

Condensed Matter Physics

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Part I

Atomic and Molecular Physics

Chapter 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 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 $[\text{Kr}]4\text{d}^{10}5\text{s}^1$: 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 ${}_{47}\text{Ag}$ 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:

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

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 μ_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 spin², which is found to be $g_s = 2$, i.e.:

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

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 $\mu_B \simeq 5.7884 \cdot 10^{-5}$ 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**.

§1.2 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 $\ell_{\max} + 1 = n$ 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**.

§1.2.1 Lamb shift

By Eq. 1.16, it is clear that states with same n and j quantum numbers are degenerate, even if their ℓ quantum numbers differ: this is a feature of the Coulombian potential, thus only valid for hydrogenoid atoms.

However, there is still another small correction which breaks the degeneracy. Indeed, accounting for the finite dimensions of the nucleus and of the electron, a correction which depends on the distance of the electron from the nucleus is determined: this is called the **Lamb shift**. In particular, this correction is greater (positively) for s-electrons, e.g. the $2S_{1/2}$ and $2P_{1/2}$ are split by ~ 10 meV.

§1.2.1.1 Electronic transitions

Due to the Lamb shift, the lowest hydrogenoid states are, with increasing energies, $1S_{1/2}$, $2P_{1/2}$ and $2S_{1/2}$. To measure the Lamb shift, we could measure the energy difference between the spectral lines $2S_{1/2} \leftrightarrow 1S_{1/2}$ and $2S_{1/2} \leftrightarrow 2P_{1/2}$: however, the former is dipole-forbidden since $\Delta\ell = 0$, while the latter is suppressed by the small energy difference of the two states. Indeed, recall that the rate for **spontaneous decay** (i.e. emission of radiation) from an initial state $|i\rangle$ to a final state $|f\rangle$ is:

$$\gamma_{if} = \frac{\hbar}{2\pi m_e^2 c^3} \frac{e^2}{4\pi\epsilon_0} \omega_{if} |\mathcal{M}_{if}(\omega_{if})|^2 \quad (1.17)$$

It is also possible to compute the rate of **stimulated decay** (or excitation) induced by an EM radiation of intensity $I(\omega)$:

$$\bar{\gamma}_{if} = \frac{4\pi^2}{m_e^2 c} \frac{e^2}{4\pi\epsilon_0} \frac{I(\omega_{if})}{\omega_{if}^2} |\mathcal{M}_{if}(\omega_{if})|^2 \quad (1.18)$$

Given the small energy split between the $2P_{1/2}$ and $2S_{1/2}$ states, with an EM radiation at the right frequency it is possible to excite both these states: the $2P_{1/2}$ state decays to the ground state $1S_{1/2}$ after $\sim 10^{-9}$ sec, while the $2S_{1/2}$ remains a metastable state, since the spontaneous decay to the ground state is dipole-forbidden and that to the $2P_{1/2}$ state is energetically suppressed.

Chapter 2

Multi-electron Atoms: Qualitative Treatment

§2.1 Alkali metals

The general Hamiltonian for an atom with N_e electrons is:

$$\mathcal{H} = \sum_{i=1}^{N_e} \frac{p_i^2}{2m_e} - \sum_{i=1}^{N_e} \frac{Ze^2}{r_i} + \frac{1}{2} \sum_{i \neq j=1}^{N_e} \frac{e^2}{r_{ij}} \quad (2.1)$$

with $r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$. Clearly, the third term cannot be treated as a perturbation, since it can be larger than the unperturbed potential.

However, a class of atoms for which an approximate solution can be found is that of alkali atoms: indeed, these atoms only have one valence electron, hence the problem reduces to that of a hydrogenoid atoms, although with a different potential. To see this, note that a completely full shell has a spherically-symmetric charge distribution, since:

$$\sum_{m=-\ell}^{\ell} |Y_{\ell,m}(\vartheta, \varphi)|^2 = \text{const.}$$

Since the $Z - 1$ core electrons screen the Coulombian potential of the nucleus, the potential acting on the valence electron is intermediate between the fully-screened potential $-e^2/r$ (which dominates for $r \rightarrow \infty$) and the un-screened potential $-Ze^2/r$ (which dominates for $r \rightarrow 0$). To express this, the energy eigenvalues for the screened potential are written as:

$$E_{n,\ell} = -\frac{E_R}{(n - \alpha_\ell)^2} \quad (2.2)$$

where the **quantum defect** α_ℓ encodes the non-Coulombian nature of the potential. Note the absence of a Z -dependence. Quantum defects are experimentally measured: e.g. for Na the relevant ones are $\alpha_s = 1.35$, $\alpha_p = 0.83$ and $\alpha_d = 0.01$, while the other ones are essentially zero (this signals the progressively increasing distance of orbitals from the nucleus).

It is possible to include the fine-structure splitting too: for non-hydrogenoid atoms, which are increasingly heavier, the kinetic term and the Darwin term rapidly become negligible, thus the relevant correction is due to the spin-orbit coupling. Recall that:

$$\mathcal{H}_{\text{s-o}} = \frac{1}{2m_e^2 c^2} \frac{1}{r} \frac{dV(r)}{dr} \mathbf{L} \cdot \mathbf{S}$$

where \mathbf{L} and \mathbf{S} are the total orbital and spin angular momenta (Eq. 2.5). Since the exact analytic expression of the potential is unknown, the spin-orbit correction is written as:

$$\Delta E_{\text{s-o}} = \frac{\xi_{n,\ell}}{2} [J(J+1) - L(L+1) - S(S+1)] \quad (2.3)$$

where the spin-orbit factor $\xi_{n,\ell}$ still depends on the n and ℓ quantum numbers.

Example 2.1.1 (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 2.1.2 (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:

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

§2.1.1 X-ray spectra

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

$$E_n \approx -\frac{E_R (Z - \alpha_n)^2}{n^2} \quad (2.4)$$

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 $L_\beta \equiv L \rightarrow N$.

§2.2 Multiple valence electrons

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:

$$\mathbf{S} := \sum_i \mathbf{s}_i \quad \mathbf{L} := \sum_i \boldsymbol{\ell}_i \quad \mathbf{J} = \mathbf{L} + \mathbf{S} \quad (2.5)$$

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.

Example 2.2.1 (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 ${}^4P_{1/2, 3/2, 5/2}$.

§2.2.1 Atoms in a magnetic field

When applying a magnetic field $\mathbf{B} \neq 0$, 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:

$$\mathbf{A}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times \mathbf{r} \quad (2.6)$$

Proposition 2.2.1 (Mono-electron Hamiltonian in constant magnetic field)

$$\mathcal{H} \simeq \mathcal{H}_0 - \boldsymbol{\mu} \cdot \mathbf{B} \quad (2.7)$$

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:

$$\boldsymbol{\mu} = \boldsymbol{\mu}_L + \boldsymbol{\mu}_S = -\frac{\mu_B}{\hbar} (\mathbf{L} + 2\mathbf{S}) \quad (2.8)$$

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

$$\mathcal{H} = \mathcal{H}_0 + \frac{\mu_B}{\hbar} (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B} + \xi(\mathbf{r}) \mathbf{L} \cdot \mathbf{S} \quad (2.9)$$

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 $\mathbf{S} = 0$ 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.

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.

Example 2.2.2 (Cadmium)

Consider ${}_{48}\text{Cd} = [\text{Kr}]4d^{10}5s^2$: in this case $L = S = J = 0$, hence the ground state is ${}^1\text{S}_0$. 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 ${}^1\text{P}_1$ and ${}^1\text{D}_2$. 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, ${}^1\text{P}_1 \rightarrow {}^1\text{S}_0$ is split into one π transition and two σ transitions, while ${}^1\text{D}_2 \rightarrow {}^1\text{P}_1$ is split into three π transitions and six σ transitions: π transitions have unperturbed energies, while σ transitions have energies perturbed by $\Delta E = \pm \mu_B B$.

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).

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 quantum description, contrary to the normal Zeeman effect).

§2.2.1.1 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:

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2} (L_+ S_- + L_- S_+) + L_z S_z \quad (2.10)$$

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:

$$\Delta E_{\text{PB}} = \mu_B B (m_L + 2m_S) + \xi m_L m_S \quad (2.11)$$

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 2.2.1 (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

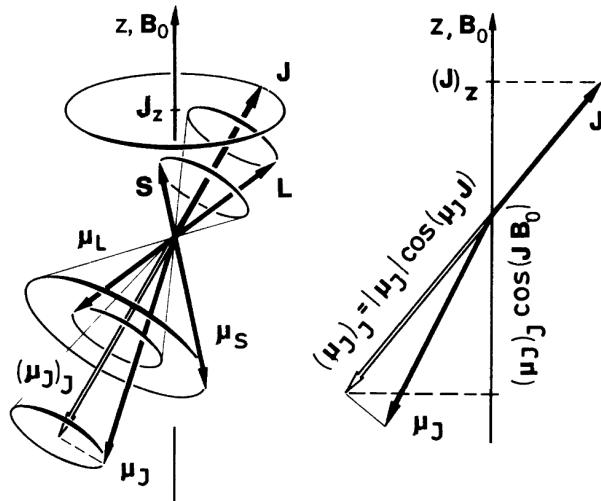


Figure 2.1: Classical view of the anomalous Zeeman effect

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

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

Geometrically $d\ell = \ell \sin \vartheta d\varphi$, where ϑ is the angle between ℓ 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 ℓ):

$$\omega = g_\ell \frac{\mu_B}{\hbar} B \quad (2.12)$$

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. 2.10, 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 $\mathbf{S}_{\text{eff}} \equiv S_z \mathbf{e}_z$.

§2.2.1.2 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. 2.2.1, 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. 2.1). 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 $\xi \gg \mu_B B$, 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. 2.1.

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. 2.1 as $(\boldsymbol{\mu}_J)_J$, i.e. the projection of $\boldsymbol{\mu}_J$ along \mathbf{J}).

Lemma 2.2.1 (Energy perturbation for the anomalous Zeeman effect)

$$\langle \boldsymbol{\mu}_J \cdot \mathbf{B} \rangle = -\frac{\mu_B B}{\hbar} \frac{3J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} m_J \quad (2.13)$$

Proof. Given the projection scheme outlined above and in Fig. 2.1, 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:

$$g_J \equiv \frac{3J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (2.14)$$

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:

$$\Delta E_{\text{AZ}} = \frac{\xi}{2} [J(J+1) - L(L+1) - S(S+1)] + g_J m_J \mu_B B \quad (2.15)$$

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 2.2.3 (Paschen–Back effect in hydrogen)

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

Solution. In this case $\mu_B B = 0.58 \text{ meV}$, while for ${}^1\text{H}$ 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 ${}^2S_{1/2}$ has no spin-orbit interaction, while the possible $n = 2$ states are ${}^2S_{1/2}$ and ${}^2P_{1/2,3/2}$: 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 ${}^2S_{1/2} \rightarrow {}^2S_{1/2}$ is dipole-forbidden, so consider ${}^2P_{1/2,3/2} \rightarrow {}^2S_{1/2}$: by Eq. 2.11, ${}^2P_{1/2,3/2}$ 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, ${}^2S_{1/2}$ 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.

§2.3 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:

$$\boldsymbol{\mu}_I = g_I \frac{\mu_N}{\hbar} \mathbf{I} \quad \mu_N \equiv \frac{e\hbar}{2m_p} \quad (2.16)$$

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**:

$$\mathcal{H}_{HF} = \frac{\xi_{HF}}{\hbar^2} \mathbf{I} \cdot \mathbf{J} \quad (2.17)$$

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

$$\Delta E_{HF} = \frac{\xi_{HF}}{2} [F(F+1) - I(I+1) - J(J+1)] \quad (2.18)$$

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

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

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

$$\xi_{\text{HF}} = \frac{g_I \mu_N B_J}{\sqrt{J(J+1)}} \quad (2.19)$$

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:

$$\xi_{\text{HF}} \simeq \frac{2}{3} \mu_0 g_J \mu_B g_I \mu_N |\psi(\mathbf{0})|^2 \quad (2.20)$$

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

Example 2.3.1 (Hyperfine interaction in hydrogen)

For ${}^1\text{H}$ we have the explicit expression in terms of the Bohr radius:

$$|\psi(\mathbf{0})|^2 = \frac{1}{\pi R_{\text{B}}^3} \quad R_{\text{B}} \simeq 52.92 \text{ pm}$$

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. 2.18, 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 2.3.2 (Hyperfine interaction in generic mono-electron atoms)

For ns states in generic mono-electron atoms, the following first-order approximation holds:

$$|\psi(\mathbf{0})|^2 \simeq \frac{Z^3}{\pi n^3 R_{\text{B}}^3}$$

For other orbitals, instead:

$$\xi_{\text{HF}} \simeq \frac{\mu_0}{4\pi} g_I \mu_B \mu_N \frac{Z^3}{R_{\text{B}}^3 n^3 J(J+1)(2L+1)}$$

§2.3.1 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 $\mu_B B \gg \mu_N B$: the total ordering is then given by the relation between ξ_{HF} and $\mu_B B$, i.e. either weak field $\xi_{\text{HF}} \gg \mu_B B$ or strong field $\mu_B B \gg \xi_{\text{HF}}$.

§2.3.1.1 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:

$$\boldsymbol{\mu}_F = \boldsymbol{\mu}_I + \boldsymbol{\mu}_J \approx \boldsymbol{\mu}_J \quad (2.21)$$

since $\mu_I \propto \mu_N \ll \mu_B$. Then, following the discussion in §2.2.1.2, 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:

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

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:

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

that is:

$$\Delta E_B = \frac{g_J \mu_B B}{2F(F+1)} m_F [F(F+1) + J(J+1) - I(I+1)] \quad (2.22)$$

This expression can be rewritten as:

$$\Delta E_B = g_F m_F \mu_B B \quad (2.23)$$

with the Landé factor for the atomic spin defined as:

$$g_F \equiv g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} \quad (2.24)$$

Each level is first split by the spin-orbit interaction, then by the hyperfine interaction and finally by the additional splitting in Eq. 2.23.

§2.3.1.2 Strong magnetic field

In this case, as per Obs. 2.2.1, 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 §2.2.1.1:

$$\Delta E_B = g_J m_J \mu_B B - g_I m_I \mu_N B + \xi_{HF} m_I m_J \quad (2.25)$$

where the negative sign before in the first terms stems from the definition Eq. 2.16, 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. 2.25), and finally by the hyperfine interaction (third term of Eq. 2.25), with the additional correction of the nuclear Zeeman energy (second term of Eq. 2.25).

Example 2.3.3 (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. 2.2, 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

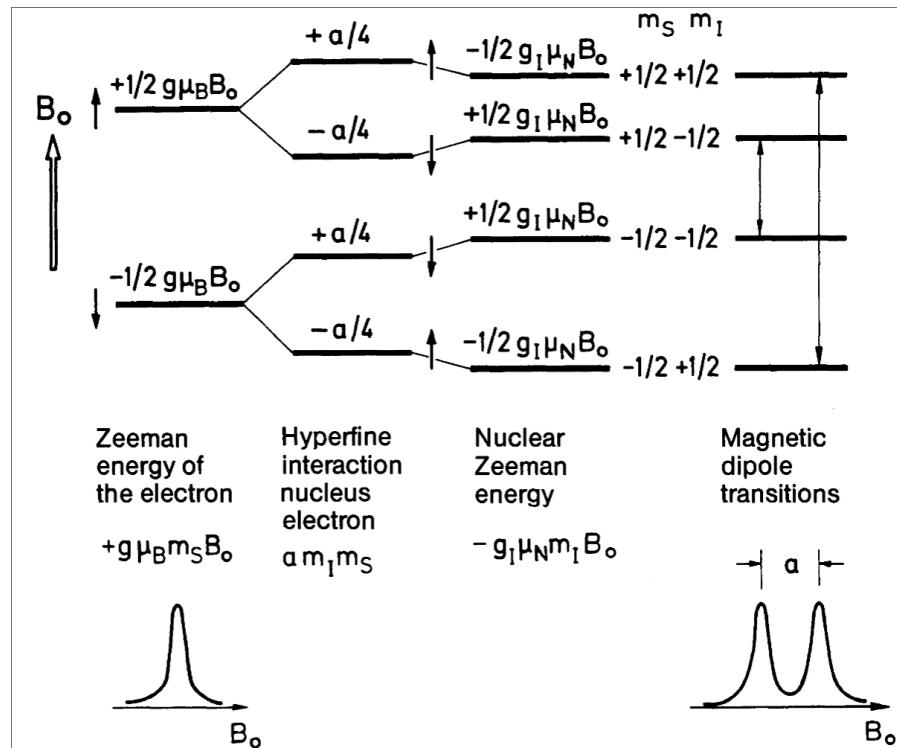


Figure 2.2: Hyperfine structure of hydrogen in a strong magnetic field.

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

$$\begin{aligned}
 E_{(+,+)} &= \frac{1}{2} (g_J \mu_B - g_I \mu_N) B + \frac{\xi_{HF}}{4} & E_{(+,-)} &= \frac{1}{2} (g_J \mu_B + g_I \mu_N) B - \frac{\xi_{HF}}{4} \\
 E_{(-,+)} &= -\frac{1}{2} (g_J \mu_B + g_I \mu_N) B - \frac{\xi_{HF}}{4} & E_{(-,-)} &= -\frac{1}{2} (g_J \mu_B - g_I \mu_N) B + \frac{\xi_{HF}}{4}
 \end{aligned}$$

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. 2.2). The energies of these transitions then are:

$$\Delta E_{(+,+)\rightarrow(-,+)} = g_J \mu_B B + \frac{\xi_{HF}}{2} \quad \Delta E_{(+,-)\rightarrow(-,-)} = g_J \mu_B B - \frac{\xi_{HF}}{2}$$

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

Chapter 3

Multi-electron Atoms: Analytic Solutions

§3.1 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:

$$\mathcal{H} = -\frac{\hbar^2}{2m}\Delta_{\mathbf{r}_1} - \frac{\hbar^2}{2m}\Delta_{\mathbf{r}_2} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \quad (3.1)$$

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 3.1.1 (Eigenfunctions of the exchange operator)

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \pm\Psi(\mathbf{r}_2, \mathbf{r}_1) \quad (3.2)$$

Proof. By definition $\mathcal{P}_{1,2}^2 = \mathbb{1}$. 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 $\lambda = \pm 1$. □

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. 3.1, 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:

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

and an antisymmetric singlet:

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

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 $S = 0$, where¹ $S \equiv s_1 + s_2$.

