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Chapter 4

Effects of the Nucleus on Atomic Structure

Until now we have discussed atoms as if the nuclei were point charges with no structure and infinite mass. Real nuclei have finite mass, possibly non-zero angular momentum, \mathbf{I} , and a charge which is spread out over a finite volume. As a result, they possess magnetic dipole moments and electric quadrupole moments coupled to the angular momentum, and possibly higher moments as well. All of these properties affect the atomic energy levels at a level about 10^{-5} rydberg. Here's a catalog of these effects:

Cause	Result	How Observed
Finite Mass	Mass Shift	Isotope shifts
Finite Volume of Charge	Volume Shift	
Magnetic Dipole ($I \geq 1/2$)	Hyperfine structure	Energy splittings
Electric Quadrupole ($I \geq 1$)	Hyperfine structure	

The first two effects produce only a small shift of the spectral line, and thus the only quantity accessible to measurement is the variation of the line position between different isotopes of the same element. (In atoms with only one or two electrons it may be possible to predict the position of a line with significant accuracy to deduce the isotope shift absolutely.) Laser spectroscopy makes it possible to measure isotope shifts to at least 10^{-9} Ry or $10^{-3} - 10^{-4}$ of the shift.

The moments of the nucleus couple to its spin which interacts with the angular momentum of the rest of the atom. This splits the energy levels of the atom according to the magnitude $|\mathbf{F}|$, where $\mathbf{F} = \mathbf{I} + \mathbf{J}$. The resulting hyperfine structure can be measured with almost limitless precision (certainly $< 10^{-18}$ Rydberg) using the techniques of RF spectroscopy. Hyperfine transitions in Cs and H are currently the best available time and frequency standards. Generally speaking, magnetic dipole interactions predominate in atoms and electric quadrupole interactions in molecules.

With the exception of the mass shift, the manifestations of nuclear structure in atomic spectra provide important information on the static properties of nuclei which are among the most precise information about nuclei. Unfortunately the great precision of the atomic measurements is generally lost in deducing information about nuclear structure because the core electrons affect the magnetic and electric interactions of the valence electrons with the nucleus.

4.1 Hyperfine interaction

4.1.1 Introduction

Hyperfine structure, as its name suggests, is extremely small on the scale of atomic interactions. To give an idea of its size, note that fine structure, which arises from relativistic effects and the spin-orbit interaction, is $O(\alpha^2)$ (i.e. of order α^2 on the scale of atomic interactions). The magnetic hyperfine interaction, which arises from the interaction of the nuclear magnetic moment with the surrounding electrons, is $O(\alpha^2 m_e/M_p)$, which is approximately 1000 times smaller. Nevertheless, studies of hyperfine structure have played an important role in the determination of nuclear properties. Perhaps more relevant today is the role of hyperfine structure in many laser-atomic experiments, particularly those that involve manipulating atoms with light. This is because hyperfine structure affects the optical selection rules and the transfer of momentum and angular momentum to atoms by light. The magnetic hyperfine interaction is most important for atoms with an unpaired electron. Consequently, the alkali-metal atoms, which are the workhorses for laser-atomic physics, all display prominent hyperfine structure, sometimes to the despair of the experimenter.

The fact that the nucleus is a charge cloud with angular momentum suggests the possibility that it might possess magnetic and electric moments. Time reversal and parity invariance restrict the possible magnetic moments to dipole, octopole, ... and the possible electric moments to monopole ($Q = Ze$), quadrupole... The magnetic dipole and electric quadrupole interactions are dominant in the hyperfine interaction.

The magnetic dipole moment can be measured only if the nucleus has $I \geq 1/2$, and it splits only those levels for which $J \geq 1/2$. Similarly, the electric quadrupole interaction is observable only when I and J are both ≥ 1 .

Note that the units used in this section are ESU.

4.1.2 Classical analysis of the magnetic hyperfine interaction

The magnetic moment of the nucleus is generally expressed in terms of the nuclear magneton,

$$\mu_N = \frac{e\hbar}{2M_p c} \quad (4.1)$$

and the nuclear g-factor, g_I

$$\mu = g_I \mu_N I. \quad (4.2)$$

In some cases it is convenient to express the nuclear moment in terms of the Bohr magneton. This is done by defining the g-factor g_I' by

$$\mu = g_I' \mu_B I. \quad (4.3)$$

To emphasize the fact that the nuclei are complex particles we note that the g-factors of the neutron and proton are

$$g_P = +5.586 \quad g_N = -3.826, \quad (4.4)$$

neither one of which is close to a simple integer.

The magnetic moment of the nucleus couples to the magnetic field produced at the nucleus by the electrons in the atom. As a result \mathbf{J} and \mathbf{I} are coupled together to form \mathbf{F} , the total angular momentum of the entire atom

$$\mathbf{F} = \mathbf{J} + \mathbf{I} \quad (4.5)$$

The magnetic coupling between \mathbf{J} and \mathbf{I} adds a term to the Hamiltonian for the magnetic dipole hyperfine structure which is the interaction between a nucleus with magnetic moment $\vec{\mu}_I$, and the magnetic field \mathbf{B}_J due to a single valence electron.

$$H = -\vec{\mu}_I \cdot \mathbf{B}_J \quad (4.6)$$

The electron's magnetic field is proportional to its angular momentum \mathbf{J} , and so we can write

$$H = ah\mathbf{I} \cdot \mathbf{J} \quad (4.7)$$

Writing $\mathbf{I} \cdot \mathbf{B}_J$ as $(\mathbf{I} \cdot \mathbf{J})(\mathbf{J} \cdot \mathbf{B}_J)/J^2$, we have

$$ah = -\frac{\mu_I}{I} \langle \frac{\mathbf{J} \cdot \mathbf{B}_J}{J^2} \rangle \quad (4.8)$$

The constant a is called the hyperfine coupling constant. By convention, it is written in units of frequency.

