

## Chemistry 21b – Spectroscopy

### Lecture # 1 – Non-Degenerate Time-Independent Perturbation Theory

In this quarter of Ch21, we will be primarily concerned with spectroscopy – the interaction of light with matter – and what it can tell us about molecules and materials. As we will see this week, perturbation theory is the simplest route to thinking about this fundamental interaction. In setting up many of the situations we will encounter, the so called matrix form of quantum mechanics will be helpful, and so before turning to perturbation theory these notes will present a brief overview of the quantum mechanical underpinnings of molecular systems that are hopefully familiar from Ch21a along with a brief review of the notation that will be followed in these notes.

### The Basic Postulates of Quantum Mechanics

As with all scientific theories, the test of quantum mechanics lies in the rigorous comparison of its predictions with observations. Building up these predictions rests on five basic postulates, that we briefly review here (in addition to Chapter 1 of the class text (Atkins & Friedman), the text by Engel has a more extensive discussion of these postulates, see *Quantum Chemistry & Spectroscopy*, Ch. 3):

#### *Postulate 1*

There exists a wave function  $\Psi(\mathbf{r}, t)$  that completely specifies the state of a quantum mechanical system. It depends on both the spatial coordinates of the particle(s) and time, and has the property that  $\Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t) dx dy dz$  denotes the probability that there is a particle located at  $\mathbf{r}$  in a volume  $dx dy dz$  and at time  $t$ , where  $\Psi^*(\mathbf{r}, t)$  is the complex conjugate of  $\Psi(\mathbf{r}, t)$ .

#### *Postulate 2*

The observables in classical mechanics (position, linear and angular momentum, energy, etc.) are represented quantum mechanically by Hermitian operators. More on this next.

#### *Postulate 3*

For each and every Hermitian operator  $\hat{A}$  associated with an observable, only certain values of this observable are possible. In particular, they must satisfy the eigenvalue equation  $\hat{A}\Psi = a\Psi$ , where  $\Psi$  is the wave function of the system. Because the operators are Hermitian, the eigenvalues are real and for non-degenerate systems the eigenfunctions (or state functions) are orthogonal. Because the wavefunctions are also probability distributions, they are best constructed to be orthonormal as well (or,  $\int \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t) dx dy dz = 1$ ). Finally, because the operators are Hermitian, it can be proven that the eigenfunctions are *complete* – meaning that any state function of the system can be decomposed into an appropriate sum of the eigenfunctions.

#### *Postulate 4*

The expectation, or average, value of an observable at time  $t$  that is represented

by an operator  $\hat{A}$  is given by the integral

$$\langle a \rangle = \int_{-\infty}^{\infty} \Psi^*(\mathbf{r}, t) \hat{A} \Psi(\mathbf{r}, t) d\mathbf{r}$$

where  $\Psi(\mathbf{r}, t)$  is the state function of the system.

#### Postulate 5

The temporal evolution of quantum mechanical systems is given by the time dependent Schrödinger equation, or  $\hat{H}\Psi(\mathbf{r}, t) = i\hbar(\partial\Psi/\partial t)$ , where  $\hbar$  is Planck's constant divided by  $2\pi$  and  $\hat{H}$  is the Hamiltonian operator (or the sum of the kinetic and potential energy of the system). Consider Hamiltonians of the form  $\hat{H} = \hat{H}(\mathbf{r})$ , that is, which are functions of the coordinates of the particles only. The separation of variables method tells us that an appropriate form of the state function under these conditions is  $\Psi(\mathbf{r}, t) = \psi(\mathbf{r})f(t)$ . Dividing both sides of the time dependent Schrödinger equation by  $\psi(\mathbf{r})f(t)$  yields

$$\frac{1}{\psi(\mathbf{r})} \hat{H}\psi(\mathbf{r}) = \frac{i\hbar}{f(t)} \frac{df}{dt} .$$

Here, the left hand side depends on the spatial coordinates only while the right hand side depends only on time; thus, each must be equal to a constant. This gives the familiar *time independent* form of the Schrödinger equation, or  $\hat{H}\psi = E\psi$ , and a time dependence of  $f(t) = e^{-iEt/\hbar}$ . In general there are a number of energy eigenvalues, which we will denote  $E_n$ . These special state functions that correspond to the permitted energies of the system are called stationary states, and are given by

$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r})e^{-iE_n t/\hbar} .$$

They are called stationary states because  $\Psi_n^*(\mathbf{r}, t)\Psi_n(\mathbf{r}, t)d\mathbf{r} = \psi_n^*(\mathbf{r})\psi_n(\mathbf{r})d\mathbf{r}$ .

