PART II APPLICATIONS

CHAPTER 6

TIME-INDEPENDENT PERTURBATION THEORY

6.1 NONDEGENERATE PERTURBATION THEORY

6.1.1 General Formulation

Suppose we have solved the (time-independent) Schrödinger equation for some potential (say, the one-dimensional infinite square well):

$$H^0 \psi_n^0 = E_n^0 \psi_n^0,$$ [6.1]

obtaining a complete set of orthonormal eigenfunctions, ψ_n^0,

$$\langle \psi_n^0 | \psi_m^0 \rangle = \delta_{nm}.$$ [6.2]

and the corresponding eigenvalues E_n^0. Now we perturb the potential slightly (say, by putting a little bump in the bottom of the well—Figure 6.1). We'd *like* to find the new eigenfunctions and eigenvalues:

$$H \psi_n = E_n \psi_n,$$ [6.3]

but unless we are very lucky, we're not going to be able to solve the Schrödinger equation exactly, for this more complicated potential. **Perturbation theory** is a systematic procedure for obtaining *approximate* solutions to the perturbed problem, by building on the known exact solutions to the *unperturbed* case.
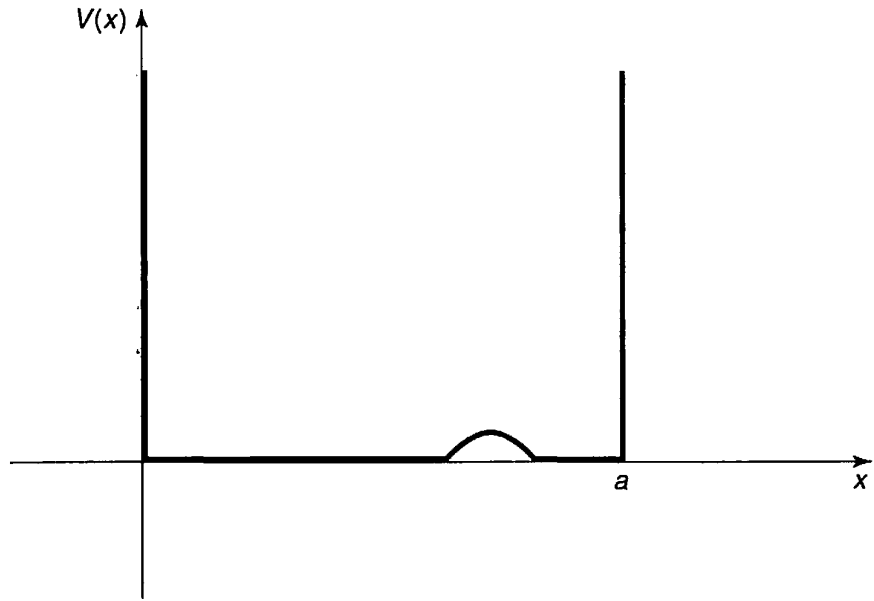
FIGURE 6.1:   Infinite square well with small perturbation.

To begin with we write the new Hamiltonian as the sum of two terms:

$$H = H^0 + \lambda H',$$ [6.4]

where H' is the perturbation (the superscript 0 always identifies the *un*perturbed quantity). For the moment we'll take λ to be a small number; later we'll crank it up to 1, and H will be the true Hamiltonian. Next we write ψ_n and E_n as power series in λ:

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots;$$ [6.5]

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots.$$ [6.6]

Here E_n^1 is the **first-order correction** to the nth eigenvalue, and ψ_n^1 is the first-order correction to the nth eigenfunction; E_n^2 and ψ_n^2 are the **second-order corrections**, and so on. Plugging Equations 6.5 and 6.6 into Equation 6.3, we have:

$$(H^0 + \lambda H')[\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots]$$

$$= (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots)[\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots],$$

or (collecting like powers of λ):

$$H^0 \psi_n^0 + \lambda (H^0 \psi_n^1 + H' \psi_n^0) + \lambda^2 (H^0 \psi_n^2 + H' \psi_n^1) + \cdots$$

$$= E_n^0 \psi_n^0 + \lambda (E_n^0 \psi_n^1 + E_n^1 \psi_n^0) + \lambda^2 (E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0) + \cdots.$$

To lowest order[1] (λ^0) this yields $H^0\psi_n^0 = E_n^0\psi_n^0$, which is nothing new (Equation 6.1). To first order (λ^1),

$$H^0\psi_n^1 + H'\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0. \qquad [6.7]$$

To second order (λ^2),

$$H^0\psi_n^2 + H'\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0, \qquad [6.8]$$

and so on. (I'm done with λ, now—it was just a device to keep track of the different orders—so crank it up to 1.)

6.1.2 First-Order Theory

Taking the inner product of Equation 6.7 with ψ_n^0 (that is, multiplying by $(\psi_n^0)^*$ and integrating),

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

But H^0 is hermitian, so

$$\langle\psi_n^0|H^0\psi_n^1\rangle = \langle H^0\psi_n^0|\psi_n^1\rangle = \langle E_n^0\psi_n^0|\psi_n^1\rangle = E_n^0\langle\psi_n^0|\psi_n^1\rangle,$$

and this cancels the first term on the right. Moreover, $\langle\psi_n^0|\psi_n^0\rangle = 1$, so[2]

$$\boxed{E_n^1 = \langle\psi_n^0|H'|\psi_n^0\rangle.} \qquad [6.9]$$

This is the fundamental result of first-order perturbation theory; as a *practical* matter, it may well be the most important equation in quantum mechanics. It says that the first-order correction to the energy is the *expectation value* of the perturbation, in the *unperturbed* state.

Example 6.1 The unperturbed wave functions for the infinite square well are (Equation 2.28)

$$\psi_n^0(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right).$$

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[1] As always (Chapter 2, footnote 25) the uniqueness of power series expansions guarantees that the coefficients of like powers are equal.

[2] In this context it doesn't matter whether we write $\langle\psi_n^0|H'\psi_n^0\rangle$ or $\langle\psi_n^0|H'|\psi_n^0\rangle$ (with the extra vertical bar), because we are using the wave function itself to "label" the state. But the latter notation is preferable, because it frees us from this specific convention.
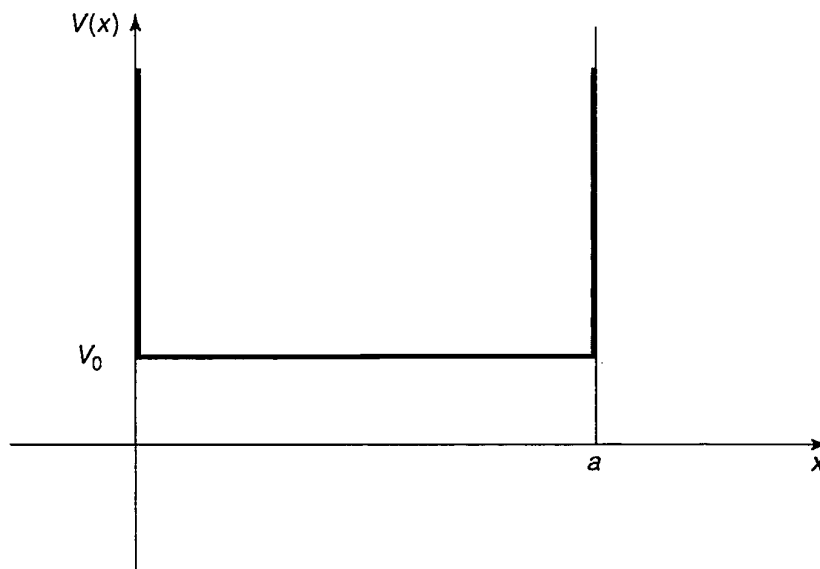
FIGURE 6.2:   Constant perturbation over the whole well.

Suppose we perturb the system by simply raising the "floor" of the well a constant amount V_0 (Figure 6.2). Find the first-order correction to the energies.

Solution: In this case $H' = V_0$, and the first-order correction to the energy of the nth state is

$$E_n^1 = \langle \psi_n^0 | V_0 | \psi_n^0 \rangle = V_0 \langle \psi_n^0 | \psi_n^0 \rangle = V_0.$$

The corrected energy levels, then, are $E_n \cong E_n^0 + V_0$; they are simply lifted by the amount V_0. Of *course*! The only surprising thing is that in this case the first-order theory yields the *exact* answer. Evidently for a *constant* perturbation all the higher corrections vanish.[3] On the other hand, if the perturbation extends only half-way across the well (Figure 6.3), then

$$E_n^1 = \frac{2V_0}{a} \int_0^{a/2} \sin^2 \left(\frac{n\pi}{a} x \right) dx = \frac{V_0}{2}.$$

In this case every energy level is lifted by $V_0/2$. That's not the *exact* result, presumably, but it does seem reasonable, as a first-order approximation.

Equation 6.9 is the first-order correction to the *energy*; to find the first-order correction to the *wave function* we first rewrite Equation 6.7:

$$(H^0 - E_n^0) \psi_n^1 = -(H' - E_n^1) \psi_n^0. \tag{6.10}$$

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[3] Incidentally, nothing here depends on the specific nature of the infinite square well—the same holds for *any* potential, when the perturbation is constant.
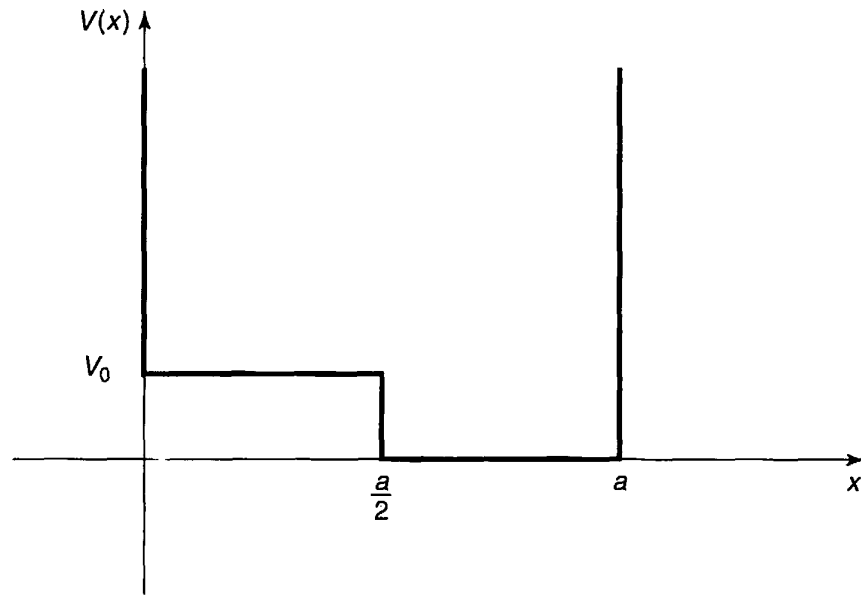
FIGURE 6.3: Constant perturbation over half the well.

The right side is a known function, so this amounts to an inhomogeneous differential equation for ψ_n^1. Now, the unperturbed wave functions constitute a complete set, so ψ_n^1 (like any other function) can be expressed as a linear combination of them:

$$\psi_n^1 = \sum_{m \neq n} c_m^{(n)} \psi_m^0.$$

[6.11]

There is no need to include $m = n$ in the sum, for if ψ_n^1 satisfies Equation 6.10, so too does $(\psi_n^1 + \alpha \psi_n^0)$, for any constant α, and we can use this freedom to subtract off the ψ_n^0 term.[4] If we could determine the coefficients $c_m^{(n)}$, we'd be done.

Well, putting Equation 6.11 into Equation 6.10, and using the fact that the ψ_m^0 satisfies the unperturbed Schrödinger equation (Equation 6.1), we have

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \psi_m^0 = -(H' - E_n^1) \psi_n^0.$$

Taking the inner product with ψ_l^0,

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \langle \psi_l^0 | \psi_m^0 \rangle = -\langle \psi_l^0 | H' | \psi_n^0 \rangle + E_n^1 \langle \psi_l^0 | \psi_n^0 \rangle.$$

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[4]Alternatively, a glance at Equation 6.5 reveals that any ψ_n^0 component in ψ_n^1 might as well be pulled out and combined with the first term. In fact, the choice $c_n^{(n)} = 0$ ensures that ψ_n —with 1 as the coefficient of ψ_n^0 in Equation 6.5—is *normalized* (to first order in λ): $\langle \psi_n | \psi_n \rangle = \langle \psi_n^0 | \psi_n^0 \rangle + \lambda (\langle \psi_n^1 | \psi_n^0 \rangle + \langle \psi_n^0 | \psi_n^1 \rangle) + \lambda^2 (\cdots) + \cdots$, but the orthonormality of the unperturbed states means that the first term is 1 and $\langle \psi_n^1 | \psi_n^0 \rangle = \langle \psi_n^0 | \psi_n^1 \rangle = 0$, as long as ψ_n^1 has no ψ_n^0 component.

If $l = n$, the left side is zero, and we recover Equation 6.9; if $l \neq n$, we get

$$(E_l^0 - E_n^0)c_l^{(n)} = -\langle \psi_l^0 | H' | \psi_n^0 \rangle,$$

or

$$c_m^{(n)} = \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0},$$

[6.12]

so

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

[6.13]

Notice that the denominator is safe (since there is no coefficient with $m = n$) as long as the unperturbed energy spectrum is nondegenerate. But if two different unperturbed states share the same energy, we're in serious trouble (we divided by zero to get Equation 6.12); in that case we need **degenerate perturbation theory**, which I'll come to in Section 6.2.

That completes first-order perturbation theory: The first-order correction to the energy, E_n^1, is given by Equation 6.9, and the first-order correction to the wave function, ψ_n^1, is given by Equation 6.13. I should warn you that whereas perturbation theory often yields surprisingly accurate energies (that is, $E_n^0 + E_n^1$ is quite close to the exact value E_n), the wave functions are notoriously poor.

∗**Problem 6.1** Suppose we put a delta-function bump in the center of the infinite square well:

$$H' = \alpha \delta(x - a/2),$$

where α is a constant.

