

Notes for Lecture 7

Symmetry, hydrogen-like atom

Having equipped ourselves with the principles of perturbation and symmetry, we should be in very good shape. We will say a few more words about symmetry, summarizing the essence of what we discussed before and giving a simple example. Then, we will have a refined look at the hydrogen-like atom problem, from the symmetry and perturbation points of view.

7.1 Short summary—symmetry

The last lecture notes have a lot of contents, and therefore it may be useful to point out simple core contents. For the rest of the section, we assume that any operator is Hermitian or unitary¹. Also, we shall assume that no operator has an explicit time dependence, when we discuss “conservation” in later parts of this section.

First, if \hat{A} and \hat{B} commute, and if $\hat{A}|A\rangle = A|A\rangle$, then $\hat{A}(\hat{B}|A\rangle) = A(\hat{B}|A\rangle)$. Second, if \hat{A} and \hat{B} commute, then they can be diagonalized simultaneously, i.e. a common natural basis (LN 1, page 8) $\{|A, B\rangle\}$ can be found so that $\hat{A}|A, B\rangle = A|A, B\rangle$ and $\hat{B}|A, B\rangle = B|A, B\rangle$.

These are the two (intertwined) core principles related to the symmetry, discussed at length in LN 6, pages 9 and 14. Both of these principles can be taken as defining what it actually means for two operators to be *compatible* (LN 1, page 9). The first principle means that a compatible operator does not mess up an eigenstate of its partner. The second principle means that two compatible operators can live harmoniously with shared eigenstates.

¹You will not suffer much even if you assume this for the entirety of this course.

A word about sharing eigenstates. In the above, and in previous lectures, you might have noticed that it is said that compatible operators *can* share eigenvectors, i.e. *can* be diagonalized simultaneously, but it is never said *how* to find common eigenvectors. A little thought, based on principle 1, can give you the following guideline. Suppose that there are two compatible operators \hat{A} and \hat{B} to diagonalize. Suppose that \hat{A} is easy to diagonalize, but its eigenvectors have degeneracy. Then, *you must write down the most general form of an A -eigenvector, i.e. an arbitrary linear combination of degenerate A -eigenvectors* and, you will know, by symmetry principle 1, that that vector is an eigenvector for \hat{B} as well. The general form of an A -eigenvector will contain undetermined coefficients. Technically, this amounts to reducing the \hat{B} matrix to a block diagonal form, where each block is characterized by a unique eigenvalue for \hat{A} . For instance, suppose that \hat{A} has eigenvalues of -1 and 1. By principle 1, \hat{B} acting on \hat{A} eigenstates with eigenvalue -1 can never produce states that have overlap with any \hat{A} eigenstate with eigenvalue 1. In general, the matrix element $\langle A | \hat{B} | A' \rangle = 0$ if $A \neq A'$, where $|A\rangle$ ($|A'\rangle$) is *any* degenerate eigenstate of \hat{A} with eigenvalue A (A'). This is what is meant by the statement that \hat{B} is block-diagonalized by \hat{A} eigenstates. The task of diagonalizing \hat{B} is now much easier: all we need to do is to diagonalize the \hat{B} matrix within each sub-space corresponding to a unique A value, instead of having to diagonalize the \hat{B} matrix in the entire Hilbert space. In other words, “we can focus one block at a time.”

Commonly, the easy-to-diagonalize matrix \hat{A} corresponds to a symmetry operator or a conserved observable corresponding to it, and the difficult-to-diagonalize matrix \hat{B} corresponds to the Hamiltonian operator.

So, the use of symmetry in a quantum mechanics problem comes down to this. By observing the full symmetry of the system, identify all conserved operators (typically these are conserved *observables*) other than the Hamiltonian itself. Find a maximal set of mutually compatible conserved operators among these, and then find the most general form of simultaneous eigenstates for them. They are then guaranteed to be Hamiltonian eigenstates, which are what we like to solve for ultimately. In addition, the symmetry protected degeneracy can be learned by using the rule described under heading “**symmetry principle 1 in action**” of page 14 of LN 6. This last step can be very technical, in general, and we will be dealing with only very simple cases, if at all, in relation to this step, during this course. However, it is quite crucial that you get the hang of carrying out the first step: writing down symmetry eigenstates that are guaranteed to be the Hamiltonian eigenstates. This is neither a trivial task nor an impossibly difficult task. However, there is no question it is one of the most important things that you must learn in doing physics. The good news is that, in quantum mechanics, a solid understanding of what it means that two operators commute, as explained above, is essentially all you need in order to become really good at this task!

