

Condensed Matter Physics

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Part I

Atomic Physics

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:

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

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, ℓ, 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}Ag atom, which has the ground state configuration $[\text{Kr}]4d^{10}5s^1$: full shells do not contribute to the orbital angular momentum, hence the ground state of ^{47}Ag has $L = 0$. As we can associate a magnetic moment¹ to an electron orbiting around a nucleus, we can study the angular

momentum of ^{47}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:

$$\ell_x = \frac{\ell_+ + \ell_-}{2} \quad \ell_y = \frac{\ell_+ - \ell_-}{2i} \quad (1.8)$$

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

By carefully orienting the magnetic field, then, $E = -\mu_z B_z$, thus the 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 μ_z .

Since $L = 0$ for the ground state of ^{47}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 spin², which is found to be $g_s = 2$, i.e.:

$$\mu_s = -2 \frac{\mu_B}{\hbar} \mathbf{s} \quad (1.9)$$

¹By 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 $\mu_B \simeq 5.7884 \cdot 10^{-5} \text{ eV/T}$ is the **Bohr magneton**.

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

$$g_s = 2 \left[1 + \frac{\alpha}{2\pi} + o(\alpha^2) \right] \quad \alpha \equiv \frac{e^2}{4\pi\epsilon_0 \hbar c} \quad (1.10)$$

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:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{rel}} \quad (1.11)$$

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

$$\mathcal{H}_{\text{rel}} = -\frac{p^4}{8m^3c^2} + \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV(r)}{dr} \boldsymbol{\ell} \cdot \mathbf{s} + \frac{\hbar^2}{8m^2c^2} \Delta V(r) \quad (1.12)$$

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:

$$\Delta E_1 = \frac{Z^4 E_R \alpha^2}{n^3} \left(\frac{3}{4n} - \frac{1}{\ell + \frac{1}{2}} \right) \quad (1.13)$$

$$\Delta E_2 = \frac{Z^4 E_R \alpha^2}{n^3 \ell (\ell + 1) (\ell + \frac{1}{2})} [j(j+1) - \ell(\ell+1) - s(s+1)] \quad (1.14)$$

$$\Delta E_3 = \frac{Z^4 E_R \alpha^2}{n^3} \delta_{\ell,0} \quad (1.15)$$

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):

$$\Delta E_{\text{rel}} = -\frac{Z^4 E_R \alpha^2}{n^4} \left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \quad (1.16)$$

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 $\ell_{\text{max}} + 1 = n$ 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

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_{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, λ_1 is associated to $3P_{1/2} \rightarrow 3S_{1/2}$ and λ_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. 1.14, hence:

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

§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 α_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

In multi-electron atoms, the potential is no longer spherically-symmetric. The corrections with respect to the unperturbed spherically-symmetric case are determined by the total angular momenta:

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

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:

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

This is **Landé's spacing law**: note that this is symmetric under $L \leftrightarrow S$. 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.

Chapter 4

Lectures 30/09–03/10

Example 4.0.1 (Spectroscopic terms from level separation)

The separation between consecutive pairs of 3 atomic levels with spin-orbit coupling is in the ratio 3 : 5 with increasing energy. Determine the spectroscopic terms.

Solution. Since the levels are ordered in increasing energy, $\xi > 0$. Denoting the two energy intervals as ΔE_1 and ΔE_2 , then $\Delta E_2/\Delta E_1 = 5/3$ and, by Landé's spacing law:

$$\frac{\xi(J_{\min} + 2)}{\xi(J_{\min} + 1)} = \frac{5}{3} \implies J_{\min} = \frac{1}{2} \implies \begin{cases} |L - S| = \frac{1}{2} \\ L + S = \frac{5}{2} \end{cases}$$

where we set to zero the energy of the lowest state. The solutions are:

$$(2L, 2S) \in \{(2, 3), (3, 2)\}$$

Since $L \in \mathbb{N}_0$, the only acceptable solution is $L = 1, S = \frac{3}{2}$, hence the spectroscopic terms are ${}^4\text{P}_{1/2, 3/2, 5/2}$.

