

Quantum Chemistry

Università degli studi di Roma "La Sapienza"
Physics and Astrophysics BSc

MATTEO CHERI

NOTES ON QUANTUM CHEMISTRY

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Written by

Matteo Cheri

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Part I

Atomic Physics

1 One Electron Atoms

§ 1.1 Interaction of Particles with EM Fields

Before diving into a full computation of an electromagnetic Hamiltonian, we need to properly “quantize” it. Having $\underline{\hat{A}}$ our vector potential operator and $\hat{\phi}$ our scalar potential operator, and knowing that $\underline{\hat{P}} = \underline{\hat{p}} - q\underline{\hat{A}}$, where $\underline{\hat{P}}$ is the minimal coupling momentum of an EM field, we have that the classical Hamiltonian for an electromagnetic field is

$$\mathcal{H} = \frac{1}{2m} (p_i - qA_i)^2 + q\phi \quad (1.1)$$

Quantizing, and noting that $[\hat{p}_i, \hat{A}_i] \neq 0$ generally, we have, setting the Coulombe gauge ($\partial_i A^i = 0, \phi = 0$) that the Hamiltonian in study for our quantum system is the following

$$\hat{\mathcal{H}} = \frac{1}{2m} \left(-\hbar^2 \nabla^2 + q^2 \hat{A}^2 + 2iq\hbar \underline{\hat{A}} \cdot \nabla \right) \quad (1.2)$$

The interaction of the field with the particle can be analyzed perturbatively, and considering first order terms in $\underline{\hat{A}}$ we have

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \frac{iq\hbar}{m} \underline{\hat{A}} \cdot \nabla \quad (1.3)$$

Where we put $\hat{\mathcal{H}}_0$ as the unperturbed Hamiltonian.

Calling the perturbative piece of the Hamiltonian $\hat{W}(t)$ we have that the perturbation on a transition between a state $|a\rangle$ and $|b\rangle$ will be given by the following integral

$$W_{ba}(t) = \frac{q}{m} \langle b | \underline{\hat{A}} \cdot \underline{\hat{p}} | a \rangle \quad (1.4)$$

Where the vector potential is the solution of the following integral

$$\hat{A}_i(x_i, t) = \frac{1}{2} \int_0^\infty A_0(\omega) \epsilon_i \left(e^{i(k_i x^i - \omega t + \delta_\omega)} + e^{-i(k_i x^i - \omega t + \delta_\omega)} \right) d\omega \quad (1.5)$$

Take now a time evolved eigenstate of the unperturbed Hamiltonian, and rewrite as a linear combination of those times an unknown time-dependent function $c_k(t)$. We can write, for a generic eigenstate $|k\rangle$, that the new perturbed state will be $|\psi\rangle$

$$|\psi\rangle = \sum_k c_k(t) e^{-\frac{iE_k t}{\hbar}} |k\rangle \quad (1.6)$$

Inserting everything in the time-dependent Schrödinger equation for the perturbed Hamiltonian, and simplifying terms, we have

$$i\hbar \sum_k \dot{c}_k(t) e^{-\frac{iE_k t}{\hbar}} |k\rangle = \sum_k c_k \hat{W}(t) e^{-\frac{iE_k t}{\hbar}} |k\rangle \quad (1.7)$$

Checking now the transition $|k\rangle \rightarrow |b\rangle$, and remembering the orthonormality between states, we have, putting $\omega_{bk} = (E_b - E_k)/\hbar$

$$\dot{c}_b(t) = \frac{1}{i\hbar} \sum_k c_k(t) \langle b | \hat{W} | k \rangle e^{-i\omega_{bk} t} \quad (1.8)$$

Approximating $c_k(t)$ to the first order in λ and making the assumption that the system will be in a state $|a\rangle$ for $t \leq 0$, therefore implying $c_k(t) = \delta_{ka}$ for $k \neq a, b$, we have, rearranging terms of the same order

$$\dot{c}_b(t) = \frac{1}{i\hbar} \langle b | \hat{W} | a \rangle e^{-i\omega_{ba} t} \quad (1.9)$$

Factoring out constants and time dependent parameters, we have that the coefficient for our perturbation is

$$c_b(t) = \frac{q}{2im\hbar} \int_0^\infty \int_0^t A_0(\omega) \langle b | e^{ik_i x_i} \epsilon \cdot \underline{\hat{p}} | a \rangle e^{-i(\omega_{ba} - \omega)t'} e^{i\delta_\omega} dt d\omega + c.c. \quad (1.10)$$

If $t \gg 2\pi/\omega$ we can approximate the radiation as a plane wave solution. Parting the integrals we have that one will be nonzero for $\omega_{ba} \simeq \omega$ and the second for $\omega_{ba} \simeq -\omega$. The first nonzero solution describes an absorption between the state with $|a\rangle$ and $|b\rangle$, with $E_b > E_a$, and the second instead describes an emission between the state $|a\rangle$ and $|b\rangle$.

Now, indicating $\langle b | e^{ik_i x_i} \epsilon \cdot \underline{\hat{p}} | a \rangle$ as M_{ba} and noting that $\langle e^{i\delta_\omega} \rangle = \delta(\omega)$ we have that the transition probability will be

$$|c_b(t)|^2 = \frac{q^2}{4m^2\hbar^2} \int_0^\infty |A_0(\omega)|^2 \left| \langle b | e^{ik_i x_i} \epsilon \cdot \underline{\hat{p}} | a \rangle \right|^2 F(t, \omega_{ba} - \omega) d\omega \quad (1.11)$$

Where the function F is defined as the square modulus of the integral of the exponential, which corresponds to a sinc^2 function. For $t \gg 1$ we have that, for the properties of the function F , Fermi's Golden Rule, and the connection between A^2 and the intensity I , we have

$$P_{a \rightarrow b}(t) = |c_b(t)|^2 = \frac{\pi q^2 t}{2\hbar^2 \epsilon_0 \omega^2 m^2 c} I(\omega) |M_{ba}|^2 \delta(\omega_{ba} - \omega) \quad (1.12)$$

Note that this probability is linearly dependent on time, therefore, the time-weighted probability of transition between the states $|a\rangle$ and $|b\rangle$ for a system in an electromagnetic field is

$$W_{ba} = \frac{\pi q^2}{\epsilon_0 \omega_{ba}^2 m^2 c \hbar^2} I(\omega_{ba}) |M_{ba}|^2 \quad (1.13)$$

§ 1.2 Dipole Approximation

In order to evaluate dipole transitions we approximate our plane wave solution to the first order, getting $e^{ik_i x^i} \approx 1$, which gives us that $M_{ba} = \langle b | \hat{\epsilon} \cdot \hat{\underline{p}} | a \rangle$. In this approximation, we can write

$$\hat{\underline{p}} = \frac{m}{i\hbar} [\hat{\underline{r}}, \hat{\mathcal{H}}_0]$$

Substituting in M_{ba} and using $\hat{\mathcal{H}}_0$'s hermiticity, we have, defining an *electric dipole operator* $\hat{\underline{D}} = -e\hat{\underline{r}}$

$$M_{ba}^{(1)} = \frac{im\omega_{ba}}{e} \langle b | \hat{\epsilon} \cdot \hat{\underline{D}} | a \rangle \quad (1.14)$$

And

$$W_{ba}^{(1)} = \frac{\pi I(\omega_{ba})}{\hbar^2 c \epsilon_0} |\langle b | \hat{\epsilon} \cdot \hat{\underline{D}} | a \rangle|^2 \quad (1.15)$$

Evaluating the square norm on the right, we have that in case of unpolarized light, the vector ϵ lays randomly on a sphere, and therefore we have that the matrix elements of M_{ba} will depend solely on $|\langle b | \hat{\underline{r}} | a \rangle|$, as follows

$$|\langle b | \hat{\epsilon} \cdot \hat{\underline{r}} | a \rangle|^2 = \frac{1}{3} \sum_k |\langle b | \hat{r}_k | a \rangle|^2 = \frac{1}{3} |\underline{r}_{ba}|^2 \quad (1.16)$$

Where we used that $\langle \cos^2(\theta) \rangle = 1/3$.

Finally, we have that in the dipole approximation

$$W_{ba} = \frac{\pi q^2 I(\omega_{ba})}{3\hbar^2 \epsilon_0 c} |\langle b | \hat{\underline{r}} | a \rangle|^2 \quad (1.17)$$

§§ 1.2.1 Dipole Selection Rules for Atomic Transitions

Consider now a Hydrogenic Hamiltonian (without spin) as our unperturbed system. In this case we choose $q = -e$.

As we have seen before, the electric dipole transition probability between two states with $E_b > E_a$ depends only on the matrix elements of $\hat{\epsilon} \cdot \hat{\underline{r}}$. Rewriting everything in terms of spherical components, we have

$$\begin{aligned} \hat{r}_{\pm 1} &= \frac{\hat{x} \pm i\hat{y}}{\sqrt{2}}, & \hat{r}_0 &= \hat{z} \\ \epsilon_{\pm 1} &= \frac{\epsilon_x \pm i\epsilon_y}{\sqrt{2}}, & \epsilon_0 &= \epsilon_z \end{aligned} \quad (1.18)$$

Considering that Spherical Harmonics are eigenfunctions of our unperturbed Hamiltonian and can also be used to describe the components of the vectors, we have $r_{\pm 1} = \sqrt{\frac{4\pi}{3}} Y_{1,\pm 1} \hat{r}$ and $r_0 = \sqrt{\frac{4\pi}{3}} Y_{1,0} \hat{r}$, hence we get that $\hat{\epsilon} \cdot \hat{\underline{r}}_{ba}$ is

$$\sum_q \langle n'l'm' | \hat{\epsilon}_{\mathbf{q}} \hat{r}_q | nlm \rangle = \sum_q \bar{\epsilon}_{\mathbf{q}} \sqrt{\frac{4\pi}{3}} \iint \bar{R}_{n'l'} R_{nl} r^3 \bar{Y}_{l'}^{m'} Y_1^q Y_l^m d\Omega dr \quad (1.19)$$

The last integral is nonzero if and only if $m' = m + q$, hence we must have that $m - m' = \pm 1$ and $q = \pm 1$. On the other hand, due to the parity of spherical harmonics, we need that $l + l' + 1$ must be even, hence summing the coefficients using Clebsch-Gordan rules, we need that $l = l' \pm 1$, and hence $l - l' = \pm 1$. In bra-ket notation this reduces to the following calculation

$$\int \bar{Y}_{l'}^{m'} Y_1^q Y_l^m d\Omega \rightarrow \sqrt{\frac{3(2l+1)}{4\pi(2l'+1)}} \langle l100|l'0 \rangle \langle l1mq|l'm' \rangle \quad (1.20)$$

Which brings back our previously found selection rules, plus one more constraint on Δm . Recapping everything, we get that for a spinless system, the selection rules for a dipole transition are

Quantum Number	Permitted Transitions
l	± 1
m	$0, \pm 1$

§§ 1.2.2 Spontaneous Emission

A situation that can't be evaluated using semiclassical methods is that of spontaneous emission, since an atom can decay spontaneously, even without having some radiation stimulating the process.

We start by evaluating an atom-photon system, for which we have three probabilities of interaction between the two: absorption (B_a), emission (B_e) and spontaneous emission (A_{se}). The B s indicate the probability in unit time that the photon induces a transition between the two states b and a with $E_b > E_a$, and A indicates the probability for unit time that the state b decays spontaneously to the state a . We already know that the B s are tied to our previous perturbation matrix as follows

$$W_{ba} = B_{ba}\rho(\omega_{ba})$$

Where ρ is a density tied to the photon number, which has the following formal expression

$$\rho(\omega) = \frac{\hbar\omega N(\omega)}{V}$$

With V the volume considered and $N(\omega)$ the number of photons in that given frequency. Given this, the number of atoms that decay from a to b is the following

$$N_{ba} = N_a B_a \rho(\omega_{ba})$$

And, vice-versa

$$N_{ab} = N_b B_e \rho(\omega_{ba}) + N_b A_{se}$$

If the system is at equilibrium we must have $N_{ab} = N_{ba}$, hence

$$\frac{N_b}{N_a} = \frac{B_a \rho(\omega_{ba})}{B_e \rho(\omega_{ba}) + A_{se}} = e^{-\beta \hbar \omega_{ba}} \quad (1.21)$$

Where $\beta = (k_B T)^{-1}$. Knowing that ρ must follow a Black-Body law, we have, solving for ρ

$$\rho(\omega_{ba}) = \frac{A_{se}}{B_a \left(e^{\beta \hbar \omega_{ba}} - \frac{B_e}{B_a} \right)} \quad (1.22)$$

Hence

$$\begin{aligned}\frac{B_e}{B_a} &= 1 \\ \frac{A_{se}}{B_a} &= \frac{\hbar\omega_{ba}^3}{\pi^2 c^3}\end{aligned}\tag{1.23}$$

We then must have that $W_{ba}^a = W_{ba}^{se} = B_a \rho(\omega_{ba})$, and coupling it to equation (1.13), we must have that

$$W_{ba}^{se} = \frac{\pi\omega_{ba}^3 e^2}{\hbar c^3 \epsilon_0} \left| \boldsymbol{\epsilon} \cdot \hat{\mathbf{r}}_{ba} \right|^2 \tag{1.24}$$

§§ 1.2.3 Thermodynamic Equilibrium

We already saw how the density of photons at a given frequency is given by the following expression, without proof.

$$\rho(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\beta\hbar\omega} - 1}$$

Proof. We need to prove this relation. We start supposing that we have a system of levels with $\Delta E = \hbar\omega$ for every level in the set. The number of photons that populate this system at a temperature T is

$$N(\omega, T) = \frac{\sum_{n=0}^{\infty} n e^{-\beta n \hbar \omega} - \frac{\beta \hbar \omega}{2}}{\sum_{n=0}^{\infty} e^{-\beta n \hbar \omega} - \frac{\beta \hbar \omega}{2}} = \frac{\sum_{n=0}^{\infty} n x^n}{\sum_{n=0}^{\infty} x^n} = -x \frac{d \log(1-x)}{dx} = \frac{1}{e^{\beta \hbar \omega} - 1} \tag{1.25}$$

Where we put, for convenience, $x = e^{-\beta \hbar \omega}$

We now need to evaluate how many states we have with frequency ω . We begin considering a box with sides of length L with periodic boundary value conditions. The number of possible modes is

$$N_m(k) = 2 \frac{\frac{4}{3} \pi k^3}{\left(\frac{2\pi}{L}\right)^3}$$

Differentiating and passing to frequency ($\omega = ck$), we get

$$dN_m(\omega) = \frac{V \omega^2}{\pi^2 c^3} d\omega \tag{1.26}$$

And, henceforth, the energy density is

$$\rho(\omega) d\omega = \frac{\hbar\omega}{V} N(\omega, T) dN_m(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\beta\hbar\omega} - 1} d\omega \tag{1.27}$$

□

§ 1.3 Relativistic Corrections and Fine Structure

Taking the full-blown relativistically invariant Dirac Hamiltonian and considering it in the limit $v/c \ll 1$ and assuming infinite nuclear mass, we get the following expression

$$\hat{\mathcal{H}} = mc^2 + \frac{\hat{p}^2}{2m} - \frac{\hat{p}^4}{8m^3c^2} + \frac{1}{2m^2c^2} \frac{1}{R} \frac{dV}{dR} \hat{\underline{L}} \cdot \hat{\underline{S}} + \frac{\hbar^2}{8m^2c^2} \nabla^2 V(R) + V(R) \quad (1.28)$$

This Hamiltonian can be divided in three parts: The non-relativistic Hamiltonian, a kinetic relativistic correction, spin-orbit interaction and the Darwin term.

§§ 1.3.1 Relativistic Correction for the Kinetic Energy

The relativistic correction for kinetic energy is given by the expansion of $E = c\sqrt{p^2 + m^2c^2}$. Expanding, we get

$$E \simeq mc^2 + \frac{\hat{p}^2}{2m} - \frac{\hat{p}^4}{8m^3c^2} \quad (1.29)$$

We have our non perturbed Hamiltonian $\hat{\mathcal{H}}_0$ with our hydrogenoid potential summed to the correction, as follows

$$\begin{aligned} \hat{\mathcal{H}} &= \frac{\hat{p}^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r} + W_p \\ W_p &= -\frac{\hat{p}^4}{8m^3c^2} \end{aligned} \quad (1.30)$$

We already know that $\hat{p}^2 = 2m(\hat{\mathcal{H}}_0 - V)$, hence $\hat{p}^4 = 4m^2(\hat{\mathcal{H}}_0 - V)^2$, and

$$W_p = -\frac{1}{2mc^2} (\hat{\mathcal{H}}_0 - V)^2$$

Surprisingly, this perturbation is diagonal in the basis of the Hydrogen atom, hence we find ourselves in need of calculating only some expectation values, as follows

$$\langle W_p \rangle = -\frac{1}{2mc^2} \langle \hat{\mathcal{H}}_0^2 + V^2 - [\hat{\mathcal{H}}_0, V] \rangle \quad (1.31)$$

Which gives

$$\langle W_p \rangle = -\frac{1}{2mc^2} \left(E_n^2 + \frac{Z^2 e^4}{(4\pi\epsilon_0)^2} \left\langle \frac{1}{r^2} \right\rangle + 2E_n \frac{Ze^2}{4\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle \right) \quad (1.32)$$

The expectation values are easy to calculate and their explicit calculation is given in appendix ???. For our specific case, we get that

$$\begin{aligned} \left\langle \frac{1}{r} \right\rangle &= \frac{Z}{a_0 n^2} \\ \left\langle \frac{1}{r^2} \right\rangle &= \frac{Z^2}{a_0^2 n^3 \left(l + \frac{1}{2}\right)} \\ \left\langle \frac{1}{r^3} \right\rangle &= \frac{Z^3}{a_0^3 n^3 l \left(l + \frac{1}{2}\right) (l + 1)} \quad l > 0 \end{aligned} \quad (1.33)$$

Putting it all into our matrix elements of the perturbation, and remembering that $E_n = -E_1/n^2$, with $E_1 = -Z^2/n^2\alpha^2mc^2$, with $\alpha = e^2/\hbar c$ is the fine structure constant, we get

$$\langle W_p \rangle = -\frac{1}{2mc^2} \left(E_n^2 + \frac{Z^4 e^4}{a_0^2 n^3 (4\pi\epsilon_0)^2 (l+1/2)} + 2E_n \frac{Z^2 e^2}{4\pi\epsilon_0 a_0 n^2} \right) \quad (1.34)$$

Substituting for E_n , we get, finally

$$\langle W_p \rangle = -E_n \frac{Z^2 \alpha^2}{2n^2} \left(\frac{3}{4} - \frac{n}{l+1/2} \right) \quad (1.35)$$

For a Hydrogen atom we have $Z = 1$, and the correction is of order $\alpha^2 E_n$. Counting that $\alpha = 137^{-1}$ the perturbation is small enough to be treated as such.

§§ 1.3.2 Darwin Term

The Darwin term $\left(\frac{\hbar^2}{8m^2 c^2} \nabla^2 V(r) \right)$, for Hydrogenoid atoms, becomes

$$\hat{W}_D = \frac{\hbar^2 Z e^2}{8\epsilon_0 m^2 c^2} \delta(r_i) \quad (1.36)$$

Where we used that $\nabla^2(1/r) = -4\pi\delta(r)$

The matrix elements of \hat{W}_D will be nonzero only for $l = 0$, and will take the following form

$$\langle W_D \rangle = \frac{\hbar^2 Z e^2}{8\epsilon_0 m^2 c^2} |\phi_{nlm}(0)|^2 \quad (1.37)$$

In general $|\phi_{n00}(0)|^2 = (4\pi)^{-1} |R_{n0}|^2$, where

$$R_{nl}(\rho) = \frac{1}{(2l+1)!} \sqrt{\left(\frac{2Z}{na_0} \right)^3 \frac{(n+l)!}{2n(n-l-1)!}} e^{\frac{\rho}{2}} r^l F(l+1-n, 2l+2, \rho) \quad (1.38)$$

With $\rho = 2Zr/na_0$. We have that $|R_{n0}(0)|^2 = \frac{4Z^3}{n^3 a_0^3}$, hence

$$|\phi_{n00}(0)|^2 = \frac{Z^3}{\pi a_0^3 n^3} \quad (1.39)$$

For which, finally we get

$$\langle W_D \rangle = \frac{\hbar^2 Z^4 e^2}{8\pi\epsilon_0 a_0^3 m^2 c^2 n^3} = \frac{\hbar^2}{2m^2 c^2} \frac{Z^2}{n^3 a_0^2} \alpha^2 m c^2 = -E_n \frac{\hbar^2 Z^2}{na_0 m^2 c^2} = -E_n \frac{Z^2 \alpha^2}{n} \quad (1.40)$$

§§ 1.3.3 Spin Orbit Coupling

The last term to evaluate, is the Spin-Orbit coupling of angular momentums, which gives the following perturbation

$$\hat{W}_{SO} = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \hat{\underline{L}} \cdot \hat{\underline{S}} \quad (1.41)$$

Explicitly

$$\hat{W}_{SO} = \frac{Ze^2}{8\pi\epsilon_0 m^2 c^2 r^3} \hat{\underline{L}} \cdot \hat{\underline{S}} \quad (1.42)$$

Its matrix elements will be, then

$$\langle W_{SO} \rangle = \frac{Ze^2}{8\pi\epsilon_0 m^2 c^2} \left\langle \frac{1}{r^3} \right\rangle \langle \hat{\underline{L}} \cdot \hat{\underline{S}} \rangle \quad (1.43)$$

Adding angular momentums and passing to the basis $|j l s m_j\rangle$, we get that

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

And remembering that

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{a_0^3 n^3 l(l+1/2)(l+1)}, \quad l > 0$$

We get

$$\langle W_{SO} \rangle = \frac{\hbar^2 Z^4 e^2}{16\pi\epsilon_0 a_0^3 n^3 l(l+1/2)(l+1) m^2 c^2} (j(j+1) - l(l+1) - s(s+1)) \quad (1.44)$$

In which, substituting in the following values

$$\begin{aligned} E_n &= -\frac{Z^2 \alpha^2 m c^2}{2n^2} \\ a_0 &= \frac{\hbar}{m c \alpha} \\ \frac{e^2}{4\pi\epsilon_0} &= \alpha \hbar c \end{aligned}$$

We have

$$\langle W_{SO} \rangle = -E_n \frac{Z^2 \alpha^2}{2n^2} \frac{j(j+1) - l(l+1) - s(s+1)}{l(l+1/2)(l+1)} \quad (1.45)$$

Which, dividing it in two cases, if we have $j = l + 1/2$ or $j = l - 1/2$, we get

$$\langle W_{SO} \rangle = -E_n \frac{Z^2 \alpha^2}{2nl(l+1/2)(l+1)} \cdot \begin{cases} l & j = l + 1/2 \\ -(l+1) & j = l - 1/2 \end{cases} \quad (1.46)$$

The total, and final, perturbation given by the relativistic approximation will not depend on l , and it's given by the following formula

$$E_{nj} = E_n \left(1 + \frac{Z^2 \alpha^2}{n^2} \left(\frac{n}{j+1/2} - \frac{3}{4} \right) \right) \quad (1.47)$$

§§ 1.3.4 Fine Structure Splitting

After summing all these perturbations to our initial energy, we have that although the non-relativistic energy levels were $2n^2$ times degenerate, we have that in the Dirac theory (i.e. relativistic quantum mechanics), we have that the n -th level splits in n different levels, each one with its own value of j . This splitting is commonly called *fine structure splitting*, and these n levels are called *fine structure multiplets*. The dimensionless *fine structure constant* $\alpha \simeq 1/137$ controls the scale of this splitting. It's important to note how in Dirac theory, two states with the same quantum numbers n, j but with $l = j \pm 1/2$, have the same energy, where the solution still has $(-1)^l$ parity. Thus for each j we have two series of $2j + 1$ solutions with opposite parity, except for $j = n - 1/2$, for which there is only a series of solutions with parity $(-1)^{n-1}$. The splitting we talked about in this paragraph is indicated as follows with spectroscopic notation.

e.g. let's say that we have $n = 3$, hence $l = 0, 1, 2$ and $j = 1/2, 3/2, 5/2$. Through the perturbed energy (1.47) we will have that the $n = 3$ level will split in 5 levels, as follows

$$3s_{1/2}, 3p_{1/2}, 3p_{3/2}, 3d_{3/2}, 3d_{5/2}$$

This splitting is accompanied by a further splitting, called *hyperfine splitting*, and its contribution is called *Lamb shift*

§§ 1.3.5 Fine Structure Dipole Transitions

We already seen how the only permitted transitions in the dipole approximation are those that have $\Delta l = \pm 1$ and $\Delta s = 0$, which implies that $\Delta j = 0, \pm 1$. Since $\underline{\hat{J}}$ eigenstates are linear combinations of eigenstates of $\underline{\hat{S}}, \underline{\hat{L}}$, we have that $\Delta j = 0$ transitions are permitted.

e.g., let's see how it works for states with $l = 1$ and $s = 1/2$. There will be 6 states, where 4 will have $j = 3/2$ and 2 will have $j = 1/2$. The six states in the $|jm_j\rangle$ basis can be written as a linear combination of states $|lsm_l m_s\rangle$. Starting with $m_j = 3/2$ we have

$$\left| \frac{3}{2}, \frac{3}{2} \right\rangle = \left| 1, \frac{1}{2}, 1, \frac{1}{2} \right\rangle$$

Operating with \hat{J}_- we have

$$\left| \frac{3}{2}, \frac{1}{2} \right\rangle = A \left| 1, \frac{1}{2}, 0, \frac{1}{2} \right\rangle + B \left| 1, \frac{1}{2}, 1, -\frac{1}{2} \right\rangle$$

Analogously, starting from $m_j = -3/2$ and working our way up the eigenstate ladder with \hat{J}_+ , we get

$$\left| \frac{3}{2}, -\frac{1}{2} \right\rangle = C \left| 1, \frac{1}{2}, 0, -\frac{1}{2} \right\rangle + D \left| 1, \frac{1}{2}, -1, \frac{1}{2} \right\rangle$$

And finally, the last two states

$$\begin{aligned} \left| \frac{1}{2}, -\frac{1}{2} \right\rangle &= -\sqrt{\frac{2}{3}} \left| 1, \frac{1}{2}, -1, \frac{1}{2} \right\rangle + \sqrt{\frac{1}{3}} \left| 1, \frac{1}{2}, 0, -\frac{1}{2} \right\rangle \\ \left| \frac{1}{2}, \frac{1}{2} \right\rangle &= E \left| 1, \frac{1}{2}, 1, -\frac{1}{2} \right\rangle + F \left| 1, \frac{1}{2}, 0, \frac{1}{2} \right\rangle \end{aligned}$$

In this situation there are 7 possible transitions, but there will be only 5 visible lines, since $\Delta j = 2$ is not permitted by the selection rules.

This can be seen as follows: before the absorption, the total angular momentum is j_i , of the electron, summed with the photon spin $s_\gamma = 1$, hence the total (initial) angular momentum will be k_i , where $|j_i - 1| < k_i < j_i + 1$. After the transition, we must have $k_f = j_f$, and since angular momentum must be conserved, we have that $k_i = k_f$, hence $|j_i - 1| < j_f < j_i + 1$, this happens analogously with emission transitions. Finally, the selection rules for dipole transitions in fine structure systems are $\Delta l = \pm 1$, $\Delta s = 0$, $\Delta j = 0, \pm 1$ where $j = 0 \rightarrow j = 0$ is not permitted

§ 1.4 Zeeman Effect

Getting back to our semiclassical EM Hamiltonian, we have that the time dependent perturbation can be written as

$$-\frac{i\hbar e}{m} \underline{\hat{A}} \cdot \nabla = \frac{e}{2m} \underline{B} \cdot \underline{\hat{L}}$$

And the quadratic perturbation as follows

$$\frac{e^2}{2m} \hat{A}^2 = \frac{e^2}{8m} (B^2 \hat{r}^2 - (\underline{B} \cdot \underline{\hat{r}})^2)$$

Since in laboratories is rare to exceed 10 T of magnetic field intensity, hence since $4a_0^2 B / 4\hbar \approx 10^{-6} B$ we suppose that the quadratic term is again negligible.

We define a Magnetic dipole moment operator as follows.

$$\underline{\hat{M}} = -\frac{e}{2m} \underline{\hat{L}} = -\frac{\mu_B}{\hbar} \underline{\hat{L}} \quad (1.48)$$

With $\mu_B = e\hbar/2m$ is Bohr's magneton, which has the value of around $9.27408 \cdot 10^{24}$ J/T or Am². The interaction Hamiltonian with this field then is

$$\hat{\mathcal{H}}_m = -\underline{\hat{M}} \cdot \underline{B} \quad (1.49)$$

To this we have to add the intrinsic magnetic moment given by the electron, which has the following shape

$$\underline{\hat{M}}_s = -\frac{g\mu_B}{\hbar} \underline{\hat{S}} \quad (1.50)$$

Where $g = 2$ is the gyromagnetic ratio of the electron And the following Hamiltonian

$$\hat{\mathcal{H}}_s = -\underline{\hat{M}}_s \cdot \underline{B} \quad (1.51)$$

Our final Hamiltonian that accounts for spin-orbit interactions and atom-magnetic field interaction is simply given via the Pauli equation, at which has been "attached" the spin-orbit coupling element. The Pauli equation will then be

$$\langle r | \hat{\mathcal{H}} | \psi \rangle = \left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + \xi(r) \underline{\hat{L}} \cdot \underline{\hat{S}} + \frac{\mu_B}{\hbar} (\underline{\hat{L}} + 2\underline{\hat{S}}) \cdot \underline{B} \right) \psi(r) = E\psi(r) \quad (1.52)$$

Where, our $\psi(r)$ not only accounts for spin, but for spin-orbit coupling also.

§§ 1.4.1 Strong Fields

Strong fields are characterized for having a magnetic field intensity of $B > Z^4$ Tesla. In this situation the spin-orbit coupling term is negligible, and our equation, after applying a rotation and having $\underline{B} \parallel \hat{z}$, we have

$$\left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \right) \psi(r_i) = \left(E - \frac{\mu_B B_z}{\hbar} (\hat{L}_z + 2\hat{S}_z) \right) \psi(r_i) \quad (1.53)$$

The perturbation is diagonal, and the shift will be

$$E_{nm_l m_s} = E_n + \mu_B B_z (m_l + 2m_s) \quad (1.54)$$

Where in this case $m_s = \pm 1/2$. Since there is no spin orbit coupling in this case, we have that levels with $m_l = 1, m_s = -1/2$ and $m_l = -1, m_s = 1/2$ coincide.

We already know from the selection rules that we must have $\Delta m_s = 0$ and $\Delta m_l = 0, \pm 1$, thus splitting the transition $n \rightarrow n'$ into three components. The two components with $\Delta m_l = \pm 1$ are called π lines, and the remaining one, with $\Delta m_l = 0$ is called the σ line.

These π transitions have the following frequencies

$$\omega_{n'n}^{\pm} = \omega_{n'n} \pm \omega_L \quad (1.55)$$

Where $\omega_L = \mu_B B_z / \hbar$ is the *Larmor frequency*. This effect is known as *normal Zeeman effect*, and the π and σ lines of this effect are said to be *Lorentz triplets*. They are also observed in atoms for which $S = 0$, hence where spin-orbit coupling is absent.

§§ 1.4.2 Paschen-Back Effect

At field strengths for which spin orbit coupling is appreciable but still small with respect to the field intensity B , we have that first order perturbation theory can be applied in order to calculate the energy shift.

We have then

$$\Delta E = \int_0^\infty r^2 R_{nl}^2 \xi(r) dr \left\langle l \frac{1}{2} m_l m_s \left| \underline{\hat{L}} \cdot \underline{\hat{S}} \right| l \frac{1}{2} m_l m_s \right\rangle = \lambda_{nl} m_l m_s \quad l \neq 0 \quad (1.56)$$

We have that $\langle ++ \rangle$

$$\lambda_{nl} = -E_n \frac{Z^2 \alpha^2}{n} \frac{1}{l(l+1/2)(l+1)} \quad (1.57)$$

Which removes the degeneracy in l . The energy difference between two different levels, when $m_s = m'_s$ ($\Delta m_s = 0$) is then the following

$$\Delta E = E_{n'} - E_n + E_z + E_{pb} = E_{n'} - E_n + \mu_B B_z (m'_l - m_l) + (\lambda_{n'l'} m'_l - \lambda_{nl} m_l) m_s \quad (1.58)$$

§§ 1.4.3 Anomalous Zeeman Effect

For weak magnetic fields, we have what's usually called the *anomalous Zeeman effect*. In this case, the spin-orbit coupling is the dominant term, and our unperturbed Hamiltonian takes the following shape

$$\hat{\mathcal{H}}_0 = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + \xi(r) \underline{\hat{L}} \cdot \underline{\hat{S}} \quad (1.59)$$

This Hamiltonian has exact wavefunctions, which are given via what's known as *Tensor Spherical Harmonics* (see appendix ??). Our unperturbed wavefunction will then be

$$\psi_{nlsm_j}(r, \theta, \phi) = R_{nl}(r) \mathcal{Y}_{ls}^{jm_j}(\theta, \phi) = C_{jm_j}^{lsm_l m_s} R_{nl}(r) Y_l^{m_l}(\theta, \phi) \chi_{s, m_s} \quad (1.60)$$

Or, in Dirac notation

$$|nl\rangle \otimes |ls\rangle \otimes |jm_j\rangle = \langle lsm_l m_s | (|jm_j\rangle \otimes |nl\rangle \otimes |lm_l\rangle \otimes |sm_s\rangle) \quad (1.61)$$

Taking the magnetic field parallel to the z axis, we have that the perturbation needed to be evaluated is

$$\hat{\mathcal{H}}' = \frac{\mu_B}{\hbar} (\hat{J}_z + \hat{S}_z) B_z \quad (1.62)$$

And, the perturbation on the energy levels is

$$\Delta E = \mu_B m_j B_z + \frac{\mu_B}{\hbar} B_z \sum_{m_s} \int \bar{\mathcal{Y}}_{l,1/2}^{jm} \hat{S}_z \mathcal{Y}_{l,1/2}^{jm} d\Omega \quad (1.63)$$

From the properties of tensor spherical harmonics, we have that the integral is of easy computation, and gives the following result

$$\int \bar{\mathcal{Y}}_{l,1/2}^{l\pm 1/2, m_j} \hat{S}_z \mathcal{Y}_{l,1/2}^{l\pm 1/2, m_j} d\Omega = \pm \frac{\hbar m_j}{2l+1} \quad (1.64)$$

Which gives our searched energy shift

$$\Delta E = \mu_B m_j B_z + \frac{\mu_B B_z}{2l+1} \sum_{m_s} m_j \quad (1.65)$$

Finally, getting back to our Hydrogenoid atoms, we now can write the total perturbation of the energy levels for an interaction with a constant magnetic field as follows

$$E_{njm_j} = E_n + \Delta E_{nj} + \Delta E_{m_j} \quad (1.66)$$

Where E_n is the unperturbed energy, ΔE_{nj} is the fine structure correction and ΔE_{m_j} is the weak field correction

§ 1.5 Stark Effect

The splitting of energy levels given by static electric fields is called *Stark effect*. We assume that the electric field is perpendicular to our z axis, and that the field strength is much larger than Spin-Orbit coupling.