(a) Find the first-order correction to the allowed energies. Explain why the energies are not perturbed for even n.

(b) Find the first three nonzero terms in the expansion (Equation 6.13) of the correction to the ground state, ψ_1^1.

∗**Problem 6.2** For the harmonic oscillator $[V(x) = (1/2)kx^2]$, the allowed energies are

$$E_n = (n + 1/2)\hbar\omega, \quad (n = 0, 1, 2, \ldots),$$

where $\omega = \sqrt{k/m}$ is the classical frequency. Now suppose the spring constant increases slightly: $k \rightarrow (1 + \epsilon)k$. (Perhaps we cool the spring, so it becomes less flexible.)

(a) Find the *exact* new energies (trivial, in this case). Expand your formula as a power series in ϵ, up to second order.

(b) Now calculate the first-order perturbation in the energy, using Equation 6.9. What is H' here? Compare your result with part (a). *Hint:* It is not necessary—in fact, it is not *permitted*—to calculate a single integral in doing this problem.

Problem 6.3 Two identical bosons are placed in an infinite square well (Equation 2.19). They interact weakly with one another, via the potential

$$V(x_1, x_2) = -aV_0\delta(x_1 - x_2)$$

(where V_0 is a constant with the dimensions of energy, and a is the width of the well).

(a) First, ignoring the interaction between the particles, find the ground state and the first excited state—both the wave functions and the associated energies.

(b) Use first-order perturbation theory to estimate the effect of the particle-particle interaction on the energies of the ground state and the first excited state.

6.1.3 Second-Order Energies

Proceeding as before, we take the inner product of the *second* order equation (Equation 6.8) with ψ_n^0:

$$\langle\psi_n^0|H^0\psi_n^2\rangle + \langle\psi_n^0|H'\psi_n^1\rangle = E_n^0\langle\psi_n^0|\psi_n^2\rangle + E_n^1\langle\psi_n^0|\psi_n^1\rangle + E_n^2\langle\psi_n^0|\psi_n^0\rangle.$$

Again, we exploit the hermiticity of H^0:

$$\langle\psi_n^0|H^0\psi_n^2\rangle = \langle H^0\psi_n^0|\psi_n^2\rangle = E_n^0\langle\psi_n^0|\psi_n^2\rangle,$$

so the first term on the left cancels the first term on the right. Meanwhile, $\langle\psi_n^0|\psi_n^0\rangle = 1$, and we are left with a formula for E_n^2:

$$E_n^2 = \langle\psi_n^0|H'|\psi_n^1\rangle - E_n^1\langle\psi_n^0|\psi_n^1\rangle. \qquad [6.14]$$

But

$$\langle\psi_n^0|\psi_n^1\rangle = \sum_{m\neq n} c_m^{(n)}\langle\psi_n^0|\psi_m^0\rangle = 0,$$

(because the sum excludes $m = n$, and all the others are orthogonal), so

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle = \sum_{m \neq n} c_m^{(n)} \langle \psi_n^0 | H' | \psi_m^0 \rangle = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle \langle \psi_n^0 | H' | \psi_m^0 \rangle}{E_n^0 - E_m^0}.$$

or, finally,

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

[6.15]

This is the fundamental result of second-order perturbation theory.

We could go on to calculate the second-order correction to the wave function (ψ_n^2), the third-order correction to the energy, and so on, but in practice Equation 6.15 is ordinarily as far as it is useful to pursue this method.[5]

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*Problem 6.4

(a) Find the second-order correction to the energies (E_n^2) for the potential in Problem 6.1. *Comment:* You can sum the series explicitly, obtaining $-2m(\alpha/\pi\hbar n)^2$ for odd n.

(b) Calculate the second-order correction to the ground state energy (E_0^2) for the potential in Problem 6.2. Check that your result is consistent with the exact solution.

Problem 6.5 Consider a charged particle in the one-dimensional harmonic oscillator potential. Suppose we turn on a weak electric field (E), so that the potential energy is shifted by an amount $H' = -qEx$.

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[5]In the short-hand notation $V_{mn} \equiv \langle \psi_m^0 | H' | \psi_n^0 \rangle$, $\Delta_{mn} \equiv E_m^0 - E_n^0$, the first three corrections to the nth energy are

$$E_n^1 = V_{nn}, \quad E_n^2 = \sum_{m \neq n} \frac{|V_{nm}|^2}{\Delta_{nm}}, \quad E_n^3 = \sum_{l,m \neq n} \frac{V_{nl}V_{lm}V_{mn}}{\Delta_{nl}\Delta_{nm}} - V_{nn} \sum_{m \neq n} \frac{|V_{nm}|^2}{\Delta_{nm}^2}.$$

The third order correction is given in Landau and Lifschitz, *Quantum Mechanics: Non-Relativistic Theory*, 3rd ed., Pergamon, Oxford (1977), page 136; the fourth and fifth orders (together with a powerful general technique for obtaining the higher orders) are developed by Nicholas Wheeler, *Higher-Order Spectral Perturbation* (unpublished Reed College report, 2000). Illuminating alternative formulations of time-independent perturbation theory include the Delgarno-Lewis method and the closely related "logarithmic" perturbation theory (see, for example, T. Imbo and U. Sukhatme, *Am. J. Phys.* **52**, 140 (1984), for LPT, and H. Mavromatis, *Am. J. Phys.* **59**, 738 (1991), for Delgarno-Lewis).

(a) Show that there is no first-order change in the energy levels, and calculate the second-order correction. *Hint:* See Problem 3.33.

(b) The Schrödinger equation can be solved directly in this case, by a change of variables: $x' \equiv x - (qE/m\omega^2)$. Find the exact energies, and show that they are consistent with the perturbation theory approximation.

6.2 DEGENERATE PERTURBATION THEORY

If the unperturbed states are degenerate—that is, if two (or more) distinct states (ψ_a^0 and ψ_b^0) share the same energy—then ordinary perturbation theory fails: $c_a^{(b)}$ (Equation 6.12) and E_a^2 (Equation 6.15) blow up (unless, perhaps, the numerator vanishes, $\langle \psi_a^0 | H' | \psi_b^0 \rangle = 0$—a loophole that will be important to us later on). In the degenerate case, therefore, there is no reason to trust even the *first*-order correction to the energy (Equation 6.9), and we must look for some other way to handle the problem.

6.2.1 Two-Fold Degeneracy

Suppose that

$$H^0 \psi_a^0 = E^0 \psi_a^0, \quad H^0 \psi_b^0 = E^0 \psi_b^0, \quad \langle \psi_a^0 | \psi_b^0 \rangle = 0. \qquad [6.16]$$

with ψ_a^0 and ψ_b^0 both normalized. Note that any linear combination of these states,

$$\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0. \qquad [6.17]$$

is still an eigenstate of H^0, with the same eigenvalue E^0:

$$H^0 \psi^0 = E^0 \psi^0. \qquad [6.18]$$

Typically, the perturbation (H') will "break" (or "lift") the degeneracy: As we increase λ (from 0 to 1), the common unperturbed energy E^0 splits into two (Figure 6.4). Going the other direction, when we turn *off* the perturbation, the "upper" state reduces down to *one* linear combination of ψ_a^0 and ψ_b^0, and the "lower" state reduces to some *orthogonal* linear combination, but we don't know a priori *what* these **"good"** linear combinations will be. For this reason we can't even calculate the *first*-order energy (Equation 6.9)—we don't know what unperturbed states to use.

For the moment, therefore, let's just write the "good" unperturbed states in generic form (Equation 6.17), keeping α and β adjustable. We want to solve the Schrödinger equation,
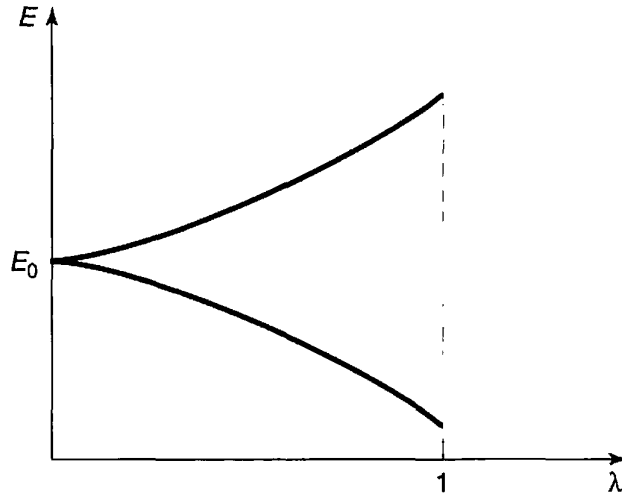
$$H\psi = E\psi, \qquad [6.19]$$

FIGURE 6.4: "Lifting" of a degeneracy by a perturbation.

with $H = H^0 + \lambda H'$ and

$$E = E^0 + \lambda E^1 + \lambda^2 E^2 + \cdots, \quad \psi = \psi^0 + \lambda \psi^1 + \lambda^2 \psi^2 + \cdots. \qquad [6.20]$$

Plugging these into Equation 6.19, and collecting like powers of λ (as before) we find

$$H^0 \psi^0 + \lambda(H' \psi^0 + H^0 \psi^1) + \cdots = E^0 \psi^0 + \lambda(E^1 \psi^0 + E^0 \psi^1) + \cdots.$$

But $H^0 \psi^0 = E^0 \psi^0$ (Equation 6.18), so the first terms cancel; at order λ^1 we have

$$H^0 \psi^1 + H' \psi^0 = E^0 \psi^1 + E^1 \psi^0. \qquad [6.21]$$

Taking the inner product with ψ_a^0:

$$\langle \psi_a^0 | H^0 \psi^1 \rangle + \langle \psi_a^0 | H' \psi^0 \rangle = E^0 \langle \psi_a^0 | \psi^1 \rangle + E^1 \langle \psi_a^0 | \psi^0 \rangle.$$

Because H^0 is hermitian, the first term on the left cancels the first term on the right. Putting in Equation 6.17 and exploiting the orthonormality condition (Equation 6.16), we obtain

$$\alpha \langle \psi_a^0 | H' | \psi_a^0 \rangle + \beta \langle \psi_a^0 | H' | \psi_b^0 \rangle = \alpha E^1,$$

or, more compactly,

$$\alpha W_{aa} + \beta W_{ab} = \alpha E^1, \qquad [6.22]$$

where

$$W_{ij} \equiv \langle \psi_i^0 | H' | \psi_j^0 \rangle, \quad (i, j = a, b). \qquad [6.23]$$

Similarly, the inner product with ψ_b^0 yields

$$\alpha W_{ba} + \beta W_{bb} = \beta E^1.$$ [6.24]

Notice that the W's are (in principle) *known*—they are just the "matrix elements" of H', with respect to the unperturbed wave functions ψ_a^0 and ψ_b^0. Multiplying Equation 6.24 by W_{ab}, and using Equation 6.22 to eliminate βW_{ab}, we find:

$$\alpha[W_{ab}W_{ba} - (E^1 - W_{aa})(E^1 - W_{bb})] = 0.$$ [6.25]

If α is *not* zero, Equation 6.25 yields an equation for E^1:

$$(E^1)^2 - E^1(W_{aa} + W_{bb}) + (W_{aa}W_{bb} - W_{ab}W_{ba}) = 0.$$ [6.26]

Invoking the quadratic formula, and noting (from Equation 6.23) that $W_{ba} = W_{ab}^*$, we conclude that

$$E_{\pm}^1 = \frac{1}{2}\left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right].$$ [6.27]

This is the fundamental result of degenerate perturbation theory: the two roots correspond to the two perturbed energies.

But what if α *is* zero? In that case $\beta = 1$, Equation 6.22 says $W_{ab} = 0$, and Equation 6.24 gives $E^1 = W_{bb}$. This is actually included in the general result (Equation 6.27), with the minus sign (the plus sign corresponds to $\alpha = 1$, $\beta = 0$). What's more, the *answers*,

$$E_+^1 = W_{aa} = \langle\psi_a^0|H'|\psi_a^0\rangle, \qquad E_-^1 = W_{bb} = \langle\psi_b^0|H'|\psi_b^0\rangle.$$

are precisely what we would have obtained using *non*degenerate perturbation theory (Equation 6.9). We have simply been *lucky*: The states ψ_a^0 and ψ_b^0 were *already* the "good" linear combinations. Obviously, it would be greatly to our advantage if we could somehow *guess* the "good" states right from the start—then we could go ahead and use *non*degenerate perturbation theory. As it turns out, we can very often do this by exploiting the following theorem:

Theorem: Let A be a hermitian operator that commutes with H^0 and H'. If ψ_a^0 and ψ_b^0 (the degenerate eigenfunctions of H^0) are also eigenfunctions of A, with distinct eigenvalues,

$$A\psi_a^0 = \mu\psi_a^0, \qquad A\psi_b^0 = \nu\psi_b^0, \qquad \text{and } \mu \neq \nu.$$

then $W_{ab} = 0$ (and hence ψ_a^0 and ψ_b^0 are the "good" states to use in perturbation theory).

Proof: By assumption, $[A, H'] = 0$, so

$$\langle \psi_a^0 | [A, H'] \psi_b^0 \rangle = 0$$

$$= \langle \psi_a^0 | A H' \psi_b^0 \rangle - \langle \psi_a^0 | H' A \psi_b^0 \rangle$$

$$= \langle A \psi_a^0 | H' \psi_b^0 \rangle - \langle \psi_a^0 | H' \nu \psi_b^0 \rangle$$

$$= (\mu - \nu) \langle \psi_a^0 | H' \psi_b^0 \rangle = (\mu - \nu) W_{ab}.$$

But $\mu \neq \nu$, so $W_{ab} = 0$.   QED

Moral: If you're faced with degenerate states, look around for some hermitian operator A that commutes with H^0 and H'; pick as your unperturbed states ones that are simultaneously eigenfunctions of H^0 and A. Then use *ordinary* first-order perturbation theory. If you can't find such an operator, you'll have to resort to Equation 6.27, but in practice this is seldom necessary.