§3.1.1 Perturbation theory

As a first attempt to solve the Schrödinger equation with Hamiltonian Eq. 3.1, 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:

$$\Psi_{1,2}^{\pm}(\sigma, \sigma') = \frac{1}{\sqrt{2}} [\psi_1(\sigma)\psi_2(\sigma') \pm \psi_1(\sigma')\psi_2(\sigma)] \quad (3.3)$$

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

Proposition 3.1.1 (Unperturbed eigenenergies)

$$E_0(\sigma, \sigma') = E_0(\sigma) + E_0(\sigma') \quad (3.4)$$

Proof. Setting² $\mathcal{H}_0 = \mathcal{H}_1 + \mathcal{H}_2$:

$$\begin{aligned} \mathcal{H}_0\Psi_{1,2}^{\pm}(\sigma, \sigma') &= \frac{1}{\sqrt{2}} [(\mathcal{H}_1 + \mathcal{H}_2)\psi_1(\sigma)\psi_2(\sigma') \pm (\mathcal{H}_1 + \mathcal{H}_2)\psi_1(\sigma')\psi_2(\sigma)] \\ &= \frac{1}{\sqrt{2}} [(E_0(\sigma) + E_0(\sigma'))\psi_1(\sigma)\psi_2(\sigma') \pm (E_0(\sigma') + E_0(\sigma))\psi_1(\sigma')\psi_2(\sigma)] \\ &= [E_0(\sigma) + E_0(\sigma')] \Psi_{1,2}^{\pm}(\sigma, \sigma') \end{aligned}$$

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 3.1.1 (Helium)

The unperturbed eigenenergies of ${}_2\text{He}$ are:

$$E_0(n_1, n_2) = -4E_R \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right)$$

For example, $E_0(1s^2) \simeq -108.8 \text{ eV}$: however, experimentally the energy to doubly ionize ${}_2\text{He}$ is 79.0 eV, thus showing the importance of the interaction term in the Hamiltonian.

¹To be precise, $S = s_1 \otimes \mathbb{1}_2 + \mathbb{1}_1 \otimes s_2$.

²To be precise, $\mathcal{H}_0 = \mathcal{H}_1 \otimes \mathbb{1}_2 + \mathbb{1}_1 \otimes \mathcal{H}_2$.

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

$$\begin{aligned}\Delta E(1s^2) &= \langle \Psi_{1,2}^+(\{1,0,0\}, \{1,0,0\}) | \mathcal{H}_{1,2} | \Psi_{1,2}^+(\{1,0,0\}, \{1,0,0\}) \rangle \\ &= 2 \int_{\mathbb{R}^6} d^3r_1 d^3r_2 |\psi_{1,0,0}(\mathbf{r}_1)|^2 |\psi_{1,0,0}(\mathbf{r}_2)|^2 \frac{e^2}{\|\mathbf{r}_1 - \mathbf{r}_2\|} = \frac{5}{4} Z E_R\end{aligned}$$

This is a classical correction, and $E_0(1s^2) + \Delta E(1s^2) \simeq -74.8$ 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 3.1.2 (Interaction correction)

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

$$\Delta E^\pm(\sigma, \sigma') = \mathcal{J}(\sigma, \sigma') \pm \mathcal{K}(\sigma, \sigma') \quad (3.5)$$

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

$$\mathcal{J}(\sigma, \sigma') \equiv \int_{\mathbb{R}^6} d^3r_1 d^3r_2 |\psi_1(\sigma)|^2 |\psi_2(\sigma')|^2 \frac{e^2}{\|\mathbf{r}_1 - \mathbf{r}_2\|} \quad (3.6)$$

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

$$\mathcal{K}(\sigma, \sigma') \equiv \int_{\mathbb{R}^6} d^3r_1 d^3r_2 \psi_1(\sigma)^* \psi_1(\sigma') \psi_2(\sigma')^* \psi_2(\sigma) \frac{e^2}{\|\mathbf{r}_1 - \mathbf{r}_2\|} \quad (3.7)$$

Proof. By direct computation:

$$\begin{aligned}\Delta^\pm E(\sigma, \sigma') &= \langle \Psi_{1,2}^\pm(\sigma, \sigma') | \mathcal{H}_{1,2} | \Psi_{1,2}^\pm(\sigma, \sigma') \rangle = \int_{\mathbb{R}^6} d^3r_1 d^3r_2 |\Psi_{1,2}^\pm(\sigma, \sigma')|^2 \frac{e^2}{\|\mathbf{r}_1 - \mathbf{r}_2\|} \\ &= \frac{e^2}{2} \int_{\mathbb{R}^6} \frac{d^3r_1 d^3r_2}{\|\mathbf{r}_1 - \mathbf{r}_2\|} [\psi_1(\sigma)^* \psi_2(\sigma')^* \pm \psi_1(\sigma')^* \psi_2(\sigma)^*] [\psi_1(\sigma) \psi_2(\sigma') \pm \psi_1(\sigma') \psi_2(\sigma)] \\ &= \frac{e^2}{2} \int_{\mathbb{R}^6} \frac{d^3r_1 d^3r_2}{\|\mathbf{r}_1 - \mathbf{r}_2\|} \left[|\psi_1(\sigma)|^2 |\psi_2(\sigma')|^2 + |\psi_1(\sigma')|^2 |\psi_2(\sigma)|^2 \right] + \\ &\quad \pm \frac{e^2}{2} \int_{\mathbb{R}^6} \frac{d^3r_1 d^3r_2}{\|\mathbf{r}_1 - \mathbf{r}_2\|} [\psi_1(\sigma)^* \psi_1(\sigma') \psi_2(\sigma')^* \psi_2(\sigma) + \psi_1(\sigma')^* \psi_1(\sigma) \psi_2(\sigma)^* \psi_2(\sigma')] \\ &= e^2 \int_{\mathbb{R}^6} \frac{d^3r_1 d^3r_2}{\|\mathbf{r}_1 - \mathbf{r}_2\|} |\psi_1(\sigma)|^2 |\psi_2(\sigma')|^2 \pm e^2 \int_{\mathbb{R}^6} \frac{d^3r_1 d^3r_2}{\|\mathbf{r}_1 - \mathbf{r}_2\|} \psi_1(\sigma)^* \psi_1(\sigma') \psi_2(\sigma')^* \psi_2(\sigma)\end{aligned}$$

which is the thesis. □

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 3.1.2 (Helium again)

Consider again ${}_2\text{He}$, and in particular its lowest states $1s^2$, $1s^12s^1$ and $1s^12p^1$:

- $1s^2$ 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 multiplet ${}^3P_{0,1,2}$ and a triplet 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).

§3.2 Many-electron atoms

Given an atom with N_e electrons, the Hamiltonian of the system (in the massive approximation for the nucleus) is:

$$\mathcal{H} = \sum_{i=1}^{N_e} \left(-\frac{\hbar^2}{2m_e} \Delta_{\mathbf{r}_i} - \frac{Ze^2}{r_i} \right) + \sum_{i=1}^{N_e} \sum_{j>i}^{N_e} \frac{e^2}{r_{ij}} \quad (3.8)$$

with $r_{ij} \equiv \| \mathbf{r}_i - \mathbf{r}_j \|$. This Hamiltonian can be rewritten as $\mathcal{H} = \sum_{i=1}^{N_e} \mathcal{H}_i$, with:

$$\mathcal{H}_i = -\frac{\hbar^2}{2m_e} \Delta_{\mathbf{r}_i} - \frac{Ze^2}{r_i} + \frac{1}{2} \sum_{j=1}^{N_e} \frac{e^2}{r_{ij}} \quad (3.9)$$

The third term cannot be treated as a perturbation; however, for valence electron we can approximate the potential generated by core electrons as a central potential, thus writing:

$$V_i(\{\mathbf{r}_k\}) = -\frac{Ze^2}{r_i} + \frac{1}{2} \sum_{j=1}^{N_e} \frac{e^2}{r_{ij}} \equiv V_c(\mathbf{r}_i) + \mathcal{H}'_i$$

where the potential \mathcal{H}'_i generated by other valence electrons can now be treated as perturbation (independent-electrons approximation). Then, the unperturbed energy of the system is:

$$E_0 = \sum_{i=1}^{N_e} E_i^{(0)} \quad E_i^{(0)} \equiv E_{n_i, \ell_i} : (\mathcal{H}_i + V_c) \psi_i = E_i^{(0)} \psi_i$$

where the wave-functions ψ_i are the single-electron wave-functions in Eq. 1.3. The total wave-function needs to be anti-symmetrized, so we set the notation $\phi_\sigma(q_i) \equiv \psi_{n_i, \ell_i, m_{\ell_i}}(\mathbf{r}_i) \mathcal{X}_{m_{s_i}}$ with $\sigma \equiv \{n, \ell, m_\ell, m_s\}$: the total anti-symmetric wave-function is then expressed as a **Slated determinant**:

$$\Phi(\{q_k\}) = \frac{1}{\sqrt{N_e!}} \begin{vmatrix} \phi_{\sigma_1}(q_1) & \phi_{\sigma_2}(q_1) & \dots & \phi_{\sigma_{N_e}}(q_1) \\ \phi_{\sigma_1}(q_2) & \phi_{\sigma_2}(q_2) & \dots & \phi_{\sigma_{N_e}}(q_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{\sigma_1}(q_{N_e}) & \phi_{\sigma_2}(q_{N_e}) & \dots & \phi_{\sigma_{N_e}}(q_{N_e}) \end{vmatrix} \quad (3.10)$$

This wave-function is anti-symmetric under exchange of two electrons, given the alternating nature of the determinant under exchange of rows/columns. Moreover, if two electrons have the same quantum numbers, then the total wave-function vanishes (since the determinant of a matrix with two equal rows/columns is zero), in accordance with the Pauli exclusion principle. Note that, in general, the Slater determinant is not an eigenfunction of the spin operator.

Example 3.2.1 (Slater determinant for ground state of helium)

Consider $[\text{He}]1\text{s}^2$: then $\phi_{\uparrow}(q_i) = \psi_{1,0,0}(\mathbf{r}_i)\mathcal{X}_i(\uparrow) \equiv \phi_i(\uparrow)$ and $\phi_{\downarrow}(q_i) = \psi_{1,0,0}(\mathbf{r}_i)\mathcal{X}_i(\downarrow) \equiv \phi_i(\downarrow)$, and the Slater determinant is:

$$\begin{aligned}\Phi_{1,2} \equiv \Phi(q_1, q_2) &= \frac{1}{\sqrt{2}} [\phi_1(\uparrow)\phi_2(\downarrow) - \phi_1(\downarrow)\phi_2(\uparrow)] \\ &= \psi_{1,0,0}(\mathbf{r}_1)\psi_{1,0,0}(\mathbf{r}_2) \frac{1}{\sqrt{2}} [\mathcal{X}_1(\uparrow)\mathcal{X}_2(\downarrow) - \mathcal{X}_1(\downarrow)\mathcal{X}_2(\uparrow)] \equiv \Psi_{1,2}\mathcal{X}_{1,2}\end{aligned}$$

where $\psi_{1,2}$ is symmetric and $\mathcal{X}_{1,2}$ is anti-symmetric. This is precisely the singlet $S = 0$ state that is the ground state of helium.

Example 3.2.2 (Slater determinant for excited state of helium)

Write the three wave-functions for the 2^3S_1 lowest energy state of helium in terms of the Slater determinant of the possible single-electron spin-orbital functions.

Solution. The 2 in the notation 2^3S_1 means that the electronic configuration considered is $[\text{He}] = 1\text{s}^1 2\text{s}^1$. The possible single-electron wave-functions are then:

$$\begin{array}{ll}\phi_{1,0,0,\uparrow}(\mathbf{r}_i) \equiv \phi_i(1 \uparrow) & \phi_{2,0,0,\uparrow}(\mathbf{r}_i) \equiv \phi_i(2 \uparrow) \\ \phi_{1,0,0,\downarrow}(\mathbf{r}_i) \equiv \phi_i(1 \downarrow) & \phi_{2,0,0,\downarrow}(\mathbf{r}_i) \equiv \phi_i(2 \downarrow)\end{array}$$

There are four possible Slater determinants:

$$\begin{aligned}\Phi_a &= \frac{1}{\sqrt{2}} [\phi_1(1 \uparrow)\phi_2(2 \uparrow) - \phi_1(2 \uparrow)\phi_2(1 \uparrow)] \\ &= \frac{1}{\sqrt{2}} [\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2) - \psi_{2s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)] \mathcal{X}_1(\uparrow)\mathcal{X}_2(\uparrow) \equiv \Psi_{1,2}^-(1s, 2s)\mathcal{X}_{1,2}^+(\uparrow, \uparrow) \\ \Phi_b &= \frac{1}{\sqrt{2}} [\phi_1(1 \downarrow)\phi_2(2 \downarrow) - \phi_1(2 \downarrow)\phi_2(1 \downarrow)] \\ &= \frac{1}{\sqrt{2}} [\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2) - \psi_{2s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)] \mathcal{X}_1(\downarrow)\mathcal{X}_2(\downarrow) \equiv \Psi_{1,2}^-(1s, 2s)\mathcal{X}_{1,2}^+(\downarrow, \downarrow) \\ \Phi_c &= \frac{1}{\sqrt{2}} [\phi_1(1 \uparrow)\phi_2(2 \downarrow) - \phi_1(2 \downarrow)\phi_2(1 \uparrow)] \\ &= \frac{1}{\sqrt{2}} [\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2)\mathcal{X}_1(\uparrow)\mathcal{X}_2(\downarrow) - \psi_{2s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)\mathcal{X}_1(\downarrow)\mathcal{X}_2(\uparrow)] \\ \Phi_d &= \frac{1}{\sqrt{2}} [\phi_1(1 \downarrow)\phi_2(2 \uparrow) - \phi_1(2 \uparrow)\phi_2(1 \downarrow)] \\ &= \frac{1}{\sqrt{2}} [\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2)\mathcal{X}_1(\downarrow)\mathcal{X}_2(\uparrow) - \psi_{2s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)\mathcal{X}_1(\uparrow)\mathcal{X}_2(\downarrow)]\end{aligned}$$

Φ_a and Φ_b are correctly anti-symmetrized, and they correspond to the states with $m_S = +1$ and $m_S = -1$ of the 2^3S_1 triplet. On the other hand, Φ_c and Φ_d are not spin eigen-functions, hence we need to consider linear combinations of them:

$$\begin{aligned}\Phi_{c+d} &\equiv \frac{1}{\sqrt{2}} [\Phi_c + \Phi_d] \\ &= \frac{1}{\sqrt{2}} [\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2) - \psi_{2s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)] \frac{1}{\sqrt{2}} [\mathcal{X}_1(\uparrow)\mathcal{X}_2(\downarrow) + \mathcal{X}_1(\downarrow)\mathcal{X}_2(\uparrow)] \\ &\equiv \Psi_{1,2}^-(1s, 2s)\mathcal{X}_{1,2}^+(\uparrow, \downarrow) \\ \Phi_{c-d} &\equiv \frac{1}{\sqrt{2}} [\Phi_c - \Phi_d] \\ &= \frac{1}{\sqrt{2}} [\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2) + \psi_{2s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)] \frac{1}{\sqrt{2}} [\mathcal{X}_1(\uparrow)\mathcal{X}_2(\downarrow) - \mathcal{X}_1(\downarrow)\mathcal{X}_2(\uparrow)] \\ &\equiv \Psi_{1,2}^+(1s, 2s)\mathcal{X}_{1,2}^-(\uparrow, \downarrow)\end{aligned}$$

It is then clear that Φ_{c+d} is the $m_S = 0$ state of the 2^3S_1 triplet, while Φ_{c-d} is the singlet state 2^1S_0 with higher energy.

To confirm that this identification of states is correct, consider the four total wave-function given as a linear combinations of Φ_a , Φ_b , Φ_c and Φ_d :

$$\Psi_j = \sum_{i=1}^4 c_{ij} \Phi_i \quad \mathcal{H}' |\Psi_j\rangle = \Delta E_j |\Psi_j\rangle$$

where $\mathcal{H}' = \frac{e^2}{r_{12}}$ is the interaction Hamiltonian. The homogeneous system can be rewritten as:

$$\sum_{i=1}^4 c_{ij} \langle \Phi_k | \mathcal{H}' | \Phi_i \rangle = c_{kj} \Delta E_j \iff \sum_{i=1}^4 (\langle \Phi_k | \mathcal{H}' | \Phi_i \rangle - \delta_{ki} \Delta E_j) c_{ij} = 0$$

This means that \mathbf{c}_j are eigenvectors of $\mathbf{H} = [H_{ij}] \equiv [\langle \Phi_k | \mathcal{H}' | \Phi_i \rangle] \in \mathbb{C}^{4 \times 4}$ with eigenvalues ΔE_j , hence we impose that $\det(\mathbf{H} - \mathbf{I}_4 \Delta E) = 0$:

$$\begin{vmatrix} H_{11} - \Delta E & H_{12} & H_{13} & H_{14} \\ H_{21} & H_{22} - \Delta E & H_{23} & H_{24} \\ H_{31} & H_{32} & H_{33} - \Delta E & H_{34} \\ H_{41} & H_{42} & H_{43} & H_{44} - \Delta E \end{vmatrix} = 0$$

Given the spin parts of Φ_a and Φ_b , it is clear that $H_{1j} \propto \delta_{1j}$ and $H_{2j} \propto \delta_{2j}$, which, given that $H_{ij} = H_{ji}^*$, reduces the matrix to a block-diagonal form:

$$\begin{vmatrix} H_{11} - \Delta E & 0 & 0 & 0 \\ 0 & H_{22} - \Delta E & 0 & 0 \\ 0 & 0 & H_{33} - \Delta E & H_{34} \\ 0 & 0 & H_{43} & H_{44} - \Delta E \end{vmatrix} = 0$$

Explicitly computing the remaining elements with Prop. 3.1.2:

$$H_{11} = H_{22} = \langle \Psi_{1,2}^-(1s, 2s) | \mathcal{H}' | \Psi_{1,2}^-(1s, 2s) \rangle = \mathcal{J}(1s, 2s) - \mathcal{K}(1s, 2s)$$

$$H_{33} = H_{44} = \frac{1}{2} [\langle 1s, 2s | \mathcal{H}' | 1s, 2s \rangle + \langle 2s, 1s | \mathcal{H}' | 2s, 1s \rangle] = \mathcal{J}(1s, 2s)$$

$$H_{34} = H_{43} = \frac{1}{2} [-\langle 1s, 2s | \mathcal{H}' | 2s, 1s \rangle - \langle 2s, 1s | \mathcal{H}' | 1s, 2s \rangle] = -\mathcal{K}(1s, 2s)$$

Setting $\mathcal{J}(1s, 2s) \equiv \mathcal{J}$ and $\mathcal{K}(1s, 2s) \equiv \mathcal{K}$:

$$\begin{vmatrix} \mathcal{J} - \mathcal{K} - \Delta E & 0 & 0 & 0 \\ 0 & \mathcal{J} - \mathcal{K} - \Delta E & 0 & 0 \\ 0 & 0 & \mathcal{J} - \Delta E & -\mathcal{K} \\ 0 & 0 & -\mathcal{K} & \mathcal{J} - \Delta E \end{vmatrix} = 0$$

The normalized eigenvectors are then trivially found:

$$\begin{aligned} \Delta E_1 &= \mathcal{J} - \mathcal{K} & \mathbf{c}_1 &= (1, 0, 0, 0) \\ \Delta E_2 &= \mathcal{J} - \mathcal{K} & \mathbf{c}_2 &= (0, 1, 0, 0) \\ \Delta E_3 &= \mathcal{J} - \mathcal{K} & \mathbf{c}_3 &= \left(0, 0, \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}\right) \\ \Delta E_4 &= \mathcal{J} + \mathcal{K} & \mathbf{c}_4 &= \left(0, 0, \frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}\right) \end{aligned}$$

which confirm the above linear combinations and identifications.

