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Presentation

0.1 Bibliography

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Capítol 1

Thermal Radiation and Photons

1.1 Blackbodies

Definició 1.1.1. *Thermal Radiation:* Radiation that a body emits because of its temperature.

Bodies emit ans absorb heat from their environment. If $T_{body} = T_{env}$, then there's a thermal equilibrium and the emission rate is equal to the absorption rate.

At high temperature, the emmited light is more intense than the reflected light, and objects become self-luminous (e.g. a piece of iron in a fire).

Important: Radiation $\neq$ Radioactivity

Definició 1.1.2. *Blackbody:* Idealized bodies that absorb all incident thermal radiation (e.g. stars). All blackbodies at the same temperature exhibit the same spectrum of emitted radiation: *blackbody radiation.*

Blackbody properties at thermal equilibrium:

- Ideal emitter (emits the largest amount of radiation at each frequency, compared with any other body at the same temperature.
- They radiate isotropically.

Definició 1.1.3. *Spectral Radiance:* Spectral distribution of thermal radiation from a blackbody, $R_v(T)$, defined as the power emitted per unit surface from an object at temperature T and in the frequency interval from ν to $\nu + d\nu$. Its units are $[R_V(T)] = Wm^{-2}Hz^{-1}$. If you integrate it for all ν, you get *radiance.*

We will not prove it in this course, but $R(T) = \frac{c}{4}\rho(T)$.

Definició 1.1.4. *(Spectral) Energy Density:* Energy contained per unit volume of the cavity at temperature T in the frequency interval from ν to $\nu + d\nu$. It is proportional to the spectral radiance. Its units are $[\rho_v(T)] = Jm^{-3}Hz^{-1}$.

1.1.1 Experimental results

The radiance increases rapidly with increasing T. This result is known as *Stefan's Law*: $R(T) = \sigma T^4$, where $\sigma := 5.67 \cdot 10^{-8} W m^{-2} K^{-4}$ is the *Stefan-Boltzmann constant.*

As T increases, the frequency at which the spectral radiance is maximum also increases. This shift is known as *Wien's Law*, and follows $\lambda_{max} T = 0.2898 cm\, K$.

Earth's atmosphere is opaque to most of the electromagnetic spectrum, and the photons emitted by the sun (visible light) are in one of the few frequency windows in which our atmosphere is transparent.

1.1.2 Classical Approach

In the late 19th century, James Jeans and Lord Rayleigh tried to explain the theory behind the blackbody phenomena with classical physics. They considered the model of a hollow metallic cube of sides L in thermal equilibrium.

When an electromagnetic wave hits a wall of the cube, the free electrons in the metal would move subject to the electrical and magnetic fields. However, this would contradict the postulate that the cube is in thermal equilibrium, so E and B must be zero at the walls. Therefore, the electromagnetic waves are standing waves.

The simplest standing wave of length L would be that with only 2 nodes (corresponding to $n = 1$). And the wavelength and frequency of each harmonic can be calculated as

$$L = n\frac{\lambda}{2} \iff n = \frac{2L}{\lambda} = \frac{2L}{c}\nu$$

If we insert waves inside the cube that are not harmonics, they must be absorbed by the walls (and possibly reemitted), as they can not be present when the cube reaches thermal equilibrium.

In order to calculate the energy density of the cube, Jeans and Rayleigh calculated the number of waves at each frequency and the average energy of each wave. Then,

$$\rho_\nu(T)d\nu = \frac{N(\nu)d\nu\langle E\rangle}{V}$$

The number of waves of frequencies lower or equal than n is simply n. Therefore, $N(\nu)d\nu = \frac{2L}{c}(\nu + d\nu - nu) = \frac{2L}{c}d\nu$. This number has to be multiplied by 2 in order to account for polarization (see E&R for more details). Thus,

$$N(\nu)d\nu = \frac{4L}{c}d\nu$$

This corresponded to the case in 1D. In 3D, it can be proved that

$$N(\nu)d\nu = \frac{8\pi}{c^3}V\nu^2 d\nu \implies \rho_\nu(T)d\nu = \frac{8\pi}{c^3}\langle E\rangle \nu^2 d\nu$$

It is known that for any system, the mean energy of its particles (or waves) is given by $\langle E\rangle = kT$, where k is the *Boltzmann's constant.* Plugging the last equation here, we get that

$$\rho_\nu(T)d\nu = \left(\frac{8\pi}{c^3}kT\right)\nu^2 d\nu$$

The problem is that this last equation does not correspond with the experimental data that was gathered before. For large ν, according to the theoretical approach, $\rho_\nu \to \infty$, while according to the experimental approach, $\rho_\nu \to 0$. This discrepancy was known as the *UV-Catastrophy*

1.2 Planck's Theory of Radiation

In order to explain the experimental results by Jeans and Rayleigh, Planck postulated that for low frequencies, $\langle E\rangle \to kT$; and for high frequencies, $\langle E\rangle \to 0$. Therefore, $\langle E\rangle$ is a function of the frequency. After lots of trial and error, he proposed that

$$E_n = nh\nu$$
$$\langle E\rangle = \frac{\sum E_n P_n}{\sum P_n} = \sum E_n P_n = h\nu \sum nP_n$$

where P_n is given by a Boltzmann distribution, so

$$P_n = \frac{e^{-E_n/kT}}{\sum e^{-E_n/kT}} \implies \langle E\rangle = h\nu \frac{\sum ne^{-nh\nu/kT}}{\sum e^{-nh\nu(kT}}$$

If we define $x := exp(-h\nu/kT)$, then the last formula is expressed as

$$\langle E\rangle = h\nu \frac{\sum nx^n}{\sum x^n}$$

$x < 1$, so we can treat the series as geometric series:

$$\langle E\rangle = h\nu \sum_{n=1}^{\infty} x^n = h\nu \frac{x}{1-x} = \frac{h\nu}{e^{h\nu/kT}-1}$$

Therefore, the spectral energy density according to Planck is given by

$$\rho_\nu d\nu = \frac{8\pi}{c^3}\frac{h\nu^3}{e^{h\nu/kT}-1}d\nu$$

Aproximating the exponential by its first order Taylor polinomial, $\langle E\rangle = kT$, which is a good aproximation for small frequencies.

Let's calculate now the total energy density for all frequencies:

$$\rho(T) = \int_0^\infty \rho_\nu d\nu = \frac{8\pi}{c^3}h\int_0^\infty \frac{\left(\frac{kT}{h}\right)^4 x^3dx}{e^x-1} = \left(\frac{8\pi k^4}{c^3h^3}\right)T^4\int_0^\infty \frac{x^3dx}{e^x-1}$$

The integral is tabulated, and is found to be equal to $\pi^4/15$. Therefore:

$$\rho(T) = \frac{8\pi^5k^4}{15c^3h^3}T^4$$

This formula can be related to the radiance:

$$R(T) = \sigma T^4 = \rho \frac{c}{4} \implies \rho = \frac{4c}{\sigma} T^4 \equiv aT^4,$$

where a is called the *radiation constant.*

An analogous formula for the energy density at small wavelength intervals can be derived from the previous one:

$$\rho_\lambda(T)d\lambda = \frac{8\pi hc \, d\lambda}{\lambda^5 \left(e^{hc/\lambda kT} - 1\right)}$$

1.3 Photons. Photoelectric & Compton Effects

There are many ways in which radiation interact with matter, but the most important are:

- **Scattering/Absoption of radiation** ⟶ Photoelectric Effect, Compton Effect, pair production
- **Production of radiation** ⟶ Bremsstrahlung, pair annihilation

1.3.1 Photoelectric Effect

In 1886, Hertz confirmed the existance of electromagnetic waves, and he started studying the emission of electrons when a catode was radiated with light.

Hertz found that for great differences of potential, there was a maximum of electrons that went from one electrode to the other (i.e. there is a moment at which the current *saturates*). When he applied a negative difference of potential, he found that some of the electrons still reached the opposite electrode. The voltage for which no electron reached the anode (V_0) is called the *stopping potential.*

Hence, he deduced that some of the electrons are emitted with an initial kinetic energy, which could be calculated by

$$K_{max} = eV_0$$

However, he was surprised to discover that V_0 did not depend on the intensity of the radiation, contradicting the current understanding of waves.

In 1914, Milikan found that V_0 does depend on the frequency of the light, and that there is a *cutoff frequency* below which no photoelectric result is obtained.

Therefore, the photoelectric effect could not be explained by classical physics, which predicted that

- K_{max} should depend on the intensity of light.
- Some electrons should be emitted for any frequency.

- There should be a noticeable time lapse between absorption of radiation and emission of the electron, during which the electron gradually accumulates the energy needed to escape.

In order to explain why this did not happen, Einstein proposed that radiant energy was quantized into entities (later known as photons). These entities interact one-to-one with electrons, and only if the energy transmitted is high enough, the electron is extracted from the metal. The kinetic energy of the electron would then be the difference between the energy provided by the photon and the minimum work required to get the electron out, also known as *work function* W_0.

$$h\nu - W = K \implies K_{max} = h\nu - W_0$$

This theory meets all the aforementioned objections:

- K_{max} does not depend on the intensity of the light $\longrightarrow$ doubling the intensity doubles the number of photons, but not its individual energy.
- For low frequencies, no electron is emitted $\longrightarrow$ Let $\nu_0 = w_0/h$. If $\nu < \nu_0$, no electron can get extracted, as they can only absorb one photon each.
- Absence of a time lag $\longrightarrow$ The energy is supplied in *packets*, so the electron gets all the energy at once and is excited almost instantaneously

Besides, this theory allowed Milikan to compute Planck's constant independently, thanks to the linear relation between V_0 and the frequency of the light.

$$K_{max} = eV_0 \implies V_0 = \frac{h\nu}{e} - \frac{w_0}{e} \implies \frac{h}{e} = \frac{dV_0}{d\nu}$$

The value of h was found to be very similar to that calculated via blackbody experiments, so the photoelectric effect constitutes an independent proof of the discontinuity of energy emission.

1.3.2 Special Relativity

Special Relativity is not the main object of this course, but there are a few formula we need to know:

$$E = (\text{rest mass energy}) m_0 c^2 + \ (\text{kinetic energy}) K,$$

where $m_0 = m/\gamma$.

$$p = mv = \frac{m_0 v}{\sqrt{1 - v^2/c^2}}$$
$$E^2 = (pc)^2 + (m_0 c)^2$$

Notice that, as the energy of a photon is finite ($E = h\nu$) and its velocity is c, in order for these formula to make sense, its mass must be zero.

1.3.3 Compton Effect

In 1923, Compton bombarded a graphite target with a beam of X-rays (high-energy photons) of wavelength λ, and measured the intensity of the scattered X-rays as a function of their wavelength for various angles of scattering.

Although the inciding beam was characterized by a single λ, Compton found that the scattered X-rays corresponded to 2 different values of λ, one being the incident λ, and the other having shifted by an amount of $\Delta\lambda$ *(Compton Shift)*. Besides, he found that this shift depended on the angle of scattering.

According to classical physics, the inciding beam would be an electromagnetic wave, which would cause the electrons in the target to oscillate with its same wavelength λ. Therefore, when radiation is later emitted, it will also have the same wavelength, contradicting the experimental results.

In order to solve this problem, Compton realized that photons must be interpreted as particles, that collide with electrons and transfer some energy to them, increasing their wavelength.

Experimentally, the frequency of the scattered radiation appears to be independent of the material of the target, so Compton suggested that scattering does not involve entire atoms, but just a photon colliding with an electron (with this simplification we suppose that the energy used to extract the electron is negligible, which is a sound approximation when working with X-rays).

Let's consider the photon approaches the elctron in 2D along the X axis. Let θ be the angle of deviation of the photon after the collision with respect to the X axis, and let ϕ be the angle of recoil of the electron (also respect to the X axis). Then the problem can be reduced to:

$$\begin{cases} E_0 + m_0c^2 = K + E_1 + m_0c^2 \\ p_0 = p_1\cos\theta + p\cos\phi \\ p_1\sin\theta = p\sin\phi \end{cases} \quad \cdots \implies \Delta\lambda = \lambda_1 - \lambda_0 = \lambda_c(1-\cos\theta),$$

where $\lambda_c := h/m_0c = 0.0243\text{Å}$ is known as the *Compton wavelength.*

Notice that the Compton shift depends on the angle of scattering: $\Delta\lambda \in [0,\ 2\lambda_c]$.

The presence of the 1st peak (at $\lambda = \lambda_{\text{incident}}$) corresponds to the case where the electron is closely bound to the atom, so the whole atom is involved in the collision and the total mass is very big $\implies \lambda_c \to 0$. This type of scattering is usually called *Rayleigh scattering.*

The ocurrence of each effect depends on the type of light:

- If the incident light is visible, microwave or radio $\longrightarrow \lambda >> \Delta\lambda \implies$ Rayleigh scattering.
- If the incident light is X-rays or gamma-rays $\longrightarrow \lambda \cong \Delta\lambda \implies$ Compton scattering.

