Condensed Matter Physics
Prof. F. D'Orazio, a.a. 2025-26

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Part I
Atomic Physics

Chapter 1

Lecture 22/09

§1.1 Mono-atomic atoms

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

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

where the Hamiltonian can be written as:

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

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**:

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

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):

$$E_n = -\frac{Z^2 E_{\mathrm{R}}}{n^2} \qquad E_{\mathrm{R}} \equiv \frac{me^4}{2\hbar^2} \simeq 13.6\,\mathrm{eV} \tag{1.4}$$

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 $_{47}\mathrm{Ag}$ atom, which has the ground state configuration $[\mathrm{Kr}]4\mathrm{d}^{10}5\mathrm{s}^1$: full shells do not contribute to the orbital angular momentum, hence the ground state of $_{47}\mathrm{Ag}$ has $L = 0$. As we can associate a magnetic moment[1] 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 $\boldsymbol{\mu}$)

$$\langle \mu_x \rangle = \langle \mu_y \rangle = 0 \tag{1.6}$$

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:

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

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:

$$\ell_x = \frac{\ell_+ + \ell_-}{2} \qquad \ell_y = \frac{\ell_+ - \ell_-}{2\mathrm{i}} \tag{1.8}$$

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

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

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

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 $\partial_y B_y \approx 0$, 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 spin[2], which is found to be $g_s = 2$, i.e.:

$$\mu_s = -2 \frac{\mu_{\mathrm{B}}}{\hbar} \boldsymbol{s} \tag{1.9}$$

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[1]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:

$$\boldsymbol{\mu} = -\frac{e}{2m_e} \boldsymbol{\ell} \equiv -\frac{\mu_{\mathrm{B}}}{\hbar} \boldsymbol{\ell} \qquad \mu_{\mathrm{B}} \equiv \frac{e\hbar}{2m_e} \tag{1.5}$$

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

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

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

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

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{rel}} \tag{1.11}$$

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

$$\mathcal{H}_{\text{rel}} = -\frac{p^4}{8m^3 c^2} + \frac{1}{2m^2 c^2}\frac{1}{r}\frac{\mathrm{d}V(r)}{\mathrm{d}r}\boldsymbol{\ell}\cdot\boldsymbol{s} + \frac{\hbar^2}{8m^2 c^2}\triangle V(r) \tag{1.12}$$

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 $\triangle V(r) = e\triangle\phi(r) = 4\pi e\rho(r)$, 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:

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

$$\Delta E_2 = \frac{Z^4 E_{\text{R}}\alpha^2}{n^3\ell\left(\ell + 1\right)\left(\ell + \frac{1}{2}\right)}\left[j\left(j + 1\right) - \ell\left(\ell + 1\right) - s\left(s + 1\right)\right] \tag{1.14}$$

$$\Delta E_3 = \frac{Z^4 E_{\text{R}}\alpha^2}{n^3}\delta_{\ell,0} \tag{1.15}$$

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

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

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

Lecture 29/09

Example 3.0.1 (Sodium transitions)

Find the wavelength of the transitions 4p $\to$ 3s and 4d $\to$ 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:

$$\lambda_{4p \to 3s} = 342.7\,\text{nm} \qquad \lambda_{4d \to 3p} = 585.9\,\text{nm}$$

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:

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

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 $3P_{1/2} \to 3S_{1/2}$ and λ_2 to $3P_{3/2} \to 3S_{1/2}$, and:

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

The mono-electron atom relation is Eq. 1.14, hence:

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

§3.1 X-ray spectra

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

$$E_n \approx -\frac{E_{\mathrm{R}}\,(Z - \alpha_n)^2}{n^2} \tag{3.1}$$

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 $1\mathrm{s}^1 2\mathrm{s}^2 2\mathrm{p}^6 \dots \to 1\mathrm{s}^2 2\mathrm{s}^2 2\mathrm{p}^5$ is denoted by $K_\alpha \equiv L \to K$, while $1\mathrm{s}^2 2\mathrm{s}^2 2\mathrm{p}^6 3\mathrm{s}^2 3\mathrm{p}^6 4\mathrm{s}^2 \to 1\mathrm{s}^2 2\mathrm{s}^2 2\mathrm{p}^6 3\mathrm{s}^2 3\mathrm{p}^6 4\mathrm{s}^1$ by $L_\beta \equiv L \to N$.

§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:

$$\mathbf{S} \coloneqq \sum_i \boldsymbol{s}_i \qquad \mathbf{L} \coloneqq \sum_i \boldsymbol{\ell}_i \qquad \mathbf{J} = \mathbf{L} + \mathbf{S} \tag{3.2}$$

This is the *Russell–Saunders coupling*: another possible coupling is the *jj coupling*, in which $\mathbf{J} = \sum_i \boldsymbol{j}_i$, 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:

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

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 weather the lowest state is that with lowest or highest total angular momentum.