7.2 Short example of symmetry—potential well

Consider a simple symmetric potential well in one dimension, $V(x) = 0$ if $|x| < a$ and $V_0 > 0$ if $|x| > a$. We assume that V_0 is finite.

What can we say about the energy eigenstates from the symmetry point of view?

The answer is simple: we can say that the energy eigenstate can be written as an even function of x or an odd function of x . However, we cannot say just what type of even function or odd function it is. That requires more physics. For the reason described in the previous section, it would be quite incorrect to write some specific even function, such as $\cos(kx)$, and claim that to be an energy eigenfunction².

This is of course due to the parity symmetry, the only symmetry of this problem. The parity operation has two eigenvalues 1 (for even functions) or -1 (for odd functions). These two eigenvalues divide the entire Hilbert space into two equal parts, and our job of diagonalizing the Hamiltonian has become half as easy as the result.

But of course, you would do better than this—you know more physics than just the parity symmetry. You would know that this problem is “free particle like³” *piecewise*. So, if $0 < E < V_0$, then for an even solution one can write down $\psi(x) = A \cos(kx)$ for $|x| < a$ and $\psi(x) = B \exp(-\kappa|x|)$ for $|x| > a$, with $k = \sqrt{2mE}/\hbar$ and $\kappa = \sqrt{2m(V_0 - E)}/\hbar$. And then, you would get down to the business of applying the boundary conditions at a , and the normalization condition, to completely determine the coefficients A, B and the energy E . For an odd solution, one can do the same with $\psi(x) = A \sin(kx)$ for $|x| < a$ and $\psi(x) = \text{sgn}(x)B \exp(-\kappa|x|)$ for $|x| > a$.

However, you would know how the parity symmetry imposed is such a delightful feature of your solution, and how it makes your life much easier! Anyone, who have tried to do this problem without using the parity symmetry, would agree how essentially helpful it is to write down the solution as an even function or as an odd function! That is the power of symmetry, and the “block diagonalization” enabled by it.

7.3 Hydrogen-like atom—symmetry point of view

From the symmetry point of view, the hydrogen-like problem as we already defined in Eq. 6.12 is a very nice example to analyze. Let us consider an electron governed

²That would be correct only if $V_0 = 0$.

³I put quotation marks here, since we need to consider a complex wave vector for some segment.

by the following Hamiltonian.

$$\hat{H} \doteq -\frac{\hbar^2 \nabla^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 r} \quad \nabla \equiv \vec{e}_1 \frac{\partial}{\partial x} + \vec{e}_2 \frac{\partial}{\partial y} + \vec{e}_3 \frac{\partial}{\partial z} \quad (6.12)$$

This Hamiltonian has the full rotational symmetry of space, both in the ordinary space and in the spin space. It also has the full parity symmetry.

The rotational symmetry can be best represented by their generators, i.e. angular momentum operators. It is well-known that for the full rotational symmetry we get two maximal commuting operators. For rotation in ordinary space, this corresponds to the orbital angular momentum operators: $\hat{L}^2 \equiv \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ and \hat{L}_z . For rotation in spin space, we get $\hat{S}^2 \equiv \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$ and \hat{S}_z . The quantum numbers for these are l, m_l, s, m_s , where $l(l+1)\hbar^2$ is the eigenvalue for \hat{L}^2 , $m_l\hbar$ is the eigenvalue for \hat{L}_z , and similarly for the spin angular momentum. This means that if we take a state

$$|\psi_a\rangle = |l, m_l, s, m_s\rangle \quad s = 1/2$$

then, it is guaranteed that this this state is an energy eigenstate⁴!

The difference in this case is that the eigenvalue—the set of eigenvalues (l, m_l, s, m_s) , taken *as a whole*—is unique. That is, the states $|l, m_l, s, m_s\rangle$ are non-degenerate.

