8.5: Discovering Electron Spin

Imagine doing a hypothetical experiment that would lead to the discovery of electron spin. Your laboratory has just purchased a microwave spectrometer with variable magnetic field capacity. We try the new instrument with hydrogen atoms using a magnetic field of 10^4 Gauss and look for the absorption of microwave radiation as we scan the frequency of our microwave generator.

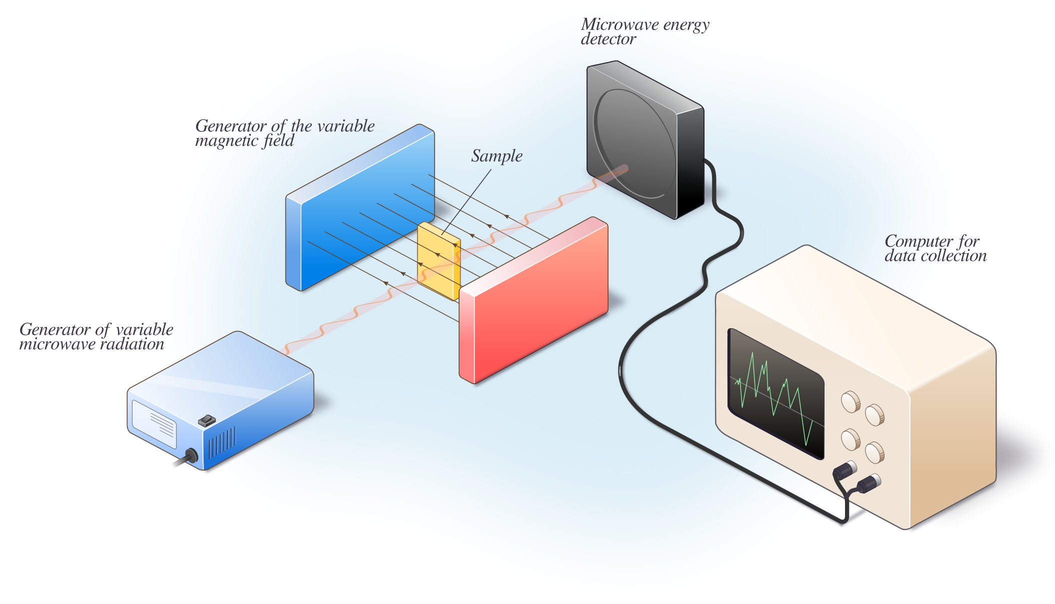

Figure 8.5.1: Schematic diagram of a microwave spectrometer with the sample in a variable magnetic field. The strength of the magnetic field is set, and the sample's absorption of microwave photons is measured for a range of microwave photon energies (or frequencies). (CC BY-NC; Ümit Kaya via LibreTexts)

Finally we see absorption at a microwave photon frequency of $28 \times 10^9\ Hz$ (28 gigahertz). This result is really surprising from several perspectives. Each hydrogen atom is in its ground state, with the electron in a 1s orbital. The lowest energy electronic transition that we predict based on existing theory (the electronic transition from the ground state (ψ_{100} to ψ_{21m}) requires an energy that lies in the vacuum ultraviolet, not the microwave, region of the spectrum. Furthermore, when we vary the magnetic field we note that the frequency at which the absorption occurs varies in proportion to the magnetic field. This effect looks like a Zeeman effect, but if you think about the situation, even if the 1s orbital were doubly degenerate, a $1s$ orbital still has zero orbital angular momentum, no magnetic moment, and therefore no predicted Zeeman effect!

To discover new things, experimentalists sometimes must explore new areas in spite of contrary theoretical predictions. Our theory of the hydrogen atom at this point gives no reason to look for absorption in the microwave region of the spectrum. By doing this crazy experiment, we discovered that when an electron is in the $1s$ orbital of the hydrogen atom, there are two different states that have the same energy. When a magnetic field is applied, this degeneracy is removed, and microwave radiation can cause transitions between the two states. In the rest of this section, we see what can be deduced from this experimental observation. This experiment actually could be done with electron spin resonance spectrometers available today.

In order to explain our observations, we need a new idea, a new model for the hydrogen atom. Our original model for the hydrogen atom accounted for the motion of the electron and proton in our three-dimensional world; the new model needs something else that can give rise to an additional Zeeman-like effect. We need a charged particle with angular momentum to produce a magnetic moment, just like that obtained by the orbital motion of the electron. We can postulate that our observation results from a motion of the electron that wasn't considered in the last section - electron spin. We have a charged particle spinning on its axis. We then have charge moving in a circle, angular momentum, and a magnetic moment, which interacts with the magnetic field and gives us the Zeeman-like effect that we observed.

