\mathbf{J} = \mathbf{L} + \mathbf{S}$, which simultaneously rotates position, momenta, and spin states. Neither \mathbf{L} nor \mathbf{S} are separately conserved. With \mathbf{J} a symmetry, states are expected to be labelled by energy and j and must be m_j independent.
2. The formula (2.4.63) works for nS states! For these $\ell = 0$ states we were supposed to add the relativistic correction and the Darwin correction, since their spin-orbit correction is zero. But we noticed that the limit $\ell \rightarrow 0$ of the spin-orbit correction reproduces the Darwin term. Whether or not this is a meaningful coincidence, it means the sum performed above gives the right answer for $\ell \rightarrow 0$.
3. While a large amount of the degeneracy of $H^{(0)}$ has been broken, for fixed n , multiplets with the same value of j , regardless of ℓ , remain degenerate. The states in each j multiplet do not split.

4. Since $S_{n,j} > 0$ all energy shifts are down. Indeed

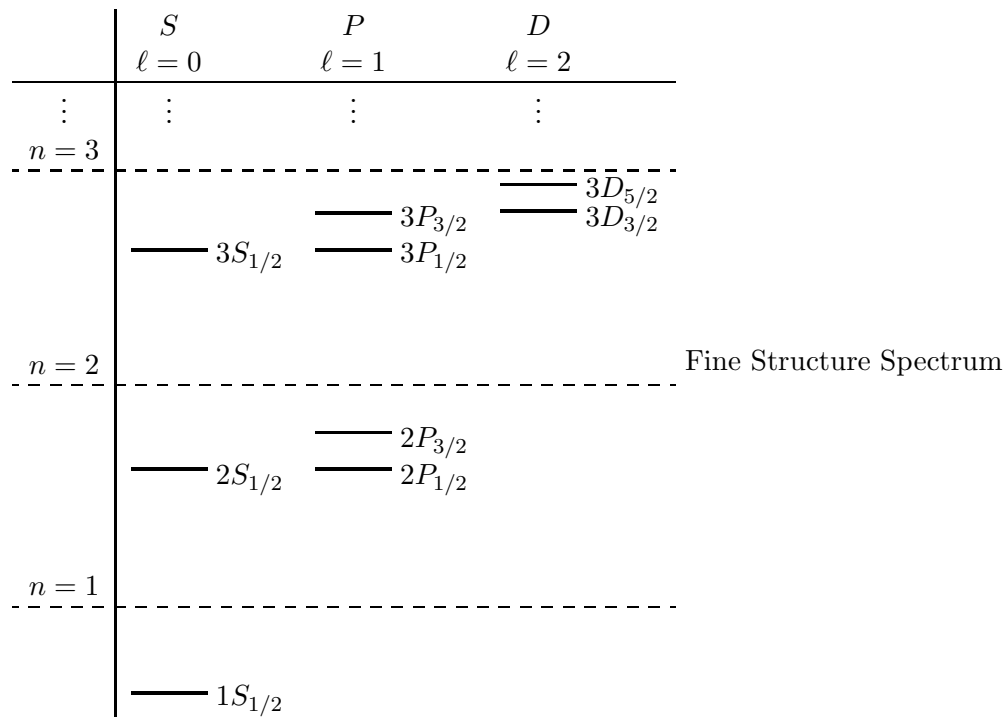
$$\frac{n}{j + \frac{1}{2}} \geq \frac{n}{j_{\max} + \frac{1}{2}} = \frac{n}{\ell_{\max} + \frac{1}{2} + \frac{1}{2}} = \frac{n}{n} = 1 \quad \rightarrow \quad \frac{n}{j + \frac{1}{2}} - \frac{3}{4} \geq \frac{1}{4}. \quad (2.4.64)$$

5. For a given fixed n , states with lower values of j get pushed further down. As n increases splittings fall off like n^{-3} .

