Notes for Lecture 8

Hydrogen-like atom

Armed with the perturbation theory and the symmetry principle, we continue to tackle some simple and some not so simple aspects of the Hydrogen-like atom problem.

8.1 Spin-orbit coupling, cont.

To the leading order of v/c, we get

$$\vec{B} \;=\; -\gamma \frac{\vec{v}}{c^2} \times \vec{E} \approx -\frac{\vec{v}}{c^2} \times \vec{E} \tag{7.17}$$

and this field couples to the spin of the electron through the Larmor-precession-like mechanism: $\hat{H} = \frac{g\mu_B}{\hbar} \hat{\vec{B}} \cdot \hat{\vec{S}}$ (Eq. 7.18 and LN 4).

Quite generally, this means that the orbital motion (represented by $\vec{v}$ in Eq. 7.17) is coupled to the spin motion (represented by $\vec{S}$ in the Hamiltonian). Let us study how this coupling occurs a bit, ignoring the operator nature of vector quantities for a while, for convenience. We shall further assume that $\vec{E}$ is due to a central potential. In particular, we assume that it is due to a Coulombic potential energy $V_c(r)$, such that

$$e\vec{E} \;=\; \nabla V_c \;=\; \vec{e}_r \frac{dV_c}{dr} \;=\; \frac{\vec{r}}{r} \frac{dV_c}{dr} \tag{8.1}$$

Regarding the notation $\vec{e}_r$ for the unit vector along the radial direction (which is *not* equal to $\hat{r}$, the quantum mechanical operator corresponding to the dynamical variable r), please re-read footnote 3 of LN 6, if you have not done so already. Note that the electrostatic potential is given by $V_c/(-e)$, where $-e$ is the charge of the electron.

Inserting this into Eq. 7.18, we get the "classical Hamiltonian" (with quotation marks, since spins do not exist in classical mechanics) as

$$\begin{aligned} H_{so} &= -\frac{g\mu_B}{\hbar e}\left(\frac{\vec{v}}{rc^2}\times\vec{r}\,\frac{dV_c}{dr}\right)\cdot\vec{S} \\ &= \frac{g\mu_B}{\hbar e m_e c^2}\,\frac{1}{r}\,\frac{dV_c}{dr}\vec{L}\cdot\vec{S} \qquad\qquad \vec{L}=-m\vec{v}\times\vec{r} \end{aligned}$$

At this point, it is clear that we can quantize this Hamiltonian by changing all dynamical variables to operators, putting hats on them. However, before we do that, let us note that our theory here is not completely correct. In Dirac's more correct treatment of the relativistic electron, the interaction is half of what we just calculated, effectively making $g \approx 2$ disappear.

Thus, we get the following quantum Hamiltonian for the spin-orbit coupling for electron in a central potential, including, of course the Hydrogen-like atom case, that we are currently interested in.

$$\hat{H}_{so} = \frac{\mu_B}{\hbar e m_e c^2}\,\frac{1}{\hat{r}}\,\frac{dV_c(\hat{r})}{d\hat{r}}\hat{\vec{L}}\cdot\hat{\vec{S}}$$

Let us recall

$$\mu_B = \frac{e\hbar}{2m_e} \qquad \text{Bohr magneton} = 5.788\times10^{-5}\ \text{eV/T} \tag{4.18}$$

using which we can rewrite the above Hamiltonian as

$$\hat{H}_{so} = \frac{1}{2m_e^2c^2}\,\frac{1}{\hat{r}}\,\frac{dV_c(\hat{r})}{d\hat{r}}\hat{\vec{L}}\cdot\hat{\vec{S}} \tag{8.2}$$

For a routine dimension check, let us note that both $\vec{L}$ and $\vec{S}$ have the dimension of $\hbar$ or have the same dimension as mvr.

Let us use the Hydrogen-like potential as we specified in Eq. 6.12: $\frac{dV_c(r)}{dr} = \frac{Ze^2}{4\pi\epsilon_0 r^2}$, which means $\hat{H}_{so} = \frac{Ze^2}{8m_e^2c^2\pi\epsilon_0}\,\frac{1}{\hat{r}^3}\hat{\vec{L}}\cdot\hat{\vec{S}} = \frac{Z\alpha\hbar}{2m_e^2c}\,\frac{1}{\hat{r}^3}\hat{\vec{L}}\cdot\hat{\vec{S}}$, where α is the fine structure constant, Eq. 6.20.

$$\hat{H}_{so} = \frac{\alpha\hbar}{2m_e^2c}\,\frac{Z}{\hat{r}^3}\hat{\vec{L}}\cdot\hat{\vec{S}} \tag{8.3}$$

Let us consider this Hamiltonian as a perturbation and consider its effect on the energy levels of a Hydrogen-like atom.