§4.1 Atoms in a magnetic field

When applying a magnetic field $\mathbf{B} \neq \mathbf{0}$, the conjugate momentum shifts as $\mathbf{P} \mapsto \mathbf{P} - q\mathbf{A}$, where q is the charge of the particle considered. Fixing the Coulomb gauge, the vector potential is uniquely defined by $\nabla \times \mathbf{A} = \mathbf{B}$ and $\nabla \cdot \mathbf{A} = 0$: for a constant magnetic field:

$$\mathbf{A}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times \mathbf{r} \quad (4.1)$$

Proposition 4.1.1 (Mono-electron Hamiltonian in constant magnetic field)

$$\mathcal{H} \simeq \mathcal{H}_0 - \boldsymbol{\mu} \cdot \mathbf{B} \quad (4.2)$$

Proof. For a mono-electron atom, the Hamiltonian becomes:

$$\mathcal{H} = \frac{1}{2m} (\mathbf{P} + e\mathbf{A})^2 - \frac{Ze^2}{r} = \frac{1}{2m} (-\hbar^2 \Delta - 2ie\hbar \mathbf{A} \cdot \nabla - i\hbar e \nabla \cdot \mathbf{A} + e^2 \mathbf{A}^2) - \frac{Ze^2}{r}$$

The third term in parentheses vanishes in the Coulomb gauge, while the last term is $\sim o(B^2)$,

hence we approximate it as negligible¹. Denoting the unperturbed Hamiltonian as \mathcal{H}_0 , then:

$$\mathcal{H} \simeq \mathcal{H}_0 - \frac{ie\hbar}{2m} (\mathbf{B} \times \mathbf{r}) \cdot \nabla = \mathcal{H}_0 - \frac{ie\hbar}{2m} (\mathbf{r} \times \nabla) \cdot \mathbf{B} = \mathcal{H}_0 + \frac{e}{2m} \mathbf{L} \cdot \mathbf{B}$$

where we used $(\mathbf{A} \times \mathbf{B}) \cdot \mathbf{C} = (\mathbf{B} \times \mathbf{C}) \cdot \mathbf{A}$. Recalling Eq. 1.5 completes the proof. \square

This expression holds in presence of spin too, summing the two magnetic moments:

$$\boldsymbol{\mu} = \boldsymbol{\mu}_L + \boldsymbol{\mu}_S = -\frac{\mu_B}{\hbar} (\mathbf{L} + 2\mathbf{S}) \quad (4.3)$$

The total Hamiltonian is then found adding the spin-orbit coupling:

$$\mathcal{H} = \mathcal{H}_0 + \frac{\mu_B}{\hbar} (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B} + \xi(\mathbf{r}) \mathbf{L} \cdot \mathbf{S} \quad (4.4)$$

The two perturbation terms are not simultaneously-diagonalizable: the first term is diagonalized in the uncoupled basis, with quantum numbers $(n, \ell, s, m_\ell, m_s)$, while the second term is diagonalized in the coupled basis, with quantum numbers (n, ℓ, s, j, m_j) . In general, to diagonalize this Hamiltonian one would have to employ degenerate perturbation theory, since the presence of these perturbation terms breaks the degeneracy of the unperturbed Hamiltonian; however, limit cases are more interesting.

Atoms with $S = 0$ In this case there is no spin-orbit interaction, and the perturbation Hamiltonian is reduced to (assuming $\mathbf{B} = B\mathbf{e}_z$):

$$\mathcal{H}' = \frac{\mu_B}{\hbar} B L_z \implies \langle \mathcal{H}' \rangle = \mu_B B m_L$$

The m_L -degeneracy is thus broken, and each state is split into $2L + 1$ equally-spaced states.

Example 4.1.1 (Cadmium)

Consider $^{48}\text{Cd} = [\text{Kr}]4d^{10}5s^2$: in this case $L = S = J = 0$, hence the ground state is 1S_0 . Now, take the two excited states with valence electrons $5s^15p^1$ and $5s^15d^1$: given the selection rule (electric-dipole approximation) $\Delta S = 0$, these states have $S = 0$ like the ground state, hence they are 1P_1 and 1D_2 . Applying a magnetic field, then, the ground state is unperturbed, the first excited state is split into three states and the second excited state is split into five states.