### Notation and the Matrix Form of Quantum Mechanics

Writing out integrals time after time can become cumbersome in quantum mechanical calculations, and so not surprisingly a number of notational shortcuts have been developed. Here we shall use the so-called *bra-ket* notation (developed by Dirac), in which the *ket* refers to a given state function, or  $|\psi_n\rangle = \psi_n$ , and in which the *bra* denotes it's complex conjugate, or  $\langle\psi_n| = \psi_n^*$ . When placed together, these symbols mean take the state function and its complex conjugate and integrate over all space. Thus, the expectation value referred to above for a system in the stationary state  $\Psi_n$  becomes

$$\langle a \rangle = \langle \Psi_n | \hat{A} | \Psi_n \rangle = \int_{-\infty}^{\infty} \Psi_n^* \hat{A} \Psi_n d\mathbf{r} .$$

What about cases where the *bra* and *ket* are not the same? The integral is then called a *matrix element*, and for two functions  $\Psi_i$  and  $\Psi_j$  the *ij*-th matrix element for operator  $\hat{A}$  would be denoted  $A_{ij}$ :

$$A_{ij} = \langle \Psi_i | \hat{A} | \Psi_j \rangle = \int_{-\infty}^{\infty} \Psi_i^* \hat{A} \Psi_j d\mathbf{r} .$$

Why would we care about matrix elements? Because observables are represented by Hermitian operators, *any* state function of the system can be decomposed into a sum over the eigenfunctions, that is, we can write with complete generality

$$|\Psi\rangle = \sum_i c_i |\varphi_i\rangle ,$$

where  $\Psi$  is the state function and the  $\varphi_i$  are the eigenfunctions of the system. The  $\langle \Psi_i | \Psi_j \rangle$  symbol alone denotes what are called *overlap integrals*.

The matrix form of a given operator, for example the Hamiltonian, consists of the matrix elements in whatever suite of orthonormal functions you care to use, or

$$\hat{H} = \begin{pmatrix} H_{11} & H_{12} & H_{13} & \dots & H_{1q} \\ H_{21} & H_{22} & H_{23} & \dots & H_{2q} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ H_{q1} & H_{q2} & H_{q3} & \dots & H_{qq} \end{pmatrix}$$

for a basis set (the suite of eigenfunctions) with  $q$  elements. If the functions chosen are eigenfunctions, the matrix will be diagonal. Thanks to efficient linear algebra routines on computers, it is now possible to use conceptually straightforward but numerically intensive basis sets to generate operator matrices which are then diagonalized to yield the actual eigenvalues and eigenfunctions of the system under study.

## Perturbation Theory in Quantum Mechanics

Before we launch into a detailed investigation of the ways in which molecules, liquids, and solids interact with electromagnetic radiation, it will be helpful to add an additional component to our quantum mechanical toolkit – perturbation theory. Ultimately, for spectroscopy we will need to utilize what is called time-dependent perturbation theory, but for starters we will look at time-independent perturbation theory to build up some necessary mathematical formalisms. Time-independent perturbation theory comes in two flavors, non-degenerate (that is, all of the eigenvalues are distinct) and degenerate (that is, a system in which some of the eigenvalues may be identical) perturbation theory.

In all cases, the basic idea is to split the total Hamiltonian into two parts, or

$$\hat{H} = \hat{H}_0 + \hat{H}' ,$$

where  $\hat{H}_0$  is called the zeroth-order Hamiltonian and  $\hat{H}'$  is the operator for the perturbation. For the approach to work well, it is best if the eigenvalues of  $\hat{H}_0$  are known. Some examples of important problems that can be treated with perturbation theory include  $\mathbf{L} \cdot \mathbf{S}$  coupling in low- $Z$  atoms, anharmonic oscillators, and the Stark and Zeeman effects (That is, the response of atoms and molecules to static electric and magnetic external fields.). The time-dependent interactions of atoms and molecules with electromagnetic fields is another important example that we will spend most of the course looking at.

In order for perturbation theory to work well, the effects of the perturbing term  $\hat{H}'$  must be, in some sense, small compared to that of  $\hat{H}_0$ . Put another way, we will assume

that the eigenstates and eigenenergies of the total Hamiltonian, let's call them  $\{\varphi_n\}$  and  $\{E_n\}$ , are only slightly different from those of the unperturbed Hamiltonian,  $\hat{H}_0$ , which we'll call  $\{\varphi_n^{(0)}\}$  and  $\{E_n^{(0)}\}$ . Provided the effects of  $\hat{H}'$  are indeed small, we can then introduce the terms  $\Delta\varphi_n$  and  $\Delta E_n$  as small corrections to the zeroth-order energies and wavefunctions, or

$$\begin{aligned}\varphi_n &= \varphi_n^{(0)} + \Delta\varphi_n \\ E_n &= E_n^{(0)} + \Delta E_n.\end{aligned}$$

