

## 6.1 Nondegenerate Perturbation Theory

Analytic solutions to the Schrödinger equation have not been found for many interesting systems. Fortunately, it is often possible to find expressions which are analytic but only *approximately* solutions.

Consider a one-dimensional example. We have already found the exact analytic solution for the one-dimensional infinite square well,  $H^0$ :  
$$H^0\psi_n^0 = E_n^0\psi_n^0, \quad \langle\psi_n^0|\psi_m^0\rangle = \delta_{nm}.$$

Suppose we change this potential only slightly; *e.g.*, we could add a slight ‘bump’ in the bottom of the well. It is not likely that we can solve for the e.s. of this new Hamiltonian  $H$  exactly, but let’s try to find an approximate solution.

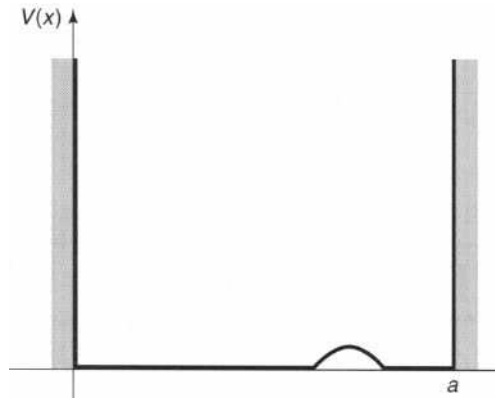


Figure 6.1 - Infinite square well with small perturbation.

Let  $H = H^0 + \lambda H'$ , where  $\lambda$  has been introduced to allow us to 'turn on' the *perturbation* as slowly as we wish.

Given the essential nonlinearity of the whole process of finding e.s., it is not surprising that the changes due to  $H'$  are not linear in  $\lambda$ , but are rather better described as a power series in  $\lambda$ :

$$\begin{aligned}\psi_n &= \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots, \\ E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots\end{aligned}$$

**NB**, the superscripts indicate *powers* of  $\lambda$  but *orders* of perturbation theory for  $\psi$  and  $E$ .

Substituting the eqs. for  $\psi$  and  $E$  into

$H\psi = E\psi$ , we obtain an equation involving all powers of  $\lambda$ . If this equation is to hold for any value of  $\lambda \in \{0, 1\}$ , then it must also hold for the coefficient of *each* power of  $\lambda$

*individually*, yielding

$$\lambda^0: H^0\psi_n^0 = E_n^0\psi_n^0 ;$$

$$\lambda^1: H^0\psi_n^1 + H^1\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0 ;$$

$$\lambda^2: H^0\psi_n^2 + H^1\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0 ;$$

and so forth.

Perturbation theory consists of satisfying

$H\psi = E\psi$  to progressively higher orders of  $\lambda$ .

The value of  $\lambda$  is of no importance now;  $\lambda$  was just a device to help us keep track of the various orders of the perturbation.

**NB**, there do exist  $H'$  for which perturbation theory *cannot* be used.

# First-order perturbation theory

The zeroth order equation has already been solved.

Take the inner product of the first order eq. with  $\psi_n^0$ , yielding

$$\langle \psi_n^0 | H^0 | \psi_n^1 \rangle + \langle \psi_n^0 | H' | \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle.$$

The first terms on each side are equal and  $\langle \psi_n^0 | \psi_n^0 \rangle = 1$ , so that  $E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle$ .

In words, the first-order correction to the energy is the expectation value of the perturbation in the unperturbed state.

To find  $\psi_n^1$ , rewrite the first-order equation as  $(H^0 - E_n^0)\psi_n^1 = -(H' - E_n^1)\psi_n^0$ .

Since the rhs is a known function, the above constitutes an inhomogeneous differential equation for  $\psi_n^1$ , which we know how to solve.

Expand  $\psi_n^1$  in the orthonormal set  $\{\psi_n^0\}$ :

$\psi_n^1 = \sum_{m \neq n} c_{nm} \psi_m^0$ . We can exclude the  $m = n$  term since  $(H^0 - E_n^0)\psi_n^0 = 0$ .