Problem 6.6 Let the two "good" unperturbed states be

$$\psi_\pm^0 = \alpha_\pm \psi_a^0 + \beta_\pm \psi_b^0.$$

where $\alpha_\pm$ and $\beta_\pm$ are determined (up to normalization) by Equation 6.22 (or Equation 6.24). Show explicitly that

(a) $\psi_\pm^0$ are orthogonal ($\langle \psi_+^0 | \psi_-^0 \rangle = 0$);

(b) $\langle \psi_+^0 | H' | \psi_-^0 \rangle = 0$;

(c) $\langle \psi_\pm^0 | H' | \psi_\pm^0 \rangle = E_\pm^1$, with $E_\pm^1$ given by Equation 6.27.

Problem 6.7 Consider a particle of mass m that is free to move in a one-dimensional region of length L that closes on itself (for instance, a bead that slides frictionlessly on a circular wire of circumference L, as in Problem 2.46).

(a) Show that the stationary states can be written in the form

$$\psi_n(x) = \frac{1}{\sqrt{L}} e^{2\pi i n x / L}, \quad (-L/2 < x < L/2).$$

where $n = 0, \pm 1, \pm 2, \ldots$, and the allowed energies are

$$E_n = \frac{2}{m} \left(\frac{n\pi \hbar}{L} \right)^2.$$

Notice that—with the exception of the ground state ($n = 0$)—these are all doubly degenerate.

(b) Now suppose we introduce the perturbation

$$H' = -V_0 e^{-x^2/a^2},$$

where $a \ll L$. (This puts a little "dimple" in the potential at $x = 0$, as though we bent the wire slightly to make a "trap.") Find the first-order correction to E_n, using Equation 6.27. *Hint:* To evaluate the integrals, exploit the fact that $a \ll L$ to extend the limits from $\pm L/2$ to $\pm\infty$; after all, H' is essentially zero outside $-a < x < a$.

(c) What are the "good" linear combinations of ψ_n and ψ_{-n}, for this problem? Show that with these states you get the first-order correction using Equation 6.9.

(d) Find a hermitian operator A that fits the requirements of the theorem, and show that the simultaneous eigenstates of H^0 and A are precisely the ones you used in (c).

6.2.2 Higher-Order Degeneracy

In the previous section I assumed the degeneracy was two-fold, but it is easy to see how the method generalizes. Rewrite Equations 6.22 and 6.24 in matrix form:

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix}. \tag{6.28}$$

Evidently the E^1's are nothing but the *eigenvalues* of the W-matrix; Equation 6.26 is the characteristic equation for this matrix, and the "good" linear combinations of the unperturbed states are the eigenvectors of **W**.

In the case of n-fold degeneracy, we look for the eigenvalues of the $n \times n$ matrix

$$W_{ij} = \langle \psi_i^0 | H' | \psi_j^0 \rangle. \tag{6.29}$$

In the language of linear algebra, finding the "good" unperturbed wave functions amounts to constructing a basis in the degenerate subspace that *diagonalizes* the

matrix **W**. Once again, if you can think of an operator A that **commutes** with H', and use the simultaneous eigenfunctions of A and H^0, then the W matrix will *automatically* be diagonal, and you won't have to fuss with solving the characteristic equation.[6] (If you're nervous about my casual generalization from 2-fold degeneracy to n-fold degeneracy, work Problem 6.10.)

Example 6.2 Consider the three-dimensional infinite cubical well (Problem 4.2):

$$V(x, y, z) = \begin{cases} 0, & \text{if } 0 < x < a, 0 < y < a, \text{ and } 0 < z < a; \\ \infty & \text{otherwise.} \end{cases} \quad [6.30]$$

The stationary states are

$$\psi^0_{n_x n_y n_z}(x, y, z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{a} y\right) \sin\left(\frac{n_z \pi}{a} z\right), \quad [6.31]$$

where n_x, n_y, and n_z are positive integers. The corresponding allowed energies are

$$E^0_{n_x n_y n_z} = \frac{\pi^2 \hbar^2}{2ma^2}(n_x^2 + n_y^2 + n_z^2). \quad [6.32]$$

Notice that the ground state (ψ_{111}) is nondegenerate; its energy is

$$E^0_0 \equiv 3\frac{\pi^2 \hbar^2}{2ma^2}. \quad [6.33]$$

But the first excited state is (triply) degenerate:

$$\psi_a \equiv \psi_{112}, \quad \psi_b \equiv \psi_{121}, \text{ and } \psi_c \equiv \psi_{211}, \quad [6.34]$$

all share the same energy

$$E^0_1 \equiv 3\frac{\pi^2 \hbar^2}{ma^2}. \quad [6.35]$$

Now let's introduce the perturbation

$$H' = \begin{cases} V_0, & \text{if } 0 < x < a/2 \text{ and } 0 < y < a/2; \\ 0, & \text{otherwise.} \end{cases} \quad [6.36]$$

---

[6]Degenerate perturbation theory amounts to diagonalization of the degenerate part of the Hamiltonian. The diagonalization of matrices (and simultaneous diagonalizability of commuting matrices) is discussed in the Appendix (Section A.5).
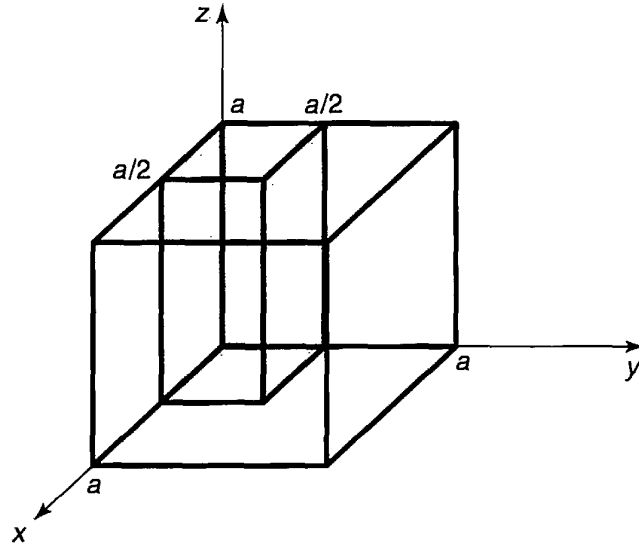
FIGURE 6.5: The perturbation increases the potential by an amount V_0 in the shaded sector.

This raises the potential by an amount V_0 in one quarter of the box (see Figure 6.5). The first-order correction to the ground state energy is given by Equation 6.9:

$$E_0^1 = \langle \psi_{111} | H' | \psi_{111} \rangle$$

$$= \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin^2\left(\frac{\pi}{a}x\right) dx \int_0^{a/2} \sin^2\left(\frac{\pi}{a}y\right) dy \int_0^a \sin^2\left(\frac{\pi}{a}z\right) dz$$

$$= \frac{1}{4}V_0, \qquad\qquad [6.37]$$

which is pretty much what we would expect.

For the first excited state we need the full machinery of degenerate perturbation theory. The first step is to construct the matrix **W**. The diagonal elements are the same as for the ground state (except that the argument of one of the sines is doubled); you can check for yourself that

$$W_{aa} = W_{bb} = W_{cc} = \frac{1}{4}V_0.$$

The off-diagonal elements are more interesting:

$$W_{ab} = \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin^2\left(\frac{\pi}{a}x\right) dx$$

$$\times \int_0^{a/2} \sin\left(\frac{\pi}{a}y\right) \sin\left(\frac{2\pi}{a}y\right) dy \int_0^a \sin\left(\frac{2\pi}{a}z\right) \sin\left(\frac{\pi}{a}z\right) dz.$$

But the z integral is zero (as it will be also for W_{ac}), so

$$W_{ab} = W_{ac} = 0.$$

Finally,

$$W_{bc} = \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin\left(\frac{\pi}{a}x\right) \sin\left(\frac{2\pi}{a}x\right) dx$$

$$\times \int_0^{a/2} \sin\left(\frac{2\pi}{a}y\right) \sin\left(\frac{\pi}{a}y\right) dy \int_0^a \sin^2\left(\frac{\pi}{a}z\right) dz = \frac{16}{9\pi^2} V_0.$$

Thus

$$\mathbf{W} = \frac{V_0}{4} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & \kappa \\ 0 & \kappa & 1 \end{pmatrix} \qquad [6.38]$$

where $\kappa \equiv (8/3\pi)^2 \approx 0.7205$.

The characteristic equation for $\mathbf{W}$ (or rather, for $4\mathbf{W}/V_0$, which is easier to work with) is

$$(1 - w)^3 - \kappa^2(1 - w) = 0,$$

and the eigenvalues are

$$w_1 = 1; \quad w_2 = 1 + \kappa \approx 1.705; \quad w_3 = 1 - \kappa \approx 0.2795.$$

To first order in λ, then,

$$E_1(\lambda) = \begin{cases} E_1^0 + \lambda V_0/4, \\ E_1^0 + \lambda(1 + \kappa)V_0/4, \\ E_1^0 + \lambda(1 - \kappa)V_0/4. \end{cases} \qquad [6.39]$$

where E_1^0 is the (common) unperturbed energy (Equation 6.35). The perturbation lifts the degeneracy, splitting E_1^0 into three distinct energy levels (see Figure 6.6). Notice that if we had naively applied *non*degenerate perturbation theory to this problem, we would have concluded that the first-order correction (Equation 6.9) is the same for all three states, and equal to $V_0/4$—which is actually correct only for the middle state.

Meanwhile, the "good" unperturbed states are linear combinations of the form

$$\psi^0 = \alpha\psi_a + \beta\psi_b + \gamma\psi_c, \qquad [6.40]$$

where the coefficients (α, β, and γ) form the eigenvectors of the matrix $\mathbf{W}$:

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & \kappa \\ 0 & \kappa & 1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = w \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}.$$
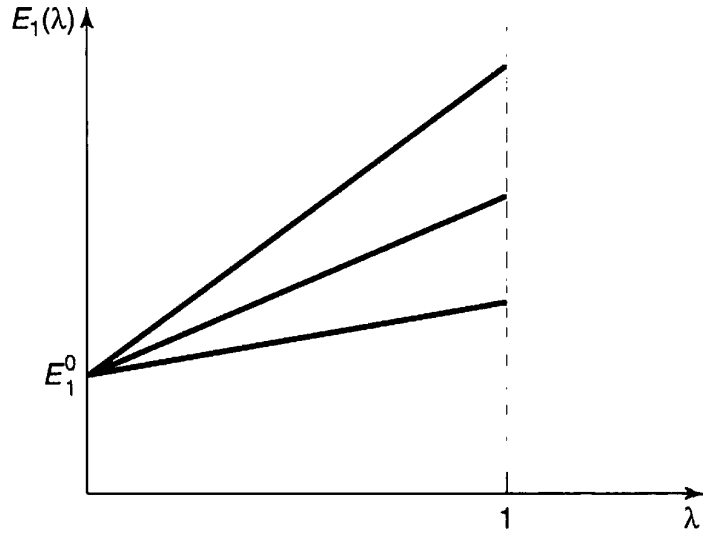
FIGURE 6.6: Lifting of the degeneracy in Example 6.2 (Equation 6.39).

For $w = 1$ we get $\alpha = 1$, $\beta = \gamma = 0$; for $w = 1 \pm \kappa$ we get $\alpha = 0$, $\beta = \pm \gamma = 1/\sqrt{2}$. (I normalized them as I went along.) Thus the "good" states are[7]

$$\psi^0 = \begin{cases} \psi_a, \\ (\psi_b + \psi_c)/\sqrt{2}, \\ (\psi_b - \psi_c)/\sqrt{2}. \end{cases} \qquad [6.41]$$

Problem 6.8 Suppose we perturb the infinite cubical well (Equation 6.30) by putting a delta function "bump" at the point $(a/4, a/2, 3a/4)$:

$$H' = a^3 V_0 \delta(x - a/4)\delta(y - a/2)\delta(z - 3a/4).$$

Find the first-order corrections to the energy of the ground state and the (triply degenerate) first excited states.

---

[7]We might have guessed this result right from the start by noting that the operator P_{xy}, which interchanges x and y, commutes with H'. Its eigenvalues are $+1$ (for functions that are *even* under the interchange), and -1 (for functions that are odd). In this case ψ_a is *already* even. $(\psi_b + \psi_c)$ is even, and $(\psi_b - \psi_c)$ is odd. This is not quite conclusive, since any linear combination of the even states would still be even. But if we also use the operator Q, which takes z to $a - z$, and note that ψ_a is an eigenfunction with eigenvalue -1, whereas the other two are eigenfunctions with eigenvalue $+1$, the ambiguity is resolved. Here the operators P_{xy} and Q together play the role of A in the theorem of Section 6.2.1.

∗Problem 6.9 Consider a quantum system with just *three* linearly independent states. Suppose the Hamiltonian, in matrix form, is

$$\mathbf{H} = V_0 \begin{pmatrix} (1 - \epsilon) & 0 & 0 \\ 0 & 1 & \epsilon \\ 0 & \epsilon & 2 \end{pmatrix}.$$

where V_0 is a constant, and ϵ is some small number ($\epsilon \ll 1$).

(a) Write down the eigenvectors and eigenvalues of the *unperturbed* Hamiltonian ($\epsilon = 0$).

(b) Solve for the *exact* eigenvalues of **H**. Expand each of them as a power series in ϵ, up to second order.

(c) Use first- and second-order *non*degenerate perturbation theory to find the approximate eigenvalue for the state that grows out of the nondegenerate eigenvector of H^0. Compare the exact result, from (a).

(d) Use *degenerate* perturbation theory to find the first-order correction to the two initially degenerate eigenvalues. Compare the exact results.

Problem 6.10 In the text I asserted that the first-order corrections to an n-fold degenerate energy are the eigenvalues of the W matrix, and I justified this claim as the "natural" generalization of the case $n = 2$. *Prove* it, by reproducing the steps in Section 6.2.1, starting with

$$\psi^0 = \sum_{j=1}^{n} \alpha_j \psi_j^0$$

(generalizing Equation 6.17), and ending by showing that the analog to Equation 6.22 can be interpreted as the eigenvalue equation for the matrix **W**.

