Chapter 21
Hydrogen Atom with Spin in External Fields

Having established the properties of irreducible tensor operators, I am now in a position to use perturbation theory to study how the energy levels of the hydrogen atom are modified in external magnetic and electric fields. Before doing so, however, I will use perturbation theory to obtain the relativistic corrections to the energy levels of hydrogen in the *absence* of any external fields. This will lead naturally to a discussion of the *fine-structure* and *hyperfine structure* of hydrogen.

In the absence of any external fields, the energy levels of hydrogen (including electron spin) are given by the solution of the Dirac equation. The Dirac equation consistently treats all relativistic effects, but does not include hyperfine structure (arising from the magnetic moment of the proton), nor the Lamb shift (to be mentioned below). Explicitly, in the absence of any external fields, the energy levels are given by

$$E_{nj} = \frac{m_e c^2}{\left\{1 + \frac{\alpha_{FS}^2}{\left[n-j-\frac{1}{2}+\sqrt{\left(j+\frac{1}{2}\right)^2-\alpha_{FS}^2}\right]^2}\right\}^{1/2}}; \quad \left\{ \begin{array}{c} n = 1, 2, \ldots; \\ j = \frac{1}{2}, \frac{3}{2} \ldots, n - \frac{1}{2} \end{array} \right. , \tag{21.1}$$

where

$$\alpha_{FS} = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137} \tag{21.2}$$

is the fine structure constant and m_e should be thought of as the reduced mass of the electron. Note that ℓ does not appear explicitly in this equation; j is the quantum number corresponding to the total angular momentum operator $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ of the electron.

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Expanding this equation in a power series in α_{FS}^2, you can show that

$$E_{nj} - m_e c^2 \approx -\frac{E_R}{n^2} - \alpha_{FS}^2 \frac{E_R}{n^4}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right) + \cdots , \tag{21.3}$$

where

$$E_R = \frac{1}{2} m_e c^2 \alpha_{FS}^2 \approx 13.6 \text{ eV} \tag{21.4}$$

is the Rydberg energy.

Even though the Schrödinger equation is a non-relativistic equation, it is possible to use perturbation theory to calculate the relativistic corrections to the hydrogenic energy levels, corrections that can be attributed to relativistic mass effects, spin–orbit interactions, and the so-called Darwin term. In this manner, the α_{FS}^2 term appearing in Eq. (21.3) can be obtained within the context of non-relativistic quantum mechanics. I have already discussed spin and the spin–orbit interaction in Chap. 12, so you should review those results.

In perturbation theory, the Hamiltonian is written as $\hat{H} = \hat{H}_0 + \hat{H}'$, where $\hat{H}'$ includes relativistic corrections, hyperfine interactions, and any atom–external field interactions, while $\hat{H}_0$ is the Hamiltonian of hydrogen in the absence of such effects. The exact eigenkets are expanded in terms of eigenkets of $\hat{H}_0$ and approximate expressions are obtained for the eigenenergies and eigenkets. If there is degeneracy and if $\hat{H}'$ couples degenerate states, I must first exactly diagonalize any degenerate sub-blocks in which there are off-diagonal matrix elements.

In dealing with any stationary state problem in quantum mechanics, *the first step is to identify the constants of the motion.* Operators corresponding to dynamic variables that are constants of the motion commute with the Hamiltonian. I can find simultaneous eigenkets of the Hamiltonian and these operators. In problems involving perturbation theory, there are *two* Hamiltonians, the unperturbed Hamiltonian $\hat{H}_0$ and the total Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}'$. If an operator $\hat{A}$ having eigenvalues labeled by a commutes with *both* $\hat{H}_0$ and $\hat{H}'$, it corresponds to an *exact* constant of the motion. As a consequence, the eigenkets of both $\hat{H}_0$ and $\hat{H}$ can be chosen as simultaneous eigenkets of $\hat{A}$. *If the eigenkets are chosen in this manner, only states having the same value of the eigenvalue a can be coupled by* $\hat{H}'$, since, under these circumstances, $\hat{H}'$ is diagonal in the $|a\rangle$ basis.

Let me be more specific. Suppose that both $\hat{L}^2$ and $\hat{L}_z$ commute with both $\hat{H}_0$ and $\hat{H}'$, and that $\hat{H}_0$ is the Hamiltonian operator for hydrogen without spin. This means that the *exact* eigenkets of $\hat{H} = \hat{H}_0 + \hat{H}'$ can be written as $|E, \ell, m\rangle$, whereas the eigenkets of $\hat{H}_0$ are given by $|E, \ell, m\rangle^{(0)} \equiv |n, \ell, m\rangle$. In carrying out perturbation theory using the $|n, \ell, m\rangle$ basis for a given n, only states having the *same* ℓ and the *same* m can be coupled by $\hat{H}'$; in other words, *no* degenerate states of $\hat{H}_0$ are coupled by the perturbation and I can use nondegenerate perturbation theory. By identifying the constants of the motion, I have dramatically simplified the problem. Note that since n does not correspond to the exact energy, states having different n (but the same ℓ and the same m) *can* be coupled by $\hat{H}'$; however, contributions from these terms are usually relatively small since they involve large energy denominators.

I first consider the hydrogen atom without spin and calculate the relativistic mass correction. Spin is then included and the modifications to the energy levels from the spin–orbit interaction are obtained. The role played by the Darwin term is discussed. Finally I allow for interactions with constant external magnetic or electric fields. The hyperfine interaction is discussed in detail in Appendix 2.

21.1 Energy Levels of Hydrogen

21.1.1 Unperturbed Hamiltonian

The Hamiltonian for the hydrogen atom without any relativistic corrections is

$$\hat{H}_0 = \frac{\hat{p}^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 r} = \frac{\hat{p}^2}{2m_e} - \frac{K_e}{r}, \tag{21.5}$$

where

$$K_e = \frac{e^2}{4\pi\epsilon_0}. \tag{21.6}$$

The eigenenergies of $\hat{H}_0$ are given by

$$E_n^{(0)} = -\frac{1}{2n^2}\alpha_{FS}^2 m_e c^2 = -\frac{1}{2n^2}\frac{e^2}{4\pi\epsilon_0 a_0} = -\frac{E_R}{n^2} = -\frac{13.6\ \text{eV}}{n^2}, \tag{21.7}$$

where a_0 is the Bohr radius. There is an n^2 degeneracy for states having a given n; for a given n, $\ell = 0, 1, \ldots (n-1)$, and for a given ℓ, m_ℓ varies from $-\ell$ to ℓ in integer steps.

21.1.2 Relativistic Mass Correction

Relativistic corrections are best treated by the exact solution of the Dirac equation for hydrogen. However I can get a perturbative solution for the relativistic mass correction (actually a relativistic energy correction, since mass is an invariant) if I replace the classical kinetic energy term by its relativistic equivalent,

$$\begin{aligned} \frac{p^2}{2m_e} &\to \sqrt{m_e^2c^4 + p^2c^2} - m_ec^2 = m_ec^2\left(\sqrt{1 + \frac{p^2}{2m_e^2c^2}} - 1\right) \\ &\approx \frac{p^2}{2m_e} - \frac{1}{8}\frac{p^4}{m_e^3c^2}, \end{aligned} \tag{21.8}$$

implying that, to lowest order, the relativistic mass correction adds a term to the Hamiltonian,

$$\hat{H}'_{\text{rel}} = -\frac{1}{8}\frac{\hat{p}^4}{m_e^3 c^2}, \tag{21.9}$$

and the total Hamiltonian is

$$\hat{H} \approx \hat{H}_0 - \frac{1}{8}\frac{\hat{p}^4}{m_e^3 c^2}. \tag{21.10}$$

The operators $\hat{H}, \hat{L}^2, \hat{L}_z$ still form a set of commuting operators allowing me to specify the states by the quantum numbers E, ℓ, m_ℓ. However, *there is no longer a single quantum number n that uniquely determines the energy.* The energy of a given level now depends on *both n and* ℓ, since the relativistic term has broken the dynamic symmetry (the classical orbit precesses—it is no longer closed and the Lenz vector is not a constant of the motion). To get the energies exactly I would need to solve the Dirac equation. To get *approximate* energies and eigenfunctions I can use the Schrödinger equation and perturbation theory.

Since the perturbation matrix is diagonal in *all* the quantum numbers except *n*, I do *not* need to use degenerate perturbation theory. The first order change in the energy is given simply by

$$\Delta E_{n\ell}^{(1)} = -\frac{1}{8m_e^3 c^2} \langle n, \ell, m | \hat{p}^4 | n, \ell, m \rangle \tag{21.11}$$

It is possible to evaluate this term as

$$\begin{aligned}
\langle n, \ell, m | \hat{p}^4 | n, \ell, m \rangle &= \int d\mathbf{r} \psi_{nlm}^*(\mathbf{r}) \hat{p}^4 \psi_{nlm}(\mathbf{r}) \\
&= \int d\mathbf{r} \left[\hat{p}^2 \psi_{nlm}(\mathbf{r})\right]^* \hat{p}^2 \psi_{nlm}(\mathbf{r}) \\
&\approx (2m_e)^2 \int d\mathbf{r} \left[\left\{\hat{H}_0 - V(r)\right\} \psi_{nlm}(\mathbf{r})\right]^* \left\{\hat{H}_0 - V(r)\right\} \psi_{nlm}(\mathbf{r}) \\
&= (2m_e)^2 \int d\mathbf{r}\, \psi_{nlm}(\mathbf{r})^* \left\{ \begin{array}{c} \hat{H}_0^2 - V(r)\hat{H}_0 \\ -\hat{H}_0 V(r) + [V(r)]^2 \end{array} \right\} \psi_{nlm}(\mathbf{r}) \\
&= (2m_e)^2 \left[\begin{array}{c} E_n^2 + 2\frac{e^2}{4\pi\epsilon_0} E_n \langle n, \ell, m | \frac{1}{r} | n, \ell, m \rangle \\ + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \langle n, \ell, m | \frac{1}{r^2} | n, \ell, m \rangle \end{array} \right].
\end{aligned} \tag{21.12}$$

The needed matrix elements can be calculated as (see Appendix 1),

$$\int d\mathbf{r}\psi^*_{nlm}(\mathbf{r})\frac{1}{r}\psi_{nlm}(\mathbf{r}) = \frac{1}{n^2 a_0}; \tag{21.13a}$$

$$\int d\mathbf{r}\psi^*_{nlm}(\mathbf{r})\frac{1}{r^2}\psi_{nlm}(\mathbf{r}) = \frac{1}{\left(\ell+\frac{1}{2}\right)n^3 a_0^2}, \tag{21.13b}$$

where a_0 is the Bohr radius. The final energy shift is

$$\Delta E_{n\ell} = -\left|E_n^{(0)}\right|\frac{\alpha_{FS}^2}{n^2}\left[\frac{n}{\ell+1/2}-\frac{3}{4}\right]. \tag{21.14}$$

You see that the energy now *now depends on both n and ℓ*; the "accidental" degeneracy is lifted by the relativistic term. Since

$$\frac{n}{\ell+1/2} \geq \frac{(\ell+1)}{\ell+1/2} > 1, \tag{21.15}$$

it follows that $\Delta E_{n\ell} < 0$ and the energy of each state is lowered, which is not surprising since H'_{rel} is negative. The energies of the low angular momentum states for a given n are lowered the most, since the electron's average speed decreases with increasing angular momentum for a fixed energy, giving a smaller relativistic correction.

The relativistic mass corrections in frequency units are given by

$$\Delta f_{n\ell}^{\text{mass}} = -\frac{175\ \text{GHz}}{n^4}\left(\frac{n}{\ell+\frac{1}{2}}-\frac{3}{4}\right). \tag{21.16}$$

For the two lowest energy states of hydrogen,

n	ℓ	$\Delta f_{n\ell}^{\text{mass}}$
1	0	– 219 GHZ
2	0	– 35.6 GHZ
2	1	– 6.38 GHZ

.

To *zeroth* order in the perturbation, the *eigenkets are unchanged.* What about higher order relativistic mass corrections to the eigenkets and eigenenergies? You can use nondegenerate perturbation theory to get higher order corrections. For example,

$$|E,\ell,m_\ell\rangle \approx |n,\ell,m_\ell\rangle + \sum_{n'\neq n}\frac{\langle n',\ell,m_\ell|\,H'_{\text{rel}}\,|n,\ell,m_\ell\rangle\,|n',\ell,m_\ell\rangle}{E_n^{(0)}-E_{n'}^{(0)}} \tag{21.17}$$

and

$$E_{n\ell} \approx E_n^{(0)} + \Delta E_{n\ell}^{(1)} + \sum_{n' \neq n} \frac{\left|\langle n', \ell, m_\ell | H'_{\text{rel}} | n, \ell, m_\ell \rangle\right|^2}{E_n^{(0)} - E_{n'}^{(0)}}, \tag{21.18}$$

where I used the fact that H'_{rel} is diagonal in both ℓ and m_ℓ, since both $\hat{L}^2$ and $\hat{L}_z$ are constants of the motion. The second order energy corrections are α_{FS}^2 times smaller than the first order corrections.[1] I neglect any such corrections throughout this chapter.

21.1.3 Spin Included

If spin is included, but spin-dependent interactions are neglected, the degeneracy of each state is doubled since the electron can have spin quantum numbers $m_s = \pm 1/2$. The total (orbital plus spin) angular momentum operator is

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}. \tag{21.19}$$

Since $\hat{J}^2$ and $\hat{J}_z$ and are constants of the motion, states can be labeled by *either* $|n, \ell, m_\ell, s, m_s\rangle$ *or* $\left|n, \ell, s, j, m_j\right\rangle$. You cannot use *both* sets of labels since $\hat{J}^2$ does not commute with $\hat{L}_z$ and $\hat{S}_z$ *separately*, only with their sum, $\hat{J}_z = \hat{L}_z + \hat{S}_z$.

The results obtained in Sect. 21.1.2 are unchanged since the relativistic mass correction to the Hamiltonian given in Eq. (21.9) is spin-independent. States having a given ℓ and different j are still degenerate. Thus, the $n = 2, \ell = 1$ state is six-fold degenerate and can be labeled *either* by $n = 2, \ell = 1, m_\ell = \pm 1, 0; m_s = \pm 1/2$ *or* by $n = 2, \ell = 1, j = 1/2, 3/2$ with $m_j = -3/2, -1/2, 1/2, 3/2$ for $j = 3/2$ and $m_j = -1/2, 1/2$ for $j = 1/2$.

21.1.4 Spin–Orbit Interaction

The spin–orbit interaction leads to an additional term in the Hamiltonian given by Eq. (12.33),

$$\hat{H}'_{\text{so}} = \frac{1}{8\pi\epsilon_0} \frac{e^2 \mathbf{S} \cdot \mathbf{L}}{m_e^2 r^3 c^2}. \tag{21.20}$$

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[1] For consistency, if I were to include such corrections, I would need to take the next term in the expansion of Eq. (21.8) and calculate its effect in first order perturbation theory.

(From this point onwards, I drop the carets on the angular momentum and spin operators, unless there is some possible cause for confusion.) For angular momentum states having $\ell = 0$ there is no spin–orbit interaction. *All equations in this subsection are restricted to values* $\ell \neq 0$.

