Quantum Mechanics

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Physics and Astrophysics BSc

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Version

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1 The Failure of Classical Physics

The failure of classical physics starts in the first years of the 1900s, when the first experimental measurements on the world of the very small begun. The first discrepancies found, after Planck's quantization of energy "trick" for avoiding the UV catastrophe, were in the experimental results given from the measurements of the wavelength of the emission of Hydrogen, Bremsstrahlung radiation and the famous photoelectric effect.
The first approaches for a correct theoretical modelization of a Hydrogen atom were put forward by Thomson, where the atom itself is considered as a charged sphere, in which there are inside positive and negative charges.
For Hydrogen we will have a sphere of radius a with charge $|q| = e = 1.6 \cdot 10^{-19}$ C. Using Gauss' theorem, we know that the flux of the electric field $\underline{E}$ will be given by the following piecewise function

$$\Phi_E(r) = \begin{cases} 4\pi e \dfrac{r^3}{a^3} & 0 \leq r \leq a \\ 4\pi e & r \geq a \end{cases} \tag{1.1a}$$

Since we are in a spherically simmetrical system, the flux of the $\underline{E}$ field will simply be $4\pi r^2 \underline{E}(r)$, and our $\underline{E}$ field will be

$$\underline{E}(r) = \begin{cases} \dfrac{er}{a}\hat{\mathbf{r}} & 0 \leq r \leq a \\ \dfrac{e}{r^2}\hat{\mathbf{r}} & r \leq a \end{cases} \tag{1.1b}$$

Since $\underline{E}$ is conservative, we can define a scalar potential ϕ such that $\nabla\phi = \underline{E}$. This function is easily determined by the solution of a 1st order ODE

$$\begin{cases} \dfrac{\mathrm{d}\phi}{\mathrm{d}r} = \begin{cases} -\dfrac{er}{a^3} & 0 \leq r \leq a \\ -\dfrac{e}{r^2} & r \geq a \end{cases} \\ \lim\limits_{r\to\infty}(\phi(r)) = 0 \end{cases} \tag{1.2a}$$

The ODE is a separable differential equation with the following solution

$$\phi(r) = \begin{cases} \dfrac{3e}{2a} - \dfrac{er^2}{2a^3} & 0 \leq r \leq a \\ -\dfrac{e^2}{r} & r \geq a \end{cases} \tag{1.2b}$$

Since the total charge of the system is $q = -e$, and the potential energy of the system will be given from the scalar potential times the total charge, we have that $V(r) = -e\phi(r)$.
Since the ionization energy is defined as $E_I = V(0)$, we get for Hydrogen,

$$E_I = -\frac{3e^2}{2a} \approx -13.6 \text{ eV}$$

For evaluating the emission frequency of this system, we write the Hamiltonian for a harmonic oscillator with the mass of an electron, m_e, coupled to a Hamiltonian with the potential $V(r)$.
The Hamiltonian will then be defined piecewise as such

$$\mathcal{H}(p,r) = \begin{cases} \dfrac{p^2}{2m_e} + \dfrac{1}{2}m_e\omega^2 r^2 \\ \dfrac{p^2}{2m_e} + \dfrac{e^2 r^2}{2a^3} \end{cases} \tag{1.3}$$

Solving the system for ω we get

$$\omega = \sqrt{\frac{e^2}{m_e a^3}}$$

Plugging the measured values of the electron mass and the radius of the charged sphere, we get a frequency $\nu \approx 1.2 \cdot 10^{15}$ Hz and a corresponding wavelength of $\lambda \approx 3 \cdot 10^3$.
Although the values obtained from this classical model of the atom core are consistent, the whole idea has been disproven by Geiger and Madsen, whom have demonstrated that if a Gold sheet is irradiated with α particles, most of them will pass through without scattering, some get sligthly deflected after interacting with the Gold atoms and another part gets deflected with angles that are completely incompatible with Thomson's model.
A different model which explains the Geiger-Madsen experiment is the Rutherford model of the atom, where the system is evaluated as two opposed charges, the nucleus positively charged, and the orbiting electrons with negative charge.
The total energy of the Rutherford atom can be calculated using the classical Virial theorem, which gives

$$E = \frac{1}{2}m_e v^2 - \frac{e^2}{a} = -\frac{e^2}{2a} \tag{1.4}$$

Forcing in the measured valued for E_I, we get for Hydrogen $a \approx 0.5$ and $\lambda \approx 455$.
Although these values are consistent with observations, the model isn't physically accurate, since the electrons in these orbits have a nonzero acceleration, which brings them to emit sincrotron radiation and consequently lose angular momentum, falling towards the nucleus.
If one explicits all the values in game with such system, will get that a random atom will have a mean life of 10^{-8} s, which is completely in contrast with observation, since atoms exist, and didn't get annihilated 10^{-8} s after their formation in the early universe.
The final blow to this huge crisis in classical physics has been given by Einstein and his discovery of the photoelectric effect, where it's shown that, if a metal is irradiated from a source with an energy $E > W$, with W a work function, there is an emission of electrons linearly proportional to the frequency of the radiation, with coupling constant being exactly Planck's constant, $h = 6.6 \cdot 10^{-34}$ Js. The inverted experiment gives instead a "stopping radiation", Bremsstrahlung in German, where at given frequencies the blackbody radiation of the source gets "stopped". This kind of behavior is not explainable with

classical physics, which gave rise to the formulation of quantum mechanics.
The photoelectric effect, with its astonishing results, gave rise to the idea that radiation is quantized, hence it behaves as a particle, and at the same time, due to the certainity behind classical optics, it has the behavior of a wave.

§ 1.1 Old Quantum Mechanics

After the discovery of Bremsstrahlung and the photoelectric effect, there has been an attempt to formalize this new mechanics of quanta by Bohr, through 3 hypotheses

Hypothesis 1 (Bound States)**.** For any atom, only states with discrete energies E_n are allowed, where E_n is a monotonically increasing succession of values, called Energy Levels. The set of these discrete states is called the set of Bound States, the minimum value of this succession is E_0 and is commonly referred to as Ground State.

Hypothesis 2 (Transition Between Levels)**.** When the system is in a bound state radiates only in transitions between levels.
Taking a level E_n and a level E_m where $m > n$, the frequency of the radiation is

$$\nu_{nm} = \frac{|E_m - E_n|}{h}$$

Where h is Planck's Constant.

Corollary 1.1.1 (Ritz Combination Principle)**.** The emission spectrum of an atom, with this hypothesis, is then given by evaluating all the energy differences of the absorption spectrum's difference, hence

$$|\nu_{0n} - \nu_{0m}| = \left| \frac{E_n - E_0}{h} - \frac{E_m - E_0}{h} \right| = \frac{|E_n - E_m|}{h} = \nu_{nm}$$

Hypothesis 3 (Bohr-Sommerfield Quantization)**.** Defining $\hbar$ as $h/2\pi$ as the reduced Planck Constant, we get that the only permitted orbits are those where $L \propto n\hbar$.
For an orbit γ then holds that

$$L = \oint_\gamma p \, \mathrm{d}q = n\hbar$$

For a circular orbit, $L = \mu v r$, hence $\mu v r = n\hbar$

For an Hydrogen atom we then get the following results.
Considering that the system is virialized, we can write the energy as such

$$E = \frac{1}{2}V = -\frac{Ze^2}{2r} \tag{1.5a}$$

The third Bohr hypothesis requires that $\mu v r = n\hbar$, with μ being the reduced mass of the system nucleus-electron.
Squaring the previous relation and inserting it in the expression of energy, we get

$$\frac{1}{2}\mu v^2 = \frac{n^2\hbar^2}{2\mu r^2} = \frac{Ze^2}{2r} \tag{1.5b}$$

From this we get that the only possible orbits are at a radius r_n, where

$$r_n = \frac{n^2\hbar^2}{\mu Z e^2} = \frac{n^2 m_e a_B}{Z\mu}$$

With $a_B = \hbar^2/m_e e^2$ a constant with dimensions of length, called Bohr radius.
Inserting what we have just derived in (1.5a) we get the succession of quantized levels of energy, with the following relation

$$E_n = -\frac{Z^2 e^2 m_e}{2a_B n^2} \tag{1.5c}$$

Inserting $Z = 1$ for restricting these levels to hydrogen, we get, with the approximation $\mu \approx m_e$ that

$$\begin{aligned} r_n &= n^2 a_B \\ a_B &= \frac{\hbar^2}{m_e e^2} = 0.53 \\ E_n &= -\frac{e^2}{2a_B n^2} \end{aligned} \tag{1.6}$$

The values obtained are in accord with experimental results, but the new "theory" of quantum mechanics had yet to be formalized with a set of fundamental principles.

§ 1.2 Wave-Particle Duality

The photoelectric effect, as said before, gave rise to the discovery of the particle-like behavior of light.
L. de Broglie, put forward the following problem:
Taking as true the wave like behavior of the electromagnetic radiation, and at the same time taking as true the particle behavior of the same, there must be a particular wavelength for any particle, for which can be then defined a *matter wave*, which has the same ondulatory behavior of classical waves, while still having all the properties of matter.
Taking as an Ansatz the Bohr-Sommerfield quantization hypothesis, we get that

$$pL = nh$$

Dividing by p we finally get that

$$L = n\frac{h}{p}$$

Since for a photon $\lambda = h/p$, we get the following hypothesis

Hypothesis 4 (de Broglie Hypothesis)**.** A wave is associated with each particle, and its wavelength is given by the relation $\lambda = h/p$. All the allowed orbits are those which contain an integer number of wavelengths.

We can then define the *de Broglie wavelength* of matter as such:
Since $p = \sqrt{2mE}$, we get

$$\lambda_{DB} = \frac{h}{\sqrt{2mE}} \tag{1.7}$$

If preferred, defining a "reduced" de Broglie wavelenght as $\lambda\!\!\!^{-} = \lambda_{DB}/2\pi$, we get, in terms of $\hbar$

$$\lambda\!\!\!^{-} = \frac{\hbar}{\sqrt{2mE}}$$

§ 1.3 Experimental Verifications of Quantum Mechanics

§§ 1.3.1 Double Slit Experiment and Quantum Measurement

In order to verify de Broglie's hypothesis of matter waves, many experiments were carried on, but the one that is really worth of notice is the *double slit experiment*.
Let a beam of monochromatic light hit a completely opaque screen, on which there are two parallel slits. Due to the wave nature of electromagnetic radiation, the light passing through the two waves interferes with itself, and if a detector is put on front of such screen, a diffraction pattern can be observed and measured, as expected from classical electromagnetism and optics. In terms of photons, this diffraction pattern indicates where more photons hit the detector and where less did, and the diffraction can be seen as mere interaction with photons that got through different slits.
The real hassle comes when the same experiment is repeated without a continuous beam of light, but with a single photon. In this case an interference pattern «*can't*» be explained with interacting photons, as there is a single photon in the whole system.
According to the corpuscular model, the photon must pass through one single slit, but the interference pattern wouldn't be observed in this case, giving a further confirmation of the wave-particle duality.
Getting back again to the first case, we can also try to interpret the interference pattern as a sum of the interference patterns of the photons passing only through one of the two slits. Introducing the idea of *state*, we can identify with $|A\rangle, |B\rangle$ the diffraction patterns of the photons passing through a single slit, and with $|C\rangle$ the interference pattern identified in the doble slit experiment.
It's easy to see that the final state isn't exactly a sum of the first two.
Leaving the world of classical physics, we can interpret the final state $|C\rangle$ as being a "mixture" of the state $|A\rangle$ and $|B\rangle$. taking a, b constants, then we can write that

$$|C\rangle = a\,|A\rangle + b\,|B\rangle$$

This result has no similar results in classical physics, since, if evaluated for a single photon, it explicitly indicates that the photon is passing through both slits at the same time!
A similar experiment uses a Mach-Zehnder interferometer, where a beam of neutrons gets shot through two different paths, where at the end of both a detector is carefully placed.
The result for a single neutron experiment are basically the same of the double slit experiment, because it is measured that the single neutron passes through both paths, and gets then measured from both detectors.
Modifying the experiment, and putting a detector on both slits, removes this indecision on which slit the particle went through (or path in the interferometer), and would let a detailed description of the construction of the interference pattern to be brought up from data.
What is observed though is extremely different from what is expected, in fact, measuring from which slit the particle goes through completely destroys the interference pattern, and what is measured is a corpuscular behavior of the particles.
This result, tells us that measuring a state, changes it. In fact, it changes the state in such a way that

we can either have an interference pattern of a wave-like behavior or a particle-like behavior.
In fact, wave-particle duality still holds, but now gets a whole different meaning: *particles aren't waves nor corpuscules, but both at the same time.* This affirmation has no meaning whatsoever in the classical world that we perceive, and it's the key factor in making quantum mechanics not understandable with physical intuition.
Although not humanly understandable, quantum mechanics can be formalized in a full fledged physical theory with a formal mathematical background, which lets us "understand" quantum mechanics through mathematics. In fact, we can grasp the mathematics of it, even without grasping the physical reality behind it.

2 The Fundamentals

§ 2.1 Dirac Notation

In order to fully grasp this and the future chapters is useful to really know how Dirac notation works in a mathematical framework. In Dirac notation, a vector of a complex Hilbert space $\mathbb{H}$ is indicated with the following notation: $|\cdot\rangle$, called a *ket*, where in place of the dot there is usually a label or an index. Hence, if we have a vector $\underline{a} \in \mathbb{H}$, this vector can be indicated as $|a\rangle \in \mathbb{H}$. Defining the dual space of $\mathbb{H}$ as the space of all linear functionals, i.e. all elements $\underline{b} \in \mathbb{H}^\star$ such that $\underline{b} \cdot \underline{a} = \lambda \in \mathbb{C}$, we define such vectors (or covectors) with the notation $\langle b|$, called *bra*. With this notation, the scalar product simply becomes $\langle b|a\rangle = \lambda$. It's also useful to remember that there exist an isomophism $\iota : \mathbb{H} \to \mathbb{H}^\star$, where it is defined as follows

$$\iota(\underline{a}) = \overline{\underline{a}}^{\mathsf{T}} = \overline{\underline{a}^{\mathsf{T}}} \in \mathbb{H}^\star \quad \forall \underline{a} \in \mathbb{H}$$

In Dirac notation, we will then have the following

$$\iota(|a\rangle) = \overline{|a\rangle}^{\mathsf{T}} = \overline{|a\rangle^{\mathsf{T}}} = \langle a| \quad \forall\, |a\rangle \in \mathbb{H}$$

§§ 2.1.1 Generalized Vectors and Tensors in Dirac Notation

Generalizing to tensor spaces, we get the following notation equivalences in the case of rank 2 tensors. Let T_{ij}, G^j_i, H^{ij} be tensors in the spaces, respectively $\mathbb{H}^\star \otimes \mathbb{H}^\star, \mathbb{H}^\star \otimes \mathbb{H}, \mathbb{H} \otimes \mathbb{H}$
In Dirac notation, since they represent the direct product of two vectors (or covectors), they can be indicated as such

$$\begin{aligned} T_{ij} &\longrightarrow \langle i| \otimes \langle j| = \langle i| \langle j| = \langle ij| \\ G^i_j &\longrightarrow |i\rangle \otimes \langle j| = |i\rangle \langle j| \\ H^{ij} &\longrightarrow |i\rangle \otimes |j\rangle = |i\rangle |j\rangle = |ij\rangle \end{aligned} \tag{2.1}$$

Remembering that the isomorphism between the space and its dual is given by a trasposition and a complex conjugation, we have that the operation of index raising and index lowering (also known as musical isomorphisms), in Dirac notation will be indicated as follows:

$$T^{ij} = \overline{T^{\mathsf{T}}_{ij}} = \overline{T_{ji}} \longrightarrow |i\rangle |j\rangle = \langle j| \langle i| \tag{2.2}$$

This is especially useful when treating the contraction of all indexes of a tensor.
Let $R_{ij} = a_i b_j$ and $S^{ij} = c^i d^j$. The product $R_{ij}S^{ij}$ will then be, using the Einstein convention for repeated indexes and the rules defined before for raising and lowering indexes,

$$R_{ij}S^{ij} = a_i b_j c^i d^j = \overline{b^j a^i} c^i d^j \to \langle b| \langle a|c\rangle |d\rangle = \langle a|c\rangle \langle b|d\rangle \tag{2.3}$$

Since a tensor product of two vector spaces is a vector space itself, it's common to directly use superindexes or labels in the labels of the kets and bras, such that a tensor $|ij\rangle = |I\rangle$, where I is the chosen label. It's not hard to then generalize the notation to rank-n tensors.
There is only one exception, irreducible tensors. Since they can't be factorized as the direct product of two vectors, they're usually directly indicated with a simple label as before.

§§ 2.1.2 Function Spaces and Linear Operators

Since quantum mechanics can be also represented with elements of function spaces, Dirac notation can be extended to indicate even functions and operators.
Let $\mathcal{F}$ be a function space, and let $\psi \in \mathcal{F}$ be an element of such.
We can write the function $\psi(x) : \mathbb{C} \to \mathbb{R}$ as the projection of the element of $\mathcal{F}$ to the field of complex numbers $\mathbb{C}$. In Dirac notation this becomes

$$\psi(x) \leftrightarrow \langle x|\psi\rangle \tag{2.4}$$

An operator, is a linear endomorphism of $\mathbb{H}$. If we have an operator $\hat{\eta}$ bounded, and an operator $\hat{\sigma}$ unbounded, their definition spaces will be the following

$$\begin{aligned} &\hat{\eta} : \mathbb{H} \to \mathbb{H} \\ &\hat{\sigma} : \mathcal{D} \subset \mathbb{H} \to \mathcal{D} \subset H \end{aligned} \tag{2.5}$$

Since they're linear, if we define a new operator $\hat{\iota}_i$, where $\hat{\iota}_1 = \hat{\eta}$ and $\hat{\iota}_2 = \sigma$, we have, that $\forall \alpha, \beta \in \mathbb{C}$ and $\forall \, |A\rangle, |B\rangle \in \mathcal{D}$, ($\in \mathbb{H}$ if we're considering a bounded operator)

$$\hat{\iota}_i \left(\alpha \, |A\rangle + \beta \, |B\rangle\right) = \alpha \hat{\iota}_i \, |A\rangle + \beta \hat{\iota}_i \, |B\rangle \tag{2.6}$$

Let's now define an operator $\hat{R}$ such that $\hat{R}\psi(x) = e^{i\pi}\psi(x)$. In Dirac notation it's simply $\hat{R} \, |\psi\rangle = e^{i\pi} \, |\psi\rangle$, nothing changes much.
Although, since operators acting on functions can be seen as tensors (or matrices) acting on vectors, we can write the (infinite) matrix representation of such objects, as such:
Let $\underline{e}_i, \underline{e}_j$ be two basis elements of $\mathcal{F}$. We then will have the following relation, if the scalar product is indicated as $\langle \cdot, \cdot \rangle$

$$R_{ij} = \langle \underline{e}_i, \hat{R}\underline{e}_j \rangle$$

In Dirac notation, its formulation it's similar in shape, and it's written as such

$$R_{ij} = \langle i| \, \hat{R} \, |j\rangle$$

If now we define the *adjoint* operation (indicated with (†) as the composition of complex conjugation and transposition ($\square^\dagger = \overline{\square} \circ \square^\intercal$), we have

$$R^\dagger_{ij} = \langle \underline{e}_i, \hat{R}\underline{e}_j \rangle^\dagger = \langle \underline{e}_j \hat{R}^\dagger, \underline{e}_i \rangle$$

Without writing the equivalent operation in Dirac notation, and just confronting how the adjoint operator works, we get immediately get how it will behave with kets and bras. The operator will act on the right, and its adjoint on the left.
Let $|a\rangle$ be an eigenvector (or eigenket) of $\hat{R}$, with eigenvalue α. We then can express the fact that the operator acts on the right, and its adjoint on the left using $\hat{R}$'s secular equation

$$\hat{R}\,|a\rangle = \alpha\,|a\rangle$$
$$\langle a|\,\hat{R}^\dagger = \langle a|\,\overline{\alpha}$$

But since applying the double adjoint means applying the identity transformation, we get that

$$\left[\left(\hat{R}\,|a\rangle\right)^\dagger\right]^\dagger = \left(\langle a|\,\hat{R}^\dagger\right)^\dagger = (\langle a|\,\overline{\alpha})^\dagger = \alpha\,|a\rangle = \hat{R}\,|a\rangle$$

Hence, an adjoint of an operator acts on the left, and the adjoint of the adjoint operator is the operator itself, and if a ket is a solution to the secular equation, its equivalent bra will be the solution to the adjoint secular equation.
Let's remember that in general, $\hat{R}^\dagger \neq \hat{R}$, hence generally $\hat{R}\,|A\rangle \neq \langle A|\,\hat{R}$

§ 2.2 Axioms of Quantum Mechanics

The first postulate of quantum mechanics used to formalize mathematically its structure is the *superposition principle*

Postulate 1 (Superposition Principle). The state of a quantum system is a vector of a separable Hilbert space ($\mathbb{H}$), and if two different vectors are proportional to eachother, they represent the same state. This space must be endowed with a Hermitian scalar product and its dimension is usually infinite.

Since this Hilbert space is a linear vector space, it's algebraically closed, which means that, for two different states $|a\rangle$ and $|b\rangle$, with $\alpha \in \mathbb{C}$, we have

$$\alpha\,(|a\rangle + |b\rangle) = \alpha\,|a\rangle + \alpha\,|b\rangle = |c\rangle \in \mathbb{H} \tag{2.7}$$

Postulate 2 (Observables). Every quantity that can be observed, hence measured, is called observable, and it's mathematically represented by a self-adjoint operator.
The eigenvalues of this operator are the possible results of the measurement.

With such definition, the eigenvectors of the self-adjoint operator will be all the states invariant to the action of the operator.
If to every eigenvalue of the observable corresponds one and only one eigenvector, the observable is said to be nondegenerate.