§3.2.1 Hartee–Fock method

In the independent-electrons approximation, the interaction potential can be written as:

$$\mathcal{H}_i = -\frac{\hbar^2}{2m_e} \Delta_{\mathbf{r}_i} - \frac{Ze^2}{r_i} + \frac{1}{2} \sum_{j \neq i} \int d^3 r_j |\psi_{\sigma_j}(\mathbf{r}_j)|^2 \frac{e^2}{\|\mathbf{r}_i - \mathbf{r}_j\|} \quad (3.11)$$

In this case, the set of equations $\mathcal{H}_i \psi_i = E_i \psi_i$ must be solved iteratively, since \mathcal{H}_i depends on the solutions $\{\psi_k\}_{k=1,\dots,N_e}$: to do so (numerically), we start with an arbitrary set of wave-functions, we solve the system of equations and then use these solutions as the starting point of another iteration of this procedure. After a number of iterations, the difference between two consecutive sets of wave-functions drops below a pre-set threshold, signaling that an acceptable solution has been found: this is the **Hartree–Fock self-consistent method**.

§3.2.2 Hund's rules

Writing $V_i = V_c + \mathcal{H}'_i$, we can derive Hund's rules for the ground state from the interaction term. As already seen, Hund's first rule stems from the exchange integral determined by \mathcal{H}'_i , while Hund's second rule is determined by the dependence on the orbital angular momenta of all the electrons of the third term in Eq. 3.11 (in addition to being justified by classical intuition). Note that, being exchange integrals generally larger than the L -dependent terms in the interaction potential, the first rule must be applied before applying the second rule.

Finally, Hund's third rule comes from the spin-orbit coupling, hence (for lighter atoms) it has less priority than the first two rules. Having already maximized S and L , the maximization or minimization depends on the sign of the spin-orbit constant ξ :

- if $\xi > 0$, then J must be minimized;

- if $\xi < 0$, then J must be maximized.

Example 3.2.3 (Chloride)

Consider ${}_{17}\text{Cl}$, which has the ground state configuration $[\text{Ne}]3s^23p^5$. To determine the spectroscopic term of the ground state, focus on the valence electrons $3p^5$: the maximum (and only) value for the spin is $S = \frac{1}{2}$, while for the orbital angular momentum is $L = 1$ (since the unpaired electron either has $m_L = 0$ or $m_L = \pm 1$). Then, regarding the spin-orbit interaction, the valence shell is full except for a hole: this can be modelled as an empty shell with a positively-charged electron, hence the spin-orbit constant changes sign (since the magnetic moment of a positively-charged electron would be opposite to that of a normal electron) and is $\xi < 0$. As a consequence, J must be maximized to $J = \frac{3}{2}$, hence the ground state of ${}_{17}\text{Cl}$ is ${}^2\text{P}_{3/2}$.

This reasoning can be generalized to an alternative expression of Hund's third rule:

- if the valence shell is less than half-full, then J must be minimized;
- if the valence shell is more than half-full, then J must be maximized.

§3.2.3 $j - j$ coupling

Hund's rule require that the spin-orbit coupling is weaker than the electromagnetic interaction between electrons: this results in the Russell-Saunders coupling for the total angular momentum, which is found as $\mathbf{J} = \mathbf{S} + \mathbf{L}$.

For heavier atoms, on the other hand, the spin-orbit coupling dominates over the electromagnetic interaction, hence each ℓ_i and s_i are coupled into $\mathbf{j}_i = \ell_i + \mathbf{s}_i$, which are then combined in $\mathbf{J} = \sum_{i=1}^{N_e} \mathbf{j}_i$: this is the $j - j$ coupling. In the $j - j$ coupling, spectroscopic terms no longer represent good quantum numbers: for two-electron atoms, we adopt the notation $(j_1, j_2)_J$.

For intermediate cases, a linear combination of states from one of these two bases needs to be considered: in this case, selection rules for electron-dipole transitions are no longer valid, and transitions between singlet and triplet (or even multiplet) states are possible.

Chapter 4

Molecules

§4.1 Born–Oppenheimer approximation

Consider a system of N_n nuclei and N_e electrons. The Hamiltonian of the system then is:

$$\mathcal{H} = -\frac{\hbar^2}{2} \sum_{\alpha=1}^{N_n} \frac{\Delta_\alpha}{M_\alpha} - \frac{\hbar^2}{2m_e} \sum_{i=1}^{N_n} \Delta_i + \frac{1}{2} \sum_{i \neq j=1}^{N_n} \frac{e^2}{r_{ij}} + \frac{1}{2} \sum_{\alpha \neq \beta=1}^{N_n} \frac{Z_\alpha Z_\beta e^2}{R_{\alpha\beta}} - \sum_{i=1}^{N_e} \sum_{\alpha=1}^{N_n} \frac{Z_\alpha e^2}{\|\mathbf{R}_\alpha - \mathbf{r}_i\|} \quad (4.1)$$

with $r_{ij} \equiv \|\mathbf{r}_i - \mathbf{r}_j\|$ and $R_{\alpha\beta} \equiv \|\mathbf{R}_\alpha - \mathbf{R}_\beta\|$. The total wave-function of the system describes both the nuclear and the electronic component, and it can be written as $\Phi \equiv \Phi(\{\mathbf{R}_\alpha\}, \{\mathbf{r}_i\})$. Since $M_\alpha \gg m_e \forall \alpha = 1, \dots, N_n$ (circa three orders of magnitudes), the timescales of nuclear processes are three orders of magnitude longer than the timescales of atomic (i.e. electronic) processes, hence we can approximate the two components of the system as factorized:

$$\Phi(\{\mathbf{R}_\alpha\}, \{\mathbf{r}_i\}) = \Phi_n(\{\mathbf{R}_\alpha\}) \Phi_e(\{\mathbf{R}_\alpha\}, \{\mathbf{r}_i\}) \quad (4.2)$$

where we approximated the nuclear state to be independent of the electronic state, while the electronic state is supposed to react instantly to changes in the nuclear state. This is the **Born–Oppenheimer approximation**, which is an adiabatic approximation¹.

In the following, we adopt the shorthands $R \equiv \{\mathbf{R}_\alpha\}_{\alpha=1, \dots, N_n}$ and $r \equiv \{\mathbf{r}_i\}_{i=1, \dots, N_e}$, and we rename the various terms of the total Hamiltonian as:

$$\mathcal{H} = T_n + T_e + V_{ee}(r) + V_{nn}(R) + V_{ne}(R, r)$$

Theorem 4.1.1 (Atomic and nuclear wave-equations)

In the Born–Oppenheimer approximation, the atomic and nuclear wave-functions respectively solve:

$$[T_e + V_{ee}(r) + V_{ne}(R, r)] \Phi_e^{(g)}(R, r) = E_e^{(g)}(R) \Phi_e^{(g)}(R, r) \quad (4.3)$$

$$\left[T_n + V_{\text{ad}}^{(g)}(R) \right] \Phi_n(R) = E \Phi_n(R) \quad (4.4)$$

where E is the total energy of the system and the **adiabatic potential**, dependent on the electronic state, is defined as:

$$V_{\text{ad}}^{(g)}(R) \equiv E_e^{(g)}(R) + V_{nn}(R) \quad (4.5)$$

¹In general, an adiabatic approximation is one in which one or more components of a system are supposed to change slowly over time, compared to the other components.

Proof. The non-trivial terms of the total Hamiltonian are the operators T_e and T_n , so we study their action of the total wave-function:

$$\begin{aligned} T_e \Phi(R, r) &= T_e [\Phi_n(R) \Phi_e(R, r)] = \Phi_n(R) T_e \Phi_e(R, r) \\ T_n \Phi(R, r) &= T_n [\Phi_n(R) \Phi_e(R, r)] \equiv -\frac{\hbar^2}{2} \sum_{\alpha=1}^{N_n} \frac{\Delta_\alpha}{M_\alpha} [\Phi_n(R) \Phi_e(R, r)] \\ &= -\frac{\hbar^2}{2} \sum_{\alpha=1}^{N_n} \frac{1}{M_\alpha} [\Phi_e(R, r) \Delta_\alpha \Phi_n(R) + \Phi_n(R) \Delta_\alpha \Phi_e(R, r) + 2 \nabla_\alpha \Phi_n(R) \cdot \nabla_\alpha \Phi_e(R, r)] \\ &= \Phi_e(R, r) T_n \Phi_n(R) - \sum_{\alpha=1}^{N_n} \frac{\hbar^2}{2M_\alpha} [\Phi_n(R) \Delta \Phi_e(R, r) + 2 \nabla_\alpha \Phi_n(R) \cdot \nabla_\alpha \Phi_e(R, r)] \end{aligned}$$

WTS the summation is negligible in the Born–Oppenheimer approximation. To do so, first consider the operator $\mathcal{O}_1 : \mathcal{O}_1 \Phi(R, r) \equiv \frac{\hbar^2}{M_\alpha} \nabla_\alpha \Phi_n(R) \cdot \nabla_\alpha \Phi_e(R, r)$ and compute its expectation value:

$$\begin{aligned} \langle \mathcal{O}_1 \rangle &= -\frac{\hbar^2}{M_\alpha} \int_{\mathbb{R}^{3(N_n+N_e)}} d^{3N_n} R d^{3N_e} r \Phi_n(R)^* \Phi_e(R, r)^* \nabla_\alpha \Phi_n(R) \cdot \nabla_\alpha \Phi_e(R, r) \\ &= -\frac{\hbar^2}{M_\alpha} \int_{\mathbb{R}^{3N_n}} d^{3N_n} R \Phi_n(R)^* \nabla_\alpha \Phi_n(R) \cdot \int_{\mathbb{R}^{3N_e}} d^{3N_e} r \Phi_e(R, r)^* \nabla_\alpha \Phi_e(R, r) \\ &\simeq -\frac{\hbar^2}{M_\alpha} \int_{\mathbb{R}^{3N_n}} d^{3N_n} R \Phi_n(R)^* \nabla_\alpha \Phi_n(R) \cdot \frac{1}{2} \nabla_\alpha \int_{\mathbb{R}^{3N_e}} d^{3N_e} r \Phi_e(R, r)^* \Phi_e(R, r) = 0 \end{aligned}$$

since the last integral is constant (assuming $\Phi_e(R, r)$ to be normalized). The main approximation employed it that $\Phi_e(R, r) \nabla_\alpha \Phi_e(R, r)^* \simeq \Phi_e(R, r)^* \nabla_\alpha \Phi_e(R, r)$: assuming this to be valid, we can suppress the second term in the summation, as its expectation value vanishes (this is another approximation).

Now, focus on the first term in the summation. The dependence of Φ_e on nuclear and atomic coordinates $\{\mathbf{R}_\alpha\}_{\alpha=1,\dots,N_n}, \{\mathbf{r}_i\}_{i=1,\dots,N_e}$ is a relative dependence, i.e. it depends on relative distances of the kind $\{\mathbf{R}_\alpha - \mathbf{r}_i\}_{\alpha=1,\dots,N_n}^{i=1,\dots,N_e}$, hence we see that:

$$-\frac{\hbar^2}{2M_\alpha} \Phi_n(R) \Delta_\alpha \Phi_e(R, r) = -\frac{\hbar^2}{2M_\alpha} \Phi_n(R) \sum_{i=1}^{N_e} \Delta_i \Phi_e(R, r) = \frac{m_e}{M_\alpha} T_e \Phi(R, r)$$

But $m_e \lesssim 10^{-3} M_\alpha \forall \alpha = 1, \dots, N_n$, hence this term too is negligible. The Schrödinger equation then becomes:

$$\begin{aligned} \Phi_e(R, r) T_n \Phi_n(R) + \Phi_n(R) T_e \Phi_e(R, r) + [V_{ee}(r) + V_{ne}(R, r) + V_{nn}(R)] \Phi_n(R) \Phi_e(R, r) \\ = E \Phi_n(R) \Phi_e(R, r) \end{aligned}$$

which can be rewritten as:

$$[\mathcal{H}_e(R, r) + \mathcal{H}_n(R)] \Phi_n(R) \Phi_e(R, r) = E \Phi_n(R) \Phi_e(R, r)$$

$$\mathcal{H}_e(R, r) \equiv T_e + V_{ee}(r) + V_{ne}(R, r) \quad \mathcal{H}_n(R) \equiv T_n + V_{nn}(R)$$

To solve for the electronic state, consider the nuclear state $\Phi_n(R)$ fixed, i.e. $\{\mathbf{R}_\alpha\}_{\alpha=1,\dots,N_n}$ fixed positions:

$$\mathcal{H}_e(R, r) \Phi_e(R, r) = E_e(R) \Phi_e(R, r)$$

where the energy $E_e(R) = E_e^{(g)}(R)$ of the electronic state g has a parametric dependence on the nuclear state through $\{\mathbf{R}_\alpha\}_{\alpha=1,\dots,N_n}$. Then, since $\mathcal{H}_n(R, r)\Phi_e(R) = \Phi_e(R)\mathcal{H}_n(R, r)$ as shown above, it is clear that the evolution of the nuclear state is given by:

$$[\mathcal{H}_n(R) + E_e^{(g)}(R)]\Phi_n(R) = E\Phi_n(R)$$

which is the thesis. \square

An example of adiabatic potential for a two-electron atom is pictured in Fig. 4.1

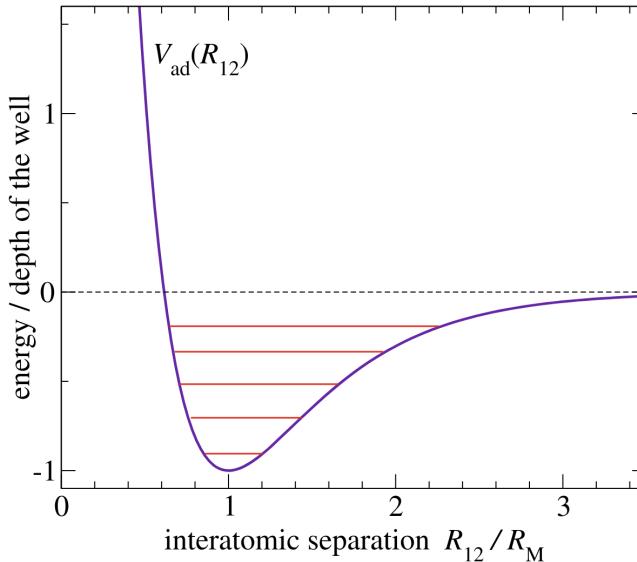


Figure 4.1: Adiabatic potential for a two-electron atom.

We now focus on the nuclear motion: in particular, we denote the nuclear wave-function as $\Phi_n(R) \equiv \Phi_\nu^{(g)}(R)$, where ν are the quantum numbers relative to the nuclear state and g those relative to the electronic state. The Schrödinger equation then becomes:

$$\left[-\sum_{\alpha=1}^{N_n} \frac{\hbar^2}{2M_\alpha} \Delta_\alpha + V_{\text{ad}}^{(g)}(R) \right] \Phi_\nu^{(g)}(R) = E_{g,\nu} \Phi_\nu^{(g)}(R) \quad (4.6)$$

§4.1.1 Biatomic molecules

In a biatomic molecule, the nuclear state can be described by a single quantity: indeed, given the positions \mathbf{R}_1 and \mathbf{R}_2 of the two nuclei, only the relative distance $\mathbf{R} \equiv \mathbf{R}_1 - \mathbf{R}_2$ is dynamically significant, since the center-of-mass motion of \mathbf{R}_{cm} is a free-particle motion which can be eliminated by working in the CM frame. In this frame:

$$\left[-\frac{\hbar^2}{2\mu} \Delta + V_{\text{ad}}^{(g)}(R) \right] \Phi_\nu^{(g)}(\mathbf{R}) = E_{g,\nu} \Phi_\nu^{(g)}(\mathbf{R}) \quad \mu \equiv \frac{M_1 M_2}{M_1 + M_2}$$

where the adiabatic potential only depends on $R \equiv \|\mathbf{R}\|$, i.e. it is a central potential. Then, the solution can be factored as:

$$\Phi_\nu^{(g)}(\mathbf{R}) = \mathcal{R}_\nu^{(g)}(R) Y_{K,M}(\vartheta, \varphi)$$

where K and M are the quantum numbers associated respectively to the orbital angular momentum and its projection on the zenithal axis. The radial Schrödinger equation is:

$$\left[-\frac{\hbar^2}{2\mu} \Delta + V_{\text{ad}}^{(g)}(R) + \frac{\hbar^2 K(K+1)}{2\mu R^2} \right] \mathcal{R}_{\nu}^{(g)}(R) = E_{g,\nu} \mathcal{R}_{\nu}^{(g)}(R) \quad (4.7)$$

Supposing that $R \approx R_{\text{eq}}$, where R_{eq} is the equilibrium distance of $V_{\text{ad}}^{(g)}(R)$, then the third term can be seen as the rotational energy of a rigid body² with $I = \mu R_{\text{eq}}^2$, since by definition $\langle \mathbf{L}^2 \rangle = \hbar^2 K(K+1)$:

$$E_{\text{rot}}(K) = \mathcal{B}K(K+1) \quad (4.8)$$

where $\mathcal{B} \equiv \frac{\hbar^2}{2I} \sim 1 \text{ meV} - 10 \text{ meV}$ is the rotational constant of the molecule. Keeping the electronic state fixed, as electronic transitions require higher energies, we can study purely-rotational transitions: these transitions have the same selection rules of electric-dipole transitions, i.e. $\Delta K = \pm 1$, hence the **purely-rotational spectrum** is:

$$\Delta E_{\text{rot}}(K) \equiv E_{\text{rot}}(K+1) - E_{\text{rot}}(K) = 2\mathcal{B}(K+1) \quad (4.9)$$

Purely-rotational spectral lines are then equidistantly spaced by an energy $2\mathcal{B}$ (typically in the IR or MW regions). The intensity I_K of the K^{th} line is proportional to the fraction $n_K \equiv \frac{N_K}{N_{\text{tot}}}$ of molecules in the state K , described by the Boltzmann distribution:

$$n_K(T) = (2K+1)e^{-\frac{\mathcal{B}K(K+1)}{k_B T}} \quad (4.10)$$

This distribution is linear at the origin and asymptotically vanishing, hence it has a finite maximum.

Lemma 4.1.1 (Maximum of Boltzmann distribution)

$$K_m(T) = \frac{1}{2} \left[\sqrt{\frac{2k_B T}{\mathcal{B}}} - 1 \right] \quad (4.11)$$

Proof. To find the maximum of $n_K(T)$ as a function of temperature, impose:

$$\frac{d}{dT} n_K(T) = 0 \implies \left[2 - \frac{\mathcal{B}}{k_B T} (2K+1)^2 \right] e^{-\frac{\mathcal{B}K(K+1)}{k_B T}} = 0$$

which is trivially solved. □

§4.1.2 Polyatomic molecules

The purely-rotational spectrum of a polyatomic molecule can be treated analogously: in this case, however, the rotation no longer follows $\mathbf{L} = I\omega$, where I is the moment of inertial (a scalar), but is in general $\mathbf{L} = \mathbf{I}\omega$, where \mathbf{I} is the inertia tensor. The inertia tensor can be diagonalized with respect to the principal axis of rotations, which we identify WLOG with the x, y, z -axis, so that the rotational energy is (promoting to operators):

$$\mathcal{H}_{\text{rot}} = \frac{L_x^2}{2I_x} + \frac{L_y^2}{2I_y} + \frac{L_z^2}{2I_z} \quad (4.12)$$

²To be precise, $I = \mu R_{\text{eq}}^2$ is the moment of inertia of a body composed of two point-like masses M_1 and M_2 , with reduced mass μ , which rotate around their center of mass at a distance R_{eq} from each other.