To keep the smallness of  $\hat{H}'$  explicitly in mind, many textbooks rewrite the first equation above as containing the term  $\lambda\hat{H}'$ , where  $\lambda$  is an infinitesimal parameter and is introduced for "bookkeeping" purposes. Thus, the equation we must solve becomes

$$(\hat{H}_0 + \lambda\hat{H}')\varphi_n = E_n\varphi_n \quad . \quad (1.1)$$

### The Perturbation Expansion

Again, we assume that the eigenstates and eigenenergies of  $\hat{H}_0$  are known, and that the eigenstates form a complete, orthonormal basis set which spans the Hilbert space of  $\hat{H}_0$ . I'll assume here that you are familiar with some of the simpler examples of problems that can be solved exactly in quantum mechanics, such as the particle-in-a-box the harmonic oscillator, and the hydrogen atom. As necessary, please review the appropriate chapters in Atkins and Friedman (esp. Ch. 2 for the particle-in-a-box/harmonic oscillator and Ch. 3 for the H atom).

Clearly, as  $\lambda \rightarrow 0$ ,  $\varphi_n \rightarrow \varphi_n^{(0)}$  and  $E_n \rightarrow E_n^{(0)}$ . Let's then expand the complete wavefunctions and energies in series in which the zeroth-order functions from  $\hat{H}_0$  are the leading terms, or

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

where the terms such as  $E_n^{(1)}$  and  $E_n^{(2)}$  are called the first- and second-order corrections to the energy (for example). Substituting these expressions into Eq. (1.1) and arranging the terms with common powers of  $\lambda$  then gives:

$$\begin{aligned}[\hat{H}_0\varphi_n^{(0)} - E_n^{(0)}\varphi_n^{(0)}] + \lambda[\hat{H}_0\varphi_n^{(1)} + \hat{H}'\varphi_n^{(0)} - E_n^{(0)}\varphi_n^{(1)} - E_n^{(1)}\varphi_n^{(0)}] \\ + \lambda^2[\hat{H}_0\varphi_n^{(2)} + \hat{H}'\varphi_n^{(1)} - E_n^{(0)}\varphi_n^{(2)} - E_n^{(1)}\varphi_n^{(1)} - E_n^{(2)}\varphi_n^{(0)}] + \dots = 0 \quad ; \quad (1.2)\end{aligned}$$

which is an equation of the form

$$F^{(0)} + \lambda F^{(1)} + \lambda^2 F^{(2)} + \lambda^3 F^{(3)} + \dots = 0 \quad .$$

Such an equation can hold for arbitrary values of  $\lambda$  only if *each* of the terms  $F^{(x)}$  is equal to zero. In such a case, the terms of Eq. (1.2) become:

$$\begin{aligned}(a) \quad \hat{H}_0\varphi_n^{(0)} &= E_n^{(0)}\varphi_n^{(0)} \\ (b) \quad (\hat{H}_0 - E_n^{(0)})\varphi_n^{(1)} &= (E_n^{(1)} - \hat{H}')\varphi_n^{(0)}\end{aligned}$$

$$\begin{aligned}
(c) \quad (\hat{H}_0 - E_n^{(0)})\varphi_n^{(2)} &= (E_n^{(1)} - \hat{H}')\varphi_n^{(1)} + E_n^{(2)}\varphi_n^{(0)} \\
(d) \quad (\hat{H}_0 - E_n^{(0)})\varphi_n^{(3)} &= (E_n^{(1)} - \hat{H}')\varphi_n^{(2)} + E_n^{(2)}\varphi_n^{(1)} + E_n^{(3)}\varphi_n^{(0)} \\
&\dots \dots \dots
\end{aligned} \tag{1.3}$$

Eq. (1.3a) simply returns the information that  $\{\varphi_n^{(0)}\}$  and  $\{E_n^{(0)}\}$  are the eigenfunctions and eigenenergies of  $\hat{H}_0$ . In the succeeding equations, the left hand sides are invariant under the substitution  $\varphi^{(s)} \rightarrow \varphi^{(s)} + a\varphi^{(0)}$ , where  $a$  is (an arbitrary) constant. Some other constraint must be applied to remove this arbitrary quality of the solution, and two are available which essentially do the same thing.

The first is to enforce a solution such that all of the corrections to the  $\{\varphi_n^{(0)}\}$  are orthogonal to the zeroth-order wavefunctions, that is

$$\langle \varphi_n^{(s)} | \varphi_n^{(0)} \rangle = 0 \quad (\text{for } s > 0 \text{ and all } n) .$$

Alternatively, we can construct the  $\{\varphi_n^{(s)}\}$  such that the total wavefunctions are normalized. Either constraint yields that same corrections to the energies, and wavefunctions which differ by at most a phase factor.