Postulate 3 (Postulate of von Neumann). If a measurement of an observable $\hat{\alpha}$ on a state $|a\rangle$ gives a degenerate eigenvalue α, the eigenstate of the observable will then be given by the projection of $|a\rangle$ onto the eigenspace of $\hat{\alpha}$, corresponding to the subspace generated by all vectors that satisfy the equation

$$\hat{\alpha}\,|r_i\rangle = \alpha\,|r_i\rangle$$

The searched state will then be

$$|s\rangle = \sum_i p_i |r_i\rangle$$

Postulate 4 (Transition Probabilities). Let $\hat{\beta}$ be an observable, hence $\hat{\beta} = \hat{\beta}^\dagger$. Consider now a state $|d\rangle$. If $\hat{\beta}|d\rangle = p|f\rangle$, we can define the probability of the transition $|d\rangle \to |f\rangle$ as follows:

$$P(|d\rangle \to |f\rangle) = \frac{|\langle f|d\rangle|^2}{\langle d|d\rangle \langle f|f\rangle} \leq 1$$

There are two main cases for the study of transition probabilities, one for nondegenerate states and one for degenerate states. Since the case for nondegenerate states is a particular case of the degenerate case, we can study directly the latter.
Let $\hat{S}$ be a degenerate observable. For a state $|A\rangle$ (with $\langle A|A\rangle = 1$), we will then have, after a projection to an orthonormal basis of eigenstates $|s_i\rangle$, as indicated in the von Neumann postulate

$$|A\rangle = \sum_i a_i |s_i\rangle$$

Let's define a state $\hat{S}|A\rangle = |k\rangle = \sum_i a_i |s_i\rangle$ The problem is straightforward. What's the transition probability from a state $|A\rangle$ to a state $|s_i\rangle$ (with i fixed)?
From the last postulate we can write

$$p_i = P(|A\rangle \to |k\rangle) = \frac{|\langle k|A\rangle|^2}{\langle k|k\rangle}$$

Due to the orthonormality of $|s_i\rangle$ ($\langle s_i|s_j\rangle = \delta_{ij}$) we will have

$$p_i = \sum_i |a_i|^2$$

Which is a direct consequence of von Neumann's postulate.
Hence, in order to treat a general state $|B\rangle$ which is not an eigenstate of a given observable $\hat{b}$, we can apply a projection, as stated from von Neumann. But how does this projection work? What's its mathematical form?
The answers to these questions are quite easy to think what shape would they take. As the projection of a state can be interpreted as a Fourier series, we get that the projection will be given by an operator that sends $|B\rangle$ to a set of eigenstates $|b_i\rangle$, multiplied by some constant which is exactly given by the scalar product $\langle B|b_i\rangle$. Summarizing, if we indicate the projected state with $|b\rangle$

$$\begin{aligned} |b\rangle &= \hat{\pi}_i |B\rangle = \sum_i \langle b_i|B\rangle |b_i\rangle \\ \hat{\pi}_i &= |b_i\rangle \langle b_i| \end{aligned} \tag{2.8}$$

Where $\hat{\pi}_i^\dagger = \hat{\pi}_i$ and $\hat{\pi}^2 = \hat{\pi}$, due to the definition of the projector operator.
Moreover, we can even define a theorem from this definition, where, if $|b_i\rangle$ is a complete orthonormal basis, then

$$|b_i\rangle \langle b_i| = \hat{\mathbb{1}} \tag{2.9}$$

Which indicates the completeness relation for a basis.
We subsequently define the expectation value of an observable, its variance, commutators and anti-commutators

Definition 2.2.1 (Mean Value). Given an observable $\hat{\eta}$, we can define its mean value on a state $|a\rangle$ as follows

$$\langle\hat{\eta}\rangle_{|a\rangle} = \langle a|\,\hat{\eta}\,|a\rangle = \sum_i \langle a|\,\hat{\pi}_i\hat{\eta}\hat{\pi}_i\,|a\rangle = \sum_i p_i\eta_i, \quad p_i = \frac{N_i}{N} \tag{2.10}$$

Due to the arbitrary definition of $\hat{\eta}$ and $|a\rangle$, what has been written is valid generally

Definition 2.2.2 (Variance). If we define the variance as $Var(x) = \sqrt{\langle x^2\rangle - \langle x\rangle^2}$, we can define the variation of an observable on a state $|a\rangle$ as such

$$Var\left(\hat{\eta}\right) = \sqrt{\langle a|\,\hat{\eta}\hat{\eta}\,|a\rangle - \langle a|\,\hat{\eta}\,|a\rangle\,\langle a|\,\hat{\eta}\,|a\rangle} = \sqrt{\langle\hat{\eta}^2\rangle_{|a\rangle} - \langle\hat{\eta}\rangle^2_{|a\rangle}} \tag{2.11}$$

Definition 2.2.3 (Commutators and Anticommutators). The commutator is an operator of operators defined for $\hat{\eta}, \hat{\gamma}$ as such:

$$[\hat{\eta}, \hat{\gamma}] = \hat{\eta}\hat{\gamma} - \hat{\gamma}\hat{\eta} \tag{2.12}$$

The anticommutator is defined as such

$$\{\hat{\eta}, \hat{\gamma}\} = \hat{\eta}\hat{\gamma} + \hat{\gamma}\hat{\eta} \tag{2.13}$$

In general, the commutator is antihermitian and bilinear, whereas an anticommutator is hermitian and bilinear.

THEOREM 2.1 (Compatibility). *Two operators $\hat{a}$ and $\hat{b}$ are said compatible, if there exists a common basis of eigenstates and their commutator is equal to 0*

Proof. If $\hat{a}$ and $\hat{b}$ are compatible, then there exists a common basis of eigenstates. Let $|A\rangle \neq 0$ be such basis, then, such statement is true

$$\begin{cases} \hat{a}\,|A\rangle = \alpha\,|a\rangle \\ \hat{b}\,|A\rangle = \beta\,|a\rangle \end{cases} \tag{2.14}$$

Then,

$$\begin{aligned} \left[\hat{a}, \hat{b}\right]|A\rangle = (\hat{a}\hat{b} - \hat{b}\hat{a})\,|A\rangle = \\ = \hat{a}\hat{b}\,|A\rangle - \hat{b}\hat{a}\,|A\rangle = \beta\hat{a}\,|A\rangle - \alpha\hat{b}\,|A\rangle = \\ = \beta\alpha\,|A\rangle - \alpha\beta\,|A\rangle = 0 \end{aligned} \tag{2.15}$$

But, if $\left[\hat{a}, \hat{b}\right]|A\rangle = 0$

$$\begin{aligned} \hat{a}\,|A\rangle = \alpha\,|A\rangle \\ \hat{b}\alpha\,|A\rangle = \alpha\beta\,|A\rangle \\ (\hat{a}\hat{b} - \hat{b}\hat{a})\,|A\rangle = 0 \end{aligned} \tag{2.16}$$

As expected from the statement of the theorem. □

Postulate 5 (Canonical Quantization). There exists a strict relation between commutators and Poisson brackets. If we define the Poisson brackets as $[\cdot,\cdot]_{PB}$, we can quantize Poisson brackets with the following relation

$$[\cdot,\cdot] = i\hbar[\cdot,\cdot]_{PB}$$

Since $[q_i, p_j]_{PB} = \delta_{ij}$, in quantum mechanics holds this fundamental relation

$$[\hat{q},\hat{p}] = i\hbar\hat{\mathbb{1}} \tag{2.17}$$

This is known as canonical quantization, where position and momentum are represented by observables.

Postulate 6 (Heisenberg Uncertainity). In quantum mechanics there is an intrinsic uncertainity on measurements.

Taking two observables $\hat{a}$ and $\hat{b}$, we define an operator $\alpha = \hat{a} + ix\hat{b}$ with $x \in \mathbb{R}$.
Its expectation value on a state $|s\rangle$ will be the following

$$\langle s|\,\hat{\alpha}^\dagger\hat{\alpha}\,|s\rangle \leq \langle s|\,\hat{\alpha}^\dagger\,|s\rangle\,\langle s|\,\hat{\alpha}\,|s\rangle$$

Since $\hat{\alpha}^\dagger\hat{\alpha} = \hat{a}^2 + x^2\hat{b}^2 + ix\left[\hat{a},\hat{b}\right]$, we get that

$$\left\langle\hat{a}^2\right\rangle + x^2\left\langle\hat{b}^2\right\rangle + ix\left\langle\left[\hat{a},\hat{b}\right]\right\rangle \geq \langle\hat{a}\rangle^2 + x^2\left\langle\hat{b}\right\rangle^2$$

Hence

$$\left\langle\hat{a}^2\right\rangle - \langle\hat{a}\rangle^2 + x^2\left(\left\langle\hat{b}^2\right\rangle - \left\langle\hat{b}\right\rangle^2\right) - ix\left\langle\left[\hat{a},\hat{b}\right]\right\rangle \geq 0$$

Rewriting $\left\langle c^2\right\rangle - \langle c\rangle^2 = \sigma_c^2$, with c arbitrary and σ its standard deviation, we get

$$\sigma_a^2 - x^2\sigma_b^2 + ix\left\langle\left[\hat{a},\hat{b}\right]\right\rangle \geq 0$$

In order for this equation to be true, the discriminant of the quadratic equation must be greater than 0, hence

$$-\left\langle\left[\hat{a},\hat{b}\right]\right\rangle^2 + 4\sigma_a^2\sigma_b^2 \geq 0$$

And finally we get

$$\sigma_a\sigma_b \geq \frac{1}{2}\left\langle\left[\hat{a},\hat{b}\right]\right\rangle$$

Taking $\hat{a} = \hat{q}$ and $\hat{b} = \hat{p}$, and following canonical quantization rules, we get that momentum and position can't be measured simultaneously due to a fundamental uncertainity, given by Heisenberg's uncertainity principle

$$\sigma_q\sigma_p \geq \frac{1}{2}\hbar \tag{2.18}$$

§ 2.3 Representation Theory

§§ 2.3.1 Heisenberg Representation

In quantum mechanics, we can define two main representations: Heisenberg representation or Schrödinger representation.
Heisenberg representation is given by matrix elements of operators, through an isomorphism between l_2 and the Hilbert space of quantum configurations $\mathbb{H}$. Defining a CON basis (complete orthonormal) $|e_i\rangle$ on $\mathbb{H}$, we get that, $\forall\, |A\rangle \in \mathbb{H}$

$$|A\rangle = \hat{\mathbb{1}}\,|A\rangle = \sum_i |e_i\rangle\,\langle e_i|A\rangle = \sum_i a_i\,|A\rangle \tag{2.19}$$

Where the operator $\hat{\pi} = |e_i\rangle\,\langle e_i|$ is defined as $\hat{\pi} : \mathbb{H} \to l_2$, which it's simply a projection, as defined in (2.8).
Hence, we can define the operation of a general operator $\hat{\rho}$ in l_2 as a combination of the projection $\hat{\pi}$ and $\hat{\rho}$. So, if $\rho\,|A\rangle = |B\rangle$, we have that

$$b_n = \langle e_n|\,\hat{\rho}\sum_i |e_i\rangle\,\langle e_i|A\rangle \to b_n = \rho_{ni}a_i \in l_2 \tag{2.20}$$

Where ρ_{ni} is the matricial representation in l_2 of the operator $\hat{\rho}$.

THEOREM 2.2 (Block Representation for Degenerate Observables)**.** *Let $\hat{a}$ and $\hat{b}$ be two observables. If they're compatible, and the basis of eigenvectors of $|a\rangle$ is degenerate, then $\hat{b}$ can be represented as a block matrix*

Proof. Let $|e_i\rangle$ be such degenerate base, then we can write b_{ij} as such

$$b_{ij} = \langle e_i|\,\hat{b}\,|e_j\rangle$$

Since $\langle e_i|e_j\rangle = 1$ for all the degenerate i, j, and it's 0 elsewhere, b_{ij} will be a block matrix. □

§§§ 2.3.1.1 Unitary Transformations

If $|e_i\rangle$ and $|r_i\rangle$ are two ON bases in $\mathbb{H}$, we can define an unitary operator of base change $\hat{U}$ with the following equation.

$$\hat{U}\,|e_i\rangle = |r_i\rangle \tag{2.21}$$

Since the two bases are ON, this operator will be defined as the projection $|r_i\rangle\,\langle r_i|$.
It follows, in order for the equation (2.21) to be true, $\langle r_i|e_j\rangle = \delta_{ij}$, and for $\hat{U}$, it must hold that

$$\hat{U}\hat{U}^\dagger = \hat{U}^\dagger\hat{U} = \hat{\mathbb{1}} \tag{2.22}$$

The last relation can be reduced to the fact that $\hat{U}$ must be left unitary and right unitary.

THEOREM 2.3 (Von Neumann Theorem)**.** *Quantization is invariant to unitary transformations*

Proof. Let $\hat{U}$ be an unitary operator, for which $\tilde{\hat{q}} = \hat{U}\hat{q}\hat{U}^\dagger$ and $\tilde{\hat{p}} = \hat{U}\hat{p}\hat{U}^\dagger$.
Then, since $\hat{U}^\dagger\hat{U} = \hat{\mathbb{1}}$

$$\begin{cases} \left[\tilde{\hat{q}}, \tilde{\hat{p}}\right] = \hat{U}\hat{q}\hat{U}^\dagger\hat{U}\hat{p}\hat{U}^\dagger - \hat{U}\hat{p}\hat{U}^\dagger\hat{U}\hat{q}\hat{U}^\dagger = \\ \qquad = \hat{U}\hat{q}\hat{\mathbb{1}}\hat{p}\hat{U}^\dagger - \hat{U}\hat{p}\hat{\mathbb{1}}\hat{q}\hat{U}^\dagger = \hat{U}[\hat{q}, \hat{p}]\hat{U}^\dagger = i\hbar\hat{\mathbb{1}} \end{cases} \tag{2.23}$$

The same holds for every commutator and anticommutator. □

§§ 2.3.2 Schrödinger Representation

Schrödinger representatio is obtained through an isomorphism between $\mathbb{H}$ and $L^2(\mathbb{R})$.
Let's consider a space $\mathbb{H}$ formed by the direct product of n Hilbert spaces, then $\mathbb{H} \simeq L^2(\mathbb{R}^n)$. The isomorphism between these two spaces is given through a projection to the space $\mathbb{R}^n$, indicated as such.
Let $|A\rangle \in \mathbb{H}$, then $\exists \hat{S} : \mathbb{H} \to L^2(\mathbb{R}^n)$ defined as such

$$\hat{S}\,|A\rangle = \langle x_i|A\rangle = \psi_A(x_i) \in L^2(\mathbb{R}^n) \tag{2.24}$$

Where the function ψ_A is called *wavefunction*.
In this space, the scalar product is defined through the following integral

$$\langle A|B\rangle \to \int_{\mathbb{R}^n} \overline{\psi_B(x_i)}\psi_A(x_j)\,\mathrm{d}^n x \tag{2.25}$$

In order to be a valid representation of quantum mechanics, canonical quantization must hold, and the momentum and position operators will be defined as such, in position space

$$\begin{cases} p_i \to -i\hbar\nabla_x \\ q_i \to \hat{x}_i \end{cases} \tag{2.26a}$$

And in momentum space as such

$$\begin{cases} p_i \to \hat{k}_i \\ q_i \to -i\hbar\nabla_p \end{cases} \tag{2.26b}$$

The canonical quantization rules will then become, for position space

$$[\hat{q}, \hat{p}]\,|A\rangle \to -i\hbar\,(x_i\nabla_j - \nabla_j x_i)\,\psi_A = i\hbar\delta_{ij}\psi_A \tag{2.27}$$

Since a quantum state must be normalizable, in order to have a proper probability of transition, we need that even the wavefunction must be normalizable.
The normalization equation will then be

$$N\,\langle A|A\rangle = 1 \to N\int_{\mathbb{R}^n} \overline{\psi_A}\psi_A\,\mathrm{d}^n x = N\int_{\mathbb{R}^n} |\psi_A|^2\,\mathrm{d}^n x = 1 \tag{2.28}$$

Since $\psi_A \in L^2$, the integral converges, and N^{-1} is the searched normalization constant.
Due to the definition of probability density function, we have that the absolute value squared of the wavefunction is the probability density of finding the particle in a certain position (in position

representation) or in a certain momentum (momentum representation). Mean values and superior statistical models are then calculated as
In order to switch between representation, we can use Fourier transforms. Defining the integral operator $\hat{\mathcal{F}}$ as the Fourier transform operator, we get, if $\phi(k_i)$ is the momentum wavefunction and $\psi(x_i)$ the position wavefunction

$$\phi(k_i) = \hat{\mathcal{F}}_k \psi(x_i) \tag{2.29}$$

And, defining an inverse Fourier transform operator $\hat{\mathcal{F}}^{-1}$

$$\psi(x_i) = \hat{\mathcal{F}}_x^{-1} \phi(k) \tag{2.30}$$

§§ 2.3.3 Hamiltonian Operators

In order to define a function for a whole system, a Lagrangian can be written. In non relativistic quantum mechanics although, its Legendre tranform is used, the Hamiltonian. We then have, for a system with a general potential, that the Hamiltonian will be given in this general form

$$\mathcal{H} = \frac{p^2}{2m} + V(x_i) \tag{2.31}$$

Quantizing, in Heisenberg representation, we will get an observable, a self adjoint operator:

$$\hat{\mathcal{H}} = \frac{\hat{p}^2}{2m} + V(x_i) \tag{2.32}$$

This operator is used, since its eigenvalues are the energy levels of the system.
Hence, given an eigenstate $|E\rangle$, we will have the following equation

$$\hat{\mathcal{H}} |E\rangle = E |E\rangle \tag{2.33}$$

Which is the secular equation of the Hamiltonian, with eigenket $|E\rangle$ and eigenvalue E.
Remembering (2.26a), we will get the Schrödinger representation of the Hamiltonian operator

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2m}\nabla^2 + V(x_i) \tag{2.34}$$

The secular equation will then become a eigenfunction equation for the differential operator $\hat{\mathcal{H}}$, and the energy levels will be the spectrum of the operator

$$\hat{\mathcal{H}}\psi = -\frac{\hbar^2}{2m}\nabla^2\psi + V(x_i)\psi = E\psi(x_i) \tag{2.35}$$

The solution to this equation, commonly called *Schrödinger equation* is the wavefunction of the system, with associated energy eigenvalue E. Due to what said before, Schrödinger and Heisenberg representations are equivalent, and a problem can be solved either as an eigenstate problem or an eigenfunction problem. The most common example of problem that can be solved with both methods is the Quantum Harmonic Oscillator, treated in the next chapter.

3 Quantum Dynamics in 1D

§ 3.1 Free Particle

The motion of a free particle is described by the following Hamiltonian:

$$\mathcal{H} = \frac{p^2}{2m} \tag{3.1}$$

Quantizing in Heisenberg representation (3.1), we get the following operatorial representation

$$\hat{\mathcal{H}} = \frac{\hat{p}^2}{2m} \tag{3.2}$$

Since $\left[\hat{\mathcal{H}}, \hat{p}\right] = 0$, there exists a common basis of eigenvectors that we will indicate with $|p\rangle$, for which

$$\hat{p}\,|p\rangle = p\,|p\rangle$$

Hence, the secular equation for the Hamiltonian will be

$$\hat{\mathcal{H}}\,|p\rangle = \frac{1}{2m}\hat{p}^2\,|p\rangle = \frac{p^2}{2m}\,|p\rangle \tag{3.3}$$

The spectrum of the Hamiltonian operator is twice degenerate, since momentum can be either negative or positive, and the final energy state will then be given by the linear combination of the two states with positive and negative momentum, with energies $\pm\frac{1}{2m}p^2$

$$\hat{\mathcal{H}}\,|E\rangle = \frac{p^2}{2m}\,|p\rangle - \frac{p^2}{2m}\,|-p\rangle \tag{3.4}$$

It's obvious, from this equation, that the particle is delocalizated, since the momentum is positive and negative at the same time, meaning that the particle is "going" both forward and backward. Representing the Hamiltonian in the Schrödinger form we will get instead

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} \tag{3.5}$$

The Schrödinger equation will then be

$$\hat{\mathcal{H}}\psi = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} - E\psi = 0 \tag{3.6}$$

Solving this simple 2nd order ODE, we get the following wavefunction

$$\psi(x) = Ae^{i\sqrt{\frac{2mE}{\hbar^2}}x} + Be^{-i\sqrt{\frac{2mE}{\hbar^2}}x} \tag{3.7}$$

Where its twofold degeneracy is obvious

THEOREM 3.1 (Degeneration Theorem). *Let $\hat{p}, \hat{\mathcal{H}}, \hat{I}$ be three observables.*
If

$$\begin{cases} \left[\hat{p}, \hat{I}\right] \neq 0 \\ \left[\hat{p}, \hat{\mathcal{H}}\right] = \left[\hat{p}, \hat{H}\right] = 0 \end{cases} \tag{3.8}$$

Then $\hat{I}$ is 2-degenerate

Proof. Considering the case of a free particle, introducing operator $\hat{I}$ as a spatial inversion operator, we have that

$$\begin{cases} \left[\hat{p}, \hat{\mathcal{H}}\right] = \left[\hat{I}, \hat{\mathcal{H}}\right] = 0 \\ \left[\hat{p}, \hat{I}\right] \neq 0 \end{cases}$$

Where $\hat{I}\left|p\right\rangle = \pm\left|-p\right\rangle$ It's obvious that $\hat{I}^2 = \hat{\mathbb{1}}$ and that $\left\{\hat{I}, \hat{p}\right\} = \left\{\hat{I}, \hat{q}\right\} = 0$.
Due to this fact, we can write a new state which is the sum of the simmetrization and antisimmetrization of a the first state found.
Since $\hat{I}\left|\pm p\right\rangle = \pm\left|\pm p\right\rangle$ we get this state, indicating the antisimmetric one with $\left|p\right\rangle_a$ and the simmetric one as $\left|p\right\rangle_s$

$$\left|p\right\rangle = \frac{1}{2}\left(\left|p\right\rangle_s + \left|-p\right\rangle_s\right) + \frac{1}{2}\left(\left|p\right\rangle_a - \left|-p\right\rangle_a\right) \tag{3.9}$$

Which is also an eigenstate of $\hat{\mathcal{H}}$, since it commutes with $\hat{I}$ □

§ 3.2 Quantum Harmonic Oscillator

§§ 3.2.1 Dirac Formulation

The classical harmonic oscillator, is described by the following Hamiltonian

$$\mathcal{H} = \frac{1}{2m}p^2 + \frac{1}{2}m\omega^2 q^2 \tag{3.10}$$

Quantizing

$$\hat{\mathcal{H}} = \frac{1}{2m}\hat{p}^2 + \frac{1}{2}m\omega^2\hat{q}^2 \tag{3.11}$$

It's evident that the Hamiltonian is an observable, hence its eigenvalues will be real.
A solution in operatorial representation can be given, defining two operators, called *creation* and *annihilation* operators, defined as follows

$$\begin{cases} \hat{\eta} = \dfrac{1}{\sqrt{2m\hbar\omega}}(\hat{p} - im\omega\hat{q}) \\ \hat{\eta}^\dagger = \dfrac{1}{\sqrt{2m\hbar\omega}}(\hat{p} + im\omega\hat{q}) \end{cases} \tag{3.12}$$

Inverting the relations and expressing position and momentum in terms of creation and distruction operators, we get

$$\begin{cases} \hat{p} = \sqrt{\dfrac{m\hbar\omega}{2}}(\hat{\eta}^\dagger + \hat{\eta}) \\ \hat{q} = -i\sqrt{\dfrac{\hbar}{2m\omega}}(\hat{\eta}^\dagger - \hat{\eta}) \end{cases} \tag{3.13}$$

In order to evaluate the commutators of these two new operators $\hat{\eta}$, we evaluate the product of the two, from the left and right, obtaining the following result

$$\hat{\eta}^\dagger\hat{\eta} = \frac{1}{2m\hbar\omega}(\hat{p}^2 + m^2\omega^2\hat{q}^2 - im\omega[\hat{q},\hat{p}]) = \frac{1}{\hbar\omega}\left(\hat{\mathcal{H}} - \frac{1}{2}\hbar\omega\hat{\mathbb{1}}\right) \tag{3.14a}$$

And

$$\hat{\eta}\hat{\eta}^\dagger = \frac{1}{2m\hbar\omega}(\hat{p}^2 + m^2\omega^2\hat{q}^2 + im\omega[\hat{q},\hat{p}]) = \frac{1}{\hbar\omega}\left(\hat{\mathcal{H}} + \frac{1}{2}\hbar\omega\hat{\mathbb{1}}\right) \tag{3.14b}$$

Having evaluated this, we therefore get

$$\begin{aligned} [\hat{\eta},\hat{\eta}^\dagger] &= \frac{1}{2m\hbar\omega}(-2im\omega[\hat{q},\hat{p}]) = \hat{\mathbb{1}} \\ [\hat{\eta}^\dagger,\hat{\eta}] &= \frac{1}{2m\hbar\omega}(2im\omega[\hat{q},\hat{p}]) = -\hat{\mathbb{1}} \end{aligned} \tag{3.15}$$

And therefore, inverting the previous relation where the Hamiltonian appears on the right hand side, and utilizing the commutators in order to switch the position of the multiplication of the two operators, we get these two new expressions for the Hamiltonian

$$\hat{\mathcal{H}} = \hbar\omega\left(\hat{\eta}^\dagger\hat{\eta} + \frac{1}{2}\hat{\mathbb{1}}\right) \tag{3.16a}$$

$$\hat{\mathcal{H}} = \hbar\omega\left(\hat{\eta}\hat{\eta}^\dagger - \frac{1}{2}\hat{\mathbb{1}}\right) \tag{3.16b}$$

The commutators between the Hamiltonian and the annihilation/creation operators is calculated easily, utilizing the latter form of the Hamiltonian and the properties of the commutator (remembering that operators in general «*do not*» commute)

$$\begin{aligned} \left[\hat{\mathcal{H}},\hat{\eta}\right] &= \hbar\omega\left(\left[\hat{\eta}^\dagger\hat{\eta},\hat{\eta}\right] + \frac{1}{2}\left[\hat{\mathbb{1}},\hat{\eta}\right]\right) = \hbar\omega\left(\hat{\eta}^\dagger[\hat{\eta},\hat{\eta}] + [\hat{\eta}^\dagger,\hat{\eta}]\hat{\eta}\right) = -\hbar\omega\hat{\eta} \\ \left[\hat{\mathcal{H}},\hat{\eta}^\dagger\right] &= \hbar\omega\left(\hat{\eta}^\dagger[\hat{\eta},\hat{\eta}^\dagger] + [\hat{\eta}^\dagger,\hat{\eta}^\dagger]\hat{\eta}\right) = \hbar\omega\hat{\eta} \end{aligned} \tag{3.17}$$

Consequently, writing the secular equation of the system we get the following results

$$\begin{aligned} \hat{\mathcal{H}}\hat{\eta}\,|E\rangle &= \left(\hat{\eta}\hat{\mathcal{H}} + \left[\hat{\mathcal{H}},\hat{\eta}\right]\right)|E\rangle = \left(\hat{\eta}\hat{\mathcal{H}} - \hbar\omega\hat{\eta}\right)|E\rangle = (E - \hbar\omega)\,\hat{\eta}\,|E\rangle \\ \hat{\mathcal{H}}\hat{\eta}^\dagger\,|E\rangle &= \left(\hat{\eta}^\dagger\hat{\mathcal{H}} + \left[\hat{\mathcal{H}},\hat{\eta}^\dagger\right]\right)|E\rangle = \left(\hat{\eta}^\dagger\hat{\mathcal{H}} + \hbar\omega\hat{\eta}^\dagger\right)|E\rangle = (E + \hbar\omega)\,\hat{\eta}^\dagger\,|E\rangle \end{aligned} \tag{3.18}$$

So, the action of these operators actually creates and annihilates quantas of energy, with a spacing of $\hbar\omega$, creating a ladder. This characteristics gives them also the name of *ladder operators*.