The perturbation acting on our Hydrogenic Hamiltonian is

$$\hat{\mathcal{H}}' = eEz \quad (1.67)$$

§§ 1.5.1 Linear Stark Effect

In order to evaluate Stark shifts with perturbations at first order, we start by calculating the perturbation given to the fundamental state.

Its first order correction is

$$E_{100}^{(1)} = eE \langle 100 | \hat{z} | 100 \rangle \quad (1.68)$$

We already see that $E_{100}^{(1)} = 0$, since the integral is null, due to it being the product of an even function ($\langle x_i | nlm \rangle$) with an odd one (z). We therefore check for excited states, starting at $n = 2$, for which we have a fourfold degeneration given by l , with energy $E_{2lm} = -mc^2\alpha^2/8$.

In this case we have that $\langle nlm | \hat{z} | n'l'm' \rangle$ doesn't vanish, if and only if $\Delta m = 0$ and $\Delta l = \pm 1$, hence, the permitted transitions are only those between $2s$ and $2p$ states, for which our perturbation (which is real, hence Hermitian) gives the following result

$$E_{2s \rightarrow 2p}^{(1)} = eE \int \bar{\psi}_{210}(x_i) z \psi_{200}(x_i) d^3x_i \quad (1.69)$$

This last integral gives us that $E^{(1)} = \pm 3eEa_0/Z$, for which we have two different energy levels, described by the following states

$$\begin{aligned} |1\rangle &= \frac{1}{\sqrt{2}} (|200\rangle + |210\rangle) \\ |2\rangle &= \frac{1}{\sqrt{2}} (|200\rangle - |210\rangle) \end{aligned} \quad (1.70)$$

§ 1.6 Hyperfine Structure and Isotope Shifts

Hyperfine structure of energy levels appears when nuclei aren't considered anymore point charges with infinite mass. The name, *hyperfine* has been given to this structure, since the deviation of the energy levels due to this additional perturbation is much smaller than that of the fine structure shifts. In general we can have two kinds of hyperfine effects: *isotope shifts*, that slightly deviate degenerate energy levels without splitting them, and proper hyperfine effects that break the degeneration on the levels and splits them.

§§ 1.6.1 Magnetic Dipole Hyperfine Structure

As for the electrons, we can define a *nuclear spin*, indicated with \hat{I} , which obey the same spin algebra of ordinary spin. As with electrons, the eigenvalues for nuclear spin can be half-integer, if the sum of the spins of the nucleons is fermionic, or integer, if the sum of the spins of the nucleons is bosonic. We denote the eigenvalues of \hat{I}^2 as $\hbar^2 I(I+1)$ and of \hat{I}_z as $\hbar M_I$.

We can define, as for electrons, a *Nuclear Magnetic Dipole Moment*, \hat{M}_I as follows

$$\hat{M}_I = \frac{g_I \mu_N}{\hbar} \hat{I} \quad (1.71)$$

Where g_I is the *Landé factor*, and μ_N is the *Nuclear magneton*, defined as

$$\mu_N = \frac{e\hbar}{2m_p} = \frac{m_e}{m_p} \mu_B \quad (1.72)$$

We now proceed to write our perturbed Hamiltonian as follows

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_{ND} \quad (1.73)$$

Since we have already solved for the fine structure Hamiltonian, it is included into the unperturbed Hamiltonian together with the Coulomb interaction.

At the zeroth order we have that the wavefunctions of $\hat{\mathcal{H}}$ are separable in electronic and nuclear variables, and are eigenfunctions of $\hat{J}^2, \hat{J}_z, \hat{I}^2, \hat{I}_z$. These wavefunction are $(2j+1)(2I+1)$ degenerate in m_j, M_I .

Examining the perturbation $\hat{\mathcal{H}}_{ND}$, we have that it will couple with both $\underline{\hat{L}}$ and $\underline{\hat{S}}$ of the electrons, hence splitting the Hamiltonian in a sum. Since this point dipole is located at the origin, we have that

$$\hat{\mathcal{H}}_{NL} = -\frac{i\hbar e}{m} \underline{\hat{A}} \cdot \nabla = \frac{\mu_0}{2\pi\hbar^2 r^3} g_I \mu_B \mu_N \underline{\hat{L}} \cdot \underline{\hat{I}} \quad (1.74)$$

For the spin-spin coupling Hamiltonian we have that, in terms of magnetic fields we can write the perturbation term as

$$\hat{\mathcal{H}}_{SS} = -\underline{\hat{M}}_s \cdot \underline{B} \quad (1.75)$$

Where

$$\underline{B} = -\frac{\mu_0}{4\pi} \left(\underline{\hat{M}}_N \nabla^2 \frac{1}{r} - \nabla(\underline{\hat{M}}_N \cdot \nabla) \frac{1}{r} \right) \quad (1.76)$$

Hence

$$\hat{\mathcal{H}}_{SS} = -\frac{2\mu_0}{4\hbar^2\pi} g_I \mu_B \mu_N \left(\underline{\hat{S}} \cdot \underline{\hat{I}} \nabla^2 \frac{1}{r} - (\underline{\hat{S}} \cdot \nabla)(\underline{\hat{I}} \cdot \nabla) \frac{1}{r} \right) \quad (1.77)$$

At $r = 0$ this perturbation will act only on s-states, and for $r \neq 0$ we get

$$\hat{\mathcal{H}}_{SS} = -\frac{\mu_0}{4\pi r^3} \left(\underline{\hat{M}}_s \cdot \underline{\hat{M}}_N - \frac{3}{r^2} \left((\underline{\hat{M}}_s \cdot \underline{\hat{r}})(\underline{\hat{M}}_N \cdot \underline{\hat{r}}) \right) \right)$$

Summing the two terms, we have that $\hat{\mathcal{H}}_{ND} = \hat{\mathcal{H}}_{NL} + \hat{\mathcal{H}}_{SS}$, and we finally have

$$\hat{\mathcal{H}}_{ND} = \frac{\mu_0}{2\hbar^2\pi} g_I \mu_B \mu_N \frac{1}{r^3} \left(\underline{\hat{L}} \cdot \underline{\hat{I}} - \underline{\hat{S}} \cdot \underline{\hat{I}} + 3 \frac{(\underline{\hat{S}} \cdot \underline{\hat{r}})(\underline{\hat{I}} \cdot \underline{\hat{r}})}{r^2} \right) \quad r \neq 0 \quad (1.78)$$

Simplifying everything, we have, at $r = 0$

$$\hat{\mathcal{H}}_{ND} = -\frac{2\mu_0}{3\pi} \underline{\hat{M}}_s \cdot \underline{\hat{M}}_N \delta(\underline{\hat{r}}) \quad r = 0 \quad (1.79)$$

This last expression is called *Fermi contact interaction*. Another way to write (1.78) is to define the new operator

$$\underline{\hat{G}} = \underline{\hat{L}} - \underline{\hat{S}} + 3 \frac{(\underline{\hat{S}} \cdot \underline{\hat{r}}) \underline{\hat{r}}}{r^2} \quad (1.80)$$

And (1.78) becomes

$$\hat{\mathcal{H}}_{ND} = \frac{\mu_0}{2\hbar^2\pi} g_I \mu_B \mu_N \frac{1}{r^3} \underline{\hat{G}} \cdot \underline{\hat{I}} \quad (1.81)$$

Before proceeding in the calculation of the energy shifts, we define a *total angular momentum* for the whole system as $\hat{\underline{F}} = \hat{\underline{I}} + \hat{\underline{J}}$, and the energy shift will be given in the total angular momentum basis as follows

$$\Delta E = \frac{\mu_0}{2\hbar^2\pi} g_I \mu_B \mu_N \langle lsjIFM_F | \frac{1}{r^3} \hat{\underline{G}} \cdot \hat{\underline{I}} | lsjIFM_F \rangle \quad (1.82)$$

We can write $\hat{\underline{G}} \cdot \hat{\underline{I}}$ as $(\hat{\underline{G}} \cdot \hat{\underline{J}})(\hat{\underline{I}} \cdot \hat{\underline{J}})/\hbar^2 j(j+1)$, and knowing that $\hat{\underline{I}} \cdot \hat{\underline{J}} = 1/2 (\hat{\underline{F}}^2 - \hat{\underline{I}}^2 - \hat{\underline{J}}^2)$ we have the total shift as

$$\Delta E = \frac{C}{2} (F(F+1) - I(I+1) - j(j+1)) \quad (1.83)$$

Where

$$C = \frac{\mu_0}{2\hbar^2 j(j+1)\pi} g_I \mu_B \mu_N \left\langle \frac{1}{r^3} \hat{\underline{G}} \cdot \hat{\underline{J}} \right\rangle \quad (1.84)$$

Noting that $\hat{\underline{G}} \cdot \hat{\underline{J}} = \hat{\underline{L}}^2$, we finally get our solution, having put a_μ as $a_0 m/\mu$, with μ the reduced mass of the electron and the nucleus

$$\Delta E_{ND} = \frac{\mu_0}{4\pi} g_I \mu_B \mu_N \frac{l(l+1)}{j(j+1)} \frac{Z^3}{a_\mu^3 n^3 l(l+1/2)(l+1)} (F(F+1) - I(I+1) - j(j+1)) \quad l \neq 0 \quad (1.85)$$

For $l = 0$ we instead get

$$\Delta E_{ND} = \frac{2\mu_0}{3\pi} g_I \mu_B \mu_N \frac{Z^3}{a_\mu^3 n^3} (F(F+1) - I(I+1) - s(s+1)) \quad (1.86)$$

In atomic units, the final result will then be

$$\Delta E_{hyp} = \frac{m_e}{m_p} \left(\frac{\mu}{m_e} \right)^3 \frac{2g_I Z^3 \alpha^2}{n^3 (j+1)(2l+1)} \cdot \begin{cases} I + \frac{1}{2} & j \leq I \\ \frac{I(j+1/2)}{j} & j \geq I \end{cases} \quad (1.87)$$

We see that the total angular momentum quantum number behaves as $\hat{\underline{J}}$, hence $\Delta F = 0, \pm 1$ are the only permitted transitions, with $0 \rightarrow 0$ being excluded

2 Two Electron Atoms

We start by directly writing the Schrödinger equation for a two electron atom in atomic units, where

$$\begin{aligned}\hbar &= 1 \\ k_e &= \frac{1}{4\pi\epsilon_0} = 1 \\ e &= 1\end{aligned}$$

We immediately have

$$\hat{\mathcal{H}} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad (2.1)$$

In this case we have that the wavefunction is symmetric to spatial exchange of the two electrons (also called para-wavefunction, similarly spatially antisymmetric wavefunction are called ortho-wavefunctions). We also must impose the Pauli exclusion principle, by taking into account the electrons' spin. We end up having our wavefunction as

$$\Psi(q_1, q_2) = \psi(x_i^1, x_i^2) \chi_{1/2, m_s}(1, 2) \quad (2.2)$$

As we know already, the basis spinor wavefunction for a system of two electrons can be either antisymmetric (singlet) or symmetric (triplet), and hence can take the following shapes

$$\begin{aligned}|00\rangle &= \frac{1}{\sqrt{2}} (|\uparrow\rangle |\downarrow\rangle - |\downarrow\rangle |\uparrow\rangle) \\ |11\rangle &= |\uparrow\rangle |\uparrow\rangle \\ |10\rangle &= \frac{1}{\sqrt{2}} (|\uparrow\rangle |\downarrow\rangle + |\downarrow\rangle |\uparrow\rangle) \\ |1\downarrow 1\rangle &= |\downarrow\rangle |\downarrow\rangle\end{aligned}$$

Due to Pauli's exclusion principle, we have that the final wavefunction must be completely antisymmetric, hence, if we have a para wavefunction ψ_+ , the final solution will take the shape

$$\Psi(q_1, q_2) = \psi_+(x_i^1, x_i^2) \chi_{00} \quad (2.3)$$

Or analogously, if we have an ortho wavefunction

$$\Psi(q_1, q_2) = \psi_-(x_i^1, x_i^2) \cdot \begin{Bmatrix} \chi_{11} \\ \chi_{10} \\ \chi_{1-1} \end{Bmatrix} \quad (2.4)$$

Written this, one may immediately ask what's then the scheme of energy levels? As an example we take an Helium atom. We have that $Z = 2 \ll 40$, hence we have a set of levels of an almost independent levels, one of ortho-triplet states and one of para-singlet states. The lowest energy levels, are divided then between singlets ($S = 0$) and triplets ($S = 1$), where S is the total spin.

Let L be the sum of the eigenvalues of the square angular momentum of both electrons and M_L the sum of the eigenvalues of the projection. We can introduce the *spectroscopic terms* as a new notation for atomic energy levels. They're written as follows

$$^{2S+1}L_{M_J} \quad (2.5)$$

The term L , analogously to the term l for particles, takes the "values" S, P, D, F, G, H, \dots , as l , which takes values s, p, d, f, g, h, \dots . In addition, on the top left of the term there is indicated the *multiplicity of the state*, which indicates whether it's a singlet or a triplet state, in terms of total spin. On the bottom right there are indicated the possible M_J values of the considered system.

§ 2.1 Independent Particle Model

In order to get a first approach to two-electron atoms, we need to develop an approximate theory, in which the $e^- - e^-$ interaction is taken as a perturbation on the system

$$\begin{aligned} \hat{\mathcal{H}} &= -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} + \hat{\mathcal{H}}' \\ \hat{\mathcal{H}}' &= \frac{1}{r_{12}} \\ \hat{\mathcal{H}} &= \hat{h}_1 + \hat{h}_2 + \hat{\mathcal{H}}' = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}' \end{aligned} \quad (2.6)$$

In this case we have that the eigenvalues of the single electron Hamiltonian (\hat{h}_i) are known to be the following

$$\hat{h}_i \psi_{nlm_i}(x_j^i) = -\frac{Z^2}{2n_i^2} \psi_{nlm_i}(x_j^i) \quad i = 1, 2; \quad j = 1, 2, 3$$

Hence, in general, we then have the following solution for the unperturbed Hamiltonian

$$\hat{\mathcal{H}}_0 \psi^0(x_i^1, x_i^2) = -\frac{Z^2}{2} \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right) \psi_{n_1 l_1 m_1}(x_i^1) \psi_{n_2 l_2 m_2}(x_i^2) \quad (2.7)$$

This solution adds up a new exchange degeneracy of the state. We already know tho that the final wavefunction must be the symmetrization or antisymmetrization of the two single electron wavefunctions. In Dirac notation, using $|1, 2\rangle$ for the full wavefunction and $|i\rangle$ for the single electron wavefunction, we must then have

$$|1, 2\rangle_{\pm} = \frac{1}{\sqrt{2}} (|1\rangle |2\rangle \pm |2\rangle |1\rangle) \quad (2.8)$$

Therefore, we can take the antisymmetric wavefunctions (ψ_-^0) as an approximation for ortho states and (ψ_+^0) for para states.

This consideration lets the ortho wavefunction vanish for the ground state of the system, in accord

with the Pauli exclusion principle, hence there can exist a single para-singlet state as ground state, for which, the associated wavefunction is the following

$$\langle 1, 2 | 1s, 1s \rangle = \psi_{GS}^0 = \psi_{1s}(x_1^1) \psi_{1s}(x_2^2) = \frac{Z^3}{\pi} e^{-Z(r_1+r_2)} \quad (2.9)$$

This result, gives then for Helium ($Z = 2$) $E_{GS}^0 = -Z^2 = -4$ a.u. (-108.8 eV), which corresponds to a ionization potential of $I_p = Z^2/2 = 2$ a.u. (54.4 eV). The experimental values are not in accord with these results, which are $E_{GS}^{exp} = -2.90$ a.u. (-79.0 eV) and a ionization potential $I_p^{exp} = 0.90$ a.u. (24.6 eV).

This final result is quite far from the experimental result, since we neglected the $e^- - e^-$ interaction.

§§ 2.1.1 Central Field Approximation

We now take again our equation (2.6) and we take a new unperturbed Hamiltonian, which is the sum of the two single particle hamiltonians

$$\hat{h}_i' = -\frac{1}{2} \nabla_i^2 + V(r_i) \quad (2.10)$$

And we modify the perturbation, getting this new formula

$$\hat{\mathcal{H}}' = \frac{1}{r_{12}} - \frac{Z}{r_1} - V(r_1) - \frac{Z}{r_2} - V(r_2) \quad (2.11)$$

In this new representation of the problem, we need to choose a central potential $V(r_i)$, for which we have that $\hat{\mathcal{H}}'$ is small enough. We choose his potential to be the following

$$V(r) = -\frac{Z - S}{r} = -\frac{Z_e}{r}$$

Where S is some constant, called *screening constant*. What we indicated with Z_e is commonly considered as an *effective charge*.

Since the new potential is a Coulomb potential, we already know the ground state wavefunction and the energy levels, since we might simply insert the substitution $Z \rightarrow Z_e$ in what we have already found. Writing u_{nlm} as the single particle equation, we will have that the single-particle energy levels will depend directly on l , breaking the degeneracy on that quantum number. Our complete wavefunction for discrete excited states will then be the following

$$\psi_{\pm}'(x_i^1, x_i^2) = \frac{1}{\sqrt{2}} (u_{100}(x_i^1) u_{nlm}(x_i^2) \pm u_{nlm}(x_i^1) u_{100}(x_i^2)) \quad (2.12)$$

The total energy of the atom will then be, simply

$$E_{nl}^0 = E_{1s} + E_{nl} \quad (2.13)$$

Where E_{nl} depends on the chosen potentia $V(r_i)$, and is $E_{nl} = -Z_{nl}^2/n^2$.

In the special case of a completely screened electron we will have $S = 1$, and the energy levels will then be described, in the non-interacting electron approximation as follows

$$E_n^0 = -\frac{Z^2}{2} - \frac{(Z - 1)^2}{2n^2} \quad (2.14)$$

§ 2.2 Ground State of Two Electron Atoms

§§ 2.2.1 Perturbation Theory

We have already seen that the ground state eigenket of two electron atoms, in its most general expression can be written as follows

$$|q_1, q_2\rangle = \frac{1}{\sqrt{2}} |1, 2\rangle (|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2) \quad (2.15)$$

Using perturbation theory, we can already get a nice guess of the ground state correction, via the calculus of the matrix elements $\langle 1s, 1s | \hat{\mathcal{H}}' | 1s, 1s \rangle$, where $\hat{\mathcal{H}}' = r_{12}^{-1}$. Writing explicitly the integral, we get

$$E_0^1 = \int_0^\infty |\psi_{1s}(r_1)|^2 \frac{1}{r_{12}} |\psi_{1s}(r_2)|^2 dr_1 dr_2 \quad (2.16)$$

Using the following conversion, and the connection between Legendre polynomials and spherical harmonics, we have that, firstly

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{\min^l(r_1, r_2)}{\max^{l+1}(r_1, r_2)} P_l(\cos \theta)$$

Hence

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \frac{\min^l(r_1, r_2)}{\max^{l+1}(r_1, r_2)} \bar{Y}_l^m(\theta_1, \phi_1) Y_l^m(\theta_2, \phi_2)$$

Plugging it into the integral, and using the properties of spherical harmonics, we get

$$E_0^1 = \frac{Z^6}{\pi^2} \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{16\pi^2}{2l+1} \int_0^\infty r_1^2 dr_1 \int_0^\infty e^{-2Z(r_1+r_2)} \frac{r_m^l}{r_M^{l+1}} \delta_{l0} \delta_{m0} dr_2$$

Contracting the indices with the sums and the Kronecker deltas, we have our final integral

$$E_0^1 = 16Z^6 \int_0^\infty e^{-2Zr_1} r_1^2 dr_1 \left(\frac{1}{r_1} \int_0^{r_1} e^{-2Zr_2} r_2^2 dr_2 + \int_{r_1}^\infty e^{-2Zr_2} r_2 dr_2 \right) \quad (2.17)$$

The integrals give the value $5/128Z^5$, hence, we get our correction

$$E_0^1 = \frac{5}{8} Z \quad (2.18)$$

The final approximate energy is then

$$E_0 \approx E_0^0 + E_0^1 = -Z^2 + \frac{5}{8} Z \quad (2.19)$$

§§ 2.2.2 Variational Methods

Proceeding instead using variational calculus, we set our $|1s\rangle$ wavefunction to be dependent from a parameter Z_e , which will be needed to minimize the following functional

$$E[\phi] = \frac{\langle \phi | \hat{\mathcal{H}} | \phi \rangle}{\langle \phi | \phi \rangle} \quad (2.20)$$

Where we set $|\phi\rangle = |1s\rangle_1 \otimes |1s\rangle_2$.

Calculating and introducing here the quantum virial theorem, we get that

$$\langle \phi | \frac{\hat{p}_1^2}{2m} | \phi \rangle = \langle \phi | \frac{\hat{p}_2^2}{2m} | \phi \rangle = \langle 1s | \frac{\hat{p}^2}{2m} | 1s \rangle = \frac{1}{2} Z_e^2 \quad (2.21)$$

We then also have

$$-\langle \phi | \frac{Z}{r_1} + \frac{Z}{r_2} | \phi \rangle = -2ZZ_e \quad (2.22)$$

And, due to our previous calculations

$$\langle \phi | \frac{1}{r_{12}} | \phi \rangle = \frac{5}{8} Z_e \quad (2.23)$$

The final result is our energy as a function of the parameter Z_e , which is

$$E(Z_e) = Z_e^2 - 2ZZ_e + \frac{5}{8} Z_e \quad (2.24)$$

We search for an extremal of this function deriving with respect to the parameter, and we get

$$\begin{aligned} \frac{\partial E}{\partial Z_e} &= 2Z_e - 2Z + \frac{5}{8} \\ Z_e &= Z - \frac{5}{16} \end{aligned} \quad (2.25)$$

Hence, since our energy was $E_0 = -Z_e^2$, we get, in atomic units, that for Helium atoms, the energy of the ground state will be approximated as follows

$$E_0^{GS} = -\left(Z - \frac{5}{16}\right)^2 = -Z^2 + \frac{5}{8}Z - \frac{25}{256} \quad (2.26)$$

Plugging in the values for Helium, we find that $E_0 = 2.84766$ au, a value that differs only by the 0.056 au from the experimental value.

Another way of finding a more precise ground state energy has been found by Hylleraas, where another set of coordinates is chosen, and the trial wavefunction has multiple variational parameters. These are the following coordinates

$$\begin{aligned} s &= r_1 + r_2 \\ t &= r_1 - r_2 \\ u &= r_{12} = \|r_1 - r_2\| \end{aligned}$$

The trial wavefunction is the following

$$\phi(s, t, u) = e^{-ks} \sum_{l=0}^N \sum_{m=0}^N \sum_{n=0}^N c_{l,2m,n} s^l t^{2m} u^n$$

Where $c_{l,2m,n}$ are linear variational parameters, and k is a nonlinear variational parameter that behaves like the effective charge Z_e .

Since the ground state must be a para state, this wavefunction must be an even function of t . Calculating for $N = 5$, we have 6 variational parameters, we have that the energy calculated is -2.90324 au, which is surprisingly close to the experimental value, differing only by $4.8 \cdot 10^{-4}$ au (0.013 eV).

§ 2.3 Excited States of Two Electron Atoms

We will now treat the excited states of Helium atoms, with the same methods used for evaluating the ground states.

§§ 2.3.1 Perturbation Theory

Firstly, we apply perturbation theory to our system, formed by the sum $\hat{H}_0 + \hat{H}'$, with $\hat{H}' = r_{12}^{-1}$. We already know that these states must either be parastates or orthostates, hence we will need our wavefunction to be either exchange-symmetric or exchange-antisymmetric. The energy perturbation will then depend on the sign of the wavefunction. We also know that $[\hat{H}', \hat{L}_z] = 0$, hence we can write the following result

$$E_{\pm}^1 = \langle \psi_{\pm}^0 | \hat{H}' | \psi_{\pm}^0 \rangle = J \pm K \quad (2.27)$$

Where

$$\begin{aligned} J &= \int_{\mathbb{R}^3 \times \mathbb{R}^3} |\psi_{100}(\underline{r}_1)|^2 \frac{1}{r_{12}} |\psi_{nlm}(\underline{r}_2)|^2 d^3r_1 d^3r_2 \\ K &= \int_{\mathbb{R}^3 \times \mathbb{R}^3} \overline{\psi_{100}(\underline{r}_1)} \overline{\psi_{nlm}(\underline{r}_2)} \frac{1}{r_{12}} \psi_{100}(\underline{r}_1) \psi_{nlm}(\underline{r}_2) d^3r_1 d^3r_2 \end{aligned} \quad (2.28)$$

Where $n \geq 2$. The integral J is called *Coulomb or direct integral* and K is called *Exchange integral*. Expanding r_{12}^{-1} in spherical harmonics, we get

$$\begin{aligned} J_{nl} &= \int_0^\infty R_{nl}(r_2) r_2^2 dr_2 \int_0^\infty R_{10}^2(r_1) \frac{r_1^2}{\max(r_1, r_2)} dr_1 \\ K_{nl} &= \frac{1}{2l+1} \int_0^\infty R_{10}(r_2) R_{nl}(r_2) r_2^2 dr_2 \int_0^\infty R_{10}(r_1) R_{nl}(r_1) \frac{\min^l(r_1, r_2)}{\max^{l+1}(r_1, r_2)} r_1^2 dr_1 \end{aligned} \quad (2.29)$$

Hence, $E_{\pm}^1 = E_{nl\pm}^1$, so the energy after this correction directly depends on n, l . At first order, we can then write

$$E_{nl\pm} \approx E_{1n}^0 + E_{nl\pm}^1 = -\frac{Z^2}{2} \left(1 + \frac{1}{n^2} \right) + J_{nl} \pm K_{nl} \quad (2.30)$$

In order to see how this perturbation acts, we can see that J_{nl} must be always positive. Seeing that for $l = n - 1$, $R_{n,n-1}$ has no nodes, hence $K_{n,n-1} > 0$. It can also be seen that, in general $K_{nl} > 0$, so,

from (2.30) we see that an orthostate has an energy lower to the corresponding parastate. This can be seen introducing spin into our calculus, as follows.

$$E_{nl\pm}^1 = J_{nl} - \frac{1}{2} (1 + \sigma_i^1 \sigma_2^i) K_{nl} \quad (2.31)$$

Where σ_i^j are the pauli matrices of the two electrons.

§§ 2.3.2 Variational Methods

Variational methods can be applied supposing that the higher-order wavefunction are orthogonal to the ground-state trial function and then calculate the variational integrals.

This method is best applied on singular states.

Starting with the 2^3S state of the atom, we have that, using variational parameters Z_i, Z_o as the inner and outer effective charge, we can write the state as follows

$$|2^3S\rangle = N (|1s\rangle |2s\rangle - |2s\rangle |1s\rangle) \quad (2.32)$$

Where

$$\begin{aligned} u_{1s}(r) &= e^{-Z_i r} \\ v_{2s}(r) &= \left(1 - \frac{Z_o r}{2}\right) e^{-\frac{Z_o r}{2}} \end{aligned} \quad (2.33)$$

Substituting into the variational integral and finding the minimum, we get $Z_i = 2.01$ au and $Z_o = 1.53$ au, which yield $E_{2^3S} = -2.167$ au. Analogously, one can use Hylleraas wavefunction in order to get a more precise result.

For 2^1P and 2^3P states, we use the following state kets

$$\begin{aligned} |2^1P\rangle &= N_+ (|1s\rangle_1 |2pm\rangle_2 + |2pm\rangle_1 |2s\rangle_2) \\ |2^3P\rangle &= N_- (|1s\rangle_1 |2pm\rangle_2 - |2pm\rangle_1 |2s\rangle_2) \end{aligned} \quad (2.34)$$

With wavefunctions

$$\begin{aligned} u_{1s}(r) &= e^{-Z_i r} \\ v_{2pm}(r) &= r e^{\frac{Z_o r}{2}} Y_m^1(\hat{\mathbf{r}}) \end{aligned} \quad (2.35)$$

The variation gives, in atomic units

$$\begin{aligned} Z_i^{2^1P} &= 2.00 \\ Z_o^{2^1P} &= 0.97 \\ E_{2^1P} &= -2.123 \\ Z_i^{2^3P} &= 1.99 \\ Z_o^{2^3P} &= 1.09 \\ E_{2^3P} &= -2.131 \end{aligned}$$

The two theoretical values are around 3 au from the experimental measurements.

3 Many Electron Atoms

§ 3.1 Central Field Approximation

In order to treat properly many-electron atoms we need to introduce an approximation, known as *central field approximation* or *Hartree's method*, in which the Coulomb potential is substituted with a new spherically symmetrical *effective potential*.

Firstly, we consider an atom with N electrons and a nucleus with charge $q_N = Ze$ and infinite nuclear mass. In our Hamiltonian we (at first) neglect all small effects (Spin-Orbit coupling, relativistic effects, etc...). Having considered this, putting $r_{ij} = \|\underline{r}_i - \underline{r}_j\|$ our many-electron Hamiltonian is

$$\hat{\mathcal{H}} = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right) + \sum_{i<j=1}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}} \quad (3.1)$$

In this case, the term r_{ij}^{-1} is too big to be treated as a perturbation, hence, we must use what's called a central field approximation. In this approximation we map our potential $V(r)$ to a new potential defined as follows

$$V_{cf}(r) = -\frac{Z}{r} + S(r) \quad (3.2)$$

Where $S(r)$ is a spherically symmetric *screening function*.

Our Hamiltonian then becomes

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_e + \hat{\mathcal{H}}_1 = \sum_{i=1}^n \hat{h}_i + \sum_{i<j=1}^N \frac{1}{r_{ij}} - \sum_{i=1}^N S(r_i) \quad (3.3)$$

This way, we can divide our calculus in two. Solving for the single electron Hamiltonian \hat{h}_i , we have

$$\begin{aligned} \sum_{i=1}^N \hat{h}_i |\psi_e\rangle &= E_e |\psi_e\rangle \\ |\psi_e\rangle &= \bigotimes_{i=1}^N |nlm_i\rangle_i \\ \hat{h}_i |nlm_i\rangle_i &= E_{ni} |nlm_i\rangle_i \end{aligned} \quad (3.4)$$

Where $|nlm_i\rangle$ is our single-electron orbital. It's important to remember that these orbitals are «not» the usual Hydrogenic orbitals, since the chosen potential is quite different.

Now there is only one simple thing missing, Spin. Our complete electronic wavefunction will then be the direct product between a spinor and the electronic wavefunction, as follows

$$u_{nlm_l m_s}(q_i) = u_{nlm_l}(r_i) \chi_{\frac{1}{2}, m_s} \leftrightarrow |nlm_l\rangle_i \otimes \left| \frac{1}{2}, \uparrow \downarrow \right\rangle \quad (3.5)$$

Now, we're ready to determine $|\psi_e\rangle$. In order to make sure that Pauli exclusion principle's requirements are solved, we know already that the total wavefunction must be zero if an electron is in the same state of another one. This is perfectly described through a determinant, called Slater determinant, which is defined as follows (let μ, ν, δ be generic states)

$$\psi_e(q_1, \dots, q_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_\mu(q_1) & u_\nu(q_1) & \cdots & u_\delta(q_1) \\ u_\mu(q_2) & u_\nu(q_2) & \cdots & u_\delta(q_2) \\ \vdots & \vdots & \ddots & \vdots \\ u_\mu(q_N) & u_\nu(q_N) & \cdots & u_\delta(q_N) \end{vmatrix} \quad (3.6)$$

It's worth noting that $(N!)^{-1/2}$ is a normalizing factor for our final wavefunction. A notable example comes for He ground state wavefunction. We will have then

$$\begin{aligned} |1, 2\rangle &= \frac{1}{\sqrt{2}} \begin{vmatrix} |100\rangle \otimes |\uparrow\rangle_1 & |100\rangle \otimes |\downarrow\rangle_1 \\ |100\rangle \otimes |\uparrow\rangle_2 & |100\rangle \otimes |\downarrow\rangle_2 \end{vmatrix} \\ |1, 2\rangle &= \frac{1}{\sqrt{2}} |100\rangle_1 \otimes |100\rangle_2 \otimes \left(|\uparrow\rangle_1 \otimes |\downarrow\rangle_2 - |\downarrow\rangle_1 \otimes |\uparrow\rangle_2 \right) \end{aligned} \quad (3.7)$$

The parity of the wavefunction ψ_e will then be $(-1)^{\sum_i l_i}$ as it should be.

Now, it's time to define new vector operators for angular momentum $\hat{\underline{L}}, \hat{\underline{S}}$ in the many-electron case, and defining both as the sum of the single electron operators we can easily demonstrate that

$$[\hat{\mathcal{H}}_e, \hat{\underline{S}}] = [\hat{\mathcal{H}}_e, \hat{\underline{L}}] = 0 \quad (3.8)$$

Therefore, we can define a new common basis between the Hamiltonian and these operator as $|LSM_l M_s\rangle$, where

$$\begin{aligned} \hat{S}^2 |LSM_l M_s\rangle &= \hbar^2 S(S+1) |LSM_l M_s\rangle \\ \hat{L}^2 |LSM_l M_s\rangle &= \hbar^2 L(L+1) |LSM_l M_s\rangle \\ \hat{S}_z |LSM_l M_s\rangle &= \hbar M_s |LSM_l M_s\rangle \\ \hat{L}_z |LSM_l M_s\rangle &= \hbar M_l |LSM_l M_s\rangle \\ \hat{\mathcal{H}}_e |LSM_l M_s\rangle &= E_{nl} |LSM_l M_s\rangle \end{aligned} \quad (3.9)$$

It's of great importance to know that in order to find the wavefunctions $\langle r_i | LSM_l M_s \rangle$, we need to find linear combinations of Slater determinants. In the case of Helium, it was fine to use a Slater determinant, since $L = S = 0$, since we were searching for 1S_0 wavefunctions for an electronic configuration of $1s^2$.

§§ 3.1.1 Shells and Subshells

As we have seen before, the total energy of atoms is directly determined by the electron configuration. We have already seen that the single electron energy grows with $n+l$, and since the spherical harmonics

and spinors are already known from previous calculations, the problem is only to find a new radial function, where the potential is central but not coulombian.

Due to this dependency with n and l we can characterize electronic *shells* and *subshells*. A shell is composed of atoms with the same value of n and subshells are composed by atoms with the same value of n and l .

As in orbital spectroscopic nomenclature, we assign a letter to each shell, as follows

$$\begin{aligned} n = 0, l = 0 &\longrightarrow K \\ n = 1, l = 0 &\longrightarrow L_I \\ n = 1, l = 1 &\longrightarrow L_{II} \\ &\vdots \end{aligned} \tag{3.10}$$

The maximum number of electrons in a subshell is $2(2l + 1)$, and if the number of electrons exactly matches it, the subshell in question is called *closed* or *filled*.