There are two contributions to \mathbf{B}_J , orbital and spin: $\mathbf{B}_J = \mathbf{B}_L + \mathbf{B}_S$. We shall first evaluate the fields classically. The magnetic moment of the electron is given by

$$\vec{\mu}_e = -g_e\mu_B\mathbf{S} \quad (4.9)$$

where μ_B is the Bohr magneton. (The negative sign is taken by convention, so that $g_e \sim 2$ is a positive number.) Then,

$$\mathbf{B}_L(0) = \int \frac{I d\mathbf{s} \times \hat{\mathbf{r}}}{r^2} \rightarrow -e\mathbf{v} \times \left(\frac{-\mathbf{r}}{r^3} \right) = -2\mu_B \frac{\mathbf{L}}{r^3} \quad (4.10)$$

$$\mathbf{B}_S(0) = -\frac{1}{r^3} [\vec{\mu}_e - 3(\vec{\mu}_e \cdot \hat{\mathbf{r}})\hat{\mathbf{r}}] = +g_e \frac{\mu_B}{r^3} [\mathbf{S} - 3(\mathbf{S} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}}] \quad (4.11)$$

$$\mathbf{B}_J(0) = -\frac{2\mu_B}{r^3} \left[\mathbf{L} - \frac{g_e}{2} (\mathbf{S} - 3(\mathbf{S} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}}) \right]. \quad (4.12)$$

We need to evaluate

$$\langle \mathbf{J} \cdot \mathbf{B}_J \rangle = -\frac{2\mu_B}{r^3} [\ell(\ell+1) - S(S+1) + \langle 3(\mathbf{S} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} \cdot (\mathbf{L} + \mathbf{S}) \rangle] \quad (4.13)$$

Using $\langle (\mathbf{S} \cdot \hat{\mathbf{r}})^2 \rangle = \langle (\hat{\sigma} \cdot \hat{\mathbf{n}}/2)^2 \rangle = 1/4$, $\hat{\mathbf{r}} \cdot \mathbf{L} = 0$, and $S(S+1) = 3/4$, we obtain

$$\langle \mathbf{J} \cdot \mathbf{B}_J \rangle = -2\mu_B \langle \frac{1}{r^3} \rangle \ell(\ell+1) \quad (4.14)$$

So after all this work, the field turns out to depend only on ℓ . From Eq. 4.8, we obtain

$$ah = +\frac{g_e\mu_I\mu_B}{I} \langle \frac{1}{r^3} \rangle \frac{\ell(\ell+1)}{J(J+1)} \quad (4.15)$$

For a hydrogenic atom

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{n^3} \frac{1}{\ell(\ell+1)(\ell+1/2)a_0^3} \quad (4.16)$$

Writing $\mu_I = g_I \mu_N I = g_I \mu_B (m_e/M_p) I$, we finally obtain

$$ah = \frac{g_e \mu_B Z^3 g_I \frac{m_e}{M_p}}{n^3 a_0^3} \frac{1}{(\ell+1/2)J(J+1)} \quad (4.17)$$

For hydrogen in the ground state, Eq. 4.17 gives

$$ah = \frac{4g_e}{3} hcR\alpha^2 g_I \frac{m_e}{M_p} \quad (4.18)$$

However, the argument has a flaw: $\langle 1/r^3 \rangle$ diverges for s -states. We must treat these states as a special case.

The orbital magnetic field is absent in s -states. However, the electron has finite probability of being at the origin and it must be regarded as a magnetic “cloud” with magnetization

$$\mathbf{M}(\mathbf{r}) = \vec{\mu}_e |\Psi(\mathbf{r})|^2 \quad (4.19)$$

The magnetization gives rise to a field at the origin

$$\mathbf{B}(0) = \mathbf{H}(0) + 4\pi\mathbf{M}(0) \quad (4.20)$$

The magnetization can be viewed as the sum of a small uniform sphere at the origin, plus a hollow sphere containing the remainder of the magnetization. It is easily shown that the field due to the hollow sphere vanishes. However, the uniform sphere give rise to a finite value of $\mathbf{H}(0)$ due to an equivalent surface magnetic charge density

$$\sigma_m = \mathbf{M}(0) \cdot \hat{\mathbf{n}} = M(0) \cos \theta \quad (4.21)$$

which acts as the source of \mathbf{H} .

$$H_z(0) = - \int \frac{\sigma \cos \theta dS}{r^2} = -\frac{4\pi}{3} M(0). \quad (4.22)$$

Since $\mathbf{M}(0) = \vec{\mu}_e |\psi(0)|^2 = -g_e \mu_B \mathbf{S} |\psi(0)|^2$,

$$\mathbf{B}(0) = -\frac{8\pi}{3} g_e f \mu_B \mathbf{S} |\Psi(0)|^2 \quad (4.23)$$

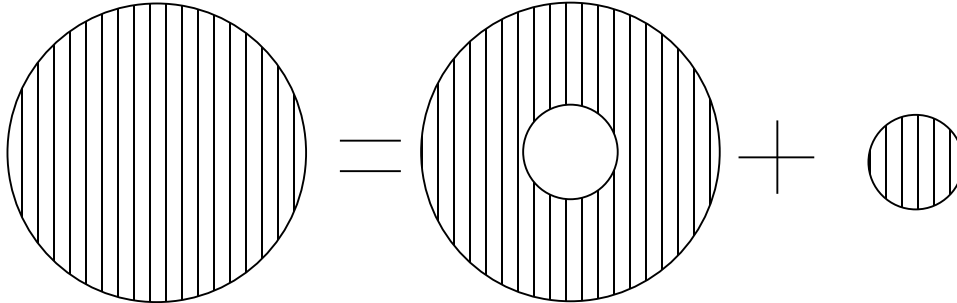


Figure 4.1. Decomposition of a spherically symmetric cloud of magnetization for finding the field at its center.

which leads to the same result as Eq. 4.17. This s -state interaction is often called the “contact” (in the sense of touch) term.

