Molecular Physics

Giacomo Fantoni

telegram: @GiacomoFantoni

Ilaria Cherchi

Telegram: @ilariacherchi

Alessia Guadagnin Pattaro

Telegram: @alessiagp

Elisa Pettinà

Telegram: @elispettina

Stefano Cretti

Telegram: @StefanoCretti

Github: https://github.com/giacThePhantom/MolecularPhysics

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Chapter 1

Revisiting classical mechanics

1.1 Physical theories

1.1.1 Experiment

An experiment performed on a physical system is a way to measure observable quantities at a determined time: $O_1(t), \ldots, O_n(t)$. By measuring more and more observables at the same time, the instantaneous state of the system becomes increasingly characterized. A maximum set of observables that leads to the complete characterization of the instantaneous state can be assumed.

1.1.1.1 Example - particle of mass m subject to an harmonic force

A particle of mass m subject to an harmonic force like one of a spring is completely characterized by:

$$(\vec{r}(t), \vec{v}(t)) = \vec{r}(t) \in \mathbb{R}^6$$

1.1.2 Definition

A physical theory is a mathematical scheme to predict the state of the system, the outcome of future observations: $O_1(t'), \ldots, O_n(t')$. In particular, an equation that can be used to compute the state at t' given the state at t is called an equation of motion. A physical theory is composed by the following elements:

- definition of the state of a system
- recipe to determine the system's equation of motion

- prediction of an observable quantity given the state of the system

1.2 Classical mechanics

In classical mechanics, the state of a system is a collection at time t of all the positions of all the particles in the system. We also need to define the velocity of the particle, or, better, the momentum. The latter is obtained, in classical mechanics, by scaling the velocity by a constant being in this way equivalent to it. The mathematical tool that allows to understand how a state evolves in time is the

time derivative of the equation of interest. Solving a classical mechanics problem means to solve a set of differential equations.

1.2.1 Newtonian mechanics

Newtonian Mechanics is a theory described by the three Newton's laws, which are in principle well stated:

1. A body will continue its state at rest or at constant speed unless a force acts. This is only true in inertial frames. The lack of an initial consensus inertial frame raises issues.

2. How does the body change when it is subject to a force. It's difficult to define exactly what is a force: here we only deal with mass and acceleration. We have an issue, stuck in a loop.

3. Whenever object A acts on object B, B acts on A with opposite sign. This is the action-reaction principle.

1.2.2 Example - point particle moving in $1D$ and subject to an harmonic force

For a point particle moving in $1D$ subject to an harmonic force (bound to a spring for example) follows the Newton's law for its equation of motion:

$$\frac{d^2}{dt^2}x(t) = -\frac{k}{m}x(t)$$

If, given λ the amplitude, L the oscillation and L_0 the distance of the point from the origin of the axis at time 0:

- $\frac{\lambda}{L} \ll 1$
- $\frac{\lambda}{L_0} \ll 1$.
- $\frac{L}{L_0} \ll 1$.

This is a second-order differential equation such that $\frac{d^2}{dt^2}f(t) = -\frac{k}{m}f(t)$. There are only two solutions:

$$f_1(t) = \sin(\omega t) \Rightarrow \frac{d^2}{dt^2}f_1(t) = -\omega^2 f_1(t)$$

$$f_2(t) = \cos(\omega t) \Rightarrow \frac{d^2}{dt^2}f_2(t) = -\omega^2 f_2(t)$$

Clearly, $f_1(t)$ and $f_2(t)$ are solutions if $\omega^2 = \frac{k}{m}$. Neither of them is a good solution: the first one is only valid if the particle starts at the origin, while the second one only holds if the particle is at rest at time 0. So the most general solution is:

$$x(t) = A\cos\sqrt{\frac{k}{m}}t + B\sin\sqrt{\frac{k}{m}}t$$

To find A and B, information about the initial conditions are used. Let the initial position $x(0) = x_0$. Then

$$x(0) = A = x_0$$

Considering initial velocity: $\frac{d}{dt}x(t)|_{t=0} = v_0$, then:

$$\frac{d}{dt}x(t) = -\sqrt{\frac{k}{m}}A\sin\sqrt{\frac{k}{m}}t + \sqrt{\frac{k}{m}}B\cos\sqrt{\frac{k}{m}}t$$

$$v_0 = \sqrt{\frac{k}{m}}B \Rightarrow B = \sqrt{\frac{m}{k}}v_0$$

So the final solution is:

$$\begin{cases} x(t) = x_0\cos\sqrt{\frac{k}{m}}t + \sqrt{\frac{m}{k}}v_0\sin\sqrt{\frac{k}{m}}t \\ v(t) = v_0\cos\sqrt{\frac{k}{m}}t - x_0\sqrt{\frac{k}{m}}\sin\sqrt{\frac{k}{m}}t \end{cases}$$

1.2.3   Phase-space

It is convenient to plot the solutions on the phase space, a plane such that on the x-axis there is the position $x = q(t)$ and on the y-axis the momentum $m \times v = p(t)$. In this way the state of the system will be described as:

$$\Gamma(t) = (q(t), p(t))$$

Cauchy's theorem implies that given a n-th order differential equation and given n initial conditions, there exists exactly one solution. Its corollary implies that trajectories in the phase-space can never intersect. Because of this classical mechanics is fully deterministic, as future $x(t)$ and $v(t)$ can be unambiguously predicted.

1.2.4   Systems in three dimension and with more than one particle

For systems with $D = 3$ and for more than one particle the equation of motion is:

$$\begin{cases} m_1\frac{d^2}{dt^2}\vec{r}_1(t) = \vec{F}_1(\vec{r}_1(t), \dots, \vec{r}_N(t)) \\ \vdots \\ m_N\frac{d^2}{dt^2}\vec{r}_N(t) = \vec{F}_N(\vec{r}_1(t), \dots, \vec{r}_N(t)) \end{cases}$$

Correspondingly, the phase-space is $6N$ dimensional. Moreover, for the N vector equations there are N scalar ones.

1.2.5   Work and energy

Let $\vec{r}$ be a trajectory followed by a particle subject to a force $\vec{F}$. The work of the force $\vec{F}$ from point A to point B of the trajectory is defined as:

$$W_{AB} = \int_{\vec{r}_a}^{\vec{r}_b} d\vec{r} \cdot \vec{F}$$

The kinetic energy of the particle is instead:

$$T = \frac{1}{2}mv^2$$

Work and energy are related:

$$\frac{d}{dt}T = \frac{d}{dt}\frac{1}{2}mv^2 = \frac{1}{2}m\frac{d}{dt}v^2 = \frac{1}{2}2m\vec{v}\underbrace{\frac{d\vec{v}}{dt}}_{\vec{a}} = \vec{v}\vec{F}$$

$$\int_{t_0}^{t_f} dt\frac{d}{dt}T = T_B - T_A = \int_{t_i}^{t_f} dt\frac{d\vec{r}}{dt}\vec{F} = \int_{\vec{r}_A}^{\vec{r}_B} d\vec{r}\cdot\vec{F} = W_{AB}$$

$$T_B - T_A = W_{A\to B}$$

1.2.5.1 Conservative forces

For conservative forces, the work from point A to point B does not depend on the path followed. In particular, for each path 1 and 2: $W_{AB}^1 = W_{AB}^2$ and:

$$-W_{AB} = U(\vec{r}_B) - U(\vec{r}_A)$$

Where $U(\vec{r})$ is the potential energy. In one dimension:

$$U(r) - U(r_0) = -w_{x_0 x} = -\int_{x_0}^{x} dyF(y) \Rightarrow$$

$$-\frac{d}{dx}U(x) = F(x)$$

1.2.5.1.1 Three dimensional case

$$\begin{cases} F_x(x,y,z) = -\frac{\partial}{\partial x}U(x,y,z) \\ F_y(x,y,z) = -\frac{\partial}{\partial y}U(x,y,z) \\ F_z(x,y,z) = -\frac{\partial}{\partial z}U(x,y,z) \end{cases}$$

Or, in short hand notation, let $\vec{r} = (x,y,z)$ and $\vec{\nabla}(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z})$, then:

$$\vec{F}(\vec{r}) = -\vec{\nabla}U(\vec{r})$$

1.2.5.1.2 Central forces

Central forces are a notable class of conservative forces, for which $\vec{F}(\vec{r}) = \hat{\omega}_r f(r)$ and $\vec{r} = \hat{U}_r|\vec{r}| = \hat{U}_r r$. Some examples:

- Coulomb: $\vec{F}_e = \hat{U}_{\vec{r}}\frac{q_1 q_2}{r_{12}^2}$
- Gravity: $\vec{F}_G = -\hat{U}_r\frac{M_1 M_2}{r_{12}^2}G$

- Harmonic $\vec{F} = -\hat{\omega}_r(\vec{r} - \vec{r}_0)$
- $\cdots$

1.2.6 Conservation of mechanical energy

Reconsidering the relationships between T and W:

$$T_B - T_A = W_{A\to B} = U_A - U_B$$

The mechanical energy H can be introduced, such that:

$$H_A = T_A + U_A = T_B + U_B = H_B$$

The mechanical energy is conserved in the system only if conservative forces act on it. Energy conservation allows us to solve Newton's equation, which is generally impossible to handle. This is because conservation laws help gaining partial information without having to solve Newton's equation. At this level, energy conservation comes in as a matter of convenience.

1.2.6.1 Example

Consider a cart going down a path with a loop. Let A be the starting highest point when it starts going and B the lowest point where it stops accelerating.

$$\begin{cases} H_A = \underbrace{T_A}_{=0} + \underbrace{U_A}_{=mgh} \\ H_B = \underbrace{T_B}_{-\frac{1}{2}mv^2} + \underbrace{U_B}_{=0} \end{cases} \Rightarrow v_B = \sqrt{2gh}$$

1.2.7 Angular momentum conservation

Let the angular momentum:

$$\vec{L}(t) = \vec{r}(t) \times m\vec{v}(t)$$

The angular momentum is also defined as the vector product of the particle position and its linear momentum.

$$\vec{L} = \bar{x} \times \bar{P}$$

There are two ways to solve a cross product: $\vec{a} \times \vec{b} \perp \vec{a}$, $\vec{a} \times \vec{b} \perp \vec{b}$ and $|\vec{a} \times \vec{b}| = |\vec{a}||\vec{b}| \sin\theta$. This implies that $\vec{a} \parallel \vec{b} \Rightarrow \vec{a} \times \vec{b} = 0$. Now considering the vectors' coordinates:

$$\vec{a} \times \vec{b} = \hat{i}(a_y b_z - a_z b_y) + \hat{j}(a_x b_z - a_z b_x) + \hat{k}(a_x b_y - a_y b_x)$$

By taking the derivative of the angular momentum with respect to time, we can asses under which conditions linear momentum is conserved. Consider that velocity and momentum are parallel, therefore the cross product depending on the angle between them is zero:

$$\frac{d}{dt}\vec{L} = \frac{d}{dt}(\vec{r} \times \vec{p}) =$$
$$= \underbrace{\frac{d\vec{r}}{dt}}_{=0} \times \vec{p} + \underbrace{\frac{d\vec{p}}{dt}}_{=F} \times \vec{r} =$$
$$= \vec{r} \times \vec{F}$$

Whenever the torque of a particle is zero, then the angular momentum of that particle is conserved. This is the case for centripetal and centrifugal forces.

$$\frac{d\vec{L}}{dt} = \bar{x} \times \vec{F} = 0$$

The following is true for any force:

$$\frac{d}{dt}\left(\vec{L}_{\text{TOT}}\right) = \frac{d}{dt}\left(\Sigma_i \vec{L}_i\right) = 0$$

If $\vec{r} \parallel \vec{F} \Rightarrow \frac{d}{dt}\vec{L} = 0$. Therefore, for a conservative force there is angular momentum conservation. Summarizing, the motion in a central force conserves energy and angular momentum.

1.3 Hamiltonian formulation of mechanics

In the Newtonian formulation, the fundamental aspect is the force:

$$m\vec{a} = \vec{F}$$

Defining a physical theory in classical mechanics corresponds to specifying what is a force.

1.3.1 Hamilton's theory

Hamilton's theory is an equivalent reformulation of mechanics in which the key concept is not the force, but the Hamiltonian H, which is closely related to energy. While from a practical standpoint the two formulation are equivalent with identical equations of motion, modern physics has shown that the notion of energy is more fundamental than the one of force. In this formulation the derivative of the position will be the derivative of H with respect to position. It can be noted that from $H(p, q)$ it is possible to retrieve Newton's equations of motion, solve them and obtain predictions to compare with experimental results following:

1. Define H.

2. Compute equation of motion.

3. Solve equation of motion.

4. Use solution to obtain predictions of experimentally observable quantities.

5. Experimentally test the prediction.

This procedure is repeated until concordance with experiments is reached. In this formulation the concept of force is never defined.

1.3.2 Hamilton's equations

From this point on, energy will be identified in an Hamiltonian:

$$H(\underbrace{\vec{p}}_{\text{momentum}}, \underbrace{\vec{q}}_{\text{position}}) = \frac{\vec{p}^2}{2m} + U(\vec{q})$$

So the equations of motion become:

$$\begin{cases} \dot{q} = +\frac{\partial H}{\partial p} \Rightarrow \dot{q} = \frac{p}{m} \Rightarrow p = \dot{q}m \\ \dot{p} = -\frac{\partial H}{\partial q} \Rightarrow \dot{p} = -\frac{\partial U(q)}{\partial q} \Rightarrow ma = F \end{cases}$$

The Hamilton's equation describes directly the evolution of a point of phase space and the state of the system. Let $\Gamma = (p, q)$ and $H = H(\Gamma)$, then:

$$\begin{cases} \dot{\Gamma}_1 = +\frac{\partial H}{\partial \Gamma_2} \\ \dot{\Gamma}_2 = +\frac{\partial H}{\partial \Gamma_1} \end{cases}$$

Definition 1 *Phase space: In dynamical system theory, a phase space is a space in which all possible states of a system are represented, with each possible state corresponding to one unique point in the phase space. For mechanical systems, the phase space usually consists of all possible values of position and momentum variables.*

For many particles in three dimensions:

$$\Gamma \overbrace{\underbrace{(\vec{p}_1, \ldots, \vec{p}_N}_{\vec{P} \in \mathbb{R}^{3N}}; \underbrace{\vec{q}_1, \ldots, \vec{q}_N)}_{\vec{Q} \in \mathbb{R}^{3N}}}^{\Gamma \in \mathbb{R}^{6N}}$$

The state of a many body system is described by the evolution of a point in a large dimensional vector space.

1.3.3 Harmonic oscillator

Consider $\omega = \sqrt{\frac{k}{m}}$:

$$\begin{cases} p(t) = -\omega q_0 \sin \omega t + v_0 \cos \omega t \\ q(t) = q_0 \cos \omega t + \frac{v_0}{\omega} \sin \omega t \end{cases}$$

Now from that:

$$\frac{p^2}{\omega^2} + q^2 = q_0^2 \sin^2 \omega t + \frac{v_0^2}{\omega^2} \cos^2 \omega t - 2\frac{q_0 v_0}{\omega} \sin \omega t \cos \omega t + q_0^2 \cos^2 \omega t + \frac{v_0^2}{\omega_2} \sin^2 \omega t + 2\frac{q_0 v_0}{\omega} \sin \omega t \cos \omega t =$$

$$= (q_0^2 + \frac{v_0^2}{\omega^2}$$

The problem has a general structure of $\frac{q^2}{A} + \frac{p^2}{B} = 1$ and the trajectories draw ellipses in the phase space.

1.4 Classical theory of the hydrogen atom

The classical theory of the hydrogen atom is defined by the classical Bohr model. The hydrogen atom is formed by a proton in the centre with an electron orbiting around it.

1.4.1 Approximations

The classical Bohr model makes some approximation to better model the atom:

- The mass of the electron divided by the mass of the proton is around $\frac{1}{2000}$ ($\frac{m_e}{M_p} \approx \frac{1}{2000}$). The center of mass of the system is very close to the nucleus, therefore we can assume that the nucleus remains still. For the sake of simplicity, an infinite proton mass $\frac{m_e}{M_p} = 0$ is assumed.

- The charge of the proton is the negative of the charge of the electron, so the overall system is neutral.

- Because $\frac{d}{dt}\vec{L} = 0$ (angular momentum conservation), the electron's motion occurs on a plane and is two dimensional.

1.4.2 Newton's equation

Let us start from Newton's equations. We wish to express the attracting force acting on the electron towards the proton. This force has an inward direction with negative sign. Since the electron coordinates x, y, z are varying with time, they can be expressed as $x(t)$, $y(t)$ and $z(t)$. The equations are coupled, meaning that we cannot solve one at a time: $y(t)$ and $z(t)$ are required for solving the first one and the same applies to the others. This is a quite tricky task, but luckily there is a way round this problem. We can employ the energy conservation that we mentioned previously though the usage of polar coordinates.

1.4.3 Mechanical energy in polar coordinates

$$H = \underbrace{\frac{p^2}{2m}}_{\text{kinetic energy}} - \underbrace{\frac{e^2}{r}}_{\text{potential energy}}$$

In this case we have a position vector r going from the proton to the electron. The Coulombic force is a radial centripetal force: it points on the same line of the position, so F is parallel to r. The mathematical expression shows that forces are anti-parallel. Rather than using Cartesian coordinates, we can use rotating coordinates. The centrality of force will imply two main results: mechanical energy is conserved and the angular momentum of the particle is the torque, but it is zero for centripetal force, so $\vec{L}$ is conserved. The second considerations lead us to understand that orbit lines are confined on a plane. This is particularly relevant, as in a plane we only need two coordinates, as the third coordinate is fixed to zero. The potential energy is derived from Coulomb's $F = -\hat{r}\frac{e^2}{|\vec{r}^2|}$, so $U(|\vec{r}|) = -\frac{e^2}{|\vec{r}|}$ Now, by using conservation to replace the differential equation, the position is divided in two components $\hat{u}_r$ and $\hat{u}_\theta$ orthogonal to each other, so that $v^2 = v_r^2 + v_\theta^2$:

$$\vec{v} = \hat{u}_\theta v_\theta + \hat{u}_r \underbrace{v_r}_{\frac{dr}{dt}} \Rightarrow v^2 = \left(\frac{dr}{dt}\right)^2 + v_\theta^2$$

Now, rewriting the angular momentum:

$$\vec{L} = m\vec{r} \times (\underbrace{\vec{v}_r}_{=0} + \vec{v}_\theta) = m\vec{r} \times \vec{v}_\theta$$

$$|L| = mrv_\theta$$

$$L^2 = m^2 r^2 v_\theta^2$$

Substituting this in the Hamiltonian:

$$H = \frac{1}{2}mv_r^2 + \frac{1}{2}mv_\theta^2 - \frac{e^2}{r} =$$
$$= \frac{1}{2}mv_r^2 + \underbrace{\frac{L^2}{2mr^2}}_{\text{Simil-potential, L constant}} - \frac{e^2}{r}$$

This term depends on r and not on θ and effectively looks like a potential energy. So $\frac{L^2}{2mr^2} - \frac{e^2}{r} \equiv V_{eff}(r)$. And:

$$H = \frac{1}{2}m\left(\frac{dr}{dt}\right)^2 + V_{eff}(r)$$

By using polar coordinates and angular momentum conservation, the mechanical energy has been written in the form of an effective one dimensional system with $U(r) \to V_{eff}(r)$. Using this trick, it is immediate to infer the qualitative structure of orbits.