Instead, there can be maximum $2n^2$ electrons in a shell, and the “closed” or “filled” names of complete subshells transfers directly to shells.

In general, the degeneracy of a configuration (g), can be determined from the degeneracy of the shells. Let $\delta_i = 2(2l_i + 1)$ be the degeneracy of the subshell, and ν_i the number of electron occupying the same subshell with energy $E_{n_i l_i}$. Henceforth, there will be d_i ways of distributing electrons in this i -th subshell, this number is

$$d_i = \frac{\delta_i!}{\nu_i! (\delta_i - \nu_i)!} \tag{3.11}$$

And, therefore, for an electronic configuration we will have that

$$g = \prod_{i=1}^n d_i$$

Where the index goes through all the n subshells. It's worth noting that for a closed subshell $d = 1$, easing the calculus. Taking Carbon as an example, we will have an electronic configuration of $[He]2s^2 2p^2$, hence

$$\begin{aligned} K &\rightarrow \nu = 2, \delta = 2, d = 1 \\ L_I &\rightarrow \nu = 2, \delta = 2, d = 1 \\ L_{II} &\rightarrow \nu = 2, \delta = 6, d = 15 \end{aligned} \tag{3.12}$$

Hence $g = 15$.

§§ 3.1.2 Aufbau Rule and the Periodic Table

Having defined properly the electronic structure of many electron atoms, we're able to discuss the Aufbau (building up) of atoms.

The “building up” of atoms is given by the Z electrons, that fill the shells in accordance with the Pauli exclusion principle. The *ground state configuration* of an atom is then given by distributing the electrons into n subshells. The first $n - 1$ (or n if the shell is complete) subshells are filled completely, and the last subshell, if incomplete, houses the so called *valence electrons*.

The screening given by the complete shells is what makes sure that the ionization potential doesn't

grow with Z , but has peaks for atoms with complete shells, that always have a ground state 1S_0 . These atoms form the set of *noble gases*, which are chemically inert. Seeing the ionization potential tables is also evident that the ionization potential of noble gases lowers with Z , since the nucleus is bigger, and the last electrons feel less attraction from the nucleus.

The stableness given by having a complete valence shell, is the reason that the *alkalis* (Li, Na, K, Rb, Cs) and the *halogens* (F, Cl, Br, I) are extremely reactive chemically, since the first ones have one weakly bound electron more, and the last ones have a “hole”, which is only a missing electron which is needed to complete the shell. The recurrence of this property is what brought chemists to build the *periodic table*, which is a table of all the known elements, ordered in base to their value of Z .

§ 3.2 Hartree-Fock Method and Self-Consistent Fields

The basic starting point of Hartree-Fock theory is the independent particle model. The complete Hartree-Fock method accounts for the Pauli exclusion principle too, whereas the Hartree method alone doesn't.

The first thing assumed for the Hartree-Fock wavefunction is that the final N -electron wavefunction is a Slater determinant, or an antisymmetric product of electron spin-orbitals. This Slater determinant is given through the variational calculus of every single electron orbital.

Seeing this in a broader way, we can see our final wavefunction being an infinite linear combination of Slater determinants, which lets this method to be well suited for calculus of even more complex systems like molecular orbitals and solid state physics. In order to keep things simple, we will treat only with the discussion of the ground state of a multi-electron atom, where the considered Hamiltonian is not relativistic.

Now, supposing we have a total Hamiltonian $\hat{\mathcal{H}} = \hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2$, where

$$\begin{aligned}\hat{\mathcal{H}}_1 &= \sum_{i=1}^N \hat{h}_i = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) \\ \hat{\mathcal{H}}_2 &= \sum_{i < j=1}^N \frac{1}{r_{ij}}\end{aligned}\tag{3.13}$$

We have that the first Hamiltonian describes the sum of N electronic Hamiltonians which include nucleus-electron attraction, and the second describes $N(N-1)/2$ terms which describe the two body interaction of electrons..

According to the variational method, if we suppose that the trial wavefunction is ϕ , we have that

$$E_0 \leq E[\phi] = \langle \phi | \hat{\mathcal{H}} | \phi \rangle$$

Where we suppose $\langle \phi | \phi \rangle = 1$, and $|\phi\rangle$ is determined through a Slater determinant of orthonormal single electron wavefunctions.

Another way to interpret this wavefunction is defining the *antisymmetrization operator* \hat{A} . We have

$$\begin{aligned}\hat{A} &= \frac{1}{N!} \sum_P (-1)^P \hat{P} \\ |\phi\rangle &= \sqrt{N!} \hat{A} |\phi_H\rangle \\ |\phi_H\rangle &= \bigotimes_{i=1}^N |u_i\rangle\end{aligned}\tag{3.14}$$

It's obvious that since \hat{A} is a linear combination of exchange operators \hat{P} , that it's also a projection operator.

The wavefunction $|\phi_H\rangle$ is what's called a *Hartree wavefunction*, which is simply the direct product of every single electron wavefunctions.

Since both Hamiltonians are invariant under permutation of electronic coordinates, we have that $[\hat{\mathcal{H}}_i, \hat{A}] = 0$, and therefore the calculation of the expectation values of the first Hamiltonian reduces to the following calculus, thanks to our definition of $|\phi\rangle$

$$\langle\phi|\hat{\mathcal{H}}_1|\phi\rangle = N! \langle\phi_H|\hat{\mathcal{H}}_1\hat{A}|\phi_H\rangle \quad (3.15)$$

Thanks to the definition of \hat{A} and $\hat{\mathcal{H}}_1$ we can reduce the calculus to the following expectation value

$$\langle\phi|\hat{\mathcal{H}}_1|\phi\rangle = \sum_{i=1}^N \sum_P (-1)^P \langle\phi_H|\hat{h}_i\hat{P}|\phi_H\rangle = \sum_{\lambda} \langle u_{\lambda}|\hat{h}_i|u_{\lambda}\rangle \quad (3.16)$$

Where the index λ runs on all possible quantum states of the single electron wavefunction. Defining $I_{\lambda} = \langle u_{\lambda}|\hat{h}_i|u_{\lambda}\rangle$ we have that $\langle\phi|\hat{\mathcal{H}}_1|\phi\rangle = \sum_{\lambda} I_{\lambda}$. Analogously with $\hat{\mathcal{H}}_2$ we get

$$\langle\phi|\hat{\mathcal{H}}_2|\phi\rangle = N! \langle\phi_H|\hat{\mathcal{H}}_2\hat{A}|\phi_H\rangle \quad (3.17)$$

Expliciting both operators, we get

$$\langle\phi|\hat{\mathcal{H}}_2|\phi\rangle = \sum_{i<j=1}^N \sum_P (-1)^P \langle\phi_H|\frac{1}{r_{ij}}\hat{P}|\phi_H\rangle = \sum_{i<j=1}^N \langle\phi_H|\frac{1}{r_{ij}}(1 - \hat{P}_{ij})|\phi_H\rangle \quad (3.18)$$

Since the exchange operator in this case exchanges spin and spatial coordinates of electrons i, j , we can also write the previous equation as follows

$$\langle\phi|\hat{\mathcal{H}}_2|\phi\rangle = \frac{1}{2} \sum_{\lambda} \sum_{\mu} \left(\langle u_{\lambda}u_{\mu}|\frac{1}{r_{ij}}|u_{\lambda}u_{\mu}\rangle - \langle u_{\lambda}u_{\mu}|\frac{1}{r_{ij}}|u_{\mu}u_{\lambda}\rangle \right) \quad (3.19)$$

We can now define two new terms, the *direct term* $J_{\lambda\mu}$ and the *exchange term* $K_{\lambda\mu}$, where they're defined as follows

$$\begin{aligned} J_{\lambda\mu} &= \langle u_{\lambda}u_{\mu}|\frac{1}{r_{ij}}|u_{\lambda}u_{\mu}\rangle \\ K_{\lambda\mu} &= \langle u_{\lambda}u_{\mu}|\frac{1}{r_{ij}}|u_{\mu}u_{\lambda}\rangle \end{aligned} \quad (3.20)$$

It's also obvious that these two matrices are real and symmetric on both indices.

This final calculus brings the following result

$$\langle\phi|\hat{\mathcal{H}}_2|\phi\rangle = \frac{1}{2} \sum_{\lambda} \sum_{\mu} (J_{\lambda\mu} - K_{\lambda\mu}) \quad (3.21)$$

The total energy functional is then the following

$$E[\phi] = \sum_{\lambda} I_{\lambda} + \frac{1}{2} \sum_{\lambda} \sum_{\mu} (J_{\lambda\mu} - K_{\lambda\mu}) \quad (3.22)$$

Introducing the N^2 Lagrange multipliers $c_{\lambda\mu}$, we have that the variational equation that we need to solve is the following

$$\delta E - \sum_{\lambda} \sum_{\mu} c_{\lambda\mu} \delta \langle u_{\lambda} | u_{\mu} \rangle \quad (3.23)$$

Diagonalizing the matrix $c_{\lambda\mu}$ with an unitary transformation, we get

$$\delta E - \sum_{\lambda} \sum_{\mu} E_{\lambda} \delta_{\lambda\mu} \delta \langle u_{\lambda} | u_{\mu} \rangle = \delta E - \sum_{\lambda} E_{\lambda} \delta \langle u_{\lambda} | u_{\lambda} \rangle \quad (3.24)$$

Projecting the previous equation in $L^2(\mathbb{R}^3 \otimes \mathbb{H}_s)$, and varying the spin-orbital electronic wavefunction we have a set of integro-differential equations, known as the *Hartree-Fock* equations

$$\begin{aligned} & \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) u_{\lambda}(q_i) + \left(\sum_{\mu} \int \bar{u}_{\mu}(q_j) \frac{1}{r_{ij}} u_{\mu}(q_j) dq_j \right) u_{\lambda}(q_i) - \\ & - \sum_{\mu} \left(\int \bar{u}_{\mu}(q_j) \frac{1}{r_{ij}} u_{\lambda}(q_j) dq_j \right) u_{\mu}(q_i) - E_{\lambda} u_{\lambda}(q_i) = 0 \end{aligned} \quad (3.25)$$

We can build a more compact version of the Hartree-Fock equation defining two new operators as follows

$$\begin{aligned} \hat{V}_{\mu}^d &= \int \bar{u}_{\mu}(q_j) \frac{1}{r_{ij}} u_{\mu}(q_j) dq_j = \langle \mu | \frac{1}{r_{ij}} | \mu \rangle \\ \hat{V}_{\mu}^{ex} f(q_i) &= \left(\int \bar{u}_{\mu}(q_j) \frac{1}{r_{ij}} f(q_j) dq_j \right) u_{\mu}(q_i) = \left(| \mu \rangle \langle \mu | \frac{1}{r_{ij}} \right) | f \rangle \end{aligned} \quad (3.26)$$

Called respectively the *direct operator* and *exchange operator*. Otherwise we can define the *direct potential* and the *exchange potential* as follows

$$\begin{aligned} \hat{\mathcal{V}}^d &= \sum_{\mu} \hat{V}_{\mu}^d = \sum_{\mu} \langle \mu | \frac{1}{r_{ij}} | \mu \rangle \\ \hat{\mathcal{V}}^{ex} &= \sum_{\mu} \hat{V}_{\mu}^{ex} = \sum_{\mu} | \mu \rangle \langle \mu | \frac{1}{r_{ij}} \end{aligned} \quad (3.27)$$

With this new addition, the Hartree-Fock equation becomes the following

$$\begin{aligned} -\frac{1}{2} \nabla_i^2 u_{\lambda}(q_i) - \frac{Z}{r_i} u_{\lambda}(q_i) + \hat{\mathcal{V}}^d u_{\lambda}(q_i) - \hat{\mathcal{V}}^{ex} u_{\lambda}(q_i) &= E_{\lambda} u_{\lambda}(q_i) \\ \frac{1}{2} \hat{p}_i^2 | \lambda \rangle - \frac{Z}{r_i} | \lambda \rangle + \hat{\mathcal{V}}^d | \lambda \rangle - \hat{\mathcal{V}}^{ex} | \lambda \rangle &= E_{\lambda} | \lambda \rangle \end{aligned} \quad (3.28)$$

Or, defining the Hartree-Fock potential as follows

$$\hat{\mathcal{V}} = -\frac{Z}{r_i} + \hat{\mathcal{V}}^d - \hat{\mathcal{V}}^{ex} \quad (3.29)$$

We can rewrite the previous equation as follows

$$\begin{aligned} -\frac{1}{2} \nabla_i^2 u_{\lambda}(q_i) + \hat{\mathcal{V}} u_{\lambda}(q_i) &= E_{\lambda} u_{\lambda}(q_i) \\ \frac{1}{2} \hat{p}^2 | \lambda \rangle + \hat{\mathcal{V}} | \lambda \rangle &= E_{\lambda} | \lambda \rangle \end{aligned} \quad (3.30)$$

§§ 3.2.1 Beryllium Ground State

A particular example of what can be calculated with the Hartree-Fock approximation is the ground state 1S of Beryllium. The Hartree-Fock potential operator, in this case is

$$\hat{V} = -\frac{4}{r_i} + \hat{V}_{1s\uparrow}^d + \hat{V}_{1s\downarrow}^d + \hat{V}_{2s\uparrow}^d + \hat{V}_{2s\downarrow}^d - \left(\hat{V}_{1s\uparrow}^{ex} + \hat{V}_{1s\downarrow}^{ex} + \hat{V}_{2s\uparrow}^{ex} + \hat{V}_{2s\downarrow}^{ex} \right) \quad (3.31)$$

The Hartree-Fock equations, since the spatial part of the two s electrons is be identical, separate into two coupled integro-differential equations, and we get then that $E_{1s} = E_{1s\uparrow} = E_{1s\downarrow}$ and $E_{2s} = E_{2s\uparrow} = E_{2s\downarrow}$. The general solution for these equation is given through a basis change to the basis of Slater orbitals, which have the following form

$$s_{nlm}(\underline{r}) = \frac{(2\alpha)^{n+\frac{1}{2}}}{\sqrt{(2n)!}} r^{n-1} e^{-\alpha r} Y_l^m(\theta, \phi) \quad (3.32)$$

The equations are then solved numerically.

Due to electronic dispositions it's obvious that the total Be wavefunction will be symmetric (S state), the total spin will be 0, and therefore we have a 1S_0 state

§ 3.3 Spin-Orbit Interactions and Fine Structure of Many-Electron Atoms

As treated before with single-electron atoms, we define an electronic Hamiltonian (\hat{H}_e) and a perturbative Hamiltonian (\hat{H}_2), where the first will be the sum of all the single electron Hamiltonians, and the second will be our spin-orbit perturbative Hamiltonian.

The total Hamiltonian will then be

$$\hat{H} = \hat{H}_e + \hat{H}_1 + \hat{H}_2 \quad (3.33)$$

Where \hat{H}_1 is the electrostatic correction, and

$$\begin{aligned} \hat{H}_2 &= \sum_i \xi(r_i) \hat{L}_i \cdot \hat{S}_i = \sum_i \frac{1}{2m^2c^2} \frac{1}{r_i} \frac{\partial V}{\partial r_i} \hat{L}_i \cdot \hat{S}_i \\ \hat{H}_e &= \sum_i \hat{h}_i = \sum_i \left(-\frac{1}{2} \nabla_i^2 + \hat{V} \right) \end{aligned} \quad (3.34)$$

Since this atom described by \hat{H} is isolated, the total parity and \hat{J} are conserved.

We shall utilize the usual perturbation theory on the energy levels obtained from the Hartree-Fock approximation, henceforth taking the Hartree-Fock energy as our "true" energy.

As we saw before, since the Hamiltonian commutes with \hat{J} (and \hat{L}, \hat{S}), hence we can say that M_L, M_S are good quantum numbers. Hence, every level will be $(2L+1)(2S+1)$ times degenerate. As usual, every level will be indicated with the usual spectroscopic notation.

§§ 3.3.1 Determination of Possible Terms in Spin-Orbit Coupling

Using the usual angular momenta addition rules, it's possible to determine straight away that, for filled subshells $L = S = 0$. Hence, an atom with its last subshell filled must have a state 1S_0 . In the

case of ions, we toss out all filled subshells, and consider only the *optically active* electrons in order to determine the possible states of the atom. We have three main cases

1. Non-equivalent electrons (in different subshells)

In this case, there can't be couples of optically active electrons that have the same set of quantum numbers, hence Pauli's exclusion principle is automatically satisfied.

We find the value of L and S by summing all optically active electrons' single values. It can be illustrated with two simple examples

(a) Configuration $np\ n'p$

In this configuration we have $l_1 = l_2 = 1$ and $s_1 = s_2 = 1/2$, hence $L = 0, 1, 2$ and $S = 0, 1$. We therefore can have the following terms for the configuration

$$^1S, ^1P, ^1D, ^3S, ^3P, ^3D$$

(b) Configuration $np\ n'd$

Here instead we have $l_1 = 1, l_2 = 2$ and $s_1 = s_2 = 1/2$, thus $L = 1, 2, 3$ and $S = 0, 1$. The possible term values are

$$^1P, ^1D, ^1F, ^3P, ^3D, ^3F$$

For more than 2 optically active electrons this calculation is repeated up until all the electrons' angular momenta are summed.

2. Equivalent electrons (in the same subshell)

This case is slightly more complicated, since Pauli's exclusion principle isn't immediately satisfied. The most simple case that might be encountered is the case ns^2 , which forces us with a 1S_0 state. A slightly more complicated case is given by np^2 configurations, where the degeneracy is $g = 15$. Due to the exclusion principle, we must immediately exclude all possible states where m_l or the m_s values of two different electrons are the same. Evaluating all the 15 states, we end up with these possible quantum number couples

$$(M_L = \pm 2, M_S = 0)$$

$$(M_L = \pm 1, M_S = \pm 1), (M_L = \pm 1, M_S = 0), (M_L = 0, M_S = 0), (M_L = 0, M_S = \pm 1)$$

We see immediately that we can only have $L = 2, 1, 0$, hence the terms will be S, P, D . From the configuration, and the absence of a $(2, 1)$ set of (M_L, M_S) , we can immediately say that all the possible 15 states must have one of these three terms

$$^1S, ^1D, ^3P$$

3. Equivalent and non-equivalent electrons

If an electronic configuration contains a group of equivalent electrons together with a group of non-equivalent electrons one must firstly determine the possible equivalent electron states, and then sum these states with the non-equivalent electron states. Then all the possible states can be determined.

3.3.1.0.1 Hund's Rules A set of two empirical rules determined by Hund is fundamental in the research of the ground state configuration. According to these rules we have that

1. The term with the largest value of S has the lowest energy
2. For a given value of S , the term with the maximum possible value of L has the lowest energy

§§ 3.3.2 Fine Structure Terms and Landé's Interval Rule

Having obtained the energy level of the previous Hamiltonian, we proceed now to the second step of the calculation, and indeed add a new perturbation $\hat{\mathcal{H}}_2$ to the previous Hamiltonian. The new total Hamiltonian $\hat{\mathcal{H}}$ will not commute with \hat{L}, \hat{S} singularly, but it will commute with $\hat{J} = \hat{L} \otimes \hat{1}_S + \hat{1}_L \otimes \hat{S}$. Since the energy of an isolated atom cannot depend on the direction of the total angular momentum, it will have degeneracy $g = (2L + 1)(2S + 1)$ associated with ^{2S+1}L term, and an additional *fine structure splitting* characterized by the possible values of J . The new term will then be $^{2S+1}L_J$, which is $2J + 1$ -fold degenerate with respect to the eigenvalues of \hat{J}_z . The degeneracy in M_J can be removed choosing a preferred direction in space, such as applying an external magnetic field in the Zeeman effect.

In this case, the possible values of M_J are $|L - S| \leq M_J \leq L + S$.

Let's take again the configuration $np\ n'p$. In this case, we have already seen that the possible values of the quantum numbers are the following

$$\begin{aligned} L &= 0, 1, 2 \\ S &= 0, 1 \\ J &= 0, 1, 2, 3 \end{aligned} \tag{3.35}$$

Without calculating the spin-orbit coupling splitting, we can have the following terms

$$^1S, ^1P, ^1D, ^3S, ^3P, ^3D$$

Applying the spin-orbit coupling we now have a additional splitting of the previous states:

$$^1S_0, ^1P_1, ^1D_2, ^3S_1, ^3P_0, ^3P_1, ^3P_2, ^3D_1, ^3D_2, ^3D_3$$

Another example comes from Carbon, which has a configuration $[\text{He}]2s^22p^2$. The two optically active electrons give rise to the following fine structure terms

$$^1S_0, ^1D_2, ^3P_0, ^3P_1, ^3P_2$$

Using Hund's Rules, we see immediately that the ground state of Carbon is 3P_0 .

Rewriting our wavefunctions as $|LSM_LM_S\rangle$ and our spin-orbit Hamiltonian as $A\hat{L} \cdot \hat{S}$, we have that it's non-diagonal in this base, but we can change basis into the new basis $|LSJM_J\rangle$, where we have

$$\begin{aligned} \langle LSJM_J | \hat{\mathcal{H}}_2 | LSJM_J \rangle &= \frac{1}{2} A \langle LSJM_J | \hat{J}^2 - \hat{L}^2 - \hat{S}^2 | LSJM_J \rangle \\ &= \frac{1}{2} A (J(J+1) - L(L+1) - S(S+1)) \end{aligned} \tag{3.36}$$

Hence, it's diagonal. From this we see that the unperturbed level splits into $2S + 1$ or $2L + 1$ if respectively we have $S \leq L$ or $S > L$. It also can be seen that $E_J - E_{J-1} = AJ$. This last result is

known as the *Landé interval rule*, which holds only in L-S coupling regimes, i.e. when $|\hat{\mathcal{H}}_2| \ll |\hat{\mathcal{H}}_1|$. Evaluating A , we get that if $A > 0$ the lowest energy is given by the term with the lowest value of J , and when $A < 0$ the lowest value of energy is given by the term with the highest level of J . These kinds of multiplet splitting are respectively called *regular multiplet splitting* and *inverted multiplet splitting*. Empirically, it has been established that regular multiplets occur in subshells that are less than half filled, while inverted multiplets appear in more than half filled subshells. In half filled subshells there is no multiplet splitting.

4 Electromagnetic Interactions

§ 4.1 Selection Rules

Having discussed in detail many-electron atoms, we can go forward and discuss the interaction between single atoms and external electromagnetic field.

We will consider only single photon interaction. The photon field Hamiltonian can be written as follows

$$\hat{\mathcal{H}}_\gamma = - \sum_{i=1}^N \frac{i\hbar e}{m} \hat{A}^i(r_i, t) \partial_i = \frac{e}{m} \hat{A}^i(r_i, t) \hat{p}_i \quad (4.1)$$

We will have $N = Z$ for neutral atoms and $N \neq Z$ for ions.

Jumping all the calculations (they're already given for single electron atoms), we get that the transition probability depends on a matrix element M_{ba} , where

$$M_{ba} = - \frac{m\omega_{ba}}{\hbar} \epsilon_j \cdot r_{ba}^j \quad (4.2)$$

The generic state $|a\rangle$ is an eigenstate of the total angular momentum and parity, hence, indicating with p the parity eigenstate, we can write M_{ba} in a different way, as follows

$$M_{ba} = - \frac{N m \omega_{ba}}{\hbar} \epsilon^j \langle p' J' M_J' | r_j | p J M_J \rangle \quad (4.3)$$

The N comes from the fact that the electrons are indistinguishable. Inserting into M_{ba} the dipole moment operator $\hat{\underline{D}} = - \sum_j e \underline{r}_j$ we have

$$M_{ba} = \frac{m \omega_{ba}}{\hbar e} \epsilon^j \langle p' J' M_J' | \hat{D}_j | p J M_J \rangle \quad (4.4)$$

From which, the probability of spontaneous emission of a photon with polarization ϵ_i can be calculated, yielding the following result

$$W_{ab}^s d\Omega = \frac{\omega_{ba}}{8\pi^2 \epsilon_0 \hbar c^3} \left| \epsilon^j \langle p' J' M_J' | \hat{D}_j | p J M_J \rangle \right|^2 d\Omega \quad (4.5)$$

We can now define the spherical vector components of the polarization versor ϵ_j and of the electric dipole operator. Using q as an index for the three possible components $(0, \pm 1)$, we have for the electric

dipole operator

$$\begin{aligned}\hat{D}_1 &= -\frac{1}{\sqrt{2}} (D_x + i\hat{D}_y) = \|\hat{D}_i\| \sqrt{\frac{4\pi}{3}} Y_1^1(\alpha, \beta) \\ \hat{D}_0 &= \hat{D}_z = \|\hat{D}_i\| \sqrt{\frac{4\pi}{3}} Y_1^0(\alpha, \beta) \\ \hat{D}_{-1} &= \frac{1}{\sqrt{2}} (\hat{D}_x - i\hat{D}_y) = \|\hat{D}_i\| \sqrt{\frac{4\pi}{3}} Y_1^{-1}(\alpha, \beta)\end{aligned}\tag{4.6}$$

And for ϵ_i

$$\begin{aligned}\epsilon_1 &= -\frac{1}{\sqrt{2}} (\epsilon_x + i\epsilon_y) \\ \epsilon_0 &= \epsilon_z \\ \epsilon_{-1} &= \frac{1}{\sqrt{2}} (\epsilon_x - i\epsilon_y)\end{aligned}\tag{4.7}$$

Using the Wigner-Eckart theorem we know that the matrix elements of a vector operator with respect to the eigenstate of the total angular momentum (squared and through the z axis) depend only on M_J, M'_J and q through the Clebsch-Gordan coefficients $\langle JM_J q | JM_J \rangle$, henceforth

$$\langle p' J' M'_J | \hat{D}_q | p J M_J \rangle = \frac{1}{\sqrt{2J'+1}} \langle JM_J q | J' M'_J \rangle \langle p' J' | \|\hat{D}_i\| | p J \rangle\tag{4.8}$$

The Clebsch-Gordan coefficient vanishes, unless

$$\begin{aligned}M_J + q &= M'_J \\ |J - 1| &\leq J' \leq J + 1 \\ J + J' &\geq 1\end{aligned}\tag{4.9}$$

Thus, obtaining the selection rule for electric dipole transition

$$\begin{aligned}\boxed{\Delta M_J = 0, \pm 1} \\ \boxed{\Delta J = 0, \pm 1}\end{aligned}\tag{4.10}$$

Be cautious, transitions $J = 0 \leftrightarrow J' = 0$ are not permitted. In addition, due to *Laporte's rule*, the state from which the transition happens, «must have the opposite parity of the initial state»

§§ 4.1.1 Spin-Orbit Coupling

In the case of spin-orbit coupling (hence weak spin-orbit interaction) we can approximate the system in a way such that \hat{L}, \hat{S} are conserved. We then obtain

$$\langle J' L' S' M'_J | \hat{D}_i | J L S M_J \rangle = \delta_{SS'} \langle J' L' S' M'_J | \hat{D}_i | J L S M_J \rangle\tag{4.11}$$

Which give the following selection rules

$$\begin{aligned}\boxed{\Delta L = 0, \pm 1} \quad (0 \leftrightarrow 0 \text{ not allowed}) \\ \boxed{\Delta S = 0}\end{aligned}\tag{4.12}$$

§ 4.2 Alkali Atoms

As we have seen for single-electron atoms, Alkali metals can be treated as such, with a single valence electron in a ns^1 orbital, shielded from the nucleus by a “core”, which is composed by a closed subshell system.

Analyzing the valence electron, it's easy to see that it «always» has $l = 0$ at its lowest level, and it's subject to a potential which is Coulombian for large r . Due to this potential, there is no degeneracy in l for a given n , this degeneracy is visible only for highly excited levels, for which the atom's wavefunction is more and more Hydrogenic. The valence electron is weakly bound to the atom, and it usually needs around 5 eV to transition into the continuum.

The ground state of Alkalis, since the core is formed by a system of closed subshells and has only a valence electron, will be $(ns^1)^2S_{1/2}$ (The core has term 1S_0 and you add a valence electron to it, where $l = 0, s = 1/2$). Excited states will be of the following form $(n_1s^1)^2S_{1/2}, (n_2p^1)^2P_{1/2,3/2}, (n_3d^1)^2D_{3/2,5/2}$ and so on.

The spectra of Alkali atoms can be determined through an approximation of the energies of single electron atoms. In atomic units, we can then write

$$E_{nl} = -\frac{1}{2} \frac{1}{(n - \mu_{nl})^2} \quad (4.13)$$

Where μ_{nl} is called *quantum defect*. This defect can be approximated to a function of l , as $\mu_{nl} \simeq \delta_l$, and with this we can write a “special” quantum number $n^* = n - \delta_l$.

This is especially useful when considering transitions. In fact, we can write that the absorption lines, in this approximation, will fall in these frequencies, at least for $p \rightarrow s$ transitions

$$\nu_{nl} = R \left(\left(\frac{1}{n_s^*} \right)^2 - \left(\frac{1}{n_p^*} \right)^2 \right) \quad (4.14)$$

In the case of emission lines, we can write, with $\tilde{Z} = Z - N + 1$, that the energy of the sequence of emission lines will have the following energies (in cm^{-1})

$$E_{nl} = -\frac{1}{2} \frac{\tilde{Z}^2}{(n^*)^2} \quad (4.15)$$

From this, it's pretty easy to generalize this to the case of fine structure. The shift induced from this is given by

$$\begin{aligned} \Delta E &= \frac{1}{2} \kappa_{nl} \left(j(j+1) - l(l+1) - \frac{3}{2} \right) \\ \kappa_{nl} &= \frac{\hbar^2}{2m^2c^2} \left\langle \frac{1}{r} \frac{\partial V}{\partial r} \right\rangle \end{aligned} \quad (4.16)$$

The value of κ_{nl} can be determined with $V(r)$, using Hartree-Fock's approximation.

§ 4.3 Alkaline Earths

Using the same reasoning of the Alkali atoms, and using the recursion properties of the periodic table, we can study Alkaline Earths as a special kind of two electron atoms.

In the case of small spin dependent interaction, we can take the total spin S as a good quantum number. As with Helium, all levels can be divided into singlet levels $S = 0$ and triplet levels $S = 1$. Since the electric dipole operator can't change spin, we have that the selection rule $\Delta S = 0$ must hold. For atoms with small nuclear charge Ze , spin-orbit and spin-spin coupling behave like small perturbations on the triplet states (where $\hat{S} \neq 0$) but aren't big enough in order to mix these states, hence L, S remain good quantum numbers, since both are conserved to a very good approximation. In general, for triplet and singlet states, we can have these two following terms

$$\begin{cases} {}^{2S+1}L_{L,L\pm 1} & L \neq 0 \\ {}^1S_1 \end{cases} \quad (4.17)$$

§ 4.4 Multiplet Structure

Thanks to Landé's interval rule, we can immediately determine that, in general

$$\Delta E_{J,J+1} = AJ$$

And in spin-orbit coupling regimes, it holds as

$$\Delta E_{J,J+1} = AS(2L + 1) = AL(2S + 1)$$

Given these two equations, it's now possible to determine level intensities for multiplet transitions. This is especially useful in L-S regimes, since, the number of atoms in each level is proportional to the statistical weight of the level, we get that, if we indicate with I_i the i -th transition intensity, we have

$$\sum_{i=1}^n I_i \propto (2J + 1) \quad (4.18)$$

A complete application of this sum rule can be done with ${}^3S_1 \rightarrow {}^3P_{012}$ (note that they're permitted transitions). We get therefore the following system

$$\begin{cases} I_1 + I_2 + I_3 = 3I_S \\ I_1 = I_P \\ I_2 = 3I_P \\ I_3 = 5I_P \end{cases} \quad (4.19)$$

With I_P the proportionality coefficient for $P \rightarrow S$ transitions and I_S analogously for $S \rightarrow P$ transitions. This simple system is basically already solved, and it immediately gives an intensity ratio of 5 : 3 : 1 between the three transitions.

§ 4.5 Magnetic Field Interaction, Zeeman Effect

Let's now consider the perturbation applied on the energy levels of multielectron atom when applying a magnetic field. Indicating our perturbing Hamiltonian with $\hat{\mathcal{H}}_B$ we have

$$\begin{aligned}\hat{\mathcal{H}} &= \hat{\mathcal{H}}_e + \hat{\mathcal{H}}_{LS} + \hat{\mathcal{H}}_B \\ \hat{\mathcal{H}}_{LS} &= \frac{\partial V}{\partial r} \hat{\underline{L}} \cdot \hat{\underline{S}} \\ \hat{\mathcal{H}}_B &= -\hat{\underline{\mu}} \cdot \hat{\underline{B}} = \mu_B g \hat{\underline{J}} \cdot \hat{\underline{B}} = -\mu_B \hat{\underline{B}} (\hat{\underline{L}} + 2\hat{\underline{S}}) \\ \mu_B &= \frac{e\hbar}{2m_e}\end{aligned}\tag{4.20}$$

Where $\hat{\mathcal{H}}_{LS}$ is our spin-orbit coupling Hamiltonian. We might immediately define two cases.

1. $|\hat{\mathcal{H}}_B| \ll |\hat{\mathcal{H}}_{LS}|$, i.e. the magnetic field is much weaker than the LS coupling, also known as *Anomalous Zeeman Effect*
2. $|\hat{\mathcal{H}}_B| \gg |\hat{\mathcal{H}}_{LS}|$, i.e. the magnetic field is much stronger than the LS coupling, also known as *Paschen-Back Effect*

§§ 4.5.1 Paschen-Back Effect, Strong Field

In this case we have that the magnetic field is much stronger than the LS-coupling, henceforth we can say easily that in this case the coupling is broken, i.e. the $\hat{\mathcal{H}}_{LS}$ is considered as perturbation, and therefore we're left with this Hamiltonian

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_e + \hat{\mathcal{H}}_B = \hat{\mathcal{H}}_e + \frac{\mu_B}{\hbar} B_z (\hat{L}_z + 2\hat{S}_z) + A\hat{L}_z\hat{S}_z\tag{4.21}$$

Where we chose for easier calculation our z axis as the magnetic field direction. Since, in this case, both Hamiltonians have the same eigenvectors $\langle n l s m_l m_s \rangle$, we have that

$$\begin{aligned}\langle l s m_l m_s | \hat{\mathcal{H}} | l s m_l m_s \rangle &= -E_n + \frac{\mu_B}{\hbar} B_z \langle l s m_l m_s | (\hat{L}_z + 2\hat{S}_z) | l s m_l m_s \rangle + \\ &+ \langle l s m_l m_s | A\hat{L}_z\hat{S}_z | l s m_l m_s \rangle = \\ &= -E_n + \mu_B B_z (M_L + 2M_S) + \hbar A M_L M_S\end{aligned}\tag{4.22}$$

Where the Paschen-Back shift is $\Delta_{PB} = \mu_B B_z (M_L + 2M_S) + \hbar A M_L M_S$.