We can summarize these results by combining Eqs. 4.12 and Eq. 4.23 taking $g_e = 2$:

$$\mathbf{B}(0) = -2\mu_B \left[\frac{\mathbf{L}}{r^3} - \frac{\mathbf{S}}{r^3} + \frac{3(\mathbf{S} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}}}{r^3} - \frac{8}{3}\pi\delta(\mathbf{r})\mathbf{S} \right] \quad (4.24)$$

The first three terms in the bracket average to zero in an s -state; the last term contributes only in an s -state.

4.1.3 Quantum mechanical treatment

The nucleus gives rise to the vector potential

$$\mathbf{A}_I = \frac{\vec{\mu}_I \times \mathbf{r}}{r^3} \quad (4.25)$$

The atomic Hamiltonian is

$$H = \frac{1}{2m}(\mathbf{p} + e\mathbf{A}_I)^2 + V(\mathbf{r}) - \vec{\mu}_e \cdot (\nabla \times \mathbf{A}_I) \quad (4.26)$$

(We continue to use the convention that e is the magnitude of the electron charge.) The last term describes the interaction of the electron and the magnetic field due to the nucleus.

We can write $H = H_0 + H_{\text{hf}}$, where, neglecting the term in A_I^2

$$H_{\text{hf}} = \frac{e}{2m}(\mathbf{p} \cdot \mathbf{A}_I + \mathbf{A}_I \cdot \mathbf{p}) + g_e\mu_B\mathbf{S} \cdot (\nabla \times \mathbf{A}_I) \quad (4.27)$$

We can take \mathbf{A}_I to obey the Coulomb gauge $\nabla \cdot \mathbf{A}_I = 0$. Then the first term in Eq. 4.27 gives

$$\mathbf{p} \cdot \mathbf{A}_I = \frac{\mathbf{p} \cdot (\vec{\mu}_I \times \mathbf{r})}{r^3} = \frac{\vec{\mu}_I \cdot (\mathbf{r} \times \mathbf{p})}{r^3} = \frac{\hbar\vec{\mu}_I \cdot \mathbf{L}}{r^3} \quad (4.28)$$

and

$$H_{\text{hf}}^{\text{orb}} = \frac{2\mu_B\vec{\mu}_I \cdot \mathbf{L}}{r^3} \quad (4.29)$$

The second term can be transformed using

$$\nabla \times \left[\frac{\vec{\mu}_I \times \mathbf{r}}{r^3} \right] = -\nabla \times \left[\vec{\mu}_I \times \nabla \frac{1}{r} \right] \quad (4.30)$$

Using this result, the second term in Eq. 4.27 can be written

$$H_{\text{hf}}^{\text{spin}} = g_e\mu_B \left[(\mathbf{S} \cdot \nabla) \left(\vec{\mu}_I \cdot \nabla \frac{1}{r} \right) - \frac{1}{3}\mathbf{S} \cdot \vec{\mu}_I \nabla^2 \frac{1}{r} \right] - \frac{2}{3}g_e\mu_B\mathbf{S} \cdot \vec{\mu}_I \nabla^2 \frac{1}{r} \quad (4.31)$$

In a spherical state the average of the first factor in the bracketed term becomes

$$\langle (\mathbf{S} \cdot \nabla) \left(\vec{\mu}_I \cdot \nabla \frac{1}{r} \right) \rangle = \left\langle \left(S_x\mu_x \frac{\partial^2}{\partial x^2} + S_y\mu_y \frac{\partial^2}{\partial y^2} + S_z\mu_z \frac{\partial^2}{\partial z^2} \right) \right\rangle \quad (4.32)$$

plus cross terms which average to zero. Consequently,

$$\langle (\mathbf{S} \cdot \nabla) \left(\vec{\mu}_I \cdot \nabla \frac{1}{r} \right) \rangle = \frac{1}{3}\mathbf{S} \cdot \vec{\mu}_I \nabla^2 \frac{1}{r}, \quad (4.33)$$

which is cancelled by the second factor. For states that vanish at the origin,

$$(\mathbf{S} \cdot \nabla)(\vec{\mu}_I \cdot \nabla \frac{1}{r}) = -\frac{\mathbf{S} \cdot \vec{\mu}_I}{r^3} + \frac{3(\mathbf{S} \cdot \hat{\mathbf{r}})(\vec{\mu}_I \cdot \hat{\mathbf{r}})}{r^3} \quad (4.34)$$

Taking $g_e = 2$, we have

$$H_{\text{hf}}^{\text{spin}} = -2\mu_B \left[\frac{\mathbf{S} \cdot \vec{\mu}_I}{r^3} - \frac{3(\mathbf{S} \cdot \hat{\mathbf{r}})(\vec{\mu}_I \cdot \hat{\mathbf{r}})}{r^3} \right] - 16\frac{\pi}{3}\mu_B \mathbf{S} \cdot \vec{\mu}_I \delta(\mathbf{r}). \quad (4.35)$$

where it is understood that the first term vanishes in S states. We finally obtain

$$H_{\text{hf}} = 2\mu_B \frac{\mu_I}{I} \mathbf{I} \cdot \left[\frac{1}{r^3} (\mathbf{L} - \mathbf{S} + 3(\mathbf{S} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}}) - \frac{8\pi}{3} \mathbf{S} \delta(\mathbf{r}) \right] \quad (4.36)$$

Writing this as $H_{\text{hf}} = ah \mathbf{I} \cdot \mathbf{J}$, we obtain the result found by the classical argument, Eq. 4.24.

4.1.4 Hyperfine structure at zero magnetic field

The Hamiltonian at zero magnetic field is

$$H = ah \mathbf{I} \cdot \mathbf{J} \quad (4.37)$$

The total angular momentum is $\mathbf{F} = \mathbf{I} + \mathbf{J}$. In zero or low field, F and m_F are good quantum numbers. A “good” quantum number is the eigenvalue of an operator. At zero field, for instance, eigenfunctions of H are eigenfunctions of $\mathbf{F} = \mathbf{I} + \mathbf{J}$.

