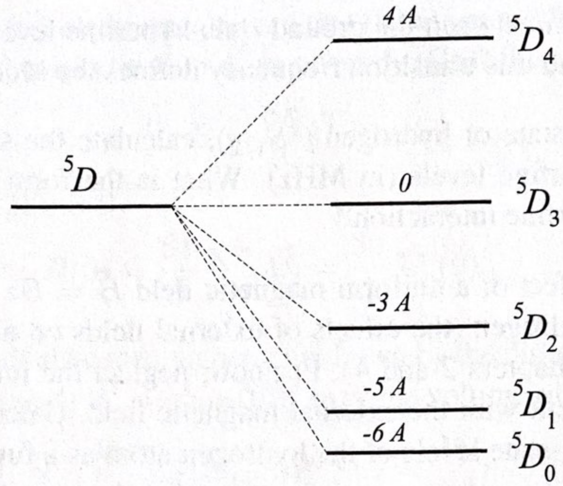

FIG. 1.2 Splitting of the ^5D term due to the spin-orbit interaction $H' = A\vec{L}\cdot\vec{S}$, with $A > 0$. We set $\hbar = 1$ for convenience.

Note that the energy difference between adjacent components is given by

$$\Delta E(J) - \Delta E(J-1) = AJ\,. \tag{1.39}$$

This formula is known as the *Landé interval rule*.

(c) The "center of gravity" of a term does not change due to the spin-orbit interaction. This answer can be guessed, since we expect the average of $\vec{L}\cdot\vec{S}$ over all possible orientations of $\vec{L}$ and $\vec{S}$ to be zero.

Alternatively, one can use the summation formulae [Eqs. (1.25)-(1.27)] to evaluate the shift of the center of gravity. For each J there are $(2J+1)$ Zeeman sublevels, so that the average energy shift $\langle \Delta E\rangle$ is given by the sum:

$$\langle \Delta E\rangle = \frac{A}{2}\sum_{J=|L-S|}^{L+S}(2J+1)[J(J+1) - S(S+1) - L(L+1)] = 0\,. \tag{1.40}$$

1.4 Hyperfine structure and Zeeman effect in hydrogen

In this classic problem, we are interested in what is known as the *hyperfine structure*, which in general arises due to the interaction of atomic electrons with the electric and magnetic multipole fields of the nucleus (the most important being the magnetic dipole and electric quadrupole). The transition between the hyperfine levels in the ground state of hydrogen is responsible for the famous 21-cm line in radio astronomy (the wavelength of the radiation is 21 cm), and the splitting between these levels has been measured extremely precisely with the hydrogen maser. The transition between the ground state hyperfine levels of cesium is used for atomic clocks and this transition frequency defines the second.

(a) For the ground state of hydrogen ($^2S_{1/2}$), calculate the splitting of the $F = 1$ and $F = 0$ hyperfine levels (in MHz). What is the form of the Hamiltonian describing the hyperfine interaction?

(b) Consider the effect of a uniform magnetic field $\vec{B} = B\hat{z}$ on the ground state energy levels of hydrogen (the effects of external fields on atoms are considered in more detail in Chapters 2 and 4). For now, neglect the interaction of the proton magnetic moment with the external magnetic field. Calculate the energies of the ground-electron-state levels of the hydrogen atom as a function of the applied magnetic field B.

(c) If one includes the interaction of the proton magnetic moment with the magnetic field, two of the energy levels cross at a certain magnetic field value. Which levels cross and at what magnetic field does the crossing occur?

Hint

For part (a), since the electron has no orbital angular momentum, one can think of the magnetic field from the electron $\vec{B}_e$ being generated by a magnetization $\vec{M}_e(r)$:

$$\vec{M}_e(r) = -g_e\mu_0\vec{S}\,|\psi_{100}(r)|^2 \,, \tag{1.41}$$

where $g_e = 2$ is the Landé g-factor for the electron,[5] and $\psi_{100}(r)$ is the $n = 1$, $l = 0$, $m_l = 0$ ground state wavefunction of hydrogen.