§§ 4.5.2 Anomalous Zeeman Effect, Weak Field

In this case the magnetic field is too weak in order to break the spin orbit coupling, and our Hamiltonian hasn't got $|n l s m_l m_s \rangle$ as eigenvectors, but rather $|n l s j m_j \rangle$. Hence we have that energy perturbation $\hat{\mathcal{H}}_B$ is

$$\Delta_{AZ} = \langle n l s j m_j | \frac{\mu_B}{\hbar} \hat{\underline{J}} \cdot \hat{\underline{B}} | n l s j m_j \rangle$$

Now, writing $\hat{J}_z - \hat{S}_z = \hat{L}_z$ we have that our calculation becomes the following

$$\Delta_{AZ} = \mu_B M_J B_z + \frac{\mu_B}{\hbar} B_z \langle nlsjm_j | S_z | nlsjm_j \rangle$$

Since the eigenkets are not eigenkets of \hat{S}_z , we use the Wigner-Eckart theorem (see appendix) in order to rewrite \hat{S}_z in a easier way to manipulate it

$$\hbar^2 J(J+1) \langle nlsjm | \hat{S}_z | nlsjm \rangle = \hbar M_J \langle nlsjm | \hat{\underline{S}} \cdot \hat{\underline{J}} | nlsjm \rangle \quad (4.23)$$

Using the definition of $\hat{\underline{J}}$ we get

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

These last operators are diagonal in our basis, hence we get, finally

$$\langle nlsjm | S_z | nlsjm \rangle = \hbar M_J \left(\frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right)$$

And, therefore

$$\Delta_{AZ} = \mu_B M_J B_z \left(1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right) = \mu_B g_J M_J B_z \quad (4.24)$$

Where g_J is the so called *Landé g factor*. As a recapitulation, we get that the Zeeman shift is the following for strong fields (Paschen-Back) and weak fields (Anomalous Zeeman)

$$\begin{aligned} \Delta E_{PB} &= -E_n + \mu_B B_z (M_L + 2M_S) + \hbar A M_L M_S \\ \Delta E_{AZ} &= -E_{n,j} + \mu_B g_J M_J B_z \end{aligned} \quad (4.25)$$

Part II

Quantum Chemistry

5 Basic Chemistry

§ 5.1 Basic Notions

Definition 5.1.1 (Compound). A «compound» is a chemical object (molecule, ion, etc...) composed by different chemical elements. The composition of a compound is defined and constant, and its properties are defined by the chemical elements that it's made of and their bonds. Compounds can be formed by both molecules and ions.

T H E O R E M 5.1 (Dalton). Given a chemical process between two compounds A and B , if we fix the amount of one of the two components and the final amount of the resultant compound, the amount of the other compound needed is always an integer multiple of the fixed amount of the other element.

Definition 5.1.2 (Atomic Number and Mass Number). The «atomic number» Z is defined as the amount of protons in an atom. If we have N neutrons, the «mass number» A is defined as follows

$$A = Z + N \quad (5.1)$$

Definition 5.1.3 (Neutral Atom). A «neutral atom» is defined as an atom where the number of electrons is equal to the atomic number Z .

Definition 5.1.4 (Isotope). Given an element with fixed Z , if we have more (or less) neutrons than protons, we call the element an «isotope». All isotopes have the same Z , but a different mass number A , also all isotopes have the same chemical properties of the "father" element.

Definition 5.1.5 (Dalton Mass). We define an «unit of atomic mass» (uma) or «Dalton» as 1/12 of the mass of Carbon-12

$$1 \text{ uma} = \frac{1}{12} m(^{12}\text{C}) = 1.66054 \cdot 10^{-27} \text{ kg} \quad (5.2)$$

We can also define the relative mass of an element as

$$m_{rel} = \frac{m}{m_{uma}} \quad (5.3)$$

Definition 5.1.6 (Relative Abundance, Atomic Mass). We define the «*relative abundance*» of an isotope as the fraction of atoms of a given isotope. From this we define the atomic mass as the weighted average of the isotope masses, with the abundances as weights

$$M_A = \sum_{i=1}^N \frac{m\%}{100} m_i \quad (5.4)$$

Another quantity which is used mainly in chemistry is the molarity of a solution. Given a solution with volume V and n moles of solvent, we define the «*molar concentration*» M also known as «*molarity*»

$$M = \frac{n}{V} \quad (5.5)$$

For an element A it's commonly indicated with $[A]$.

§ 5.2 Chemical Nomenclature

The huge number of possible compounds gives rise to the necessity of building a comfortable and useful way of naming compounds, which eases their distinction.

The first step is recognizing that the names of the elements give the root of the compound name, like *Hydrogen bromide* or *Sodium bicarbonate*. After that, it's important to distinguish the class and category of the compound.

The two main categories of compounds are

1. Binary compounds
2. Ternary compounds

Binary compounds include the following classes:

- Basic oxides, composed by a metal and oxygen
- Acid oxides, composed by a non metal and oxygen
- Hydrides, composed by hydrogen and a metal or a non metal (excluding sulfur and halogens)
- Hydroacids, composed by hydrogen with sulfur or a halogen
- Binary salts, composed by a metal and a non metal

Ternary compounds include the following classes:

- Hydroxides, composed by oxygen, a metal and hydrogen
- Oxyacids, composed by hydrogen, a non metal and oxygen
- Ternary salts, composed by hydrogen, a non metal and oxygen

Independently from the subdivisions we also have a set of prefixes in order to indicate the amount of atoms there will be in a given formula, in order, we have

1. *Mono-*, usually omitted
2. *Di-* or *Bi-*
3. *Tri-*
4. *Tetra-*
5. *Penta-*
6. *Hepta-*
7. *Hexa-*
8. *Hepta-*

In chemistry, it's useful to define a new quantity, in order to better grasp how compounds are formed, and with how many atoms they are formed, this quantity is known as «*electronegativity*».

Definition 5.2.1 (Electronegativity). Electronegativity quantifies the amount of electrons that an atom uses (in excess or in defect) with respect to the ground state configuration. It follows some basic rules:

- Hydrogen (H) has always $E_n = 1$, except when it's in a hydride, then $E_n = -1$
- Oxygen (O) has always $E_n = -2$, except in *peroxides* where $E_n = -1$ and *superoxides* where $E_n = -\frac{1}{2}$ and in the compound OF_2 where $E_n = 2$
- For an unbound atom $E_n = 0$
- In metals $E_n > 0$. Metals of the i -th group have $E_n = i$, $i = 1, 2, 3$
- In a molecule, $\sum_i E_{ni} = 0$
- Charged ions have $E_n = q$, where q is their charge. If the ion is polyatomic this continues to hold
- Halogens (group 7), always have $E_n = -1$, except when bound to O, F, where $E_n > 0$

§§ 5.2.1 Binary Compounds

§§§ 5.2.1.1 Basic Oxides

The nomenclature for oxides works as follows:

- It always keeps the word *oxide*
- When elements can have more than one oxidation state E_n , a suffix *-ic* for the max value and *-ous* for the min value

Therefore, we can build immediately a simple example table using all the previous rules, also including the traditional nomenclature.

Compound	Traditional	IUPAC
Na_2O	Sodium oxide	Sodium oxide
FeO	Ferrous oxide	Iron oxide
Fe_2O_3	Ferric oxide	Diiron trioxide
CuO	Cuprous oxide	Copper oxide
Cu_2O	Cupric oxide	Dicopper oxide
PbO	Plumbous oxide	Lead oxide
PbO_2	Plumbic oxide	Lead dioxide

Table 5.1: Basic oxide nomenclature

§§§ 5.2.1.2 Acid Oxides/Anhydrides

For anhydrides the rules are basically the same, but when we have more than two possible oxidation states we add the “ipo-/ous” prefix/suffix for the lowest possible oxidation number and “per-/ic” prefix/suffix

Compound	Traditional	IUPAC
CO	Carbonious anhydride	Carbon oxide
CO_2	Carbonic anhydride	Carbon dioxide
N_2O_3	Nitrous anhydride	Dinitrogen trioxide
N_2O_5	Nitric anhydride	Dinitrogen pentoxide
P_2O_3	Phosphoric anhydride	Diphosphorus trioxide
P_2O_5	Phosphorous anhydride	Diphosphorous pentoxide
Cl_2O	Ipochlorous anhydride	Dichlorine oxide
Cl_2O_3	Chlorous anhydride	Dichlorine trioxide
Cl_2O_5	Chloric anhydride	Dichlorine pentoxide
Cl_2O_7	Perchloric anhydride	Dichlorine heptoxide

Table 5.2: Anhydride nomenclature

§§§ 5.2.1.3 Hydracids

For hydracids the nomenclature slightly differs between IUPAC and traditional nomenclature, in the traditional nomenclature, the compounds get the adjective *acid* and the prefix *hydro-*, while in the IUPAC nomenclature they get the *-ane* suffix. The traditional nomenclature is the most used with this class of compounds

Compound	Traditional	IUPAC
HF	Hydrofluoric acid	Fluorane/Hydrogen fluoride
HCl	Hydrochloric acid	Chlorane/Hydrogen chloride
HBr	Hydrogen bromide	Bromane/Hydrogen bromide
HI	Hydrogen iodide	Iodane/Hydrogen iodide
H_2S	Hydrogen sulfide	Dihydrogen sulfide

Table 5.3: Hydracid nomenclature

§§§ 5.2.1.4 Hydrides

For hydrides the traditional and IUPAC nomenclatures differ particularly, due to the existence of multiple compounds of common use, like ammonia, which has already its common name.

Compound	Traditional	IUPAC
NaH	Sodium hydride	Sodium hydride
CaH ₂	Calcium hydride	Calcium dihydride
AlH ₃	Aluminum hydride	Aluminum trihydride
NH ₃	Ammonia	Nitrogen trihydride
PH ₃	Phosphine	Phosphor trihydride
AsH ₃	Arsine	Arsenic trihydride
CH ₄	Methane	Carbon tetrahydride
SiH ₄	Silane	Silicium tetrahydride
B ₂ H ₆	Diborane	Diboron hexahydride

Table 5.4: Hydrides nomenclature

§§§ 5.2.1.5 Peroxides

Peroxides follow the same rules of oxides, with an added *per-* suffix, as with H₂O₂, *hydrogen peroxide*

§§§ 5.2.1.6 Binary Salts

Same rules as for hydric acids, without *per* and *ipo* prefixes.

Compound	Traditional	IUPAC
NaCl	Sodium chloride	Sodium chloride
Na ₂ S	Sodium sulfide	Disodium sulfide
CaI ₂	Calcium iodide	Calcium diiodide
AlF ₃	Aluminum fluoride	Aluminum trifluoride
FeCl ₂	Ferrous chloride	Iron dichloride
FeCl ₃	Ferric chloride	Iron trichloride
CsBr	Cesium bromide	Cesium bromide

Table 5.5: Binary salts

§§§ 5.2.1.7 Hydroxides

Same as oxides, but with *hydroxide* instead of oxide. Note that hydroxide ions go in groups

§§§ 5.2.1.8 Oxyacids

The rules for naming oxyacids are the same used for anhydrides, but with the term *acid* substituting the term *anhydride*. In the IUPAC naming standard instead, the quantitative prefixes are followed by the infix *-osso-* and the suffix *-ic* and the oxidation number of the metal written between parentheses in roman numerals, as in the following table

Compound	Traditional	IUPAC
H_2CO_3	Carbonic acid	Trioxocarbonic acid(IV)
HNO_2	Nitrous acid	Dioxonitric acid(III)
HNO_3	Nitric acid	Trioxonitric acid(IV)
H_2SO_3	Sulfurous acid	Trioxosulfuric acid(IV)
H_2SO_4	Sulfuric acid	Tetraoxosulfuric acid(IV)
HClO	Ipclorous acid	Ossocloric acid(I)
HClO_2	Chlorous acid	Dioxocloric acid(III)
HClO_3	Chloric acid	Trioxochloric acid(V)
HClO_4	Perchloric acid	Tetraoxochloric acid(VII)
HBrO_3	Bromic acid	Trioxobromic acid(V)
HIO	Ipoioudous acid	Ossiodic acid(I)

Table 5.6: Oxyacids

§§§ 5.2.1.9 Ions - Acid Radicals

Acid radicals are what remains of an oxyacid after a partial or total loss of the hydrogens composing the acid molecule. For obvious reasons, the total negative charge of this ion will be equal to the amount of lost hydrogens.

In traditional nomenclature we have

- *acid becomes ion*

- For monoatomic ions: there is only one suffix, *-ide*

- For polyatomic ions:
 - *-ous becomes -ite*
 - *-ic becomes -ate*

As in the following table

Acid	Radical	Traditional name
HCl	Cl^-	Chloride ion
H_2S	S^{2-}	Sulfide ion
H_2SO_4	SO_4^{2-}	Sulphate ion
H_2SO_4	HSO_4^-	Hydrogensulfate ion
H_2CO_3	CO_3^{2-}	Carbonate ion
H_2CO_3	HCO_3^-	Hydrogencarbonate ion
HClO	ClO^-	Ipochlorite ion
HClO_2	ClO_2^-	Chlorite ion
HClO_3	ClO_3^-	Chlorate ion
HClO_4	ClO_4^-	Perchlorate ion
H_3PO_4	PO_4^{3-}	Phosphate ion
H_3PO_4	HPO_4^{2-}	Hydrogenphosphate ion
H_3PO_4	H_2PO_4^-	Dihydrogenphosphate ion
HNO_3	NO_2^-	Nitrite ion
HNO_4	NO_3^-	Nitrate ion

Table 5.7: Ions

For positive ions (cations), the nomenclature follows closely the rules for oxides and hydroxides by substituting the term oxide or hydroxide with the term ion. Another nomenclature is the stock nomenclature for cations, which indicates in roman numerals the amount of positive charges. Some ions are special in this regard, and these are some special ions of hydrogen:

Ion	Traditional
H^+	Hydrogenium ion
H_3O^+	Oxonium ion
NH_4^+	Ammonium ion

Table 5.8: Special cations

§§ 5.2.2 Ternary Salts

Ternary salts are the most complex compounds we're gonna treat, and are composed by a metallic cation and a polyatomic anion (acid radical).

In traditional nomenclature the salt name is given by the attributes of the acid radical with suffixes and prefixes, followed by the name of the cation with the -ic/-ous suffixes, depending on the oxidation numbers

§ 5.3 Chemical Reactions

Every chemical species is unequivocally represented by a unique formula. There are three possible formulas for a compound:

Definition 5.3.1 (Minimal/Empirical Formula). The minimal, or empirical formula is a kind of chemical notation which represents a compound with the atomic symbols of the elements composing the

aggregate, indicating the number of atoms present in the molecular composition with a number below. An example of this is the commonly known formula for water H_2O

Definition 5.3.2 (Structure Formula). The structure formula is another unique way of describing a chemical species. The structure formula arranges the atoms in space and shows the molecular structure of the molecule studied

Note that in ionic compounds the cation *always comes before the anion*.

§§ 5.3.1 Acids and Bases

Definition 5.3.3 (Arrhenius Acids). An arrhenius acid is a substance which cedes hydrogenium cations, while bases are substances which cede hydroxide OH^- ions. We can then define

- Binary acids

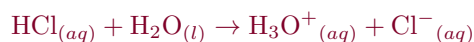


- Ternary acids

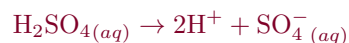


Definition 5.3.4 (Brønsted-Lowry Acids). Acids, as defined by Brønsted and Lowry get two additional categories, as *weak acids* and *strong acids*. The difference between the two is given again by how they dissociate in water, but more specifically, we have

- Strong monoprotic acids



- Strong polyprotic acids



- Weak monoprotic acids



Or also



From this definition of acid, we have also the appearance of the *conjugated bases*. For any given acid there will be defined a basic compound which differs only by one hydrogenium ion. As an example, we have that

- Hydrochloric acid is the conjugated acid of the chloride ion
- Water is the conjugated basis of the oxonium ion

An easier way of understanding this definition is that strong acids are completely soluble in aqueous solutions. Those which do not completely dissolve are then weak acids and weak bases

§§ 5.3.2 Chemical Formulas

Method 1 (Determination of the Chemical Formula). Given the percent abundance of the elements creating compound (obtained empirically), it's possible to find the molecular formula of the compound via the following method:

Suppose that we have a recombination reaction where two elements A and B combine into the composite AB. If we have $\%_A$ and $\%_B$ abundances, after converting them into moles we have

$$n_B \text{ (mol)} = \frac{\%_A \text{ (g)}}{M_A \text{ (g/mol)}} \quad n_B \text{ (mol)} = \frac{\%_B \text{ (g)}}{M_B \text{ (g/mol)}}$$

Then, if the compound is A_xB_y we have

$$\alpha = \left\lfloor \frac{\max(n_A, n_B)}{\min(n_A, n_B)} \right\rfloor$$

The minimal formula will then be

$$A_\alpha B, \quad \text{or} \quad AB_\alpha$$

Depending whether $n_A \geq n_B$ or vice versa.

Supposing that $n_A > n_B$, the complete formula will then be obtained noting that

$$M_{A_\alpha B} = \alpha M_A + M_B$$

If the molar mass of the experimental compound is known, being \tilde{M} , we can find a multiplier μ as

$$\mu = \left\lfloor \frac{\tilde{M}}{M_{A_\alpha B}} \right\rfloor$$

The full chemical formula will be then

$$A_{\mu\alpha}B_\mu$$

§§ 5.3.3 Redox Reactions

All chemical reactions can be reduced into 6 categories, depending on the reaction type

- Synthesis reactions, aka recombination reactions



- Decomposition reactions



- Dissociation reactions



- Exchange reactions



- Redox reactions, where a substance in the reagents accepts electrons and one loses them
- Combustion reactions



The kind of reactions which we're gonna treat with more care are redox reactions, where electrons gets exchanged between the reactants.

The electron transfer happens from a compound that cedes electrons (*reducing agent*) and one that accepts these electrons (*oxidizing agent*). Essentially, the reaction can be divided in two, an oxidation and a reduction, although physically they are simultaneous.

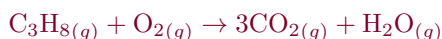
Remembering that mass is conserved, all chemical equations have to be balanced, indicating the numbers of moles needed of the reagents and the number of moles obtained in the resultants. This is known as *stoichiometric balancing*. For redox reactions, if they don't happen in an aqueous solution, this balancing can be obtained by simply balancing the masses.

EXERCISE 5.3.1. *Given the following redox reaction of propane, find the correct equation via stoichiometric balancing*

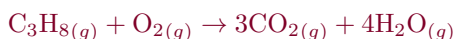


SOLUTION. We have two ways to solve the problem: using a system of equations, or slowly balancing the masses, since the redox is not in an aqueous solution.

We choose the second path, and we immediately see that we have one compound containing carbon on both sides, thus, we have



We then proceed by balancing the hydrogen atoms



And lastly the oxygen atoms



This is valid only in case the reaction doesn't happen in an aqueous solution. Let's consider an example of reaction in an aqueous solution and develop a new method for balancing the equation.

Method 2 (Semireaction Method). Consider the following redox in an aqueous solution



We begin by dissociating every compound in the composing ions and find which of those gets oxidized and which gets reduced.

We see immediately that in order for the reaction to work we must have that

- Strontium oxidized
- The nitrate ion gets reduced

We can then write two semireactions for the two ions



Before balancing the masses we have to check whether the reaction is happening in acid or basic environment.

Using Arrhenius' definition of acid we immediately see that the reaction is acid, thus we balance the two ionic equations by adding H^+ to the reactants and H_2O to the products, while also balancing charges at the same time, by adding electrons



We now proceed to multiply by a coefficient which lets us sum the two semireactions and cross out all the added electrons. We immediately note that multiplying the first row by 4 is enough to accomplish this task, thus



Adding them up and rebalancing if needed, we get the *ionic form* of reaction



Recombining the compounds and checking the stoichiometric coefficients of the compounds we have the fully balanced equation



§§ 5.3.4 Stoichiometry

The importance of balancing the stoichiometric coefficient lays directly on the fact that they indicate the molar proportions of the compounds acting in the reaction. As an example consider the reaction between phosphorus and chlorine, generating phosphorus trichloride in the following way



This equation means that for consuming all the phosphorus in the reaction we need 6 times as much moles of chlorine

Example 5.3.1 (Phosphorus Trichloride). Suppose that we have $m_P = 1.45$ g and we want to know how much phosphorus trichloride is produced if we consume all the phosphorus.

Noting that $M_P = 30.794$ g/mol, we have

$$n_P = \frac{1.45}{4 * 30.794} \text{ mol} = 0.01170 \text{ mol}$$

This means that we will need $n_{Cl} = 0.07022$ mol, which corresponds to 4.98 g. Since all the phosphorus gets consumed, we have that the limiting reactant in this situation is phosphorus itself. We have that for a mole of phosphorus consumed, 4 of phosphorus trichloride are produced, which in this case is

$$n_{PCl_3} = 4n_P = 0.04680 \text{ mol}$$

The molar mass of the product is

$$M_{PCl_3} = M_P + 3M_{Cl} = 137.3 \text{ g/mol}$$

Thus we get 6.43 g of product

The calculation is better made by creating a table with the initial and final amounts of all products indicated in moles, simply because the reagents won't be used wholly in every reaction.

Example 5.3.2 (Limiting Reagent). Consider again the previous reaction, but this time we have 1.45 g of phosphorus reacting with 3.50 g of chlorine. The amount of moles of chlorine is 0.04937 mol, which is less than what we need to burn through all the phosphorus, making chlorine the limiting reagent of the reaction.

We want now to calculate the amount of phosphorus that will remain unused in the reaction. We begin by building the table that we described before

	P ₄	Cl ₂	PCl ₃
IS	0.01170	0.04937	0
FS	x	0	y

Table 5.9: Stoichiometric table

As before, for 1 mol of phosphorus we need 6 mol of chlorine, which means that the amount of phosphorus that will react is 1/6 the amount we have, precisely 0.008228 mol. By simple subtraction we can find the amount of phosphorus that remains after the reaction, i.e. 0.003472 mol.

With the same logic we have that the amount of phosphorus trichloride produced is 6/4 the amount of chlorine that we have, thus we produce 0.03291 mol, or 4.52 g.

The updated and completed stoichiometric table is

	P ₄	Cl ₂	PCl ₃
IS	0.01170	0.04937	0
FS	0.003472	0	0.03291

Table 5.10: Completed stoichiometric table

EXERCISE 5.3.2 (Combustion of Glucose). Consider the combustion of glucose

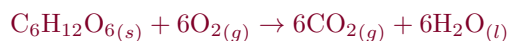


Balance the equation and calculate how many grams of oxygen are needed for burning completely 25.0 g of glucose

	C ₆ H ₁₂ O ₆	O ₂	CO ₂	H ₂ O
IS	0.1388	0.8328	0	0
FS	0	0	?	?

Table 5.11: Glucose combustion stoichiometric table

S O L U T I O N. We begin by balancing the equation. We see immediately that we have 8 oxygen atoms on the left and 3 on the right, while we have 12 hydrogen atoms on one side and two on the other side. Balancing hydrogen and carbon simultaneously we get 18 oxygens, and thus the balanced equation is



Since

$$M_{gl} = 6M_C + 12M_H + 6M_O = 180.156 \text{ g/mol}$$

We have, initially

$$n_{gl} = \frac{m_{gl}}{M_{gl}} = 0.1388 \text{ mol}$$

Using the previous formula we have that for burning a mole of glucose we need 6 moles of oxygen, thus

$$n_{O_2} = 6n_{gl} = 0.8328 \text{ mol}$$

Which corresponds to

$$[H]m_{O_2} = 2M_O n_{O_2} = 12M_O n_{gl} = 26.65 \text{ g} \quad (5.12)$$

We have now found the first data needed to compile our table. The glucose - carbon dioxide rate is exactly the same as the one between glucose and oxygen, thus the amount of carbon dioxide produced is known. We can do the same for water, but we can also use mass conservation in order to find the amount of water produced.

The completed table will then be

	C ₆ H ₁₂ O ₆	O ₂	CO ₂	H ₂ O
IS	0.1388	0.8328	0	0
FS	0	0	0.8328	0.8328

Table 5.12: Completed table for the combustion of glucose

The moles can be easily converted into grams then.

Method 3 (Stoichiometric Table). The previous method can be easily generalized. Consider a (balanced) chemical reaction as the following, where without loss of generality we will have only two reagents and two products:



Supposing that we want to consume all the composite A we will need then

$$n_B = \frac{b}{a} n_A$$

And the amounts of products generated in the reaction are

$$n_C = \frac{c}{a} n_A$$

$$n_D = \frac{d}{a} n_A$$

And the table will simply be

	A	B	C	D
IS	n_A	$\frac{b}{a} n_A$	0	0
FS	0	0	$\frac{c}{a} n_A$	$\frac{d}{a} n_A$

Table 5.13: Table for the stoichiometric analysis of a reaction where there's no limiting reagent

In case that we have an excess of composite A, or a deficit of the composite B, i.e when

$$n_B < \frac{b}{a} n_A = n_{lim}$$

For mass conservation then we must have that the amount that rea

$$n_A^f = n_A - \frac{a}{b} n_B = n_A - n_A^r$$

Which modifies the table into the following one

	A	B	C	D
IS	n_A	n_B	0	0
FS	$n_A - \frac{a}{b} n_B$	0	$\frac{c}{a} n_A^r$	$\frac{d}{a} n_A^r$

Table 5.14: Table for the stoichiometric analysis of a reaction with a limiting agent

§ 5.4 Molecular Bonding and Structure

§§ 5.4.1 The Periodic Table

The periodic table is the pinnacle of modern chemistry. The table lists all known elements in a way such that the periodic properties of the elements can be quickly seen and understood, and compacted in an ordered table of «groups» (columns) and «periods» (rows). The physical details of these properties will be treated later in depth in the atomic physics part, but it's clear by simply considering purely classical electromagnetism, that there must be a total charge Z of an atom, but also an effective charge Z^* due to screening processes between electrons.

Other periodic properties which are well ordered in the periodic table are the ionization energy of atoms and *electronic affinity*, a purely chemical idea which gives a quantification to the capacity of an atom to accept electrons. In the same way we can define the *electronegativity* χ of an atom as the capacity of forming bonds with other elements. All these properties have their own preferred direction of growth in the table, specifically

- Atomic radius grows going down along a column (group) and decreases going left along a row (period)
- Electron affinity grows along periods going right and decreases going down along a group
- Ionization energy grows and decreases exactly in the same way as electron affinity
- the metallic characteristics of elements grow going left along a period and down along a group, i.e. moving diagonally from left to right

Each group of the periodic table can be seen to have similar properties of the elements in it, letting us define special categories for the elements sharing the same group.

In the modern periodic table, we have 18 groups:

- 8 “A” main groups
- 10 “B” transitional groups

The groups are indicated with roman numerals, going from I to VIII. We are interested mainly in the A category of groups. Specifically, the elements of these groups will get a special name.

- Group IA: Hydrogen and Alkali metals. Also known in physics as “hydrogenoid” atoms.
- Group IIA: Alkaline Earths
- Group IIIA: Triels
- Group IVA: Tetrels
- Group VA: Pnictogens or Pentels
- Group VIA: Chalcogens
- Group VIIA: Halogens
- Group VIIIA: Noble gases

§§ 5.4.2 Molecular Bonding

In order to have chemistry in itself, we must have molecules, and the only way to get them is via *molecular bonds*. There are three types of bonding in general:

1. Metallic bonds
2. Covalent bonds
3. Ionic bonds

Definition 5.4.1 (Lewis Structures). If we consider firstly covalent bonding, one of the best ways to grasp graphically and conceptually how electrons get shared between atoms in the molecule is using «Lewis structures». These structures are formed by drawing as many dots as the *valence electrons* (outer shell electrons which participate in the bond), drawn sequentially going around each side of the symbol, and indicating the bonds as solid lines connecting the electrons of the bonding atoms.

A rule of thumb for understanding how many lines we can make is the «octet rule», which states that every element bonds in order to reach the same amount of chemical reactivity of the noble gases of the VIIIA group. As an example, for completing the octet rule, fluorine F only needs one electron from another substance, as in HF.

More generally, in order to properly draw a Lewis diagram we need to take into account 5 simple rules

1. Determine the central atom, generally the one with the smallest electron affinity
2. Determine the total amount of valence electrons
3. Dispose the remaining atoms around the central element and create bonds by putting electronic couples between each bonding atom and the central one
4. Dispose the electrons in a way that the peripheral atoms satisfy the octet rule
5. If the central atom didn't satisfy the octet rule, create multiple bonds between it and the peripherals atoms

Molecules with the same amount of external electrons have the same Lewis structure and are said to be «isoelectronic».

From Lewis structures we can define the «formal charge» of a molecule, i.e. the electrostatic charge that an atom would have in a molecule if the electrons are uniformly distributed between atoms.

Said N_{ve-} the number of valence electrons and N_{be-} the number of bonding electrons and with N_{lp} the amount of «lone pairs» (unbounded couples of electrons), we have

$$Q_F = N_{ve-} - N_{lp} - \frac{1}{2}N_{be-} \quad (5.13)$$

For having a well defined molecule with charge Q , each atom must have $Q_{F,i}$ such that

$$Q = \sum_i Q_{F,i} \quad (5.14)$$

Examples of Lewis structures are the following

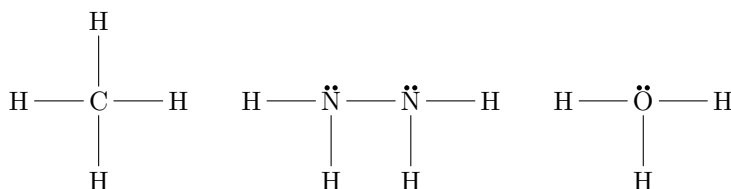


Figure 5.1: Lewis structure for methane CH₄, hydrazine N₂H₄ and oxonium H₃O⁺

§§§ 5.4.2.1 Resonance and Exceptions to the Octet Rule

It's possible to find molecules for which there are two valid Lewis structures. This was explained by Pauli as *resonance*, i.e. we have a superposition between two possible structures, creating a «resonance hybrid» structure.

An example of resonant structure is ozone O₃, in which there are two possible position of a double

bond between the central oxygen and one of the two external oxygen atoms, the two possible diagrams are

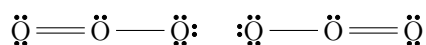


Figure 5.2: Ozone resonant hybrid Lewis formula

Other particularities are the exceptions to the octet rule, found in elements from the third period and onward, where the central atoms form composite with more than eight electrons. These elements are called «*hypervalent composites*».

Another case of violation of the octet rule is found in a small class of compounds which have an uneven number of electron in the valence shell. In these cases, on the central atom remains a single unpaired electron.

These compounds are highly reactive and get the name of «*free radicals*». An example of one of these compounds is nitrogen dioxide NO_2

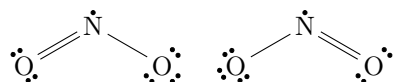


Figure 5.3: Resonant hybrid structure of nitrogen dioxide

§§§ 5.4.2.2 VSEPR Model

Lewis structures are fundamental in the description of molecular structure using the «*Valence Shell Electron Pair Repulsion*», which states that the best spatial disposition of the atoms in the molecule is the one that minimizes the electrostatic repulsion between the electron pairs. With a single table we can indicate all these rules easily, when we indicate with X_n the numbers of bound atoms and with E_n the number of lone pairs on the central atom.

Composition	Structure	Planar Angles	Vertical Angles	Example Compound
AX ₂	Linear	180°	//	BeCl ₂ , CO ₂
AX ₂ E	Bent	120° (119°)	//	NO ₂ ⁻ , SO ₂
AX ₂ E ₂	Bent	109.5° (104.48°)	//	H ₂ O, OF ₂
AX ₂ E ₃	Linear	180°	//	XeF ₂ , I ₃ ⁻
AX ₃	Trigonal Planar	120°	//	BF ₃ , SO ₃
AX ₃ E	Trigonal Pyramidal	109.5° (106.8°)	//	NH ₃ , PCl ₃
AX ₃ E ₂	T-Shaped	180° (175°)	90° (87.5°)	ClF ₃ , BrF ₃
AX ₄	Tetrahedral	120°	109.5°	CH ₄ , XeO ₄
AX ₄ E	Seesaw	180°	120°	SF ₄
AX ₄ E ₂	Square Pyramidal	180°	90°	XeF ₄
AX ₅	Trigonal Bipyramidal	120°	90°	PCl ₅
AX ₅ E	Square Pyramidal	90°	90°	ClF ₅ , BrF ₅
AX ₅ E ₂	Pentagonal Planar	72°	144°	XeF ₅ ⁻
AX ₆	Octahedral	90°	90°	SF ₆
AX ₆ E	Pentagonal Pyramidal	72°	90°	XeOF ₅ ⁻ , IOF ₅ ²⁻
AX ₇	Pentagonal Bipyramidal	72°	90°	IF ₇
AX ₈	Square Antiprismatic	//	//	IF ₈ ⁻ , XeF ₈ ²⁻
AX ₉	Tricapped Trigonal Prismatic	//	//	ReH ₉ ²⁻

Table 5.15: VSEPR table for determining the molecular structure of compounds from their Lewis structure

Note that the presence of multiple bonds doesn't change the molecular geometry, since double bonds occupy the same amount of space of single bonds.

§§§ 5.4.2.3 Bond Polarity and Bond Order

There are two main types of covalent bond

- Homopolar bonds
- Heteropolar bond

The determination of the kind of bond we're facing can be made by checking the difference in electronegativity between the two atoms considered, and if

$$\Delta\chi \begin{cases} = 0 & \text{Homopolar} \\ \neq 0 & \text{Heteropolar} \end{cases}$$

In the second case the charge imbalance can be indicated in the structure diagram with δ^{\pm} indicating the partial charge of the atoms.

Note that in the special case of

$$0.4 \leq \Delta\chi \leq 1.7$$

The bond is known as a covalent polar bond.

We can also define the bond order of a bond as the number of bond between equal atoms. It's calculated with the following technique

- For each n -ple bond add n
- Divide by the number of participating atoms

§§§ 5.4.2.4 Intermolecular Forces

Being molecules particularly small and electrically charged, we have to consider a class of intermolecular forces, known as *Van der Waals forces* which permit the creation of weakly bound structures only via electrostatic interaction.

Van der Waals forces can be of two kinds:

1. Ion-dipole interaction
2. Dipole-dipole interaction

The first kind of interaction is found when a polar compound gets close to an ionic compound, like water. This is really common in aqueous ionic solutions. When an ion gets hydrated, it also liberates energy as *hydration enthalpy*.

Dipole dipole interactions are instead found in interactions between polar molecules, due to the presence of an electric dipole generated from the electron imbalance between the atoms. A particular case of molecular dipole interaction is given by *hydrogen bonds*, where hydrogen forms a ionic bond with a strongly electronegative atom. Two molecules of this kind then form a strong dipole-dipole interaction which creates the bonds.