What do these states look like? For the (ordinary) spatial part, they correspond to the spherical Harmonics, $Y_{lm}(\theta, \phi)$. For the spin part, they correspond to the spin up state or the spin down state. We do not have a colorful function like Y_{lm} for the spin part, since we do not know what spin really is⁵. All we can do is to do something like: $|s = 1/2, m_s = 1/2\rangle \equiv |\uparrow\rangle \doteq \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, and $|s = 1/2, m_s = -1/2\rangle \equiv |\downarrow\rangle \doteq \begin{pmatrix} 0 \\ 1 \end{pmatrix}$.

Now, if what we said so far sounds too good to be true, then it is because it is. The general wave function must have a radial part as well as angular part, and so we must recognize that we need an additional quantum number for the radial part. So, the full energy eigenstate must be written as

$$|\psi\rangle = |n, l, m_l, s, m_s\rangle \quad s = 1/2 \quad (7.1)$$

where n is a quantum number associated with the radial degree of freedom.

⁴You may wonder why, in this discussion, we do not include the parity operator, \hat{P}_z , which is compatible with \hat{L}^2 and \hat{L}_z . In fact, we must include \hat{P}_z if we were to define a *maximal* set of compatible operators. However, Y_{lm} 's are already \hat{P}_z eigenstates, and so we do not gain any more practical benefit by adding \hat{P}_z .

⁵However, notice that we can do a lot of spin algebra without knowing what spin really is. Keep this in mind when you do calculation on *orbital* angular momentum. For many calculations, you do *not* need to know what Y_{lm} looks like! The angular momentum operator algebra and the orthonormality of $|l, m\rangle$'s are quite sufficient for them.

Now, the state $|\psi\rangle$ remains to be an eigenstate of \hat{L}^2 , \hat{L}_z , \hat{S}^2 , and \hat{S}_z . However, it is a *massively degenerate* eigenstate of them now that we are considering the radial quantum number n as well.

This is not news to you, of course. You probably learned how to separate variables for the differential equation

$$-\frac{\hbar^2 \nabla^2}{2m_e} \psi(\vec{r}) - \frac{Ze^2}{4\pi\epsilon_0 r} \psi(\vec{r}) = E\psi(\vec{r}) \quad (7.2)$$

so that you get two angular equations and a radial equation. Two angular equations correspond to eigenvalue equations for \hat{L}^2 and \hat{L}_z ! And, the only equation that depends on the form of the central potential to solve is the radial equation.

The symmetry argument alone cannot determine the radial wave function. However, the virtue of the symmetry argument is that it reduced the problem into a differential equation involving only one variable, r !

By the way, you will note that \hat{L}^2 , \hat{L}_z , \hat{P}_z (see footnote 4), \hat{S}^2 , and \hat{S}_z are not a unique choice of operators that commute with \hat{H} . We can choose \hat{L}^2 , \hat{P}_x , \hat{P}_y , \hat{P}_z , \hat{S}^2 , \hat{S}_z , instead, where \hat{P} 's are parity/reflection operators. With this other choice of “maximal mutually compatible symmetry operators,” what would be the symmetry eigenstates? Since the spin part remains the same, we consider the orbital part only.

For $l = 0$ state, i.e. the so-called s states in the spectroscopic notation, we have nothing to do. An s state, represented by Y_{00} , is a constant, fully invariant under any rotation and reflection.

For $l = 1$ states, i.e. the so-called p states, we have something to do. In fact, what we did the in the last lecture, p_x , p_y , p_z states are just those—parity eigenstates, as well as \hat{L}^2 eigenstates.

For $l = 2$ states, i.e. the so-called d states, we have the following states⁶: d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$, $d_{3z^2-r^2}$ (or “ d_{z^2} ”⁷). These five (orthonormal) states can be formed by linear combinations of $Y_{l=2,m}$ states, and are parity eigenstates, but not \hat{L}_z eigenstates.