6.3 THE FINE STRUCTURE OF HYDROGEN

In our study of the hydrogen atom (Section 4.2) we took the Hamiltonian to be

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi \epsilon_0} \frac{1}{r} \qquad [6.42]$$

(electron kinetic energy plus coulombic potential energy). But this is not quite the whole story. We have already learned how to correct for the motion of the

TABLE 6.1:   Hierarchy of corrections to the
Bohr energies of hydrogen.

Bohr energies:	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	$(m/m_p)\alpha^4 mc^2$

nucleus: Just replace m by the reduced mass (Problem 5.1). More significant is the so-called **fine structure**, which is actually due to two distinct mechanisms: a **relativistic correction**, and **spin-orbit coupling**. Compared to the Bohr energies (Equation 4.70), fine structure is a tiny perturbation—smaller by a factor of α^2, where

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} \cong \frac{1}{137.036} \qquad [6.43]$$

is the famous **fine structure constant**. Smaller still (by another factor of α) is the **Lamb shift**, associated with the quantization of the electric field, and smaller by yet another order of magnitude is the **hyperfine structure**, which is due to the magnetic interaction between the dipole moments of the electron and the proton. This hierarchy is summarized in Table 6.1. In the present section we will analyze the fine structure of hydrogen, as an application of time-independent perturbation theory.

Problem 6.11

(a) Express the Bohr energies in terms of the fine structure constant and the rest energy (mc^2) of the electron.

(b) Calculate the fine structure constant from first principles (i.e., without recourse to the empirical values of ϵ_0, e, $\hbar$, and c). *Comment:* The fine structure constant is undoubtedly the most fundamental pure (dimensionless) number in all of physics. It relates the basic constants of electromagnetism (the charge of the electron), relativity (the speed of light), and quantum mechanics (Planck's constant). If you can solve part (b), you have the most certain Nobel Prize in history waiting for you. But I wouldn't recommend spending a lot of time on it right now; many smart people have tried, and all (so far) have failed.

6.3.1 The Relativistic Correction

The first term in the Hamiltonian is supposed to represent kinetic energy:

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m}, \qquad [6.44]$$

and the canonical substitution $\mathbf{p} \to (\hbar/i)\nabla$ yields the operator

$$T = -\frac{\hbar^2}{2m}\nabla^2.$$ [6.45]

But Equation 6.44 is the *classical* expression for kinetic energy; the *relativistic* formula is

$$T = \frac{mc^2}{\sqrt{1-(v/c)^2}} - mc^2.$$ [6.46]

The first term is the *total* relativistic energy (not counting *potential* energy, which we aren't concerned with at the moment), and the second term is the *rest* energy—the *difference* is the energy attributable to motion.

We need to express T in terms of the (relativistic) momentum,

$$p = \frac{mv}{\sqrt{1-(v/c)^2}},$$ [6.47]

instead of velocity. Notice that

$$p^2c^2 + m^2c^4 = \frac{m^2v^2c^2 + m^2c^4[1-(v/c)^2]}{1-(v/c)^2} = \frac{m^2c^4}{1-(v/c)^2} = (T+mc^2)^2.$$

so

$$T = \sqrt{p^2c^2 + m^2c^4} - mc^2.$$ [6.48]

This relativistic equation for kinetic energy reduces (of course) to the classical result (Equation 6.44), in the nonrelativistic limit $p \ll mc$; expanding in powers of the small number (p/mc), we have

$$T = mc^2\left[\sqrt{1+\left(\frac{p}{mc}\right)^2} - 1\right] = mc^2\left[1 + \frac{1}{2}\left(\frac{p}{mc}\right)^2 - \frac{1}{8}\left(\frac{p}{mc}\right)^4 \cdots - 1\right]$$

$$= \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \cdots.$$ [6.49]

The lowest-order[8] relativistic correction to the Hamiltonian is evidently

$$H_r' = -\frac{p^4}{8m^3c^2}.$$ [6.50]

---

[8]The kinetic energy of the electron in hydrogen is on the order of 10 eV. which is miniscule compared to its rest energy (511,000 eV), so the hydrogen atom is basically nonrelativistic, and we can afford to keep only the lowest-order correction. In Equation 6.49. p is the *relativistic* momentum (Equation 6.47), *not* the classical momentum mv. It is the former that we now associate with the quantum operator $-i\hbar\nabla$, in Equation 6.50.

In first-order perturbation theory, the correction to E_n is given by the expectation value of H' in the unperturbed state (Equation 6.9):

$$E_r^1 = \langle H_r' \rangle = -\frac{1}{8m^3c^2}\langle \psi | p^4 \psi \rangle = -\frac{1}{8m^3c^2}\langle p^2\psi | p^2\psi \rangle. \qquad [6.51]$$

Now, the Schrödinger equation (for the unperturbed states) says

$$p^2\psi = 2m(E - V)\psi, \qquad [6.52]$$

and hence[9]

$$E_r^1 = -\frac{1}{2mc^2}\langle (E - V)^2 \rangle = -\frac{1}{2mc^2}[E^2 - 2E\langle V \rangle + \langle V^2 \rangle]. \qquad [6.53]$$

So far this is entirely general; but we're interested in hydrogen, for which $V(r) = -(1/4\pi\epsilon_0)e^2/r$:

$$E_r^1 = -\frac{1}{2mc^2}\left[E_n^2 + 2E_n\left(\frac{e^2}{4\pi\epsilon_0}\right)\left\langle\frac{1}{r}\right\rangle + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle\right], \qquad [6.54]$$

where E_n is the Bohr energy of the state in question.

To complete the job, we need the expectation values of $1/r$ and $1/r^2$, in the (unperturbed) state ψ_{nlm} (Equation 4.2.1). The first is easy (see Problem 6.12):

$$\left\langle\frac{1}{r}\right\rangle = \frac{1}{n^2a}, \qquad [6.55]$$

where a is the Bohr radius (Equation 4.72). The second is not so simple to derive (see Problem 6.33), but the answer is[10]

$$\left\langle\frac{1}{r^2}\right\rangle = \frac{1}{(l + 1/2)n^3a^2}. \qquad [6.56]$$

It follows that

$$E_r^1 = -\frac{1}{2mc^2}\left[E_n^2 + 2E_n\left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{1}{n^2a} + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{1}{(l + 1/2)n^3a^2}\right],$$

---

[9]There is some sleight-of-hand in this maneuver, which exploits the hermiticity of p^2 and of $(E - V)$. In truth, the operator p^4 is *not* hermitian for states with $l = 0$ (see Problem 6.15), and the applicability of perturbation theory to Equation 6.50 is therefore called into question (for the case $l = 0$). Fortunately, the *exact* solution is available; it can be obtained by using the (relativistic) Dirac equation in place of the (nonrelativistic) Schrödinger equation, and it confirms the results we obtain here by less rigorous means (see Problem 6.19).

[10]The general formula for the expectation value of *any* power of r is given in Hans A. Bethe and Edwin E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms*, Plenum, New York (1977), p. 17.

or, eliminating a (using Equation 4.72) and expressing everything in terms of E_n (using Equation 4.70):

$$E_r^1 = -\frac{(E_n)^2}{2mc^2}\left[\frac{4n}{l+1/2} - 3\right]. \qquad [6.57]$$

Evidently the relativistic correction is smaller than E_n, by a factor of about $E_n/mc^2 = 2 \times 10^{-5}$.

You might have noticed that I used *non*degenerate perturbation theory in this calculation (Equation 6.51), in spite of the fact that the hydrogen atom is highly degenerate. But the perturbation is spherically symmetrical, so it commutes with L^2 and L_z. Moreover, the eigenfunctions of these operators (taken together) have distinct eigenvalues for the n^2 states with a given E_n. Luckily, then, the wave functions ψ_{nlm} *are* the "good" states for this problem (or, as we say, n, l, and m are the **good quantum numbers**), so as it happens the use of nondegenerate perturbation theory was legitimate (see the "Moral" to Section 6.2.1).

∗Problem 6.12 Use the virial theorem (Problem 4.40) to prove Equation 6.55.

Problem 6.13 In Problem 4.43 you calculated the expectation value of r^s in the state ψ_{321}. Check your answer for the special cases $s = 0$ (trivial), $s = -1$ (Equation 6.55), $s = -2$ (Equation 6.56), and $s = -3$ (Equation 6.64). Comment on the case $s = -7$.

∗∗Problem 6.14 Find the (lowest-order) relativistic correction to the energy levels of the one-dimensional harmonic oscillator. *Hint:* Use the technique in Example 2.5.

∗∗∗Problem 6.15 Show that p^2 is hermitian, but p^4 is *not*, for hydrogen states with $l = 0$. *Hint:* For such states ψ is independent of θ and ϕ, so

$$p^2 = -\frac{\hbar^2}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)$$

(Equation 4.13). Using integration by parts, show that

$$\langle f|p^2 g\rangle = -4\pi\hbar^2\left(r^2 f\frac{dg}{dr} - r^2 g\frac{df}{dr}\right)\Bigg|_0^\infty + \langle p^2 f|g\rangle.$$

Check that the boundary term vanishes for ψ_{n00}, which goes like

$$\psi_{n00} \sim \frac{1}{\sqrt{\pi}(na)^{3/2}}\exp(-r/na)$$

near the origin. Now do the same for p^4, and show that the boundary terms do *not* vanish. In fact:

$$\langle \psi_{n00} | p^4 \psi_{m00} \rangle = \frac{8\hbar^4}{a^4} \frac{(n-m)}{(nm)^{5/2}} + \langle p^4 \psi_{n00} | \psi_{m00} \rangle.$$

6.3.2 Spin-Orbit Coupling

Imagine the electron in orbit around the nucleus; from the *electron's* point of view, the proton is circling around *it* (Figure 6.7). This orbiting positive charge sets up a magnetic field **B**, in the electron frame, which exerts a torque on the spinning electron, tending to align its magnetic moment (μ) along the direction of the field. The Hamiltonian (Equation 4.157) is

$$H = -\boldsymbol{\mu} \cdot \mathbf{B}. \qquad [6.58]$$

To begin with, we need to figure out the magnetic field of the proton (**B**) and the dipole moment of the electron (μ).

The magnetic field of the proton. If we picture the proton (from the electron's perspective) as a continuous current loop (Figure 6.7), its magnetic field can be calculated from the Biot-Savart law:

$$B = \frac{\mu_0 I}{2r},$$

with an effective current $I = e/T$, where e is the charge of the proton and T is the period of the orbit. On the other hand, the orbital angular momentum of the *electron* (in the rest frame of the *nucleus*) is $L = rmv = 2\pi m r^2/T$. Moreover, **B** and **L** point in the same direction (up, in Figure 6.7), so

$$\mathbf{B} = \frac{1}{4\pi\epsilon_0} \frac{e}{mc^2 r^3} \mathbf{L}. \qquad [6.59]$$

(I used $c = 1/\sqrt{\epsilon_0 \mu_0}$ to eliminate μ_0 in favor of ϵ_0.)
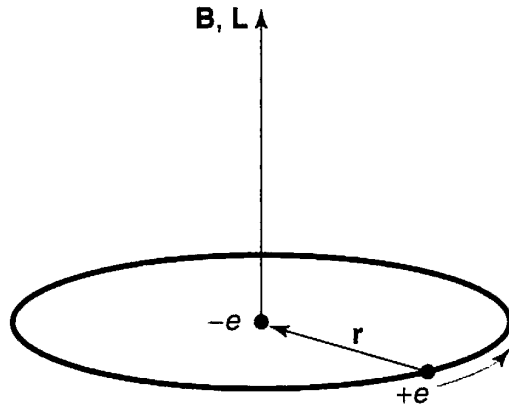

FIGURE 6.7: Hydrogen atom, from the electron's perspective.

The magnetic dipole moment of the electron. The magnetic dipole moment of a spinning charge is related to its (spin) angular momentum; the proportionality factor is the gyromagnetic ratio (which we already encountered in Section 4.4.2). Let's derive it, this time, using classical electrodynamics. Consider first a charge q smeared out around a ring of radius r, which rotates about the axis with period T (Figure 6.8). The magnetic dipole moment of the ring is defined as the current (q/T) times the area (πr^2):

$$\mu = \frac{q \pi r^2}{T}.$$

If the mass of the ring is m, its angular momentum is the moment of inertia (mr^2) times the angular velocity $(2\pi/T)$:

$$S = \frac{2\pi m r^2}{T}.$$

The gyromagnetic ratio for this configuration is evidently $\mu/S = q/2m$. Notice that it is independent of r (and T). If I had some more complicated object, such as a sphere (all I require is that it be a figure of revolution, rotating about its axis), I could calculate μ and S by chopping it into little rings, and adding up their contributions. As long as the mass and the charge are distributed in the same manner (so that the charge-to-mass ratio is uniform), the gyromagnetic ratio will be the same for each ring, and hence also for the object as a whole. Moreover, the directions of μ and S are the same (or opposite, if the charge is negative), so

$$\mu = \left(\frac{q}{2m}\right) S.$$

That was a purely *classical* calculation, however; as it turns out the electron's magnetic moment is *twice* the classical value:
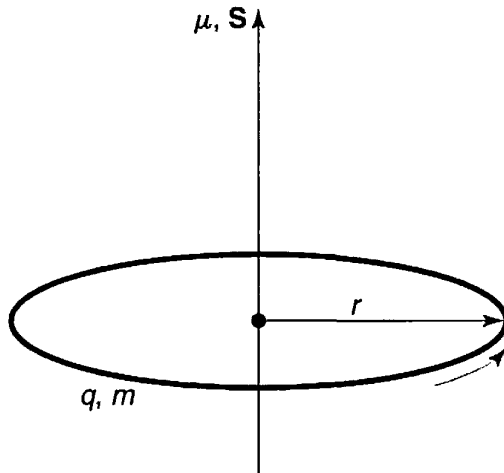
$$\mu_e = -\frac{e}{m} S. \qquad [6.60]$$

FIGURE 6.8: A ring of charge, rotating about its axis.

