

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):

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

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

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

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:

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

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.

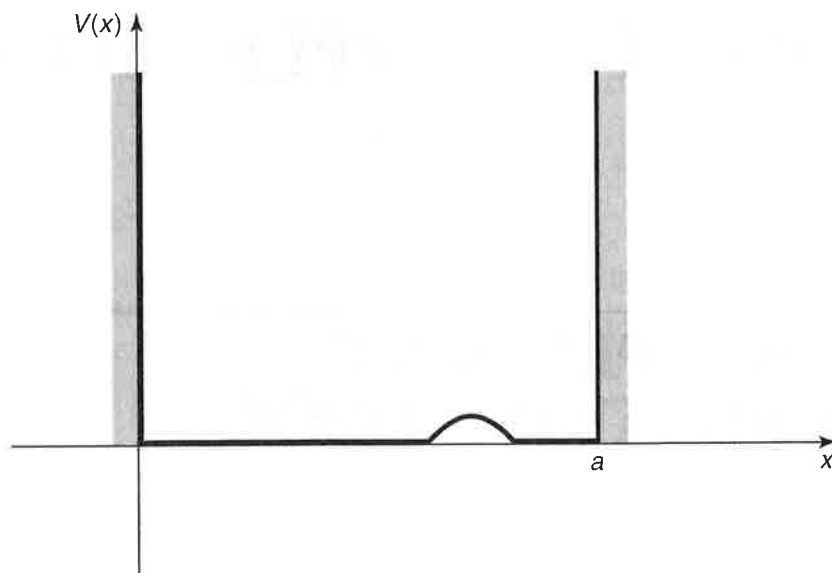


FIGURE 6.1: Infinite square well with small perturbation.

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

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

where H' is the perturbation (the superscript 0 always identifies the *unperturbed* 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 :

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

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

Here E_n^1 is the **first-order correction** to the n th eigenvalue, and ψ_n^1 is the first-order correction to the n th 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:

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

or (collecting like powers of λ):

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

To lowest order¹ (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),

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

To second order (λ^2),

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

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, $\langle \psi_n^0 | \psi_n^0 \rangle = 1$, so²

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle. \quad [6.9]$$

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)

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

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

²In 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.

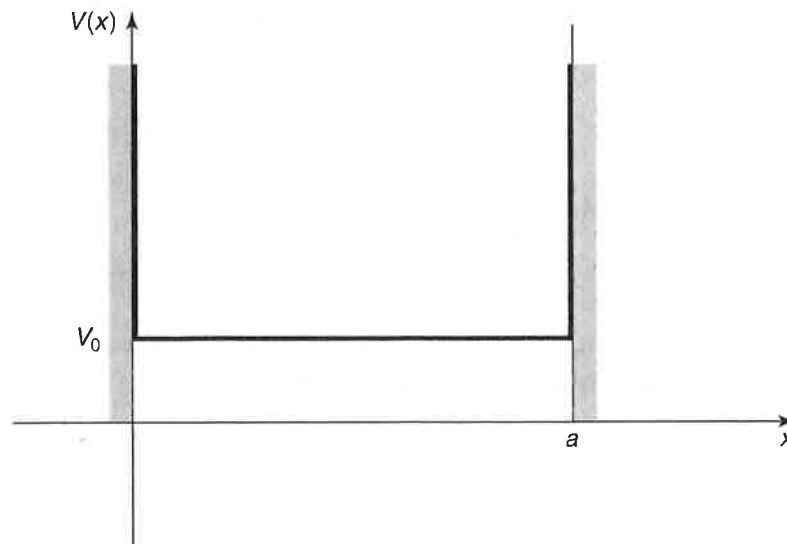


FIGURE 6.2: Constant perturbation over the whole well.

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 n th 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:

$$(H^0 - E_n^0)\psi_n^1 = -(H' - E_n^1)\psi_n^0. \quad [6.10]$$

³Incidentally, nothing here depends on the specific nature of the infinite square well—the same holds for *any* potential, when the perturbation is constant.