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:

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

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 ${}^4\mathrm{P}_{1/2,3/2,5/2}$.

§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 $\boldsymbol{\nabla} \times \mathbf{A} = \mathbf{B}$ and $\boldsymbol{\nabla} \cdot \mathbf{A} = 0$: for a constant magnetic field:

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

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

$$\mathcal{H} \simeq \mathcal{H}_0 - \boldsymbol{\mu} \cdot \mathbf{B} \tag{4.2}$$

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

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

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

hence we approximate it as negligible[1]. Denoting the unperturbed Hamiltonian as $\mathcal{H}_0$, then:

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

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:

$$\boldsymbol{\mu} = \boldsymbol{\mu}_L + \boldsymbol{\mu}_S = -\frac{\mu_{\mathrm{B}}}{\hbar}(\mathbf{L} + 2\mathbf{S}) \tag{4.3}$$

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

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

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 diagonalized 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 $\mathbf{B} = B\mathbf{e}_z$):

$$\mathcal{H}' = \frac{\mu_{\mathrm{B}}}{\hbar}BL_z \qquad \Longrightarrow \qquad \langle\mathcal{H}'\rangle = \mu_{\mathrm{B}}Bm_L$$

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

Example 4.1.1 (Cadmium)

Consider $_{48}\mathrm{Cd} = [\mathrm{Kr}]4\mathrm{d}^{10}5\mathrm{s}^2$: in this case $L = S = J = 0$, hence the ground state is $^1\mathrm{S}_0$. Now, take the two excited states with valence electrons $5\mathrm{s}^1 5\mathrm{p}^1$ and $5\mathrm{s}^1 5\mathrm{d}^1$: given the selection rule (electric-dipole approximation) $\Delta S = 0$, these states have $S = 0$ like the ground state, hence they are $^1\mathrm{P}_1$ and $^1\mathrm{D}_2$. 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, $^1\mathrm{P}_1 \rightarrow \,^1\mathrm{S}_0$ is split into one π transition and two σ transitions, while $^1\mathrm{D}_2 \rightarrow \,^1\mathrm{P}_1$ is split into three π transitions and six σ transitions: π transitions have unperturbed energies, while σ transitions have energies perturbed by $\Delta E = \pm\mu_{\mathrm{B}}B$.

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).

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

Atoms with $S \neq 0$ We can distinguish between 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:

$$\mathcal{H}' \simeq \frac{\mu_{\mathrm{B}}}{\hbar} B \left(L_z + 2S_z \right) \quad \Longrightarrow \quad \langle \mathcal{H}' \rangle = \mu_{\mathrm{B}} B \left(m_L + 2m_S \right)$$

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:

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

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 pertubation energy as:

$$\Delta E_{\mathrm{PB}} = \mu_{\mathrm{B}} B \left(m_L + 2m_S \right) + \xi m_L m_S \tag{4.6}$$

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

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 $\mathbf{B}$, precede 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 $\boldsymbol{\mu}$ precedes along the direction of $\mathbf{B}$ according to the torque $\boldsymbol{\tau} = \boldsymbol{\mu} \times \mathbf{B}$:

$$\boldsymbol{\tau} = \frac{\mathrm{d}\boldsymbol{\ell}}{\mathrm{d}t} = \frac{\mathrm{d}\boldsymbol{\ell}}{\mathrm{d}\varphi} \frac{\mathrm{d}\varphi}{\mathrm{d}t} \quad \Longrightarrow \quad \tau = \omega \frac{\mathrm{d}\boldsymbol{\ell}}{\mathrm{d}\varphi}$$

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

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

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

$$\omega = g_\ell \frac{\mu_{\mathrm{B}}}{\hbar} B \tag{4.7}$$

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 precede 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 $\mathbf{L}_{\mathrm{eff}} \equiv L_z \mathbf{e}_z$ and $\mathbf{S}_{\mathrm{eff}} \equiv S_z \mathbf{e}_z$.
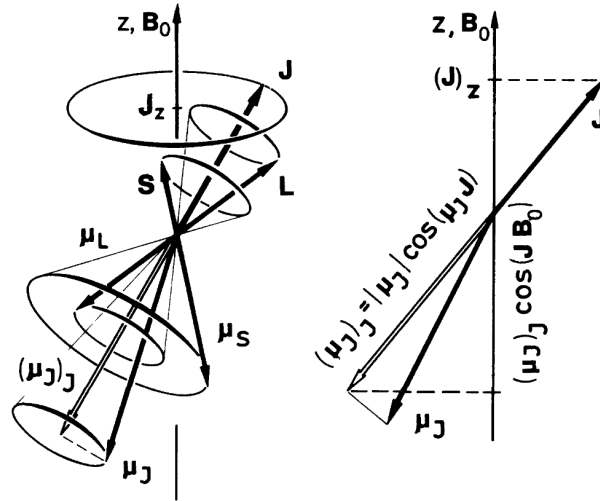
Figure 4.1: Classical view of the anomalous Zeeman effect