A modest amount of manipulation yields

$$|\psi_n^1\rangle = \sum_{m \neq n} |\psi_m^0\rangle \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0}.$$

**NB**, the derivation which led to this equation breaks down if  $E_m^0 = E_n^0$ , so that its validity is restricted to nondegenerate  $\{\psi_n^0\}$ .

In practice, while  $E^0 + E^1$  is frequently a good approximation for the actual energy,  $\psi^0 + \psi^1$  is often a poor approximation for the w.f.

## Second-order perturbation theory

An expression can be derived for the second-order correction to the energy using the coefficient for  $\lambda^2$  and again taking the inner product with  $\psi_n^0$  and performing a few manipulations:

$$E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}.$$

One could follow this procedure to derive the second-order correction to the e.f., the third-order correction to the e.v., and so forth, but these expressions involve higher order sums over the unperturbed states and are not usually practical to use.

## 6.2 Degenerate Perturbation Theory

Suppose that  $\psi_a^0$  and  $\psi_b^0$  are both e.s. of  $H^0$ , with a common e.v., and that  $\langle \psi_a^0 | \psi_b^0 \rangle = 0$ .

We know that any linear combination of these two states is also an e.s. of  $H^0$  with the same e.v.

Assuming for the moment that  $H'$  will 'lift' this degeneracy, let's replace  $\psi^0$  with  $\alpha\psi_a^0 + \beta\psi_b^0$ , and find the (two sets of) values of  $\alpha$  and  $\beta$  which satisfy the  $\lambda^1$  equation.

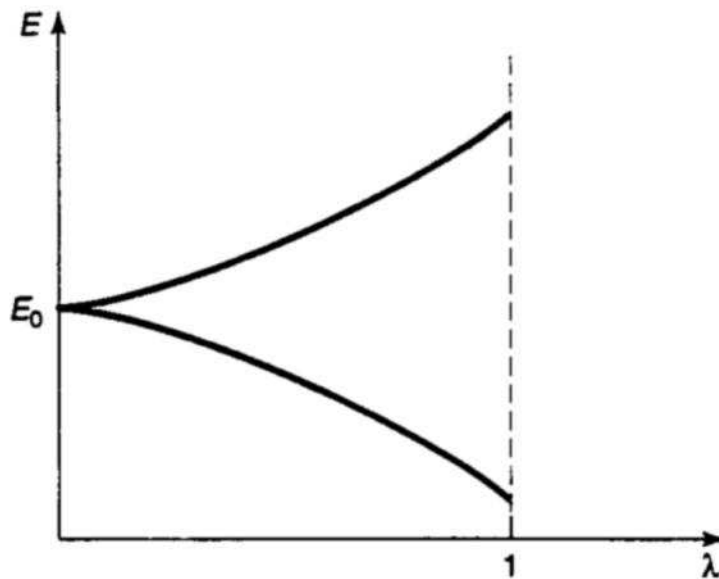


Figure 6.4 - 'Lifting' of a degeneracy by a perturbation.

Substituting for  $\psi^0$  and taking the inner product with  $\psi_a^0$ , we find  $\alpha W_{aa} + \beta W_{ab} = \alpha E^1$ , where  $W_{ij} \equiv \langle \psi_i^0 | H' | \psi_j^0 \rangle$ .

Similarly, the inner product with  $\psi_b^0$  yields  $\alpha W_{ba} + \beta W_{bb} = \beta E^1$ .

These two equations can be written as

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix}.$$

We already know how to solve this set of two coupled linear equations to obtain the two values of  $E^1$  and the corresponding two sets of values of  $\alpha$  and  $\beta$ . The resulting two e.s. are e.s. of both  $H^0$  and  $H'$ .



If  $W_{ab} = 0$ , then  $H'$  does not 'lift' the degeneracy between  $\psi_a^0$  and  $\psi_b^0$ . In that case, the resultant  $\psi$  need not involve both e.s., and the sum over  $m \neq n$  can be modified to exclude in turn each of the degenerate states from the sum to obtain the other.