1.4 X-Rays

Definició 1.4.1. X-rays are defined as electromagnetic waves with λ from 0.01 to 10 nm.

X-rays can be produced when a beam of electrons is accelerated by a voltage of KVs and then stopped upon hitting a target. This effect is usually known as *bremsstrahlung.*

Classical physics predicted that the deceleration of a particle would emit radiation in a continous spectre. However, experimental data showed that there existed a wavelength threshold λ_{max} below which no radiation was emitted. This wavelength threshold was found to only depend on the voltage V used to accelerate the particle.

The quantized intepretation of energy allows us to give an easy explanation to this phenomena. When the electron interacts with a nucleus (a particle much more massive than itself), it transfers momentum to it and loses energy. The lost energy is expelled in the form of an X-ray photon, with an energy of

$$h\nu = K_0 - K_f \implies \lambda = \frac{hc}{K_0 - K_f}$$

The more energy an electron loses, the shortest the wavelength of the photon will be. Then,

$$\lambda_{min} = \frac{hc}{K - 0} = \frac{hc}{eV}.$$

If $h \to 0$, then $\lambda_{min} \to 0$, and we would get the classical result.

1.5 Pair Production and Annihilation

1.5.1 Pair Production

The pair production phenomenon happens when a high-energy photon loses all its energy in an encounter with a nucleus, thereby creating a pair particle (electron - positron).

In this process, it is usually considered that the nucleus has a big mass, so it absorbs a negligible amount of energy. Therefore, by conservation of energy:

$$h\nu = E_- + E_+ = (m_0c^2 + K_-) + (m_0c^2 + K_+) = K_- + K_+ + 2m_0c^2$$

Usually, K_- and K_+ are considered to be equal, though this might not always be the case (the difference in charge causes one to be more atracted to the nucleus than the other).

Conservation of momentum prevents this process to ocurr in empty space (i.e. without the nucleus to mediate).

Electron-positron pairs are produced in nature by *cosmic-ray photons*, and in the lab through *bremsstrahlung photons* in particle accelerators. It is much harder to obtain any other pair of particles, as the energy needed to create a pair of particles depends on its rest mass, and protons or neutrons are much more massive than electrons. However, with photons of high enough frequency, it is theoretically possible.

1.6 Annihilation

If an electron and positron are at rest, they atract each other and eventually collide and annihilate, creating photons. It isn't possible that a single photon is created, as then momentum wouldn't be conserved, so usually 2 photons are created, moving in opposite directions (and in some cases, 3 photons or more). The frequency of the 2 photons must be equal:

$$p_1 + p_2 = 0 \implies |p_1| = |p_1| \implies \frac{h\nu_1}{c} = \frac{h\nu_2}{c} \implies \nu_1 = \nu_2$$

Energy conservation requires that

$$2m_0c^2 = 2h\nu \implies h\nu = 511 \text{ KeV}$$

Definició 1.6.1. *Positronium:* Short-lived pseudo-atom formed by a positron and an electron. Depending on its specific configuration, it can lead to emission or annihilation.

Capítol 2

Quantization and Early Atomic Models

2.1 Wave-Particle Duality

2.1.1 Matter Waves

De Broglie, in 1924, suggested that the dual behaviour of radiation apllies equally well to matter. Therefore, he suggested a relation between the energy or momentum of the particle and the frequency of the associated wave. The relativistic energy of a particle is defined as

$$E^2 = p^2c^2 + m_0^2c^4$$

For photons, $m_0 = 0 \implies p = E/c = h/\lambda$. In analogy to photons, De Broglie proposed that each particle had a wavelength $\lambda_{DB} = h/p$.

At first, De Broglie theory was considered to be original but unreal. However, only 5 years later it had became widely accepted and he was given a Nobel Prize. Nowadays, particles are treated as matter or waves indistinctly, and their properties are related by

$$E = h\nu$$

$$\lambda = \frac{h}{p}$$

Wave aspects of matter manifest in the phenomena of diffraction and interference. However, for this phenomena to be noticeable, the wavelength of the wave must be similar to the size of the interacting matter. That's the reason why we don't usually treat macroscopic objects as waves. Their wavelengths are so small that they can not interact with ordinary matter.

Diffraction effects in light with an apparatus of size D are confined to angles $\theta \cong \lambda/D$. For example, in the case of a circular aperture, the area between the first minimum and the centre of the image (also called the airy disk), is given by an angle of $\theta \cong 1.22\lambda/D$. Thus, diffraction effects are hardly noticeable when $\lambda << D$.

In order to prove that electrons are also waves, Davidson & Germer did an experiment in 1925 in which they observed the interference patterns produced by the reflection of an electron beam on a crystal. Let d be the distance between two layers of crystal, and let ϕ be the angle between the inciding electrons and the surface of the crystal. Then, the extra path travelled by an electron that goes one layer deeper before bouncing is $2l = d \sin \phi$. Therefore, the maxima (constructive interference points) are obtained when $d \sin \phi = n\lambda$, which is commonly referred to as the *Bragg Relation.* With the results of the experiment, the wavelength of the electron was confirmed to be $\lambda = h/p$.

2.1.2 Wave-particle Duality

We have seen that both matter and radiation have wave and particle effects. Due to Planck's constant being so small, the momentum of a particle needs to be very small for the wavelength to be noticeable (remember $\lambda = h/p$). Therefore, wave effects are only observed in objects of a microscopic scale.

Consequences of wave-particle duality:

- If an entity is detected, it acts as a particle (localized); if an entity is moving, it acts as a wave (not localized).
- Bohr's *principle of complementarity:* If the wave or particle character of an entity is proved in a measurement, then it is impossible to prove the converse character in the same measurement.
- The link between wave and particle models: probability interpretation (probability waves).

If we consider light is made of photons, its energy density can be expressed as $\rho = Nh\nu$, where N is the number of photons per cubic meter. If we consider light as a wave, then its energy density is given by $\rho = \varepsilon_0 \langle E^2 \rangle$, where

$$E(x,t) = A \sin 2\pi \left(\frac{x}{\lambda} - vt \right).$$

When we combine both interpretations, we get that $Nh\nu = \varepsilon_0 \langle E^2 \rangle \implies N \propto \langle E^2 \rangle$ (i.e. the number of photons is proportional to the square mean of the magnitude of the electric field).

In analogy to that, Max Born introduced the wave function to represent matter waves:

$$\Psi(x,t) = A \sin 2\pi \left(\frac{x}{\lambda} - vt \right)$$

Just like the square of the electric field gave a way to quantify the number of photons, the square of the wave function ($|\Psi^2|$) gives the *probability density* of the wave, that is, the probability of finding a particle per unit volume at a given place and time.

The principle of superposition applies to matter waves just as it did to radiation. Thus, if we have two matter waves with wave functions Ψ_1 and Ψ_2, their superposition will give a wave with wave density $\Psi = \Psi_1 + \Psi_2$.

This effect can be seen for example in the double-slid experiment with electrons:

Let d be the distance between slids, let θ be the angle for which we will calculate the interference and let d_1 and d_2 be the paths travelled by two electrons from different slids. Then, $d_2 - d_1 = d \sin \theta$. Therefore, the angles of maximum intensity will be the ones that satisfy $n\lambda = d \sin \theta$.

2.2 Uncertainty Principle

The probabilistic interpretation of matter waves implies that quantum mechanics can not be deterministic. This intuition is formalized by *Heisenberg's Uncertainty Principle*, that states that we cannot measure simultaneously the position and momentum (or energy and time intervals) of matter or radiation with arbitrarily good precision, as the precision of the measurement is limited by

$$\Delta p_x \Delta x \geq \frac{\hbar}{2}$$
$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

where $\hbar := h/2\pi$. The idea behind this principle comes from a thought experiment called *Heisenberg's microscope*:

Let's suppose we want to observe an electron. In order to do so, we illuminate it with light of frequency λ, and we detect the reflected light with a microscope of diameter D, and focal length f. Also let θ be the angle comprised by the line that goes from the electron to the center of the lens, and the line that goes from the electron to the edge of the lens.

We can suppose that the momentum of the electron before the scattering is $p = 0$. But when the photon collides with the electron, it conveys a momentum to it. Its maximum value is $p_{max} = h \sin\theta / l$, and its minimum value is $p_{min} = -h \sin\theta / l$.

In order to interfere as less as we can with the electron, we make θ very small, and therefore we can assume that $\sin\theta \cong \theta$ and that the wavelength of the photon stays constant.

$$\Delta p_x = p_{max} - p_{min} = 2\frac{h}{\lambda}\sin\theta \cong 2\frac{h\theta}{l}$$

The diffraction limit (i.e. the smallest angular size we can measure) is $theta \cong \lambda/D$. Then, when we to calculate the x position of the electron, $\Delta x \cong f\theta \cong f\lambda/D \cong \lambda/\theta$. Therefore, if λ is large, Δx becomes large, and if λ is small, then Δp_x becomes large.

Following this line of reasoning, we can also get an estimate of the value of the product of uncertainties:

$$\Delta p_x \Delta x \cong \frac{2h\theta}{\lambda}\frac{\lambda}{\theta} = 2h.$$

The second version of the Uncertainty Principle (the one about energy and time) can be derived from the first:

Let's consider a particle moving along the x-axis.

$$E = \frac{p_x^2}{2m} \implies \Delta E = \frac{\partial E}{\partial p_x}\Delta p_x = v_x \Delta p_x$$
$$\Delta x = v_x \Delta t \implies \Delta t = \frac{\Delta x}{v_x}$$

Multiplying both equations, we get

$$\Delta E \Delta t = v_x \Delta p_x \frac{\Delta x}{v_x} = \Delta p_x \Delta x \implies \Delta E \Delta t \geq \frac{\hbar}{2}$$

Quantum theory probabilistic nature can be intepretated in different ways:

- **Copenhagen Interpretation:** Probabilistic/Indeterminate nature of quantum theory is a fundamental part of physical reality.
- **Einstein - De Broglie Interpretation:** Reality is deterministic but the current theories are not sufficiently advanced to explain it.

The Copenhaguen Interpretation is the most widely accepted one nowadays.

Propagation of a matter wave

Let's suppose we have a matter wave with wave function $\Psi(x,t) = A \sin 2\pi(x/\lambda - \nu t)$. The position of a node is given by $\Psi(x,t) == 0 \implies x_n = \lambda \nu t$. Therefore, the velocity of the wave is

$$w := \frac{\partial x_N}{\partial t} = \lambda \nu = \frac{h}{p}\frac{E}{h} = \frac{E}{p} = \frac{v}{2}$$

This seems to imply that the wave is lagging behind the particle, as its velocity is half of the velocity of the particle! Besides, the wave is not localized, as it extends from $-\infty$ to ∞.

In order to solve these problems, we need to consider the superposition of several wave functions. Let's suppose we havea wave function formed by the superposition of two waves of slightly different wavelengths and frequencies:

$$\begin{aligned} \Psi(x,t) = \Psi_1(x,t) + \Psi_2(x,t) &== \sin 2\pi \left(kx - \nu t\right) + \sin 2\pi \left((k+dk)x - (\nu + d\nu)t\right) \\ &= 2 \cos 2\pi \left(\frac{dk}{2}x - \frac{d\nu}{2}t\right) \sin 2\pi \left(kx - \nu t\right) \end{aligned}$$

Then the wavelength of the envelope is given by $\lambda_{env} = 2/dk$, and the velocity of the envelope g (also called *group velocity*) is given by

$$\frac{dk}{2}x - \frac{d\nu}{2}t = 0 \implies g = \frac{dx}{dt} = \frac{d\nu}{dk} = \frac{dE/h}{dp/h} = \frac{dE}{dp} = v.$$

By superposing a group of waves in a range Δk, which will form an envelope with spatial extent Δx, it can be shown that

$$\Delta x \Delta k \geq \frac{1}{4}\pi$$
$$\Delta t \Delta \nu \geq \frac{1}{4}\pi$$

This result is obtained by going from an envelope (i.e. finite superposition of waves) to a well-localized infinite superposition of waves, using Fourier integrals:

$$\int_0^\infty A(k)\cos 2\pi kx\,dk$$

The details of the proof, however, are not relevant to this course, and can be found in the Appendix D of E&R.

Deriving the Uncertainty Principle is easy once we've got these expressions, as $E = h\nu$ and $p = h/\lambda = kh$.

2.3 Atomic Models

2.3.1 Thomson's Model

This model of the atom was proposed by J.J. Thomson, and is commonly known as the *plum pudding* model. It has the following characteristics:

- Negatively charged electrons are distributed within a continuous uniform distribution of positive charge
- In the lowest energy state of the atom, the electrons are fixed
- In excited atoms, the electrons vibrate (i.e. accelerate and emit EM radiation)

According to this model, the atraction force experimented by an electron at distance r to the center would be $F = kr$, so when an excited electron oscillates, it would do so in a simple harmonic motion, so it would only emit radiation of a single frequency (in the case of the hydrogen atom, where there is only one electron), and experimentally, radiation was found at different frequencies.