Since the energies of an harmonic oscillator can't obtain negative values, there must exist a state for which the application of the annihilation operators "annihilates" the system, returning back zero. Indicating the energy eigenvalues with $|n\rangle$, we identify such state with $|0\rangle$ (watch out, this is «*not*» the null vector of the Hilbert space, 0 is simply a label), such state is usually called *vacuum* state.
Its energy can be determinated without much hassle, noting that the square norm of 0 is still 0 (obviously). Rewriting 0 as $\hat{\eta}\,|0\rangle$, we get, in Dirac notation, and remembering (3.14a)

$$\langle 0|\,\hat{\eta}^\dagger\hat{\eta}\,|0\rangle = \frac{1}{\hbar\omega}\,\langle 0|\left(\hat{\mathcal{H}} - \frac{1}{2}\hbar\omega\hat{\mathbb{1}}\right)|0\rangle = E_0 - \frac{1}{2}\hbar\omega = 0 \tag{3.19}$$

It's clear then, that the minimum possible value of energy is $E_0 = \frac{1}{2}\hbar\omega$, usually called *zero point energy*
In order to properly see how the annihilation and creation operators act on the energy eigenstates it's useful to normalize their succession.
We know, as for (3.18), that creation operators increase by one the number of quants in the system, hence, knowing that there is a ground state, indicated with $|0\rangle$, we can write the n-th state as follows

$$\hat{\eta}^n\,|0\rangle = \nu\,|n\rangle$$

With $\nu \in \mathbb{C}$. Since the normalization condition asks that the square braket of the vector must be equal to one, we simply get the following expression

$$\langle 0|\,\hat{\eta}^n\hat{\eta}^{\dagger n}\,|0\rangle = |\nu|^2\,\langle n|n\rangle \tag{3.20}$$

Since the former operator multiplication can be written as $\hat{\eta}^{n-1}\left[\hat{\eta},\hat{\eta}^{\dagger n}\right]$. It can be easily demonstrated that the previous commutator gives the following value

$$\left[\hat{\eta},\hat{\eta}^{\dagger n}\right] = n\hat{\eta}^{\dagger(n-1)}$$

We can then write (3.20) as

$$n\,\langle 0|\,\hat{\eta}^{n-1}\hat{\eta}^{\dagger(n-1)}\,|0\rangle = \nu^2\,\langle n-1|n-1\rangle$$

Iterating, we get the following condition

$$\nu^2 = \frac{1}{n!} \tag{3.21}$$

Henceforth, we get $\nu = \frac{1}{\sqrt{n!}}$, without any loss of generality.
The normalization of the n-th state, can then be defined recursively starting from $|0\rangle$

$$|n\rangle = \frac{1}{\sqrt{n!}}\hat{\eta}^{\dagger n}\,|0\rangle \tag{3.22}$$

Since all eigenstates must be normalized, we get that the action of the creation and annihilation operators will be, respectively

$$\begin{aligned}\hat{\eta}^\dagger\,|n\rangle &= \sqrt{n+1}\,|n+1\rangle\\ \hat{\eta}\,|n\rangle &= \sqrt{n}\,|n-1\rangle\end{aligned} \tag{3.23}$$

Defining a *particle number operator* as follows

$$\hat{N} = \hat{\eta}^\dagger\hat{\eta} \tag{3.24}$$

We get the following commutation relations

$$\begin{cases} \left[\hat{N}, \hat{\eta}^\dagger\right] = \hat{\eta}^\dagger \\ \left[\hat{N}, \hat{\eta}\right] = -\hat{\eta} \end{cases} \tag{3.25}$$

And the new Hamiltonian in terms of $\hat{N}$ becomes, evidently

$$\hat{\mathcal{H}} = \hbar\omega\left(\hat{N} + \frac{1}{2}\hat{\mathbb{1}}\right) \tag{3.26}$$

Calculating the commutator $\left[\hat{\mathcal{H}}, \hat{N}\right]$ explicitly we get

$$\begin{aligned} \left[\hat{\mathcal{H}}, \hat{N}\right] = \left[\hbar\omega\left(\hat{N} + \frac{1}{2}\hat{\mathbb{1}}\right), \hat{N}\right] = \hbar\omega\left[\hat{N} + \frac{1}{2}\hat{\mathbb{1}}, \hat{N}\right] = \\ = \hbar\omega\left(\left[\hat{N}, \hat{N}\right] + \frac{1}{2}\left[\hat{\mathbb{1}}, \hat{N}\right]\right) = 0 \end{aligned} \tag{3.27}$$

Since $\left[\hat{\mathcal{H}}, \hat{N}\right] = 0$, we get from Theorem 2.1 on the compatibility of operators, that there exist a common ON basis between $\hat{N}$ and $\hat{\mathcal{H}}$. This basis will obviously be the energy eigenstates of the Hamiltonian, and remembering the action of $\hat{\eta}$ and $\hat{\eta}^\dagger$ on the energy eigenkets, we get that the number operator will act on these states as such

$$\hat{N}\left|n\right\rangle = n\left|n\right\rangle \tag{3.28}$$

It's now obvious why such operator is called *particle number* operator, since applying it to an energy eigenstate, it will give as an eigenvalue the "number of particles" present.
Since these eigenstates are eigenstates for both the particle number operator and the Hamiltonian, we can write the secular equation of the Hamiltonian (3.26), which gives immediately the following result

$$\hat{\mathcal{H}}\left|n\right\rangle = \hbar\omega\left(n + \frac{1}{2}\right)\left|n\right\rangle \tag{3.29}$$

Since $\hat{\mathcal{H}}\left|n\right\rangle = E_n\left|n\right\rangle$, we get that energy is quantized, and has the following expression

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \tag{3.30}$$

From this definition, we can define the ground state of the system as $\left|0\right\rangle$, since, applying the annihilation operator on $\left|0\right\rangle$ the state gets "annihilated" and its action gives 0, we get our ground state energy (also known as *zero point energy*)

$$\hat{\mathcal{H}}\left|0\right\rangle = \frac{1}{2}\hbar\omega\left|0\right\rangle \tag{3.31}$$

Switching to a Schrödinger representation for the definition (3.22), we can also find the eigenfunctions of the Hamiltonian, $\langle x|n\rangle = \psi_n(x)$. Since the operator $\hat{\eta}^\dagger$ and $\hat{\eta}$ are defined in (3.12), we can then

write the normalized eigenfunctions as the solutions for the following differential equation. For the ground state, we will have, applying the annihilation operator

$$\hat{\eta}\psi_0(x) = -\frac{1}{\sqrt{2m\hbar\omega}}\left(i\hbar\nabla + im\omega x\right)\psi_0(x) = 0 \tag{3.32}$$

Its solution is simply given by the following exponential

$$\psi_0(x) = Ae^{-\frac{m\omega}{2\hbar}x^2}$$

The normalization condition will be given by the fact that $\psi_0 \in L^2(\mathbb{R})$, hence it must be square integrable. Using Gauss' identity, we get

$$|A|^2\int_{-\infty}^{\infty} e^{-\frac{m\omega}{\hbar}x^2}\,\mathrm{d}x = \sqrt{\frac{\hbar\pi}{m\omega}}$$

The constant A is easily determined, and the normalized wavefunction for the ground state is

$$\psi_0(x) = \sqrt{\sqrt{\frac{m\omega}{\hbar\pi}}}e^{-\frac{m\omega}{2\hbar}x^2} \tag{3.33}$$

Now, applying the operator $\hat{\eta}^\dagger$ multiple times we can get the n-th wavefunction. In formulae, we get that

$$\frac{1}{\sqrt{n!}}\hat{\eta}^{\dagger n}\psi_0(x) = \frac{1}{(2m\hbar\omega)^{\frac{n}{2}}}\left(im\omega x - i\hbar\nabla\right)^n\psi_0(x) = \psi_n(x)$$

Substituting the function we found for ψ_0, we get the following differential equation of the n-th order

$$\psi_n(x) = \frac{1}{\sqrt[n]{2m\hbar\omega}}\sqrt{\frac{1}{n!}\sqrt{\frac{m\omega}{\hbar\pi}}}\left(im\omega x - i\hbar\frac{\mathrm{d}}{\mathrm{d}x}\right)^n e^{-\frac{m\omega}{2\hbar}x^2} \tag{3.34}$$

Using the substitution $\xi = \sqrt{\frac{m\omega}{\hbar}}x$ we can write the solution in terms of *Hermite polynomials*, where they're defined through *Rodrigues formula*

$$H_n(\xi) = (-1)^n e^{\xi^2}\frac{\mathrm{d}^n}{\mathrm{d}\xi^n}e^{-\xi^2} \tag{3.35}$$

The normalization constant for Hermite polynomials can be calculated to be exactly $(2^n n!)^{-1/2}$, and the eigenfunction succession of the quantum harmonic oscillator will be the following

$$\psi_n(x) = \sqrt{\frac{1}{2^n n!}\sqrt{\frac{m\omega}{\hbar\pi}}}H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right)e^{-\frac{m\omega}{\hbar}x^2} \tag{3.36}$$

§§ 3.2.2 Coherent States of the Quantum Harmonic Oscillator

The coherent states of a quantum harmonic oscillator, are those states defined as the eigenvalues of the annihilation operator $\hat{\eta}$. Hence, we are finding all states $|h\rangle$ such that $\hat{\eta}\,|h\rangle = h\,|h\rangle$. Since we're in

the Hilbert space of the quantum harmonic oscillator (obviously) we can use Von Neumann's principle in order to Fourier transform our state $|h\rangle$ to an eigenstate of the Hamiltonian. We then get, applying a projection $\hat{\pi}_h^{(i)} = |h\rangle\langle h|$, the following Fourier series

$$|h\rangle = \sum_{n=0}^{\infty} \langle h|n\rangle |h\rangle \tag{3.37}$$

Applying $\hat{\eta}$ to its eigenstate $|h\rangle$, we get, knowing its action to the energy eigenstates

$$\hat{\eta}|h\rangle = \sum_{n=0}^{\infty} \langle h|n\rangle \hat{\eta}|n\rangle = \sum_{n=0}^{\infty} \langle h|n\rangle \sqrt{n}|n-1\rangle = h|h\rangle \tag{3.38a}$$

Changing the indexes of our sum to $k = n - 1$ we get

$$\sum_{k=0}^{\infty} \langle h|k+1\rangle \sqrt{k+1}|k\rangle = h\sum_{k=0}^{\infty} \langle h|k\rangle |k\rangle \tag{3.38b}$$

We henceforth get the following relation between $\langle h|k+1\rangle$ and $\langle h|k\rangle$

$$\langle h|k+1\rangle = \frac{h}{\sqrt{k+1}}\langle h|k\rangle \tag{3.38c}$$

Through induction we get, after substituting again the index,

$$\begin{aligned} \langle h|n\rangle &= \frac{h^n}{\sqrt{n!}}\langle h|0\rangle \\ |h\rangle &= \langle h|0\rangle \sum_{n=0}^{\infty} \frac{h^n}{\sqrt{n!}}|n\rangle \end{aligned} \tag{3.38d}$$

In order to find $\langle h|0\rangle$ we normalize the state $\langle h|h\rangle$

$$\langle h|h\rangle = |\langle h|0\rangle|^2 \sum_{n=0}^{\infty} \frac{|h|^{2n}}{n!} = 1 \tag{3.38e}$$

We finally get $\langle h|0\rangle = e^{-\frac{|h|^2}{2}}$, hence, our coherent state will be

$$|h\rangle = e^{-\frac{|h|^2}{2}} \sum_{n=0}^{\infty} \frac{h^n}{\sqrt{n!}}|n\rangle \tag{3.38f}$$

Writing $|n\rangle$ as in (3.22) we get a new form of this state, in terms of $\hat{\eta}^\dagger$

$$|h\rangle = e^{\frac{|h|^2}{2}} \sum_{n=0}^{\infty} \frac{h^n}{n!}\hat{\eta}^{\dagger n}|0\rangle \tag{3.39}$$

Summing, we then find a new representation for this coherent state, in terms of both annihilation and creation operators

$$|h\rangle = e^{-\frac{\overline{h}h}{2} + h\hat{\eta}}|0\rangle = e^{h\hat{\eta}^\dagger - \overline{h}\hat{\eta}}|0\rangle \tag{3.40}$$

§§ 3.2.3 Schrödinger Formulation

The Schrödinger equation for the quantum harmonic oscillator is simply given converting momentum and position operator to their representation in $L^2(\mathbb{R})$. Taking (3.11) and converting, we get the following differential equation for $\psi_n(x)$ as follows

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi_n}{\mathrm{d}x^2}+\frac{1}{2}m\omega^2x^2\psi_n(x)=E_n\psi_n(x) \tag{3.41}$$

In order to ease the equation, we utilize the following change of variables

$$\xi=\sqrt{\frac{m\omega}{\hbar}}x$$

Through this change of variables we get that the second derivative of ψ_n will become

$$\frac{\mathrm{d}^2\psi_n}{\mathrm{d}x^2}=\frac{m\omega}{\hbar}\frac{\mathrm{d}^2\psi_n}{\mathrm{d}\xi^2}$$

Hence, the Schrödinger equation will become

$$-\frac{\hbar\omega}{2}\frac{\mathrm{d}^2\psi_n}{\mathrm{d}\xi^2}+\left(\frac{\hbar\omega}{2}\xi^2-E_n\right)\psi_n(\xi)$$

Rearranging everything, we get the following "easier" to tackle equation

$$\frac{\mathrm{d}^2\psi_n}{\mathrm{d}\xi^2}-\left(\xi^2-\frac{2E_n}{\hbar\omega}\right)\psi_n(\xi)=0 \tag{3.42}$$

Considering the limit where $\xi >> \frac{2E_n}{\hbar\omega}$, we can define an asymptotic differential equation for ψ_n

$$\psi_a(\xi)-\xi^2\psi_a(\xi)=0$$

Its solution will be a linear combination of esponentials

$$\psi_a(\xi)=Ae^{\frac{\xi^2}{2}}+Be^{-\frac{\xi^2}{2}}$$

Due to normalization problems, we choose $A=0$.
Through the definition of ξ, we can easily find the normalization constant B, which it is, simply

$$B=\sqrt{\sqrt{\frac{m\omega}{\hbar\pi}}}$$

Henceforth, the asymptotic solution will simply be the following

$$\psi_a(x)=\sqrt{\sqrt{\frac{m\omega}{\hbar\pi}}}e^{-\frac{m\omega}{\hbar}x^2} \tag{3.43}$$

The complete solution, will then be the product of a function $h(\xi)$ with the asymptotic solution

$$\psi_n(\xi)=h(\xi)\psi_a(\xi) \tag{3.44}$$

Where, $h(x)$ is a power series, defined as follows

$$h(\xi) = \sum_{j=0}^{\infty} a_j \xi^j \tag{3.45}$$

Deriving the new definition of $\psi_n(\xi)$, we get the following relation

$$\frac{\mathrm{d}^2\psi_n}{\mathrm{d}\xi^2} = \psi_a(\xi)\frac{\mathrm{d}^2 h}{\mathrm{d}\xi^2} + 2\frac{\mathrm{d}h}{\mathrm{d}\xi}\frac{\mathrm{d}\psi_a}{\mathrm{d}\xi} + h(\xi)\frac{\mathrm{d}^2\psi_a}{\mathrm{d}\xi^2}$$

Due to ψ_a being known, we end up with the following equation

$$\frac{\mathrm{d}^2\psi_n}{\mathrm{d}\xi^2} = \sqrt{\sqrt{\frac{m\omega}{\hbar\pi}}}\frac{\mathrm{d}^2 h}{\mathrm{d}\xi^2}e^{-\frac{\xi^2}{2}} - 2\xi\sqrt{\sqrt{\frac{m\omega}{\hbar\pi}}}\frac{\mathrm{d}h}{\mathrm{d}\xi}e^{-\frac{\xi^2}{2}} + (\xi^2-1)\sqrt{\sqrt{\frac{m\omega}{\hbar\pi}}}h(\xi)e^{-\frac{\xi^2}{2}}$$

The Schrödinger equation will, finally, become the following, after cleaning up multiplicative constants and nonvanishing exponentials

$$\frac{\mathrm{d}^2 h}{\mathrm{d}\xi^2} - 2\xi\frac{\mathrm{d}h}{\mathrm{d}\xi} + \left(\frac{2E_n}{\hbar\omega} - 1\right)h(\xi) = 0 \tag{3.46}$$

The derivatives of $h(\xi)$ are easy to calculate, and they give the following result

$$\frac{\mathrm{d}h}{\mathrm{d}\xi} = \sum_{j=1}^{\infty} j a_j \xi^{j-1} = \sum_{n=0}^{\infty} \alpha a_\alpha \xi^{\alpha-1}$$
$$\frac{\mathrm{d}^2 h}{\mathrm{d}\xi^2} = \sum_{j=2}^{\infty} j(j-1) a_j \xi^{j-2} = \sum_{\alpha=0}^{\infty} (\alpha+1)(\alpha+2) a_{\alpha+2}\xi^{\alpha}$$

Inserting in our Schrödinger equation, we get the following

$$\sum_{\alpha=0}^{\infty}\left[(\alpha+1)(\alpha+2)a_{\alpha+2} + \left(\frac{2E_n}{\hbar\omega} - 2\alpha - 1\right)a_\alpha\right]\xi^\alpha = 0$$

For which, the only non trivial solutions will be given if the summand is zero, thing that'll be true only and only if persists a recursive relation

$$a_{\alpha+2} = \frac{2\alpha + 1 - \frac{2E_n}{\hbar\omega}}{(\alpha+1)(\alpha+2)}a_\alpha \tag{3.47}$$

Since we want the sum to converge, we suppose that $\exists n \in \mathbb{N} : \forall \alpha > n \; a_\alpha = 0$, hence, using the recursive relation we get

$$\frac{2E_n}{\hbar\omega} = 2n + 1 \tag{3.48}$$

Solving for E_n we get the quantization of energy

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \tag{3.49}$$

Getting a closer look on (3.46), we get that a general solution for this differential equation is known, and it's the Hermite polynomials $H_n(\xi)$. The final product solution will then be our eigenfunctions of the Hamiltonian

$$\psi_n(x) = \sqrt{\frac{1}{2^n n!}\sqrt{\frac{m\omega}{\hbar\pi}}} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) e^{-\frac{m\omega}{2\hbar}x^2} \tag{3.50}$$

The factor $(2^n n!)^{-1/2}$ is given by the normalization of Hermite polynomials.

§ 3.3 Infinite Square Well

Let's consider now a massive particle inside an infinite square well, i.e., where the potential is defined as follows

$$V(x) = \begin{cases} 0 & 0 \leq x \leq a \\ \infty & \text{elsewhere} \end{cases}$$

Since this problem is simple enough with the Schrödinger approach, we immediately write the Schrödinger equation for the problem

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -k^2\psi(x) \tag{3.51}$$

Where we define k as $k^2 = 2mE/\hbar^2$.
The general solution is easily computed as being

$$\psi(x) = A\sin(kx) + B\cos(kx) \tag{3.52}$$

Since ψ must be square integrable in all space, we impose its continuity at the borders of the well, hence we must have $\psi(0) = \psi(a) = 0$, which gives us $B = 0$ and $A\sin(ka) = 0$. Since $A = 0$ would give a trivial solution, we impose $\sin(ka) = 0$, and we get a restriction on the possible values of k.

$$ka = n\pi \longrightarrow k_n = \frac{n\pi}{a} \tag{3.53}$$

Due to the definition of k, we get that energy must be quantized, with the following succession

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \tag{3.54}$$

Integrating over all space the square modulus of what we have defined, finally, lets us determine the normalization factor A

$$|A|^2 \int_0^a \sin^2(k_n x)\,\mathrm{d}x = |A|^2\frac{a}{2} = 1 \tag{3.55}$$

The complete solution will be, finally

$$\begin{aligned} \psi_n(x) &= \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right) \\ E_n &= \frac{n^2\pi^2\hbar^2}{2ma^2} \end{aligned} \tag{3.56}$$

§ 3.4 Infinite Wall

In order to treat the idea of an infinite wall in quantum mechanics, we have to first define two particular states, *scattering states* and *bound states*

Definition 3.4.1 (Bound State). We define a bound state, as the set of configurations of the system where $E < V(x)$, and the particle is henceforth "trapped"

Definition 3.4.2 (Scattering State). A scattering state is defined as the set of configurations of the system for which $E > V(x)$, hence, the particle coming from $-\infty$ will simply interact with the potential without getting trapped by it.

Getting back to our problem, we define an infinite wall as a system whose potential is described by a Dirac delta function $\delta(x)$. Using a potential $V(x) = -\alpha\delta(x)$, we get that the Hamiltonian will be

$$\hat{\mathcal{H}} = \frac{\hat{p}^2}{2m} - \alpha\delta(x) \tag{3.57}$$

The associated Schrödinger equation will be

$$\hat{\mathcal{H}}\psi(x) = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} - \alpha\delta(x)\psi(x) = E\psi(x) \tag{3.58}$$

It's obvious that we can both have bound states and scattering states. Considering first the bound states, in the region $x < 0$, $V(x) = 0$, we get the following equation, where $\kappa = (-2mE)^{1/2}/\hbar$ ($E < 0$ by assumption, since we're considering bound states only).