1.4.4 Case 1 - $E > 0$

The case in which $E > 0$ is the case of an unbound orbit. The electron approaches the proton and accelerates. There is an inversion point and:

$$\begin{cases} H = \frac{1}{2}m\left(\frac{dr}{dt}\right)^2 + V_{eff}(r) \\ \| \\ E < V_{eff}(r) \end{cases} \Rightarrow \left(\frac{dr}{dt}\right)^2 < 0$$

And that is impossible.

1.4.5 Case 2 - $E < 0$

The case in which $E < 0$ is the case of the bound orbit. The electron is trying to escape the proton and there are two inversion points.

1.4.6 Conclusion

Whenever a charge changes its velocity it emits $\frac{e}{m}$ radiations. The energy loss per unit time is:

$$P = \frac{2}{3}\frac{m_e r_e}{c}a^2 \qquad a = \omega^2 r$$

According to Larmer's law, the electron would spiral into the nucleus in $10^{-15}s$. Because of this, classical atoms are unstable.

Chapter 2

Breakdown of classical mechanics

2.1 The fall of determinism

2.1.1 Double slit experiment

The double-slit experiment is a virtual experiment, because it cannot be performed as we will describe it due to technological limitations. However, we can treat is as a real experiment, as it can summarize many technically feasible and performed experiments. The setup of this experiment consists of a gun shooting particles through a screen with two holes and a detection screen behind the first one.

2.1.1.1 Case 1 - particles are macroscopic bullets
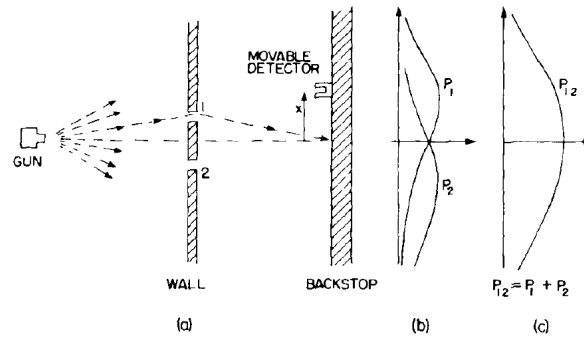
Figure 2.1: Double-slit experiment with bullets

In the case in which the gun shoots macroscopic bullets, we imagine the distance gun-screen to be large, implying that the bullets might arrive at different locations due to error, vibrations, wind, etc. Therefore, we expect bullets to arrive as a beam.

2.1.1.1.1 Results Most of the bullets will not reach the second wall, as they will remain stuck on the first one. However, the ones directed towards the holes will pass through. We expect to

obtain a distribution of bullets for hole 1 and hole 2. If we shut down one hole 2, nothing will pass through it leading to a p_1 distribution. Conversely, if we shut down hole 1, we will observe p_2. Summarizing, we will find the following observations:

1. Bullets arrive one-by-one, we can recognize the sound of each bullet impacting the screen (if sufficient resolution is available for the recording)

2. $P(z)$, the probability of a bullet reaching a point, can be obtained by plotting a histogram of the times a bullet has hit the point of interest. Through a statistical model we could then predict future locations.

3. Considering the experiment with one of the holes shut, a Gaussian like probability of detection P_1 can be seen such that μ is directly perpendicular to the hole.

4. If both holes are open there is a **ballistic behaviour** and the resulting distribution of detection P_{12} is the sum of the two deriving for each hole open by itself. As a consequence,P_1 and P_2 are disjoint events:

$$P_{12} = P_1 + P_2$$

2.1.1.2 Case 2 - macroscopic waves in a tank
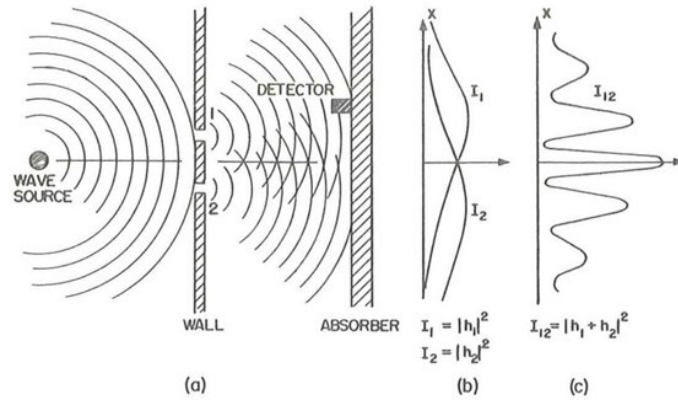
Figure 2.2: Double-slit experiment with waves

Suppose that rather than having a screen, we have a tank of water with a wall with two holes. In this case, we have an instrument producing waves e.g. something touching water. Since the source is very far, waves that will reach the wall will be plane waves. We want to measure whether the waves manage to impact the second wall. From each of the holes, we will observe circular waves. We can repeat the previous procedure of shutting each hole at a time. The maximum intensity (square of max amplitude) will be observed at the hole.

2.1.1.2.1 Results   When the wave arrives, it reaches different locations at the same time (delocalization), very differently from bullets. A second difference is what we obtain when we let waves pass through both holes. The obtained pattern has alternating minima and maxima and it can be seen that $P_{12} \neq P_1 + P_2$. Consider the Ps as the intensities of the waves, and A as the amplitudes. In this case we obtain an **interference pattern**, as waves can sum and subtract in a non-trivial way (waves are complex objects). So, deriving from wave theory:

$$P_1 = |A_1|^2 = A_1^* A_1$$

$$P_2 = |A_2|^2 = A_2^* A_2$$

$$A_{12} = A_1 + A_2 \rightarrow P_{12} = |A_1 + A_2|^2 =$$
$$= A_1^* A_1 + A_2^* A_2 + \underbrace{A_1^* A_2 + A_1 A_2^*}_{\text{interference}}$$

Unlike bullets, wave hit the entire screen and not at a precise time. This results in a wave-like behaviour with delocalization.

2.1.1.3 Case 3 - cathode as an electron gun
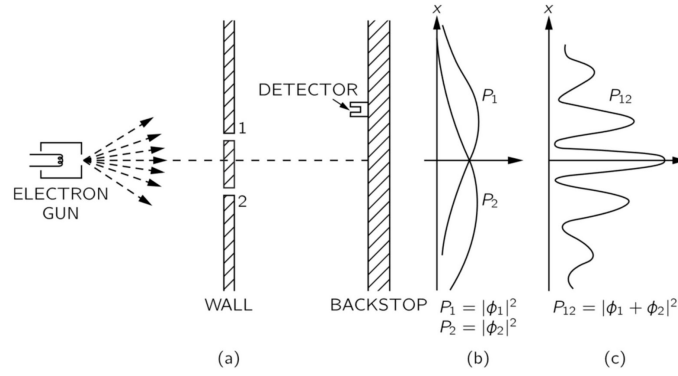
Figure 2.3: Double-slit experiment with electrons

Finally, let us have a cathode electron gun shooting electrons at a wall with very small holes - which need to be so small that the effect becomes evident. As before, we close one of the holes and the screen will record the arrival of electrons on the wall through a detector (device producing a small signal as soon as an electron arrives). If we place many detectors on the wall, we will retrieve when and where the electron has arrived. The electron signals arrive one at a time, as a "rain". If we open both holes, an interference pattern will be observed: P_{tot} is not the sum of the single probabilities, implying that the two are not disjoint events.

2.1.1.3.1 Results Result: we observe either a particle-like behaviour (one hole closed) or a wave-like behaviour (both holes open).

2.1.1.3.2 Particle detector at the holes To verify whether the electron goes through both holes simultaneously, an apparatus that emits a signal if an electron travels nearby is put near the holes. Detection on the screen happens only if the signal is emitted. The two apparatuses never trigger a signal together, meaning that the electron travels through one of the holes like a particle.

We can define P_{A_1} as the probability that counts only events in which A_1 is triggered, and P_{A_2} the results of counting only events triggering A_2. By counting all the events, it can be seen that the
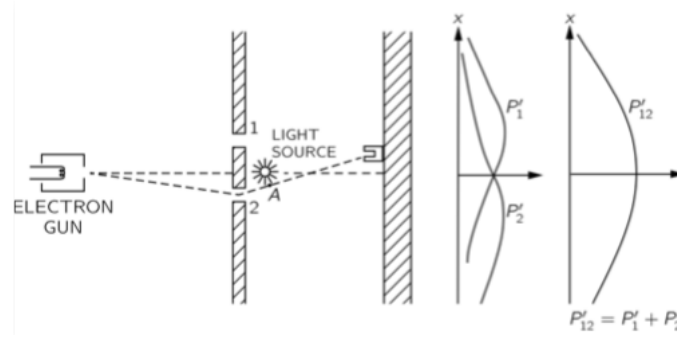
Figure 2.4: Double-slit experiment with electrons and apparatus emitting a signal

resulting pattern is $P_{A_1} + P_{A_2}$. In the case in which $P_{A_1+A_2} = P_{A_1} + P_{A_2}$, delocalization is lost and the electron assumes a **ballistic behaviour**.

2.1.1.3.3 Summary Summarizing, measurement affects the nature of the electron and can change the state of the system. When we try to measure where the particle goes, we observe a ballistic behaviour. Conversely, if we do not impose any measurement, we will obtain an interference pattern. The result depends on the kind of behaviour we are trying to detect.

2.1.1.3.3.1 Example Suppose that we are blind. We can detect a ball by throwing something smaller at it e.g. pen cap. If instead we throw a pen cap towards with another pen cap, we will have a collision and both objects will end up in a different location. The act of measuring has changed the system! Throwing photons at electrons perturbs the system, as they are comparable in size.

2.1.1.4 Conclusions

The notion of trajectory loses significance for microscopic particles. This is quantified by **Heisemberg's uncertainty principle**:

$$\underbrace{\Delta p}_{\text{Uncertainty on } p} \underbrace{\Delta q}_{\text{Uncertainty on } q} \geq \frac{\hbar}{2}$$

It is impossible to simultaneously measure with arbitrary accuracy the position and the velocity of a microscopic particle.

2.2 The photoelectric effect

By considering the classical theory of the hydrogen atom and ignoring that energy loss through electromagnetic radiation would be unstable, this model can transfer any amount of energy to the electron by shining light on it. In classical electromagnetism, the energy of radiation comes from the intensity of the electromagnetic wave. It would be expected that, irregardless of the frequency or wave-length, the amount of electron extracted would scale with the intensity of the electromagnetic wave.

2.2.1 Experimental findings

Electrons are extracted only if the light has a $\nu > \nu_{\min}$ or $\lambda < \lambda_{\max}$. If $\nu > \nu_{\min}$, the amount of electrons scales with the intensity. Also, the velocity of those electrons, extracted, would depend on the difference between $\nu - \nu_{min}$.
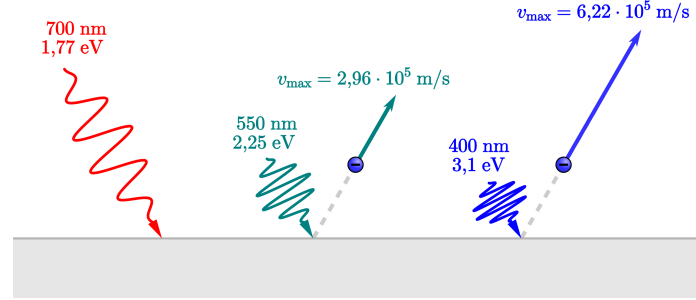
Figure 2.5: Photoelectric effect. Only certain frequencies allow the ejection of an electron from the metal plate.

2.2.2 Conclusions

This experiment determined that the energy transfer depends on the frequency ν of the electromagnetic radiation. Moreover, electrons can only acquire certain quanta of energy. This led to the introduction of two pivotal concepts of modern physics.

2.2.2.1 Energy quantization

The amount of energy transfer to a bound system cannot be arbitrary small.

2.2.2.2 Photons

Light is made by the photon particle which carries energy $E = h\nu$, where $\omega = 2\pi\nu$ and $\hbar = \frac{h}{2\pi}$, so:

$$E = \hbar\omega$$

Photons, like electrons, share wave-like and particle-like properties. Therefore, electrons can be considered as waves of matter and photons as particles of light.

2.3 Quantization and atomic spectra

2.3.1 Experiment

A beam of light goes through an atom and a prism. The prism splits the frequencies and those frequencies are collected on a screen.
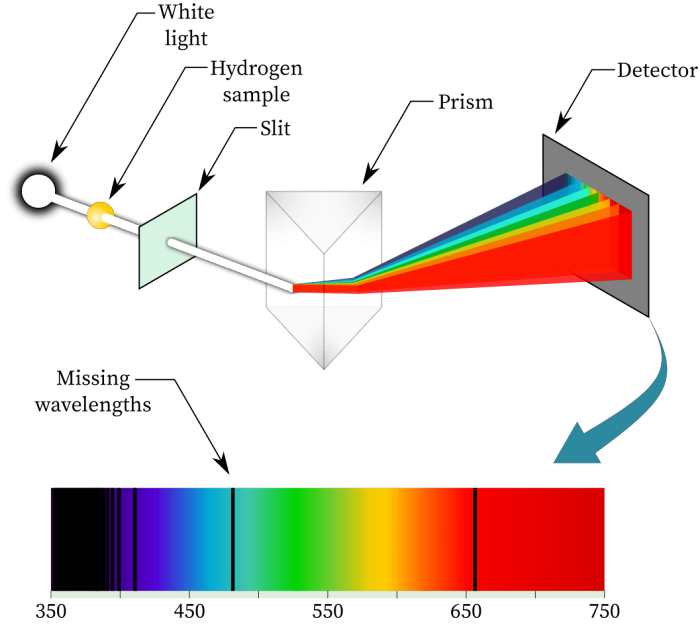
Figure 2.6: Hydrogen emission spectrum: the bright lines in the spectrum are the wavelengths emitted by the excited sample of hydrogen.

2.3.2 Finding

By performing this experiment, it has been found that only certain frequencies can be absorbed by atoms.

2.3.3 Conclusion

Only certain excitation energies are permitted and those form a characteristic signature of atoms:

$$\hbar\omega = E_n - E_m$$

Where E_n and E_m are two energy level of the electron in the atom. Because of this finding, classical mechanics can be seen as a non-fundamental theory: it perfectly describes observations in some limited range of length, mass, temperature. Any more fundamental theory must contain classical mechanics as an approximation in the macroscopic regime, according to the correspondence principle.

2.4 Stern Gerlach experiment

2.4.1 Experiment

An electron beam shoots electrons with different momenta $\vec{\mu}$ through an inhomogeneous magnetic field SG. Behind this there is a screen that detects those electron. If we shut off the magnetic field, the electrons will not interact with anything and we will obtain a high peak. When we activate a magnetic field, there will be some electrons with magnetic moment aligned with velocity and

basically left unchanged, while others will be deflected either up or down. We expect to see a wider distribution as a result.

2.4.2 Finding

Figure 2.7: Stern Gerlach experiment
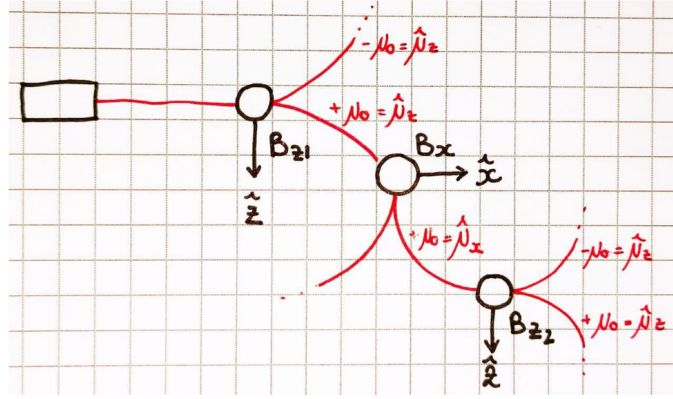
Classically, the electrons are expected to be bended by SG more or less depending on the orientation of $\vec{\mu}$, with an expected density shaped like a Gaussian with μ at the middle. Since $\hat{z}$ has been selected by SG_1, SG_3, it would be expected to find only $\mu_z = +\mu_0$. Instead, the final beam contains $\mu_z = \pm\mu_0$. In real experiments what we see are two narrow peaks; the position of the peaks is compatible with a scenario in which all particles are completely aligned or completely anti-aligned with the z-axis. Somehow, the z component of the magnetic moment is QUANTIZED. It can only take maximum or negative maximum values. Other atoms provide different shapes e.g. up, down, zero. But let's stick to the case in which we observe two peaks. Suppose that now we insert a second device aligned to the x-axis. This time we are measuring the x-component of the magnetic field. Not only the z component is quantised, but also the x and y components.

1. Select z component.

2. Filter positive z component.

3. Select x component.

4. Filter positive x component.

5. Measure z component.

We already measured the z component, so we expect x to be deflected in a single direction. Surprisingly, x will deflect to both positive and negative with equal probability.