8.1.1 Symmetry

This perturbation, $\hat{H}_{so}$, breaks the full rotation symmetry both in the ordinary space and in the spin space. In other words, it does not commute with any of $\hat{S}_x, \hat{S}_y, \hat{S}_z$ operators, nor does it commute with any of $\hat{L}_x, \hat{L}_y, \hat{L}_z$ operators. This is easy to see as follows.

$$\hat{H}_{so} = \frac{\alpha\hbar}{2m_e^2 c}\frac{Z}{\hat{r}^3}\left(\hat{L}_x\hat{S}_x + \hat{L}_y\hat{S}_y + \hat{L}_z\hat{S}_z\right)$$

Let us compute $\left[\hat{H}_{so}, \hat{L}_z\right]$. Since $\hat{L}_z$ commutes with $\hat{r}^2$ (Homework 3.3(d)), all we need to worry about[1] is the commutator of $\hat{L}_z$ with $\hat{L}_x$ and $\hat{L}_y$. Thus, using the standard commutator, $\left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x$, etc., we get

$$\left[\hat{H}_{so}, \hat{L}_z\right] = \frac{\alpha\hbar}{2m_e^2 c}\frac{Z}{\hat{r}^3}\, i\hbar\left(-\hat{L}_y\hat{S}_x + \hat{L}_x\hat{S}_y\right)$$

which is clearly not zero. Other commutators of $\hat{H}_{so}$ with $\hat{L}_{x,y}$ and $\hat{S}_{x,y,z}$ are obtained in a completely analogous way with the same conclusion.

However, it is clear that $\hat{H}_{so}$ commutes with both $\hat{L}^2$ and $\hat{S}^2$, since $\hat{L}^2$ commutes with any component of $\hat{\vec{L}}$ and similarly for $\hat{S}^2$.

It is important to note that $\hat{H}_{so}$ has the full rotational symmetry, in the sense discussed in Section 6.3.3, i.e. when both the spin space and the ordinary space are rotated together. This is seen by the fact that the above Hamiltonian commutes with all $\hat{J}_x, \hat{J}_y, \hat{J}_z$ operators, where $\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$. This can be most clearly seen if one notes that

$$\hat{\vec{L}}\cdot\hat{\vec{S}} = \frac{1}{2}\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right) \tag{8.4}$$

and that *any* component of $\hat{\vec{J}}$ commutes with *all* of $\hat{r}^2, \hat{J}^2, \hat{L}^2, \hat{S}^2$.

8.1.2 Magnitude

We have assumed that $\hat{H}_{so}$ is a perturbation, which makes sense only if the energy scale of $\hat{H}_{so}$ is smaller than the typical energy level spacing of the Hydrogen-like atom

[1] In case you are unsure, note that $\hat{\vec{L}}$ and $\hat{\vec{S}}$ must commute since they belong in different Hilbert spaces—they are apple and orange, so to speak.

problem. From Eq. 8.3, one can estimate the magnitude of $\hat{H}_{so}$ as

$$\begin{aligned} E_{so} &\sim \frac{\alpha\hbar}{m_e^2 c}\frac{Z^4}{a_B^3}\hbar^2 && \langle r^{-3}\rangle \sim Z^3/a_B^3 \quad \text{(Eqs. 7.6–7.9); also, see Eq. 8.9} \\ &= \frac{\alpha\hbar}{m_e^2 c}\frac{Z^4 m_e^3 c^3 \alpha^3}{\hbar^3}\hbar^2 && a_B = \frac{\hbar}{m_e c\,\alpha} \quad \text{(Eq. 6.19)} \\ &= Z^4 m_e c^2 \alpha^4 \\ &\sim |E_n^{(0)}|\, Z^2\alpha^2 && E_n^{(0)} = -\frac{Z^2}{n^2}\frac{m_e c^2\alpha^2}{2} \quad \text{(Eq. 7.12)} \end{aligned} \tag{8.5}$$

The main notable thing here is that the order of magnitude of this spin orbit term is just like the relativistic kinematical correction term (Eq. 7.16 and the discussion below it). Two things must be noted: both are $O(\alpha^2)$, in comparison to the unperturbed energy, and both are proportional to Z^4. There are two notable things here. While the first assures that the spin orbit interaction is small, the second means that the effect increase rapidly as the atomic mass increases. This is why the spin orbit interaction becomes important for heavy atoms, and recent materials (e.g. "topological insulators") for which the spin orbit interaction plays a critical role involves heavy atoms (see below).

8.1.3 Solution

Having looked at the symmetry and the magnitude of the spin orbit interaction, we are now in a very good position to simply produce the perturbative solution.

