Lecture 35

Relevant sections in text: §5.2

Degenerate Perturbation Theory

We now consider the case where the unperturbed eigenvalue is degenerate, that is, there are d linearly independent eigenvectors $|E_n\rangle_i^{(0)},\ i = 1, 2, \ldots, d$ for the unperturbed eigenvalue $E_n^{(0)}$. These eigenvectors span the "degenerate subspace" D, which is a d-dimensional vector space sitting inside the full Hilbert space of state vectors. Degeneracy is associated with a symmetry of the (unperturbed, in this case) Hamiltonian. The full Hamiltonian (with the perturbation included) will typically not have all the symmetry of the unperturbed Hamiltonian. Thus the *true* eigenvalues that are approximated by the unperturbed eigenvalue will usually not all be degenerate. Put differently, as the perturbation is "turned on", by mathematically varying λ from 0 to 1, some of the unperturbed eigenvectors with the same unperturbed eigenvalue become eigenvectors with a distinct eigenvalue, so that the degeneracy can be lifted by the perturbation. One says that the energy levels "split" as the perturbation is "turned on".

Consider for example an atom modeled as a particle moving in a central potential. Its excited state energies are degenerate because the (unperturbed) Hamiltonian H_0 is rotationally invariant. In particular, since H_0 commutes with $\vec{L}$, it is easy to see that all states differing only by their m values must have the same energy. In detail, if $|n, l, m\rangle$ is an eigenvector of H_0, then so is $L_\pm|n, l, m\rangle$. Thus all such states will have the same energy. Suppose this atom is put in a uniform electric field (Stark effect), so that the perturbation is

$$V = e\vec{E} \cdot \vec{X}.$$

This potential breaks the rotational symmetry (to just that of rotations about the direction of $\vec{E}$), so that the degeneracy is lifted. Treating V as a perturbation, the first-order approximation to the eigenvalue/eigenvectors will not exhibit degeneracy.

But now there is a subtlety in the perturbative account of this phenomenon. Recall that in the unperturbed system any linear combination of eigenvectors with the same eigenvalue will again define a state with the (degenerate) energy. But in the perturbed theory, the energies will shift and, in general, no longer be degenerate. Which of the infinite set of vectors in D will provide the correct zeroth order approximation to the energy eigenvectors? Somehow the perturbation theory must select a preferred basis of unperturbed eigenvectors, namely, the ones that the correct eigenvectors collapse to as $\lambda \to 0$. The way in which this happens is the new feature appearing in "degenerate perturbation theory".

Repeating our perturbative analysis but allowing for the unperturbed eigenvalue to be degenerate leads to the following conclusions (see the text for details of the derivation). To compute the first-order corrections to the energies and eigenvectors when there is degeneracy in the unperturbed eigenvalue $E_n^{(0)}$ one proceeds as follows.

Step 1

Consider the restriction, $\tilde{V}$ of the perturbation V to the d-dimensional degenerate subspace D. $\tilde{V}$ is defined as follows. The action of V on a vector from D is some other vector in the Hilbert space. Take the component of this vector along D, *i.e.,* project this vector back into D. This process defines a Hermitian linear mapping $\tilde{V}$ from D to itself. In practice, the most convenient way to compute $\tilde{V}$ is to pick a basis for D. Compute the matrix elements of V in this basis. One now has a $d \times d$ Hermitian matrix representing $\tilde{V}$ on D.

Step 2

Find the eigenvectors $|\mu_i\rangle$ and eigenvalues μ_i, $i = 1, 2, \ldots, d$ of $\tilde{V}$. Again, it is most convenient to do this using the matrix representation of $\tilde{V}$. For simplicity we assume all these eigenvalues are distinct. (Otherwise the analysis gets a bit more involved.)

Step 3

There will be d separate first-order energy corrections $E_{ni}^{(1)}$ to $E_n^{(0)}$; these are the eigenvalues of $\tilde{V}$:

$$E_{ni} \approx E_n^{(0)} + \mu_i + \mathcal{O}(V^2).$$

The zeroth order approximation to the eigenvector corresponding to E_{ni} is

$$|E_{ni}\rangle \approx |\mu_i\rangle + \mathcal{O}(V).$$

Step 4

The first-order correction to the eigenvectors are given by the same formula as before, but now one excludes vectors from D in the summation.

These steps are, at first sight, rather complicated looking. It is not really that bad, though. An example will help clear things up.

Example: Hyperfine structure

The hyperfine structure is a feature of atomic spectra which results from the interaction of the nuclear and electronic spin. Specializing to a hydrogen atom we can model it as

follows. We model the electron as a particle with spin 1/2, so it has both translational and spin degrees of freedom. We will model the nucleus (proton) as a point particle, fixed in space; so we model it as a spin 1/2 system. The total system then is defined on the Hilbert space which is a direct product of the space of states of the electron and another spin 1/2 system. A basis for this space is given by the product states of the form

$$|\psi; S_{(e)z}, \pm; S_{(p)z}, \pm\rangle := |\psi\rangle \otimes |S_{(e)z}, \pm\rangle \otimes |S_{(p)z}\pm\rangle,$$

where $|\psi\rangle$ runs over a basis for the Hilbert space of a spinless particle (*e.g.,* the energy eigenfunctions for the hydrogen atom Hamiltonian), $|S_{(e)z}, \pm\rangle$ is the usual basis for the spin 1/2 system – here used for the electron, and $|S_{(p)z}, \pm\rangle$ is the usual basis for the spin 1/2 system – here used for the proton.

The magnetic moments for the electron and proton are given by*

$$\vec{\mu}_e = -\frac{e}{m_e}\vec{S}_{(e)}, \quad \vec{\mu}_p = \frac{ge}{2m_p}\vec{S}_{(p)},$$

where g is the proton "g-factor", which is about 5.6.

It is a nice exercise to check that a pure point magnetic dipole (which is how we are modeling the proton) is the source of the following magnetic field

$$\vec{B}(\vec{r}) = \frac{\mu_0}{4\pi}\left\{\frac{3\vec{n}(\vec{n}\cdot\vec{\mu}_p) - \vec{\mu}_p}{r^3} + \frac{8\pi}{3}\vec{\mu}_p\delta(\vec{r})\right\},$$

where

$$\vec{n} = \frac{\vec{r}}{r}.$$

Here the first term represents the familiar dipole term in a multipole expansion of the magnetic field outside a localized current distribution. The second term is used to model the limit in which one assumes the spatial dimensions of the current distribution vanish while keeping the magnetic moment $\vec{\mu}_p$ fixed. The energy of the electron in the presence of this field is given by

$$V := -\vec{\mu}_e \cdot \vec{B}.$$

Let us treat this energy as a perturbation of the usual hydrogenic energy and study the effects of this perturbation on the ground state of hydrogen in our current model.

The unperturbed ground state of hydrogen does not "know" about the magnetic field of the proton. Therefore its energy is the usual $-13.6\ eV$. However, since we have taken account of the spin degrees of freedom of both the proton and the electron we now have a four-fold degeneracy corresponding to the different possible states of orientation of the

* For this example I am using SI units.

spins, and superpositions thereof. The degenerate subspace D of the ground state energy is spanned by the four orthonormal vectors

$$|\psi_{ground}; S_{(e)z}, \pm, S_{(p)z}, \pm\rangle,$$

where

$$|\psi_{ground}\rangle = |n = 1, l = 0, m_l = 0\rangle.$$

To be continued...