The generalization to  $n$  degenerate states is straightforward, leading to the e.v. and e.f. in all instances of degeneracy.

The influence of all the nondegenerate e.s. of  $H^0$  can be handled using nondegenerate perturbation theory.

## 6.3 Fine Structure of Hydrogen

In solving for the e.s. of the hydrogen atom, we took  $H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$ . This led to e.f. and e.v. which were in remarkable qualitative agreement with both the original Bohr model and experiment.

But we know that the actual situation is more complicated. For instance, a correct treatment of the masses will assume that both proton and electron rotate about the center of mass. To a first approximation, this can be accommodated by replacing  $m$  with the reduced mass, resulting in no change in the functional form of the e.s.

More significant for the *functional form* are a number of small corrections to the Hamiltonian:

1. The kinetic energy  $T$  must reflect relativity.
2. The spin of the electron couples with the angular momentum of its orbit.

These two corrections are known together as the **fine structure** correction.

3. The **Lamb shift** is associated with quantization of the Coulomb field.
4. The **hyperfine splitting** is due to the interaction between the magnetic dipole moments of the electron and proton.

The hierarchy of these corrections to the Bohr energies of hydrogen is

Bohr energy	of order $\alpha^2 mc^2$
fine structure	of order $\alpha^4 mc^2$
Lamb shift	of order $\alpha^5 mc^2$
hyperfine splitting	of order $(m/m_p)\alpha^4 mc^2$

where  $\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137.036}$  is the fine structure constant.

Apart from the Lamb shift, each of these corrections is considered in turn.

## Relativistic correction

The operator form for  $T$  is based on the formula  $T = \frac{p^2}{2m}$ . Relativistic arguments suggest that  $T$  is given correctly as the total relativistic energy less the rest energy:

$$T = \frac{mc^2}{\sqrt{1 - (v/c)^2}} - mc^2 = mc^2 \left[ \sqrt{1 + \left(\frac{p}{mc}\right)^2} - 1 \right].$$

Assuming that  $\frac{p}{mc}$  is a small number, the square root can be expanded in powers of that number to yield  $T = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \dots$

The lowest-order relativistic contribution is accordingly  $H'_r = -\frac{\hat{p}^4}{8m^3c^2}$ , where  $\hat{p} = (\hbar/i)\nabla$ .

The first-order correction to the energy is given by the expectation value of  $H'$  in the unperturbed state:

$$E_r^1 = -\frac{1}{8m^3c^2} \langle \psi_0 | \hat{p}^4 | \psi_0 \rangle \rightarrow -\frac{1}{8m^3c^2} \langle \hat{p}^2 \psi_0 | \hat{p}^2 \psi_0 \rangle.$$

But  $H\psi_0 = (\frac{\hat{p}^2}{2m} + V)\psi_0 = E\psi_0$ , so that  
 $\hat{p}^2\psi_0 = 2m(E - V)\psi_0$ .

$$\begin{aligned}\therefore E_r^1 &= -\frac{1}{2mc^2} \langle (E - V)^2 \rangle \\ &= -\frac{1}{2mc^2} (E^2 - 2E\langle V \rangle + \langle V^2 \rangle).\end{aligned}$$

The expectation values of  $V$  and  $V^2$  depend only on  $\langle \frac{1}{r} \rangle$  and  $\langle \frac{1}{r^2} \rangle$ , and these can be evaluated in  $\psi^0$ , yielding

$$E_r^1 = -\frac{(E_n^0)^2}{2mc^2} \left( \frac{4n}{l + \frac{1}{2}} - 3 \right).$$

This correction is smaller than  $E_n^0$  by  $\sim 10^{-5}$ .

**NB:** *Nondegenerate* perturbation theory was used in this case even though the  $\psi^0$  are highly degenerate. This worked only because we are using e.f. which are e.s. of  $\hat{L}^2$  and  $\hat{L}_z$  as well as  $H_0$ , and which have unique sets of e.v. when all these operators are *taken together*. In addition,  $H_r'$  commutes with  $\hat{L}^2$  and  $\hat{L}_z$ . Therefore, these e.f were acceptable for this *particular* application of nondegenerate perturbation theory.