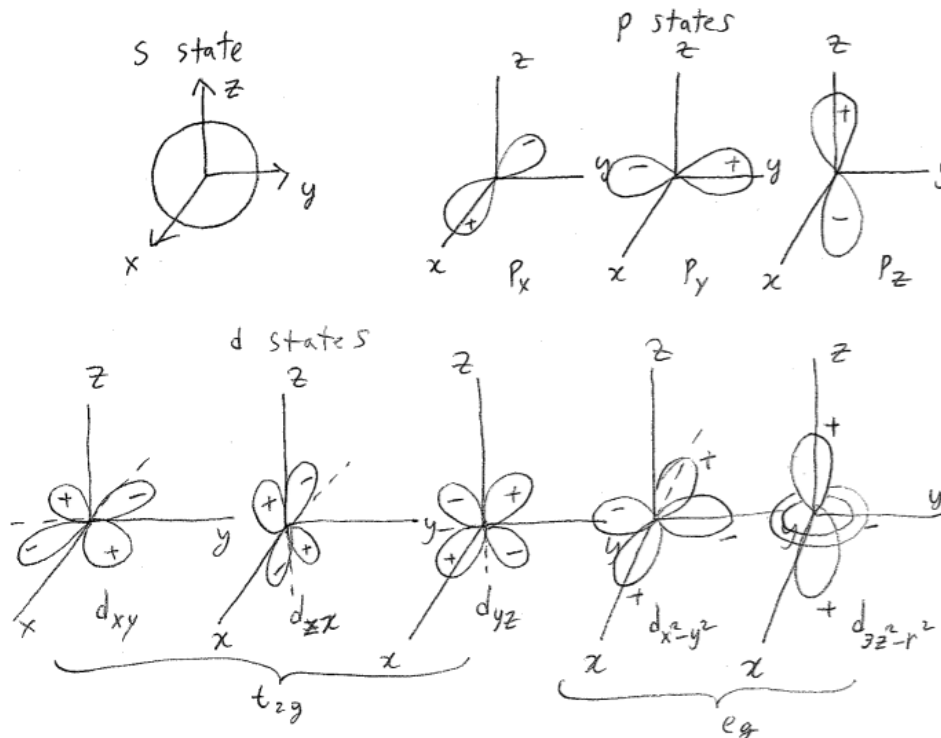
These orbitals are sketched below. I hope you will see easily that these are parity eigenstates. These orbitals are essential in chemistry and materials science, due to the fact that as soon as atoms form molecules and crystals the full rotational symmetry is broken (only discrete rotational symmetry will remain in typical cases) while

⁶These are very important states in condensed matter physics. The first three are so-called “ t_{2g} orbitals” and the last two are so-called “ e_g orbitals.”

⁷This is the designation in some literature. However, note that an angular wave function $\propto z^2$ is not orthogonal to an isotropic wave function (s state). So, $3z^2 - r^2$ is the correct one, and “ z^2 ” should be understood as an unfortunate short-hand notation for it.

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the parity symmetries tend to survive. So, these “chemistry-type” orbitals remain relevant in molecules and crystals, while spherical harmonic states generally do not.



7.4 Hydrogen-like atom—perturbation point of view

It is often said that the fine structure constant is what makes this world what it looks and feels like to us now. This is indeed the case, since the fine structure constant is what determines the hierarchy of all atomic energies (thus the chemistry).

The fine structure constant α was already introduced in LN 6. Here is some information repeated.

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} = \frac{1}{137.0} \quad \text{Fine structure constant} \quad (6.20)$$

$$a_B \equiv \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = \frac{\hbar}{m_e c} \frac{1}{\alpha} = 0.5292 \text{ \AA} \quad \text{Bohr radius} \quad (6.19)$$

$$\frac{\hbar}{m_e c} = 386.2 \text{ fm} \quad \text{(Reduced) } e \text{ Compton wavelength} \quad (6.21)$$

where fm = femto meter = fermi = 10^{-15} m.

Also, let us note that the followings are very useful numbers to remember.

$$\hbar c = 1973 \text{ eV } \text{\AA} \quad (7.3)$$

$$m_e c^2 = 0.5110 \text{ MeV} = 511.0 \text{ keV} \quad (7.4)$$

The expression for a_B can be “derived” conveniently from Bohr’s atomic model, which hinges on the assumption that $mvr = n\hbar$, with $n = 1, 2, 3, \dots$. With this assumption and the classical centripetal force equation (which amounts to the “virial theorem”), $\frac{mv^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2}$, it is possible to show (by eliminating v ; left for your exercise)

$$\frac{1}{r} = \frac{Z}{n^2 a_B} \quad (7.5)$$

The reason why this equation is presented in terms of $1/r$, instead of r , is because the exact quantum mechanics results for energy eigenstates are

