Lecture 15

Hydrogen-like Atom-II

Study Goal of This Lecture

- Orbital angular momentum and atomic spectra
- Electron spins
- Zeeman effect

15.1 Introduction

Before we move on to treat many-electron atoms, we will consider the effect of an electron in an atomic orbital under the influence of and external magnetic field. So far we have considered a free hydrogen-like atom, which has the energy levels:

$$E_n = -\frac{1}{2}\frac{Z^2}{n^2}E_h, \quad E_h = \frac{e^2}{4\pi\epsilon_0 a_0}. \tag{15.1}$$

When an external magnetic field is present, the degenerate energy levels will split $\rightarrow$ Zeeman effect. Also, up to now, we have explored mainly the energy levels and shapes of the hydrogen atomic orbitals. These energy levels explain the hydrogen-atom spectrum, i.e. experimental proofs. How about the shape? Are there experimental evidence for atomic orbitals with different angular momentum quantum number(m_l)? To answer this question, we ought to discuss the effects of magnetic field too.

Again, notice that "orbitals" means "single electron wavefunction"!

15.1.1 Orbital Angular Momentum

We first consider the consequences of having the orbital angular momentum. In atomic physics, angular momentum leads, to two key rules:

1. Selection rule of atomic spectrum requires $\Delta l = \pm 1$ in a single photo transition. This is because a photon is quantized and exhibit an angular momentum, spin of $m = \pm 1$(photon is boson.) In quantum mechanics, the conservation of angular momentum must be obeyed. So when a photon is destroyed or created, the total angular momentum of the photon + atom system must be conserved. Therefore, the atomic system must change its angular momentum $\Delta l = \pm 1$. This rules will be more clearly explaned later when we actually consider the matter-field interations and spectroscopy. At this point, you can simply take this as an experimental fact/empirical rule. As a result, the "allowed transition" is limited to $s \longleftrightarrow p$, $p \longleftrightarrow d$, ...

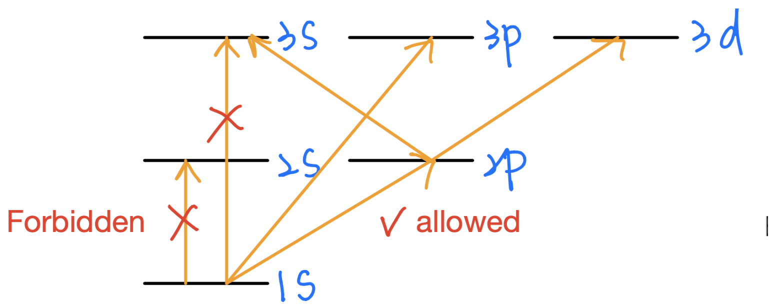

Figure 15.1: Diagram of selection rule for light absorbing transition.

2. States which $l \neq 0$ splits into $2l + 1$ states under the influence of magnetic field. The orbital angular momentum means the electron is "moving" around the nucleus(remember, electron has $-e$ charge!) A rotating charge will generate a magnetic field $\rightarrow$ this will interact with an external magnetic field!

15.2 Zeeman Effect

For a hydrogen atom in a external magnetic field $\vec{B}$ aligned along the z-direction. The potential energy caused by the B-field is