# Magnetic moment of the electron

It has been said that experiments on the electron *require* that one attribute to it a magnetic moment, *as though* it were a ball of charge spinning about its own axis. The relationship between this magnetic moment and the spin angular momentum can be shown to be  $\boldsymbol{\mu} = -\frac{e}{m}\mathbf{S}$  using relativistic quantum mechanics.

Once you accept that the electron possesses a magnetic moment even when it is not in motion, you need to account for the interaction between this  $\boldsymbol{\mu}$  and magnetic fields which arise in many ways: the orbital motion of the proton (as seen in the rest frame of the electron); the magnetic moment of the proton; an externally applied magnetic field; and so forth ...

# Spin-orbit coupling

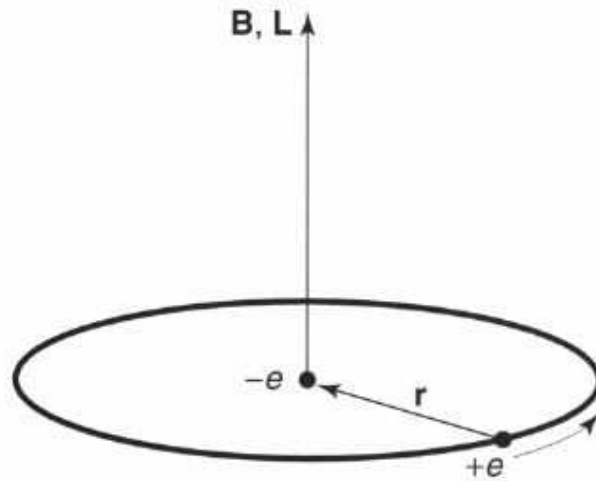


Figure 6.7 - Hydrogen atom from the electron's perspective.

In the rest frame of the electron, the proton is orbiting about it. This circling charge gives rise to a magnetic field which can be calculated classically to be  $\mathbf{B} = \frac{1}{4\pi\epsilon_0} \frac{e}{mc^2 r^3} \mathbf{L}$ , where  $\mathbf{L}$  is the orbital angular momentum of the *electron*:

$$\therefore H'_{so} = -\boldsymbol{\mu} \cdot \mathbf{B} = \frac{e^2}{8\pi\epsilon_0} \frac{1}{m^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L}.$$



Note that this equation already reflects a correction factor of  $1/2$  to account approximately for the fact that the rest frame of the electron is actually *accelerating* in the rest frame of the atom. This effect is known as the Thomas precession.

With the addition of  $H'_{so}$ ,  $H$  no longer commutes with  $\mathbf{L}$  and  $\mathbf{S}$ , so the spin and orbital angular momenta are no longer separately conserved. However, it can be shown that  $H'_{so}$  does commute with  $L^2$ ,  $S^2$ , and  $\mathbf{J} \equiv \mathbf{L} + \mathbf{S}$ , and hence these three quantities *are* conserved.

Therefore, the e.s. of  $L^2$ ,  $S^2$ ,  $J^2$ , and  $J_z$  (jointly) are 'good states' to use in perturbation theory.

It can be shown that  $\mathbf{L} \cdot \mathbf{S} = \frac{1}{2}(J^2 - L^2 - S^2)$ , so that the e.v. of that operator are  $\frac{\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)]$ . Evaluating  $\langle \frac{1}{r^3} \rangle$ , one obtains

$$E_{so}^1 = \frac{(E_n^0)^2 n [j(j+1) - l(l+1) - \frac{3}{4}]}{mc^2 l(l + \frac{1}{2})(l+1)}.$$

$$\therefore E_{fs}^1 = E_r^1 + E_{so}^1 = \frac{(E_n^0)^2}{2mc^2} \left( 3 - \frac{4n}{j + \frac{1}{2}} \right).$$

The fine structure correction breaks the degeneracy in  $l$ . The resulting energies are determined by  $n$  and  $j$ .

