

# **Condensed Matter Physics**

Prof. F. D'Orazio, a.a. 2025-26

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**Part I**

**Atomic Physics**



## Chapter 1

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# Lecture 22/09

## §1.1 Mono-atomic atoms

To describe a mono-electron atom, consider the Schrödinger equation for a single-particle quantum system:

$$\mathcal{H}\psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (1.1)$$

where the Hamiltonian can be written as:

$$\mathcal{H} = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) \quad (1.2)$$

A particularly interesting case is that of a spherically-symmetric potential  $V(\mathbf{r}) = V(r)$ . This allows for a separation of variables of the kind  $\psi(\mathbf{r}) = R(r)Y(\vartheta, \varphi)$ : the angular part is uniquely determined, as it is not affected by the potential, and is given by the **spherical harmonics**:

$$\psi_{n,\ell,m}(\mathbf{r}) = R_{n,\ell}(r)Y_{\ell,m}(\vartheta, \varphi) \quad (1.3)$$

A quantization of the wave-functions has appeared, with three quantum numbers  $n, \ell, m$ : note that the energy eigenvalue  $E = E_{n,\ell}$  does not depend on  $m$ . In the specific case of the mono-electron atom:

$$V(\mathbf{r}) = -\frac{Ze^2}{r}$$

and the radial solutions are given by the Laguerre polynomials, while the energy eigenvalues are the **Bohr energies** (expressed in terms of the Rydberg energy):

$$E_n = -\frac{Z^2 E_R}{n^2} \quad E_R \equiv \frac{me^4}{2\hbar^2} \simeq 13.6 \text{ eV} \quad (1.4)$$

These solutions contains several approximations: the mass of the electron is assumed negligible with respect to the mass of the nucleus (since  $m_e/m_p \sim 2000$ ) and both the electron's spin and the relativistic effects of its motion (which have the same order of magnitude) have been ignored.

### §1.1.1 Stern-Gerlach experiment

The Stern-Gerlach experiment has proved the existence of the electron's spin. Consider the  $^{47}\text{Ag}$  atom, which has the ground state configuration  $[\text{Kr}]4\text{d}^{10}5\text{s}^1$ : full shells do not contribute to the orbital angular momentum, hence the ground state of  $^{47}\text{Ag}$  has  $L = 0$ . As we can associate a magnetic moment<sup>1</sup> to an electron orbiting around a nucleus, we can study the angular

momentum of  $^{47}\text{Ag}$  using a magnetic field: classically  $E = -\boldsymbol{\mu} \cdot \mathbf{B}$ , but quantistically  $\boldsymbol{\mu}$  is an operator, so we have to consider its expectation value.

**Lemma 1.1.1 (Expectation value of  $\boldsymbol{\mu}$ )**

$$\langle \mu_x \rangle = \langle \mu_y \rangle = 0 \quad (1.6)$$

*Proof.* Since  $\langle \boldsymbol{\mu} \rangle \propto \langle \boldsymbol{\ell} \rangle$ , WTS  $\langle \ell_x \rangle = \langle \ell_y \rangle = 0$ . Recall the action of the raising and lowering operators on the spherical harmonics:

$$\ell_{\pm} |Y_{\ell,m}\rangle = c_{\ell,m} |Y_{\ell,m\pm 1}\rangle \quad c_{\ell,m} = \hbar \sqrt{\ell(\ell+1) - m(m \pm 1)} \quad (1.7)$$

with an abuse of notation. By direct calculation:

$$\langle \ell_{\pm} \rangle \equiv \langle Y_{\ell,m} | \ell_{\pm} | Y_{\ell,m} \rangle = c_{\ell,m} \langle Y_{\ell,m} | Y_{\ell,m\pm 1} \rangle = 0$$

by the orthonormality of the spherical harmonics. Now, consider that:

$$\ell_x = \frac{\ell_+ + \ell_-}{2} \quad \ell_y = \frac{\ell_+ - \ell_-}{2i}$$

This shows that  $\langle \ell_x \rangle = \langle \ell_y \rangle = 0$ . □

By carefully orienting the magnetic field, then,  $E = -\mu_z B_z$ , thus each atom is subjected to a force given by:

$$\mathbf{F} = \mu_z \nabla B_z$$

The magnetic field is constructed in such a way that it is well-collimated with the axis of the experimental apparatus, hence  $\partial_x B_z = 0$  and  $\partial_y B_z \approx 0$ , and the force to be measured is  $F_z = \mu_z \partial_z B_z$ . Assuming that  $\partial_z B_z$  is constant and known for the apparatus, the atoms follow parabolic trajectories on the  $z$ -axis dependent on  $\mu_z$ .

Since  $L = 0$  for the ground state of  $^{47}\text{Ag}$ , there should be only one observed outgoing trajectory corresponding to  $F_z = 0$ , but two parabolic trajectories are observed instead: this proves the existence of an additional intrinsic angular momentum in the valence electron, i.e. the spin, which has two quantized values, i.e.  $s = \pm \frac{1}{2}$ . Moreover, this experiment also allows us to compute the **Landé factor** for the spin<sup>2</sup>, which is found to be  $g_s = 2$ , i.e.:

$$\mu_s = -2 \frac{\mu_B}{\hbar} s \quad (1.8)$$

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<sup>1</sup>By the correspondence principle of Quantum Mechanics, we can associate to the classical magnetic moment for an electron with orbital angular momentum  $\boldsymbol{\ell}$  a quantum analogous:

$$\boldsymbol{\mu} = \frac{e}{2m_e} \boldsymbol{\ell} \equiv -\frac{\mu_B}{\hbar} \boldsymbol{\ell} \quad \mu_B \equiv \frac{e\hbar}{2m_e} \quad (1.5)$$

where  $\mu_B \simeq 5.7884 \cdot 10^{-5}$  eV/T is the **Bohr magneton**.

<sup>2</sup>To be precise, the Landé factor for the spin is computed in QED to be:

$$g_s = 2 \left[ 1 + \frac{\alpha}{2\pi} + o(\alpha^2) \right] \quad \alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} \quad (1.9)$$

where  $\alpha \simeq \frac{1}{137}$  is the **fine structure constant**.

### §1.1.2 Relativistic correction

Relativistic correction are found writing  $E = T + V$ , with  $T^2 = p^2c^2 + m^2c^4$ , and quantizing  $E \mapsto i\hbar\partial_t$  and  $\mathbf{p} \mapsto -i\hbar\nabla$ . By expanding  $T$  up to order  $p^4$ , the Hamiltonian of the system can be written as:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{rel}} \quad (1.10)$$

where  $\mathcal{H}_0$  is the Hamiltonian in Eq. 1.2 and  $\mathcal{H}_{\text{rel}}$  includes the relativistic corrections:

$$\mathcal{H}_{\text{rel}} = -\frac{p^4}{8m^3c^2} + \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV(r)}{dr} \boldsymbol{\ell} \cdot \mathbf{s} + \frac{\hbar^2}{8m^2c^2} \Delta V(r) \quad (1.11)$$

The first term is a kinetic correction, and it dominates for electrons closer to the nucleus (in particular s-electrons), while the third term (the **Darwin term**) can be rewritten as  $\Delta V(r) = e\Delta\phi(r) = 4\pi e\rho(r)$ , where  $\rho(r)$  is the charge distribution which generates the potential acting on the considered electron, i.e.  $\rho(r) = Ze\delta(r)$ : since  $E[\psi] = \langle\psi|\mathcal{H}_{\text{rel}}|\psi\rangle$ , this last term is non-vanishing only for s-electrons, as only  $R_{n,0}(r)$  is non-vanishing at  $r = 0$ . On the other hand, the second term is the **spin-orbit** term and is non-vanishing only for  $\ell \neq 0$ .