Recall that, from the electric-dipole approximation, we can derive the selection rule $\Delta m_L = 0, \pm 1$, where $\Delta m_L = 0$ is associated to a linear polarization of the EM wave along the z -axis, while $\Delta m_L = \pm 1$ are circular polarizations in the xy -plane. Historically, $\Delta m_L = 0$ transitions are called π transitions and $\Delta m_L = \pm 1$ ones σ transitions.

Then, $^1P_1 \rightarrow ^1S_0$ is split into one π transition and two σ transitions, while $^1D_2 \rightarrow ^1P_1$ is split into three π transitions and six σ transitions: π transitions have unperturbed energies, while σ transitions have energies perturbed by $\Delta E = \pm \mu_B B$.

This example shows that we cannot distinguish $S = 0$ atoms from one another by only applying a magnetic field, since their spectra are all equally perturbed: in particular, each line is split into three lines (corresponding to $\Delta m_L = 0, \pm 1$), an effect historically known as **normal Zeeman effect** (as it can be derived classically).

¹Indeed, a field $B \sim 1$ T is associated to an energy $\mu_B B \sim 60 \mu\text{eV}$, which can be treated as a perturbation.

Atoms with $S \neq 0$ We can distinguish between two cases: the magnetic field dominates or the spin-orbit coupling dominates, which are respectively known as **Paschen–Back effect** and **anomalous Zeeman effect** (as it requires a quantistic description, contrary to the normal Zeeman effect).

§4.1.1 Paschen–Back effect

In this case, we approximate the perturbation Hamiltonian at first order as:

$$\mathcal{H}' \simeq \frac{\mu_B}{\hbar} B (L_z + 2S_z) \implies \langle \mathcal{H}' \rangle = \mu_B B (m_L + 2m_S)$$

To include the spin-orbit coupling, we have to rewrite $\mathbf{L} \cdot \mathbf{S}$ in a way best suited for the uncoupled basis, which has been fixed by the first-order approximation:

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2} (L_+ S_- + L_- S_+) + L_z S_z \quad (4.5)$$

where we used Eq. 1.8. Clearly, then, on the uncoupled basis $\langle \mathbf{L} \cdot \mathbf{S} \rangle = \hbar^2 m_L m_S$, so we can write the total perturbation energy as:

$$\Delta E_{\text{PB}} = \mu_B B (m_L + 2m_S) + \xi m_L m_S \quad (4.6)$$

This expression suggests how to establish whether the magnetic field or the spin-orbit coupling dominates: the Paschen–Back effect takes place if $\mu_B B \gg \xi$.

Observation 4.1.1 (Classical treatment of Larmor precession)

From a classical point of view, \mathbf{L} and \mathbf{S} are vectors which, in the presence of a magnetic field \mathbf{B} , precess along the direction of \mathbf{B} . Indeed, ignoring at first order the spin-orbit coupling, \mathbf{L} and \mathbf{S} are associated to independent magnetic moments $\boldsymbol{\mu}_L$ and $\boldsymbol{\mu}_S$, but in a magnetic field a magnetic moment $\boldsymbol{\mu}$ precesses along the direction of \mathbf{B} according to the torque $\boldsymbol{\tau} = \boldsymbol{\mu} \times \mathbf{B}$:

$$\boldsymbol{\tau} = \frac{d\boldsymbol{\ell}}{dt} = \frac{d\boldsymbol{\ell}}{d\varphi} \frac{d\varphi}{dt} \implies \boldsymbol{\tau} = \omega \frac{d\boldsymbol{\ell}}{d\varphi}$$

Geometrically $d\ell = \ell \sin \vartheta d\varphi$, where ϑ is the angle between $\boldsymbol{\ell}$ and \mathbf{B} , hence:

$$\mu B \sin \vartheta = \omega \ell \sin \vartheta \implies \omega = \frac{\mu B}{\ell}$$

Recalling Eq. 1.5 we find the angular velocity of the precession of $\boldsymbol{\mu}$ (i.e. of $\boldsymbol{\ell}$):

$$\omega = g_\ell \frac{\mu_B}{\hbar} B \quad (4.7)$$

where we included the Landé factor for a general angular momentum. This phenomenon is known as **Larmor precession**.