Physically, \mathbf{I} and \mathbf{J} are tightly coupled by the $ah\mathbf{I} \cdot \mathbf{J}$ interaction: they precess about each other, and about \mathbf{F} . Using $\mathbf{F}^2 = (\mathbf{I} + \mathbf{J})^2$, we obtain

$$\langle \mathbf{I} \cdot \mathbf{J} \rangle = [F(F+1) - J(J+1) - I(I+1)]/2 \quad (4.38)$$

and for the energy levels

$$W(F, m) = \frac{ah}{2} [F(F+1) - J(J+1) - I(I+1)]. \quad (4.39)$$

Note that $m = \langle F_z \rangle$ remains a good quantum number at all fields. (The symbols F and I are used both for operators and eigenvalues: the meaning is clear from the context). F has values $|I - J|, |I - J + 1| \cdots |I + J|$. The interval between adjacent terms is

$$W(F) - W(F-1) = haF \quad (4.40)$$

This result, known as the Landé Interval Rule, played an important role in the early development of the theory of hyperfine structure. Furthermore, it is easy to show that

$$\sum_F (2F+1)W(F) = 0 \quad (4.41)$$

so that the “center of gravity” of a hyperfine multiplet is zero.

4.1.5 Electric quadrupole interaction

If the nucleus does not have a spherically symmetric charge distribution, it probably has a non-zero electric quadrupole moment

$$Q = \frac{1}{e} \int d^3r \rho(\mathbf{r}) [3z^2 - r^2] \quad (4.42)$$

which is < 0 for an oblate charge distribution. In contrast to the nuclear magnetic dipole, which is predominantly determined by the unpaired nucleons, Q is sensitive to collective deformations of the nucleus. Some nuclei are observed with 30% differences between polar and equatorial axes, so Q can be comparable to $\langle r^2 \rangle$, i.e. $\approx 10^{-24} \text{ cm}^2$.

The interaction energy of the quadrupole moment Q with the electron can be found by expanding the term $|\mathbf{r}_e - \mathbf{r}_N|^{-1}$ in spherical harmonics and evaluating the resulting expressions in terms of Clebsch-Gordon coefficients. The resulting energy shifts are then

$$E_{hf}^Q = BC(C + 1) \quad (4.43)$$

where

$$B = \frac{3(Q/a_o^2)}{8I(2I - 1)J(J + 1)} < \frac{1}{r^3} > R_\infty \quad (4.44)$$

and

$$C = [F(F + 1) - J(J + 1) - I(I + 1)] \quad (4.45)$$

[Note that $\mathbf{I} \cdot \mathbf{J}/\hbar^2$, which was involved in $H_{\text{mag}}^{\text{hf}}$, is equal to $C/2$].

The preceding expressions, like the corresponding ones for the magnetic interactions, have several significant omissions. The most important are relativistic corrections and core shielding corrections. Calculations of core shielding have been made by Sternheimer [2], and the quadrupole shielding by the core is sometimes prefixed by his name.

4.1.6 Order of magnitude of hyperfine structure

If one examines the magnetic hyperfine structure in Eq. 4.15, it is obviously quite similar to the expression for the fine structure expression in Chapter 3. The ratio is

$$\frac{E^{\text{mag}_{\text{hfs}}}}{E^{\text{fs}}} \approx g_I \left(\frac{m}{M_p} \right) \frac{1}{Z} \quad (4.46)$$

which is typically 10^{-3} to 10^{-4} . For a neutral atom, one can estimate

$$\frac{E_{\text{mag}}^{\text{hfs}}}{\hbar} = (\ell + 3/4)^{-3} \text{ GHz} \quad (4.47)$$

with a factor of 10 spread in either direction.

The quadrupole interaction is generally considerably smaller. An estimate is

$$B/\hbar \approx 0.01 Z(\ell + 1/2)^{-3} \text{ GHz} \quad (4.48)$$

Thus one generally expects that magnetic hyperfine structure dominates electric hyperfine structure in atoms. The opposite is generally true in molecules for two reasons: unpaired electrons are relatively rare, and the molecular binding mechanism can create large electric field gradients at the sites of the nuclei.

In concluding this discussion of hyperfine structure in atoms I would like to point out that the preceding formulae are, except in hydrogenic atoms, only approximations and never permit one to extract the nuclear dipole or quadrupole moment with the full accuracy of laser spectroscopy experiment—let alone R.F. spectroscopy experiments. Thus A and B in the combined hyperfine energy formula

$$E^{\text{hfs}} = E_{\text{mag}}^{\text{hfs}} + E_{\text{el}}^{\text{hfs}} = \frac{1}{2}AC + BC(C + 1)$$

(with C from Eq. 4.45) should be regarded primarily as empirical constants from the standpoint of atomic physics. Even if the problems of connecting A and B with the nuclear moments could be solved, the principal result would be better measurements of nuclear properties.

4.2 Isotope Effects

When comparing the spectral lines originating from atoms whose nuclei differ only in the number of neutrons (eg. different isotopes of the same element), effects due to the finite mass and volume of the nucleus become apparent. Even neglecting hyperfine structure (by taking the center of gravity of the observed splitting), the spectral lines of the different isotopes vary slightly in position—generally at the many parts per million level. The difference between the lines of the various isotopes is referred to as the isotope shift: it is observed to have both positive (heavier isotope has higher energy spacing) and negative values.

General speaking, light ($A < 40$) elements have positive frequency shift whereas heavy elements ($A > 60$) have negative shifts. This reflects the contribution of two distinct physical processes to the shift; the finite mass shift (almost always positive), and the nuclear volume shift (almost always negative). These will be discussed separately.