The rotational Hamiltonian is in general non-diagonalizable, since the three components of \mathbf{L} do not commute, but we can analyze particular cases of interest.

Linear molecule Identifying the z -axis with the axis of the molecule, then $I_z = 0$ and $I_x = I_y \equiv I$, and consequently $L_z = 0$, hence:

$$\mathcal{H}_{\text{rot}} = \frac{L_x^2 + L_y^2}{2I} = \frac{\mathbf{L}^2}{2I}$$

which is precisely the result previously found.

Cylindrical molecule In presence of a cylindrical symmetry, identifying the z -axis with the axis of the molecule, then $I_x = I_y \equiv I_{\perp}$, but now $I_z \neq 0$, hence:

$$\mathcal{H}_{\text{rot}} = \frac{L_x^2 + L_y^2}{2I_{\perp}} + \frac{L_z^2}{2I_z} = \frac{\mathbf{L}^2 - L_z^2}{2I_{\perp}} + \frac{L_z^2}{2I_z}$$

whose expectation value is:

$$E_{\text{rot}} = \frac{\hbar^2 K(K+1)}{2I_{\perp}} + \frac{\hbar^2 M^2}{2} \left(\frac{1}{I_z} - \frac{1}{I_{\perp}} \right)$$

The sign of the second term allows us to classify the various molecules:

- if $I_{\perp} < I_z$, the molecule is oblate (e.g. benzene C₆H₆);
- if $I_z < I_{\perp}$, the molecule is prolate (e.g. ammonia NH₃).

The purely-rotational spectrum of cylindrical molecule is more complex than that of linear molecules, since the M -degeneracy is broken by the second term and the K^{th} level is split into $M + 1$ levels. Note that the electric-dipole selection rules in this case are $\Delta K = \pm 1$ and $\Delta M = 0$.

Spherical molecule The spherically-symmetric case is trivial, since $I_x = I_y = I_z \equiv I$:

$$\mathcal{H}_{\text{rot}} = \frac{L_x^2 + L_y^2 + L_z^2}{2I} = \frac{\mathbf{L}^2}{2I}$$

which is analogous to the linear case. However, a spherically-symmetric molecule has no electric dipoles (e.g. methane CH₄), hence it is harder to be studied via EM interactions.

§4.1.2.1 Electronic state

Although most diatomic molecules have ground state with $\Lambda = 0$ (electronic angular momentum projected on the axis of the molecule), i.e. are Σ states, there are some molecules with ground state Π , i.e. $\Lambda = 1$, like NO and OH. In this case, then:

$$\mathcal{H}_{\text{rot}} = \frac{L_x^2 + L_y^2}{2I} + \frac{L_z^2}{2I_e} \implies E_{\text{rot}} = \frac{\hbar^2 K(K+1)}{2I} + \frac{\hbar^2 \Lambda^2}{2} \left(\frac{1}{I_e} - \frac{1}{I} \right)$$

where $I_e \sim m_e$ is the electronic moment of inertia. Note that, since $m_e \ll \mu$, it is $I_e \ll I$, hence the second term is positive; however, it is usually not observed, since transitions which change the quantum numbers Λ require much more energy ($\sim 1 \text{ eV}$) than rotational transitions ($\sim 1 \text{ meV}$), and doing so would change the electronic state of the molecule and, as per Eq. 4.5, the geometry of the molecule.

§4.1.3 Molecular vibrations

We now solve the radial Schrödinger equation Eq. 4.7 for diatomic molecules. First, explicitly write the Laplacian in spherical coordinates (recalling that $\mathcal{R}_\nu^{(g)}(R)$ only depends on the radial coordinate):

$$\left[-\frac{\hbar^2}{2\mu} \frac{1}{R^2} \frac{d}{dR} \left(R^2 \frac{d}{dR} \right) + V_{\text{eff}}^{(g)}(R, K) \right] \mathcal{R}_\nu^{(g)}(R) = E_{g,\nu} \mathcal{R}_\nu^{(g)}(R) \quad (4.13)$$

where we defined an effective potential to include the effect of the orbital angular momentum on the adiabatic potential. Now, focus on the first term:

$$\frac{1}{R^2} \frac{d}{dR} \left(R^2 \frac{d}{dR} \right) \mathcal{R}(R) = \frac{1}{R} \left[R \frac{d^2 \mathcal{R}(R)}{dR^2} + 2 \frac{d \mathcal{R}(R)}{dR} \right]$$

To simplify this expression, introduce an auxiliary function:

$$u_\nu^{(g)}(R) \equiv R \mathcal{R}_\nu^{(g)}(R) \quad (4.14)$$

Then, trivially:

$$\frac{1}{R^2} \frac{d}{dR} \left(R^2 \frac{d}{dR} \right) \mathcal{R}_\nu^{(g)}(R) = \frac{1}{R} \frac{d^2}{dR^2} u_\nu^{(g)}(R)$$

so that the radial equation can be recast in the simpler form:

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V_{\text{eff}}^{(g)}(R, K) \right] u_\nu^{(g)}(R) = E_{g,\nu} u_\nu^{(g)}(R) \quad (4.15)$$

To solve this equation, we employ a **harmonic approximation**, assuming $R \approx R_{\text{eq}}$:

$$V_{\text{ad}}^{(g)}(R) \simeq V_{\text{ad}}^{(g)}(R_{\text{eq}}) + \frac{1}{2} \frac{d^2 V_{\text{ad}}^{(g)}(R)}{dR^2} \Big|_{R=R_{\text{eq}}} (R - R_{\text{eq}})^2 \quad \frac{\hbar^2 K(K+1)}{2\mu R^2} \simeq \frac{\hbar^2 K(K+1)}{2\mu R_{\text{eq}}^2}$$

The adiabatic potential then reduces to a harmonic potential with elastic constant:

$$\kappa \equiv \frac{d^2 V_{\text{ad}}^{(g)}(R)}{dR^2} \Big|_{R=R_{\text{eq}}} \quad (4.16)$$

and the system to a simple harmonic oscillator:

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{1}{2} \kappa (R - R_{\text{eq}})^2 \right] u_\nu^{(g)}(R) = E_{\text{vib}}(n) u_\nu^{(g)}(R) \quad (4.17)$$

where:

$$E_{\text{vib}}(n) \equiv E_{g,\nu} - E_{\text{rot}}(K) - V_{\text{ad}}^{(g)}(R_{\text{eq}}) \quad (4.18)$$

clearly is the vibrational energy of the molecule, since it is the difference between the total energy with respect to the equilibrium energy $E_{g,\nu} - V_{\text{ad}}^{(g)}(R_{\text{eq}})$ and the rotational energy $E_{\text{rot}}(K)$. The degrees of freedom (and the quantum numbers) of the system are therefore separated into electronic (g), rotational (K, M) and vibrational (n) degrees of freedom. The eigenfunctions of Eq. 4.17 are the Hermite functions, and its spectrum is:

$$E_{\text{vib}}(n) = \left(n + \frac{1}{2} \right) \hbar \omega \quad \omega \equiv \sqrt{\frac{\kappa}{\mu}} \quad (4.19)$$

The molecules with the biggest vibrational energies are those with the lowest reduced mass, i.e. H_2 (with $\hbar \omega \simeq 0.546 \text{ eV}$) and HCl (with $\hbar \omega \simeq 0.36 \text{ eV}$): clearly, then, $E_{\text{rot}} \ll E_{\text{vib}} \ll E_e^{(g)}$, which justifies the separation of the degrees of freedom.

§4.1.3.1 Vibrational transitions

As noted previously, homo-nuclear molecules are IR-inactive³, since they have no electric dipoles, hence their interactions are mediated by higher-order terms in the multipole expansion of the EM field.

We then consider etero-nuclear molecules and analyze their electric-dipole transitions: it can be shown that, for vibrational transitions, the selection rule $\Delta n = \pm 1$ holds, i.e. $\Delta E_{\text{vib}} = \hbar\omega$. Note that at standard temperature, since $k_B T \simeq 26 \text{ meV}$, contrary to rotational levels, only the ground state of the vibrational spectrum is populated.

Anarmonic correction It is possible to treat the cubic term in the expansion of $V_{\text{ad}}^{(g)}(R)$ at $R = R_{\text{eq}}$ using perturbation theory, and the corrected energies are found to be:

$$E_{\text{vib}}(n) = \left(n + \frac{1}{2}\right) \hbar\omega - a \left(n + \frac{1}{2}\right)^2 \hbar\omega \quad (4.20)$$

with $a \in \mathbb{R}^+ : a \ll 1$, e.g. $a \simeq 0.018$ for HCl. Clearly, the correction becomes commensurable to the unperturbed energy for sufficiently large $n \sim a^{-1}$, and approaching this asymptotic value the energy levels become increasingly less spaced: when these levels approximately overlap, no elastic force is present in the molecule, i.e. the molecule has dissociated into its two constituent atoms. This phenomenon can estimate⁴ the dissociation energy of the molecule.

Lemma 4.1.2 (Dissociation energy)

$$E_{\text{diss}} \simeq \frac{\hbar\omega}{4a} \quad (4.21)$$

Proof. To find $n_{\text{diss}} : E_{\text{vib}}(n_{\text{diss}} + 1) = E_{\text{vib}}(n_{\text{diss}})$, impose:

$$\frac{dE_{\text{vib}}(n)}{dn} = 0 \implies \hbar\omega - 2a \left(n + \frac{1}{2}\right) \hbar\omega = 0 \implies n = \frac{1}{2a} - \frac{1}{2}$$

Then $E_{\text{diss}} \simeq E_{\text{vib}}(n_{\text{diss}})$. □

This result also allows to estimate the anarmonic coefficient from the dissociation energy. Moreover, it is possible to phenomenologically express the adiabatic potential in terms of the dissociation energy:

$$V_{\text{ad}}^{(g)}(R) = E_{\text{diss}} [1 - e^{-\beta(R-R_{\text{eq}})}]^2 - E_{\text{diss}} \quad (4.22)$$

which is known as **Morse potential**. Note that this expression fails for $R \rightarrow 0$, since it does not reproduce the singularity of the adiabatic potential, but this region has little phenomenological interest. An interesting property of the Morse potential is that it allows for an analytic solution of the radial Schrödinger equation, with exact eigenenergies Eq. 4.20.

The addition of an anarmonic correction also changes the selection rule for electric-dipole transitions: in this case $\Delta n \in \mathbb{Z} - \{0\}$, but the peaks in the spectrum are progressively suppressed as $|\Delta n|$ becomes larger than 1.

³Recall that IR transitions have energies $\sim 0.1 \text{ eV}$.

⁴This is only an estimate as, since the correction term is comparable to unperturbed energy, the perturbative analysis is no longer valid, and one would have to include higher-order corrections.

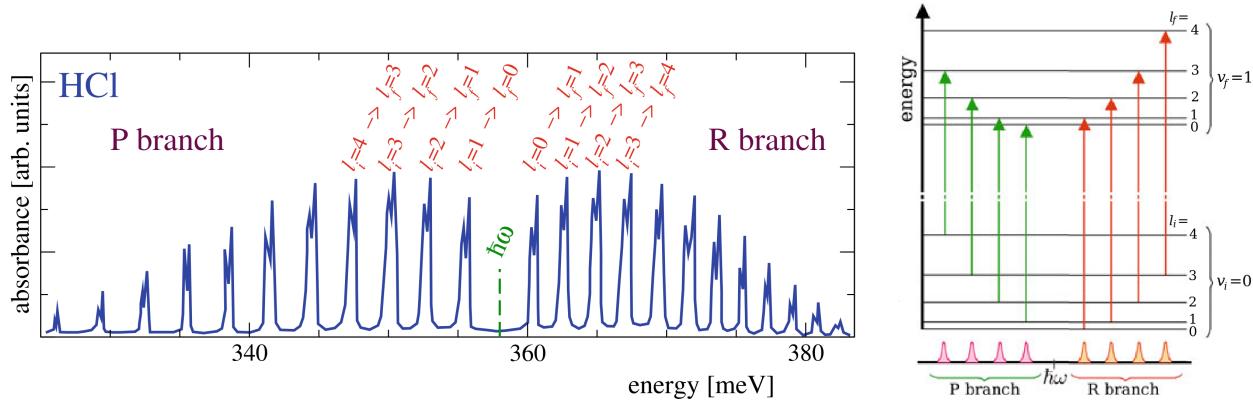


Figure 4.2: Observed roto-vibrational absorption spectrum of gas-phase HCl and scheme of electric-dipole transitions between $n = 0$ and $n = 1$ rotational levels.

Roto-vibrational spectrum In the harmonic approximation, the absorption of IR radiation can only excite molecules from the $n = 0$ state to the $n = 1$ state. However, since $E_{\text{rot}} \ll E_{\text{vib}}$, this absorption also induces multiple rotational transitions, hence both these states are split into multiple rotational levels with various values of K , as shown in Fig. 4.2. The roto-vibrational spectrum then is:

$$\Delta E_{\text{rot-vib}}(K) = \hbar\omega \pm 2\mathcal{B}(K + 1) \quad (4.23)$$

Note that the selection rule $\Delta K = \pm 1$ is valid if the electronic state is $\Lambda = 0$, i.e. for Σ states. If instead $\Lambda \neq 0$, then $\Delta K = 0, \pm 1$, hence a central peak at $\hbar\omega$ between the P and R branches is present, denoted as Q peak.

Including the anarmonic terms in the vibrational and rotational potentials, one finds the following corrections to the roto-vibrational energy:

$$E_{\text{rot-vib}}^{(1)} = -a_1 \hbar\omega \left(n + \frac{1}{2}\right)^2 - a_2 \left(n + \frac{1}{2}\right) K(K + 1) - a_3 K^2(K + 1)^2 \quad (4.24)$$

where a_1 is the previously discussed anarmonic coefficients and $a_2, a_3 \in \mathbb{R}^+ : a_2, a_3 \ll \mathcal{B}$. In particular, the third term is called centrifugal distortion term: it reduces the energy of the molecule since, in classical analogy, it represents a distortion of the spring due to the rotation, increasing the moment of inertia. On the other hand, the second term intuitively represents the fact that, at an excited state $n > 0$, the equilibrium distance is increased, hence so is the moment of inertia. From a perturbative analysis, the centrifugal coefficients are:

$$a_2 = \frac{6\mathcal{B}^2}{\hbar\omega} \quad a_3 = \frac{4\mathcal{B}^3}{(\hbar\omega)^2} \quad (4.25)$$

Electronic transitions Transitions between two electronic states, in the Born–Oppenheimer approximation, happen instantly as the radiation is absorbed by the molecule, hence it induces an instantaneous vertical shift between two adiabatic potential surfaces as in Fig. 4.3: this is the **Frank–Condon principle**. To study this transition, consider the general matrix element between two molecular states $|g, \nu\rangle$ and $|g', \nu'\rangle$:

$$\langle g', \nu' | \boldsymbol{\mu}_e | g, \nu \rangle = \int_{\mathbb{R}^{3(N_n+N_e)}} d^{3N_n} R d^{3N_e} r \Phi_e^{(g')*}(R_{\text{fin}}, r) \Phi_n^{(\nu')*}(R) [\boldsymbol{\mu}_e^{(e)} + \boldsymbol{\mu}_e^{(n)}] \Phi_e^{(g)}(R_{\text{in}}, r) \Phi_n^{(\nu)}(R)$$

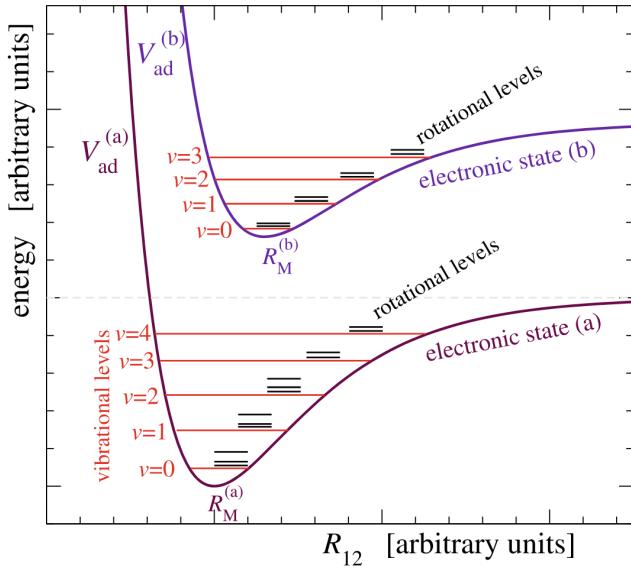


Figure 4.3: Electronic transition between two adiabatic potential surfaces.

where we separated the electronic and nuclear electric dipoles. Their expressions are:

$$\boldsymbol{\mu}_e^{(e)} = -e \sum_{i=1}^{N_e} \mathbf{r}_i \quad \boldsymbol{\mu}_e^{(n)} = +e \sum_{j=1}^{N_n} \mathbf{R}_j \quad (4.26)$$

By the Frank–Condon principle, $R_{\text{in}} = R_{\text{fin}}$ at the instant of the transition, hence the two contributions can be written as:

$$\int_{\mathbb{R}^{3(N_n+N_e)}} d^{3N_n} R d^{3N_e} r \Phi_e^{(g')*}(R_{\text{in}}, r) \Phi_n^{(\nu')*}(R) \boldsymbol{\mu}_e^{(n)} \Phi_e^{(g)}(R_{\text{in}}, r) \Phi_n^{(\nu)}(R) = \langle g' | g \rangle \langle \nu' | \boldsymbol{\mu}_e^{(n)} | \nu \rangle$$

$$\int_{\mathbb{R}^{3(N_n+N_e)}} d^{3N_n} R d^{3N_e} r \Phi_e^{(g')*}(R_{\text{in}}, r) \Phi_n^{(\nu')*}(R) \boldsymbol{\mu}_e^{(e)} \Phi_e^{(g)}(R_{\text{in}}, r) \Phi_n^{(\nu)}(R) = \langle \nu' | \nu \rangle \langle g' | \boldsymbol{\mu}_e^{(e)} | g \rangle$$

Since the electronic eigenfunctions are orthonormal, $\langle g' | g \rangle = \delta_{g',g}$, but in an electronic transition $g' \neq g$, therefore the nuclear contribution vanishes. On the other hand, the electronic contribution has two terms:

- $\langle g' | \boldsymbol{\mu}_e^{(e)} | g \rangle$ is the matrix element for electric-dipole transitions between electronic states, which results in the usual selection rules $\Delta \Lambda = 0, \pm 1$ and $\Delta S = 0$;
- $\langle \nu' | \nu \rangle \neq 0$ since the equilibrium point changes between the two adiabatic potential surfaces, hence the eigenfunctions associated to $|\nu'\rangle$ are a different set of eigenfunctions when compared to those of $|\nu\rangle$, as both I and ω change with R_{eq} . As a consequence, this term determines no selection rules, but simply determines the relative intensity of particular nuclear transitions (e.g. due to the form of Hermite functions, if R_{eq} shifts to the right, then $\nu = 0 \rightarrow \nu' > 0$ is more intense than $\nu = 0 \rightarrow \nu' = 0$).