Since the states having the same n are degenerate, it is best to use a basis in which the levels *within* a given n manifold are not coupled. In that way I do not have to use degenerate perturbation theory. To find such a basis, I write

$$\mathbf{S}\cdot\mathbf{L} = S_xL_x + S_yL_y + S_zL_z = \frac{J^2 - L^2 - S^2}{2}. \tag{21.21}$$

Clearly, $\mathbf{S}{\cdot}\mathbf{L}$ is *not* diagonal in the $|n,\ell,s;m_\ell,m_s\rangle$ basis; however in the $|n,\ell,s,;j,m\rangle$ basis

$$\begin{aligned}
&\langle n,\ell,s,;j,m|\,\frac{\mathbf{S}\cdot\mathbf{L}}{r^3}\,\left|n',\ell',s,;j',m'\right\rangle \\
&= \langle n,\ell,s,;j,m|\,\frac{J^2-L^2-S^2}{2r^3}\,\left|n',\ell',s,;j',m'\right\rangle \\
&= \hbar^2\frac{j(j+1)-\ell(\ell+1)-3/4}{2} \\
&\quad\times \langle n,\ell,s,;j,m|\,\frac{1}{r^3}\,\left|n',\ell,s,;j,m\right\rangle \delta_{\ell,\ell'}\delta_{j,j'}\delta_{m,m'}.
\end{aligned} \tag{21.22}$$

In the $|n,\ell,s,;j,m\rangle$ basis, there *is* coupling between *different* electronic state manifolds (which I already said I will neglect), but *within* a given n state manifold, there is no coupling! The quantum numbers ℓ, j, m are said to be *good* quantum numbers since they correspond to exact constants of the motion. In effect I am exploiting the fact that the total angular momentum is conserved, even if $\mathbf{L}$ and $\mathbf{S}$ are not conserved separately.

Thus, to lowest order perturbation theory (that is, neglecting coupling between different electronic state manifolds),

$$\begin{aligned}
E_{n\ell j} &= E_n^{(0)} + \frac{1}{8\pi\epsilon_0}\frac{e^2\hbar^2}{m_e^2c^2}\frac{j(j+1)-\ell(\ell+1)-3/4}{2} \\
&\quad\times \langle n,\ell,s,;j,m|\,\frac{1}{r^3}\,|n,\ell,s,;j,m\rangle
\end{aligned} \tag{21.23}$$

and $j = \ell \pm 1/2$. The matrix elements of r^{-3} can be evaluated analytically (see Appendix 1) as

$$\begin{aligned}
\langle n,\ell,s,;j,m|\,\frac{1}{r^3}\,|n,\ell,s,;j,m\rangle &= \int d\mathbf{r}\psi_{nlm}^*(\mathbf{r})\frac{1}{r^3}\psi_{nlm}(\mathbf{r}) \\
&= \frac{1}{\ell\left(\ell+\frac{1}{2}\right)(\ell+1)\,n^3a_0^3},
\end{aligned} \tag{21.24}$$

leading to

$$E_{n\ell,j=\ell-\frac{1}{2}} = E_n^{(0)} - \frac{\alpha_{FS}^2}{2n}\left|E_n^{(0)}\right|\frac{1}{\ell\left(\ell+\frac{1}{2}\right)}; \tag{21.25a}$$

$$E_{n\ell,j=\ell+\frac{1}{2}} = E_n^{(0)} + \frac{\alpha_{FS}^2}{2n}\left|E_n^{(0)}\right|\frac{1}{\left(\ell+\frac{1}{2}\right)(\ell+1)}. \tag{21.25b}$$

The *fine structure splitting* for a state having $\ell \neq 0$ is equal to

$$\delta E_{n\ell}^{\mathrm{so}} = E_{n\ell j=\ell+\frac{1}{2}} - E_{n\ell j=\ell-\frac{1}{2}} = \frac{\alpha_{FS}^2}{n}\left|E_n^{(0)}\right|\frac{1}{\ell(\ell+1)}. \tag{21.26}$$

For the $2P$ state of hydrogen, this splitting is equal to 4.53×10^{-5} eV which is about 11 GHz in frequency units. For the alkali atoms the fine structure splitting is much larger—it is about 515 GHz for the $3P$ state of sodium (in sodium the ground state is a $3S$ state and the first excited states are $3P$ states).

The spin orbit corrections in frequency units are given by

$$\Delta f_{n\ell,j=\ell-\frac{1}{2}}^{\mathrm{so}} = -\frac{175\text{ GHz}}{2n^3}\frac{1}{\ell\left(\ell+\frac{1}{2}\right)}; \tag{21.27}$$

$$\Delta f_{n\ell,j=\ell+\frac{1}{2}}^{\mathrm{so}} = \frac{175\text{ GHz}}{2n^3}\frac{1}{(\ell+1)\left(\ell+\frac{1}{2}\right)}; \tag{21.28}$$

$$\delta f_{n\ell}^{\mathrm{so}} = \Delta f_{n\ell,j=\ell+\frac{1}{2}}^{\mathrm{so}} - \Delta f_{n\ell,j=\ell-\frac{1}{2}}^{\mathrm{so}} = \frac{175\text{ GHz}}{n^3}\frac{1}{\ell(\ell+1)}. \tag{21.29}$$

For the $n = 2$ state

$$\begin{array}{cccc} n & \ell & j & \Delta f_{n\ell j}^{\mathrm{so}} \\ 2 & 1 & 1/2 & -7.30\text{ GHZ} \\ 2 & 1 & 3/2 & 3.65\text{ GHZ} \end{array}; \qquad \begin{array}{ccc} n & \ell & \delta f_{n\ell}^{\mathrm{so}} \\ 2 & 1 & 10.94\text{ GHZ} \end{array}.$$

The prediction for the fine structure splitting obtained using the Dirac equation is 10.943 GHz, when the reduced mass is used in the calculation, while the experimental value is 10.969 GHz. There are corrections to the Dirac equation arising from the finite size of the nucleus and radiative corrections, involving fluctuations of the vacuum field. When these are included, experiment and theory are in excellent agreement.

21.1.5 Darwin Term

Although $\ell = 0$ states are not shifted by the spin–orbit interaction, they *are* shifted by what is called the *Darwin term* (named for Charles Galton Darwin). The Darwin term shifts only states having $\ell = 0$. In some rough sense this term arises owing to the fact that the electron cannot have a speed greater than c. As a consequence of the uncertainty principle, the electron wave packet must then always be constrained to a sphere of radius of order of the Compton wavelength to insure that $\Delta v < c$. The potential energy is averaged over this sphere. That is, the average potential seen by the electron is

$$\begin{aligned} V(\mathbf{r}) &= \frac{1}{\frac{4}{3}\pi\bar{\lambda}_c^3}\int_{\text{sphere}} d\boldsymbol{\epsilon}\, V(\mathbf{r}+\boldsymbol{\epsilon}) \\ &\approx V(\mathbf{r}) + \frac{1}{\frac{4}{3}\pi\bar{\lambda}_c^3}\int_{\text{sphere}} d\boldsymbol{\epsilon}\left[\boldsymbol{\epsilon}\cdot\nabla V(\mathbf{r}) + \frac{1}{2}\sum_{i,j=1}^{3}\epsilon_i\epsilon_j\frac{\partial^2 V(\mathbf{r})}{\partial x_i\partial x_j}\right], \end{aligned} \tag{21.30}$$

where the integral is over a sphere having radius $\bar{\lambda}_c = \hbar/m_e c$ centered at position $\mathbf{r}$ and $V(\mathbf{r})$ is the Coulomb potential. The first term in the integral vanishes on integrating over $\boldsymbol{\epsilon}$ and the second contributes only for $i = j$. In this manner, you can obtain

$$H'^{\text{Darwin}}(\mathbf{r}) = \frac{1}{\frac{4}{3}\pi\bar{\lambda}_c^3}\frac{1}{2}\int_{\text{sphere}} d\boldsymbol{\epsilon}\sum_i^3 \epsilon_i^2\frac{\partial^2 V(\mathbf{r})}{\partial x_i^2} \tag{21.31}$$

But

$$\int_{\text{sphere}} d\boldsymbol{\epsilon}\,\epsilon_i^2 = \frac{1}{3}\int_{\text{sphere}} d\boldsymbol{\epsilon}\,\epsilon^2 = 4\pi\frac{\bar{\lambda}_c^5}{15} \tag{21.32}$$

since each component gives the same result. As a consequence,

$$H'^{\text{Darwin}}(\mathbf{r}) \approx \frac{\bar{\lambda}_c^2}{10}\sum_i^3\frac{\partial^2 V(\mathbf{r})}{\partial x_i^2} = \frac{\bar{\lambda}_c^2}{10}\nabla^2 V(\mathbf{r}) = \frac{e^2\bar{\lambda}_c^2}{10\epsilon_0}\delta(\mathbf{r}), \tag{21.33}$$

which is of the same order of magnitude as the result that can be derived from the Dirac equation,

$$H'^{\text{Darwin}}(\mathbf{r}) = \frac{e^2\bar{\lambda}_c^2\delta(\mathbf{r})}{8\epsilon_0}. \tag{21.34}$$

The energy shift vanishes for all but $\ell = 0, j = 1/2$ states. The (correct) Darwin energy shift is given by

$$\Delta E_n^{\text{Darwin}} = \frac{e^2 \bar{\lambda}_c^2}{8\epsilon_0} \langle n00 | \delta(\mathbf{r}) | n00 \rangle , \tag{21.35}$$

where $|n\ell m_\ell\rangle$ is an eigenket of the hydrogen atom neglecting spin. The matrix element is evaluated easily [see Eq. (21.108) in Appendix 2] and one finds

$$\Delta E_n^{\text{Darwin}} = \frac{E_R \alpha_{FS}^2}{n^3}; \tag{21.36a}$$

$$\Delta f_n^{\text{Darwin}} = \frac{175\text{ GHz}}{n^3}. \tag{21.36b}$$

The frequency shifts for $n = 1, 2$ states are given by

n	ℓ	j	$\Delta f_n^{\text{Darwin}}$
1	0	1/2	175 GHZ .
2	0	1/2	21.9 GHZ

21.1.6 Total Fine Structure

The total fine structure (mass+spin-orbit+Darwin terms) is obtained by combining Eqs. (21.14), (21.25), and (21.36). The result is

$$\Delta E_{nj}^{\text{tot}} = -\alpha_{FS}^2 \frac{E_R}{n^4} \left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right); \quad j = \frac{1}{2}, \frac{3}{2} \ldots, n - \frac{1}{2}; \tag{21.37a}$$

$$\Delta f_{nj}^{\text{tot}} = -\frac{175\text{ GHz}}{n^4} \left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right); \quad j = \frac{1}{2}, \frac{3}{2} \ldots, n - \frac{1}{2}. \tag{21.37b}$$

These results agree with the solutions of the Dirac equation [see Eq. (21.3)], if corrections of order $\alpha_{FS}^4 E_R$ are neglected. Note that the ℓ-dependence is now implicit, with $j = \ell \pm \frac{1}{2}$. For $n = 1, 2$

n	ℓ	j	$\Delta f_{n\ell}^{\text{tot}}$
1	0	1/2	− 43.8 GHZ
2	0	1/2	− 13.7 GHZ .
2	1	1/2	− 13.7 GHZ
2	1	3/2	− 2.74 GHZ

All energies are lowered, a result attributable mainly to the relativistic mass correction. States having the same values of n and j are still degenerate.

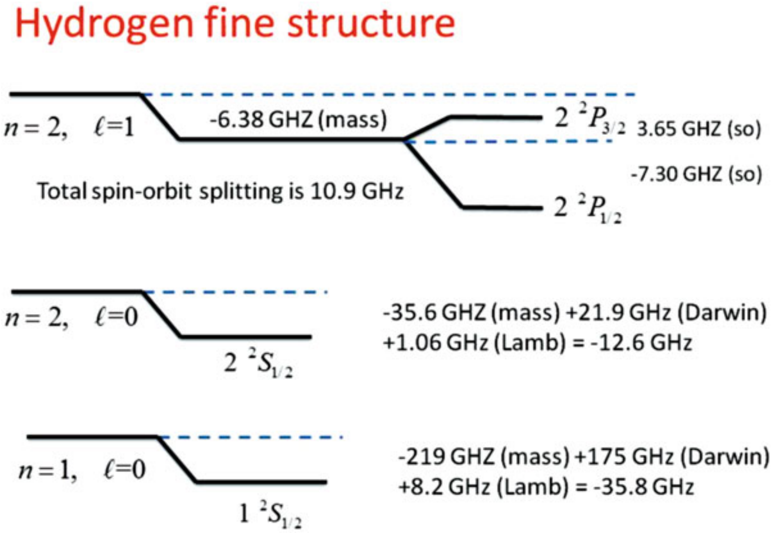

Fig. 21.1 Hydrogen fine structure for the $n = 1$ and $n = 2$ states (not to scale), including relativistic mass, spin-orbit and Darwin contributions, as well as the Lamb shift. The values shown are those obtained using the results of perturbation theory with m_e equal to the reduced mass and differ slightly from the experimental values

21.1.7 Lamb Shift

The Lamb shift [named for Willis E. Lamb, Jr. (my thesis advisor)] arises from quantum electrodynamic corrections, that is, effects related to changes in atomic energy levels resulting from fluctuations of the vacuum radiation field. The Lamb shift affects mainly $\ell = 0$ states. The $n = 2$, $\ell = 0$, $j = 1/2$ level is shifted *up* by about 1.06 GHz and the $n = 1$, $\ell = 0$, $j = 1/2$ level is shifted *up* by about 8.17 GHz. The Lamb shift breaks the degeneracy of states having the same n but different j.

In Fig. 21.1,the relativistic corrections to the $n = 1, 2$ states of hydrogen are illustrated. In the remainder of this chapter, I neglect the Lamb shift.

21.1.8 Hyperfine Structure

As does the electron, the proton in hydrogen possesses an intrinsic spin angular momentum having quantum number $I = 1/2$ and an intrinsic magnetic moment. In hydrogen, this results in an interaction of the magnetic moment of the proton with the magnetic field produced by the electron. The magnetic moment of the proton is

$$\mathbf{m}_p = \frac{eg_p\mathbf{I}}{2m_p}, \tag{21.38}$$

where m_p is the proton mass and g_p is the proton *g-factor*, equal to 5.586. The hyperfine interaction strength is roughly $m_e/m_p = 1/1836$ times smaller than the fine structure interaction strength. A calculation of the energy level shifts produced by the hyperfine interaction is given in Appendix 2. It is possible to define a total (orbital plus electronic spin plus nuclear spin) angular momentum operator by

$$\mathbf{F} = \mathbf{J} + \mathbf{I}, \tag{21.39}$$

having associated quantum number $f = j \pm 1/2$. In frequency units, the hyperfine level shifts, $\Delta f^{\mathrm{hf}}_{n\ell jf}$, and splittings, $\delta f^{\mathrm{hf}}_{n\ell j}$, for the $n = 1, 2$ states of hydrogen are:

n	ℓ	j	f	$\Delta f^{\mathrm{hf}}_{n\ell jf}$
1	0	1/2	0	– 1.06 GHZ
1	0	1/2	1	0.355 GHZ
2	0	1/2	0	– 133 MHZ
2	0	1/2	1	44.4 MHZ
2	1	1/2	0	– 44.4 MHZ
2	1	1/2	1	14.8 MHZ
2	1	3/2	1	– 14.8 GHZ
2	1	3/2	2	8.88 MHZ

n	ℓ	j	$\delta f^{\mathrm{hf}}_{n\ell j}$
1	0	1/2	1.42 GHZ
2	0	1/2	177 MHZ .
2	1	1/2	59.2 MHZ
2	1	3/2	23.7 MHZ

These results are indicated schematically in Fig. 21.2.