2.4.3 Conclusion

The act of measuring μ_x completely destroys the information about the state of μ_z. According to the uncertainty principle, μ_x and μ_z cannot be simultaneously determined. Instead, we only find two possible orientations of the magnetic moment, that is in fact quantizied. Considering three SGs in series with different orientations: $\hat{z} \to \hat{x} \to \hat{z}$: The first selects $\hat{\mu}_z = +\mu_0$ and the second $\hat{\mu}_x = +\mu_0$. It can be seen, measuring μ_z in the last SG how the information selected about μ_z in the first SG is lost.
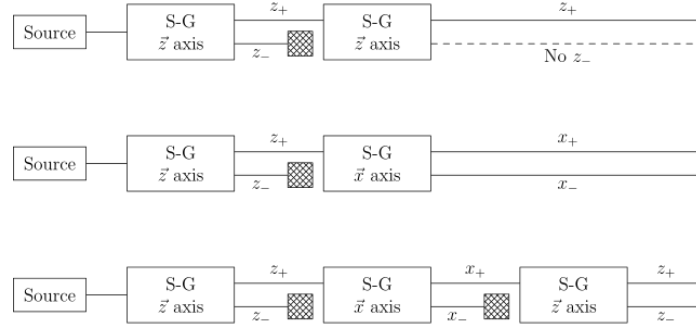
Figure 2.8: Stern-Gerlach experiment summary

2.5 Finding the Schrödinger equation

Particle propagation is not ballistic:

$$P_{12} \neq P_1 + P_2$$

Probability P_2 displayed interference pattern. Interference pattern naturally arises when taking squared modules of complex amplitudes:

$$
\begin{aligned}
I_{12} = |A_1 + A_2|^2 &= \\
&= (A_1 + A_2)(A_1^* + A_2^*)^* = \\
&= (A_1 A_1^* + \underbrace{A_1 A_2^* + A_2 A_1^*}_{interference\ pattern} A_2 A_2^*)
\end{aligned}
$$

Considering $E = n\nu$ a wave function for the electron, a propagating wave can be written as:

$$f(x,t) = f_>(x - vt) + f_<(x + vt)$$

And:

$$
\left(\frac{1}{v^2} \frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2} \right) \begin{cases} f_>(x + vt) \\ f_<(x - vt) \end{cases} = 0
$$

$$
\frac{1}{v^2} \frac{\partial}{\partial t} \left(\frac{\partial}{\partial t} f_>(x - vt) \right) - \frac{\partial}{\partial x} \left(\frac{\partial}{\partial x} f_>(x - vt) \right) =
$$

$$
-\frac{1}{v} \frac{\partial}{\partial t} [f_>'(x - vt)] = f_>''(x - vt)
$$

$$
f_>''(x - vt) = f_>''(x - vt)
$$

Now an electron is assumed to propagate as a wave $\psi(x.t)$ for which: $|\psi(x,t)|^2 = P(x,t)$. Trying to apply a photon wave to the electron:

$$\psi(x,t) = A_o e^{i(\nu t - kx)} = \cos(\nu t - kx) + i \sin(\nu t - kx)$$

Considering that both the real and imaginary part oscillate:

$$\begin{cases} \frac{\partial^2}{\partial t^2} A_0 e^{i(\nu t - kx)} = A_0(-\nu^2 e^{i(\nu t - kx)}) \\ \frac{\partial^2}{\partial x^2} A_0 e^{i(\nu t - kx)} = A_0(-k^2 e^{i(\nu t - kx)}) \end{cases} \rightarrow \frac{1}{v^2}\left[-A_0\nu^2 e^{i(\nu t - kx)} + A_0 k^2 e^{i(\nu t - kx)}\right] = 0$$

$$\Rightarrow \nu = v^2 k^2 \text{ frequency or velocity of propagation}$$

From this it can be seen that $E = \nu h \propto v$, but because of the mass of the electron it should be that $E \propto v^2$. So the Schrödinger equation is a modified wave equation to accomodate this:

$$ia\frac{\partial}{\partial t}\psi = -b\frac{\partial^2}{\partial x^2}\psi(x,t)$$

2.5.1 Free particle Schrödinger equation

In this equation, particle interactions and potential energy are not considered:

$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t)$$

2.5.2 Complete Schrödinger equation

By allowing the electron to react, we can introduce the operator H, which is composed by a kinetic energy and a potential energy component (as the classical Hamiltonian). Based on this, we can refer to the operator as Quantum Hamiltonian. It can be seen how the potential energy is more important than the force:

$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = \underbrace{\left[-\underbrace{\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}}_{\text{kinetic energy operator}} + \underbrace{\hat{U}(x)}_{\text{quantum energy operator}}\right]}_{\text{Quantum Hamiltonian}}\psi(x,t) = \hat{H}\psi(x,t)$$

This is a partial differential equation describing the evolution over time of the wave function. Uncertainty is reflected by the fact that we do not talk about a space trajectory. The interpretation is stochastic ,as the wave function is a probability. Therefore, quantum mechanics is not about the nature itself, but rather about predicting the outcomes of experiments on nature. The entire foundation of quantum mechanics is computing the probability for an outcome of an experiment.

Chapter 3

Waves of matter

3.1 The Schrödinger equation

Physical laws can never be demonstrated, but only inferred from experiments and then verified or falsified by other ones.

3.1.1 Double-slit experiment

The propagation of the electrons in the double-slit experiment has wave-like properties. The probability of an electron being detected in certain points of the screen is described by complex-wave amplitudes, which are functions of x and t. Being $A(x,y)$ a wave, its intensity:

$$Intensity(x,t) = A^*(x,t) \cdot A(x,t)$$

The state of the electron in the beams is assumed to be described by a complex amplitude called the wave-function:

$$\psi(x,t) \rightarrow Prob(x,t)$$
$$= \psi^*(x,t)\psi(x,t)$$
$$\equiv |\psi(x,t)|^2$$

3.1.2 Main assumption

Electrons behave exactly like photons: they both have a dual particle and wave nature. As a consequence, we can assume that for an electron the energy is proportional to frequency:

$$E = \hbar\omega = h\nu = \frac{p^2}{2m}$$

Photons propagate according to a wave equation:

$$\left(\underbrace{\frac{1}{c^2}}_{\text{speed of light}} \frac{\partial^2}{\partial t^2} - \nabla^2 \right) \underbrace{A}_{\text{Maxwell equation}} = 0$$

There is a need to find if the same equation describes the propagation of a massive particle like the electron. Let the electron wave particle be:

$$\psi(x,t) = Ae^{\frac{i}{\hbar}(Et-px)}$$

Then: $\frac{\partial^2}{\partial t^2}\psi = \omega^2\psi$ and $\frac{\partial^2}{\partial x^2}\psi = p^2\psi$. So it is obtained that:

$$p^2 \propto \underbrace{\omega^2}_{\propto E^2}$$

Then $E = cons|p|$. This is true for light, but it is false for massive particles. The correspondence principle implies that:

$$E = \frac{p^2}{2m} \rightarrow E \propto p^2$$

And not just to $|p|$.

3.1.3 Defining the Schrödinger equation

There is a need to use a different wave equation with respect to the photon's one. Noticing that $E^2 \propto p^2$ follows from having two time derivatives, we can try a first time derivative to obtain $E \propto p^2$. Then the equation to solve becomes:

$$\left(C_1\frac{\partial}{\partial t} - C_2\frac{\partial^2}{\partial x^2}\right)\psi = 0$$

$$\begin{cases} \frac{\partial\psi}{\partial t} = A\frac{i}{\hbar}E\psi(x,t) \\ \frac{\partial^2\psi}{\partial x^2} = A\frac{-1}{\hbar^2}p^2\psi(x,t) \end{cases}$$
$$\left(C_1\frac{\partial}{\partial t} - C_2\frac{\partial^2}{\partial x^2}\right)\psi(x,t) = 0$$
$$\left(C_1\frac{i}{\hbar}E - C_2\left(-\frac{1}{\hbar^2}p^2\right)\right)\psi(x,t) = 0$$
$$\left(C_1\frac{i}{\hbar}E - C_2\left(-\frac{1}{\hbar^2}p^2\right)\right) = 0$$

Now, considering $\frac{C_1}{C_2} = R \rightarrow \hbar^2$:

$$\begin{cases} i\ \underbrace{\hbar\frac{\partial}{\partial t}\psi}_{\text{kinetic energy}}\ -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi = 0 \\ E = \frac{p^2}{2m} \\ E = \hbar\omega \end{cases}$$

Now:

$$\hbar\omega = E \propto p^2$$

Recall that $\hbar$ is the Dirac's constant, obtained by the following formula: $\hbar = \frac{h}{2\pi}$, where h is Planck's constant.

For a free electron, H equals the kinetic energy and is approximately the Hamiltonian. For an interacting electron:

$$H_0 \rightarrow H_0 + \underbrace{V(\vec{r})}_{\text{potential energy}} = H$$

Finally, the Schrödinger equation is:

$$i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right)\psi(x,t)$$

3.1.3.1 Quantum Hamiltonian

The quantum Hamiltonian can be defined as:

$$\hat{H} \equiv -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)$$

Comparing it with a classical Hamiltonian, it can be seen that $\frac{p^2}{2m} \xrightarrow{\text{quantization}} -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \Rightarrow p^2 \rightarrow \hbar^2\frac{\partial^2}{\partial x^2}$. Then, due to the fact that the forward propagating wave has a positive momentum, $\hat{p} \rightarrow i\hbar\frac{\partial}{\partial x}$. The same happens in three dimensions, where:

$$i\hbar\frac{\partial}{\partial x}\psi(\vec{x},t) = \left(-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{x})\right)\psi(\vec{x},t)$$

The Schrödinger equation is then recast as:

$$i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t) = \hat{H}\psi(\vec{r},t)$$

To solve this equation there is a need to solve a partial differential equation that defines the state of a system. The operators are:

$$\hat{H} = \left(-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right)$$

$$\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

3.2 Stationary Schrödinger equation

Assuming that the system conserves mechanical energy:

$$H(p,q,\not{t}) = \frac{p^2}{2m} + U(q,\not{t})$$

Considering the plane wave:

$$\psi(\vec{r},t) = \phi(\vec{r})e^{-i\frac{E}{\hbar}t}$$

By formulating a guess for the form of the solution and plugging it into the Schrödinger equation:

$$E\phi e^{-i\frac{i}{\hbar}(Et)} = He^{-\frac{i}{\hbar}Et}\phi$$

Which gives:

$$\hat{H}\phi(\vec{r}) = E\phi(\vec{r})$$

Where E is unknown. This is an eigen problem: given $\hat{H}$, a function $\psi(\vec{r})$ has to be found such that $\hat{H}\psi(\vec{r})$ is a function proportional to $\psi(\vec{r})$ through some constant E. In other words, the energy of a quantum system is an eigenvalue of the quantum Hamiltonian operator. Energy quantization is obtained and:

$$E = \underbrace{E_0}_{\text{ground state energy}} < \underbrace{E_1 < \cdots < E_n}_{\text{excited state energies}}$$

And:

$$\hat{H}\psi(\vec{r}) = E_0\psi_0(\vec{r})$$
$$\hat{H}\psi(\vec{r}) = E_1\psi_1(\vec{r})$$
$$\vdots$$
$$\hat{H}\psi(\vec{r}) = E_n\psi_n(\vec{r})$$

3.3 Ground state of the quantum harmonic oscillator

The quantum Hamiltonian for the quantum harmonic oscillator is:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$

The solution for the ground state should be in the form $\hat{H}\psi_0 = E$.

3.3.1 Form of the ground state

The ground state will be in the form:

$$\psi(x) = \mathcal{N}e^{-\frac{\alpha x^2}{4}}$$

So:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\phi_0 = -\frac{\hbar^2}{2m}\mathcal{N}\frac{d}{dx}\left[-\frac{\alpha}{2}xe^{-\frac{\alpha x^2}{4}}\right] =$$
$$= -\frac{\hbar^2}{2m}\left[-\frac{\alpha}{2}e^{-\frac{\alpha x^2}{4}} + \frac{\alpha^2}{4}x^2 e^{-\frac{\alpha x^2}{4}}\right]\mathcal{N}$$

So:
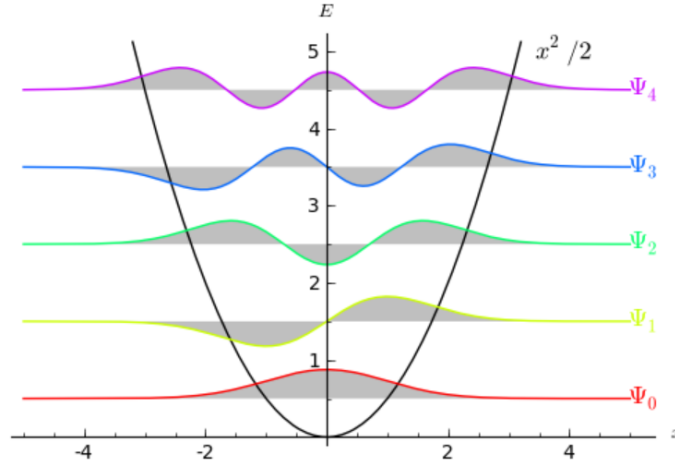
Figure 3.1: Quantum mechanics oscillator

$$\hat{H}\phi_0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\phi_0 + \frac{1}{2}m\omega^2 x^2 \phi_0 =$$
$$= \frac{\alpha}{4}\frac{\hbar^2}{m}\phi_0 - \frac{\hbar^2\alpha^2}{8m}x^2\phi_0 + \frac{1}{2}m\omega^2 x^2\phi_0$$

For ϕ_0 to be an eigenstate $\hat{H}\psi_0 = const \cdot \psi_0$, so the dependence on x^2 must be cancelled:

$$-\frac{\hbar^2}{8m}\alpha^2 x^2\phi_0 + \frac{1}{2}m\omega^2 x^2\phi_0 = 0$$

From this:

$$\alpha^2 = \frac{4m^2\omega^2}{\hbar^2} \Rightarrow \alpha = \frac{2m\omega}{\hbar}$$

So the solution is:

$$\phi_0(x) = \mathcal{N}e^{-\frac{2m\omega}{\hbar}x^2}$$

3.3.2 Solution of the ground state of the quantum mechanic oscillator

The one dimensional quantum mechanic oscillator is the most used model:

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2$$

A wave function for a one particle system contains zero nodes for the ground state. It is expected that the ground state is different from zero and we assume a Gaussian for a solution:

$$\phi_0(x) = \mathcal{N}e^{\alpha x^2}$$

The objective is to compute $\hat{H}\phi_0 = n\phi_0(x)$:

$$\hat{H}\phi_0 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}(\mathcal{N}e^{-\alpha x^2}) = -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}(-2\alpha x e^{-\alpha x^2})\mathcal{N} =$$

$$= -\frac{\hbar^2}{2m}(-2\alpha e^{-\alpha x^2} + 4\alpha^2 x^2 e^{-\alpha x^2})\mathcal{N} =$$

$$= \frac{\hbar^2}{2m}2\alpha\phi_0 - \frac{\hbar^2}{2m}4\alpha^2 x^2 \phi_0$$

$$\hat{H}\phi_0 = \underbrace{\frac{\hbar^2}{m}\alpha\phi_0(x)}_{n\phi_0(x)} + \underbrace{\left(\frac{1}{2}m\omega^2 - \frac{\hbar^2}{m}2\alpha^2\right)x^2\phi_0(x)}_{\text{depends on } x^2}$$

The solutions are found for values of α that set to 0 the part dependent on x^2:

$$\frac{1}{2}m\omega^2 - \frac{\hbar^2}{m}2\alpha^2 = 0$$

$$\alpha = \frac{m\omega}{2\hbar}$$

Therefore the Gaussian is a good solution:

$$\phi_0(x) = \mathcal{N}e^{-\frac{m\omega x^2}{2\hbar}}$$

3.3.2.1 Normalization evaluation

Consider that $\frac{1}{\sigma^2} = \frac{2m\omega}{\hbar} \rightarrow \sigma^2 = \frac{\hbar}{2m\omega} \rightarrow \sigma = \sqrt{\frac{\hbar}{2m\omega}}$. Then consider:

$$\mathcal{N}\int_{-\infty}^{\infty} e^{-\frac{m\omega x^2}{\hbar}}$$

And solve the Gaussian integral:

$$\int e^{-\sigma x^2} = \sqrt{2\pi}\sigma$$

Then:

$$\mathcal{N}^2 = \frac{1}{\int|\phi_0|^2 dx} = \frac{1}{(2\pi\sigma^2)^{\frac{1}{2}}} = \frac{1}{(2\pi\frac{\hbar}{2m\omega})^{\frac{1}{2}}}$$

$$\mathcal{N} = \frac{1}{(2\pi\frac{\hbar}{2m\omega})^{\frac{1}{4}}} = \left(\frac{m\omega}{\pi\hbar}\right)^{-\frac{1}{4}}$$

3.3.2.2 Compute the average value of kinetic and potential energy

Due to the fact that operations are stochastic, the outcome cannot be predicted. We can only compute the probability or the average values. Let $\langle U \rangle$ be the average value of the potential energy, then:

$$\langle U \rangle = \int P_0(x)U(x)dx = \frac{\int dx e^{-\frac{m\omega x^2}{\hbar}} \frac{1}{2}m\omega^2 x^2}{\int dx e^{-\frac{m\omega x^2}{\hbar}}} =$$

$$= \frac{1}{2}m\omega^2 \underbrace{\langle x^2 \rangle}_{\text{variance } \sigma^2} = \frac{1}{2}m\omega^2 \frac{\hbar}{2m\omega} =$$

$$= \frac{1}{4}\hbar\omega$$

So considering $E_0 = \frac{1}{2}\hbar\omega$, the energy remains the same, but the potential energy changes stochastically. Then:

$$E_0 = \langle U \rangle + \langle T \rangle$$

In order to compute the kinetic energy, we need to consider that in quantum mechanics anything that can be measured except time is an observable. So, starting with classical mechanics, the observable $o(p,q)$ momentum and position, and after quantization and using the position representation:

$$O(\underbrace{\hat{p}}_{-i\hbar\vec{\nabla}}, \underbrace{\hat{q}}_{\vec{q}}) \to \hat{O}$$

$$T = \frac{p^2}{2m} \to \hat{T} = \frac{\hat{p}^2}{2m} = \frac{(-i\hbar\nabla)^2}{2m} = -\frac{\hbar^2\nabla^2}{2m}$$

$$U(q) \to \hat{U}$$

Now considering the orbital angular momentum $\vec{L} = \vec{r} \cdot \vec{p}$:

$$\begin{vmatrix} i & j & k \\ x & y & z \\ P_x & P_y & P_z \end{vmatrix}$$

Then:

$$L_z = xP_y - yP_x \xrightarrow{\text{quantization}} x\left(-i\hbar\frac{\partial}{\partial y}\right) - y\left(-i\hbar\frac{\partial}{\partial x}\right)$$

