

## Chapter 5

### APPROXIMATION METHODS FOR STATIONARY STATES

As we have seen, the task of predicting the evolution of an isolated quantum mechanical can be reduced to the solution of an appropriate eigenvalue equation involving the Hamiltonian of the system. Unfortunately, only a small number of quantum mechanical systems are amenable to an exact solution. Moreover, even when an exact solution to the eigenvalue problem is available, it is often useful to understand the behavior of the system in the presence of weak external fields that may be imposed in order to probe the structure of its stationary states. In these situations an approximate method is required for calculating the eigenstates of the Hamiltonian in the presence of a perturbation that renders an exact solution untenable. There are two general approaches commonly taken to solve problems of this sort. The first, referred to as the variational method, is most useful in obtaining information about the ground state of the system, while the second, generally referred to as time-independent perturbation theory, is applicable to any set of discrete levels and is not necessarily restricted to the solution of the energy eigenvalue problem, but can be applied to any observable with a discrete spectrum.

#### 5.1 The Variational Method

Let  $H$  be a time-independent observable (e.g., the Hamiltonian) for a physical system having (for convenience) a discrete spectrum. The normalized eigenstates  $\{|\phi_n\rangle\}$  of  $H$  each satisfy the eigenvalue equation

$$H|\phi_n\rangle = E_n|\phi_n\rangle \quad (5.1)$$

where for convenience in what follows we assume that the eigenvalues and corresponding eigenstates have been ordered, so that

$$E_0 \leq E_1 \leq E_2 \cdots \quad (5.2)$$

Under these circumstances, if  $|\psi\rangle$  is an arbitrary normalized state of the system it is straightforward to prove the following simple form of the **variational theorem**: the mean value of  $H$  with respect to an arbitrary normalized state  $|\psi\rangle$  is necessarily greater than the actual ground state energy (i.e., lowest eigenvalue) of  $H$ , i.e.,

$$\langle H \rangle_\psi = \langle \psi | H | \psi \rangle \geq E_0. \quad (5.3)$$

The proof follows almost trivially upon using the expansion

$$H = \sum_n |\phi_n\rangle E_n \langle \phi_n| \quad (5.4)$$

of  $H$  in its own eigenstates to express the mean value of interest in the form

$$\langle H \rangle_\psi = \sum_n \langle \psi | \phi_n \rangle E_n \langle \phi_n | \psi \rangle = \sum_n |\psi_n|^2 E_n, \quad (5.5)$$

and then noting that each term in the sum is itself bounded, i.e.,  $|\psi_n|^2 E_n \geq |\psi_n|^2 E_0$ , so that

$$\sum_n |\psi_n|^2 E_n \geq \sum_n |\psi_n|^2 E_0 = E_0 \quad (5.6)$$

where we have used the assumed normalization  $\langle \psi | \psi \rangle = \sum_n |\psi_n|^2 = 1$  of the otherwise arbitrary state  $|\psi\rangle$ . Note that the equality holds only if  $|\psi\rangle$  is actually proportional to the ground state of  $H$ .

Thus, the variational theorem proved above states that the ground state minimizes the mean value of  $H$  taken with respect to the normalized states of the space. This has interesting implications. It means, for example, that one could simply choose random vectors in the state space of the system and evaluate the mean value of  $H$  with respect to each. The smallest value obtained then gives an upper bound for the ground state energy of the system. By continuing this random, or ‘‘Monte Carlo’’, search it is possible, in principle, to get systematically better (i.e., lower) estimates of the exact ground state energy.

It is also possible to prove a stronger statement that includes the simple bound given above as a special case: the mean value of  $H$  is actually *stationary* in the neighborhood of each of its eigenstates  $|\phi\rangle$ . This fact, which is a more complete and precise statement of the variational theorem, is compactly expressed in the language of the calculus of variations through the relation

$$\delta \langle H \rangle_\phi = 0. \quad (5.7)$$

To see what this means physically, let  $|\phi\rangle$  be a normalizable state of the system about which we consider a family of kets

$$|\phi(\lambda)\rangle = |\phi\rangle + \lambda|\eta\rangle \quad (5.8)$$

that differ by a small amount from the original state  $|\phi\rangle$ , where  $|\eta\rangle$  is a fixed but arbitrary normalizable state and  $\lambda$  is a real parameter allowing us to parameterize the small but arbitrary variations

$$\delta|\phi\rangle = |\phi(\lambda)\rangle - |\phi\rangle = \lambda|\eta\rangle \quad (5.9)$$

of interest about the ket  $|\phi\rangle = |\phi(0)\rangle$ .

Let us now denote by

$$\varepsilon(\lambda) = \langle H \rangle_\lambda = \frac{\langle \phi(\lambda) | H | \phi(\lambda) \rangle}{\langle \phi(\lambda) | \phi(\lambda) \rangle} \quad (5.10)$$

the mean value of  $H$  with respect to the varied state  $|\phi(\lambda)\rangle$ , in which we have included the normalization in the denominator so that we do not have to worry about constraining the variation to normalized states. With these definitions, then, we wish to prove the following: the state  $|\phi\rangle$  is an eigenstate of  $H$  if and only if, for arbitrary  $|\eta\rangle$ ,

$$\left. \frac{\partial \varepsilon}{\partial \lambda} \right|_{\lambda=0} = 0. \quad (5.11)$$

To prove the statement we first compute the derivative of  $\varepsilon(\lambda)$  using the chain rule, i.e., introducing the notation

$$|\phi'\rangle = \frac{\partial |\phi(\lambda)\rangle}{\partial \lambda} = |\eta\rangle \quad \langle \phi'| = \frac{\partial \langle \phi(\lambda) |}{\partial \lambda} = \langle \eta | \quad (5.12)$$

we have (since  $H$  is independent of  $\lambda$ )

$$\left. \frac{\partial \varepsilon}{\partial \lambda} \right|_{\lambda=0} = \frac{\langle \phi' | H | \phi \rangle}{\langle \phi | \phi \rangle} + \frac{\langle \phi | H | \phi' \rangle}{\langle \phi | \phi \rangle} - \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle^2} [\langle \phi' | \phi \rangle + \langle \phi | \phi' \rangle]. \quad (5.13)$$

This can be multiplied through by  $\langle \phi | \phi \rangle$  and the identity  $|\phi'\rangle = |\eta\rangle$  used to obtain the relation

$$\langle \phi | \phi \rangle \left. \frac{\partial \varepsilon}{\partial \lambda} \right|_{\lambda=0} = \langle \eta | H | \phi \rangle + \langle \phi | H | \eta \rangle - \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} [\langle \eta | \phi \rangle + \langle \phi | \eta \rangle]. \quad (5.14)$$

Now denote by  $E$  the mean value of  $H$  with respect to the unvaried state, i.e., set

$$E = \varepsilon(0) = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} \quad (5.15)$$

and write  $E[\langle \eta | \phi \rangle + \langle \phi | \eta \rangle] = \langle \eta | E | \phi \rangle + \langle \phi | E | \eta \rangle$  to put the above expression in the form

$$\langle \phi | \phi \rangle \left. \frac{\partial \varepsilon}{\partial \lambda} \right|_{\lambda=0} = \langle \eta | (H - E) | \phi \rangle + \langle \phi | (H - E) | \eta \rangle. \quad (5.16)$$

We now note that if  $|\phi\rangle$  is an actual eigenstate of  $H$  its eigenvalue must be equal to  $E = \varepsilon(0)$ , in which case the right hand side of the last expression vanishes (independent of the state  $|\eta\rangle$ ). Since  $|\phi\rangle$  is nonzero, we conclude that the derivative in (5.11) and (5.16) vanishes for arbitrary variations  $\delta|\phi\rangle = \lambda|\eta\rangle$  about *any* eigenstate  $|\phi\rangle$  of  $H$ .