$$E = -\vec{\mu} \cdot \vec{B} = -\vec{\mu_z} \cdot \vec{B}. \tag{15.2}$$

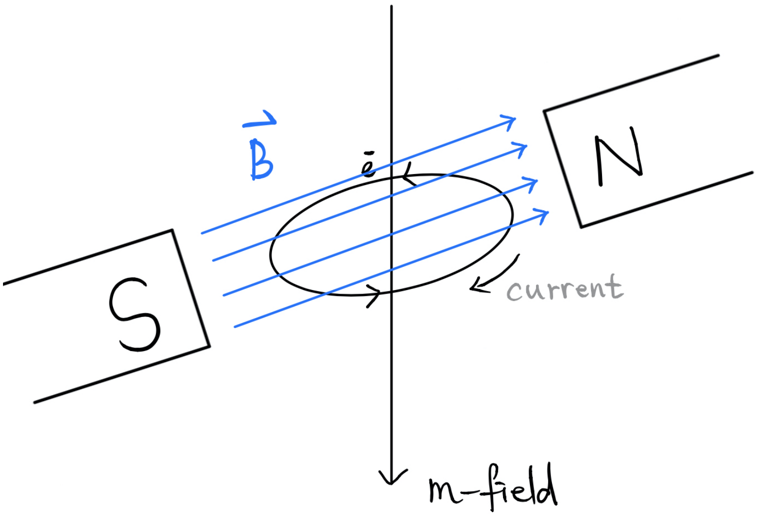

Figure 15.2: Under magetic field.

By definition

$$\hat{\mu} = \gamma_e \hat{L}, \tag{15.3}$$

γ_e is gyromagnetic ratio, the ratio of magnetic moment to angular momentum, $\gamma_e = \frac{-e}{2m_e}$.

therefore

$$\hat{\mu}_z = \frac{-e}{2m_e}\hat{L}_z \tag{15.4}$$

in eigenstate of $\hat{L}_z \to Y_l^m(\theta, \phi)$

$$\hat{\mu_z} Y_l^m(\theta,\phi) = -\frac{e}{2m_e}\hbar m Y_l^m(\theta,\phi). \tag{15.5}$$

Thus, the Hamiltonian with the field:

$$\hat{H} = \hat{H}_0 - \hat{\mu}_z \cdot B = \hat{H}_0 + \frac{eB}{2m_e}\hat{L}_z. \tag{15.6}$$

Clearly, the eigenstates remain the same as the original hydrogen atom:

$$\psi_{n,l,m_l} = R_{n,l}(r) \times Y_l^m(\theta,\phi), \tag{15.7}$$

$$\hat{H}\psi_{n,l,m_l} = \Big(-\frac{m_e e^4 Z^2}{2(4\pi\epsilon_0)^2 n^2 \hbar^2} + \mu_B m B \Big)\psi_{n,l,m_l}. \tag{15.8}$$

We find the eigenvalue, i.e. the energy level, changes. The additional term depends on the quantum number m_l. Thus, under the influence of external magnetic field, the energy will split, and this spliting is called Zeeman effect.

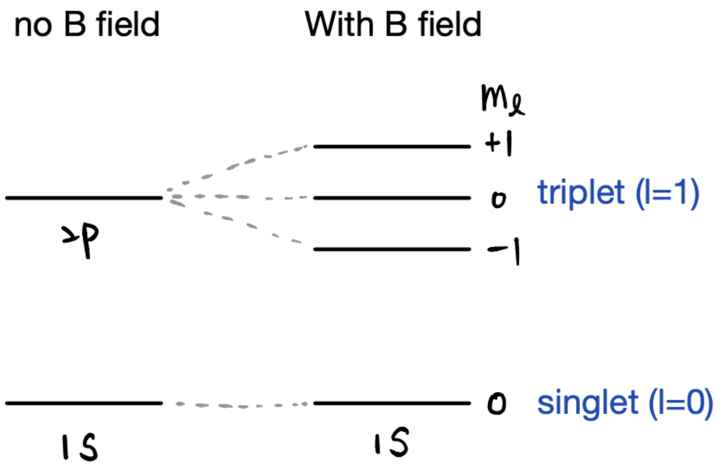

Figure 15.3: Zeeman spliting.

For the hydrogen atom under a 1T(tesla) magnetic field, the splitting is $\simeq 9.274\times 10^{-24}J$. Compare to the $1s \to 2p$ transition energy $\simeq 1.63 \times 10^{-18}J$, the ratio is $\simeq 5.69 \times 10^{-6}$, very small value. (Which means that it is hard to detect.)