§4.1.2 Anomalous Zeeman effect

We now consider the case $\xi \gg \mu_{\mathrm{B}}B$ 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 $\mathbf{S}$ precede 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, $\mathbf{J}$ precedes along its direction: since we are assuming $\xi \gg \mu_{\mathrm{B}}B$, 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)

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

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

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

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

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

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:

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

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:

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

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 $B = 10\,\mathrm{T}$ magnetic field.
Solution. In this case $\mu_B B = 0.58\,\mathrm{meV}$, while for $^1\mathrm{H}$ the spin-orbit constant has the exact expression given by Eq. 1.14:

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

The ground state $^2\mathrm{S}_{1/2}$ has no spin-orbit interaction, while the possible $n = 2$ states are $^2\mathrm{S}_{1/2}$ and $^2\mathrm{P}_{1/2,3/2}$: in the latter case the spin-orbit constant is $\xi_{2,1} = 0.03\,\mathrm{meV}$, hence the magnetic field induces a Paschen–Back effect.
The transition $^2\mathrm{S}_{1/2} \to {}^2\mathrm{S}_{1/2}$ is dipole-forbidden, so consider $^2\mathrm{P}_{1/2,3/2} \to {}^2\mathrm{S}_{1/2}$: by Eq. 4.6, $^2\mathrm{P}_{1/2,3/2}$ 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, $^2\mathrm{S}_{1/2}$ 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 $(m_L, \pm\frac{1}{2}) \to (0, \pm\frac{1}{2})$, which, given the degeneracy above, produce five spectral lines.

Lecture 10/10

§5.1 Hyperfine interaction

Like the electrons, the nucleus too has a total angular momentum I, given by the momenta of the individual protons and neutrons. We only consider the angular momentum of the ground state, since nuclear reactions (which change the spin state of the nucleus) in general require high energies.

There are three possible cases for the nuclear spin in the ground state, depending on the number of protons Z and neutrons N:

- Z, N odd: I is an integer and the nucleus is a boson;

- Z odd, N even (or vice versa): I is a half-integer and the nucleus is a fermion;

- Z, N even: $I = 0$.

Although the nucleus is a composite body, the magnetic moment associated to the nuclear spin is still proportional to I, so we write:

$$\boldsymbol{\mu}_I = g_I \frac{\mu_{\mathrm{N}}}{\hbar} \mathbf{I} \qquad \mu_{\mathrm{N}} \equiv \frac{e\hbar}{2m_p} \tag{5.1}$$

where we introduced the Landé factor for the nuclear spin g_I (which is to be determined experimentally: e.g. $g_I \simeq 5.59$ for a proton and $g_I \simeq -3.83$ for a neutron) and the nuclear Bohr magneton μ_{N}.

Analogously to the spin-orbit coupling, which leads to the fine interaction and the fine-structure splitting, the angular momenta J and I couple too, leading to the **hyperfine interaction**:

$$\mathcal{H}_{\mathrm{HF}} = \frac{\xi_{\mathrm{HF}}}{\hbar^2} \mathbf{I} \cdot \mathbf{J} \tag{5.2}$$

We can then define the total atomic angular momentum $\mathbf{F} \equiv \mathbf{I} + \mathbf{J}$, so that:

$$\Delta E_{\mathrm{HF}} = \frac{\xi_{\mathrm{HF}}}{2} \left[F(F+1) - I(I+1) - J(J+1) \right] \tag{5.3}$$

To qualitatively describe the hyperfine constant ξ_{HF}, rewrite the hyperfine interaction Hamiltonian as:

$$\mathcal{H}_{\mathrm{HF}} = -\boldsymbol{\mu}_I \cdot \mathbf{B}_J = -g_I \frac{\mu_{\mathrm{N}}}{\hbar^2} \mathbf{I} \cdot \mathbf{B}_J = g_I \frac{\mu_{\mathrm{N}}}{\hbar^2} \mathbf{I} \cdot \frac{\mathbf{J}}{\|\mathbf{J}\|} B_J = \frac{g_I \mu_{\mathrm{N}} B_J}{\hbar^2 \sqrt{J(J+1)}} \mathbf{I} \cdot \mathbf{J}$$

where we used the fact that $\mathbf{B}_J$ and $\mathbf{J}$ are antiparallel. Then:

$$\xi_{\text{HF}} = \frac{g_I \mu_{\text{N}} B_J}{\sqrt{J(J+1)}} \tag{5.4}$$

The magnetic field $\mathbf{B}_J$ generated by $\mathbf{J}$ at the position of the nucleus is difficult to be measured directly; nonetheless, we expect this magnetic field to be larger for electrons closer to nucleus: indeed, for a mono-electron atom, it is possible to prove the following expression:

$$\xi_{\text{HF}} \simeq \frac{2}{3} \mu_0 g_J \mu_{\text{B}} g_I \mu_{\text{N}} \left| \psi(\mathbf{0}) \right|^2 \tag{5.5}$$

where $\psi(\mathbf{r})$ is the electron's wave-function. In general, the hyperfine correction is significant for s-electrons.