First, symmetry. The unperturbed solution has the full symmetry in rotation in either the ordinary space and the space. This means that $\hat{L}_z$ and $\hat{S}_z$ are conserved. In other words, m_l (= $L_z/\hbar$) and m_s (= $S_z/\hbar$) are good quantum numbers. However, with the spin-orbit interaction, these are no longer conserved, excluding them from good quantum numbers. However, note that the unperturbed problem can be described either in the $\{|l, m_l, s, m_s\rangle\}$ basis or in the $\{|l, s, j, m_j\rangle\}$ basis, due to the angular momentum addition rules. In other words, the following two sets of operators are equivalent sets, each consisting of mutually compatible operators.

$$\{\hat{J}^2, \hat{J}_z, \hat{L}^2, \hat{S}^2\} \;\Leftrightarrow\; \{\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z\} \tag{8.6}$$

The good news is that the first set is *still* good as symmetry operators, while the second set is not. In other words, $\hat{H}_{so}$ is not diagonal if we use the second set as the basis, but $\hat{H}_{so}$ *is* diagonal if we use the first set as the basis. Therefore, different from the relativistic kinematical correction, here we *do* have a degenerate perturbation theory, *if* we insist on using the $\{|l, m_l, s, m_s\rangle\}$ basis. **This is because the symmetry of the system got lowered (cf. Section 6.5) due to this spin-orbit perturbation.** On the other hand, we hardly need to do any real matrix diagonalization to

treat this degenerate perturbation theory. Why is this? It is because we know that the first set of symmetry operators remain good for the perturbation term! There is a perfect analogy of the current case with the much simpler case of a particle in 1D (Sections 5.1 and 6.5): in that case, too, the unperturbed Hamiltonian allowed alternative basis sets, θ-translation eigenkets or θ-parity eigenkets, while with the perturbation breaking the θ-translation but still preserving the θ-parity, it *turned out* that θ-parity states were *good zeroth order states* for the degenerate perturbation. That is, in the current case, we *could* do the same type of matrix diagonalization, except that it is now much harder; it is no longer a simple 2×2 matrix problem; we have a $2(2l+1) \times 2(2l+1)$ matrix problem for each value of l. But, we know the answer for the good zeroth order eigenstates, already! By symmetry principle 2 (LN 6), we know that the first set of operators $\{\hat{J}^2, \hat{J}_z, \hat{L}^2, \hat{S}^2\}$ and the Hamiltonian operator can be simultaneously diagonalized, and since the set of eigenvalues l, s, j, m_j are non-degenerate, we just know that $|l, s, j, m_j\rangle$'s *are* energy eigenstates! **Realizing this is not just a great time saver but also an essential step.** It would be sub-optimal, to put it mildly, to try and diagonalize the $2(2l+1) \times 2(2l+1)$ matrix problem. To do so would be akin to trying to solve a collision problem in classical mechanics without using known conservation laws.

So, from the symmetry argument alone, we know that *good* zeroth order states can be written as

$$|n, l, s, j, m_j\rangle \tag{8.7}$$

Second, the magnitude. Here, we go ahead and calculate the first order correction in energy, due to $\hat{H}_{so}$. Since we already have the diagonal basis, all we need to evaluate is

$$E_{so}^{(1)} \;=\; \left\langle n, l, s, j, m_j \left| \hat{H}_{so} \right| n, l, s, j, m_j \right\rangle \tag{8.8}$$

Note that the radial wave function of a Hydrogen-like problem depends only on n, l and its expectation value for various powers of r can be computed readily (e.g. Problem T6.34). For the current case, the following is what we need.

$$\left\langle n, l, ... \left| \frac{1}{\hat{r}^3} \right| n, l, ... \right\rangle \;=\; \frac{2\,Z^3}{a_B^3\, n^3 l(l+1)(2l+1)} \tag{8.9}$$

where ... represents the *same* quantum numbers omitted for bra and ket. Therefore,

we get

$$E_{so}^{(1)} = \frac{\alpha\hbar Z^4}{m_e^2 c a_B^3 n^3 l(l+1)(2l+1)} \left\langle lsjm_j \left| \hat{\vec{L}} \cdot \hat{\vec{S}} \right| lsjm_j \right\rangle \tag{8.10}$$

$$= \frac{\alpha\hbar Z^4 m_e^3 c^3 \alpha^3}{m_e^2 c\hbar^3 n^3 l(l+1)(2l+1)} \left\langle lsjm_j \left| \hat{\vec{L}} \cdot \hat{\vec{S}} \right| lsjm_j \right\rangle \qquad a_B = \frac{\hbar}{m_e c\alpha} \quad \text{(Eq. 6.19)}$$

$$= \frac{Z^4 m_e c^2 \alpha^4}{\hbar^2 n^3 l(l+1)(2l+1)} \left\langle lsjm_j \left| \hat{\vec{L}} \cdot \hat{\vec{S}} \right| lsjm_j \right\rangle$$

$$= \frac{2\left|E_n^{(0)}\right| Z^2\alpha^2}{\hbar^2 nl(l+1)(2l+1)} \left\langle lsjm_j \left| \hat{\vec{L}} \cdot \hat{\vec{S}} \right| lsjm_j \right\rangle \qquad E_n^{(0)} = -\frac{Z^2}{n^2}\frac{m_e c^2\alpha^2}{2} \quad \text{(Eq. 7.12)}$$