The quantum kinetic energy operator is obtained as following from the classical kinetic energy $T = \frac{p^2}{2m} \to \hat{T} = \frac{\hat{p}^2}{2m} = \frac{(-i\hbar\vec{\nabla})^2}{2m} = \frac{\hbar^2}{2m}\nabla^2$

In order to compute the expected value of operators, we need to consider $\langle \varphi | O | \varphi \rangle$ that specifies the state and that is equivalent to $\langle O \rangle$, where:

$$\langle O \rangle = \frac{\int dx \varphi^*(x)(O(x) \cdot \varphi(x))}{\int dx \varphi^*(x)\varphi(x)}$$

3.3.2.2.1 Potential energy operator

$$\langle \varphi | \hat{U} | \varphi \rangle = \frac{\int dx \varphi^*(x)(\hat{U}\varphi(x))}{\int dx |\varphi|^2} = \int dx U(x)|\varphi|^2$$

3.3.2.2.2 Kinetic energy operator : Consider $\varphi = e^{-\frac{\alpha x^2}{2}}$

$$\langle\varphi|\hat{T}|\varphi\rangle = \frac{\int dx\varphi^*(x)(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\varphi(x))}{\int dx|\varphi|^2} = e^{-\frac{\alpha x^2}{2}}\frac{\partial^2}{\partial x^2}e^{-\frac{\alpha x^2}{2}} = e^{-\frac{\alpha x^2}{2}}\frac{\partial}{\partial x}(-2\alpha x e^{-\frac{\alpha x^2}{2}}) =$$

$$= e^{-\frac{\alpha x^2}{2}}(-\alpha e^{-\frac{\alpha x^2}{2}} + \alpha^2 x^2 e^{-\frac{\alpha x^2}{2}}) =$$

$$= -\alpha|\varphi|^2 + \alpha^2 x^2|\varphi|^2$$

We can then substitute for $\alpha = \frac{m\omega}{\hbar}$ and $\langle x^2\rangle = \sigma^2 = \frac{\hbar}{2\omega m}$:

$$\langle\varphi|\hat{T}|\varphi\rangle = -\frac{\hbar^2}{2m}\alpha(\alpha x^2 - 1) = \frac{\hbar\omega}{4}$$

3.4 Quantum particle in a one dimensional infinite square well

We previously discussed at the classical level that a physical system can be bound or unbound. In quantum physics, a bound state is a quantum state of a particle subject to a potential such that the particle has a tendency to remain localized in one or more regions of space. Ultimately, matter and life exist because of bound systems, which allow the presence of macro structures. While trying to solve a bound system problem, we will require a toy model - a model deliberately too simple to be realistic, which is not meant to predict the outcome of an experiment, but rather to understand the qualitative nature of the object under study. While implementing a toy model, if the scale where a detail occurs is very small compared with the size of the box, its effect can be neglected. As a consequence, everything which occurs within the box is idealized, allowing us to solve the problem. It's all a matter of scale e.g. λ is the scale for details, L the size of the physical system, η the energy we are interested in, E the unbounding energy. If the ratio $\frac{\lambda}{L} \ll 1$ and $\frac{\eta}{E} \ll 1$, we can neglect the detail.

For the case of a quantum particle in a one dimensional infinite square well, we will consider
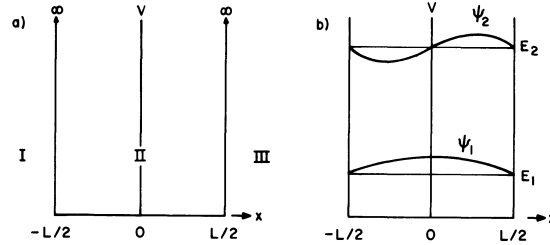
Figure 5.1. (a) The box potential. (b) The first two levels and wave functions in the box.

Figure 3.2: Particle trapped in 1D infinite square well

a particle constrained in a trap where interactions are so strong that it cannot escape and with two confining directions much narrower than the third. We can consider a box with size $L/2$ and $-L/2$ and find the eigenvalues and eigenvectors for the Schrödinger equation in this specific condition. This can be modelled with a one dimensional confining potential:

$$U(x) = \begin{cases} 0, & -\frac{L}{2} < x < \frac{L}{2} \\ \infty & |x| > \frac{L}{2} \end{cases}$$

Inside the box $U = 0$, so the Schrödinger equation is:

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

Mathematically this looks like the Newton's equation for the harmonic oscillator:

$$+m\frac{d^2}{dt^2}x(t) = -kx(t)$$

Where $x \to t$ and $\psi \to x$. However, the constraints are different. Instead of the classical initial values $x(0) = x_0$ and $\frac{d}{dt}x|_{t=0} = 0$, there is a boundary value $\psi\left(\pm\frac{L}{2}\right) = 0$.

3.4.1 Solution

Given the mathematical similarity between the two equations, the general structure of the solution should be:

$$\psi(x) = \begin{cases} A_1 \cos k_1 x \\ A_2 \sin k_2 x \end{cases}$$

Where A_1, A_2, k_1, k_2 need to be fixed.

3.4.1.1 Option 1

$A_1 \cos\left(k_1 \frac{L}{2}\right) = 0$, then:

$$k_1 \frac{L}{2} = \pm\frac{\pi}{2} \pm n\pi \Rightarrow$$
$$\Rightarrow k_1^{(n)} = \pm\frac{\pi}{L}, \pm\frac{3\pi}{L}, \cdots =$$
$$= \pm 2(n-1)\frac{\pi}{L} \qquad n = \mathbb{N}$$

For this option, the possible quantized energy levels are:

$$E^{(n)} = \frac{\hbar^2}{2m}\frac{\pi^2}{L^2}(2n-1)^2$$

3.4.1.2 Option 2

$A_1 \sin\left(k_2 \frac{L}{2}\right) = 0$, then:

$$k_2 \frac{L}{2} = \pm\pi \pm n\pi \Rightarrow$$
$$\Rightarrow k_2^{(n)} = \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \cdots =$$
$$= \pm 2n\frac{\pi}{L} \qquad n = \mathbb{N}$$

For this option, the possible quantized energy levels are:

$$E^{(n)} = \frac{\hbar^2}{2m}\frac{\pi^2}{L^2}(2n)^2$$

3.4.1.3 A_1 and A_2

A_1 and A_2 can be determined by applying the normalization conditions. The probability of finding the particle somewhere in the box is one, so:

$$\int_{-\frac{L}{2}}^{\frac{L}{2}} dx |\psi(x)|^2 = 1$$

$$1 = \int_{-\frac{L}{2}}^{\frac{L}{2}} dx \begin{cases} A_1^2 \cos^2 k_1 x \\ A_2^2 \sin^2 k_2 x \end{cases} \Rightarrow \begin{cases} A_1 = \\ A_2 = \end{cases}$$

3.4.1.4 Summary

Summarizing the results:

3.4.1.4.1 Energy spectrum

$$E_n = \frac{\hbar^2}{2m} \frac{\pi^2}{L^2} \mathcal{L}^2$$

3.4.1.4.2 Energy eigenstates   The energy eigenstates of the stationary wave-functions are:

$$\psi_m(x) = \begin{cases} A_1 \cos k_1 x & n \ odd \\ A_2 \sin k_2 x & n \ even \end{cases}$$

3.4.2 Discussion

3.4.2.1 Quantized momenta

From the quantized energy:

$$E_n = \frac{1}{2m} \left(\underbrace{\frac{\pi^2 \hbar^2}{L_2} m^2}_{=p_m^2} \right)$$

So the quantized momenta is $p_m = \pm \frac{\pi \hbar}{L} m$.

3.4.2.2 Lowest energy state

In classical mechanics, the lowest energy state is $p = 0 \Rightarrow E = 0$. Differently, in quantum mechanics the lowest energy level is:

$$E_1 = \frac{\hbar^2}{2m} \left(\frac{\pi}{L} \right)^2 > 0$$

Recalling that $E_1 = \frac{p_1^2}{2m}$, it is inferred that:

$$p_1 = \pm \frac{\hbar \pi}{L} \neq 0$$

p_1 can point in $+$ or $-$ direction with equal probability, so the quantum uncertainty is $\Delta p = \frac{2\hbar\pi}{L}$. On the other hand, $\Delta q \sim L$, so there is quantum delocalization for $\psi_1(x)$. However in the classical ground state:

$$T = \frac{p^2}{2m} = 0 \Rightarrow p = 0 \Rightarrow \Delta p = 0$$

But $\Delta q = L$, hence there is a violation of the uncertainty principle:

$$\Delta q \Delta p = 0$$

3.4.2.3 Correspondence principle

By considering that for $L \to \infty$ and $m \to \infty$ $E_0 = 0$, there is no uncertainty in classical mechanics. In addition, $E_{n+1} - E_n \to 0$, so there is no quantization. As a consequence, classical mechanics is contained in quantum mechanics in the macroscopic limit, for large size and heavy masses.

3.4.2.4 Excited states

The wave function of the n-th excited state has N nodes, a general result that holds for any quantum system.

3.5 Two dimensional square well

Consider a quantum particle in a two dimensional square well with dimensions L_1 and L_2. Then:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}$$

Any H can be separated as: $H(x,y) = H_1(x) + H_2(y)$. Anytime the Hamiltonian factorizes, i.e. $\hat{H} = \sum_i \hat{h}_i$, the solution of the Schrödinger equation can be written as the product of two wave functions $\phi(x,y) = \phi_1(x)\phi_2(y)$. The corresponding energy will be obtained by summing the two energies $E = E_1 + E_2$. By applying this property, we can write the solution to the Hamiltonian for our problem.

3.5.1 Solution

Then the solution is:

$$\begin{cases} \phi(x,y) = \phi_1(x)\phi_2(y) \\ H\phi = (E_1 + E_2)\phi \end{cases}$$

Where $H_1\phi_1 = E_1\phi_1$ and $H_2\phi_2 = E_2\phi_2$ So:

$$(H_1 + H_2)\phi_1(x)\phi_2(y) = H_1\phi_1(x)\phi_2(y) + H_2\phi_1(x)\phi_2(y) =$$
$$= \phi_2(y)\hat{H}_1\phi_1(x) + \phi_1(x)H_2\phi_2(y) =$$
$$= \phi_2 E_1 \phi_1 + \phi_1 E_2 \phi_2 =$$
$$= (E_1 + E_2)\phi_1\phi_2$$

Resulting in:

$$\phi_n(x) = \begin{cases} \sqrt{\frac{2}{L_x}} \sin k_n x \\ \sqrt{\frac{2}{L_x}} \cos k_n x \end{cases}$$

$$\phi_m(x) = \begin{cases} \sqrt{\frac{2}{L_y}} \sin k_m y \\ \sqrt{\frac{2}{L_y}} \cos k_m y \end{cases}$$

For $n = 1$ and $m = 1$:

$$\psi_1 = \sqrt{\frac{2}{L_x} \frac{2}{L_y} \cos k_1^x x \cos k_1^y y}$$

$$k_1^x = \frac{\pi}{L_x} n = \frac{\pi}{L_x}$$

$$k_1^y = \frac{\pi}{L_y} m = \frac{\pi}{L_y}$$

For $n = 2$ and $m = 1$:

$$\psi_2 = \sqrt{\frac{2 \cdot 2}{L_x L_y}} \sin k_2^x x \cos k_1^y y$$

The total energy can be obtained as $E_{n,m} = E_n^x + E_m^y = -\frac{\hbar^2}{2m} \pi^2 \left(\frac{n^2}{L_x^2} + \frac{m^2}{L_y^2} \right)$. Then the ground state is $E_{11} = E_1^x + E_1^y$ and the system is doubly degenerative in opposite directions:

$$E_{12} + E_1^x + E_2^y + E_{21} = E_2^x + E_1^y$$

3.6 Lattice discretization

Lattice discretization is a technique by which a numerical solution is obtained by exploiting the connection between operators and matrices.

We know that the wavefunction should be normlized and localized in a certain position of the space. By going towards the end and beginning of the x-axis, the function will go to zero, meaning that we have a maximum and minimum after which the function value can be neglected. We can either stop at maximum/minimum point, and this would be a first approximation. But let us divide the axis into little dots, such that the function can be considered almost constant in each dot. We are going to obtain a very accurate step-wise representation of the function, and we can proceed until the result is good enough i.e. when the lattice space is smaller than the scale at which the wavefunction changes. Though discretization, we can tune the number of dots required to obtain an accurate result.

A large but finite number of equally spaced possible position is used. The possible positions are $x = x_{\min} + \Delta x$, where $\Delta x = \frac{x_{\max} - x_{\min}}{N}$. After discretization, the wave function is represented by a list $\psi(x) \rightarrow (\psi_1, \ldots, \psi_N)$. Thus, the wave function becomes a vector and the Hamiltonian a matrix.

3.6.1 Discrete representation of the derivative

$$\frac{d}{dx}\psi(x) \to \frac{\psi_{i+1} - \psi_i}{\Delta x}$$

$$\frac{d^2}{dx^2}\psi(x) \to \frac{\psi_{i+1} + \psi_{i-1} - 2\psi_i}{\Delta x^2}$$

Let the Kronecker delta be:

$$\delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases} \Rightarrow S_{ij} \to \begin{pmatrix} 1 & 0 & \cdots \\ \vdots & \ddots & \vdots \\ 0 & \cdots & 1 \end{pmatrix}$$

Now:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \to T_{ij} = -\frac{\hbar^2}{2m\Delta x^2}(\delta_{ij+1} + \delta_{ij-1} - 2\delta_{ij})$$

Indeed:

$$\sum_j T_{ij}\psi_i = -\frac{\hbar^2}{2m}(\psi_{i+1} + \psi_{i-1} - 2\psi_i)\frac{1}{\Delta x^2}$$

Now $V(x) \to V_{ij} = V_i\delta_{ij}$, so:

$$\sum_j V_{ij}\psi_j = V_i\psi_i$$

Finally, the matrix lattice representation is obtained as:

$$H_{ij} = T_{ij} + V_{ij}$$

$$H_{ij} = \begin{pmatrix} \frac{\hbar^2}{m\Delta x^2} + V_1 & -\frac{\hbar^2}{2m\Delta x} & 0 & \cdots \\ -\frac{\hbar^2}{2m\Delta x^2} & \frac{\hbar^2}{m\Delta x^2} + V_2 - \frac{\hbar^2}{2m\Delta x^2} & 0 & \cdots \\ 0 & -\frac{\hbar^2}{2m\Delta x^2} & \frac{\hbar^2}{m\Delta x^2} + V_3 - \frac{\hbar^2}{2m\Delta x^2} & \cdots \end{pmatrix}$$

Solving the matrix eigenproblem $\sum_i H_{ij}\psi_i = E_i\psi_i$ yields $\{E_i\}_{i=\{1,\dots,N\}}$ and $\{y_j\}_i$.

The dimensionality grows with the number of mesh points N. The exact case is $N \to \infty$. Quantum mechanics is described by an infinite dimensional vector space called the Hilbert space. After discretization, changing from coordinate representation to momentum representation (and opposite), i.e. performing Fourier transformation, basically involves changing a basis in the vector space that describes the state of the system. Lattice discretization allows us to go from quantum mechanics mathematics to linear algebra.

3.7 Time evolution operators

Consider the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \psi(x,t) = \hat{H}\psi(x,t)$$

Where:

$$\psi(x,t) = e^{-\frac{i}{\hbar}\hat{H}(t-t_0)}\psi(x,t_0)$$

And the time-evolution operator:

$$U(t,t_0) = e^{-\frac{i}{\hbar}\hat{H}(t-t_0)}$$

If the argument of the Taylor expansion is too large, we will infinitely many operators, unless it is a special quantum mechanics operators such that it is the eigenvalues of the Hamiltonian. Let $\vec{a}_k$ be an eigenvector, then:

$$e^{\hat{A}}\vec{a}_k = e^{a_k}\vec{a}_n$$

As a consequence, the time-evolution operator for the eigenvectors of the Hamiltonian can be easily evaluated. If $\psi(x, t = t_0) = \phi_n(x)$, where $\hat{H}\phi_n(x) = E_n\phi_n(x)$, then:

$$\psi(x,t) = e^{-\frac{i}{\hbar}(t-t_0)E_n}\phi_n(x)$$

And:

$$P(x,t) = |\psi(x,t)|^2 = |e^{-\frac{i}{\hbar}(t-t_0)E_n}|^2|\phi_n(x)|^2$$

If it has a pure phase: $|e^{ia}|^2 = e^{ia}(e^{ia})^* = e^{i(a-a)} = 1$, then:

$$P(x,t) = |\phi_n(x)|^2 = P(x,t_0)$$

And it is the same as the initial time.

Chapter 4

Quantum mechanics

4.1 State of a system

The instantaneous state of a system is represented by points in a Hilbert space: $|\psi(t)\rangle$. More precisely, states are associated to rays - since $a|\psi\rangle$ and $|\psi\rangle$ represent the same state. Let $|\psi_3\rangle = a|\psi_2\rangle$, $|\psi_1\rangle$ and $|\psi_2\rangle$ represent different states and $|\psi_1\rangle$ and $|\psi_3\rangle$ represent the same one.

The wavefunction $\psi(Q,t)$ describes the state of a quantum system, where $Q = \vec{q_1}, ..., \vec{q_N}$ are coordinates for the position of all the particles. Keep in mind that ψ cannot be measured, it is a mere mathematical tool that we use for computing and making predictions.

4.2 Observable quantities

Observable quantities are associated to an Hermitian Operator, for example:

- $\underbrace{x}_{\text{position}} \rightarrow \underbrace{\hat{x}}_{\text{position operator}}$

- $\underbrace{h}_{\text{energy}} \rightarrow \underbrace{\hat{H}}_{\text{Hamiltonian operator}}$

The only exception is time, which is not associated to an operator.

$$O(p,q) \rightarrow \hat{O}(\underbrace{-i\hbar\vec{\nabla}}_{\text{p}}, \bar{q})$$

4.3 Outcomes of measurement

The possible outcomes of measurement of an observable O are the eigenvalues of the corresponding operator $\hat{O}$:

$$\hat{O}|o_n\rangle = o_n|o_n\rangle$$

If the system is in the quantum state $|\psi\rangle$, the probability of finding the value o_n when measuring $\hat{O}$ is:

$$P(o_n) = |\langle o_n|\psi\rangle|^2$$

Immediately after the measurement of $\hat{O}$, yielding o_n, the state of the system is described by:

$$\psi(Q, t_0) = f_n^\circ(Q)$$

By measuring we observe the **collapse of the wavefunction** e.g. the state of the cat collapses to either dead or alive when we open the box.