Thomson's Model was also put in doubt by *Rutherford's Experiment.* In this experiment, Rutherford shot alpha particles towards a thin gold foil, and studied the scattering patterns.

We can consider that each alpha particle collides with N atoms and is deflected by each of them by an angle of θ. The total reflection angle Θ can be calculated statistically, and the calculations yield a probability of having a $\Theta > 90°$ of 10^{-3500}. However, when Rutherford's experiment was carried out in the laboratory, a probability of 10^{-4} was obtained, giving an error of 3496 orders of magnitude!?

Therefore, Thomson's Model can not correspond to reality.

2.3.2 Rutherford's Model

Rutherford's experiment gave rise to a new model of the atom, where all the positive mass of the atom (nearly the total mass of the atom) is concentrated in a zone called nucleus. Then, the alpha particles are deflected by the electromagnetic repulsion with the atom nuclei.

The deflection angle of an alpha particle when it encounters an atom is given by $\cot\frac{\theta}{2} = 2b/D$, where b is the *impact parameter*, or the distance between the initial trajectory of the α-particle and the parallel line that goes through the nucleus of the atom; and D is defined as

$$D \equiv \frac{1}{4\pi\varepsilon_0}\frac{zZe^2}{Mv^2/2}$$

By operating with this formula, we get that the probability of having large total scattering angles is much higher than that of the Thomson's Model, so this interpretation of the atom gives a more precise account of reality. We are not going to derive the formula in this course, but we might use it in some problems, so here it is:

$$N(\Theta)d\Theta = \left(\frac{1}{4\pi\varepsilon_0}\frac{zZe^2}{2Mv^2}\right)^2 \frac{I\rho t 2\pi \sin\Theta d\Theta}{\sin^4(\Theta/2)},$$

where I is the incoming particle rate, t is the thickness of the foil and ρ is the number of nuclei by cm^3.

Now that we've characterized the nucleus of the atom, it's natural to wonder where the negative charge (the electrons) is. Rutherford conjectured that the electrons orbited the nucleus in a planetary-like model, but this would mean that the electrons would lose energy in the form of radiation (due to being accelerated) and would quickly collapse into the nucleus, so the resulting atom would not be stable.

2.3.3 Bohr's Model

A more accurate description of the atom was found when studying the spectral lines of the hidrogen atom. In atomic spectroscopy, the emitted radiation does not form a continuum (like a blackbody would), but it forms discrete spectral lines. This characteristic is also shared by the spectral absorption lines.

In 1913, Niels Bohr developed a model which could explain the spectroscopy data, and that was based in four postulates:

- An atomic electron moves in a circular orbit around the nucleus, under Coulomb attractive force.
- Only orbits with angular momentum $L = n\hbar$ are allowed
- Despite being accelerated, the electrons in an atom do not radiate electromagnetic energy.
- If an electron changes from an orbit with energy E_i to an orbit of energy E_f, it radiates electromagnetic radiation with a frequency given by
$$\nu = \frac{E_i - E_f}{h}$$

Following Bohr's interpretation, we get that

$$F = \frac{Ze^2}{4\pi\varepsilon_0 r^2} = \frac{mv^2}{r}$$
$$L = mvr = n\hbar$$

From this equations, we can derive the radii of the possible orbits:

$$r = \frac{4\pi\varepsilon_0 n^2\hbar^2}{mZe^2}$$

$$v = \frac{n\hbar}{mr} = \frac{Ze^2}{4\pi\varepsilon_0 n\hbar}$$

The velocities we have obtained are much lower than c for small n, so we can safely assume that we are in a non-relativistic setting. The energy of the orbiting electrons can be calculated as $E = K + V$, getting the following formula:

$$E = -\frac{mZ^2e^4}{n^2(4\pi\varepsilon_0)^2 2\hbar^2} = -V$$

That result means that the energy of the electrons in an atom is quantized. We also know that the most stable situation will be the one with the lower energy, that in this case corresponds to $n = 1$. As $n \to \infty$, $E \to 0 \implies$ if n were to get to ∞, the electron would be free from the attraction of the atom (i.e. $E > 0$).

The value of $-E_1$ is sometimes called the *binding energy* or *Bohr's energy*, and has an approximate value of -13.606 eV.

If we used the last energy formula to calculate the ΔE of a transition between two different states, we would get the wavelength and frequency formula that we saw before, which was an experimental result that came from atomic spectroscopy.

In the preceding discussion, we have considered that the mass of the nucleus is infinitely larger than the mass of the electron. However, this is not entirely accurate, so a more precise formula can be found if we replace R_∞ by $R_M := \frac{M}{m+M}R_\infty$, which is known as the *finite mass correction.*

Capítol 3

Schrödinger's Theory of Quantum Mechanics

3.1 Schrödinger's Equation

In this section, we are going to explore the insight that lead Schrodinger to derive his famous equation. Let's suppose we've got a free particle. The simplest assumption would be that its wave function is a sinusoidal wave, such as

$$\Psi(x,t) = \sin 2\pi\left(\frac{x}{\lambda} - \nu t\right) = \sin\left(\frac{2\pi}{\lambda}x - 2\pi\nu t\right) = \sin(kx - \omega t),$$

where k is called the *wave number* ([rad/m]) and ω is the *angular frequency* ([rad/s]).

In order for this equation to accurately describe quantum mechanics, it must have the following properties:

- Compatible with $E = h\nu$ and $\lambda = h/p$
- Energy Conservation: $E = K + V = \frac{1}{2}mv^2 + V = \frac{p^2}{2m} + V$, where V is the potential energy (not the potential), and we consider the classical kinetic energy formula (no relativistic effects yet).
- Linearity: Ψ_1, Ψ_2 solutions $\implies \Psi = c_1\Psi_1 + c_2\Psi_2$ is also a solution for any $c_1, c_2 \in k$.
- Potential energy is just a function of space ($V \equiv V(x)$). When we consider the case of a free particle (no net force acting on the particle), then $V = V_0$ (constant), because $F = -dV/dx = 0 \implies V = \texttt{ctt}$.

Once we have listed all the assumptions. We can try to get a law that defines Ψ. We start with the definition of energy, and change the variables to those we were working with in Ψ:

$$\frac{p^2}{2m} + V = E \implies \frac{h^2}{2m\lambda^2} + V_0 = h\nu \implies \frac{\hbar^2 k^2}{2m} + V_0 = \hbar\omega$$

If we are to obtain an equation that gives Ψ as a result, it seems plausible to think it will be a differential equation. When we calculate some derivatives of Ψ, we get:

$$\begin{aligned}\frac{\partial\Psi}{\partial t} &= -\omega\cos(kx-\omega t)\\ \frac{\partial\Psi}{\partial x} &= k\cos(kx-\omega t)\\ \frac{\partial^2\Psi}{\partial x^2} &= -k^2\sin(kx-\omega t) = -k^2\Psi\end{aligned}$$

Therefore, plugging this into our last equation, it looks like Schrödinger's Equation might be of the following form:

$$\alpha\frac{\partial^2\Psi}{\partial x^2} + V_0 = \beta\frac{\partial\psi}{\partial t}$$

but this equation does not satisfy lineality, so Schrödinger artificially modified the potential energy term, getting the following equation:

$$\alpha\frac{\partial^2\Psi}{\partial x^2} + V_0\Psi = \beta\frac{\partial\psi}{\partial t},$$

Substituting Ψ, we get

$$-\alpha k^2\sin(kx-\omega t) + V_0\sin(kx-\omega t) + \beta\omega\cos(kx-\omega t) = 0,$$

but there is not an easy way to find the coefficients α and β, so if we are to find a useful equation, we are in need of another interpretation.

Taking into account that the solution of the wave function is a complex exponential, it looks reasonable to suppose that Ψ is also be a complex exponential, of the form $\Psi = \cos(kx-\omega t) + \gamma\sin(kx-\omega t)$, where $\gamma \in \mathbb{C}$. In this case, after plugging the derivatives in our equation, we get

$$\left(-\alpha k^2 + V_0 + \beta\omega\gamma\right)\cos(kx-\omega t) + (-\alpha k^2\gamma + V_0\gamma - \beta\omega)\sin(kx-\omega t) = 0$$

This equality is valid for any x and t, so both coefficients must be zero. Therefore:

$$-\beta\omega\gamma = \frac{\beta\omega}{\gamma} \implies \gamma^2 = -1 \implies \gamma = \pm i$$

Thus, the possible wave functions are

$$\Psi(x,t) = \cos(kx-\omega t) \pm i\sin(kx-\omega t) = e^{\pm i(kx-\omega t)},$$

the values of the coefficients are

$$\begin{aligned}\alpha &= \frac{-\hbar^2}{2m}\\ \beta &= \pm i\hbar,\end{aligned}$$

and the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V_0\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

3.2 Born's Interpretation

In the beginnings of the quantum theory, there was no known physical intepretation for the wavefunction Ψ. In 1926, Max Born proposed what today is known as the Born Rule, that is, that the probability of finding a particle around location x at time t is given by

$$P(x,t)dx = \Psi^*\Psi dx$$

As the particle must be somewhere, the sum of all probabilities for a given time must equal 1:

$$\int_{-\infty}^{\infty} P(x,t)dx = \int_{-\infty}^{\infty} \Psi^*\Psi dx = 1$$

This normalization equation it's useful to calculate the amplitude of Ψ.

3.2.1 Expectation value

The average value of any physical magnitude (such as the position x of the particle) can be calculated by Born's Law by *sandwiching* it in between Ψ^* and Ψ:

$$\bar{x} = \langle x \rangle = \int_{-\infty}^{\infty} \Psi^* x \Psi dx$$
$$f(\bar{x}) = \langle f(x) \rangle = \int_{-\infty}^{\infty} \Psi^* f(x) \Psi dx$$

3.3 Momentum and Energy Operators

We are going to try to derive an expression for the momentum of a free particle. We have supposed previously that the wave function of a free particle is given by

$$\Psi(x,t) = e^{i(kx-\omega t)} \implies \frac{\partial \Psi}{\partial x} = ik\Psi$$

Using the De Broglie's relation, we get

$$\lambda = \frac{h}{p} \implies k = \frac{2\pi p}{h} \implies \frac{\partial \Psi}{\partial x} = i\frac{p}{\hbar}\Psi$$

From this equation we can derive a formula for the momentum operator:

$$p\Psi = \frac{\hbar}{i}\frac{\partial \Psi}{\partial x} \implies p \equiv -i\hbar\frac{\partial}{\partial x}$$

Similarly, we could relate the derivative of Ψ with respect to time to the function itself:

$$\frac{\partial \Psi}{\partial t} = -i\omega\Psi$$

Using Planck's relation, we get

$$E = h\nu \implies \omega = \frac{E}{\hbar} \implies \frac{\partial \Psi}{\partial t} = -i\frac{E}{\hbar}\Psi$$

From this equation we get an expression of the energy operator:

$$E\Psi = i\hbar\frac{\partial \Psi}{\partial t} \implies E \equiv i\hbar\frac{\partial}{\partial t}$$

From the expressions of momentum and energy operators, we could derive again Schrödinger's Equation:

$$E = K + V = \frac{p^2}{2m} + V \implies i\hbar\frac{\partial}{\partial t} = \frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)^2 + V = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V$$

3.4 Time-Independent Schrödinger Equation

In some cases, $\Psi(x,t) \equiv \psi(x)\phi(t)$. When this separation of variables is possible, the Schrödinger equation takes the following form:

$$-\frac{\hbar^2}{2m}\phi(t)\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\phi(t) = i\hbar\psi(x)\frac{d\phi(t)}{dt} \implies$$
$$\implies -\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + V(x) = i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt}$$

The LHS only depends on x, while the RHS only depends on t, so in order for this equation to be consistent for any x and t, both LHS and RHS must be constant. This constant is usually referred to as the *separation constant* and is equivalent to the total energy.

Let's tackle first the RHS:

$$i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt} = G \implies \frac{d\phi}{\phi} = -\frac{iG}{\hbar}dt \implies \phi = e^{(-iG/\hbar)t}$$

This is the form that the time-dependent part of the Schrödinger equation will take when the separation of variables is possible. Notice that we don't bother with the integration constant, as we'll later have to normalize $\Psi(x,t)$, so it won't matter anyway.