To describe electron spin from a quantum mechanical perspective, we must have spin wavefunctions and spin operators. The properties of the spin states are deduced from experimental observations and by analogy with our treatment of the states arising from the orbital angular momentum of the electron.

The important feature of the spinning electron is the spin angular momentum vector, which we label S by analogy with the orbital angular momentum L. We define spin angular momentum operators with the same properties that we found for the rotational and orbital angular momentum operators. After all, angular momentum is angular momentum.

We found that (in Bra-ket notation)

$$\hat{L}^2 |Y_l^{m_l}\rangle = l(l+1)\hbar^2 |Y_l^{m_l}\rangle \tag{8.5.1}$$

so by analogy for the spin states, we must have

$$\hat{S}^2 |\sigma_s^{m_s}\rangle = s(s+1)\hbar^2 |\sigma_s^{m_s}\rangle \tag{8.5.2}$$

where σ is a spin wavefunction with quantum numbers s and m_s that obey the same rules as the quantum numbers l and m_l associated with the spherical harmonic wavefunction Y. We also found

$$\hat{L}_z |Y_l^{m_l}\rangle = m_l \hbar |Y_l^{m_l}\rangle \tag{8.5.3}$$

so by analogy, we must have

$$\hat{S}_z |\sigma_s^{m_s}\rangle = m_s \hbar |\sigma_s^{m_s}\rangle \tag{8.5.4}$$

Since m_l ranges in integer steps from $-l$ to $+l$, also by analogy m_s ranges in integer steps from $-s$ to $+s$. In our hypothetical experiment, we observed one absorption transition, which means there are two spin states. Consequently, the two values of m_s must be $+s$ and $-s$, and the difference in m_s for the two states, labeled f and i below, must be the smallest integer step, i.e. 1. The result of this logic is that

$$\begin{aligned} m_{s,f} - m_{s,i} &= 1 \\ (+s) - (-s) &= 1 \\ 2s &= 1 \\ s &= \frac{1}{2} \end{aligned} \tag{8.5.5}$$

Therefore our conclusion is that the magnitude of the spin quantum number is 1/2 and the values for ms are +1/2 and -1/2. The two spin states correspond to spinning clockwise and counter-clockwise with positive and negative projections of the spin angular momentum onto the z-axis. The state with a positive projection, m_s = +1/2, is called α; the other is called β. These spin states are arbitrarily labeled α and β, and the associated spin wavefunctions also are designated by α and β.

From Equation 8.5.4 the magnitude of the z-component of spin angular momentum, S_z, is given by

$$S_z = m_s \hbar \tag{8.5.6}$$

so the value of S_z is $+\hbar/2$ for spin state α and $-\hbar/2$ for spin state β. Using the same line of reasoning we used for the splitting of the m_l states in Section 8.4, we conclude that the α spin state, where the magnetic moment is aligned against the external field direction, has a higher energy than the β spin state.

Even though we don’t know their functional forms, the spin wavefunctions are taken to be normalized and orthogonal to each other.

$$\int \alpha^* \alpha d\tau_s = \int \beta^* \beta d\tau_s = 1 \tag{8.5.7}$$

and

$$\int \alpha^* \beta d\tau_s = \int \beta^* \alpha d\tau_s = 0 \tag{8.5.8}$$

where the integral is over the spin variable τ_s.

Now let's apply these deductions to the experimental observations in our hypothetical microwave experiment. We can account for the frequency of the transition (ν= 28 gigahertz) that was observed in this hypothetical experiment in terms of the magnetic moment of the spinning electron and the strength of the magnetic field. The photon energy, $h\nu$, is given by the difference between the energies of the two states, E_α and E_β

$$\Delta E = h\nu = E_\alpha - E_\beta \tag{8.5.9}$$

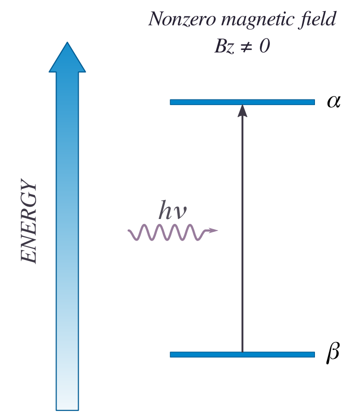

Figure 8.5.2: Absorption of a photon to cause a transition from the β to the α state. (CC BY-NC; Ümit Kaya via LibreTexts)