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{n^2 a_B} \quad (7.6)$$

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{Z^2}{n^3 a_B^2 (l + \frac{1}{2})} \quad (7.7)$$

$$\langle r \rangle = \frac{a_B}{2Z} (3n^2 - l(l+1)) \quad (7.8)$$

$$\langle r^2 \rangle = \frac{a_B^2 n^2}{2Z^2} (5n^2 + 1 - 3l(l+1)) \quad (7.9)$$

The total energy is given correctly by the Bohr model, which was the fundamental reason why that model became so celebrated:

$$E_n = -\frac{Z^2 e^2}{8\pi\epsilon_0 n^2 a_B} = -\frac{Z^2 R}{n^2} \quad R = 13.61 \text{ eV} = \text{Rydberg} \quad (7.10)$$

Using Eq. 7.6, we can see that

$$E_n = \frac{1}{2} \langle \hat{V} \rangle = -\langle \hat{T} \rangle \quad \hat{V} = -\frac{Ze^2}{4\pi\epsilon_0 \hat{r}}, \quad \hat{T} = \frac{\hat{p}^2}{2m_e} \quad (7.11)$$

The latter equality comes from the fact that $E_n = \langle \hat{T} + \hat{V} \rangle$ and that $E_n = \frac{1}{2} \langle \hat{V} \rangle$. On the other hand, we could have used the virial theorem, $\langle \hat{T} \rangle = -\frac{1}{2} \langle \hat{V} \rangle$ (cf. Homework 3), to *derive* Eq. 7.6.

Now, one can note that $R = \frac{e^2}{8\pi\epsilon_0 a_B} = \frac{e^2 m_e c \alpha}{8\pi\epsilon_0 \hbar} = \frac{1}{2} m_e c^2 \alpha^2$. Therefore, one can write

$$E_n = -\frac{Z^2 m_e c^2}{2n^2} \alpha^2 \quad (7.12)$$

The fact that the inverse atomic length scale $1/a_B$ is α times the intrinsic length scale of the electron (Eq. 6.19) and the atomic energy scale is α^2 times the intrinsic energy scale of the electron (Eq. 7.12) is a hint that α is a perturbation parameter and these atomic scale phenomena are the results of perturbation to the intrinsic energy scale of the electron. Indeed, such is the picture that emerges from quantum electro-dynamics (QED). In this case, the perturbation involves a small probability that an otherwise free electron will absorb or emit a photon at random time and place.

Finally, let us discuss the wave functions for the Hydrogen-like atom, defined by the Hamiltonian, Eq. 6.12. One way to view this problem is to regard it as the Hydrogen atom problem with $\epsilon_0 \rightarrow \epsilon_0/Z$. Then, from Eq. 6.19, we see that the change $a_B \rightarrow a_B/Z$ is necessary to make. Indeed, this is the only change that is necessary when rewriting the energy eigenstates for the Hydrogen atom as the energy eigenstates for the Hydrogen-like atom. With this change in mind, the Z dependence in the integrals of Eqs. 7.6 through 7.9 can be readily understood⁸.

7.5 Hydrogen-like atom—relativistic effect

While the QED was mentioned in passing in the last section, that is not what we are up to in this course. Now we will discuss effects that are within the reach of our calculation. These are fine structures and hyperfine structures that occur when we include perturbative terms to the Hamiltonian of Eq. 6.12.

Relativistic kinematic correction

In relativity, $E = \sqrt{m_e^2 c^4 + p^2 c^2}$. The kinetic energy is given by $E - m_e c^2$. Expanding to the fourth powers of p , we get

$$T = \frac{p^2}{2m_e} - \frac{1}{8} \frac{p^4}{m_e^3 c^2} + \dots \quad (7.13)$$

Therefore, we identify the perturbing Hamiltonian

$$\hat{H}_1 = -\frac{1}{8} \frac{\hat{p}^4}{m_e^3 c^2} \quad (7.14)$$

The first order correction to the atomic energy levels, Eq. 7.12, is given by

$$E_n^{(1)} = -\frac{1}{8m_e^3 c^2} \langle \hat{p}^4 \rangle \quad (7.15)$$

⁸Also, notice that this mapping makes it easy to understand why $E_n \propto Z^2$, since $E_n \propto 1/(a_B \epsilon_0)$.