To prove the converse we note that, if the derivative of  $\varepsilon(\lambda)$  with respect to  $\lambda$  does indeed vanish for *arbitrary* kets  $|\eta\rangle$ , then it must do so for any *particular* ket we choose; for example, if we pick

$$|\eta\rangle = (H - E)|\phi\rangle. \quad (5.17)$$

then, (5.16) above reduces to the relation

$$0 = \langle \eta | (H - E) | \phi \rangle + \langle \phi | (H - E) | \eta \rangle = \langle \phi | (H - E)^2 | \phi \rangle. \quad (5.18)$$

Because, by assumption,  $H$  is Hermitian and  $E$  real we can now interpret this last equation as telling us that

$$\langle \phi | (H - E)^2 | \phi \rangle = \|(H - E)|\phi\rangle\|^2 = 0, \quad (5.19)$$

which means that the vector  $(H - E)|\phi\rangle$  must vanish, and that  $|\phi\rangle$  is therefore an eigenstate of  $H$  with eigenvalue  $E$  whenever the derivative (5.11) vanishes for arbitrary variations  $\delta|\phi\rangle = \lambda|\eta\rangle$ , completing the proof.

In practice, use of this principle is referred to as the variational method, the basic steps of which we enumerate below:

1. Choose an appropriate family  $\{|\phi(\alpha)\rangle\}$  of normalized trial kets which depend parameterically on a set of variables  $\alpha = \{\alpha_1, \alpha_2, \dots, \alpha_n\}$ , referred to as variational parameters.
2. Calculate the mean value

$$\langle H(\alpha) \rangle = \langle \phi(\alpha) | H | \phi(\alpha) \rangle \quad (5.20)$$

as a function of the parameters  $\alpha$ .

3. Minimize  $E(\alpha) = \langle H(\alpha) \rangle$  with respect to the variational parameters by finding the values  $\alpha_0$  for which

$$\left. \frac{\partial \langle H \rangle}{\partial \alpha_i} \right|_{\alpha=\alpha_0} = 0 \quad i = 1, 2, \dots, n. \quad (5.21)$$

The value  $E(\alpha_0)$  so obtained is the variational estimate of the ground state energy with respect to this family of trial kets, and the corresponding state  $|\phi(\alpha_0)\rangle$  provides the corresponding variational approximation to the ground state.

It should be noted that if the family  $\{|\phi(\alpha)\rangle\}$  of trial kets actually contains the ground state (or any excited state), the variational principle shows that the technique described above will find it and the corresponding energy exactly. This can sometimes be exploited. For example, if symmetry properties of the ground state are known (parity, angular momentum, etc.) it is often possible to choose a family of trial kets that are orthogonal to the exact ground state of the system. In this situation, the variational method will then yield an upper bound to the energy of the lowest lying excited state of the system that is not orthogonal to the family of trial kets employed. We also note, in passing, that our derivation of the variational principle shows that an approximation to the ground state  $|\phi_0\rangle$  that is correct to order  $\varepsilon$  (i.e.,  $|\phi(\varepsilon)\rangle = |\phi_0\rangle + \varepsilon|\eta\rangle$ ) will yield an estimate of the ground state energy  $E_0$  which is correct to order  $\varepsilon^2$ . This follows from the fact that in an expansion

$$E(\varepsilon) = E_0 + \varepsilon \left. \frac{\partial E}{\partial \varepsilon} \right|_{\varepsilon=0} + \frac{\varepsilon^2}{2!} \left. \frac{\partial^2 E}{\partial \varepsilon^2} \right|_{\varepsilon=0} + \dots \quad (5.22)$$

of the mean energy about that of the actual ground state, the linear term vanishes due to the stationarity condition derived above. This explains the often observed phenomenon that a rather poor approximation to the eigenstate can yield a relatively good estimate of the ground state energy.

A particularly useful application of the variational method involves what is referred to as the Rayleigh-Ritz method, which overcomes to some extent the usual difficulty of dealing with an infinite dimensional space. Suppose for example that we were to take as a trial ket a state

$$|\phi\rangle = \sum_i \phi_i |i\rangle \quad (5.23)$$

expanded in terms of some orthonormal set of vectors  $\{|i\rangle\}$ , and take the expansion coefficients  $\phi_i$  (or their real and imaginary parts) as our variational parameters. If the set  $\{|i\rangle\}$  is complete, then the family  $\{|\phi\rangle\}$  of trial kets includes all physical vectors in the state space, and the resulting variational procedure will just generate the exact eigenvectors of  $H$ . Suppose, on the other hand, that the states  $\{|i\rangle\}$  are not complete, but span some  $N$ -dimensional subspace  $S_N$ . The variational procedure would then search through this finite dimensional subspace to find those states that are closest to being actual eigenstates of the full system. The resulting vectors would then extremize the mean value

$$\langle H \rangle = \langle \phi | H | \phi \rangle = \sum_{i,j} \phi_i^* H_{ij} \phi_j \quad (5.24)$$

taken with respect to the states  $|\phi\rangle$  in this subspace. In this last expression,  $H_{ij} = \langle i | H | j \rangle$  denotes the matrix elements of  $H$  with respect to the orthonormal states  $\{|i\rangle\}$  spanning the subspace  $S_N$ . Suppose, however, we introduce a new Hermitian operator  $H^{(S)}$  defined *only* on the subspace  $S_N$  and having the same matrix elements

$$H_{ij}^{(S)} = \langle i | H | j \rangle = H_{ij} \quad (5.25)$$

as  $H$  *within* that subspace (but which vanishes outside of  $S_N$ ); the  $N$  eigenvectors of this restricted operator  $H^{(S)}$  will be those states  $|\phi\rangle$  in  $S_N$  which extremize the mean value

$$\langle H^{(S)} \rangle = \sum_{i,j} \phi_i^* H_{ij}^{(S)} \phi_j = \sum_{i,j} \phi_i^* H_{ij} \phi_j, \quad (5.26)$$

i.e., they will be precisely the variational eigenstates of the full Hamiltonian  $H$  that we are looking for. Thus, in this case, application of the variational method simply amounts to diagonalizing the matrix representing  $H$  restricted to some finite subspace of interest. Moreover, as implied by our previous comments on the variational method, the Rayleigh-Ritz method described above will exactly find any actual eigenvectors of  $H$  that lie entirely within the chosen subspace  $S_N$ .

## 5.2 Perturbation Theory for Nondegenerate Levels

We now turn to a more general and systematic method for determining the eigenvector and eigenvalues for observables with a discrete spectrum. As in the last section we use the language of energy eigenstates and Hamiltonians even though the method itself is perfectly applicable to other observables. For the purposes of stating the initial problem of interest, however, we consider the eigenvalue problem for a time-independent Hamiltonian

$$H = H^{(0)} + H^{(1)} = H^{(0)} + \lambda V \quad (5.27)$$

having a discrete *nondegenerate* spectrum. In writing the Hamiltonian in this form, the eigenvalue problem for the operator  $H^{(0)}$ , which will be referred to as the “unperturbed part” of the Hamiltonian, is assumed to have been solved, and the perturbation  $H^{(1)} = \lambda V$  is presumed to be, in some sense, small compared to  $H^{(0)}$ . Our goal is to obtain expressions for the eigenstates  $|n\rangle = |n(\lambda)\rangle$  and eigenvalues  $\varepsilon_n = \varepsilon_n(\lambda)$  of  $H$  as an expansion in powers of the small, real parameter  $\lambda$ . These eigenstates of the full Hamiltonian  $H$  are to be expressed as linear combinations and simple functions of the known eigenstates  $|n^{(0)}\rangle$  and eigenvalues  $\varepsilon_n^{(0)}$  of the unperturbed Hamiltonian  $H^{(0)}$ . Thus, the exact and unperturbed states of the system are assumed to satisfy the equations

$$(H - \varepsilon_n)|n\rangle = 0 \quad \langle n|m\rangle = \delta_{n,m} \quad \sum_n |n\rangle\langle n| = 1 \quad (5.28)$$

$$(H^{(0)} - \varepsilon_n^{(0)})|n^{(0)}\rangle = 0 \quad \langle n^{(0)}|m^{(0)}\rangle = \delta_{n,m} \quad \sum_n |n^{(0)}\rangle\langle n^{(0)}| = 1, \quad (5.29)$$

the two relations on the right of the last two lines indicating that both sets of states form an ONB for the space of interest. We wish to identify, in particular, the unperturbed eigenstates  $|n^{(0)}\rangle$  as those to which the exact states  $|n\rangle$  tend as  $\lambda \rightarrow 0$ . This still leaves the relative phase of the two sets of basis vector undetermined, as we could multiply the basis vectors of one set by an arbitrary set of phases  $e^{i\phi_n}$  without affecting the validity of the equations above. For nonzero values of  $\lambda$ , therefore, we further fix the relative phase between these two sets of states by requiring that the inner product  $\langle n|n^{(0)}\rangle$  between corresponding elements of these two basis sets be real and positive.