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \kappa^2\psi(x)$$

Its solution will simply be $\psi(x) = A\exp(-\kappa x) + B\exp(\kappa x)$, that for normalization reasons, in the region $x < 0$, becomes simply

$$\psi(x) = Be^{\kappa x} \tag{3.59}$$

In the region $x > 0$, instead, we get the following solution

$$\psi(x) = Ae^{-\kappa x} \tag{3.60}$$

Since $\psi(x)$ must be «*always*» continuous, we get that the solution for our bound states must have $A = B$, and our general solution becomes

$$\psi(x) = \begin{cases} Be^{\kappa x} & x \leq 0 \\ Be^{-\kappa x} & x \geq 0 \end{cases} \tag{3.61}$$

Since $\psi(x)$ must also be a square integrable function, we need that its derivative must be continuous too, hence for $x = 0$, we have to check another few things.
The first idea that comes up to mind is to utilize the properties of the delta function and integrate in a infinitesimal interval around 0, henceforth, we get

$$-\frac{\hbar^2}{2m}\int_{-\epsilon}^{\epsilon}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}\,\mathrm{d}x - \alpha\int_{-\epsilon}^{\epsilon}\delta(x)\psi(x)\,\mathrm{d}x = E\int_{-\epsilon}^{\epsilon}\psi(x)\,\mathrm{d}x \tag{3.62}$$

Which becomes the following general relation

$$\lim_{x\to 0^{\pm}} \Delta\psi'(x) = -\frac{2m\alpha}{\hbar^2}\psi(0) \tag{3.63}$$

Calculating the derivatives from the left and from the right of our solution, and imposing what has been found previously, we get

$$\frac{\mathrm{d}\psi}{\mathrm{d}x} = \begin{cases} -B\kappa & x \to 0^+ \\ B\kappa & x \to 0^- \end{cases} \tag{3.64}$$

From this, we get $\Delta\psi'(x) = -2B\kappa$ and, then, since $\kappa = (-2mE)^{1/2}/\hbar$, we get from (3.63)

$$E = -\frac{m\alpha^2}{2\hbar^2} \tag{3.65}$$

Normalizing ψ, we get

$$2|B|^2 \int_{\mathbb{R}} e^{-2\kappa x}\,\mathrm{d}x = \frac{|B|^2}{\kappa} = 1 \tag{3.66}$$

The final solution for the wavefunction of the bound states, will then be

$$\begin{aligned} \psi(x) &= \frac{\sqrt{m\alpha}}{\hbar} e^{-\frac{m\alpha}{\hbar^2}|x|} \\ E &= -\frac{m\alpha^2}{2\hbar^2} \end{aligned} \tag{3.67}$$

It's obvious that there is only «*one*» bound state.
For scattering states, we define $k = (2mE)^{1/2}/\hbar$, and the Schrödinger equation becomes the following

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -k^2\psi(x) \tag{3.68}$$

The solution will be formed by the superposition of two complex esponentials, since neither of the two blows up for $x \to \pm\infty$. Hence, we will get

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Fe^{ikx} + Ge^{-ikx} & x > 0 \end{cases} \tag{3.69}$$

Considering again their derivatives coming from left and right, we get the following

$$\frac{\mathrm{d}\psi}{\mathrm{d}x} = \begin{cases} ik(A-B) & x \to 0^- \\ ik(F-G) & x \to 0^+ \end{cases} \tag{3.70}$$

Since $\Delta\psi'(x) = ik(F-G-A+B)$ and $\psi(0) = A+B$, we get from (3.63) the following

$$ik\,(F-G-A+B) = -\frac{2m\alpha}{\hbar^2}\,(A+B)$$

Defining $\beta = m\alpha/\hbar^2 k$, we can write the previous relation in a much more compact way

$$F - G = A(1+2i\beta) - B(1-2i\beta) \tag{3.71}$$

In this case normalizating $\psi(x)$ won't help, since this state is absolutely non normalizable. In order to give a viable solution we reason on how the particle would scatter in this potential. Imagine shooting this quantum particle from $-\infty$, since a negative complex exponential describes a wave coming from $+\infty$ to $-\infty$ we can easily set $G = 0$, and get the following result:

$$\begin{cases} B = \dfrac{i\beta}{1 - i\beta} A \\ F = \dfrac{1}{1 - i\beta} A \end{cases} \tag{3.72}$$

Reasoning in a physical way, we can deduce then that A is the amplitude of the incident wave, B of the reflected wave and F of the trasmitted wave. Since the probability in quantum mechanics is given by the square modulus of the wavefunction, we get that the probability of having a particle reflected back or trasmitted forward, will be given by two coefficients, respectively R and T, where they're defined as follows

$$\begin{aligned} R &= \frac{|B|^2}{|A|^2} = \frac{\beta^2}{1 + \beta^2} \\ T &= \frac{|F|^2}{|A|^2} = \frac{1}{1 + \beta^2} \end{aligned} \tag{3.73a}$$

Since their sum must be 1, being probabilities themselves, we get

$$R + T = \frac{|B|^2 + |F|^2}{|A|^2} = 1 \tag{3.73b}$$

And substituting β with its full expression,

$$\begin{aligned} R &= \frac{1}{1 + \frac{2\hbar^2 E}{m\alpha^2}} \\ T &= \frac{1}{1 + \frac{m\alpha^2}{2\hbar^2 E}} \end{aligned} \tag{3.73c}$$

A fun thing to do, with this potential, is to change the sign of α and reason on what is happening really.
First of all, since $E \propto \alpha$, we get that the only bound state we found gets brutally killed since $E \not< 0$ everywhere, but since $R, T \propto \alpha^2$, they stay unchanged.
Naively evaluating this as a classical problem, we get that this "particle" is thrown towards an infinitely strong wall n times and passes through nT times, and bounces back nR times. This is obviously impossible in the classical world, but instead in the quantum world is much more than possible. This effect is known commonly as *quantum tunneling*. This phenomenon is not restricted to infinite potential walls, let's take a finite potential wall V, for which exists a maximum V_{max}. If the energy E of the particle is $E < V_{max}$ we get that it might pass through with a nonzero probability T, and for $E > V_{max}$ there is still a probability of it bouncing back, expressed with R.

§ 3.5 Finite Square Well

After having considered an infinite square well and the difference between bound and scattering states, we can describe properly the finite square well problem, where the potential is defined as such

$$V(x) = \begin{cases} -V_0 & -a \leq x \leq a \\ 0 & |x| > a \end{cases}$$

It's obvious how this potential admits both scattering and bound states.
Let's consider first the region $x < -a$, where the potential is 0, from the previous problem on the infinite wall, we can write directly the solution

$$\psi(x) = Be^{\kappa x} \quad \kappa = \frac{\sqrt{-2mE}}{\hbar},\ x < -a \tag{3.74}$$

Inside the well, the problem is similar, but it's useful to directly write Schrödinger's equation

$$\hat{\mathcal{H}}\psi(x) = \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} - \frac{2m}{\hbar^2}(V_0 + E)\psi(x) = 0 \tag{3.75}$$

Replacing $[2m(E+V_0)^{-1/2}]/\hbar$ with l it reduces, yet again, to the following equation

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -l^2\psi(x)$$

Since $E > V_{min}$, the solution must be real and positive, hence, we can write it as follows

$$\psi(x) = C\sin(lx) + D\cos(lx) \quad -a < x < a \tag{3.76}$$

In the outer region, for $x > a$, we have again an exponential solution, this time decreasing

$$\psi(x) = Fe^{\kappa x} \quad x > a \tag{3.77}$$

Now, we need to impose the boundary conditions for ψ and ψ', that due to the potential being odd, can only be of two kinds, either odd or even.
Choosing the even solution, we get immediately that $C = 0$, and $\psi(x)$ becomes

$$\psi(x) = \begin{cases} Fe^{-\kappa x} & x > a \\ D\cos(lx) & 0 < x < a \\ \psi(-x) & x < 0 \end{cases} \tag{3.78}$$

For the continuity of ψ, ψ' at $x = a$, we get the following system

$$\begin{cases} Fe^{-\kappa a} = D\cos(la) \\ -\kappa Fe^{-\kappa a} = -lD\sin(la) \end{cases} \tag{3.79}$$

Dividing the two, we get $\kappa = l\tan(la)$. This is clearly a restriction on energies, due to the definition of κ, but it's a trascendental equation, that can't be solved directly. Applying the transformation $z = la$ and $z_0 = a(2mV_0)^{1/2}/\hbar$ we end with the following trascendental equation

$$\tan(z) = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1} \tag{3.80}$$

We can also approximate energy eigenvalues for the case of a deep well or a shallow well. In the first case we get that the solutions to the aforementioned equation will be at $z_n = n\pi/2$ with n odd, and follows that

$$E_n + V_0 \approx \frac{n^2\pi^2\hbar^2}{8ma^2}$$

In the second case instead, the intersections between the tangent and the square root get fewer and fewer, until, for $z_0 < \pi/2$ we end up with a single eigenstate, no matter how shallow is the well.
The only thing we miss to properly evaluate this problem (other than compute the normalization constant for $\psi(x)$) is to check the scattering states of the system.
We assume an ian incoming wave from the right, with a wavefunction $\psi(x) = Fe^{ikx}$, with $k^2 = 2mE/\hbar^2$. Putting, as before, A as the incident amplitude, B as the reflected amplitude and F the transmitted amplitude, for continuity of ψ and its derivative, we get that the following systems must hold. At $x = -a$ we have

$$\begin{cases} Ae^{-ika} + Be^{ika} = D\cos(la) - C\sin(la) \\ ik\left[Ae^{-ika} - Be^{ika}\right] = l\left[C\cos(la) + D\sin(la)\right] \end{cases} \tag{3.81}$$

At $x = a$, instead we get the following system

$$\begin{cases} C\sin(la) + D\cos(la) = Fe^{ika} \\ l\left[C\cos(la) - D\sin(la)\right] = ikFe^{ika} \end{cases} \tag{3.82}$$

Eliminating C and D and solving for B and F, we get the following

$$\begin{aligned} B &= i\frac{\sin(2la)}{2kl}\left(l^2 - k^2\right)F \\ F &= \frac{e^{-2ika}}{\cos(2la) - i\frac{k^2+l^2}{2kl}\sin(2la)}A \end{aligned} \tag{3.83}$$

Substituting everything back to the original variables, we get that the transmission coefficient T is

$$\frac{1}{T} = 1 + \frac{V_0^2}{4E(E+V_0)}\sin^2\left(\frac{2a}{\hbar}\sqrt{2m\left(E+V_0\right)}\right) \tag{3.84}$$

The reflection coefficient can be calculated knowing that $R = 1 - T$.

§§ 3.5.1 Scattering and Transfer Matrices

In order to treat efficiently scattering problems for general potentials, we first of all, suppose that the wavefunction will be the following:
For an incoming particle, since it's a free particle, we get that $\psi(x)$ will be a superposition of complex exponentials

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \tag{3.85}$$

The same goes for the post-scattering region, but with changed coefficients due to the interaction with the potential

$$\psi(x) = Fe^{ikx} + Ge^{-ikx} \tag{3.86}$$

In the interaction region, we can still suppose that the wavefunction will be a superposition of two functions $f(x), g(x)$, albeit both will remain unknown, until a specific potential is given.

$$\psi(x) = Cf(x) + Dg(x) \tag{3.87}$$

Using this systems, we can write a linear system of equations for B and F (the reflected and trasmitted amplitudes), as follows

$$\begin{aligned} B &= S_{11}A + S_{12}G \\ F &= S_{21}A + S_{22}G \end{aligned} \tag{3.88}$$

Reuniting everything in a *scattering matrix*, also known as *S-matrix*, we get the following matrix equation

$$\begin{pmatrix} B \\ F \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} A \\ G \end{pmatrix} \tag{3.89}$$

In this formalism, the transmission and reflection coefficients will be:
For a particle coming from the left

$$\begin{aligned} R_l &= \frac{|B|^2}{|A|^2} = |S_{11}|^2 \\ T_l &= \frac{|F|^2}{|A|^2} = |S_{21}|^2 \end{aligned} \tag{3.90}$$

For a scattering from the right instead, we get

$$\begin{aligned} R_r &= \frac{|F|^2}{|G|^2} = |S_{22}|^2 \\ T_r &= \frac{|B|^2}{|G|^2} = |S_{12}|^2 \end{aligned} \tag{3.91}$$

The scattering matrix, hence, gives us the outgoing amplitudes in terms of the incoming amplitudes. In case we'd like to have the amplitudes on the right of the potential in terms of the amplitudes on the left of the potential, we can "build" a second matrix, called *transfer matrix* or *M-matrix*

$$\begin{pmatrix} F \\ G \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} \tag{3.92}$$

The usefulness of this matrix, is that if the potential is formed by two separated pieces, the complete M-matrix of the system, will be given as the product of the two M-matrices of the single pieces of the potential, hence $\underline{M} = \underline{M}_2\underline{M}_1$. It's easy then to generalize this product to multiple pieces of the potential.

§ 3.6 One Dimensional Motion in Generic Potentials

What has been studied with the one dimensional quantum system that have been solved before, can be generalized to a one-dimensional Hamiltonian with a general potential $V(x)$. Without passing through

the operatorial representation, we write directly the Schrödinger equation for a general system. We will have

$$\hat{\mathcal{H}}\psi(x) = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x)\psi(x) = E\psi(x)$$

Rewriting the equation in its normal form, we will have the following

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} - \frac{2m}{\hbar^2}\left(V(x) - E\right)\psi(x) = 0 \tag{3.93}$$

We can immediately bring up three conclusions

1. If $\psi(x)$ is normalizable, there exists a *discrete spectrum* of eigenvalues of $\hat{\mathcal{H}}$, E_n
2. If $\psi(x)$ is «*not*» normalizable, there exists a *continuous spectrum* of $\hat{\mathcal{H}}$, $\sigma(E)$
3. Since $\psi : \mathbb{R} \to \mathbb{C}$, from the theory of differential equations, we will have that $\mathfrak{Re}\psi(x)$ will be a solution.

Again, if we consider what we derived for scattering and bound states, we can derive from (3.93) two considerations on $\psi(x)$ and its second derivative, that we will indicate with $\psi''(x)$ in order to avoid heavy notations.

1. If we are evaluating a bound state, then $\psi''(x)/\psi < 0$
2. If we are evaluating a scattering state, then $\psi''(x)/\psi > 0$
3. In passing from a bound state to a scattering state there is an inversion point, where $\psi''(x)/\psi(x) = 0$, $\psi(x) \neq 0$ and $E = V(x)$

It can be demonstrated that, if $E < \min(V)$ there won't be any eigenvalues E, for $\min(V) < E < 0$ there will be at least one eigenvalue E, if there is more than one in this region, they will be discrete and nondegenerate. For $0 < E < \max(V)$ we will have nondegenerate continue eigenvalues $\sigma(E)$, and for $E > \max(V)$ they will be continuous and twice degenerate.
Utilizing this general potential Schrödinger equation, we can also define a quite useful theorem

THEOREM 3.2 (Theorem of the Oscillations)**.** *Let $\hat{D}_s$ be a differential operator that acts in the following way:*

$$\hat{D}_s = \frac{\mathrm{d}^2}{\mathrm{d}x^2} - \frac{2m}{\hbar^2}\left(V(x) - E\right)$$

Suppose then that there exist two functions $\psi(x)$ and $\phi(x)$, for which $\hat{D}_s\psi(x) = 0$ and $\hat{D}_s\phi(x) = 0$, then ψ and ϕ are linearly dependent with n zeroes.

Proof. We begin writing directly the action of the operator $\hat{D}_s$ on the two functions $\psi(x)$ and $\phi(x)$

$$\begin{cases} \hat{D}_s\psi(x) = \dfrac{\mathrm{d}^2\psi}{\mathrm{d}x^2} - \dfrac{2m}{\hbar^2}\left(V(x) - E\right)\psi(x) = 0 \\ \hat{D}_s\phi(x) = \dfrac{\mathrm{d}^2\phi}{\mathrm{d}x^2} - \dfrac{2m}{\hbar^2}\left(V(x) - E\right)\phi(x) = 0 \end{cases}$$

We solve this linear system multiplying the first equation by $\phi(x)$ and the second by $\psi(x)$, and then subtracting the two rows, obtaining the following relation

$$\phi(x)\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} - \psi(x)\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = 0$$

It's easy to see that this it's the derivative of $\phi(x)\psi'(x) - \psi(x)\phi'(x)$, and since this derivative must be zero, we know that it must be a constant k

$$\phi\frac{\mathrm{d}\psi}{\mathrm{d}x} - \psi(x)\frac{\mathrm{d}\phi}{\mathrm{d}x} = k$$

Since both functions must be normalizable, we must have $k = 0$, hence we can write the equation in the following way

$$\frac{\psi'(x)}{\psi(x)} = \frac{\phi'(x)}{\phi(x)}$$

Integrating once, we get that $\psi(x) = \lambda\phi(x)$, hence they're linearly independent, and hence essentially the same. □

Corollary 3.6.1. Since $\phi(x), \psi(x)$ are eigenfunctions of the Hamiltonian, we know that there is a direct relation between the energy eigenvalue E_n and the eigenfunction $\psi_n(x)$, hence, analyzing everything, we get that it must have n zeroes.

Another interesting feature of quantum dynamics, is given by the quantum version of the virial theorem, which states the following

THEOREM 3.3. *Let $\hat{T}$ be the kinetic energy operator, and $\hat{V}$ the potential energy operator, then the expectation value of the kinetic energy on an energy eigenstate is equal to the expectation value of $qV'(q)$.*

Proof. In order to demonstrate this theorem we first calculate the commutator between the Hamiltonian operator and the product operator $\hat{q}\hat{p}$.
The Hamiltonian in question is

$$\hat{\mathcal{H}} = \frac{\hat{p}^2}{2m} + V(q)$$

Then the desired commutator will be the following

$$\left[\hat{\mathcal{H}}, \hat{q}\hat{p}\right] = \hat{q}\left[\hat{\mathcal{H}}, \hat{p}\right] + \left[\hat{\mathcal{H}}, \hat{q}\right]\hat{p}$$

In order to evaluate the previous commutators, we write the Poisson brackets of each, and then quantize, deforming the brackets through mltiplication by $i\hbar$

$$[\mathcal{H}, p]_{PB} = \frac{\partial\mathcal{H}}{\partial q}\frac{\partial p}{\partial p} - \frac{\partial\mathcal{H}}{\partial p}\frac{\partial p}{\partial q} = \frac{\partial V}{\partial q}$$
$$[\mathcal{H}, q]_{PB} = \frac{\partial\mathcal{H}}{\partial q}\frac{\partial q}{\partial p} - \frac{\partial\mathcal{H}}{\partial p}\frac{\partial q}{\partial q} = -\frac{p}{m}$$

Quantizing, we get the following

$$\left[\hat{\mathcal{H}}, \hat{p}\right] = i\hbar\frac{\partial V}{\partial q}$$
$$\left[\hat{\mathcal{H}}, \hat{q}\right] = -i\hbar\frac{\hat{p}}{m}$$

And the searched commutator will be

$$\hat{q}\left[\hat{\mathcal{H}},\hat{p}\right]+\left[\hat{\mathcal{H}},\hat{q}\right]\hat{p}=i\hbar\hat{q}\frac{\partial V}{\partial q}-i\hbar\frac{\hat{p}^2}{m}$$

Rearranging, and remembering how $\hat{T}$ is defined, we get the following

$$\left[\hat{\mathcal{H}},\hat{q}\hat{p}\right]=i\hbar\left(\hat{q}\frac{\partial V}{\partial q}-2\hat{T}\right)$$

We calculate the expectation value of this commutator in the energy eigenstate

$$\left\langle\left[\hat{\mathcal{H}},\hat{q}\hat{p}\right]\right\rangle=i\hbar\left\langle\hat{q}\frac{\partial V}{\partial q}-2\hat{T}\right\rangle$$

We first calculate the left side, and we get the following

$$\left\langle\hat{q}\hat{\mathcal{H}}\hat{p}-\hat{q}\hat{p}\hat{\mathcal{H}}+\hat{\mathcal{H}}\hat{q}\hat{p}-\hat{q}\hat{\mathcal{H}}\hat{p}\right\rangle=\left\langle\hat{\mathcal{H}}\hat{q}\hat{p}-\hat{q}\hat{p}\hat{\mathcal{H}}\right\rangle=E\left\langle\hat{q}\hat{p}-\hat{q}\hat{p}\right\rangle=0$$

Hence, using the linearity of the $\langle\cdot\rangle$ operator, we get the virial theorem

$$i\hbar\left\langle\hat{q}\frac{\partial V}{\partial q}\right\rangle-2i\hbar\left\langle\hat{T}\right\rangle=0$$
$$2\left\langle\hat{T}\right\rangle=\left\langle\hat{q}\frac{\partial V}{\partial q}\right\rangle$$

□

Corollary 3.6.2. Considering the particular case of potentials of the form $V(q)=c\hat{q}^{\alpha}$, we get the following

$$\left\langle\hat{T}\right\rangle=\frac{\alpha}{2}\left\langle\hat{V}\right\rangle$$

Proof. We use the previous identity used in the general case, and we get that $\hat{q}V'(q)=c\alpha\hat{q}^{\alpha}=\alpha\hat{V}$, hence

$$2\left\langle\hat{T}\right\rangle=\alpha\left\langle\hat{V}\right\rangle$$

□

The next theorem that will be stated, will be directly generalized to n-dimensions.

THEOREM 3.4 (Probability Conservation). *Defining $J_i(x_j)$ as the probability current density vector, for a time-independent system the following continuity equation holds*

$$\frac{\partial J_i}{\partial x_i}=0$$

If $J_i(x_j)$ is defined as follows

$$J_i(x_j)=-\frac{i\hbar}{2m}\left(\overline{\psi}(x_j)\frac{\partial\psi}{\partial x_i}-\psi(x_j)\frac{\partial\overline{\psi}}{\partial x_i}\right)$$

Or, in operatorial form

$$\hat{J}_i = \frac{1}{2m}\left(\langle\psi|\,\hat{p}_i\,|\psi\rangle\,\hat{\mathbb{1}} - |\psi\rangle\,\hat{p}_i\,\langle\psi|\right)$$

Proof. We will begin by writing the Schrödinger equation for both ψ and $\overline{\psi}$. We will then have the following system

$$\begin{cases} -\dfrac{\hbar^2}{2m}\dfrac{\partial^2\psi}{\partial x_i\partial x_i} + V(x_i)\psi(x_j) = E\psi(x_j) \\ -\dfrac{\hbar^2}{2m}\dfrac{\partial^2\overline{\psi}}{\partial x_i\partial x_i} + V(x_i)\overline{\psi}(x_j) = E\overline{\psi}(x_j) \end{cases}$$

Multiplying the first by $\overline{\psi}_i(x_j)$ and the second by $\psi_i(x_j)$ and adding the second to the first we get the following

$$-\frac{\hbar^2}{2m}\left(\overline{\psi}(x_j)\frac{\partial^2\psi}{\partial x_i\partial x_i} - \psi(x_j)\frac{\partial^2\overline{\psi}}{\partial x_i\partial x_i}\right) + V(x_i)\left(|\psi(x_j)|^2 - |\psi(x_j)|^2\right) = E\left(|\psi|^2 - |\psi|^2\right)$$

Simplifying everything, we get

$$-\frac{\hbar^2}{2m}\left(\overline{\psi}(x_j)\frac{\partial^2\psi}{\partial x_i\partial x_i} - \psi(x_j)\frac{\partial^2\psi}{\partial x_i\partial x_i}\right) = 0$$

Bringing outside the gradient operator we get

$$-\frac{\hbar^2}{2m}\frac{\partial}{\partial x_i}\left(\overline{\psi}(x_j)\frac{\partial\psi}{\partial x_i} - \psi(x_j)\frac{\partial\psi}{\partial x_i}\right) = \frac{\partial J_i}{\partial x_i} = 0$$

This theorem, in one dimension, reduces simply to the equation

$$\mathfrak{Im}(\overline{\psi}(x)\psi'(x)) = \mathfrak{Im}(\psi(x)\overline{\psi}'(x))$$

□

§ 3.7 Time Evolution of Quantum Systems

§§ 3.7.1 General Remarks and Schrödinger's Picture

The problems we studied in the previous sections never found how the eigenstate of the system evolves in time.
Time evolution of a system can be seen as a traslation, hence taking the eigenstate of the time independent problem and "moving" it to a time $t \neq 0$. It's not hard to imagine then how time evolution can be seen as the action of an unitary group with a single parameter, which will be t, our time.
The first question that comes up to the mind is actually how this group is defined in quantum mechanics. Here, the following theorem comes to our rescue

THEOREM 3.5 (Stone Theorem). *Let U_t be a strongly continuous one-parameter unitary group. Then*

$$\exists! \hat{A} : D_a \subset \mathbb{H} \to \mathbb{H},\ A = A^\dagger \text{ in } D_a \text{ then } \hat{\mathcal{U}}(t) = e^{it\hat{A}} \in U_t$$

Where holds the following relation $\hat{\mathcal{U}}(t_1+t_2) = \hat{\mathcal{U}}(t_1)\hat{\mathcal{U}}(t_2)$ where $\hat{\mathcal{U}}(t_1+t_2) \in U_{t_1}U_{t_2}$ and $\hat{\mathcal{U}}(t_1) \in U_{t_1}$, $\hat{\mathcal{U}}(t_2) \in U_{t_2}$ (i.e., $\hat{\mathcal{U}}$ is an homomorphism)
The set D_a is defined as follows

$$D_a := \left\{ |\psi\rangle \in \mathbb{H} \;\middle|\; \exists \lim_{\epsilon\to 0} \frac{-i}{\epsilon}\left(\hat{\mathcal{U}}(\epsilon)|\psi\rangle - \hat{\mathbb{1}}|\psi\rangle\right) \right\}$$