$$= \frac{\left|E_n^{(0)}\right| Z^2\alpha^2}{nl(l+1)(2l+1)} \Big[j(j+1) - l(l+1) - s(s+1) \Big] \qquad \text{using Eq. 8.4; will put } s = 1/2$$

$$= \frac{\left|E_n^{(0)}\right| Z^2\alpha^2}{nl(l+1)(2l+1)} \times \begin{cases} l & \text{if } j = l + 1/2 \\ -(l+1) & \text{if } j = l - 1/2 \end{cases} \tag{8.11}$$

$$= \frac{\left|E_n^{(0)}\right| Z^2\alpha^2}{n(2l+1)} \times \begin{cases} \frac{1}{l+1} & \text{if } j = l + 1/2 \\ -\frac{1}{l} & \text{if } j = l - 1/2 \end{cases} \tag{8.12}$$

Due to the spin orbit splitting, the higher angular momentum state becomes higher in energy than the lower angular momentum state, breaking the degeneracy in the unperturbed state. The fact that the energy splitting is proportional to $2l + 1 = 2(l + 1/2)$, i.e. proportional to the larger of the two possible j values goes by the name "Lande interval rule." The spectroscopic notation for spin orbit split orbitals is $p_{1/2}$ and $p_{3/2}$, and $d_{3/2}$ and $d_{5/2}$, etc., where the subscript is the j value. For valence electrons, the spin orbit interaction for light atoms is very small, on the order of meV or less. However, it can be quite significant, on the order of several 100 meV, for a heavy atom (e.g. Bi).

8.1.4 Fine structure—summary of relativistic effects

For historical reason, the relativistic correction, Eq. 7.16 and the spin-orbit interaction result that we just obtained, is called the "fine structure."

$$E_{fs}^{(1)} = Z^2 \left|E_n^{(0)}\right| \alpha^2 \times \begin{cases} \frac{1}{n(2l+1)(l+1)} - \frac{2}{n(2l+1)} + \frac{3}{4n^2} & j = l + \frac{1}{2} \\ -\frac{1}{n(2l+1)l} - \frac{2}{n(2l+1)} + \frac{3}{4n^2} & j = 1 - \frac{1}{2} \end{cases}$$

$$= E_n^{(0)} Z^2\alpha^2 \left(\frac{1}{n\left(j + \frac{1}{2}\right)} - \frac{3}{4n^2} \right) \tag{8.13}$$

8.2 Zeeman effect

In Lecture 4, we have already considered the effect of the electron spin in a constant uniform magnetic field. At that time, we did not consider the coupling of the orbital moment to the magnetic field. However, this is not hard to do. In general, according to our discussion in Lecture 4, the total magnetic moment of an electron is given by

$$\hat{\vec{\mu}} = -\frac{\mu_B}{\hbar}\left(g\hat{\vec{S}} + \hat{\vec{L}}\right) \approx -\frac{\mu_B}{\hbar}\left(2\hat{\vec{S}} + \hat{\vec{L}}\right) \tag{8.14}$$

$$\mu_B = \frac{e\hbar}{2m_e} \qquad \text{Bohr magneton} = 5.788 \times 10^{-5}\ \text{eV/T} \tag{4.18}$$

Now, let us say that a constant uniform field $\vec{B} = B_0\,\vec{e}_3$ is applied. Then, the Hamiltonian is given by, through $\hat{H} = -\hat{\vec{\mu}} \cdot \vec{B}$,

$$\hat{H}_Z = \frac{\mu_B B_0}{\hbar}\left(2\hat{S}_z + \hat{L}_z\right) \tag{8.15}$$

This is the so-called **Zeeman term**.

8.2.1 Symmetry

The Zeeman term definitely breaks the rotational symmetry of the system, both in the ordinary space and in the spin space. In fact, it reduces the full spherical symmetry of the Hamiltonian of Eq. 6.12 to a cylindrical rotational symmetry, where only $\hat{L}_z$ and $\hat{S}_z$ are conserved, but not $\hat{L}_x, \hat{L}_y, \hat{S}_x, \hat{S}_y$. Of course, $\hat{L}^2$ and $\hat{S}^2$ remain conserved, as they commute with $\hat{H}$. This means that we *can* continue to use spherical harmonics $|l, m_l, s, m_s\rangle$ as good eigenstates, where m_l and m_s are angular momentum quantum numbers along the z axis. However, $|p_x\rangle, |p_y\rangle, |p_z\rangle$ basis is no longer good, and neither is the $|l, m_{l,x}\rangle$ basis or the $|l, m_{l,y}\rangle$ basis.