Now, by assumption, there exist expansions of the full eigenstate  $|n\rangle$  and the corresponding eigenenergy  $\varepsilon_n$  of the form

$$|n\rangle = |n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \dots \quad (5.30)$$

$$\varepsilon_n = \varepsilon_n^{(0)} + \lambda\varepsilon_n^{(1)} + \lambda^2\varepsilon_n^{(2)} + \dots \quad (5.31)$$

We will refer to the terms  $\lambda^k \varepsilon_n^{(k)}$  and  $\lambda^k |n^{(k)}\rangle$  as the  $k$ th order correction to the  $n$ th eigenenergy and eigenstate, respectively. The corresponding correction to the energy is also generally referred to as the  $k$ th order energy *shift*, for obvious reasons. To determine these corrections, we will simply require that the exact eigenstate  $|n\rangle$  satisfy the appropriate eigenvalue equation

$$(H - \varepsilon_n)|n\rangle = 0 \quad (5.32)$$

to all orders in  $\lambda$ . Upon substitution of the expansions for  $|n\rangle$  and  $\varepsilon_n$  into the eigenvalue equation we obtain

$$(H^{(0)} + \lambda V) \sum_{k=0}^{\infty} \lambda^k |n^{(k)}\rangle = \sum_{k=0}^{\infty} \lambda^k \varepsilon_n^{(k)} \sum_{j=0}^{\infty} \lambda^j |n^{(j)}\rangle = \sum_{k,j=0}^{\infty} \lambda^{j+k} \varepsilon_n^{(k)} |n^{(j)}\rangle \quad (5.33)$$

or

$$\sum_{k=0}^{\infty} \left[ \lambda^k H^{(0)} |n^{(k)}\rangle + V \lambda^{k+1} |n^{(k)}\rangle - \sum_{j=0}^{\infty} \lambda^{j+k} \varepsilon_n^{(k)} |n^{(k)}\rangle \right] = 0. \quad (5.34)$$

For this equation to hold for small but arbitrary values of  $\lambda$ , the coefficients of each power of that parameter must vanish separately. The reason for this is essentially that the polynomials  $f_k(\lambda) = \lambda^k$  form a linearly independent set of functions on  $R$ , so any relation of the form  $\sum_{k=0}^{\infty} c_k \lambda^k = 0$  can only be satisfied for all  $\lambda$  in  $R$  if  $c_k = 0$  for all  $k$ . Applying this requirement to the last equation generates an infinite hierarchy of coupled equations, one for each power of  $\lambda$ . The equation generated by setting the coefficient of  $\lambda^k$  equal to zero is referred to as the  $k$ th order equation. Collecting coefficients of the first few powers of  $\lambda$  we obtain after a little rearrangement the zeroth order equation

$$(H^{(0)} - \varepsilon_n^{(0)}) |n^{(0)}\rangle = 0, \quad (5.35)$$

the first order equation

$$(H^{(0)} - \varepsilon_n^{(0)}) |n^{(1)}\rangle + (V - \varepsilon_n^{(1)}) |n^{(0)}\rangle = 0, \quad (5.36)$$

the second order equation

$$(H^{(0)} - \varepsilon_n^{(0)}) |n^{(2)}\rangle + (V - \varepsilon_n^{(1)}) |n^{(1)}\rangle - \varepsilon_n^{(2)} |n^{(0)}\rangle = 0, \quad (5.37)$$

the third order equation

$$(H^{(0)} - \varepsilon_n^{(0)}) |n^{(3)}\rangle + (V - \varepsilon_n^{(1)}) |n^{(2)}\rangle - \varepsilon_n^{(2)} |n^{(1)}\rangle - \varepsilon_n^{(3)} |n^{(0)}\rangle = 0, \quad (5.38)$$

and finally, after inspecting those which precede it, we deduce for  $k \geq 2$  the form of the general  $k$ th order equation

$$(H^{(0)} - \varepsilon_n^{(0)}) |n^{(k)}\rangle + (V - \varepsilon_n^{(1)}) |n^{(k-1)}\rangle - \sum_{j=2}^k \varepsilon_n^{(j)} |n^{(k-j)}\rangle = 0. \quad (5.39)$$

As we will demonstrate, the structure of these equations allows for the general  $k$ th order solutions to be obtained from those solutions of lower order, allowing for the development of a systematic expansion of the eigenstates and eigenenergies in powers of  $\lambda$ . To begin the demonstration we note that the zeroth order equation (5.35) is already satisfied, by assumption. From knowledge of the unperturbed states and eigenenergies, Eq. (5.36) can be solved to give the first order correction  $\varepsilon_n^{(1)}$  to the energy. This is most easily done by simply multiplying (5.36) on the left by the unperturbed eigenbra  $\langle n^{(0)}|$ , i.e.,

$$\langle n^{(0)}| (H^{(0)} - \varepsilon_n^{(0)}) |n^{(1)}\rangle + \langle n^{(0)}| (V - \varepsilon_n^{(1)}) |n^{(0)}\rangle = 0. \quad (5.40)$$

Since  $H^{(0)}$  is Hermitian (and  $\varepsilon_n^{(0)}$  therefore real) it follows that  $\langle n^{(0)}| (H^{(0)} - \varepsilon_n^{(0)}) = 0$ , and so the first order equation reduces to the relation

$$\varepsilon_n^{(1)} = \langle n^{(0)}| V |n^{(0)}\rangle \quad \lambda \varepsilon_n^{(1)} = \langle n^{(0)}| H^{(1)} |n^{(0)}\rangle. \quad (5.41)$$

Thus, the first order correction to the energy eigenvalue for the  $n$ th level is simply the mean value of the perturbing Hamiltonian taken with respect to the unperturbed eigenfunctions. Note that the first order correction to the energy comes from a mean value taken with respect to the zeroth order approximation to the state, consistent with the remarks made earlier in the context of the variational method. As we will see, a similar structure persists to all orders of perturbation theory, namely, an approximation of the state to  $k$ th order generates an approximation to the energy that is correct to order  $k + 1$ .

Now that we have  $\varepsilon_n^{(1)}$ , we can put it back in to the first order equation (5.36) to find an expansion for the first order correction  $|n^{(1)}\rangle$  to the eigenstate. Since we want to express this correction as an expansion

$$|n^{(1)}\rangle = \sum_m |m^{(0)}\rangle \langle m^{(0)}|n^{(1)}\rangle \quad (5.42)$$

in unperturbed eigenstates  $|m^{(0)}\rangle$  of  $H^{(0)}$ , we obviously need to evaluate the expansion coefficients  $\langle m^{(0)}|n^{(1)}\rangle$ . Thus, we now take inner products of the first order equation (5.36) with the other members of this complete set of states, i.e., for the states with  $m \neq n$ . Multiplying (5.36) on the left by  $\langle m^{(0)}|$  we obtain

$$\langle m^{(0)}|(H^{(0)} - \varepsilon_n^{(0)})|n^{(1)}\rangle + \langle m^{(0)}|(V - \varepsilon_n^{(1)})|n^{(0)}\rangle = 0 \quad (5.43)$$

and observe that for the first term on the left of this expression

$$\langle m^{(0)}|(H^{(0)} - \varepsilon_n^{(0)})|n^{(1)}\rangle = (\varepsilon_m^{(0)} - \varepsilon_n^{(0)})\langle m^{(0)}|n^{(1)}\rangle, \quad (5.44)$$

while orthogonality of the unperturbed states implies that, for the second term,

$$\langle m^{(0)}|\varepsilon_n^{(1)}|n^{(0)}\rangle = \varepsilon_n^{(1)}\langle m^{(0)}|n^{(0)}\rangle = 0 \quad \text{for } m \neq n. \quad (5.45)$$