Let's repeat the same process with the LHS:

$$-\frac{\hbar}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + V(x) = G \implies -\frac{\hbar}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = G\psi(x)$$

Recalling that the momentum operator was defined as $p \equiv -i\hbar\ \partial/\partial x$, the last equation can be written as

$$\frac{p^2\psi}{2m} + V\psi = G\psi \implies K + V = G$$

Therefore, the constant G has been found to be equal to the energy E. Thus, the previous are usually expressed as:

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar},$$

where $\psi(x)$ must satisfy the following ODE:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x),$$

which is usually known as the *Time-Independent Schrödinger Equation (TISE).*

3.5 Examples

3.5.1 Free Particle

Let's consider the case where the net force acting upon the particle is equal to zero. $F = -dV/dx$, so $V(x)$ is constant, and we can assume that $V(x) = 0 \quad \forall x$. Then, the Schrödinger equation takes the following form:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = E\psi(x)$$

In previous lessons, we obtained the result that $\Psi(x,t) = e^{i(kx-\omega t)}$. We know that

$$\omega = 2\pi\nu = \frac{E}{\hbar}$$
$$k = \frac{2\pi}{\lambda} = \frac{p}{\hbar} = \frac{\sqrt{2mE}}{\hbar}$$

where we have used the fact that $E = K$, as $V = 0$. Substituting the value of ω, we get

$$\Psi(x,t) = e^{ikx}e^{-iEt/\hbar}$$

From here on, E&R try to give a physical meaning to $\psi(x) = e^{ikx}$, but JJ believes that this approach is conceptually wrong, as the wave function has no physical interpretation on its own, and E&R restrict their analysis to the real part of $\Psi(x,t)$ only. Therefore, we will use a different approach.

Let's compute the expectation value of the linear momentum:

$$\bar{p} = \int_{-\infty}^{\infty}\Psi(x,t)^* p\Psi(x,t) = \int_{-\infty}^{\infty}\Psi^*\left(-i\hbar\frac{\partial\Psi}{\partial x}\right) = k\hbar\int_{-\infty}^{\infty}\Psi(x,t)^*\Psi(x,t) = k\hbar > 0$$

The momentum is positive (i.e. directed to the right), so the wave function can be interpreted as a travelling wave, which moves to the right.

It is also interesting to see that $\psi(x) = Ae^{ikx} + Be^{-ikx}$ is a solution to TISE (it can be easily proved by plugging it into the equation). In the next subsection we derive this from the original differential equation.

Uncertainty Principle

When we have a free particle moving to the right, the momentum is fixed, so $\sigma_p = 0$. This doesn't actually violate Heisenberg's Principle, as $\sigma_x^2 = \bar{x}^2 - \bar{x^2} = \infty - 0 = \infty$.

The same happens with energy and time. $E = \texttt{ctt} \implies \sigma_E = 0$, so σ_t must be infinite. JJ doesn't like E&R's explanation of this phenomenon. He thinks that the simplest explanation is that the time scale of a process is related to the speed at which it changes it energy. Therefore, in some way, a system with no energy change at all would correspond to an infinite time scale.

3.5.2 Mathematical Interlude

It will be very useful for our purposes to find solutions of the homogeneous ODEs of the form

$$a\frac{d^2y}{dx^2} + b\frac{dy}{dx} + cy = 0$$

We can use a guess solution $y = e^{mx}$ to derive the characteristic polynomial:

$$am^2 + bm + c = 0 \implies m = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

From there, we get the following cases:

- $b^2 > 4ac \longrightarrow$ 2 real roots $\longrightarrow y(x) = c_1 e^{m_1 x} + c_2 e^{m_2 x}$
- $b^2 = 4ac \longrightarrow$ 1 real root $\longrightarrow y(x) = (c_1 + c_2 x)e^{mx}$
- $b^2 < 4ac \longrightarrow$ 2 conjugate complex roots $\longrightarrow y(x) = c_1 e^{(\alpha + i\beta)x} + c_2 e^{(\alpha - i\beta)x}$

Applying this procedure to the TISE with null potential, we get

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\Psi = 0 \implies m = \pm i\frac{\sqrt{2mE}}{\hbar} = \pm ik \implies \psi(x) = Ae^{ikx} + Be^{-ikx}$$

as we wanted to prove.

3.5.3 Step Potential

In this section, we suppose that the potential takes the form of a step function:

$$V(x) = \begin{cases} 0, & x < 0 \\ V_0, & x > 0 \end{cases}$$

We'll divide our study of this case in 2 sections, depending on whether the energy of the particle is bigger than its potential energy.

$\underline{E < V_0}$**:**

We have a particle with energy E approaching an energy barrier of $V_0 > E$. In classic physics, one would expect that the particle bounces off, as it doesn't have enough energy to cross it. However, quantum physics is not that simple.

Where $x < 0$, the TISE of the particle is:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \implies \psi_I(x) = Ae^{ik_1 x} + Be^{-ik_1 x},$$

where $k_1 = \frac{\sqrt{2mE}}{\hbar} = \frac{\sqrt{2m(E-0)}}{\hbar}$.

Where $x > 0$, the TISE of the particle is:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V_0\psi(x) = E\psi(x) \implies -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = (E-V)\psi(x) \implies$$
$$\implies \psi_{II}(x) = Ce^{ik_2' x} + De^{-ik_2' x},$$

where $k_2' = \frac{\sqrt{2m(E-V_0)}}{\hbar} = i\frac{\sqrt{2m(V_0-E)}}{\hbar} =: ik_2$, and $k_2 \in \mathbb{R}$. Substituting this value in the solution to TISE, the exponentials turn out to be real:

$$\psi_{II}(x) = Ce^{k_2 x} + De^{-k_2 x}$$

The coefficients A, B, C, D can be reduced to just one coefficient by imposing that ψ is finite, and that $\psi \in \mathcal{C}(0)$:

- $\psi(x)$ finite $\implies C = 0$.
- $\psi(x)$ continuous at 0 $\implies A + B = D$.
- $\frac{d\psi}{dx}(x)$ is continuous at 0 $\implies ik_1 A - ik_1 B = -k_2 D$.

We'll express A and B in function of D:

$$2ik_1 A = (ik_1 - k_2)D \implies A = \frac{ik_1 - k_2}{2ik_1}D = \frac{k_1 + ik_2}{2k_1}D = \frac{D}{2}\left(1 + i\frac{k_2}{k_1}\right)$$
$$B = D - A = \frac{D}{2}\left(1 - i\frac{k_2}{k_1}\right)$$

We might substitute this relations in the expression of $\psi(x)$:

$$\psi(x) = \begin{cases} \frac{D}{2}\left(1 + i\frac{k_2}{k_1}\right)e^{ik_1 x} + \frac{D}{2}\left(1 - i\frac{k_2}{k_1}\right)e^{-ik_1 x}, & x < 0 \\ \\ De^{-k_2 x}, & x > 0 \end{cases}$$

The expression of $\psi(x)$ when $x < 0$ is the sum of two travelling waves, one moving to the right (corresponding to the original particle), and another one moving to the left (corresponding to the reflected particle). When $x > 0$, on the contrary, we get an exponential that decreases as x gets bigger. Therefore, there is a slight chance for the particle to be found beyond the potential barrier (but close to it), which contradicts the classical and intuitive explanation.

Definició 3.5.1. *Reflection coefficient:*

$$R := \frac{\psi^*\psi_{\text{reflect.}}}{\psi^*\psi_{\text{incid.}}} = \frac{B^*B}{A^*A}$$

Plugging in the values of A, and B with respect to D, it can be checked that $R = 1$, so all the particles are going to get reflected (even if they get a little beyond the classical limit).

By substituting the negative exponentials by trigonometric functions, an alternative expression for $\psi_I(x)$ can be found:

$$\psi_I(x) = D\cos k_1 x - D\frac{k_2}{k_1}\sin k_1 x$$

$\underline{E > V_0:}$

For the first region (where $x < 0$), the TISE is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi,$$

so its solution is

$$\psi_I = Ae^{ik_1x} + Be^{ik_1x}, \qquad k_1 = \frac{\sqrt{2mE}}{\hbar}$$

For the second region ($x > 0$), the TISE is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = (E - V_0)\psi,$$

so its solution is

$$\psi_{II} = Ce^{ik_2x} + De^{ik_2x}, \qquad k_2 = \frac{\sqrt{2m(E - V_0)}}{\hbar}$$

Imposing that $\psi \in \mathcal{C}^1(0)$, we get that

$$\begin{cases} A + B = C + D \\ ik_1A - ik_1B = ik_2C - ik_2D \end{cases}$$

We also need to impose that $D = 0$, as there is nothing to reflect the wave at region II, so there would be no wave in the right-to-left direction.

Solving the system, we get that

$$C = \frac{2k_1}{k_1 + k_2}A$$
$$B = \frac{k_1 - k_2}{k_1 + k_2}A$$

so the wavefunction of the particle is the following:

$$\psi(x) = \begin{cases} Ae^{ik_1x} + A\left(\dfrac{k_1-k_2}{k_1+k_2}\right)e^{-ik_1x}, & x<0 \\ \\ A\left(\dfrac{2k_1}{k_1+k_2}\right)e^{ik_2x}, & x>0 \end{cases}$$

When a particle reaches the discontinuity at $x=0$, it can either get reflected or transmitted. Let R be the reflection coefficient and let T be the transmission coefficient. Then, $R+T=1$. We can calculate the coefficients as

$$R = \frac{\psi^*\psi_{\text{refl}}}{\psi^*\psi_{\text{inc}}}\frac{v_{\text{refl}}}{v_{\text{inc}}} = \frac{B^*B}{A^*A} = \left(\frac{k_1-k_2}{k_1+k_2}\right)^2$$

$$T = \frac{\psi^*\psi_{\text{transm}}}{\psi^*\psi_{\text{inc}}}\frac{v_{\text{transm}}}{v_{\text{inc}}} = \frac{C^*C}{A^*A}\frac{k_2}{k_1} = \frac{4k_1k_2}{(k_1+k_2)^2}$$

where we have used the fact that $v = p/m = k\hbar/2m$. From these formula it is trivial to check that

$$R+T = \frac{4k_1k_2+(k_1-k_2)^2}{(k_1+k_2)^2} = 1$$

3.5.4 Barrier Potential

We now turn our attention to the case where $V=0$ for all points except for an interval where $V=V_0>0$.

For the regions outside the barrier (I and III),

$$\begin{aligned}\psi_I &= Ae^{ik_1x}+Be^{-ik_1x}\\ \psi_{III} &= Ce^{ik_3x}+De^{ik_3x},\end{aligned}$$

as we have seen before. For the region inside the barrier, we have 3 possibilities:

- $E<V_0 \implies \psi_{II} = Fe^{k_2'x}+Ge^{-k_2'x}$
- $E=V_0 \implies \psi_{II} = Fx+G$
- $E>V_0 \implies \psi_{II} = Fe^{ik_2x}+Ge^{-ik_2x}$,

where $k_2 = \sqrt{2m(V_0-E)}/\hbar$, and $k_2' = \sqrt{2m(E-V_0)}/\hbar$.

Imposing that $\psi \in \mathcal{C}^1$ at the discontinuity points, we get 4 equations. The extra equation we need comes from imposing that $D=0$, as there is nothing to reflect the wave back at region III.

Let's write the system of equations for the case $E<V_0$:

$$\psi \in \mathcal{C}^0(0) \implies A+B = F+G$$
$$\psi \in \mathcal{C}^1(0) \implies ik_1 A - ik_1 B = k_2' F - k_2' G$$
$$\psi \in \mathcal{C}^0(a) \implies Fe^{k_2' a} + Ge^{-k_2' a} = Ce^{ik_1 a}$$
$$\psi \in \mathcal{C}^1(a) \implies k_2' Fe^{k_2' a} - k_2' Ge^{k_2' a} = ik_1 Ce^{ik_1 a}$$

Solving this system of equations we would get the values of B, C, D, F and G in function of A. A complete solution can be found at 2016's Partial Exam.

The transmission coefficient from region I to III is given by

$$T = \frac{C^* C}{A^* A} = \left(1 + \frac{\sinh^2 k_2' a}{4\frac{E}{V_0}\left(1 - \frac{E}{V_0}\right)} \right)^{-1}$$

When $k_2' a >> 1$, the hyperbolic sine reduces to the positive exponential, and the 1 at the beggining is negligible. Therefore:

$$T \cong \frac{16}{V_0}\left(1 - \frac{E}{V_0}\right) e^{2k_2' a}$$

When $E > V_0$,

$$T = \frac{C^* C}{A^* A} = \left(1 + \frac{\sin^2 k_2 a}{\frac{4E}{V_0}\left(\frac{E}{V_0} - 1\right)} \right)^{-1}$$

From this formula, it can be deduced that, no matter how big E/V_0 is, $T = 1$ (i.e. 100% of transmission) only when $a = n\lambda/2$.

This corresponds to the cases when there is destructive interference between the two reflected waves (the one that starts at $x = a$ and the one that starts at $x = 0$.

3.5.5 Infinite Well Potential

Let's suppose we have a potential that is infinite everywhere except for $0 < x < a$, where it is null. (Appendix H of E&R). If V is infinite there is no possibility that the particle is found outside the well, so $\psi_I = \psi III = 0$. Inside the well, we get the usual $\psi_{II} = Ae^{ikx} + Be^{-ikx}$. Imposing continuity of ψ:

$$\psi \in \mathcal{C}^0(0) \implies A+B=0 \implies A=-B \implies \psi II = 2Ai\sin kx = A'\sin kx$$
$$\psi \in \mathcal{C}^0(a) \implies A'\sin ka = 0 \implies ka = n\pi \implies k = \frac{\sqrt{2mE}}{\hbar} = \frac{n\pi}{a}$$

Solving out for the energy, we get

$$E_n = \frac{n^2\hbar^2\pi^2}{2ma^2}$$

It is interesting to see that the case where $E = 0$ is physically impossible, as $n = 0 \implies k = 0 \implies \lambda = \infty$. Besides, if $E = 0$, Heisenberg's Principle would be violated, as $E = 0 \implies \Delta p = 0 \implies \Delta x \Delta p \ngtrsim 0$.