4.2.1 Mass effect

The origin of the mass effect is obvious from the Bohr energy level formula

$$E_n = E_n^{\circ} \left(\frac{M}{m + M} \right) \approx E_n^{\circ} \left(1 - \frac{m}{M} \right) \quad (4.49)$$

where the term involving m/M comes from solving the two body electron-nucleus (of mass M) system using the relative coordinate and associated reduced mass. Obviously increasing M increases E_n .

In two (or more) electron atoms the situation becomes more complicated due to the relative motion of the electrons. It would, for example, be possible to arrange the electrons symmetrically on opposite sides of the nucleus in which case there would be zero isotope effect. The virial theorem assures us that the mean value of the kinetic energy equals the negative of the total energy, so if we treat the nuclear motion as a perturbation on a fixed nucleus solution, the mass effect will be:

$$\Delta E_{n,M} = \frac{-p^2}{2M} = -\frac{1}{2M} \left[\sum_i \mathbf{p}_i \right]^2 = -\frac{m}{M} \left[\underbrace{\frac{1}{2m} \sum p_i^2}_{\text{Normal Shift}} + \underbrace{\frac{1}{2m} \sum_{i \neq j} \mathbf{p}_i \cdot \mathbf{p}_j}_{\text{Specific Shift}} \right] \quad (4.50)$$

The first term is called the normal shift since (using the virial theorem again) it is

$$\Delta E_{n,M}^{\text{Normal}} = -\frac{m}{M} E_n^0 \quad (4.51)$$

The second term is called specific because it depends on the atom's quantum state. A discussion can be found in Sobel'man (pp. 224-6). $\Delta E^{\text{Specific}} = 0$ unless there are two or more valence electrons. For electronic configuration specified by quantum numbers n, s, ℓ , Sobel'man finds:

$$\Delta E_{ns,n'\ell}^{\text{specific}} = (1 - 2S) \frac{m}{M} \frac{3f_{ns,n'\ell}}{2} \hbar \omega_{n's',n\ell} \quad (4.52)$$

where $3f_{ns,n'\ell}$ is the oscillator strength (see Chapter ??). Thus the specific shift has opposite signs for $S = 1$ and $S = 0$ states—a reflection of the fact that the specific isotope shift is closely related to the exchange interaction. Eq. 4.52 also reflects the general result that $\Delta E^{\text{Specific}} = 0$ unless the two electrons are connected by an allowed dipole transition (otherwise f will vanish). Furthermore the specific isotope shift is of the same order of magnitude as the normal isotope shift: for $f > 2/3$, in fact, it can be larger (reversing the sign of the mass dependence of the isotope effect.)

The preceding discussion shows that the fractional energy shift of a level due to the mass of the nucleus decreases rapidly with increasing mass of the nucleus. The normal part of this shift has a variation in the fractional magnitude due to a change ΔM in the mass of the isotope of

$$\frac{\Delta E_{n,M+\Delta M}^{\text{Normal}} - \Delta E_{n,M}^{\text{Normal}}}{E_n} = \left(\frac{m}{M + \Delta M} - \frac{m}{M} \right) = \frac{m}{M} \left(\frac{\Delta M}{M} \right) \quad (4.53)$$

which decreases as M^{-2} , reaching 10 parts per million for a nucleus with $A = 54$ (assuming $\Delta M = 1$).

4.2.2 Volume effect

Inside the nucleus, the electrostatic potential no longer behaves like Ze/r , but is reduced from this value. If the valence electron(s) penetrate significantly into this region (eg. for s electrons) then its energy will rise, relative to the value for a point nucleus, because of this reduced potential. Adding neutrons to the nucleus generally spreads out the charge distribution, causing a further rise in its energy. This reduction in the binding energy results in a decrease of the transition energy and therefore to a negative mass shift (assuming that the s state is the lower energy state involved in the transition).

For an s state, the density of the electron probability distribution at the nucleus is given by the semi-empirical Fermi-Segré formula [1]:

$$|\Psi_s(0)|^2 = \frac{Z_a^2 Z}{\pi a_0^2 n^*3} \left(1 + \left| \frac{\partial \delta_s}{\partial n} \right| \right) \quad (4.54)$$

where δ_s is the quantum defect and $Z_a e$ the charge of the atomic core. Combining this with a model of the nuclear charge cloud results (Sobel'man p. 229) in the nuclear volume correction to the energy (of an s electron):

$$\Delta E_n^V = Z_a^2 \frac{R_\infty}{n^*3} \left(1 + \left| \frac{\partial \delta_s}{\partial n} \right| \right) C \quad (4.55)$$

with

$$C = \frac{4(\gamma + 1)}{[\Gamma(2\gamma + 1)]^2} B(\gamma) \left(\frac{2Zr_o}{a_o} \right)^{2\gamma} \frac{\delta r_o}{r_o} \quad (4.56)$$

where

$$\gamma = [1 - \alpha^2 Z^2]^{1/2} \quad (4.57)$$

Γ is the gamma function $\Gamma(N + 1) = N!$, $B(\gamma)$ is a factor which depends on the nuclear charge distribution. For a charged shell

$$B(\gamma) = (2\gamma + 1)^{-1} \quad (4.58)$$

and for a uniform charge

$$B(\gamma) = (2\gamma + 1)^{-1} \left(\frac{3}{2\gamma + 3} \right) \quad (4.59)$$

The nuclear radius is taken as (for atomic number A)

$$r_o = 1.15 \times 10^{-15} A^{1/3} m. \quad (4.60)$$

so that

$$\frac{\delta r_o}{r_o} = \frac{\delta A}{3A} \quad (4.61)$$

There are obviously a number of assumptions in these equations, and they should not be expected to work as well as expressions for the nuclear mass shift. Sobel'man states that the observed shift is generally 1/2 to 3/4 of the one given above except for non-spherical nuclei (eg. rare-earth nuclei) which have anomalously large shifts.

References for Chapter 4

- [1] E.Fermi and E. Segré, Memorie dell 'Accademia d'Italia **4**(Fisica), 131. An English translation is in Hindmarsh p. 259.
- [2] R.M. Sternheimer, Phys. Rev. **164**, 10 (1967).

