Phys 487 Discussion 7 – Degenerate Perturbation Theory

Today we will learn and use the procedure for applying perturbation theory to degenerate states; in the next lecture, we will derive the procedure.

The Procedure

Perturbation theory always starts with an "unperturbed" Hamiltonian H_0 whose eigenstates $\left\{ \left|n^{(0)}\right\rangle \text{ or } \psi_n^{(0)} \right\}$ and eigenvalues $\left\{ E_n^{(0)} \right\}$ can be obtained exactly. A small perturbing Hamiltonian $H' << H_0$ is then added to H_0 to produce the full Hamiltonian $H = H_0 + \varepsilon H'$. This is the Hamiltonian whose eigen-things we would like to obtain. I have attached a dimensionless scale factor $\varepsilon << 1$ to H' so that I can easily keep track of orders of smallness. (Sometimes such a small scale factor is an intrinsic part of the problem, sometimes not.)

Suppose that a subset of the unperturbed eigenenergies $\left\{ E_n^{(0)} \right\}$ are **degenerate**, i.e. have the same value E_α. Let the quantum numbers of these degenerate eigenstates be { $\alpha 1, \alpha 2, \alpha 3, \ldots, \alpha n$ }. If we write H_0 in matrix form using as basis the unperturbed eigenstates $\left\{ \left|n^{(0)}\right\rangle \right\}$, we get the diagonal matrix $\left(\mathbf{H}_0\right)_{mn} \equiv \left\langle m^{(0)} \middle| \hat{H}_0 \middle| n^{(0)} \right\rangle$:

$$\mathbf{H}_0 = \begin{pmatrix} E_1^{(0)} & & & & & \\ & E_2^{(0)} & & & & \\ & & \boldsymbol{E_\alpha} & & & \\ & & & \boldsymbol{E_\alpha} & & \\ & & & & E_5^{(0)} & \\ & & & & & \ldots \end{pmatrix}$$ where all the empty elements are 0.

I have bold-faced the degenerate energies and left off the superscript (0) so that you can spot them easily. The degenerate states $\left\{ \left|\alpha_1^{(0)}\right\rangle, \ldots, \left|\alpha_n^{(0)}\right\rangle \right\}$, which are just $\left\{ \left|3^{(0)}\right\rangle, \left|4^{(0)}\right\rangle \right\}$ here, form a **degenerate subspace** where any linear combination of the $|\alpha_i\rangle$'s is *also* an eigenstate of H_0 with the same eigenvalue E_α.

Degenerate perturbation theory is accomplished by finding a **particular set of linear combinations** of the $|\alpha_i\rangle$'s, i.e. within the degenerate subspace, that **diagonalizes the perturbation matrix** $\left(\mathbf{H}'\right)_{ij} \equiv \left\langle i^{(0)} \middle| \hat{H}' \middle| j^{(0)} \right\rangle$.

Once you have found these linear combinations $\left\{ \left|\beta_1^{(0)}\right\rangle, \ldots, \left|\beta_n^{(0)}\right\rangle \right\}$, i.e. the eigenvectors of H' within the degenerate subspace, find their corresponding eigenvalues and you will have your first-order corrections

$$E_{\beta i}^{(1)} = \left\langle \beta_i^{(0)} \middle| H' \middle| \beta_i^{(0)} \right\rangle$$

If you all goes well, these 1st-order energy corrections should be **non-degenerate**, i.e. they should **break the degeneracy** of the $\alpha 1, \ldots \alpha n$ subspace.

Problem 1 : The Last Part of Discussion 6 Problem 3 *Griffiths 6.9(d)*

In last week's discussion you had this Hamitonian :

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

where V_0 is a constant and ε is a small number << 1. Have a look at the posted questions and solution to remind yourself: you used various techniques to find the 1st and 2nd order corrections to this 3-state Hamiltonian's energies. Today, use <u>degenerate</u> perturbation theory to find the first-order correction to the two initially degenerate eigenvalues. Compare with your various results from last week!

Problem 2 : Stark Effect *Griffiths 6.36*

When an atom is placed in a uniform external electric field E_{ext}, the energy levels are shifted — a phenomenon known as the **Stark effect**. In this problem we analyze the Stark effect for the n = 1 and n = 2 states of hydrogen. Let the field point in the z direction, so the potential energy of the electron is

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

Treat this as a perturbation on the simple "Bohr" Hamiltonian for the hydrogen atom,

$$H_0 = -\frac{\hbar^2\nabla^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r}\,.$$

Spin is irrelevant to this problem so ignore it.

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

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

(c) What are the "β" wave functions for part (b), i.e. the ones that diagonalize the perturbation H'_S? (Griffiths calls these "good" wavefunctions.) Find the expectation value of the electric dipole moment ($\vec{p}_e = -e\vec{r}$) in each of these "good" states. Notice that the results are independent of the applied field — evidently hydrogen in its first excited state can carry a *permanent* electric dipole moment.

HINT: There are a lot of integrals in this problem, but almost all of them are ZERO. So study each one carefully, before you do any calculations! For example, if the ϕ integral vanishes, there's not much point in doing the r and θ integrals! Partial answer: $H'_{13} = H'_{31} = -3ea_0 E_{\text{ext}}$ where a_0 is the Bohr radius as usual; all other elements of $\mathbf{H}'_{ij} \equiv \langle \beta_i^{(0)} | H' | \beta_j^{(0)} \rangle$ are zero ☺.