The "extra" factor of 2 was explained by Dirac, in his relativistic theory of the electron.[11]

Putting all this together, we have

$$H = \left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{1}{m^2c^2r^3}\mathbf{S}\cdot\mathbf{L}.$$

But there is a serious fraud in this calculation: I did the analysis in the rest frame of the electron, but that's *not an inertial system*—it *accelerates*, as the electron orbits around the nucleus. You can get away with this if you make an appropriate kinematic correction, known as the **Thomas precession**.[12] In this context it throws in a factor of $1/2$:[13]

$$H'_{so} = \left(\frac{e^2}{8\pi\epsilon_0}\right)\frac{1}{m^2c^2r^3}\mathbf{S}\cdot\mathbf{L}. \qquad [6.61]$$

This is the **spin-orbit interaction**; apart from two corrections (the modified gyromagnetic ratio for the electron and the Thomas precession factor—which, coincidentally, exactly cancel one another) it is just what you would expect on the basis of a naive classical model. Physically, it is due to the torque exerted on the magnetic dipole moment of the spinning electron, by the magnetic field of the proton, in the electron's instantaneous rest frame.

Now the quantum mechanics. In the presence of spin-orbit coupling, the Hamiltonian no longer commutes with **L** and **S**, so the spin and orbital angular momenta are not separately conserved (see Problem 6.16). However, H'_{so} *does* commute with L^2, S^2 and the *total* angular momentum

$$\mathbf{J} \equiv \mathbf{L} + \mathbf{S}, \qquad [6.62]$$

---

[11] We have already noted that it can be dangerous to picture the electron as a spinning sphere (see Problem 4.25), and it is not too surprising that the naive classical model gets the gyromagnetic ratio wrong. The *deviation* from the classical expectation is known as the **g-factor**: $\mu = g(q/2m)\mathbf{S}$. Thus the g-factor of the electron, in Dirac's theory, is exactly 2. But **quantum electrodynamics** reveals tiny corrections to this: g_e is actually $2 + (\alpha/\pi) + \ldots = 2.002\ldots$. The calculation and measurement (which agree to exquisite precision) of the so-called **anomalous magnetic moment** of the electron were among the greatest achievements of twentieth-century physics.

[12] One way of thinking of it is that the electron is continually stepping from one inertial system to another; Thomas precession amounts to the cumulative effect of all these Lorentz transformations. We could avoid the whole problem, of course, by staying in the *lab* frame, in which the nucleus is at rest. In that case the field of the proton is purely *electric*, and you might wonder why it exerts any torque on the electron. Well, the fact is that a moving *magnetic* dipole acquires an *electric* dipole moment, and in the lab frame the spin-orbit coupling is due to the interaction of the *electric* field of the nucleus with the *electric* dipole moment of the electron. Because this analysis requires more sophisticated electrodynamics, it seems best to adopt the electron's perspective, where the physical mechanism is more transparent.

[13] More precisely, Thomas precession subtracts 1 from the g factor. See R. R. Haar and L. J. Curtis, *Am. J. Phys.*, **55**, 1044 (1987).

and hence these quantities *are* conserved (Equation 3.71). To put it another way, the eigenstates of L_z and S_z are not "good" states to use in perturbation theory, but the eigenstates of L^2, S^2, J^2, and J_z *are*. Now

$$J^2 = (\mathbf{L} + \mathbf{S}) \cdot (\mathbf{L} + \mathbf{S}) = L^2 + S^2 + 2\mathbf{L} \cdot \mathbf{S},$$

so

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2}(J^2 - L^2 - S^2), \tag{6.63}$$

and therefore the eigenvalues of $\mathbf{L} \cdot \mathbf{S}$ are

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

In this case, of course, $s = 1/2$. Meanwhile, the expectation value of $1/r^3$ (see Problem 6.35(c)) is

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{l(l+1/2)(l+1)n^3a^3}, \tag{6.64}$$

and we conclude that

$$E_{so}^1 = \langle H_{so}' \rangle = \frac{e^2}{8\pi\epsilon_0} \frac{1}{m^2c^2} \frac{(\hbar^2/2)[j(j+1) - l(l+1) - 3/4]}{l(l+1/2)(l+1)n^3a^3}.$$

or, expressing it all in terms of E_n:[14]

$$E_{so}^1 = \frac{(E_n)^2}{mc^2} \left\{ \frac{n[j(j+1) - l(l+1) - 3/4]}{l(l+1/2)(l+1)} \right\}. \tag{6.65}$$

It is remarkable, considering the totally different physical mechanisms involved, that the relativistic correction and the spin-orbit coupling are of the same order (E_n^2/mc^2). Adding them together, we get the complete fine-structure formula (see Problem 6.17):

$$E_{fs}^1 = \frac{(E_n)^2}{2mc^2} \left(3 - \frac{4n}{j+1/2} \right). \tag{6.66}$$

---

[14]Once again, the case $l = 0$ is problematic, since we are ostensibly dividing by zero. On the other hand, the numerator is *also* zero, since in this case $j = s$, so Equation 6.65 is indeterminate. On physical grounds there shouldn't be any spin-orbit coupling when $l = 0$. One way to resolve the ambiguity is to introduce the so-called **Darwin term** (see, for instance, G. K. Woodgate, *Elementary Atomic Structure*, 2nd ed., Oxford (1983), p. 63). Serendipitously, even though both the relativistic correction (Equation 6.57) and the spin-orbit coupling (Equation 6.65) are questionable in the case $l = 0$, their *sum* (Equation 6.66) is correct for *all* l (see Problem 6.19).
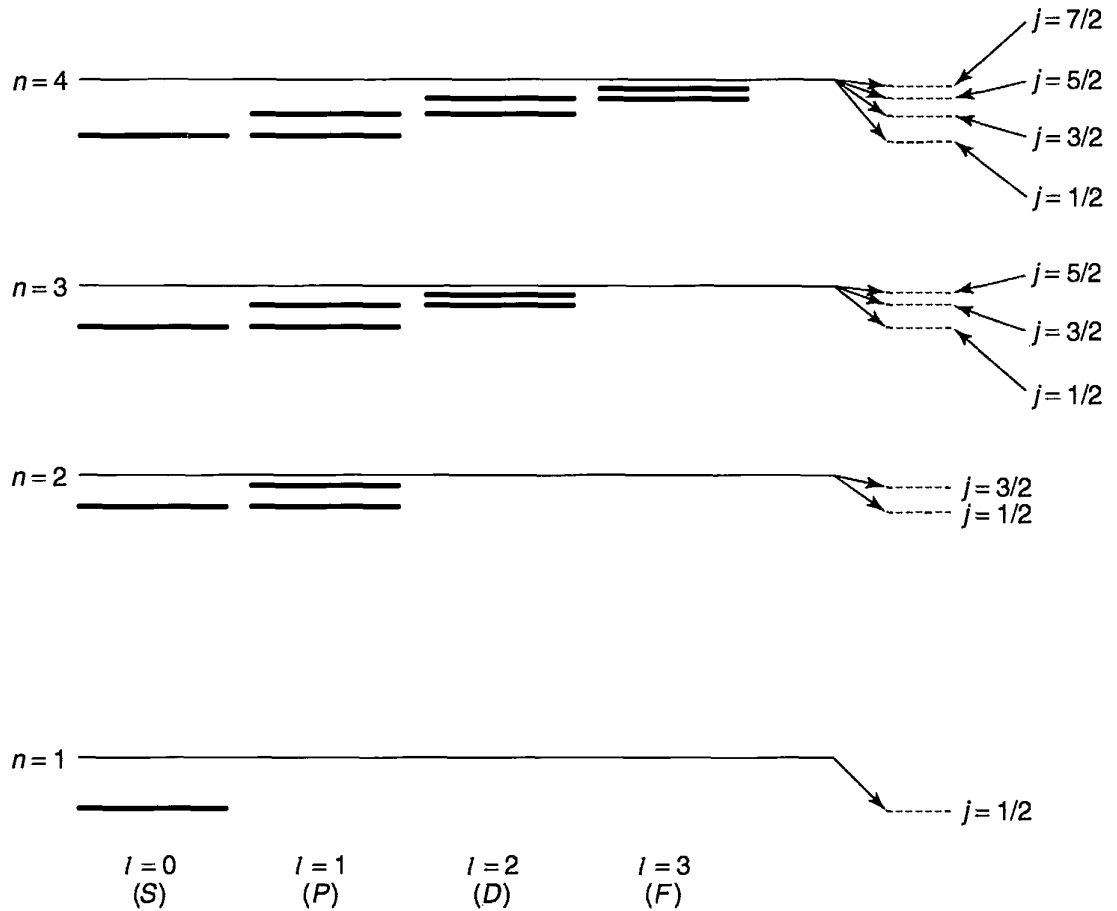
FIGURE 6.9: Energy levels of hydrogen, including fine structure (not to scale).

Combining this with the Bohr formula, we obtain the grand result for the energy levels of hydrogen, with fine structure included:

$$E_{nj} = -\frac{13.6\,\text{eV}}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)\right]. \qquad [6.67]$$

Fine structure breaks the degeneracy in l (that is, for a given n, the different allowed values of l do not all carry the same energy), but it still preserves degeneracy in j (see Figure 6.9). The z-component eigenvalues for orbital and spin angular momentum (m_l and m_s) are no longer "good" quantum numbers—the stationary states are linear combinations of states with different values of these quantities; the "good" quantum numbers are n, l, s, j, and m_j.[15]

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[15]To write $|j\,m_j\rangle$ (for given l and s) as a linear combination of $|l\,m_l\rangle|s\,m_s\rangle$ we would use the appropriate Clebsch-Gordan coefficients (Equation 4.185).

Problem 6.16 Evaluate the following commutators: (a) $[\mathbf{L} \cdot \mathbf{S}, \mathbf{L}]$, (b) $[\mathbf{L} \cdot \mathbf{S}, \mathbf{S}]$, (c) $[\mathbf{L} \cdot \mathbf{S}, \mathbf{J}]$, (d) $[\mathbf{L} \cdot \mathbf{S}, L^2]$, (e) $[\mathbf{L} \cdot \mathbf{S}, S^2]$, (f) $[\mathbf{L} \cdot \mathbf{S}, J^2]$. *Hint:* $\mathbf{L}$ and $\mathbf{S}$ satisfy the fundamental commutation relations for angular momentum (Equations 4.99 and 4.134), but they commute with each other.

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*Problem 6.17 Derive the fine structure formula (Equation 6.66) from the relativistic correction (Equation 6.57) and the spin-orbit coupling (Equation 6.65). *Hint:* Note that $j = l \pm 1/2$; treat the plus sign and the minus sign separately, and you'll find that you get the same final answer either way.

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* *Problem 6.18 The most prominent feature of the hydrogen spectrum in the visible region is the red Balmer line, coming from the transition $n = 3$ to $n = 2$. First of all, determine the wavelength and frequency of this line according to the Bohr theory. Fine structure splits this line into several closely spaced lines; the question is: *How many*, and *what is their spacing*? *Hint:* First determine how many sublevels the $n = 2$ level splits into, and find E_{fs}^1 for each of these, in eV. Then do the same for $n = 3$. Draw an energy level diagram showing all possible transitions from $n = 3$ to $n = 2$. The energy released (in the form of a photon) is $(E_3 - E_2) + \Delta E$, the first part being common to all of them, and the ΔE (due to fine structure) varying from one transition to the next. Find ΔE (in eV) for each transition. Finally, convert to photon frequency, and determine the spacing between adjacent spectral lines (in Hz)—*not* the frequency interval between each line and the *unperturbed* line (which is, of course, unobservable), but the frequency interval between each line and the *next* one. Your final answer should take the form: "The red Balmer line splits into (???) lines. In order of increasing frequency, they come from the transitions (1) $j = (???)$ to $j = (???)$, (2) $j = (???)$ to $j = (???)$, ... The frequency spacing between line (1) and line (2) is (???) Hz, the spacing between line (2) and line (3) is (???) Hz, ..."

Problem 6.19 The *exact* fine-structure formula for hydrogen (obtained from the Dirac equation without recourse to perturbation theory) is[16]

$$E_{nj} = mc^2 \left\{ \left[1 + \left(\frac{\alpha}{n - (j + 1/2) + \sqrt{(j + 1/2)^2 - \alpha^2}} \right)^2 \right]^{-1/2} - 1 \right\}.$$

Expand to order α^4 (noting that $\alpha \ll 1$), and show that you recover Equation 6.67.

---

[16]Bethe and Salpeter (footnote 10), page 238.

6.4 THE ZEEMAN EFFECT

When an atom is placed in a uniform external magnetic field $\mathbf{B}_{ext}$, the energy levels are shifted. This phenomenon is known as the **Zeeman effect**. For a single electron, the perturbation is

$$H'_Z = -(\boldsymbol{\mu}_l + \boldsymbol{\mu}_s) \cdot \mathbf{B}_{ext},$$ [6.68]

where

$$\boldsymbol{\mu}_s = -\frac{e}{m}\mathbf{S}$$ [6.69]

is the magnetic dipole moment associated with electron spin, and

$$\boldsymbol{\mu}_l = -\frac{e}{2m}\mathbf{L}$$ [6.70]

is the dipole moment associated with orbital motion.[17] Thus

$$H'_Z = \frac{e}{2m}(\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B}_{ext}.$$ [6.71]

The nature of the Zeeman splitting depends critically on the strength of the external field in comparison with the *internal* field (Equation 6.59) that gives rise to spin-orbit coupling. If $B_{ext} \ll B_{int}$, then fine structure dominates, and H'_Z can be treated as a small perturbation, whereas if $B_{ext} \gg B_{int}$, then the Zeeman effect dominates, and fine structure becomes the perturbation. In the intermediate zone, where the two fields are comparable, we need the full machinery of degenerate perturbation theory, and it is necessary to diagonalize the relevant portion of the Hamiltonian "by hand." In the following sections we shall explore each of these regimes briefly, for the case of hydrogen.

Problem 6.20 Use Equation 6.59 to estimate the internal field in hydrogen, and characterize quantitatively a "strong" and "weak" Zeeman field.