Thus, we obtain after a little rearrangement the following result

$$\langle m^{(0)}|n^{(1)}\rangle = -\frac{\langle m^{(0)}|V|n^{(0)}\rangle}{\varepsilon_m^{(0)} - \varepsilon_n^{(0)}} \quad m \neq n. \quad (5.46)$$

for the expansion coefficients of interest. This procedure for obtaining the expansion coefficients for the state  $|n^{(1)}\rangle$  does not work for the term with  $m = n$ , since it just leads, again, to the expression  $\varepsilon_n^{(1)} = \langle n^{(0)}|V|n^{(0)}\rangle$  for the first order energy correction. As it turns out, however, the one remaining expansion coefficient  $\langle n^{(0)}|n^{(1)}\rangle$  can be evaluated from the normalization condition  $\langle n|n\rangle = 1$  and our already chosen phase convention. The normalization condition implies the expansion

$$\begin{aligned} 1 &= \left[ \langle n^{(0)}| + \lambda \langle n^{(1)}| + \lambda^2 \langle n^{(2)}| + \dots \right] \left[ |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots \right] \\ &= \langle n^{(0)}|n^{(0)}\rangle + \lambda \left[ \langle n^{(1)}|n^{(0)}\rangle + \langle n^{(0)}|n^{(1)}\rangle \right] + O(\lambda^2). \end{aligned} \quad (5.47)$$

Since, by assumption,  $\langle n^{(0)}|n^{(0)}\rangle = 1$ , all of the remaining terms on the right-hand side of this expansion must vanish, term-by-term. Thus, to first order normalization of the eigenstates requires that

$$0 = \langle n^{(1)}|n^{(0)}\rangle + \langle n^{(0)}|n^{(1)}\rangle = 2 \operatorname{Re} \left( \langle n^{(0)}|n^{(1)}\rangle \right). \quad (5.48)$$

On the other hand, we have chosen our phase convention so that the inner product

$$\begin{aligned} \langle n|n^{(0)}\rangle &= \left[ \langle n^{(0)}| + \lambda \langle n^{(1)}| + \lambda^2 \langle n^{(2)}| + \dots \right] |n^{(0)}\rangle \\ &= \langle n^{(0)}|n^{(0)}\rangle + \lambda \langle n^{(1)}|n^{(0)}\rangle + \lambda^2 \langle n^{(2)}|n^{(0)}\rangle + \dots \end{aligned} \quad (5.49)$$

is real and positive. Setting the imaginary part equal to zero gives the condition

$$\sum_{k=1}^{\infty} \lambda^k \operatorname{Im} \left[ \langle n^{(k)} | n^{(0)} \rangle \right] = 0, \quad (5.50)$$

which again requires, for arbitrary  $\lambda$ , that each inner product in the sum be separately real. Combining this with (5.48) we deduce, therefore, that

$$\langle n^{(0)} | n^{(1)} \rangle = 0. \quad (5.51)$$

By our simple choice of phase, then, the first order correction  $|n^{(1)}\rangle$  is forced to be orthogonal to the unperturbed eigenstate  $|n^{(0)}\rangle$ . Using this fact we then end up with the following expansion

$$|n^{(1)}\rangle = - \sum_{m \neq n} \frac{|m^{(0)}\rangle \langle m^{(0)} | V | n^{(0)} \rangle}{\varepsilon_m^{(0)} - \varepsilon_n^{(0)}} \quad (5.52)$$

for the first order correction, and similar expansions

$$|n\rangle = |n^{(0)}\rangle - \sum_{m \neq n} \frac{\langle m^{(0)} | \lambda V | n^{(0)} \rangle}{\varepsilon_m^{(0)} - \varepsilon_n^{(0)}} |m^{(0)}\rangle + O(\lambda^2) \quad (5.53)$$

$$|n\rangle = |n^{(0)}\rangle - \sum_{m \neq n} \frac{\langle m^{(0)} | H^{(1)} | n^{(0)} \rangle}{\varepsilon_m^{(0)} - \varepsilon_n^{(0)}} |m^{(0)}\rangle + O(\lambda^2) \quad (5.54)$$

for the full eigenstate, correct to first order in the perturbation. This expression shows that the perturbation  $H^{(1)}$  “mixes” the eigenstates of  $H^{(0)}$ , by which is referred to the fact that the eigenstates of  $H$  are linear combinations of the unperturbed eigenstates. Note also that the presence of the “energy denominators”  $\varepsilon_m^{(0)} - \varepsilon_n^{(0)}$  appearing in the expansion coefficients in this expression tend to mix together states close together in energy more strongly than states that are energetically disparate. This makes it clear why we assumed from the outset that the unperturbed spectrum was non-degenerate, since the method we have developed clearly must fail when applied to perturbations that connect degenerate states. It is also clear that an implicit condition for the perturbation expansion to converge, i.e., that the correction terms be sufficiently small is that

$$|\langle m^{(0)} | H^{(1)} | n^{(0)} \rangle| \ll \left| \varepsilon_m^{(0)} - \varepsilon_n^{(0)} \right| \quad (5.55)$$

for all states  $|m^{(0)}\rangle$  connected to the state  $|n^{(0)}\rangle$  by the perturbing Hamiltonian.

When the first order correction to the energy vanishes, or higher accuracy is required, it is necessary to go to higher order in the perturbation expansion. To obtain the second order energy correction we proceed as follows: multiply the second order equation (5.37) on the left by the unperturbed eigenbra  $\langle n^{(0)} |$  to obtain

$$\langle n^{(0)} | (H^{(0)} - \varepsilon_n^{(0)}) | n^{(2)} \rangle + \langle n^{(0)} | (V - \varepsilon_n^{(1)}) | n^{(1)} \rangle - \varepsilon_n^{(2)} \langle n^{(0)} | n^{(0)} \rangle = 0. \quad (5.56)$$

Again using the fact that  $\langle n^{(0)} |$  is an eigenbra of  $H_0$ , along with the orthogonality relation  $\langle n^{(0)} | n^{(1)} \rangle = 0$  deduced above, we find that

$$\varepsilon_n^{(2)} = \langle n^{(0)} | V | n^{(1)} \rangle. \quad (5.57)$$

Inserting the expansion deduced above for  $|n^{(1)}\rangle$ , we then obtain the second order energy shift

$$\lambda^2 \varepsilon_n^{(2)} = - \sum_{m \neq n} \frac{\langle n^{(0)} | \lambda V | m^{(0)} \rangle \langle m^{(0)} | \lambda V | n^{(0)} \rangle}{\varepsilon_m^{(0)} - \varepsilon_n^{(0)}} = - \sum_{m \neq n} \frac{|\lambda V_{mn}|^2}{\varepsilon_m^{(0)} - \varepsilon_n^{(0)}} \quad (5.58)$$



where the quantities  $\lambda V_{mn} = \langle m^{(0)} | \lambda V | n^{(0)} \rangle = H_{mn}^{(1)}$  are just the matrix elements of the perturbation between the unperturbed eigenstates. Thus, the full eigenenergies, correct to second order, are given by the expression

$$\varepsilon_n = \varepsilon_n^{(0)} + H_{nn}^{(1)} - \sum_{m \neq n} \frac{|H_{mn}^{(1)}|^2}{\varepsilon_m^{(0)} - \varepsilon_n^{(0)}} + O(\lambda^3). \quad (5.59)$$

In problems involving weak perturbations it usually suffices to determine corrections and energy shifts to lowest non-vanishing order in the perturbation, and so it is unusual that one needs to go beyond second order for “simple” problems in perturbation theory. Exceptions to this general observation arise quite often when dealing with many-body problems, where diagrammatic methods have been developed that take the ideas of perturbation theory to an extremely high level, and where it is not uncommon to find examples where effects of the perturbation are calculated to all orders.

It is worth pointing out, however, that the first order correction to the energy contains no information in it about any changes that occur in the eigenstates of the system as a result of the perturbation. This information appears for the first time in the second order energy shift, as the derivation above makes clear. In many cases it is not possible to perform the sum in (5.59) exactly, and so it is useful to develop simple means for estimating the magnitude of the second order energy shift. As it turns out, it is often straightforward to develop upper and lower bounds for the magnitude of the change in energy that occurs in any given eigenstate.