> **Example 5.1.1** (Hyperfine interaction in hydrogen)
>
> For ^{1}H we have the explicit expression in terms of the Bohr radius:
>
> $$\left| \psi(\mathbf{0}) \right|^2 = \frac{1}{\pi R_{\text{B}}^3} \qquad R_{\text{B}} \simeq 52.92 \, \text{pm}$$
>
> Hence, since $g_I \simeq 5.59$ for the proton, we can compute the hyperfine constant for the ground state $^2\text{S}_{1/2}$:
>
> $$\xi_{\text{HF}} \approx 5.9 \, \mu\text{eV}$$
>
> Moreover, in this case $I = \frac{1}{2}$ and $J = \frac{1}{2}$, hence the atomic spin can be either $F = 0$ or $F = 1$: from Eq. 5.3, these two states are separated by $5.9 \, \mu\text{eV}$, i.e. the transition between $F = 1$ and $F = 0$ corresponds to a well known spectral line $\lambda \approx 21.0 \, \text{cm}$, which is of astrophysical interest.

> **Example 5.1.2** (Hyperfine interaction in generic mono-electron atoms)
>
> For ns states in generic mono-electron atoms, the following first-order approximation holds:
>
> $$\left| \psi(\mathbf{0}) \right|^2 \simeq \frac{Z^3}{\pi n^3 R_{\text{B}}^3}$$
>
> For other orbitals, instead:
>
> $$\xi_{\text{HF}} \simeq \frac{\mu_0}{4\pi} g_I \mu_{\text{B}} \mu_{\text{N}} \frac{Z^3}{R_{\text{B}}^3 n^3 J(J+1)(2L+1)}$$

§5.1.1 Hyperfine structure in magnetic fields

To study how the hyperfine strucure is affected by magnetic fields, consider first that $\xi \gg \xi_{\text{HF}}$ and $\mu_{\text{B}} B \gg \mu_{\text{N}} B$: the total ordering is then given by the relation between ξ_{HF} and $\mu_{\text{B}} B$, i.e. either weak field $\xi_{\text{HF}} \gg \mu_{\text{B}} B$ or strong field $\mu_{\text{B}} B \gg \xi_{\text{HF}}$.

§5.1.1.1 Weak magnetic field

In the weak-field regime we adopt the coupled basis with $\mathbf{F} = \mathbf{I} + \mathbf{J}$. The atomic magnetic moment is then:

$$\boldsymbol{\mu}_F = \boldsymbol{\mu}_I + \boldsymbol{\mu}_J \approx \boldsymbol{\mu}_J \tag{5.6}$$

since $\mu_I \propto \mu_N \ll \mu_B$. Then, following the discussion in §4.1.2, we project $\boldsymbol{\mu}_F$ onto $\mathbf{F}$, since this is the only component which does not vanish in the mean over many precession periods:

$$(\mu_F)_F \approx \boldsymbol{\mu}_J \cdot \frac{\mathbf{F}}{\|\mathbf{F}\|} = -g_J \frac{\mu_B}{\hbar} \mathbf{J} \cdot \frac{\mathbf{J} + \mathbf{I}}{F} = -g_J \frac{\mu_B}{2\hbar F} \left[\mathbf{F}^2 + \mathbf{J}^2 - \mathbf{I}^2 \right]$$

Identifying $\boldsymbol{\mu}_F$ with this projection (an "effective" magnetic moment), the energy correction due to the magnetic field $\mathbf{B} = B\mathbf{e}_z$ is:

$$\mathcal{H}_B = -\boldsymbol{\mu}_F \cdot \mathbf{B} = -(\mu_F)_F \frac{\mathbf{F}}{\|\mathbf{F}\|} \cdot \mathbf{B} = \frac{g_J \mu_B B}{2\hbar F^2} \left[F^2 + J^2 - I^2 \right] F_z$$

that is:

$$\Delta E_B = \frac{g_J \mu_B B}{2F(F+1)} m_F \left[F(F+1) + J(J+1) - I(I+1) \right] \tag{5.7}$$

This expression can be rewritten as:

$$\Delta E_B = g_F m_F \mu_B B \tag{5.8}$$

with the Landé factor for the atomic spin defined as:

$$g_F \equiv g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} \tag{5.9}$$

Each level is first split by the spin-orbit interaction, then by the hyperfine interaction and finally by the additional splitting in Eq. 5.8.