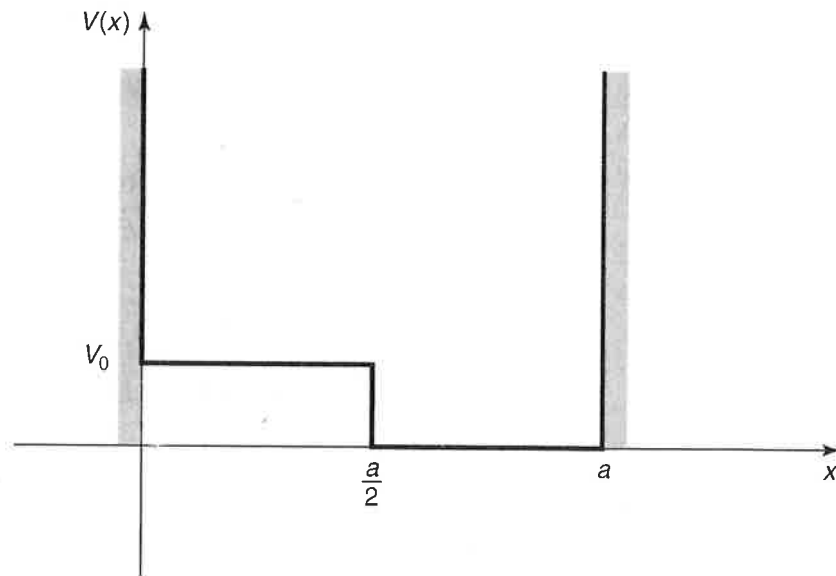


FIGURE 6.3: Constant perturbation over half the well.

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:

$$\psi_n^1 = \sum_{m \neq n} c_m^{(n)} \psi_m^0. \quad [6.11]$$

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 ,

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

⁴Alternatively, 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): $\langle \psi_n | \psi_n \rangle = \langle \psi_n^0 | \psi_n^0 \rangle + \lambda(\langle \psi_n^1 | \psi_n^0 \rangle + \langle \psi_n^0 | \psi_n^1 \rangle) + \lambda^2(\dots) + \dots$, 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

$$c_m^{(n)} = \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0}, \quad [6.12]$$

so

$$\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} \psi_m^0. \quad [6.13]$$

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.

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

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

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 :

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

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,

$$E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}. \quad [6.15]$$

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

*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 $H' = -qEx$.

⁵In 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 n th 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

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

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

$$\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0, \quad [6.17]$$

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

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

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,

$$H\psi = E\psi, \quad [6.19]$$

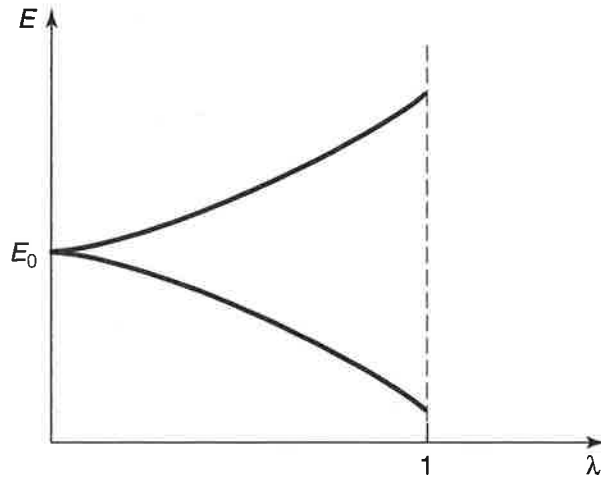


FIGURE 6.4: “Lifting” of a degeneracy by a perturbation.

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

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

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

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

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

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

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,

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

where

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

Similarly, the inner product with ψ_b^0 yields

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

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:

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

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

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

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

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

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*,

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

are precisely what we would have obtained using *nondegenerate* 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 *nondegenerate* 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,

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

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

$$\begin{aligned} \langle \psi_a^0 | [A, H'] \psi_b^0 \rangle &= 0 \\ &= \langle \psi_a^0 | A H' \psi_b^0 \rangle - \langle \psi_a^0 | H' A \psi_b^0 \rangle \\ &= \langle A \psi_a^0 | H' \psi_b^0 \rangle - \langle \psi_a^0 | H' \nu \psi_b^0 \rangle \\ &= (\mu - \nu) \langle \psi_a^0 | H' \psi_b^0 \rangle = (\mu - \nu) W_{ab}. \end{aligned}$$

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 α_{\pm} and β_{\pm} are determined (up to normalization) by Equation 6.22 (or Equation 6.24). Show explicitly that

- (a) ψ_{\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 $n = 0, \pm 1, \pm 2, \dots$, 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:

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

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 \mathbf{W} .

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

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

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 \mathbf{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

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

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

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

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:

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

all share the same energy

$$E_1^0 \equiv 3 \frac{\pi^2 \hbar^2}{ma^2}. \quad [6.35]$$

Now let's introduce the perturbation

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

⁶Degenerate 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).