The azimuthal e.v. for orbital and spin angular momentum are no longer 'good' quantum numbers. The appropriate 'good' quantum numbers are  $n$ ,  $l$ ,  $s$ ,  $j$ , and  $m_j$ .

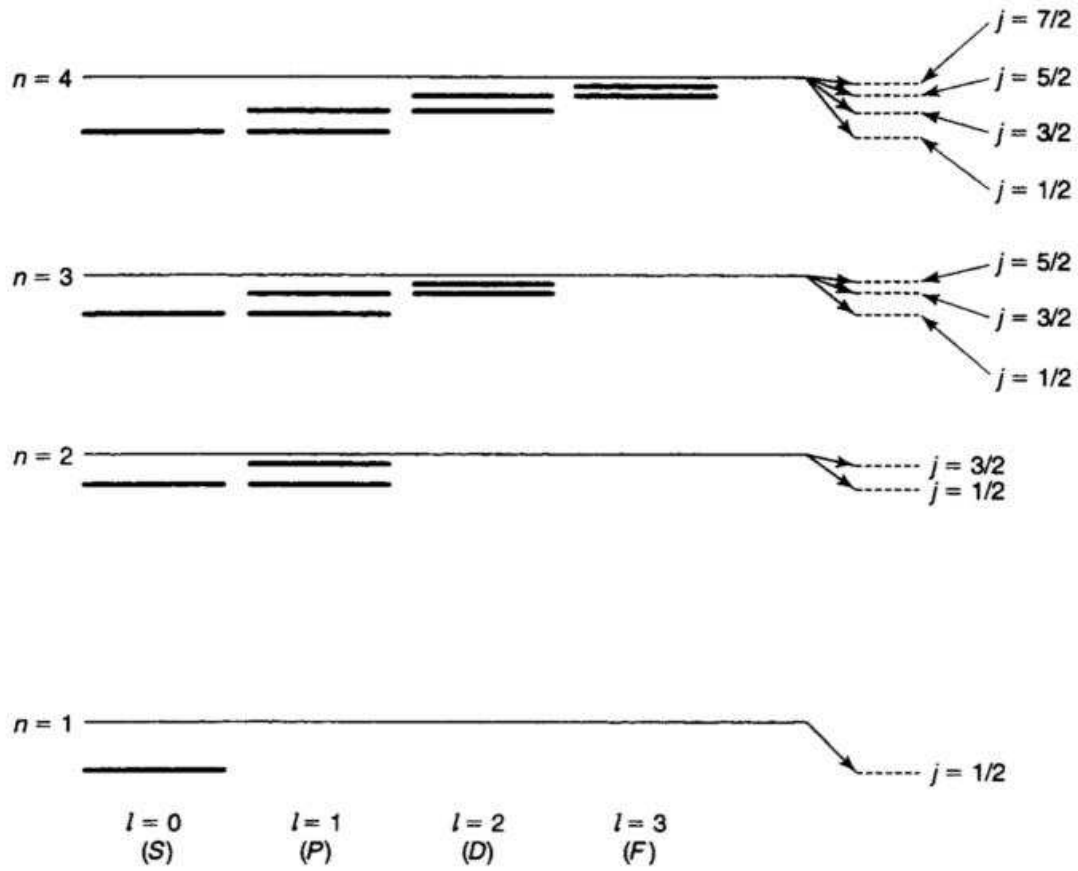


Figure 6.9 - Hydrogen energy levels including fine structure (not to scale).

## 6.4 The Zeeman Effect

When an atom is placed in an external magnetic field, the perturbing term in  $H$  is  $H'_Z = -(\boldsymbol{\mu}_l + \boldsymbol{\mu}_s) \cdot \mathbf{B}_{ext}$ , where  $\boldsymbol{\mu}_l = -\frac{e}{2m}\mathbf{L}$  and  $\boldsymbol{\mu}_s = -\frac{e}{m}\mathbf{S}$ . [There is an extra factor of 2 in  $\boldsymbol{\mu}_s$ , arising from relativistic arguments.]

$$\therefore H'_Z = \frac{e}{2m}(\mathbf{L} + \mathbf{S}) \cdot \mathbf{B}_{ext}.$$

There are three regimes in which we will consider the implications of this equation, depending on the relative values of  $B_{ext}$  and  $B_{int}$ .