For example, a general *upper bound* for the second order shift can be obtained for any nondegenerate level by observing that

$$\varepsilon_n^{(2)} = \sum_{m \neq n} \frac{|H_{mn}^{(1)}|^2}{\varepsilon_n^{(0)} - \varepsilon_m^{(0)}} \leq \sum_{m \neq n} \frac{|H_{mn}^{(1)}|^2}{|\varepsilon_n^{(0)} - \varepsilon_m^{(0)}|} \quad (5.60)$$

where in the right hand side we have a sum of positive definite terms that will always be larger in magnitude than a similar sum in which some of the corresponding terms are positive and some negative, depending upon where the energy of each level lies relative to the one of interest. Moreover, each term in the sum on the right can itself be bounded, since the energy denominators are bounded from below by that associated with the level closest in energy to the state  $|n^{(0)}\rangle$ . If we denote by  $\Delta\varepsilon_n$  the energy spacing between level  $n$  and the state closest in energy to it, then  $|\varepsilon_n^{(0)} - \varepsilon_m^{(0)}| \geq \Delta\varepsilon_n$  and so

$$\varepsilon_n^{(2)} \leq \frac{1}{\Delta\varepsilon_n} \sum_{m \neq n} |H_{mn}^{(1)}|^2 = \frac{\lambda^2}{\Delta\varepsilon_n} \sum_{m \neq n} |V_{mn}|^2$$

We can perform the infinite sum by “removing” the restriction on the summation index. We do this latter trick by adding and subtracting the quantity  $|V_{nn}|^2 = |\langle V \rangle_n|^2$ , where  $\langle V \rangle_n = V_{nn} = \langle n^{(0)} | V | n^{(0)} \rangle$  is the mean value of the perturbation taken with respect to the unperturbed eigenstate. (It is, essentially, just the first order energy correction  $\varepsilon_n^{(1)}$ ). Performing this operation allows us to write the upper bound above in the form

$$\varepsilon_n^{(2)} \leq \frac{\lambda^2}{\Delta\varepsilon_n} \left[ \sum_m |\langle m^{(0)} | V | n^{(0)} \rangle|^2 - |\langle V \rangle_n|^2 \right]. \quad (5.61)$$

where the sum is now unrestricted. But since the unperturbed states form a complete set

of states we can now rewrite the sum as

$$\begin{aligned} \sum_m |\langle m^{(0)} | V | n^{(0)} \rangle|^2 &= \sum_m \langle n^{(0)} | V | m^{(0)} \rangle \langle m^{(0)} | V | n^{(0)} \rangle \\ &= \langle n^{(0)} | V | n^{(0)} \rangle = \langle V^2 \rangle_n \end{aligned} \quad (5.62)$$

which is just the mean value of the square of the perturbation taken with respect to the unperturbed eigenstate. Making this substitution above and recognizing the root-mean-square statistical uncertainty

$$\Delta^2 V = \langle V^2 \rangle - \langle V \rangle^2 \quad (5.63)$$

associated with the perturbing operator taken with respect to the unperturbed state of interest, we obtain our final result for the upper bound

$$\varepsilon_n^{(2)} \leq \frac{\lambda^2 \Delta^2 V}{\Delta \varepsilon_n} = \frac{\Delta^2 H^{(1)}}{\Delta \varepsilon_n} \quad (5.64)$$

in the second order energy shift. We note in passing that this gives another intuitively reasonable measure for determining the validity of the perturbation expansion, which requires for the smallness of  $\varepsilon_n^{(2)}$  that the uncertainty in  $H^{(1)}$  be small relative to the energy level spacing associated with the unperturbed states, i.e., that  $\Delta H^{(1)} / \Delta \varepsilon_n \ll 1$ .

For the *ground state energy* (or more generally the extremal eigenvalue) it is also possible to determine a *lower bound* on the magnitude of the second order energy shift. For the ground state, such a bound follows from the fact that in this case the second order energy shift

$$\varepsilon_0^{(2)} = - \sum_{m \neq n} \frac{|H_{mn}^{(1)}|^2}{\varepsilon_m^{(0)} - \varepsilon_0^{(0)}} \quad (5.65)$$

is always negative (the change in state always leads to a lower energy, consistent with the variational principle), because the energy denominators are always positive. We can thus write

$$\left| \varepsilon_0^{(2)} \right| = \sum_{m \neq n} \frac{|H_{mn}^{(1)}|^2}{\varepsilon_m^{(0)} - \varepsilon_0^{(0)}} \geq \frac{|H_{mn}^{(1)}|^2}{\varepsilon_m^{(0)} - \varepsilon_0^{(0)}} \quad (5.66)$$

where in the right-hand side we have used the fact that any single term in the sum is less than or equal to the total sum of all the positive definite terms therein. The maximal term in the sum (which is usually one of the low-lying excited states closest in energy to the ground state) can thus be used to provide a reasonable lower bound for the the second order shift in the ground state energy.

As an application of the techniques of nondegenerate perturbation theory we consider the example of a harmonically bound electron to which a uniform electric field is applied. Thus, we take for our Hamiltonian

$$H = H_0 + \hat{V} \quad (5.67)$$

where

$$H_0 = \frac{P^2}{2m} + \frac{1}{2} m \omega^2 X^2 \quad (5.68)$$

is a simple one-dimensional harmonic oscillator describing the bound electron, and the perturbing field is described by the potential

$$\hat{V} = -eEX = -fX. \quad (5.69)$$

Our goal is to treat  $\hat{V}$  as a small perturbation and calculate relevant corrections to the energy levels and eigenstates in the presence of the applied electric field. To this end we recall the standard transformations

$$q = \sqrt{\frac{m\omega}{\hbar}} X \quad p = \frac{P}{\sqrt{m\hbar\omega}} \quad (5.70)$$

$$a = \frac{1}{\sqrt{2}}(q + ip) \quad a^+ = \frac{1}{\sqrt{2}}(q - ip) \quad N = a^+ a \quad (5.71)$$

that allow us to put the harmonic oscillator part of the problem in a simpler, dimensionless form

$$H_0 = \left[ N + \frac{1}{2} \right] \hbar\omega \quad \hat{V} = -f \sqrt{\frac{\hbar}{m\omega}} q = -\lambda q = -\frac{\lambda}{\sqrt{2}}(a^+ + a) \quad (5.72)$$

where

$$\lambda = f \sqrt{\frac{\hbar}{m\omega}} \quad (5.73)$$

is a (presumed small) measure of the strength of the applied field. With these definitions, the unperturbed states of  $H_0$  are the usual oscillator states  $|n\rangle$  which obey

$$N|n\rangle = n|n\rangle \quad H_0|n\rangle = (n + \frac{1}{2})\hbar\omega|n\rangle = \varepsilon_n^{(0)}|n\rangle \quad \langle n|n'\rangle = \delta_{n,n'}. \quad (5.74)$$

We also have the relations

$$a^+|n\rangle = \sqrt{n+1}|n+1\rangle \quad a|n\rangle = \sqrt{n}|n-1\rangle \quad (5.75)$$

in terms of which we readily determine that the first order energy shift due to the applied field

$$\begin{aligned} \varepsilon_n^{(1)} &= \langle n|\hat{V}|n\rangle = \frac{-\lambda}{\sqrt{2}} \langle n|(a^+ + a)|n\rangle \\ &= -\frac{\lambda}{\sqrt{2}} \{ \langle n|a^+|n\rangle + \langle n|a|n\rangle \} = -\frac{\lambda}{\sqrt{2}} \{ \sqrt{n+1}\langle n|n+1\rangle + \sqrt{n}\langle n|n-1\rangle \} \\ &= 0 \end{aligned} \quad (5.76)$$

vanishes due to the orthogonality of the unperturbed states. So the first order energy shift vanishes and we must go to second order to calculate the energy shift. Physically this vanishing of the first order energy shift occurs for the unperturbed states because they have equal weight on each side of the origin, and so the net change in energy due to the linear applied potential vanishes. We can anticipate that the second order correction will cause a lowering of the energy as the electron displaces in the presence of the field, lowering its potential energy in the process. To see this we first calculate the first order correction to the eigenstates. In the present problem we will denote by  $|\hat{n}\rangle$  the exact eigenstates of the system that are presumed to have an expansion

$$|\hat{n}\rangle = |n\rangle + \lambda|n\rangle^{(1)} + \lambda^2|n\rangle^{(2)} + \dots \quad (5.77)$$

in powers of the small parameter  $\lambda$ . The first order correction is given, according to the results of the last section, by the expression

$$\lambda|n\rangle^{(1)} = \sum_{m \neq n} \frac{\langle m|\hat{V}|n\rangle}{\varepsilon_n^{(0)} - \varepsilon_m^{(0)}} |m\rangle = -\frac{\lambda}{\sqrt{2}} \sum_{n' \neq n} \frac{\langle m|(a^+ + a)|n\rangle}{(n-m)\hbar\omega} |m\rangle. \quad (5.78)$$

