

*Lecture 32**Relevant sections in text: §5.2***Degenerate Perturbation Theory (cont.)**

Degenerate perturbation theory 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 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} .

Step 2

Find the eigenvectors and eigenvalues of \tilde{V} . Again, it is most convenient to do this using the matrix representation of \tilde{V} .

Step 3

The first-order energy corrections to $E_n^{(0)}$ are the eigenvalues of \tilde{V} . The zeroth order limit of the true eigenvectors that correspond to the true eigenvalues are the eigenvectors of \tilde{V} that correspond to the first-order eigenvalue corrections.

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. The zeroth order eigenvectors are those identified in Step 3.

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 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 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

$$\mu_e = -\frac{e}{m_e} \mathbf{S}_{(e)}, \quad \mu_p = \frac{ge}{2m_p} \mathbf{S}_{(p)},$$

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

$$\mathbf{B}(\mathbf{r}) = \frac{3\mathbf{n}(\mathbf{n} \cdot \mu_p) - \mu_p}{r^3} + \frac{8\pi}{3} \mu_p \delta(\mathbf{r}),$$

where

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

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 μ_p fixed. The energy of the electron in the presence of this field is given by

$$U := -\mu_e \cdot \mathbf{B}.$$

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

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

where

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

According to degenerate perturbation theory our first step is to compute the matrix elements of the perturbation in the degenerate subspace. For each of the basis states we have a matrix element of the form

$$(\text{constant}) \times \int d^3x \frac{1}{4\pi} |R_{10}(r)|^2 \left[\frac{3\mathbf{n}(\mathbf{n} \cdot \mathbf{a}) - \mathbf{a}}{r^3} + \frac{8\pi}{3} \mathbf{a} \delta(\mathbf{r}) \right] \cdot \mathbf{b},$$

where the vectors \mathbf{a} and \mathbf{b} represent the matrix elements of the magnetic moment vectors:

$$\mathbf{a} = \langle S_{(p)z}, \pm | \mu_p | S_{(p)z}, \pm \rangle,$$

$$\mathbf{b} = \langle S_{(e)z}, \pm | \mu_e | S_{(e)z}, \pm \rangle.$$

Now, it is a standard result from E&M that the *quadrupole tensor*,

$$Q(\mathbf{a}, \mathbf{b}) = (\mathbf{r} \cdot \mathbf{a})(\mathbf{r} \cdot \mathbf{b}) - \frac{1}{3} r^2 \mathbf{a} \cdot \mathbf{b},$$

here evaluated on a pair of constant vectors, has a vanishing average over the unit sphere:

$$\frac{1}{4\pi} \int_0^\pi d\theta \int_0^{2\pi} d\phi Q(\mathbf{a}, \mathbf{b}) = 0.$$

One way to check this is to write out this tensor in spherical polar coordinates. You will find that the angular dependence of this tensor is that of the spherical harmonic $Y_{l=2,m}$, which integrates to zero over a sphere (since it is orthogonal to constants, i.e., Y_{00}). This result implies (exercise) that only the delta function portion of \mathbf{B} plays a role in the matrix of the perturbation in the ground states.

To be continued...