Notes 2: Degenerate Perturbation Theory

We saw above that a difficulty arises when there are degenerate eigenstates of the unperturbed Hamiltonian. This difficulty occurs routinely e.g. consider the hydrogen atom or a two-dimensional infinite square well. Degeneracy typically arises due to underlying symmetries in the Hamiltonian. These symmetries can sometimes be exploited to allow non-degenerate perturbation theory to be used. However, we will begin my considering a general approach.

First, we consider the case in which a degenerate subspace, corresponding to energy E^0, is spanned by two orthogonal wave functions, ψ_a and ψ_b. Any linear combination of ψ_a and ψ_b will also be an eigenvector of the unperturbed Hamiltonian. Let $\psi = \alpha\psi_a + \beta\psi_b$, so that

$$H^0\psi = E^0\psi. \tag{2.1}$$

The perturbation to the Hamiltonian (usually) lifts the degeneracy. The perturbed Hamiltonian will have orthogonal wave functions with different energies. If we gradually turn off the perturbation (i.e. let $\lambda \to 0$) these orthogonal wave functions will tend to two orthogonal wave functions of the unperturbed Hamiltonian, i.e. to two specific linear combinations of ψ_a and ψ_b. Griffiths refers to these combinations as the 'good' states. Noting that the first order correction to an energy in the non-degenerate case involves the expectation value of the perturbation to the Hamiltonian in the *unperturbed* state, we see that for the degenerate case all we need to do is find the two sets of values of α and β that correspond to the good states.

Now

$$\left(H^0 + \lambda H^1\right)\psi = \left(E^0 + \lambda E^1 + \cdots\right)\psi \tag{2.2}$$

leads to

$$\begin{aligned} H^0\psi &= E^0\psi, \\ H^1\psi &= E^1\psi. \end{aligned} \tag{2.3}$$

The first equation is satisfied for any values of α and β. Taking the inner product of the second equation with first ψ_a and then ψ_b, we get

$$\begin{aligned} \left\langle \psi_a \middle| H^1\left(\alpha\psi_a + \beta\psi_b\right)\right\rangle = E^1\left\langle \psi_a \middle| \left(\alpha\psi_a + \beta\psi_b\right)\right\rangle \Rightarrow \alpha\left\langle \psi_a \middle| H^1\psi_a\right\rangle + \beta\left\langle \psi_a \middle| H^1\psi_b\right\rangle = \alpha E^1, \\ \left\langle \psi_b \middle| H^1\left(\alpha\psi_a + \beta\psi_b\right)\right\rangle = E^1\left\langle \psi_b \middle| \left(\alpha\psi_a + \beta\psi_b\right)\right\rangle \Rightarrow \alpha\left\langle \psi_b \middle| H^1\psi_a\right\rangle + \beta\left\langle \psi_b \middle| H^1\psi_b\right\rangle = \beta E^1. \end{aligned} \tag{2.4}$$

Introducing the notation

$$W_{ab} = \left\langle \psi_a \middle| H^1\psi_b\right\rangle, \tag{2.5}$$

the two equations (2.4) can be written as

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix}, \tag{2.6}$$

which is a familiar eigen-problem.

Note that since

$$W_{ab} = \langle \psi_a | H^1 \psi_b \rangle = \langle H^1 \psi_a | \psi_b \rangle = \langle \psi_b | H^1 \psi_a \rangle^* = W_{ba}{}^*, \tag{2.7}$$

the matrix is Hermitian and E^1 is real.

Non-trivial solutions for E^1 requires that

$$\begin{vmatrix} W_{aa} - E^1 & W_{ab} \\ W_{ba} & W_{bb} - E^1 \end{vmatrix} = 0. \tag{2.8}$$

The two values of E^1 are

$$E^1 = \frac{(W_{aa} + W_{bb}) \pm \sqrt{(W_{aa} - W_{bb})^2 + 4W_{ab}W_{ba}}}{2}. \tag{2.9}$$

Once the energy corrections have found, the good states are obtained by using equation (2.6).

The generalization of this method to higher order degeneracies is straightforward (see problem 7.13).

A major simplification results if we can find the good states right from the start. The off-diagonal elements of the W matrix will be zero and the diagonal elements (which are the energy corrections) are the same as for non-degenerate perturbation theory.

$$W_{aa} = \langle \psi_a | H^1 \psi_a \rangle. \tag{2.10}$$

A way to find the good states

Suppose we can find a Hermitian operator A that commutes with H^0 **and** H^1. If ψ_a^0 and ψ_b^0 are degenerate eigenfunctions of H^0 and are also nondegenerate eigenfunctions of A, then they are good states.