$\hat{A}$ is called the infinitesimal generator of the unitary group, and can be computed as follows

$$\hat{A}|\psi\rangle = -i \lim_{\epsilon\to 0} \frac{1}{\epsilon}\left(\hat{\mathcal{U}}(\epsilon)|\psi\rangle - \hat{\mathbb{1}}|\psi\rangle\right)$$

As a spoiler, we can say that this infinitesimal generator is the Hamiltonian of the system, and the operator $\hat{\mathcal{U}}$ has the form $\hat{\mathcal{U}} = e^{-\frac{i}{\hbar}\hat{\mathcal{H}}t}$. In order to see how this works out, informally, we write the time-dependent Schrödinger equation, which can be derived considering energy as a differential operator $E \to i\hbar\partial_t$. Substituting, we get the following equation

$$\hat{E}|\psi\rangle = \hat{\mathcal{H}}|\psi\rangle \to i\hbar\frac{\partial\psi}{\partial t} = \hat{\mathcal{H}}\psi(x,t) \tag{3.94a}$$

In the case that $\hat{\mathcal{H}}$ is time-independent, we get that the solution to the differential equation in time will be the following

$$\psi(x,t) = c(x)e^{-\frac{i}{\hbar}\hat{\mathcal{H}}t} \tag{3.94b}$$

It's obvious then that the time-evolved state will be the time-independent state at which gets applied the time evolution operator.

$$\psi(x,t) = \hat{\mathcal{U}}(t)\psi(x) \tag{3.94c}$$

In case the Hamiltonian is time dependent, the operator easily becomes the following

$$\hat{\mathcal{U}}(t) = e^{-\frac{i}{\hbar}\int_0^t \hat{\mathcal{H}}\,\mathrm{d}t} \tag{3.94d}$$

In order to see how this operator actually acts on the states, it's quite useful to utilize the fact that all complex exponentials are holomorphic, and can be written as a power series. This holds even when we talk about operator exponentials, hence $\hat{\mathcal{U}}(t)$ becomes:

$$\hat{\mathcal{U}}(t) = \sum_{n=0}^{\infty} \frac{1}{n!}\left(-\frac{i}{\hbar}\hat{\mathcal{H}}t\right)^n \tag{3.95a}$$

Applying this to an eigenstate of the Hamiltonian $|\psi\rangle$, we get the following

$$\begin{aligned} \hat{\mathcal{U}}(t)|\psi\rangle &= \sum_{n=0}^{\infty} \frac{1}{n!}\left(-\frac{i}{\hbar}\hat{\mathcal{H}}t\right)|\psi\rangle \\ \hat{\mathcal{U}}(t) &= \sum_{n=0}^{\infty} \frac{1}{n!}\left(-\frac{i}{\hbar}\hat{\mathcal{H}}t\right)^{n-1}\left(-\frac{i}{\hbar}\hat{\mathcal{H}}t\right)|\psi\rangle \end{aligned} \tag{3.95b}$$

Using Schrödinger's equation and iterating, we finally get, retransforming the series to an exponential, the following result for eigenstates

$$\hat{\mathcal{U}}(t)\left|\psi\right\rangle = e^{-\frac{i}{\hbar}Et}\left|\psi\right\rangle \tag{3.95c}$$

For a general state $|s\rangle$, we then get using Von Neumann's principle, the following result

$$\hat{\mathcal{U}}(t)\left|s\right\rangle = e^{-\frac{i}{\hbar}\hat{\mathcal{H}}t}\sum_n \left\langle\psi|s\right\rangle\left|\psi\right\rangle = \sum_n c_n e^{-\frac{i}{\hbar}Et}\left|\psi\right\rangle \tag{3.95d}$$

Since all the problems that we discussed were with a time-independent Hamiltonian, they're quite easy to generalize to a time-evolved problem without solving a time dependent Schrödinger equation or even redoing any calculus. This stress on time evolution on the state, is commonly called *Schrödinger picture* of time evolution.
Having now described time evolution in quantum mechanics, the next step is redescribing the probability conservation equation. Since now we have that the wavefunction is time-dependent, we have now that the time dependent probability amplitude will be defined as follows

$$\langle s(t)|s(t)\rangle = \langle s|\hat{\mathcal{U}}^\dagger\hat{\mathcal{U}}\left|s\right\rangle \to \int_{-\infty}^{\infty}\overline{\psi_s}(x,t)\psi_s(x,t)\,\mathrm{d}x = \rho(t)$$

Having defined this time dependent probability amplitude with $\rho(t)$. We now have an advanced version of the theorem

THEOREM 3.6 (Time Dependent Probability Conservation)**.** *The probability amplitude of a wavefunction that solves the Schrödinger's time-dependent equation must always solve the following equation*

$$\frac{\partial\rho}{\partial t} + \frac{\partial J_i}{\partial x_i} = 0$$

Where

$$\rho(x_j,t) = \overline{\psi}(x_j,t)\psi(x_j,t)$$
$$J_i(x_j,t) = -\frac{i\hbar}{2m}\left(\overline{\psi}(x_j,t)\frac{\partial\psi}{\partial x_i} - \psi(x_j,t)\frac{\partial\overline{\psi}}{\partial x_i}\right)$$

Proof. The first thing to write is the time dependent Schrödinger equation for ψ and its complex conjugate, since both must solve it as a proposition of the theorem.

$$\begin{cases} i\hbar\dfrac{\partial\psi}{\partial t} = -\dfrac{\hbar^2}{2m}\dfrac{\partial^2\psi}{\partial x_i\partial x_i} + V(x_j)\psi(x_j,t) \\ -i\hbar\dfrac{\partial\overline{\psi}}{\partial t} = -\dfrac{\hbar^2}{2m}\dfrac{\partial^2\overline{\psi}}{\partial x_i\partial x_i} + V(x_j)\psi(x_j,t) \end{cases}$$

We then multiply the first line by $\overline{\psi}$ and the second by ψ

$$\begin{cases} i\hbar\overline{\psi}(x_j,t)\dfrac{\partial\psi}{\partial t} = -\dfrac{\hbar^2}{2m}\overline{\psi}(x_j,t)\dfrac{\partial^2\psi}{\partial x_i\partial x_i} + \overline{\psi}(x_j,t)V(x_j)\psi(x_j,t) \\ -i\hbar\psi(x_j,t)\dfrac{\partial\overline{\psi}}{\partial t} = -\dfrac{\hbar^2}{2m}\psi(x_j,t)\dfrac{\partial^2\overline{\psi}}{\partial x_i\partial x_i} + \psi(x_j,t)V(x_j)\overline{\psi}(x_j,t) \end{cases}$$

We then subtract the first line to the second, and we obtain the following equation

$$-i\hbar\left(\overline{\psi}(x_j,t)\frac{\partial\psi}{\partial t}+\psi(x_j,t)\frac{\partial\overline{\psi}}{\partial t}\right)=\frac{\hbar^2}{2m}\left(\overline{\psi}(x_j,t)\frac{\partial^2\psi}{\partial x_i\partial x_i}-\psi(x_j,t)\frac{\partial^2\overline{\psi}}{\partial x_i\partial x_i}\right)$$

We recognize immediately the left part being exactly equal to $\partial_t\rho(x_j,t)$, hence we substitute it in the equation

$$-i\hbar\frac{\partial\rho}{\partial t}=\frac{\hbar^2}{2m}\left(\overline{\psi}(x_j,t)\frac{\partial^2\psi}{\partial x_i\partial x_i}-\psi(x_j,t)\frac{\partial^2\overline{\psi}}{\partial x_i\partial x_i}\right)$$

Bringing out a gradient operator (∂_i), we recognize the part on the right being the probability density current J_i, to which has been applied a gradient operator ∂_i (Einstein summation convention is implied, hence it's a divergence)

$$-i\hbar\frac{\partial\rho}{\partial t}=i\hbar\frac{\partial J_i}{\partial x_i}$$

We simplify everything and bring the right hand side on the left of the equation and we finally have demonstrated the theorem

$$\frac{\partial\rho}{\partial t}+\frac{\partial J_i}{\partial x_i}=0$$

□

§§ 3.7.2 Heisenberg Picture and Constants of Motion

In the Heisenberg picture, the stress on time dependence is given only on operators. It may not be immediately clear how this is equivalent to Schrödinger's picture, where the time dependence is always on the state.
In order to clearly see this equivalence, we calculate the expectation state of an operator $\hat{A}$ on a time evolved state $|s(t)\rangle$. We get the following relation

$$\left\langle\hat{A}\right\rangle_t=\langle s(t)|\,\hat{A}\,|s(t)\rangle=\langle s|\,\hat{\mathcal{U}}^\dagger(t)\hat{A}\hat{\mathcal{U}}(t)\,|s\rangle \tag{3.96}$$

It's immediate to write the previous relation as $\left\langle\hat{A}(t)\right\rangle_s$, where the time evolved operator is defined as $\hat{A}(t)=\hat{\mathcal{U}}^\dagger(t)\hat{A}\hat{\mathcal{U}}(t)$. Using this definition, we can also calculate the derivative of an operator, in the following way

$$\begin{aligned}\frac{\mathrm{d}\hat{A}}{\mathrm{d}t}&=\frac{\mathrm{d}}{\mathrm{d}t}\left(\hat{\mathcal{U}}^\dagger(t)\hat{A}\hat{\mathcal{U}}(t)\right)\\&=\frac{\mathrm{d}\hat{\mathcal{U}}^\dagger}{\mathrm{d}t}\hat{A}\hat{\mathcal{U}}(t)+\hat{\mathcal{U}}^\dagger\hat{A}\frac{\mathrm{d}\hat{\mathcal{U}}}{\mathrm{d}t}=\\&=\frac{i}{\hbar}\left(\hat{\mathcal{H}}\hat{\mathcal{U}}^\dagger\hat{A}\hat{\mathcal{U}}-\hat{\mathcal{U}}^\dagger\hat{A}\hat{\mathcal{H}}\hat{\mathcal{U}}\right)=\\&=\frac{i}{\hbar}\hat{\mathcal{U}}^\dagger\left[\hat{\mathcal{H}},\hat{A}\right]\hat{\mathcal{U}}\end{aligned} \tag{3.97}$$

Or, using the full fledged Heisenberg picture, we can write the last line as follows, for a time-independent Hamiltonian

$$\frac{\mathrm{d}\hat{A}}{\mathrm{d}t}=\frac{i}{\hbar}\left[\hat{\mathcal{H}},\hat{A}(t)\right] \tag{3.98}$$

Remembering the connection to the Poisson brackets, we already know that if the $[\mathcal{H}, A]_{PB} = 0$, then A is a constant of motion. In quantum mechanics, this will be represented as follows

$$\frac{\mathrm{d}\hat{A}}{\mathrm{d}t} = 0 \longrightarrow \left[\hat{\mathcal{H}}, \hat{A}\right] = 0 \tag{3.99}$$

The operator $\hat{A}$, is then called a *constant of motion* in quantum mechanics.

4 Angular Momentum

§ 4.1 Rotations

Taking as granted the knowledge that in classical physics rotations around the same axis commute and around different axes do not (it's easy to prove, even mentally by yourself).
A classical rotation around a certain axis can be writted in tensor notation as follows. Let v_i be a vector in the fixed system and v_i' the same vector in the rotated system. We can then write the following relation (where $i, j = x, y, z$ or $i, j = 1, 2, 3$)

$$v_i' = R_{ij} v_j$$

Whereas

$$R_{ij} R_{ji} = R_{ji} R_{ij} = \delta_{ij} \longrightarrow R^{\mathsf{T}} = R^{-1}$$

The second equation is obvious, since applying an identical but opposed rotation on the same axis is exactly like letting act the identity rotation onto the vector (basically doing nothing to it).
Due to this matrix being then, orthogonal, we know from linear algebra that the following relation holds, and is automatically satisfied.

$$\sqrt{v_1^2 + v_2^2 + v_3^2} = \sqrt{v_1^{2'} + v_2^{2'} + v_3^{2'}}$$

From this relation, we can define pretty easily, that for a finite rotation of an angle ϕ, the matrix $R_{ij}^{(z)}(\phi)$, will have the following general form

$$R_{ij}^{(z)}(\phi) = \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{4.1}$$

The infinitesimal form all the rotation matrices, in order $\mathcal{O}(\varepsilon^3)$, will be the following, using the taylor expansions of the trigonometric functions

$$R_{ij}^{(z)}(\varepsilon) = \begin{pmatrix} 1 - \frac{\varepsilon^2}{2} & -\varepsilon & 0 \\ \varepsilon & 1 - \frac{\varepsilon^2}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{4.2a}$$

$$R_{ij}^{(x)}(\varepsilon) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1-\frac{\varepsilon^2}{2} & -\varepsilon \\ 0 & \varepsilon & 1-\frac{\varepsilon^2}{2} \end{pmatrix} \tag{4.2b}$$

$$R_{ij}^{(y)}(\varepsilon) = \begin{pmatrix} 1-\frac{\varepsilon^2}{2} & 0 & \varepsilon \\ 0 & 1 & 0 \\ -\varepsilon & 0 & 1-\frac{\varepsilon^2}{2} \end{pmatrix} \tag{4.2c}$$

It's obvious, that the rotations commute only for $\mathcal{O}(\varepsilon)$, and that they follow a cyclic relation. We might write this as follows for rotations of order $\mathcal{O}\left(\varepsilon^3\right)$

$$[R_x(\varepsilon), R_y(\varepsilon)] = R_x(\varepsilon^2) - R_{(i)}(0) \tag{4.3}$$

Where $R_{(i)}(0)$ is a null rotation along a generic axis, which is exactly an identity matrix, for every axis we choose.

§§ 4.1.1 Infinitesimal Rotations in Quantum Mechanics

In order to "quantize" the previous section, we assign to the rotation matrix, a rotation operator $\hat{\mathcal{D}}(R)$, with D as in *Drehung*, which means rotation in German.
Calling $|\cdot\rangle_r$ the rotated ket, we will have that this operator will act in the following way

$$|s\rangle_r = \hat{\mathcal{D}}(R)\,|s\rangle \tag{4.4}$$

Using an analogy with classical mechanics, and knowing that angular momentum is the generator for infinitesimal rotations, we can imagine that in quantum mechanics, this generator $\hat{G}$ will simply be the following $\hat{\underline{J}}/\hbar$, where we indicated with $\hat{\underline{J}}$ a generic angular momentum operator, and an $\hbar$ added for dimensionality reasons.
In first approximation, we can see the Drehung operator to the first order, for a rotation of $\mathrm{d}\phi$ degrees, as follows

$$\hat{\mathcal{D}}(\hat{\mathbf{n}}, \mathrm{d}\phi) = 1 - i\left(\frac{\hat{\underline{J}}\cdot\hat{\mathbf{n}}}{\hbar}\right)\,\mathrm{d}\phi$$

Repeating this rotation N times and sending this N to infinity, we can see this as a finite rotation, and due to the way it's written, we can immediately see how the Drehung operator for a finite rotation is shaped. Taking without loss of generality a rotation around the z axis, we get the following result for a rotation of ϕ degrees.

$$\hat{\mathcal{D}}(\phi) = \lim_{N\to\infty}\left(1 - \frac{i\hat{J}_z\phi}{N\hbar}\right)^N = e^{-\frac{i\hat{J}_z\phi}{\hbar}} \tag{4.5}$$

From this simple result, we can immediately see how the Drehung operator is tied to classical rotation, as it has the same group properties of the classical rotation matrices, which are the following

1. Identity: $\hat{\mathcal{D}}(R)\cdot\hat{\mathbb{1}} = \hat{\mathcal{D}}(R)$
2. Closure: $\hat{\mathcal{D}}(R_1)\hat{\mathcal{D}}(R_2) = \hat{\mathcal{D}}(R_3)$
3. Invertibility: $\hat{\mathcal{D}}^{-1}(R)\hat{\mathcal{D}}(R) = \hat{\mathcal{D}}(R)\hat{\mathcal{D}}^{-1}(R) = \hat{\mathbb{1}}$

4. Associativity: $\hat{\mathcal{D}}(R_1)\left(\hat{\mathcal{D}}(R_2)\hat{\mathcal{D}}(R_3)\right) = \left(\hat{\mathcal{D}}(R_1)\hat{\mathcal{D}}(R_2)\right)\hat{\mathcal{D}}(R_3) = \hat{\mathcal{D}}(R_1)\hat{\mathcal{D}}(R_2)\hat{\mathcal{D}}(R_3)$

Now it's quick to ask how do these operators commute, then we use the analogy with the R matrices and use the commutation relations (4.3). We obviously use the approimation to the second order of $\hat{\mathcal{D}}(R)$

$$\left(1 - \frac{i\hat{J}_x\varepsilon}{\hbar} - \frac{\hat{J}_x^2\varepsilon^2}{2\hbar^2}\right)\left(1 - \frac{i\hat{J}_y\varepsilon}{\hbar} - \frac{\hat{J}_y^2\varepsilon^2}{2\hbar^2}\right) - \left(1 - \frac{i\hat{J}_y\varepsilon}{\hbar} - \frac{\hat{J}_y^2\varepsilon^2}{2\hbar^2}\right)\left(1 - \frac{i\hat{J}_x\varepsilon}{\hbar} - \frac{\hat{J}_x^2\varepsilon^2}{2\hbar^2}\right) =$$
$$= 1 - \frac{i\hat{J}_z\varepsilon^2}{\hbar} - 1$$

Equating the terms of order $\mathcal{O}(\varepsilon^2)$, we get that $\left[\hat{J}_x, \hat{J}_y\right] = i\hbar\hat{J}_z$, and through cyclic permutations (using the ϵ_{ijk} tensor) we get the following result

$$\left[\hat{J}_i, \hat{J}_j\right] = i\hbar\epsilon_{ijk}\hat{J}_k \tag{4.6}$$

These are the fundamental commutation relations of angular momentum, and they are said to generate a non-Abelian group of rotations, since two different operators of the same group do not commute. Since we have defined angular momentum from rotations, we can easily say that these relations hold for «*every kind*» of angular momentum we find.

§ 4.2 Eigenvalues and Eigenstates of Angular Momentum

We have already seen how angular momentum operators between different axes do not commute, hence, in order to find a suitable eigenbasis we build a new operator starting from $\underline{\hat{J}}$. From (4.6) we can immediately imagine that the simplest operator we can find is $\hat{J}^2$, defined as follows

$$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 = \underline{\hat{J}} \cdot \underline{\hat{J}}$$

This operator commutes with every $\hat{J}_i$, and hence, we have another commutation relations

$$\left[\hat{J}^2, \hat{J}_i\right] = 0 \tag{4.7}$$

We know already that there exists simultaneously an eigenbasis for any operator $\hat{J}_i$ and $\hat{J}^2$. As a convention we take $\hat{J}_3 = \hat{J}_z$ as our main direction, and we will call the eigenkets as $|a, b\rangle$, for which holds the already known secular equation

$$\hat{J}^2 |a, b\rangle = a |a, b\rangle$$
$$\hat{J}_z |a, b\rangle = b |a, b\rangle$$

In order to work out the results, we define two non hermitian operators, that we will call $\hat{J}_+$ and $\hat{J}_+^\dagger = \hat{J}_-$. These operators are defined as follows

$$\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y \tag{4.8}$$

These operators satisfy the commutation relations

$$\begin{aligned}\left[\hat{J}_z, \hat{J}_\pm\right] &= \pm\hbar\hat{J}_\pm \\ \left[\hat{J}_\pm, \hat{J}_\mp\right] &= \pm 2\hbar\hat{J}_z \\ \left[\hat{J}^2, \hat{J}_\pm\right] &= 0\end{aligned} \tag{4.9}$$

Defined as such, these are the ladder operators of angular momentum, but why are they called ladder operators? It's easy to see why if we let them act on an eigenstate and utilize the previous commutation relations. We then get

$$\hat{J}_z\hat{J}_\pm |a,b\rangle = \left(\left[\hat{J}_z, \hat{J}_\pm\right] + \hat{J}_\pm\hat{J}_z\right)|a,b\rangle = (b \pm \hbar)\,\hat{J}_\pm |a,b\rangle$$

In an analogy with the quantum harmonic oscillator, we see then really why these operators are called "ladder" operators, since they move up or down of one step ($\hbar$ long) the "measured" value.
We now redo the same calculations with $\hat{J}^2$, and using (4.9), we get

$$\hat{J}^2\hat{J}_\pm |a,b\rangle = \hat{J}_\pm\hat{J}^2 |a,b\rangle = a\hat{J}_\pm |a,b\rangle \tag{4.10}$$

Remembering that $|a,b\rangle$ are simultaneous eigenstates for both $\hat{J}_z$ and $\hat{J}^2$, we can summarize everything in the following way

$$\hat{J}_\pm |a,b\rangle = c_\pm |a, b \pm \hbar\rangle \tag{4.11}$$

Now, let's use what we found with this ladder operator machinery for finding the actual eigenstates and eigenvalues of angular momentum. We give the following Ansatz:

$$a \geq b^2$$

But why should the eigenvalue of $\hat{J}_z$ be limited? Let's write a new operator, made through a combination of $\hat{J}^2$ and $\hat{J}_z$

$$\hat{J}^2 - \hat{J}_z^2 = \frac{1}{2}\left(\hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+\right) = \frac{1}{2}\left(\hat{J}_+\hat{J}_+^\dagger + \hat{J}_+^\dagger\hat{J}_+\right) \tag{4.12}$$

Now, $\hat{J}_+^\dagger\hat{J}_+$ and $\hat{J}_+\hat{J}_+^\dagger$ must be positive definite, hence it follows that

$$\langle a,b|\left(\hat{J}^2 - \hat{J}_z^2\right)|a,b\rangle \geq 0$$

Which implies the previous Ansatz. It follows, then, that there exists a value b_{max} and b_{min} for the following relations hold

$$\begin{aligned}\hat{J}_+ |a, b_{max}\rangle &= 0 \\ \hat{J}_- |a, b_{min}\rangle &= 0\end{aligned} \tag{4.13}$$

Studying the first case, we know that it also implies $\hat{J}_-\hat{J}_+ |a, b_{max}\rangle = 0$, but analyzing further and utilizing the definition of the ladder operators, we get that

$$\hat{J}_-\hat{J}_+ = \hat{J}_x^2 + \hat{J}_y^2 - i\left[\hat{J}_y, \hat{J}_x\right] = \hat{J}^2 - \hat{J}_z^2 - \hbar\hat{J}_z$$

Hence, we get the following important result

$$\left(\hat{J}^2 - \hat{J}_z^2 - \hbar\hat{J}_z\right)|a, b_{max}\rangle = 0 \tag{4.14}$$

Now, since $|a, b_{max}\rangle$ is an eigenket of every operator acting on it, and for such can't be a null ket, it must hold that

$$\begin{aligned} a - b_{max}^2 - \hbar b_{max} &= 0 \\ a &= b_{max}(b_{max} + \hbar) \end{aligned} \tag{4.15}$$

Similarly, letting $\hat{J}_-$ on the ket $|a, b_{min}\rangle$, we obtain that a must also be equal to

$$a = b_{min}(b_{min} - \hbar)$$

Hence, it's obvious that $b_{max} = -b_{min}$, and hence $-b_{max} \leq b \leq b_{max}$, with $b_{max} \geq 0$.
Due to how $\hat{J}_+$ acts on the eigenkets, it must definitely hold that $b_{max} = b_{min} + n\hbar$, with $n \in \mathbb{N}$.
Then, it must hold definitely that

$$b_{max} = \frac{n\hbar}{2}$$

Due to convention it's usual to define directly the eigenvalue j as $n/2$, hence, we get that

$$a = \hbar^2 j(j+1) \tag{4.16}$$

Defining another integer eigenvalue m, such that we have

$$b = m\hbar \tag{4.17}$$

Due to what we found before, j is an half-integer, hence all m must be half-integers too, and they can only take the following values

$$m = \underbrace{-j, -j+1, \cdots, j-1, j}_{2j+1 \text{ times}} \tag{4.18}$$

For a little recap, after renaming a, b with j, m we have that the simultaneous eigenkets of $\hat{J}^2$ and $\hat{J}_z$ are the following

$$\begin{aligned} \hat{J}^2|j, m\rangle &= \hbar^2 j(j+1)|j, m\rangle \\ \hat{J}_z|j, m\rangle &= \hbar m|j, m\rangle \end{aligned} \tag{4.19}$$

§§ 4.2.1 Matrix Elements of the Ladder Operators of Angular Momentum

Now that we have defined the eigenvalues of the $\hat{J}^2$ and $\hat{J}_z$ angular momentum operators, is immediately seen that their tensor representation will be the following:

$$\begin{aligned} J^2_{\overline{j},\overline{m},j,m} &= \langle\overline{j}, \overline{m}|\hat{J}^2|j, m\rangle = \hbar^2 j(j+1)\delta_{\overline{j}j}\delta_{\overline{m}m} \\ J^{(z)}_{\overline{j},\overline{m},j,m} &= \langle\overline{j}, \overline{m}|\hat{J}_z|j, m\rangle = \hbar m\delta_{\overline{j}j}\delta_{\overline{m}m} \end{aligned} \tag{4.20}$$

The first question that might pop up is, then, what are the matrix elements of the ladder operators? Hence, what's their action on the eigenkets of angular momentum?