A table of values of $S_{n,j}$ is given here below

n	j	$S_{n,j}$
1	$\frac{1}{2}$	$\frac{1}{8}$
2	$\frac{1}{2}$	$\frac{5}{128}$
	$\frac{3}{2}$	$\frac{1}{128}$
3	$\frac{1}{2}$	$\frac{1}{72}$
	$\frac{3}{2}$	$\frac{1}{216}$
	$\frac{5}{2}$	$\frac{1}{648}$

The energy diagram for states up to $n = 3$ is given here (not to scale)



For the record, the total energy of the hydrogen states is the zeroth contribution plus the fine structure contribution. Together they give

$$E_{n\ell jm_j} = -\frac{e^2}{2a_0} \frac{1}{n^2} \left[1 + \frac{\alpha^2}{n^2} \left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right]. \quad (2.4.65)$$

This is the fine structure of hydrogen! There are, of course, finer corrections. The so-called Lamb shift, for example, breaks the degeneracy between $2S_{1/2}$ and $2P_{1/2}$ and is of order α^5 . There is also hyperfine splitting, which arises from the coupling of the magnetic moment of the proton to the magnetic moment of the electron. Such coupling leads to a splitting that is a factor m_e/m_p smaller than fine structure.

2.5 Zeeman effect

In remarkable experiment done in 1896, the Dutch physicist Pieter Zeeman (1865-1943) discovered that atomic spectral lines are split in the presence of an external magnetic field. For this work Zeeman was awarded the Nobel Prize in 1902. The proper understanding of this phenomenon had to wait for Quantum Mechanics.

The splitting of atomic energy levels by a constant, uniform, external magnetic field, the *Zeeman effect*, has been used as a tool to measure inaccessible magnetic fields. In observing the solar spectrum, a single atomic line, as seen from light emerging from outside a sunspot, splits into various lines inside the sunspot. We have learned that magnetic fields inside a sunspot typically reach 3,000 gauss. Sunspots are a bit darker and have lower temperature than the rest of the solar surface. They can last from hours to months, and their magnetic energy can turn into powerful solar flares.

The external magnetic field interacts with the total magnetic moment of the electron. The electron has magnetic moment due to its orbital angular momentum and one due to its spin

$$\boldsymbol{\mu}_\ell = -\frac{e}{2mc} \mathbf{L}, \quad \boldsymbol{\mu}_s = -\frac{e}{mc} \mathbf{S}, \quad (2.5.1)$$

where we included the $g = 2$ factor in the spin contribution. The Zeeman Hamiltonian is thus given by

$$\delta H_{\text{Zeeman}} = -(\boldsymbol{\mu}_\ell + \boldsymbol{\mu}_s) \cdot \mathbf{B} = \frac{e}{2mc} (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B}. \quad (2.5.2)$$

Conventionally, we align the magnetic field with the positive z axis so that $\mathbf{B} = B \mathbf{z}$ and thus get

$$\delta H_{\text{Zeeman}} = \frac{eB}{2mc} (\hat{L}_z + 2\hat{S}_z). \quad (2.5.3)$$

When we consider the Zeeman effect on Hydrogen we must not forget fine structure. The full Hamiltonian to be considered is

$$H = H^{(0)} + \delta H_{\text{fs}} + \delta H_{\text{Zeeman}}. \quad (2.5.4)$$

Recall that in fine structure, there is an internal magnetic field B_{int} associated with spin-orbit coupling. This is the magnetic field seen by the electron as it goes around the proton. We have therefore two extreme possibilities concerning the external magnetic field B of the Zeeman effect:

- (1) Weak-field Zeeman effect: $B \ll B_{\text{int}}$. In this case the Zeeman effect is small compared with fine structure effects. Accordingly, the original Hamiltonian $H^{(0)}$ together with the fine structure Hamiltonian H_{fs} are thought as the “known” Hamiltonian $\tilde{H}^{(0)}$, and the Zeeman Hamiltonian is the perturbation:

$$H = \underbrace{H^{(0)} + \delta H_{\text{fs}}}_{\tilde{H}^{(0)}} + \delta H_{\text{Zeeman}}. \quad (2.5.5)$$

