

Lecture 33

Relevant sections in text: §5.2, 5.6

Example: Hyperfine structure (cont.)

We are evaluating the matrix elements of the perturbation, which now takes the form

$$-\mu_e \cdot \mathbf{B} = -\frac{8\pi}{3} \mu_e \cdot \mu_p \delta(\mathbf{r})$$

in the degenerate subspace spanned by

$$|1, 0, 0\rangle \otimes |\pm\rangle \otimes |\pm\rangle.$$

The “translational part” of the unperturbed degenerate subspace is just the usual ground state of hydrogen and so when computing the matrix elements of the perturbation we get a common factor of:

$$\langle 1, 0, 0 | \delta(\mathbf{r}) | 1, 0, 0 \rangle = \int d^3x |\psi_{100}(r)|^2 \delta(\mathbf{r}) = |\psi_{100}(0)|^2.$$

 Using $|\psi_{100}(0)|^2 = \frac{1}{\pi a^3}$, the 4×4 the perturbation takes the form

$$\frac{4ge^2}{3m_p m_e a} (\mathbf{S}_p \cdot \mathbf{S}_e)_{ij},$$

where a is the Bohr radius and the $i j$ refer to the basis $|S_{(e)z}, S_{(p)z}\rangle = |++\rangle, |+-\rangle, |-+\rangle, |--\rangle$. So, for example,

$$(\mathbf{S}_p \cdot \mathbf{S}_e)_{12} = \langle + | \mathbf{S}_e | + \rangle \cdot \langle + | \mathbf{S}_p | - \rangle = 0.$$

A very straightforward computation of the matrix elements yields

$$(\mathbf{S}_p \cdot \mathbf{S}_e)_{ij} = \frac{\hbar^2}{4} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

The eigenvalues and (normalized) eigenvectors of this matrix are (exercise)

$$\begin{aligned} \text{eigenvalue : } \frac{\hbar^2}{4}, \quad \text{eigenvectors : } & \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}, \\ \text{eigenvalue : } -\frac{3\hbar^2}{4}, \quad \text{eigenvectors : } & \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ -1 \\ 0 \end{pmatrix}. \end{aligned}$$

Of course, the eigenvalue $\frac{\hbar^2}{4}$ is triply degenerate; any linear combination of its three eigenvectors is also suitable.

You can also get this result by setting

$$\mathbf{S} = \mathbf{S}_p + \mathbf{S}_e$$

and computing

$$\mathbf{S}_p \cdot \mathbf{S}_e = \frac{1}{2}(S^2 - S_p^2 - S_e^2) = \frac{1}{2}S^2 - \frac{3}{4}\hbar^2 I.$$

Recall that the singlet and triplet states are eigenvectors of S^2 with eigenvalues of 0 and $2\hbar^2$ respectively. Thus the singlet state is an eigenvector of $\mathbf{S}_p \cdot \mathbf{S}_e$ with eigenvalue $-\frac{3}{4}\hbar^2$ and the triplet states all have the eigenvalue $\frac{1}{4}\hbar^2$. The components of the eigenvectors in the product basis which we found above are indeed the components of the singlet and triplet states and the eigenvalues then follow. Our particular choice of basis for the triply degenerate eigenvalue corresponds to states of total spin of $\sqrt{2}\hbar$ and $S_z = \pm\hbar, 0$, of course.

We thus see that the spin-spin interaction of the electron and proton is such that (to first order in the perturbation) the “triplet” spin states are increased in energy by an amount

$$\Delta E_{triplet} = \frac{g\hbar^4}{3m_p m_e a^3},$$

and the “singlet” spin state has its energy decreased:

$$\Delta E_{singlet} = -\frac{g\hbar^4}{m_p m_e a^3}.$$

Taking account of the hyperfine interaction, we see that the singlet state is the correct (zeroth order approximation to the) ground state. The difference in energy between the singlet and triplet states is given by

$$\Delta E_{triplet} - \Delta E_{singlet} = 5.9 \times 10^{-6} \text{ eV}.$$

If we consider transitions between these states associated with emission or absorption of a photon this energy difference corresponds to a photon wavelength of about 21 *cm*. This leads to an explanation for the famous “21 centimeter” spectral line that is observed in the microwave spectrum by radio telescopes. It is attributed to vast amounts of interstellar hydrogen undergoing transitions from the triplet to the singlet state.