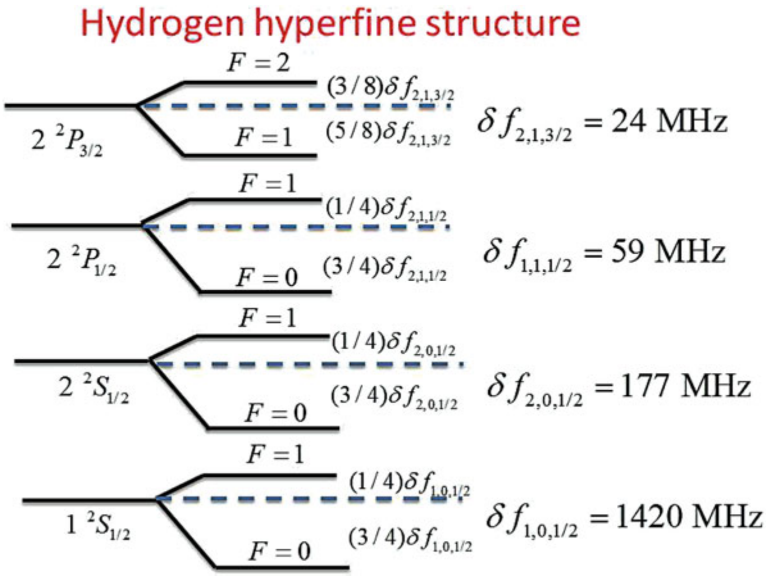

Fig. 21.2 Hydrogen hyperfine structure for the $n = 1$ and $n = 2$ states (not to scale) with splittings $\delta f_{n,\ell,j}$

21.1.9 Addition of a Magnetic Field

I now want to consider the influence of external magnetic and electric fields on the energy levels of hydrogen. Although external magnetic fields couple different hyperfine levels much more strongly than different fine structure levels (see Appendix 2), I neglect hyperfine structure in discussing magnetic and electric field effects. This is not because they are unimportant, but simply because I want to illustrate some physical concepts that are more easily understood if the hyperfine interaction is neglected.

The modifications of the energy levels of atoms by an external magnetic field are often referred to as the *Zeeman effect* (after Pieter Zeeman). If a magnetic field is present along the z direction, a term

$$\hat{H}'_B = \frac{\beta_0 B}{\hbar}\left(L_z + 2S_z\right) = \frac{\beta_0 B}{\hbar}\left(J_z + S_z\right) \tag{21.40}$$

must be added to the Hamiltonian. Recall that $\beta_0 = e\hbar/2m_e$ is the Bohr magneton and that $\beta_0/h \approx 14$ GHz/T. The total Hamiltonian then consists of the unperturbed Hamiltonian of hydrogen plus contributions from both the relativistic corrections (relativistic mass, spin-orbit, and Darwin terms) and the Zeeman effect. The only constants of the motion for the total Hamiltonian are E, L^2, S^2, J_z. The magnitude of the total angular momentum is not a constant of the motion since $\hat{J}^2$ does not commute with $\hat{S}_z$, and the z-components of the orbital and spin angular momenta are not constants of the motion since $\hat{L}_z$ and $\hat{S}_z$ do not commute with $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$, which appears as a factor in the spin-orbit term of the Hamiltonian. Thus the eigenkets can be labeled by $\left|E, \ell, s = 1/2, m_j\right\rangle$. I will drop the s label since $s = 1/2$. In a given n manifold, the energy E of a state having a given ℓ, m_j now depends on some complicated combination of the spin–orbit and Zeeman interactions.

To apply degenerate perturbation theory, I can use either the $\left|n, \ell, j, m_j\right\rangle$ or the $\left|n, \ell, m_\ell, m_s\right\rangle$ basis kets, remembering that only states having the same ℓ and the same $m_j = m_\ell + m_s$ can be coupled since L^2 and J_z are constants of the motion. In other words, ℓ and $m_j = m_\ell + m_s$ remain good quantum numbers in the presence of an external magnetic field. It is relatively easy to calculate the matrix elements in either basis in a state of given n. Once the matrix elements are calculated, you need to diagonalize each degenerate sub-block. If the spin-orbit coupling is much larger than the magnetic field interaction strength, then j is an *approximate* good quantum number since J^2 is an approximate constant of the motion. In this limit the $\left|n, \ell, j, m_j\right\rangle$ are *approximate* eigenkets that can be used to carry out *nondegenerate perturbation theory* for the magnetic-field interaction. On the other hand, if the magnetic field interaction strength is much larger than the spin-orbit coupling strength, then m_ℓ and m_s are *approximate* good quantum number since L_z and S_z are an approximate constants of the motion. In this case, the $\left|n, \ell, m_\ell, m_s\right\rangle$ are *approximate* eigenkets that can be used to carry out *nondegenerate perturbation theory* for the spin–orbit and other relativistic interactions.

In the $\left|n,\ell,j,m_j\right\rangle$ basis, the only matrix elements that are a little tricky to evaluate are those involving $\left\langle n,\ell,j,m_j\right|\hat{S}_z\left|n,\ell,j',m_j\right\rangle$. You must convert the $\left|n,\ell,j,m_j\right\rangle$ kets back to the $|n,\ell,m_\ell,m_s\rangle$ basis using

$$\left|n,\ell,j,m_j\right\rangle=\sum_{m_\ell,m_s}\begin{bmatrix}\ell & s=1/2 & j\\ m_\ell & m_s & m_j\end{bmatrix}|n,\ell,m_\ell,m_s\rangle \tag{21.41}$$

to arrive at

$$\left\langle n,\ell,j,m_j\right|\hat{S}_z\left|n,\ell,j',m_j\right\rangle=\hbar\sum_{m_\ell,m_s}m_s\begin{bmatrix}\ell & \frac{1}{2} & j\\ m_\ell & m_s & m_j\end{bmatrix}\begin{bmatrix}\ell & \frac{1}{2} & j'\\ m_\ell & m_s & m_j\end{bmatrix}. \tag{21.42}$$

In this way, using tabulated values of the Clebsch-Gordan coefficients, you can obtain

$$\begin{aligned}&\left\langle n,\ell,j,m_j\right|\hat{H}\left|n,\ell,j',m_j\right\rangle=E_n^{(0)}\delta_{j,j'}\\&-\frac{\alpha_{FS}^2}{4n^2}\left(\frac{4n}{\ell+1/2}-3\right)\left|E_n^{(0)}\right|\delta_{j,j'}\\&+\frac{\alpha_{FS}^2}{2n}\left(\frac{\delta_{j,\ell+1/2}}{(\ell+1/2)(\ell+1)}-\frac{\delta_{j,\ell-1/2}}{\ell(\ell+1/2)}\right)\left|E_n^{(0)}\right|\delta_{j,j'}\\&+\beta_0Bm_j\left[\left(1+\frac{1}{2\ell+1}\right)\delta_{j,\ell+1/2}+\left(1-\frac{1}{2\ell+1}\right)\delta_{j,\ell-1/2}\right]\delta_{j,j'}\\&-\beta_0B\frac{\sqrt{(\ell+1/2)^2-m_j^2}}{2\ell+1}\left(\delta_{j,\ell+1/2}\delta_{j',\ell-1/2}+\delta_{j,\ell-1/2}\delta_{j',\ell+1/2}\right),\end{aligned} \tag{21.43}$$

or

$$\begin{aligned}&\left\langle n,\ell,j,m_j\right|\hat{H}\left|n,\ell,j',m_j\right\rangle=E_n^{(0)}\delta_{j,j'}\\&-\frac{\alpha_{FS}^2}{n^2}\left(\frac{n}{j+1/2}-\frac{3}{4}\right)\left|E_n^{(0)}\right|\delta_{j,j'}\\&+\beta_0Bm_j\left[\left(1+\frac{1}{2\ell+1}\right)\delta_{j,\ell+1/2}+\left(1-\frac{1}{2\ell+1}\right)\delta_{j,\ell-1/2}\right]\delta_{j,j'}\\&-\beta_0B\frac{\sqrt{(\ell+1/2)^2-m_j^2}}{2\ell+1}\left(\delta_{j,\ell+1/2}\delta_{j',\ell-1/2}+\delta_{j,\ell-1/2}\delta_{j',\ell+1/2}\right).\end{aligned} \tag{21.44}$$

On the other hand, in the $|n,\ell,m_\ell,m_s\rangle$ basis it is simple to evaluate matrix elements of the magnetic field interaction, but the $\mathbf{S}\cdot\mathbf{L}$ factor in the spin–orbit interaction has to be written as $(L_+S_-+L_-S_+)/2+L_zS_z$ to evaluate its matrix elements. In this manner you can find

$$\begin{aligned}
\left\langle n,\ell,m_\ell,m_s\right|\hat{H}\left|n,\ell,m_\ell',m_s'\right\rangle &= E_n^{(0)}\delta_{m_\ell,m_\ell'}\delta_{m_s,m_s'} \\
&-\frac{\alpha_{FS}^2}{n^2}\left(\frac{n}{\ell+1/2}-\frac{3}{4}\right)\left|E_n^{(0)}\right|\delta_{m_\ell,m_\ell'}\delta_{m_s,m_s'} \\
&+\frac{\alpha_{FS}^2\left|E_n^{(0)}\right|(1-\delta_{\ell,0})}{n\ell\left(\ell+1/2\right)\left(\ell+1\right)}\left\{m_\ell m_s\delta_{m_\ell,m_\ell'}\delta_{m_s,m_s'}\right. \\
&+\frac{1}{2}\sqrt{\left(\ell-m_\ell'\right)\left(\ell+m_\ell'+1\right)}\delta_{m_\ell,m_\ell'+1}\delta_{m_s,-1/2}\delta_{m_s',1/2} \\
&\left.+\frac{1}{2}\sqrt{\left(\ell+m_\ell'\right)\left(\ell-m_\ell'+1\right)}\delta_{m_\ell,m_\ell'-1}\delta_{m_s,1/2}\delta_{m_s',-1/2}\right\} \\
&+\frac{\alpha_{FS}^2\left|E_n^{(0)}\right|\delta_{\ell,0}\delta_{m_s,m_s'}}{n}+\beta_0 B\left(m_\ell+2m_s\right)\delta_{m_\ell,m_\ell'}\delta_{m_s,m_s'}. \qquad (21.45)
\end{aligned}$$

To obtain the exact (exact only in the sense that I neglect coupling between different electronic state manifolds) eigenkets and eigenenergies, I must diagonalize these matrices for a given value of n and ℓ. Before doing so, let me look at the weak and strong field limits.

Consider the $n = 2, \ell = 1$ manifold which consists of six degenerate levels in the absence of any magnetic fields and any relativistic corrections. The fine structure splitting is about 11 GHz and, since $\beta_0/h = 14.0$ GHz/T, the magnetic and fine structure interactions are comparable for field strengths of 1 T or above. In weak fields of much less than 1 T, the $\left|n,\ell,j,m_j\right\rangle$ are *approximate* eigenkets. That is, to lowest order I can neglect the magnetic field interaction entirely. The corrections arising from the magnetic field interaction can then be calculated using nondegenerate perturbation theory in the $\left|n,\ell,j,m_j\right\rangle$ basis. In this limit, the change in the energy levels produced by the magnetic field is given approximately by the diagonal matrix elements in Eq. (21.44), namely

$$\begin{aligned}
\Delta E_{n=2,\ell=1j,m_j} &= \left\langle 2,1,j,m_j\right|\hat{H}-\hat{H}_0\left|2,1,j,m_j\right\rangle \\
&= -\frac{\alpha_{FS}^2}{4}\left(\frac{2}{j+1/2}-\frac{3}{4}\right)\left|E_2^{(0)}\right| \\
&\quad+\beta_0 B m_j\left[\frac{4}{3}\delta_{j,3/2}+\frac{2}{3}\delta_{j,1/2}\right], \qquad (21.46)
\end{aligned}$$

which implies that

$$\frac{\Delta E_{n=2,\ell=1,3/2,m_j}}{h} = \left[-2.74 + 18.7 m_j B(\mathrm{T})\right]\mathrm{GHz}; \tag{21.47a}$$

$$\frac{\Delta E^{(0)}_{n=2,\ell=1,1/2,m_j}}{h} = \left[-13.7 + 9.33 m_j B(\mathrm{T})\right]\mathrm{GHz}, \tag{21.47b}$$

where $B(\mathrm{T})$ is the magnetic induction in units of Tesla.

On the other hand, in fields much greater than 1 T, the spin–orbit interaction can be neglected to lowest order compared with the magnetic field interaction. In that limit, the $|n, \ell, m_\ell, m_s\rangle$ are approximate eigenkets and the magnetic field coupling strength is sufficiently large to allow me to use nondegenerate perturbation theory in this basis to approximate the changes in the energy levels produced by the spin–orbit interaction. These changes are given approximately by the diagonal matrix elements in Eq. (21.45), namely

$$\begin{aligned}\Delta E_{n=2,\ell=1,m_\ell,m_s} &= \langle 2,1,m_\ell,m_s|\,\hat{H}-\hat{H}_0\,|2,1,m_\ell,m_s\rangle \\ &= -\alpha_{FS}^2\frac{7}{48}\left|E_2^{(0)}\right| + \beta_0 B\,(m_\ell+2m_s) + \frac{\alpha_{FS}^2\left|E_2^{(0)}\right|}{6}m_\ell m_s,\end{aligned} \tag{21.48}$$

which implies that

$$\frac{\Delta E_{n=2,\ell=1,m_\ell,m_s}}{h} = \left[-6.38 + 14.0\,(m_\ell+2m_s)\,B(\mathrm{T}) + 7.30 m_\ell m_s\right]\mathrm{GHz}. \tag{21.49}$$

Note that the energy of the $m_\ell = 1, m_s = 1/2$ level in Eq. (21.49) agrees with that of the $j = 3/2, m_j = 3/2$ level in Eq. (21.47a), as does the energy of the $m_\ell = -1, m_s = -1/2$ level in Eq. (21.49) with that of the $j = 3/2, m_j = -3/2$ level in Eq. (21.47a). These pairs of states are identical in both bases.

For arbitrary field strengths I can use either basis. I will use $|n = 2, \ell = 1, m_\ell, m_s\rangle$ basis kets, for which the perturbation Hamiltonian in frequency units, obtained using Eqs. (21.45), is

$$\frac{\Delta \underline{\mathrm{H}}}{h} = \begin{pmatrix} -2.73+28B & 0 & 0 & 0 & 0 & 0 \\ 0 & -10.0 & 5.16 & 0 & 0 & 0 \\ 0 & 5.16 & -6.38+14B & 0 & 0 & 0 \\ 0 & 0 & 0 & -6.38-14B & 5.16 & 0 \\ 0 & 0 & 0 & 5.16 & -10.0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -2.73-28B \end{pmatrix}\mathrm{GHz} \tag{21.50}$$

where the order for $|m_\ell, m_s\rangle$ is

$$\left|1,\frac{1}{2}\right\rangle, \left|1,-\frac{1}{2}\right\rangle, \left|0,\frac{1}{2}\right\rangle, \left|0,-\frac{1}{2}\right\rangle, \left|-1,\frac{1}{2}\right\rangle, \left|-1,-\frac{1}{2}\right\rangle. \tag{21.51}$$

The eigenenergies and eigenkets are obtained easily by diagonalizing the 2 × 2 sub-matrices of the Hamiltonian. The eigenkets $\left|E, \ell = 1, m_j\right\rangle$ are of the form

$$|E_1, 1, 3/2\rangle = |2, 1, 1, 1/2\rangle\,; \tag{21.52a}$$

$$|E_2, 1, 1/2\rangle = \alpha\,|2, 1, 1, -1/2\rangle + \beta\,|2, 1, 0, 1/2\rangle\,; \tag{21.52b}$$

$$|E_3, 1, 1/2\rangle = \gamma\,|2, 1, 1, -1/2\rangle + \delta\,|2, 1, 0, 1/2\rangle\,; \tag{21.52c}$$

$$|E_4, 1, -1/2\rangle = \alpha'\,|2, 1, 0, -1/2\rangle + \beta'\,|2, 1, -1, 1/2\rangle\,; \tag{21.52d}$$

$$|E_5, 1, -1/2\rangle = \gamma'\,|2, 1, 0, -1/2\rangle + \delta'\,|2, 1, -1, 1/2\rangle\,; \tag{21.52e}$$

$$|E_6, 1, -3/2\rangle = |2, 1, -1, -1/2\rangle\,, \tag{21.52f}$$

where the coefficients $\alpha, \beta, \gamma, \delta, \alpha', \beta', \gamma', \delta'$ emerge in the diagonalization procedure, but are not written explicitly. The corresponding eigenfrequencies in GHZ are

$$\Delta f_1 = -2.74 + 28B; \tag{21.53a}$$

$$\Delta f_2 = -8.21 + 7B + 7\sqrt{0.611 + 0.521B + B^2}; \tag{21.53b}$$

$$\Delta f_3 = -8.21 + 7B - 7\sqrt{0.611 + 0.521B + B^2}; \tag{21.53c}$$

$$\Delta f_4 = -8.21 - 7B + 7\sqrt{0.611 - 0.521B + B^2}; \tag{21.53d}$$

$$\Delta f_5 = -8.21 - 7B - 7\sqrt{0.611 - 0.521B + B^2}; \tag{21.53e}$$

$$\Delta f_6 = -2.74 - 28B, \tag{21.53f}$$

where B is in Tesla. The eigenvalues (change in frequency, Δf) in GHz are plotted in Fig. 21.3 as a function of magnetic field strength in Tesla (T).