Letting  $a$  and  $a^+$  act to the right we find after a little calculation that, except for the ground state, this reduces to a sum of just two terms

$$\begin{aligned}\lambda|n\rangle^{(1)} &= -\frac{\lambda}{\sqrt{2}} \left[ \frac{\sqrt{n+1}}{-\hbar\omega} |n+1\rangle + \frac{\sqrt{n}}{\hbar\omega} |n-1\rangle \right] \\ &= \frac{\lambda}{\sqrt{2\hbar\omega}} [\sqrt{n+1}|n+1\rangle - \sqrt{n}|n-1\rangle].\end{aligned}\quad (5.79)$$

Thus, to first order the exact eigenstates of  $H$  can be written

$$|\hat{n}\rangle = |n\rangle + \frac{\lambda}{\sqrt{2\hbar\omega}} [\sqrt{n+1}|n+1\rangle - \sqrt{n}|n-1\rangle] + O(\lambda^2). \quad (5.80)$$

Thus, the perturbation mixes only the states immediately above and below the unperturbed level. Note that the corresponding expression for the ground state does not contain the second term in the above expression, i.e.,

$$|\hat{0}\rangle = |0\rangle + \frac{\lambda}{\sqrt{2\hbar\omega}} |1\rangle + O(\lambda^2). \quad (5.81)$$

We now consider the second order energy shift

$$\varepsilon_n^{(2)} = \sum_{m \neq n} \frac{|\langle m|\hat{V}|n\rangle|^2}{\varepsilon_n^{(0)} - \varepsilon_m^{(0)}} \quad (5.82)$$

which will also (except for the ground state) contain just two terms:

$$\begin{aligned}\varepsilon_n^{(2)} &= \frac{\lambda^2}{2} \left\{ \frac{|\langle n+1|a^+|n\rangle|^2}{-\hbar\omega} + \frac{|\langle n-1|a|n\rangle|^2}{\hbar\omega} \right\} \\ &= \frac{\lambda^2}{2} \left\{ -\frac{n+1}{\hbar\omega} + \frac{n}{\hbar\omega} \right\} = -\frac{\lambda^2}{2\hbar\omega} = -\frac{f^2}{2m\omega^2}.\end{aligned}\quad (5.83)$$

Thus, to second order, we find

$$\varepsilon_n = \varepsilon_n^{(0)} - \frac{\lambda^2}{2\hbar\omega} = -\frac{f^2}{2m\omega^2}. \quad (5.84)$$

We note that for this particular problem the energy shift is the same for all states, that is, all of the energies of the system are lowered by the same amount in the presence of the field. It turns out that the second order energy correction for this problem gives the exact eigenenergies (even though the first order correction to the state does not give the exact eigenstates). This result is physically intuitive, since it corresponds to the fact that a classical mass-spring system when hung in a gravitational field simply stretches, or displaces, to a new equilibrium position, thereby lowering its potential energy, but continues to oscillate with the same frequency as it would if it were left unperturbed. To establish this result in the present context we perform a canonical transform to a new set of variables

$$\hat{q} = q - \frac{\lambda}{\hbar\omega} \quad \hat{p} = p \quad (5.85)$$

which has the position coordinate now centered at the new force center at  $q = \lambda/\hbar\omega$ . This transformation preserves the commutation relations

$$[\hat{q}, \hat{p}] = [q, p] = i \quad (5.86)$$

and allows us to write the Hamiltonian in terms of the new coordinate and momenta in the form

$$\begin{aligned}
 H &= \frac{\hbar\omega}{2}(q^2 + p^2) - \lambda q \\
 &= \frac{\hbar\omega}{2} \left[ \hat{q}^2 + \frac{2\lambda}{\hbar\omega} \hat{q} + \frac{\lambda^2}{\hbar^2\omega^2} + \hat{p}^2 \right] - \lambda \left( \hat{q} + \frac{\lambda}{\hbar\omega} \right) \\
 &= \frac{\hbar\omega}{2}(\hat{q}^2 + \hat{p}^2) - \frac{\lambda^2}{2\hbar\omega}.
 \end{aligned} \tag{5.87}$$

We can now introduce operators

$$\begin{aligned}
 \hat{a} &= \frac{\hat{q} + i\hat{p}}{\sqrt{2}} & \hat{a}^+ &= \frac{\hat{q} - i\hat{p}}{\sqrt{2}} \\
 \hat{N} &= \hat{a}^+ \hat{a}
 \end{aligned}$$

in the usual way, so that the Hamiltonian takes the form

$$H = \left( \hat{N} + \frac{1}{2} \right) \hbar\omega - \frac{\lambda^2}{2\hbar\omega}$$

of an oscillator of frequency  $\omega$  lowered uniformly in energy by an amount  $\lambda^2/2\hbar\omega$ . Of course this oscillator has its equilibrium position at  $\hat{q} = q - \lambda/\hbar\omega = 0$ , i.e., shifted with respect to the unperturbed oscillator, and its energy levels are in exact agreement with those found to second order in the applied field using perturbation theory. In fact, this displacement of the oscillator under the action of the field makes it clear that the exact eigenstates of the system satisfy the equation

$$\langle \hat{q} | \hat{n} \rangle = \phi_n(\hat{q}) = \phi_n(q - \lambda/\hbar\omega) = \phi_n(q - \varepsilon),$$

where  $\varepsilon = \lambda/\hbar\omega$ , i.e., they are just the unperturbed oscillator states shifted along the  $x$ -axis, and centered at the new equilibrium position  $q = \varepsilon$ . The unitary operator which effects this transformation is the corresponding translation operator

$$T(\varepsilon) = e^{-ip\varepsilon}$$

which, in the position representation has the effect of displacing the wave function, i.e.,  $T(\varepsilon)\psi(q) = \psi(q - \varepsilon)$ . Thus, we expect that the unperturbed and perturbed eigenstates are related through the relation

$$|\hat{n}\rangle = T(\varepsilon)|n\rangle = e^{-ip\varepsilon}|n\rangle.$$

For small  $\varepsilon$  (or small  $\lambda$ ) we can expand the exponential as  $T(\varepsilon) \simeq 1 - ip\varepsilon$  so that

$$|\hat{n}\rangle \simeq (1 - ip\varepsilon)|n\rangle = |n\rangle - ip\varepsilon|n\rangle.$$

Using the fact that  $-ip\varepsilon = \varepsilon(a^+ - a)/\sqrt{2}$  and substituting back in the definition of  $\varepsilon = \lambda/\hbar\omega$  we recover the result

$$|\hat{n}\rangle \simeq |n\rangle + \frac{\lambda}{\sqrt{2}\hbar\omega}|n+1\rangle - \frac{\lambda}{\sqrt{2}\hbar\omega}|n-1\rangle$$

that we obtained using the techniques of first order perturbation theory.

### 5.3 Perturbation Theory for Degenerate States

The expressions that we derived above for the first order correction to the ground state and the second order correction to the energy are clearly inappropriate to situations in which degenerate or nearly-degenerate eigenstates are connected by the perturbation, since the corresponding corrections all diverge as the spacing between the energy levels goes to zero. This divergence is an indication of the strength with which the perturbation tries to mix together states that are very-nearly degenerate (or exactly so), and suggest that we might wish to treat differently those states that are known in advance to be very closely related in energy. In this section, therefore, we discuss the general approach taken to deal with problems of this sort.