- (2) Strong-field Zeeman effect: $B \gg B_{\text{int}}$. In this case the Zeeman effect is much larger than fine structure effects. Accordingly, the original Hamiltonian $H^{(0)}$ together with the Zeeman Hamiltonian are thought as the “known” Hamiltonian $\tilde{H}^{(0)}$ and the fine structure Hamiltonian H_{fs} is viewed as the perturbation:

$$H = \underbrace{H^{(0)} + \delta H_{\text{Zeeman}}}_{\tilde{H}^{(0)}} + \delta H_{\text{fs}}. \quad (2.5.6)$$

You may think that $H^{(0)} + \delta H_{\text{Zeeman}}$ does not qualify as known, but happily, as we will confirm soon, this is actually a very simple Hamiltonian.

When the Zeeman magnetic field is neither weak nor strong, we must take the sum of the Zeeman and fine structure Hamiltonians as the perturbation. No simplification is possible and one must diagonalize the perturbation.

Weak-field Zeeman effect. The approximate eigenstates of $\tilde{H}^{(0)}$ are the coupled states $|n\ell jm_j\rangle$ that exhibit fine structure corrections and whose energies are a function of n and j , as shown in the Fine Structure diagram. Degeneracies in this spectrum occur for different values of ℓ and different values of m_j .

To figure out the effect of the Zeeman interaction on this spectrum we consider the matrix elements:

$$\langle n\ell jm_j | \delta H_{\text{Zeeman}} | n\ell' jm'_j \rangle. \quad (2.5.7)$$

Since $\delta H_{\text{Zeeman}} \sim L_z + 2S_z$ we see that δH_{Zeeman} commutes with \mathbf{L}^2 and with \hat{J}_z . The matrix element thus vanishes unless $\ell' = \ell$ and $m'_j = m_j$ and the Zeeman perturbation is diagonal in the degenerate fine structure eigenspaces. The energy corrections are therefore

$$E_{n\ell jm_j}^{(1)} = \frac{e\hbar}{2mc} B \langle n\ell jm_j | (\hat{L}_z + 2\hat{S}_z) | n\ell jm_j \rangle \frac{1}{\hbar}, \quad (2.5.8)$$

where we multiplied and divided by \hbar to make the units of the result manifest. The result of the evaluation of the matrix element will show a remarkable feature: a linear dependence

$E^{(1)} \sim \hbar m_j$ on the azimuthal quantum numbers. The states in each j multiplet split into equally separated energy levels! We will try to understand this result as a property of matrix elements of vector operators. First, however, note that $\hat{L}_z + 2\hat{S}_z = \hat{J}_z + \hat{S}_z$ and therefore the matrix element of interest in the above equation satisfies

$$\langle n\ell jm_j | (\hat{L}_z + 2\hat{S}_z) | n\ell jm_j \rangle = \hbar m + \langle n\ell jm_j | \hat{S}_z | n\ell jm_j \rangle. \quad (2.5.9)$$

It follows that we only need to concern ourselves with \hat{S}_z matrix elements.

Let's talk about vector operators. The operator $\hat{\mathbf{V}}$ is said to be a vector operator under an angular momentum operator $\hat{\mathbf{J}}$ if the following commutator holds for all values of $i, j = 1, 2, 3$:

$$[\hat{J}_i, \hat{V}_j] = i\hbar \epsilon_{ijk} \hat{V}_k. \quad (2.5.10)$$

It follows from the familiar $\hat{\mathbf{J}}$ commutators that $\hat{\mathbf{J}}$ is a vector operator under $\hat{\mathbf{J}}$. Additionally, if $\hat{\mathbf{V}}$ is a vector operator it has a standard commutation relation with $\hat{\mathbf{J}}^2$ that can be quickly confirmed:

$$[\hat{\mathbf{J}}^2, \hat{\mathbf{V}}] = 2i\hbar (\hat{\mathbf{V}} \times \hat{\mathbf{J}} - i\hbar \hat{\mathbf{V}}). \quad (2.5.11)$$