Hydrogen bonding explains the numerous peculiarities of water, like the strong solvent power.

Dipole-dipole interactions can also happen between polar and non-polar compounds via electrostatic repulsion of the electrons of the non-polar molecule, creating an electric dipole. The bigger is the non-polar molecule and higher is its polarizability.

A special case of induced dipoles is «*London dispersion interaction*», where the polarized molecules interact weakly.

§ 5.5 Thermochemistry

The branch of thermodynamics interested in the study of chemical reactions is *thermochemistry*. Here, the most used potentials are enthalpy and the Gibbs' free energy.

Remembering the definition of enthalpy we have that in chemical reactions, being isobaric processes, we have

$$\Delta H = Q \begin{cases} > 0 & \text{endothermic reaction} \\ < 0 & \text{exothermic reaction} \end{cases} \quad (5.15)$$

The terms «*endothermic*» and «*exothermic*» come directly from the direction of heat flow from (to) the surroundings, considering the reaction as our thermodynamic system.

In order to standardize and define properly enthalpy variations, a *standard atmosphere* for measuring, where

$$T_0 = 25^\circ\text{C} = 298.15 \text{ K}, \quad p_0 = 1 \text{ bar} \approx 1 \text{ atm} \quad (5.16)$$

In this precise state chemists measure enthalpy variations for the different chemical processes that can happen.

The additivity of enthalpy and its extensive nature, we can say, that for a generic reaction of multiple elements with formation enthalpy ΔH_f^0 , we define the reaction enthalpy via Hess' law

$$\Delta H_r^0 = \sum_{prod} c_i \Delta H_{f,i}^0 - \sum_{rea} d_i \Delta H_{f,i}^0 \quad (5.17)$$

Where c_i, d_i are the stoichiometric coefficients of each compound.

Example 5.5.1 (Combustion of Methane). Consider as an example the combustion of methane, with the following chemical reaction



By Hess' law, the combustion enthalpy will then be

$$\Delta H_{comb}^0 = \Delta H_f^0(\text{CO}_2) + 2\Delta H_f^0(\text{H}_2\text{O}) - \Delta H_f^0(\text{CH}_4) \quad (5.19)$$

Note that since oxygen is in its stable form, its formation enthalpy in standard atmosphere is taken to be 0.

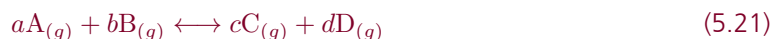
Since in chemistry we're usually dealing with first order phase changes, it's also really useful to redefine Hess' law in terms of the Gibbs' free energy as

$$\Delta G_r^0 = \sum_{prod} c_i \Delta G_{f,i}^0 - \sum_{rea} d_i \Delta G_{f,i}^0 \quad (5.20)$$

Always remember that the formation enthalpy and Gibbs free energy of a single element are always 0.

§§ 5.5.1 Equilibrium in Gases

Consider a system in thermal and chemical equilibrium, with the following equilibrium formula



Considered the molar concentrations of each element to the power of their corresponding stoichiometric coefficient, we have that the ratio of the product concentrations and the reagent concentrations is constant, and known as the «equilibrium constant» κ_C . Thus, for the previous generic case

$$\kappa_C = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \quad (5.22)$$

For gaseous equilibrium, the equilibrium constant is defined in terms of the partial pressure of each gas. It's tied to the previous definition via the ideal gas law as

$$\kappa_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} = \kappa_C (RT)^{c+d-a-b} \quad (5.23)$$

Thanks to its definition, we can define two scenarios

1. $\kappa_c \gg 1$, the equilibrium is moved towards the products, i.e. when the mix reaches equilibrium the molar concentrations of products are greater than those of the reagents
2. $\kappa_c \ll 1$ the equilibrium is moved towards the reagents.

The equilibrium constant is used to determine the direction of equilibrium of a reaction which is not in equilibrium, and to calculate the final equilibrium concentrations given some initial conditions.

Given the same reaction as before, together with an initial condition on the concentrations we can calculate the reaction quotient $Q_c(t)$. Considered a fixed generic time t we have

$$Q_c = \frac{[C]_t^c [D]_t^d}{[A]_t^a [B]_t^b} \quad (5.24)$$

Note that, at equilibrium $Q(t_{eq}) = \kappa_c$!

Therefore, by the same logic as before

1. $Q_c < \kappa_c$ the reaction is not in equilibrium and it will tend to create products, i.e. "move right"
2. $Q_c > \kappa_c$ the reaction will tend to create reagents i.e. "move left"
3. $Q_c = \kappa_c$ the reaction is in equilibrium

Chemical equilibrium, due to the nature of matter can be of two different kinds

1. Homogeneous, if all the participating compounds are in the same phase
2. Heterogeneous, if the compounds are in different phases

For a heterogeneous equilibrium, the concentrations of pure liquids and solids are omitted, since they don't contribute to the gaseous equilibrium.

Equilibrium can be perturbed only via variations of temperature, pressure or by a variation of concentrations. In the case of a variation of temperature, we can use the following theorem

T H E O R E M 5.2 (Le Chatelier). *A system in equilibrium will respond to a perturbation in a way such the changes are minimized.*

In terms of enthalpy, we have

1. $\Delta H^0 > 0$, the reaction is endothermic and the equilibrium moves right, i.e. $\Delta \kappa > 0$
2. $\Delta H^0 < 0$, the reaction is exothermic and the equilibrium moves left, i.e. $\Delta \kappa < 0$

A quick way to summarize everything, we can use the relationship between κ and the Gibbs' free energy to check what happens after a variation of temperature.

$$\Delta G^0 = -RT \log \kappa \quad (5.25)$$

Using thermodynamics we can derive what's known as the «Van 't Hoff equation». From the definition of the standard Gibbs free energy, we have

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (5.26)$$

Combined with the previous equation we have that

$$-RT \log \kappa = \Delta H^0 - T \Delta S^0 \quad (5.27)$$

Dividing by $-RT$ and then derivind with respect to temperature, we get the final equation that we can use to determine the variation of the equilibrium constant. The evaluation is immediate, giving

$$\frac{d \log \kappa}{dT} = \frac{\Delta H^0}{RT^2} \quad (5.28)$$

In case of a pressure variation, equilibrium will move towards the direction where moles of gas are the least, while it will go the opposite way for a variation of volume

§§ 5.5.2 Equilibrium in Aqueous Solutions

In order to define equilibrium in aqueous solutions we need to define two things:

Definition 5.5.1 (Electrolyte). An «electrolyte» is a substance that dissolves in water producing ions. A non-electrolyte is defined analogously as an element soluble in water that doesn't produce ions

An electrolyte can either be an ion or a molecule, and can be both strong or weak depending on how much it dissolves in water.

A special example is water, it itself is a weak electrolyte, with the following dissociation reaction, known as the «self ionization reaction of water»



The “wet” equilibrium constant is then determined by considering only the elements in an aqueous solution, ignoring liquids, solids and gases. For the dissociation of water, we have

$$\kappa_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = 1.0 \cdot 10^{-14} \quad (5.30)$$

Remembering the Brønsted-Lowry definition of acid, we have that water can then behave as both a base and an acid, getting the title of «anfiprotic».

Note that

1. The conjugate basis of a strong acid is a weak basis
2. The conjugate basis of a weak acid has strength depending on the strength of the acid
3. The conjugate acid of a strong basis is a very weak basis
4. The conjugate acid of a weak basis has strength depending on the basis

We can define then an *acid and basic equilibrium constant* as

$$\left\{ \begin{array}{l} \kappa_A = \frac{[\text{H}_3\text{O}^+] [\text{A}^-]}{[\text{HA}]} \\ \kappa_B = \frac{[\text{HB}^+] [\text{OH}^-]}{[\text{B}]} \end{array} \right. \quad (5.31)$$

Where A, B are our generic acid and base. The bigger is the equilibrium constant, the stronger is the base/acid. Note that polyprotic acids will have more than one constant since they can donate more than one proton. Obviously, the more protons does the acid donate and the more the constant reduces.

Definition 5.5.2 (pH and pOH). For qualitatively determining the acidity of a solution, we can calculate the «pH», defined as follows

$$pH = -\log_{10} [H_3O^+] = -\log_{10} [H^+] \quad (5.32)$$

Analogously, we define the «pOH» as

$$pOH = -\log_{10} [OH^-] \quad (5.33)$$

And the « $p\kappa_w$ » as

$$p\kappa_w = -\log_{10} \kappa_w = pH + pOH = 14 \quad (5.34)$$

A solution is then

- Acid, if $pH < 7$ or $pOH > 7$
- Basic, if $pH > 7$ or $pOH < 7$
- Neutral, if $pH = pOH = 7$

Method 4 (Calculation of the pH of a Solution). Suppose that we have a solution of CH_3COOH (acetic acid), where $[CH_3COOH] = 0.100$ M, the dissociation reaction is the following



Being acetic acid a weak acid, only a small part is dissociated in water. In fact, we have

$$\kappa_A = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} \simeq 1.80 \cdot 10^{-5} \ll 1$$

For evaluating the reaction and finding the pH of the solution we write the stoichiometric table of the reaction, in terms of the concentrations of the various species

	CH_3COOH	H_2O	CH_3COO^-	H_3O^+
IS	0.100	/	0	0
FS	$100 - x$	/	x	x

Table 5.16: Stoichiometric table for the dissociation of acetic acid

Since κ_A is known, we can write a second order equation in terms of the concentrations of acetic acid and oxonium

$$\kappa_A = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

The solution is immediate if we approximate for a weak acid, therefore

$$x = \sqrt{0.100\kappa_A} = 0.0013 \text{ M} \Rightarrow pH = \log_{10} x = 2.87$$

The general method is then, given a dissociation reaction for a weak Brønsted acid ($\kappa_A \ll 1$) and concentration c_A

$$\kappa_A = \frac{x^2}{c_A - x} \quad (5.36)$$

When the acid is really weak ($c_A > 100\kappa_A$), then $x \ll c_A$, and the solution is straightforward

$$x = \sqrt{c_A \kappa_A} \Rightarrow pH = -\log_{10}(\sqrt{c_A \kappa_A})$$

For a weak Brønsted basis the process will be similar, although we need to take into account that the κ_B gives us the concentration of OH^- . Thus, due to the completely analogous process and calculation we get, with a basis concentration of c_B

$$\kappa_B = \frac{x^2}{c_B - x} \quad (5.37)$$

If the basis is really weak, i.e. $c_B < 100\kappa_B$ we can again approximate the denominator to c_B , and therefore, the concentration of $[OH^-] = x$ ions is

$$x = \sqrt{c_B \kappa_B} \Rightarrow pOH = -\log_{10}(c_B \kappa_B)$$

For recovering the pH of the solution we use the definition of $p\kappa_w$, and get

$$pH = 14 - pOH$$

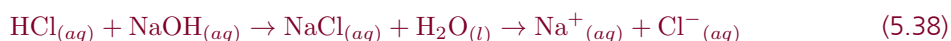
Note that for polyprotic acids and bases, the process must be repeated each time (just note that the κ is different each time), although for evaluating the pH only the first constant is used.

§ 5.6 Acid-Base Reactions

§§ 5.6.1 Saline Hydrolysis

Acids and bases are not the only elements that have acidic or basic properties in water. There exists a relation between weak acids and bases for which when a salt is dissolved in water, it dissociates into either an acid or a basis in water, giving rise to an acid-base reaction.

Note that if we dissolve a *strong* acid and a *strong* base, the formed salt will have the conjugated ions of the two dissolved elements, which will dissociate again. A common example reaction is the one between hydrochloric acid and sodium hydroxide, which will form sodium chloride (table salt). The reaction is the following



The strength of the chloride ion and sodium cation is almost null, and therefore the final pH will be the one of water, i.e. $pH = 7$. This reasoning is valid *only* for strong acids and strong bases. If we introduce a perturbation on the concentration of hydrogenium or hydroxide, we will have a change in pH in either direction, in a reaction known as (acid/basic) saline hydrolysis.

A good example reaction is the one which generates ammonium ions from ammonium chloride

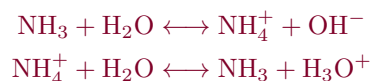
Example 5.6.1 (Ammonium Chloride in an Aqueous Solution). The dissociation of ammonium chloride follows this reaction



Since ammonium chloride is basic, we have that ammonium is the conjugated acid in the reaction. It will react again with water creating ammonia, in the following reaction



Having ceded a proton to water, we've seen why ammonium is acid, because it also increases the concentration of oxonium cations. The pH will get then lower than 7 and we're looking at an acid saline hydrolysis. Here we have two acid-base reactions



Clearly, the greater is κ_A the smaller κ_B will be, corresponding to our previous consideration on the strength of acids and bases.

In general, for this kind of reactions we will have that

$$\kappa_A \kappa_B = [\text{H}_3\text{O}^+] [\text{OH}^-] = \kappa_w \quad (5.39)$$

Thus explaining why strong acids combined with strong bases will give rise to a neuter solution. Note that, as an example for table salt, the opposite reaction is *not* possible. If everything is calculated out one sees that $\kappa_A \rightarrow \infty$, making the dissolution reaction *not reversible*.

§§§ 5.6.1.1 Common Ion Effect

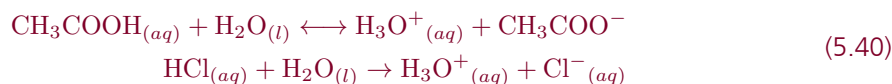
If we try to calculate the pH of an aqueous solution obtained via mixing 200 ml of acetic acid 0.200 M and 100 ml of hydrochloric acid 0.150 M, after writing the reactions and remembering that $\kappa_A = 1.80 \cdot 10^{-5}$ we have

$$\begin{aligned}V_{\text{acetic}} &= 0.200 \text{ l} & [\text{CH}_3\text{COOH}] &= 0.200 \text{ M} \\ V_{\text{hydrochloric}} &= 0.100 \text{ l} & [\text{HCl}] &= 0.150 \text{ M}\end{aligned}$$

The calculation of the amount of moles of each compound is straightforward and gives $n = 0.0400$ mol for acetic acid and $n = 0.0150$ mol for hydrochloric acid. The new concentrations after mixing the two compounds are

$$\begin{aligned}[\text{CH}_3\text{COOH}] &= 0.133 \text{ M} \\ [\text{HCl}] &= 0.0500 \text{ M}\end{aligned}$$

Being both acids, we have to write separately the two dissociation reactions, as



The two reactions have both as product a mole of oxonium, thus making it a «common ion». This means that

$$[\text{H}_3\text{O}^+] = [\text{H}_3\text{O}^+]_{\text{HCl}} \quad (5.41)$$

This simply because hydrochloric acid is a stronger acid than acetic acid. Note that due to Le Chatelier's theorem we have that the strong acid dissociation will perturb the weak acid dissociation moving the equilibrium towards the reagents.

§§ 5.6.2 Buffer Solutions

A special kind of reactions containing acid-base couples are «*buffer solutions*», in which the adding of strong acids and strong bases *does not vary the pH of the solution*.

In order to keep the pH stable it's *necessary* to have a base and his conjugated acid in the same solution in similar quantities.

Suppose now that we let acetic acid react with sodium hydroxide (a strong basis) and we add to it a mole more of acid than the base.

The reaction is



The products of the reaction are sodium acetate and water. Due to acetic acid being a weak acid it will be present in the solution together with the conjugated basis in similar quantities, creating a buffer solution.

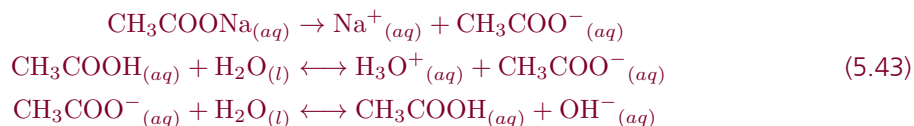
Buffer solutions can be created by

- Weak acid in solution with their conjugated basis, e.g. acetic acid (CH_3COOH) and sodium acetate (CH_3COONa)
- Weak bases in solution with their conjugated acids, e.g. ammonia and ammonium chloride
- Solution of mixed polyprotic acids, e.g. phosphoric acid and dihydrogen phosphate, or bicarbonate and carbonate

Concentrating ourselves only on the reaction between a weak acid and a salt containing his conjugated basis we have three reactions in water:

1. Salt dissociation
2. Acid dissociation
3. Basic saline hydrolysis

In terms of chemical formulas we have



What's happening here is that we have a double common ion effect, moving the equilibrium reactions to the left and leaving unchanged the two initial configurations. The pH will then be evaluated only using the acid dissociation.

Knowing that for acetic acid we have $\kappa_A = 1.80 \cdot 10^{-5}$, we can find the oxonium concentration from the definition of κ_A , thus

$$[\text{H}_3\text{O}^+] = \kappa_A \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

Which indicates that the oxonium concentration is completely determined by the acid strength and by the (initial) concentrations of the acid and of the conjugated salt.

The capacity to block pH variations of these solutions is known as buffering power. The max buffering power is when the acid-base couple has exactly the same concentration. The variability field is instead the interval of pH for which the buffer is efficient. Usually the efficiency is around 1 unit of pH from the $\text{p}\kappa_A$ of the acid

§§ 5.6.3 Solubility

The solubility S is the maximum concentration possible of a compound dissolved in water at a given fixed temperature. It's measured in mol/l or also g/l.

It's deeply tied to the concentration of ions dissociated from the saline compound, via the stoichiometric coefficients of the dissociation reaction. Many compounds are not really soluble, and the equilibrium of the concentrations of the ions and the undissolved salt is known as a «saturated solution». The reaction in question is of the following kind



The equilibrium constant will depend on temperature and on the amount of solid remaining, It's indicated as κ_{ps} and is known as the «solubility product».

$$\kappa_{ps} = [M^{m+}]^n [X^{n-}]^m \quad (5.45)$$

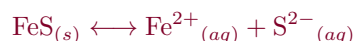
The solubility is then defined as the ion concentration divided by their stoichiometric coefficient

$$S = \frac{1}{n} [M^{m+}]^n = \frac{1}{m} [X^{n-}]^m \quad (5.46)$$

At constant temperature it's influenced by the common ion effect, the pH of the solution and eventual reactions in the solution.

§§§ 5.6.3.1 Variations of pH

Consider the dissolution reaction of iron sulfide in water. Sulfates are usually not easily dissolvable salts, in fact, for this reaction



The solubility product is

$$\kappa_{ps} = 5.0 \cdot 10^{-18}$$

Adding an acid like hydrochloric acid we see that the sulfide ion will react with the free protons creating hydrogen sulfide ion and dihydrogen sulfide. Being the second in the gaseous phase it will be ceded to the ambient, reducing the concentration of sulfur. For the Le Chatelier theorem the reaction will move to the right, increasing the solubility product and thus dissolving completely the salt.

§§§ 5.6.3.2 Common Ion Effect in Dissolutions

Since the solubility product depends only on temperature, and must be always defined then, we have that the solubility of a not really soluble salt must get smaller when it encounters a common ion effect. Considering the generic case (5.44) and the generic definition of the solubility product, we can determine a Q factor (reaction quotient) which will give us more knowledge on the reaction. We have:

$$Q_s = \frac{[M^{m+}]^n [X^{n-}]^m}{[M_n X_m]} \quad (5.47)$$

Its values can be interpreted as follows

- $Q_s > \kappa_{ps}$, the solution is oversaturated and precipitation will follow
- $Q_s = \kappa_{ps}$, the solution is saturated
- $Q_s < \kappa_{ps}$, the solution is unsaturated and the salt will continue to dissolve

6 Molecular Structure

§ 6.1 Introductory Remarks

In order to begin to appreciate physically how a molecule can be described is by considering a few conditions:

Obviously the nuclei of the molecules have comparatively a much bigger mass than all the electrons combined, therefore, the center of mass of the nuclei can be thought as being “fixed” in space, at a certain average distance from both atoms, called the *equilibrium spacing* which depends on the considered molecule.

Let’s now consider valence electrons. They’re distributed all around the molecule, and their charge distribution gives the force needed to keep the molecule bound. Now, if a is an average distance between the two nuclei, we have a rough estimate of the energy levels of the valence electrons of the molecule. Using the uncertainty principle, we get that the magnitude of the electronic energies is approximately the following

$$E_e \approx \frac{\hbar^2}{ma^2}$$

Since $a \approx 1 \text{ \AA}$, we have that E_e is on the order of some eV.

Let’s now consider motions. A molecule, in general, can rotate and translate in space, which can be reduced to the calculation of vibrations around the equilibrium distance of the molecule and the rotation of itself, after separating the center of mass.

The nuclear vibrational energies can be calculated by supposing that both nuclei are tied by an elastic force, for which the oscillation frequency is $\omega_N = (k/M)^{1/2}$ (where M is the nuclear mass, and k is a parameter). Comparing it to the electronic oscillation, we get that the energy levels associated to vibration will have the following spacing (in relation to electronic levels)

$$\frac{E_v}{E_e} = \frac{\hbar\omega_N}{\hbar\omega_e} = \sqrt{\frac{m}{M}}$$

Hence

$$E_v \simeq \sqrt{\frac{m}{M}} E_e$$

Inserting the approximate values for the mass ratio m/M we have that E_v is around 10^2 times smaller than E_e .

Let's now consider the rotation of a diatomic molecule. In this simplified case, we have that the moment of inertia is $Ma^2/2$, and the energy associated will then be

$$E_r \simeq \frac{\hbar^2}{Ma^2} \simeq \frac{m}{M} E_e$$

Which gives has an even smaller value than E_v . Therefore we can say that $E_r < E_v < E_e$, and we can imagine E_r, E_v as a first and second order splitting of the initial energy levels E_e

§ 6.2 Born-Oppenheimer Approximation

We now consider a diatomic molecule with nuclei A and B with mass M_a, M_b with together N electrons. The internuclear coordinate will be indicated with $\underline{R} = \underline{R}_B - \underline{R}_A$ and the electronic positions with respect to the center of mass will be indicated by \underline{r}_i . The Schrödinger equation for this system is straightforward, and neglecting spin we have

$$(\hat{T}_N + \hat{T}_e + \hat{V}) |\psi\rangle = E |\psi\rangle \quad (6.1)$$

Where \hat{T}_N is the kinetic energy of the nuclei, \hat{T}_e of the electrons, and \hat{V} is the potential operator. Rewriting everything explicitly, where μ is taken as the reduced mass of the two nuclei, we have

$$\begin{aligned} & -\frac{\hbar^2}{2\mu} \nabla_R^2 \psi(R_j, r_k) - \frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 \psi(R_j, r_k) - \left(\sum_{i=1}^N \frac{Z_A e^2}{4\pi\epsilon_0 |r_i - R_A|} - \right. \\ & \left. - \sum_{i=1}^N \frac{Z_B e^2}{4\pi\epsilon_0 |r_i - R_B|} + \sum_{i>j=1}^N \frac{e^2}{4\pi\epsilon_0 |r_i - r_j|} + \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R} \right) \psi(R_j, r_k) = E \psi(R_j, r_k) \end{aligned} \quad (6.2)$$

This equation is clearly unsolvable. In this case tho, we can suppose that the total wavefunction $|\psi\rangle$ is the product of two wavefunctions, an electronic wavefunction, and a nuclear wavefunction, hence, respectively $|\psi\rangle = |\Phi_q\rangle \otimes |F_q\rangle$.

Here, we have that the electronic wavefunction will depend parametrically by the internuclear distance, and the wave equation searched is the following

$$\begin{aligned} & \hat{T}_e |\Phi_q\rangle + \hat{V} |\Phi_q\rangle = E_q(R) |\Phi_q\rangle \\ & -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 \Phi_q(r_k; R) = E_q(R) \Phi_q(r_k; R) \end{aligned} \quad (6.3)$$

These wavefunctions form a complete basis set for each R , and therefore, we can expand the total molecular wavefunction as follows

$$\psi(R_i, r_k) = \sum_q F_q(R) \Phi_q(r_k; R) \quad (6.4)$$

Reinserting it back on the initial equation, we have that, projecting into the $|\Phi\rangle$ basis, we have

$$\sum_q \int \overline{\Phi_s} \left(\hat{T}_N + \hat{T}_e + \hat{V} - E \right) F_q(R) \Phi_q \, d^N r_i = 0 \quad (6.5)$$

Usin the fact that Φ_q is an eigenfunction for the electronic kinetic energy operator and the potential operator, we have, also considering the orthonormality condition $\langle \Phi_s | \Phi_q \rangle = \delta_{sq}$ we have

$$\sum_q \int \overline{\Phi_s} \hat{T}_N \Phi_q F_q(R) d^N r_i + (E_s(R) - E) F_s(R) = 0 \quad (6.6)$$

Where the operator \hat{T}_N acts as follows

$$\langle x_i | \hat{T}_N | \Phi_q \rangle | F_q \rangle = -\frac{\hbar^2}{2\mu} (F_q \nabla_R^2 \Phi_q + 2 \nabla_R F_q \cdot \nabla_R \Phi_q + \Phi_q \nabla_R^2 \Phi_q) \quad (6.7)$$

Here comes the important piece, as we said before, the motion of the nuclei around the equilibrium value doesn't affect particularly electrons, hence all the $\nabla_R^2 \Phi_q$ parts of the differential equation can be neglected, and we're left with the Nuclear wave equation

$$-\frac{\hbar^2}{2\mu} \nabla_R^2 F_q(R) + (E_q(R) - E) F_q(R) = 0 \quad (6.8)$$

Thus, we have finally that the differential equation (6.2) will be solved with two different equations with the following conditions

$$\begin{aligned} -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 \Phi_q + V(r_k, R) \Phi_q &= E_q(R) \Phi_q \\ -\frac{\hbar^2}{2\mu} \nabla_R^2 F_q + E_q(R) F_q &= E F_q \end{aligned}$$

Where

$$\begin{aligned} \nabla_R \Phi_q &= 0 \\ \psi(R_i, r_k) &= F_q(R_i) \Phi_q(r_k; R_i) \end{aligned}$$

It's of particular interest the fact that the energies found solving the electronic equation $E_q(R)$, while using the Born-Oppenheimer approximation, behave as a potential energy for the nuclear Schrödinger equation.

§ 6.3 Rovibronic States

Let's now analyze properly the nuclear wavefunction. Analyzing the symmetries of the system, it's obvious that this wavefunction will be the product of a radial and an angular part. Already knowing how ∇_R^2 can be written, we have that it must be an eigenfunction of the total angular momentum \hat{J}^2 , \hat{J}_z , and plugging it into (6.8) we get our desired radial equation

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2 \mathcal{F}_{s\nu J}}{\partial R^2} + \frac{\hbar^2}{2\mu R^2} J(J+1) \mathcal{F}_{s\nu J} + (E_s(R) - E_{s\nu J}) \mathcal{F}_{s\nu J} = 0 \quad (6.9)$$

Here ν works as a "principal" quantum number for the quantized levels of the oscillation of the two nuclei, and together with the quantum number J forms the set of Rovibronic States. Another problem ensues from this equation, the "potential" $E_s(R)$ hasn't been determined, and it can't properly be

determined. Hence we approximate it in a power series around the equilibrium position R_0 up to the second order, and since $E'_s(R_0) = 0$, we're left with the following expression

$$E_s(R_0) = E_s(R_0) + \frac{1}{2} \frac{\partial^2 E_s}{\partial R_0^2} + \mathcal{O}((R - R_0)^2) \quad (6.10)$$

Rewriting the second derivative as k , and putting $k/\mu = \omega_0$ we see already how it behaves like a harmonic potential. We immediately write from this that the total energy will be $E_{s\nu J} = E_s(R_0) + E_\nu + E_r$, with the last one being the rotational energy

$$E_r = \frac{\hbar^2}{2\mu R_0^2} J(J+1) = BJ(J+1)$$

Where B is called the rotational constant.

Due to the harmonicity of the new $E_s(R)$ potential, we will have obviously the following result for E_ν

$$E_\nu = \hbar\omega_0 \left(\nu + \frac{1}{2} \right)$$

We can then rewrite our Schrödinger equation as follows, with $\mathcal{F}_{s\nu J} Y_J^M(\theta, \phi) \rightarrow |\nu JM\rangle$

$$\hat{\mathcal{H}}_N |\nu JM\rangle = \left(E_s(R_0) + \hbar\omega_0 \left(\nu + \frac{1}{2} \right) + \frac{\hbar^2}{2\mu R_0^2} J(J+1) \right) |\nu JM\rangle \quad (6.11)$$

A better approximation is given by the empirical Morse potential $V_M(R)$, where

$$V_M(R) = D_e \left(e^{-2\alpha(R-R_0)} - 2e^{\alpha(R-R_0)} \right)$$

With D_e, α constants.

We plug it into our equation as a correction of $E_s(R)$, as $E_s(R) = E_s(\infty) + V(R)$, which then yields D_e as a minimum for $R \rightarrow \infty$, that gives its name as the *dissociation constant* for the molecule.

Approximating again $E_s(R)$ to the second order and equating the coefficients of $E_s(R)$ and $V_M(R)$, we get the following equality

$$D_e \alpha^2 = \frac{1}{2} k \quad (6.12)$$

Now, taking $V_M(R)$ into account, we get the new vibrational energy, which has now an anharmonic correction

$$E_\nu = \hbar\omega_0 \left[\left(\nu + \frac{1}{2} \right) - \beta \left(\nu + \frac{1}{2} \right)^2 \right] \quad (6.13)$$

β is our anharmonicity constant, and from the previous considerations, we get that

$$\beta\omega_0 = \frac{\hbar\omega_0}{4D_e}$$

From the new energy, we now know that at the ground vibrational state $\nu = 0$, is not 0, which gives us the true dissociation energy D_0 as

$$D_0 = E_s(\infty) - E_s(R_0) - \frac{\hbar\omega_0}{2}$$

Or, more explicitly

$$D_0 = D_e - \frac{\hbar\omega_0}{2} \quad (6.14)$$

§§ 6.3.1 Centrifugal Distortion

Now we have determined that the oscillations of the two nuclei are quantized, hence there exists a series of values R_k , which modifies the energies of the system. We now rewrite the nuclear Hamiltonian as follows

$$\hat{\mathcal{H}}_N = \frac{\hat{p}_R^2}{2\mu} + \hat{V}_{eff} - \tilde{E}_{s\nu J} \quad (6.15)$$

Where

$$\begin{aligned} \hat{V}_{eff} &= \hat{V}_M + \frac{\hat{j}^2}{2\mu R^2} \\ \tilde{E}_{s\nu J} &= E_{s\nu J} - E_s(\infty) \end{aligned}$$

Starting from this, we begin to evaluate the energies at $R = R_1$. We start by approximating the effective potential at the new minimum R_1 up until the 4th order

$$V_{eff}(R) \simeq V_0 + \frac{1}{2}\tilde{k}(R - R_1)^2 + c_1(R - R_1)^3 + c_2(R - R_1)^4$$

We search iteratively the exact value of R_1 by deriving $V_{eff}(R)$, and we finally get

$$R_1 \simeq R_0 + \frac{\hbar^2}{2\mu\alpha^2 R_0^3 D_e} J(J+1) \quad (6.16)$$

Where for a simpler calculus we put $c_1 = c_2 = 0$, $D_e\alpha^2 = k/2$ and $\tilde{k} = k$.

Using what we found, and applying the third and fourth order of the approximation as a second order perturbation, we finally get our effective energy $\tilde{E}_{s\nu J}$

$$\begin{aligned} \tilde{E}_{s\nu J} &= -D_e + \hbar\omega_0 \left[\left(\nu + \frac{1}{2} \right) - \beta \left(\nu + \frac{1}{2} \right)^2 \right] + \frac{\hbar^2 J(J+1)}{2\mu R_0^2} - \\ &\quad - \frac{3\hbar^3 \omega_0 J(J+1)}{4\mu\alpha R_0^3 D_e} \left(1 - \frac{1}{\alpha R_0} \right) \left(\nu + \frac{1}{2} \right) - \frac{\hbar^4 J^2(J+1)^2}{4\mu^2 \alpha^2 R_0^6 D_e} \end{aligned} \quad (6.17)$$

This effective energy includes the anharmonic correction to the quantum oscillator, a rotation-vibration coupling correction and a correction to the energy of the rigid rotor. This lets us evaluate directly the centrifugal distortions, since for large ν the average distance $R > R_0$. The same goes for large values of J .

7 Molecular Spectra

§ 7.1 Diatomic Molecules

Let's now consider again the vibration of diatomic molecules, where now we also consider cases where $\Lambda \neq 0$. We then define two "new" operators, $\hat{\underline{N}}$, the angular momentum of the molecule, $\hat{\underline{N}}$, the angular momentum of the two nuclei and the associated total angular momentum operator $\hat{\underline{J}} = \hat{\underline{A}} + \hat{\underline{N}}$. We shall consider cases where the spin-orbit coupling is negligible and no relativistic corrections are considered.

We get back to the definition of $\hat{\underline{N}}$. From the definition of angular momentum, we already know that

$$\hat{\underline{N}} = \hat{\underline{R}} \wedge \hat{\underline{P}} \implies \hat{\underline{N}} \cdot \hat{\underline{R}} = 0$$

Where $\hat{\underline{R}}$ is the internuclear distance operator.

We define the projection on the internuclear axis of the total angular momentum as follows, and we already know that it must have the same value of the projection of $\hat{\underline{A}}$ on the internuclear axis, since $\hat{\underline{N}} \cdot \hat{\underline{R}} = 0$ so

$$\hat{J}_R = \frac{\hat{\underline{J}} \cdot \hat{\underline{R}}}{\hat{R}} = \hat{A}_R$$

Considering now all the symmetries of the system, we can with ease say that $[\hat{\mathcal{H}}, \hat{J}_R] = [\hat{\mathcal{H}}, \hat{J}^2] = 0$, and we can define the eigenstate of the molecule as $|sJM\Lambda\rangle$, where s is a set of quantum numbers which do not intervene in the rotovibration of the molecule

We begin by analyzing the nuclear Schrödinger equation for the diatomic molecule, and we get

$$\begin{aligned} \hat{\mathcal{H}}\mathcal{F}_{s\nu J} &= \left(-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{\langle \hat{N}^2 \rangle}{2\mu R_0^2} \right) \mathcal{F}_{s\nu J} + (E_s(R_0) - E) \mathcal{F}_{s\nu J} = 0 \\ \langle \hat{N}^2 \rangle &= \langle (\hat{J}^2 - \hat{A}^2) \rangle = \hbar^2 J(J+1) + \langle \hat{A}^2 \rangle - 2 \langle \hat{\underline{J}} \cdot \hat{\underline{A}} \rangle \\ \hat{\mathcal{H}}\mathcal{F}_{s\nu J} &= \left(-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{\hbar^2}{2\mu R_0^2} J(J+1) + (E'_s(R_0) - E) \right) \mathcal{F}_{s\nu J} = 0 \\ E'_s(R_0) &= E_s(R_0) + \frac{1}{2\mu R_0} \left(\langle \hat{A}^2 \rangle - 2 \langle \hat{\underline{J}} \cdot \hat{\underline{A}} \rangle \right) = \\ &= E_s(R_0) + \frac{1}{2\mu R_0} \left(\langle \hat{A}^2 \rangle - 2\hbar^2 \Lambda^2 \right) \end{aligned} \tag{7.1}$$

The choice of redefining $E_s(R_0)$ is immediate, by noting how the terms defining $E'_s(R_0)$ all depend on the electronic terms of the molecule.