We assume, as before, that the Hamiltonian of interest can be separated into two parts, which we now write in the simplified form

$$H = H_0 + V \quad (5.88)$$

where, since we will not be developing a systematic expansion in powers of the perturbation we have no need for the more complex notation used previously. We again seek the exact eigenstates and eigenenergies of  $H$ , expressed as an expansion in eigenstates of  $H_0$ , the latter of which are assumed to be at least partially degenerate. We will denote by  $\{|\phi_n, \tau\rangle\}$  an arbitrary orthonormal basis of eigenstates of  $H_0$ , where the index  $\tau$  is included to distinguish between the different linearly independent basis states of  $H_0$  having the same unperturbed energy  $\varepsilon_n^{(0)}$ . The basis states

$$\{|\phi_n, \tau\rangle \mid \tau = 1, \dots, N_n\} \quad (5.89)$$

with fixed energy  $\varepsilon_n^{(0)}$  form a basis for an eigensubspace  $S(\varepsilon_n^{(0)})$  of  $H_0$  corresponding to that particular degenerate energy. The dimension  $N_n$  of this subspace is just the degeneracy of the corresponding eigenvalue  $\varepsilon_n^{(0)}$  of  $H_0$ . It is important to point out that, due to the degeneracy, our choice of the basis set  $\{|\phi_n, \tau\rangle\}$  is not unique; any unitary transformation carried out *within* any one of the eigenspaces  $S(\varepsilon_n^{(0)})$  generates a new basis  $\{|\chi_n, \tau\rangle\}$  that can be used as readily as any other for expanding the exact eigenstates of  $H$ . Any such basis set will satisfy the obvious eigenvalue, orthogonality, and completeness relations

$$\begin{aligned} H_0|\phi_n, \tau\rangle &= \varepsilon_n^{(0)}|\phi_n, \tau\rangle & \langle\phi_{n'}, \tau'|\phi_n, \tau\rangle &= \delta_{n',n}\delta_{\tau',\tau} & \sum_{n,\tau} |\phi_n, \tau\rangle\langle\phi_n, \tau| &= 1 \\ H_0|\chi_n, \tau\rangle &= \varepsilon_n^{(0)}|\chi_n, \tau\rangle & \langle\chi_{n'}, \tau'|\chi_n, \tau\rangle &= \delta_{n',n}\delta_{\tau',\tau} & \sum_{n,\tau} |\chi_n, \tau\rangle\langle\chi_n, \tau| &= \mathbf{1} \end{aligned} \quad (5.90)$$

We now observe that the divergences that render the formulae of nondegenerate perturbation theory inapplicable really only arise if the perturbation actually *connects* states within each eigensubspace, i.e., if there exists non-zero matrix elements  $V_{n\tau, n'\tau'} = \langle\phi_n, \tau|V|\phi_n, \tau'\rangle$  of the perturbation connecting basis states of the same energy. Thus, our previous formulae can, in fact be applied (at least to the level that we have developed them), under two conceivable circumstances, one involving the diagonal matrix elements of  $V$  and one involving the off-diagonal elements:

1. If the first order correction  $\varepsilon_{n,\tau}^{(1)} = \langle\phi_n, \tau|V|\phi_n, \tau\rangle$  is *distinct* for all the basis states  $|\phi_n, \tau\rangle$  in each eigenspace  $S(\varepsilon_n^{(0)})$ , then the degeneracy is “lifted” in the first order of the perturbation. Provided the magnitude of this splitting of the energy levels by the perturbation is large compared to the matrix elements of  $V$  that connect these states

we can then simply “redefine” what we call the unperturbed and the perturbing part of the Hamiltonian. In other words, although we originally decomposed the Hamiltonian in the form  $H = H_0 + V$ , where, in a representation of eigenstates of  $H_0$ ,

$$\begin{aligned} H_0 &= \sum_{n,\tau} |\phi_n, \tau\rangle \varepsilon_n^{(0)} \langle \phi_n, \tau| \\ V &= \sum_{n,\tau;n',\tau'} |\phi_n, \tau\rangle V_{n\tau,n'\tau'} \langle \phi_{n'}, \tau'|, \end{aligned}$$

we can now *include* the diagonal part of  $V$  in a redefined  $\hat{H}_0$  such that  $H = \hat{H}_0 + \hat{V}$ , but now,

$$\begin{aligned} \hat{H}_0 &= \sum_{n,\tau} |\phi_n, \tau\rangle [\varepsilon_n^{(0)} + \varepsilon_{n,\tau}^{(1)}] \langle \phi_n, \tau| \\ \hat{V} &= \sum_{n,\tau \neq n',\tau'} |\phi_n, \tau\rangle V_{n\tau,n'\tau'} \langle \phi_{n'}, \tau'| \end{aligned}$$

where the perturbation  $\hat{V}$  now has no diagonal matrix elements in this representation. In this situation, states within  $S(\varepsilon_n^{(0)})$  are now no longer degenerate, so we can proceed as before to apply the formulae of non-degenerate perturbation theory, with the energy denominators now including the first order shifts, so no divergences occur.

2. If, on the other hand, the *off-diagonal* part of the perturbation  $\hat{V}$  just happens to vanish between all the basis states *within a given eigensubspace*  $S(\varepsilon_n^{(0)})$ , then (at least to second order) the problematic terms in the perturbation expansion never actually arise; thus if the submatrix  $[V]_n$  representing the perturbation *within* the degenerate subspace is *diagonal*, we can actually proceed as though there were no degeneracy.

In passing we might comment regarding the first of these circumstances that the act of including the diagonal part of the perturbation  $V$  in a redefined  $\hat{H}_0$  can always be performed, even when it does not entirely lift the degeneracy. We may therefore assume without loss of generality in what follows that such an operation has already been carried out, and hence that the perturbation has no diagonal components in the basis of interest.

Regarding the second circumstance mentioned above, it might be thought that, in actual practice, the vanishing of the off-diagonal matrix elements of  $V$  within  $S(\varepsilon_n^{(0)})$  would occur in so few circumstances that it hardly merits attention. To the contrary, there is a sense in which it *always* can be *made* to occur. To understand this comment, and in the process reveal the basic technique that is generally employed for dealing with degenerate states, we note that the off-diagonal matrix elements of the perturbation  $V$  taken between basis states in a given degenerate subspace of  $H_0$  depend upon *which* set of basis states of  $H_0$  we choose to begin with. If, e.g., we choose a set  $\{|\phi_n, \tau\rangle\}$  we get one set of matrix elements

$$V_{n\tau;n\tau'} = \langle \phi_n, \tau | V | \phi_n, \tau' \rangle,$$

defining a certain submatrix  $[V]_n$ , while if we choose, instead, any other set  $\{|\chi_n, \tau\rangle\}$  we obtain a completely different set of matrix elements

$$\tilde{V}_{n\tau;n\tau'} = \langle \chi_n, \tau | V | \chi_n, \tau' \rangle$$

defining a different submatrix  $[\tilde{V}]$  representing the perturbation  $V$  within this degenerate eigensubspace.

Thus, as we would expect, the *submatrix*  $[V]_n$  or  $[\tilde{V}]_n$  representing the perturbation within the eigenspace  $S(\varepsilon_n^{(0)})$  depends upon the particular basis set ( $\{|\phi_n, \tau\rangle\}$  or  $\{|\chi_n, \tau\rangle\}$ ) that we chose to work in. In light of circumstance 2, above, the question that arises is the following: under what circumstances can we find a representation of basis states  $\{|\chi_n, \tau\rangle\}$  *within*  $S(\varepsilon_n^{(0)})$  for which the submatrix  $[\tilde{V}]$  representing the perturbation in that subspace is strictly *diagonal*?