6.4.1 Weak-Field Zeeman Effect

If $B_{ext} \ll B_{int}$, fine structure dominates (Equation 6.67); the "good" quantum numbers are n, l, j, and m_j (but not m_l and m_s, because—in the presence of spin-orbit coupling—$\mathbf{L}$ and $\mathbf{S}$ are not separately conserved).[18] In first-order perturbation

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[17]The gyromagnetic ratio for *orbital* motion is just the classical value $(q/2m)$—it is only for *spin* that there is an "extra" factor of 2.

[18]In this problem we have a perturbation (Zeeman splitting) piled on top of a perturbation (fine structure). The "good" quantum numbers are those appropriate to the dominant perturbation—in this case the fine structure. The secondary perturbation (Zeeman splitting) lifts the remaining degeneracy in J_z, which plays here the role of the operator A in the theorem of Section 6.2.1. Technically, J_z does not commute with H'_Z, but it does in the time average sense of Equation 6.73.
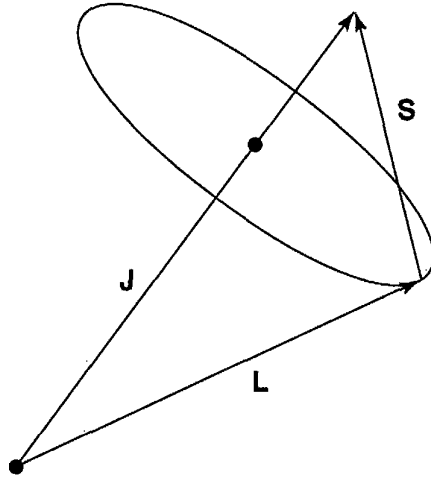
FIGURE 6.10: In the presence of spin-orbit coupling, L and S are not separately conserved; they precess about the fixed total angular momentum, J.

theory, the Zeeman correction to the energy is

$$E_Z^1 = \langle nljm_j | H_Z' | nljm_j \rangle = \frac{e}{2m} \mathbf{B}_{ext} \cdot \langle \mathbf{L} + 2\mathbf{S} \rangle. \qquad [6.72]$$

Now $\mathbf{L} + 2\mathbf{S} = \mathbf{J} + \mathbf{S}$. Unfortunately, we do not immediately know the expectation value of $\mathbf{S}$. But we can figure it out, as follows: The total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is constant (Figure 6.10); $\mathbf{L}$ and $\mathbf{S}$ precess rapidly about this fixed vector. In particular, the (time) *average* value of $\mathbf{S}$ is just its projection along $\mathbf{J}$:

$$\mathbf{S}_{ave} = \frac{(\mathbf{S} \cdot \mathbf{J})}{J^2} \mathbf{J}. \qquad [6.73]$$

But $\mathbf{L} = \mathbf{J} - \mathbf{S}$, so $L^2 = J^2 + S^2 - 2\mathbf{J} \cdot \mathbf{S}$, and hence

$$\mathbf{S} \cdot \mathbf{J} = \frac{1}{2}(J^2 + S^2 - L^2) = \frac{\hbar^2}{2}[j(j+1) + s(s+1) - l(l+1)]. \qquad [6.74]$$

from which it follows that

$$\langle \mathbf{L} + 2\mathbf{S} \rangle = \left\langle \left(1 + \frac{\mathbf{S} \cdot \mathbf{J}}{J^2}\right) \mathbf{J} \right\rangle = \left[1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)}\right] \langle \mathbf{J} \rangle. \qquad [6.75]$$

The term in square brackets is known as the **Landé g-factor**, g_J.

We may as well choose the z-axis to lie along $\mathbf{B}_{ext}$; then

$$E_Z^1 = \mu_B g_J B_{ext} m_j. \qquad [6.76]$$

where

$$\mu_B \equiv \frac{e\hbar}{2m} = 5.788 \times 10^{-5} \text{ eV/T} \qquad [6.77]$$

is the so-called **Bohr magneton**. The *total* energy is the sum of the fine-structure part (Equation 6.67) and the Zeeman contribution (Equation 6.76). For example,

the ground state ($n = 1$, $l = 0$, $j = 1/2$, and therefore $g_J = 2$) splits into two levels:

$$-13.6 \text{ eV}(1 + \alpha^2/4) \pm \mu_B B_{\text{ext}},$$
[6.78]

with the plus sign for $m_j = 1/2$, and minus for $m_j = -1/2$. These energies are plotted (as functions of B_{ext}) in Figure 6.11.

∗Problem 6.21 Consider the (eight) $n = 2$ states, $|2ljm_j\rangle$. Find the energy of each state, under weak-field Zeeman splitting, and construct a diagram like Figure 6.11 to show how the energies evolve as B_{ext} increases. Label each line clearly, and indicate its slope.

6.4.2 Strong-Field Zeeman Effect

If $B_{\text{ext}} \gg B_{\text{int}}$, the Zeeman effect dominates;[19] with B_{ext} in the z direction, the "good" quantum numbers are now n, l, m_l, and m_s (but not j and m_j because—in the presence of the external torque—the total angular momentum is not conserved, whereas L_z and S_z *are*). The Zeeman Hamiltonian is

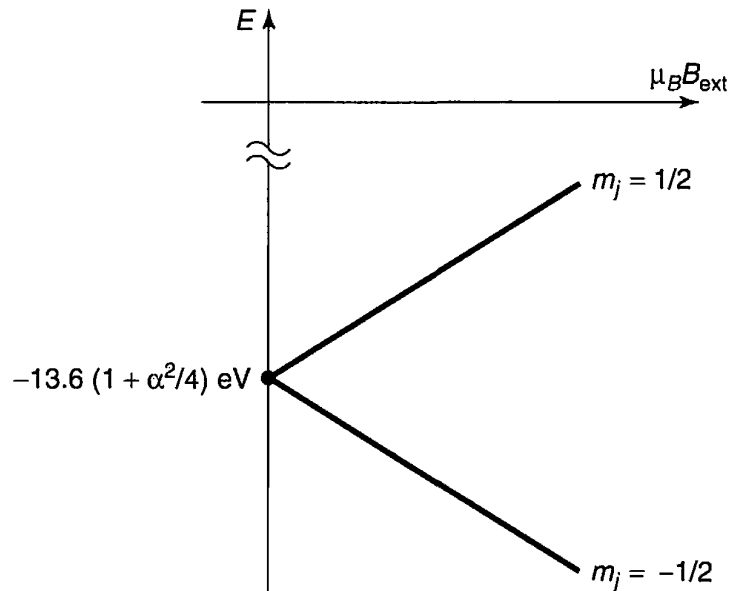$$H'_Z = \frac{e}{2m} B_{\text{ext}} (L_z + 2S_z),$$

FIGURE 6.11: Weak-field Zeeman splitting of the ground state of hydrogen; the upper line ($m_j = 1/2$) has slope 1, the lower line ($m_j = -1/2$) has slope −1.

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[19]In this regime the Zeeman effect is also known as the **Paschen-Back effect**.

and the "unperturbed" energies are

$$E_{nm_lm_s} = -\frac{13.6 \text{ eV}}{n^2} + \mu_B B_{\text{ext}}(m_l + 2m_s). \tag{6.79}$$

That's the *answer*, if we ignore fine structure completely. But we can do better.
    In first-order perturbation theory the fine-structure correction to these levels is

$$E_{\text{fs}}^1 = \langle nl \, m_l \, m_s | (H_r' + H_{\text{so}}') | nl \, m_l \, m_s \rangle. \tag{6.80}$$

The relativistic contribution is the same as before (Equation 6.57); for the spin-orbit term (Equation 6.61) we need

$$\langle \mathbf{S} \cdot \mathbf{L} \rangle = \langle S_x \rangle \langle L_x \rangle + \langle S_y \rangle \langle L_y \rangle + \langle S_z \rangle \langle L_y \rangle = \hbar^2 m_l m_s \tag{6.81}$$

(note that $\langle S_x \rangle = \langle S_y \rangle = \langle L_x \rangle = \langle L_y \rangle = 0$ for eigenstates of S_z and L_z). Putting all this together (Problem 6.22), we conclude that

$$E_{\text{fs}}^1 = \frac{13.6 \text{ eV}}{n^3} \alpha^2 \left\{ \frac{3}{4n} - \left[\frac{l(l+1) - m_l m_s}{l(l + 1/2)(l+1)} \right] \right\}. \tag{6.82}$$

(The term in square brackets is indeterminate for $l = 0$; its correct value in this case is 1—see Problem 6.24.) The *total* energy is the sum of the Zeeman part (Equation 6.79) and the fine structure contribution (Equation 6.82).

Problem 6.22 Starting with Equation 6.80, and using Equations 6.57, 6.61, 6.64, and 6.81, derive Equation 6.82.

∗∗**Problem 6.23** Consider the (eight) $n = 2$ states, $|2 l \, m_l \, m_s \rangle$. Find the energy of each state, under strong-field Zeeman splitting. Express each answer as the sum of three terms: the Bohr energy, the fine-structure (proportional to α^2), and the Zeeman contribution (proportional to $\mu_B B_{\text{ext}}$). If you ignore fine structure altogether, how many distinct levels are there, and what are their degeneracies?

Problem 6.24 If $l = 0$, then $j = s$, $m_j = m_s$, and the "good" states are the same ($|n \, m_s \rangle$) for weak *and* strong fields. Determine E_Z^1 (from Equation 6.72) and the fine structure energies (Equation 6.67), and write down the general result for the $l = 0$ Zeeman effect—*regardless* of the strength of the field. Show that the strong-field formula (Equation 6.82) reproduces this result, provided that we interpret the indeterminate term in square brackets as 1.

6.4.3 Intermediate-Field Zeeman Effect

In the intermediate regime neither H'_Z nor H'_{fs} dominates, and we must treat the two on an equal footing, as perturbations to the Bohr Hamiltonian (Equation 6.42):

$$H' = H'_Z + H'_{fs}. \qquad [6.83]$$

I'll confine my attention here to the case $n = 2$, and use as the basis for degenerate perturbation theory the states characterized by l, j, and m_j.[20] Using the Clebsch-Gordan coefficients (Problem 4.51 or Table 4.8) to express $|j\, m_j\rangle$ as a linear combination of $|l\, m_l\rangle|s\, m_s\rangle$, we have:

$$l = 0 \begin{cases} \psi_1 \equiv |\tfrac{1}{2}\ \tfrac{1}{2}\rangle\ = |0\,0\rangle|\tfrac{1}{2}\ \tfrac{1}{2}\rangle. \\[1em] \psi_2 \equiv |\tfrac{1}{2}\ \tfrac{-1}{2}\rangle = |0\,0\rangle|\tfrac{1}{2}\ \tfrac{-1}{2}\rangle. \end{cases}$$

$$l = 1 \begin{cases} \psi_3 \equiv |\tfrac{3}{2}\ \tfrac{3}{2}\rangle\ = |1\ 1\rangle|\tfrac{1}{2}\ \tfrac{1}{2}\rangle. \\[1em] \psi_4 \equiv |\tfrac{3}{2}\ \tfrac{-3}{2}\rangle = |1\,-1\rangle|\tfrac{1}{2}\ \tfrac{-1}{2}\rangle. \\[1em] \psi_5 \equiv |\tfrac{3}{2}\ \tfrac{1}{2}\rangle\ = \sqrt{2/3}|1\,0\rangle|\tfrac{1}{2}\ \tfrac{1}{2}\rangle\ + \sqrt{1/3}|1\ 1\rangle|\tfrac{1}{2}\ \tfrac{-1}{2}\rangle. \\[1em] \psi_6 \equiv |\tfrac{1}{2}\ \tfrac{1}{2}\rangle\ = -\sqrt{1/3}|1\,0\rangle|\tfrac{1}{2}\ \tfrac{1}{2}\rangle\ + \sqrt{2/3}|1\ 1\rangle|\tfrac{1}{2}\ \tfrac{-1}{2}\rangle. \\[1em] \psi_7 \equiv |\tfrac{3}{2}\ \tfrac{-1}{2}\rangle = \sqrt{1/3}|1\,-1\rangle|\tfrac{1}{2}\ \tfrac{1}{2}\rangle\ + \sqrt{2/3}|1\,0\rangle|\tfrac{1}{2}\ \tfrac{-1}{2}\rangle. \\[1em] \psi_8 \equiv |\tfrac{1}{2}\ \tfrac{-1}{2}\rangle = -\sqrt{2/3}|1\,-1\rangle|\tfrac{1}{2}\ \tfrac{1}{2}\rangle + \sqrt{1/3}|1\,0\rangle|\tfrac{1}{2}\ \tfrac{-1}{2}\rangle. \end{cases}$$

In this basis the nonzero matrix elements of H'_{fs} are all on the diagonal, and given by Equation 6.66; H'_Z has four off-diagonal elements, and the complete matrix $-\mathbf{W}$ is (see Problem 6.25):

$$\begin{pmatrix} 5\gamma - \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 5\gamma + \beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \gamma - 2\beta & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \gamma + 2\beta & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \gamma - \tfrac{2}{3}\beta & \tfrac{\sqrt{2}}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & \tfrac{\sqrt{2}}{3}\beta & 5\gamma - \tfrac{1}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \gamma + \tfrac{2}{3}\beta & \tfrac{\sqrt{2}}{3}\beta \\ 0 & 0 & 0 & 0 & 0 & 0 & \tfrac{\sqrt{2}}{3}\beta & 5\gamma + \tfrac{1}{3}\beta \end{pmatrix}$$

---

[20]You can use l, m_l, m_s states if you prefer—this makes the matrix elements of H'_Z easier, but those of H'_{fs} more difficult; the $\mathbf{W}$ matrix will be more complicated, but its eigenvalues (which are independent of basis) are the same either way.

where

$$\gamma \equiv (\alpha/8)^2 13.6 \text{ eV} \quad \text{and} \quad \beta \equiv \mu_B B_{\text{ext}}.$$