## Weak-field Zeeman effect

If  $B_{ext} \ll B_{int}$ , the energy spectrum will be dominated by the fine structure. It therefore makes sense to start with ‘unperturbed’ states for which  $n$ ,  $l$ ,  $j$ , and  $m_j$  are ‘good’ quantum numbers.

The first-order Zeeman correction to the energy of *these* states is

$$E_Z^1 = \langle n l j m_j | H'_Z | n l j m_j \rangle = \frac{e}{2m} \mathbf{B}_{ext} \cdot \langle \mathbf{L} + 2\mathbf{S} \rangle.$$

In the presence of spin-orbit coupling,  $\mathbf{J}$  is a constant vector, but  $\mathbf{L}$  and  $\mathbf{S}$  are not. They precess rapidly about  $\mathbf{J}$ . Let  $\mathbf{L} + 2\mathbf{S} \rightarrow \mathbf{J} + \mathbf{S}$ . The time-average value of  $\mathbf{S}$  is in fact its projection along  $\mathbf{J}$ :  $\mathbf{S}_{avg} = \frac{\mathbf{S} \cdot \mathbf{J}}{J^2} \mathbf{J}$ .

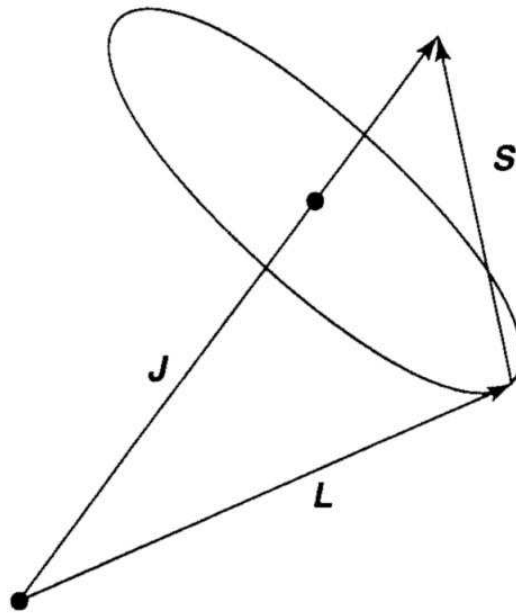


Figure 6.10 -  $\mathbf{J} = \mathbf{L} + \mathbf{S}$ .

But  $\mathbf{L} = \mathbf{J} - \mathbf{S} \Rightarrow L^2 = J^2 + S^2 - 2\mathbf{J} \cdot \mathbf{S}$ .

$$\therefore \mathbf{S} \cdot \mathbf{J} = \frac{1}{2}(J^2 + S^2 - L^2) =$$

$$\frac{\hbar^2}{2}[j(j+1) + s(s+1) - l(l+1)].$$

$$\therefore \langle \mathbf{L} + 2\mathbf{S} \rangle = \left\langle \left(1 + \frac{\mathbf{S} \cdot \mathbf{J}}{J^2}\right) \mathbf{J} \right\rangle =$$

$$\left[ 1 + \frac{j(j+1) - l(l+1) + \frac{3}{4}}{2j(j+1)} \right] \langle \mathbf{J} \rangle, \text{ where the term in}$$

square brackets is known as the Landé g-factor,  $g_J$ .

Choosing the  $z$ -axis to lie along  $\mathbf{B}_{ext}$ ,

$$E_Z^1 = \mu_B g_J B_{ext} m_j, \text{ where}$$

$\mu_B \equiv \frac{e\hbar}{2m} = 5.788 \times 10^{-5} \text{ eV/T}$  is the Bohr magneton.

The total energy of the resulting state is the sum of the energy of  $H^0$ , the fine structure correction, and the Zeeman effect. For the ground state, for example, this totals  $-13.6\text{eV}(1 + \alpha^2/4) \pm \mu_B B_{ext}$ .

