

## Chapter 3: Addition of angular momenta and magnetic effects

### 3.1 Magnetic Moments and Electron Spin

### 3.2 The Angular Momentum Addition Theorem

### 3.3 Spin–Orbit Interaction

### 3.4 Magnetic Energy

In this chapter, we delve deeper into the properties of hydrogen-like atoms, focusing primarily on their magnetic characteristics. This includes their response to external magnetic fields and the interaction of the electron with the nucleus's magnetic field. We will introduce the concept of electron spin, examine the crucial angular momentum addition theorem, and utilize the time-independent perturbation theory you studied last semester to analyse the effects of these additional interactions on hydrogen-like atoms.

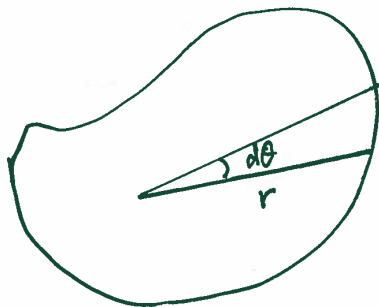
### 3.1 Magnetic moment and electron spin

A small loop of area  $A$  carrying a current  $I$  will produce a magnetic field. We define a magnetic moment

$$\boldsymbol{\mu} = I\mathbf{A},$$

where  $\mathbf{A}$  is the area vector normal to the plane of the loop. We can in fact express this magnetic moment in term of the angular momentum  $\mathbf{L}$  as follows.

Assume the current loop is due to the motion of an electron, we have  $I = -e/T$  with the period  $T$ . The magnitude of the area (as shown in the figure) is given by the integral



$$A = \int_0^{2\pi} \frac{1}{2} r^2 d\theta = \int_0^T \frac{1}{2} r^2 \frac{d\theta}{dt} dt.$$

In terms of the orbital angular momentum  $L$  of the electron,

$$\frac{1}{2} r^2 \frac{d\theta}{dt} = \frac{L}{2m_e},$$

where  $m_e$  is the electron's mass. Hence

$$A = \int_0^T \frac{L}{2m_e} dt = \frac{LT}{2m_e} \quad \text{or} \quad \mathbf{A} = \frac{T}{2m_e} \mathbf{L}.$$

The magnetic moment of the current loop is therefore given by

$$\boldsymbol{\mu} = I\mathbf{A} = -\frac{e}{2m_e}\mathbf{L}.$$

We therefore have the magnetic moment operator in QM as

$$\hat{\boldsymbol{\mu}} = -\frac{e}{2m_e}\hat{\mathbf{L}}. \quad (1)$$

Hence the  $z$  component is

$$\hat{\mu}_z = -\frac{e}{2m_e}\hat{L}_z, \quad \text{with eigenvalues} \quad -\frac{e\hbar}{2m_e}m_l, \quad (2)$$

where  $m_l (= 0, \pm 1, \pm 2, \dots, \pm l)$  is the quantum number of  $\hat{L}_z$ . The unit of magnetic moment, called Bohr magneton,

$$\mu_B = \frac{e\hbar}{2m_e} = 9.3 \times 10^{-24} \text{ J T}^{-1}. \quad (3)$$

Historically, the magnetic moments of atoms were first measured in the Stern-Gerlach experiment. A beam of atoms is fired through an inhomogeneous magnetic field, created by a shaped permanent magnet, see the diagram below. A neutral particle would not be bent by a constant magnetic field, but in a gradient  $\partial B_z/\partial z$  a particle with a magnetic dipole moment  $\mu$  is bent by a force

$$F_z = \mu_z \frac{\partial B_z}{\partial z}.$$

Classically, for atoms of a given total angular momentum  $|\mathbf{L}|$ , one would expect a range of results with  $L_z$  between  $\pm|\mathbf{L}|$ . Instead, a set of spots was observed, corresponding to  $L_z$  values  $m_l\hbar$ ,  $|m_l| \leq l$ . The first important result of the Stern-Gerlach experiment was the fact that angular momentum is indeed quantized. There are many nice variants one can do; for example, by making several measurements along different axes, one can test their incompatibility and the fact that measuring the angular momentum along the  $x$  axis, destroys information about the angular momentum along the  $z$  axis.