We use the definition in (4.12) in order to find this out. From that equation, we can write the two following useful relations

$$\begin{aligned}\hat{J}_-\hat{J}_+ &= \left(\hat{J}_x - i\hat{J}_y\right)\left(\hat{J}_x + i\hat{J}_y\right) = \hat{J}_x^2 + \hat{J}_y^2 + i\left[\hat{J}_x, \hat{J}_y\right] = \hat{J}^2 - \hat{J}_z^2 - \hbar\hat{J}_z \\ \hat{J}_+\hat{J}_- &= \left(\hat{J}_x + i\hat{J}_y\right)\left(\hat{J}_x - i\hat{J}_y\right) = \hat{J}_x^2 + \hat{J}_y^2 - i\left[\hat{J}_x, \hat{J}_y\right] = \hat{J}^2 - \hat{J}_z^2 + \hbar\hat{J}_z\end{aligned} \tag{4.21}$$

Let's now calculate the matrix elements for these operators, bearing in mind that $\hat{J}_- = \hat{J}_+^\dagger$

$$\begin{aligned}\langle j.m|\, \hat{J}_+^\dagger\hat{J}_+ \,|j,m\rangle &= \langle j,m|\left(\hat{J}^2 - \hat{J}_z^2 - \hbar\hat{J}_z\right)|j,m\rangle = \hbar^2 j(j+1) - \hbar^2 m^2 - \hbar^2 m \\ \langle j,m|\, \hat{J}_-^\dagger\hat{J}_- \,|j,m\rangle &= \langle j,m|\left(\hat{J}^2 - \hat{J}_z^2 + \hbar\hat{J}_z\right)|j,m\rangle = \hbar^2 j(j+1) - \hbar^2 m^2 + \hbar^2 m\end{aligned} \tag{4.22}$$

But, we can also write the following relations

$$\hat{J}_\pm |j,m\rangle = c_\pm |j, m\pm 1\rangle$$

And, in order to find $c_\pm$, we impose that $\left\|\hat{J}_\pm |j,m\rangle\right\| = 1$, and confronting with (4.22), we can conclude that

$$|c_\pm|^2 = \hbar^2\left(j(j+1) - m(m\pm 1)\right) \longrightarrow c_\pm = \hbar\sqrt{j(j+1) - m(m\pm 1)} \tag{4.23}$$

And we can conclude, definitely, that the action of the ladder operators will be the following

$$\hat{J}_\pm |j,m\rangle = \hbar\sqrt{j(j+1) - m(m\pm 1)}\,|j, m\pm 1\rangle \tag{4.24}$$

The tensor representations of the operators will then be

$$\begin{aligned}J^{(+)}_{\bar{j},\overline{m},j,m} &= \hbar\sqrt{j(j+1) - m(m-1)}\,\delta_{\overline{m}m+1}\delta_{\bar{j}j} \\ J^{(-)}_{\bar{j},\overline{m},j,m} &= \hbar\sqrt{j(j+1) - m(m+1)}\,\delta_{\overline{m}m-1}\delta_{\bar{j}j}\end{aligned} \tag{4.25}$$

§ 4.3 Orbital Angular Momentum

We have seen how a general angular momentum, seen as a generator of rotations can be quantized, and be represented as an operator. To delve deeper on the physical meaning of this, we then quantize the classical angular momentum, where it can be written quantum mechanically as follows

$$\hat{\underline{L}} = \hat{\underline{q}} \wedge \hat{\underline{p}} = \epsilon_{ijk}\hat{q}_j\hat{p}_k \tag{4.26}$$

It is immediately seen that it satisfies the main commutation relation of angular momentum, and hence it must be a generator of rotations. In fact, it's easy to demonstrate that

$$\left[\hat{L}_i, \hat{L}_j\right] = i\hbar\epsilon_{ijk}\hat{L}_k \tag{4.27}$$

Since this must be a generator of rotations, we can write at the first order the Drehung operator as follows

$$\hat{\mathcal{D}}_z(\delta\phi) = 1 - \left(\frac{i\delta\phi}{\hbar}\right)\hat{L}_z = 1 - \left(\frac{i\delta\phi}{\hbar}\right)(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x) \tag{4.28}$$

It's already clear from the beginning, that letting this act on a ket $|x, y, z\rangle$ is uncomfortable, hence we choose a spherical coordinate set $|r, \theta, \phi\rangle$, and we see that the action, to the first order, of the Drehung operator will be the following, considering a toy wavefunction $|\alpha\rangle$

$$\langle r, \theta, \phi| \left(1 - \left(\frac{i\delta\phi}{\hbar}\right)\hat{L}_z\right)|\alpha\rangle = \langle r, \theta, \phi - \delta\phi|\alpha\rangle = \langle r, \theta, \phi|\alpha\rangle - \frac{\partial}{\partial\phi}\langle r, \theta, \phi|\alpha\rangle\,\delta\phi \tag{4.29}$$

Since $|r, \theta, \phi\rangle$ is arbitrary, we easily identify the following representation of $\hat{L}_z$

$$\langle r_i|\,\hat{L}_z\,|\alpha\rangle = -i\hbar\frac{\partial}{\partial\phi}\langle r_i|\alpha\rangle \tag{4.30}$$

Identically, doing the same evaluation with $\hat{L}_x$ and $\hat{L}_y$, we get the following representations

$$\begin{aligned}\langle r_i|\,\hat{L}_x\,|\alpha\rangle &= -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)\langle r_i|\alpha\rangle \\ \langle r_i|\,\hat{L}_y\,|\alpha\rangle &= -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)\langle r_i|\alpha\rangle\end{aligned} \tag{4.31}$$

Now, defining two new ladder operators for orbital angular momentum as $\hat{L}_\pm$, we have, combining the representations (4.31), the following result

$$\langle r_i|\,\hat{L}_\pm\,|\alpha\rangle = -i\hbar e^{\pm i\phi}\left(\pm i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\phi}\right)\langle r_i|\alpha\rangle \tag{4.32}$$

As for $\hat{J}^2$, we can write $\hat{L}^2$ as follows

$$\hat{L}^2 = \hat{L}_z^2 + \frac{1}{2}\left(\hat{L}_+\hat{L}_- + \hat{L}_-\hat{L}_+\right) \tag{4.33}$$

Applying to our wavefunction $|\alpha\rangle$ we, hence get

$$\langle r_i|\,\hat{L}^2\,|\alpha\rangle = -\hbar^2\left(\csc^2\theta\frac{\partial^2}{\partial\phi^2} + \csc\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right)\langle r_i|\alpha\rangle \tag{4.34}$$

Which is only the angular part of the Laplacian in spherical coordinates.
Using the property (**??**) of the tensor ϵ_{ijk}, we can also write $\hat{L}^2$ in operatorial form as follows

$$\hat{L}^2 = \hat{q}^2\hat{p}^2 - \left(\underline{\hat{q}}\cdot\underline{\hat{p}}\right)^2 + i\hbar\underline{\hat{q}}\cdot\underline{\hat{p}} \tag{4.35}$$

Using this last expression, we manage to get the following results

$$\begin{aligned}\langle r_i|\,\hat{q}^j\hat{p}_j\,|\alpha\rangle &= \hat{q}^j\left(-i\hbar\frac{\partial}{\partial x_j}\langle r_i|\alpha\rangle\right) \\ \langle r_i|\left(\hat{q}^j\hat{p}_j\right)^2|\alpha\rangle &= -\hbar^2 r\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\langle r_i|\alpha\rangle\right)\end{aligned}$$

Thus, we have

$$\langle r_i|\,\hat{L}^2\,|\alpha\rangle = r^2\langle r_i|\,\hat{p}^2\,|\alpha\rangle + \hbar^2\left(r^2\frac{\partial^2}{\partial r^2} + 2r\frac{\partial}{\partial r}\right)\langle r_i|\alpha\rangle \tag{4.36}$$

Now, having $\hat{p}^2$ in the definition of $\hat{L}^2$, we can write the kinetic energy as follows

$$\hat{T}\langle r_i|\alpha\rangle = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}\langle r_i|\alpha\rangle + \frac{2}{r}\frac{\partial}{\partial r}\langle r_i|\alpha\rangle - \frac{\langle r_i|\hat{L}^2|\alpha\rangle}{\hbar^2 r^2}\right) \tag{4.37}$$

Let's now write the actual eigenfunctions $\langle r_i|l,m\rangle$[1] of $\hat{L}^2, \hat{L}_z$. Solving for both $\hat{L}_z$ and $\hat{L}^2$, it's easy to see that they are the Spherical Harmonics $Y_l^m(\theta,\phi)$, hence $\langle r_i|l,m\rangle = Y_l^m(\theta,\phi)$, and

$$\begin{aligned}\hat{L}_z Y_l^m(\theta,\phi) &= \hbar m Y_l^m(\theta,\phi)\\ \hat{L}^2 Y_l^m(\theta,\phi) &= \hbar^2 l(l+1) Y_l^m(\theta,\phi)\end{aligned} \tag{4.38}$$

The treatment of the spherical harmonics and its derivation is given in the appendices.

§ 4.4 Spin

So far we managed to define how the algebra of angular momentum works, and how the quantization of orbital angular momentum follows it. A main question arises: due to how orbital angular momentum is defined, it can only have integer eigenvalues, but as we've seen in the general picture, the eigenvalues can also be half-integers, which cannot be explained by orbital angular momentum. This problem arises, where there is this kind of intrinsic angular momentum, which cannot be defined through the quantization of classical objects! This new angular momentum, is called *Spin Angular Momentum* or simply *Spin*, and it's represented through a vector operator $\underline{\hat{S}}$.
Since it's an angular momentum, it follows every single commutation rule of a generator of rotations, hence it satisfies the following rules

$$\begin{aligned}\left[\hat{S}_i, \hat{S}_j\right] &= i\hbar\epsilon_{ijk}S_k\\ \left[\hat{S}^2, \hat{S}_i\right] &= 0\\ \hat{S}^2|s,m\rangle &= \hbar^2 s(s+1)|s,m\rangle\\ \hat{S}_z|s,m\rangle &= \hbar m_s|s,m\rangle\end{aligned} \tag{4.39}$$

Due to the previous statements, we already know that s takes half integer values, but using the algebraic definition of angular momentum, it's obvious that it can also take integer values.
The simplest case that comes to mind, is the case where $s = 1/2$. In this case we have, since $-s \leq m \leq s$, that

$$\begin{aligned}\hat{S}_z\left|\frac{1}{2},\pm\frac{1}{2}\right\rangle &= \pm\frac{\hbar}{2}\left|\frac{1}{2},\pm\frac{1}{2}\right\rangle\\ \hat{S}^2\left|\frac{1}{2},\pm\frac{1}{2}\right\rangle &= \frac{3\hbar^2}{4}\left|\frac{1}{2},\pm\frac{1}{2}\right\rangle\end{aligned} \tag{4.40}$$

[1] The two integers l and m, are usually identified in literature as *principal quantum number* and *magnetic quantum number*, respectively, due to experimental reasons

Due to the two different possible values of m_s, we can split the ket, in order to have the following result

$$\begin{aligned}\hat{S}_z\left|\frac{1}{2},\frac{1}{2}\right\rangle &= \frac{\hbar}{2}\left|\frac{1}{2},\frac{1}{2}\right\rangle \\ \hat{S}_z\left|\frac{1}{2},-\frac{1}{2}\right\rangle &= -\frac{\hbar}{2}\left|\frac{1}{2},-\frac{1}{2}\right\rangle\end{aligned} \tag{4.41}$$

Immediately, it's easy to define then, two possible states, either spin "up" or spin "down". This new notation follows the previous rules, although adding some day to day physical intuition that this argument completely lacks:

$$\begin{aligned}\hat{S}_z\left|\uparrow\right\rangle &= \frac{\hbar}{2}\left|\uparrow\right\rangle \\ \hat{S}_z\left|\downarrow\right\rangle &= -\frac{\hbar}{2}\left|\downarrow\right\rangle \\ \hat{S}^2\left|\uparrow\right\rangle = \hat{S}^2\left|\downarrow\right\rangle &= \frac{3\hbar^2}{4}\left|\uparrow\right\rangle = \frac{3\hbar^2}{4}\left|\downarrow\right\rangle\end{aligned} \tag{4.42}$$

The $\hat{S}_z$ is diagonal in this basis, hence we can immediately write it in matrix form as follows

$$\hat{S}_z \to \frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} \tag{4.43}$$

And $\hat{S}^2$, as

$$\hat{S}^2 \to \frac{3\hbar^2}{4}\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} \tag{4.44}$$

It jumps immediately to the eye that we're now working on a 2D Hilbert space. This space is spanned by the kets $|\uparrow\rangle$ and $|\downarrow\rangle$, which, due to their nature as spin eigenkets, are called *spinors*.
Immediately, a question comes to mind: how do the other spin components act on these spinors? Firstly, let's define our spin ladder operators $\hat{S}_\pm$ as usual. Since the only possible values of m are $m = -1/2, 1/2$ they'll be represented by the following matrices

$$\begin{aligned}\hat{S}_+ &\to \hbar\begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix} \\ \hat{S}_- &\to \hbar\begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}\end{aligned} \tag{4.45}$$

The $\hbar$ pops out remembering the following rule of angular momentum ladder operators

$$\hat{S}_\pm\left|s,m\right\rangle = \hbar\sqrt{s(s+1)-m(m\pm1)}\left|s,m\pm1\right\rangle \tag{4.46}$$

Now it's easy to answer our first question! We remember how the ladder operators are defined, and we invert them in order to find how we can define $\hat{S}_x$ and $\hat{S}_y$ in terms of these operators, their calculation is quite straightforward, and we get

$$\begin{aligned}\hat{S}_x &= \frac{1}{2}\left(\hat{S}_+ + \hat{S}_-\right) \\ \hat{S}_y &= \frac{1}{2i}\left(\hat{S}_+ - \hat{S}_-\right)\end{aligned} \tag{4.47}$$

Their representation is then easy to find

$$\begin{aligned}\hat{S}_x &\to \frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\\ \hat{S}_y &\to \frac{\hbar}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\end{aligned} \tag{4.48}$$

Putting it all together, the $\underline{\hat{S}}$ is then represented as follows

$$\begin{aligned}\hat{S}_x &\to \frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} = \frac{\hbar}{2}\hat{\sigma}_x\\ \hat{S}_y &\to \frac{\hbar}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix} = \frac{\hbar}{2}\hat{\sigma}_y\\ \hat{S}_z &\to \frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} = \frac{\hbar}{2}\hat{\sigma}_z\end{aligned} \tag{4.49}$$

Using index notation, we get that $\hat{S}_i = \frac{\hbar}{2}\hat{\sigma}_i$, where $\hat{\sigma}_i$ is the i-th *Pauli matrix* for a spin $1/2$ system. These matrices have the following properties, inherited from the properties of Spin

$$\begin{aligned}[\hat{\sigma}_i, \hat{\sigma}_j] &= 2i\epsilon_{ijk}\hat{\sigma}_k\\ \{\hat{\sigma}_i, \hat{\sigma}_j\} &= 2\delta_{ij}\hat{\mathbb{1}}\end{aligned} \tag{4.50}$$

From these, it's easy to derive some additional properties

$$\begin{aligned}\hat{\sigma}_i\hat{\sigma}_j &= \delta_{ij}\hat{\mathbb{1}} + \epsilon_{ijk}\hat{\sigma}_k\\ A_{ij} &= c_0\delta_{ij} + c_k\hat{\sigma}^k\\ \hat{\sigma}^2 &= \delta_{ij}\\ \hat{\sigma}_i\hat{\sigma}^i &= 3\delta_{ij}\end{aligned}$$

§ 4.5 Addition of Angular Momenta

In order to add up two different angular momenta, we need, first of all, to understand how the underlying maths works.
The two operators act on two different Hilbert spaces, and the *total* angular momentum must act on both. This constraints bring us to the definition of the total angular momentum Hilbert space, which «*must*» be given by the tensor product of the two, as follows

$$\mathbb{H} = \mathbb{H}_1 \otimes \mathbb{H}_2 \tag{4.51}$$

The operator $\underline{\hat{J}}$ will then be defined as

$$\underline{\hat{J}} = \underline{\hat{J}}_1 \otimes \hat{\mathbb{1}} + \hat{\mathbb{1}} \otimes \underline{\hat{J}}_2 \tag{4.52}$$

From this definition, the two following commutation relations are then obvious

$$\begin{aligned}\left[\hat{J}_2^2, \hat{J}^2\right] &= 0 \\ \left[\hat{J}^2, \hat{J}_1^2\right] &= 0\end{aligned} \tag{4.53}$$

Although, it follows that $\hat{J}^2$ and $\hat{J}_1^z, \hat{J}_2^z$ do not commute.

$$\left[\hat{J}_2^z, \hat{J}^2\right] = \left[\hat{J}^2, \hat{J}_1^z\right] = 2i\hbar\left(\hat{J}_1^x\hat{J}_2^y - \hat{J}_1^y\hat{J}_2^x\right) \neq 0 \tag{4.54}$$

Due to the last relation a common basis of eigenvalues between $\hat{J}^2$ and $\hat{J}_1^z, \hat{J}_2^z$ cannot be formed, but two choices are possible:

1. Since $\hat{J}_1^2$ commutes with $\hat{J}_2^2, \hat{J}_1^z, \hat{J}_2^z$ and each of them commutes, we can utilize a basis $B := |j_1, m_1\rangle \otimes |j_2, m_2\rangle$
2. Since $\hat{J}^2$ commutes only with $\hat{J}_1^2, \hat{J}_2^2, \hat{J}_z$, we can also define a second basis $C := |j_1, j_2\rangle \otimes |j, m\rangle$

We will then have the following eigenvalues (where we avoid writing the tensor product between states in order to ease the notation)

$$\begin{aligned}\hat{J}^2 |j_1, j_2, j, m\rangle &= \hbar^2 j(j+1) |j_1, j_2, j, m\rangle \\ \hat{J}_z |j_1, j_2, j, m\rangle &= \hbar m |j_1, j_2, j, m\rangle \\ \hat{J}_1^2 |j_1, j_2, j, m\rangle &= \hbar^2 j_1(j_1+1) |j_1, j_2, j, m\rangle \\ \hat{J}_2^2 |l.s.j.m\rangle &= \hbar^2 j_2(j_2+1) |j_1, j_2, j.m\rangle \\ \hat{J}_2^z |j_1, j_2, m_1, m_2\rangle &= \hbar m_2 |j_1, j_2, m_1, m_2\rangle \\ \hat{J}_1^z |j_1, j_2, m_1, m_2\rangle &= \hbar m_1 |j_1, j_2, m_1, m_2\rangle\end{aligned} \tag{4.55}$$

We can obviously define an unitary transformation in $\mathbb{H}$ that lets us switch between the two basi

$$|j_1, j_2, j, m\rangle = \hat{\mathcal{U}} |j_1, j_2, m_1, m_2\rangle \tag{4.56}$$

The shape of $\hat{\mathcal{U}}$ will obviously be that of a projection, and hence we will have the following result

$$|j_1, j_2, j, m\rangle = \sum_{m_1, m_2} |j_1, j_2, m_1, m_2\rangle \langle j_1, j_2, m_1, m_2 | j_1, j_2, j, m\rangle \tag{4.57}$$

Where here we utilized the completeness relation

$$\sum_{m_1, m_2} |j_1, j_2, m_1, m_2\rangle \langle j_1, j_2, m_1, m_2| = \hat{\mathbb{1}}$$

Looking at the braket on the right of (4.57), we immediately see the property of these coefficients, called *Clebsch-Gordan coefficients*. These coefficients vanish, unless we have that $m = m_1 + m_2$, but how?

Proof. We know that the following assertation is true

$$\left(\hat{J}_z - \hat{J}_1^z - \hat{J}_2^z\right) |j_1, j_2, j, m\rangle = 0$$

We simply multiply the relation with $\langle j_1, j_2, m_1, m_2|$ and we get our proof

$$(m - m_1 - m_2) \langle j_1, j_2, m_1, m_2 | j_1, j_2, j, m\rangle$$

Where the last braket are our Clebsch-Gordan coefficients □

Similarly, we have that the Clebsch-Gordan coefficients are nonzero also if only the $\hat{J}^2$ eigenvalue j holds the following values

$$|j_1 - j_2| \leq j \leq j_1 + j_2 \tag{4.58}$$

One might now ask how many states we can count, after adding the two angular momentums.
We can already count $2j_1 + 1$ possible values of m_1 and $2j_2 + 1$ values of m_2. Summing it all up we get that there will be N states, counted as follows

$$\begin{aligned} N = \sum_{j=j_1-j_2}^{j_1+j_2} (2j+1) &= \frac{1}{2}\left(2(j_1 - j_2) + 1 + 2(j_1 + j_2) + 1\right)(2j_2 + 1) \\ &= (2j_1 + 1)(2j_2 + 1) \end{aligned} \tag{4.59}$$

The Clebsch-Gordan coefficients are taken to be real by covention, hence the inverse coefficients are equal to the coefficient themselves, since it's a unitary transformation.
Another way that these coefficients can be written, is with the *Wigner 3-j symbols*, through this relation

$$\langle j_1, j_2, m_1, m_2 | j_1, j_2, j, m\rangle = (-1)^{j_1 - j_2 + m} \sqrt{2j+1} \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix} \tag{4.60}$$

The values that the "matrix" can take are tabulated, and therefore, even the Clebsch-Gordan coefficients.