By noting that $\hat{p}^4 = (2m_e(\hat{H} - \hat{V}))^2$, using the fact \hat{H} turns into $E_n^{(0)}$ (Eq. 7.12) when acting on the zeroth order state, and using Eq. 7.6, 7.7, we get

$$E_n^{(1)} = -\frac{(E_n^{(0)})^2}{2m_e c^2} \left(\frac{4n}{l + \frac{1}{2}} - 3 \right) \quad (7.16)$$

Note that, compared to the zero order energy, this correction is small by a factor of $\sim \frac{E_n^{(0)}}{m_e c^2}$, ignoring other numerical factors. Since $E_n^{(0)} \sim m_e c^2 \alpha^2$ (Eq. 7.12), we see that the relativistic correction given here is α^2 times smaller than the Rydberg scale. These corrections due to the relativistic effect is the so-called fine-structure.

Now, let us note something about the symmetry related to this perturbation that we just dealt with. One notable thing is that this perturbation has exactly the same symmetry as the unperturbed Hamiltonian: the full rotational symmetry and the full parity symmetry. Therefore, we do not expect the perturbation to split any energy levels, except for splitting any accidental degeneracy (LN 6, page 13). Indeed, the perturbation *did* split the accidental degeneracy⁹ since now the energy values depend on l as well! Regardless, note that the perturbing Hamiltonian and the unperturbed Hamiltonian have exactly the same structure as far as symmetry eigenstates, e.g. $|l, m_l, s, m_s\rangle$'s, are concerned: both Hamiltonians are already diagonal in this symmetry eigenstate basis. For a fixed set of values (l, m_l, s, m_s) , the perturbation changes the *radial* part of the wave function, but the way that happens is *exactly the same* for different values of m_l, m_s ($s = 1/2$ is fixed). This is the reason why we do not, and should not, use the degenerate perturbation theory for this problem, even though technically there is a $(2l + 1) \times 2$ degeneracy for a given set of values (n, l) .

Spin-orbit coupling

Consider an electron moving in an electric field. By relativity, the electron sees a magnetic field as well. Why? It is because in the electron's moving frame, some of the electric field is seen as a magnetic field. An easy way to understand this is to consider an electron moving in the field generated by other charges, like charges of nuclei.

If the electron is moving in the field by these other charges, which we assume to be at rest in the lab frame, then it is clear that in the rest frame of the electron, these charges are moving. Naturally, those moving charges generate a magnetic field.

⁹However, readers must be warned here—the “accidental degeneracy” in a Hydrogen-like atom problem (Eq. 6.12) with energy eigenvalues 7.10 is not really accidental, since there is a hidden symmetry. You can google for something like “Laplace-Runge-Lenz vector in quantum mechanics.”

For an electron moving at velocity \vec{v} in an electric field \vec{E} , the magnetic field is given by (please see any of your favorite E&M book to see the derivation of this formula):

$$\vec{B} = -\gamma \frac{\vec{v}}{c^2} \times \vec{E} \approx -\frac{\vec{v}}{c^2} \times \vec{E} \quad (7.17)$$

How does an electron at rest interact with this magnetic field? Effectively, we have already dealt with this type of problem in Lecture 4. There, we ignored any magnetic moment generated by the electron's orbital motion, assuming, e.g., an electron in an s shell. However, this would also be the case, i.e. there would be no contribution of the electron's orbital motion to the magnetic moment, in the rest frame of the electron. So, the electron couples to the magnetic field, via $\hat{H} = -\hat{\vec{\mu}} \cdot \hat{\vec{B}}$, only through the spin-generated magnetic moment $\vec{\mu}$. Thus, the Hamiltonian is given by, as in LN 4,

$$\hat{H} = \frac{g\mu_B}{\hbar} \hat{\vec{B}} \cdot \hat{\vec{S}} \quad g \approx 2 \text{ is the gyromagnetic ratio for electron spin} \quad (7.18)$$

Thus, one sees that the orbital motion (generating the \vec{B} field) and the spin degree of freedom (interacting with the \vec{B} field) will be coupled by these two equations. This is the so-called “spin-orbit coupling.”

Note that this is a relativistic effect as well.