The second important result of the Stern-Gerlach experiment was that the details of the magnetic moments measured did not fit the pattern predicted by  $\mu_z = -\mu_B L_z/\hbar$ . In particular, it was found that even electrons in  $s$  orbitals ( $l = 0$ ) have a magnetic moment. Eventually, understanding the pattern of results for different atoms, resulted in the discovery that electrons have a fundamental property (like charge or mass) which we call intrinsic angular momentum or "spin".

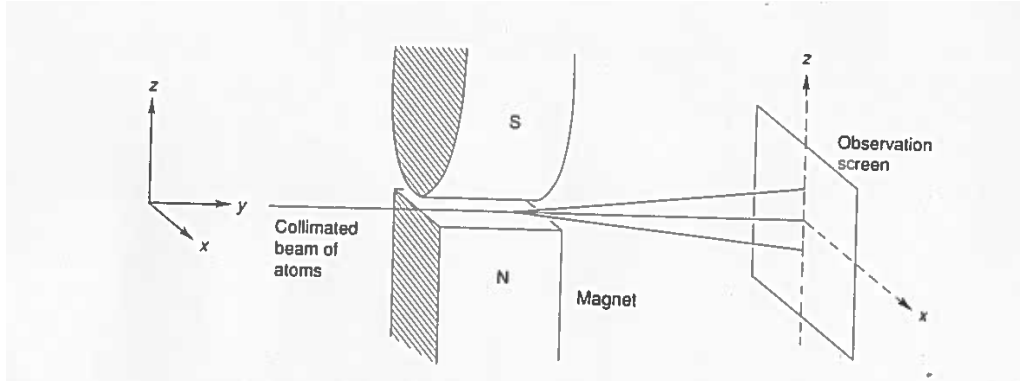


Figure 1: Schematic diagram of the Stern-Gerlach apparatus (copy from F Mandl's *Quantum Mechanics*, page 46).

All electrons have a spin quantum number  $s = 1/2$ , with all other properties defined by analogy with orbital angular momentum:

$$\text{Eigenvalues of } \hat{S}^2 : s(s+1)\hbar^2;$$

$$\text{Eigenvalues of } \hat{S}_z : m_s\hbar, \quad \text{with } m_s = -s, -s+1, \dots, s-1, s.$$

However, the magnetic moment is not given by  $\mu_z = -\mu_B m_s$ , as would be expected classically, but rather by

$$\mu_z = -g\mu_B m_s, \quad (4)$$

where  $g$  is called the gyromagnetic ratio. It is one of the best measured quantities in physics, with a value  $g = 2.0023\dots$  known to better than 10 significant figures. For the purposes of this course, however, we will define it to be  $g = 2$ . Eventually, a variant of the Stern-Gerlach experiment used an electric field to counteract the Lorentz force on an electron and was able to measure the spin of free electrons directly, in agreement with the value of  $g \approx 2$ .

Now we know the electron in a Hydrogen atom has also spin degree of freedom, we need to include it in the complete description of hydrogen state. Therefore the complete set of quantum numbers for a Hydrogen state is now given by  $(n, l, m_l, m_s)$ , with the new quantum number  $m_s = \pm 1/2$  for the  $z$  component of the spin operator  $\hat{S}_z$ . The usual notation for the electron spin wave function is  $\chi_{\pm}$ :

$$\hat{S}_z \chi_{\pm} = \pm \frac{\hbar}{2} \chi_{\pm}. \quad (5)$$

Another popular notation is  $\chi_{\uparrow, \downarrow}$ , obviously indicating the spin-up ( $m_s = 1/2$ ) or spin-down ( $m_s = -1/2$ ) state. A complete wave function for a Hydrogen atom can

be written as the product of the orbital wave function  $\psi_{n,l,m_l} = R_{nl}(r)Y_{lm}(\theta, \phi)$  and the spin wave function  $\chi_{m_s}$

$$\Psi_{n,l,m_l,m_s} = \psi_{n,l,m_l}\chi_{m_s}, \quad (6)$$

with the complete set of good quantum numbers  $(n, l, m_l, m_s)$  of the hydrogen wave function. In Dirac notation, this corresponds to the state  $|n, l, m_l, m_s\rangle$ . You may also recall the matrix representation of the spin operator  $\hat{S}_z$  and the spin state  $|m_s\rangle \rightarrow \chi_{m_s}$ . For all our purposes in this course, we only need to know the values of the quantum number, namely  $m_s = \pm 1/2$ .