§5.1.1.2 Strong magnetic field

In this case, as per Obs. 4.1.1, the precessions of $\mathbf{I}$ and $\mathbf{J}$ along $\mathbf{B}$ can be treated as independent, hence we work in the uncoupled basis. The derivation is analogous to that in §4.1.1:

$$\Delta E_B = g_J m_J \mu_B B - g_I m_I \mu_N B + \xi_{HF} m_I m_J \tag{5.10}$$

where the negative sign before in the first terms stems from the definition Eq. 5.1, which lacks a negative sign (since the nucleus is positively charged). Note that this is the most common occurrence, given that ξ_{HF} is smaller than ξ.

Now, each level is first split by the spin-orbit interaction, then by electronic Zeeman splitting (first term of Eq. 5.10), and finally by the hyperfine interaction (third term of Eq. 5.10), with the additional correction of the nuclear Zeeman energy (second term of Eq. 5.10).

Example 5.1.3 (Measure of ξ_{HF} for hydrogen)

Consider the ground state $^2S_{1/2}$ of ^1H, which has $I = \frac{1}{2}$, and apply a strong magnetic field. This state has no spin-orbit interaction, hence, according to Fig. 5.1, it first gets split into two $m_J = +\frac{1}{2}$ and $m_J = -\frac{1}{2}$ levels by the magnetic field, and then each of these levels is split into two $m_I = +\frac{1}{2}$ and $m_I = -\frac{1}{2}$ by the hyperfine interaction. We then have four levels
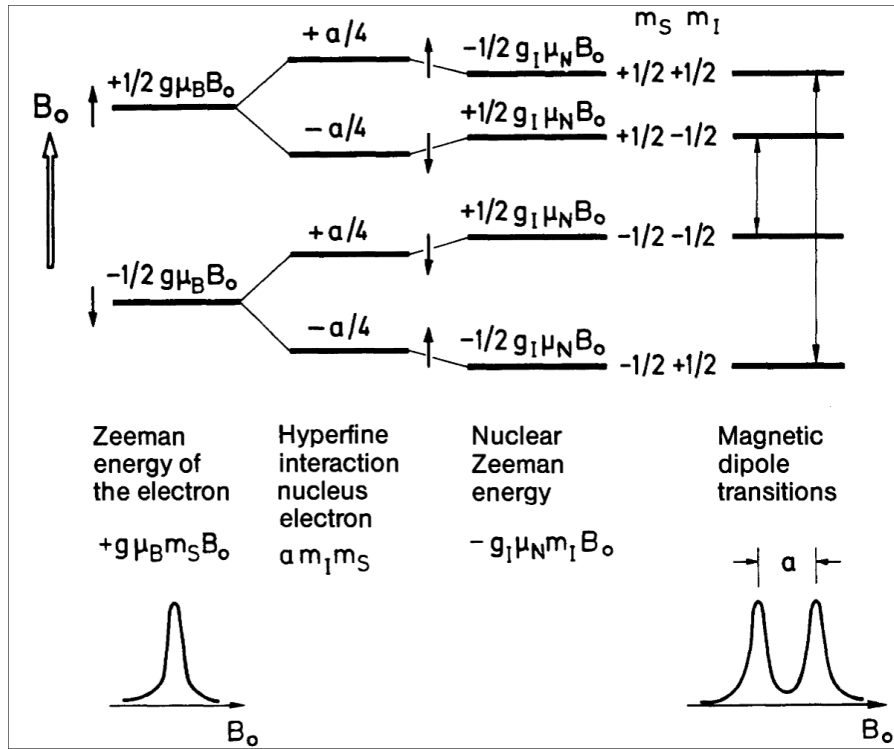
Figure 5.1: Hyperfine structure of hydrogen in a strong magnetic field.

(m_J, m_I), with energies (setting $E_{1S_{1/2}} \equiv 0$):

$$E_{(+,+)} = \frac{1}{2} \left(g_J \mu_{\mathrm{B}} - g_I \mu_{\mathrm{N}} \right) B + \frac{\xi_{\mathrm{HF}}}{4} \qquad E_{(+,-)} = \frac{1}{2} \left(g_J \mu_{\mathrm{B}} + g_I \mu_{\mathrm{N}} \right) B - \frac{\xi_{\mathrm{HF}}}{4}$$

$$E_{(-,+)} = -\frac{1}{2} \left(g_J \mu_{\mathrm{B}} + g_I \mu_{\mathrm{N}} \right) B - \frac{\xi_{\mathrm{HF}}}{4} \qquad E_{(-,-)} = -\frac{1}{2} \left(g_J \mu_{\mathrm{B}} - g_I \mu_{\mathrm{N}} \right) B + \frac{\xi_{\mathrm{HF}}}{4}$$

Note that no electric-dipole transitions are possible between these four states, since the orbital angular momentum of the electron is always zero, but two magnetic-dipole transitions are allowed: the selection rule in this case is $\Delta S = \pm 1$, and additionally $\Delta I = 0$ since we exclude nuclear transitions, hence $(+,+) \leftrightarrow (-,+)$ and $(+,-) \leftrightarrow (-,-)$ are possible (see Fig. 5.1). The energies of these transitions then are:

$$\Delta E_{(+,+) \to (-,+)} = g_J \mu_{\mathrm{B}} B + \frac{\xi_{\mathrm{HF}}}{2} \qquad \Delta E_{(+,-) \to (-,-)} = g_J \mu_{\mathrm{B}} B - \frac{\xi_{\mathrm{HF}}}{2}$$

The hyperfine constant ξ_{HF} is thus found by measuring the splitting in the ESR (electron spin resonance) spectrum of ^{1}H.