5 Quantum Dynamics

In this chapter, we will treat problems defined by Hamiltonians of the following kind

$$\hat{\mathcal{H}} = \frac{\hat{p}^2}{2m} + V(r) \tag{5.1}$$

Where

$$\begin{cases} \hat{p}^2 = p_i p^i \\ \hat{r} = \sqrt{\hat{q}_i \hat{q}^i} \end{cases} i = 1, 2, 3$$

Due to this definition, it's evident that this Hamiltonian is *spherically symmetrical*, because it's easy to show that angular momentum is conserved. In fact

$$\left[\hat{L}_i, \hat{p}^2\right] = \left[\hat{L}_i, \hat{q}^2\right] = 0$$

Due to how the Hamiltonian is defined, we have

$$\left[\hat{L}_i, \hat{\mathcal{H}}\right] = \left[\hat{L}^2, \hat{\mathcal{H}}\right] = 0 \tag{5.2}$$

Which, indicates that angular momentum is conserved. The fact that the commutator between every element of the angular momentum and the Hamiltonian brings our problem to the search of common eigenstates of angular momentum and energy, that for simplicity we will call $|Elm\rangle$.
The secular equations that we need to solve simultaneously are the following three

$$\begin{aligned} \hat{\mathcal{H}} |Elm\rangle &= E |Elm\rangle \\ \hat{L}^2 |Elm\rangle &= \hbar^2 l(l+1) |Elm\rangle \\ \hat{L}_z |Elm\rangle &= \hbar m |Elm\rangle \end{aligned} \tag{5.3}$$

Using what we found for angular momentum, we write $\langle x_i| \hat{p}^2 |Elm\rangle$ in spherical coordinates, and, we then get

$$\begin{aligned} \langle x_i| \hat{\mathcal{H}} |Elm\rangle = -\frac{\hbar^2}{2mr^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \psi_{Elm}(x_i) + \\ + \frac{\hbar^2 l(l+1)}{2mr^2} \psi_{Elm}(x_i) + V(r) \psi_{Elm}(x_i) = E \psi_{Elm}(x_i) \end{aligned} \tag{5.4}$$

As we seen for angular momentum, $\hat{L}^2$ takes the angular dependence, hence this equation can be reduced to a single variable differential equation on r through separation of variable, utilizing the fact

that $\langle\theta,\phi|lm\rangle \neq 0$ for all θ,ϕ. As a convention, we will call the radial part $R_{El}(r)$
We simplify the equation (the *radial* equation), introducing a new radial function, and an effective potential

$$\begin{cases} R_{El} = \dfrac{u_{El}(r)}{r} \\ V_{eff}(r) = \dfrac{\hbar^2 l(l+1)}{2mr^2} + V(r) \end{cases} \tag{5.5}$$

The new equation then becomes the following

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2 u_{El}}{\mathrm{d}r^2} + V_{eff}(r)u_{El}(r) = Eu_{El}(r) \tag{5.6}$$

Considering the behavior in an infinitesimal ball around $r = 0$, and supposing that our potential is regular enough to have $\lim_{r\to 0} V(r) = 0$, we have that our equation becomes the following

$$\frac{\mathrm{d}^2 u_{El}}{\mathrm{d}r^2} = \frac{l(l+1)}{r^2}u_{El}(r) \tag{5.7}$$

Which has the following general solution

$$u(r) = Ar^{l+1} + Br^{-l}$$

For our needs, we set $B = 0$, since r^{-l} blows up at $r \to 0$. We have now a restriction for R_{El}, which imposes that $R_{El}(r) \to r^l$ for $r \to 0$.
For $r \to \infty$ we get a new equation, of simple solution

$$\frac{\mathrm{d}^2 u_E}{\mathrm{d}r^2} = \kappa^2 u_E(r) \quad \kappa^2 = -\frac{2mE}{\hbar^2} > 0 \tag{5.8}$$

It's solution is a decaying exponential $u_E(r) \propto e^{-\kappa r}$
Introducing a new dimensionless variable $\rho = \kappa r$, we can write our radial function as a product of the asymptotic behaviors and a new unknown function $w(\rho)$

$$u_{El} = \rho^{l+1}e^{-\rho}w(\rho)$$

The function $w(\rho)$ is well behaved, and satisfies the following differential equation

$$\rho\frac{\mathrm{d}^2 w}{\mathrm{d}\rho^2} + 2\left(l+1-\rho\right)\frac{\mathrm{d}w}{\mathrm{d}\rho} + \left(\frac{V(\rho/\kappa)}{E}\rho - 2(l+1)\right)w(\rho) = 0 \tag{5.9}$$

This equation depends on the potential $V(r)$, hence a formal solution can't yet be defined.

§ 5.1 Free Particles and Infinite Wells Revisited

Starting from the radial equation, we define as before $\rho = kr$ and $E = \hbar^2 k^2/2m$. Plugging it all into the radial equation, we then get the following

$$\frac{\mathrm{d}^2 R}{\mathrm{d}\rho^2} + \frac{2}{\rho}\frac{\mathrm{d}R}{\mathrm{d}\rho} + \left(1 - \frac{l(l+1)}{\rho^2}\right)R(\rho) = 0 \tag{5.10}$$

This differential equation is solved immediately including the *spherical Bessel functions* j_l, n_l, defined as follows

$$\begin{aligned} j_l(\rho) &= (-1)^l \rho^l \left(\frac{1}{\rho}\frac{\mathrm{d}}{\mathrm{d}\rho}\right)^l \left(\frac{\sin\rho}{\rho}\right) \\ n_l(\rho) &= (-1)^{l+1} \rho^l \left(\frac{1}{\rho}\frac{\mathrm{d}}{\mathrm{d}\rho}\right)^l \left(\frac{\cos\rho}{\rho}\right) \end{aligned} \tag{5.11}$$

This result can be applied directly to the problem of a particle confined inside an infinite spherical well ($V(\rho) = 0$ in $r < a$) through the imposition of the condition $j_l(ka) = 0$. At $l = 0, 1, 2$ the levels are non degenerate, and for $l = 0$ we then have the following energy values

$$E_{nl} = E_{n0} = \frac{\hbar^2 (n\pi)^2}{2ma} \tag{5.12}$$

§ 5.2 Isotropic Harmonic Oscillator

The Hamiltonian for a 3D isotropic oscillator can be written as follows

$$\hat{\mathcal{H}} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{r}^2 \tag{5.13}$$

We introduce immediately the two following dimensionless variables and introduce them in the radial equation

$$E = \frac{1}{2}\hbar\omega\lambda$$
$$r = \sqrt{\frac{\hbar}{m\omega}}\rho$$

We obtain the following equation

$$\frac{\mathrm{d}^2 u}{\mathrm{d}\rho^2} - \frac{l(l+1)}{\rho^2} u(\rho) + (\lambda - \rho)^2 u(\rho) = 0 \tag{5.14}$$

We separate immediately the asymptotic behavior of $u(\rho)$, and since the potential diverges for $r \to \infty$, we write

$$u(\rho) = \rho^{l+1} e^{-\frac{\rho^2}{2}} f(\rho) \tag{5.15}$$

Inserting it back into (5.14), we get an equation on $f(\rho)$

$$\rho \frac{\mathrm{d}^2 f}{\mathrm{d}\rho^2} + 2\left(l + 1 - \rho^2\right) \frac{\mathrm{d}f}{\mathrm{d}\rho} + (\lambda - 2l + 3)\rho f(\rho) = 0 \tag{5.16}$$

This equation is solvable by writing $f(\rho)$ as a power series, and after manipulating it analogously to how it's done for a simple linear quantum harmonic oscillator, we get, after plugging it back into (5.16)

$$\sum_{n=2}^{\infty} \left[(n+2)(n+1)a_{n+2} + 2(l+1)(n+2)a_{n+2} - 2na_n + (\lambda - 2l + 3)a_n\right] \rho^{l+1} = 0 \tag{5.17}$$

Which gives the following recursion relation

$$a_{n+2} = \frac{2n + 2l + 3 - \lambda}{(n+2)(n+2l+3)} a_n \tag{5.18}$$

It's immediate to see that $\lim_{n\to\infty} a_{n+2}/a_n = 2/n = q^{-1}$, therefore, we get that $\lim_{\rho\to\infty} f(\rho) \propto e^{\rho^2}$, which gives us a non normalizable wavefunction. Due to this, the series must terminate for some even $q = 2n$, which gives the quantization of energy

$$\lambda = 2n + 2l + 3 \tag{5.19}$$

Which, gives finally

$$E_{ql} = \hbar\omega \left(2q + l + \frac{3}{2}\right) = \hbar\omega \left(N + \frac{3}{2}\right) \tag{5.20}$$

It's easy so see how energy is degenerate in l, and how for even (or odd) N we can only have even (or odd) values for l.
Another way to solve this problem is by seeing how the Hamiltonian is simply the sum of three Hamiltonians, one for each coordinate

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_x + \hat{\mathcal{H}}_y + \hat{\mathcal{H}}_y$$

And write each in terms of creation and destruction operators as follows

$$\hat{\mathcal{H}}_i = \hbar\omega \left(\hat{\eta}_i^\dagger \hat{\eta}_i + \frac{1}{2}\hat{\mathbb{1}}\right)$$

Labeling the eigenstates as $|n_x\rangle \otimes |n_y\rangle \otimes |n_z\rangle = |n_x, n_y, n_z\rangle$, we get then the simple result

$$\hat{\mathcal{H}} |n_x, n_y, n_z\rangle = \hbar\omega \left(n_x + \frac{1}{2} + n_y + \frac{1}{2} + n_z + \frac{1}{2}\right) |n_x, n_y, n_z\rangle$$

It's obvious that in this basis, the degeneration is the same of the previous, and it can be seen changing the basis using the following unitary transformation matrix $\langle n_x, n_y, n_z | qlm \rangle$

§ 5.3 Particle in a Coulomb Potential, Hydrogen Atom

We basically treated most of the common problems in 3 dimensions, but there is one potential that we didn't treat in a single dimension that will pop up various times in this book, especially when we'll start touching particular themes such as atomic physics and quantum chemistry: **The Coulomb potential**.
We write our potential in Gaussian units as follows

$$V(r) = -\frac{Ze^2}{r} \tag{5.21}$$

We already know the shape of this potential and what do the constants really mean, since we already treated it in the old quantum theory, so we immediately write our Schrödinger equation, remembering

how on the general case, the assumption of $V(r) \propto r^{-1}$ brought the equation (5.9).
Considering that bound states happen only for $E < 0$ and defining a ρ_0 as

$$\rho_0 = \sqrt{-\frac{2m}{E}}\frac{Ze^2}{\hbar} = \sqrt{-\frac{2mc^2}{E}}Z\alpha$$

Where $\alpha = e^2/\hbar c \approx 137^{-1}$ is the fine structure constant. Inserting everything in (5.9) we get a particular differential equation

$$\rho\frac{\mathrm{d}^2 w}{\mathrm{d}\rho^2} + 2(l+1-\rho)\frac{\mathrm{d}w}{\mathrm{d}\rho} + (\rho_0 - 2l + 2)w(\rho) = 0 \tag{5.22}$$

This equation is immediately solved by a confluent hypergeometric function[1], with parameters $\alpha = l + 1 - \rho$, $\gamma = 2l + 2$ and $z = 2\rho$, so

$$w(\rho) = F\left(2l + 2 - \rho_0, 2l + 2, 2\rho\right) \tag{5.23}$$

Approximating w with a power series for large N we get that

$$w(\rho) = \sum_{N=0}^{\infty} \frac{(2l+2-2\rho_0)_N}{(2l+2)_N}\frac{(2\rho)^N}{N!} \approx \sum_{N=0}^{\infty} \frac{(N/2)^N(2\rho)^N}{N^N N!} \approx \sum_{N=0}^{\infty} \frac{\rho^N}{N!} \approx e^{\rho}$$

Hence, this series must terminate, for some $n \geq \tilde{N}$, defined as $n = N + l + 1$. This number is called the *principal quantum number*[2].
Since we defined ρ_0 as $2N + 2l + 2$, we can write the energy eigenvalues as follows

$$\rho_0 = \sqrt{-\frac{E}{2mc^2}} = 2n$$

And therefore, solving for E, we get the energy quantization rule

$$E_n = -\frac{1}{2}mc^2\frac{Z^2\alpha^2}{n^2} \tag{5.24}$$

Now we can define properly our eigenfunction $\langle r, \theta, \phi | nlm \rangle$. As we know already the symmetries of the system, we know it will be composed by a radial part and a spherical part, multiplied together tensorially. Therefore, we have our wavefunction as follows

$$\begin{aligned}\psi_{nlm}(r,\theta,\phi) = &\frac{1}{(2l+1)!}\left(\frac{2Zr}{na_0}\right)^l \\ &\sqrt{\left(\frac{2Z}{na_0}\right)^3\left(\frac{(n+l)!}{2n(n-l-1)!}\right)}F\left(-n+l+1, 2l+2, \frac{2Zr}{na_0}\right)Y_l^m(\theta,\phi)\end{aligned} \tag{5.25}$$

Where $a_0 = \hbar/mc\alpha$ is Bohr's radius. The appearance of Bohr's radius in this equation is not casual, since the solution of the Schrödinger equation for a Coulomb potential is «*identical*» to the direct solution of the equation for a Hydrogen atom (non-relativistic). This finally closes at least partially all the questions that the old quantum theory left, and gave a proper solution to the main problem of atomic physics: the Hydrogen atom.

[1] See appendix B.2

[2] So far we found 3 quantum numbers, n the principal quantum number, l the angular quantum number and m the magnetic quantum number.

6 Approximation Methods

§ 6.1 Perturbation Theory

Since most problems in quantum mechanics can't be solved directly, there are various methods in order to approximate the results. In perturbation theory, we have two main problems and two cases: time-independent and time-dependent perturbations with or without degeneration. As a first approach, we will consider nondegenerate and time independent perturbations.

§§ 6.1.1 Rayleigh-Schrödinger Perturbation Theory, Nondegenerate Case

Let $\hat{\mathcal{H}}$ be our non directly solvable Hamiltonian, divisible in a sum of a solvable Hamiltonian $\hat{\mathcal{H}}_0$ and a perturbation $\hat{V}$.

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{V} \tag{6.1}$$

For $\hat{\mathcal{H}}_0$ we already know the solution of the secular equation, and we label them as follows

$$\hat{\mathcal{H}}_0 \left|n_0\right\rangle = E_n^{(0)} \left|n_0\right\rangle \tag{6.2}$$

Where the 0 should be seen strictly as a label, otherwise told.
The full secular equation will then be the following

$$\hat{\mathcal{H}} \left|n\right\rangle = \left(\hat{\mathcal{H}}_0 + \hat{V}\right) \left|n\right\rangle = E_n \left|n\right\rangle \tag{6.3}$$

It is customary to have $\hat{V}' = \lambda \hat{V}$, where $0 \leq |\lambda| \leq 1$ is a parameter that can be manipulated in order to see the effect of the perturbation.
A nice example on how this works is given by a two state system, defined as follows

$$\begin{aligned} \hat{\mathcal{H}}_0 &= E_1^{(0)} \left|1_0\right\rangle \left\langle 1_0\right| + E_2^{(0)} \left|2_0\right\rangle \left\langle 2_0\right| \\ \hat{V} &= \lambda V_{12} \left|1_0\right\rangle \left\langle 2_0\right| + \lambda V_{21} \left|2_0\right\rangle \left\langle 1_0\right| \end{aligned} \tag{6.4}$$

In matrix representation, our Hamiltonian will then be the following

$$\mathcal{H}_{ij} = \begin{pmatrix} E_1^{(0)} & \lambda V_{12} \\ \lambda V_{21} & E_2^{(0)} \end{pmatrix} \tag{6.5}$$

Since it must be (obviously) an Hermitian operator, we have $V_{12} = V_{21}$ Calculating the eigenvalues is simple, and we get

$$E_{1,2} = \frac{E_1^{(0)} + E_2^{(0)}}{2} \pm \sqrt{\frac{(E_1^{(0)} - E_2^{(0)})^2}{4} + \lambda^2 V_{12}^2} \tag{6.6}$$

Since we are considering perturbations tied to a parameter, if $\lambda|V_{12}| << \left|E_1^{(0)-E_2^{(0)}}\right|$ we can approximate the square root with a power series, obtaining the following result

$$\begin{aligned} E_1 &= E_1^{(0)} + \frac{\lambda^2 |V_{12}|^2}{E_1^{(0)} - E_2^{(0)}} \\ E_2 &= E_2^{(0)} + \frac{\lambda^2 |V_{12}|^2}{E_2^{(0)} - E_1^{(0)}} \end{aligned} \tag{6.7}$$

Which are the perturbation-corrected eigenvalues.
Now it's simpler to grasp the «*formal*» development of the theory. We take our two secular equations (6.2) and (6.3), and rename the difference of eigenvalues found in the approximation (6.7) as follows $\Delta_n = E_n - E_n^{(0)}$.
Our new approximate Schrödinger equation can then be written as follows

$$\left(E_n^{(0)} - \hat{\mathcal{H}}_0\right)|n\rangle = \left(\lambda\hat{V} - \Delta_n\right)|n\rangle \tag{6.8}$$

And now here a little precaution: $E_n^{(0)} - \hat{\mathcal{H}}_0$ and $\lambda\hat{V} - \Delta_n$ «*are operators*», and must be treated as such.
Back to our perturbation theory, we see right away that inverting the operator on the left isn't the way to go. It may act both on $|n_0\rangle, |n\rangle$, and therefore it's inverse is ill-defined, but the right hand side comes to our rescue, and we can impose the following condition as an Ansatz

$$\langle n_0|\left(\lambda\hat{V} - \Delta_n\right)|n\rangle = 0 \tag{6.9}$$

Now, we want to define properly the inverse of the operator on the left hand side, and we start by using a *complementary projection operator* $\hat{\phi}_n$ defined as follows

$$\hat{\phi}_n = 1 - |n_0\rangle\langle n_0| = \sum_{k\neq n} |k_0\rangle\langle k_0| \tag{6.10}$$

Now, in order to well-define the inverse operator we simply apply a projection beforehand

$$\frac{1}{E_n^{(0)} - \hat{\mathcal{H}}_0}\hat{\phi}_n = \sum_{k\neq n} \frac{1}{E_n^{(0)} - E_k^{(0)}} |k_0\rangle\langle k_0| \tag{6.11}$$

From the Ansatz (6.9) we have, evidently

$$\left(\lambda\hat{V} - \Delta_n\right)|n\rangle = \hat{\phi}_n\left(\lambda\hat{V} - \Delta_n\right)|n\rangle$$

So everything looks set up and fine, and it's tempting to find the perturbed eigenstates simply by inverting the first operator, but it simply doesn't work. Why? First of all, for $\lambda \to 0$ we «*must*» have

$|n\rangle \to |n_0\rangle$, and Δ_0, secondly because we need to add the solution to the homogeneous equation, hence, finally, we get the following result, naming this solution $c_n\,|n\rangle$

$$|n\rangle = c_n(\lambda)\,|n_0\rangle + \frac{1}{E_n^{(0)} - \hat{\mathcal{H}}_0}\hat{\phi}_n\left(\lambda\hat{V} - \Delta_n\right)|n\rangle \tag{6.12}$$

Where we have $c_n(\lambda) \to 1$ for $\lambda \to 0$, and $c_n(\lambda) = \langle n_0|n\rangle$.
Simplifying the successive equations, we put $c_n(\lambda) = \langle n_0|n\rangle = 1$ as our normalization condition, effectively removing a common multiplicative factor that appears. Then, easing the notation, we get

$$|n\rangle = |n_0\rangle + \frac{\hat{\phi}_n}{E_n^{(0)} - \hat{\mathcal{H}}_0}\left(\lambda\hat{V} - \Delta_n\right)|n\rangle \tag{6.13}$$

We also note that, from (6.9) that

$$\Delta_n = \lambda\,\langle n_0|\,\hat{V}\,|n\rangle \tag{6.14}$$

Now everything is set. What we are searching depends only on the equations (6.13) and (6.14), and using the "smallness" of λ we approximate everything using power series, hence

$$\begin{aligned} |n\rangle &= \sum_{k=0}^{\infty}\lambda^k\,|n_k\rangle \\ \Delta_n &= \sum_{k=0}^{\infty}\lambda^k\Delta_n^{(k)} \end{aligned} \tag{6.15}$$

So, in order to evaluate the energy shift up to an order $\mathcal{O}(\lambda^N)$ it's sufficient to equate the coefficients of the powers of λ, putting simply the following condition $\Delta_n^{(N)} = \langle n_0|\,\hat{V}\,|n_{N-1}\rangle$. It's evident how we need to know $|n_k\rangle$ only up to $\mathcal{O}(\lambda^{N-1})$. Adding all this in (6.15), we get

$$|n_0\rangle + \lambda\,|n_1\rangle + \cdots = |n_0\rangle + \frac{\hat{\phi}_n}{E_n^{(0)} - \hat{\mathcal{H}}_0}\left(\lambda\hat{V} - \lambda\Delta_n^{(1)} - \cdots\right)(|n_0\rangle + \lambda\,|n_1\rangle + \cdots)$$

Therefore, for $\mathcal{O}(\lambda)$ we will get the following (remembering that $\hat{\phi}_n\Delta_n^{(1)}\,|n_0\rangle = 0$)

$$|n_1\rangle = \frac{\hat{\phi}_n}{E_n^{(0)} - \hat{\mathcal{H}}_0}\hat{V}\,|n_0\rangle \tag{6.16}$$

For $\mathcal{O}(\lambda^2)$ it gets trickier. Firstly we use the definition of $\Delta_n^{(2)}$, where

$$\Delta_n^{(2)} = \langle n_0|\,\hat{V}\frac{\hat{\phi}_n}{E_n^{(0)} - \hat{\mathcal{H}}_0}\hat{V}\,|n_0\rangle$$

Plugging it into the power series approximation up to order 2, we get therefore

$$\begin{aligned} |n_2\rangle = &\frac{\hat{\phi}_n}{E_n^{(0)} - \hat{\mathcal{H}}_0}\hat{V}\frac{\hat{\phi}_n}{E_n^{(0)} - \hat{\mathcal{H}}_0}\,|n_0\rangle - \\ &- \frac{\hat{\phi}_n}{E_n^{(0)} - \hat{\mathcal{H}}_0}\,\langle n_0|\,\hat{V}\,|n_0\rangle\,\frac{\hat{\phi}_n}{E_n^{(0)} - \hat{\mathcal{H}}_0}\hat{V}\,|n_0\rangle \end{aligned} \tag{6.17}$$

Defining $\hat{\Phi} = \hat{\phi}/(E_n^{(0)} - \hat{\mathcal{H}}_0)$, we get the previous equations compacted

$$\begin{aligned} |n_1\rangle &= \hat{\Phi}\hat{V}\,|n_0\rangle \\ |n_2\rangle &= \hat{\Phi}\hat{V}\hat{\Phi}\hat{V}\,|n_0\rangle - \hat{\Phi}\left\langle \hat{V}\right\rangle_0 \hat{\Phi}\hat{V}\,|n_0\rangle \end{aligned} \tag{6.18}$$

It's evident that there is a trend in how next-order perturbations can be found, in this not-so-simple pattern.
Written explicitly, it's evident how this works

$$\begin{aligned} |n\rangle = |n_0\rangle + \lambda \sum_{k\neq n} \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}}\,|k_0\rangle + \lambda^2 \sum_{k\neq n}\sum_{l\neq n} \frac{V_{kl}V_{ln}}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_l^{(0)})}\,|k_0\rangle - \\ - \lambda^2 \sum_{k\neq n} \frac{V_{nn}V_{kn}}{(E_n^{(0)} - E_k^{(0)})^2}\,|k_0\rangle + \cdots \end{aligned}$$

§§ 6.1.2 Rayleigh-Schrödinger Perturbation Theory, Degenerate Case

What we have defined so far, fails when the eigenstates we perturb are degenerate, since we supposed that there was only one well-defined eigenvalue $E_n^{(0)}$ for each eigenket.
Let's now suppose that we have a system, for which there is a g-fold degeneracy, hence there are g unperturbed eigenkets $|m_0\rangle$ for one single $E_D^{(0)}$ eigenvalue. Let's define the degenerate eigenspace as $D := \left\{ |m_0\rangle \in \mathbb{H} \,\middle|\, \hat{\mathcal{H}}\,|m_0\rangle = E_D^{(0)}\,|m_0\rangle\,,\ m = 1, \cdots, g \right\}$. In general, the perturbation breaks the degeneracy, forming a new set of eigenkets $|l\rangle$ that do not coincide with the unperturbed set $|l_0\rangle$, although we can use the following projection

$$|l_0\rangle = \sum_{|m\rangle\in D} \langle m_0|l_0\rangle\,|m_0\rangle$$

Let's rewrite the Schrödinger equation for the new states $|l\rangle$, and define the projections $\hat{\pi}_0 = |m_0\rangle\langle m_0|$ and its coprojection $\hat{\pi}_1 = \hat{\mathbb{1}} - \hat{\pi}_0$. The Schrödinger equation then becomes

$$\left(E - \hat{\mathcal{H}}_0 - \lambda\hat{V}\right)|l\rangle = \left(E - E_D^{(0)} - \lambda\hat{V}\right)(\hat{\pi}_0\,|l\rangle + \hat{\pi}_1\,|l\rangle) = 0 \tag{6.19}$$