Chapter 5

Atoms in Magnetic Fields

5.1 The Landé g -factor

In this section we treat the interaction of the electron's orbital and spin angular momentum with external static magnetic fields. Previously, in the chapter on fine structure, we have considered the spin-orbit interaction: the coupling of electron spin to the magnetic field generated by the nucleus (which appears to move about the electron in the electron's rest frame). The spin orbit interaction causes the orbital and spin angular momenta of the electron to couple together to produce a total spin which then couples to the external field; the magnitude of this coupling is calculated here for weak external fields.

5.1.1 Magnetic moment of circulating charge (classical)

The energy of interaction of a classical *magnetic moment* $\vec{\mu}$ with a magnetic field \mathbf{B} is

$$U = -\vec{\mu} \cdot \mathbf{B} \quad (5.1)$$

indicating that the torque tends to align the moment along the field. In classical electrodynamics the magnetic moment of a moving point particle about some point in space is independent of the path which it takes, but depends only on the product of the ratio of its charge to mass m , and angular momentum ℓ . This result follows from the definitions of angular momentum

$$\mathbf{L} \equiv \mathbf{r} \times \mathbf{p} = m[\mathbf{r} \times \mathbf{v}] \quad (5.2)$$

and magnetic moment

$$\vec{\mu} \equiv \frac{1}{2} \mathbf{r} \times \mathbf{i} = \frac{q}{2} [\mathbf{r} \times \mathbf{v}] \quad (5.3)$$

where \mathbf{i} is the current and \mathbf{v} the velocity (see Jackson Ch.5). The equality of the bracketed terms implies

$$\vec{\mu} = \frac{q}{2m} \mathbf{L} \equiv \gamma_\ell \mathbf{L} \quad (5.4)$$

where γ_ℓ is referred to as the *gyromagnetic ratio*. This is a general result for any turbulently rotating blob provided only that it has a constant ratio of charge to mass throughout.

For an electron with orbital angular momentum ℓ

$$\vec{\mu}_\ell = -\frac{e}{2m} \mathbf{L} \equiv -\mu_B \mathbf{L} / \hbar \quad (5.5)$$

which is the classical result, and μ_B is the *Bohr magneton*:

$$\mu_B = \frac{e\hbar}{2m} = 9.27408(4) \times 10^{-24} \text{ J T}^{-1} \rightarrow 1.39983 \times 10^4 \text{ MHz} \times B/(\text{Tesla}) \quad (5.6)$$

5.1.2 Intrinsic electron spin and magnetic moment

When Uhlenbeck and Goudsmit suggested [1] that the electron had an intrinsic spin $S = \frac{1}{2}$, it soon became apparent that it had a magnetic moment twice as large as would be expected on the basis of Eq. 5.4. (This implies that the electron cannot be made out of material with a uniform ratio of charge to mass.) This is accounted for by writing for the *intrinsic electron moment*

$$\vec{\mu}_s = -g_e \mu_B \mathbf{S} / \hbar \quad (5.7)$$

where the quantity $g_e = 2$ is called the electron g -factor. (The negative sign permits treating g_e as a positive quantity, which is the convention.) This factor was predicted by the Dirac theory of the electron, probably its greatest triumph. Later, experiments by Kusch, followed by Crane et al., and then by Dehmelt and coworkers, have shown (for both electrons and positrons).

$$\frac{g_e}{2} = 1.0011596521869(41) \quad (5.8)$$

This result has been calculated from quantum electrodynamics, which gives

$$\frac{g_e}{2} = 1 + \frac{1}{2} \left(\frac{\alpha}{\pi} \right) - 0.3258 \left(\frac{\alpha}{\pi} \right)^2 + 0.13 \left(\frac{\alpha}{\pi} \right)^3 + \dots \quad (5.9)$$

The agreement between the prediction of quantum electrodynamics and experiment on the electron g -factor is often cited as the most precise test of theory in all of physics.

5.1.3 Vector model of the Landé g -factor

In zero or weak magnetic field the spin orbit interaction couples \mathbf{S} and \mathbf{L} together to form $\mathbf{J} = \mathbf{L} + \mathbf{S}$, and this resultant angular momentum interacts with the applied magnetic field with an energy

$$U = -g_j \mu_B \mathbf{B} \cdot \mathbf{J} / \hbar \quad (5.10)$$

which defines g_j .

The interaction of the field is actually with $\vec{\mu}_s$ and $\vec{\mu}_\ell$, however g_j is not simply related to these quantities because $\vec{\mu}_s$ and $\vec{\mu}_\ell$ precess about \mathbf{J} instead of the field. As Landé showed in investigations of angular momentum coupling of different electrons [2], it is a simple matter to find g_j by calculating the sum of the projections of $\vec{\mu}_s$ and $\vec{\mu}_\ell$ onto \mathbf{J} .

The projection of $\vec{\mu}_\ell$ on \mathbf{J} is

$$\mu_{\ell j} = \frac{-\mu_B |\mathbf{L}|}{\hbar} \frac{\mathbf{L} \cdot \mathbf{J}}{|\mathbf{L}| |\mathbf{J}|} \quad (5.11)$$

The projection of $\vec{\mu}_s$ on \mathbf{J} is

$$\mu_{s j} = -g_e \mu_B \frac{|\mathbf{S}|}{\hbar} \frac{\mathbf{S} \cdot \mathbf{J}}{|\mathbf{S}| |\mathbf{J}|} \quad (5.12)$$

The definition of g_j gives

$$g_j = -\frac{(\mu_{\ell j} + \mu_{s j})}{|\mathbf{J}|\mu_B/\hbar} \quad (5.13)$$

Taking $g_e = 2$

$$g_j = \frac{\mathbf{L} \cdot (\mathbf{L} + \mathbf{S}) + 2\mathbf{S} \cdot (\mathbf{L} + \mathbf{S})}{|\mathbf{J}|^2} \quad (5.14)$$

$$= 1 + \frac{j(j+1) + s(s+1) - \ell(\ell+1)}{2j(j+1)} \quad (5.15)$$

using $2\mathbf{L} \cdot \mathbf{S} = \mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2$.