Since $g_L = 1$ and $g_S = 2$, the orbital angular momentum and the spin precess at different velocities, hence their sum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is no longer an integral of motion, which quantistically corresponds to j not being a good quantum number. However, note that Larmor precession leaves the components of \mathbf{L} and \mathbf{S} along \mathbf{B} unchanged: this is reflected in Eq. 4.5, since $\langle \mathbf{L} \cdot \mathbf{S} \rangle = \hbar^2 m_L m_S$ which are still good quantum numbers. A classical way of putting this is that, over an extended time interval, \mathbf{L} and \mathbf{S} can be replaced with “effective” angular momenta given by their mean values $\mathbf{L}_{\text{eff}} \equiv L_z \mathbf{e}_z$ and $\mathbf{S}_{\text{eff}} \equiv S_z \mathbf{e}_z$.

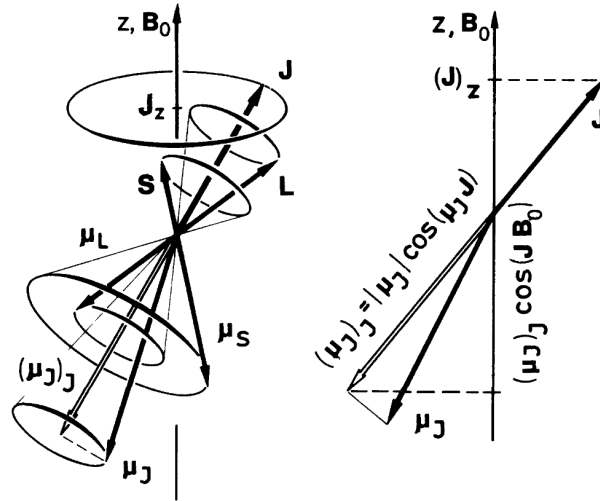


Figure 4.1: Classical view of the anomalous Zeeman effect

§4.1.2 Anomalous Zeeman effect

We now consider the case $\xi \gg \mu_B B$ in which the spin-orbit interaction dominates, so we work in the coupled basis.

As per Obs. 4.1.1, since $g_L = 1$ and $g_S = 2$, the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ and its magnetic moment $\boldsymbol{\mu}_J = \boldsymbol{\mu}_L + \boldsymbol{\mu}_S$ are not aligned (see Fig. 4.1). In absence of an external magnetic field, \mathbf{J} is a constant vector and \mathbf{L} and \mathbf{S} precess along its direction, since they are affected by each other's magnetic moment (i.e. generated magnetic field), and so do their magnetic moments and the total magnetic moment $\boldsymbol{\mu}_J$. Then, adding an external magnetic field, \mathbf{J} precesses along its direction: since we are assuming $\xi \gg \mu_B B$, the precession of \mathbf{L} , \mathbf{S} and $\boldsymbol{\mu}_J$ along \mathbf{J} is much faster than the precession of \mathbf{J} along \mathbf{B} , hence we can assume them to be independent, as represented in Fig. 4.1.

Given the greater angular frequency of the precession of $\boldsymbol{\mu}_J$ along \mathbf{J} , the only component of $\boldsymbol{\mu}_J$ that interacts with \mathbf{B} is the mean component during the precession (denoted in Fig. 4.1 as $(\boldsymbol{\mu}_J)_J$), i.e. the projection of $\boldsymbol{\mu}_J$ along \mathbf{J} .

Lemma 4.1.1 (Energy perturbation for the anomalous Zeeman effect)

$$\langle \boldsymbol{\mu}_J \cdot \mathbf{B} \rangle = -\frac{\mu_B B}{\hbar} \frac{3J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} m_J \quad (4.8)$$

Proof. Given the projection scheme outlined above and in Fig. 4.1, first project $\boldsymbol{\mu}_J$ along \mathbf{J} :

$$(\boldsymbol{\mu}_J)_J \equiv \frac{\boldsymbol{\mu}_J \cdot \mathbf{J}}{\|\mathbf{J}\|} \frac{\mathbf{J}}{\|\mathbf{J}\|} = \frac{(\boldsymbol{\mu}_L + \boldsymbol{\mu}_S) \cdot \mathbf{J}}{J^2} \mathbf{J} = -\frac{\mu_B}{\hbar J^2} (\mathbf{L} + 2\mathbf{S}) \cdot (\mathbf{L} + \mathbf{S}) \mathbf{J}$$