Another way of considering the rotation of a molecule, is given by starting from the basic approximation that a molecule could be seen as an almost completely rigid body, and therefore, in the system of the center of mass of the molecule, we can write that the kinetic energy operator will be the following in the coordinates where the inertia tensor is diagonal:

$$\hat{T} = \frac{1}{2I_a} \hat{J}_a^2 + \frac{1}{2I_b} \hat{J}_b^2 + \frac{1}{2I_c} \hat{J}_c^2 \quad (7.2)$$

Since in a diatomic molecule one of the eigenaxis will be the internuclear axis, let's say it's the c axis, we get that $I_a = I_b$, and $\hat{J}_c = \hat{\Lambda}_R$

$$\hat{T} = \frac{1}{2I_a} (\hat{J}_a^2 + \hat{J}_b^2) + \left(\frac{1}{2I_c} + \frac{1}{2I_b} \right) \hat{\Lambda}_R^2$$

This equation is the same equation of a symmetric top. For a diatomic molecule we have that $I_a = \mu R_0^2$ and that I_c depends directly on the electronic terms of the molecule

From this we have

$$E_r = \frac{\hbar^2}{2\mu R_0^2} J(J+1) + \left(\frac{1}{2I_c} + \frac{1}{2I_b} \right) \hbar^2 \Lambda^2 \quad (7.3)$$

This point of view makes the generalization to polyatomic molecules much more easy to derive.

§ 7.2 Rovibrational Spectra of Diatomic Molecules

Let's begin considering interaction with the radiation field and the possible transition for the rovibronic states. We define as usual the dipole operator as the sum of the dipole moments of the nuclei and of the electrons

$$\hat{D}_j = e \left(\sum_i Z_i \hat{R}_{ij} - \sum_i \hat{r}_{ij} \right) \quad (7.4)$$

As we did before, we approximate the system by considering no coupling between angular momentums and by neglecting rotovibrational motions.

The molecular wavefunction in study will then be a product of the electronic wavefunction, a vibrational wavefunction and a rotational wavefunction, with the following quantum numbers

$$|\Psi\rangle = \frac{1}{R} |s\rangle_{e-} |\nu\rangle |JM\Lambda\rangle \quad (7.5)$$

Where, $|\nu\rangle$ is the standard eigenfunction of the quantum harmonic oscillator.

Disregarding spin in our calculations, we define the *permanent electric dipole moment* δ of the molecule as the diagonal elements of the \hat{D}_i operator.

$$\hat{D}_{\alpha\alpha} = \langle \alpha | \hat{D} | \alpha \rangle = \delta$$

These matrix elements always vanish if $|\alpha\rangle$ is a nondegenerate state, but also it doesn't fade if there is an excess of charge in one of the two nuclei, which is always true when we consider heteronuclear

molecules.

Since homonuclear molecules are symmetric, all elements of the dipole operator will be zero, and therefore transition can happen only if there is an electronic transition, since $J \geq |\Lambda|$. So, for the already known transition rules for $\Lambda = 0$

$$\begin{aligned}\Delta J &= \pm 1 \\ \Delta M &= 0, \pm 1\end{aligned}$$

We have, for $\Lambda \neq 0$

$$\begin{aligned}\Delta J &= 0, \pm 1 & \Delta J &= 0 \text{ if only if } \Lambda \neq 0 \\ \Delta M &= 0, \pm 1 \\ \Delta \Lambda &= 0\end{aligned}$$

The spectrum found will lay on the far IR or the microwave region of frequencies for diatomic molecules, which will have a definite energy

$$\hbar\Delta\omega_{\Delta J} = E_r(J+1) - E_r(J) = 2B(J+1) \quad (7.6)$$

As we said before, vibrational transitions can happen if and only if the vibrational matrix elements of the dipole operator are nonzero, i.e. if the following integral is nonzero

$$\hat{D}_{\nu\nu'} = \langle \nu | \hat{D} | \nu' \rangle \quad (7.7)$$

Expanding the integral in power series, and using the definition of Hermite polynomials, we have that the integral depends only on $(R - R_0)$.

$$\begin{aligned}\hat{D}(R) &\simeq \hat{D}(R_0) + \left. \frac{\partial \hat{D}}{\partial R} \right|_{R=R_0} (R - R_0) + \dots \\ I(\nu, \nu') &= \int \overline{\psi_{\nu'}}(R - R_0) \psi_{\nu} dR \\ \psi_{\nu}(x) &= N_{\nu} H_{\nu}(\alpha x) e^{-\frac{\alpha^2 x^2}{2}}\end{aligned} \quad (7.8)$$

Using the following recursion relation of the Hermite polynomials

$$2\alpha x H_{\nu}(\alpha x) = 2\nu H_{\nu-1}(\alpha x) + H_{\nu+1}(\alpha x)$$

We have that the integral will be nonzero if and only if $\Delta\nu = \pm 1$

The selection rules then are the following

$$\begin{aligned}\Delta J &= 0, \pm 1 \\ \Delta M &= 0, \pm 1 \\ \Delta \Lambda &= 0 \\ \Delta \nu &= \pm 1\end{aligned} \quad (7.9)$$

We can delve deeper into the $\Delta J = \pm 1$ transitions. We can define two different branches, i.e. R branches, if $\Delta J = -1$, and P branches when $\Delta J = 1$. The two sets will have the following separations between levels

$$\begin{aligned}\hbar\omega_R &= E_r(\nu+1, J+1) - E_r(\nu, J) = 2B(J+1) + \hbar\omega_0 \\ \hbar\omega_P &= E_r(\nu-1, J-1) - E_r(\nu, J) = \hbar\omega_0 - 2BJ\end{aligned} \quad (7.10)$$

Both branches form what's usually called as *vibrational-rotational branch*, which is formed by lines spaced by $2B/h$.

There exists a third branch of the spectrum given by the anharmonicity of the oscillation of the molecule, the Q branch. If $B_\nu = B_{\nu+1}$, we have that

$$\hbar\omega_Q = E_r(\nu + 1, J) - E(\nu, J) = \hbar\omega_0 \quad (7.11)$$

§§ 7.2.1 Raman Scattering

We get back to our consideration of homonuclear diatomic molecules. We saw that for $\Lambda = 0$ no transitions are possible due to the symmetry of the molecule, this is not properly true, since there can be a particular kind of transitions given by an inelastic scattering, called Raman scattering.

Raman scattering works as a second order process, where a photon with energy $\hbar\omega$ is absorbed from an atom or a molecule, which is excited from a state a to a state n , and then emits a second photon with energy $\hbar\omega'$ while decaying to the final state b . In this case, if $a = b$, we get again Rayleigh scattering. In other cases, using the conservation of energy we have

$$\hbar\omega' = \hbar\omega + \Delta E_{ab} \quad (7.12)$$

In general, this kind of scattering permits the existence of another selection rule, valid only for Raman scattering

$$\Delta J = 0, \pm 2 \quad (7.13)$$

Let's consider now two particular cases. If the state a is the ground state of the molecule, the state b must have higher energy, so $\omega' < \omega$, and the observed line is called a *Stokes line*, whereas in the opposite case, we have that $\omega' > \omega$ and this line is called the *Anti-Stokes line*

§ 7.3 Electronic Spectra

The electronic spectra of diatomic molecules is given by combined electronic-rovibronic transitions. The lines associated with this transitions lay on the visible or in the UV part of the light spectrum. We can immediately say that the frequency separation of these lines will be

$$\omega = \frac{(E_{s'} + E_{\nu'} + E_{r'}) - (E_s + E_\nu + E_r)}{\hbar} \quad (7.14)$$

This is obviously given by three different components, i.e. the *vibrational* or *band structure*, the *rotational structure* and the *fine structure* of the total band.

Keeping only the first two terms and ignoring rotational variations we can see that in general, the transitions will have the following energy separation

$$\hbar\omega = \hbar\omega_{s's} + \hbar\omega'_0 \left(\nu' + \frac{1}{2} \right) - \hbar\omega_0 \left(\nu + \frac{1}{2} \right) \quad (7.15)$$

Or, introducing again the anharmonicity of the oscillator, we get the *Deslandres formula*

$$\hbar\omega_D = \hbar\omega_{s's} + \hbar\omega'_0 \left(\nu' + \frac{1}{2} \right) - \hbar\beta'\omega'_0 \left(\nu' + \frac{1}{2} \right)^2 - \hbar\omega_0 \left(\nu + \frac{1}{2} \right) + \hbar\beta\omega_0 \left(\nu + \frac{1}{2} \right)^2 \quad (7.16)$$

The series of lines obtained from these transitions is called a ν progression.

Adding back the E_r term, we are obliged to use the selection rules for J .

If we now consider spin, in absence of coupling we get $\Delta S = 0$ and for transitions between Σ states we have $\Sigma^+ \leftrightarrow \Sigma^+$ and $\Sigma^- \leftrightarrow \Sigma^-$. Due to symmetry reasons we also have the selection rule $g \leftrightarrow u$.

The three branches, having considered the new selection rules and considering the centrifugal distortion

$$\begin{aligned}\hbar\omega_P &= \hbar\omega_D + B'J(J-1) - BJ(J+1) \\ \hbar\omega_Q &= \hbar\omega_D + B'J(J+1) - BJ(J+1) \\ \hbar\omega_R &= \hbar\omega_D + B'(J+1)(J+2) - BJ(J+1)\end{aligned}\quad (7.17)$$

It's evident that these formulas, after substituting the Deslandres equation for $\hbar\omega_D$, are not linear nor quadratic in J , but rather *parabolic* in J , which give a *Fortrat parabola*. Since $B' \neq B$ we also see that the lines aren't equally spaced, which is closely tied to the centrifugal distortion that we have already treated

§§ 7.3.1 The Franck-Condon Principle

The Franck-Condon principle is based on the idea that the atoms of the molecule do not move during the electronic transition but after. This is represented on the energy graph of the molecule as a vertical line between two electronic curves, where the centrifugal distortion gets considered.

This principle can be seen in action considering the total wavefunction $\Psi_\alpha = R^{-1}\Phi_s\psi_\nu\phi_{JMA}$ and evaluating the dipole moment operator's matrix elements

$$\hat{D}_{\alpha'\alpha} = e \int R^{-2} d^3R \int \overline{\Phi_{s'}\psi_{\nu'}\phi_{J'M'\Lambda'}} \left(\sum_{i=1}^2 Z_i R_{ij} - \sum_i r_{ij} \right) \Phi_s\psi_\nu\phi_{JMA} d^3r \quad (7.18)$$

From the definition of the dipole moment operator we take only the electronic part of the dipole operator

$$\hat{D}_{e-}(R) = -e \langle s | \sum_i \hat{r}_{ij} | s \rangle \rightarrow -e \int \overline{\Phi_s} \sum_i \hat{r}_{ij} \Phi_s d^3r$$

The Franck-Condon principle then amounts to saying that this operator is independent of R , so that the transition amplitudes will be always proportional to the *Franck-Condon factor*

$$f_{\nu'\nu} = \int \overline{\psi_{\nu'}} \psi_\nu dR \quad (7.19)$$

This simply represents the overlap integral between two vibrational wavefunctions in different electronic states.

§§§ 7.3.1.1 Fluorescence and Phosphorescence

One event that can be explained using the Franck-Condon principle is fluorescence and phosphorescence, which is an effect given by some molecules, where the radiation absorbed in the near-UV gets re-emitted at a longer wavelength, whereas in phosphorescence, it's involved the decay from an excited state to a second state with different multiplicity.

Fluorescence can be graphed as a transition from an electronic level to a second level, respecting the Franck-Condon principle. Let's take as an example a molecule in the ground state 1X , which get

excited to a second state 1A , which slowly decays level by level up until getting back down to the 1X state.

In this case, the effect of fluorescence can be seen as the slow decay from the excited state 1A to the ground state 1X , where all the decays emit photons in the range of visible and near-UV light.

Phosphorescence, instead, can be seen as a process $^1X \rightarrow ^1A \rightarrow ^3A \rightarrow ^1X$, where the molecule “slips” from the state 1A to the state 3A due to the nonzero multiplicity of this state.

§ 7.4 Inversion Spectrum of Ammonia (NH_3)

The ammonia molecule is a pyramidal molecule composed by a nitrogen atom at the summit and three hydrogens at the basis

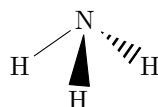


Figure 7.1: Structure of the Ammonia molecule (NH_3)

This geometry is twice degenerate, since we can invert the molecule using the nitrogen atom as an inversion point.

The vibrational modes of this molecule can be seen as an umbrella opening and closing with respect to the hydrogen plane of the molecule. The nitrogen atom can overpass this plane, hence the vibrational potential must have two wells for the two possible stable oscillation points.

Considering this well and doing a couple calculations, we can see that the transition between vibrational states $\nu = 0 \rightarrow \nu = 1$ is classically forbidden, but possible in the framework of quantum tunneling.

The tunneling of the wavefunction permits the removal of the degeneracy, hence forming a doublet. In order to define properly this situation we consider the whole molecule as a two level system, where the upper level is the “up” configuration, where the nitrogen atom rests above the hydrogen plane, and a second “down” configuration where the nitrogen atom is below the hydrogen plane.

The wavefunctions representing these states are eigenvalues of the parity operator, and therefore we can write

$$\begin{aligned} |1\rangle &= \frac{1}{\sqrt{2}} (|u\rangle + |d\rangle) \\ |2\rangle &= \frac{1}{\sqrt{2}} (|u\rangle - |d\rangle) \end{aligned} \quad (7.20)$$

We also have that the nitrogen atom could *probably* be above or below the hydrogen plane, so we can also write a third wavefunction. We will directly write the time-dependent wavefunction of the system, which is the following

$$\Psi(z, t) = \frac{1}{\sqrt{2}} \left(\psi_1(z) e^{-i \frac{E_1 t}{\hbar}} + \psi_2(z) e^{-i \frac{E_2 t}{\hbar}} \right) = \frac{1}{\sqrt{2}} \left(\psi_1(z) + \psi_2(z) e^{-2\pi i \omega t} \right) e^{-i \frac{E_1 t}{\hbar}} \quad (7.21)$$

Where we used $\Delta E = \hbar \omega$.

Explicating the two wavefunctions and setting $t = 1/4\pi\omega$ we get

$$\Psi(z, t) = \psi_d(z) e^{-i \frac{E_1 t}{\hbar}} \quad (7.22)$$

So that we have that the probability density of the wavefunction is simply $|\psi_d(z)|^2$

8 Molecular Electronic Structure

It's now time to analyze the electronic structure of diatomic molecules. We begin with the usual multielectron Hamiltonian without fine and hyperfine corrections. We choose for easier calculus the z -axis as the internuclear axis, and in this case we can immediately say that

$$[\hat{\mathcal{H}}, \hat{L}_z] = 0$$

It's also obvious that due to the nature of the system, $\hat{L}_x, \hat{L}_y, \hat{L}^2$ «do not» commute with the Hamiltonian of this system (this can be proved through direct calculus). Due to the previous statement, we know that the electronic eigenfunctions of the molecular Hamiltonian Φ_s are simultaneous eigenfunctions of $\hat{\mathcal{H}}$ and \hat{L}_z .

Since $\hat{L}_z \rightarrow i\hbar\partial_\phi$, we can solve directly for the angular part through separation of variables. We suppose that $\Phi_s(r_i; R) = f_r(R; r_i)\eta(\phi)$, solving then for η we have

$$\eta(\phi) = e^{iM_L\phi} \quad (8.1)$$

In molecular physics tho is common to use a new quantum number, $\Lambda = |M_L|$, therefore, we can then write for Φ_s (with appropriate normalization)

$$\Phi_s(R; r_i) = \frac{1}{\sqrt{2\pi}} f_s(r) e^{\pm i\Lambda\phi} \quad (8.2)$$

In the usual spectroscopic notation, we now have m_l for single particles, M_L for atoms and Λ for molecules, and it follows a similar pattern. It's also used $\lambda = |m_l|$ for single molecular electrons

Quantum Number	0	1	2	3...
m_l	s	p	d	f...
M_L	S	P	D	F...
Λ	Σ	Π	Δ	$\Phi...$
λ	σ	π	δ	$\phi...$

Table 8.1: Table of quantum numbers in spectroscopic notation

Let's get back to our molecular system. Through a quick sketch of a diatomic molecule it's obvious that, if the z -axis is taken as the intermolecular axis, the system is invariant for reflections along the

$x - y$ plane. Let's call this reflection operator \hat{A}_{xy} . Since it's a reflection we know that $\hat{A}_{xy}^2 = \hat{1}$ and its eigenvalues are ± 1 , and from the previous consideration that

$$[\hat{\mathcal{H}}, \hat{A}_{xy}]$$

Writing out explicitly the angular momentum operator $\hat{L}_z = \hat{\Lambda}_z$ (using $\hat{\Lambda}$ makes it easier to distinguish this operator from the usual angular momentum operators) in Cartesian form ($\hat{\Lambda}_z \rightarrow i\hbar y \partial_x - i\hbar x \partial_y$), and knowing that \hat{A}_{xy} maps $y \rightarrow -y$, we also have that these two operators anticommute.

$$\{\hat{\Lambda}_z, \hat{A}_{xy}\} = 0$$

We therefore have that, for states with $\Lambda \neq 0$

$$\hat{\Lambda}_z \hat{A}_{xy} |\Lambda\rangle = -\hat{A}_{xy} \hat{\Lambda}_z |\Lambda\rangle = \pm \hbar \Lambda |\Lambda\rangle \quad (8.3)$$

Depending on the symmetry of the wavefunction, this brings up what is usually called Λ -doubling, i.e. a two-fold degeneracy on levels given by the symmetries of the system.

A particular case happens when $\Lambda = 0$, in this case we can construct simultaneous eigenfunctions of $\hat{\mathcal{H}}, \hat{\Lambda}_z, \hat{A}_{xy}$, and the degeneracy is broken into two non-degenerate states, Σ^+, Σ^- , where for the first the wavefunction is unchanged on reflections along the internuclear axis, and for the second state that the wavefunction changes sign ($\hat{A}_{xy} |a\rangle = \pm |a\rangle$).

Therefore, for inversions of the kind $\underline{r}_i \rightarrow -\underline{r}_i$, we can define states which are invariant and non-invariant to this transformation, these will be indicated by either a subscript g or u , which come from the German *gerade* and *ungerade*, which mean respectively "even" and "odd".

For homonuclear diatomic molecules, the behavior of the Σ wavefunctions through the inversions $y_i \rightarrow -y_i$ and $\underline{r}_i \rightarrow -\underline{r}_i$, give the additional definition of 4 non degenerate Σ states, respectively $\Sigma_g^+, \Sigma_g^-, \Sigma_u^+, \Sigma_u^-$.

These states can be determined precisely by considering the inversion $\underline{R} \rightarrow -\underline{R}$, made by the composition of the inversion $y_i \rightarrow -y_i$ and $\underline{r}_i \rightarrow -\underline{r}_i$. The result of these inversion will be an unchanged sign for Σ_g^+, Σ_u^- wavefunctions and a changed sign for Σ_g^-, Σ_u^+ wavefunctions.

Considering now the spin of the molecular electrons, we're left with the usual operator \hat{S} , with the usual eigenvalues. With spin, we can write the terms as follows

$$^{2S+1}\Lambda_{g/u}$$

The ground states are usually indicated as $X^{2S+1}\Lambda_{g/u}$, and for diatomic molecules, they are usually $X^1\Sigma^+$ and $X^1\Sigma_g^+$ for homonuclear diatomic molecules, with some exceptions¹

§ 8.1 Approximation Methods and the H₂ Molecule

§§ 8.1.1 Linear Combination Of Atomic Orbitals (LCAO-MO)

A great example of a molecular system that can be analyzed, is the *Dihydrogen cation*, i.e. the molecule H_2^+ .

¹See O_2 and NO , which have as ground states $X^3\Sigma_g$ and $X^2\Pi$, respectively

Considering all particles present in the system, we can write our Hamiltonian as follows (using atomic units $\hbar = 1, k_e = 1, e = 1, m_e = 1$)

$$\hat{\mathcal{H}}_{H_2^+} = -\frac{1}{2}\nabla_r^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R} \quad (8.4)$$

Where r, r_a, r_b are not independent, given in terms of the distance between the two nuclei R , as

$$\begin{aligned} r_a &= r + \frac{R}{2} \\ r_b &= r - \frac{R}{2} \end{aligned}$$

The Schrödinger equation can be exactly solved, but it's useful to firstly develop the Linear Combination of Atomic Orbitals (LCAO) approximation technique.

As we have already seen, at great distances, we must have that the system is a simple hydrogen atom, hence

$$|\Phi\rangle = |1s\rangle$$

Where the $1s$ orbital takes into consideration whether it's bound to the nucleus a or b .

From this, we can construct two molecular wavefunctions with either an even (gerade) symmetry or an uneven (ungerade) symmetry.

We have

$$\begin{aligned} |g\rangle &= \frac{1}{\sqrt{2}} (|1s\rangle_a + |1s\rangle_b) \\ |u\rangle &= \frac{1}{\sqrt{2}} (|1s\rangle_a - |1s\rangle_b) \end{aligned} \quad (8.5)$$

We then can find our molecular energy levels by plugging it into our variational equation

$$E_{g,u}(R) = \frac{\langle g, u | \hat{\mathcal{H}} | g, u \rangle}{\langle g, u | g, u \rangle}$$

Let's calculate firstly the normalization of the state $|g, u\rangle$. We have

$$\begin{aligned} \langle g, u | g, u \rangle &= \frac{1}{2} (\langle 1s|_a \pm \langle 1s|_b) (\langle 1s|_a \pm |1s\rangle_b) \\ &= \frac{1}{2} (\langle 1s|1s\rangle_a + \langle 1s|1s\rangle_b \pm 2 \langle 1s|1s\rangle_{ab}) = \\ &= 1 \pm \langle 1s|1s\rangle_{ab} = 1 \pm I(R) \end{aligned} \quad (8.6)$$

Where $I(R) = \langle 1s|1s\rangle_{ab}$ is an overlap integral, which can be calculated, considering that

$$\langle r | 1s \rangle = \psi_{1s}(r) = \frac{1}{\pi} e^{-r}$$

A piece-by-piece calculation of this and some further integrals will be given in an appendix, but for now, we have that the result is

$$I(R) = \left(1 + R + \frac{1}{3}R^2\right) e^{-R}$$

We then evaluate the numerator, keeping in mind that these two Schrödinger equations also hold

$$\begin{aligned}\left(\frac{1}{2}\hat{p}_r^2 - \frac{1}{r_a}\right) |1s\rangle_a &= E_{1s} |1s\rangle_a \\ \left(\frac{1}{2}\hat{p}_r^2 - \frac{1}{r_b}\right) |1s\rangle_b &= E_{1s} |1s\rangle_b\end{aligned}$$

So, we then have, expanding $|g, u\rangle$ in its composing kets

$$\begin{aligned}\langle g, u | \hat{H} | g, u \rangle &= \frac{1}{2} (\langle 1s |_a \pm \langle 1s |_b) \hat{H} (|1s\rangle_a \pm |1s\rangle_b) \\ &= \langle 1s | \hat{H} | 1s \rangle_a \pm \langle 1s | \hat{H} | 1s \rangle_{ab}\end{aligned}\tag{8.7}$$

Writing the Hamiltonian and distributing once again, we get

$$\begin{aligned}\langle g, u | \hat{H} | g, u \rangle &= \left(E_{1s} + \frac{1}{R}\right) - \langle 1s | \frac{1}{r_b} | 1s \rangle_a \pm \left(E_{1s} + \frac{1}{R}\right) \langle 1s | 1s \rangle_{ab} \pm \langle 1s | \frac{1}{r_b} | 1s \rangle_{ab} \\ &= E_{1s} (1 \pm I(R)) \pm \frac{1}{R} I(R) + \frac{1}{R} - \langle 1s | \frac{1}{r_b} | 1s \rangle_a \pm \langle 1s | \frac{1}{r_b} | 1s \rangle_{ab}\end{aligned}\tag{8.8}$$

Solving the two last integrals and putting everything together, we finally get

$$E_{g,u}(R) = E_{1s} + \frac{(1+R)e^{-2R} \pm (1 - \frac{2}{3}R^2)e^{-R}}{R \pm (1+R + \frac{1}{3}R^2)Re^{-R}}\tag{8.9}$$

From this, we can then define the two following levels

$$\begin{aligned}\hat{H}_{H_2^+} |g\rangle &= E_g(R) |g\rangle \\ \hat{H}_{H_2^+} |u\rangle &= E_u(R) |u\rangle\end{aligned}$$

The first energy is the one for which the wavefunction is symmetrical ($\pm \rightarrow +$). For this wavefunction, if plotted or calculated, it's easy to see that there exists a well, for which the molecule can bond, and therefore, this molecular orbital is said to be a *bonding orbital*, indicated by the term σ_g , in the other case, for the uneven wavefunction, there is no energetic well, hence it's easy to see how this orbital doesn't contribute to the bonding of the molecule, hence it's called an *antibonding orbital*, and it's indicated by the term σ_u^* . The second approach, after the molecule H_2^+ , is the actual hydrogen molecule H_2 , which has two electrons.

We shall build its electronic wavefunctions using what we found for the dihydrogen cation.

We already know that the eigenspinors must either be a singlet state $S = \sum_i s_i = 0$ or a triplet state. We can immediately write these spinors, starting from the singlet state (remembering that $a \otimes b \neq b \otimes a$, for two vectors $a, b \in \mathbb{H}$, here due to the indistinguishability of the two electrons it only matters to know that the first ket is referring to the first electron and the second ket, obviously, to the second and last electron)

$$\begin{aligned}|00\rangle &= \frac{1}{\sqrt{2}} [|\uparrow\rangle \otimes |\downarrow\rangle - |\downarrow\rangle \otimes |\uparrow\rangle] \\ |11\rangle &= |\uparrow\rangle \otimes |\uparrow\rangle \\ |10\rangle &= \frac{1}{\sqrt{2}} [|\uparrow\rangle \otimes |\downarrow\rangle + |\downarrow\rangle \otimes |\uparrow\rangle] \\ |1-1\rangle &= |\downarrow\rangle \otimes |\downarrow\rangle\end{aligned}\tag{8.10}$$

Using the two eigenfunctions $|u\rangle, |g\rangle$ we can then form four combinations of the two

$$\begin{aligned} |A\rangle &= [|g\rangle \otimes |g\rangle] \otimes |00\rangle \\ |B\rangle &= [|u\rangle \otimes |u\rangle] \otimes |00\rangle \\ |C\rangle &= \frac{1}{\sqrt{2}} [|g\rangle \otimes |u\rangle + |u\rangle \otimes |g\rangle] \otimes |00\rangle \\ |D\rangle &= \frac{1}{\sqrt{2}} [|g\rangle \otimes |u\rangle - |u\rangle \otimes |g\rangle] \otimes |1, M_S\rangle \end{aligned} \quad (8.11)$$

It's immediate to see that, since $|g\rangle, |u\rangle$, as calculated previously for H_2^+ , are either σ_g or σ_u^* states, that $|A\rangle, |B\rangle$ represent $^1\Sigma_g^+$, while $|C\rangle$ represents a $^1\Sigma_u^+$ state, and $|D\rangle$ represents the remaining $^3\Sigma_u^+$ states. The exact Hamiltonian for the Hydrogen molecule is, in atomic units

$$\hat{H}_{H_2} = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) - \sum_{i=1}^2 \frac{1}{r_{ai}} - \sum_{i=1}^2 \frac{1}{r_{bi}} + \frac{1}{r_{12}} + \frac{1}{R} \quad (8.12)$$

Regrouping the two single electron Hamiltonians as \hat{h}_i , and remembering that

$$\hat{h}_i |g, u\rangle = \left(E_{g,u}(R) - \frac{1}{R} \right) |g, u\rangle$$

We get by using the eigenket $|A\rangle$, imposing without loss of generality that $\langle g, u | g, u \rangle = 1$, that the associated energy will be, after plugging everything into the Rayleigh-Ritz variational expression, that

$$\begin{aligned} E_A &= \langle 00 | \langle g | \otimes \langle g | \hat{H} | g \rangle \otimes | g \rangle | 00 \rangle \\ &= \langle 00 | \langle g | \otimes \langle g | \sum_{i=1}^2 \hat{h}_i + \frac{1}{r_{12}} | g \rangle \otimes | g \rangle | 00 \rangle \\ &= 2E_g(R) - \frac{1}{R} + \langle 00 | \langle g | \otimes \langle g | \frac{1}{r_{12}} | g \rangle \otimes | g \rangle | 00 \rangle \end{aligned} \quad (8.13)$$

The last expression, corresponds to the following integral

$$\iint \bar{\Phi}_g(r_1) \bar{\Phi}_g(r_2) \frac{1}{r_{12}} \Phi_g(r_1) \Phi_g(r_2) d^3r_1 d^3r_2 = \iint \frac{|\Phi_g(r_1)|^2 |\Phi_g(r_2)|^2}{r_{12}} d^3r_1 d^3r_2$$

This integral can be computed using the approximate LCAO form, or the "exact" solution of the Schrödinger equation for the H_2^+ molecule.

Using the LCAO form of $|g\rangle$, we can then write in extensive form

$$\begin{aligned} |A\rangle &= |g\rangle_1 \otimes |g\rangle_2 |00\rangle = \\ &= \frac{1}{2} (|1s\rangle_a \otimes |1s\rangle_b + |1s\rangle_b \otimes |1s\rangle_a + |1s\rangle_a \otimes |1s\rangle_a + |1s\rangle_b \otimes |1s\rangle_b) |00\rangle \end{aligned} \quad (8.14)$$

Or, using directly the Schrödinger representation of eigenstates

$$\begin{aligned} \langle r_{ij} | A \rangle &= \Phi_A = \frac{1}{2} (\psi_{1s}(r_{a1}) \psi_{1s}(r_{b2}) + \psi_{1s}(r_{b1}) \psi_{1s}(r_{a2}) + \\ &\quad + \psi_{1s}(r_{a1}) \psi_{1s}(r_{a2}) + \psi_{1s}(r_{b1}) \psi_{1s}(r_{b2})) \chi_{00}(r_1, r_2) \end{aligned} \quad (8.15)$$

It's easy to see how this eigenstate can be expressed by a superposition of two states, as $|A\rangle = |A\rangle_{cov} + |A\rangle_{ion}$, which represent two types of molecular bonding already known in chemistry: *covalent* and *ionic bonding*. Using the previous expression, we can write these two kinds of bonding as follows

$$\begin{aligned} |A\rangle_{cov} &= \frac{1}{2} (|1s\rangle_a \otimes |1s\rangle_b + |1s\rangle_b \otimes |1s\rangle_a) |00\rangle \\ |A\rangle_{ion} &= \frac{1}{2} (|1s\rangle_a \otimes |1s\rangle_a + |1s\rangle_b \otimes |1s\rangle_b) |00\rangle \end{aligned} \quad (8.16)$$

It's immediate to see how the covalent eigenstate ($|A\rangle_{cov}$) represents a situation where the two electrons (remember that we're working in a Hilbert space of the kind $\mathbb{H}_1 \otimes \mathbb{H}_2$) are bound to both nuclei, whereas the ionic eigenstate represents a situation where both electrons are bound to one nucleus. Using the LCAO approximation, in the limit $R \rightarrow \infty$, the covalent bond yields two hydrogen atoms ($H_2 \rightarrow H + H$), whereas the second yields one proton and a negative hydrogen ion ($H_2 \rightarrow H^- + p^+$).

A better approximation can be given using the Rayleigh-Ritz variational principle, with a trial eigenket $|\lambda\rangle$, formed by an equal mixture of the two states $|A\rangle$ and $|B\rangle$, which both have symmetry $^1\Sigma_g^+$. Noting that the state $|B\rangle$ is the following

$$|B\rangle = \frac{1}{2} (|1s\rangle_A \otimes |1s\rangle_A - |1s\rangle_A \otimes |1s\rangle_B - |1s\rangle_B \otimes |1s\rangle_A + |1s\rangle_B \otimes |1s\rangle_B) |00\rangle$$

The eigenstate $|\lambda\rangle$ will then have the following definition

$$\begin{aligned} |\lambda\rangle &= |A\rangle + \lambda |B\rangle \\ |\lambda\rangle &= \frac{1}{2} [(1 - \lambda) (|1s\rangle_A \otimes |1s\rangle_B + |1s\rangle_B \otimes |1s\rangle_A) \\ &\quad + (1 + \lambda) (|1s\rangle_A \otimes |1s\rangle_A + |1s\rangle_B \otimes |1s\rangle_B)] |00\rangle \\ |\lambda\rangle &= (1 - \lambda) |A\rangle_{cov} + (1 + \lambda) |A\rangle_{ion} \end{aligned} \quad (8.17)$$

Using the Rayleigh Ritz variational method, it's possible to calculate the energy of the system in relation to the parameter λ , as follows

$$E(\lambda) = \frac{\langle \lambda | \hat{H} | \lambda \rangle}{\langle \lambda | \lambda \rangle} \quad (8.18)$$

Finding the extremum, (i.e. where $\delta E(\lambda) = 0$, i.e. $\partial_\lambda E = 0$ and λ_0 is an extremum) it is possible to find values closer to the experimental values than the previous approximations.

§§ 8.1.2 Heiter-London Valence Bond Method (VB-MO)

Considering now the *Valence Bond method*, we approximate the wavefunction for H_2 basing ourselves on the separated atom wavefunctions.