The first four eigenvalues are already displayed along the diagonal; it remains only to find the eigenvalues of the two 2×2 blocks. The characteristic equation for the first of these is

$$\lambda^2 - \lambda(6\gamma - \beta) + \left(5\gamma^2 - \frac{11}{3}\gamma\beta\right) = 0,$$

and the quadratic formula gives the eigenvalues:

$$\lambda_\pm = -3\gamma + (\beta/2) \pm \sqrt{4\gamma^2 + (2/3)\gamma\beta + (\beta^2/4)}. \quad [6.84]$$

The eigenvalues of the second block are the same, but with the sign of β reversed. The eight energies are listed in Table 6.2, and plotted against B_{ext} in Figure 6.12. In the zero-field limit ($\beta = 0$) they reduce to the fine-structure values; for weak fields ($\beta \ll \gamma$) they reproduce what you got in Problem 6.21; for strong fields ($\beta \gg \gamma$) we recover the results of Problem 6.23 (note the convergence to five distinct energy levels, at very high fields, as predicted in Problem 6.23).
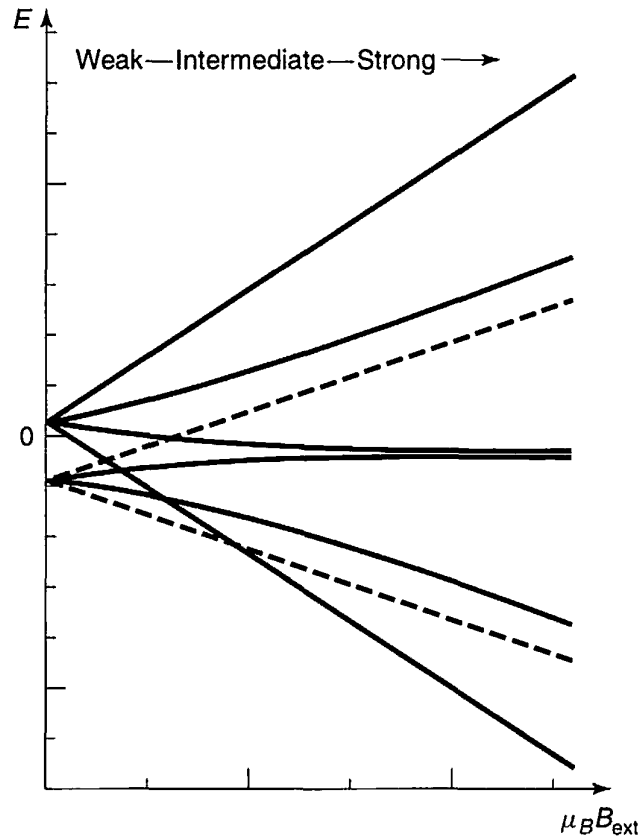

FIGURE 6.12: Zeeman splitting of the $n = 2$ states of hydrogen, in the weak, intermediate, and strong field regimes.

TABLE 6.2:   Energy levels for the $n = 2$ states of hydrogen, with fine structure and Zeeman splitting.

ϵ_1	=	$E_2 - 5\gamma + \beta$
ϵ_2	=	$E_2 - 5\gamma - \beta$
ϵ_3	=	$E_2 - \gamma + 2\beta$
ϵ_4	=	$E_2 - \gamma - 2\beta$
ϵ_5	=	$E_2 - 3\gamma + \beta/2 + \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4}$
ϵ_6	=	$E_2 - 3\gamma + \beta/2 - \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4}$
ϵ_7	=	$E_2 - 3\gamma - \beta/2 + \sqrt{4\gamma^2 - (2/3)\gamma\beta + \beta^2/4}$
ϵ_8	=	$E_2 - 3\gamma - \beta/2 - \sqrt{4\gamma^2 - (2/3)\gamma\beta + \beta^2/4}$

Problem 6.25 Work out the matrix elements of H'_Z and H'_{fs}, and construct the W-matrix given in the text, for $n = 2$.

★ ★ ★**Problem 6.26** Analyze the Zeeman effect for the $n = 3$ states of hydrogen, in the weak, strong, and intermediate field regimes. Construct a table of energies (analogous to Table 6.2), plot them as functions of the external field (as in Figure 6.12), and check that the intermediate-field results reduce properly in the two limiting cases.

6.5 HYPERFINE SPLITTING

The proton itself constitutes a magnetic dipole, though its dipole moment is much smaller than the electron's because of the mass in the denominator (Equation 6.60):

$$\mu_p = \frac{g_p e}{2m_p}\mathbf{S}_p, \qquad \mu_e = -\frac{e}{m_e}\mathbf{S}_e. \tag{6.85}$$

(The proton is a composite structure, made up of three quarks, and its gyromagnetic ratio is not as simple as the electron's—hence the explicit g-factor (g_p), whose measured value is 5.59, as opposed to 2.00 for the electron.) According to classical electrodynamics, a dipole μ sets up a magnetic field[21]

$$\mathbf{B} = \frac{\mu_0}{4\pi r^3}[3(\mu \cdot \hat{r})\hat{r} - \mu] + \frac{2\mu_0}{3}\mu\delta^3(\mathbf{r}). \tag{6.86}$$

---

[21] If you are unfamiliar with the delta function term in Equation 6.86, you can derive it by treating the dipole as a spinning charged spherical shell, in the limit as the radius goes to zero and the charge goes to infinity (with μ held constant). See D. J. Griffiths. *Am. J. Phys.*. **50**, 698 (1982).

So the Hamiltonian of the electron, in the magnetic field due to the proton's magnetic dipole moment, is (Equation 6.58)

$$H'_{hf} = \frac{\mu_0 g_p e^2}{8\pi m_p m_e} \frac{[3(\mathbf{S}_p \cdot \hat{r})(\mathbf{S}_e \cdot \hat{r}) - \mathbf{S}_p \cdot \mathbf{S}_e]}{r^3} + \frac{\mu_0 g_p e^2}{3 m_p m_e} \mathbf{S}_p \cdot \mathbf{S}_e \delta^3(\mathbf{r}).$$ [6.87]

According to perturbation theory, the first-order correction to the energy (Equation 6.9) is the expectation value of the perturbing Hamiltonian:

$$E^1_{hf} = \frac{\mu_0 g_p e^2}{8\pi m_p m_e} \left\langle \frac{3(\mathbf{S}_p \cdot \hat{r})(\mathbf{S}_e \cdot \hat{r}) - \mathbf{S}_p \cdot \mathbf{S}_e}{r^3} \right\rangle$$

$$+ \frac{\mu_0 g_p e^2}{3 m_p m_e} \langle \mathbf{S}_p \cdot \mathbf{S}_e \rangle |\psi(0)|^2.$$ [6.88]

In the ground state (or any other state for which $l = 0$) the wave function is spherically symmetrical, and the first expectation value vanishes (see Problem 6.27). Meanwhile, from Equation 4.80 we find that $|\psi_{100}(0)|^2 = 1/(\pi a^3)$, so

$$E^1_{hf} = \frac{\mu_0 g_p e^2}{3\pi m_p m_e a^3} \langle \mathbf{S}_p \cdot \mathbf{S}_e \rangle.$$ [6.89]

in the ground state. This is called **spin-spin coupling**, because it involves the dot product of two spins (contrast spin-orbit coupling, which involves $\mathbf{S} \cdot \mathbf{L}$).

In the presence of spin-spin coupling, the individual spin angular momenta are no longer conserved; the "good" states are eigenvectors of the *total* spin,

$$\mathbf{S} \equiv \mathbf{S}_e + \mathbf{S}_p.$$ [6.90]

As before, we square this out to get

$$\mathbf{S}_p \cdot \mathbf{S}_e = \frac{1}{2}(S^2 - S_e^2 - S_p^2).$$ [6.91]

But the electron and proton both have spin 1/2, so $S_e^2 = S_p^2 = (3/4)\hbar^2$. In the triplet state (spins "parallel") the total spin is 1, and hence $S^2 = 2\hbar^2$; in the singlet state the total spin is 0, and $S^2 = 0$. Thus

$$E^1_{hf} = \frac{4 g_p \hbar^4}{3 m_p m_e^2 c^2 a^4} \begin{cases} +1/4, & \text{(triplet)}; \\ -3/4, & \text{(singlet)}. \end{cases}$$ [6.92]

Spin-spin coupling breaks the spin degeneracy of the ground state, lifting the triplet configuration and depressing the singlet (see Figure 6.13). The energy gap is evidently

$$\Delta E = \frac{4 g_p \hbar^4}{3 m_p m_e^2 c^2 a^4} = 5.88 \times 10^{-6} \text{ eV}.$$ [6.93]
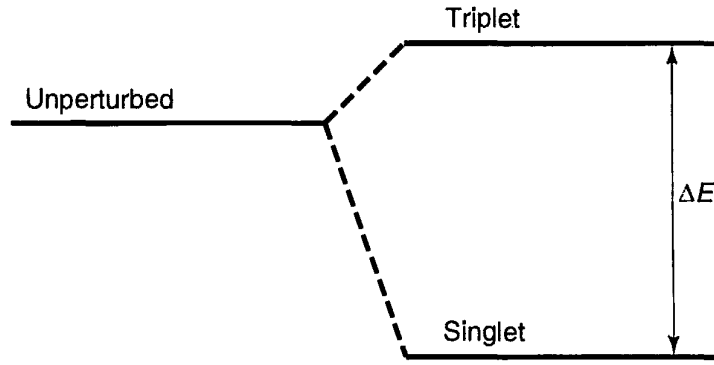
Triplet

Unperturbed

ΔE

Singlet

FIGURE 6.13:   Hyperfine splitting in the ground state of hydrogen.

The frequency of the photon emitted in a transition from the triplet to the singlet state is

$$v = \frac{\Delta E}{h} = 1420 \text{ MHz.} \qquad [6.94]$$

and the corresponding wavelength is $c/v = 21$ cm, which falls in the microwave region. This famous **21-centimeter line** is among the most pervasive and ubiquitous forms of radiation in the universe.

Problem 6.27 Let **a** and **b** be two constant vectors. Show that

$$\int (\mathbf{a} \cdot \hat{r})(\mathbf{b} \cdot \hat{r}) \sin\theta \, d\theta \, d\phi = \frac{4\pi}{3}(\mathbf{a} \cdot \mathbf{b}) \qquad [6.95]$$

(the integration is over the usual range: $0 < \theta < \pi, \ 0 < \phi < 2\pi$). Use this result to demonstrate that

$$\left\langle \frac{3(\mathbf{S}_p \cdot \hat{r})(\mathbf{S}_e \cdot \hat{r}) - \mathbf{S}_p \cdot \mathbf{S}_e}{r^3} \right\rangle = 0.$$

for states with $l = 0$. *Hint:* $\hat{r} = \sin\theta \cos\phi\, \hat{\imath} + \sin\theta \sin\phi\, \hat{\jmath} + \cos\theta\, \hat{k}$.

Problem 6.28 By appropriate modification of the hydrogen formula, determine the hyperfine splitting in the ground state of (a) **muonic hydrogen** (in which a muon—same charge and g-factor as the electron, but 207 times the mass—substitutes for the electron), (b) **positronium** (in which a positron—same mass and g-factor as the electron, but opposite charge—substitutes for the proton), and (c) **muonium** (in which an anti-muon—same mass and g-factor as a muon, but opposite charge—substitutes for the proton). *Hint:* Don't forget to use the reduced mass (Problem 5.1) in calculating the "Bohr radius" of these exotic "atoms." Incidentally, the answer you get for positronium (4.82×10^{-4} eV) is quite far from the experimental value (8.41×10^{-4} eV); the large discrepancy is due to pair annihilation ($e^+ + e^- \rightarrow \gamma + \gamma$), which contributes an extra $(3/4)\Delta E$, and does not occur (of course) in ordinary hydrogen, muonic hydrogen, or muonium.

FURTHER PROBLEMS FOR CHAPTER 6

Problem 6.29 Estimate the correction to the ground state energy of hydrogen due to the finite size of the nucleus. Treat the proton as a uniformly charged spherical shell of radius b, so the potential energy of an electron inside the shell is *constant:* $-e^2/(4\pi\epsilon_0 b)$; this isn't very realistic, but it is the simplest model, and it will give us the right order of magnitude. Expand your result in powers of the small parameter (b/a), where a is the Bohr radius, and keep only the leading term, so your final answer takes the form

$$\frac{\Delta E}{E} = A(b/a)^n.$$

Your business is to determine the constant A and the power n. Finally, put in $b \approx 10^{-15}$ m (roughly the radius of the proton) and work out the actual number. How does it compare with fine structure and hyperfine structure?

Problem 6.30 Consider the isotropic three-dimensional harmonic oscillator (Problem 4.38). Discuss the effect (in first order) of the perturbation

$$H' = \lambda x^2 yz$$

(for some constant λ) on

(a) the ground state;

(b) the (triply degenerate) first excited state. *Hint:* Use the answers to Problems 2.12 and 3.33.

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* * *Problem 6.31** **Van der Waals interaction.** Consider two atoms a distance R apart. Because they are electrically neutral you might suppose there would be no force between them, but if they are polarizable there is in fact a weak attraction. To model this system, picture each atom as an electron (mass m, charge $-e$) attached by a spring (spring constant k) to the nucleus (charge $+e$), as in Figure 6.14. We'll assume the nuclei are heavy, and essentially motionless. The Hamiltonian for the unperturbed system is

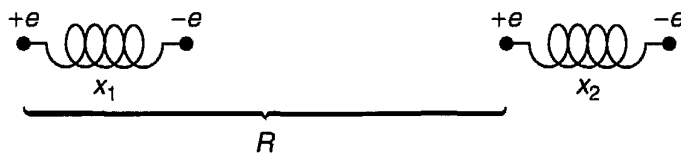$$H^0 = \frac{1}{2m}p_1^2 + \frac{1}{2}kx_1^2 + \frac{1}{2m}p_2^2 + \frac{1}{2}kx_2^2. \tag{6.96}$$

FIGURE 6.14:   Two nearby polarizable atoms (Problem 6.31).