Insofar as the perturbation  $V$  itself is presumed to be an observable (and thus Hermitian), any submatrix  $[V]_n$  or  $[\tilde{V}]_n$  representing  $V$  within such a subspace must itself be a Hermitian, and related to any of the other matrices representing  $V$  within this subspace by a unitary (sub)transformation. For a finite  $N_n$  dimensional subspace, however, we know that it is *always* possible to find a representation that diagonalizes *any* Hermitian matrix. For each subspace we just have to go through the usual procedure of finding the roots  $\tilde{\varepsilon}_{n,\tau}$  to the characteristic equation

$$\det([V]_n - \varepsilon) = 0$$

for the  $N_n$  dimensional submatrix  $[V]_n$  that represents  $V$  within a given eigenspace  $S(\varepsilon_n^{(0)})$ , and then solve the resulting linear equations to find those combinations  $\{|\chi_n, \tau\rangle\}$  of the original basis vectors  $\{|\phi_n, \tau\rangle\}$  that are also eigenvectors of the submatrix  $[V]_n$ . In this new representation, by construction, no elements of the new basis set  $\{|\chi_n, \tau\rangle\}$  having the same energy unperturbed energy are connected to one another by nonzero matrix elements of the perturbation. Moreover, the diagonalization of  $V$  within each eigenspace  $S(\varepsilon_n^{(0)})$  provides a new set of eigenvalues  $\tilde{\varepsilon}_{n,\tau}$  (the roots of the characteristic equation  $\det[V - \varepsilon]_n$  computed within the subspace) which will form the diagonal elements of the matrix representing  $V$  in this representation. These diagonal elements can then be combined with those of  $H_0$  to obtain new unperturbed eigenenergies (correct to first order)

$$\varepsilon_{n,\tau} = \varepsilon_n^{(0)} + \tilde{\varepsilon}_{n,\tau}$$

that will themselves often at least partially lift the degeneracy. The particular states found during the diagonalization can then be chosen as a new set of zeroth order states with which to pursue higher order corrections, according to the techniques of nondegenerate perturbation theory. Thus, the basic result of degenerate perturbation theory is not an explicit formula, as it is in the nondegenerate case. Rather it is a simple prescription: diagonalize the perturbation  $V$  within the degenerate subspaces of  $H_0$  to determine a new basis for proceeding, if necessary, with the determination of higher order corrections using standard techniques.

### 5.3.1 Application: Stark Effect of the $n = 2$ Level of Hydrogen

We consider as an application of the ideas developed above the splitting of the spectral lines observed in the absorption and emission spectra of the hydrogen atom when it is placed in a uniform DC electric field, the so-called Stark effect. The relevant Hamiltonian can be written in the expected form

$$H = H_0 + V,$$

where

$$H = \frac{p^2}{2m} - \frac{e^2}{r}$$

is the usual one describing a single electron bound to the proton of a hydrogen atom, and the perturbation

$$V = Fz = Fr \cos \theta$$



describes the constant force  $F = eE$  exerted on the electron by a uniform field oriented along the negative  $z$ -axis. We initially take as our unperturbed states the standard bound eigenstates  $|n, l, m\rangle$  of the hydrogen atom

$$H_0|n, l, m\rangle = \varepsilon_n^{(0)}|n, l, m\rangle \quad \varepsilon_n^{(0)} = -\frac{\varepsilon_0}{n^2}$$

which have both a rotational and an accidental degeneracy of the energy levels. The degeneracy  $g_n$  of the  $n$ th eigenenergy (or the dimension  $N_n$  of the associated eigenspace  $S_n$ ) is given by the expression

$$g_n = n^2 = \sum_{\ell=0}^{n-1} (2\ell + 1).$$

The first order correction to the energy of the state  $|n, l, m\rangle$  due to the applied electric field vanishes, i.e.,

$$\varepsilon_{nlm}^{(1)} = F\langle nlm|Z|nlm\rangle = 0$$

reflecting the fact that the mean position of the electron in any of the standard hydrogen atom eigenstates is the origin. To use perturbation theory to find non-vanishing corrections to the energy due to the applied field we must handle the degeneracies. Consider, e.g., the four-fold degenerate  $n = 2$  level, which is spanned by the four  $|nlm\rangle$  states

$$|2, 0, 0\rangle \quad |2, 1, 0\rangle \quad |2, 1, 1\rangle \quad |2, 1, -1\rangle.$$

Within the subspace  $S_2$  the submatrix representing  $H_0$  is, of course, diagonal

$$[H_0] = \begin{bmatrix} \varepsilon_2^{(0)} & 0 & 0 & 0 \\ 0 & \varepsilon_2^{(0)} & 0 & 0 \\ 0 & 0 & \varepsilon_2^{(0)} & 0 \\ 0 & 0 & 0 & \varepsilon_2^{(0)} \end{bmatrix}.$$

To proceed we need to construct the matrix  $[V]$  representing the perturbation within this subspace. Thus we need to evaluate the matrix elements

$$\langle 2, l, m|z|2, l', m'\rangle = \int d^3r \psi_{2,\ell,m}^* z \psi_{2,\ell',m'}.$$

But the perturbing operator is clearly just the  $z$  component of the vector operator  $\vec{R}$ . According to the Wigner-Eckart theorem such an operator can only connect states having the same  $z$ -component of angular momentum, i.e., those for which  $m = m'$ . Thus, of the states in the  $n = 2$  manifold, the only nonzero matrix elements for this perturbation occur between the state  $|2, 0, 0\rangle$  and the state  $|2, 1, 0\rangle$ . Hence, within this subspace the matrix of interest has the form

$$[V] = \begin{bmatrix} 0 & \eta & 0 & 0 \\ \eta^* & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix},$$

where  $\eta = \langle 2, 0, 0|Fz|2, 1, 0\rangle$ . This latter integral is readily evaluated in the position representation, using the known form

$$\langle \vec{r}|2, 0, 0\rangle = \psi_{2,0,0}(\vec{r}) = \frac{1}{\sqrt{8a^3}} \left(2 - \frac{r}{a}\right) e^{-r/2a} Y_0^0(\theta, \phi)$$

$$\langle \vec{r} | 2, 1, 0 \rangle = \psi_{2,1,0}(\vec{r}) = \frac{1}{\sqrt{8a^3}} \frac{1}{\sqrt{3}} \frac{r}{a} e^{-r/2a} Y_1^0(\theta, \phi)$$

of the hydrogen  $n = 2$  wave functions. Substituting into the integral of interest we find after a short calculation that

$$\eta = \frac{F}{16a^4} \left[ \int_0^\infty r^4 \left(2 - \frac{r}{a}\right) e^{-r/a} dr \right] \left[ \int_0^\pi \sin \theta \cos^2 \theta d\theta \right] = -3Fa.$$

Thus,

$$[V] = \begin{bmatrix} 0 & -3Fa & 0 & 0 \\ -3Fa & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}.$$

Diagonalizing  $[V]$  we set  $\det(V - \varepsilon) = -\varepsilon^2[\varepsilon^2 - (3Fa)^2] = 0$  and find the eigenvalues

$$\begin{aligned} \hat{\varepsilon}_{2,1,1} &= \hat{\varepsilon}_{2,1,-1} = 0 \\ \hat{\varepsilon}_{2,+} &= +3Fa \\ \hat{\varepsilon}_{2,-} &= -3Fa \end{aligned}$$

which we can add to the  $n = 2$  hydrogenic energies to provide the *first order* corrections. Thus, to first order, the  $n = 2$  eigenenergies in the presence of the field take the form

$$\begin{aligned} \varepsilon_{2,+} &= \varepsilon_2^{(0)} + 3Fa \\ \varepsilon_{2,-} &= \varepsilon_2^{(0)} - 3Fa \\ \varepsilon_{2,1,1} &= \varepsilon_{2,1,-1} = \varepsilon_2^{(0)} \end{aligned}$$

which correspond, respectively, to new zeroth order states

$$\begin{aligned} |2, +\rangle &= \frac{|2, 0, 0\rangle + |2, 0, 1\rangle}{\sqrt{2}} \\ |2, -\rangle &= \frac{|2, 0, 0\rangle - |2, 0, 1\rangle}{\sqrt{2}} \\ &|2, 1, 1\rangle \\ &|2, 1, -1\rangle. \end{aligned}$$

Qualitatively we see that the four-fold degenerate  $n = 2$  hydrogenic level is split by the field into three separate levels, with the nondegenerate lower and higher energy states splitting off linearly in the applied field from the remaining two-fold degenerate subspace corresponding to the unperturbed energies. With these new basis states (in which  $\ell$  is no longer a necessarily good quantum) one can, in principle, investigate higher order corrections to the energy.