Denoting these terms by  $\mathcal{H}_1$ ,  $\mathcal{H}_2$  and  $\mathcal{H}_3$ , we can compute the corresponding energy corrections:

$$\Delta E_1 = \frac{Z^4 E_R \alpha^2}{n^3} \left( \frac{3}{4n} - \frac{1}{\ell + \frac{1}{2}} \right) \quad (1.12)$$

$$\Delta E_2 = \frac{Z^4 E_R \alpha^2}{n^3 \ell (\ell + 1) (\ell + \frac{1}{2})} [j(j+1) - \ell(\ell+1) - s(s+1)] \quad (1.13)$$

$$\Delta E_3 = \frac{Z^4 E_R \alpha^2}{n^3} \delta_{\ell,0} \quad (1.14)$$

where  $\mathbf{j} = \boldsymbol{\ell} + \mathbf{s}$  is the total angular momentum of the electron. These three corrections have the same order of magnitude, since they are all proportional to  $Z^4 E_R \alpha^2 / n^3$ , and can be combined in a single relativistic correction (using  $s = \frac{1}{2}$  for electrons):

$$\Delta E_{\text{rel}} = -\frac{Z^4 E_R \alpha^2}{n^4} \left( \frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \quad (1.15)$$

Note that the total angular momentum has quantized values  $|\ell - s| \leq j \leq \ell + s$ , hence the maximum value for  $j + \frac{1}{2}$  is  $\ell_{\max} + 1 = n$  and the relativistic correction is always negative.

This relativistic correction introduces a dependence of the energy eigenvalue on  $j$ , hence it induces a splitting of the previously-degenerate energy levels: this is the **fine-structure splitting**.

## **Chapter 2**

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# **Lecture 23/09**

Da recuperare, no registrazione: Lamb shift and alkali atoms.

## Chapter 3

# Lecture 29/09

### Example 3.0.1 (Sodium transitions)

Find the wavelength of the transitions  $4p \rightarrow 3s$  and  $4d \rightarrow 3p$  of sodium, knowing that  $\alpha_s = 1.35$ ,  $\alpha_p = 0.86$  and  $\alpha_d = 0.01$ .

*Solution.* Since Na is an alkali atom, the energy gap between two levels can be written in terms of the respective quantum defects as:

$$\Delta E = E_R \left[ \frac{1}{(n_1 - \alpha_{\ell_1})^2} - \frac{1}{(n_2 - \alpha_{\ell_2})^2} \right]$$

Then, defining the **Rydberg wavelength**  $\lambda_R \equiv \frac{hc}{E_R} \simeq 91.127 \text{ nm}$ , since  $\lambda = \frac{hc}{\Delta E}$  we get:

$$\lambda_{4p \rightarrow 3s} = 342.7 \text{ nm} \quad \lambda_{4d \rightarrow 3p} = 585.9 \text{ nm}$$

The first transition is UV, while the second transition is visible.

### Example 3.0.2 (Yellow doublet of sodium)

The yellow doublet of sodium consists of two lines  $\lambda_1 = 589.6 \text{ nm}$  and  $\lambda_2 = 589.0 \text{ nm}$  associated to the transitions of the valence electron from the first excited state to the ground state. Compute the spin-orbit constant and the effective charge  $Z_{\text{eff}}$  that should be assumed in the spin-orbit relation for mono-electron atoms.