This analysis shows that electronic transitions do not require etero-nuclear molecules, since nuclear dipoles play no role in them: these so-called **vibronic transitions** can thus be used to study the vibrational spectrum of homo-nuclear molecules⁵.

⁵Typically, since vibronic transitions require energies $\sim 1 \text{ eV}$, the detector is not capable to resolve rotational transitions, hence the roto-vibrational spectrum requires finer methods to be studied in homo-nuclear molecules.

§4.2 Vibrations of polyatomic molecules

Consider a generic molecule with N atoms and let $\mathbf{R}_{\text{eq}} \equiv \{\mathbf{R}_i^{\text{eq}}\}_{i=1,\dots,N} \in \mathbb{R}^{3N}$ be the equilibrium positions: then, in a neighborhood of R_{eq} , the interactions between each pair of atoms can be modelled by an elastic force. This molecule has $3N$ degrees of freedom: 3 of them are translational and describe the free-particle motion of the CM of the system, and 3 are rotational⁶, hence the remaining $3N - 6$ degrees of freedom are vibrational.

To study the dynamics of this system, define the positions relative to the equilibrium positions as $\mathbf{Q} \equiv \{\mathbf{Q}_i\}_{i=1,\dots,N} \in \mathbb{R}^{3N}$, with $\mathbf{Q}_i \equiv \mathbf{R}_i - \mathbf{R}_i^{\text{eq}}$, and the total force vector $\mathbf{F} \equiv \{\mathbf{F}_i\}_{i=1,\dots,n}$, where \mathbf{F}_i is the net force acting on the i^{th} atom. The dynamics is then given by a generalized Hook's law:

$$\mathbf{F} = -K\mathbf{Q} \quad (4.27)$$

To give an explicit expression for the **force-constants matrix** K , we first set a suitable representation of \mathbf{Q} and \mathbf{F} :

$$\mathbf{Q} = (Q_{1,x} \ \dots \ Q_{N,x} \ Q_{1,y} \ \dots \ Q_{N,y} \ Q_{1,z} \ \dots \ Q_{N,z})^T$$

$$\mathbf{F} = (F_{1,x} \ \dots \ F_{N,x} \ F_{1,y} \ \dots \ F_{N,y} \ F_{1,z} \ \dots \ F_{N,z})^T$$

Then, the force-constants matrix can be represented as:

$$K = \begin{bmatrix} k_{x,x}^{1,1} & \dots & k_{x,x}^{1,N} & k_{x,y}^{1,1} & \dots & k_{x,y}^{1,N} & k_{x,z}^{1,1} & \dots & k_{x,z}^{1,N} \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ k_{x,x}^{N,1} & \dots & k_{x,x}^{N,N} & k_{x,y}^{N,1} & \dots & k_{x,y}^{N,N} & k_{x,z}^{N,1} & \dots & k_{x,z}^{N,N} \\ k_{y,x}^{1,1} & \dots & k_{y,x}^{1,N} & k_{y,y}^{1,1} & \dots & k_{y,y}^{1,N} & k_{y,z}^{1,1} & \dots & k_{y,z}^{1,N} \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ k_{y,x}^{N,1} & \dots & k_{y,x}^{N,N} & k_{y,y}^{N,1} & \dots & k_{y,y}^{N,N} & k_{y,z}^{N,1} & \dots & k_{y,z}^{N,N} \\ k_{z,x}^{1,1} & \dots & k_{z,x}^{1,N} & k_{z,y}^{1,1} & \dots & k_{z,y}^{1,N} & k_{z,z}^{1,1} & \dots & k_{z,z}^{1,N} \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ k_{z,x}^{N,1} & \dots & k_{z,x}^{N,N} & k_{z,y}^{N,1} & \dots & k_{z,y}^{N,N} & k_{z,z}^{N,1} & \dots & k_{z,z}^{N,N} \end{bmatrix} \quad (4.28)$$

where the general $k_{a,b}^{i,j}$ is the elastic constant which gives the contribution of $Q_{j,b}$ to $F_{i,a}$, i.e.:

$$F_{i,a} = - \sum_{j=1}^N \sum_{b=x,y,z} k_{a,b}^{i,j} Q_{j,b} \quad (4.29)$$

Note that the third Newton's law implies that K must be symmetric, since exchanging the two interacting atoms must yield the same force between them.

Since $\mathbf{F}_i = m_i \ddot{\mathbf{Q}}_i$, we can use the ansatz $\mathbf{Q}_i = \mathbf{A}_i \exp(i\omega t)$: therefore, $\ddot{\mathbf{Q}}_i = -\omega^2 \mathbf{Q}_i$, and Eq. 4.27 becomes:

$$(K - \omega^2 M) \mathbf{Q} = \mathbf{0} \quad (4.30)$$

where the the **mass matrix** is define as (in the representation we fixed):

$$M = \text{diag}(m_1, \dots, m_N, m_1, \dots, m_N, m_1, \dots, m_N) \quad (4.31)$$

⁶Actually, for linear molecules the rotational degrees of freedom are only 2, hence the vibrational degrees of freedom are $3N - 5$.

In general, Eq. 4.30 has $3N$ solutions for ω^2 : among these, we expect to find a number (5 of 6, as per the above observations) of trivial $\omega = 0$ solutions, which correspond to translational and rotational normal modes (which are not subject to a Hook-type force and have no period), while the non-vanishing solutions are the frequencies of vibrational normal modes.

Moreover, note that, in general, the force-constants matrix can be expressed in terms of the potential of interaction between the various atoms as:

$$k_{a,b}^{i,j} = \frac{\partial^2 V(Q)}{\partial Q_{i,a} \partial Q_{j,b}} \quad (4.32)$$

since $\mathbf{F}_i = -\nabla_i V(Q)$ and given Eq. 4.29.

Example 4.2.1 (Biatomc molecule)

For the biatomic molecule, the interaction potential can be modelled as a simple harmonic potential, in a neighborhood of \mathbf{R}_{eq} :

$$V(Q) = \frac{1}{2}k(Q_{1,x} - Q_{2,x})^2$$

where we set the x -axis to be the axis of the molecule. Then, the force-constants matrix is:

$$\mathbf{K} = \begin{bmatrix} k & -k & 0 & 0 & 0 & 0 \\ -k & k & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

Consequently, Eq. 4.30 becomes:

$$\begin{bmatrix} k - \omega^2 m_1 & -k & 0 & 0 & 0 & 0 \\ -k & k - \omega^2 m_2 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\omega^2 m_1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\omega^2 m_2 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\omega^2 m_1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\omega^2 m_2 \end{bmatrix} \begin{pmatrix} Q_{1,x} \\ Q_{2,x} \\ Q_{1,y} \\ Q_{2,y} \\ Q_{1,z} \\ Q_{2,z} \end{pmatrix} = \mathbf{0}$$

The last four rows correspond to four $\omega^2 = 0$ solutions, which correspond to translations along the y - and z -axis and rotations in the xy - and zx - planes, so we focus on the first 2×2 submatrix:

$$\begin{bmatrix} k - \omega^2 m_1 & -k \\ -k & k - \omega^2 m_2 \end{bmatrix} \begin{pmatrix} Q_{1,x} \\ Q_{2,x} \end{pmatrix} = \mathbf{0}$$

Since this is a homogeneous system, the solutions are found imposing that the determinant of the matrix vanishes:

$$(k - \omega^2 m_1)(k - \omega^2 m_2) - k^2 = 0 \implies \omega^2 \left[\omega^2 - k \frac{m_1 + m_2}{m_1 m_2} \right] = 0$$

Now, the $\omega^2 = 0$ solution corresponds to a translation along the x -axis, while the non-vanishing solution is the expected vibration along the molecular axis with frequency:

$$\omega^2 = \frac{k}{\mu}$$

All in all, we recovered the five roto-translational and the single vibrational normal modes of biatomic molecules.

Example 4.2.2 (Carbon dioxide)

Consider a CO_2 molecule, identifying the two oxygen atoms as 1 and 3 and the carbon atom as 2. Fixing the molecular axis along the x -axis, we can model the interaction between the atoms as a sum of harmonic potentials:

$$V(Q) = \frac{1}{2}k_x(Q_{1,x} - Q_{2,x})^2 + \frac{1}{2}k_x(Q_{2,x} - Q_{3,x})^2 + \frac{1}{2}k'_x(Q_{1,x} - Q_{3,x})^2 \\ + \frac{1}{2}k_y(Q_{1,y} + Q_{3,y} - 2Q_{2,y})^2 + \frac{1}{2}k_z(Q_{1,z} + Q_{3,z} - 2Q_{2,z})^2$$

where k_x is the elastic constant for the elastic interaction $\text{C} - \text{O}$, k'_x is that for $\text{O} - \text{O}$, and k_y and k_z are responsible for the recall force which maintains the molecule linear, i.e. opposes to the bending of the molecule. Since the two oxygen atoms are further apart, with respect to the carbon atom, $k'_x \ll k_x$, hence we can suppress the $\text{O} - \text{O}$ interaction at first-order approximation. Moreover, due to cylindrical symmetry, $k_y = k_z$, so we set $k_x \equiv k$ and $k_y = k_z \equiv \kappa$. The force-constants matrix then is:

$$\mathbf{K} = \begin{bmatrix} k_x + k'_x & -k_x & -k'_x & 0 & 0 & 0 & 0 & 0 & 0 \\ -k_x & 2k_x & -k_x & 0 & 0 & 0 & 0 & 0 & 0 \\ -k'_x & -k_x & k_x + k'_x & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & k_y & -2k_y & k_y & 0 & 0 & 0 \\ 0 & 0 & 0 & -2k_y & 4k_y & -2k_y & 0 & 0 & 0 \\ 0 & 0 & 0 & k_y & -2k_y & k_y & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & k_z & -2k_z & k_z \\ 0 & 0 & 0 & 0 & 0 & 0 & -2k_z & 4k_z & -2k_z \\ 0 & 0 & 0 & 0 & 0 & 0 & k_z & -2k_z & k_z \end{bmatrix}$$

$$\simeq \begin{bmatrix} k & -k & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -k & 2k & -k & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -k & k & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \kappa & -2\kappa & \kappa & 0 & 0 & 0 \\ 0 & 0 & 0 & -2\kappa & 4\kappa & -2\kappa & 0 & 0 & 0 \\ 0 & 0 & 0 & \kappa & -2\kappa & \kappa & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \kappa & -2\kappa & \kappa \\ 0 & 0 & 0 & 0 & 0 & 0 & -2\kappa & 4\kappa & -2\kappa \\ 0 & 0 & 0 & 0 & 0 & 0 & \kappa & -2\kappa & \kappa \end{bmatrix}$$

This is a block-diagonal matrix, hence Eq. 4.30 reduces from a 9×9 homogeneous system to a three 3×3 homogeneous systems. Setting $m_1 = m_3 \equiv M$ and $m_2 \equiv m$, the solutions for the x -system are:

$$\begin{vmatrix} k - \omega^2 M & -k & 0 \\ -k & 2k - \omega^2 m & -k \\ 0 & -k & k - \omega^2 M \end{vmatrix} = (k - \omega^2 M) [(k - \omega^2 M)(2k - \omega^2 m) - 2k^2] = 0$$

whose solutions are:

$$\omega^2 = \frac{k}{M} \quad \omega^2 = \frac{2M + m}{mM} k \quad \omega^2 = 0$$

The third solution is a translation along the x -axis (since it produces a system with solutions to $Q_{1,x} = Q_{2,x} = Q_{3,x}$), while the other two are vibrations along the x -axis: the first one

is a vibration of oxygen atoms with opposite phases, while the carbon atom remains fixed (since it corresponds to $Q_{2,x} = 0$ and $Q_{1,x} = -Q_{3,x}$), while in the second one the two oxygen atoms vibrate with equal phase, while the carbon atom vibrates with opposite phase (since $Q_{1,x} = Q_{3,x}$ and $Q_{2,x} = -\frac{2M}{m}Q_{1,x}$, to leave the CM fixed). These vibrations are respectively called **symmetric** and **asymmetric stretching**: note that in the antisymmetric stretching the two bonds oscillate asymmetrically, hence the distribution of positive and negative are displaced (i.e. their barycenters do not coincide), and an electric dipole is present, contrary to the symmetric stretching, which means that the asymmetric stretching is IR-active.

The y - and z -systems are equivalent, so WLOG we solve the y -system:

$$\begin{vmatrix} \kappa - \omega^2 M & -2\kappa & \kappa \\ -2\kappa & 4\kappa - \omega^2 m & -2\kappa \\ \kappa & -2\kappa & \kappa - \omega^2 \kappa \end{vmatrix} = 0$$

which results into:

$$\begin{aligned} 0 &= (\kappa - \omega^2 M)^2 (4\kappa - \omega^2 m) - 8\kappa^2 (\kappa - \omega^2 M) - \kappa^2 (4\kappa - \omega^2 m) + 8\kappa^3 \\ &= (4\kappa - \omega^2 m) (\omega^4 M^2 - 2\kappa \omega^2 M) + 8\kappa^2 \omega^2 M \\ &= \omega^2 M [(4\kappa - \omega^2 m) (\omega^2 M - 2\kappa) + 8\kappa^2] = \omega^4 M (2\kappa m + 4\kappa M - \omega^2 m M) \end{aligned}$$

whose solutions are:

$$\omega^2 = 0 \quad \omega^2 = 2 \frac{2M + m}{mM} \kappa$$

The first one is a two-fold solution, representing a translation along the y -axis and a rotation in the xy -plane, while the second one is a vibration where the carbon atom oscillates with opposite phase with respect to the oxygen atoms (since $y_1 = y_3$ and $y_2 = -\frac{2M}{m}y_1$), called **symmetric bending**. It is clear that in this vibrational mode an electric dipole is present, hence the symmetric bending is IR-active.

All in all, we correctly find 5 roto-translations and 4 vibrations.

Part II

Solid-state Physics

Chapter 5

Crystal Lattices

§5.1 Bravais lattices

Definition 5.1.1 (Crystal)

A **crystal** is a collection of atoms with a translational symmetry.

The presence of a translational symmetry means that it is possible to define a **periodic lattice** (or Bravais lattice) \mathcal{B} and a **basis**, i.e. a set of atoms which repeats in each point of the lattice. Given the periodicity of the lattice, it is possible to write the general element of the lattice as:

$$\mathbf{R} = n_1 \mathbf{R}_1 + n_2 \mathbf{R}_2 + n_3 \mathbf{R}_3$$

where $n_1, n_2, n_3 \in \mathbb{Q}$ and $\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3 \in \mathbb{R}^3$ LI are the principal directions or *generators* of the lattice. In particular, if the generators are the “smallest” possible (non-unique definition), they form a **primitive cell**, i.e. the minimal volume which contains all translationally-unequivalent points of the lattice: clearly, the whole lattice is a repetition of the primitive cell under discrete translations.

Proposition 5.1.1 (Wigner–Seitz cell)

Given a point in a Bravais lattice $\mathbf{R} \in \mathcal{B}$, the **Wigner–Seitz cell** in \mathbf{R} is defined as the cell $V_{\text{WS}} := \{\mathbf{r} \in \mathbb{R}^3 : \|\mathbf{r} - \mathbf{R}\| < \|\mathbf{r} - \mathbf{R}'\| \ \forall \mathbf{R}' \in \mathcal{B} - \{\mathbf{R}\}\}$. This is a primitive cell of \mathcal{B} .

The Wigner–Seitz cell eliminates the arbitrariness of the primitive cell. However, it is convenient to consider conventional (or unitary) cells, which are composed of one or more primitive cells to obtain a macro-cell with a simple shape (preferably cubic, like for the sc, bcc and fcc lattices, see Fig. 5.1).

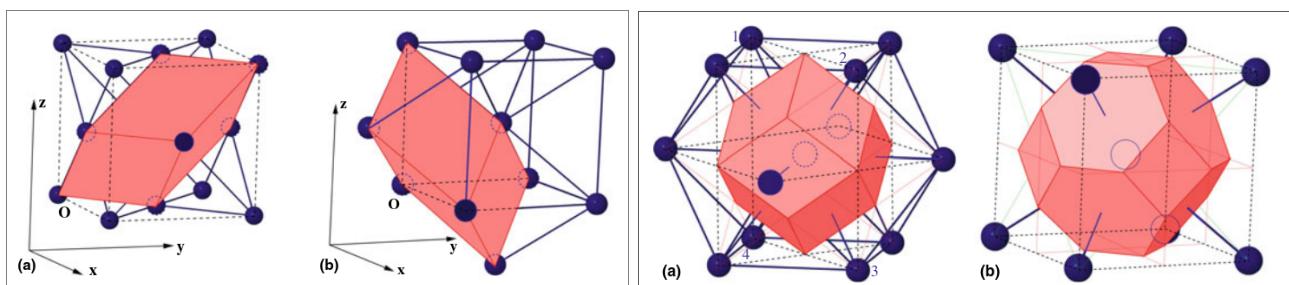


Figure 5.1: Arbitrary primitive cells and Wigner–Seitz cells for the fcc and bcc lattices.

All of the physical information of the lattice is present in the Wigner–Seitz cell (or in a general primitive cell): nonetheless, we study conventional cell for their simpler geometries, even though they present redundant information. In general, fix an atom in the conventional cell as the origin, we denote the position of the other atoms as (n_1, n_2, n_3) , with coefficients given by Eq. 5.1; on the contrary, **directions** are denoted by $[h \ k \ \ell]$, with $h, k, \ell \in \mathbb{Z}$ (with the same meaning as in Eq. 5.1), while **crystal planes** by $(h \ k \ \ell)$, with Miller indices $h, k, \ell \in \mathbb{Z}$ being the minimal integer multiples of the inverses of the plane's intercepts with the principal directions of the conventional cell. Note that both the notations for directions and crystal planes do not univocally define directions and crystal planes, but rather collections of equivalent (i.e. parallel) directions and crystal planes.

Lemma 5.1.1 (Directions and crystal planes)

$$[h \ k \ \ell] \perp (h \ k \ \ell) \quad \forall h, k, \ell \in \mathbb{Z} \quad (5.1)$$

Example 5.1.1 (Crystal planes in cubic lattices)

Consider a lattice with a cubic unitary cell with sides of length a . Then, given a collection of crystal planes with Miller indices $(h \ k \ \ell)$, the distance between two consecutive planes in this collection is:

$$d_{h,k,\ell} = \frac{a}{\sqrt{h^2 + k^2 + \ell^2}} \quad (5.2)$$

§5.1.1 Diffraction

When a plane EM wave scatters on a single atom, it makes the electronic cloud oscillate, thus emitting spherical EM waves. In presence of multiple atoms, the various spherical waves start interfering with each other, analogously to the diffraction grating. The main difference now is that the atoms are arranged in a 3D lattice and that they are in number $\sim N_A$, hence, if the constructive-interference condition is not satisfied (even slightly), then no outgoing radiation is observed, as it is always possible to find an atom which produces an EM wave with π phase shift, thus causing destructive interference.