This argument does not apply to the total angular momentum $\vec{J}$. It is easy to see that $\left[\hat{H}_Z, \hat{J}_z\right] = 0$, making m_j a good quantum number, while $\hat{H}_Z$ does *not* commute with $\hat{\vec{J}}^2$. [Exercise: compute $\left[\hat{\vec{J}}^2, \hat{S}_z\right]$ (which is non-zero) to verify this last point.] So, states $|l, s, j, m_j\rangle$'s are generally not good.

Thus, in comparison to the Hamiltonian of Eq. 6.12, the Zeeman term definitely lowers the symmetry, and we expect that the degeneracy of the $|l, m_l, s, m_s\rangle$ to be lifted by the Zeeman term. In comparison to the fine structure Hamiltonian, the Zeeman term has a higher symmetry in some aspects (cylindrical rotational symmetry for $\vec{L}$ and $\vec{S}$) while showing a lower symmetry in some other aspect (only cylindrical symmetry for $\vec{J}$).

8.2.2 Magnitude

As we discussed in Lecture 4, the man-made magnetic field gives only a few meV energy scale at the most due to the above Hamiltonian. This is a definitely small energy scale compared to the energy scale (~ Rydberg) of the unperturbed Hamiltonian, Eq. 6.12, justifying our treatment of the above Hamiltonian as a perturbation.

However, how does $\hat{H}_Z$ compare in relation to the fine structure term: $\hat{E}_{fs}^{(1)}$ (Eq. 8.13)? It depends. For heavy atom or in a small $\vec{B}$ field, the fine structure term dominates. For light atom or in a large $\vec{B}$ field, the Zeeman term dominates. Usually, the first case is simply referred to as the **"weak field limit,"** while the second case is simply referred to as the **"strong field limit"** (or **the Paschen-Back limit**). However, it is worth keeping in mind that the atomic number matters greatly in this distinction as well. With this point clarified, we will follow the conventional terminology.

8.2.3 Solution—weak field limit

If the Zeeman term is smaller than the fine structure energy scale, then it follows that we must define the unperturbed Hamiltonian as follows.

$$\hat{H}_0 = \frac{\hat{p}^2}{2m_e} + V_c(\hat{r}) + \hat{H}_{fs} \qquad V_c(\hat{r}) = -\frac{Ze^2}{4\pi\epsilon_0 \hat{r}} \tag{8.16}$$

$$\hat{H}_{fs} = -\frac{\hat{p}^4}{8m_e^3c^2} + \frac{1}{2m_e^2c^2}\frac{1}{\hat{r}}\frac{dV_c(\hat{r})}{d\hat{r}}\hat{\vec{L}}\cdot\hat{\vec{S}} \qquad \text{Eqs. 7.14, 8.2 (or 8.3)} \tag{8.17}$$

The perturbation is $\hat{H}_Z$, Eq. 8.15, and the unperturbed states are $|n,l,s,j,m_j\rangle$. Then, the Zeeman correction is[2]

$$E_Z^{(1)} = \frac{\mu_B B_0}{\hbar}\left\langle 2\hat{S}_z + \hat{L}_z\right\rangle = \mu_B B_0\left(m_j + \frac{\langle S_z\rangle}{\hbar}\right) \tag{8.18}$$

where the expectation value is on the unperturbed state $|n,l,s,j,m_j\rangle$. For the expec-

[2]Note that the use of the non-degenerate perturbation theory here is justified since the degeneracy of $|n,l,s,j,m_j\rangle$ states exists for different m_j values, for fixed n,l, while the Zeeman Hamiltonian commutes with $\hat{J}_z$ so that m_j *is* a good quantum number for the Zeeman term.

tation value of spin, we use

$$\left|j = l \pm \frac{1}{2}, m_j\right\rangle = \pm\sqrt{\frac{l \pm m_j + \frac{1}{2}}{2l+1}}\left|m_l = m_j - \frac{1}{2}, m_s = \frac{1}{2}\right\rangle + \sqrt{\frac{l \mp m_j + \frac{1}{2}}{2l+1}}\left|m_l = m_j + \frac{1}{2}, m_s = -\frac{1}{2}\right\rangle \tag{8.19}$$

For derivation, see problem T4.51 (which uses a slightly different sign convention, but has the same physical content). Thus, we get

$$\langle S_z\rangle = \frac{\hbar}{2}\left(\frac{l \pm m_j + \frac{1}{2}}{2l+1} - \frac{l \mp m_j + \frac{1}{2}}{2l+1}\right) \tag{8.20}$$

$$= \frac{\pm m_j \hbar}{2l+1} \tag{8.21}$$

which gives the final result:

$$E_Z^{(1)} = \mu_B B_0 m_j \left(1 \pm \frac{1}{2l+1}\right) \tag{8.22}$$

which also satisfies Lande interval rule, mentioned in page 6. The term in the parenthesis is called **Lande g factor**, g_J.