For weak fields ($B \ll 1$ T), the frequencies are given by Eq. (21.47), and for strong fields ($B \approx 1$ T), the frequencies begin to approach those given by Eq. (21.49). Note that in very strong fields the states having $m_\ell = 1, m_s = -1/2$ and $m_\ell = -1, m_s = 1/2$ approach degeneracy, a result predicted in Eq. (21.49). The strong field region is referred to as the *Paschen-Back* region.

21.1.10 Addition of an Electric Field

If, instead of a magnetic field, there is a constant electric field having amplitude $\mathcal{E}_0$ along the z axis, then an additional term,

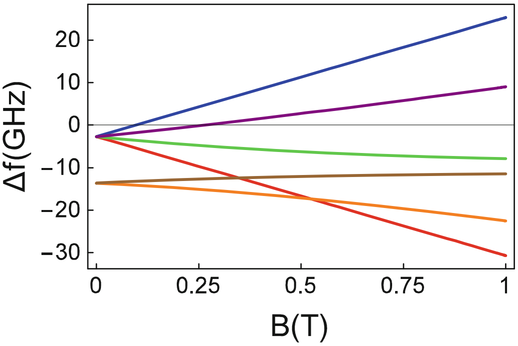

Fig. 21.3 Changes in the eigenfrequencies of the $n = 2$, $\ell = 1$ states of hydrogen produced by a constant external magnetic field

$$\hat{H}'_E = e\mathcal{E}_0\hat{z}, \tag{21.54}$$

must be added to the Hamiltonian.[2] The splitting of atomic energy levels by an electric field is commonly referred to as the Stark effect (Johannes Stark discovered this effect in 1913). I have already discussed the linear Stark effect in hydrogen in the context of degenerate perturbation theory, but relativistic corrections and spin were neglected in that discussion. In the presence of a constant external electric field, L^2, $\mathbf{L}$, and J^2 are no longer constants of the motion for the total Hamiltonian. The only constants of the motion are E, S^2, and J_z. For example, in the $n = 2$ manifold there are eight states that can be characterized by their energy and m_j values. The states having $m_j = 3/2$ $[m_\ell = 1, m_s = 1/2]$ and $m_j = -3/2$ $[m_\ell = -1, m_s = -1/2]$ are not coupled to any other states by the field and remain a degenerate doublet. The other states break up into two *triplets* of states coupled by both the spin–orbit and electric field interactions. It turns out that the energies of the levels do not depend on the sign of m_j.

In the $|n, \ell, m_\ell, m_s\rangle$ basis it is simple to evaluate matrix elements of the electric field interaction since

$$\langle n, \ell, m_\ell, m_s| \hat{z} \left|n', \ell', m'_\ell, m'_s\right\rangle = \frac{\delta_{m_\ell, m'_\ell}\delta_{m_s, m'_s}}{\sqrt{2\ell + 1}} \begin{bmatrix} \ell' & 1 & \ell \\ m_\ell & 0 & m_\ell \end{bmatrix} \langle n, \ell \| z \left\| n', \ell' \right\rangle . \tag{21.55}$$

The Clebsch-Gordan coefficients restrict $\Delta\ell = \ell - \ell'$ to values $\pm 1, 0$, but $\Delta\ell = 0$ is ruled out owing to parity considerations; in other words, the reduced matrix elements vanish if $\Delta\ell = 0$. A general formula for the reduced matrix elements can be given in terms of hypergeometric functions, but I do not give it here. The matrix

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[2] Technically there are no longer any bound states of hydrogen in an external electric field. However, the lifetimes of the low-lying energy states are effectively infinite for static fields and the shifts of these levels can be calculated using perturbation theory.

elements for the entire Hamiltonian in a state of fixed n are

$$\begin{aligned}
&\langle n,\ell,m_\ell,m_s|\,\hat{H}\,\left|n,\ell',m'_\ell,m'_s\right\rangle = E_n^{(0)}\delta_{m_\ell,m'_\ell}\delta_{m_s,m'_s}\delta_{\ell,\ell'}\\
&-\frac{\alpha_{FS}^2}{4n^2}\left(\frac{4n}{\ell+1/2}-3\right)\left|E_n^{(0)}\right|\delta_{m_\ell,m'_\ell}\delta_{m_s,m'_s}\delta_{\ell,\ell'}\\
&+\frac{\alpha_{FS}^2\left|E_n^{(0)}\right|(1-\delta_{\ell,0})}{n\ell\,(\ell+1/2)\,(\ell+1)}\left\{m_\ell m_s\delta_{m_\ell,m'_\ell}\delta_{m_s,m'_s}\right.\\
&+\frac{1}{2}\sqrt{\left(\ell-m'_\ell\right)\left(\ell+m'_\ell+1\right)}\delta_{m_\ell,m'_\ell+1}\delta_{m_s,-1/2}\delta_{m'_s,1/2}\\
&\left.+\frac{1}{2}\sqrt{\left(\ell+m'_\ell\right)\left(\ell-m'_\ell+1\right)}\delta_{m_\ell,m'_\ell-1}\delta_{m_s,1/2}\delta_{m'_s,-1/2}\right\}\delta_{\ell,\ell'}\\
&+\frac{\alpha_{FS}^2\left|E_n^{(0)}\right|\delta_{\ell,0}\delta_{m_s,m'_s}}{n}\\
&+e\mathcal{E}_0\,\langle n,\ell,m_\ell|\,\hat{z}\,\left|n,\ell',m_\ell\right\rangle\delta_{m_\ell,m'_\ell}\delta_{m_s,m'_s}. \qquad (21.56)
\end{aligned}$$

For the $n=2$ manifold, $\langle 2,1,0,|\,\hat{z}\,|2,0,0\rangle = -3a_0$, and, with the states denoted by $|n,\ell;m_\ell,m_s\rangle$, there are eight unperturbed eigenkets that can be written as

$$|1\rangle = \left|2,0;0,\frac{1}{2}\right\rangle;\quad m_j = 1/2, \qquad (21.57a)$$

$$|2\rangle = \left|2,0;0,-\frac{1}{2}\right\rangle;\quad m_j = -1/2, \qquad (21.57b)$$

$$|3\rangle = \left|2,1;1,\frac{1}{2}\right\rangle;\quad m_j = 3/2, \qquad (21.57c)$$

$$|4\rangle = \left|2,1;1,-\frac{1}{2}\right\rangle;\quad m_j = 1/2, \qquad (21.57d)$$

$$|5\rangle = \left|2,1;0,\frac{1}{2}\right\rangle;\quad m_j = 1/2, \qquad (21.57e)$$

$$|6\rangle = \left|2,1;0,-\frac{1}{2}\right\rangle;\quad m_j = -1/2, \qquad (21.57f)$$

$$|7\rangle = \left|2,1;-1,\frac{1}{2}\right\rangle;\quad m_j = -1/2, \qquad (21.57g)$$

$$|8\rangle = \left|2,1;-1,-\frac{1}{2}\right\rangle;\quad m_j = -3/2. \qquad (21.57h)$$

If I set

$$A = -3.84 \times 10^{-5} \mathcal{E}_0(\text{V/m}) \tag{21.58}$$

and use Eq. (21.56), I can write the perturbation Hamiltonian sub-matrix for the $n = 2$ manifold as

$$\frac{\Delta \underset{=}{\mathrm{H}}}{h} = \begin{pmatrix} -13.7 & 0 & 0 & 0 & A & 0 & 0 & 0 \\ 0 & -13.7 & 0 & 0 & 0 & A & 0 & 0 \\ 0 & 0 & -2.74 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -10.0 & 5.16 & 0 & 0 & 0 \\ A & 0 & 0 & 5.16 & -6.38 & 0 & 0 & 0 \\ 0 & A & 0 & 0 & 0 & -6.38 & 5.16 & 0 \\ 0 & 0 & 0 & 0 & 0 & 5.16 & -10.0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -2.74 \end{pmatrix} \text{GHz} \tag{21.59}$$

States $|3\rangle$ and $|8\rangle$ having $m_j = \pm 3/2$ are degenerate and are uncoupled to other states by the field. States $|1\rangle$,$|4\rangle$,$|5\rangle$ having $m_j = 1/2$ are coupled to each other as are states $|2\rangle$,$|6\rangle$,$|7\rangle$ having $m_j = -1/2$. However, *the eigenvalues do not depend on the sign of* m_j. Thus, these six states break up into three degenerate pairs of levels, with one state in each doublet having $m_j = 1/2$ and the other $m_j = -1/2$. These six states contain an admixture of both $\ell = 1$ and $\ell = 0$ states.

The eigenfrequencies (change in frequency) in GHz, obtained by numerically diagonalizing Eq. (21.59), are plotted in Fig. 21.4 as a function of electric field strength in units of 10^5 V/m. Note that there are four distinct energies. The horizontal straight line in the figure corresponds to the $m_j = \pm 3/2$ states, while each other line corresponds to a doublet having $m_j = \pm 1/2$. Explicit expressions for eigenenergies and eigenkets are not given, but can be obtained easily by numerically diagonalizing the Hamiltonian. The energy degeneracy is not totally lifted by the field, which implies there is still some remaining symmetry in the problem. The Hamiltonian for a hydrogen atom in an external electric field remains invariant under time reversal. Since the time-reversal operator effectively reverses the sign of m_j in the eigenkets, the energy must be independent of the sign of m_j.[3] In the case of hydrogen in an external magnetic field, time reversal symmetry is broken since the magnetic moment operator changes sign under time reversal; as a consequence, the magnetic field can totally lift the degeneracy of the different magnetic sublevels.

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[3] In other words, the time-reversal operator $\hat{T}$ (see Problem 19.12) acting on a ket $\left|Em_j\right\rangle$ produces $\left|E,-m_j\right\rangle$, but $\hat{T}\left|Em_j\right\rangle$ must be an eigenket of the Hamiltonian having the same energy as that associated with $\left|Em_j\right\rangle$ if the Hamiltonian is invariant under time-reversal, implying that there is a two-fold degeneracy for states having $m_j \neq 0$.

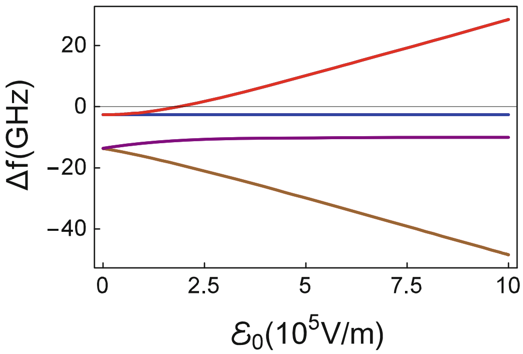

Fig. 21.4 Frequency shift Δf in GHz of the $n = 2$, $\ell = 1$ states of hydrogen as a function of electric field amplitude in units of 10^5 V/m

21.2 Multi-Electron Atoms in a Magnetic Field: Vector Model

In multi-electron atoms the coupling of the orbital and spin angular momentum of all the electrons constitutes a very difficult problem. For atoms having atomic number $Z \lesssim 30$, however, it is often a good approximation to couple the spin angular momentum of the valence band electrons into a total spin angular momentum **S** and the orbital angular momentum of the valence band electrons into a total orbital angular momentum **L**. The total angular momentum of all the electrons is then $\mathbf{J} = \mathbf{L} + \mathbf{S}$ (*Russel-Saunders* or L-S coupling scheme).[4] If a multi-electron atom whose structure can be approximated by an L-S coupling scheme is placed in a magnetic field, it is relatively easy to calculate the level splitting *approximately* in the limits that the spin-orbit coupling is much less than or much greater than the Zeeman splitting. Moreover, there is a *classical vector model* that can be used in each of these cases. In all cases, I take the magnetic field along the z-axis. In an external magnetic field, L, S, and $m_J = m_L + m_s$ remain good quantum numbers.

21.2.1 *Zeeman Splitting Much Greater Than Spin-Orbit Splitting*

As in the case of hydrogen, I can simply ignore the spin-orbit coupling to lowest order. In this limit the magnetic field splitting in a state of given S and L is

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[4] In the opposite limit of high Z atoms, a j–j coupling scheme can be used in which the total angular momentum of the atom is the sum of the total angular momenta of the individual electrons.

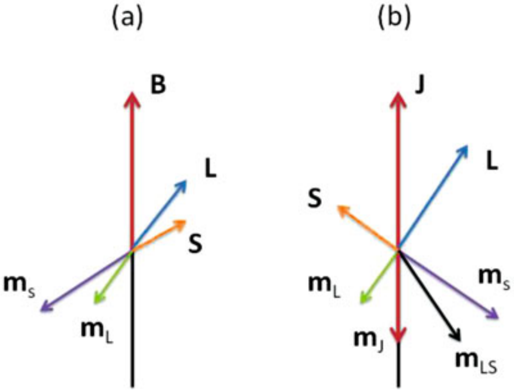

Fig. 21.5 Vector coupling schemes for calculating the Zeeman splitting. (**a**) Strong field limit (**b**) Weak field limit

$$\Delta E_{LS} \approx \beta_0 B \left(m_L + 2m_S\right). \tag{21.60}$$

In a vector model [see Fig. 21.5 (a)], the magnetic field is sufficiently strong to cause the total spin and total orbital angular momentum to precess *separately* around the field vector. All components of the spin and orbital magnetic moments average to zero owing to the precession, *except* their components along the z-axis. These projections account for ΔE_{LS}.