In a 3D lattice, there are three conditions for constructive interference. First of all, assuming that the periodic lattice of atoms is divided into parallel (crystal) planes:

1. the plane determined by the incoming wave-vector and the outgoing wave-vector is perpendicular to the planes determined by the atoms, which guarantees that all the atoms in the same position on different planes receive and emit EM radiation with the same phase;
2. the angle of incidence is equal to the angle of emission, which guarantees that all the atoms on the same plane receive and emit EM radiation with the same phase;

These conditions impose that each crystal plane behaves like a perfect mirror. The last condition is obtained imposing that two consecutive planes determine a constructive interference:

$$2d \sin \vartheta = n\lambda \quad (5.3)$$

where $d = d_{h,k,\ell}$ is the distance between the consecutive planes, ϑ is the angle of incidence, λ is the wavelength of the incident EM radiation and $n \in \mathbb{N}$ is the diffraction order. This is known as the **Bragg relation**.

The diffraction order can be always fixed to $n \equiv 1$ by adding n intermediate (imaginary) planes between the two consecutive planes: this is done by multiplying each Miller index by n , that is $d_{h,k,\ell} \mapsto d_{nh,hk,n\ell} \equiv d$. Then, since $\sin \vartheta \leq 1$, the incident radiation has a maximum-wavelength condition to be able to diffract off of the considered lattice:

$$\lambda < 2d \quad (5.4)$$

Hence, since $d \sim 0.1 \text{ nm}$, only X-rays and gamma rays with $\lambda \lesssim 0.1 \text{ nm}$ can produce a diffraction pattern.

§5.1.2 Reciprocal lattice

It is possible to rewrite the Bragg condition in terms of the wave-vectors \mathbf{k}, \mathbf{k}' of the incoming and outgoing EM radiation. In particular, geometrically $\|\mathbf{k}' - \mathbf{k}\| = 2k \sin \vartheta$ (since for elastic scattering $k = k'$), thus the Bragg condition can be recast in vectorial form as:

$$\mathbf{k}' - \mathbf{k} = \frac{2\pi}{d_{h,k,\ell}} \hat{\mathbf{n}}_{h,k,\ell} \equiv \mathbf{G}_{h,k,\ell} \quad (5.5)$$

where $\hat{\mathbf{n}}_{h,k,\ell}$ is the normal vector of the family of crystal planes with Miller indices $(h \ k \ \ell)$. Note that the same vector in the reciprocal lattice is obtained by multiple non-equivalent choices for \mathbf{k} and \mathbf{k}' . It is trivial to see that:

$$\mathbf{G}_{h,k,\ell} = h\mathbf{A}_1 + k\mathbf{A}_2 + \ell\mathbf{A}_3 \quad (5.6)$$

where $\{\mathbf{A}_i\}_{i=1,2,3} \in \mathbb{R}^3$ are the generators of the reciprocal lattice, which are related to the generators $\{\mathbf{R}_i\}_{i=1,2,3} \in \mathbb{R}^3$ of the real lattice by:

$$\mathbf{R}_i \cdot \mathbf{A}_j = 2\pi\delta_{ij} \quad (5.7)$$

Defining the volume of the primitive cell of the real lattice $V_p \equiv (\mathbf{R}_1 \times \mathbf{R}_2) \cdot \mathbf{R}_3$ (assuming a right-handed triplet of primitive vectors), the generators of the reciprocal lattice are clearly given by:

$$\mathbf{A}_1 = \frac{2\pi}{V_p} \mathbf{R}_2 \times \mathbf{R}_3 \quad \mathbf{A}_2 = \frac{2\pi}{V_p} \mathbf{R}_3 \times \mathbf{R}_1 \quad \mathbf{A}_3 = \frac{2\pi}{V_p} \mathbf{R}_1 \times \mathbf{R}_2 \quad (5.8)$$

These expressions allow to express the volume \tilde{V}_p of the primitive cell of the reciprocal lattice in terms of V_p :

$$\tilde{V}_p = \frac{(2\pi)^3}{V_p} \quad (5.9)$$

Example 5.1.2 (Reciprocal lattices)

The reciprocal of an sc lattice with side a is an sc lattice with side $\frac{2\pi}{a}$, while the reciprocal of a bcc(fcc) lattice with side a is an fcc(bcc) lattice with side $\frac{4\pi}{a}$.

Note that, by Eq. 5.5, the Bragg scattering of X rays on a crystal lattice can be studied in the reciprocal lattice using the **Ewald construction**: fixed the incoming wave-vector \mathbf{k} pointing to a point of the reciprocal lattice, draw a sphere with \mathbf{k} as radius, so that the possible \mathbf{G} vectors (and so $\mathbf{k}' = \mathbf{k} + \mathbf{G}$) are determined by other points of the reciprocal lattice which intersect the sphere (see Fig. 5.2).

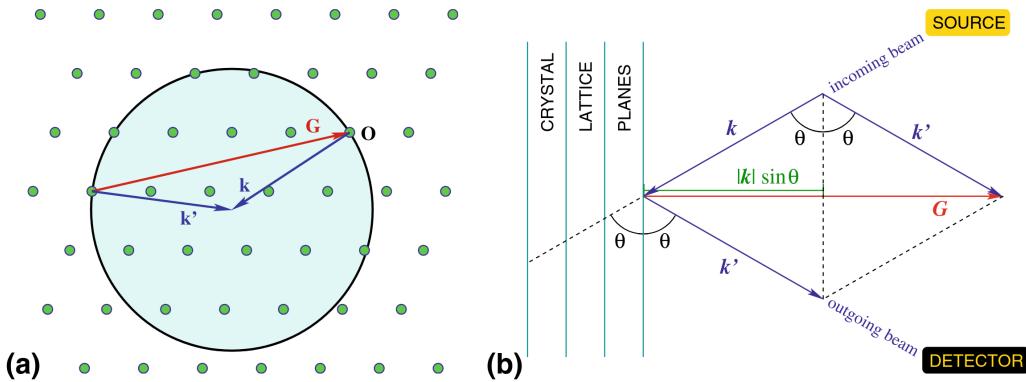


Figure 5.2: Ewald construction.

In practice, to generate an X-ray diffraction on a single crystal, the reciprocal lattice is moved with respect to the Ewald construction until there are at least two points of the reciprocal lattice intersecting the sphere: this is achieved either varying the wavelength of the incoming radiation (thus modifying the radius of the Ewald sphere), or rotating the crystal sample (since the reciprocal lattice rotates in the same manner as the real lattice).

§5.2 Lattice vibrations

Like for molecules, we expect to find multiple normal modes, since the crystal can be seen as a molecule with an extremely large number of atoms: in particular, since for a molecule with N atoms there are $3N - 6$ normal frequencies, for a crystal we similarly expect $\sim 3N$ normal frequencies.

§5.2.1 Linear chain

Consider a monoatomic linear chain, and adopt the approximation where the only interactions are between neighbouring atoms and have a harmonic nature. Then, label each atom with $s = 0, 1, \dots, N - 1$ and assume that their equilibrium distance is a , so that the total length of the chain is $L = (N - 1)a$, and that their mass is M . Defining u_s as the longitudinal displacement (analogous to stretching modes in molecules) from its equilibrium position of the atom s , then its equation of motion is:

$$C(u_{s+1} - 2u_s + u_{s-1}) = M\ddot{u}_s \quad (5.10)$$

where $C \in \mathbb{R}^+$ is the spring constant of the harmonic interaction between neighbouring atoms. The wave ansatz reads:

$$u_s(t) = u_0 e^{i(ksa - \omega t)} \quad (5.11)$$

where we set the $s = 0$ atom at the origin. Inserting this ansatz into Eq. 5.10:

$$-\omega^2 M = C(e^{ika} + e^{-ika} - 2) = 2C(\cos ka - 1)$$

which results in the **dispersion relation** for vibrations in a crystal:

$$\omega = 2\sqrt{\frac{C}{M}} \left| \sin \frac{ka}{2} \right| \quad (5.12)$$

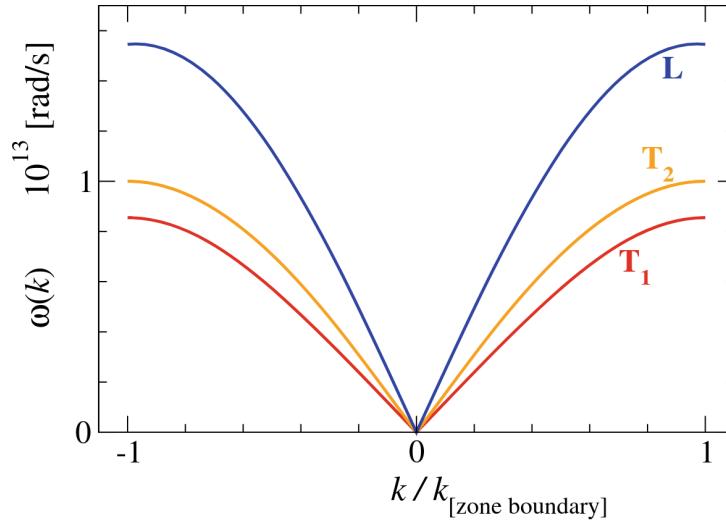


Figure 5.3: Acoustic branches in a monoatomic crystal.

Contrary to waves in a continuous medium (EM waves in vacuum $\omega = ck$, sound waves in air $\omega = v_s k$), crystal vibrations propagate in a discrete medium, hence their dispersion relation is non-linear (see Fig. 5.3).

Note that this analysis holds for all atoms in the linear chains, except for the endpoints: since $N \sim N_A$, these endpoints can be ignored, and the chain can be assumed to be infinite. To do so, it is necessary to impose **periodic boundary conditions**, i.e.:

$$u(L) = u(0) \quad u'(L) = u'(0) \quad (5.13)$$

These imply that $\exp ikL = 1$, i.e. they make the normal frequencies discrete. It is trivial to see that two waves whose wave-vectors differ by a vector in the discrete lattice. i.e. k and $k + 2\pi n/a$, determine the same normal mode: all of the physical information is then contained in the interval $k \in (-\frac{\pi}{a}, \frac{\pi}{a}]$, as pictured in Fig. 5.3. The discrete normal frequencies then are:

$$k_n = \frac{2\pi n}{L} \quad n = 0, \pm 1, \pm 2, \dots, +\frac{N}{2} \quad (5.14)$$

where N is assumed even. The total number of normal modes has been computed as:

$$\frac{2\pi}{a} \div \frac{2\pi}{L} = \frac{L}{a} = N$$

Note that the $n = 0$ normal mode is a translation, since $k = 0$ and $\omega = 0$. Moreover, we again see a reciprocity between real space and momentum space: the finiteness of the chain determines discrete normal frequencies, while its discreteness determines a finite number of normal frequencies.

Consider now the limit for $|k| \ll \frac{\pi}{a}$, i.e. $\lambda \gg 2a$: since the wavelength is much larger than the separation between atoms, the oscillation is not affected by the discreteness of the medium, hence the dispersion curve is linear:

$$\lim_{k \rightarrow 0} \omega = \sqrt{\frac{C}{M}} ak \equiv v_s k$$

where v_s is the “sound wave” in the 1D crystal considered. In general, the **group velocity**, i.e. the velocity in the transfer of mechanical energy in the crystal, is defined as:

$$v_g(k) := \frac{d\omega}{dk} \quad (5.15)$$

For the 1D crystal:

$$v_g(k) = \text{sgn}(k) \sqrt{\frac{C}{M}} \cos \frac{ka}{2}$$

Note that the group velocity vanishes at the boundary $v_g(\pm \frac{\pi}{a}) = 0$. To understand this, consider the displacement of the atoms:

$$u_s(t) = u_0 e^{\pm i\pi s - \omega t} = (-1)^s u_0 e^{-i\omega t}$$

which is a stationary wave.

§5.2.2 3D crystal

In the case of a 3D crystal, it is still possible to have both longitudinal and transversal: however, contrary to the 1D crystal, the elastic constant of the oscillation is an “effective” elastic constant, since each atom has multiple “closest” atoms.

Consider an oscillation with wave-vector k along a principal crystal direction in an sc crystal, WLOG [1 0 0]. Since this is a wave, it can undergo Bragg scattering, and in particular there could be the phenomenon of **back-scattering**, i.e. the wave is reflected backward: from the Bragg relation Eq. 5.3 with $n = 1$ and $\vartheta = \frac{\pi}{2}$ (reflection), since the distance between two atoms in the [1 0 0] direction is $d = a$, it is trivial to find:

$$\lambda = 2a \iff k = \pm \frac{\pi}{a}$$

Now, note that if the wave is totally reflected, the total oscillation given by the sum of the two waves is a stationary wave, hence the same result as for the 1D crystal is recovered.

If instead the oscillation propagates along the [1 1 0] crystal direction, then $d = \frac{a}{\sqrt{2}}$ and the back-scattering condition becomes:

$$\lambda = \sqrt{2}a \iff k = \pm \sqrt{2} \frac{\pi}{a}$$

In the general case, the back-scattering happens for all wave-vector which lie on the boundary of the primitive cell of the reciprocal lattice, which is called **first Brillouin zone** (1BZ): indeed, it is possible to show that, given a wave-vector \mathbf{k} on the boundary of the 1BZ and its diffracted wave-vector \mathbf{k}' according to Bragg diffraction, then $\|\mathbf{k}' - \mathbf{k}\| = \frac{2\pi}{a}$, i.e. a stationary wave.

§5.2.2.1 Vibrational bands

Example 5.2.1 (Biatomlic linear chain)

Consider a 1D crystal where two kinds of atoms, with masses M_1 and M_2 , alternate: the primitive cell is then composed of a couple of nearby atoms, and define $s \in \mathbb{N}_0$ the index of the primitive cells in the chain (of periodicity a).

In the first-order harmonic approximation where only nearby atoms interact with an elastic constant C , denoting the displacement of the mass M_1 in the s cell as u_s and that of the mass M_2 as v_s , the equations of motion read:

$$M_1 \ddot{u}_s = C(v_s - 2u_s + v_{s-1}) \quad M_2 \ddot{v}_s = C(u_{s+1} - 2v_s + u_s)$$

The plane-wave ansatz now reads:

$$u_s(t) = u_0 \exp(i\omega ka - i\omega t) \quad v_s(t) = v_0 \exp(i\omega ka - i\omega t + i\varphi) \equiv v'_0 \exp(i\omega ka - i\omega t)$$

with $u_0, v_0 \in \mathbb{R}$ and $v'_0 \in \mathbb{C}$. Inserting these expressions in the equations of motion:

$$-\omega^2 M_1 = C [v'_0 (1 + e^{-ika}) - 2u_0] \quad -\omega^2 M_2 = C [u_0 (e^{ika} + 1) - 2v'_0]$$

which reduce to a linear system:

$$\begin{bmatrix} 2C - \omega^2 M_1 & -C (1 + e^{-ika}) \\ -C (1 + e^{ika}) & 2C - \omega^2 M_2 \end{bmatrix} \begin{pmatrix} u_0 \\ v'_0 \end{pmatrix} = \mathbf{0} \quad \Rightarrow \quad \begin{vmatrix} 2C - \omega^2 M_1 & -C (1 + e^{-ika}) \\ -C (1 + e^{ika}) & 2C - \omega^2 M_2 \end{vmatrix} = 0$$

The equation for ω^2 then is:

$$M_1 M_2 \omega^4 - 2C (M_1 + M_2) \omega^2 + 2C^2 (1 - \cos ka) = 0$$

which in general has two solutions for ω^2 . The interesting behavior is in the limits for $k \rightarrow 0$ and $k \rightarrow \pm\frac{\pi}{a}$. For $k \rightarrow 0$:

$$M_1 M_2 \omega^2 - 2C (M_1 + M_2) \omega^2 + C^2 (ka)^2 = 0$$

whose solutions are:

$$\begin{aligned} \omega^2 &= \frac{C (M_1 + M_2) \pm \sqrt{C^2 (M_1 + M_2)^2 - C^2 M_1 M_2 (ka)^2}}{M_1 M_2} \\ &= \frac{C}{\mu} \left[1 \pm \sqrt{1 - \mu(ka)^2} \right] \approx \frac{C}{\mu} \left[1 \pm 1 \mp \frac{\mu}{2(M_1 + M_2)} (ka)^2 + o(k^3) \right] \end{aligned}$$

where $\mu = M_1 M_2 / (M_1 + M_2)$ is the reduced mass of the primitive cell. Then, at first order:

$$\omega_+ = \sqrt{\frac{2C}{\mu}} + o(k^2) \quad \omega_- = \sqrt{\frac{C}{2(M_1 + M_2)}} ak + o(k^2) \equiv v_s k + o(k^2)$$

The ω_- is analogous to that of the monoatomic linear chain, while ω_+ is new. Substituting ω_+ in the above linear system and setting $k = 0$:

$$\begin{cases} \left(1 - \frac{M_1}{\mu}\right) u_0 - v'_0 = 0 \\ -u_0 + \left(1 - \frac{M_2}{\mu}\right) v'_0 = 0 \end{cases} \iff v'_0 = -\frac{M_1}{M_2} u_0$$

This means that the two atoms in the primitive cell oscillate in phase-opposition, corresponding to a stationary wave: this justifies the dispersion curve being parallel to the k -axis, since the group velocity of a stationary wave is $v_g = 0$. Note that, on the other hand, $\omega_- = 0$ at $k = 0$, which is not a vibration, but a translation ($u_0 = v'_0$).

Now, consider $k \rightarrow \pm\frac{\pi}{a}$:

$$M_1 M_2 \omega^4 - 2C (M_1 + M_2) \omega^2 + 4C^2 = 0$$

which has solutions:

$$\omega^2 = \frac{C (M_1 + M_2) \pm \sqrt{C^2 (M_1 + M_2)^2 - 4C^2 M_1 M_2}}{M_1 M_2} = \frac{C (M_1 + M_2) \pm C (M_1 - M_2)}{M_1 M_2}$$

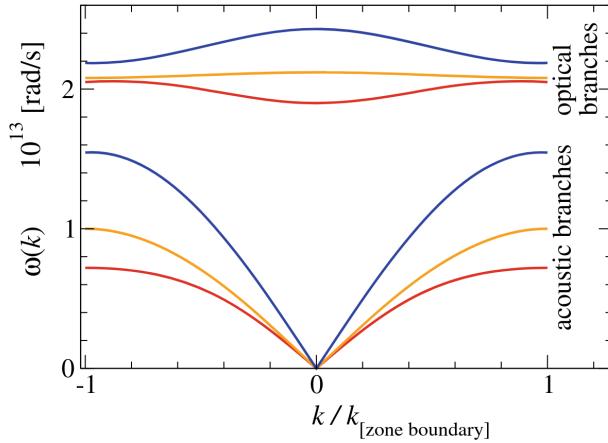


Figure 5.4: Phonon dispersion curves for an $n_d = 2$ crystal.

where $M_1 > M_2$ is assumed WLOG. The two solutions then read:

$$\omega_+ = \frac{2C}{M_2} + o\left(\left(k \mp \frac{\pi}{a}\right)^2\right) \quad \omega_- = \frac{2C}{M_1} + o\left(\left(k \mp \frac{\pi}{a}\right)^2\right)$$

To show that these correctly are stationary waves, insert these expressions in the above linear system with $k = \pm \frac{\pi}{a}$: for ω_+ it is $u_0 = 0$, and indeed the frequency only depends on M_2 , and conversely for ω_- it is $v'_0 = 0$, and the frequency only depends on M_1 .