4.4 Expectation value

The average over many measurement of $\hat{O}$ or expectation value is given by:

$$\langle \hat{O} \rangle = \frac{\langle \psi | \hat{O} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\int d^{3N}Q\, \psi^*(Q, t) \hat{O} \psi(Q, t)}{\int d_Q^{3N} \psi^*(Q, t) \psi(Q, t)}$$

As a corollary, the mean-square deviation of the measurement is:

$$\Delta^2 \hat{O} = \frac{\langle \psi | \hat{O}^2 | \psi \rangle}{\langle \psi | \psi \rangle} - \left(\frac{\langle \psi | \hat{O} | \psi \rangle}{\langle \psi | \psi \rangle} \right)^2$$

It $|\psi\rangle$ is an eigenstate of $\hat{O}$ $|\psi\rangle = |o_n\rangle$), then $\Delta^2 \hat{O} = 0$

4.5 Time evolution

The time evolution of $|\psi(t)\rangle$ is described by the Schrödinger equation:

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H |\psi(t)\rangle$$

The formal solution of this equation is given by the time evolution operator:

$$|\psi(t)\rangle = \hat{U}(t - t_0) |\psi(t_0)\rangle$$

$$\hat{U}(t - t_0) = e^{-\frac{i}{\hbar} \hat{H}(t - t_0)}$$

4.6 Remarks

$\hat{O}_1, \hat{O}_2, ..., \hat{O}_N$ are Hermitian operators.
Let O_l where $l = 1, ..., M < N$ be the subset of mutually commuting operators. Then, for $[O_l, O_m] = 0$ with $O_l, O_m \in M$ there will be a common set of eigenstates.
$\hat{O}_l f_i = o_i^{(l)} f_i$, where f_i are the eigenstates. By measuring immediately after a previous measurement M, the result will be equal, as the M measurement will provide the maximum information possible on the quantum system. Any other measurement will destroy the information e.g. if we measure the momentum (non-commuting) after the position, we will not know the position any more.

4.6.1 Proof for non commutation of momentum's components

Check whether L_x and L_y do not commute.

$$\bar{L} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = \hat{i} \underbrace{(yp_z - zp_y)}_{L_x} + \hat{j} \underbrace{(zp_x - xp_z)}_{L_y} + \hat{k} \underbrace{(xp_y - yp_x)}_{L_z}$$

Quantization leads to:

$$\hat{L}_x = -i\hbar \left(y\frac{\partial}{dz} - z\frac{\partial}{\partial y} \right)$$

$$\hat{L}_y = -i\hbar \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right)$$

$$\hat{L}_z = -i\hbar \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right)$$

Find $\left[\hat{L}_x, \hat{L}_y \right]$:

$$\underbrace{(-i\hbar)^2}_{\text{collect}} \left[\hat{L}_x\hat{L}_y\varphi - \hat{L}_y\hat{L}_x\varphi \right\} =$$

Apply definition:

$$(-i\hbar)^2 \left\{ \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right) \left[\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right) \varphi(x,y,z) \right] \right\} - (-ih)^2 \left\{ \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right) \left[\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right) \varphi(x,y,z) \right] \right\}$$

Solving:

$$(-i\hbar)^2 \left\{ \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right) \left[z\frac{\partial}{\partial x}\varphi - x\frac{\partial}{\partial z}\varphi \right] \right\} - (-i\hbar)^2 \left\{ \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right) \left[y\frac{\partial}{\partial z}\varphi - z\frac{\partial}{\partial y}\varphi \right] \right\} =$$

$$= (-i\hbar)^2 \left\{ y\frac{\partial}{\partial x}\varphi + yz\frac{\partial}{\partial z}\frac{\partial}{\partial x}\varphi - yx\frac{\partial^2}{\partial z^2}\varphi - z^2\frac{\partial}{\partial y}\frac{\partial}{\partial x}\varphi + zx\frac{\partial}{\partial y}\frac{\partial}{\partial z}\varphi \right\}$$

$$- (-i\hbar)^2 \left\{ zy\frac{\partial}{\partial x}\frac{\partial}{\partial z}\varphi - z^2\frac{\partial}{\partial x}\frac{\partial}{\partial y}\varphi - xy\frac{\partial^2}{\partial z^2}\varphi + x\frac{\partial}{\partial y}\varphi + xz\frac{\partial}{\partial z}\frac{\partial}{\partial y}\varphi \right\} =$$

$$= (-i\hbar)(-i\hbar)\left[y\frac{\partial}{\partial x}\varphi - x\frac{\partial}{\partial y}\varphi \right] = i\hbar\hat{L}_z\varphi \qquad \text{By deleting terms}$$

As a result, $\left[\hat{L}_x, \hat{L}_y \right] = i\hbar\hat{L}_z$.

The other relationships are the following:

- $\left[\hat{L}_z, \hat{L}_x \right] = -i\hbar \hat{L}_y$
- $\left[\hat{L}_y, \hat{L}_z \right] = -i\hbar \hat{L}_x$

Keep in mind that $[\hat{L}^2, \hat{L}_x] = 0, [\hat{L}^2, \hat{L}_y] = 0, [\hat{L}^2, \hat{L}_z] = 0$.

Summarizing, $\hat{L}_x, \hat{L}_y, \hat{L}_z$ are not mutually commuting, i.e., we can only know one component of the orbital momentum and the squared modulus (total length of the orbital momentum) at the same time.

4.7 Harmonic magnetic trap problem

In experiments on dilute cold gases, atoms are confined to a certain region of space by a magnetic trap formed by an appropriately configured magnetic field. Close to the center of the trap, the effect of the magnetic field can be described as a harmonic potential, which is defined by the Hamiltonian.

Imagine that we perform an experimental measurement at time t_0, giving as outcome $x_0 = 0$
By exploiting this result, we can obtain an approximation for the wave function:

$$\psi(x, t = 0) = \mathcal{N} e^{-\frac{mx^2\omega}{2\hbar}}$$

$$\left(\frac{m\omega}{\pi\hbar} \right)^{1/4} = \mathcal{N}$$

At time t_0 the trap is removed and the energy is measured. We then need to compute the expectation value for E:

$$\langle E \rangle = \frac{(\psi, \hat{H}\psi)}{(\psi, \psi)} = \left(\frac{m\omega}{\pi\hbar} \right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} dx \, \psi^*(x) \hat{H} \psi(x) =$$

$$= \left(\frac{m\omega}{\pi\hbar} \right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} dx \, e^{-\frac{m\omega x^2}{2\hbar}} \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x) \right) e^{-\frac{m\omega x^2}{2\hbar}} =$$

$$= \langle T \rangle + \langle U \rangle$$

$$\langle T \rangle = -\frac{\hbar^2}{2m} \left(\frac{m\omega}{\pi\hbar} \right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} dx \, e^{-\frac{mx^2\omega}{2\hbar}} \frac{\partial^2}{\partial x^2} e^{-\frac{mx^2\omega}{2\hbar}} = \frac{1}{4}\hbar\omega$$

$$\langle U \rangle = \left(\frac{m\omega}{\pi\hbar} \right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} dx \, e^{-\frac{mx^2\omega}{2\hbar}} U(x) e^{-\frac{mx^2\omega}{2\hbar}} = 0$$

While the trap is present, the function never gets to the infinity boundary, as it gets suppressed beforehand (the trap is narrower than the box). Therefore, the whole integral equals zero.

$$\langle U \rangle = 0 \rightarrow \langle E \rangle = \langle T \rangle = \frac{1}{4}\hbar\omega$$

Before t_0, the Hamiltonian is the trap. Let's check if the Hamiltonian at t_0 is the box. Usually, for a free particle in a one dimension box, $E_n = \left(\frac{\pi^2 n^2}{L^2} \right) \frac{\hbar^2}{2m}$.

4.7.1 Trap larger than the particle

By assuming that the trap is much larger than the particle, the particle behaves as a free particle. As a consequence, it has many degrees of freedom and we can measure only its kinetic energy, as the probability of finding particles near the edges of the box is way lower than the average value (only kinetic component).

If the outcome of $\hat{O}$ is O_n, given a state $|\psi\rangle$, the probability of finding O_n is:

State (initial ψ) : $\psi(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega x^2}{2\hbar}}$, where $P_n = |\langle n|\psi\rangle|^2 = |(f_0^n(x), \psi(x))|^2$ overlap integral, with $f_0^n(x) = \langle x|n\rangle$

$$P(E_1) = \left|\int_{-\infty}^{+\infty} dx\, \varphi_1^*(x)\psi(x)\right|^2 \qquad \text{with } \varphi_1(x) = \sqrt{\frac{2}{L}} \cos\frac{\pi}{L}x \in \mathbb{R}$$

$$= \left(\int_{-\infty}^{+\infty} dx\, \sqrt{\frac{2}{L}} \cos\frac{\pi}{L} \cdot \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{2}} e^{-\frac{m\omega x^2}{2\hbar}}\right)^2 =$$

$$= \frac{m\omega}{\pi\hbar}\frac{2}{L}\left[\int_{-\infty}^{+\infty} dx\, \cos\frac{\pi}{L}x e^{-\frac{m\omega x^2}{2\hbar}}\right]^2$$

4.7.2 Trap smaller than the box

Let's now assume that the trap is much narrower than the box.

$$\text{Kronecker delta: } \delta_{ij} = \begin{cases} 1,\ i = j \\ 0,\ i \neq j \end{cases} \quad \rightarrow \delta(x, x') \sim \begin{cases} 1,\ \ |\,x - x'\,| < a \\ 0,\ \ x \neq x' \end{cases}$$

If $a \ll 1$, $1/a \sim 1$

I can also use a Gaussian delta function $\delta(x - x') = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{(x-x')^2}{2\sigma^2}}$, which becomes narrower as σ gets smaller.

In our case $\sigma^2 = \frac{\hbar}{2m\omega}$, so we can multiply and divide for the Gaussian normalization factor:

$$P(E_1) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{2}} \frac{2}{L} \left(\int_{-\infty}^{+\infty} dx\, \frac{e^{-\frac{x^2}{2\sigma^2}}}{\sqrt{2\pi}\sqrt{\frac{\hbar}{2m\omega}}} \cos\frac{\pi}{L}x\right)^2 \frac{\pi\hbar}{m\omega}$$

$$= \left(\frac{\pi\hbar}{m\omega}\right)\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{2}} \frac{2}{L}\int_{-\infty}^{+\infty} dx\, \delta(x - 0)\cos\frac{\pi}{L}x = \cos\frac{\pi}{L} \cdot 0 = 1 \qquad \text{Applying the Delta function}$$

Check that $P(E_1)$ is dimensionless:

$$P(E_1) = \frac{2}{L}\left(\frac{\pi\hbar}{m\omega}\right)^{\frac{1}{2}} \rightarrow \sqrt{\frac{[J][S]}{[kg][S]^{-1}}} = \sqrt{[\frac{[kg][m]^2[S]^{-2}[S]}{[kg][S]^{-1}} \cdot \frac{1}{[m]}}$$

$P(E_1)$ is dimensionless.

4.7.3 Conclusion

The probability has actually a value larger than one, energy levels tend to overlap heavily when considering ground state at small oscillations. Anyway, the average value of energy is $\frac{1}{4}\hbar\omega$.

Part II

Quantum chemistry

Chapter 5

Approximation methods

How do we solve quantum mechanical problems? Or to be more specific, how to solve the (stationary) Schrodinger equation $H\psi = E\psi$? There are some "solvable" problems, for which we get a wave function to fit any desired value. As the problems become more complicated, even by relying on super computers it is impossible to design algorithms that provide for an exact solution. There is the need for approximation methods. Approximation methods can be "ideal" and "non-ideal" (not conventional names). An ideal approximation method can become an exact method by tuning some parameters, the non-ideal ones will always remain an approximation, even with huge computational power (many in biology are non-ideal, like the Hartree-Fock, and are developed upon a physical intuition that allows to make important assumptions). Some assumption concern the shape of the Hamiltonian (like confining a particle in a box instead of a complex potential), some concern the solution of a given Hamiltonian. The question we ask ourselves as biologist is "do we want to be more accurate or insightful?". If our aim is a biological application of quantum mechanics we are more interested in accuracy rather than completely understanding a structure $\rightarrow$ approximation.

5.1 Truncated eigenstate expansion (Generalized Fourier)

Most quantum mechanical problems have an infinite number of functions in the basis set of functions that should be used to represent the problem. We can simplify our calculations and make a useful and accurate approximate solution by considering a finite subset of all the possible functions, especially those that have energies close to the state of the system of interest.

5.1.1 Operators

An Hermitian operator $\hat{O}$ defined such as it is complete and orthonormal $\hat{O}^\dagger = \hat{O}$ can be applied to a wave function $\hat{O}\psi_n(x) = o_n\psi_n(x)$ such as $(\psi_n(x), \psi_m(x)) = \delta_{mn}$
Remember that *complete* and *orthonormal* means:

- *orthonormal*: $(\psi_n(x), \psi_m(x)) = \delta_{mn}$, or using Dirac notation $\langle o_k|o_n\rangle = \delta_{mn}$

- *complete*: $|\psi\rangle = \sum_n \langle o_k|\psi\rangle|o_n\rangle$.

5.1.2 Generalized Fourier series

If given $g(x) \in L^2$ I can write the projection of function onto a basis of functions. The **Generalized Fourier Series of a L^2 function** is

$$g(x) = \sum_n \big(\psi_n(x), g(x)\big)\psi_n(x) = \sum_{n=1}^{\infty} c_n\psi_n(x)$$

Where $\big(\psi_n(n), g(n)\big)$ are coefficient of the inner product with $c_n \in \mathbb{C}$.

5.1.2.1 Expansion

Any wave function can be expanded, just like $\vec{v} = \sum_n c_n\vec{e}_n$, where $c_n = \vec{v}\,\vec{e}_n$. But the expansion can be truncated. For example, if we have a vector projected to its components $\vec{v} = v_1\hat{e}_1 + v_r\hat{e}_r$, we can choose a smart basis $\vec{w}_1, \vec{w}_2$, so that we can describe the vector with fewer elements and end up with something like $\vec{v} \cong (\vec{v} \cdot \vec{w}_1)\vec{w}_1$. We shall truncate the sum to a finite number, not to infinite, such as there is no projection onto the third coordinate but only to a two dimensional plane. Such an example is reported in figure 5.1.
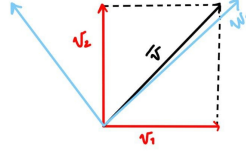
Figure 5.1: Example of an approximation using the vector example.

5.1.2.2 Momentum operator

Suppose $\hat{O} = \hat{P}$ (momentum operator) $\rightarrow$ eigenstates are represented by plane waves that are continuous. It can be integrated:

$$g(x) = \int_{-\infty}^{\infty} \frac{dp}{2\pi}(e^{ipx}, g(x)) \cdot e^{i\frac{px}{\hbar}}$$

This is an integral of a function over phase (where $\frac{dp}{2\pi}$ serves as normalization constant). The inner product represents a coefficient with a continuous label so it's a function of the label.

$$\tilde{g}(p) = \int dx \cdot e^{-ipx}g(x) \ \rightarrow \ g(x) = \int \frac{dp}{2\pi} \cdot \tilde{g}(p) \cdot e^{-ipx}$$

The latter is an integral over momentum of Fourier transform with a negative sign. $\tilde{\mathbf{g}}(\mathbf{p})$ is the **Fourier transform**, that is a measurable quantity and it's also one of the most successful algorithms (FFT).

5.1.3 Quantum system composed by a nucleus and an electron

Suppose we have a quantum system composed by a nucleus with an electron flying by. $|\psi(x)|^2$ needs to be computed by solving the Schrödinger equation. With scattering experiments the Fourier transform $|\tilde{\psi}(\mathbf{p})|^2$ can be measured. This method is used in X-Ray Diffraction Crystallography, IR spectroscopy and so on.

5.1.3.1 Truncating the expansion

So, how do we truncate the expansion? Example:

$$(g,g) = \left(\sum_n c_n \psi_n(x), \sum_m c_m \psi_m(x) \right) = \sum_{m,n} c_n^* \cdot c_m (\psi_n, \psi_m)$$

Where $(\psi_n, \psi_m) = \delta_{nm}$ and for the Kronecker delta properties I get:

$$(g,g) = \sum_n c_n^* \cdot c_m \cdot 1 \rightarrow (g,g) = \sum_{n=0}^{\infty} |c_n|^2$$

That is the square module of Fourier coefficient. If $g(x)$ is a wave function then $(g,g) = 1$, which is the probability of finding the electron in the region delimited by the function (obviously, the electron will *always* be somewhere). From $(g,g) = 1$ we get the **SUM RULE**: $\sum_{n=0}^{\infty} |c_n|^2 = 1$. The aim of the approximation method is finding a M integer that indicates how far from one is the wave function that needs to be approximated. E.g.: $\sum_{n=0}^{M} |c_n|^2 \simeq 0.98$

5.1.4 The art of approximation

For example, we might want to use the harmonic oscillator ground state to approximate a sum of Gaussian. Meaning "use problem B to solve problem A". Clearly, problem B shall be as close as possible to problem A. Our aim is to solve the Schrödinger equation written as $\hat{H}\varphi_n = E_n \varphi_n$, assuming we can solve $\hat{H}_0 \psi_n = \lambda_n \psi_n$ that represents an harmonic oscillator (shown in figure 5.2).
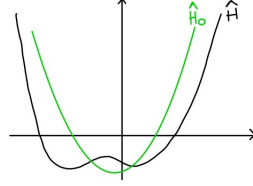
Figure 5.2: How to approximate an otherwise very difficult function with a known, simpler one.