### First-Order Corrections

Recall that we have constructed the  $\{\varphi_n^{(0)}\}$  such that they are a complete, orthonormal basis set. We may therefore arbitrarily expand the  $\{\varphi_n^{(1)}\}$  wavefunctions in terms of the zeroth-order basis set, or

$$|\varphi_n^{(1)}\rangle = \sum_i c_{ni} |\varphi_i^{(0)}\rangle .$$

If this expansion is substituted into Eq. (1.3b), we find

$$(\hat{H}_0 - E_n^{(0)}) \sum_i c_{ni} |\varphi_i^{(0)}\rangle = (E_n^{(1)} - \hat{H}') |\varphi_n^{(0)}\rangle .$$

If we then “mutiply from the left” with  $\langle \varphi_j^{(0)} |$ , and use the fact that the  $\{\varphi_n^{(0)}\}$  are orthonormal (that is,  $\langle \varphi_i^{(0)} | \varphi_j^{(0)} \rangle = \delta_{ij}$ ), we are left with

$$(E_j^{(0)} - E_n^{(0)})c_{nj} + H'_{jn} = E_n^{(1)}\delta_{jn} , \tag{1.4}$$

where the  $H'_{jn}$  are the matrix elements of the  $\hat{H}'$  operator in the  $\{\varphi_n^{(0)}\}$  representation, or

$$H'_{jn} = \langle \varphi_j^{(0)} | \hat{H}' | \varphi_n^{(0)} \rangle .$$

Now, for  $j \neq n$ , eq. (1.4) gives the coefficients  $\{c_{nj}\}$ , which we need to construct the first order corrections to the wavefunctions, in terms of the zeroth-order energies and wavefunctions that are known *a priori*, namely

$$c_{ni} = H'_{in} / (E_n^{(0)} - E_i^{(0)})$$

$$\varphi_n^{(1)} = \sum_{i \neq n} \frac{H'_{in}}{E_n^{(0)} - E_i^{(0)}} \varphi_i^{(0)} + c_{nn} \varphi_n^{(0)} .$$

From either the orthogonality or normalization constraint noted above, it is found that  $c_{nn} = 0$ . Given this, we find that the first order correction to the energy is simply the diagonal matrix elements of the perturbing  $\hat{H}'$  operator, or  $E_n^{(1)} = H'_{nn}$ . Reinserting the now known value of  $E_n^{(1)}$  into eq. (1.4), setting  $\lambda = 1$ , and slight rearrangement yields the following expressions for the first order wavefunctions and energies:

$$\begin{aligned} \varphi_n &= \varphi_n^{(0)} + \sum_{i \neq n} \frac{H'_{in}}{E_n^{(0)} - E_i^{(0)}} \varphi_i^{(0)} \\ E_n &= E_n^{(0)} + H'_{nn} . \end{aligned}$$

These equations are valid provided the expansion coefficients are less than one, that is provided the perturbation is small. Numerically, it must be true that  $|H'_{in}| \ll |E_n^{(0)} - E_i^{(0)}|$  and  $|H'_{nn}| \ll |E_n^{(0)}|$ .

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### Lecture # 1 (cont'd) – Second Order Non-Degenerate Perturbation Theory

Now that we derived the first-order corrections to the eigenenergies and eigenfunctions for the total Hamiltonian  $\hat{H} = \hat{H}_0 + \hat{H}'$ , we can insert them into Eq. (1.3c) to generate the corresponding second order corrections in the non-degenerate case. As before, we first proceed to calculate the second-order corrections to the energies,  $E_n^{(2)}$ . At this point, all of the terms in Eq. (1.3c) are known *except* the  $\{\varphi_n^{(2)}\}$  second-order corrections to the wavefunctions, whose solution is therefore straightforward.

It is worth considering for a moment the form of the equations in (1.3). Specifically, as the first lecture outlines, in order to generate the first-order corrections to the energies it is only necessary to know the wavefunctions to zeroth-order. The first-order corrections for the wavefunctions are more involved, and in principle may require the off-diagonal matrix elements involving *all* of the zeroth-order eigenfunctions – which in many cases are infinite in number! This is a specific example of the Brillouin-Wigner theorem, which states that if the corrections to the wavefunctions of order ( $m$ ) are known, these are sufficient to calculate the corrections to the energies of order ( $2m + 1$ ). We will come back to this point during our discussion of time-dependent perturbation theory.