Note that $\omega_+(0) > \omega_+(\pm \frac{\pi}{a})$ and $\omega_-(0) < \omega_-(\pm \frac{\pi}{a})$. The full solutions $\omega_+(k)$ and $\omega_-(k)$ are plotted in Fig. 5.4 (where both the longitudinal and the two transversal normal modes are present): these are called bands, and in particular $\omega_-(k)$ is an **acoustic band**, since it is linear for $k \rightarrow 0$ and the atoms oscillate in phase, while $\omega_+(k)$ is an **optical band**, since it is constant for $k \rightarrow 0$ and the atoms oscillate in phase-opposition.

In general, a crystal with $n_d \in \mathbb{N}$ atoms in its primitive cell presents 3 acoustic bands and $3n_d - 3$ optical bands, for a total of $3n_d$ bands.

To experimentally measure vibrational bands, consider an EM waves scattering on the sample crystal: the interaction with the EM waves makes electric charge oscillate, with positive charges and negative charges oscillating in opposite directions. To make the crystal vibrate, the EM wave $\omega(\mathbf{k})$ must resonate with the vibrational bands $\Omega(\mathbf{K})$, i.e. $\mathbf{k} = \mathbf{K}$ and $\Omega(\mathbf{k}) = \omega(\mathbf{k}) = \frac{c}{n}k$, where n is the refractive index of the crystal. This method only allows to study optical bands¹, since for acoustic bands $v_s \ll \frac{c}{n}$. Quantitatively, these resonance conditions correspond to an energy-momentum conservation condition for the transformation² of a photon of energy $\hbar\omega$ and momentum $\hbar\mathbf{k}$ to a phonon of energy $\hbar\Omega$ and momentum $\hbar\mathbf{K}$.

²A scattering $\gamma \rightarrow \gamma + \varphi$ is also possible, but energetic photons are needed: IR photons generate resonances, visible photons generate scatterings. In general, three peaks are observed: one for the resonance and two smaller ones, one for $\gamma \rightarrow \gamma + \varphi$ at $\omega - \Omega$ and one for $\gamma + \varphi \rightarrow \gamma$ at $\omega + \Omega$ (Brillouin anelastic scattering). For even higher energies, e.g. X-rays, it is possible to combine Brillouin scattering and Bragg scattering, so that the total energy-momentum conservation becomes:

$$\mathbf{k} - \mathbf{G} = \mathbf{k}' \pm \Omega \quad \omega = \omega' \pm \Omega$$

since the crystal momentum \mathbf{G} does not determine an energy transfer between the EM wave and the crystal.

²Acoustic bands can be studied using neutrons, since their dispersion relations $E = \frac{\hbar^2 k^2}{2m_n}$ allows for an intersection even with acoustic bands, which have lower frequencies than optical bands.

§5.2.3 Thermal properties

For a perfect gas composed of N particles, the mean energy of the system is found by the *equipartition principle* for energy:

$$\langle E \rangle = \frac{3}{2} N k_B T$$

Then, recalling that $dQ = dE + PdV$, its specific heat and molar specific heat at constant volume are:

$$C_V := \frac{dQ}{dT} = \frac{3}{2} N k_B \quad c_V := \frac{C_V}{n} = \frac{3}{2} R$$

with $R \equiv N_A k_B$.

The same classical treatment can be performed for a crystal: in this case, there are both kinetic and potential degrees of freedom, hence there is twice the total number of degrees of freedom, i.e. the expected classical result is $c_V = 3R$.

However, the crystal is a quantum system, hence the treatment must be extended to account for quantum effects. A crystal at $T > 0$ has all its atoms randomly oscillating: this random motion can be expressed as a linear combination of normal modes.

Suppose that we can filter a particular frequency ω : in general, the equation $\omega(k) = \omega$ has multiple solutions for k in multiple bands, and they all depend on the crystal direction considered (since bands in different directions are generally different). Nonetheless, quantistically the energy only depends on ω and it is quantized (for oscillations in a single direction) as:

$$E_n = \left(n + \frac{1}{2} \right) \hbar\omega \quad (5.16)$$

where the population of the n^{th} energy level follows a Boltzmann distribution:

$$P(n) = A e^{-\frac{E_n}{k_B T}} \quad (5.17)$$

Taking the ground state as reference $E_0 \equiv 0$, then:

$$\langle E \rangle = \frac{\sum_{n \in \mathbb{N}_0} n \hbar\omega P(n)}{\sum_{n \in \mathbb{N}_0} P(n)} = \frac{\sum_{n \in \mathbb{N}_0} n \hbar\omega e^{-n \frac{\hbar\omega}{k_B T}}}{\sum_{n \in \mathbb{N}_0} e^{-n \frac{\hbar\omega}{k_B T}}} = \hbar\omega \frac{\sum_{n \in \mathbb{N}_0} n e^{nx}}{\sum_{n \in \mathbb{N}_0} e^{nx}}$$

where $x \equiv -\frac{\hbar\omega}{k_B T}$. Since $e^x \in (0, 1)$:

$$\langle E \rangle = \hbar\omega \left(\frac{1}{1 - e^x} \right)^{-1} \frac{d}{dx} \frac{1}{1 - e^x} = \frac{\hbar\omega}{e^{-x} - 1}$$

i.e.:

$$\langle E \rangle = \frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} \quad (5.18)$$

Note that $\lim_{T \rightarrow \infty} \langle E \rangle = k_B T$: since there are three directions of oscillation (each with its own quantum number n_j), the classical limit $c_V = 3R$ is found. Moreover, writing $\langle E \rangle = \hbar\omega n(\omega, T)$ from Eq. 5.16, the **phonon distribution** is found:

$$n(\omega, T) = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} \quad (5.19)$$

where phonons are the quanta of vibrational energy. This is the Bose-Einstein distribution, hence phonons are bosons. At fixed temperature, the singularity at $\omega = 0$ means that lower

level are more populated, since they require less energy; at fixed frequency, the distribution is asymptotically linear in T with angular coefficient $k_B/(\hbar\omega)$, which means that lower frequencies are more easily populated since they require less energy.

Experimentally, the classical limit $\lim_{T \rightarrow \infty} c_V = 3R$ is confirmed. Moreover, we find that $\lim_{T \rightarrow 0} c_V \sim T^3$: this is compatible with the quantum description, since for a sufficiently small temperature the energy will not be enough to excite the atoms to the first excited state, hence only the ground state will be populated and $c_V = 0$.

§5.2.3.1 Einstein model

To study the limit of $c_V(T)$ as $T \rightarrow 0$, make the (erroneous) simplification that all atoms oscillate with the same frequency ω_E , thus ignoring the vibrational bands. Therefore:

$$E_E = \frac{3N\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} \implies c_V = 3R \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{\frac{\hbar\omega}{k_B T}}}{\left(e^{\frac{\hbar\omega}{k_B T}} - 1 \right)^2} \quad (5.20)$$

In the low-temperature limit:

$$c_V \approx 3R \left(\frac{\hbar\omega}{k_B T} \right)^2 e^{-\frac{\hbar\omega}{k_B T}}$$

which correctly goes to $c_V = 0$, but it does not reproduce the experimental behavior.

§5.2.3.2 Debye model

An improved model accounts for the various possible frequencies. The simplification adopted in this case is that these frequencies are continuously-distributed (i.e. we assume $a \rightarrow 0$). Hence:

$$E_D = \int_{\mathbb{R}^+} d\omega D(\omega) \frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} \quad (5.21)$$

where $D(\omega)$ is the density of state, defined so that the number of states between ω and $\omega + d\omega$ is $dN = D(\omega)d\omega$. To perform the computation, switch to the k variable, so that $dN = D(\omega)d\omega = \tilde{D}(k)dk$: then, for the monoatomic linear chain of total length L :

$$\tilde{D}(k) = \frac{dN}{dk} = \frac{1}{\frac{2\pi}{L}} = \frac{L}{2\pi}$$

since the spacing between discretized wave-vectors is $\frac{2\pi}{L}$.

High-temperature limit In the high-temperature limit:

$$E_D \simeq k_B T \int_{\mathbb{R}^+} d\omega D(\omega) = 3Nk_B T$$

since the total number of states is approximately $3N$ (for $N \gg 1$). This is the expected classical result.

Low-temperature limit In the low-temperature limit, on the other hand, due to the functional expression of the Bose–Einstein distribution, only low frequencies contribute to the integral, since high frequencies are exponentially suppressed: this means that only acoustic bands contribute to the integral, and we can set $\omega \approx v_s k$. Supposing an isotropic crystal, so that $v_s = \text{const.}$ in all directions, then near the origin in the k -space (reciprocal space) the $\omega = \text{const.}$ surfaces are spheres, i.e. $k = \text{const.}$: this allows to directly count the number of states between ω and $\omega + d\omega$. The number of states inside the sphere of frequency ω is simply given by:

$$N(\omega) = \frac{\frac{4}{3}\pi k^3}{\left(\frac{2\pi}{L}\right)^3} = \frac{V}{6\pi^2 v_s^3} \omega^3 \quad (5.22)$$

where $(2\pi)^3/V$ is the volume of a single state in the reciprocal space. Then:

$$D(\omega) = \frac{dN(\omega)}{d\omega} = \frac{V}{2\pi^2 v_s^3} \omega^2 \quad (5.23)$$

Since this only holds for low-frequencies, we introduce a cut-off frequency ω_D , called **Debye frequency**, so that $D(\omega) = 0$ for $\omega > \omega_D$ and:

$$\int_0^{\omega_D} d\omega D(\omega) = 3N \implies \omega_D = v_s \sqrt[3]{6\pi^2 \frac{N}{V}} \quad (5.24)$$

The energy then becomes:

$$E_D = \frac{V}{2\pi^2 v_s^3} \int_0^{\omega_D} d\omega \frac{\hbar\omega^3}{e^{\frac{\hbar\omega}{k_B T}} - 1} = \frac{3\hbar V}{2\pi^2 v_s^3} \left(\frac{k_B T}{\hbar}\right)^4 \int_0^{x_D} dx \frac{x^3}{e^x - 1}$$

If $T \ll \hbar\omega_D/k_B \equiv \theta_D$ (Debye temperature), then $x_D \rightarrow \infty$ and the integral is equal to $\frac{\pi^4}{15}$:

$$E_D \simeq \frac{\pi^2 k_B^4 V}{10\hbar^3 v_s^3} T^4 \quad (5.25)$$

The specific heat then is:

$$C_V = \frac{2}{5} \frac{\pi^2 k_B^4 V}{\hbar^3 v_s^3} T^3 = \frac{12\pi^4}{5} N k_B \left(\frac{T}{\theta_D}\right)^3 \quad (5.26)$$

which is the expected classical result.

Chapter 6

Electronic Properties of Crystals

Our main interest is in the description of metals. In the roughest approximations, the independent non-interacting electrons model, the valence electrons in the metal are assumed to be free and only bound to move inside the crystal: this approximation ignores the screening due to the interaction between electrons, since these are unaffected by any potential (except for the exclusion potential, since electrons are fermions).

This approximation best describes alkali metals, where the single valence electron can be assumed to be free in the metal, while it fails for more complex systems.

§6.1 Linear chain

§6.1.1 Monodimensional case

Consider a 1D linear chain, assuming it is infinite. The free-electron Schrödinger equation reads:

$$-\frac{\hbar^2}{2m_e} \frac{d^2\psi}{dx^2} = E\psi \implies \psi \sim e^{-i(kx - \frac{E}{\hbar}t)}$$

Denoting the distance between adjacent atoms with a and the total length of the chain with L , the periodic boundary condition (so to have an infinite chain) impose:

$$k_n = \frac{2\pi}{L}n \quad n \in \mathbb{Z} - \{0\} \quad (6.1)$$

analogously to the treatment of crystal vibrations. Inserting the functional expression for the wave-function in the Schrödinger equation, the dispersion curve for the free electron is recovered:

$$E_n = \frac{\hbar^2 k_n^2}{2m_e} = \frac{2\pi^2 \hbar^2}{m_e L^2} n^2 \quad (6.2)$$

Note that there is a double degeneracy: one due to $E_n = E_{-n}$ and one due to spin. This means that the energy levels of these free electrons can be labelled with $n \in \mathbb{N}$, and each state has degeneracy $g = 4$. Then, due to the Fermi–Dirac statistics, if there are N_e electrons, only the lowest $N_e/4$ states are populated, and the energy of the highest state is called the **Fermi energy**:

$$E_F = \frac{\pi^2 \hbar^2}{8m_e} \left(\frac{N_e}{L} \right)^2 \quad (6.3)$$

Since $N_e = n_v N_a$, where n_v is the number of valence electrons of the considered atomic species and N_a is the number of atoms in the linear chain, then $N_a/L = 1/a$ is the linear density of atoms.

It is useful to define a density of states $D(E)$ in this case too. The number of states up to energy E , ignoring the spin degeneracy, is:

$$E(N) = \frac{\pi^2 \hbar^2}{8m_e} \left(\frac{N}{L} \right)^2 \implies N(E) = \frac{L}{\pi \hbar} \sqrt{2m_e E}$$

and the density of states is:

$$D(E) = \frac{dN}{dE} = \frac{L}{\pi \hbar} \sqrt{\frac{m}{2E}} \quad (6.4)$$

§6.1.2 Tridimensional case

Generalizing to the 3D case:

$$-\frac{\hbar^2}{2m_e} \Delta \psi = E\psi \implies \psi \sim e^{-i(\mathbf{k} \cdot \mathbf{x} - \frac{E}{\hbar} t)}$$

and the periodic boundary conditions impose:

$$k_i = \frac{2\pi}{L} n_i \quad n_i \in \mathbb{Z} - \{0\} \quad (6.5)$$

for $i = x, y, z$. Then, the dispersion relation becomes:

$$E = \frac{\hbar^2 k^2}{2m_e} = \frac{2\pi^2 \hbar^2}{m_e L^2} (n_x^2 + n_y^2 + n_z^2) \quad (6.6)$$

In this case, the $E = \text{const.}$ surfaces are *always* spheres in reciprocal space (while for vibrations this was true only for small frequencies). Then:

$$N(E) = 2 \frac{\frac{4}{3}\pi k^3}{\left(\frac{2\pi}{L}\right)^3} = \left(\frac{2m_e E}{\hbar^2} \right)^{3/2} \frac{V}{3\pi^2} \quad (6.7)$$

and the density of states reads:

$$D(E) = \frac{dN}{dE} = \frac{V}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{3/2} \sqrt{E} \quad (6.8)$$

While in the 1D case $D(E)$ decreases as E increases, since the gaps between levels become wider, in the 3D the opposite happens, as the number of states between E and $E + dE$ increases as E increases. It is possible to show that in 2D the density of states is constant.

To determine the Fermi energy, we can impose $N(E_F) = N_e$, since we already accounted for spin in the expression for $N(E)$. Solving this equation yields:

$$N_e = \frac{V}{3\pi^2} k_F^3 \implies k_F = \sqrt[3]{3\pi^2 n_e} \quad (6.9)$$

where $n_e \equiv N_e/V \sim a^{-1}$ is the electron number density. This result allows for the computation of the Fermi energy and all other sensible quantities at the Fermi threshold.

Moreover, the electronic contribution to the specific heat can be estimated. First, recall the expression of the Fermi–Dirac distribution:

$$f(E, T) = \frac{1}{e^{\frac{E-\mu}{k_B T}} + 1} \quad (6.10)$$

where $\mu = \mu(T)$ is the chemical potential. As $T \rightarrow 0$, this distribution becomes a Heaviside distribution $f(E, 0) = \theta(\mu(0) - E)$, but at $T = 0$ the highest-energy states which are filled are precisely those at $E = E_F$, hence $\mu(0) = E_F$. In general:

$$\mu(T) = E_F - \frac{\pi^2}{6} \frac{D'(E_F)}{D(E_F)} (k_B T)^2 + o(T^3) \quad (6.11)$$

Recall that in d -dimensions $D(E) \propto E^{\frac{d}{2}-1}$, for $d = 1, 2, 3$, hence the chemical potential can be expressed as:

$$\mu(T) = E_F \left[1 - \frac{\pi^2}{6} \frac{d-2}{2} \left(\frac{T}{T_F} \right)^2 \right]$$

which shows that the chemical potential increases as temperature increases in 1D, remains constant in 2D and decreases in 3D. Since for metals $T \ll T_F$ (as T_F is always way larger than the fusion threshold of the metal), it is always possible to approximate $\mu \simeq E_F$.

Now, to estimate the electronic contribution to the specific heat, we employ the classical relation $E = \frac{3}{2}Nk_B T$, but with a correct for the number of electrons: indeed, the only electrons which contribute to the specific heat are those above the Fermi threshold, whose fraction of the total number of electron can be estimated as T/T_F for $T \ll T_F$. Then:

$$E \simeq \frac{3}{2}N_{\text{eff}}k_B T = \frac{3}{2}N_e k_B \frac{T^2}{T_F} \implies C_V(T) \simeq 3N_e k_B \frac{T}{T_F}$$

§6.2 Free electrons in metals

The estimate for the electronic contribution to the specific heat of a metal can be refined with the free-electron model, which assumes that the valence electrons of the atoms in a metal can be treated as free electrons, due to the nature of the metallic bond.

Proposition 6.2.1 (Electronic specific heat)

The electronic contribution to the specific heat of a metal is:

$$C_V(T) \simeq \frac{\pi^2}{2} N_e k_B \frac{T}{T_F} \quad (6.12)$$

where T_F is the Fermi temperature of the electron ensemble.

Proof. The total energy of the system is:

$$U = \int_0^\infty dE D(E) f(E, T) E$$

where $f(E, T)$ is the Fermi–Dirac distribution. Then, $C_V = \frac{dU}{dT}$, so consider first the following integral:

$$\int_0^\infty dE D(E) \frac{\partial f(E, T)}{\partial T} E_F$$

For metals $T \ll T_F$, hence the variation with temperature of the distribution is, expressed as a function of energy, just two delta functions peaked at $E = E_F$ (this is an approximation): one negative at $E \rightarrow E_F^-$, which represents the states which are devoid of electrons due to

the increase in temperature, and one positive at $E \rightarrow E_F^+$, which represents the states which are filled by those electrons. Then, since these delta functions peak the value of $D(E)$ at $D(E_F)$ and since they have the same area with opposite sign, the integral vanishes. This allows to rewrite:

$$C_V = \int_0^\infty dE D(E) \frac{\partial f(E, T)}{\partial T} (E - E_F)$$

With the same reasoning, $D(E)$ gets peaked at $D(E_F)$ by the partial derivative. The latter can be written as:

$$\frac{\partial f(E, T)}{\partial T} = \frac{\partial}{\partial T} [e^{(E-E_F)/k_B T} + 1]^{-1} = \frac{e^{(E-E_F)/k_B T}}{[e^{(E-E_F)/k_B T} + 1]^2} \frac{E - E_F}{k_B T^2} \equiv \frac{e^x}{[e^x + 1]^2} \frac{x}{T}$$

which results in:

$$C_V = D(E_F) k_B^2 T \int_{-\frac{E_F}{k_B T}}^\infty dx \frac{x^2 e^x}{(e^x + 1)^2} \simeq D(E_F) k_B^2 T \int_{-\infty}^\infty dx \frac{x^2 e^x}{(e^x + 1)^2} = \frac{\pi^2}{3} D(E_F) k_B^2 T$$

since $T \ll T_F$. By Eq. 6.7-6.8:

$$D(E) = \frac{3}{2} \frac{N(E)}{E} \implies D(E_F) = \frac{3}{2} \frac{N_e}{E_F} \implies C_V \simeq \frac{\pi^2}{2} N_e k_B \frac{T}{T_F}$$

which is the thesis. □

Then, the total specific heat of a metal at low temperature can be expressed as:

$$C_V(T) = \gamma T + AT^3$$

where the linear term is the electronic contribution, valid for $T \ll T_F \sim 12'000$ K, and the cubic term is the lattice contribution. For insulators (non-metals) $\gamma = 0$.