$$E_z^{(1)} = g_J \mu_B B_0 m_j \tag{8.23}$$

$$g_J = 1 \pm \frac{1}{2l+1} \tag{8.24}$$

8.2.4 Solution—strong field limit

If the Zeeman effect dominates over the fine structure effect, then we must take

$$\hat{H}_0 = \frac{\hat{p}^2}{2m_e} + V_c(\hat{r}) + \hat{H}_Z \qquad V_c(\hat{r}) = -\frac{Ze^2}{4\pi\epsilon_0 \hat{r}} \tag{8.25}$$

$$\hat{H}_1 = \hat{H}_{fs} = -\frac{\hat{p}^4}{8m_e^3c^2} + \frac{1}{2m_e^2c^2}\frac{1}{\hat{r}}\frac{dV_c(\hat{r})}{d\hat{r}}\hat{\vec{L}}\cdot\hat{\vec{S}} \qquad \text{Eqs. 7.14, 8.2 (or 8.3)} \tag{8.26}$$

treating the fine structure Hamiltonian as a perturbation.

The eigenstates of $\hat{H}_0$ are

$$|n, l, m_l, s, m_s\rangle \tag{8.27}$$

whose energy values now must contain the first order correction due to the Zeeman term

$$E_Z^{(1)} = \mu_B B_0 (2m_s + m_l) \tag{8.28}$$

On top of this, the fine structure term contributes. The kinematic term remains the same since it is dependent only on l, and it is diagonal in the $|n,l,m_l,s,m_s\rangle$ basis.

For the spin-orbit coupling, some care is necessary. Note that the perturbation is, as far as the angular momentum is concerned, of the form $\hat{L}_z\hat{S}_z + \hat{L}_x\hat{S}_x + \hat{L}_y\hat{S}_y$. As $\hat{L}_x$ (or $\hat{L}_y$) raises or lowers m_l by 1, and similarly for $\hat{S}_x$ (or $\hat{S}_y$), we see that the spin orbit Hamiltonian *may not be* diagonal in the $|n,l,m_l,s,m_s\rangle$ basis. This possibility matters only if we have the case of a degenerate perturbation. And, actually we do have a degenerate perturbation. The above Zeeman correction has split the originally $2(2l+1)$ degenerate energy levels, but some energy levels remain degenerate after the perturbation. Those are energy levels for which $2m_s + m_l$ remains the same. What are those levels? Since m_s must change between $1/2$ and $-1/2$, what we have is a double degeneracy between $m_l = m, m_s = 1/2$ and $m_l + 2, m_s = -1/2$. Fortunately, these doubly degenerate states *already diagonalize* the spin orbit interaction, since, as explained above, the spin-orbital coupling connects only those states whose m_l values differ by 1 or 0: the matrix element of $\vec{L}$ between those states whose m_l values differ by 2 or more vanishes.

It may be instructive to consider the case of $l = 1$ (p orbitals). Under the Zeeman term, the following hierarchy of levels happen.

$$E_Z^{(1)} = \mu_B B_0 \cdot \begin{cases} 2 & m_s = 1/2, m_l = 1 \\ 1 & m_s = 1/2, m_l = 0 \\ 0 & m_s = 1/2, m_l = -1 \quad \text{or} \quad m_s = -1/2, m_l = 1 \\ -1 & m_s = -1/2, m_l = 0 \\ -2 & m_s = -1/2, m_l = -1 \end{cases} \tag{8.29}$$

In any case, since $\hat{H}_{fs}$ is already diagonal in the $|n,l,m_l,s,m_s\rangle$ basis, all we need to do for the leading order calculation is to take the expectation value of $\hat{H}_{fs}$. This calculation is very similar to what we already carried out for Eq. 8.13. The only difference is that we need to re-evaluate $\left\langle \hat{\vec{L}} \cdot \hat{\vec{S}} \right\rangle$. In the calculation that led to Eq. 8.13, the expectation value for the j, m_j basis was $(j-1/2)\hbar/2$ (i.e., $l\hbar/2$ for $j = l+1/2$ and $-(l+1)\hbar/2$ for $j = l - 1/2$: see Eq. 8.11). In the current case, however, we must use the m_l, m_s basis, and we get

$$\left\langle \hat{\vec{L}} \cdot \hat{\vec{S}} \right\rangle = \hbar^2 m_l m_s \tag{8.30}$$

since the expectation value for $\hat{L}_x$, $\hat{L}_y$, $\hat{S}_x$, or $\hat{S}_y$ vanishes (these operators raise or lower m_l or m_s). With this, the equation just before Eq. 8.13 can be re-written for

the current case, and we get

$$\begin{aligned} E_{fs}^{(1)} &= Z^2 \left|E_n^{(0)}\right| \alpha^2 \left(\frac{2m_l m_s}{nl(l+1)(2l+1)} - \frac{2}{n(2l+1)} + \frac{3}{4n^2} \right) \\ &= E_n^{(0)} \frac{Z^2\alpha^2}{n} \left(\frac{l(l+1) - m_l m_s}{l(l+1)\left(l+\frac{1}{2}\right)} - \frac{3}{4n} \right) \end{aligned} \tag{8.31}$$