We begin taking the triplet sigma wavefunction $|D\rangle$, for which, the covalent part is the following

$$|D\rangle_{cov} = \frac{1}{2} (|1s\rangle_A \otimes |1s\rangle_B - |1s\rangle_B \otimes |1s\rangle_A) |1M_S\rangle \quad (8.19)$$

This wavefunction has the symmetry $^3\Sigma_u^+$. Now, substituting this and $|A\rangle_{cov}$ for the $^1\Sigma_g^+$ term in the variational equation, we get that the searched energy for gerade and ungerade states is the following

$$E_{g,u}(R) = 2E_{1s} + \frac{J \pm K}{1 \pm I^2} + \frac{1}{R} \quad (8.20)$$

Where (using Schrödinger's representation), we have that

$$\begin{aligned} I &= \int \psi_{1s}(r_{A1}) \psi_{1s}(r_{B1}) d^3r_1 \\ J &= \iint |\psi_{1s}(r_{A1})|^2 \left(\frac{1}{r_{12}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} \right) |\psi_{1s}(r_{B2})|^2 d^3r_1 d^3r_2 \\ K &= \iint \bar{\psi}_{1s}(r_{A1}) \bar{\psi}_{1s}(r_{B2}) \left(\frac{1}{r_{12}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} \right) \psi_{1s}(r_{A2}) \psi_{1s}(r_{B1}) \end{aligned}$$

In order to get these two results we begin by inserting everything into the Rayleigh-Ritz equation. For the ${}^3\Sigma_u^+$ we have

$$E_u(R) = \frac{\langle D | \hat{H} | D \rangle_c}{\langle D | D \rangle_c}$$

We begin calculating the normalization factor $\langle D | D \rangle$

$$\begin{aligned} \langle D | D \rangle_c &= \frac{1}{4} (\langle 1s |_A \otimes \langle 1s |_B - \langle 1s |_B \otimes \langle 1s |_A) \otimes (|1s \rangle_A \otimes |1s \rangle_B - |1s \rangle_B \otimes |1s \rangle_A) = \\ &= \frac{1}{4} (2 \langle 1s | 1s \rangle_A \langle 1s | 1s \rangle_B - 2 \langle 1s | 1s \rangle_{AB} \langle 1s | 1s \rangle_{BA}) = \\ &= \frac{1}{2} (1 - \langle 1s | 1s \rangle_{AB1}^2) \end{aligned}$$

Where, $\langle 1s | 1s \rangle_{AB1} = \langle 1s | 1s \rangle_{AB2} = I$

Secondly, we find the expectation value of the Hamiltonian $\langle \hat{H} \rangle_{D_c}$. We begin by noting that the Hamiltonian can be separated into the sum of three Hamiltonians

$$\begin{aligned} \hat{H} &= \hat{h}_a + \hat{h}_b + \hat{h}_{12} = 2\hat{h}_a - \hat{h}_{12} \\ \hat{h}_a &= \frac{\hat{p}^2}{2} - \frac{1}{r_{a1}} \\ \hat{h}_b &= \frac{\hat{p}^2}{2} - \frac{1}{r_{b2}} \\ \hat{h}_{12} &= \frac{1}{r_{12}} + \frac{1}{R} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} \end{aligned}$$

In order to ease the notation in this calculation we will indicate $|1s \rangle_i \otimes$ as $|1 \rangle_i$ and $\otimes |1s \rangle_i$ as $|2 \rangle_i$. In this notation, we have $|D \rangle_c = 1/2(|1 \rangle_A |2 \rangle_B - |1 \rangle_B |2 \rangle_A)$, and therefore, remembering that $\hat{H}^\dagger = \hat{H}$ always holds, we have

$$\begin{aligned} \langle D | \hat{H} | D \rangle_c &= 2 \langle D | \hat{h}_a | D \rangle_c - \langle D | \hat{h}_{12} | D \rangle_c = \\ &= 2 (h_{1212}^a + h_{2112}^a) + h_{1212}^{12} - h_{2112}^{12} = \\ &= \left(4E_{1s} + \frac{2}{R} \right) (1 - \langle 1s | 1s \rangle_{AB1}^2) + \hat{h}_{1212}^{12} - \hat{h}_{2112}^{12} \end{aligned}$$

Writing explicitly the integrals in the last equation for the matrix elements of \hat{h}_{12} , we get the J integral for the first and the K integral for the second, therefore obtaining the results

$$\begin{aligned}\langle D | \hat{H} | D \rangle_c &= \left(4E_{1s} + \frac{2}{R} \right) (1 - I^2) + \frac{1}{2} (J - K) \\ \langle D | D \rangle_c &= \frac{1}{2} (1 - I^2)\end{aligned}\tag{8.21}$$

Putting it up altogether, we get for the ${}^3\Sigma_u^+$

$$E_u(R) = 2E_{1s} + \frac{1}{R} + \frac{J - K}{1 - I^2}\tag{8.22}$$

For the ${}^1\Sigma_g^+$ state, everything remains equal, except for the sign $-$, that becomes a $+$ due to the definition of $|A\rangle_c$, and therefore we have

$$E_g(R) = 2E_{1s} + \frac{1}{R} + \frac{J + K}{1 + I^2}\tag{8.23}$$

A question arises now, after all these calculations. One might ask what do I, J, K actually mean physically. The first is the overlap integral between the nucleus A and the nucleus B of the two electrons (it is squared since the two electrons are indistinguishable), J is the Coulomb integral which represents the interactions between the charge densities of the two electrons ($-e|\psi_{1s}(r_{A1})|^2$ and $-e|\psi_{1s}(r_{B2})|^2$) and K is the exchange integral, each of these already known through the Hartree-Fock approximation for many-electron atoms.

§ 8.2 Homonuclear Diatomic Molecules

In general, for homonuclear diatomic molecules, we can write the electronic wavefunction for the molecular orbitals in the LCAO approximation as

$$|g, u\rangle = N_{g,u} (|a\rangle_{Ai} \pm |b\rangle_{Bi})$$

Where $N_{g,u}$ is an appropriate normalization factor, and $|a\rangle, |b\rangle$ are two (non necessarily equal) atomic orbitals, with respect to the first or the second atom.

Studying more the molecular orbitals we have that

1. MOs with a given value of λ must connect with atomic orbitals with the same value of $|m_l|$.
2. The parity of the wavefunction (g, u) must be preserved

From spatial MOs it's possible to build spinorbitals for each electrons, using Slater determinants.

As an example, we can write the state $|A\rangle$ for H_2 as follows

$$|A\rangle = \frac{1}{\sqrt{2}} \det_2 \begin{vmatrix} |g\rangle |\uparrow\rangle_1 & |g\rangle |\downarrow\rangle_1 \\ |g\rangle |\uparrow\rangle_2 & |g\rangle |\downarrow\rangle_2 \end{vmatrix}\tag{8.24}$$

In this case, both electrons of the H atoms can be in the bonding σ_g orbital, but in higher electron number systems, due to Pauli's principle, is not possible anymore.

For He_2 , He_2^+ we have in the first case that the molecular configuration is $\sigma_g^2\sigma_u^2$, which is unstable and hence bond-breaking. For the second case instead we're left with one less electron in the antibonding σ_u orbital, which corresponds to a weakly bond molecule.

Next in line of homonuclear diatomic molecules, there is Li_2 , each atom with electronic configuration $[\text{He}]2s$. The molecule will be formed through the bonding of the $2s$ valence electron, forming a $(\sigma_g 2s)^2$ molecular orbital, which is a stable bond.

Going forward in the periodic table, we have Be_2 , which must have a $\sigma_g^2\sigma_u^2$ unstable configuration. For B_2 we have a $(\sigma_g 2p)^2$ state, given by the uncomplete LII atomic subshell, which corresponds to the $2p$ atomic orbital (the complete shell would be the $2s^2 2p$ valence shell for Boron). Going forwards, we reach the C_2 molecule. The C atom has a configuration $[\text{He}]2s^2 2p^2$. The 4 p electrons form two bonding orbitals, $\sigma_g^2\pi_u^2$, which are both bonding, hence giving a stable molecule.

Finally we consider the O_2 molecule. Each atom has a configuration $[\text{He}]2s^2 2p^4$, which gives a molecular configuration $\sigma_g^2\pi_u^4\pi_g^2$. Following the Aufbau rules we know that the unfilled antibonding π_u orbital, must have one electron in the π_x^* and one in the π_y^* (remember that the star is usually used in literature to indicate an antibonding orbital, in our case the π_g orbital)

§§ 8.2.1 Valency and Chemical Bonding

It's interesting to see now what valence electrons and chemical bonds really mean in physics. Usually, in order to form a bonding molecular orbital we need to form a singlet spin state. Let's now imagine what happens when we bring an hydrogen atom close to an helium atom. Both the electrons in He are in a singlet spin state, and the Hydrogen atom can't pair with Helium, since it can't exchange with neither of the two He electrons, since such bond would have two electrons in the same state, violating Pauli's principle. We quickly study this three electron system. The total wavefunction will be the following Slater determinant

$$|\Phi\rangle = N \det_3 \begin{vmatrix} |1s\rangle_{\text{He}} |\uparrow\rangle_1 & |1s\rangle_{\text{He}} |\downarrow\rangle & |1s\rangle_{\text{H}} |\uparrow\rangle_1 \\ |1s\rangle_{\text{He}} |\uparrow\rangle_2 & |1s\rangle_{\text{He}} |\downarrow\rangle_2 & |1s\rangle_{\text{H}} |\uparrow\rangle_2 \\ |1s\rangle_{\text{He}} |\uparrow\rangle_3 & |1s\rangle_{\text{He}} |\downarrow\rangle_3 & |1s\rangle_{\text{H}} |\uparrow\rangle_3 \end{vmatrix} \quad (8.25)$$

With N our normalization constant. Substituting this wavefunction into the Rayleigh-Ritz variational expression, we have that $E(R) = J - K$, where J is the following direct integral

$$\begin{aligned} J &= N^2 \langle 1s |_{\text{He}} \langle 1s |_{\text{He}} \langle 1s |_{\text{H}} \hat{H} | 1s \rangle_{\text{He}} | 1s \rangle_{\text{He}} | 1s \rangle_{\text{H}} \\ J &= N^2 \int \overline{\psi_{1s}(1)\psi_{1s}(2)\phi_{1s}(3)} \hat{H} \psi_{1s}(1)\psi_{1s}(2)\phi_{1s}(3) d^3r_1 d^3r_2 d^3r_3 \\ \phi_{1s}(i) &= \langle r_i | 1s \rangle_{\text{H}} \\ \psi_{1s}(i) &= \langle r_i | 1s \rangle_{\text{He}} \end{aligned} \quad (8.26)$$

And K is the following exchange integral

$$K = N^2 \int \overline{\psi_{1s}(1)\psi_{1s}(2)\phi_{1s}(3)} \hat{H} \psi_{1s}(3)\psi_{1s}(2)\phi_{1s}(1) d^3r_1 d^3r_2 d^3r_3 \quad (8.27)$$

The only exchange happening from this integral is between the electron 1 and the electron 3, which have the same spin, thus introducing a repulsion, which makes the existence of a stable HHe molecule impossible. The two electrons in the He atom are said to be *paired*, and only *unpaired* electrons

contribute to chemical bonding. Due to this, since for atoms with closed valence subshells we have only paired valence electrons, they are said to be *chemically inert*. A chemical bond forms principally singlet states using unpaired electrons, forming states with $S = 0$, with the exception of the O_2 molecule, in which the two electrons in the antibonding π_g orbitals are in a relative triplet state, giving O_2 's ground state a relative triplet state.

§ 8.3 Heteronuclear Diatomic Molecules

These methods of forming molecular orbitals can also be applied to heteronuclear molecules, formed by two different atoms. Since in this case there is no reflection symmetry along the internuclear axis, orbitals can't be classified as gerade or ungerade.

In general we will write our molecular orbital as a weighted combination of atomic orbitals of the atom A and the atom B

$$|\Phi\rangle = \lambda |u\rangle_A + \mu |v\rangle_B \quad (8.28)$$

A rule of thumb in order to write these molecular orbital comes from the chemical properties of the two elements, in fact, the more electronegative atom's atomic orbitals will have a greater weight, represented in a MO diagram as having a lower energy than the other atom's orbitals.

A quick way to grasp these concepts is to dive directly into the examples, in our case these will be LiH, HCl and NaCl molecules.

§§ 8.3.1 Lithium Hydride LiH

We begin by writing out the valence orbitals of these two compounds. We have that Lithium has a configuration $[\text{He}]2s$, and Hydrogen has a configuration $1s$. The lowest lying molecular orbital will be the $1\sigma^2$ orbital formed by the complete K shell of Lithium, going higher in energy we find the 2σ orbital, that should be formed by the $1s$ orbital of Hydrogen and the $2s$ orbital of Lithium. Using the variational LCAO method, where as a trial function we take the superposition of the $2s$ and $2p$ orbitals of Lithium, in what is usually called *hybridization*, we can then find a lower energy eigenvalue. The new hybrid orbital is called an sp orbital, and will have a wavefunction of the following kind, if we write the atomic hydrogenoid orbitals as $|nlm\rangle$

$$|sp\rangle = c_1 |200\rangle + c_2 |210\rangle \quad (8.29)$$

This hybridization causes an excess negative charge, which gives a permanent electric dipole moment. In other hydrides like BH, NH and HF, this negative charge excess still exists, but with an opposite sign.

§§ 8.3.2 Hydrogen Chloride HCl

The configuration of Chlorine is $[\text{He}]3s^2 3p^5$, with the K and L shells completely filled and not participating in the chemical bonding.

Since energies of the $3s$ orbital of Chlorine aren't similar to the energies of Hydrogen's $1s$ orbital, these two do not mix, but the bond will be formed between the $1s$ orbital of Hydrogen and the $3p$ orbital of Chlorine. Only the p_z orbital can form a σ orbital, and therefore the searched bond will be formed by a superposition of the $3p_z$ of Chlorine with the $1s$ of Hydrogen.

The weight on the $3p_z$ in this case will be greater than the weight on the $1s$, therefore representing at $R \rightarrow \infty$ the combination $H^+ + Cl^-$, which represents a *ionic bond*

§§ 8.3.3 Sodium Chloride NaCl

Really good examples of molecules characterized by ionic bonds are compounds of an alkali atom with a halogen. In this case, the alkalis have a single valence electron outside a closed shell ($X^3S_{1/2}$), whereas halogens miss only an electron in order to close the last shell.

This configuration makes sure that both atoms end up with a closed shell through bonding, which happens through a ionic bonding. Considering Sodium Chloride, we have that the lowest energy configuration is given by the combination of the ions $\text{Na}^+ + \text{Cl}^-$. At small distances, this system works like inert gases, and is strongly repulsive.

Empirically, one can then write

$$E_s(R) = E_s(\infty) - \frac{1}{R} + Ae^{-cR} \quad (8.30)$$

§ 8.4 Triatomic Molecules

§§ 8.4.1 Hybridization

The construction of molecular orbitals for polyatomic molecules works in a similar way as it does for diatomic molecules.

We begin taking our molecular orbital $|\psi\rangle$ and expanding it into a basis of Gauss-wavefunctions or atomic orbitals $|\phi\rangle$

$$|\psi\rangle = \sum_{i=1}^n c_i |\phi\rangle$$

The coefficients c_i are determined through the Rayleigh-Ritz variational calculus. Due to the importance of geometry and symmetry groups (see Appendix ??), we need this wavefunction as a basis of an irreducible translation of the molecular point groups.

We begin by searching the minimal potential energy for every wavefunction $|\psi\rangle_k$, with electronic state $|k\rangle$ for every single nucleus

$$\nabla_{R_i} V_k = 0$$

As noted before, in case we have different atoms participating in the binding, if the energy differences given by two different orbitals aren't too different, we get what's usually called hybrid orbital. Since in polyatomic molecules we mostly have heterogeneous systems, we might get different kinds of orbital hybridizations given by the intermixing of orbitals.

As we have already seen, with s and p orbitals, we can get what's called a sp orbital, if an s orbital intermixes with a p_z orbital.

It's not actually the only kind of hybridization that can happen between s and p orbitals, in fact we have a couple more possibilities.

One of these possibility is the sp^2 hybrid orbital, given by the triple mixing of an s orbital and two p_x, p_y

orbitals, following the following pattern

$$|sp^2\rangle = \begin{cases} \frac{1}{\sqrt{3}} (|s\rangle + \sqrt{2}|p_x\rangle) \\ \frac{1}{\sqrt{3}} |s\rangle - \frac{1}{\sqrt{6}} |p_x\rangle + \frac{1}{\sqrt{2}} |p_y\rangle \\ \frac{1}{\sqrt{3}} |s\rangle - \frac{1}{\sqrt{6}} |p_x\rangle - \frac{1}{\sqrt{2}} |p_y\rangle \end{cases} \quad (8.31)$$

Adding up to this mix the orbital p_z , we get the sp^3 hybrid orbital, formed as follows

$$|sp^3\rangle = \begin{cases} \frac{1}{2} (|s\rangle + \sqrt{3}|p_z\rangle) \\ \frac{1}{2} |s\rangle + \sqrt{\frac{2}{3}} |p_x\rangle - \frac{1}{2\sqrt{3}} |p_z\rangle \\ \frac{1}{2} |s\rangle - \frac{1}{\sqrt{6}} |p_x\rangle + \frac{1}{\sqrt{2}} |p_y\rangle - \frac{1}{2\sqrt{3}} |p_z\rangle \\ \frac{1}{2} |s\rangle - \frac{1}{\sqrt{6}} |p_x\rangle - \frac{1}{\sqrt{2}} |p_y\rangle - \frac{1}{2\sqrt{3}} |p_z\rangle \end{cases} \quad (8.32)$$

There are more kinds of hybridization, and each one of these gives a different kind of geometry to the molecule, mainly written up on the following table

Hybrid Orbital	Geometry
sp, dp	Linear
p^2, sd	Bent
sp^2, s^2d	Trigonal Planar ($\alpha = 120^\circ$)
p^3	Trigonal Pyramidal
sp^3	Tetrahedral
sp^3d	Bipyramidal
sp^3d^2	Octahedral

Table 8.2: Different kinds of hybridization and subsequent molecular geometry

§§ 8.4.2 Beryllium Dihydride (BeH_2)

Our first real example will be Beryllium Dihydride. This molecule is linear, and considering that the valence shell of Beryllium is $[\text{He}]2s^2$ we have that our complete molecular orbital can be written as an intermixing of s orbitals of the 3 atoms.

In formulae

$$|\psi\rangle_{\text{BeH}_2} = c_1 |1s\rangle_H + c_2 |2s\rangle_{\text{Be}} + c_3 |1s\rangle_H \quad (8.33)$$

This molecular orbital has σ symmetry (it's not hard to see this, it's a superposition of s orbitals). Following the hybridization method of orbitals we can also find 3 more orbitals

$$|\psi\rangle_i = \begin{cases} |\psi\rangle_1 = |1s\rangle + \lambda |2s\rangle + |1s\rangle \\ |\psi\rangle_2 = |1s\rangle + \mu |2p_z\rangle - |1s\rangle \\ |\psi\rangle_3 = |1s\rangle - \nu |2s\rangle + |1s\rangle \\ |\psi\rangle_4 = -|1s\rangle + \omega |2p_z\rangle + |1s\rangle \end{cases} \quad (8.34)$$

All of these configurations represent the state $X^1\Sigma_g$ of Beryllium Dihydride.

It's easy also to verify that this molecule (like all linear molecules) can have either a $C_{\infty h}$ symmetry or a $D_{\infty h}$ symmetry

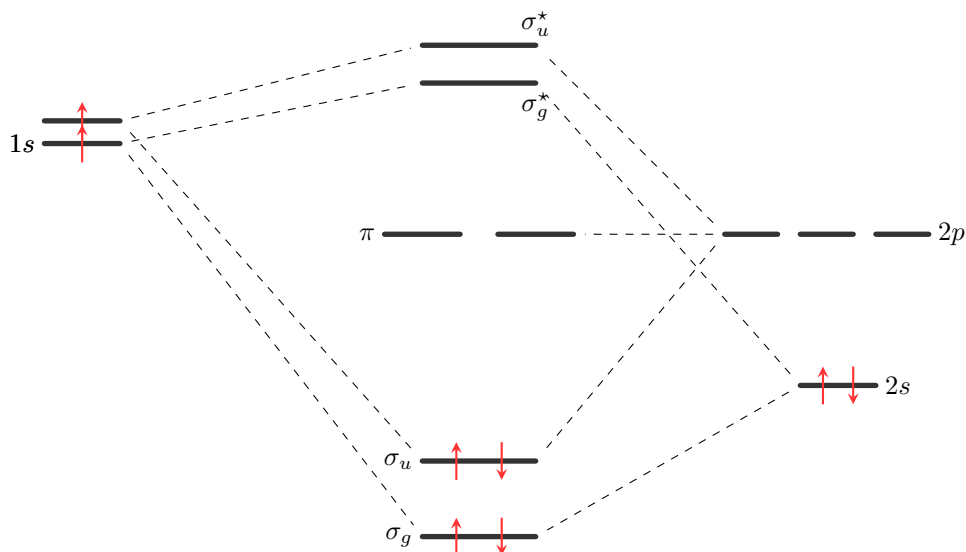


Figure 8.1: The Beryllium Hydride molecular orbital diagram



Figure 8.2: The Beryllium Hydride molecule

§§ 8.4.3 Water (H_2O)

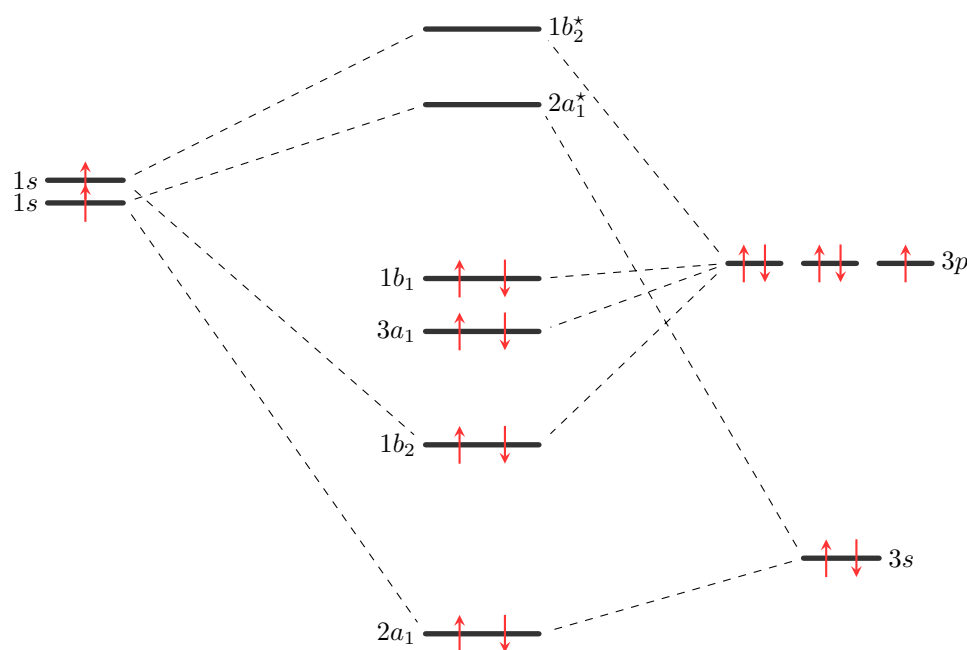
For water the situation is completely different. The two $1s$ orbitals of the hydrogen mix with the $2p$ orbitals of Oxygen, forming a sp^2 hybridization. In this case, we know already that this molecule has a bent symmetry, and the Hamiltonian will be invariant to all transformations of the group C_{2v} , due to the planar hybridization with the p_x, p_y orbitals of Oxygen.

The two hybrid orbitals will then be the following 2

$$\begin{aligned} |sp^2\rangle_1 &= |1s\rangle_H + \lambda |2p_x\rangle_O \\ |sp^2\rangle_2 &= |1s\rangle_H + \lambda |2p_y\rangle_O \end{aligned} \quad (8.35)$$

Due to the symmetry of the molecule it's possible to determine that the angle of separation of the two Hydrogen atoms is $\alpha = 105^\circ$. Note that since this molecule is bent, usual molecular states do not apply to molecular orbitals, therefore, another notation based on group theory is used, and we get that the ground state of the water molecule is X^1A_1 and the electronic configuration is

$$2a_1^2 1b_2^2 3a_1^2 1b_1^2$$

Figure 8.3: The molecular orbital diagram for water (H_2O)

Where the first two orbitals, a_1, b_2 are bonding orbitals.

The new notation for electronic structure of the molecule is given directly by group theory. This notation takes into account the bending of the molecule, which changes the energies of the usual σ, π, \dots molecular orbitals. This can be seen by taking a C_{2v} transformation and applying it to these molecular orbitals. Through this change of coordinates we see that the p orbitals transform as follows

$$\begin{aligned} |p'_x\rangle &= \frac{1}{\sqrt{2}} (|p_x\rangle + |p_y\rangle) \\ |p'_y\rangle &= \frac{1}{\sqrt{2}} (|p_x\rangle - |p_y\rangle) \end{aligned} \quad (8.36)$$

Looking closely at this definition, we see that the state $|2s\rangle$ and $|2p_x\rangle$ transform into themselves, thus they have a a_1 symmetry, whereas we see that $|2p'_y\rangle$ changes sign upon this C_2 rotation, and therefore has a b_2 symmetry, and last, the state $|2p_z\rangle$ changes sign upon reflection σ_v , and therefore has b_1 symmetry.

Putting this all together we get the previous molecular configuration, which through a simple direct calculus (evaluating sign changes and symmetries) gives back the X^1A_1 spectroscopic term for water.

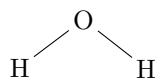


Figure 8.4: The Water molecule

§§ 8.4.4 Carbon Dioxide (CO₂) and Lone Pairs

For this molecule, we have 16 valence electrons, and we can form a bond using the $2s, 2p_x, 2p_y, 2p_z$ molecular orbitals of both atomic species.

Since the molecule is linear with an inversion point it is a $D_{\infty h}$ molecule, and the only possible σ_g atoms are given by the three $2s$ orbitals of Carbon and the two $2p_z$ orbitals of the two Oxygen atoms. We choose the internuclear axis as our z axis, and we build our orbitals as usual through the projection of $\hat{\Lambda}$ and $\hat{\lambda}$. The hybrid atomic orbitals will then be a superposition of $2s, 2p_z$ orbitals ($\Lambda = 0, \Sigma$ symmetry) and of $2p_x, 2p_y$ orbitals ($\Lambda = 1, \Pi$ symmetry) which give a π bond.

Therefore, the electronic configuration of CO₂ will be, using the usual Aufbau rules for molecular orbitals

$$(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(1\pi_u)^4(1\pi_g^*)^4 \quad (8.37)$$

The antibonding molecular orbitals do not contribute to the bonding, and therefore lead to a destabilization of the molecule. These are usually called (in chemistry) as *lone pairs*, and are indicated by couples of electrons which do not participate in the bonding.

The *bond order* of the molecule is given by this simple calculus

$$B_o = \frac{1}{2} (N_B - N_A) \quad (8.38)$$

Where N_B is the number of bonding electrons and N_A is the number of antibonding electrons.

From this we can immediately see that if the electrons involved in the lone pair had participated into the bonding, placing themselves into an antibonding orbital, would have brought the bond order $B_o = 0$, which means that there are *no bonds* in the molecule. This is clearly not what happens in nature in a standard atmosphere, because we are quite certain that this molecule exists!

Talking about the bond order again, it is also used in order to determine the number of bonds of a molecule, i.e. if $B_o = 3$ it means that this molecule has a triple bond, and so on.

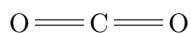


Figure 8.5: The Carbon Dioxide molecule

§ 8.5 Rayleigh-Ritz Variational Method

It's useful to check a different approach on the LCAO method, by introducing a variational form of this approximation.

We start by defining our unnormalized Hamiltonian eigenstate as follows, indicating with the subscript A the first atom, and with the subscript B the second atom.

$$|\Phi\rangle = c_1 |\psi\rangle_A + c_2 |\psi\rangle_B \quad (8.39)$$

Normalizing, and considering, without loss of generality that $\langle\psi|\psi\rangle_i = 1 \ i = A, B$, we get the new normalized eigenstate

$$|\Psi\rangle = \frac{1}{\sqrt{c_1^2 + c_2^2 + 2c_1c_2 \langle\psi|\psi\rangle_{AB}}} (c_1 |\psi\rangle_A + c_2 |\psi\rangle_B) \quad (8.40)$$

Inserting this eigenstate in the Rayleigh-Ritz variational equation, we have

$$E = \langle \Psi | \hat{H} | \Psi \rangle$$

$$E = \frac{1}{c_1^2 + c_2^2 + 2c_1c_2 \langle \psi | \psi \rangle_{AB}} (\langle \psi |_A c_1 + \langle \psi |_B c_2) \hat{H} (c_1 | \psi \rangle_A + c_2 | \psi \rangle_B)$$

We continue calculating by bringing to the left the normalization factor

$$E (c_1^2 + c_2^2 + 2c_1c_2 \langle \psi | \psi \rangle_{AB}) = c_1^2 \langle \psi | \hat{H} | \psi \rangle_{AA} + c_2^2 \langle \psi | \hat{H} | \psi \rangle_{BB} + 2c_1c_2 \langle \psi | \hat{H} | \psi \rangle_{AB}$$

$$c_1^2 E + c_2^2 E + 2c_1c_2 E \langle \psi | \psi \rangle_{AB} - c_1^2 \langle \psi | \hat{H} | \psi \rangle_{AA} - c_2^2 \langle \psi | \hat{H} | \psi \rangle_{BB} - 2c_1c_2 \langle \psi | \hat{H} | \psi \rangle_{AB} = 0$$

Now, we impose the condition $\partial_{c_i} \langle \Psi | \hat{H} | \Psi \rangle = 0$ in order to find the extremal value for the coefficients, and simplifying the constants and regrouping, we get the following system of equation

$$c_1 \left(\langle \psi | \hat{H} | \psi \rangle_{AA} - E \right) + c_2 \left(\langle \psi | \hat{H} | \psi \rangle_{AB} - E \langle \psi | \psi \rangle_{AB} \right) = 0$$

$$c_1 \left(\langle \psi | \hat{H} | \psi \rangle_{AB} - E \langle \psi | \psi \rangle_{AB} \right) + c_2 \left(\langle \psi | \hat{H} | \psi \rangle_{BB} - E \right) = 0 \quad (8.41)$$

Writing the matrix elements of the Hamiltonian as \mathcal{H}_{ij} , with $i, j = A, B$ and the overlap integral as S_{AB} , we have that the previous system, in the basis of the two coefficients is represented by the following matrix

$$A_{ij} = \begin{pmatrix} \mathcal{H}_{AA} - E & \mathcal{H}_{AB} - ES_{AB} \\ \mathcal{H}_{AB} - ES_{AB} & \mathcal{H}_{BB} - E \end{pmatrix}$$

It's easy to note how this matrix is given by the following matrix equation

$$\langle \psi | \hat{H} | \psi \rangle_{ij} - E \langle \psi | \psi \rangle_{ij} = \mathcal{H}_{ij} - ES_{ij}$$

$$\mathcal{H}_{ij} = \begin{pmatrix} \langle \psi | \hat{H} | \psi \rangle_{AA} & \langle \psi | \hat{H} | \psi \rangle_{AB} \\ \langle \psi | \hat{H} | \psi \rangle_{AB} & \langle \psi | \hat{H} | \psi \rangle_{BB} \end{pmatrix}$$

$$S_{ij} = \begin{pmatrix} 1 & \langle \psi | \psi \rangle_{AB} \\ \langle \psi | \psi \rangle_{AB} & 1 \end{pmatrix}$$

This matrix gives the searched solution for $\det_2(A_{ij}) = 0$, hence we get the following second order linear equation on E

$$(\mathcal{H}_{AA} - E)(\mathcal{H}_{BB} - E) - (\mathcal{H}_{AB} - ES_{AB})^2 = 0$$

Noting that $|\psi\rangle_A = |\psi\rangle_B$ we have that $\mathcal{H}_{AA} = \mathcal{H}_{BB}$, and the solution to the equation are

$$E_+(R) = \frac{\mathcal{H}_{AA} + \mathcal{H}_{AB}}{1 + S_{AB}}$$

$$E_-(R) = \frac{\mathcal{H}_{AA} - \mathcal{H}_{AB}}{1 - S_{AB}} \quad (8.42)$$

$$|c_1|^2 = |c_2|^2 \longrightarrow c_1 = \pm c_2$$

Where, expressing the matrix elements of the Hamiltonian in Schrödinger notation, we get

$$\begin{aligned}\mathcal{H}_{AA} &= \int \bar{\psi}(r_A) \hat{\mathcal{H}} \psi(r_A) d^3r_A = J \\ \mathcal{H}_{AB} &= \iint \bar{\psi}(r_A) \hat{\mathcal{H}} \psi(r_B) d^3r_A d^3r_B = K \\ S_{AB} &= \iint \bar{\psi}(r_A) \psi(r_B) d^3r_A d^3r_B = I\end{aligned}\quad (8.43)$$

Which are the already known Coulomb integral (J), Exchange integral (K) and the Overlap integral (I). The energies therefore represent the bonding-antibonding state couple

§§ 8.5.1 Hückel Theory

Further approximations can be made using this variational method. Commonly one chooses a minimal LCAO basis (overlap of $|1s\rangle$ states) in order to complete the calculations, but this is not always the best choice. An example are organic molecules and molecules with weak overlaps of orbitals (like in π bonds). Therefore, as an example, suppose taking a planar hydrocarbon. The π bond of carbon can be thought, as for the Rayleigh-Ritz theory described before, as a linear sum of $|p_z\rangle$ states.

$$|\pi\rangle = c_1 |p_z^1\rangle + c_2 |p_z^2\rangle \quad (8.44)$$

The energies will therefore be the solution of the following secular equation

$$\begin{vmatrix} \mathcal{H}_{11} - ES_{11} & \mathcal{H}_{12} - ES_{12} \\ \mathcal{H}_{21} - ES_{21} & \mathcal{H}_{22} - ES_{22} \end{vmatrix} = 0 \quad (8.45)$$

In order to solve this equation, we impose the two main approximation of Hückel theory

1. We assume an orthonormal basis, therefore $S_{ij} = \langle p_z^i | p_z^j \rangle = \delta_{ij}$
2. We assume that the p_z orbitals interact only with their next closest orbital, therefore $\mathcal{H}_{ij} = \alpha$ if $i = j$, or $\mathcal{H}_{ij} = \beta$ if the orbitals are adjacent. Otherwise it's considered to be zero

The secular equation therefore becomes

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = (\alpha - E)^2 - \beta^2 = 0 \quad (8.46)$$

Solving for E we get $E_{\pm} = \alpha \pm \beta$, which gives E_+ as our bonding π_u orbital and E_- as the antibonding π_g^* orbital

§ 8.6 π Electron Systems and Unlocalized Orbitals

From now on we will consider a different class of molecules, where the electronic wavefunction isn't precisely localized in a certain position, permitting the existence of *unlocalized orbitals*. These particular molecules include chains of Carbon atoms, where double and single bonds alternate and aren't localized. The electrical polarizability of these molecules is much larger than the usual molecules with localized bonds. This phenomenon is given by overlapping p orbitals, i.e. π bonds.