Solution

(a) The $\psi_{100}(r)$ wavefunction is spherically symmetric, so we can envision the average magnetization produced by the electron (1.41) to consist of the contributions of a series of concentric spherical balls each with constant magnetization $\vec{M}_i$, so that

$$\sum_i \vec{M}_i = \vec{M}_e(r) \,. \tag{1.42}$$

[5] Note that the standard sign convention for the Bohr magneton is positive, so the magnetic dipole moment of the electron is $\mu_e = -g_e\mu_0$.

Recalling from classical electromagnetism that the magnetic field inside a spherical ball with constant magnetization $\vec{M}$ is given by (Griffiths 1999)

$$\vec{B} = \frac{8\pi}{3}\vec{M} \tag{1.43}$$

we have for the field at $r = 0$

$$\vec{B}(0) = \frac{8\pi}{3}\sum_i \vec{M}_i = \frac{8\pi}{3}\vec{M}_e(0) , \tag{1.44}$$

from which we can calculate the magnetic field seen by the proton using Eq. (1.41).

We assume that $|\psi_{100}(r)|^2 = |\psi_{100}(0)|^2$ over the volume of the proton,[6] so

$$\vec{B}_e = -\frac{16\pi}{3}\mu_0 |\psi_{100}(0)|^2 \vec{S} = -\frac{16}{3a_0^3}\mu_0 \vec{S} , \tag{1.45}$$

where we have made use of the fact that

$$|\psi_{100}(0)|^2 = \frac{1}{\pi a_0^3} . \tag{1.46}$$

The Hamiltonian H_{hf} describing the interaction of the magnetic moment of the proton $\vec{\mu}_p$ with this magnetic field is thus

$$H_{\text{hf}} = -\vec{\mu}_p \cdot \vec{B}_e = \frac{16}{3a_0^3} g_p \mu_N \mu_0 \vec{I} \cdot \vec{S} , \tag{1.47}$$

where $g_p = 5.58$ is the proton g-factor and μ_N is the nuclear magneton.

Using the same trick employed in the derivation of the fine structure splitting in Problem 1.3, we find that the Hamiltonian has the form

$$H_{\text{hf}} = a\vec{I} \cdot \vec{S} = \frac{a}{2}\left(F^2 - I^2 - S^2\right) . \tag{1.48}$$

In units where $\hbar = 1$,

$$a \approx 5.58 \frac{16}{3a_0^3}\mu_N \mu_0 \approx 1420 \text{ MHz} , \tag{1.49}$$

and in terms of the eigenvalues of the angular momentum operators,

$$\boxed{H_{\text{hf}} = \frac{a}{2}[F(F+1) - I(I+1) - S(S+1)] .} \tag{1.50}$$

Therefore the hyperfine splitting in the ground state of hydrogen is

$$\boxed{\Delta E_{\text{hf}} \approx 1420 \text{ MHz} ,} \tag{1.51}$$

which corresponds to electromagnetic radiation of wavelength $\lambda = 21$ cm.

[6] An important point is that the hyperfine interaction in this case arises due to the wavefunction overlap between the proton and electron. This is somewhat subtle, as can be seen by comparing this analysis to that carried out in Problem 2.5 for a small ball carved out of a uniformly magnetized ball.

(b) From Eq. (1.50), we see that the energy eigenstates for the Hamiltonian describing the hyperfine interaction are also eigenstates of the operators $\{F^2, F_z, I^2, S^2\}$. Therefore if we write out a matrix for this Hamiltonian in the coupled basis, it is diagonal. However, the Hamiltonian H_B for the interaction of the magnetic moment of the electron with the external magnetic field

$$H_B = -\vec{\mu}_e \cdot \vec{B} = 2\mu_0 B S_z \tag{1.52}$$

is diagonal in the uncoupled basis (which is made up of eigenstates of the operators $\{I^2, I_z, S^2, S_z\}$).