Here, one may note that the first term in the big parenthesis becomes problematic when $l = 0$: it is indeterminate. However, the $l = 0$ case is a special case where the $|j, m_j\rangle$ basis and the $|m_l, m_s\rangle$ basis are identical, since $j = s$ and $l = m_l = 0$. Therefore, the same basis diagonalizes $\hat{H}_Z$ as well as $\hat{H}_{fs}$, and so we can read off what the fine structure energy correction would be in *all* cases from Eq. 8.13. Namely, Eqs. 8.13 and 8.31 must be identical if $l = 0$. Then, we see that the expression $\frac{l(l+1)-m_l m_s}{l(l+1)\left(l+\frac{1}{2}\right)}$ must be interpreted as 1, when $l = 0$.

8.2.5 Intermediate case

When neither limit is applicable, the solution can not be obtained in a nice closed form. One has to diagonalize the perturbing Hamiltonian, $\hat{H}_Z + \hat{H}_{fs}$, following the degenerate perturbation theory, per appropriate angular momentum sub-space. An example of this is worked out in Section T6.4.3, which I recommend you to read.

8.3 Hyperfine splitting

We have already covered a few very important constants of nature.

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0 \hbar c} = \frac{1}{137.0} \qquad \text{Fine structre constant} \tag{6.20}$$

$$\hbar c = 1973 \text{ eV Å} \tag{7.3}$$

$$m_e c^2 = 0.5110 \text{ MeV} = 511.0 \text{ keV} \tag{7.4}$$

Let us introduce another important constant of nature, which is good to know in general.

$$k_B = 25.85 \text{ meV / } 300 \text{ K} \qquad \text{Boltzmann constant} \tag{8.32}$$

This means that 300 K ("room temperature") corresponds to 25.85 meV. Notice then that the temperature scale for the atomic energy scale, a Rydberg, is very high—this is why molecules, crystals, and all stuff around us are stable at room temperature: their

binding energy is much higher (which is generally not quite as high as Rydberg, but often a good fraction of it) than room temperature. Typically fine structure energy scale (or Zeeman energy scale) is much lower than room temperature, although there are some important exceptions. Assuming then that the fine structure energy level spacing is much smaller than the room temperature scale, we can say the following. Suppose that an atom is in the lowest energy state. Just above it, say that there is an excited energy level, whose spacing from the ground state is determined to be the fine structure energy scale. Then, at room temperature, we know that that excited state is occupied significantly. Materials and their environment (such as the gas of photons) are in constant thermal equilibrium and not only the lowest fine structure energy level but also excited fine structure energy levels will be occupied because there is sufficient thermal energy to occupy them.

It turns out that, in our Universe, there is one important wavelength of photons that can tell us how hydrogen atoms are distributed in the Universe. Such a distribution is interpreted as fingerprint of early Universe when it was just forming. But the Universe is generally a very cold place. For a neutral Hydrogen atom under no field, note that the energy level does not split at all due to the fine structure, while it may shift in energy. The excited state is 2s, which is too high in energy to be relevant in the cold Universe. However, there *is* a splitting of the 1s orbital! The wavelength that corresponds to this splitting is 21 cm, and the splitting arises due to the so-called "hyperfine interaction," which we look at now.

A magnetic dipole $\vec{\mu}$ generates a $\vec{B}$ field

$$\vec{B}(\vec{\mu}) \;=\; \frac{\mu_0}{4\pi r^3}\,[3(\vec{\mu}\cdot\vec{e}_r)\vec{e}_r - \vec{\mu}] + \frac{2\mu_0}{3}\,\vec{\mu}\delta(\vec{r}) \tag{8.33}$$

(Note that $\delta(\vec{r}) \equiv \delta(x)\delta(y)\delta(z)$.) Here, the first term is the usual $\vec{B}$ field due to a magnetic dipole, while the second term is the local term, that is typically not considered in elementary textbooks. This term is very important for correctly deriving the so-called "Fermi contact interaction term," as we shall see below. Physically, it can be seen to arise from a current loop whose magnetic moment is held constant and whose radius vanishes[3].

We shall consider only s orbitals of an electron in Hydrogen[4]. Thus,

$$\hat{\vec{\mu}}_e \;=\; -\frac{e}{m_e}\hat{\vec{S}}_e \tag{8.34}$$

[3]For the derivation of this term, please use the reference given in the textbook. However, you can calculate the field at the center of a circular current loop using the elementary Biot-Savart law. In the limit of the radius going to zero, one can justify the above term up to a numerical factor, or even exactly if luck is on your side.