### 3.2 Angular momentum addition theorem

In the previous section we saw that an electron's intrinsic angular momentum must be added to its orbital angular momentum to give its total angular momentum,

$$\hat{J} = \hat{L} + \hat{S}.$$

We will see that this is a special case of a more general theorem for combining any two sources of angular momentum.

In this subsection we discuss the addition of two angular momenta  $\mathbf{L}_1$  and  $\mathbf{L}_2$ , of a two particle system or a single particle with two independent angular momenta such as the orbital angular momentum and the spin as mentioned above. We denote the total angular momentum as

$$\hat{\mathbf{J}} = \hat{\mathbf{L}}_1 + \hat{\mathbf{L}}_2. \quad (7)$$

The components  $\hat{J}_x, \hat{J}_y, \hat{J}_z$  and  $\hat{J}^2$  obey the usual commutation rules of angular momentum operators discussed before. Namely

$$\begin{aligned} [\hat{J}_x, \hat{J}_y] &= i\hbar\hat{J}_z, \\ [\hat{J}_y, \hat{J}_z] &= i\hbar\hat{J}_x, \\ [\hat{J}_z, \hat{J}_x] &= i\hbar\hat{J}_y, \\ [\hat{J}^2, \hat{J}_z] &= 0. \end{aligned}$$

Hence we have the usual eigenvalues for angular momentum operators  $\hat{J}^2$  and  $\hat{J}_z$  as

$$\begin{aligned} \text{Eigenvalues of } \hat{J}^2 &: j(j+1)\hbar^2; \\ \text{Eigenvalues of } \hat{J}_z &: m_j\hbar, \quad \text{with } m_j = -j, -j+1, \dots, j-1, j, \end{aligned}$$

with the corresponding quantum numbers  $j$  and  $m_j$  respectively.

**But how to find  $j$ ?**

Let us consider the possible values of  $m_j$ . The largest value it can have is  $m_j = l_1 + l_2$ , the smallest is  $m_j = -l_1 - l_2$ , and it can have all integer-spaced values in between. Therefore it could be that  $j = l_1 + l_2$ .

However,  $m_j = l_1 + l_2 - 1$  can be made in two different ways,  $m_j = l_1 + l_2 - 2$  can be made in three different ways, and so on. But from  $j = l_1 + l_2$ , each  $m_j$  is only covered once.

It must be that the combination  $j = l_1 + l_2 - 1$  (with  $m_j = -j, \dots, j$ ) is also possible. And also  $j = l_1 + l_2 - 2$ , and so on.

In the end we conclude:

**Addition Theorem:** States with  $l_1$  and  $l_2$  combine to give a set of states with

$$j = l_1 + l_2, l_1 + l_2 - 1, \dots, |l_1 - l_2|. \quad (8)$$

**Example:** Show that the total number of the states of the total angular momentum described by  $(j, m_j)$  is precisely equal to  $(2l_1 + 1)(2l_2 + 1)$ .

**Proof:** Assume  $l_1 > l_2$ . We list all terms as follows,

$j$	no. of $m_j = 2j + 1$
$l_1 + l_2$	$2(l_1 + l_2) + 1$
$l_1 + l_2 - 1$	$2(l_1 + l_2 - 1) + 1$
$l_1 + l_2 - 2$	$2(l_1 + l_2 - 2) + 1$
$\dots$	$\dots$
$l_1 + l_2 - 2l_2$	$2(l_1 + l_2 - 2l_2) + 1$

There are  $(2l_2 + 1)$  lines. Sum all the numbers of possible  $m_j$  values to give the total number of states as

$$\begin{aligned}
& 2[(l_1 + l_2)(2l_2 + 1) - (1 + 2 + 3 + \dots + 2l_2)] + (2l_2 + 1) \\
& = 2[(l_1 + l_2)(2l_2 + 1) - (2l_2)(2l_2 + 1)/2] + (2l_2 + 1) \\
& = [2(l_1 + l_2) - (2l_2)/2 + 1](2l_2 + 1) \\
& = (2l_1 + 1)(2l_2 + 1).
\end{aligned}$$

Notice that the eigenfunctions of  $\hat{J}^2$  and  $\hat{J}_z$  are in general given by linear combinations of the eigenfunctions of  $\hat{L}_1^2$  and  $\hat{L}_2^2$  with the coefficients known as Clebsch-Gordan coefficients, which you can find tabulated in many textbooks. For all our purposes in this course we do not need to know the details of these linear combinations.