The relationship between the coupled and uncoupled bases is as follows

$$|F=1, M_F=1\rangle = |+\rangle_S|+\rangle_I\,, \tag{1.53}$$

$$|F=1, M_F=0\rangle = \frac{1}{\sqrt{2}}(|+\rangle_S|-\rangle_I + |-\rangle_S|+\rangle_I)\,, \tag{1.54}$$

$$|F=1, M_F=-1\rangle = |-\rangle_S|-\rangle_I\,, \tag{1.55}$$

$$|F=0, M_F=0\rangle = \frac{1}{\sqrt{2}}(|+\rangle_S|-\rangle_I - |-\rangle_S|+\rangle_I)\,. \tag{1.56}$$

Employing Eqs. (1.50) and (1.52), one finds for the matrix $\mathbf{H}$ for the overall Hamiltonian $(H_{\text{hf}} + H_B)$ in the coupled basis:

	$\|1,1\rangle$	$\|1,-1\rangle$	$\|1,0\rangle$	$\|0,0\rangle$
$\langle 1,1\|$	$\frac{a}{4} + \mu_0 B$	0	0	0
$\langle 1,-1\|$	0	$\frac{a}{4} - \mu_0 B$	0	0
$\langle 1,0\|$	0	0	$\frac{a}{4}$	$-\mu_0 B$
$\langle 0,0\|$	0	0	$-\mu_0 B$	$-\frac{3a}{4}$

We can use this matrix to solve for the energies of the states as a function of B by employing the Schrödinger equation

$$\mathbf{H}|\psi\rangle = E|\psi\rangle \tag{1.57}$$

which implies that

$$(\mathbf{H} - E\mathbf{1})|\psi\rangle = 0\,, \tag{1.58}$$

where $\mathbf{1}$ is the identity matrix. If $(\mathbf{H} - E\mathbf{1})$ had an inverse, then we could multiply both sides of Eq. (1.58) by $(\mathbf{H} - E\mathbf{1})^{-1}$ to show that $|\psi\rangle = 0$. Assuming $|\psi\rangle \neq 0$, in order to satisfy Eq. (1.58), the matrix $(\mathbf{H} - E\mathbf{1})$ must be singular. This implies that its determinant is zero:

$$\begin{vmatrix} \frac{a}{4}+\mu_0 B-E & 0 & 0 & 0 \\ 0 & \frac{a}{4}-\mu_0 B-E & 0 & 0 \\ 0 & 0 & \frac{a}{4}-E & -\mu_0 B \\ 0 & 0 & -\mu_0 B & -\frac{3a}{4}-E \end{vmatrix} = 0\,. \tag{1.59}$$

The above expression is known as the *secular equation*. The matrix is block diagonal, so the energies are obtained by solving

$$\frac{a}{4}+\mu_0 B-E=0\,, \tag{1.60}$$

$$\frac{a}{4}-\mu_0 B-E=0\,, \tag{1.61}$$

$$\left(\frac{a}{4}-E\right)\left(-\frac{3a}{4}-E\right)-\mu_0^2B^2=0\,. \tag{1.62}$$

This gives the following energies

$$E_1=\frac{a}{4}+\mu_0 B\,, \tag{1.63}$$

$$E_2=\frac{a}{4}-\mu_0 B\,, \tag{1.64}$$

$$E_3=-\frac{a}{4}+\frac{a}{2}\sqrt{1+4\frac{\mu_0^2B^2}{a^2}}\,, \tag{1.65}$$

$$E_4=-\frac{a}{4}-\frac{a}{2}\sqrt{1+4\frac{\mu_0^2B^2}{a^2}}\,, \tag{1.66}$$

which are plotted as a function of B in Fig. 1.3.