To actually derive the second order corrections we proceed as before. That is, we expand the  $\{\varphi_n^{(2)}\}$  in terms of the complete, orthonormal  $\{\varphi_n^{(0)}\}$  eigenfunctions, or

$$|\varphi_n^{(2)}\rangle = \sum_i d_{ni} |\varphi_i^{(0)}\rangle .$$

Inserting this expression into Eq. (1.3c) we find

$$\sum_i E_i^{(0)} d_{ni} |\varphi_i^{(0)}\rangle + \hat{H}' |\varphi_n^{(1)}\rangle = E_n^{(0)} \sum_i d_{ni} |\varphi_i^{(0)}\rangle + E_n^{(1)} |\varphi_n^{(1)}\rangle + E_n^{(2)} |\varphi_n^{(0)}\rangle .$$

Again we multiply from the left with an eigenstate of  $\hat{H}_0$ , call it  $\langle \varphi_j^{(0)} |$ , which leads to

$$(E_j^{(0)} - E_n^{(0)}) d_{nj} + \langle \varphi_j^{(0)} | \hat{H}' | \varphi_n^{(1)} \rangle = E_n^{(2)} \delta_{jn} + E_n^{(1)} \langle \varphi_j^{(0)} | \varphi_n^{(1)} \rangle . \quad (1.5)$$

If  $j = n$ , then eq. (1.5) simplifies to

$$\begin{aligned} E_n^{(2)} &= \langle \varphi_n^{(0)} | \hat{H}' | \varphi_n^{(1)} \rangle \\ &= \langle \varphi_n^{(0)} | \sum_{i \neq n} \frac{\hat{H}' H'_{in}}{E_n^{(0)} - E_i^{(0)}} | \varphi_i^{(0)} \rangle \\ &= \sum_{i \neq n} \frac{H'_{ni} H'_{in}}{E_n^{(0)} - E_i^{(0)}} . \end{aligned}$$

Recall, however, that the Hamiltonian operator is Hermitian, and thus we may rewrite the above simply as

$$E_n^{(2)} = \sum_{i \neq n} \frac{|H'_{ni}|^2}{E_n^{(0)} - E_i^{(0)}} .$$

Now that we have obtained the second-order corrections to the energies, the only unknown terms in eq. (1.5) are the coefficients  $\{d_{ni}\}$ . All we need do now is consider the case where  $j \neq n$ , which yields

$$\begin{aligned} (E_n^{(0)} - E_j^{(0)})d_{nj} &= \langle \varphi_j^{(0)} | \sum_{k \neq n} \hat{H}' \frac{H'_{kn}}{E_n^{(0)} - E_k^{(0)}} | \varphi_k^{(0)} \rangle \\ &\quad - H'_{nn} \langle \varphi_j^{(0)} | \sum_{k \neq n} \frac{H'_{kn}}{E_n^{(0)} - E_k^{(0)}} | \varphi_k^{(0)} \rangle . \end{aligned}$$

In the second sum, only the  $k = j$  term survives the  $\langle \varphi_j^{(0)} | \varphi_k^{(0)} \rangle$  inner product (the  $H'_{kn}$  are just numbers). All terms in the first term remain. There results

$$d_{nj} = \frac{1}{E_n^{(0)} - E_j^{(0)}} \left( \sum_{k \neq n} \frac{H'_{jk} H'_{kn}}{E_n^{(0)} - E_k^{(0)}} \right) - \frac{H'_{nn} H'_{jn}}{(E_n^{(0)} - E_j^{(0)})^2} .$$

As in the treatment of first-order perturbation theory, the orthogonality or normalization constraints impose  $d_{nn} = 0$ , and in this manner we obtain the complete corrections for the energies and wavefunctions through second-order as:

$$\begin{aligned} E_n &= E_n^{(0)} + H'_{nn} + \sum_{i \neq n} \frac{|H'_{ni}|^2}{E_n^{(0)} - E_i^{(0)}} \\ \varphi_n &= \varphi_n^{(0)} + \sum_{i \neq n} \left[ \frac{H'_{in}}{E_n^{(0)} - E_i^{(0)}} - \frac{H'_{nn} H'_{in}}{(E_n^{(0)} - E_i^{(0)})^2} \right. \\ &\quad \left. + \sum_{k \neq n} \frac{H'_{ik} H'_{kn}}{(E_n^{(0)} - E_i^{(0)})(E_n^{(0)} - E_k^{(0)})} \right] \varphi_i^{(0)} \end{aligned}$$

## Chemistry 21b – Spectroscopy

### Lecture # 1 – Supplemental Notes Degenerate Time-Independent Perturbation Theory

In Lecture 1 we examined how perturbation theory may be used to derive first- and second-order corrections to the eigenenergies and eigenfunctions of the zeroth-order Hamiltonian,  $\hat{H}_0$ , in the case where each of the eigenenergies of  $\hat{H}_0$  is distinct. For many quantum mechanical systems, particularly those in three dimensions, degenerate eigenstates abound. Consider angular momentum, for example, in either the hydrogen atom or in the rigid rotor, both of which you examined in Ch21a. For each, the zeroth-order Hamiltonian involves considering the energetics of the system in a spatial coordinate system which is isotropic.