21.2.2 Spin-Orbit Splitting Much Greater Than Zeeman Splitting

In analogy with hydrogen, J is now an approximate good quantum number and the magnetic field splitting in a state of given J is

$$\begin{aligned}\Delta E_{Jm_J} &= \frac{\beta_0 B}{\hbar}\left\langle L,S,J,m_J\right|\hat{J}_z + \hat{S}_z\left|L,S,J,m_J\right\rangle \\ &= \beta_0 B m_J + \frac{\beta_0 B}{\hbar}\left\langle L,S,J,m_J\right|\hat{S}_z\left|L,S,J,m_J\right\rangle. \end{aligned}\tag{21.61}$$

To calculate $\left\langle L,S,J,m_J\right|\hat{S}_z\left|L,S,J,m_J\right\rangle$, I can use the Wigner-Eckart theorem. First, I prove the following lemma: For any vector operator $\hat{A}$,

$$\left\langle \alpha',J,m_J'\right|\hat{A}_1^q\left|\alpha,J,m_J\right\rangle = \frac{\left\langle \alpha',J,m_J\right|\hat{\mathbf{J}}\cdot\hat{\mathbf{A}}\left|\alpha,J,m_J\right\rangle}{\hbar^2 J\left(J+1\right)}\left\langle \alpha,J,m_J'\right|\hat{J}_1^q\left|\alpha,J,m_J\right\rangle, \tag{21.62}$$

where the $\hat{A}_1^q$ are the components of an irreducible tensor operator of rank 1 given by Eq. (20.41) and α, α' represent additional quantum numbers. The proof is relatively simple. It follows from the Wigner-Eckart theorem that

$$\begin{aligned}\left\langle \alpha', J, m_J' \right| \hat{A}_1^q \left| \alpha, J, m_J \right\rangle &= \frac{1}{\sqrt{2J+1}} \begin{bmatrix} J & 1 & J \\ m_J & q & m_J' \end{bmatrix} \left\langle \alpha', J \right\| A^{(1)} \left\| \alpha, J \right\rangle \\ &= \frac{\left\langle \alpha', J \right\| A^{(1)} \left\| \alpha, J \right\rangle}{\left\langle \alpha, J \right\| J^{(1)} \left\| \alpha, J \right\rangle} \left\langle \alpha, J, m_J' \right| J_1^q \left| \alpha, J, m_J \right\rangle . \quad (21.63)\end{aligned}$$

Since $\hat{\mathbf{J}} \cdot \hat{\mathbf{A}}$ is a scalar or irreducible tensor of rank zero, it also follows from the Wigner-Eckart theorem that

$$\left\langle \alpha', J, m_J \right| \hat{\mathbf{J}} \cdot \hat{\mathbf{A}} \left| \alpha, J, m_J \right\rangle = \frac{1}{\sqrt{2J+1}} \left\langle \alpha', J \right\| \mathbf{J} \cdot \mathbf{A} \left\| \alpha, J \right\rangle . \quad (21.64)$$

In other words, these matrix elements are independent of m_J. Moreover, if you expand

$$\hat{\mathbf{J}} \cdot \hat{\mathbf{A}} = -\hat{J}_1^1 \hat{A}_1^{-1} - \hat{J}_1^{-1} \hat{A}_1^1 + \hat{J}_1^0 \hat{A}_1^0 = -\frac{\left(\hat{J}_+ \hat{A}_1^{-1} + \hat{J}_- \hat{A}_1^1 \right)}{\sqrt{2}} + \hat{J}_1^0 \hat{A}_1^0, \quad (21.65)$$

use Eqs. (22.123) and the Wigner-Eckart theorem, you will find that the left-hand side of Eq. (21.64) is proportional $\langle \alpha', J \| \mathbf{J} \cdot \mathbf{A} \| \alpha, J \rangle$, with a proportionality constant that appears to depend on J and m_J, but *not* on $\hat{\mathbf{A}}$, α, and α'. However, I know from Eq. (21.64) that the proportionality constant is independent of m_J, so

$$\left\langle \alpha', J, m_J \right| \hat{\mathbf{J}} \cdot \hat{\mathbf{A}} \left| \alpha, J, m_J \right\rangle = C(J) \left\langle \alpha', J \right\| A^{(1)} \left\| \alpha, J \right\rangle , \quad (21.66)$$

where the constant $C(J)$ is independent of α, α', and the properties of the operator $\hat{A}$. As a consequence,

$$\begin{aligned}\frac{\left\langle \alpha', J \right\| A^{(1)} \left\| \alpha, J \right\rangle}{\left\langle \alpha, J \right\| J^{(1)} \left\| \alpha, J \right\rangle} &= \frac{\left\langle \alpha', J, m_J \right| \hat{\mathbf{J}} \cdot \hat{\mathbf{A}} \left| \alpha, J, m_J \right\rangle}{\left\langle \alpha, J, m_J \right| \hat{\mathbf{J}} \cdot \hat{\mathbf{J}} \left| \alpha, J, m_J \right\rangle} \\ &= \frac{\left\langle \alpha', J, m_J \right| \hat{\mathbf{J}} \cdot \hat{\mathbf{A}} \left| \alpha, J, m_J \right\rangle}{\hbar^2 J (J+1)} . \quad (21.67)\end{aligned}$$

By combining Eqs. (21.67), and (21.63), I arrive at Eq. (21.62).

Using Eq. (21.62), I find that the diagonal matrix elements of $\hat{S}_z$ are

$$\begin{aligned}\langle L,S,J,m_J|\,\hat{S}_z\,|L,S,J,m_J\rangle &= \frac{\langle L,S,J,m_J|\,\hat{\mathbf{J}}\cdot\hat{\mathbf{S}}\,|L,S,J,m_J\rangle}{\hbar^2 J\,(J+1)}\,\langle J,m_J|\,\hat{J}_z\,|J,m_J\rangle \\ &= \hbar m_J \frac{\langle L,S,J,m_J|\,\hat{J}^2+\hat{S}^2-\hat{L}^2\,|L,S,J,m_J\rangle}{2\hbar^2 J\,(J+1)} \\ &= \hbar m_J \frac{J\,(J+1)+S\,(S+1)-L\,(L+1)}{2J\,(J+1)},\end{aligned} \tag{21.68}$$

having used the relationship

$$\mathbf{J}\cdot\mathbf{S} = (\mathbf{L}+\mathbf{S})\cdot\mathbf{S} = \mathbf{L}\cdot\mathbf{S}+\mathbf{S}^2 = \frac{J^2-S^2-L^2}{2}+S^2. \tag{21.69}$$

When this result is substituted into Eq. (21.61), I obtain the Zeeman splitting

$$\Delta E_{Jm_J} = \beta_0 B g_J m_J, \tag{21.70}$$

where

$$g_J = 1+\frac{J\,(J+1)+S\,(S+1)-L\,(L+1)}{2J\,(J+1)} \tag{21.71}$$

is referred to as the Landé *g* factor (after Alfred Landé).

In the vector model, the spin-orbit coupling couples **L** and **S** into **J**. Both **L** and **S** precess rapidly about **J**, as do the magnetic moments. Only the projection of the total magnetic moment $\mathbf{m}_{LS}$ onto **J** does not average to zero. In other words, in terms of Fig. 21.5 (b),

$$\begin{aligned}\mathbf{m}_J &\approx -\frac{e}{2m_e}\frac{(\mathbf{L}+2\mathbf{S})\cdot\mathbf{J}}{J}\frac{\mathbf{J}}{J} \\ &= -\frac{e}{2m_e}\left[L\cos\left(\mathbf{L}\cdot\mathbf{J}\right)+2S\cos\left(\mathbf{S}\cdot\mathbf{J}\right)\right]\frac{\mathbf{J}}{J} \\ &= -\frac{e\mathbf{J}}{2m_e}\left[\frac{-S^2+L^2+J^2}{2J^2}+\frac{-L^2+S^2+J^2}{J^2}\right] \\ &= -\frac{e\mathbf{J}}{2m_e}\left[1+\frac{J^2+S^2-L^2}{2J^2}\right] \\ &\Rightarrow -\frac{e\mathbf{J}}{2m_e}\left[1+\frac{J\,(J+1)+S\,(S+1)-L\,(L+1)}{2J\,(J+1)}\right],\end{aligned} \tag{21.72}$$

where I replaced J^2, S^2, L^2 by their quantum equivalents. The interaction energy $\Delta E = -\mathbf{m}_J \cdot \mathbf{B} = -(\mathbf{m}_J)_z B$ agrees with Eq. (21.70) if J_z in Eq. (21.72) is replaced by $\hbar m_J$.

21.3 Summary

I have presented a rather detailed account of the relativistic corrections to the energy levels of hydrogen. In addition, the modifications of the energy levels produced by external magnetic and electric fields were calculated. Special emphasis was placed on the role played by approximate constants of the motion. The vector model of coupling of angular momentum was introduced and used to calculate the Zeeman splitting of atomic energy levels characterized by some total angular momentum quantum number. A calculation of the hyperfine splitting in hydrogen is given in Appendix 2, where the Zeeman splitting, including the hyperfine interaction, is also discussed.

21.4 Appendix A: Radial Integrals for Hydrogen

In this Appendix, I calculate matrix elements of the form

$$\left\langle r^\beta \right\rangle = \int d\mathbf{r}\psi^*_{nlm}(\mathbf{r}) r^\beta \psi_{nlm}(\mathbf{r}) = \int_0^\infty dr \left[u_{nl}(r)\right]^2 r^\beta, \tag{21.73}$$

where the $\psi_{nlm}(\mathbf{r})$ are hydrogenic wave functions and the $u_{nl}(r) = rR_{n\ell}(r)$ are radial wave functions. These matrix elements can be calculated using the generating function for the associated Laguerre polynomials. Each integral is simply the integral of a power with an exponential, so the integrals are fairly simple to carry out. However there is a simpler method for obtaining the results that involves a few "tricks." To start I derive a recursion relation for $\left\langle r^\beta \right\rangle$.

The equation for the radial wave function $u_{n\ell}$ for hydrogen is

$$\frac{d^2 u_{n\ell}}{dr^2} + \left(-\frac{1}{n^2 a_0^2} + \frac{2}{a_0 r} - \frac{\ell(\ell+1)}{r^2} \right) u_{n\ell} = 0, \tag{21.74}$$

where $a_0 = 4\pi\epsilon_0 \hbar^2 / m_e e^2$ is the Bohr radius. I start from

$$\begin{aligned} \int_0^\infty dr \frac{d^2 u_{n\ell}(r)}{dr^2} r^\beta u_{nl}(r) &= \int_0^\infty dr \left(\frac{1}{n^2 a_0^2} - \frac{2}{a_0 r} + \frac{\ell(\ell+1)}{r^2} \right) r^\beta \left[u_{nl}(r)\right]^2 \\ &= \frac{1}{n^2 a_0^2} \left\langle r^\beta \right\rangle - \frac{2}{a_0} \left\langle r^{\beta-1} \right\rangle + \ell(\ell+1) \left\langle r^{\beta-2} \right\rangle. \end{aligned} \tag{21.75}$$

As $r \to 0$, $u_{n\ell}(r) d^2 u_{n\ell}(r)/dr^2 \sim r^{2\ell}$ for $\ell \neq 0$ and as $\sim r$ for $\ell = 0$; as a consequence, the integral on the left-hand side of Eq. (21.75) is convergent only if

$$\begin{cases} \beta > -2 & \ell = 0 \\ \beta > -2\ell - 1 & \ell > 0 \end{cases}. \tag{21.76}$$

Integrating the left-hand side of this equation by parts and using the fact that the endpoint contributions vanish if condition (21.76) is satisfied, I find

$$\int_0^\infty dr \frac{d^2 u_{n\ell}(r)}{dr^2} r^\beta u_{nl}(r) = -\int_0^\infty dr \frac{du_{n\ell}(r)}{dr}\left(\beta r^{\beta-1} u_{nl}(r) + r^\beta \frac{du_{n\ell}(r)}{dr}\right). \tag{21.77}$$

Integration by parts can be used on the first term on the right-hand side of this equation to transform it into

$$\begin{aligned} &-\int_0^\infty dr \frac{du_{n\ell}(r)}{dr} \beta r^{\beta-1} u_{nl}(r) \\ &\quad = \int_0^\infty dr u_{n\ell}(r) \left(\beta(\beta-1) r^{\beta-2} u_{nl}(r) + \beta r^{\beta-1} \frac{du_{n\ell}(r)}{dr}\right), \end{aligned} \tag{21.78}$$

which implies that

$$-\int_0^\infty dr \frac{du_{n\ell}(r)}{dr} \beta r^{\beta-1} u_{nl}(r) = \frac{1}{2}\beta(\beta-1)\left\langle r^{\beta-2}\right\rangle. \tag{21.79}$$

I integrate the second term in Eq. (21.77) by parts and use Eq. (21.74) to obtain

$$\begin{aligned} -\int_0^\infty dr\, r^\beta \left[\frac{du_{n\ell}(r)}{dr}\right]^2 &= 2\int_0^\infty dr \frac{r^{\beta+1}}{\beta+1} \frac{du_{n\ell}(r)}{dr} \frac{d^2 u_{n\ell}(r)}{dr^2} \\ &= 2\int_0^\infty dr \frac{r^{\beta+1}}{\beta+1} \frac{du_{n\ell}(r)}{dr} \left(\frac{1}{n^2 a_0^2} - \frac{2}{a_0 r} + \frac{\ell(\ell+1)}{r^2}\right) u_{n\ell}(r). \end{aligned} \tag{21.80}$$

I can now use Eq. (21.79) to rewrite this equation as

$$-\int_0^\infty dr\, r^\beta \left[\frac{du_{n\ell}(r)}{dr}\right]^2 = \frac{1}{\beta+1}\left[\begin{array}{c} -\frac{(\beta+1)\left\langle r^\beta\right\rangle}{n^2 a_0^2} + \frac{2\beta\left\langle r^{\beta-1}\right\rangle}{a_0} \\ -\ell(\ell+1)(\beta-1)\left\langle r^{\beta-2}\right\rangle \end{array}\right]. \tag{21.81}$$

Combining Eqs. (21.75)–(21.81), I arrive at the recursion relation

$$\frac{1}{n^2 a_0^2}\left\langle r^\beta\right\rangle - \frac{(2\beta+1)}{(\beta+1)a_0}\left\langle r^{\beta-1}\right\rangle + \frac{\beta}{4}\frac{\left[(2\ell+1)^2 - \beta^2\right]}{(\beta+1)}\left\langle r^{\beta-2}\right\rangle = 0. \tag{21.82}$$

Equation (21.82) is valid only when conditions (21.76) hold, consistent with the fact that $\left\langle r^{\beta-2}\right\rangle$ is non-divergent only for $\beta > -2\ell - 1$ (a result that is also derived easily using the fact that $u_{n\ell}(r) \sim r^{\ell+1}$ as $r \rightarrow 0$).

Since the wave functions are normalized, it follows immediately that $\left\langle r^0\right\rangle = 1$. By choosing $\beta = 0$ in Eq. (21.82), I then find

$$\left\langle r^{-1}\right\rangle = \frac{1}{n^2 a_0}, \tag{21.83}$$

a result that also follows from the Virial theorem. Using this result and the fact that $\left\langle r^0\right\rangle = 1$, you can take $\beta = 1$ in Eq. (21.82) to obtain

$$\frac{1}{n^2 a_0^2}\langle r\rangle - \frac{3}{2a_0} + \frac{1}{4}\frac{\left[(2\ell+1)^2 - 1\right]}{2}\frac{1}{n^2 a_0} = 0, \tag{21.84}$$

or

$$\langle r\rangle = \frac{a_0}{2}\left[3n^2 - \ell(\ell+1)\right]. \tag{21.85}$$

All higher powers of $\langle r^q\rangle$ can be generated in the same manner by taking $\beta = q$ in Eq. (21.82); for example, with $q = 2$,

$$\begin{aligned}\left\langle r^2\right\rangle &= \frac{5n^2 a_0}{3}\langle r\rangle - \frac{n^2 a_0^2}{2}\frac{\left[(2\ell+1)^2 - 4\right]}{3}\left\langle r^0\right\rangle \\ &= \frac{n^2 a_0^2}{2}\left[5n^2 + 1 - 3\ell(\ell+1)\right].\end{aligned} \tag{21.86}$$

To get values of $\langle r^{-q}\rangle$ for $q \geq 2$, I first set $\beta = -1$ in Eq. (21.82) and find

$$\left\langle r^{-2}\right\rangle = \ell(\ell+1)\, a_0\left\langle r^{-3}\right\rangle. \tag{21.87}$$

By setting $\beta = -q$ in Eq. (21.82) with $q \geq 2$, you can get expressions for $\left\langle r^{-q-2}\right\rangle$ in terms of $\left\langle r^{-q-1}\right\rangle$ and $\langle r^{-q}\rangle$. Thus, to obtain *all* values of $\langle r^{-q}\rangle$ for $q \geq 2$, it is sufficient to calculate since $\left\langle r^{-2}\right\rangle$ and $\left\langle r^{-3}\right\rangle$, since all the others can be expressed in terms of these quantities; moreover I need only calculate $\left\langle r^{-2}\right\rangle$, since $\left\langle r^{-3}\right\rangle$ can then be determined from Eq. (21.87).