(c) If we include the effect of the proton's magnetic moment, we have

$$\vec{\mu}=\vec{\mu}_e+\vec{\mu}_p\,, \tag{1.67}$$

so

$$H_B=-\vec{\mu}\cdot\vec{B}=g_e\mu_0 BS_z-g_p\mu_N BI_z\,. \tag{1.68}$$

In the high field limit we expect that the highest energy state should be the $|+\rangle_S|-\rangle_I$ state. In the low field limit, the $|1,1\rangle=|+\rangle_S|+\rangle_I$ state is the highest energy state, so these two levels must cross at some magnetic field.

In part (b), where we neglected the proton magnetic moment, for sufficiently high fields ($2\mu_0 B/a \gg 1$), the difference in energy between the two highest lying energy levels is [see Eqs. (1.63) and (1.65)]:

$$E_1-E_3\approx\frac{a}{2}\,. \tag{1.69}$$

When the difference in energy between $|+\rangle_I$ and $|-\rangle_I$ due to the interaction of the proton's magnetic moment with the magnetic field is equal to this energy

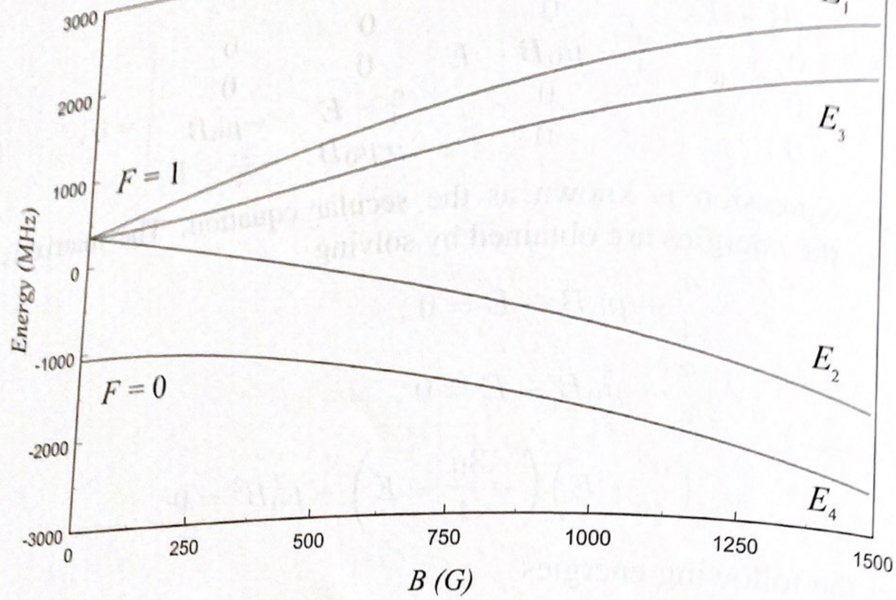

FIG. 1.3 Energies of the ground-state hyperfine manifold of hydrogen as a function of applied magnetic field. Such a plot is known as the *Breit-Rabi diagram*. At low fields, the system is well described in the coupled basis ($F = 1, 0$), while at high fields the energy eigenstates are best approximated by the uncoupled basis. The energies of the $|F = 1, M_F = 1\rangle$ and $|F = 1, M_F = -1\rangle$ states are linear in the magnetic field because they are not mixed with other states by the magnetic field [see Eqs. (1.53) and (1.55)].

difference, then the levels will cross. This occurs for the magnetic field:

$$B \approx \frac{a}{2 \times 5.58 \times \mu_N} \approx 167 \text{ kG} . \tag{1.70}$$

1.5 Hydrogenic ions

Hydrogen is an attractive object for the study of atomic structure because its simplicity allows accurate theoretical calculations which can be compared to experiment. A number of features in the energy-level structure of hydrogen are more pronounced in hydrogenic ions (atoms consisting of one electron bound to a nucleus with $Z > 1$) due to the larger nuclear charge. Hydrogenic ions are of interest for precision experiments testing quantum electrodynamics (Silver 2001), measuring the mass of the electron (Quint 2001), determining the fine structure constant (Quint 2001), and testing the Standard Model of electroweak interactions (Zolotorev and Budker 1997), to name a few.