**Example:** A hydrogen atom is in the  $(3d)$  orbital. Determine its possible  $j$  values.

**Solution:** For the (3d) orbital,  $l = 2$ . Hence the possible values of  $j$  of the hydrogen are:  $j = 2 + 1/2 = 5/2$ , and  $2 - 1/2 = 3/2$ .

**Home Exercise:** Enumerate all possible values of the total angular momentum quantum number  $j$ , for  $l_1 = 2$  and  $l_2 = 3$ , where  $\hat{\mathbf{J}} = \hat{\mathbf{L}}_1 + \hat{\mathbf{L}}_2$ .

### 3.3 Spin-orbit interaction

Since the electron of a hydrogen carries an intrinsic magnetic moment, it will interact with the magnetic field due to the nucleus (in the rest frame of the electron, the proton is moving around hence produces a magnetic field). This magnetic field is proportional to the orbital angular momentum hence the we have an additional (relativistic) term in the Hamiltonian of a Hydrogen atom as

$$V_{\text{SO}} = f(r)\mathbf{L} \cdot \mathbf{S}, \quad (9)$$

where  $f(r)$  depends only on the magnitude of  $\mathbf{r}$ . We leave the details to year 3 and just quote  $f(r)$  as

$$f(r) = \frac{1}{2m_e^2 c^2} \frac{1}{r} \frac{dV(r)}{dr} = \frac{e^2}{8\pi\epsilon_0 m_e^2 c^2 r^3}$$

with Coulomb attraction potential  $V(r)$  for the electron. Note the factor of  $1/c^2$ , which shows clearly that this is a relativistic effect.

In quantum mechanics, we can simply promote each of the variables in  $V_{\text{SO}}$  to operators:

$$\hat{H} = \hat{H}_0 + \hat{V}_{\text{SO}} = \hat{H}_0 + f(r)\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \quad (10)$$

where  $\hat{H}_0$  is the hydrogen Hamiltonian already studied and  $\hat{V}_{\text{SO}}$  is referred as the spin-orbit coupling. It is important in physics of atoms, molecules and solids, and now plays a central role in two-dimensional topological materials in the current research. Thomas (1926) first derived this formula using Bohr model, Schrödinger quantum mechanics and relativistic kinematics, in complete agreement with the result of the relativistic quantum mechanics of Dirac.

To get an idea of the expected size of this effect, we can estimate  $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \sim \hbar^2$ , and  $r \sim a_0$  (the Bohr radius),

$$\langle \hat{V}_{\text{SO}} \rangle \sim 10^{-3} \text{ eV}.$$

This is much smaller than the spacing between hydrogen energy levels (about a few eV), so we can reliably use first order perturbation theory to calculate them, but it is large enough to be observed. In fact, the effects we will calculate to what is called the 'fine structure' of the atom.

But now we have a major complication:  $\hat{L}_z$  no longer commutes with  $\hat{H}$  of Eq. (10) (it is no longer a central potential). Therefore, states of definite  $L_z$  will no longer be

stationary states and  $m_l$  will not be a good quantum number. The same goes for  $S_z$  and  $m_s$ .

Will we be able to find some other good quantum numbers that describe stationary states of the atom?

Let us try the total angular momentum,  $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ . Squaring it

$$\hat{J}^2 = \hat{L}^2 + 2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} + \hat{S}^2,$$

hence

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2} (\hat{J}^2 - \hat{L}^2 - \hat{S}^2).$$

Therefore, if we are in a definite state of  $J^2, L^2$  and  $S^2$ , then

$$\langle \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \rangle = \frac{1}{2} [j(j+1) - l(l+1) - s(s+1)]. \quad (11)$$

**Exercise:** use the commutation relations of  $\hat{L}$  and  $\hat{S}$  to show that  $\hat{J}^2$ ,  $\hat{L}^2$  and  $\hat{S}^2$  all commute with each other (therefore also with  $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ ), and that  $\hat{J}_z$  commutes with all three, but that  $\hat{L}_z$  and  $\hat{S}_z$  do not.