In this limit, the  $|nlm_l\rangle$  wavefunctions of the hydrogen atom, where  $n$  is the principal quantum number and  $l$  is the electron orbital angular momentum (with  $0 \leq l \leq n - 1$ ,  $-l \leq m_l \leq l$ ), are  $n^2$  degenerate since the energy depends only on  $n$ . For the rigid rotor, the angular momentum quantum number is again  $l$ , but now the states are of degeneracy  $(2l + 1)$  thanks to the  $m_l$  states. If the isotropy of space is broken in some manner, say by the application of electric or magnetic fields, these degeneracies can be partially or completely lifted. Clearly, non-degenerate perturbation theory cannot be applied in this case (just look at the denominators of the eigenenergy and eigenfunction corrections through first- and second-order in the Lectures notes above!), and so we'll need to look at things slightly differently in the degenerate case.

Consider, for the sake of argument, a system in which the ground state of the  $\hat{H}_0$  Hamiltonian is  $q$ -fold degenerate. If the perturbing term  $\hat{H}'$  completely lifts the degeneracy, then there will be  $q$  distinct energy levels; and the goal of perturbation theory is to calculate these new energies and the altered wavefunctions associated with the now distinct eigenenergies. As before, we can expand the first-order wavefunction in terms of the zeroth-order eigenstates,

$$|\varphi_n^{(1)}\rangle = \sum_i c_{ni} |\varphi_i^{(0)}\rangle ,$$

where the coefficients  $\{c_{ni}\}$  are given by

$$c_{ni} = H'_{in} / (E_n^{(0)} - E_i^{(0)}) .$$

If the ground state, call it  $E_1^{(0)}$ , is  $q$ -fold degenerate, then

$$E_1^{(0)} = E_2^{(0)} = \dots = E_q^{(0)}$$

and the  $\{c_{ni}\}$  are infinite for  $n, i \leq q$ . How do we get out of this predicament? The idea is to construct a new set of basis functions *based on a linear combination* of the set  $\{\varphi_n^{(0)}\}$  which diagonalize the submatrix  $H'_{in}$  (for  $n, i \leq q$ ). Once diagonalized, the  $i \neq n$  matrix elements are, by definition, zero. The corresponding singular  $\{c_{ni}\}$  coefficients in the equations above also vanish, and the remainder of the problem may be solved just as we proceeded in the first-order non-degenerate case.

Indeed, the diagonal elements constructed in this revised basis set will, of course, be the corrections to the zeroth-order energies; which when added to the  $E_n^{(0)}$  values give the total eigenenergies including the perturbation. Let's call the first-order wavefunctions which diagonalize the  $H'_{in}$  ( $n, i \leq q$ ) matrix elements  $\bar{\varphi}_n$ . As before, we will generate the  $\bar{\varphi}_n$  as linear combinations of the zeroth-order wavefunctions  $\{\varphi_n^{(0)}\}$ , that is

$$\bar{\varphi}_n = \sum_i^q a_{ni} |\varphi_i^{(0)}\rangle ,$$

where the coefficients  $\{a_{ni}\}$  are constructed such that

$$\langle \bar{\varphi}_n | \hat{H}' | \bar{\varphi}_p \rangle = H'_{np} \delta_{np} \quad (n, p \leq q) . \quad (1.6)$$

If all the other  $\hat{H}_0$  eigenstates are non-degenerate (an unlikely scenario!), then the total basis set  $\mathcal{B}$  would be given by

$$\mathcal{B} = \{\bar{\varphi}_1, \bar{\varphi}_2, \dots, \bar{\varphi}_q, \varphi_{q+1}^{(0)}, \varphi_{q+2}^{(0)}, \dots\} ,$$

otherwise each of the suite of degenerate states must be treated like the  $n = 1 \rightarrow q$  eigenstates.