Time-dependent perturbation theory

Time-dependent perturbation theory (TDPT) is an extremely important approximation technique for extracting dynamical information from a quantum system when the

Schrödinger equation cannot be solved explicitly.* TDPT can be viewed as a technique for iteratively approximating solutions to differential equations. Many key physics results appear via TDPT. It leads, for example, to the fundamental picture of quantum dynamics as a sequence of transitions between (formerly) stationary states, *e.g.*, , for atoms interacting with electromagnetic radiation. It leads to “Fermi’s Golden Rule”, it leads to the idea of “forbidden transitions”, and it yields an amusing form of the time energy uncertainty principle. And there’s more.

The basic idea of TDPT is quite simple, we suppose that the Hamiltonian for a given quantum system can be decomposed into two parts,

$$H = H_0 + V,$$

where H_0 describes physics that is well-understood and V represents the interactions that we are trying to understand. So, for example, H_0 could be the Hamiltonian for an electron in the hydrogen atom, and V could represent the interaction with an incident electromagnetic wave – an example I hope to get to. The key assumption is that the effect of V on the dynamics is suitably small (compared to H_0) so that the dynamics generated by H can be expressed in terms of some small modifications due to the *perturbation* V to the dynamics generated by H_0 . The technique of TDPT is valid whether or not H , H_0 and/or V depend explicitly on time. For simplicity we will restrict attention to situations where H_0 can be chosen to be time independent; V may be time dependent.

The basic scheme is the following (see your text for an alternative description). In the Schrödinger picture the state vector at time t satisfies

$$i\hbar \frac{d}{dt} |\psi, t\rangle = (H_0 + V) |\psi, t\rangle.$$

Our goal is to find (an approximation scheme for) the state vector at time t given the initial state. We expand $|\psi, t\rangle$ in the basis of eigenvectors of H_0 :

$$|\psi, t\rangle = \sum_n c_n(t) e^{-\frac{i}{\hbar} E_n t} |n\rangle,$$

where

$$H_0 |n\rangle = E_n |n\rangle,$$

and we assume the spectrum is discrete only for simplicity in our general development. Note that we have inserted a convenient phase factor into the definition of the expansion coefficients c_n . This phase factor is such that (1) the $c_n(0)$ are the expansion coefficients at $t = 0$, and (2) if $V = 0$ (*i.e.*, we “turn off” or neglect the effect of the perturbation) then

* The usual comments apply about non-trivial physical systems and the lack of explicit solubility.

the c_n are constant in time (exercise). Thus, the time dependence of the $c_n(t)$ is solely due to the perturbation.

The Schrödinger equation can be viewed as a system of ODEs for the $c_n(t)$. To see this, substitute the expansion of $|\psi, t\rangle$ into the Schrödinger equation and take components in the basis $|n\rangle$. We get (exercise)

$$i\hbar \frac{d}{dt} c_n(t) = \sum_m e^{\frac{i}{\hbar}(E_n - E_m)t} V_{nm}(t) c_m(t), \quad V_{nm} = \langle n | V(t) | m \rangle.$$

Up until now everything we have done has involved no approximations. The system of ODE's displayed above is equivalent to the Schrödinger equation.

Now we suppose that the effect of the matrix elements V_{nm} is suitably small and we make a sequence of approximations to the right-hand side of the differential equations. First, if we ignore V_{nm} altogether then we can approximate the differential equation as

$$\frac{dc_n}{dt} \approx 0.$$

This is the zeroth order approximation in that the right hand side of the differential equation is correct to zeroth order in the perturbation (*i.e.*, accurate up to terms of zeroth order in the matrix elements of the perturbation) and, by the same token, the expansion coefficients are correct to zeroth order. Thus we find that the $c_n(t)$ are constant in time in this lowest order approximation. You will recall that we defined the phases of the c_n so this would happen. Of course, physically this means that the probability distribution for H_0 is time-independent. We call this the “zeroth-order approximation” and we denote the expansion coefficients in this approximation as $c_n^{(0)}$.

We can now get a better approximation to the right hand side of the equation by substituting the zeroth order solution there. This gives an equation which approximates the Schrödinger equation accurately to first order in the potential. As we shall see, it is easy to solve this approximate form of the equation by simply integrating both sides. We then have an approximate solution which involves some time dependence because of the potential. The potential appears linearly in this “first order approximation”. We can substitute the first-order approximation into the right hand side of the equation to get a better approximation to the equation. Solving this equation gives the “second order approximation”; the solution is quadratic in V . The idea is that if V is sufficiently “small” one can continue this iterative process to get better and better approximations to the solution of the Schrödinger equation. We will content ourselves with studying the first-order approximation, which has a number of important physical features and applications.