Lecture 13/10

§**6.1** Atoms with two electrons

Consider an atom with Z protons and two electrons. Approximating the nucleus as unaffected by the electrons (i.e. massive approximation), the Hamiltonian of the system is:

$$\mathcal{H} = -\frac{\hbar^2}{2m}\triangle_{\mathbf{r}_1} - \frac{\hbar^2}{2m}\triangle_{\mathbf{r}_2} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \tag{6.1}$$

with $r_{12} \equiv \|\mathbf{r}_1 - \mathbf{r}_2\|$. Note that $\mathcal{H}$ is symmetric under $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$, i.e. under exchange of the two electrons: as a consequence, if $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ is an eigenfunction of the Hamiltonian, then $\Psi(\mathbf{r}_2, \mathbf{r}_1)$ is still an eigenfunction of $\mathcal{H}$ with the same eigenvalue, i.e. with the same energy. Moreover, defining the exchange operator $\mathcal{P}_{1,2} : \mathcal{P}_{1,2}f(\mathbf{r}_1, \mathbf{r}_2) := f(\mathbf{r}_2, \mathbf{r}_1)$, then $[\mathcal{H}, \mathcal{P}_{1,2}] = 0$, hence we can diagonalize the Hamiltonian by diagonalizing the exchange operator.

> **Lemma 6.1.1** (Eigenfunctions of the exchange operator)
>
> $$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \pm\Psi(\mathbf{r}_2, \mathbf{r}_1) \tag{6.2}$$

> *Proof.* By definition $\mathcal{P}_{1,2}^2 = \mathrm{id}$. However, eigenfunctions satisfy $\mathcal{P}_{1,2}\Psi(\mathbf{r}_1, \mathbf{r}_2) = \lambda\Psi(\mathbf{r}_1, \mathbf{r}_2)$, thus:
> $$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \mathcal{P}_{1,2}^2\Psi(\mathbf{r}_1, \mathbf{r}_2) = \lambda^2\Psi(\mathbf{r}_1, \mathbf{r}_2)$$
> Solving for λ yields $\lambda = \pm 1$. $\qquad\square$

The Hamiltonian is then diagonalized on the eigenbasis of symmetric and antisymmetric functions. Note that $\Psi(\mathbf{r}_1, \mathbf{r}_2) \equiv \Psi_{1,2}$ is the spatial part of the total wave-function of the system: for a complete description, we have to include the spin part $\mathcal{X}_{1,2}$, so to define the total wave-function $\Phi_{1,2} \equiv \Psi_{1,2}\mathcal{X}_{1,2}$. This definition is well-posed if the Hamiltonian of the system is independent of the spin of the two electrons: this is the case for Eq. 6.1, where we implicitly assumed that the Coulomb interaction term dominates over the spin-orbit interaction term, which has been suppressed; however, this approximation does not hold for increasingly-heavier atoms, for which the spin-orbit coupling dominates.

Since electrons are fermions, the total wave-function must be antisymmetric: $\Phi_{1,2} = -\Phi_{2,1}$. This means that if $\Psi_{1,2} = \pm\Psi_{2,1}$, then $\mathcal{X}_{1,2} = \mp\mathcal{X}_{2,1}$. Starting from the individual spinors $\mathcal{X}_i(\uparrow)$ and $\mathcal{X}_i(\downarrow)$, with $i = 1, 2$, we can build a symmetric triplet:

$$\mathcal{X}_1(\uparrow)\mathcal{X}_2(\uparrow) \qquad\qquad \frac{1}{\sqrt{2}}\left[\mathcal{X}_1(\uparrow)\mathcal{X}_2(\downarrow) + \mathcal{X}_1(\downarrow)\mathcal{X}_2(\uparrow)\right] \qquad\qquad \mathcal{X}_1(\downarrow)\mathcal{X}_2(\downarrow)$$

and an antisymmetric singlet:

$$\frac{1}{\sqrt{2}} \left[\mathcal{X}_1(\uparrow)\mathcal{X}_2(\downarrow) - \mathcal{X}_1(\downarrow)\mathcal{X}_2(\uparrow) \right]$$

Note that for the symmetric triplet $m_S = 1, 0, -1$, while for the antisymmetric singlet $m_S = 0$: it is then clear that the symmetric triplet has $S = 1$, while the antisymmetric singlet has $S = 0$, where[1] $S \equiv s_1 + s_2$.