It is stated above that the diagonal elements of the  $q \times q$  submatrix of  $\hat{H}'$  are the first-order corrections to  $E'_n$ , or

$$E'_n = \langle \bar{\varphi}_n | \hat{H}' | \bar{\varphi}_n \rangle = H'_{nn} \quad (n \leq q) .$$

To show this, recall that for  $n \leq q$  we have set  $\varphi_n = \bar{\varphi}_n$  and  $E_n = E_n^{(0)} + E'_n$ . Plugging these into the total Schrödinger equation and recalling that the  $\bar{\varphi}_n$  are a linear combination of degenerate states (which means that the  $\bar{\varphi}_n$  are also eigenfunctions of  $\hat{H}_0$ ), we are left with

$$\hat{H}' \bar{\varphi}_n = E'_n \bar{\varphi}_n \quad (n \leq q) . \quad (1.7)$$

If the  $\{\bar{\varphi}_n\}$  are taken to comprise an orthonormal sequence, Eq. (1.7) is the operator equation form of the matrix elements of  $\hat{H}'$  in the  $\{\bar{\varphi}_n\}$  basis set outlined in Eq. (1.6). Thus, the diagonal elements of  $\hat{H}'$  in the  $\{\bar{\varphi}_n\}$  basis set are indeed the first-order energy corrections for the total Hamiltonian (for  $n \leq q$ ).

In order to generate the coefficients we need to construct the  $\{\bar{\varphi}_n\}$  basis, substituting the expansion into Eq. (1.7) yields:

$$\hat{H}' \sum_i^q a_{ni} |\varphi_i^{(0)}\rangle = E'_n \sum_i^q a_{ni} |\varphi_i^{(0)}\rangle .$$

Again, it is best to now multiply from the left, say with  $\langle \varphi_p^{(0)} |$  to produce the equation

$$\sum_i^q a_{ni} H'_{pi} = E'_n \sum_i^q a_{ni} \delta_{pi} = E'_n a_{np} \quad (\text{for fixed } n, p \leq q) ,$$

which may be rewritten as

$$\sum_i^q (H'_{pi} - E'_n \delta_{pi}) a_{ni} = 0 \quad (n, p \leq q) . \quad (1.8)$$

The coefficients  $\{a_{ni}\}$ , for a fixed value of  $n$ , are simply the column vector representation of  $\bar{\varphi}_n$  in the sub-basis  $\{\varphi_l^{(0)}, l \leq q\}$ . Similarly, the  $H'_{pi}$  are the matrix elements of  $\hat{H}'$  in the same basis. For each value of  $n$  and  $p$ , Eq. (1.8) is one equation for  $E'_n$  and the  $q$  components  $\{a_{ni}\}$ . In total, there are  $q$  such matrix equations corresponding to the  $q$  values of  $p$ . For  $n = 1$ , for example, the equations may be written in matrix notation as

$$\begin{pmatrix} H'_{11} - E'_1 & H'_{12} & H'_{13} & \cdots & H'_{1q} \\ H'_{21} & H'_{22} - E'_1 & H'_{23} & \cdots & H'_{2q} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ H'_{q1} & H'_{q2} & H'_{q3} & \cdots & H'_{qq} - E'_1 \end{pmatrix} \begin{pmatrix} a_{11} \\ a_{12} \\ \vdots \\ a_{1q} \end{pmatrix} = 0$$

For  $n = 2$ , the diagonal terms now contain  $E'_2$  instead of  $E'_1$ , and the column vector  $\{a_{1i}\}$  is replaced with  $\{a_{2i}\}$ , and so on up to  $q$ . In order that there be a non-trivial solution  $\{a_{ni}\}$  for any one of these  $q$  matrix equations is that the determinant of the coefficient matrix vanish, that is, the following secular equation must hold:

$$\det|H'_{pi} - E'_n \delta_{pi}| = 0 .$$

In purely operator form this equation may be written

$$\det|\hat{H}' - E'_n \hat{I}| = 0 ,$$

where  $\hat{I}$  is the  $q \times q$  unit matrix, or identity operator.

The  $q$  roots of the algebraic secular equation are the eigenvalues we are after, and substituting the various values of  $E'$  so obtained into the matrix equation above permits the various coefficients  $\{a_{ni}\}$  to be calculated. Once determined, the construction of the new basis set  $\{\bar{\varphi}_n\}$  is straightforward. If all of the degeneracies are lifted by the perturbing term, we may then proceed to second order just as we did for the non-degenerate case above. If the degeneracy is not completely lifted, then it is necessary to continue the degenerate approach outlined above. This is beyond what is needed for this course, but if you are interested a good place to look further would be a text like *Quantum Mechanics* by L.I. Schiff (McGraw-Hill, New York).

## The Two-Dimensional Harmonic Oscillator as a Simple Example

Let's consider the following total Hamiltonian:

$$\hat{H} = \frac{p_x^2 + p_y^2}{2m} + \frac{K}{2}(x^2 + y^2) + K'xy ,$$

which is, of course, a symmetric two-dimensional harmonic oscillator of force constant  $K$  perturbed by a  $\hat{H}' = K'xy$  term. For the unperturbed case, the zeroth-order eigenfunctions are clearly

$$\varphi_{np} = \varphi_n(x)\varphi_p(y) \quad ,$$

which we'll label  $|np\rangle$ . The corresponding zeroth-order eigenenergy is

$$E_{np} = \hbar\omega_0(n + p + 1)$$

and is  $(n + p + 1)$  degenerate.