Definició 3.5.2. *Zero-point energy:* Minimum value of the energy in a system with quantized values of energy (i.e. in this last example, it is E_1).

Let's find an approximate value for the uncertainties of x and p in the case E_1:

$$\begin{cases} \Delta x \cong a \\ \Delta p \cong 2\sqrt{2mE} \end{cases} \implies \Delta x \Delta p \cong 2a\sqrt{2mE} = 2\pi\hbar \geq \frac{\hbar}{2}$$

3.5.6 Simple Harmonic Oscillator

Solved in an appendix of E&R. It uses some advanced mathematical tools such as Hermite Polynomials.

Capítol 4

One-electron Atoms

4.1 Introduction

In this chapter we will study the quantic properties of one-electron atoms. This term mainly refers to hidrogen, including its two main isotopes: protium (^{1}H) and deuterium (^{2}H), but we might also consider He$^+$, Be^{3+} or fancier particles such as a muonium (1 muon, 1 electron) or a positronium (1 positron, 1 electron).

We will base our approach in Coulomb's potential which is more realistic than the ones we considered in the last chapter. We will also work in 3 dimensions, so the mathematical work is going to be more complicated, but we'll be able to make much more accurate predictions of reality.

One of the advantages of the quantic approach compared to Bohr's model is that the probability density of the electron is constant with time. This means that the atom has a static charge distribution, so it does not emit radiation and it can be stable.

Exemple 4.1.1. Let's suppose we have a mix of states with energies E_1 and E_2. The wavefunction of the mixed state will be the linear combination of the wavefunctions of each state:

$$\Psi(x,t) = c_1\psi_1(x)e^{-iE_1t/\hbar} + c_2\psi_2(x)e^{-iE_2t/\hbar}$$
$$P = \Psi^*\Psi = c_1^*c_1P_1 + c_2^*c_2P_2 + c_2^*c_1\psi_2^*\psi_1e^{i(E_2-E_1)t/\hbar} + c_2c_1^*\psi_1^*\psi_2e^{-i(E_2-E_1)t/\hbar}$$

The oscillatory terms (the ones that depend on time) can be expressed in trigonometric form as $Ce^{i\omega t} = Ce^{i2\pi\nu t}$, so the frequency of the photons emitted in the transition state is

$$\nu = \frac{E_2 - E_1}{2\pi\hbar} = \frac{E_2 - E_1}{h},$$

as it was predicted by Bohr's model.

4.1.1 Reduced mass

Because the nucleus has finite mass, both the electron and the nucleus orbit around their center of mass.

The distance of the center of mass from the nucleus is

$$d = \frac{m}{M+m} r$$

By Newton's second law, the force acting on the nucleus is $\vec{F}_n = M\vec{a}_n$, and the force acting on the electron is $\vec{F}_e = m\vec{a}_e$, while by the third law, $\vec{F}_n = -\vec{F}_e$. Therefore:

$$\vec{a}_n = -\frac{m}{M}\vec{a}_e \implies \vec{a}_{\text{rel}} := \vec{a}_e - \vec{a}_n = \frac{m+M}{M}\vec{a}_e$$

Substituting the second law formula for the electron:

$$\vec{F}_e = \frac{Mm}{M+m}\vec{a}_{\text{rel}} = \mu\vec{a}_{\text{rel}},$$

where μ is called the *reduced mass*, and $\vec{a}_{\text{rel}}$ is the acceleration of the electron with respect to the nucleus.

Exemple 4.1.2. The finite mass correction can be applied, for example, to the Rydberg formula. For a nucleus of infinite mass, we saw previously that

$$R_\infty = \left(\frac{1}{4\pi\varepsilon_0}\right)^2 \frac{me^4}{4\pi\hbar^3 c}$$

If we consider the nucleus mass not to be infinite, then Rydberg's constant must be multiplied by μ/m:

$$R_M = \frac{\mu}{m} R_\infty$$

and in some cases, such as for a positronium, the difference is quite significant.

4.2 TDSE in 3D

We will develop the Time-Dependent Schrödinger Equation for 3 dimensions in the same fashion we did for the one-dimensional case.

$$E = K + V = \frac{1}{2\mu}(p_x^2 + p_y^2 + p_z^2) + V(x,y,z) \implies E\psi = -\frac{\hbar^2}{2\mu}\nabla^2\Psi + V\Psi \implies$$

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2\mu}\nabla^2\Psi + V\Psi$$

By considering $\Psi \equiv \psi(x,y,z)\phi(t)$, we get that

$$\Psi = \psi(x,y,z)e^{-iEt/\hbar}$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z) + V(x,y,z)\psi(x,y,z) = E\psi(x,y,z)$$

The last equation is the Time-Independent Schrödinger Equation in 3D.

We will know solve the TISE for Coulomb's Potential. As this potential has spherical symmetry, so we will solve the equation in spherical coordinates. The Laplacian operator in spherical coordinates takes the following form (see appendix M of E&R for a complete proof):

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

Let's suppose that we can separate the variables and express the eigenfunction as $\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$. By substuting into the TISE and multiplying both sides of the equation by the following factor

$$-\frac{2\mu r^2\sin^2\theta}{R\Theta\Phi\hbar^2}$$

we end up with

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{2\mu}{\hbar^2}r^2\sin^2\theta\left(E - V(r)\right)$$

Only the LHS depends on ϕ, so we know that both the LHS and the RHS must be constant. From there we get the *azimuthal equation*:

$$\frac{d^2\Phi}{d\phi^2} = -m_l^2\Phi,$$

where we have taken $-m_l^2$ as the separation constant. The reason for this will be evident later. From the RHS, we get that

$$-\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{2\mu}{\hbar^2}r^2\left(E - V(r)\right) = -\frac{m_l^2}{\sin^2\theta}$$

We might rearrange this equation into

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}\left(E - V(r)\right) = \frac{m_l^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)$$

Again, by the same argument, both the LHS and the RHS must be constant, and we call this separation constant $l(l+1)$, for reasons that will become apparent later. The two equations that we get are

$$\begin{gathered}-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{m_l^2\Theta}{\sin^2\theta} = l(l+1)\Theta \\ \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}\left(E - V(r)\right)R = l(l+1)\frac{R}{r^2}\end{gathered}$$

In the next part of this section we are going to solve this 3 equations (azimuthal, polar and radial), and we are going to find that these equations only have valid solutions for certain values of m_l, l and E.

4.2.1 Azimuthal Equation

We've seen that the azimuthal angle is given by

$$\frac{d^2\Phi}{d\phi^2} = -m_l^2\Phi \implies \Phi(\phi) = e^{im_l\phi}$$

In order for this function to be valid, it needs to be single-valued, continuous and finite. From the fact that it is single-valued, we get that

$$\Phi(0) = \Phi(2\pi) \implies 1 = e^{im_l 2\pi} = \cos(2\pi m_l) + i\sin(2\pi m_l) \implies |m_l| = 0, 1, 2, 3, \ldots$$

4.2.2 Polar Equation

The polar angle was given by

$$-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{m_l^2\Theta}{\sin^2\theta} = l(l+1)\Theta$$

We will use the following change of variable:

$$z = \cos\theta \implies \begin{cases} \sin\theta = \sqrt{1-z^2} \\ \dfrac{d}{d\theta} = -\sqrt{1-z^2}\dfrac{d}{dz} \end{cases}$$

Then the polar equation becomes:

$$\frac{d}{dz}\left((1-z^2)\frac{d\Theta}{dz}\right) + \left(l(l+1) - \frac{m_l^2}{1-z^2}\right)\Theta = 0$$

The solutions are associated Legendre functions given by

$$\Theta_{l,m_l}(z) = (1-z^2)^{|m_l|/2} \cdot \frac{d^{|m_l|}P_l(z)}{dz^{|m_l|}},$$

where P_l are the Legendre Polynomials, given by

$$(1-z^2)\frac{d^2P_l}{dz^2} - 2z\frac{dP_l}{dz} + l(l+1)P_l = 0$$

This can be proven by applying $d^{|m_l|}/dz^{|m_l|}$ to the last equation. We then get

$$(1-z^2)\frac{d^{|m_l|+2}P_l}{dz^{|m_l|+2}} - 2z(|m_l|+1)\frac{d^{|m_l|+1}P_l}{dz^{|m_l|}} + \left[l(l+1) - |m_l|\left(|m_l|+1\right)\right]\frac{d^{|m_l|}P_l}{dz^{|m_l|}}$$

By plugging $\Theta = (1-z^2)\Gamma$ into the polar equation, and using the relation we just derived, we get that the solution must satisfy the condition given before.

We are now going to solve the equation of P_l, and from that solution we have seen that we can find the solutions of Θ_{l,m_l}. Let's take the power series expansion of P_l:

$$P_l(z) = \sum_{k=0}^{\infty} a_k z^k$$

By plugging it into the 2nd order ODE we had, we get

$$\sum_{k=0}^{\infty}\Big(\left(l(l+1)-k(k+1)\right)z^k a_k + k(k-1)a_k z^{k-2}\Big) = 0$$

We can regroup the terms with the same powers of z:

$$\sum_{j=0}^{\infty}\left(\left(l(l+1)-j(j+1)\right)a_j + a_{j+2}(j+2)(j+1)\right)z^j = 0$$

This power series must be zero for all values of z, so all the terms of the sum must equal zero. We then get the following recurrence relation:

$$a_{j+2} = a_j\frac{j(j+1)-l(l+1)}{(j+2)(j+1)}$$

that must hold for any power series that gives a solution for z.

We want all our solutions of the TISE to be finite, so P_l must be finite too. Therefore, we need to truncate the power series at some point. We do this by setting one of the two initial values (a_0 or a_1) to zero, thereby getting rid of either the odd or the even coefficients. To truncate the other series, we need to set l to an integer of the same parity as the non-vanishing series, as then a_{l+2} will be equal to 0, and all the terms will be zero onwards.

By constructing P_l with this method, P_l turns out to be a polynomial of degree l. Therefore, taking into account that

$$\Gamma = \frac{d^{|m_l|}P_l}{dz^{|m_l|}},$$

we get that $|m_l|$ can't be bigger than l, as then $\Gamma = 0$ and our solution would be $z \equiv 0$.

Exemple 4.2.1. Some examples of Legendre polynomials are $P_0 = 1$, $P_1 = z$, $P_2 = 1 - 3z^2$, $P_3 = 3z - 5z^2, \dots$. Their associated Legendre functions are

$$\Theta_{0,0} = 1,\ \Theta_{1,0} = z,\ \Theta_{1,\pm1} = (1-z^2)^{1/2},\ \dots$$

4.2.3 Radial Equation

The radial equation was

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}\left(E - V(r)\right)R = l(l+1)\frac{R}{r^2}$$

We define the following parameters:

$$\rho := 2\beta r \qquad \beta^2 := -\frac{2\mu E}{\hbar^2} \qquad \gamma := \frac{\mu Z e^2}{4\pi\varepsilon_0\hbar\beta}$$

Plugging them into the radial equation, we get

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{d\rho}\right)+\left[-\frac{1}{4}-\frac{l(l+1)}{\rho^2}+\frac{\gamma}{\rho}\right]R=0$$

For large ρ (i.e. the electron is far away from the nucleus), this equation becomes

$$\frac{d^2R}{d\rho^2}=\frac{R}{4}\implies R(\rho)=e^{-\rho/2}$$

We only take the negative exponential, as the positive one would not be finite.

From this solution, we might assume that the general solutions will have the form

$$R(\rho)=F(\rho)\cdot e^{-\rho/2}$$

Substituting this function in the radial equation, we get:

$$\frac{d^2F}{d\rho^2}+\left(\frac{2}{\rho}-1\right)\frac{dF}{d\rho}+\left[\frac{\gamma-1}{\rho}-\frac{l(l+1)}{\rho^2}\right]F=0$$

Next we apply the power series method. We suppose F has a polynomic form:

$$F(\rho)=\rho^s\sum_{k=0}^{\infty}a_k\rho^k$$

The factor ρ^s will be needed to keep the series finite.

By substituting the power series in the differential equation, we get the following recursive relation:

$$a_{j+1}=\frac{j+l+1-\gamma}{(j+l+1)(j+l+2)-l(l+1)}a_j$$

We also find that $s=l$ (details in the pdf in Atenea).

We want the series to be truncated at some point (as otherwise F would not be finite and thus ψ would not be finite). Therefore, we need γ to be an integer such that $\gamma=l+1+i$, for some $i\in\mathbb{N}$, as then the numerator of the recurrence factor would vanish.