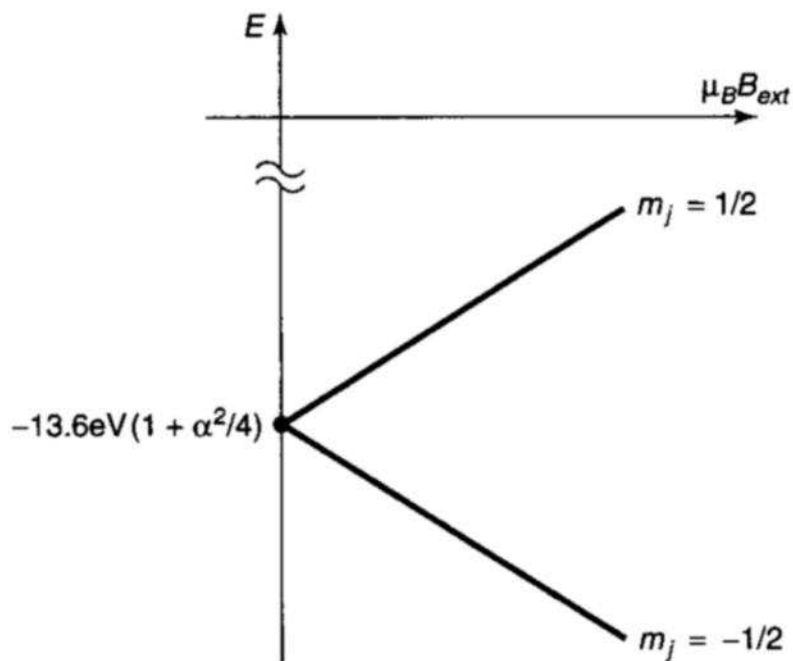


Figure 6.11 - Weak-field Zeeman splitting of the ground state; the upper and lower lines ( $m_j = \pm\frac{1}{2}$ ) have slopes  $\pm 1$ .

## Strong-field Zeeman effect

If  $B_{ext} \gg B_{int}$ , the effect of the external source of torque dominates over the effect which produces the fine structure. The total angular momentum is no longer conserved, but  $L_z$  and  $S_z$  are, and the 'good' quantum numbers become  $n$ ,  $l$ ,  $m_l$ , and  $m_s$ .

The 'unperturbed' Hamiltonian includes the external field, and is given by

$$H^0 + \frac{e}{2m} B_{ext} (L_z + 2S_z), \text{ which has e.v. given by } E_{nm_l m_s} = -\frac{13.6\text{eV}}{n^2} + \mu_B B_{ext} (m_l + 2m_s).$$

The perturbation term is due to the fine structure effects, and is

$$E_{fs}^1 = \langle nlm_l m_s | (H'_r + H'_{so}) | nlm_l m_s \rangle.$$



The  $H'_r$  part is evaluated as before, but for  $H'_{so}$  we need to evaluate  $\langle \mathbf{S} \cdot \mathbf{L} \rangle$ . Since these vectors do not couple with one another, we can average them separately. Thus,

$$\langle \mathbf{S} \cdot \mathbf{L} \rangle = \langle S_x \rangle \langle L_x \rangle + \langle S_y \rangle \langle L_y \rangle + \langle S_z \rangle \langle L_z \rangle.$$

But, for e.s. of  $S_z$  and  $L_z$ ,

$$\langle S_x \rangle = \langle S_y \rangle = \langle L_x \rangle = \langle L_y \rangle = 0.$$

Putting this together, the fine structure correction is given by

$$E_{fs}^1 = \frac{13.6\text{eV}}{n^3} \alpha^2 \left\{ \frac{3}{4n} - \left[ \frac{l(l+1) - m_l m_s}{l(l+\frac{1}{2})(l+1)} \right] \right\},$$

to which must be added  $E_{nm_l m_s}$ .

## Intermediate-field Zeeman effect

In this regime, neither the Zeeman effect nor the fine structure effect can be considered to be a perturbation on the effect of the other. Thus it is necessary to let  $H' = H'_Z + H'_{fs}$  and use degenerate perturbation theory.