The Coulomb interaction between the atoms is

$$H' = \frac{1}{4\pi\epsilon_0}\left(\frac{e^2}{R} - \frac{e^2}{R - x_1} - \frac{e^2}{R + x_2} + \frac{e^2}{R - x_1 + x_2}\right). \qquad [6.97]$$

(a) Explain Equation 6.97. Assuming that $|x_1|$ and $|x_2|$ are both much less than R, show that

$$H' \cong -\frac{e^2 x_1 x_2}{2\pi\epsilon_0 R^3}. \qquad [6.98]$$

(b) Show that the total Hamiltonian (Equation 6.96 plus Equation 6.98) separates into two harmonic oscillator Hamiltonians:

$$H = \left[\frac{1}{2m}p_+^2 + \frac{1}{2}\left(k - \frac{e^2}{2\pi\epsilon_0 R^3}\right)x_+^2\right] + \left[\frac{1}{2m}p_-^2 + \frac{1}{2}\left(k + \frac{e^2}{2\pi\epsilon_0 R^3}\right)x_-^2\right], \qquad [6.99]$$

under the change of variables

$$x_\pm \equiv \frac{1}{\sqrt{2}}(x_1 \pm x_2), \quad \text{which entails} \quad p_\pm = \frac{1}{\sqrt{2}}(p_1 \pm p_2). \qquad [6.100]$$

(c) The ground state energy for this Hamiltonian is evidently

$$E = \frac{1}{2}\hbar(\omega_+ + \omega_-), \quad \text{where} \quad \omega_\pm = \sqrt{\frac{k \mp (e^2/2\pi\epsilon_0 R^3)}{m}}. \qquad [6.101]$$

Without the Coulomb interaction it would have been $E_0 = \hbar\omega_0$, where $\omega_0 = \sqrt{k/m}$. Assuming that $k \gg (e^2/2\pi\epsilon_0 R^3)$, show that

$$\Delta V \equiv E - E_0 \cong -\frac{\hbar}{8m^2\omega_0^3}\left(\frac{e^2}{2\pi\epsilon_0}\right)^2 \frac{1}{R^6}. \qquad [6.102]$$

Conclusion: There is an attractive potential between the atoms, proportional to the inverse sixth power of their separation. This is the **van der Waals interaction** between two neutral atoms.

(d) Now do the same calculation using second-order perturbation theory. *Hint:* The unperturbed states are of the form $\psi_{n_1}(x_1)\psi_{n_2}(x_2)$, where $\psi_n(x)$ is a one-particle oscillator wave function with mass m and spring constant k; ΔV is the second-order correction to the ground state energy, for the perturbation in Equation 6.98 (notice that the *first*-order correction is zero).

★ ★**Problem 6.32** Suppose the Hamiltonian H, for a particular quantum system, is a function of some parameter λ; let $E_n(\lambda)$ and $\psi_n(\lambda)$ be the eigenvalues and

eigenfunctions of $H(\lambda)$. The **Feynman-Hellmann theorem**[22] states that

$$\frac{\partial E_n}{\partial \lambda} = \left\langle \psi_n \left| \frac{\partial H}{\partial \lambda} \right| \psi_n \right\rangle$$ [6.103]

(assuming either that E_n is nondegenerate, or—if degenerate—that the ψ_n's are the "good" linear combinations of the degenerate eigenfunctions).

(a) Prove the Feynman-Hellmann theorem. *Hint:* Use Equation 6.9.

(b) Apply it to the one-dimensional harmonic oscillator, (i) using $\lambda = \omega$ (this yields a formula for the expectation value of V), (ii) using $\lambda = \hbar$ (this yields $\langle T \rangle$), and (iii) using $\lambda = m$ (this yields a relation between $\langle T \rangle$ and $\langle V \rangle$). Compare your answers to Problem 2.12, and the virial theorem predictions (Problem 3.31).

∗∗Problem 6.33 The Feynman-Hellmann theorem (Problem 6.32) can be used to determine the expectation values of $1/r$ and $1/r^2$ for hydrogen.[23] The effective Hamiltonian for the radial wave functions is (Equation 4.53)

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}.$$

and the eigenvalues (expressed in terms of l)[24] are (Equation 4.70)

$$E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2(j_{max}+l+1)^2}.$$

(a) Use $\lambda = e$ in the Feynman-Hellmann theorem to obtain $\langle 1/r \rangle$. Check your result against Equation 6.55.

(b) Use $\lambda = l$ to obtain $\langle 1/r^2 \rangle$. Check your answer with Equation 6.56.

∗∗∗Problem 6.34 Prove **Kramers' relation**:[25]

$$\frac{s+1}{n^2}\langle r^s \rangle - (2s+1)a\langle r^{s-1} \rangle + \frac{s}{4}[(2l+1)^2 - s^2]a^2\langle r^{s-2} \rangle = 0,$$ [6.104]

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[22]Feynman obtained Equation 6.103 while working on his undergraduate thesis at MIT (R. P. Feynman. *Phys. Rev.* **56**. 340. 1939): Hellmann's work was published four years earlier in an obscure Russian journal.

[23]C. Sánchez del Rio. *Am. J. Phys.* **50**. 556 (1982): H. S. Valk. *Am. J. Phys.* **54**, 921 (1986).

[24]In part (b) we treat l as a continuous variable: n becomes a function of l, according to Equation 4.67, because j_{max}, which must be an integer, is fixed. To avoid confusion, I have eliminated n, to reveal the dependence on l explicitly.

[25]This is also known as the (second) **Pasternack relation.** See H. Beker, *Am. J. Phys.* **65**, 1118 (1997). For a proof based on the Feynman-Hellmann theorem (Problem 6.32). see S. Balasubramanian, *Am. J. Phys.* **68**, 959 (2000).

which relates the expectation values of r to three different powers (s, $s - 1$, and $s - 2$), for an electron in the state ψ_{nlm} of hydrogen. *Hint:* Rewrite the radial equation (Equation 4.53) in the form

$$u'' = \left[\frac{l(l+1)}{r^2} - \frac{2}{ar} + \frac{1}{n^2 a^2} \right] u,$$

and use it to express $\int (u r^s u'') dr$ in terms of $\langle r^s \rangle$, $\langle r^{s-1} \rangle$, and $\langle r^{s-2} \rangle$. Then use integration by parts to reduce the second derivative. Show that $\int (u r^s u') dr = -(s/2) \langle r^{s-1} \rangle$, and $\int (u' r^s u') dr = -[2/(s + 1)] \int (u'' r^{s+1} u') dr$. Take it from there.

Problem 6.35

(a) Plug $s = 0$, $s = 1$, $s = 2$, and $s = 3$ into Kramers' relation (Equation 6.104) to obtain formulas for $\langle r^{-1} \rangle$, $\langle r \rangle$, $\langle r^2 \rangle$, and $\langle r^3 \rangle$. Note that you could continue indefinitely, to find *any* positive power.

(b) In the *other* direction, however, you hit a snag. Put in $s = -1$, and show that all you get is a relation between $\langle r^{-2} \rangle$ and $\langle r^{-3} \rangle$.

(c) But if you can get $\langle r^{-2} \rangle$ by some *other* means, you can apply the Kramers' relation to obtain the rest of the negative powers. Use Equation 6.56 (which is derived in Problem 6.33) to determine $\langle r^{-3} \rangle$, and check your answer against Equation 6.64.

∗ ∗ ∗Problem 6.36 When an atom is placed in a uniform external electric field $\mathbf{E}_{\text{ext}}$, the energy levels are shifted—a phenomenon known as the **Stark effect** (it is the electrical analog to the Zeeman effect). In this problem we analyze the Stark effect for the $n = 1$ and $n = 2$ states of hydrogen. Let the field point in the z direction, so the potential energy of the electron is

$$H'_S = eE_{\text{ext}}z = eE_{\text{ext}}r\cos\theta.$$

Treat this as a perturbation on the Bohr Hamiltonian (Equation 6.42). (Spin is irrelevant to this problem, so ignore it, and neglect the fine structure.)

(a) Show that the ground state energy is not affected by this perturbation, in first order.

(b) The first excited state is 4-fold degenerate: ψ_{200}, ψ_{211}, ψ_{210}, ψ_{21-1}. Using degenerate perturbation theory, determine the first-order corrections to the energy. Into how many levels does E_2 split?

(c) What are the "good" wave functions for part (b)? Find the expectation value of the electric dipole moment ($\mathbf{p}_e = -e\mathbf{r}$) in each of these "good" states.

Notice that the results are independent of the applied field—evidently hydrogen in its first excited state can carry a *permanent* electric dipole moment.

Hint: There are a lot of integrals in this problem, but almost all of them are zero. So study each one carefully, before you do any calculations: If the ϕ integral vanishes, there's not much point in doing the r and θ integrals! *Partial answer:* $W_{13} = W_{31} = -3ea E_{\text{ext}}$; all other elements are zero.

***Problem 6.37** Consider the Stark effect (Problem 6.36) for the $n = 3$ states of hydrogen. There are initially nine degenerate states, ψ_{3lm} (neglecting spin, as before), and we turn on an electric field in the z direction.

(a) Construct the 9×9 matrix representing the perturbing Hamiltonian. *Partial answer:* $\langle 300|z|310\rangle = -3\sqrt{6}a$, $\langle 310|z|320\rangle = -3\sqrt{3}a$, $\langle 31\pm 1|z|32\pm 1\rangle = -(9/2)a$.

(b) Find the eigenvalues, and their degeneracies.

Problem 6.38 Calculate the wavelength, in centimeters, of the photon emitted under a hyperfine transition in the ground state ($n = 1$) of **deuterium**. Deuterium is "heavy" hydrogen, with an extra neutron in the nucleus; the proton and neutron bind together to form a **deuteron**, with spin 1 and magnetic moment

$$\mu_d = \frac{g_d e}{2m_d} \mathbf{S}_d;$$

the deuteron g-factor is 1.71.

***Problem 6.39** In a crystal, the electric field of neighboring ions perturbs the energy levels of an atom. As a crude model, imagine that a hydrogen atom is surrounded by three pairs of point charges, as shown in Figure 6.15. (Spin is irrelevant to this problem, so ignore it.)

(a) Assuming that $r \ll d_1$, $r \ll d_2$, and $r \ll d_3$, show that

$$H' = V_0 + 3(\beta_1 x^2 + \beta_2 y^2 + \beta_3 z^2) - (\beta_1 + \beta_2 + \beta_3)r^2,$$

where

$$\beta_i \equiv -\frac{e}{4\pi\epsilon_0}\frac{q_i}{d_i^3}, \quad \text{and} \quad V_0 = 2(\beta_1 d_1^2 + \beta_2 d_2^2 + \beta_3 d_3^2).$$

(b) Find the lowest-order correction to the ground state energy.

(c) Calculate the first-order corrections to the energy of the first excited states ($n = 2$). Into how many levels does this four-fold degenerate system split, (i) in the case of **cubic symmetry**, $\beta_1 = \beta_2 = \beta_3$; (ii) in the case of **tetragonal symmetry**, $\beta_1 = \beta_2 \neq \beta_3$; (iii) in the general case of **orthorhombic symmetry** (all three different)?
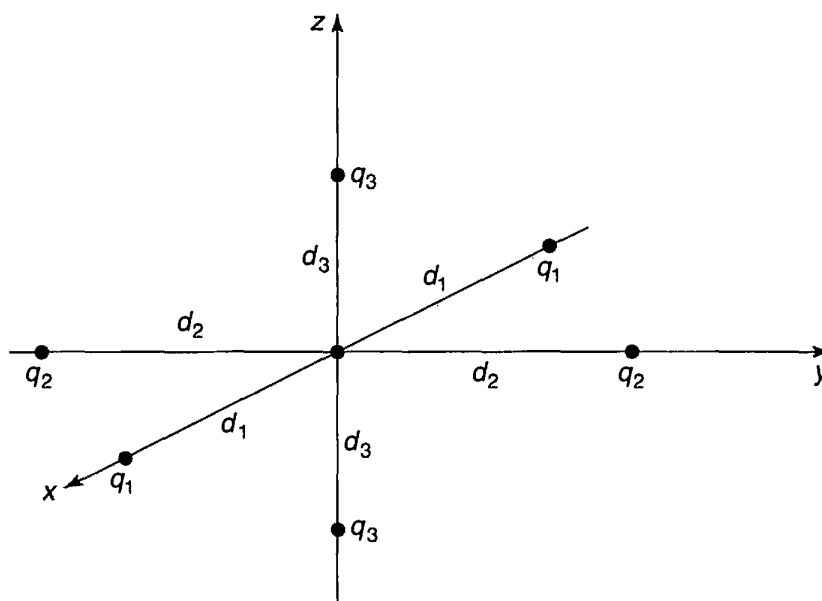
FIGURE 6.15:   Hydrogen atom surrounded by six point charges (crude model for a crystal lattice); Problem 6.39.

★ ★ ★Problem 6.40 Sometimes it is possible to solve Equation 6.10 directly, without having to expand ψ_n^1 in terms of the unperturbed wave functions (Equation 6.11). Here are two particularly nice examples.

(a) **Stark effect in the ground state of hydrogen.**

(i) Find the first-order correction to the ground state of hydrogen in the presence of a uniform external electric field E_{ext} (the Stark effect—see Problem 6.36). *Hint:* Try a solution of the form

$$(A + Br + Cr^2)e^{-r/a}\cos\theta;$$

your problem is to find the constants A, B, and C that solve Equation 6.10.

(ii) Use Equation 6.14 to determine the second-order correction to the ground state energy (the first-order correction is zero, as you found in Problem 6.36(a)). *Answer:* $-m(3a^2eE_{\text{ext}}/2\hbar)^2$.

(b) If the proton had an *electric* dipole moment p, the potential energy of the electron in hydrogen would be perturbed in the amount

$$H' = -\frac{ep\cos\theta}{4\pi\epsilon_0 r^2}.$$

(i) Solve Equation 6.10 for the first-order correction to the ground state wave function.

(ii) Show that the *total* electric dipole moment of the atom is (surprisingly) *zero*, to this order.

(iii) Use Equation 6.14 to determine the second-order correction to the ground state energy. What is the *first*-order correction?