On this basis, we conclude that  $n$ ,  $l$ ,  $j$  and  $m_j$  are good quantum numbers (but that  $m_l$  and  $m_s$  are not).

**Example:** Assume that a hydrogen atom is in  $(3d)$  state. Determine the energy level splitting due to the spin-orbit coupling.

**Solution:** For the  $(3d)$  state,  $l = 2$ . By the angular momentum theorem, there are two possible values,  $j = 5/2$  and  $j = 3/2$ . The energy shifts/splitting are given by

$$\Delta E = \langle \hat{V}_{\text{SO}} \rangle = \begin{cases} \frac{1}{2} \langle f(r) \rangle \times 2\hbar^2, & \text{for } j = \frac{5}{2}; \\ -\frac{1}{2} \langle f(r) \rangle \times 3\hbar^2, & \text{for } j = \frac{3}{2}, \end{cases}$$

where the integral involving only the radial part of the wave function

$$\langle f(r) \rangle = \int_0^\infty R_{3,2}^*(r) f(r) R_{3,2}(r) r^2 dr.$$

**Home Exercise:** Study the energy level splitting of a hydrogen atom in the  $2n$  state due to the spin-orbit coupling. Note that the  $n = 2$  level has two orbitals: the  $2s$  orbital with  $l = 0$  and the  $2p$  orbital with  $l = 1$ . You need to consider the energy shift for both of them. See Example3, Q4.

### 3.4 Magnetic energy: the Zeeman effects



Classically, a magnetic dipole  $\mu$  in a magnetic field  $\mathbf{B}$  in the  $z$  direction has energy  $-\mu \cdot \mathbf{B}$ , so we have a perturbation to our Hamiltonian

$$\hat{V}_{\text{mag}} = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B} = -B\hat{\mu}_z = -B(\hat{\mu}_{z,L} + \hat{\mu}_{z,S}) = \frac{eB}{2m_e} (\hat{L}_z + g\hat{S}_z) . \quad (12)$$

Recall that  $g$  is the gyromagnetic ratio of the electron, which we will take to be 2.

To estimate the size of this effect, we can again estimate that the angular momenta are of order  $\hbar$  and obtain

$$\Delta E_{\text{mag}} \sim \frac{e\hbar B}{2m_e} \approx 9.3 \times 10^{-24} \text{ J} \approx 5.8 \times 10^{-5} \text{ eV T}^{-1} \times B .$$

Therefore, these energy shifts will be of the same order of magnitude as the spin-orbit splitting if  $B \sim 1 \text{ T}$ .

If we wish to use first-order perturbation theory, it is a problem for the two effects to be of a similar size – we would prefer to think of one of them as a small perturbation to the other. We therefore distinguish:

- the strong Zeeman effect,  $B \gg 1 \text{ T}$ : the spin-orbit interaction is a small correction to the magnetic energy;
- the weak Zeeman effect,  $B \ll 1 \text{ T}$ : the magnetic energy is a small correction to the spin-orbit interaction.

Both are named after Dutch physicist Pieter Zeeman, who discovered them experimentally. smaller by a factor of 10 than that of the spin-orbit coupling estimated earlier. We can certainly apply the first order PT for its effects.

**Strong Zeeman effect:** If the magnetic field is strong enough, the spin-orbit interaction is a small correction to the magnetic energy. We can therefore calculate the magnetic energy as a perturbation of the unperturbed hydrogen orbitals:

$$\langle \hat{V}_{\text{mag}} \rangle = \mu_B B (m_l + 2m_s) . \quad (13)$$

Since  $m_l$  and  $m_s$  are good quantum numbers of the unperturbed atom, this is straightforward to calculate, see example below.

