

Lecture 36

Relevant sections in text: §5.2, 5.5, 5.6

Hyperfine structure (cont.)

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

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

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

$$\vec{a} = \langle S_{(p)z}, \pm | \vec{\mu}_p | S_{(p)z}, \pm \rangle,$$

$$\vec{b} = \langle S_{(e)z}, \pm | \vec{\mu}_e | S_{(e)z}, \pm \rangle.$$

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

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

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

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

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 \vec{B} plays a role in the matrix of the perturbation in the ground states.

We thus need to evaluate matrix elements of

$$\tilde{V} = -\frac{2\mu_0}{3} \vec{\mu}_e \cdot \vec{\mu}_p \delta(\vec{r})$$

in the 4-dimensional 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:

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

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

$$\frac{ge^2\mu_0}{3\pi m_p m_e a^3} (\vec{S}_p \cdot \vec{S}_e)_{ij},$$

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,

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

A very straightforward computation of the matrix elements yields

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

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

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

and computing

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

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 $\vec{S}_p \cdot \vec{S}_e$ 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

$$\Delta E_{triplet} = \frac{ge^2\mu_0\hbar^2}{12\pi m_p m_e a^3},$$

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

$$\Delta E_{singlet} = -\frac{ge^2\mu_0\hbar^2}{4\pi m_p m_e a^3}.$$

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 and is similar in spirit to TIPT. 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

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

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 . Unlike TIPT, TDPT is designed to approximate solutions to the “time-dependent” Schrödinger equation. The techniques of TDPT can be applied 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 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. However, when the matrix elements of V are suitably “small”, an iterative approximation method can be used to extract information from the Schrödinger equation when written in this form. This is our next topic.