As we have just reviewed, we have considered many aspects of the Hamiltonian and eigenfunctions for hydrogen-like atoms, but there is still a big piece missing!$\Rightarrow$ electron spin!

15.3 Electron Spin

The electron has two spin states; we say that the electron is a spin-1/2 system. The electron spin occurs naturally in the relativistic equation for the quantum mechanics $\to$ called the Dirac equation. The Dirac equation is out of the scope of this class. Since we only consider the non-relativistic version of quantum mechanic, i.e. the Schrödinger equation. So at here, the electron spin has to be treated as an additional postulate. Note that this is ”okay” since many experimental results support the existense of electron spins. Most notably:

- The periodic table.
- Finite structure of atoms.

- Stem-Gerlach experiment.

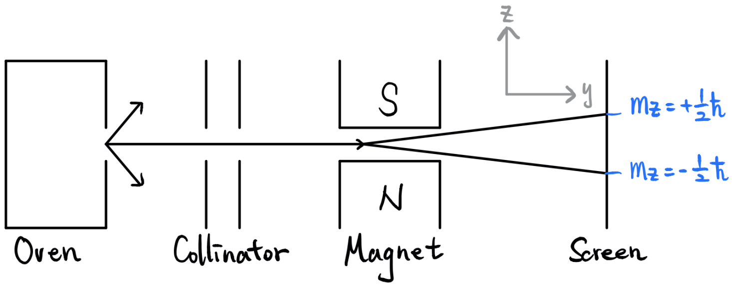

Figure 15.4: Stem-Gerlach experiment.

Since there is no classical analogue of it, we directly postulate:

> An electron has an intrinsic spin angular momentum, with the spin quantum number $S = 1/2$.

Using the term "angular momentum" could be misleading, but there is a reason for it.

Note that the electron spin is not angular momentum of electron actually spining.

Recall that for rotational motions, even on a plane defined by $\hat{L}_z$, the cyclic boundary condition requires $m_l = 0, \pm 1, \pm 2, \cdots \Rightarrow$ rotational motions cannot give $m_l = \frac{1}{2}$! So why say "angular momentum"? This is because we can define the spin angular momentum operator $\hat{S}$, which follows all the operator rules for angular momentum $\hat{L}$. Therefore, we can define $\hat{S}^2$ and $\hat{S}_z$, and then consider their shared eigenfunctions.

Electron spin looks like $l = \frac{1}{2}(S = \frac{1}{2}$ angular momentum!

For a single spin, the spin quantum number is $S = \frac{1}{2}$, and there are two possible eigenstates for $\hat{S}_z$, usually denotes as $|+\rangle, |-\rangle$ or $|\alpha\rangle, |\beta\rangle$.

$$\hat{S}_z \alpha(s) = \frac{1}{2}\hbar\alpha(s), \tag{15.9}$$

$$\hat{S}_z \beta(s) = -\frac{1}{2}\hbar\beta(s), \tag{15.10}$$

$\alpha(s)$ and $\beta(s)$ are spin eigenfunctions and s is spin variable. In addition,

$$\hat{S}^2\alpha(s) = \hat{S}^2\beta(s) = S(S+1)\hbar^2 = \frac{3}{4}\hbar^2. \tag{15.11}$$

So

$$|\langle S\rangle| = \frac{\sqrt{3}}{2}\hbar. \tag{15.12}$$

S denotes magnitude of spin angular momentum.

A complete assignment of the state of an electron in a hydrogen-like atom thus requires the inclusion of the spin state, i.e.

$$\Psi_{n,l,m_l,m_s} = R_{nl}(r)Y_l^m(\theta,\phi)f_{m_s}(s) \tag{15.13}$$

We call the orbital not including the spin part "spatial orbital" and those including the spin part "spin orbital".