**Weak field Zeeman effects:** If the magnetic field is weak enough, the magnetic energy is a small correction to the spin-orbit interaction. We therefore have to start from the states described by the good quantum numbers of the spin-orbit interaction,  $j$  and  $m_j$ . We write

$$\langle \hat{V}_{\text{mag}} \rangle = \frac{\mu_B B}{\hbar} (\langle \hat{L}_z \rangle + 2\langle \hat{S}_z \rangle) = \frac{\mu_B B}{\hbar} (\langle \hat{J}_z \rangle + \langle \hat{S}_z \rangle) . \quad (14)$$

with  $\hat{J}_z = \hat{L}_z + \hat{S}_z$ . The first term is straightforward, since  $m_j$  is a good quantum number,  $\langle \hat{J}_z \rangle = m_j \hbar$ . The second term is more involved, and we just quote its result:

$$\langle \hat{S}_z \rangle = \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} m_j \hbar.$$

We therefore have

$$\langle \hat{V}_{\text{mag}} \rangle = g_L \mu_B B m_j, \quad (15)$$

where  $g_L$  is the Landé  $g$  factor defined by

$$g_L = 1 + \frac{j(j+1) + 3/4 - l(l+1)}{2j(j+1)}. \quad (16)$$

There are some exercises of the weak-field Zeeman effects in Examples 4, where you only need to use the above formulas to calculate the energy shift  $\Delta E = \langle \hat{V}_{\text{mag}} \rangle$ .

**Example:** A hydrogen atom in the ( $3d$ ) orbital is placed in a strong magnetic field of magnitude  $B$ . Sketch the energy level splitting and labeled with appropriate quantum numbers.

**Solution:** For the ( $3d$ ) state,  $l = 2$ . So  $m_l = 2, 1, 0, -1, -2$ . The spin always has  $m_s = \pm 1/2$ . Therefore,  $(m_l + 2m_s)$  gives seven different values as listed in Fig. 2. The energy level spacing is given by the magneton energy  $\mu_B B$ . We notice that the middle three levels are doubly degenerate.

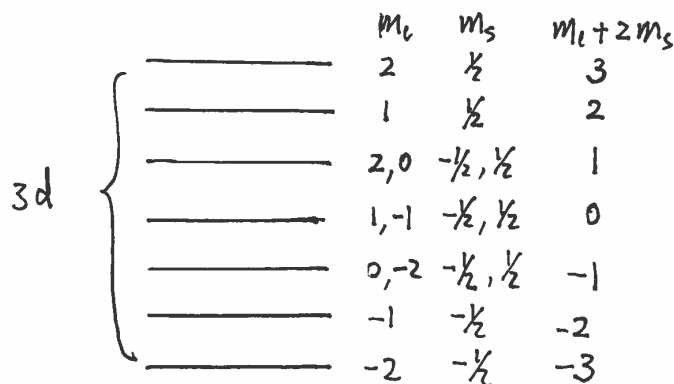


Figure 2: The ( $3d$ ) orbital splitting of hydrogen atom in presence of a strong magnetic field with the energy spacing  $\mu_B B$ .

### Summary of Chapter 3

- An electron in an orbital with angular momentum  $\mathbf{L}$  gives a magnetic moment  $\mu = -\frac{e}{2m_e}\mathbf{L}$ .
- In particular, any component of magnetic moment is quantized in integer steps of  $\mu_B = \frac{e\hbar}{2m_e}$ , the Bohr magneton.
- The Stern-Gerlach experiment separates out different values of  $\mu_z$  using an inhomogeneous magnetic field.
- Electrons have internal angular momentum ("spin") with  $s = 1/2$ ; and in general  $S^2 = s(s+1)\hbar^2$ ,  $S_z = m_s\hbar$ ,  $m_s = -s, \dots, s$ .
- Electrons have magnetic moment  $\mu_z = -g\mu_B m_s$ , where  $g \approx 2$ .
- Two sources of angular momentum (e.g. orbital and internal, or of two electrons in different orbitals) with  $\mathbf{J} = \mathbf{L}_1 + \mathbf{L}_2$  can be combined:  $j$  values in integer steps from  $|l_1 - l_2|$  to  $l_1 + l_2$  are allowed, with  $m_j = -j, \dots, j$  for each  $j$ .
- Hydrogen energy levels splitting in a strong field:  $\langle \hat{V}_{mag} \rangle = \mu_B B(m_l + 2m_s)$ .
- Hydrogen energy levels splitting due in a weak field:  $\langle \hat{V}_{mag} \rangle = g_L \mu_B B m_j$ .