§6.2.1 Electrical conductivity

Electrical conductivity is a unique property of metals, since electrons in insulators are not free to oscillate. In presence of an EM field, an electron is subject to the Lorentz force, resulting in the following equation of motion:

$$\hbar \frac{d\mathbf{k}}{dt} = -e \left(\mathbf{E} + \frac{\hbar}{m_e} \mathbf{k} \times \mathbf{B} \right) \quad (6.13)$$

recalling that $m_e \mathbf{v} = \mathbf{p} = \hbar \mathbf{k}$. If $\mathbf{B} = \mathbf{0}$, the solution is:

$$\mathbf{k}(t) = \mathbf{k}(0) - \frac{eE}{\hbar} t$$

Since the filled electronic states are inside the Fermi sphere $k \leq k_F$ (this is exact at $T = 0$, while at $T > 0$ this is approximately true since small variations only happen near the boundary of the Fermi sphere), this means that an electric field shifts the Fermi sphere in an opposite direction with respect to itself.

This result does not agree with experiments: the measured current in the metal is $i \propto v$, which means that if v increases linearly so must do i , a phenomenon which is not observed. On

the contrary, applying a constant electric field to a metal, a constant current and a constant potential difference are observed: this is known as **Ohm's law**, which hints to the fact that the motion of the electrons in the metal is similar to the motion of a body in a viscous fluid (indeed, the free-electron model is only an approximation, and the electrons in the metal are not really free). Adding a viscous term to Eq. 6.13:

$$\hbar \frac{d\mathbf{k}}{dt} = -e\mathbf{E} - \frac{\hbar\mathbf{k}}{\tau} \quad (6.14)$$

This viscous term $-m_e\mathbf{v}/\tau$ represents the dissipative force determined by the random scatterings between electrons: τ is then the mean time between collisions. To derive Ohm's law, impose $\frac{d\mathbf{k}}{dt} = \mathbf{0}$, which has solution:

$$\mathbf{v}_d = -\frac{e\tau}{m_e}\mathbf{E} \equiv -\mu\mathbf{E} \quad (6.15)$$

which is called *drift velocity*, while μ is the *electrical mobility* of the metal. The drift velocity is the average velocity at which electrons move in the metal.

§6.2.1.1 Macroscopic analysis

Consider a volume of section S and length ℓ : the total charge inside the volume is $Q = N_q q$, with $N_q = n_q \ell S$ and n_q numeric density of the charges. The density current then is:

$$J = \frac{Q}{St} = \frac{n_q q \ell S}{S \frac{\ell}{v_d}} = n_q q v_d$$

Inserting Eq. 6.15:

$$\mathbf{J} = \frac{n_q q^2 \tau}{m_q} \mathbf{E} \quad (6.16)$$

For a metal the charges are the electrons, i.e. $q = -e$, but note that Ohm's law is insensitive to the sign of the charges. This relation allows to defined both resistivity ρ and conductivity $\sigma \equiv \frac{1}{\rho}$:

$$\sigma = \frac{n_q q^2 \tau}{m_q} \quad (6.17)$$

Example 6.2.1 (Copper)

For Cu, resistivity is experimentally found to be $\rho \simeq 1.80 \cdot 10^{-8} \Omega \text{ m}$, while its density is $d = 8930 \text{ kg m}^{-3}$. Since copper has a single valence electron:

$$n_e = \frac{N_e}{V} = \frac{N_e d}{M} = \frac{N_a d}{M} = \frac{d}{M_{\text{Cu}}}$$

Hence, the mean time between electronic collisions is:

$$\tau = \frac{m_e M_{\text{Cu}}}{d e^2 \rho} \simeq 2.33 \cdot 10^{-14}$$

Then, it is possible to estimate the mean free path for the electrons in Cu:

$$\lambda = \tau v_F = \tau \frac{\hbar}{m_e} k_F = \tau \frac{\hbar}{m_e} \sqrt[3]{3\pi^2 n_e}$$

The Fermi velocity, which is the maximum velocity of the electrons, is $v_F \simeq 1.57 \cdot 10^6 \text{ m s}^{-1}$, and the mean free path is $\lambda \simeq 36.6 \text{ nm}$, i.e. $\lambda \gg a$: this justifies the free-electron approximation, since the electrons are effectively free in the primitive cell of the lattice, and it also confirms that the viscous effect on their motion is determined by electron-electron scattering, not by electron-nucleus scattering.

The shift Δk of the Fermi sphere can be estimated from $\hbar\Delta k = m_e v_d$:

$$\Delta k = \frac{m_e}{\hbar} v_d = \frac{m_e}{\hbar} \frac{e}{m_e} \tau E = \frac{e\tau}{m_e} \rho J$$

For a current density $J = 1 \text{ A m}^{-2}$ the shift is $\Delta k \simeq 0.64 \text{ m}^{-1}$, which is extremely small if compared to $k_F \simeq 1.34 \cdot 10^{10} \text{ m}^{-1}$: since the only electrons which contribute to the current density are those affected by the shift, which is extremely close to the boundary of the Fermi sphere, this justifies the computation of the mean free path using the Fermi velocity. This implies that $v_d \ll v_F$, which is true since $v_d \simeq 7.4 \cdot 10^{-5} \text{ m s}^{-1}$.

§6.2.2 Hall effect

Now, consider Eq. 6.14 with a magnetic field $\mathbf{B} \neq 0$:

$$m_e \frac{d\mathbf{v}}{dt} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B}) - \frac{m_e}{\tau} \mathbf{v} \quad (6.18)$$

Assuming $\mathbf{B} = B\hat{\mathbf{e}}_z$:

$$\begin{aligned} m_e \left(\frac{d}{dt} + \frac{1}{\tau} \right) v_x &= -e(E_x + Bv_y) & m_e \left(\frac{d}{dt} + \frac{1}{\tau} \right) v_y &= -e(E_y - Bv_x) \\ m_e \left(\frac{d}{dt} + \frac{1}{\tau} \right) v_z &= -eE_z \end{aligned}$$

The EM field is assumed to be stationary, hence the electron reaches a constant velocity due to the viscous term. To find this drift velocity, it is useful to adopt the **Hall geometry**: the z -axis has been fixed by \mathbf{B} , while the x -axis is fixed by the current density $\mathbf{J} = J\hat{\mathbf{e}}_x$, which is applied externally. In this geometry, it is intuitive to see that the drift velocity only has an x -component: indeed, the current density puts the electrons in motion along $\hat{\mathbf{e}}_x$, so they are subject to a Lorentz force along $-\hat{\mathbf{e}}_y$ due to \mathbf{B} , but this has only a transitory effect: indeed, due to the finite dimension of the metal sample we are considering (WLOG a parallelepiped), the electrons will accumulate on the side in the $-\hat{\mathbf{e}}_y$, thus negatively charging it and positively charging the opposite side, and this generates a potential difference and an electric field which balance the magnetic Lorentz force. Then, setting $v_x \equiv v_d$, the above system becomes:

$$m_e \frac{v_d}{\tau} = -eE_x \quad 0 = -e(E_y - v_d B) \quad 0 = 0$$

which has solutions:

$$v_d = -\frac{e\tau}{m_e} E_x \quad E_y = -\frac{e\tau}{m_e} E_x B$$

Note that the drift velocity is the same as in the case without magnetic field. Recalling that $J = -n_e e v_d$, the transverse electric field can be written as:

$$E_y = -\frac{1}{n_e e} J B \quad (6.19)$$

Note that this quantity is indeed sensitive to the sign of the charges, as for general charges the constant is $(n_q q)^{-1}$.

§6.2.3 Optical properties of metals

Empirically, no transparent metal is observed.

§6.2.3.1 Electric fields in metals

Consider a metal sample (WLOG a parallelepiped) and apply a stationary electric field \mathbf{E} perpendicular to one of its sides: in a transient the electrons accumulate on the side opposite to the direction of the electric field, hence at equilibrium the sides are electrically charged and inside the metal an electric field $-\mathbf{E}$ is present, since in stationary conditions the electric field inside a conductive object vanishes.

Now, suppose that the external electric field is instantaneously turned off. To study how electrons return to their equilibrium conditions, notice that the two sides along \mathbf{E} have been charged with superficial charge densities $\pm\sigma$: assuming that the electron distribution has been displaced by a displacement u and denoting the section of the metal in the direction of \mathbf{E} as S , then $Q = Sun_e e$ and $\sigma \equiv \frac{Q}{S} = un_e e$. The equation of motion for the displacement of the electron distribution is:

$$m_e \ddot{u} = -eE = -e \frac{\sigma}{\epsilon_0} = -\frac{ne^2}{\epsilon_0} u$$

where we are neglecting the viscous term $-m_e \dot{u}/\tau$. The solution is a displacement which oscillates around the equilibrium configuration $u = 0$ with a frequency:

$$\omega_p = \sqrt{\frac{n_e e^2}{m_e \epsilon_0}} \quad (6.20)$$

which is called the **plasma frequency** of the metal (a plasma is a gas with ions). Accounting for the viscous term makes the oscillation damped.

§6.2.3.2 EM waves on metals

Consider the same setup as before, but now consider a time-dependent external electric field $E(t) = E_0 e^{i\omega t}$, so that $u(t) = u_0 e^{i\omega t}$ (now accounting for the viscous term would introduce a phase shift φ). The equation of motion then becomes:

$$-m_e \omega^2 u_0 = -eE_0 \implies u(t) = \frac{e}{m_e \omega^2} E(t)$$

Since the displacement of the electron distribution determines a shift of the positive-charge (holes) distribution too, an electric dipole is formed with electric-dipole moment $p = qu = -eu$:

$$p(t) = -\frac{e^2}{m_e \omega^2} E(t) \quad (6.21)$$

The polarization is defined as $P = \frac{1}{V} \sum_i p_i$, but since all the electrons have the same electric-dipole moment $\sum_i p_i = N_e p = V n_e p$, i.e.:

$$P(t) = -\frac{n_e e^2}{m_e \omega^2} E(t) \quad (6.22)$$

Recall that the electric displacement is defined as $\mathbf{D} = \epsilon_0 \epsilon_r \mathbf{E} = \epsilon_0 \mathbf{E} - \mathbf{P}$, hence the relative dielectric constant of the metal is found as:

$$\epsilon_r = 1 + \frac{P}{\epsilon_0 E} \quad (6.23)$$

Since the time dependence cancels in the fraction, the relative dielectric constant is only dependent on the incoming frequency, and it can be expressed in terms of the plasma frequency:

$$\epsilon_r(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \quad (6.24)$$

The relative dielectric constant is related to the refractive index by $n = \sqrt{\epsilon_r}$ (neglecting the relative magnetic permeability, which is assumed to be $\mu_r = 1$), so, assuming that the EM wave propagates in the x -direction inside the metal, the complex exponential becomes:

$$\exp[i(kx - \omega t)] = \exp\left[i\omega\left(\frac{n}{c}x - t\right)\right]$$

where we used the dispersion relation $\omega(k) = ck$. Note that the first term is real if $\omega > \omega_p$, which results in the oscillatory behavior of EM waves, while it is complex if $\omega < \omega_p$: this results in an exponential damping factor, which would mean that the medium is optically opaque. For metals $\hbar\omega_p \sim 10$ eV (in the UV region), which means that metals are opaque to optical radiation, as empirically observed.

§6.2.4 Electronic bands

§6.2.4.1 Linear chain

Consider a 1D metal modelled as a linear chain of atoms separated by a . Since electrons can be considered free in a (ideal) metal, they are represented by waves $\psi \propto e^{ikx}$. Being interal waves of the linear chain, they must satisfy the back-scattering condition, so that $k = \frac{\pi}{a}n$ with $n \in \mathbb{Z} - \{0\}$. Then, consider the interference between the $n = +1$ and the $n = -1$ waves:

$$\psi^\pm \propto \frac{1}{\sqrt{2}} [e^{i\frac{\pi}{a}x} \pm e^{-i\frac{\pi}{a}x}] \propto \begin{cases} \sqrt{2} \cos \frac{\pi}{a}x & (+) \\ \sqrt{2} \sin \frac{\pi}{a}x & (-) \end{cases}$$

Recall that the charge density is $\rho \propto |\psi|^2$: clearly, the + configuration is energetically favourable when compared to the - configuration, since ρ^+ peaks at na , i.e. at the lattice positions where atoms are places and where the potential is deeper (more negative), as opposed to ρ^- which vanishes at na . To be precise:

$$\rho^+(x) \propto 2 \cos^2 \frac{\pi}{a}x \quad \rho^-(x) \propto 2 \sin^2 \frac{\pi}{a}x$$

Note that $\rho_0 \propto |\psi_0|^2 \propto |e^{\pm i\frac{\pi}{a}x}|^2 = 1$, and defining its energy $E_0(k) = \hbar^2 k^2 / (2m_e)$ it is clear that $E^+ < E_0(\frac{\pi}{a}) < E^-$ (values on the boundary of the 1BZ): the energy transitions smoothly from the parabola $E_0(k)$ inside the 1BZ to a function with horizontal tangent at $k = \pm \frac{\pi}{a}$ and with value $E(\pm \frac{\pi}{a}) = E^\pm$. Then, for $\frac{\pi}{a} < k < \frac{2\pi}{a}$, the energy has again the behavior of a parabola at the center, while becoming horizontal on the boundary: in particular, at $k = \frac{\pi}{a}$ it has value $E(\frac{\pi}{a}) = E^-$. It is clear that the boundary of the 1BZ presents a discontinuity, i.e. a **gap**.

To study how wide this gap is, note that it is determined by the periodic potential determined by the atoms placed in the lattice positions, which perturbs the otherwise free electrons. Since this potential $V(x)$ is periodic, it is possible to express it as a Fourier series:

$$V(x) = \sum_{h \in \mathbb{Z}} v_h e^{i \frac{2\pi}{a} h x} \quad (6.25)$$

In particular, in the case of the linear chain $V(x)$ is an even function, i.e. $V(-x) = V(x)$, hence the Fourier series reduces to a cosine series:

$$V(x) = \sum_{h \in \mathbb{N}_0} v_h \cos \frac{2\pi h}{a} x \quad (6.26)$$

The normalized wavefunctions are:

$$\psi_n^+ = \sqrt{\frac{2}{a}} \cos \frac{\pi n}{a} x \quad \psi_n^- = \sqrt{\frac{2}{a}} \sin \frac{\pi n}{a} x \quad (6.27)$$

It is now possible to compute the n^{th} energy gap:

$$\begin{aligned} E_g^{(n)} &\equiv \langle \psi_n^- | V(x) | \psi_n^- \rangle - \langle \psi_n^+ | V(x) | \psi_n^+ \rangle \\ &= \frac{2}{a} \sum_{h \in \mathbb{N}_0} v_h \int_0^a dx \cos \frac{2\pi h}{a} x \left[\sin^2 \frac{\pi n}{a} x - \cos^2 \frac{\pi n}{a} x \right] \\ &= -\frac{2}{a} \sum_{h \in \mathbb{N}_0} v_h \int_0^a dx \cos \frac{2\pi h}{a} x \cos \frac{2\pi n}{a} x = -\frac{2}{a} \sum_{h \in \mathbb{N}_0} v_h \frac{a}{2} \delta_{hn} = -v_n \end{aligned}$$

Note that $v_h < 0 \forall n \in \mathbb{N}$, since the potential is attractive, hence $E_g^{(n)} > 0$ as expected. Qualitatively, this shows that free-electron states (i.e. atomic orbitals) subject to a periodic potential naturally quantize in **energy bands** separated by gaps: this is an intermediate behavior between free electrons (continuous spectrum) and atomic orbitals (discrete spectrum).

§6.2.4.2 Tridimensional case

The quantization into energy bands generalizes trivially to the tridimensional case. In particular, focusing on the 1BZ with $-\frac{\pi}{a} < k < \frac{\pi}{a}$, it is possible to count how many states are present in the energy band, i.e. how many electrons it can contain:

$$N = 2 \frac{V}{a^3} \equiv 2N_c \quad (6.28)$$

where the 2 comes from the spin degrees of freedom and N_c is the number of primitive cells (in real space). This number of available states is to be compared to the number of electrons: indeed, $N_e = n_v N_c$, where n_v is the number of valence electrons in the primitive cell (e.g. $n_d = 1$ for alkali metals¹, $n_d = 2$ for alkali-earth metals, etc.).

Semiconductors A particular case is that of semiconductors, i.e. elements of the IV group (in particular C, Si and Ge), which are characterized by large gaps between energy bands: for example, diamond has gaps of 5.4 eV, which is way larger than visible light, and in fact it is transparent, while Si has gaps of 1.17 eV (IR) and is opaque.

If a sample of IV-group metals is doped with V-group (or higher) metals, the excess of electrons fills the second energy band, which becomes a conductive band, thus obtaining a semiconductor from what normally is an insulator (due to the large gaps). The same result is achieved with a III-group (or lower) doping, where now the valence band itself becomes a conducting band (even if there are few available conducting states) since it is no longer full. In

¹This justifies the treatment of alkali metals using the free-electron approximation: only half of the energy band is filled with electrons, i.e. the energy can be approximated with the free-electron parabola.

both cases, the energy band as seen by active electrons, i.e. those near the Fermi energy, can be approximated as a parabola:

$$E(k) = \frac{\hbar^2 k^2}{2m_{\text{eff}}} \quad (6.29)$$

where $m_{\text{eff}} \in \mathbb{R}$ is an effective mass (positive for V-group or higher and negative for III-group or lower). Therefore, all the results in the free-electron approximation are still valid, with the substitution $m_e \mapsto |m_{\text{eff}}|$ and $q = -e \mapsto -\text{sgn}(m_{\text{eff}})e$: if $m_{\text{eff}} < 0$, the freed conducting states at the boundary of the energy band behave like positively-charged particles. For example, the value of the effective mass can be probed measuring the plasma frequency, while its sign can be determined with a Hall experiment; moreover, since there are few conducting states in semiconductors, the electric field generated by the Hall effect is stronger than in the metal case ($E_y \propto n_q^{-1}$), at the cost of requiring a stronger current density due to the higher resistance of the medium.

The effective mass is a general concept. Given an energy band $E(k)$, the effective mass is defined by the curvature of the band:

$$m_{\text{eff}} := \hbar^2 \left[\frac{d^2 E(k)}{dk^2} \right]^{-1} \quad (6.30)$$

Intuitively, this effective mass is determined by the potential which perturbs the free electrons, modifying their inertia.