If $\hat{\mathbf{V}}$ is chosen to be $\hat{\mathbf{J}}$ the left-hand side vanishes by the standard property of $\hat{\mathbf{J}}^2$ and the right-hand side vanishes because the $\hat{\mathbf{J}}$ commutation relations can be written as $\hat{\mathbf{J}} \times \hat{\mathbf{J}} = i\hbar \hat{\mathbf{J}}$. Finally, by repeated use of the above identities you will show (homework) that the following formula holds

$$\frac{1}{(2i\hbar)^2} [\hat{\mathbf{J}}^2, [\hat{\mathbf{J}}^2, \hat{\mathbf{V}}]] = (\hat{\mathbf{V}} \cdot \hat{\mathbf{J}}) \hat{\mathbf{J}} - \frac{1}{2} (\hat{\mathbf{J}}^2 \hat{\mathbf{V}} + \hat{\mathbf{V}} \hat{\mathbf{J}}^2). \quad (2.5.12)$$

Consider $(\hat{\mathbf{J}}^2, \hat{J}_z)$ eigenstates $|k; jm_j\rangle$ where k stands for other quantum number that bear no relation to angular momentum. The matrix elements of the left-hand side of (2.5.12) on such eigenstates is necessarily zero:

$$\langle k'; jm'_j | [\hat{\mathbf{J}}^2, [\hat{\mathbf{J}}^2, \hat{\mathbf{V}}]] | k; jm_j \rangle = 0, \quad (2.5.13)$$

as can be seen by expanding the outer commutator and noticing that $\hat{\mathbf{J}}^2$ gives the same eigenvalue when acting on the bra and on the ket. Therefore the matrix elements of the right-hand side gives

$$\langle k'; jm'_j | (\hat{\mathbf{V}} \cdot \hat{\mathbf{J}}) \hat{\mathbf{J}} | k; jm_j \rangle = \hbar^2 j(j+1) \langle k'; jm'_j | \hat{\mathbf{V}} | k; jm_j \rangle, \quad (2.5.14)$$

which implies that

$$\langle k'; jm'_j | \hat{\mathbf{V}} | k; jm_j \rangle = \frac{\langle k'; jm'_j | (\hat{\mathbf{V}} \cdot \hat{\mathbf{J}}) \hat{\mathbf{J}} | k; jm_j \rangle}{\hbar^2 j(j+1)}. \quad (2.5.15)$$

This is the main identity we wanted to establish. Using the less explicit notation $\langle \dots \rangle$ for the matrix elements we have found that

$$\langle \hat{\mathbf{V}} \rangle = \frac{\langle (\hat{\mathbf{V}} \cdot \hat{\mathbf{J}}) \hat{\mathbf{J}} \rangle}{\langle \hat{\mathbf{J}}^2 \rangle}. \quad (2.5.16)$$

This is sometimes called the projection lemma: the matrix elements of a vector operator $\hat{\mathbf{V}}$ are those of the conventional projection of $\hat{\mathbf{V}}$ onto $\hat{\mathbf{J}}$. Recall that the projection of a vector \mathbf{v} along the vector \mathbf{j} is $(\mathbf{v} \cdot \mathbf{j})\mathbf{j}/j^2$.