The value of $\left\langle r^{-2}\right\rangle$ can be found using a "trick." Suppose the hydrogen atom is subjected to a perturbation $H' = \epsilon/r^2$. The first order energy change produced by this perturbation is

$$\delta E_{n\ell} = \int d\mathbf{r}\psi^*_{nlm}(\mathbf{r})\frac{\epsilon}{r^2}\psi_{nlm}(\mathbf{r}) = \epsilon\left\langle r^{-2}\right\rangle. \tag{21.88}$$

However, the total Hamiltonian is exactly solvable in this case since the $\hbar^2\ell(\ell+1)/2m_er^2$ term in the effective potential is replaced by

$$\frac{\hbar^2}{2m_er^2}\left[\ell(\ell+1)-\frac{2m_e\epsilon}{\hbar^2}\right]\equiv\frac{\hbar^2}{2m_e}\ell'\left(\ell'+1\right)/r^2, \tag{21.89}$$

where

$$\ell'\left(\ell'+1\right)=\ell(\ell+1)-\frac{2m_e\epsilon}{\hbar^2} \tag{21.90}$$

and ℓ' is *not* an integer. To have an acceptable solution of the Schrödinger equation, it is necessary that $q=n-\ell'-1$ be an integer (note that n is no longer an integer, except in the limit that $\epsilon\rightarrow 0$). In that case the energy is

$$E_{n\ell}=-\frac{e^2}{4\pi\epsilon_0}\frac{1}{2a_0n^2}=-\frac{e^2}{4\pi\epsilon_0}\frac{1}{2a_0(q+\ell'+1)^2}. \tag{21.91}$$

Expanding this result to first order in ϵ, I find

$$\begin{aligned}\delta E_{n\ell}&\approx\left.\frac{\partial E_{n\ell}}{\partial\ell'}\right|_{\epsilon=0}\left.\frac{\partial\ell'}{\partial\epsilon}\right|_{\epsilon=0}\epsilon\\&=-\frac{e^2}{4\pi\epsilon_0}\left(\frac{-1}{a_0n^3}\right)\frac{m_e}{\hbar^2(\ell+1/2)}\epsilon.\end{aligned} \tag{21.92}$$

Comparing this result with Eq. (21.88), I can identify

$$\left\langle r^{-2}\right\rangle=\frac{1}{\left(\ell+\frac{1}{2}\right)n^3a_0^2} \tag{21.93}$$

and, using Eq. (21.87), that

$$\left\langle r^{-3}\right\rangle=\frac{1}{\ell\left(\ell+\frac{1}{2}\right)(\ell+1)n^3a_0^3};\quad\ell\neq 0. \tag{21.94}$$

Remember that $\left\langle r^{\beta}\right\rangle$ is defined only if $\beta>-2\ell-3$ or $\ell>-(\beta+3)/2$.

21.5 Appendix B: Hyperfine Interactions

All baryons have half-integral nuclear spin. Both the neutron and proton have nuclear spin $I=1/2$. They also have associated magnetic moments given by

$$\hat{\mathbf{m}}_p = \frac{eg_p\mathbf{I}_p}{2m_p}; \tag{21.95a}$$

$$\hat{\mathbf{m}}_n = \frac{eg_n\mathbf{I}_n}{2m_n}, \tag{21.95b}$$

where m_p is the proton mass, m_n is the neutron mass, and $g_{p,n}$ is a *nuclear g-factor*. For the proton $g_p \approx 5.586$ and for the neutron $g_n \approx -3.826$. Note that the neutron has a magnetic moment even though it is neutral. The reason for this is that the neutron, like the proton, is a composite particle, composed of three quarks bound by gluons. Whereas the magnetic moment of the electron arises naturally from the Dirac equation, there is no analogous equation that gives the nuclear magnetic moments. Theories based on *quantum chromodynamics* attempt to predict the values of nuclear magnetic moments by considering the baryons to be composed of quarks and gluons.

For hydrogen, the nucleus consists of a single proton, whose magnetic moment interacts with the magnetic field produced by the electron. There are two contributions to the magnetic field produced by the electron, one from its orbital motion and one from its intrinsic spin. There is no Thomas precession in calculating the hyperfine interaction as there was for the fine structure calculation since the proton is in an inertial frame whereas the electron was in an accelerating frame. Classically, the electron can be modeled as a point magnetic dipole having mass m_e, magnetic moment $\mathbf{m}_s$, and charge $-e$. If this point dipole is located at position $\mathbf{r}$ and has orbital angular momentum $\mathbf{L}$ about the origin, it produces a field at the origin given by

$$\mathbf{B}(0) = \frac{\mu_0}{4\pi}\left[\frac{8\pi}{3}\mathbf{m}_s\delta(\mathbf{r}) + \frac{3\mathbf{u}_r\left(\mathbf{u}_r\cdot\mathbf{m}_s\right) - \mathbf{m}_s}{r^3} + \frac{2\mathbf{m}_\ell}{r^3}\right], \tag{21.96}$$

where $\mathbf{u}_r$ is a unit vector in the radial direction,

$$\mathbf{m}_\ell = -\frac{e\mathbf{L}}{2m_e} \tag{21.97}$$

is the orbital magnetic moment, and μ_0 is the vacuum permeability. The first two terms in Eq. (21.96) give the field associated with the point magnetic moment of the electron—the delta function term is necessary for the consistency of Maxwell's equations and is related to the fact that the field at the center of a "point" dipole diverges. The third term is the field arising from the orbital motion of the electron.

The proton is modeled classically as a point dipole at the origin having magnetic moment $\mathbf{m}_p$. The interaction energy of the proton's magnetic moment with the magnetic field of the electron is

$$H = -\mathbf{m}_p\cdot\mathbf{B}(0). \tag{21.98}$$

To go over to a quantum description, I replace $\mathbf{m}_p$ by Eq. (21.95a), $\mathbf{m}_s$ by

$$\hat{\mathbf{m}}_s = -\frac{e\mathbf{S}}{m_e}, \tag{21.99}$$

and all angular momenta by operators (although I leave off the carets) to arrive at the *hyperfine interaction* contribution to the Hamiltonian,

$$\begin{aligned}\hat{H}_{hf} &= -\hat{\mathbf{m}}_p \cdot \mathbf{B}(0)\\ &= \frac{\mu_0 e^2 g_p}{8\pi m_e m_p}\left[\frac{8\pi\delta(\mathbf{r})}{3}\mathbf{S}\cdot\mathbf{I} + \frac{3\left(\mathbf{u}_r\cdot\mathbf{S}\right)\ \left(\mathbf{u}_r\cdot\mathbf{I}\right) - \mathbf{S}\cdot\mathbf{I}}{r^3} + \frac{\mathbf{L}\cdot\mathbf{I}}{r^3}\right].\end{aligned} \tag{21.100}$$

If I define the total angular momentum as

$$\mathbf{F} = \mathbf{J} + \mathbf{I} = \mathbf{L} + \mathbf{S} + \mathbf{I}, \tag{21.101}$$

then it is convenient to use basis kets labeled by $\left|n\ell j f m_f\right\rangle$ where the electron spin quantum number $S = 1/2$ and the proton spin quantum number $I = 1/2$ have been suppressed in the label. In perturbation theory, the change in the energy levels produced by the hyperfine interaction is given by

$$\Delta E_{n\ell jf} = \left\langle n\ell j f m_f\right| \hat{H}_{hf} \left|n\ell j f m_f\right\rangle. \tag{21.102}$$

The ket $\left|n\ell j f m_f\right\rangle$ is the eigenket in the absence of the hyperfine interaction. The constants of the motion are $L^2, S^2, J^2, I^2, F^2, F_z$.

21.5.1 Hyperfine Splitting

I first derive the contribution to $\Delta E_{n\ell jf}$ from the first term in Eq. (21.100), the so-called *contact interaction*. I will then outline a method for calculating the other terms. Only $\ell = 0$ states contribute to the contact interaction since they are the only states for which the eigenfunctions do not vanish at the origin. If $\ell = 0$, then $j = 1/2$, and f can be equal to 0 or 1 Thus, the contact term gives rise to a hyperfine splitting of S states. To evaluate this term I need to calculate

$$\begin{aligned}\Delta E_{nf}^{\text{contact}} &= \left\langle n, \ell = 0, j = 1/2, f, m_f\right| \hat{H}_{hf} \left|n, \ell = 0, j = 1/2, f, m_f\right\rangle\\ &= \frac{\mu_0 e^2 g_p}{3 m_e m_p}\left\langle n, \ell = 0, j = 1/2, f, m_f\right| \delta(\mathbf{r})\mathbf{S}\cdot\mathbf{I} \left|n, \ell = 0, j = 1/2, f, m_f\right\rangle.\end{aligned} \tag{21.103}$$

However, since $\ell = 0$, it follows that $\mathbf{F} = \mathbf{S} + \mathbf{I}$, implying that

$$\begin{aligned}\mathbf{S}\cdot\mathbf{I} &= \frac{F^2 - I^2 - S^2}{2};\\ \left\langle n,f,m_f\right|\delta(\mathbf{r})\mathbf{S}\cdot\mathbf{I}\left|n,f,m_f\right\rangle &= \hbar^2\frac{f(f+1)-3/2}{2}\\ &\quad\times\left\langle n,f,m_f\right|\delta(\mathbf{r})\left|n,f,m_f\right\rangle. \end{aligned} \tag{21.104}$$

The hyperfine energy shifts of the $f = 0, 1$ levels are given by

$$\Delta E^{\text{contact}}_{f=1} = \beta\hbar^2\,\frac{f(f+1)-3/2}{2} = \frac{\beta\hbar^2}{4}; \tag{21.105a}$$

$$\Delta E^{\text{contact}}_{f=0} = -\frac{3\beta\hbar^2}{4}, \tag{21.105b}$$

where

$$\beta = \frac{e^2\mu_0 g_p}{3m_p m_e}\left\langle n,f,m_f\right|\delta(\mathbf{r})\left|n,f,m_f\right\rangle. \tag{21.106}$$

It is straightforward to show that

$$\left\langle n,\ell,j,f,m_f\right|g(\mathbf{r})\left|n,\ell,j,f,m_f\right\rangle = \left\langle n,\ell,m_\ell\right|g(\mathbf{r})\left|n,\ell,m_\ell\right\rangle \tag{21.107}$$

for any function $g(\mathbf{r})$ that does not depend on electron or nuclear spin. Therefore,

$$\begin{aligned}\beta &= \frac{e^2\mu_0 g_p}{3m_p m_e}\left\langle n00\right|\delta(\mathbf{r})\left|n00\right\rangle\\ &= \frac{e^2\mu_0 g_p}{3m_p m_e}\int d\mathbf{r}\,\left|\psi_{n00}(r)\right|^2\delta(\mathbf{r})\\ &= \frac{e^2\mu_0 g_p}{3m_p m_e}\int d\mathbf{r}\,\left|R_{n0}(r)\right|^2\left|Y_{00}(\theta,\phi)\right|^2\delta(\mathbf{r})\\ &= \frac{e^2\mu_0 g_p}{3m_p m_e}\frac{\left|R_{n0}(0)\right|^2}{4\pi},\end{aligned} \tag{21.108}$$

where $R_{n0}(0)$ is the value of the radial wave function at the origin.[5] The hyperfine splitting of any S ($\ell = 0$) state of hydrogen is then

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[5] In spherical coordinates

$$\int d\mathbf{r}\delta(\mathbf{r}) = \int_0^{2\pi} d\phi\int_{-1}^{1} d\left(\cos\theta\right)\int_0^{\infty} dr r^2\frac{\delta(r)\delta(\cos\theta)\delta(\phi)}{r^2}$$

$$\delta E_{n,\ell=0}^{\text{contact}} = \Delta E_{n,\ell=0,f=1}^{\text{contact}} - \Delta E_{n,\ell=0,f=0}^{\text{contact}} = \frac{\mu_0 e^2 g_p \hbar^2}{3m_e m_p} \frac{|R_{n0}(0)|^2}{4\pi}. \tag{21.109}$$

The value of $|R_{n0}(0)|^2$ can be obtained from Eq. (10.114) as

$$|R_{n0}(0)|^2 = \frac{1}{a_0^3}\left(\frac{4}{n^5}\right)\left[L_{n-1}^1(0)\right]^2 = \frac{1}{a_0^3}\left(\frac{4}{n^3}\right), \tag{21.110}$$

where $a_0 = \hbar/(\alpha_{FS} m_e c)$ is the Bohr radius and $L_{n-1}^1(0) = n$ is a Laguerre polynomial. Combining Eqs. (21.109) and (21.110) and using the fact that $\mu_0 \epsilon_0 = 1/c^2$, I find for the ground state of the hydrogen atom that

$$\begin{aligned} \delta E_{1,\ell=0} &= \frac{\mu_0 e^2 g_p}{3m_p m_e} \frac{\hbar^2}{\pi a_0^3} \\ &= \left|E_1^{(0)}\right| \frac{8 g_p \alpha_{FS}^2 m_e}{3m_p} = 5.88 \times 10^{-6}\ \text{eV}; && (21.111\text{a}) \\ \frac{\delta E_{1,\ell=0}}{h} &= 1.42\ \text{GHz}; && (21.111\text{b}) \\ \lambda &= c/f = 21.1\ \text{cm}. && (21.111\text{c}) \end{aligned}$$

This corresponds to the famous 21 cm astrophysical line of radio astronomy.

It turns out that the spin–spin interaction [second term in Eq. (21.100)] averages to zero for $\ell = 0$ states; moreover, the contribution to the hyperfine interaction from the orbital motion of the electron also vanishes for $\ell = 0$ states. As a consequence, the *only* contribution to the hyperfine splitting of $\ell = 0$ states arises from the contact interaction term. This is why the "contact" label was suppressed in Eqs. (21.111).

For $\ell \neq 0$, the calculation is more complicated and is given at the end of this Appendix. The hyperfine shift for $\ell \neq 0$ is

$$\Delta E_{n\ell jf} = \left|E_n^{(0)}\right| \frac{g_p \alpha_{FS}^2 m_e}{n m_p} \frac{f(f+1) - j(j+1) - 3/4}{j(j+1)(2\ell+1)} \tag{21.112}$$

and the hyperfine splitting is

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is somewhat ambiguous owing to the endpoint contributions to the integrals. I use the convention that, for any spherically symmetric function $f(r)$,

$$\int d\mathbf{r}\delta(\mathbf{r}) f(r) = f(0).$$

This will insure that $\int d\mathbf{r}\delta(\mathbf{r}) = 1$.

$$\delta E_{n\ell j} = \Delta E_{n\ell jf=j+1/2} - \Delta E_{n\ell jf=j-1/2} = \left|E_n^{(0)}\right| \frac{g_p \alpha_{FS}^2 m_e}{n m_p} \frac{2j+1}{j\,(j+1)\,(2\ell+1)}. \tag{21.113}$$

Equations (21.112) and (21.113) are also valid for $\ell = 0$ states [see Eq. (21.111a)], even though they are derived assuming $\ell \neq 0$.

For a spin 1/2 atom such as hydrogen, the only contribution to the hyperfine interaction is associated with the magnetic dipole moment of the proton. Nuclei having spin $I \geq 1$ possess an electric quadrupole moment as well, which also gives rise to a hyperfine interaction. In this case, the additional hyperfine interaction results from the interaction of the nuclear quadrupole with the electric field gradient at the nucleus produced by the atomic electrons.