We know that γ must be a natural number. Let n be that number. Then, the maximum term of the series will correspond to $j=n-(l+1)$, so the degree of $F(\rho)$ will be $n-1$. Thus, $l\in\{1,2,\ldots,n-1\}$.

Besides, $n=\gamma$ was defined in function of β, and β depended on E, so the possible values of energy will be given by

$$E=-\frac{\beta^2\hbar^2}{2\mu}=\frac{-\mu^2Z^2e^4\hbar^2}{(4\pi\varepsilon_0)^2\hbar^4n^22\mu}\implies E_n=-\frac{\mu Z^2e^4}{(4\pi\varepsilon_0)^22\hbar^2}\cdot\frac{1}{n^2},\quad n=1,2,\ldots$$

which turns out to be the same formula that Bohr predicted in his model of the atom!

Exemple 4.2.2. Some examples of possible values of F (which are called Laguerre Polynomials) are

$$F_{1,0}=1,\ F_{2,0}=2-\rho,\ F_{2,1}=\rho,\ F_{3,0}=6-6\rho+\rho^2,\ldots$$

4.2.4 Solutions of the Eigenfunction

Now that we've solved all the three parts of the eigenfunction, let's look at what form does it take. We have seen that ψ depends on 3 parameters (n, l and m_l). Then,

$$R_{n,l}(r)\Theta_{l,m_l}(\theta)\Phi_{m_l}(\phi) = R'_{n,l}(r)Y_{l,m_l}(\theta,\phi),$$

where Y are called *spherical harmonics*, and are defined as

$$Y_{l,m_l} = \sqrt{\frac{(2l+1}{4\pi}\frac{(l-m_l)!}{(l+m_l)!}}\Theta_{l,m_l}(\theta)\Phi_{m_l}(\phi)$$

We can normalize ψ by applying the usual condition, that is, that

$$\int_V P(r,\theta,\phi)dV = 1,$$

where P is the probability density (probability per unit of volume) and it is calculated as $P = \psi^*\psi$.

In spherical coordinates, the differential unit of volume can be expressed as

$$dV = r^2 \sin\theta dr d\theta d\phi,$$

so plugging this into the normalization condition,

$$\int_0^\infty |R_{n,l}|^2 r^2 dr \int_0^{2\pi} |\Phi_{m_l}|^2 d\phi \int_0^\pi |\Theta_{l,m_l}|^2 \sin\theta d\theta = 1$$

Some of the normalization constants for the hydrogen atom can be found at the form in Atenea. However, in some cases, such as when we want to calculate the radial distribution, we are going to have to renormalize the eigenfunction and compute these factors ourselves.

4.3 Interpretation of Results

4.3.1 Quantum Numbers and Degeneracy

Solving the TISE in 3D, we found 3 quantum numbers:

- Principal quantum number: $n = 1, 2, \dots$
- Azimuthal quantum number: $l = 01, 2, \dots n-1$
- Magnetic quantum number: $m_l = -l, -l+1, \dots, 0, \dots, l-1, l$

This introduces the concept of *degeneracy*. The energy values only depend on n, but ψ depends on n, l and m_l, so two states with different eigenfunctions (different behaviour) can have the same total energy (the same eigenvalue).

As a remnant of the historical evolution of quantum theory, the value of l is usually expressed with a letter code:

- $l = 0 \longrightarrow$ s
- $l = 1 \longrightarrow$ p
- $l = 2 \longrightarrow$ d
- $l = 3 \longrightarrow$ f

How many possible states can exist for a given value of n? For each n, there are n possible values of l, and for each l, there are $2l + 1$ possible values of m_l, so there are a total of n^2 possible eigenfunctions for each given n.

4.3.2 Eigenfunctions

The full eigenfunctions solutions for the simplest states of the hydrogen atoms can be found in the form at Atenea. Note that the solutions take the form:

$$\Phi_{m_l}(\phi) = e^{im_l\phi}$$
$$\Theta_{l,m_l}(\theta) = \sin^{|m_l|}\theta \cdot P[\cos\theta]$$
$$R_{n,l}(r) = e^{-Cr/n}r^l \cdot P[r]$$

where $P[x]$ denotes a polynomial on x.

4.3.3 Probability densities

Radial Probability Density

The radial probability density is the probability of finding the electron at a certain distance of the atom, and can be calculated as

$$P_{n,l}(r)dr = R^*_{n,l}(r)R_{n,l}(r)4\pi r^2 dr$$

When plotting these functions for different eigenfunctions (see slides in Atenea), we find that the radial probability density has the following characteristics:

- It is contained (i.e. restricted to a certain region of space).
- Their shape is non-trivial (in contrast to Bohr's).
- The shape of the $P(r)dr$ depends heavily on the principal quantum number n and not so much on l.

The expectation value of the radius of the electron for a certain eigenfunction is calculated as

$$\bar{r}_{n,l} = \int_0^\infty rP_{n,l}(r)dr$$

which from the known form of $R_{n,l}$, can be proved to yield

$$\bar{r}_{n,l} = \frac{n^2 a_0}{Z}\left[1 + \frac{1}{2}\left(1 - \frac{l(l+1)}{n^2}\right)\right]$$

Take into account that, due to the fact that $P_{n,l}(r)$ is not symmetric, the expectation value of r does not match the radius of maximum probability.

Exemple 4.3.1. For example, let's take the case $n = 0 \implies l, m_l = 0$ of the hydrogen atom ($Z = 1$).

$$P_{1,0}(r) = Cr^2 e^{-2r/a_0} \implies (\dots) \implies r_{\text{maxProb}} = a_0$$

On the other hand, the expectation value of r is

$$\bar{r} = \int_0^\infty 4\pi r^3 \psi_{1,0}^2 dr = (\dots) = \frac{3}{2}a_0$$

Angular Probability Density

The angular probability density can be calculated as $\Theta^*_{l,m_l}\Theta_{l,m_l}\Phi^*_{m_l}\Phi_{m_l} = \Theta^*\Theta$, so the angular probability density is indepent of the azimuthal coordinate, and only depends on the polar angle.

We will usually represent the angular probability density in polar diagrams, examples of which can be found in the lecture slides at Atenea.

4.4 Spin and Orbital Angular Momentum

4.4.1 Angular Momentum Operator

As the force we are considering (Coulomb's Force) is radial, it doesn't produce any torque, so the angular momentum of the electrons must be constant. In the following discussion we are going to calculate the angular momentum and we are going to relate it with the quantum numbers we have seen.

From the definition $\vec{L} = \vec{r} \times \vec{p}$, and $\vec{p_{x_i}} = -i\hbar\partial/\partial x_i$, so

$$L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$
$$L_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$
$$L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

Which in spherical coordinates translates to

$$L_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$
$$L_y = i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$
$$L_z = -i\hbar\frac{\partial}{\partial\phi}$$

(details can be found in appendix M of E&R).

By adding the squares of each component, we can quantify the square of the modulus of the angular momentum as

$$L^2 = L_x^2 + L_y^2 + L_z^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

We can find the expectation value of the operator L_z as

$$\bar{L_z} = \iiint \Psi^* L_z \Psi \underbrace{r^2\sin\theta dr d\theta d\phi}_{=dV} = \int_V \psi^* L_z \psi dV = \int_V \psi^* R\Theta\left(-i\hbar\frac{d\Phi}{d\phi}\right)dV$$
$$= \int_V \psi^* R\Theta m_l\hbar\Phi dV = m_l\hbar\int_V \psi^*\psi dV = m_l\hbar$$

Similarly we will now calculate the expectation value of $\bar{L^2}$. In order to do that, let's calculate first what is the effect of the L^2 operator to ψ:

$$L^2\psi = L^2(\Theta R\Phi) = -\hbar^2 R\left[\frac{\Phi}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{\Theta}{\sin^2\theta}\left(-m_l^2\Phi\right)\right]$$
$$= (...) = l(l+1)\hbar^2\psi$$

Therefore, the expectation value of L^2 is

$$\bar{L^2} = \int_V \psi^* L^2\psi dV = l(l+1)\hbar^2\int_V \psi^*\psi dV = l(l+1)\hbar^2$$

Until now, we have only calculated expectation values, that is, the mean of all measurements of a variable. We will now prove that L_z and L^2 are constant, and that when we measure them, the expectation values we found are always obtained. We will prove it by finding that the square of their mean equals the mean of their square, so their standard deviation is zero.

$$\bar{L_z^2} = \int \psi^* L_z^2\psi d\tau = m_l^2\hbar^2 = (\bar{L_z})^2,$$

and similarly with L^2. Therefore, the values of L_z and L^2 operators are fixed and equal to

$$L_z = m_l\hbar$$
$$L^2 = l(l+1)\hbar$$

No similar expression can be found for L_x and L_y, which are not quantized. Their expectation value can be found by calculating the integral and give the result

$$\bar{L_x} = \bar{L_y} = 0$$

4.4.2 Vector Model for $\vec{L}$

The vector Model is an interpretation of the angular momentum of the electron as a vector, where its magnitude is given by

$$L = \sqrt{L^2} = \sqrt{l(l+1)}\hbar,$$

and thus depends only on l, while its orientation is given by m_l, which corresponds to the projection of $\vec{L}$ onto the Z-axis.

The other components of $\vec{L}$, L_x and L_y, are not clearly defined, so $\vec{L}$ can be anywhere inside a cone that goes around the Z-axis. For the case $m_l = +l$, the cone is given by the angle

$$\theta = \arccos\left(\frac{l}{\sqrt{l(l+1)}}\right),$$

so when $l \to \infty$, $\theta \to 0$.

This phenomenon is sometimes called *space quantization*, as the quantization of L^2 and L_z means that the magnitude and orientation of $\vec{L}$ are both quantized.

When $m_l = 0$, $\vec{L}$ is in the XY plane, so the electron moves on a plane containing the Z-axis, while if $m_l = l$, as l gets large, $\vec{L}$ gets closer to the Z-axis, so the motion of the electrons gets closer to the XY-plane. This corresponds to the trend in the *flatness* of the orbitals that we observed in the orbital diagrams. For $m_l = l \to \infty$, we get the classical limit, where $\vec{L}$ is aligned with the Z-axis and the electron orbits in the XY-plane.

Observació 4.4.1. When f is a dynamical quantity and $f_{\text{op}}\psi = F\psi$, then ψ is called *eigenfunction* and F is called *eigenvalue.*

This is what happened with L_z and L^2, symbols we used to denote both the operator and its eigenvalue, although the two are conceptually different. Formally speaking,

$$L_{z,\text{op}}\psi = L_z\psi$$
$$L^2_{\text{op}}\psi = L^2\psi$$

4.4.3 Magnetic Dipole

The angular momentum is related to the magnetic dipole moment. An electron in a Bohr-like orbit produces a magnetic dipole moment which is given by $\mu_l \propto q\vec{r} \times \vec{v}$, while $\vec{L} = m\vec{r} \times \vec{v}$, so we see that both vectors are going to be proportional.

The electric current is given by

$$I = \frac{e}{T} = \frac{ev}{2\pi r},$$

so the magnetic dipole moment can be calculated as

$$\mu_l = IA = I\pi r^2 = \mu_l = \frac{evr}{2}$$

Therefore, we can calculate the explicit relation between L and μ_l:

$$\frac{\mu_l}{L} = \frac{evr}{2mvr} = \frac{e}{2m}$$

The *Bohr magneton* is a constant defined as

$$\mu_b := \frac{e\hbar}{2m} \cong 0.93 \times 10^{23} A \cdot m^2$$

Therefore, the magnetic dipole moment can be expressed as

$$\frac{\mu_l}{L} = \frac{g_l \mu_b}{\hbar},$$

where g_l is the orbital g factor, which for the moment we define as an adimensional quantity equal to one, (its use will become apparent later).

As both vectors are antiparallel, we also have that

$$\vec{\mu}_l = -\frac{g_l \mu_b}{\hbar} \vec{L}$$

Therefore, since the values of L and L_z are quantized, the magnetic dipole moment's magnitude and z-component will also be quantized:

$$\mu_l = g_l \mu_b \sqrt{l(l+1)}$$
$$\mu_{l,z} = -g_l \mu_b m_l$$

When subjected to a magnetic field $\vec{B}$, a magnetic dipole moment $m\vec{u}$ will experience a torque given by

$$\vec{\tau} = \vec{\mu} \times \vec{B},$$

and so $\vec{\mu}$ will tend to align itself with $\vec{B}$.

Deriving from this torque, one might also define a potential energy of orientation, given by

$$\Delta E = -\vec{\mu}_l \cdot \vec{B}$$

and its maximum value is

$$\Delta E_{\text{max}} = 2\mu_l B \cong 1.2 \cdot 10^6 eV$$

If the magnetic field $\vec{B}$ is not uniform, the magnetic dipole will also experience a net translational force in the direction of increasing B.

4.4.4 Stern-Gerlach Experiment

In the Stern-Gerlach Experiment, a beam of silver atoms goes through a magnet with a non-uniform magnetic field. Therefore, the particles suffer a net translational force depending on their magnetic dipole $\vec{\mu}_l$.