Let us now return to the question of interest; the computation of the the expectation value of \hat{S}_z in (2.5.20). Since $\hat{\mathbf{S}}$ is a vector operator under $\hat{\mathbf{J}}$ we can use (2.5.15). Specializing to the z -component

$$\langle n\ell jm_j | \hat{S}_z | n\ell jm_j \rangle = \frac{\hbar m_j \langle n\ell jm_j | \hat{\mathbf{S}} \cdot \hat{\mathbf{J}} | n\ell jm_j \rangle}{\hbar^2 j(j+1)}. \quad (2.5.17)$$

We already see the appearance of the predicted $\hbar m_j$ factor. The matrix element in the numerator is still to be calculated but it will introduce no m_j dependence. In fact $\hat{\mathbf{S}} \cdot \hat{\mathbf{J}}$ is a scalar operator (it commutes with all \hat{J}_i) and therefore it is diagonal in m_j . But even more is true; the expectation value of a scalar operator is in fact independent of m_j ! We will not show this here, but will just confirm it by direct computation. Since $\hat{\mathbf{L}} = \hat{\mathbf{J}} - \hat{\mathbf{S}}$ we have

$$\hat{\mathbf{S}} \cdot \hat{\mathbf{J}} = \frac{1}{2}(\hat{\mathbf{J}}^2 + \hat{\mathbf{S}}^2 - \hat{\mathbf{L}}^2), \quad (2.5.18)$$

and therefore

$$\langle n\ell jm_j | \hat{S}_z | n\ell jm_j \rangle = \frac{\hbar m_j}{2j(j+1)} (j(j+1) - \ell(\ell+1) + \frac{3}{4}). \quad (2.5.19)$$

Indeed, no further m_j dependence has appeared. Back now to (2.5.20) we get

$$\langle n\ell jm_j | (\hat{L}_z + 2\hat{S}_z) | n\ell jm_j \rangle = \hbar m_j \left(1 + \frac{j(j+1) - \ell(\ell+1) + \frac{3}{4}}{2j(j+1)} \right). \quad (2.5.20)$$

The constant of proportionality in parenthesis is called the **Lande g-factor** $g_J(\ell)$:

$$g_J(\ell) \equiv 1 + \frac{j(j+1) - \ell(\ell+1) + \frac{3}{4}}{2j(j+1)} \quad (2.5.21)$$

We finally have for the Zeeman energy shifts in (2.5.8)

$$E_{n\ell jm_j}^{(1)} = \frac{e\hbar}{2mc} B g_J(\ell) m_j. \quad (2.5.22)$$

Here the Bohr magneton $\frac{e\hbar}{2mc} \simeq 5.79 \times 10^{-9} \text{eV/gauss}$. This is our final result for the weak-field Zeeman energy corrections to the fine structure energy levels. Since all degeneracies within j multiplets are broken and j multiplets with different ℓ split differently due to the ℓ dependence of $g_J(\ell)$, the weak-field Zeeman effect removes all degeneracies!

Strong-field Zeeman effect. We mentioned earlier that when the Zeeman effect is larger than the fine structure corrections we must take the original hydrogen Hamiltonian together with the Zeeman Hamiltonian to form the ‘known’ Hamiltonian $\check{H}^{(0)}$:

$$\check{H}^{(0)} = H^{(0)} + \frac{e}{2mc} (\hat{L}_z + 2\hat{S}_z) B. \quad (2.5.23)$$

Actually $\check{H}^{(0)}$ is simple because the Zeeman Hamiltonian commutes with the zero-th order hydrogen Hamiltonian

$$[\hat{L}_z + 2\hat{S}_z, H^{(0)}] = 0. \quad (2.5.24)$$

We can thus find eigenstates of both simultaneously. Those are in fact the uncoupled basis states! We have

$$\begin{aligned} H^{(0)}|n\ell m_\ell m_s\rangle &= E_n^{(0)}|n\ell m_\ell m_s\rangle \\ (\hat{L}_z + 2\hat{S}_z)|n\ell m_\ell m_s\rangle &= \hbar(m_\ell + 2m_s)|n\ell m_\ell m_s\rangle. \end{aligned} \quad (2.5.25)$$

and therefore the uncoupled basis states are the *exact* energy eigenstates of $\check{H}^{(0)}$ and have energies

$$E_{n\ell m_\ell m_s} = E_n^{(0)} + \frac{e\hbar}{2mc}B(m_\ell + 2m_s). \quad (2.5.26)$$