§6.1.1 Perturbation theory

As a first attempt to solve the Schrödinger equation with Hamiltonian Eq. 6.1, consider the interaction term as a perturbation, i.e. write:

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{1,2}$$

Then, a general eigenfunction can be written in a separated way as $\Psi_{1,2} = \psi_1\psi_2$, where ψ_1 and ψ_2 are eigenfunctions of the mono-electron Hamiltonians $\mathcal{H}_1$ and $\mathcal{H}_2$, i.e. $\psi_i = \psi_{n,\ell,m}(\mathbf{r}_i)$. In particular, denoting the set of quantum number as $\sigma \equiv (n, \ell, m)$, the bi-electron eigenfunctions can be written as:

$$\Psi^{\pm}_{1,2}(\sigma, \sigma') = \frac{1}{\sqrt{2}} \left[\psi_1(\sigma)\psi_2(\sigma') \pm \psi_1(\sigma')\psi_2(\sigma) \right] \tag{6.3}$$

with the notation $\psi_i(\sigma) \equiv \psi_{n,\ell,m}(\mathbf{r}_i)$.

> **Proposition 6.1.1** (Unperturbed eigenenergies)
>
> $$E_0(\sigma, \sigma') = E_0(\sigma) + E_0(\sigma') \tag{6.4}$$

Proof. Setting[2] $\mathcal{H}_0 = \mathcal{H}_1 + \mathcal{H}_2$:

$$\mathcal{H}_0 \Psi^{\pm}_{1,2}(\sigma, \sigma') = \frac{1}{\sqrt{2}} \left[(\mathcal{H}_1 + \mathcal{H}_2)\,\psi_1(\sigma)\psi_2(\sigma') \pm (\mathcal{H}_1 + \mathcal{H}_2)\,\psi_1(\sigma')\psi_2(\sigma) \right]$$

$$= \frac{1}{\sqrt{2}} \left[(E_0(\sigma) + E_0(\sigma'))\,\psi_1(\sigma)\psi_2(\sigma') \pm (E_0(\sigma') + E_0(\sigma))\,\psi_1(\sigma')\psi_2(\sigma) \right]$$

$$= \left[E_0(\sigma) + E_0(\sigma') \right] \Psi^{\pm}_{1,2}(\sigma, \sigma')$$

which is the thesis. $\square$

This confirms that $\Psi^{+}_{1,2}$ and $\Psi^{-}_{1,2}$ (i.e. $\Psi_{1,2}$ and $\Psi_{2,1}$) have the same eigenenergies.

> **Example 6.1.1** (Helium)
>
> The unperturbed eigenenergies of $_2$He are:
>
> $$E_0(n_1, n_2) = -4E_\mathrm{R} \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right)$$
>
> For example, $E_0(1s^2) \simeq -108.8\,\mathrm{eV}$: however, experimentally the energy to doubly ionize $_2$He is $79.0\,\mathrm{eV}$, thus showing the importance of the interaction term in the Hamiltonian.

---

[1] To be precise, $S = s_1 \otimes \mathrm{id}_2 + \mathrm{id}_1 \otimes s_2$.
[2] To be precise, $\mathcal{H}_0 = \mathcal{H}_1 \otimes \mathrm{id}_2 + \mathrm{id}_1 \otimes \mathcal{H}_2$.

Accounting for this perturbation, since $1s^2$ is an $S = 0$ singlet:

$$\Delta E(1s^2) = \langle \Psi_{1,2}^+(\{1,0,0\},\{1,0,0\})|\mathcal{H}_{1,2}|\Psi_{1,2}^+(\{1,0,0\},\{1,0,0\})\rangle$$

$$= 2 \int_{\mathbb{R}^6} \mathrm{d}^3 r_1 \mathrm{d}^3 r_2 \, |\psi_{1,0,0}(\mathbf{r}_1)|^2 \, |\psi_{1,0,0}(\mathbf{r}_2)|^2 \, \frac{e^2}{\|\mathbf{r}_1 - \mathbf{r}_2\|} = \frac{5}{4} Z E_{\mathrm{R}}$$

This is a classical correction, and $E_0(1s^2) + \Delta E(1s^2) \simeq -74.8\,\mathrm{eV}$, which is closer to the experimental value but still shows the limitation of the perturbative approach.

We now have to compute the correction due to the interaction Hamiltonian.