When the beams leave the magnet, they collide with a detector. In classical physics, μ is not quantized, so the deflection angles would lay in a continuous range.

However, when this experiment was performed, the deflection angles were observed to be discretized, so this was accepted as a proof of the quantization of μ.

The problem is that the beam was observed to split in two, and according to the angular momentum theory, it should have been split in an odd number of beams $(2l + 1)$.

These results were actually an evidence for another intrinsic magnetic dipole moment of the electron: *spin*.

4.4.5 Electron Spin

The spin of the electron is a quantum number that does not come from the resolution of Schrödinger Equation, but that is added as an additional postulate to make the theory correspond to experimental results. However, in some formulations of quantum mechanics (such as in Dirac's one) it does come naturally from its basic postulates.

Spin is based in a fourth quantum number, m_s, that can take only two different values: $m_s = \pm 1/2$. By analogy with the formulas we developed earlier, the magnetic dipole and angular momentum associated with spin are given by

$$\begin{gathered} S = \sqrt{s(s+1)\hbar} \\ S_z = m_s \hbar \\ \vec{\mu}_s = -\frac{g_s \mu_b}{\hbar} \vec{S} \\ \mu_{s,z} = -g_s \mu_b m_s \end{gathered}$$

As we want m_s to increase in steps of length 1, $s = \frac{1}{2}$.

The force that acts on the electron can be calculated as

$$F_z = -\frac{\partial B_z}{\partial z} \mu_z = -\frac{\partial B_z}{\partial z} \mu_b g_s m_s$$

Experimentally, the product $g_s m_s$ was found to be equal to ± 1, so $g_s = 2$. This value is bigger than $g_l = 1$, so, in some way, the spin is more efficient in deviating the atom than the orbital angular momentum.

4.5 Spin-Orbit Coupling

In the reference frame at which the electron is at rest, the atomic nucleus orbits around the electron at a velocity $-\vec{v}$, and the movement of the nuclear charge induces a magnetic field. Its value can be calculated as

$$\vec{B} = \frac{\mu_0}{4\pi} \frac{\vec{j} \times \vec{r}}{r^3} = -\frac{Zev_0}{4\pi} \frac{\vec{v} \times \vec{r}}{r^3} = -\frac{1}{c^2} \vec{v} \times \vec{E}$$

The electric force can be expressed as

$$-e\vec{E} = \vec{F} = -\frac{dV}{dr}\frac{\vec{r}}{r},$$

so substituting in $\vec{B}$,

$$\vec{B} = -\frac{1}{ec^2}\frac{1}{r}\frac{dV}{dr}\vec{v} \times \vec{r} = \frac{1}{ec^2}\frac{1}{r}\frac{dV}{dr}\vec{L}$$

Here we have also used that $\vec{L} = -m\vec{v} \times \vec{r}$.

The intrinsic spin magnetic dipole of the electron experiences a torque from this magnetic field, and its associated orientation potential energy is given by

$$\Delta E = \frac{1}{2}\frac{g_s \mu_b}{\hbar}\vec{S} \cdot \vec{B} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\vec{S} \cdot \vec{L}$$

From these formulas we see that for $L = 0$, $B = 0$. A classical interpretation might be that in the ground state the electron does not rotate around the nucleus, and therefore its angular momentum is null.

Note also that the torque that acts on $\vec{S}$ depends on $\vec{L}$, so these vectors must be linked together.

We are not going to derive it in this course, but $\vec{L}$ and $\vec{S}$ precess around the total angular momentum vector $\vec{J} := \vec{L} + \vec{S}$.

4.5.1 Total Angular Momentum

The total angular momentum is quantized analogously to the spin and the orbital angular momentum:

$$J = \sqrt{j(j+1)}\hbar$$
$$J_z = m_j \hbar$$
$$m_j = -j, \dots, j$$
$$j = \begin{cases} l \pm \frac{1}{2}, & l > 0 \\ \frac{1}{2}, & l = 0 \end{cases}$$

The fact that $j = l \pm \frac{1}{2}$ happens because the vectors $\vec{L}$ and $\vec{S}$ can either be aligned or misaligned, so depending on the direction of $\vec{S}_z$, the modulus of its sum might be bigger or smaller than L.

Hence, in the absence of spin-orbit coupling, we describe states with the quantum numbers n, l, m_l, m_s, while when there is spin-orbit coupling, we describe states with the quantum numbers n, l, j, m_j. In both cases, the total number of states if $2n^2$.

4.5.2 Spin-Orbit Energy

We have defined $\vec{J} = \vec{L} + \vec{S}$, so

$$J^2 = L^2 + S^2 + 2\vec{S} \cdot \vec{L} \implies \vec{S} \cdot \vec{L} = \frac{J^2 - S^2 - L^2}{2}$$

Plugging in the quantum numbers, we find that $\vec{S} \cdot \vec{L}$ is also quantized:

$$\vec{S} \cdot \vec{L} = \frac{\hbar^2}{2} \left[j(j+1) - l(l+1) - s(s+1) \right]$$

The orientation potential energy was defined in function of $\vec{S} \cdot \vec{L}$, so substituting in there, we get:

$$\Delta E = \frac{\hbar^2}{4m^2c^2} \left[j(j+1) - l(l+1) - s(s+1) \right] \frac{1}{r} \frac{dV(r)}{dr}$$

The last factor is a function of the radius, so it might change in different states. Therefore, the spin-orbit interaction energy is the expectation value of ΔE:

$$\overline{\Delta E} = \frac{\hbar^2}{4m^2c^2} \left[j(j+1) - l(l+1) - s(s+1) \right] \overline{\frac{1}{r} \frac{dV(r)}{dr}}$$

4.5.3 Fine and Hyperfine Structure

For non-zero values of l, spin-orbit interaction splits energy levels in two and gives rise to what is called *fine structure.* For example, $2p$ level ($n = 2, l = 1$) is split in $2p_{1/2}$ ($j = 1/2$) and $2p_{3/2}$ ($j = 3/2$).

This effect can be proved experimentally by the observation of the split of spectral lines (e.g. sodium doublet at 5896Å and 5890Å).

Even in $l = 0$ states, where there is no orbital angular momentum, there might be an interaction between the intrinsic angular momentum (spin) of the electron and the nucleus. This interaction gives rise to the *hyperfine structure* and is responsible for the famous $21cm$ line of hydrogen.

4.6 Selection rules and transition rates

4.6.1 Selection Rules

Having four different quantum numbers implies that there is a high number of states. However, not all transitions between those states is possible. For example, photons are detected only at frequencies corresponding to transitions that satisfy

$$\Delta l = \pm 1$$
$$\Delta j = 0, \pm 1$$

In order to quantify the probability of ocurrence of these transitions, we use *transition rates*:

Definició 4.6.1. *Transition rate:* Number of atoms per second emitting a photon corresponding to a given frequency. It is proportional to the intensity of the emission line, and it can be calculated as

$$R = \frac{1}{t},$$

where t is the expected lifetime of the excited state (the state with a higher energy).

In previous sections, we saw that the probability density of a mix of two states E_1 and E_2 oscillates with a frequency of

$$\nu = \frac{E_2 - E_1}{\hbar}$$

Let's recall that the electric dipole moment was given by $\vec{p} = -e\vec{r}$.

To quantify the transition rates, we assume that the electric dipole moment is oscillating like the probability density.

Then, from classical electromagnetism, one might deduce that

$$\tilde{R} = \frac{4\pi^3\nu^4}{3\varepsilon_0 c^3} p^2$$

Taking into account that each photon has an energy of $E = h\nu$, the rate of emission of photons is

$$R = \frac{\tilde{R}}{h\nu} = \frac{4\pi^3\nu^3}{3\varepsilon_0 h c^3} p^2$$

Each atomic transition emits one photon, so R is also a measure of the number of transitions per second.

In a mixed state, the wave function is expressed as

$$\Psi = \Psi_f e^{\frac{-iE_f t}{\hbar}} + \Psi_i e^{\frac{-iE_i t}{\hbar}}$$

So the expectation value of the electric dipole moment is given by

$$\langle\vec{p}\rangle \propto \int \Psi_f^* e\vec{r}\Psi_f dV + \int \Psi_i^* e\vec{r}\Psi_i dV + \frac{e^{i(E_i - E_f)t}}{\hbar} \int \psi_i^* e\vec{r}\psi_f dV + \frac{e^{-i(E_i - E_f)t}}{\hbar} \int \psi_f^* e\vec{r}\psi_i dV$$

The first two integrals are odd with respect to r, so their value is zero. The other two terms are complex conjugates, so their sum will give twice their real part. Therefore, $\langle\vec{p}\rangle$ is proportional to the *matrix element of the electric dipole*:

$$\vec{p}_{fi} = \left| \int \Psi_f^* e\vec{r}\Psi_i dV \right|$$

Substituting in the expression of R, we get that

$$R \propto \frac{\nu^3 p_{fi}^2}{\varepsilon_0 h c^3}$$

and by more sophisticated arguments we might find that

$$R = \frac{16\pi^3\nu^3 p_{fi}^2}{3\varepsilon_0 h c^3}$$

4.6.2 Rates and selection rules

The selection rules are given by the parity of ψ_f and ψ_i with respect to $\vec{r}$:

$$p_{fi} = \left| \int \psi_f^* e\vec{r}\psi_i dV \right| \implies \begin{cases} \psi_f \text{ and } \psi_i \text{ have the same parity} \implies R = 0 \\ \psi_f \text{ and } \psi_i \text{ have different parity} \implies R \neq 0 \end{cases}$$

The parity of ψ can be found according to the following rule:

$$\psi_{n,l,m_l}(-\vec{r}) = \psi_{n,l,m_l}(r, \pi - \theta, \pi - \phi) = (-1)^l \psi_{n,l,m_l}(r, \theta, \phi)$$

Therefore, in order for a photon to be emitted, ψ_f and ψ_i need to have different parity, so this gives rise to the first selection rule ($\Delta l = \pm 1$). By angular momentum conservation we get the second rule ($\Delta j = 0, \pm 1$). Note that $\Delta j = 0$ is allowed by a rearrangement of the atomic angular momentum, and $\Delta l = 3$ would be allowed by parity but would violate angular momentum conservation.

4.6.3 Spontaneous Emission

With Schrödinger's quantum mechanics we can not explain how an electron in a pure state might get to a mixed state. This kind of phenomena is explained by QED (Quantum ElectroDynamics).

Capítol 5

Introduction to Elementary Particles

5.1 Two-Particle Systems. Indistinguishability

Let's suppose we have a system with two particles. Then, the wave function depends on both position vectors, and we can write it as $\Psi(\vec{r}_1, \vec{r}_2, t)$.

This wave function has to satisfy Schrödinger's Equation, which for two particles takes the following form:

$$\underbrace{-\frac{\hbar^2}{2m}\nabla_1^2\Psi(\vec{r}_1, \vec{r}_2, t)}_{\cong K_1\Psi}\underbrace{-\frac{\hbar^2}{2m}\nabla_2^2\Psi(\vec{r}_1, \vec{r}_2, t)}_{\cong K_2\Psi}+V(\vec{r}_1, \vec{r}_2, t) = i\hbar\frac{\partial\Psi}{\partial t}$$

We will consider the case where the potential is time-independent (i.e. $V \equiv V(\vec{r}_1, \vec{r}_2)$). Then, we can divide the wave function in 2 parts, one depending on time and the other depending on spatial coordinates. The time dependent part is equivalent to the one we found for systems of one particle:

$$\Psi(\vec{r}_1, \vec{r}_2, t) = \psi(\vec{r}_1, \vec{r}_2)\phi(t) = \psi(\vec{r}_1, \vec{r}_2)e^{-iEt/\hbar}$$

Let's assume that the two particles are identical but have two different quantum states α and β.

According to quantum formalism, and for reasons that will be discussed in more detail in following courses, two identical particles are *indistinguishable*, that is, we can not tell which particle is which.

If we suppose that the particles are non-interactive and that there is no entanglement involved, then we can separate the eigenfunction in two factors, each depending on the position of one of the particles:

$$\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_1)\psi(\vec{r}_2)$$

We suppose one particle is in state α and the other is in state β, so ψ can take the following form:

$$\psi = \begin{cases} \psi_\alpha(\vec{r}_1)\psi_\beta(\vec{r}_2) \\ \psi_\alpha(\vec{r}_2)\psi_\beta(\vec{r}_1) \end{cases}$$

Let's suppose both particles are in an infinite potential well of length a (and centered around $x = 0$) and that state α corresponds to $n = 1$ and state β corresponds to $n = 2$. Then

$$\psi_\alpha = B\cos\left(\frac{\pi x}{a}\right)$$
$$\psi_\beta = A\sin\left(\frac{2\pi x}{a}\right)$$

The problem with this approach is that substituting in ψ, both conformations give different wave functions, so there would be a way to tell the states of the two particles apart by experiment, which violates indistinguishability.