For simplicity, let's look at the  $2 \times 2$  problem formed by the state with an energy of  $2\hbar\omega_0$ , which has two degenerate eigenstates formed by  $|10\rangle$  and  $|01\rangle$ . For this simple case, the two new  $\bar{\varphi}$  wavefunctions may be written

$$\bar{\varphi}_1 = a_{11}\varphi_{10} + a_{12}\varphi_{01}$$

$$\bar{\varphi}_2 = a_{21}\varphi_{10} + a_{22}\varphi_{01}$$

The sub-matrix of  $\hat{H}'$  in the basis set  $\{\varphi_{10}, \varphi_{01}\}$  is then just

$$\hat{H}' = K' \begin{pmatrix} \langle 10|xy|10\rangle & \langle 10|xy|01\rangle \\ \langle 01|xy|10\rangle & \langle 01|xy|01\rangle \end{pmatrix} = \mathcal{E} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

where  $\mathcal{E} = 2\hbar K'/m\omega_0$ .

The last step in the above equation can be looked at two ways. First, we know for a simple one-dimensional harmonic oscillator that the eigenfunctions (which are Hermite polynomials) are even or odd. Since  $x$  and  $y$  are odd functions, this implies the product of the wavefunctions in the matrix elements must be odd or the integral will vanish. Thus, the diagonal terms are zero by symmetry, but the off-diagonal terms can be finite, in principle. The best way to actually calculate their value is to use the creation and annihilation operators. An excellent discussion of these useful operators may be found in *Quantum Mechanics*, Claude Cohen-Tannoudji, Bernad Diu & Frank Laloë (New York, Wiley & Sons 1977), pp. 483-500. A brief summary is presented below.

For a harmonic oscillator with natural frequency  $\omega$  and mass  $m$ , the observables

$$\hat{X} = \sqrt{m\omega/\hbar} x$$

$$\hat{P} = \sqrt{1/m\hbar\omega} p$$

are dimensionless. In terms of  $\hat{X}$  and  $\hat{P}$ , the creation and annihilation operators  $a^\dagger$  and  $a$  are defined by:

$$a^\dagger = \sqrt{\frac{1}{2}}(\hat{X} - i\hat{P}) \quad (1.9)$$

$$a = \sqrt{\frac{1}{2}}(\hat{X} + i\hat{P})$$

from which it can be shown that  $\hat{H} = aa^\dagger - \frac{1}{2}$ . Thus,  $x \propto (a + a^\dagger)$ , and if the operations of  $a$  and  $a^\dagger$  on the harmonic oscillator wavefunctions are known, the expectation value of  $x$  can be expressed in terms of the expectation values of the creation and annihilation operators. To make a somewhat long, but interesting, story short, these operators get their names because they have the following effect on harmonic oscillator wavefunctions:

$$\begin{aligned} a^\dagger|\varphi_n\rangle &= \sqrt{(n+1)}|\varphi_{n+1}\rangle \\ a|\varphi_n\rangle &= \sqrt{(n)}|\varphi_{n-1}\rangle \end{aligned} \quad (1.10)$$

It is therefore true that  $\hat{X}$ , and by extension  $x$ , connects a state of  $|n\rangle$  with  $|n\pm 1\rangle$ . The magnitude of  $\mathcal{E}$  follows directly from the definition of  $\hat{X}$  and the creation and annihilation operator relations in eqs. (1.9) and (1.10).

The secular equation which must be solved is thus

$$\begin{vmatrix} -E' & \mathcal{E} \\ \mathcal{E} & -E' \end{vmatrix} = 0 \quad ,$$

which has the solutions  $E' = \pm\mathcal{E}$ . Thus, the perturbation separates the first excited state by the amount  $2\mathcal{E}$ . For the theory to be valid  $\mathcal{E} \ll E_1^{(0)}$  (and so  $K'$  must be small w.r.t.  $K$ ). The wavefunctions are also straightforward to generate, and we find

$$\begin{aligned} E' = \mathcal{E} &\rightarrow \hat{\varphi}_1 = \sqrt{\frac{1}{2}}(\varphi_{10} + \varphi_{01}) \\ E' = -\mathcal{E} &\rightarrow \hat{\varphi}_2 = \sqrt{\frac{1}{2}}(\varphi_{10} - \varphi_{01}) \end{aligned}$$

for the new wavefunctions which diagonalize  $\hat{H}'$ .