*Solution.* For heavier atoms, the kinetic correction and the Darwin term become smaller, and the relativistic corrections are determined by the spin-orbit term, which can be written as:

$$\Delta E_{\text{s-o}} = \frac{\xi_{\ell,s}}{2} [J(J+1) - L(L+1) - S(S+1)]$$

In particular, the ground state  $3S$  remains unchanged, while the first excited state is split in  $3P_{1/2}$  and  $3P_{3/2}$ : since Na has a single valence electron, we expect  $\xi_{\ell,s} \geq 0$  like for H, hence  $3P_{1/2}$  is energetically closer to the ground state. Then,  $\lambda_1$  is associated to  $3P_{1/2} \rightarrow 3S_{1/2}$  and  $\lambda_2$  to  $3P_{3/2} \rightarrow 3S_{1/2}$ , and:

$$\frac{hc}{\lambda_2} - \frac{hc}{\lambda_1} = \frac{\xi}{2} \left[ \frac{3}{2} \left( \frac{3}{2} + 1 \right) - \frac{1}{2} \left( \frac{1}{2} + 1 \right) \right] = \frac{3}{2} \xi \quad \Rightarrow \quad \xi = \frac{2hc}{3} \left( \frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right) \approx 1.46 \text{ meV}$$

The mono-electron atom relation is Eq. 1.13, hence:

$$\xi_{\ell,s} = \frac{Z_{\text{eff}}^4 E_R \alpha^2}{n^3 \ell (\ell+1) (\ell+\frac{1}{2})} \quad \Rightarrow \quad Z_{\text{eff}} = \sqrt[4]{3^3 \cdot 1 \cdot 2 \cdot \frac{3}{2} \frac{\xi}{E_R \alpha^2}} \approx 3.56$$

## §3.1 X-ray spectra

For general multi-electron atoms, the energy eigenvalues for internal electrons can be empirically expressed by **Mosley's law**:

$$E_n \approx -\frac{E_R (Z - \alpha_n)^2}{n^2} \quad (3.1)$$

where  $\alpha_n$  are the screening constants determined by inner electrons (empirically  $\alpha_1 < \alpha_2 < \alpha_3 < \dots$ ). Since chemical bonds only affect valence electrons, at the first order of approximation, the energies of internal electrons should remain unperturbed independently of the state of the sample.

Transition between core states, i.e. electronic configurations with different internal electrons, are described by this notation: a hole in a shell  $n = 1, 2, 3, 4, \dots$  is denoted by  $K, L, M, N, \dots$ , while the difference  $\Delta n = 1, 2, 3, \dots$  is denoted by  $\alpha, \beta, \gamma, \dots$ . For example, the transition  $1s^1 2s^2 2p^6 \dots \rightarrow 1s^2 2s^2 2p^5$  is denoted by  $K_\alpha \equiv L \rightarrow K$ , while  $1s^2 2s^2 2p^5 3s^2 3p^6 4s^2 \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$  by  $L_\beta \equiv L \rightarrow N$ .

## §3.2 Multi-electron atoms

When accounting for multiple valence electrons, the potential is no longer spherically-symmetric. The corrections with respect to the unperturbed spherically-symmetric case are determined by the total angular momenta:

$$\mathbf{S} := \sum_i \mathbf{s}_i \quad \mathbf{L} := \sum_i \boldsymbol{\ell}_i \quad \mathbf{J} = \mathbf{L} + \mathbf{S} \quad (3.2)$$

This is the *Russell-Saunders coupling*: another possible coupling is the *jj coupling*, in which  $\mathbf{J} = \sum_i \mathbf{j}_i$ , which is more effective for heavier atoms where the spin-orbit interaction dominates the potential. The total orbital  $\mathbf{L}$  gives rise to non-central correction terms, while the total spin  $\mathbf{S}$  imposes conditions on the possible states due to the Pauli exclusion principles, which are linked to the swap integral.

The spin-orbit interaction splits the atomic states into multiplets (since  $S \neq \frac{1}{2}$  in general). For a multiplet with fixed  $L$  and  $S$ , the split levels are energetically separated by:

$$\Delta E(L, S) = \frac{\xi}{2} [(J+1)(J+2) - J(J+1)] = \xi (J+1)$$

A measurement of the ordering of these split levels can then determine if  $\xi > 0$  or  $\xi < 0$ , depending on whether the lowest state is that with lowest or highest total angular momentum.