Some of the degeneracy of $H^{(0)}$ has been removed, but some remains. For a fixed principal quantum number n there are degeneracies among $\ell \otimes \frac{1}{2}$ states and degeneracies among such multiplets with ℓ and ℓ' different. This is illustrated in Figure 2.2.

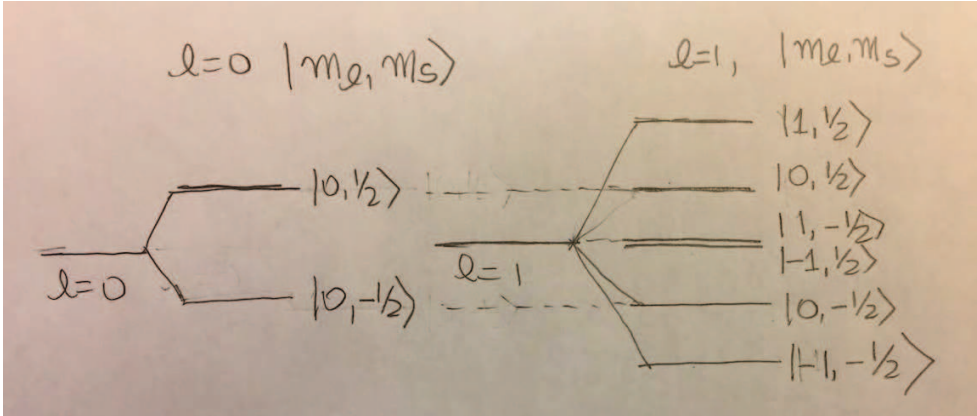


Figure 2.2: Illustrating the degeneracies remaining for $\ell = 0$ and $\ell = 1$ after the inclusion of Zeeman term in the Hamiltonian. Accounting for the spin of the electron there two degenerate states in the $\ell = 1$ multiplet $1 \otimes \frac{1}{2}$ and each of the two states in the $\ell = 0$ multiplet $0 \otimes \frac{1}{2}$ is degenerate with a state in the $\ell = 1$ multiplet.

The problem now is to compute the corrections due to δH_{fs} on the non-degenerate and on the degenerate subspaces of $\check{H}^{(0)}$. The non-degenerate cases are straightforward, but the degenerate cases could involve diagonalization. We must therefore consider the matrix elements

$$\langle n\ell' m'_\ell m'_s | \delta H_{\text{fs}} | n\ell m_\ell m_s \rangle, \quad (2.5.27)$$

with the condition

$$m'_\ell + 2m'_s = m_\ell + 2m_s, \quad (2.5.28)$$

needed for the two states in the matrix element to belong to a degenerate subspace. Since $\hat{\mathbf{L}}^2$ commutes with δH_{fs} the matrix elements vanish unless $\ell = \ell'$ and therefore it suffices to consider the matrix elements

$$\langle n\ell'm'_\ell m'_s | \delta H_{\text{fs}} | n\ell m_\ell m_s \rangle, \quad (2.5.29)$$

still with condition (2.5.28). Ignoring $\ell = 0$ states, we have to re-examine the relativistic correction and spin orbit. The relativistic correction was computed in the uncoupled basis and one can use the result because the states are unchanged and the perturbation was shown to be diagonal in this basis. For spin-orbit the calculation was done in the coupled basis because spin-orbit is *not diagonal* in the original $H^{(0)}$ degenerate spaces using the uncoupled basis. But happily, it turns out that spin-orbit is diagonal in the more limited degenerate subspaces obtained after the Zeeman effect is included. All these matters are explored in the homework.

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