[4]The textbook discussion is not so clear on this assumption, which must be made early on. Otherwise, the orbital angular momentum will contribute as well.

For the nucleus (= proton), we get

$$\hat{\vec{\mu}}_p = \frac{g_p e}{2m_p}\hat{\vec{S}}_p \tag{8.35}$$

where $g_p = 5.59$ is the gyromagnetic ratio for the proton. Now, the Hamiltonian is given by

$$\begin{aligned}\hat{H}_{hf} &= -\hat{\vec{\mu}}_e \cdot \hat{\vec{B}}(\hat{\vec{\mu}}_p) \\ &= \frac{\mu_0 g_p e^2}{3m_p m_e}\,\hat{\vec{S}}_e \cdot \hat{\vec{S}}_p\,\delta(\hat{\vec{r}}) + ...\end{aligned} \tag{8.36}$$

where ... means the term that arises from the first term of Eq. 8.33. For a given fixed but arbitrary time, we can define the direction of $\left\langle \hat{\vec{S}}_p \right\rangle$ to be the z axis, and then define the angle between that and $\left\langle \hat{\vec{S}}_e \right\rangle$ to be γ, with these two spins defining the xz plane. Then, the expectation value of the omitted term satisfies

$$\begin{aligned}\langle ... \rangle &\propto \left\langle 3\left(\hat{z}\cos\gamma + \hat{x}\sin\gamma\right)\hat{z} - \hat{r}^2\cos\gamma \right\rangle \\ &= \left\langle 3\hat{z}^2 - \hat{r}^2 \right\rangle \cos\gamma + 3\left\langle \hat{z}\hat{x} \right\rangle \sin\gamma\end{aligned}$$

Both the $3z^2 - r^2$ symmetry and the zx symmetry belong in the d symmetry (cf. Section 7.3, especially the figure therein), and so when both terms vanish since we are taking the expectation value over an s state, whose angular wave function is a constant ($\int d\Omega\, Y_{00}^* Y_{2m} Y_{00} = \int d\Omega\, Y_{00}^* Y_{2m} = 0$ where the first step is due to the fact that Y_{00} is a constant, and the second step is due to the orthogonality of wave functions with different l values. $d\Omega = d(\cos\theta)d\phi$.)

Therefore for an s shell electron the hyperfine interaction is only due to the delta function term, and is given by

$$E_{hf}^{(1)} = \frac{\mu_0 g_p e^2}{3m_p m_e}\left\langle \hat{\vec{S}}_e \cdot \hat{\vec{S}}_p \right\rangle |\psi_{ns}(0)|^2$$

Let us concentrate on the $1s$ orbital, for which $|\psi_{1s}(0)|^2 = \frac{1}{\pi a_B^3}$. We also note that

$$\hat{\vec{S}}_e \cdot \hat{\vec{S}}_p = \frac{1}{2}\left(\hat{S}_{tot}^2 - \hat{S}_e^2 - \hat{S}_p^2\right) \tag{8.37}$$

$$= \hbar^2 \times \begin{cases} \frac{1}{4} & \text{if } s_{tot} = 1 \\ -\frac{3}{4} & \text{if } s_{tot} = 0 \end{cases} \tag{8.38}$$

where $\hat{\vec{S}}_{tot}$ is the total spin, $\hat{\vec{S}}_e + \hat{\vec{S}}_p$, with its magnitude given by $\hbar\sqrt{s_{tot}(s_{tot}+1)}$. Using $\mu_0 = 1/(c^2\epsilon_0)$, we get

$$\begin{aligned} E^{(1)}_{hf} &= \frac{g_p e^2}{3\pi m_p m_e c^2 a_B^3 \epsilon_0} \left\langle \hat{\vec{S}}_e \cdot \hat{\vec{S}}_p \right\rangle \\ &= \frac{g_p 4\hbar^2}{3 m_p m_e^2 c^2 a_B^4} \left\langle \hat{\vec{S}}_e \cdot \hat{\vec{S}}_p \right\rangle \qquad \frac{e^2}{\pi\epsilon_0} = \frac{4\hbar^2}{m_e a_B} \text{ (Eq. 6.19)} \end{aligned}$$

Therefore, combining the above result for the spin, we get

$$E^{(1)}_{hf} = \frac{4 g_p \hbar^4}{3 m_p m_e^2 c^2 a_B^4} \times \begin{cases} \frac{1}{4} & \text{if } s_{tot} = 1 \\ -\frac{3}{4} & \text{if } s_{tot} = 0 \end{cases} \tag{8.39}$$

This hyperfine splitting corresponds to 5.88 μ eV and wave length 21 cm (ν = 1420 MHz). It arises due to the loss of spin isotropy due to the "Fermi contact interaction."

Note that in the ground state of a neutral Hydrogen in the absence of any field, the Hyperfine interaction gives the first excited state, since there is no splitting of the $1s$ orbital due to the fine structure.