If a transition from a level with angular momentum j' is to a level with j'' takes place in a magnetic field, the resulting spectral line will be split into three or more components—a phenomenon known as the *Zeeman* effect. For transitions with a particular Δm , say $\Delta m = -1$, the components will have shifts

$$\Delta E_{z,m,-1} = [g_{j'}m - g_{j''}(m-1)]\mu_B B = [(g_{j'} - g_{j''})m - g_{j''}]\mu_B B \quad (5.16)$$

If $g_{j'} = g_{j''}$ (or if j' or $j'' = 0$) then $\Delta E_{z,m,-1}$ will not depend on m (or there will be only one transition with $\Delta m = -1$) and there will be only 3 components of the line ($\Delta m = +1, 0, -1$); this is called the normal Zeeman splitting. If neither of these conditions holds, the line will be split into more than 3 components and the Zeeman structure is termed “anomalous”—it can't be explained with classical atomic models.

5.2 Hyperfine structure in an applied field

The Hamiltonian in an applied field \mathbf{B}_0 is

$$H = ah\mathbf{I} \cdot \mathbf{J} - \vec{\mu}_J \cdot \mathbf{B}_0 - \vec{\mu}_I \cdot \mathbf{B}_0 = ah\mathbf{I} \cdot \mathbf{J} + g_j\mu_B\mathbf{J} \cdot \mathbf{B}_0 - g_I\mu_B\mathbf{I} \cdot \mathbf{B}_0 \quad (5.17)$$

By convention, we take $\vec{\mu}_J = -g_j\mu_B\mathbf{J}$. Note that we are expressing the nuclear moment in terms of the Bohr magneton, and that $g_I \ll g_j$. (The nuclear moment is often expressed in terms of the nuclear magneton, in which case $\vec{\mu}_I = g'_I\mu_N\mathbf{I}$, where μ_N is the nuclear magneton.) What are the quantum numbers and energies? Before discussing the general solution, let us look at the limiting cases.

5.2.1 Low field

The total angular momentum is $\mathbf{F} = \mathbf{I} + \mathbf{J}$. In low field, F and m_F are good quantum numbers. Each level F contains $(2F+1)$ degenerate states. In a weak field \mathbf{B}_0 the $(2F+1)$ fold degeneracy is lifted. We can treat the terms

$$H_z = -(\vec{\mu}_j + \vec{\mu}_I) \cdot \mathbf{B}_0 \quad (5.18)$$

as a perturbation. \mathbf{J} and \mathbf{I} are not good quantum numbers, only their components parallel to \mathbf{F} are important. Thus

$$\langle \mathbf{J} \cdot \mathbf{B}_0 \rangle = \frac{\langle \mathbf{J} \cdot \mathbf{F} \rangle \mathbf{F} \cdot \mathbf{B}_0}{F^2} \quad (5.19)$$

$$H_z = -\mu_B[-g_j(\mathbf{J} \cdot \mathbf{F}) + g_I(\mathbf{I} \cdot \mathbf{F})] \frac{\mathbf{F} \cdot \mathbf{B}_0}{F^2} \quad (5.20)$$

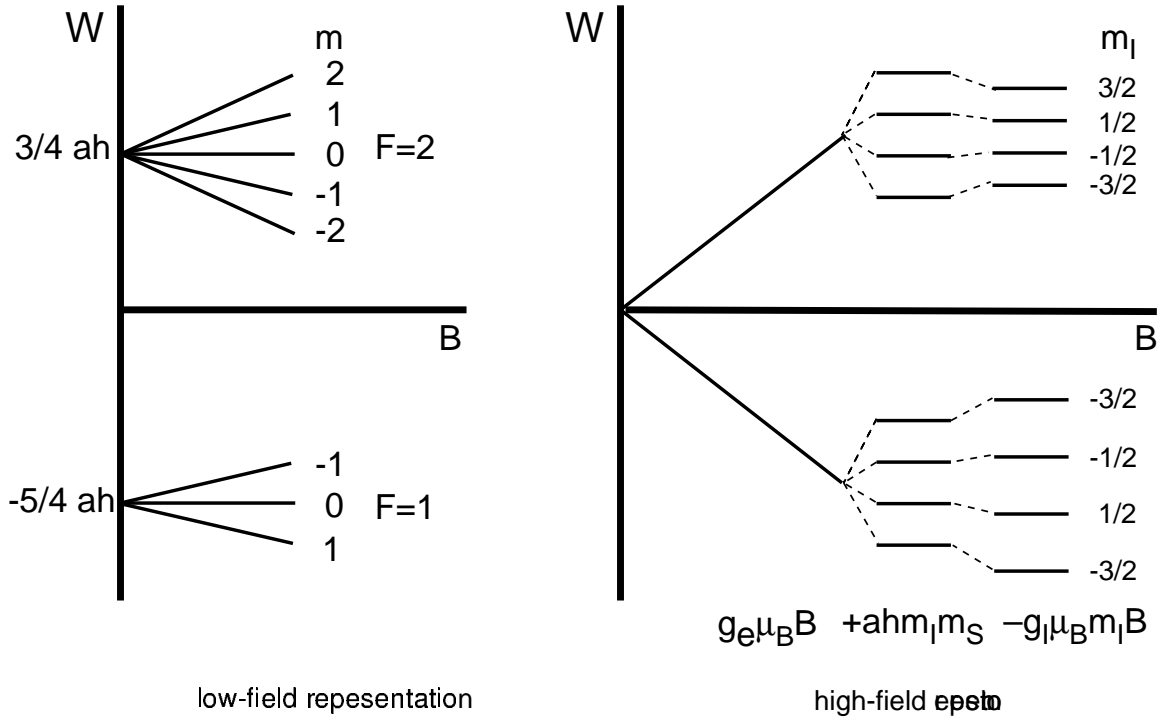


Figure 5.1. Energy level structure for a single-electron atom with nuclear spin $3/2$ in the limits of low and high fields.