21.5.2 Zeeman Splitting

In the presence of an external magnetic field, there is an additional interaction Hamiltonian that is still given approximately by Eq. (21.40) (the interaction of the *nuclear* magnetic moment with the field can be neglected since it is about m_e/m_p times smaller than the electronic contribution). Within a given fine structure manifold j there are two hyperfine levels having $f = j \pm 1/2$. The calculation of the effect of a magnetic field on these levels is similar to that of a magnetic field on the two fine structure levels $j = \ell \pm 1/2$ within a given ℓ manifold that was considered in Sect. 21.1.9. In other words, in weak magnetic fields, m_f is approximately a good quantum number and each hyperfine level splits into $(2f+1)$ components. With increasing field strength there is a transition to the Paschen-Back region in which m_j and m_I are approximately good quantum numbers. This region actually corresponds to the *weak field regime* of the Zeeman splitting of a state characterized by quantum number j—that is, the components coalesce into a set of $(2j+1)$ distinct energy levels, each of which is doubly-degenerate, owing to the nuclear spin. The $(2j+1)$ energy levels are those of the weak field Zeeman effect for this $j = 1/2$ state. I concentrate mainly on the weak field regime, since the strong-field regime reproduces the weak field results that were obtained neglecting hyperfine structure.

I first consider S states, for which the hyperfine and Zeeman interaction Hamiltonian can be written as

$$\hat{H}' = \frac{\mu_0 e^2 g_p}{3 m_e m_p} \delta(\mathbf{r}) \mathbf{S} \cdot \mathbf{I} + \frac{\beta_0 B}{\hbar} \left(J_z + S_z\right). \tag{21.114}$$

Using the $\left|m_I m_j\right\rangle$ basis and writing

$$\mathbf{S} \cdot \mathbf{I} = \mathbf{J} \cdot \mathbf{I} = \frac{J_+ I_- + J_- I_+}{2} + J_z I_z \tag{21.115}$$

($\mathbf{S} = \mathbf{J}$ since $\ell = 0$), I calculate matrix elements of $\hat{H}'$ for n, $\ell = 0$ states as

$$\frac{\underline{\mathrm{H}}'_n}{h} = \begin{pmatrix} \frac{A_n}{4} - bB(T) & 0 & 0 & 0 \\ 0 & -\frac{A_n}{4} - bB(T) & \frac{A_n}{2} & 0 \\ 0 & \frac{A_n}{2} & -\frac{A_n}{4} + bB(T) & 0 \\ 0 & 0 & 0 & \frac{A_n}{4} + bB(T) \end{pmatrix}, \quad (21.116)$$

where the order is

$$\left|m_I, m_j\right\rangle = \left|-\frac{1}{2}, -\frac{1}{2}\right\rangle, \left|-\frac{1}{2}, \frac{1}{2}\right\rangle, \left|\frac{1}{2}, -\frac{1}{2}\right\rangle, \left|\frac{1}{2}, \frac{1}{2}\right\rangle, \quad (21.117)$$

$A_n = \left(1.42/n^3\right)$ GHZ, $b = 14$ GHZ, and $B\,(T)$ is the magnetic induction in units of Tesla. The eigenkets and eigenergies are

$$|E_1\rangle = \left|-\frac{1}{2}, -\frac{1}{2}\right\rangle; \quad E_1 = A_n/4 - bB(T); \quad (21.118a)$$

$$|E_2\rangle = a_{22}\left|-\frac{1}{2}, \frac{1}{2}\right\rangle + a_{23}\left|\frac{1}{2}, -\frac{1}{2}\right\rangle;$$

$$E_2 = -A_n/4 - \sqrt{A_n^2 + 4b^2B(T)^2}/2; \quad (21.118b)$$

$$|E_3\rangle = a_{32}\left|-\frac{1}{2}, \frac{1}{2}\right\rangle + a_{33}\left|\frac{1}{2}, -\frac{1}{2}\right\rangle;$$

$$E_3 = -A_n/4 + \sqrt{A_n^2 + 4b^2B(T)^2}/2; \quad (21.118c)$$

$$|E_4\rangle = \left|\frac{1}{2}, \frac{1}{2}\right\rangle; \quad E_4 = A_n/4 + bB(T), \quad (21.118d)$$

where

$$a_{22} = NA_n; \quad (21.119a)$$

$$a_{23} = -N\left[-2bB(T) + \sqrt{A_n^2 + 4\left[bB(T)\right]^2}\right]; \quad (21.119b)$$

$$a_{32} = -N\left[2bB(T) - \sqrt{A_n^2 + 4\left[bB(T)\right]^2}\right]; \quad (21.119c)$$

$$a_{33} = NA_n; \quad (21.119d)$$

$$N = 1/\left\{\left(2bB(T) - \sqrt{A_n^2 + 4\left[bB(T)\right]^2}\right)^2 + A_n^2\right\}^{1/2}. \quad (21.119e)$$

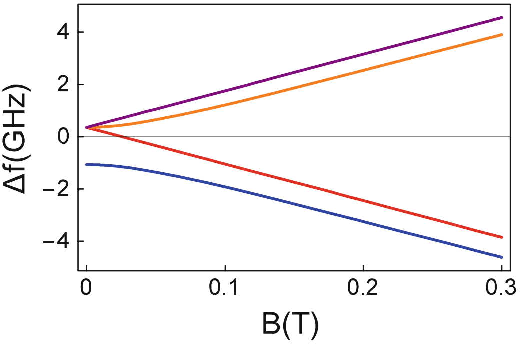

Fig. 21.6 Frequency shifts of the ground state of hydrogen resulting from the hyperfine interaction and the interaction with an external magnetic field

Each S-state manifold consists of four non-degenerate levels (one $f = 0$ level and three $f = 1$ levels) in weak magnetic fields. With increasing field strength, these levels approximately coalesce into two pairs of levels (the $m_j = \pm 1/2$ levels of the $j = 1/2$ state). For $B(T) \ll A_n/b$, the eigenkets and eigenenenergies are those associated with the $\left|fm_f\right\rangle$ basis. For $B\,(T) \gg A_n/b$, the eigenkets and eigenvalues are those associated with the $\left|jm_j\right\rangle$ basis, with an (almost) two-fold degeneracy for each energy. The eigenfrequencies for the ground state sublevels as a function of magnetic induction are plotted in Fig. 21.6.

There is an important difference from the Zeeman effect that we encountered for fine structure levels. Since the hyperfine splitting is 10 to a 1000 times smaller than the fine structure splitting, the crossover to the Paschen-Back region occurs at much lower field strengths for hyperfine levels. In fact, the ability to tune the energy of the hyperfine levels using magnetic field strengths that are easily accessible in the laboratory plays an important role in modern atomic spectroscopy.

In weak fields for other than S states, the Zeeman shift of the energy levels of a hydrogenic state characterized by quantum numbers $n\ell jfm_f$ is given approximately by

$$\begin{aligned}\Delta E_{\ell jfm_f} &= (\beta_0 B/\hbar)\left\langle n\ell jfm_f\right|\hat{L}_z + 2\hat{S}_z\left|n\ell jfm_f\right\rangle/\hbar \\ &= (\beta_0 B/\hbar)\sum_{m_j,m_j',m_I,m_I'}\begin{bmatrix} j & 1/2 & f \\ m_j & m_I & m_f\end{bmatrix}\begin{bmatrix} j & 1/2 & f \\ m_j' & m_I' & m_f\end{bmatrix} \\ &\quad\times\left\langle n\ell jm_j\right|\hat{L}_z + 2\hat{S}_z\left|n\ell jm_j\right\rangle\delta_{m_I,m_I'}\delta'_{m_j,m_j}. \qquad (21.120)\end{aligned}$$

The matrix element $\left\langle n\ell jm_j\right|\hat{L}_z+2\hat{S}_z\left|n\ell jm_j\right\rangle$ is the one we encountered in the Zeeman effect without hyperfine structure—it is equal to $\hbar g_j m_j$; moreover, m_j must equal $\left(m_f - m_I\right)$, owing to the properties of the Clebsch-Gordan coefficients. Therefore

$$\Delta E_{\ell j f m_f} = \beta_0 B g_j \sum_{m_I=-1/2}^{1/2} \left(m_f - m_I\right) \begin{bmatrix} j & 1/2 & f \\ m_f - m_I & m_I & m_f \end{bmatrix}^2 . \tag{21.121}$$

The sum can be carried out to give

$$\Delta E_{\ell j f m_f} = \beta_0 B g_f m_f$$

where the Landé g_f factor is

$$g_f = g_j \frac{f(f+1) + j(j+1) - 3/4}{2f(f+1)}, \tag{21.122}$$

with g_j given by Eq. (21.71) with $J = j$, $L = \ell$, and $S = 1/2$. For a multi-electron, multi-nucleon atom characterized by angular momentum quantum numbers L, S, J, I, and F, the corresponding result is

$$g_f = g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)}, \tag{21.123}$$

with g_J given by Eq. (21.71). The same result can be obtained using a vector model in which the vector $\mathbf{F} = \mathbf{J} + \mathbf{I}$ precesses about the magnetic field direction.

In the strong field vector model, $\mathbf{J}$ and $\mathbf{I}$ and their magnetic moments precess separately about the magnetic field direction; however, the contribution to level shifts resulting from the nuclear spin magnetic moment is m_e/m_p times smaller than that of the electronic magnetic moment. This is the reason the strong field result approximately reproduces the weak field results neglecting hyperfine interactions.

21.5.3 Contribution to the Hyperfine Splitting from Non-contact Interaction Terms

I now give some details of the calculation of the hyperfine level shifts from the second and third terms in Eq. (21.100). The hyperfine splitting from these non-contact interaction terms can be written as

$$\Delta E_{n\ell jf} = \frac{\mu_0 e^2 g_p}{8\pi m_e m_p} \left(A_{n\ell jf} + 3B_{n\ell jf}\right), \tag{21.124}$$

where

$$A_{n\ell jf} = \langle n, \ell, j, f, 0| \frac{\left(\hat{\mathbf{L}} - \hat{\mathbf{S}}\right) \cdot \hat{\mathbf{I}}}{r^3} |n, \ell, j, f, 0\rangle \tag{21.125}$$

and

$$B_{n\ell jf} = \langle n,\ell,j,f,0| \frac{\left(\mathbf{u}_r\cdot\hat{\mathbf{S}}\right)\,\left(\mathbf{u}_r\cdot\hat{\mathbf{I}}\right)}{r^3} |n,\ell,j,f,0\rangle\,. \tag{21.126}$$

I have set $m_f = 0$, since the result is independent of m_f. I now calculate $A_{n\ell jf}$ and $B_{n\ell jf}$ separately.

21.5.3.1 $\mathbf{A}_{n\ell jf}$

If Eq. (21.62) is written as a vector equation involving $\hat{\mathbf{A}}$ and $\hat{\mathbf{J}}$ with $\hat{\mathbf{A}} = \hat{\mathbf{L}}$, it follows that[6]

$$\begin{aligned}\langle n,\ell,j,f,0|\,\hat{\mathbf{L}}\cdot\hat{\mathbf{I}}\,|n,\ell,j,f,0\rangle &= \frac{\langle n,\ell,j,f,0|\,\hat{\mathbf{L}}\cdot\hat{\mathbf{J}}\,|n,\ell,j,f,0\rangle}{\hbar^2 j\,(j+1)}\\ &\times\langle n,\ell,j,f,0|\,\hat{\mathbf{I}}\cdot\hat{\mathbf{J}}\,|n,\ell,j,f,0\rangle\\ &=\hbar^2\left[\frac{j(j+1)+\ell(\ell+1)-3/4}{2j\,(j+1)}\right]\left[\frac{f(f+1)-j(j+1)-3/4}{2}\right],\end{aligned} \tag{21.127}$$

where I used the relations $\mathbf{S} = (\mathbf{J}-\mathbf{L})$ and $\mathbf{F} = (\mathbf{J}+\mathbf{I})$. Similarly,

$$\begin{aligned}\langle n,\ell,j,f,0|\,\hat{\mathbf{S}}\cdot\hat{\mathbf{I}}\,|n,\ell,j,f,0\rangle &= \frac{\langle n,\ell,j,f,0|\,\hat{\mathbf{S}}\cdot\hat{\mathbf{J}}\,|n,\ell,j,f,0\rangle}{\hbar^2 j\,(j+1)}\\ &\times\langle n,\ell,j,f,0|\,\hat{\mathbf{I}}\cdot\hat{\mathbf{J}}\,|n,\ell,j,f,0\rangle\\ &=\hbar^2\left[\frac{j(j+1)-\ell(\ell+1)+3/4}{2j\,(j+1)}\right]\left[\frac{f(f+1)-j(j+1)-3/4}{2}\right].\end{aligned} \tag{21.128}$$

Combining Eqs. (21.125), (21.127), and (21.128), I obtain

$$A_{n\ell jf} = \hbar^2\left[\frac{\ell(\ell+1)-3/4}{j\,(j+1)}\right]\left[\frac{f(f+1)-j(j+1)-3/4}{2}\right]\left\langle r^{-3}\right\rangle, \tag{21.129}$$

where $\left\langle r^{-3}\right\rangle$ is given by Eq. (21.94).

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[6] Equations (21.127) and (21.128) can also be obtained by expanding the kets in the uncoupled basis and directly evaluating the matrix elements (see the *Supplementary Material* at the book's web site).

21.5.3.2 $B_{n\ell jf}$

To evaluate Eq. (21.126), I use the fact that

$$\mathbf{u}_r = \sin\theta\cos\phi\mathbf{u}_x + \sin\theta\sin\phi\mathbf{u}_y + \cos\theta\mathbf{u}_z \tag{21.130}$$

to write

$$\frac{(\mathbf{u}_r\cdot\mathbf{S})\ (\mathbf{u}_r\cdot\mathbf{I})}{r^3} = \sum_{q,q'=-1}^{1}(-1)^{q+q'}\frac{u_q I_{-q} u_{-q'} S_{q'}}{r^3}, \tag{21.131}$$

where

$$u_{\pm1} = \mp\frac{(u_r)_x \pm i\,(u_r)_y}{\sqrt{2}} = \mp\frac{\sin\theta e^{\pm i\phi}}{\sqrt{2}};\qquad u_0 = \cos\theta. \tag{21.132}$$

Then, to evaluate the matrix elements needed in Eq. (21.126), I expand the basis kets as

$$\begin{aligned}|n,\ell,j,f,0\rangle = &\sum_{m_I,m_s=-1/2}^{1/2}\begin{bmatrix}\ell & 1/2 & j\\ -m_I-m_s & m_s & -m_I\end{bmatrix}\begin{bmatrix}j & 1/2 & f\\ -m_I & m_I & 0\end{bmatrix}\\ &\times|n,\ell,m_\ell=-m_I-m_s\rangle\,|Im_I\rangle\,|Sm_s\rangle\end{aligned} \tag{21.133}$$

with a corresponding equation for the bra, and use the relationships

$$\hat{G}_{\pm1}\left|g,m_g\right\rangle = \hbar\sqrt{\left(g\mp m_g\right)\left(g\pm m_g+1\right)}\left|g,m_g\pm1\right\rangle; \tag{21.134a}$$

$$\hat{G}_0\left|g,m_g\right\rangle = m_g\hbar\left|g,m_g\right\rangle, \tag{21.134b}$$

where the $\hat{G}_{\pm1}$,$\hat{G}_0$ ($\hat{G}=\hat{S},\hat{I}$) are components of an irreducible tensor operator of rank 1. It then follows that

$$\begin{aligned}B_{n\ell jf} = \left\langle r^{-3}\right\rangle &\sum_{m_I,m_s=-1/2}^{1/2}\sum_{q,q'=-1}^{1}(-1)^{q+q'}\begin{bmatrix}\ell & 1/2 & j\\ -m_I-m_s & m_s & -m_I\end{bmatrix}\\ &\times\begin{bmatrix}j & 1/2 & f\\ -m_I & m_I & 0\end{bmatrix}\begin{bmatrix}\ell & 1/2 & j\\ -m_I'-m_s' & m_s' & -m_I'\end{bmatrix}\begin{bmatrix}j & 1/2 & f\\ -m_I' & m_I' & 0\end{bmatrix}\\ &\times S_{q'm_s'm_s}I_{qm_I'm_I}B_\ell(q,q',-m_I'-m_s',-m_I-m_s),\end{aligned} \tag{21.135}$$

where

$$B_\ell(q,q',m_\ell',m_\ell) = \left\langle\ell,m_\ell'\right|u_q u_{-q'}\left|\ell,m_\ell\right\rangle \tag{21.136}$$

and

$$S_{qm_s'm_s} = \left\langle Sm_s'\right| \hat{S}_1^q \left|Sm_s\right\rangle = \hbar \left[\begin{array}{c} m_s\delta_{q,0}\delta_{m_s,m_s'} \\ +\frac{1}{\sqrt{2}}\left(\begin{array}{c} -\delta_{q,1}\delta_{m_s,-1/2}\delta_{m_s',1/2} \\ +\delta_{q,-1}\delta_{m_s,1/2}\delta_{m_s',-1/2} \end{array}\right) \end{array}\right]; \quad (21.137a)$$

$$I_{qm_s'm_s} = \left\langle Im_I'\right| \hat{I}_1^q \left|Im_I\right\rangle = \hbar \left[\begin{array}{c} m_I\delta_{q',0}\delta_{m_I,m_I'} \\ +\frac{1}{\sqrt{2}}\left(\begin{array}{c} -\delta_{q,1}\delta_{m_I,-1/2}\delta_{m_I',1/2} \\ +\delta_{q,-1}\delta_{m_I,1/2}\delta_{m_I',-1/2} \end{array}\right) \end{array}\right]. \quad (21.137b)$$