5.1.4.1 Schröedinger equation with truncated basis set

First we proceed by writing the Schröedinger equation with the truncated basis set.

$$\hat{H} \left(\sum_{m=1}^{M} c_m^{(n)} \psi_m(x) \right) = E_n \left(\sum_{m=1}^{M} c_m^{(n)} \psi_m(x) \right) \text{ where } c_m^{(n)} = \int dx\, \psi_m^*(x) \varphi_n(x)$$

Since the Hamiltonian operator is a function it can be propagated through the equation. Right now we are expanding n and projecting it onto m.

$$\sum_{m=1}^{M} c_m^{(n)} \hat{H} \psi_m = E_n \sum_{m=1}^{M} c_m^{(n)} \psi_m$$

5.1.4.2 Projection on the basis

We project both functions on the basis (scalar product). We multiply both sides for an arbitrary wave function ψ_l (that we can supposedly solve).

$$\sum_{m=1}^{M} (\psi_l, \hat{H}\psi_m) c_m^{(n)} = E_n \sum_{m=1}^{M} c_m^{(n)} (\psi_l, \psi_m)$$

The inner product between two functions gives an integer. $H_{lm} = H_{ml}^*$ is an hermitian matrix that can be diagonalized to get the eigenvalues.

$$\sum_{m}^{M} H_{lm} c_m^{(n)} = E^{(n)} c_l$$

We reduced a complex problem to a conventional eigenvalue problem with a H_{lm} matrix. The pain is to compute the M integrals and to find an appropriate "problem B". As a results, this method is hardly applicable to any problems with more of 3 dimensions.

5.2 Quantum tunnelling - The Landau problem
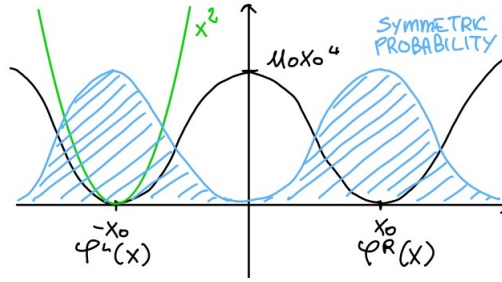
Figure 5.3: ass problem

The ass problem (because the potential kinda looks like an ass) is the gate to the understanding of quantum tunneling (necessary for quantum bonds, which are a reflection of the quantum tunneling behaviour). The potential is: $U(x) = U_0(x^2 - x_0^2)^2$.

5.2.1 Hamiltonian

The Hamiltonian for the wave function: $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U_0 \cdot (x^2 - x_0^2)^2$. Note that this is a symmetric function, roughly composed by two gaussians, so we can approximate the function with an harmonic oscillator. Considering the potential to its lowest points it can be approximated and then expanded. We have two basis elements, the two eigenstates $n = 0, 1$ (ground state and first excited state), and we wish to solve $\hat{H}\varphi_n = E_n\varphi_n$, with $n = 0, 1$:

$$\hat{H}\varphi_n = E_n\varphi_n \begin{cases} \varphi_0 \cong C_L^0 \, \psi^L(x) + C_R^0 \, \psi^R(x) \\ \varphi_1 \cong C_L^1 \, \psi^L(x) + C_R^1 \, \psi^R(x) \end{cases}$$

C_L and C_R are coefficients for each part of the function, one for each eigenstate. The values φ_o and φ_1 are the two eigenvalues of a 2×2 matrix. We then proceed to calculate the value of the matrices for the expansion.

$$H_{RR} = (\psi_R, \hat{H}\,\psi_R) = \int \psi_R^*(x) \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U_0 \cdot (x^2 - x_0^2)^2 \right] \psi_R(x)\,dx$$

$$= \int \psi_R^*(x) \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 \cdot (x^2 - x_0^2)^2 \right] \psi_R(x)\,dx$$

U_0 has been substituted with the potential energy of the harmonic oscillator approximation. The integral is computable with Taylor expansion because we consider the minimum of the function.

$$U(x) = U(x_0) + U'(x_0)(x - x_0) + \frac{1}{2}\,U''(x_0)(x - x_0)^2 + \ldots$$

The final result is:

$$H_{RR} = \frac{1}{2}\hbar\omega$$

And since this is a symmetrical problem we can also foresee that $H_{LL} \cong \frac{1}{2}\hbar\omega$. The result of $H_{LR} = H_{RL}$ is expected to be very small because the probability of finding the particle in the middle of the harmonic oscillator is very small, i.e. when $\psi_L(x)$ is large, $\psi_R(x)$ is going to be small and viceversa.

$$H_{RL} = H_{LR} = \int dx\,\psi_L(x)\hat{H}\psi_R(x) = \varepsilon$$

Now we can calculate the matrix

$$H_{mn} = \begin{pmatrix} E_0 & -\varepsilon \\ -\varepsilon & E_0 \end{pmatrix} = \begin{pmatrix} \frac{1}{2}\hbar\omega & -\varepsilon \\ -\varepsilon & \frac{1}{2}\hbar\omega \end{pmatrix} = E_0 \begin{pmatrix} 1 & -\frac{\varepsilon}{E_0} \\ -\frac{\varepsilon}{E_0} & 1 \end{pmatrix}$$

$E_0 \gg \varepsilon$ because of the energy barrier due to H_{mn}. We reduced a complex problem to a linear algebra problem: $\hat{H}\psi = E\psi \rightarrow H_{mn}C_n^{(l)} = E_l C_n^{(l)}$.

5.2.2 Ground state

In the ground state there is a 50% probability of finding the particle in the left part and 50% of finding it in the right one.

$$\begin{pmatrix} 1 & -\frac{\varepsilon}{E_0} \\ -\frac{\varepsilon}{E_0} & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 - \frac{\varepsilon}{E_0} \\ 1 - \frac{\varepsilon}{E_0} \end{pmatrix}$$

This ground state has slightly lower energy than the normal ground state

$$1^{st}\ \text{ex.st.:}\ \begin{pmatrix} 1 & -\frac{\varepsilon}{E_0} \\ -\frac{\varepsilon}{E_0} & 1 \end{pmatrix} \begin{pmatrix} 1 \\ -1 \end{pmatrix} = \left(1 + \frac{\varepsilon}{E_0}\right) \cdot E_0 \cdot \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

5.2.3 Quantum superposition

If the barrier is infinite the ground state is trivially degenerate. I then have two independent quantum systems. The particle cannot change its state. Instead, if the barrier is finite (slightly determined end of the barrier at very high energies) it splits into two states (**splitting states**) that interact with each other. The particle goes back to a 100% probability of being in either one or another system. This is called **quantum superposition**. Since the barrier is at very high energy, we could expect to find the correspondence principle at some point. Classical interpretation of the system at this point says that the particle could "decay" from a state of very high energy into one of the two ground states (50% probability for each state, fair game). Quantum interpretation gives the 100% probability to the electron of being in both the states at the same time.

$$\begin{cases} \varphi_0(x) = \frac{1}{\sqrt{2}}[\psi^L(x) + C_R^0\,\psi^R(x)] \\ \varphi_1(x) = \frac{1}{\sqrt{2}}[\psi^L(x) + C_R^0\,\psi^R(x)] \end{cases}$$

5.2.4 Quantum tunnelling

So, if at $t = 0$, the particle is on the left $|\psi_0\rangle = |\psi_L\rangle$, the function immediately after will be $\psi_L(x)$. However, if we wait long enough, the probability to find it in each state will be 50% - 50%. What is the probability of finding the particle on the right at given time t? $(P_R(t > 0) = ?)$ $P_L(t > 0) = 1 - P_R(t > 0)$ By definition $E_0 = 0, E_1 = \varepsilon$. Consequently, $\varepsilon = E_1 - E_0$, To find the probability of the particle being on the right/left, $(P_{R/L}(t) = |\langle \psi_{R/L} | \varphi(t) | \psi_{R/L} | \varphi(t)\rangle|^2)$, we will use the time evolution operator.

$$P_R(t) = |\langle\psi_R|e^{-\frac{i}{\hbar}\cdot t\hat{H}}|\psi_L\rangle|^2$$

Minding that ψ_R occurs at time t whilst ψ_L occurs at $t = 0$. If I want to check whether the particle is still on the left

$$P_L(t) = |\langle\psi_L|e^{-\frac{i}{\hbar}\cdot t\hat{H}}|\psi_L\rangle|^2$$

Let's first compute the probability for a small t. We perform the Taylor expansion of $e^{-\frac{i}{\hbar}\cdot t\hat{H}} = \mathbb{1} - \frac{i}{\hbar}\cdot t\hat{H}$.

$$|\psi_L\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \ |\psi_R\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \ \hat{H} = \begin{pmatrix} 0 & \varepsilon \\ \varepsilon & 0 \end{pmatrix}$$

$$P_R(t) \cong \left|\langle\psi_R|\mathbb{1} - \frac{i}{\hbar}\cdot t\hat{H}|\psi_L\rangle\right|^2 \cong \left|(0, 1)\left[\mathbb{1} - \frac{i}{\hbar}\cdot t\hat{H}\begin{pmatrix} 1 \\ 0 \end{pmatrix}\right]\right|^2$$

$$\cong \frac{t^2}{\hbar^2}\varepsilon^2$$

But since $\frac{t\varepsilon}{\hbar} << 1$ we get $t << \frac{\hbar}{\varepsilon}$. This is telling us that by waiting a little time the probability of finding the particle on the other side increases. This phenomenon is called **quantum tunnelling**. The conclusion up until this point is:

- A quantistic particle can cross an energy barrier, and the probability (or rate at which the transitions happen) is given by

$$k = \frac{\varepsilon}{\hbar}$$

  Which is an exponentially small amount. There is an analogy between thermal kinetic activation and quantum tunnelling, both happen because of stochastic fluctuations. ($K \propto e^{\frac{\Delta V}{K_B T}}$). The difference is that in a quantum system this happens in quantum time and is not influenced by the temperature of the system.

- In quantum tunnelling, the superposition between the higher energy levels that is caused by the lowering of the potential barrier causes the splitting of the lower energy levels. This is remarkably important when considering the **formation of the hydrogen bond → electron sharing is quantum tunneling!** At infinite distance we don't have any sharing because it's like having an infinite energy barrier. When the two atoms get close to each other, they share an electron via quantum tunneling, because of this then the energy levels split and create the two orbitals (bonding, antibonding).

5.2.5 Quantum pulsation

For the final t we cannot expand the exponent like we did before. Given $e^{-\frac{it}{\hbar}\hat{H}} |\psi_R\rangle$, we don't know $H\psi_R$, but can rewrite ψ_R as linear combination of eigenstates of H:

$$\text{ground state: } |0\rangle = \left(\frac{|L\rangle + |R\rangle}{\sqrt{2}}\right) \to \sqrt{2}\,|0\rangle = |L\rangle + |R\rangle$$

$$\text{first excited state: } |1\rangle = \left(\frac{|L\rangle - |R\rangle}{\sqrt{2}}\right) \to \sqrt{2}\,|1\rangle = |L\rangle - |R\rangle$$

By summing and subtracting,

$$\begin{cases} |L\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle) \\ |R\rangle = \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle) \end{cases}$$

So we can substitute them and use Hamiltonian operator:

$$e^{-\frac{it}{\hbar}\hat{H}} |R\rangle = \frac{e^{-\frac{it}{\hbar}\hat{H}}}{\sqrt{2}} \cdot (|0\rangle - |1\rangle) = \frac{1}{\sqrt{2}}\,|0\rangle - \frac{e^{-\frac{it}{\hbar}\varepsilon}}{\sqrt{2}}\,|1\rangle$$

Where $e^{-\frac{it}{\hbar}\varepsilon}$ is the relative weight of quantum superposition for the first excited state ($E_1 = \varepsilon$). Ground state has an eigenvalue $E_0 = 0$ as stated above. Let's calculate the probability for the particle to be on the left.

$$P_L = |\langle L|\psi(t)\rangle|^2 = \left| \left\langle L \middle| \left(\frac{1}{\sqrt{2}}\,|0\rangle - \frac{1}{\sqrt{2}} \cdot e^{-\frac{it}{\hbar}\varepsilon}\,|1\rangle\right) \right\rangle \right|^2$$

Knowing that $\langle L|L\rangle = \frac{1}{\sqrt{2}}$ and $\langle L|R\rangle = 0$,

$$= \left| \left\langle L \left| \frac{|L\rangle + |R\rangle}{\sqrt{2}} - e^{-\frac{it}{\hbar}\varepsilon} \cdot \frac{|L\rangle - |R\rangle}{\sqrt{2}} \right\rangle \right|^2 =$$

$$= \left(\frac{1}{2} - \frac{1}{2} \cdot e^{-\frac{it}{\hbar}\varepsilon} \right)^2 =$$

$$= \left[\frac{1}{2} - \frac{1}{2} \left(\cos\frac{\varepsilon t}{\hbar} + i\sin\frac{\varepsilon t}{\hbar} \right) \right]^2$$

$$P_L = \frac{1}{2}\left(1 - \cos^2\frac{\varepsilon}{\hbar}t \right)$$

For $t = 0$, $P = 0$ then $\cos^2 x$ grows with a t^2 rate. There is an oscillation (figure 5.4) with a given period $T = \frac{\hbar}{2\varepsilon}$.
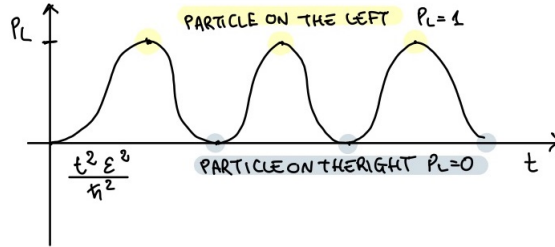
Figure 5.4: The oscillatory behaviour here represented is called **quantum pulsation**.

5.3   Ritz-Rayleigh variational principle

Suppose we want to estimate the ground state energy E_0 and corresponding wave function of the stationary Schrödinger equation. We define $\varphi_n(x)$ as a set of functions approximating $\psi_0(x)$. Variational principle gives an upper bound for the ground state energy. The chosen function's expectation value for energy normally overestimates the ground state energy; if the chosen function (unfortunately) represent an excited state, the expected value of energy for chosen function will highly overcome E_0. This set of function is assumed to be complete, so it can always be written as a sum of the linear combination of all the functions:

$$\varphi(x) = \sum_n^\infty c_n\psi_n(x), \quad \hat{H}\psi_n = E_n\psi_n \text{ furthermore } \sum_{n=0}|c_n|^2 = 1$$

The set of functions is normalized and orthonormal, too. Normalization implies $\sum_{n=0}|c_n|^2 = 1$. We need to find any function approximating $\psi_0^{(x)}$. The expectation value for φ is:

$$\langle \varphi | \hat{H} | \varphi \rangle = \sum_{mn} c_n^* c_m \langle \psi_n | \hat{H} | \psi_m \rangle =$$

$$= \sum_{n,m} c_n^* c_m E_m \delta_{nm} =$$

$$= \sum_n |c_n|^2 E_n =$$

$$= E_n \sum_n |c_n|^2$$

We recall that for a normalized set of functions $\sum_{n=0} |c_n|^2 = 1$ so $\langle \varphi | \hat{H} | \varphi \rangle = E_n$. And, of course, by assuming $c_n \geq 0$, the whole operation is $\geq E_0$ but this is true only if $\psi_n = \psi_0$. If $\varphi(x) = \psi_0$ then we have a projection on a vector on itself:

$$\begin{cases} c_n = 0, & n \neq 0 \\ c_n = 1, & n = 0 \end{cases}$$

The point here is that if we guess a function, compute the eigenvalues, and do the same with another function, the one that lowers the energy the most is the most accurate approximation of the wavefunction. If given two functions ψ_0 and ψ_1 such that they have respectively expected value E_0 and E_1, such that $E_0 < E_1$, E_0 is a better approximation for the wave function.

5.3.1 Example

Given $\varphi(x, \alpha)$, which is a family of wave functions, find $\psi_0(x)$ such as it is the best approximation of the family. In other words, we need to evaluate the following equation:

$$\langle \varphi_\alpha(x) | \hat{H} | \varphi_\alpha(x) \rangle = E(\alpha)$$

For which E is minimum. We must find the minimum of the function. This is done zeroing its gradient.

$$\frac{\partial}{\partial \alpha} E(\alpha) = 0 \text{ solve for } \alpha = \alpha_{\min}$$

Find α such as $E_{\alpha_{\min}}$ is the best approximation of E_0 and $\varphi_{\alpha_{\min}}(x)$ is the best approximation of ψ_0. Putting it formally, if we have multiple parameters: $\varphi_{\alpha \ldots \alpha_n(x)}$

$$\langle \varphi_{\alpha \ldots \alpha_n(x)} | \hat{H} | \varphi_{\alpha \ldots \alpha_n(x)} \rangle = E_{\alpha \ldots \alpha_n}$$

We need to calculate the minimum of the multidimensional function:

$$\nabla_\alpha E = 0 \rightarrow \begin{cases} \frac{\partial}{\partial \alpha_1} = 0 \rightarrow \alpha_1 = \alpha_{1,min} \\ \ldots \\ \frac{\partial}{\partial \alpha_n} = 0 \rightarrow \alpha_n = \alpha_{n,min} \end{cases}$$

Doing so we find a collection of energies and wavefunctions. The more parameters we have, the more we can explore the space, but we have no guarantee of finding the exact solution. Indeed, the probability of getting the right ground state is very low.

5.3.2 Quantum harmonic oscillator

Let's use the quantum harmonic oscillator to determine the steps necessary to perform this approximation method. Given the Hamiltonian equation for harmonic oscillator: $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 = \langle T \rangle + \langle U \rangle$.