Since $g_I \ll g_j$, we can usually neglect it. We can rewrite this result as

$$H_z = g_F \mu_B m B_0 \quad (5.21)$$

$$g_F = \frac{\langle \mathbf{J} \cdot \mathbf{F} \rangle}{F^2} g_j = \frac{g_j}{2} \frac{F(F+1) + j(j+1) - I(I+1)}{F(F+1)} \quad (5.22)$$

For example, let $I = 3/2, j = 1/2; F = 2, 1$. Then

$$F = 2; \quad W(2) = (3/4)ah; \quad g_F = g_j/4 \quad (5.23)$$

$$F = 1; \quad W(1) = -(5/4)ah; \quad g_F = -g_j/4 \quad (5.24)$$

5.2.2 High field

If $\vec{\mu}_j \cdot \mathbf{B}_0 \gg ah\mathbf{I} \cdot \mathbf{J}$, then \mathbf{J} is quantized along \mathbf{B}_0 . Although $\vec{\mu}_I \cdot \mathbf{B}_0$ is not necessarily large compared to the hyperfine interaction, the $\mathbf{I} \cdot \mathbf{J}$ coupling assures that \mathbf{I} is also quantized along \mathbf{B}_0 . Thus m_I and m_j are good quantum numbers. In this case, Eq. 5.17 can be written

$$H = ahm_j m_i + g_j \mu_B m_j B_0 - g_I \mu_B m_I B_0 \quad (5.25)$$

The second term on the right is largest. Usually the first term is next largest, and the nuclear terms is smallest. The diagram below shows low and high field behavior for hyperfine structure for $I = 3/2, j = 1/2$.

5.2.3 General solution

Finding eigenfunctions and eigenvalues of the hyperfine Hamiltonian for arbitrary field requires diagonalizing the energy matrix in some suitable representation. To obtain a rough idea of the expected results, one can smoothly connect the energy levels at low and high field, bearing in mind that $m = m_I + m_j$ is a good quantum number at all fields.

For $J = 1/2$, the eigenvalues of (Eq. 5.17) can be found exactly. The energies are given by the Breit-Rabi formula

$$W(m) = -\frac{1}{2} \frac{\Delta W}{2I+1} - g_I \mu_B B_0 m \pm \frac{\Delta W}{2} \sqrt{1 + \frac{4mx}{2I+1} + x^2}, \quad (5.26)$$

where the + sign is for $F = I + 1/2$, and the - sign is for $F = I - 1/2$. ΔW is the zero field energy separation.

$$\Delta W = W(F = I + 1/2) - W(F = I - 1/2) = ah \left(\frac{2I+1}{2} \right) \quad (5.27)$$

The parameter x is given by

$$x = \frac{(g_e + g_I) \mu_B B_0}{\Delta W} \quad (5.28)$$

Physically, x is the ratio of the paramagnetic interaction (the “Zeeman energy”) to the hyperfine separation. The Breit-Rabi energy level diagram for hydrogen and deuterium are shown below. The units reflect current interest in atom trapping. Low-field quantum numbers are shown. It is left as an exercise to identify the high field quantum numbers.

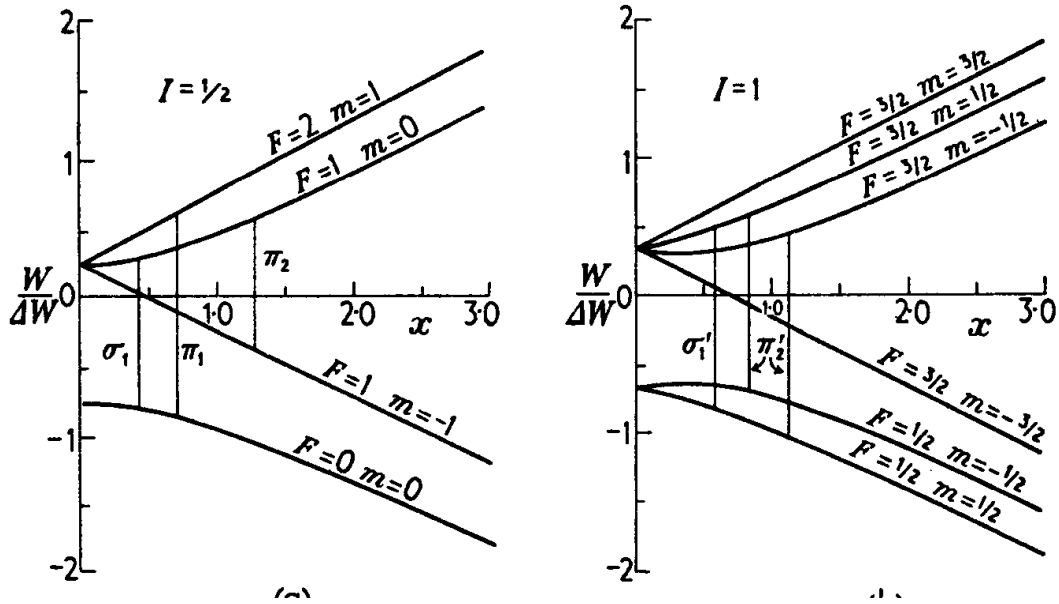


Figure 5.2. Energy level structure for a single-electron atom with nuclear spin $I = 1/2$, such as hydrogen (left), and $I = 1$, such as deuterium (right). From *Molecular Beams* by N.F. Ramsey.

References for Chapter 5

- [1] G.E. Uhlenbeck and S. Goudsmit, *Nature* **117**, 264 (1926).
- [2] A. Landé, *Zeitschrift für Physik* **15**, 189 (1923), English translation on p. 186 of Hindmarsh.