This is worked out in the text for a particular example using states characterized by  $n = 2$ ,  $l$ ,  $j$ , and  $m_j$ . The Clebsch-Gordan coefficients are used to express  $|jm_j\rangle$  as a linear combination of  $|lm_l\rangle|sm_s\rangle$ . The resulting Hamiltonian matrix is diagonalized to yield analytic expressions for the e.v.

It is then shown that, in the weak- and strong-field limits, those e.v. smoothly approach the limiting expressions found earlier. This demonstrates the correctness of all three developments.

## 6.5 Hyperfine Splitting

This splitting results from the magnetic dipole–magnetic dipole interaction between proton and electron. For the proton,  $\boldsymbol{\mu}_p = \frac{g_p e}{2m_p} \mathbf{S}_p$ , where  $g_p \doteq 5.59$  instead of 2 as for the electron.

According to classical electrodynamics, a magnetic dipole gives rise to the following field:

$$\mathbf{B}_p = \frac{\mu_0}{4\pi r^3} [3(\boldsymbol{\mu} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \boldsymbol{\mu}] + \frac{2\mu_0}{3} \boldsymbol{\mu} \delta^3(\mathbf{r}).$$

The electron Hamiltonian correction in the presence of this field is  $H'_{hf} = -\boldsymbol{\mu}_e \cdot \mathbf{B}_p$ .

In the ground state (or any other state for which  $l = 0$ ), the spherical symmetry of the e.f. causes the term in  $E_{hf}^1$  corresponding to the first term in the field to vanish.

$\therefore E_{hf}^1 \rightarrow \frac{\mu_0 g e^2}{3\pi m_p m_e a^3} \langle \mathbf{S}_p \cdot \mathbf{S}_e \rangle$ . This is called spin–spin coupling for obvious reasons.

In the presence of spin–spin coupling, the individual spin angular momenta are no longer conserved; the ‘good’ states are e.s. of the total spin  $\mathbf{S} \equiv \mathbf{S}_e + \mathbf{S}_p$ . As before, we can form  $\mathbf{S} \cdot \mathbf{S}$  to obtain  $\mathbf{S}_p \cdot \mathbf{S}_e = \frac{1}{2}(S^2 - S_e^2 - S_p^2)$ , where  $S_e^2 = S_p^2 = (3/4)\hbar^2$ .

In the triplet state (*i.e.*, spins ‘parallel’), the total spin is 1, so  $S^2 = 2\hbar^2$ ; in the singlet state the total spin is zero, and  $S^2 = 0$ .

$$\therefore E_{hf}^1 = \frac{4g_p\hbar^4}{3m_p m_e^2 c^2 a^4} \begin{cases} +1/4, & \text{(triplet);} \\ -3/4, & \text{(singlet).} \end{cases}$$

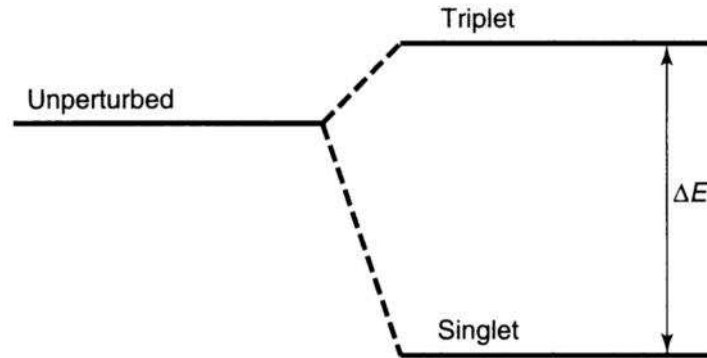


Figure 6.13 - Hyperfine splitting in the ground state of hydrogen.

Thus, spin–spin coupling breaks the spin degeneracy of the ground state, lifting the energy of the triplet and depressing the singlet. The energy gap is  $\sim 5.88 \times 10^{-6} \text{eV}$ , or a photon frequency of 1420 MHz, or a photon wavelength of 21 cm, which falls in the microwave region. The radiation due to this transition is the amongst the most pervasive and ubiquitous in the universe.