5.3.2.1 Guessing a normalized Gaussian

Guess a normalized (the 4 term is used for normalization) Gaussian to best represent the harmonic oscillator: $\varphi_\alpha(x) = \left(\frac{1}{\sqrt{2\pi}\alpha}\right)^{\frac{1}{2}} e^{-\frac{x^2}{4\alpha^2}}$

5.3.2.2 Computation of the energy

Computation of $E(\alpha)$ by first evaluating the Hamiltonian function of $\varphi_\alpha(x)$ (first fragment, so to say)

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\varphi_\alpha(x) =$$

$$= \frac{\hbar^2}{2m}\left(\frac{1}{\sqrt{2\pi}\alpha}\right)^{\frac{1}{2}}\frac{d}{dx}e^{-\frac{x^2}{4\alpha^2}} =$$

$$= \frac{\hbar^2}{2m}\left(\frac{1}{\sqrt{2\pi}\alpha}\right)^{\frac{1}{2}}\cdot\frac{d}{dx}\frac{x}{2\alpha^2}e^{-\frac{x^2}{4\alpha^2}}$$

$$= \frac{\hbar^2}{2m}\left(\frac{1}{\sqrt{2\pi}\alpha}\right)^{\frac{1}{2}}\cdot\left(\frac{1}{2\alpha^2}e^{-\frac{x^2}{4\alpha^2}} - \frac{x^2}{2\alpha^2}e^{-\frac{x^2}{4\alpha^2}}\right)$$

$$= \frac{\hbar^2}{2m}\left(\frac{1}{\sqrt{2\pi}\alpha}\right)^{\frac{1}{2}}\cdot\frac{1}{2\alpha^2}\cdot\left(1 - \frac{x}{2\alpha^2}\right)e^{-\frac{x^2}{4\alpha^2}}$$

The total kinetic energy for this approximation of the quantum oscillator is:

$$\langle T \rangle = \frac{\hbar^2}{4m\alpha^2}\left[1 - \frac{x^2}{2\alpha^2}\right]e^{-\frac{x^2}{4\alpha^2}}\cdot\frac{1}{(\sqrt{2\pi}\alpha)^{\frac{1}{2}}}$$

And go on with the evaluation of $E(\alpha)$.

$$E(\alpha) = \frac{1}{\sqrt{2\pi}\alpha}\cdot\int dx\, e^{\frac{x^2}{2\alpha^2}}\left[\frac{\hbar^2}{4m\alpha^2}\left(1 - \frac{x^2}{2\alpha^2}\right) + \frac{1}{2}m\omega^2 x^2\right] =$$

$$= \frac{1}{\sqrt{2\pi}\alpha} - \left(\frac{\hbar^2}{8m\alpha^4} + \frac{1}{2}m\omega^2\right)\cdot\int dx\,\frac{e^{\frac{x^2}{2\alpha^2}}}{\sqrt{2\pi}\alpha}x^2$$

The integrand is called **Gaussian variance** and it is equal to $\alpha^{\mathbf{2}}$. So:

$$E(\alpha) = \left(\frac{1}{4} - \frac{1}{8}\right)\frac{\hbar^2}{m\alpha^2} + \frac{\alpha^2}{2}m\omega^2 = \frac{1}{8}\frac{\hbar^2}{m\alpha^2} + \frac{\alpha^2}{2}m\omega^2$$

The latter sum is a sum of two energy values.

To find $\alpha_{min} \rightarrow \frac{\partial}{\partial \alpha} E(\alpha) = 0$

$$\frac{\partial}{\partial \alpha} E(\alpha) = -2 \cdot \frac{1}{8} \frac{\hbar}{m\alpha^3} + \alpha m\omega^2 = 0$$
$$\frac{\partial}{\partial \alpha} E(\alpha) = -\frac{\hbar}{4m} + \alpha^4 m\omega^2 = 0 \qquad \text{Multiply by } \alpha^3 \text{ both sides}$$
$$\alpha^2 = \sqrt{\frac{\hbar^2}{4m^2\omega^2}}$$

This is the same result we got for the quantum harmonic oscillation problem! Keep in mind that this method only applies to the ground state.
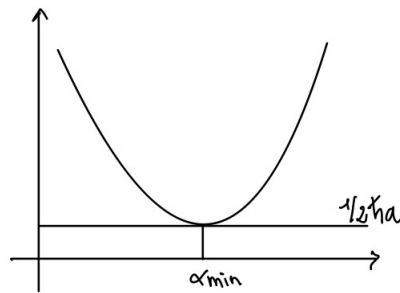
Figure 5.5: In this picture we can see a point of intersection because we get the exact result.

Chapter 6

Atomic physics

6.1 Quantum theory of the Hydrogen atom

6.1.1 Evaluation of conservation of energy

Remember that when talking about classical theory of the hydrogen atom we simplified the problem by switching from Cartesian to polar coordinates and, by applying the conservation laws, we obtained:

$$E = \frac{1}{2} m \left(\frac{d}{dt} n \right)^2 + \frac{L^2}{2mr^2} + U(r)$$

That can be represented in quantum mechanics with the Hamiltonian. The Hamiltonian in polar coordinates is written as

$$\hat{H} = (-\frac{\hbar^2}{2m^2} \nabla - \frac{e^2}{r})$$

6.1.1.1 Spherical coordinates

The best evaluation of the Hamiltonian for the quantum analysis of the hydrogen atom is obtained by using the **spherical coordinates**. Nabla (the Laplacian) in spherical coordinates (r, θ, φ) is hence written as:

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

The Hamiltonian then becomes:

$$\hat{H} = \frac{\hbar^2}{2mr^2} \frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2mr^2} \cdot \left(\frac{\partial^2}{\partial \theta^2} + \frac{1}{\tan \theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin \theta} \frac{\partial^2}{\partial \varphi^2} \right) - \frac{e^2}{r}$$

The first part is called **radial part** because it's r-dependent only, the other is the **angular part** and depends on r, θ, and φ.

6.1.1.2 Angular momentum

Now we can consider the angular momentum in classical mechanics and quantum mechanics:

$$\vec{L} = \vec{r} \times \vec{p} = \vec{r} \times (-i\vec{\nabla}\hbar)$$

$$Fact \rightarrow \hat{\vec{L}}^2 = \hat{L}_x\hat{L}_x + \hat{L}_y\hat{L}_y + \hat{L}_z\hat{L}_z = \vec{\nabla}^2\hbar^2$$

This is corresponding to the angular part of the Hamiltonian that can be rewritten in spherical coordinates with the inclusion of the angular momentum multiplied by $\hbar^2$.

$$\hat{H} = \frac{\hbar^2}{2mr^2}\frac{\partial^2}{\partial r^2} + \frac{\hat{L}^2}{2mr^2} - \frac{e^2}{r}$$

The fact that the angular momentum is not present in the radial part of the Hamiltonian means that the two operators must commute $[\hat{H}, \hat{L}^2] = 0$ and they must also share the same eigenstates. It's also important to note that the individual components of the angular momentum only commute with $\hat{L}^2$ but not with each other.

$$\begin{cases} [\hat{L}_i, \hat{L}_j] \neq 0 & i,j = 1,2,3,\dots \\ [\hat{L}_i, \hat{L}^2] = 0 \end{cases}$$

6.1.1.3 Spherical coordinates

The following functions are called **spherical harmonics**, these functions are defined on the surface of a sphere and form a complete and orthonormal set of functions. For this latter reason they can be expressed as a linear combination. In quantum mechanics, spherical harmonics are the eigenfunctions of $\hat{L}^2$ and actually generate a rotation of azimuthal angle (φ). They depend on two quantum numbers because they use two different operators and are only part of the angular part of the Hamiltonian.

$$\begin{cases} \hat{L}_z Y_{lm}(\theta,\varphi) = \hbar m Y_{l,m}(\theta,\varphi) & m = l, -l+1, \dots, 0, \dots, -l \text{ (projection)} \\ \hat{L}^2 Y_{lm}(\theta,\varphi) = \hbar^2 l(l+1) Y_{l,m}(\theta,\varphi) & l = 0,1,2,\dots \text{ (max length,)} \, m < l^2 \end{cases}$$

In this way we obtain the quantization of $\hat{L}_j$ and $\hat{L}^2$. Where m represents the projection (bounded to l), and l the length. Note that we wrote $l(l+1)$ and not l^2, the difference only matters in the quantum realm and it is noticeable when l is small. For larger l we go back to the classical realm (correspondence principle).

6.1.1.4 One-dimensional Schröedinger equation

The wave function can then undergo variables separation, this implies the fact that eigenstates of the Hamiltonian are also eigenstates of the square of the angular momentum.

$$\psi_{n,l,m}(r,\theta,\varphi) = R(r) \cdot Y_{l,m}(\theta,\varphi)$$

I can calculate the Hamiltonian of the newly obtained wave function.

$$\hat{H}\psi_{n,l,m} = \left[\frac{-\hbar^2}{2mr^2}\frac{\partial^2 r}{\partial r^2}R_n Y_{l,m} + \frac{\hbar^2 l(l+1)}{2mr^2}R_n Y_{l,m} - \frac{e^2}{r}R_n Y_{l,m}\right] = E_{n,m,l}R_n Y_{l,m}$$

By eliminating $Y_{l,m}$ we obtain the **one-dimensional Schrödinger equation**, with one equation for each value of l. Each equation is referred to a different expression of energy.

$$\frac{-\hbar^2}{2mr^2}\frac{\partial^2 r}{\partial r^2}R_n + \frac{\hbar^2 l(l+1)}{2mr^2}R_n - \frac{e^2}{r}R_n = E_{n,m,l}R_n$$

6.1.2   Angular momentum conservation

6.1.2.1   Kinetic energy

We can also rewrite kinetic energy in a polar form.

$$-\frac{\hbar^2}{2m}\nabla^2 \rightarrow -\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}\dot{r} + \frac{\hat{L}^2}{2mr^2} = \hat{T}_r + \hat{T}_{(\theta,\varphi)}$$

Where $\hat{T}_r$ is the radial component of kinetic energy, $\hat{T}_{(\theta,\varphi)}$ is the angular component of kinetic energy. Note that if the radial part is applied to a radial function $rR(r)$, the second derivative applies to the product of r and the function, not just to r.

$$R(r) = \frac{1}{r}\frac{\partial^2(r \cdot R(r))}{\partial r^2}$$

As we said before, the Hamiltonian commutes with the square of the angular momentum $[\hat{H}, \hat{L}^2] = 0$ because the angular momentum doesn't have any derivatives with respect to r. By considering the Hamiltonian as $\hat{H} = \hat{T}_r + \hat{V}$ with $\hat{V}$ as describing the coulomb potential, these commutations are possible:

$$[\hat{T}_r, \hat{L}^2] = 0, \quad [\hat{V}, \hat{L}] = 0, \quad [\hat{L}^2, \hat{L}^2] = 0$$

All these have common sets of eigenstates. Note that $[\hat{T}_r, \hat{L}^2] = 0$ is possible because $\hat{T}_r$ doesn't depend on θ.

6.1.2.2   Family of equation for each unit of angular momentum

We can implement the fact that the operators, as said above, share a common set of eigenstate by plugging in the following:

$$\psi_{nml}(r,\theta,\varphi) = R_n(r)Y_{lm}(\theta,\varphi)$$

In the Schrödinger equation, obtaining a family of equations, one for each unit of angular momentum:

$$\frac{-\hbar^2}{2mr^2}\frac{\partial^2 r}{\partial r^2}R_n + \frac{\hbar^2 l(l+1)}{2mr^2}R_n - \frac{e^2}{r}R_n = E_{n,m,l}R_n$$

$$l = 0 \rightarrow \textbf{s-state}: \frac{-\hbar^2}{2mr^2}\frac{\partial^2 r}{\partial r^2}R_n - \frac{e^2}{r}R_n = E_{n,l}R_n$$

$$l = 1 \rightarrow \textbf{p-state}: \frac{-\hbar^2}{2mr^2}\frac{\partial^2 r}{\partial r^2}R_n + \frac{3\hbar^2}{2mr^2}R_n - \frac{e^2}{r}R_n = E_{n,m,l}R_n$$

$$l = 2 \rightarrow \textbf{d-state}: \frac{-\hbar^2}{2mr^2}\frac{\partial^2 r}{\partial r^2}R_n + \frac{6\hbar^2}{2mr^2}R_n - \frac{e^2}{r}R_n = E_{n,m,l}R_n$$
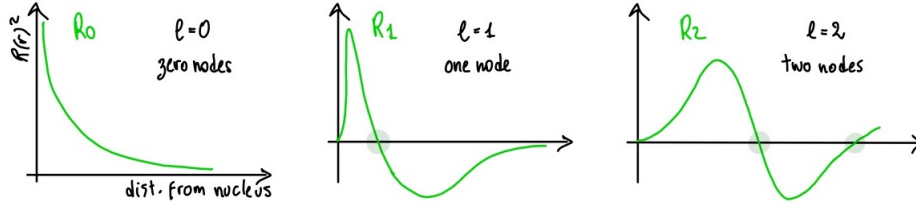
Figure 6.1: Representation of the probability of a particle to be found at distance r from nucleus

We can infer from these equation that we get stronger repulsions between states as l grows (graphs of such functions shown in figure 6.1).

Defining $U(r) \equiv rR(r)$ implies

$$-\frac{\hbar}{2m}\frac{d^2}{dr^2}U(r) + \frac{\hbar l(l+1)}{2mr^2}U(r) - \frac{e^2}{r}u(r) = EU(r)$$

Where $u(r)$ is not a potential. When we tried to solve the H-atom with classical mechanics, the analogy with the kinetic energy was perfect. This is not quite the case?

6.1.2.3   Probability of a particle to be at a certain distance

Finally we want to calculate the probability of a particle to be at distance r.

$$dr\, Prob(r) = |R(r)|^2 r^2 dr$$

$$P(\vec{r}, \vec{r} + dr) = \int_{\vec{r}}^{\vec{r}+dr} dr\, r^2 \iint d\theta\, d\varphi\, |R(r)\, Y(\theta, \varphi)|^2 = \int_{\vec{r}}^{\vec{r}+dr} dr\, r^2 R^2(r) \iint_{sph} d\theta\, d\varphi |Y|^2$$

Since the function is not dependent on θ or φ, the integral equals 1.

$$P(\vec{r}, \vec{r} + dr) = \vec{r}^2 R^2(r) dr$$

Depending on the value of l the probability of the electron depending on θ and φ can be obtained. At $l = 0$ the probability is more concentrated on the centre and then fades out (s orbital). At $l = 1$ the function depends on θ but not on φ, the function is cylindrically symmetrical (p orbital). It is important to remember that there is no orbit in an atom, for the concept of trajectory breaks down on a quantum level.

6.2   Relationship between spin and statistics: Quantum many-body systems

6.2.1   The importance of spin

Spin statistics can explain chemistry, quantum entanglement, and quantum computers. The Stern Gerlach experiments confirm the fact that electrons have a magnetic moment, which is quantised in integers or half integers, because they can interact with a magnetic field. Generally, particles behave differently and may have different states of being. What we know is that we cannot measure more than one component of the magnetic moment (quantum uncertainty) and this **intrinsic** magnetic

moment behaves like an angular momentum. The rotation of the electron upon itself generates a magnetic field and a magnetic moment. This is called **spin**, $\hat{S}^2, \hat{S}_z$ a property of particles that **doesn't change with time** and that can distinguish a particle from one another.
We assume that:

$$[\hat{S}_x , \hat{S}_y] = i\hbar\hat{S}_z$$

$$[\hat{S}_z , \hat{S}^2] = \hat{0}$$

The values of $\hat{S}^2$ characterize the behaviour of the particle.

$$\hat{L}^2 \rightarrow l = 0, 1, 2, \ldots$$

$$\hat{S}^2 \rightarrow s = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$$

Electrons, neutrons, and protons have $s = 1/2$. Photons, for instance, have $s = 1$.

6.2.2 Spin-Statistics theorem for identical particles

Let's consider a wave function of many identical particles ψ, for instance n identical electrons with spin s, $\hat{S}_z$, and position r. All the particles have the same velocity.

$$\psi(\vec{r_1}, s_1^z, \vec{r_2}, s_2^z, \ldots, \vec{r_n}, s_n^z) \text{ ,with } \vec{q} = (\vec{r}, \vec{s_z})$$

For identical particles: $\psi(\vec{q_1}, \vec{q_2}, \ldots, \vec{q_n}) A[\psi(\vec{q_1}, \vec{q_2}, \ldots, \vec{q_n}) \pm \psi(\vec{q_1}, \vec{q_2}, \ldots, \vec{q_n})]$

6.2.2.1 Antisymmetric wave function

An antisymmetric wave function is a wave-function that under the exchange of pairs of identical particles has a total spin, s, that is an **half integer** (1/2, 3/2, ...). Swapping the wave function **changes** it.

$$\psi(\vec{q_1}, \vec{q_2}, \ldots, \vec{q_n}) = -\psi(\vec{q_1}, \vec{q_2}, \ldots, \vec{q_n})$$

The particles that have an antisymmetric wavefunction are called **fermions**.

6.2.2.2 Symmetric wave functions

A symmetric wave function is a wave function that under the exchange of pairs of identical particles has a total spin, s, that is an **integer** (1, 2, 3, ...). Swapping the wave function **doesn't change** it.

$$\psi(\vec{q_1}, \vec{q_2}, \ldots, \vec{q_n}) = \psi(\vec{q_1}, \vec{q_2}, \ldots, \vec{q_n})$$

The particles that have a symmetric wave function are called **bosons**.

6.2.2.3 Pauli's exclusion principle

In a quantum wave function, there cannot be two fermions with identical state or else two identical fermions cannot be found in the same quantum state.

$$\psi(q_1, q_2) = -\psi(q_2, q_1)$$

The two electrons are the same, $q_1 = q_2 = q$

$$\psi(q, q) = -\psi(q, q)$$

The only condition for which this equality is true is for $\psi = 0$, there is no wave function that can describe a system of two identical fermions with identical state. This is called **Pauli's exclusion principle** and applies to all identical fermions.

6.2.3 Mean Field Approximation

Solving the Schrödinger equation for more than one particle rapidly becomes challenging, even resorting to High Performance Computing. However, much of the global, qualitative structure of the Mondelyev table can be understood within a simple **mean field** picture: instead of accounting for all pairwise Coulomb interactions, we assume that the effect on each electron, due to all other electrons and the protons can be represented by an overall confining potential. Suppose we are dealing with two electrons:

$$\left(-\frac{\hbar^2}{2m} \sum_i^N \nabla_i^2 + U(\vec{r_1} \cdots \vec{r_n}) \right) \psi(\varphi_1 \cdots \varphi_n) = E\psi(q_1 \cdots q_n)$$

The solution to the eigenvalue problem that is also antisymmetric to the potential depends on the position.

$$U(\vec{r_1} \cdots \vec{r_n}) = \sum_{i,j} \frac{e^2}{|\vec{r_i} - \vec{r_j}|} - e^2 \frac{\mathbb{Z}}{r_i}$$

Instead of keeping track of all the interactions of particles on one another, we consider the average of the whole many-body system, e.g., mean coulombic repulsion. The interaction between single electron and average electron density is computed. The larger symmetry is the ground state, which for the H-atom this is **1s**, as shown in figure 6.2.
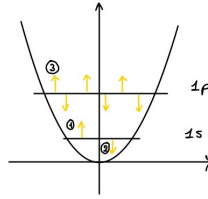

Figure 6.2: Position of electrons in the 1p and 1s states with relative spin (up or down)

The structure of the wave function is influenced by spin even if it doesn't appear in the Hamiltonian and can be used not only for electrons but for all subatomic/subnuclear particles.