To evaluate the $B_\ell(q, q', m_\ell', m_\ell)$, I use the identities

$$(u_0)^2 = \cos^2\theta = \frac{\sqrt{4\pi}Y_0^0(\theta,\phi) + \sqrt{\frac{16\pi}{5}}Y_2^0(\theta,\phi)}{3}, \quad (21.138a)$$

$$u_1u_{-1} = -\frac{\sin^2\theta}{2} = \frac{\sqrt{\frac{16\pi}{5}}Y_2^0(\theta,\phi) - 2\sqrt{4\pi}Y_0^0(\theta,\phi)}{6}, \quad (21.138b)$$

$$u_0u_{\pm1} = \mp\frac{\cos\theta\sin\theta e^{\pm i\phi}}{\sqrt{2}} = \sqrt{\frac{4\pi}{15}}Y_2^{\pm1}(\theta,\phi), \quad (21.138c)$$

$$(u_{\pm1})^2 = \frac{\sin^2\theta e^{\pm2i\phi}}{2} = \sqrt{\frac{8\pi}{15}}Y_2^{\pm2}(\theta,\phi), \quad (21.138d)$$

and

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \left[Y_{\ell_3}^{m_3}(\theta,\phi)\right]^* Y_{\ell_2}^{m_2}(\theta,\phi)\, Y_{\ell_1}^{m_1}(\theta,\phi)$$
$$= \sqrt{\frac{(2\ell_1+1)(2\ell_2+1)}{4\pi(2\ell_1+1)}} \begin{bmatrix} \ell_1 & \ell_2 & \ell_3 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & m_3 \end{bmatrix} \quad (21.139)$$

to obtain

$$B_\ell(1,1,m_\ell',m_\ell) = B_\ell(-1,-1,m_\ell',m_\ell) = \frac{1-\ell(\ell+1)-m_\ell^2}{(2\ell+3)(2\ell-1)}\delta_{m_\ell,m_\ell'}; (21.140a)$$

$$B_\ell(1,0,m_\ell',m_\ell) = B_\ell(0,-1,m_\ell',m_\ell)$$
$$= \frac{\left(2m_\ell'-1\right)\sqrt{\ell(\ell+1)-m_\ell'\left(m_\ell'-1\right)}}{\sqrt{2}(2\ell+3)(2\ell-1)}\delta_{m_\ell,m_\ell'-1}; \quad (21.140b)$$

$$B_\ell(1,-1,m_\ell',m_\ell) = -\frac{\sqrt{(1+\ell-m_\ell')\left(2+\ell-m_\ell'\right)(\ell+m_\ell'-1)\left(\ell+m_\ell'\right)}}{(2\ell+3)\,(2\ell-1)} \times\delta_{m_\ell,m_\ell'-2}; \tag{21.140c}$$

$$\begin{aligned} B_\ell(0,1,m_\ell',m_\ell) &= B_\ell(-1,0,m_\ell',m_\ell) \\ &= -\frac{\left(2m_\ell'+1\right)\sqrt{\ell(\ell+1)-m_\ell'\left(m_\ell'+1\right)}}{\sqrt{2}\,(2\ell+3)\,(2\ell-1)}\delta_{m_\ell,m_\ell'+1}; \end{aligned}$$

$$B_\ell(0,0,m_\ell',m_\ell) = \frac{2\ell(\ell+1)-2m_\ell^2-1}{(2\ell+3)\,(2\ell-1)}\delta_{m_\ell,m_\ell'}; \tag{21.140d}$$

$$B_\ell(-1,1,m_\ell',m_\ell) = -\frac{\sqrt{(\ell-m_\ell'-1)\left(2+\ell+m_\ell'\right)(\ell+m_\ell'+1)\left(\ell-m_\ell'\right)}}{(2\ell+3)\,(2\ell-1)} \times\delta_{m_\ell,m_\ell'+2}. \tag{21.140e}$$

The sum in Eq. (21.135) can then be carried out to arrive at

$$B_{n\ell jf} = \hbar^2\frac{4\,[f(f+1)-j\,(j+1)]-3}{32j\,(j+1)}\left\langle r^{-3}\right\rangle. \tag{21.141}$$

Using Eqs. (21.129) and (21.141), I find

$$A_{n\ell jf} + 3B_{n\ell jf} = \hbar^2\frac{\ell(\ell+1)}{j\,(j+1)}\left[\frac{f(f+1)-j(j+1)-3/4}{2}\right]\left\langle r^{-3}\right\rangle, \tag{21.142}$$

which, when combined with Eqs. (21.124) and (21.94), leads to Eq. (21.112). Note that the right-hand side of Eq. (21.142) vanishes if a small volume about the origin is excluded in evaluating $\left\langle r^{-3}\right\rangle$, implying that the only contributing term to the hyperfine level shifts from $\ell = 0$ states arises from the contact interaction. The hyperfine splitting associated with the non-contact, spin–spin interaction alone can be obtained from Eqs. (21.124)–(21.126), (21.128), and (21.141) as

$$\begin{aligned} \Delta E_{n\ell jf}^{\text{spin-spin}} &= -\frac{\mu_0 e^2 g_p\hbar^2}{8\pi m_e m_p}\left[\frac{j(j+1)+\ell(\ell+1)+3/4}{2j\,(j+1)}\right] \\ &\quad\times\left[\frac{f(f+1)-j(j+1)-3/4}{2}\right]\left\langle r^{-3}\right\rangle \\ &\quad+3\frac{\mu_0 e^2 g_p\hbar^2}{8\pi m_e m_p}\frac{4\,[f(f+1)-j\,(j+1)]-3}{32j\,(j+1)}\left\langle r^{-3}\right\rangle \end{aligned}$$

$$= -\frac{\mu_0 e^2 g_p \hbar^2}{8\pi m_e m_p}\left[\frac{j(j+1)-\ell(\ell+1)-3/4}{4j\,(j+1)}\right]$$
$$\times\,[f(f+1)-j(j+1)-3/4]\left\langle r^{-3}\right\rangle, \qquad (21.143)$$

which vanishes for $\ell = 0, j = 1/2$ states.

21.6 Problems

1. What is meant by a "good" quantum number. If the spin-orbit coupling in hydrogen is much greater than the Zeeman splitting produced by an external magnetic field, what are the *approximate* good quantum numbers? In the opposite limit, what are the *approximate* good quantum numbers? For hydrogen in an external magnetic field, what are the only good eigenvalue labels? Explain. For hydrogen in an external electric field, what are the only good eigenvalue labels? Explain. For hydrogen in both external electric and magnetic fields, what are the only good eigenvalue labels? Explain.

2. Given a Hamiltonian of the form

$$\hat{H} = \frac{\hat{p}^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 r} - \frac{1}{8}\frac{\hat{p}^4}{m_e^3 c^2},$$

use the facts that $\hat{p}^4$ commutes with $\hat{L}^2$ and $\hat{L}_z$ to prove that

$$\langle n,\ell,m|\,\hat{p}^4\,\left|n',\ell',m'\right\rangle \propto \delta_{\ell,\ell'}\delta_{m,m'}.$$

Why isn't the matrix element also diagonal in the n quantum number?

3. Calculate the change in the 2P-1S transition frequencies in GHz (a) including only the relativistic mass corrections and (b) including both the relativistic mass, spin-orbit, and Darwin corrections. For case (b) compare your result with the exact result of the Dirac equation given in Eq. (21.1).

4. For an electron in a spherically symmetric potential *plus* a constant magnetic field, prove that L^2 is a constant of the motion, but $\mathbf{L}$ is not a constant of the motion. For an electron in a spherically symmetric potential *plus* a constant electric field, prove that L^2 and $\mathbf{L}$ are not constants of the motion. Neglect any spin–orbit interactions. Give a simple physical explanation of the results based on classical considerations.

5–7. Consider the hydrogen atom in the $n = 2$, $\ell = 1$ manifold of levels. Calculate the eigenvalues and eigenkets when the atom is subjected to an external, constant magnetic field along the z axis. Use the $\left|n\ell jm_j\right\rangle$ basis. Plot the energy eigenvalues divided by h in units of GHZ as a function of magnetic field strength for fields between 0 and 10 T. Plot this in two graphs, one for 0 T$\leq B \leq$ 1 T and one for 1 T$\leq B \leq$ 10 T. Show that the slopes of your energy graphs agree with perturbation theory predictions in the limits of weak and strong fields. Include all relativistic corrections.

8. For a hydrogen atom in a constant electric field $\mathbf{E} = \mathcal{E}_0\mathbf{u}_z$ aligned along the z axis, the perturbation Hamiltonian is

$$\hat{H}' = \frac{1}{8\pi\epsilon_0}\frac{e^2\mathbf{S}\cdot\mathbf{L}}{m_e^2 r^3 c^2} + e\mathcal{E}_0\hat{z},$$

where the relativistic mass and Darwin correction terms have been neglected. Write matrix elements of H' in both the $|n\ell s m_\ell m_s\rangle$ and $|n\ell s j m_j\rangle$ bases, allowing for all values of the quantum numbers. You need not evaluate the radial integrals, but determine the states that are coupled by the perturbation in each basis. What are the only exact constants of the motion in this problem?

9–10. For a hydrogen atom in a constant electric field aligned along the x axis, prove that $\hat{L}_x$ is a constant of the motion. Now consider the $n = 2$ electronic state manifold of hydrogen, neglecting all relativistic corrections. Find the eigenkets of the $n = 2$ manifold in this field. Show that the *nondegenerate* eigenkets of the Hamiltonian are eigenkets of $\hat{L}_x$ (as they must be), and that a linear combination of the degenerate eigenkets of the Hamiltonian can be chosen such that they are eigenkets of $\hat{L}_x$. Conversely show that the *nondegenerate* eigenkets of $\hat{L}_x$ are eigenkets of the Hamiltonian (as they must be), and that a linear combination of the degenerate eigenkets of $\hat{L}_x$ can be chosen such that they are eigenkets of the Hamiltonian.

11. Consider the hyperfine plus Zeeman interaction Hamiltonian for the *ground* state of hydrogen in the $|m_I m_j\rangle$ basis. Take the interaction Hamiltonian in frequency units as

$$\hat{H}'/h = 1.42\ \text{GHz}\ \frac{\mathbf{S}\cdot\mathbf{I}}{\hbar^2} + \left(\frac{2S_z}{\hbar}\right) 14\ \text{GHz/T}\ B(\text{T})$$

Use the fact that $\mathbf{S} = \mathbf{J}$ and obtain an explicit form for the interaction Hamiltonian matrix. Diagonalize the Hamiltonian to obtain the eigenkets and eigenfrequencies. Show that for $B(T) = 0$, the eigenkets and eigenvalues are those associated with states characterized by $f = 0, 1$, and, for $B(T) \gg 0.1$ T, the eigenkets and eigenvalues are those associated with a (doubly-degenerate) $j = 1/2$ state whose magnetic sublevels are split by the Zeeman effect.

12–13. The ground state of ^{87}Rb is a $5^2S_{1/2}$ state having $L = 0, S = 1/2, J = 1/2$ while the first excited states are a $5^2P_{1/2}$ state having $L = 1, S = 1/2, J = 1/2$ and a $5^2P_{3/2}$ state having $L = 1, S = 1/2, J = 3/2$. The ^{87}Rb has nuclear spin $I = 3/2$. What are the possible total angular momentum states for each of these levels? When a pair of off-resonant, optical fields that are counter-propagating in the Z-direction drive a transition between the $F = 1$ hyperfine levels of the $5^2S_{1/2}$ state and the $F = 2$ hyperfine levels of the $5^2P_{1/2}$ state, they produce an effective perturbation Hamiltonian for the $F = 1$ ground state hyperfine levels whose matrix elements are given by[7]

$$H'_{m_F,m'_F} = A\sum_{j,j'=1}^{2}\sum_{K,Q} e^{i\mathbf{k}_{jj'}\cdot\mathbf{R}}(-1)^{K+Q+1}$$

$$\times\epsilon_Q^K(j,j')(-1)^{m'_F}\begin{bmatrix}1 & 1 & K\\ m_F & -m'_F & Q\end{bmatrix}\begin{Bmatrix}1 & 1 & K\\ 1 & 1 & 2\end{Bmatrix},$$

where

$$\mathbf{k}_{jj'} = \mathbf{k}_j - \mathbf{k}_{j'};\quad \mathbf{k}_1 = -\mathbf{k}_2 = k\mathbf{u}_z;$$

$$\epsilon_Q^K(1,1) = -\frac{1}{\sqrt{3}}\delta_{K,0}\delta_{Q,0} + \delta_{K,2}\left[-\frac{1}{\sqrt{6}}\delta_{Q,0} + \frac{1}{2}\left(\delta_{Q,2} + \delta_{Q,-2}\right)\right];$$

$$\epsilon_Q^K(2,2) = -\frac{1}{\sqrt{3}}\delta_{K,0}\delta_{Q,0} - \delta_{K,2}\left[\frac{1}{\sqrt{6}}\delta_{Q,0} + \frac{1}{2}\left(\delta_{Q,2} + \delta_{Q,-2}\right)\right];$$

$$\epsilon_Q^K(1,2) = \left[\epsilon_{-Q}^K(2,1)\right]^* = \frac{i}{\sqrt{2}}\left[\delta_{K,1}\delta_{Q,0} + \frac{1}{\sqrt{2}}\delta_{K,2}\left(\delta_{Q,2} - \delta_{Q,-2}\right)\right],$$

A is a constant proportional to the field intensity and inversely proportional to the frequency difference between the applied field and the atomic transition, and the curly bracket term is a 6-J symbol [Mathematica symbol, SixJSymbol[{1, 1, K}, {1, 1, 2}]. Diagonalize the perturbation matrix and plot the eigenenergies E/A as a function of kZ to obtain the *optical lattice potentials.* Counter-propagating optical fields can be used to cool atoms to microKelvin temperatures and the optical potentials associated with these fields can be used to trap the atoms.

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[7] See, for example, P. R. Berman and V. Malinovsky, *Principles of Laser Spectroscopy and Quantum Optics* (Princeton University Press, Princeton, N.J., 2011) pp. 414–418. The atoms are pre-cooled using *Doppler cooling* (see Sect. 5.5.3 in the cited work) before these fields produce *sub-Doppler cooling* (see Chap. 18 in the cited work).