§§ 8.6.1 Butadiene (C_4H_6)

Transbutadiene is an isomer of Butadiene (molecule with the same composition of Butadiene) which is planar. It's formed by a single σ bond between two CH radicals, which are themselves doubly bonded with two CH_2 radicals. In this case there exist 4 π bonds which are linear combinations of the p orbitals of the Carbon atoms, with the following wavefunction

$$|\pi\rangle = \sum_{n=1}^4 c_n |2p\rangle_n \quad (8.47)$$

These 4 c_n coefficients can be determined using the Rayleigh-Ritz variational equation, which corresponds to the eigenvalue problem

$$[\mathcal{H}_{ij} - ES_{ij}] = 0$$

In order to solve easily these equations we impose some approximations

1. $\mathcal{H}_{ii} = \alpha$, with α a parameter
2. $\mathcal{H}_{ij} = \beta < 0$, $i \neq j$ only for adjacent atoms
3. $S_{ij} = \delta_{ij}$

These assumptions are the basis of the *Hückel method*. After some calculations, for Transbutadiene, we obtain the following wavefunction for the π bonds

$$\begin{aligned} |\pi_1\rangle &= 0.37 |1\rangle + 0.60 |2\rangle + 0.60 |3\rangle + 0.37 |4\rangle \\ |\pi_2\rangle &= 0.60 |1\rangle + 0.37 |2\rangle - 0.37 |3\rangle - 0.60 |4\rangle \\ |\pi_3\rangle &= 0.60 |1\rangle - 0.37 |2\rangle - 0.37 |3\rangle + 0.60 |4\rangle \\ |\pi_4\rangle &= 0.37 |1\rangle - 0.60 |2\rangle + 0.60 |3\rangle - 0.37 |4\rangle \end{aligned} \quad (8.48)$$

The orbital π_1 is completely unlocalized over the whole Transbutadiene molecule.

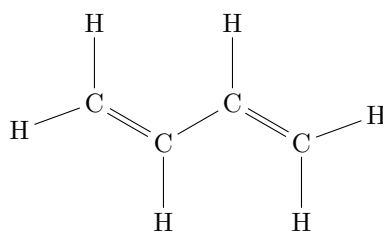


Figure 8.6: The Transbutadiene Molecule

§§ 8.6.2 Methane and Ethylene(CH_4 , C_2H_4)

As a continuation to our examples, we take the Methane molecule, CH_4 . Carbon bonds readily in an excited state $1s^2 2s^2 2p^3$ which is very close in energy, forming, for Methane, an sp^3 hybridization. We

can construct the usual 4 combinations for the wavefunction of the molecular orbitals

$$\begin{aligned}
 |1\rangle &= |2s\rangle + |2p_x\rangle + |2p_y\rangle + |2p_z\rangle \\
 |2\rangle &= |2s\rangle + |2p_x\rangle - |2p_y\rangle - |2p_z\rangle \\
 |3\rangle &= |2s\rangle - |2p_x\rangle + |2p_y\rangle - |2p_z\rangle \\
 |4\rangle &= |2s\rangle - |2p_x\rangle - |2p_y\rangle + |2p_z\rangle
 \end{aligned}
 \tag{8.49}$$

Since all $|2p_i\rangle$ eigenstates are proportional to the standard euclidean basis, we can immediately determine that the direction of the maximum are respectively

$$\begin{aligned}
 (1, 1, 1) \\
 (1, -1, -1) \\
 (-1, 1, -1) \\
 (-1, -1, 1)
 \end{aligned}$$

Calculating the cosine between these directions we obtain a bond angle of 109.6° , giving CH_4 a tetrahedral structure.

In case of a planar molecule like Ethylene, we can form sp^2 hybrids as follows

$$\begin{aligned}
 |1\rangle &= |2s\rangle + \sqrt{2}|2p_x\rangle \\
 |2\rangle &= |2s\rangle + \sqrt{\frac{3}{2}}|p_y\rangle - \sqrt{\frac{1}{2}}|p_x\rangle \\
 |3\rangle &= |2s\rangle - \sqrt{\frac{3}{2}}|p_y\rangle - \sqrt{\frac{1}{2}}|p_x\rangle
 \end{aligned}
 \tag{8.50}$$

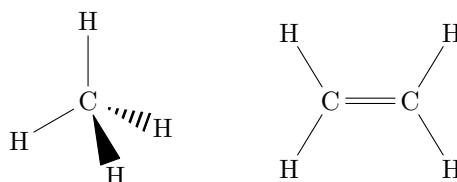


Figure 8.7: The Methane and Ethylene molecules

§ 8.7 Cyclic Molecules

§§ 8.7.1 Ideal Homonuclear Trimer

We can begin our treatment of polyatomic molecules by studying a toy problem, as the homonuclear trimer, i.e. a triangular molecule composed from 3 atoms of the same element. We begin evaluating the system by immediately finding that there is a C_3 axis of symmetry, passing through the center of the triangle. Having considered this, we already know that the electronic Hamiltonian and the \hat{C}_3 operator, which applicates a rotation of $\frac{2}{\pi}3$ radians, commutes $[\hat{\mathcal{H}}_e, \hat{C}_3] = 0$, thus there exists a common diagonalizing base.

We search this base by taking the minimal LCAO base orbitals. In this base, the electronic Hamiltonian $\hat{\mathcal{H}}_e$ has the energy of the single orbitals in the diagonal, and these base kets diagonalize the \hat{C}_3 operator. We have

$$\hat{C}_3 |\alpha\rangle = c_m |\alpha\rangle = c_1 |1s\rangle_1 + c_2 |1s\rangle_2 + c_3 |1s\rangle_3$$

Since these eigenvalues must have norm $\|c_m\| = 1$ and must also express a rotation, have the shape of a complex exponential

$$c_i = e^{\frac{2im\pi}{3}}$$

Therefore, we can write

$$\hat{C}_3 |\alpha_m\rangle = e^{\frac{2im\pi}{3}} |\alpha_m\rangle = |1s\rangle_1 + e^{\frac{2im\pi}{3}} |1s\rangle_2 + e^{-\frac{2im\pi}{3}} |1s\rangle_3, \quad m = 0, \pm 1$$

Where we ignored general phases.

This base is made from a linear combination of bases of the electronic Hamiltonian $\hat{\mathcal{H}}_e$, hence we can easily write that $\text{diag } \mathcal{H}_{ij}^{(e)} = (\epsilon, \epsilon, \epsilon)$, with ϵ the single atomic orbital energy, and the diagonal elements are all the same $\mathcal{H}_{ij} = -t \forall i \neq j$ at the same time we can also say easily that the Schrödinger equation holds

$$\hat{\mathcal{H}}_e |\alpha_m\rangle = E_m |\alpha_m\rangle$$

And therefore, applying the Hamiltonian matrix to the matrix representation of this vector (with normalization), we obtain

$$\begin{aligned} \mathcal{H}_{ij} \alpha_j^{(m)} &= \frac{1}{\sqrt{3}} \begin{pmatrix} \epsilon & -t & -t \\ -t & \epsilon & -t \\ -t & -t & \epsilon \end{pmatrix} \begin{pmatrix} 1 \\ e^{\frac{2im\pi}{3}} \\ e^{-\frac{2im\pi}{3}} \end{pmatrix} = \\ &= \frac{1}{\sqrt{3}} \begin{pmatrix} \epsilon - t \left(e^{\frac{2im\pi}{3}} + e^{-\frac{2im\pi}{3}} \right) \\ \epsilon - t \left(e^{\frac{2im\pi}{3}} + e^{-\frac{4im\pi}{3}} \right) \\ \epsilon - t \left(e^{\frac{4im\pi}{3}} + e^{-\frac{2im\pi}{3}} \right) \end{pmatrix} = \\ &= \frac{1}{\sqrt{3}} \left[\epsilon - t \left(e^{\frac{2im\pi}{3}} + e^{\frac{2im\pi}{3}} \right) \right] \begin{pmatrix} 1 \\ e^{\frac{2im\pi}{3}} \\ e^{-\frac{2im\pi}{3}} \end{pmatrix} = \\ &= \frac{1}{\sqrt{3}} \left[\epsilon - 2t \cos \left(\frac{2m\pi}{3} \right) \right] \alpha_j^{(m)} = E_m \alpha_j^{(m)} \end{aligned} \tag{8.51}$$

Which are the energies of the three $|\alpha_m\rangle$ molecular orbitals, where two are degenerate and shifted upwards from the single orbital by $+t$ and one is shifted downwards of $-2t$.

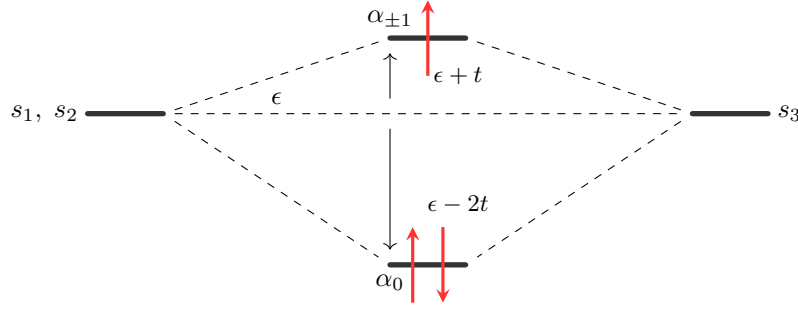


Figure 8.8: LCAO diagram for the homonuclear trimer

These energy levels though, are «not» optimized. In fact it's energetically convenient to distort the molecule from a triangular symmetry to a isosceles symmetry, breaking the degeneracy for the orbitals $|\alpha_{\pm 1}\rangle$. This effect is known as *Jahn-Teller effect*.

§§ 8.7.2 Ideal Polyatomic Ring and the Tight Binding Approximation

After treating the ideal homonuclear trimer it's possible to generalize the calculations to a generic ring formed by N atoms. Suppose having a ring of such N atoms with one valence electron, this ring will be a regular polyhedron with the nuclei at its vertexes. We must obviously have $[\hat{\mathcal{H}}, \hat{C}_N] = 0$ which means that the eigenstates of the Hamiltonians must also be eigenstates of the rotation operator \hat{C}_N with eigenvalue $e^{\pm 2mi\pi/N}$ with $m = 0, \pm 1, \dots, \pm(N/2 - 1), N/2$ if $N \bmod 2n = 0$ with $n \in \mathbb{N}$. Considering a minimal LCAO basis $|1s_n\rangle = |n\rangle$, all the eigenvectors of $\hat{\mathcal{H}}$ will be therefore linear combinations of 1s orbitals of the following kind

$$|\alpha_m\rangle = \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{\frac{2imn\pi}{N}} |n\rangle \quad (8.52)$$

Note how the state $|\alpha_0\rangle, |\alpha_{N/2}\rangle$ correspond respectively to the normalized sum of the orbitals (generalization of a bonding orbital) and to the alternated sum of orbitals (generalization of an antibonding orbital).

Considering the $|n\rangle$ basis as a complete orthonormal system we have that the energies of the system will be the matrix elements of the Hamiltonian, as follows

$$\epsilon_m = \langle \alpha_m | \hat{\mathcal{H}} | \alpha_m \rangle = \frac{1}{N} \sum_{n'=1}^N \sum_{n=1}^N e^{\frac{2im(n'-n)\pi}{N}} \langle n' | \hat{\mathcal{H}} | n \rangle \quad (8.53)$$

Calling the diagonal elements of the Hamiltonian as ϵ and the off diagonal as $\langle n \pm k | \hat{\mathcal{H}} | n \rangle = -t^{(k)}$ we can safely suppose that $t^{(k)} = 0$ for $k > 1$ since the atomic eigenfunction must decay exponentially with the distance. This approximation is known as the *tight binding approximation*. Calculating the energies as we did for the trimer we get, analogously, the following expression

$$\epsilon_m = \epsilon - \frac{1}{N} \sum_{k=1}^{N-1} \sum_{n=1}^N t^{(k)} \left(e^{\frac{2^k im\pi}{N}} + e^{\frac{2^k im\pi}{N}} \right) = \epsilon - 2 \sum_{k=1}^{N-1} t^{(k)} \cos \left(\frac{2^k m\pi}{N} \right)$$

Including the tight binding approximation, the levels become

$$\epsilon_m = \epsilon - 2t \cos\left(\frac{2m\pi}{N}\right) \quad (8.54)$$

Note how this is a reformulation of the previously discussed Hückel theory.

All the energy levels will lay in the interval $[\epsilon - 2t, \epsilon + 2t]$ ($\epsilon + 2t$ included if the number of atoms is even).

We therefore will have, for the minimum and maximum value of the energies

$$\epsilon_m \rightarrow \begin{cases} \epsilon_0 = \epsilon - 2t \\ \epsilon_{\frac{N}{2}} = \epsilon + 2t \\ \epsilon_{\pm \frac{N-1}{2}} = \epsilon - 2t \cos\left(\frac{2\pi(N-1)}{N}\right) \end{cases} \begin{matrix} N \bmod 2n = 0 \\ N \bmod (2n+1) = 0 \end{matrix} \quad n \in \mathbb{N} \quad (8.55)$$

The minimum will be ϵ_0 and the remaining 2 will be the maximum levels of energy, for even and uneven N .

Generally, from this property of energy we have that the energy levels will move from the median value ϵ by $\pm 2t$, defining the band of permitted energies. Note that since we have to fill these orbitals with electrons (2 per time due to the spin degeneracy and the Pauli exclusion principle), therefore if the single atoms have only one valence electron, only half of these N orbitals will be occupied.

§§ 8.7.3 Benzene (C_6H_6)

Benzene is a planar molecule, formed by a ring of carbon atoms, for which each one of those is bonded with a hydrogen atom. This symmetry structure indicates an sp^2 hybridization of the carbon atom's orbitals.

This molecule has a C_{6v} symmetry which lets us hypothesize immediately an sp^2 hybridization of the orbitals of the carbon atoms, or more precisely of the orbitals of the Methyl group CH. Again using the symmetry of the molecule, we can write our eigenfunctions as follows, noting that there exist 3 combinations possible for a sp^2 hybridization

$$|\psi_j\rangle = \frac{1}{\sqrt{6}} \sum_{n=1}^6 e^{\frac{i\pi n}{3}} |sp^2\rangle_j \quad j = 1, 2, 3 \quad (8.56)$$

We need simply to add to these 3 hybrid orbitals another 2 orbitals participating in the bonding, which are given by the CH group.

Solving everything, we find that the sp^2 hybrids are well localized in the molecule, and instead the remaining $2p_z$ orbitals, which participate in the bonding, are loosely bound in a unlocalized π bond.

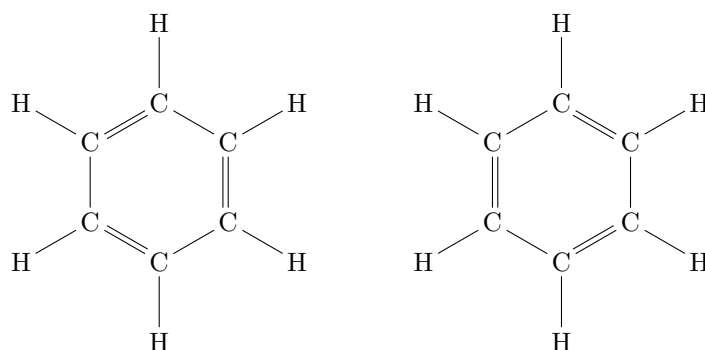


Figure 8.9: The Benzene molecule and its resonance of the double π bonds

Another way to treat this organic molecule, is to use its rotational symmetry for $C - C$ bonds and tight binding for tying everything up. Since there are 6 C atoms we have that there will be 6 α_m orbitals, combination of the basis orbitals. Mathematically

$$|\alpha_m\rangle = \frac{1}{\sqrt{6}} \sum_{n=1}^6 e^{\frac{2im\pi}{6}} |n\rangle \quad (8.57)$$

Adding up the hydrogens and supposing that only the $2s2p$ orbitals of carbon will partake in the bonding, considering also the three previously mentioned sp^2 hybrid orbitals, we will have a grand total of 30 atomic orbitals. Since carbon is tetravalent and hydrogen is univalent, we will have $4 * 6 + 6 = 30$ electrons. Due to the doubly degenerate nature of molecular orbitals, only the first 15 will be completely occupied, leaving 15 free orbitals.

It's not easy to solve easily a 30×30 Hamiltonian for such problem, but it's possible to greatly reduce the dimensionality of the problem. We have that the interacting orbitals in this system must be 4 for the carbons and only one for hydrogen.

We identify with α, β the two orbitals of carbon coplanar with the ring, the first in the clockwise direction and vice versa, with p the perpendicular p_z orbital, with γ the orbital between carbon and hydrogen, and with s the remaining hydrogen orbital.

Using therefore these $\alpha, \beta, \gamma, p, s$ orbitals end up, using the previous formula, with the following general

expression for their linear combination

$$\begin{aligned}
 |C\alpha_m\rangle &= \frac{1}{\sqrt{6}} \sum_{n=1}^6 e^{\frac{2im\pi}{6}} |\alpha_n\rangle \\
 |C\beta_m\rangle &= \frac{1}{\sqrt{6}} \sum_{n=1}^6 e^{\frac{2im\pi}{6}} |\beta_n\rangle \\
 |C\gamma_m\rangle &= \frac{1}{\sqrt{6}} \sum_{n=1}^6 e^{\frac{2im\pi}{6}} |\gamma_n\rangle \\
 |Cp_m\rangle &= \frac{1}{\sqrt{6}} \sum_{n=1}^6 e^{\frac{2im\pi}{6}} |p_n\rangle \\
 |Hs_m\rangle &= \frac{1}{\sqrt{6}} \sum_{n=1}^6 e^{\frac{2im\pi}{6}} |s_n\rangle
 \end{aligned} \tag{8.58}$$

Approximating with the tight binding model we have that 2 of each of these orbitals are orthogonal for different m and have 0 Hamiltonian matrix element, imposing these two constraints

$$\begin{aligned}
 \langle I|J\rangle &= \delta_{mm'} S_{IJ}(m) \\
 \langle I|\hat{\mathcal{H}}|J\rangle &= \delta_{mm'} \mathcal{H}_{IJ}(m)
 \end{aligned} \tag{8.59}$$

This reduces the complete 30×30 problem in 6 5×5 problems.

To this first reduction, we apply the tight binding approximation therefore rendering the S matrix nonzero only on the diagonal and on the first elements above and below the diagonal. We apply the same reasoning for the Hamiltonian, giving finally

$$\begin{aligned}
 S_{IJ} &= \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & S_{\alpha\beta} & 0 & 0 \\ 0 & S_{\beta\alpha} & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & S_{\gamma s} \\ 0 & 0 & 0 & S_{s\gamma} & 1 \end{pmatrix} \\
 \mathcal{H}_{IJ} &= \begin{pmatrix} \epsilon_m & 0 & 0 & 0 & 0 \\ 0 & \epsilon_{\alpha\beta\gamma} & -t_{CC\sigma} & 0 & 0 \\ 0 & -t_{CC\sigma} & \epsilon_{\alpha\beta\gamma} & 0 & 0 \\ 0 & 0 & 0 & \epsilon_{\alpha\beta\gamma} & -t_{CH\sigma} \\ 0 & 0 & 0 & -t_{CH\sigma} & \epsilon_s \end{pmatrix}
 \end{aligned} \tag{8.60}$$

Where $I, J = p, \alpha, \beta, \gamma, s$ and

$$\begin{aligned}
 \epsilon_m &= \epsilon_p - 2t_{pp\pi} \cos\left(\frac{2m\pi}{6}\right) \\
 \epsilon_{\alpha\beta\gamma} &= \langle C\alpha|\hat{\mathcal{H}}|C\alpha\rangle = \langle C\beta|\hat{\mathcal{H}}|C\beta\rangle = \langle C\gamma|\hat{\mathcal{H}}|C\gamma\rangle \\
 \epsilon_s &= \langle Hs|\hat{\mathcal{H}}|Hs\rangle - t_{CC\sigma} = \langle C\alpha|\hat{\mathcal{H}}|C\beta\rangle \\
 &\quad - t_{CH\sigma} = \langle C\gamma|\hat{\mathcal{H}}|Hs\rangle
 \end{aligned} \tag{8.61}$$

Note how the energies for the sigma bonds are localized to either the $C - C$ or $C - H$ bonds and are localized to one single orbital, while the energy for the p_z orbitals of each carbon are dependent on m and are delocalized over the whole ring.

Ordering the orbital energies and filling up the orbitals using the usual rules we have that the two hybrid sp^2 orbitals σ_{CH}, σ_{CC} are completely filled, while the delocalized π_{CC} orbital is filled only in the lower levels with $m = 0, \pm 1 < ++ >$

9 Introduction to Solid State Physics

§ 9.1 Infinite Linear Chain

The first idea of solid we can imagine is the direct generalization of an ideal cyclic molecule with N atoms, where N is a pretty big number but not infinite, in general $N \sim 10^7 - 10^8$.

This regular polygon with so many vertices can be approximated without problems to a chain long $2\pi R \simeq Na$ where a is the distance between two atoms. Taking a single atom of the chain as our coordinate origin we see easily that a finite rotation of $2\pi N^{-1}$, for $N \rightarrow \infty$ is almost indistinguishable from a discrete translation of a along an infinite chain.

From this symmetry we can immediately say, that if we define a translation operator \hat{T}_a that moves this chain, if we write the Hamiltonian of the system as $\hat{\mathcal{H}}$, we have that $[\hat{\mathcal{H}}, \hat{T}_a] = 0$. Since we're generalizing the ideal polyatomic cyclic molecule for N univalent atoms, we take our usual minimal LCAO basis. We will have $|\alpha_m\rangle$ orbitals, where $m = 0, \dots, N$, and our translation operator on our basis kets will act as follows

$$\hat{T}_a |\alpha_m\rangle = e^{\frac{2i\pi m}{N}} |\alpha_m\rangle \quad (9.1)$$

The induced phase, which depends on m , can now be redefined with a new quantum number, due to the properties of this chain.

We must have, for the electronic wavefunction

$$\psi_{e-}(x) = \psi_{e-}(x + L), \quad L = Na \quad (9.2)$$

Supposing the electron completely free we have that the wavefunction must be of the form $\psi \propto e^{ikx}$. Imposing the previous condition in order to constrain the electron wavefunction to the chain we must have

$$Ae^{ikx} = Ae^{ik(x+Na)} \Rightarrow k = \frac{2\pi m}{Na}, \quad m = 0, \dots, N \quad (9.3)$$

This is the quantization relation for the chain, which gives us a new quantum number k_m , that due to its definition is called the «wavenumber» of the chain, where

$$k_m = \begin{cases} \frac{2\pi m}{Na} = 0, \dots, \pm \left(\frac{N-1}{N} \right) \frac{\pi}{a} & N = 2k + 1, \quad k \in \mathbb{N} \\ \frac{2\pi m}{Na} = 0, \dots, \pm \frac{\pi}{a} & N = 2k \end{cases} \quad (9.4)$$

It's easy to see from its definition that $k_m \in [-\pi/a, \pi/a]$, which is called the «1st Brillouin zone». It's also obvious that for $N \rightarrow \infty$, $k_m \rightarrow k$, where k is a continuous variable defined in the same Brillouin

interval.

With this definition, we will have that applying \hat{T}_a on our basis states, we have

$$\hat{T}_a |\alpha_k\rangle = e^{ik_m a} |\alpha_k\rangle \quad (9.5)$$

Where we substituted $m \rightarrow k_m$, our new quantum (wave)number. As we said before the Hamiltonian commutes with the translation operator, therefore, since $|\alpha_k\rangle$ are eigenstates of \hat{T}_a , they must also be eigenstates of the Hamiltonian, such that

$$\begin{aligned} \langle k | k' \rangle &= \delta_{kk'} \\ \langle k | \hat{\mathcal{H}} | k' \rangle &= \epsilon_k \delta_{kk'} \end{aligned} \quad (9.6)$$

Where $|\alpha_k\rangle = |k\rangle$.

Since basically everything is equal to the case of the N -atomic cyclic molecule, supposing that $|\alpha_m\rangle = |1s\rangle_m$ (i.e. $|\alpha\rangle$ is a minimal LCAO base for every single atom) we can say, imposing the tight binding approximation, that

$$\begin{aligned} |k\rangle &= \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{ikna} |1s\rangle_n \\ \epsilon_k &= \epsilon_0 - 2t \cos(ka) \end{aligned} \quad (9.7)$$

All of this is generalizable to 2 and 3 dimensions, with the definition of a Bravais lattice

Definition 9.1.1 (Bravais Lattice). A Bravais lattice is defined as a set of discrete points which can be described with a lattice vector $\underline{R} = n_1 \underline{a}_1 + n_2 \underline{a}_2 + n_3 \underline{a}_3$, where $n_1, n_2, n_3 \in \mathbb{Z}$ and \underline{a}_i are linearly independent basis vectors. Therefore

$$\begin{aligned} R &= na && \text{in 1D} \\ \underline{R} &= n_1 \underline{a}_1 + n_2 \underline{a}_2 && \text{in 2D} \\ \underline{R} &= n_1 \underline{a}_1 + n_2 \underline{a}_2 + n_3 \underline{a}_3 && \text{in 3D} \end{aligned} \quad (9.8)$$

And with the usage of the Bloch theorem, which states

T H E O R E M 9.1 (Bloch Theorem). Given a Hamiltonian with a lattice-periodic potential $V(\underline{r}) = V(\underline{r} + \underline{R})$, where \underline{R} is a lattice vector, the eigenfunctions of the system will be of the following shape

$$\psi_{\underline{k}}(\underline{r}) = e^{i\underline{k}\underline{r}} u_{\underline{k}}(\underline{r}) \quad (9.9)$$

Where $u_{\underline{k}}$ is a lattice-periodic function. The wavefunction $\psi_{\underline{k}}$ is known as a Bloch wave.

All this summed up, for a 3D lattice, we will have

$$\begin{aligned} |k\rangle &= \frac{1}{\sqrt{N_1 N_2 N_3}} \sum_{n_1=1}^{N_1} \sum_{n_2=1}^{N_2} \sum_{n_3=1}^{N_3} e^{ia(k_x n_1 + k_y n_2 + k_z n_3)} |n_1 n_2 n_3\rangle \\ \epsilon_{\underline{k}} &= \epsilon_0 - 2t \cos(k_x a) - 2t \cos(k_y a) - 2t \cos(k_z a) \end{aligned} \quad (9.10)$$

§ 9.2 Fermi Level

As seen in Statistical Mechanics, the electrons, being fermions with $s = 1/2$ must obey the Fermi-Dirac statistic, where the density of states is some function $g(\epsilon)$. The number of states will be given by the integral of this probability density function $g(\epsilon)$, remembering that if dN is the number of states between $\epsilon, \epsilon + d\epsilon$ and g is the degeneracy of the levels, we have

$$\int_{-\infty}^{\infty} g(\epsilon) d\epsilon = \frac{N}{g}$$

Since for electrons we have a degeneracy of 2, since $m_s = \pm 1/2$ we can say that in general, the number of states possible is $2g(\epsilon)d\epsilon$. It's obvious that the Fermi-Dirac distribution must be a Dirac delta for discrete spectra (like the QHO), where

$$g(\epsilon) = \sum_i \delta(\epsilon - \epsilon_i)$$

Where i is a quantum number.

In general, for solids we will search the density of states in a certain energy interval, given by $g(\epsilon)/V$ where V is either the length, surface or volume (in 1D, 2D or 3D) of the lattice.

Due to the high number of atoms in the crystals we treat it's common to employ the following approximation, where we will move everything from the discrete sums to a continuous integral, where in 3 dimensions, we have

$$\frac{1}{V} \sum_i \rightarrow \frac{1}{(2\pi)^3} \int_B d^3k$$

Where we also approximated $\underline{k}_m \rightarrow \underline{k}$, considering it as a continuous quantum number. Note that B is Brillouin's first zone.

Using the definition of $\epsilon_{\underline{k}}$ given in (9.10) the integral is solvable in 1D, and therefore, we get

$$g(\epsilon) = \begin{cases} \frac{1}{\pi a} \frac{1}{\sqrt{4t^2 - (\epsilon - \epsilon_0)}} & |\epsilon - \epsilon_0| < 2t \\ 0 & |\epsilon - \epsilon_0| > 2t \end{cases} \quad (9.11)$$

The Fermi level of a crystal, is defined as the level with energy ϵ_F such that the highest possible state is occupied by fermions at $T = 0$. For electrons we have, supposing a univalent crystal with only one basis orbital (a one level system) for N atoms, we have that

$$N_{e-}(\epsilon_F) = N = 2 \int_{-\infty}^{\epsilon_F} g(\epsilon) d\epsilon \quad (9.12)$$

Note that the integral must be equal to the number of atoms, since that's the number of electrons in the system, since each atom is univalent.

By sheer logic, since each cell of the crystal can be occupied by two electrons, we have that $N/2$ cells are occupied and $N/2$ are unoccupied, therefore at $T = 0$ K, noting that the energy band is symmetric with respect to ϵ_0 ($|\cos(x)| \leq 1$), we can immediately say that having the first $N/2$ cells occupied, it implies that the Fermi level must lay at the center of the band, giving $\epsilon_F = \epsilon_0$.

If this is generalized to two or three dimensional lattices, we can define a Fermi surface, i.e. a surface Σ_F defined as follows

$$\Sigma_F := \{\underline{k} \in \mathbb{R}^3 \mid \epsilon_{\underline{k}} = \epsilon_F\}$$

i.e. it's the set of all wavevectors \underline{k} such that $\epsilon_{\underline{k}} = \epsilon_0$.

For a tight-binding Hamiltonian in 3D, where all the atoms are in an univalent lattice, we can immediately say that since $\epsilon_0 = \epsilon_F$, the Fermi surface will be the solution of the following equation

$$\cos(k_x a) + \cos(k_y a) + \cos(k_z a) = 0 \quad (9.13)$$

§ 9.3 Free Electron Approach to Metals

§§ 9.3.1 Drude Theory of Conduction

The idea of conduction theorized by Drude is a completely classical idea.

Suppose having a metal with Z valence electrons and N atoms with charge $+Z_a e$. These electrons move almost freely on the surface of the metal, where their only interaction is through collisions with the ions.

Supposing these collisions as “conduction collisions” we can write Newton’s equation of motion for this system

$$m\underline{a} = e\underline{E} \implies \underline{a} = -\frac{e\underline{E}}{m} \quad (9.14)$$

By integrating on t and including $\langle \underline{v}_0 \rangle = 0$ by hypothesis, we have that on average, for each electron

$$\langle \underline{v}_{e-} \rangle = \left\langle \frac{e\underline{E}}{m} t \right\rangle = \frac{e\underline{E}}{m} \tau \quad (9.15)$$

Where τ is the “relaxation time” of the metal, i.e. the average time between the collisions of the electrons.

By definition of current we can see that it will be proportional to the average velocity of the electrons times the number density of electrons in the metal, therefore, writing Ohm’s law

$$\underline{J} = -ne \langle \underline{v}_{e-} \rangle = \sigma \underline{E} \implies \sigma = \frac{ne^2}{m} \tau \quad (9.16)$$

Where σ is the conductivity of the metal.

Since the system is completely classical, we have that the electrons will follow a Maxwell-Boltzmann distribution of velocities, and since $\langle E \rangle = 3k_B T/2$ we also have that the electron speed is tied to the temperature of the metal with the following formula

$$\langle \underline{v}_{e-} \rangle (T) = \sqrt{\frac{3k_B T}{m}} \quad (9.17)$$

The mean free path of the electrons on the metal will obviously be given by the formula $\lambda = |\langle \underline{v}_{e-} \rangle| \tau$.

§§ 9.3.2 Sommerfeld Theory of Metals and Conduction

The Sommerfeld theory is basically a quantum approach to Drude's classical theory. The first idea behind this is to evaluate the free electrons of the solid inside a box of volume $V = L^3$. The Schrödinger equation for such system will be

$$\begin{aligned}\frac{\hbar^2}{2m}\nabla^2\psi &= \epsilon_{\underline{k}}\psi \\ \psi(\underline{r} + \underline{L}) &= \psi(\underline{r})\end{aligned}\tag{9.18}$$

This equation has a solution a plane wave with normalization $V^{-1/2}$, and a quantization of the wavenumber $\underline{k}_n = 2\pi L^{-1}(n_x, n_y, n_z)$. Note that since we didn't consider a lattice structure the electrons are completely free and \underline{k} isn't confined to Brillouin's first zone.

From this we can say that since the particles considered must obey Fermi-Dirac's statistic, we have that at $T = 0$ the density of states will be confined inside a minimal volume V_F in k space it, where

$$V_F = \frac{4}{3}\pi k_F^3$$

The Fermi momentum is implicitly defines Fermi's momentum k_F , where

$$\epsilon_F = \frac{\hbar^2 k_F^2}{2m} \implies k_F = \sqrt{\frac{2m}{\hbar^2} \epsilon_F}$$

The density of states will be $\rho(k) = 2V/8\pi^3$ for electrons ($g = 2$) and the total number of states will therefore be

$$N_s = \rho(k)V_F = \frac{V}{3\pi^2} k_F^3$$

Which, if we write $n = N_s/V$ as the number density of states gives

$$k_F = \sqrt[3]{3n\pi^2}\tag{9.19}$$

Rearranging everything using (9.19) we end up having the following expressions for the Fermi energy in terms of the density of electrons

$$\begin{aligned}\epsilon_F(n) &= \frac{\hbar^2}{2m} (3n\pi^2)^{\frac{2}{3}} \\ n(\epsilon_F) &= \frac{1}{3\pi^2} \left(\frac{2m\epsilon_F}{\hbar^2} \right)^{\frac{3}{2}} \\ n(k_F) &= \frac{k_F^3}{3\pi^2}\end{aligned}\tag{9.20}$$

Another intrinsic characteristic of the metal is the Fermi temperature T_F of such, which is simply $T_F = k_B^{-1}\epsilon_F$.

Using statistical mechanics we can approximate the energy distribution for electrons, and expanding around ϵ_F we get

$$g(\epsilon) = \frac{4}{3} \frac{n}{\epsilon_F} \sqrt{\frac{\epsilon}{\epsilon_F}} \quad \epsilon \geq 0$$

Inserting this into the Fermi-Dirac distribution we have that

$$\mu \approx \epsilon_F - \frac{\pi^2}{6} \frac{g'(\epsilon_F)}{g(\epsilon_F)} = \epsilon_F \left[1 - \frac{1}{3} \left(\frac{\pi}{2} \frac{T}{T_F} \right) \right]$$

Indicating that since $T/T_F \ll 1$ at room temperature, Sommerfeld's free electron approach is a good approximation for what happens in a metal, since $\epsilon \approx \epsilon_F$

Suppose now that we want to calculate another property of the metal itself, the specific heat at constant volume.

Using statistical mechanics again we have that the energy per single electron is given by

$$\frac{E}{N} = \frac{u}{n} = \frac{u_0}{n} + \frac{\pi^2}{6} \frac{2g(\epsilon_F)}{n} (k_B T)^2$$

Where $g(\epsilon_F)$ is our well known Fermi-Dirac distribution evaluated at the Fermi energy.

Using the well known formula for calculating the specific heat we get

$$c_V = \frac{\partial u}{\partial T} = \frac{\pi^2}{2} \left(\frac{k_B T}{\epsilon_F} \right) k_B T = \frac{\pi^2}{2} \left(\frac{T}{T_F} \right) n k_B$$

§ 9.4 blah blah

hi this is a test <++>