Proof: (Note the proof in GS is opaque and possibly wrong, so here is the much simpler proof from the second edition of Griffiths Quantum Mechanics). For ψ_a^0 and ψ_b^0 to be good states, we require $W_{ab} = \langle \psi_a^0 | H^1 \psi_b^0 \rangle = 0.$ Since H^1 commutes with A, we have

$$
\begin{aligned}
0 &= \left\langle \psi_a^0 \middle| \left[A, H^1\right] \psi_b^0 \right\rangle = \left\langle \psi_a^0 \middle| A H^1 \psi_b^0 \right\rangle - \left\langle \psi_a^0 \middle| H^1 A \psi_b^0 \right\rangle = \left\langle A \psi_a^0 \middle| H^1 \psi_b^0 \right\rangle - \left\langle \psi_a^0 \middle| H^1 A \psi_b^0 \right\rangle \\
&= \left(\mu - \nu\right) \left\langle \psi_a^0 \middle| H^1 \psi_b^0 \right\rangle,
\end{aligned}
\tag{2.11}
$$

where μ and ν are real and distinct eigenvalues of the Hermitian operator *A*. Hence $W_{ab} = 0$ as required.

Problem 7.9 Consider a particle of mass *m* that is free to move in a one-dimension region of length *L* that closes on itself.

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

$$
\psi_n\left(x\right) = \frac{1}{\sqrt{L}} e^{2\pi i n x/L}, \tag{2.12}
$$

where *n* = 0, ±1, ±2, …, and the allowed energies are

$$
E_n = \frac{2}{m}\left(\frac{n\pi\hbar}{L}\right)^2. \tag{2.13}
$$

Note that, with the exception of the ground state, these are all doubly degenerate.

(b) Now suppose we introduce the perturbation

$$
H^1 = -V_0 e^{-x^2/a^2}, \tag{2.14}
$$

where $a \ll L.$ Find the first order correction to E_n, using degenerate perturbation theory.

(c) What are the good linear combinations of ψ_n and ψ_{-n}, for this problem? Show that for the good states you get the first order correction using non-degenerate perturbation theory.

(d) Find a Hermitian operator *A* that fits the requirement of the theorem, and show that the simultaneous eigenvalues of H_0 and *A* are precisely the ones you used in (c).

Solution. **(a)** The wave functions for a free particle are of form $\psi\left(x\right) = Ae^{ikx}$ and the energy eigenvalues are $E = \hbar^2 k^2 / \left(2m\right).$ Since the region of length *L* closes on itself, we impose the condition $\psi\left(x\right) = \psi\left(x+L\right).$ Then *k* must satisfy $e^{ikL} = 1.$ The solutions are $k = 2n\pi/L,$ where *n* is an integer. The normalized wave functions are $\psi_n\left(x\right) = e^{2\pi i n x/L}/\sqrt{L}$, and the energies are $E_n = \hbar^2\left(2n\pi/L\right)^2/\left(2m\right) = 2\left(n\pi\hbar\right)^2/\left(mL^2\right).$

(b). There is no degeneracy for the lowest energy state for which *n* = 0. The correction to the energy is

$$E_0^1 = \left\langle \psi_0 \middle| H^1 \psi_0 \right\rangle = -\frac{V_0}{L} \int_{-L/2}^{L/2} e^{-x^2/a^2} dx \approx -\frac{V_0}{L} \int_{-\infty}^{\infty} e^{-x^2/a^2} dx = -V_0 \frac{a}{L} \sqrt{\pi}.$$

For non-zero *n*, there is two-fold degeneracy. We need to calculate the components of the W matrix. We have

$$\begin{aligned}
W_{aa} &= \left\langle \psi_n \middle| H^1 \psi_n \right\rangle = \left\langle \psi_0 \middle| H^1 \psi_0 \right\rangle \approx -V_0 \frac{a}{L} \sqrt{\pi}, \\
W_{ba} &= \left\langle \psi_{-n} \middle| H^1 \psi_n \right\rangle = -\frac{V_0}{L} \int_{-L/2}^{L/2} e^{2\pi inx/L} e^{-x^2/a^2} e^{2\pi inx/L} dx \approx -\frac{V_0}{L} \int_{-\infty}^{\infty} e^{4\pi inx/L} e^{-x^2/a^2} dx \\
&= -\frac{V_0}{L} \int_{-\infty}^{\infty} e^{4\pi inx/L - x^2/a^2} dx = -\frac{V_0}{L} \int_{-\infty}^{\infty} e^{-\left(x - 2\pi ina^2/L\right)^2 / a^2 - (2\pi na/L)^2} dx = -V_0 \frac{a}{L} \sqrt{\pi} e^{-(2\pi na/L)^2}, \\
W_{ab} &= W_{ba}, \quad W_{bb} = W_{aa}.
\end{aligned}$$

Let $\eta = e^{-(2\pi na/L)^2}$. This is close to unity for $na \ll L.$ The corrections to the energies from equation (2.9) are

$$E^1 = W_{aa} \pm W_{ab} = -V_0 \frac{a}{L} \sqrt{\pi} (1 \pm \eta).$$

(c) Let the good state corresponding to the + sign be $\psi = \alpha \psi_n + \beta \psi_{-n}.$ Then equation (2.6) gives

$$\begin{pmatrix} 1 & \eta \\ \eta & 1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = (1 + \eta) \begin{pmatrix} \alpha \\ \beta \end{pmatrix}.$$