The energies of these two states consist of the sum of the energy of an electron in a 1s orbital, E_{1s}, and the energy due to the interaction of the spin magnetic dipole moment of the electron, μ_s, with the magnetic field, B (as in Section 8.4). The two states with distinct values for spin magnetic moment μ_s are denoted by the subscripts α and β.

$$E_\alpha = E_{1s} - \mu_{s,\alpha} \cdot B \tag{8.5.10}$$

$$E_\beta = E_{1s} - \mu_{s,\beta} \cdot B \tag{8.5.11}$$

Substituting the two equations above into the expression for the photon energy gives

$$h\nu = E_\alpha - E_\beta \tag{8.5.12}$$

$$= (E_{1s} - \mu_{s,\alpha} \cdot B) - (E_{1s} - \mu_{s,\beta} \cdot B) \tag{8.5.13}$$

$$= (\mu_{s,\beta} - \mu_{s,\alpha}) \cdot B \tag{8.5.14}$$

Again by analogy with the orbital angular momentum and magnetic moment discussed in Section 8.4, we take the spin magnetic dipole of each spin state, $\mu_{s,\alpha}$ and $\mu_{s,\beta}$, to be related to the total spin angular momentum of each state, S_α and S_β, by a constant spin gyromagnetic ratio, γ_s, as shown below.

$$\mu_s = \gamma_s S \tag{8.5.15}$$

$$\mu_{s,\alpha} = \gamma_s S_\alpha \tag{8.5.16}$$

$$\mu_{s,\beta} = \gamma_s S_\beta \tag{8.5.17}$$

With the magnetic field direction defined as z, the scalar product in Equation 8.5.14 becomes a product of the z-components of the spin angular momenta, $S_{z,\alpha}$ and $S_{z,\beta}$, with the external magnetic field.

Inserting the values for $S_{z,\alpha} = +\frac{1}{2}\hbar$ and $S_{z,\alpha} = -\frac{1}{2}\hbar$ from Equation 8.5.6 and rearranging Equation 8.5.14 yields

$$\frac{h\nu}{B} = -\gamma_s \hbar \tag{8.5.18}$$

Calculating the ratio $\frac{h\nu}{B}$ from our experimental results, $\nu = 28 \times 10^9\ Hz$ when $B = 10^4\ gauss$, gives us a value for

$$-\gamma_s \hbar = 18.5464 \times 10^{-21}\ erg/gauss. \tag{8.5.19}$$

This value is about twice the Bohr magneton, $-\gamma_e \hbar$ with $\gamma_s \hbar = 2.0023$, $\gamma_e \hbar$, or

$$\gamma_s = 2.0023 \gamma_e \tag{8.5.20}$$

The factor of 2.0023 is called the **g-factor** and accounts for the deviation of the spin gyromagnetic ratio from the value expected for orbital motion of the electron. In other words, it accounts for the spin transition being observed where it is instead of where it would be if the same ratio between magnetic moment and angular momentum held for both orbital and spin motions. The value 2.0023 applies to a freely spinning electron; the coupling of the spin and orbital motion of electrons can produce other values for g.

Exercise 8.5.1

Carry out the calculations that show that the g-factor for electron spin is 2.0023.

Interestingly, the concept of electron spin and the value g = 2.0023 follow logically from *Dirac's relativistic quantum theory*, which is beyond the scope of this discussion. Electron spin was introduced here as a postulate to explain experimental observations. Scientists often introduce such postulates parallel to developing the theory from which the property is naturally deduced.

Now that we have discovered electron spin, we need to determine how the electron spin changes when radiation is absorbed or emitted, i.e. what are the selection rules for electron spin of a single electron? Unlike orbital angular momentum, which can have several values, the spin angular momentum can have only the value

$$|S| = \sqrt{s(s+1)\hbar} = \frac{\sqrt{3}}{2}\hbar \tag{8.5.21}$$

Since s = ½, one spin selection rule is

$$\Delta s = 0 \tag{8.5.22}$$

When a magnetic field is applied along the z-axis to remove the m_s degeneracy, another magnetic field applied in the x or y direction exerts a force or torque on the magnetic dipole to turn it. This transverse field can “flip the spin,” and change the projection on the z-axis from $\frac{1}{+2}\hbar$ to $\frac{1}{-2}\hbar$ or from $\frac{1}{-2}\hbar$ to $\frac{1}{+2}\hbar$. So the other spin selection rule for a single electron is

$$\Delta m_s = \pm 1 \tag{8.5.23}$$