We separate the equation (6.19) multiplying on the left firstly by $\hat{\pi}_0$ and then by $\hat{\pi}_1$

$$\begin{aligned} \left(E - E_D^{(0)} - \lambda\hat{\pi}_0\hat{V}\right)\hat{\pi}_0\,|l\rangle - \lambda\hat{\pi}_0\hat{V}\hat{\pi}_1\,|l\rangle = 0 \\ \left(E + \hat{\mathcal{H}}_0 - \lambda\hat{\pi}_1\hat{V}\right)\hat{\pi}_1\,|l\rangle - \lambda\hat{\pi}_1\hat{V}\hat{\pi}_0\,|l\rangle = 0 \end{aligned} \tag{6.20}$$

From this equation we can then solve for $\hat{\pi}_1\,|l\rangle$ and $\hat{\pi}_0\,|l\rangle$

$$\begin{aligned} \hat{\pi}_1 = \hat{\pi}_1 \frac{\lambda}{E - \hat{\mathcal{H}}_0 - \lambda\hat{\pi}_1\hat{V}\hat{\pi}_1}\hat{\pi}_1\hat{V}\hat{\pi}_0\,|l\rangle \\ \left(E - E_D^{(0)} - \lambda\hat{\pi}_0\hat{V}\hat{\pi}_0 - \lambda^2\hat{\pi}_0\hat{V}\hat{\pi}_1\frac{1}{E - \hat{\mathcal{H}}_0\lambda\hat{V}}\hat{\pi}_1\hat{V}\hat{\pi}_0\right)\hat{\pi}_0\,|l\rangle = 0 \end{aligned} \tag{6.21}$$

The general approximation to $\mathcal{O}(\lambda^n)$ will be given from the following general expression

$$\hat{\pi}_1 |l_1\rangle = \sum_{|k\rangle \notin D} \frac{V_{kl}}{E_D^{(0)} - E_k^{(0)}} |k_0\rangle$$

And, henceforth, in order to solve for $\mathcal{O}(\lambda)$, we get the following equation

$$\left(E - E_D^{(0)} - \lambda \hat{\pi}_0 \hat{V} \hat{\pi}_0\right) \hat{\pi}_0 |l_0\rangle = 0 \tag{6.22}$$

The energy shifts $\Delta^{(1)}$ will then be the diagonal elements of the perturbation $\langle l_0| \hat{V} |l_0\rangle$
We can immediately ask why a λ^2 appears in (6.21). This is given simply by the substitution we made in order to get the equation, but we already know that the energy shift at the first order is $E_i^{(1)} = E_D^{(0)} + \lambda v_i$, where v_i are the eigenvalues of the operator $\hat{\pi}_0 \hat{V} \hat{\pi}_0$. We assume that the degeneracy is completely resolved after the application of the perturbation, hence we get $E_i^{(1)} = \lambda(v_i - v_j) \neq 0$. Since there isn't anymore degeneration in this system, we solve using nondegenerate Rayleigh-Schrödinger perturbation theory, obtaining the corrections

$$\hat{\pi}_0 \left|l_i^1\right\rangle = \lambda \sum_{j \neq i} \frac{\hat{\pi}_0}{v_j - v_i} \left|l_j^0\right\rangle \left\langle l_j^0\right| \hat{V} \hat{\pi}_1 \frac{1}{E_D^{(0)} - \hat{\mathcal{H}}_0} \hat{\pi}_1 \hat{V} \left|l_i^0\right\rangle \tag{6.23}$$

Since $\hat{\pi}_0 \left|l_j^0\right\rangle$ are eigenvectors of $\hat{V}$ we get that the energy shift at the second order is simply

$$\Delta_l^{(2)} = \sum_{k \notin D} \frac{|V_{kl}|^2}{E_D^{(0)} - E_k^{(0)}} \tag{6.24}$$

§ 6.2 Variational Methods

Approximating through variational methods is done when searching for approximate ground states energies E_0 when exact values aren't available.
We start to "guess" the ground state by defining a trial ket $\left|\emptyset\right\rangle$. We then define the following

$$\left\langle \hat{\mathcal{H}} \right\rangle = \frac{\langle \emptyset | \hat{\mathcal{H}} | \emptyset \rangle}{\langle \emptyset | \emptyset \rangle} \tag{6.25}$$

THEOREM 6.1. *There exists an upper bound to E_0, hence*

$$\left\langle \hat{\mathcal{H}} \right\rangle \geq E_0$$

Proof. We can expand $\left|\emptyset\right\rangle$ as follows

$$\left|\emptyset\right\rangle = \sum_{k=0}^{\infty} |k\rangle \langle k|\emptyset\rangle$$

Where, $\hat{\mathcal{H}}\left|k\right\rangle = E_k\left|k\right\rangle$, hence it's an exact eigenket.
We can write $E_k = E_k - E_0 + E_0$ and evaluating $\left\langle\hat{\mathcal{H}}\right\rangle$ we have

$$\left\langle\hat{\mathcal{H}}\right\rangle = \frac{\sum_{k=0}^{\infty}\left|\left\langle k|\emptyset\right\rangle\right|^2 E_k}{\sum_{k=0}^{\infty}\left|\left\langle k|\emptyset\right\rangle^2\right|} = \frac{\sum_{k=0}^{\infty}\left|\left\langle k|\emptyset\right\rangle\right|^2 (E_k - E_0)}{\sum_{k=0}^{\infty}\left|\left\langle k|\emptyset\right\rangle^2\right|} + E_0 \geq E_0$$

Obviously, the equality is given iff $\left|\emptyset\right\rangle$ is the exact ground eigenket □

This method is really powerful, since for even a poor trial ket we have $\left\langle k|\emptyset\right\rangle \sim \mathcal{O}(\epsilon)$ and $\left\langle\hat{\mathcal{H}}\right\rangle - E_0 \sim \mathcal{O}(\epsilon^2)$.
Another way to say this is saying that if we variate $\left|\emptyset\right\rangle$, the Hamiltonian will be stationary with respect to $\delta\left|\emptyset\right\rangle$.
This method doesn't say what shape does the ket $\left|\emptyset\right\rangle$ has, hence we must guess them, using the system as a guide.
Practically, it's much more useful to define a parameter vector λ_i which will appear in the considered eigenket, and then find the minimum of $\left\langle\hat{\mathcal{H}}\right\rangle$, imposing the following equation

$$\frac{\partial\left\langle\hat{\mathcal{H}}\right\rangle}{\partial\lambda_i} = 0 \tag{6.26}$$

§ 6.3 Time Dependent Perturbation Theory

§§ 6.3.1 Dirac Interaction Picture

Let's begin considering a time dependent Hamiltonian that can be split in two parts

$$\hat{\mathcal{H}}(t) = \hat{\mathcal{H}}_0 + \hat{V}(t) \tag{6.27}$$

Where one piece is time independent and the other is time dependent. We suppose that $\hat{\mathcal{H}}_0$ is exactly solvable.
Let's suppose that at $t = 0$ the state ket is given by the following relation

$$\left|\alpha\right\rangle = \sum_n c_n(0)\left|n\right\rangle \tag{6.28}$$

Where $\left|n\right\rangle$ is the eigenvalue of $\hat{\mathcal{H}}_0$.
Our objective is to find some $c_n(t)$ such that

$$\left|\alpha(t)\right\rangle = \sum_n c_n(t)e^{-\frac{iE_n t}{\hbar}}\left|n\right\rangle \tag{6.29}$$

Now, in order to simplify our problem, we define the *Dirac picture*, or *Interaction picture*, where, having considered our Hamiltonian, we have

$$\left|\alpha(t)\right\rangle_I = e^{\frac{i\hat{\mathcal{H}}_0 t}{\hbar}}\left|\alpha(t)\right\rangle_S \tag{6.30}$$

The observables in this picture will be defined as follows, in particular, for our perturbation $\hat{V}$, we have

$$\hat{V}_I = e^{\frac{i\hat{\mathcal{H}}_0 t}{\hbar}} \hat{V} e^{-\frac{i\hat{\mathcal{H}}_0 t}{\hbar}} \tag{6.31}$$

Remembering the relation between Schrödinger and Heisenberg picture, we have that

$$\begin{aligned} |\alpha\rangle_H &= e^{\frac{i\hat{\mathcal{H}}t}{\hbar}} |\alpha(t_0)\rangle_S \\ |\alpha(t_0)\rangle_S &= e^{-\frac{i\hat{\mathcal{H}}(t-t_0)}{\hbar}} |\alpha\rangle \\ \hat{A}_H &= e^{\frac{i\hat{\mathcal{H}}t}{\hbar}} \hat{A} e^{-\frac{i\hat{\mathcal{H}}t}{\hbar}} \end{aligned} \tag{6.32}$$

Hence, we have that the Dirac interaction picture will satisfy the following time dependent Schrödinger equation (remembering that $i\hbar\partial_t |\alpha(t)\rangle_I = i\hbar\partial_t(\exp\left(i\hat{\mathcal{H}}_0 t/\hbar\right) |\alpha(t)\rangle_S)$

$$i\hbar \frac{\partial}{\partial t} |\alpha(t)\rangle_I = \hat{V}_I |\alpha(t)\rangle_I \tag{6.33}$$

Where the perturbation takes the place of the Hamiltonian in the time dependent equation.
It is also demonstrable that, for an observable $\hat{A}$, its interaction picture will satisfy the following differential equation

$$\frac{\mathrm{d}\hat{A}_I}{\mathrm{d}t} = \frac{1}{i\hbar}\left[\hat{A}_I, \hat{\mathcal{H}}_0\right] \tag{6.34}$$

It's obvious that this Dirac Interaction picture is the halfway between a Schrödinger and a Heisenberg representation picture.
Going back to (6.29), we hae that in interaction picture it will simply become this

$$|\alpha(t)\rangle_I = \sum_n c_n(t) |n\rangle \tag{6.35}$$

We can now write a differential equation for $c_n(t)$.

$$i\hbar \frac{\partial}{\partial t} \langle n|\alpha(t)\rangle_I = \sum_m \langle n| \hat{V}_I |m\rangle \langle m|\alpha(t)\rangle_I \tag{6.36}$$

By definition, we have $c_n(t) = \langle n|\alpha(t)\rangle_I$, henceforth

$$i\hbar \frac{\mathrm{d}c_n}{\mathrm{d}t} = \sum_m V_{nm} e^{i\omega_{nm}t} c_m(t) \tag{6.37}$$

Where we have expanded the interaction-picture time dependence, and we have by definition of frequency

$$\omega_{nm} = \frac{E_n - E_m}{\hbar} = -\omega_{mn} \tag{6.38}$$

§§ 6.3.2 Dyson Series

Usually, exact solutions for $c_n(t)$ are not available, hence we must find a suitable approximation for our solution. One good way to start is to suppose that $c_n(t)$ can be expressed via the sum of different functions as follows

$$c_n(t) = \sum_{i=0}^{\infty} c_n^{(i)}$$

Where $c_n^{(i)}$ indicates the $i-$th transition amplitude.
This problem can be attacked, using that $c_n^{(0)} = \delta_{in}$ and then using it to define a differential equation for $c_n^{(1)}(t)$ and so on. Using operator theory, this problem can be solved even in a better way.
The time evolution operator in the Dirac picture is defined as follows

$$|\alpha(t)\rangle = \hat{\mathcal{U}}_I(t)\,|\alpha\rangle$$

For which, we know already that it's solution to the following ODE

$$\begin{cases} i\hbar \dfrac{\mathrm{d}\hat{\mathcal{U}}_I}{\mathrm{d}t} = \hat{V}_I \hat{\mathcal{U}}_I \\ \hat{\mathcal{U}}(t_0) = \hat{\mathbb{1}} \end{cases}$$

This differential equation is equivalent to the following integral equation

$$\hat{\mathcal{U}}_I(t) = \hat{\mathbb{1}} - \frac{i}{\hbar}\int_{t_0}^{t} \hat{V}_I(t_1)\hat{\mathcal{U}}_I(t_1)\,\mathrm{d}t_1$$

Iterating, we get

$$\hat{\mathcal{U}}_I(t) = \sum_{n=0}^{\infty}\prod_{k=1}^{\infty}\left(\frac{-i\hat{\mathbb{1}}}{\hbar}\right)^n \int_{t_0}^{t_{k-1}} V_I(t_k)\,\mathrm{d}t_k \tag{6.39}$$

Which is equivalent to writing the following expression

$$\begin{aligned} \hat{\mathcal{U}}_I(t) \approx \hat{\mathbb{1}} - \frac{i}{\hbar}\int_{t_0}^{t} V_I(t_1)\,\mathrm{d}t_1 \approx \\ \hat{\mathbb{1}} - \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} V_I(t_1)V_I(t_2)\,\mathrm{d}t_1\mathrm{d}t_2 + \cdots \\ \cdots + \left(\frac{-i}{\hbar}\right)^n \int_{t_0}^{t}\int_{t_0}^{t_1}\cdots\int_{t_0}^{t_{n-1}} V_I(t_1)\cdots V_I(t_n)\,\mathrm{d}t_1\cdots\,\mathrm{d}t_n \end{aligned}$$

Through this approximation, it's virtually possible to compute $\hat{\mathcal{U}}_I(t)$ to any order, and therefore $c_n(t)$. This kind of computation is fundamental in fields like atomic physics, as we will see later.

7 Identical Particles

While in classical physics, two identical particles can be distinguished, in quantum mechanics they're truly indistinguishable. Let's suppose that we have two particles, for which you have a configuration (Hilbert) space $\mathbb{H}_1$ for the first particle, and $\mathbb{H}_2$ for the second particle. The general state of the system will then be described by a ket in $\mathbb{H}_1 \otimes \mathbb{H}_2$. Hence, labeling particle 1 as α and the second as β, we then will write that a state $|s\rangle$ can be written as

$$|s\rangle = |\alpha\rangle \otimes |\beta\rangle = |\alpha\rangle\,|\beta\rangle \tag{7.1}$$

It's obvious that, since the particles in study are impossible to distinguish, that the state $|s\rangle$ can also be written also as $|\beta\rangle \otimes |\alpha\rangle$, hence, for the principle of quantum superposition, we must have that the most general state will be the following, for a two particle system

$$|s\rangle = c_1\,|\alpha\rangle \otimes |\beta\rangle + c_2\,|\beta\rangle \otimes |\alpha\rangle \tag{7.2}$$

This definition brings us what's known as *exchange degeneracy*. This degeneracy brings us a huge problem, since in this case, the eigenvalue of the complete basis doesn't completely define the state ket.
Before diving into the nature of exchange degeneracy, we define a new operator, called *exchange operator*, or just $\hat{P}_{ij}$. It will act as follows:
Let $|a_i\rangle \in \mathbb{H}_1$ and $|a_j\rangle \in \mathbb{H}_2$, and consider the new state $|a_i\rangle \otimes |a_j\rangle \in \mathbb{H}_1 \otimes \mathbb{H}_2$. We will have

$$\begin{aligned}
\hat{P}_{ij}\,|a_i\rangle \otimes |a_j\rangle &= \lambda\,|a_j\rangle \otimes |a_i\rangle \\
\hat{P}_{ij} &= \hat{P}_{ji} \\
\hat{P}_{ij}^2 &= \hat{\mathbb{1}} \to \lambda = \pm 1
\end{aligned}$$

In general, if we have an observable $\hat{a}$, such that

$$\begin{aligned}
\hat{a}_i\,|a_i\rangle &= a\,|a_i\rangle \\
\hat{a}_j\,|a_j\rangle &= b\,|a_j\rangle
\end{aligned}$$

We get, after applying an exchange transformation

$$\begin{aligned}
\hat{P}_{ij}\hat{a}_i\hat{P}_{ij}^{-1}\,|a_i\rangle\,|a_j\rangle &= a\,|a_i\rangle\,|a_j\rangle \\
\hat{P}_{ij}\hat{a}_i\hat{P}_{ij}^{-1}\,|a_j\rangle\,|a_i\rangle &= a\,|a_j\rangle\,|a_i\rangle
\end{aligned}$$

This is valid only if $\hat{P}_{ij}\hat{a}_i\hat{P}_{ij}^{-1} = \hat{a}_j$, hence, this exchange operator, applied on a system observable, changes its label, hence basically in which space of the two of the tensor space $\mathbb{H}_1 \otimes \mathbb{H}_2$ the operator $\hat{a}_i$ will act.
Let's now consider a general two-particle Hamiltonian. It will be the following

$$\hat{\mathcal{H}} = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} + V\left(\left|x_1^i - x_2^i\right|\right) + V_e(x_1^i) + V_e(x_2^i) \tag{7.3}$$

This Hamiltonian is obviously invariant to exchange of particles, hence $\left[\hat{\mathcal{H}}, \hat{P}_{12}\right] = 0$ and $\hat{P}_{12}$ is a constant of motion
If we call the Hamiltonian's eigenket $|a_1\rangle |a_2\rangle$, we can select two main common basis eigenkets as follows

$$|s\rangle = \frac{1}{\sqrt{2}}\left(|a_1\rangle |a_2\rangle + |a_2\rangle |a_1\rangle\right)$$
$$|a\rangle = \frac{1}{\sqrt{2}}\left(|a_1\rangle |a_2\rangle - |a_2\rangle |a_1\rangle\right)$$

Where they are tied through two operators, the *symmetrization* operator and the *antisymmetrization* operator, defined as follows

$$\begin{aligned}\hat{T}_+ &= \frac{1}{2}\left(\hat{\mathbb{1}} + \hat{P}_{12}\right)\\ \hat{T}_- &= \frac{1}{2}\left(\hat{\mathbb{1}} - \hat{P}_{12}\right)\end{aligned} \tag{7.4}$$

Hence, applied to a ket $|a_1\rangle \otimes |a_2\rangle$, we have

$$\hat{T}_\pm\left(c_1 |a_1\rangle \otimes |a_2\rangle + c_2 |a_2\rangle \otimes |a_1\rangle\right) = \frac{c_1 \pm c_2}{2}\left(|a_1\rangle \otimes |a_2\rangle \pm |a_2\rangle \otimes |a_1\rangle\right)$$

This finally gives the final symmetry of the system.

§ 7.1 Symmetrization Postulate

We will now delve shortly into quantum statistical mechanics. Here we have two statistics, *Fermi-Dirac statistics* and *Bose-Einstein statistics*. Particles that satisfy Fermi-Dirac statistics are said to be *fermions* and those who satisfy Bose-Einstein statistics are said to be *bosons*. Under exchange of two particles, we have that, if we indicate with $|b\rangle$ bosons and with $|f\rangle$ fermions, that for a system of N identical particles

$$\begin{aligned}\hat{P}_{ij}\bigotimes_{i=1}^{N}|b\rangle_i &= \hat{P}_{ij}|B\rangle_i = |B\rangle_j = \bigotimes_{j=1}^{N}|b\rangle_j\\ \hat{P}_{ij}\bigotimes_{i=1}^{N}|f\rangle_i &= \hat{P}_{ij}|F\rangle_i = -|F\rangle_j = -\bigotimes_{j=1}^{N}|f\rangle_j\end{aligned} \tag{7.5}$$

This change of sign is dependent from the spin-wavefunction, determining that antisymmetric particle wavefunctions have half-integer spin, and symmetric particle wavefunctions have integer spin.
Empirically for fermions (half-integer spin particles), it's known that they must obey the *Pauli exclusion principle*, which states that two identical fermions cannot share the same quantum state.

For only two fermions, if we want to write the ground state wavefunction, we know that due to its antisymmetry, it must be the following

$$|GS\rangle_f = \frac{1}{\sqrt{2}}\left(|f_1\rangle\,|f_2\rangle - |f_2\rangle\,|f_1\rangle\right) \tag{7.6}$$

This is the only possible configuration. For bosons, instead, we have three possible configurations

$$|GS\rangle_b = |b_1\rangle\,|b_1\rangle\,, \quad |b_2\rangle\,|b_2\rangle\,, \quad \frac{1}{\sqrt{2}}\left(|b_1\rangle\,|b_2\rangle + |b_2\rangle\,|b_1\rangle\right) \tag{7.7}$$

§§ 7.1.1 Two Electron System

The most simple system composed by two fermions is the two-electron system. Since it's fermionic, we already know that the eigenvalue of the exchange operator must be -1.
Let's say that our base kets are specified by $|i, m_{s_i}\rangle$ where $i = 1, 2$ indicates the electron and m_{s_i} indicates the particle's spin magnetic quantum number. The most general state will then be given by a linear combination of these basis kets as follow

$$|\psi\rangle = \sum_{m_{s_1}}\sum_{m_{s_2}} |s_1, s_2, m_{s_1}, m_{s_2}\rangle\,\langle s_1, s_2, m_{s_1}, m_{s_2}|\psi\rangle$$

Or, in terms of wavefunctions

$$\psi_{jm}(x_1^i, x_2^i) = \sum_{m_{s_2}}\sum_{m_{s_1}} C(m_{s_1}, m_{s_2})\psi_{m_{s_1}m_{s_2}}(x_1^i, x_2^i)$$

Where with $C(m_{s_1}, m_{s_2})$ we indicated the Clebsch-Gordan coefficients for the sum of two spin $1/2$ systems.
Analogously, if $\left[\hat{\mathcal{H}}, \hat{S}^2_{tot}\right] = 0$, we have that the eigenvalues (and hence eigenfunctions) of the system will be given by the tensor product $|E\rangle \otimes |sm\rangle$. Since the wavefunction associated with $|sm\rangle$ is a spinor, we will have that our wavefunction will be given by

$$\psi_{jm}(x_1^i, x_2^i) = \phi(x_1^i, x_2^i)\chi_\pm$$

With $\chi_\pm$ as our basis spinor.
Due to the properties requested by the fermion statistics, we must have that, if $\chi_\pm = |\pm\rangle$, it «*must*» be one of these four

$$|\pm\rangle = \begin{cases} |+\rangle\,|+\rangle \\ \dfrac{1}{\sqrt{2}}\left(|+\rangle\,|-\rangle + |-\rangle\,|+\rangle\right) \\ |-\rangle\,|-\rangle \\ \dfrac{1}{\sqrt{2}}\left(|+\rangle\,|-\rangle - |-\rangle\,|+\rangle\right) \end{cases} \tag{7.8}$$

Applying our exchange operator we have that the first three are symmetric, which are commonly called triplet states, and the last one is antisymmetric with respect to exchange of particles, and it's called a

singlet state.
Another particular relation of the particle exchange operator is obvious if we see how it acts on our kets.
We have that $\langle s_1 s_2 m_{s_1} m_{s_2}| \hat{P}_{12} |\alpha\rangle = \langle s_2 s_1 m_{s_1} m_{s_2}|\alpha\rangle$, and we also know that $\langle s_1 s_2 m_{s_1} m_{s_2}|\alpha\rangle = -\langle s_2 s_1 m_{s_2} m_{s_1}|\alpha\rangle$ from the Fermi-Dirac statistic, followed by electrons.
Hence, a full exchange operator $\hat{P}_{12}$ will be given instead by the tensor product of the spatial particle exchange operator and the spin exchange operator, as

$$\hat{P}_{12} = \hat{P}^p_{12} \otimes \hat{P}^s_{12}$$

A thorough application of this theory for $s = 1/2$ systems will be treated in a further section where it will be studied together with atomic physics.

§ 7.2 Multiparticle States

As we've already seen previously, multiparticle states can be defined as a multiple tensor product of single particle states. As we've already seen, the particle exchange operator is idempotent, i.e. $\hat{P}^2_{ij} = \hat{\mathbb{1}}$, thus the possible eigenvalues are ± 1. It must be noted tho, that in general

$$\left[\hat{P}_{ij}, \hat{P}_{kl}\right] = \hat{P}_{ij}\hat{P}_{kl} - \hat{P}_{kl}\hat{P}_{ij} \neq 0 \tag{7.9}$$

Let's now consider a 3 particle state. We have that there are $3!$ possible combinations of the single particle states $|p_1\rangle |p_2\rangle |p_3\rangle$. If we insist on our symmetrization postulate, we have that we can either have a single completely antisymmetric state or a single fully symmetric state. This states must hence be a linear combination of 6 equally probable states, formed by the tensor product of the different particles. This state is an eigenstate for $\hat{P}_{12}, \hat{P}_{23}, \hat{P}_{13}$. Defining a new exchange operator $\hat{P}_{123} = \hat{P}_{12} \otimes \hat{P}_{13}$, we have that a completely symmetrical state can be written, (remember that if two indices are equal then there can't be a completely antisymmetric state)