Thus

$$\alpha + \beta \eta = (1 + \eta) \alpha \Rightarrow \beta = \alpha.$$

For the – sign good state, we get $\beta = -\alpha.$ The two good states are orthogonal, and when normalized are

$$\psi_a = \frac{1}{\sqrt{2}} (\psi_n + \psi_{-n}) = \sqrt{\frac{2}{L}} \cos\left(2\pi \frac{nx}{L}\right), \quad \psi_b = \frac{1}{\sqrt{2}} (\psi_n + \psi_{-n}) = \sqrt{\frac{2}{L}} i \sin\left(2\pi \frac{nx}{L}\right).$$

For *a* small enough, ψ_b is essentially zero at the position of the perturbation to the potential, i.e. this eigenstate doesn't 'see' the potential dip and hence the correction to the energy s close to zero.

The corrections from non-degenerate perturbation theory are

$$E_a^1 = \langle \psi_a | H^1 \psi_a \rangle = \frac{1}{2}\langle (\psi_n + \psi_{-n}) | H^1 (\psi_n + \psi_{-n}) \rangle = \frac{1}{2}(W_{aa} + W_{ab} + W_{ab} + W_{bb}) = W_{aa} + W_{ab},$$

$$E_b^1 = \langle \psi_b | H^1 \psi_b \rangle = \frac{1}{2}\langle (\psi_n - \psi_{-n}) | H^1 (\psi_n - \psi_{-n}) \rangle = \frac{1}{2}(W_{aa} - W_{ab} - W_{ab} + W_{bb}) = W_{aa} - W_{ab}.$$

These are the results from degenerate perturbation theory.

(d) We can take *A* to be the parity operator (see section 6.4 of GS), which is related to spatial inversion $(x \to -x)$. Spatial inversion leaves the perturbation to the Hamiltonian unchanged. Since applying parity operation twice is equivalent to no inversion, the parity operator has eigenvalues +1 and -1. The cosine good state is corresponds to eigenvalue 1 and the sine good state to eigenvalue -1.

Problem 7.11 Suppose we perturb the infinite cubic well by putting a delta function bump at the point (*a*/4, *a*/2, 3*a*/4):

$$H^1 = a^3 V_0 \delta\left(x - \frac{a}{4}\right)\delta\left(y - \frac{a}{2}\right)\delta\left(z - \frac{3a}{4}\right).$$

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

Solution: The potential for the infinite cubic well is

$$V(x,y,z) = \begin{cases} 0, & x, y, z \text{ all between 0 and } a; \\ \infty, & \text{otherwise.} \end{cases}$$

The stationary-state wave functions are

$$\psi_{lmn}(x,y,z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{l\pi x}{a}\right)\sin\left(\frac{m\pi y}{a}\right)\sin\left(\frac{n\pi z}{a}\right),$$

and the energies are

$$E_{lmn} = \frac{\hbar^2 \pi^2}{2Ma^2}\left(l^2 + m^2 + n^2\right).$$

The ground state wave function is

$$\psi_{111}(x,y,z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{\pi y}{a}\right)\sin\left(\frac{\pi z}{a}\right),$$

so that the first-order correction to the energy is

$$E_{111}^{1} = \langle \psi_{111} | H^1 \psi_{111} \rangle = \left(\frac{2}{a}\right)^3 \int_0^a \int_0^a \int_0^a \sin^2\left(\frac{\pi x}{a}\right) \sin^2\left(\frac{\pi y}{a}\right) \sin^2\left(\frac{\pi z}{a}\right) a^3 V_0 \delta\left(x - \frac{a}{4}\right) \delta\left(y - \frac{a}{2}\right) \delta\left(z - \frac{3a}{4}\right) dxdydz$$

$$= 8V_0 \sin^2\left(\frac{\pi}{4}\right) \sin^2\left(\frac{\pi}{2}\right) \sin^2\left(\frac{3\pi}{4}\right) = 2V_0.$$

For the triply degenerate first excited state the wave functions are $\psi_a = \psi_{211}$, $\psi_b = \psi_{121}$, and $\psi_c = \psi_{112}$.

We need to diagonalize the W matrix where $W_{aa} = \langle \psi_a | H^1 \psi_a \rangle$, $\quad W_{ab} = \langle \psi_a | H^1 \psi_b \rangle$, etc. We find

$$\mathsf{W} = 4V_0 \begin{pmatrix} 1 & 0 & -1 \\ 0 & 0 & 0 \\ -1 & 0 & 1 \end{pmatrix}.$$

From the second row of the matrix and the sum of the first and third row of the matrix, we see that two of its eigenvalues are zero. From the trace of the matrix we deduce that the third eigenvalue is 2. Thus to first order, the perturbation to the Hamiltonian splits the triply degenerate state into a doubly-degenerate state with the original and energy, and a non-degenerate state with energy correction $8V_0$.