Physically, electron also interacts with magnetic fields; we define spin magnetic dipole moment for electron:

In fact, spins are magnetic moment of the electron. It is the magnetic properties of electron and it will show up naturally when we consider relativistic effect. Note that in classical electromagnetism, the transformation between electron field and magnetic fied is due to relativistc effect(Lorentz transformation).

$$\hat{\mu_s} = -\frac{g_e e}{2m_e}\hat{S} = -\frac{g_e\mu_B}{\hbar}\hat{S}, \tag{15.14}$$

g_e is electron g factor(dimensionless magentic momentum). Thus, for spin $\hat{\mu}_z$

$$\hat{\mu_z} = \frac{-g_e\mu_B}{\hbar}\hat{S}_z. \tag{15.15}$$

So, the full Hamiltonian for a hydrogen-like atom with electron spin in a magnetic field:

$$\begin{aligned}\hat{H} &= \hat{H}_0 + \frac{\mu_B B}{\hbar}\hat{L}_z + \frac{g_e\mu_B B}{\hbar}\hat{S}_z \\ &= \hat{H}_0 + \frac{\mu_B B}{\hbar}(\hat{L}_z + g_e\hat{S}_z),\end{aligned} \tag{15.16}$$

note that $g_e = 2.002322 \simeq 2$.
By the fact:

$$\left[\hat{H}_0, \hat{L}_z\right] = \left[\hat{H}_0, \hat{S}_z\right] = 0, \tag{15.17}$$

the hydrogen-like orbitals still are good eigenfunctions, therefore:

$$\hat{H}\psi_{n,l,m_l,m_s} = \left[E_n + \mu_B B(m_l + g_e m_s)\right]\psi_{n,l,m_l,m_s}. \tag{15.18}$$

Consider 1s and 2p orbitals:

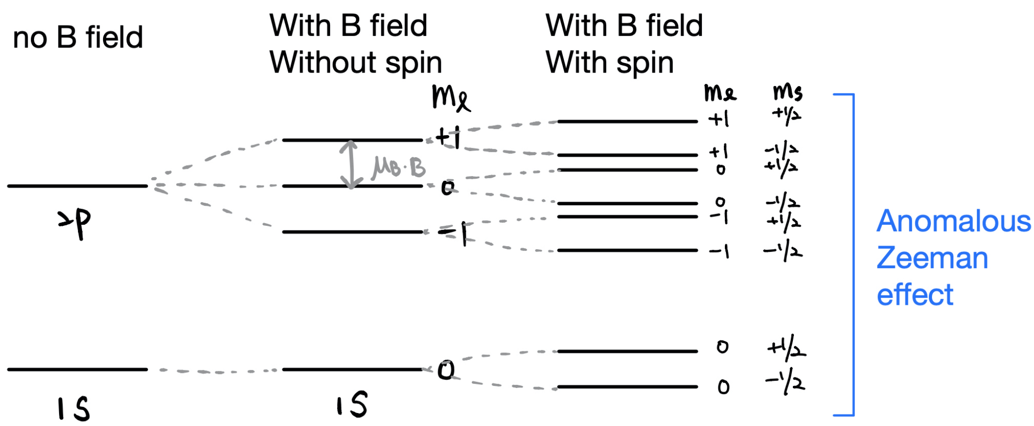

Figure 15.5: Energy splitting for considering electron spin.

The splitting due to electron spin is also called "Anomalous Zeeman effect".

There still other additional terms can be included in the Hamiltonian, including:

- Spin-orbit coupling(also a relativistic effect described in the Dirac equation); L-S coupling ⇒ fine structure in the atomic spectrum.
- Electron-nucleus spin-spin coupling; L-S-I coupling ⇒ hyperfine structures.

These are more complicated effect. To some extend, the hydrogen Hamiltonian that we considered is approximated. But, note that these effects are very small! (For fine structure term, it is 10^4 times smaller than H_0 and the hyperfine structure is 2000 times smaller than L-S term. This is because the magnetic interaction are intincially smaller than electrostatic interactions.)