Proposition 6.1.2 (Interaction correction)

The correction due to $\mathcal{H}_{1,2}$ can be written as:

$$\Delta E^{\pm}(\sigma, \sigma') = \mathcal{J} \pm \mathcal{K} \tag{6.5}$$

where the **Coulomb integral** is defined as:

$$\mathcal{J} \equiv \int_{\mathbb{R}^6} \mathrm{d}^3 r_1 \mathrm{d}^3 r_2 \, |\psi_1(\sigma)|^2 \, |\psi_2(\sigma')|^2 \, \frac{e^2}{\|\mathbf{r}_1 - \mathbf{r}_2\|} \tag{6.6}$$

and the **exchange integral** is defined as:

$$\mathcal{K} \equiv \int_{\mathbb{R}^6} \mathrm{d}^3 r_1 \mathrm{d}^3 r_2 \, \psi_1(\sigma)^* \psi_1(\sigma') \psi_2(\sigma')^* \psi_2(\sigma) \frac{e^2}{\|\mathbf{r}_1 - \mathbf{r}_2\|} \tag{6.7}$$

Proof. By direct computation:

$$\Delta^{\pm} E(\sigma, \sigma') = \langle \Psi_{1,2}^{\pm}(\sigma, \sigma')|\mathcal{H}_{1,2}|\Psi_{1,2}^{\pm}(\sigma, \sigma')\rangle = \int_{\mathbb{R}^6} \mathrm{d}^3 r_1 \mathrm{d}^3 r_2 \, \left|\Psi_{1,2}^{\pm}(\sigma, \sigma')\right|^2 \frac{e^2}{\|\mathbf{r}_1 - \mathbf{r}_2\|}$$

$$= \frac{e^2}{2} \int_{\mathbb{R}^6} \frac{\mathrm{d}^3 r_1 \mathrm{d}^3 r_2}{\|\mathbf{r}_1 - \mathbf{r}_2\|} \left[\psi_1(\sigma)^* \psi_2(\sigma')^* \pm \psi_1(\sigma')^* \psi_2(\sigma)^*\right] \left[\psi_1(\sigma) \psi_2(\sigma') \pm \psi_1(\sigma') \psi_2(\sigma)\right]$$

$$= \frac{e^2}{2} \int_{\mathbb{R}^6} \frac{\mathrm{d}^3 r_1 \mathrm{d}^3 r_2}{\|\mathbf{r}_1 - \mathbf{r}_2\|} \left[|\psi_1(\sigma)|^2 \, |\psi_2(\sigma')|^2 + |\psi_1(\sigma')|^2 \, |\psi_2(\sigma)|^2\right] +$$

$$\pm \frac{e^2}{2} \int_{\mathbb{R}^6} \frac{\mathrm{d}^3 r_1 \mathrm{d}^3 r_2}{\|\mathbf{r}_1 - \mathbf{r}_2\|} \left[\psi_1(\sigma)^* \psi_1(\sigma') \psi_2(\sigma')^* \psi_2(\sigma) + \psi_1(\sigma')^* \psi_1(\sigma) \psi_2(\sigma)^* \psi_2(\sigma')\right]$$

$$= e^2 \int_{\mathbb{R}^6} \frac{\mathrm{d}^3 r_1 \mathrm{d}^3 r_2}{\|\mathbf{r}_1 - \mathbf{r}_2\|} \, |\psi_1(\sigma)|^2 \, |\psi_2(\sigma')|^2 \pm e^2 \int_{\mathbb{R}^6} \frac{\mathrm{d}^3 r_1 \mathrm{d}^3 r_2}{\|\mathbf{r}_1 - \mathbf{r}_2\|} \psi_1(\sigma)^* \psi_1(\sigma') \psi_2(\sigma')^* \psi_2(\sigma)$$

which is the thesis. $\qquad \square$

The Coulomb integral is classical, while the exchange integral has a quantum nature: indeed, $\mathcal{J}$ is equivalent to the interaction of two charge distributions, while $\mathcal{K}$ stems from the antisymmetrization of the total wave-function.

Note that $\mathcal{J}, \mathcal{K} > 0$, hence the singlet state has a higher energy correction than the triplet states: this is an instance of **Hund's first rule**, which is an empirical rule that states that maximizing the total electronic spin of an atom minimizes its energy. **Hund's second rule** is also illustrated by these integrals: indeed, it states that maximizing the total orbital angular

momentum minimizes the energy of the atom, which is justified by the fact that electrons which orbit in the same direction are close to one another less often than electrons which orbit in opposite directions, thus minimizing the repulsive potential interaction.

Example 6.1.2 (Helium again)

Consider again $_2$He, and in particular its lowest states $1s^2$, $1s^1 2s^1$ and $1s^1 2p^1$:

- $1s^2$ only has a singlet state $S = 0$, hence it can only be $^1S_0$;

- 1s2s is split by the exchange interaction into a triplet (lower energy) and a singlet (higher energy), with respective spectroscopic terms $^3S_1$ and $^1S_0$;

- 1s2p is split into a triplet $^3P_{0,1,2}$, which can be further split by the spin-orbit interaction, and a singlet $^1P_1$.

In particular, the lowest levels are $^1S_0$ and $^3S_1$: since a transition between them is dipole-forbidden (as $\Delta S \neq 0$), historically these were thought as two different species of helium: para-helium ($S = 0$ singlet) and ortho-helium ($S = 1$ triplet).