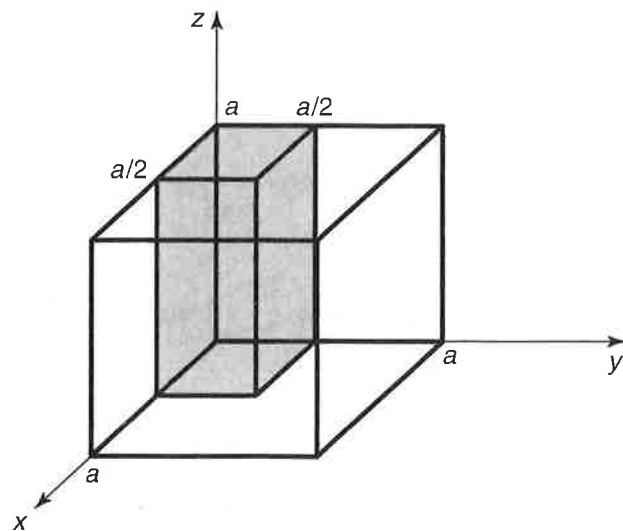


FIGURE 6.5: The perturbation increases the potential by an amount V_0 in the shaded sector.

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:

$$\begin{aligned}
 E_0^1 &= \langle \psi_{111} | H' | \psi_{111} \rangle \\
 &= \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin^2\left(\frac{\pi}{a}x\right) dx \int_0^{a/2} \sin^2\left(\frac{\pi}{a}y\right) dy \int_0^a \sin^2\left(\frac{\pi}{a}z\right) dz \\
 &= \frac{1}{4}V_0,
 \end{aligned} \tag{6.37}$$

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 \mathbf{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:

$$\begin{aligned}
 W_{ab} &= \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin^2\left(\frac{\pi}{a}x\right) dx \\
 &\quad \times \int_0^{a/2} \sin\left(\frac{\pi}{a}y\right) \sin\left(\frac{2\pi}{a}y\right) dy \int_0^a \sin\left(\frac{2\pi}{a}z\right) \sin\left(\frac{\pi}{a}z\right) dz.
 \end{aligned}$$

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

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

Finally,

$$\begin{aligned} W_{bc} &= \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin\left(\frac{\pi}{a}x\right) \sin\left(\frac{2\pi}{a}x\right) dx \\ &\quad \times \int_0^{a/2} \sin\left(\frac{2\pi}{a}y\right) \sin\left(\frac{\pi}{a}y\right) dy \int_0^a \sin^2\left(\frac{\pi}{a}z\right) dz = \frac{16}{9\pi^2} V_0. \end{aligned}$$

Thus

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

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,

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

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 *nondegenerate* 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

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

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

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & \kappa \\ 0 & \kappa & 1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = w \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}.$$

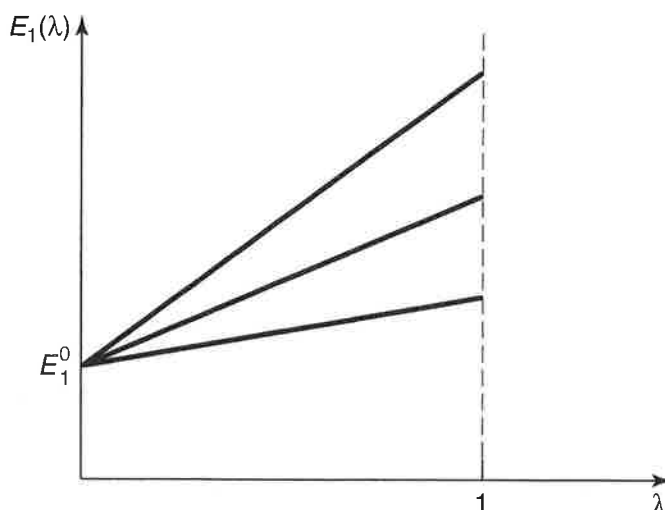


FIGURE 6.6: Lifting of the degeneracy in Example 6.2 (Equation 6.39).

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 are⁷

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

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 (triple degenerate) first excited states.

⁷We 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 ($\epsilon \ll 1$).

- Write down the eigenvectors and eigenvalues of the *unperturbed* Hamiltonian ($\epsilon = 0$).
- Solve for the *exact* eigenvalues of \mathbf{H} . Expand each of them as a power series in ϵ , up to second order.
- Use first- and second-order *nondegenerate* 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).
- 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 \mathbf{W} .

6.3 THE FINE STRUCTURE OF HYDROGEN

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

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

(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