Then, project $(\boldsymbol{\mu}_J)_J$ along $\mathbf{B} = B\mathbf{e}_z$:

$$(\boldsymbol{\mu}_J)_J \cdot \mathbf{B} = -\frac{\mu_B B}{\hbar J^2} (\mathbf{L} + 2\mathbf{S}) \cdot (\mathbf{L} + \mathbf{S}) J_z$$

To solve the scalar product, recall that $2\mathbf{L} \cdot \mathbf{S} = J^2 - L^2 - S^2$:

$$(\mathbf{L} + 2\mathbf{S}) \cdot (\mathbf{L} + \mathbf{S}) = L^2 + 2S^2 + 3\mathbf{L} \cdot \mathbf{S} = \frac{3J^2 + S^2 - L^2}{2}$$

Putting everything together:

$$(\boldsymbol{\mu}_J)_J \cdot \mathbf{B} = -\frac{\mu_B B}{\hbar} \frac{3J^2 + S^2 - L^2}{2J^2} J_z$$

The expectation value is easily found. □

We define the Landé factor for J as:

$$g_J \equiv \frac{3J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (4.9)$$

so that $\boldsymbol{\mu}_J = g_J \frac{\mu_B}{\hbar} \mathbf{J}$ (truly this is $(\boldsymbol{\mu}_J)_J$, but we identify the magnetic moment with its mean over many precession periods) the energy correction due to the anomalous Zeeman effect is:

$$\Delta E_{AZ} = \frac{\xi}{2} [J(J+1) - L(L+1) - S(S+1)] + g_J m_J \mu_B B \quad (4.10)$$

Note that the g_J is not always between $1 = g_L$ and $2 = g_S$: for example, for $(L, S, J) = (1, \frac{3}{2}, \frac{1}{2})$ it is $g_J = \frac{8}{3} > 2$, while for $(L, S, J) = (3, \frac{5}{2}, \frac{1}{2})$ it is $g_J = -\frac{2}{3} < 0$.

Example 4.1.2 (Paschen–Back effect in hydrogen)

Determine the spectrum observed for transitions between $n = 2$ and $n = 1$ of hydrogen atoms in a $B = 10$ T magnetic field.

Solution. In this case $\mu_B B = 0.58$ meV, while for ^1H the spin-orbit constant has the exact expression given by Eq. 1.14:

$$\xi_{n,\ell} = \frac{E_R Z^4 \alpha^2}{n^3 \ell (\ell + 1) (\ell + \frac{1}{2})}$$

The ground state $^2\text{S}_{1/2}$ has no spin-orbit interaction, while the possible $n = 2$ states are $^2\text{S}_{1/2}$ and $^2\text{P}_{1/2,3/2}$: in the latter case the spin-orbit constant is $\xi_{2,1} = 0.03$ meV, hence the magnetic field induces a Paschen–Back effect.

The transition $^2\text{S}_{1/2} \rightarrow ^2\text{S}_{1/2}$ is dipole-forbidden, so consider $^2\text{P}_{1/2,3/2} \rightarrow ^2\text{S}_{1/2}$: by Eq. 4.6, $^2\text{P}_{1/2,3/2}$ splits into six levels, for $m_L = -1, 0, 1$ and $m_S = -\frac{1}{2}, \frac{1}{2}$, but $m_L + 2m_S = 0$ for $(m_L, m_S) = (-1, \frac{1}{2}), (1, -\frac{1}{2})$, hence the non-degenerate split levels are five: on the other hand, $^2\text{S}_{1/2}$ splits into the two levels $m_S = -\frac{1}{2}, \frac{1}{2}$. The relevant selection rule in this transition is $\Delta m_S = 0$: the possible transitions are then $(m_L, \pm\frac{1}{2}) \rightarrow (0, \pm\frac{1}{2})$, which, given the degeneracy above, produce five spectral lines.