For this reason, we take

$$\psi = \frac{1}{\sqrt{2}}\left[\psi_\alpha(\vec{r}_1)\psi_\beta(\vec{r}_2) + \psi_\alpha(\vec{r}_2)\psi_\beta(\vec{r}_1)\right]$$

which remains constant when we switch the labels of the particles. We will call this eigenfunction ψ_S, where the S stands for symmetric. We will also use ψ_A (antysimmetric wave function), which changes sign when switching the labels. In our two-particle case, ψ_A takes the following form:

$$\psi_A = \frac{1}{\sqrt{2}}\left[\psi_\alpha(\vec{r}_1)\psi_\beta(\vec{r}_2) - \psi_\alpha(\vec{r}_2)\psi_\beta(\vec{r}_1)\right]$$

The antysimmetric wave function does not violate indistinguishability either, as the probability density is given by $\Psi^*\Psi$ and by taking this product the sign vanishes.

Let's find the coefficients A and B. Supposing that A and B are real, and given that both particles are confined inside the box, we have that

$$\int_{-a/2}^{a/2}\psi_\alpha^*\psi_\alpha dx = 1 \implies B^2\int_{-a/2}^{a/2}\cos^2\left(\frac{\pi x}{a}\right)dx = \frac{B^2}{2}\int_{-a/2}^{a/2}\left(1+\cos\left(\frac{2\pi x}{a}\right)\right)dx = 1$$
$$\implies \frac{B^2}{2}\left(a + \frac{a}{2\pi}\sin\frac{2\pi x}{a}\bigg|_{-a/2}^{a/2}\right) = 1 \implies B = \sqrt{\frac{2}{a}}$$
$$\int_{-a/2}^{a/2}\psi_\beta^*\psi_\beta dx = 1 \implies \int_{-a/2}^{a/2}A^2\sin^2\frac{2\pi x}{a}dx = \frac{A^2}{2}\int_{-a/2}^{a/2}\left(1-\cos\frac{4\pi x}{a}\right)dx = 1$$
$$\implies \frac{A^2}{2}\left(x - \frac{a}{4\pi}\cos\frac{4\pi x}{a}\bigg|_{-a/2}^{a/2}\right) = 1 \implies A = \sqrt{\frac{2}{a}}$$

5.1.1 Systems with more than 2 particles

For systems with more than 2 particles, we can symmetrize or antisymmetrize the total eigenfunction just as we would do with a tensor. We have to take into account the normalization constant though.

$$\psi_S = \frac{1}{\sqrt{n!}}\sum_{\sigma\in S_n}\psi_{\sigma(1)}\cdots\psi_{\sigma(n)}$$
$$\psi_A = \frac{1}{\sqrt{n!}}\sum_{\sigma\in S_n}\mathrm{sgn}(\sigma)\,\psi_{\sigma(1)}\cdots\psi_{\sigma(n)}$$

5.2 Exclusion Principle

Proposició 5.2.1. Weak Exclusion Principle: In a multi-electron system, there can not be two different electrons with the same quantum state.

Proposició 5.2.2. Strong Exclusion Principle: Electrons in a multi-electron system can only be described by antysimmetric eigenfunction.

It's easy to see how the strong formulation of the Exclusion Principle implies the weak formulation. If we have two electrons in the same state, then their combined wave function will be

$$\psi_A = \frac{1}{\sqrt{2}}\left(\psi_\alpha(1)\psi_\alpha(2) - \psi_\alpha(1)\psi_\alpha(2)\right) = 0$$

so the eigenfunction vanishes (and thus it does not have any physical meaning).

This principle motivates the definition of *antisymmetric particles* (i.e. particles that follow the exclusion principle like the electrons) and *symmetric particles* (i.e. particles that do not follow the principle).

Examples of antysimmetrical particles are *fermions*, while examples of symmetrical particles are *bosons*.

5.3 Elementary Particles

The fundamental particles can be divided among *fermions*, that act as matter constituents, and *bosons*, that act as force carriers. The gravitational boson has not been discovered yet.

Fermions in turn can be classified in *leptons* (formed by electrons, muons, taus and their associated neutrinos) and *quarks* (which come in 6 different flavours).

Protons and neutrons are *hadrons*, that is, particles made by the association of quarks, just like *baryons* and *mesons*.

5.4 Neutrinos

Neutrinos are the only elementary particles that are stable alone (besides protons and electrons) and take part in some of the most fundamental phenomena of nature, such as the emission of beta radiation.

In the early universe ($t < 0.5s$), energy density was dominated by photons, electrons, positrons and neutrinos, all in thermal equilibrium.

By the reaction

$$e^- + e^+ \longleftrightarrow \nu + \bar{\nu}$$

and others, the electron and neutrino gases were equilibrated. The universe has since cooled down, so this reactions are now rare, and the population of neutrinos has remained more or less constant.

Neutrinos scarcely interact with matter. About 65 billion solar neutrinos hit each cm^2 of our bodies every second, and the expected number of interactions is of 1 in 70 years.

Capítol 6

Multi-electron Atoms

6.1 Introduction

Multi-electron atoms are almost as old as the Universe itself. A few minutes after Big Bang, 74% of matter was H, 26% was ^{4}He and less than 0.01% were other elements or isotopes (^{2}H, ^{3}He, ^{7}Si, ...). Elements up to ^{54}Fe were created in thermonuclear reactions in stars, while elements beyond ^{54}Fe were made in stellar explosions and related phenomena.

The interaction among electrons makes the problem of finding analytical solutions to Schrödinger's Equation very difficult. Therefore, numerical methods are usually employed to study multi-electron atoms.

In general, we need to take into account:

- Electrostatic interaction with the nucleus
- Electrostatic interaction with the other electrons
- Spin and other interactions

Therefore, the net potential will not be the simple Coulomb potential we used before.

6.2 Pauli and Symmetry

6.2.1 Non-interacting particles

For a system of two non-interacting particles in 1D,

$$\frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V_1(x_1)V_2(x_2) = E$$

Therefore, the TDSE is

$$-\frac{\hbar^2}{2m_1}\frac{\partial^2\Psi}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2\Psi}{\partial x_2^2} + V_1(x_1)\Psi + V_2(x_2)\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

The particles do not interact with each other, so we can separate the variables:

$$\Psi(x_1, x_2, t) = \psi_A(x_1)\psi_B(x_2)f(t) = \psi_A(x_1)\psi_B(x_2)e^{-iEt/\hbar}$$

Plugging it into the TDSE, we get

$$\underbrace{\left[-\frac{\hbar^2}{2m_1}\frac{d^2\psi_A}{dx_1^2} + V_1(x_1)\psi_A\right]\frac{1}{\psi_A}}_{=E_A} + \underbrace{\left[-\frac{\hbar^2}{2m_2}\frac{d^2\psi_B}{dx_2^2} + V_2(x_2)\psi_B\right]\frac{1}{\psi_B}}_{=E_B} = \frac{i\hbar}{f}\frac{df}{dt}$$

The total energy will be $E = E_1 + E_2$, and the probability density is given by

$$dP = |\Psi|^2 dx_1 dx_2 = |\psi_A(x_1)|^2 dx_1 |\psi_B(x_2)|^2 dx_2,$$

and represents the probability that the first particle is infinitessimally close to x_1 and the second particle is infinitessimally close to x_2.

6.2.2 Exchange Symmetry

The problem of the composite wave function used above is that it does not respect *exchange symmetry*, that is, $\Psi(x_1, x_2, t) \neq \Psi(x_2, x_1, t)$ (because in general $\psi_A \neq \psi_B$).

In order to make the two composite states (particle 1 in state A and particle 2 in state B `vs` particle 2 in state A and particle 1 in state B) indistinguishable, the square of the norm of the wave function must be equal in both cases, so

$$\Psi(x_1, x_2, t) = \pm\Psi(x_2, x_1, t)$$

When $\Psi(x_1, x_2, t) = \Psi(x_2, x_1, t)$ we'll say Ψ is *symmetric*, while if $\Psi(x_1, x_2, t) = -\Psi(x_2, x_1, t)$, we will say Ψ is *antisymmetric.*

In order to compute the symmetric and antisymmetric Ψ for a system, we apply the same procedure we would use to symmetrize or antisymmetrize a tensor.

6.3 Combined spin states

Let's take a system of two particles with two possible individual states α and β (that can be identified with spin up and down). We then have three possible symmetric states:

$$\alpha(1)\alpha(2) \qquad \beta(1)\beta(2) \qquad \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \alpha(2)\beta(1)\right]$$

but only one possible antysimmetric state:

$$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]$$

These states are called *triplet* and *singlet* states, respectively.

6.3.1 Triplet states

In the triplet states, the two added spins are parallel ($s = s_1 + s_2 = 1$), and the three possible wave functions correspond to the cases $m_s = +1, 0, -1$.

As electrons are fermions, their total wave function must be antisymmetric, so the space wave function must be antysimmetric. That implies that when the two electrons are close, the wave function tends to zero, so there is a repulsive force between both particles. This repulsion is an example of *exchange forces.*

6.3.2 Singlet state

In the singlet state, the two spins are anti-parallel, so $s = s_1 + s_2 = 0$. Therefore, m_s can only take the value $m_s = 0$, which corresponds to the only possible wave function.

The spin eigenfunction is antysimmetric, so in order to keep the total wave function antysimmetric, the space function must be symmetric. Therefore, when the two particles are close, the wave function increases, and so there is an attraction between both electrons.

6.4 Helium atom

In this section we are going to study the system formed by the two electrons of an helium atom, subjected to different types of forces.

6.4.1 No interaction

Let's suppose that the two electrons are in states n_1 and n_2 and that they are non-interacting. Then, the total energy can be calculated as

$$E = -\frac{\mu Z^2 e^4}{(4\pi\varepsilon_0)^2 2\hbar^2 n_1^2} - \frac{\mu Z^2 e^4}{(4\pi\varepsilon_0)^2 2\hbar^2 n_2^2}$$

For example, for the ground state ($n_1 = n_2 = 1$), the energy is predicted to be $E = -108.8eV$, so the energy of ionization would be $54.4eV$. Experimentally, this energy is found to be $24.5eV$, so this model is not very accurate.

6.4.2 Bohr orbits + Coulomb force

Now, we consider the electrons to describe a Bohr orbit. We also consider that at any time they are at opposite points of the orbit. The radius of the orbit will be $a_0/2$ (as the charge of the nucleus is twice of that of the hydrogen). The electromagnetic Coulomb force between the electrons will be

$$E_c = \frac{e^2}{4\pi\varepsilon_0} a_0 \cong 27.2eV$$

Then, the total energy of the system with both electrons in the ground state is

$$E = -108.8 + 27.2 = -81.6eV$$

The ionization energy will be the difference between this energy and the energy of He$^+$ (the ionized atom, with one electron less):

$$\Delta E = -54.4 + 81.6 = 27.2eV$$

We can see that this ionization energy is closer to the experimental value.

6.4.3 QM + Coulomb force

A more accurate model is created by considering that both particles satisfy the TISE:

$$\left[\left(-\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{2e^2}{r_1}\right) + \left(-\frac{\hbar^2}{2m_2}\nabla_2^2 - \frac{2e^2}{r_2}\right)\right]\psi = E\psi$$

The interference created by one electron in the Coulomb force between the other electron and the nucleus is called *effective shielding*. This interference depends on the orbital angular momentum, so the states with $l = 0$ and $l = 1$ will have different ionization energies.

Even more accurate predictions can be made by taking into account the exchange forces between the electrons. Thus, depending on whether the system is in a triplet or a singlet state, the ionization energy will also be different.

6.5 Hartree-Fock

For multielectron atoms, a more sophisticated method is used. The method can be summarized in the following points:

1. Approximate a *net potential* that behaves like Coulomb's potential near the nucleus with $Z = Z$, and far from it with $Z = 1$. We interpolate between those to get an approximated potential in between.
2. Solve the TISE numerically for the net potential we found.
3. Find ground state E and Ψ.
4. Evaluate charge distribution.
5. Find the electric field created by the distribution and integrate to find the real potential.
6. If this potential is substantially different from the one in step 1, turn back to step 2 using this new potential as our initial guess.

6.5.1 Eigenfunctions

For multielectron atoms, the eigenfunctions are spherically symmetric, so the angular part vanishes (just like it did in the Hydrogen atom) and the probability density only depends on the radius. Therefore,

$$P_{n,l,m_l,m_s}(r) = \underbrace{2(2l+1)}_{\#\text{ of electrons}} P_{n,l}(r)$$

as there are 2 possible values of m_s and $2l+1$ possible values of m_l.

Radial eigenfunctions take the form

$$V(r) = -\frac{Z(r)e^2}{4\pi\varepsilon_0 r}$$

which does not always take Coulomb's form, as Z depends on the radius. This is explained because if there is another electron between the electron we are studying and the nucleus, then this intermediate electron will *shield* the nuclear charge, and the effective Z will be lower.

In general, we consider that for $r \to 0$, $Z_e = Z$; for $r \to \infty$, $Z_e = 1$; and for $r = r_1$, $Z_e \cong Z - 2$.