6.2.3.1 Stable nuclei

A nucleus is divided into two different type of nucleons, protons and neutrons. Nucleons can have two different states: spin up (protons) and spin down (neutrons). Actually, the spin is really the only thing that allow us to differentiate the two, since their mass is basically the same (neutrons have a little heavier mass). For each spin there's an isospin up and an isospin down (isospin measures the charge). An example of (impossible) nucleus decay is shown in figure 6.3.
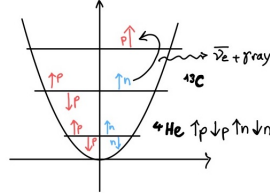
Figure 6.3: In this picture the $_2^4\text{He}^{2+}$ nucleus is represented. It it the most stable nucleus (α-particle). The thing is that the difference in mass ($m_n > m_p$) $\Delta m \to$ energy is not sufficient to reach the higher energy state and become a proton. Because of spin theory there is no other way that it can be. So, even if in principle a neutron could decay into a proton, ultimately Pauli's exclusion principle does not allow to have the same spin.

6.2.4 Quantum Entanglement

In an external/mean potential, the Schrödinger equation has a potential of a single coordinate that depends on where that potential is located, thanks to the mean field approximation.

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i=1}^N U(q_i) = \sum_i h_i$$

When $\hat{H}$ is separable into two parts, the wave function is the product of these two parts.

6.2.4.1 Identical bosons

Consider N identical spin-0 bosons (simplest system that represents the sum of all possible permutations for $N > 2$):

$$\psi(r_1, \ldots, r_n) = \prod_K^n \varphi_n(r_i) = \varphi_1(r_1) \cdot \cdots \cdot \varphi_n(r_n)$$

If I swap two excited states eg., $\varphi_s(r_3)$ and $\varphi_p(r_1)$, I do not obtain the same wave function (I get $\varphi_s(r_1)$ and $\varphi_p(r_3)$) so they are antisymmetric. If I swap two ground states they stay the same (they are symmetric). This system is also used for distinguishable particles (boltzmanions) or identical particles in semiclassic regimes.

6.2.4.2 Identical fermions

Consider now two identical fermions described by single-electron wave functions.

$$\psi(r_1, s_1^2, r_2, s_2^2) = \varphi_\uparrow(r_1)\varphi_\downarrow(r_2)$$

We can prove that the wave function of the two different fermions (hence each one is described by a different spin state) system is antisymmetric. This is called **Slater determinant** for N>2 fermions.

$$\psi = \frac{1}{\sqrt{2}} \big(\varphi_\uparrow(r_1)\varphi_\downarrow(r_2) + \varphi_\uparrow(r_2)\varphi_\downarrow(r_1) \big)$$

By swapping their indices

$$\psi' = \frac{1}{\sqrt{2}} \big(\varphi_\uparrow(r_2)\varphi_\downarrow(r_1) - \varphi_\uparrow(r_1)\varphi_\downarrow(r_2) \big)$$

And it's noticeable how $\psi = -\psi'$. The two functions are antisymmetric. This represents a quantum superposition of states. In order to follow Pauli's principle, each state has a 50% of probability to occur and when r_1 is $\uparrow$, r_2 must necessarily be $\downarrow$. We found out that Pauli's principle **entangles** particles. In our case with two fermions, the state of particle n.2 is entangled to the state of particle 1.

> **Quantum entanglement**: a physical phenomenon that occurs when a group of particles are generated, interact, or share spatial proximity in a way such that the quantum state of each particle of the group cannot be described independently of the state of the others, including when the particles are separated by a large distance.

6.2.4.3 Bell state

The two particles are said to be an **EPR pair** (Einstein-Podolsky-Rosen) and the state of the two particles is called a **Bell state**. If I measure spin 1, the wave function collapses into spin value 1 and spin 2 consequently collapses into spin value 2. The concept of **quantum entanglement** has no correspondences in classical mechanics and is used to develop quantum computers. In classical computers the information is carried on in one single state out of two (either the gate is open or is closed, binary system). In quantum computers there are N states, 2^N states entangled with each other at the same time. Much more information in 2^N can be stored compared to 1 [1].

6.2.4.4 Slater matrix

The antisymmetric equation is the determinant of this matrix:

$$\frac{1}{\sqrt{2}} \begin{pmatrix} \varphi_1(r_1) & \varphi_2(r_1) \\ \varphi_1(r_2) & \varphi_2(r_2) \end{pmatrix}$$

That can be generalized into

$$\frac{1}{\sqrt{2}} \begin{pmatrix} \varphi_1(r_1) & \ldots & \varphi_n(r_1) \\ \ldots & & \ldots \\ \varphi_1(r_m) & \ldots & \varphi_n(r_m) \end{pmatrix}$$

This latter matrix is called **Slater matrix** and the Slater determinant guarantees that the wave function is antisymmetric.

---

[1] With N bits in classical computer we can ultimately have just one number, even if we have N possible ways to arrange the bits. Instead, a quantum architecture supports 2^N states *simultaneously*. This more expressive power contributes to the idea of "quantum supremacy".

6.2.5 Mathematical formalism of Stern-Gerlach experiment

The spin $\hat{S}^2$ doesn't have a classical correspondence, we cannot directly obtain a formula for $\hat{S}^2$ in classical mechanics. Objects that have two states need to be found. Consider spin 1/2 only and choose an Hillbert space and an operator that acts on it. Since a particle with $s = 1/2$ can have two different states, the most natural choice for a Hillbert space would be L^2.

6.2.5.1 Eigenstates of the z-component

The eigenstates of the z-component are:

$$|\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \; |\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$\hat{S}_x$, $\hat{S}_y$, and $\hat{S}_z$ are represented by 2x2 matrices that must obey the commutation rule of $[\hat{S}^2, \hat{S}_z] = 0$ and $[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z$

6.2.5.2 Pauli's matrices

$$\hat{S}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \; \hat{S}_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \; \hat{S}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

6.2.5.3 Normalized eigenstates for the x-component

The normalized eigenstates for the x-component are:

$$|\rightarrow\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \; |\leftarrow\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

6.2.5.4 Conditional probability of spin given another

We can find the conditional probability of finding spin up with the condition of being in a state of spin left (but also spin up given spin up, etc.).

$$P(|\uparrow\rangle \,|\, |\leftarrow\rangle) = \left(\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \right)^2 = \frac{1}{2}$$

$$P(|\uparrow\rangle \,|\, |\uparrow\rangle) = \left(\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \right)^2 = 1$$

$$P(|\leftarrow\rangle \,|\, |\uparrow\rangle) = \left(\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \right)^2 = \frac{1}{2}$$

This is also the mathematical formalism that represents the Stern Gerlach experiment. In fact, if we calculate $P(|\uparrow\rangle \,|\, |\leftarrow\rangle) = \frac{1}{2}$, then $P(|\uparrow\rangle \,|\, |\uparrow\rangle) = 1$, we will get again $P(|\uparrow\rangle \,|\, |\leftarrow\rangle) = \frac{1}{2}$.

6.2.5.5 Total spin

We can calculate $\hat{S}^2 = \hat{S_x}^2 + \hat{S_y}^2 + \hat{S_z}^2$ that results in a sum of identity matrices, in fact

$$\hat{S}^2 = \frac{3}{4}\hbar^2 \big(\mathbb{1}_e\big)$$

The identity matrix $\mathbb{1}_e$ allows $\hat{S}^2$ to commute with every component of the spin operator.

6.2.6 Tensor product states

6.2.6.1 Tensor product

Up until now, we learned how to deal with spin's degrees of freedom only. But how do we integrate spin in the L_2 space of the wave function? We'll use the tensor product. Given two vectors, the definition of tensor product is:

$$\begin{pmatrix} a_1 \\ a_2 \\ \dots \\ a_n \end{pmatrix} \otimes \begin{pmatrix} b_1 \\ b_2 \\ \dots \\ b_n \end{pmatrix} = \begin{pmatrix} a_1 b_1 \\ a_1 b_2 \\ \dots \\ a_1 b_n \\ a_2 b_1 \\ a_2 b_2 \\ \dots \\ a_m b_n \end{pmatrix}$$

Tensor product is obtained by multiplying each a term with every b term. It creates another vector space (a larger Hillbert space) that is used to combine spins for many particles, spin and particle space of one particle ect. Tensor product is used to describe the *combination of two quantum states*.

6.2.6.2 Combination of two quantum states

Quantum state of particle 1: $\begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = \alpha_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \alpha_2 \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \alpha_1 \left|\uparrow\right\rangle + \alpha_2 \left|\downarrow\right\rangle = \left|\vec{\alpha}\right\rangle$

Quantum state of particle 2: $\begin{pmatrix} \beta_1 \\ \beta_2 \end{pmatrix} = \beta_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \beta_2 \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \beta_1 \left|\uparrow\right\rangle + \beta_2 \left|\downarrow\right\rangle = \left|\vec{\beta}\right\rangle$

These two single quantum states represent qubits.

Combination of the two states: $\left|\vec{\alpha}\right\rangle \otimes \left|\vec{\beta}\right\rangle \equiv \left|\vec{\alpha}\vec{\beta}\right\rangle = \begin{pmatrix} \alpha_1 \beta_1 \\ \alpha_1 \beta_2 \\ \alpha_2 \beta_1 \\ \alpha_2 \beta_2 \end{pmatrix}$

6.2.6.3 Resulting wave-function

The combination of the two states creates a wave function which amplitude corresponds to the observation of all the combinations of the particles. For example, $\alpha_1 \beta_1$ is the amplitude of observing the first particle $\uparrow$ and the second particle $\uparrow$. We can build the basis for a vector product of two particles and with this we can describe four different states since $\mathbb{R}^2 \otimes \mathbb{R}^2 = \mathbb{R}^4$

$$\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} = |\uparrow\uparrow\rangle \left.\begin{matrix} \alpha_1 = 1 \\ \beta_1 = 1 \end{matrix}\right| \quad \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} = |\uparrow\downarrow\rangle \left.\begin{matrix} \alpha_1 = 1 \\ \beta_2 = 1 \end{matrix}\right| \quad \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} = |\downarrow\uparrow\rangle \left.\begin{matrix} \alpha_2 = 1 \\ \beta_1 = 1 \end{matrix}\right| \quad \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} = |\downarrow\downarrow\rangle \left.\begin{matrix} \alpha_2 = 1 \\ \beta_2 = 1 \end{matrix}\right|$$

We can also derive the most general quantum mechanical state description of the EPR pair:

$$\left|\vec{\alpha}\vec{\beta}\right\rangle = \alpha_1\beta_1 |\uparrow\uparrow\rangle + \alpha_1\beta_2 |\uparrow\downarrow\rangle + \alpha_2\beta_1 |\downarrow\uparrow\rangle + \alpha_2\beta_2 |\downarrow\downarrow\rangle$$

In this way information about multiple state can be carried simultaneously.

6.2.6.4 Spinor

Given $\varphi(x)$ wavefunction lives in a L^2 Hillbert space.

$$\varphi(x) \otimes (\alpha |\uparrow\rangle + \beta |\downarrow\rangle) = \begin{pmatrix} \alpha\varphi(x) \\ \beta\varphi(x) \end{pmatrix} = \begin{pmatrix} \varphi_\uparrow(x) \\ \varphi_\downarrow(x) \end{pmatrix}$$

This latter matrix is called a **spinor**, which is a wave function that includes spin amplitude (usually wave function doesn't have information about spin of the particle).

6.2.6.4.1 Non-entangled state

$$|\psi\rangle = \frac{1}{\sqrt{2}} |\uparrow\uparrow\rangle + \frac{1}{\sqrt{2}} |\uparrow\downarrow\rangle = |\alpha \uparrow\rangle$$

The two measures are independent of each other, particle 2 can be found with a probability which is independent of the measurement of particle 1. It is said to be factorizable.

6.2.6.4.2 Entangled state

$$|\psi\rangle = \frac{1}{\sqrt{2}} \big(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \big) = \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ 0 \end{pmatrix}$$

Note that the expression cannot be factorized now.

6.2.6.5 Generation of entangled states

We can generate an operator that generates entangled states:

$$\frac{\big(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \big)}{\sqrt{2}} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \end{pmatrix} \big(U \big) \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

6.2.6.5.1 Quantum gates U is called **quantum gate** in quantum computing. Quantum gates can be defined as a **time evolution operators** that acts on the function to solve time-dependent Schrödinger equation and provide the dynamics of the system. $\hat{U}(\Delta t) = e^{i\hat{H}\Delta t}$ at state $|\psi(0)\rangle$ can be approximated with $(1 - \hat{H}\Delta t)$ and this latter can be solved by a quantum gate to give out $|\psi(t)\rangle$. This operation cannot be solved by classical computers, dynamics is naturally given out by quantum computers.

6.2.6.6 Three-electrons system

Remember that thanks to the mean field approximation (needed for many-body calculations) we have the advantage that:

$$\sum_{i<j} U(r_{ij}) \simeq \sum_i \bar{U}(r_i)$$

Making the computation piece-wise and therefore, much easier to solve. The Hamiltonian becomes the sum of many small Hamiltonians:

$$H = \sum_{ij} h_i \rightarrow \phi(q_1, \ldots, q_n) = \prod_i \phi(q_i)$$

With $q_i = (\bar{r}_i, S_i^z)$ representing the position. The thing is that a simple product generally does not respect the spin and its rules (e.g.Pauli blocking). This factorization works well for distinguishable particles, like in Boltzmanions systems. These are almost classical settings.

6.2.6.7 Two particle systems

Let's assume we have the following systems:

$$\textbf{Bosons} \quad \frac{1}{\sqrt{2}}(\phi_0(r_1)\phi_1(r_2) + \phi_0(r_2)\phi_1(r_1))$$

$$\textbf{Fermions} \quad \frac{1}{\sqrt{2}}(\phi_0(r_1)\phi_1(r_2) + \phi_0(r_2)\phi_1(r_1))$$

While for bosons for systems with $N > 2$ the sum of permutations is sufficient (symmetry), for fermions we'll need to calculate the Slater determinant (since it's guaranteed that the wave-function is antisymmetric). For this application ($N = 3$) we need two energy levels. Indeed if we try to force the three particles in the same s-state, the Slater determinant will eventually go to zero.

$$\det \frac{1}{\sqrt{N!}} \begin{pmatrix} \phi_s^{\uparrow}(r_1) & \phi_s^{\uparrow}(r_2) & \phi_s^{\uparrow}(r_3) \\ \phi_s^{\downarrow}(r_1) & \phi_s^{\downarrow}(r_2) & \phi_s^{\downarrow}(r_3) \\ \phi_p^{\uparrow}(r_1) & \phi_p^{\uparrow}(r_2) & \phi_p^{\uparrow}(r_3) \end{pmatrix} =$$

$$= \frac{1}{\sqrt{N!}} \big[\phi_s^{\uparrow}(r_1)\phi_s^{\downarrow}(r_2)\phi_p^{\uparrow}(r_3) - \phi_s^{\uparrow}(r_1)\phi_s^{\downarrow}(r_3)\phi_p^{\uparrow}(r_2) -$$

$$\phi_s^{\uparrow}(r_2)\phi_s^{\uparrow}(r_3)\phi_p^{\uparrow}(r_1) + \phi_s^{\uparrow}(r_2)\phi_s^{\downarrow}(r_1)\phi_p^{\uparrow}(r_3) + \phi_s^{\uparrow}(r_3)\phi_s^{\downarrow}(r_1)\phi_p^{\uparrow}(r_2) - \phi_s^{\uparrow}(r_3)\phi_s^{\downarrow}(r_2)\phi_p^{\uparrow}(r_1) \big]$$

This is a six-term determinant and is complicated to evaluate.

6.2.6.8 Application of the mean-field approximation to calculate the density of electrons in a point with $N = 2$

6.2.6.8.1 Density operator We can define a *density operator*

$$\hat{\rho}(x) = \sum_i \delta(x - r_i)$$

And apply it to a wave function that defines a point with two electrons (basically we want to calculate how much space these electrons occupy). We want to calculate $\langle \psi | \hat{\rho}(x) | \psi \rangle$ The wave function is:

$$\psi(\vec{r_1}, \vec{r_2}, s_1^z, s_2^z) = \frac{1}{\sqrt{2}} \big(\phi_\uparrow(r_1)\phi_\downarrow(r_2) - \phi_\downarrow(r_1)\phi_\uparrow(r_2) \big) \quad \text{Six-dimensional integral}$$

$$\langle \psi | \hat{\rho}(x) | \psi \rangle = \frac{1}{2} \int d\vec{r_1} d\vec{r_2} \, \psi^*(\vec{r_1}, \vec{r_2}, s_1^z, s_2^z) \cdot \left(\sum_i \delta(\vec{x} - \vec{r_i}) \right) \cdot \psi(\vec{r_1}, \vec{r_2}, s_1^z, s_2^z) =$$

$$= \frac{1}{2} \int d\vec{r_1} d\vec{r_2} \big(\phi_\uparrow^*(r_1)\phi_\downarrow^*(r_2) - \phi_\downarrow^*(r_1)\phi_\uparrow^*(r_2) \big) \cdot \big(\delta(\vec{x} - \vec{r_1}) + \delta(\vec{x} - \vec{r_2}) \big) \cdot \big(\phi_\uparrow(r_1)\phi_\downarrow(r_2) - \phi_\downarrow(r_1)\phi_\uparrow(r_2) \big)$$

$$= \frac{1}{2} \int_1 \int_2 \Big[\phi_1^{*\uparrow} \phi_2^{*\downarrow} \delta_1 \phi_1^\uparrow \phi_2^\downarrow + \phi_1^{*\uparrow} \phi_2^{*\downarrow} \delta_2 \phi_1^\uparrow \phi_2^\downarrow - \phi_1^{*\uparrow} \phi_2^{*\downarrow} \delta_1 \phi_2^\uparrow \phi_1^\downarrow - \phi_1^{*\uparrow} \phi_2^{*\downarrow} \delta_2 \phi_1^\downarrow \phi_2^\uparrow -$$

$$- \phi_1^{*\downarrow} \phi_2^{*\uparrow} \delta_1 \phi_1^\uparrow \phi_2^\downarrow \phi_1^{*\downarrow} \phi_2^{*\uparrow} \delta_2 \phi_1^\uparrow \phi_2^\downarrow + \phi_1^{*\downarrow} \phi_2^{*\uparrow} \delta_1 \phi_1^\downarrow \phi_2^\uparrow + \phi_1^{*\downarrow} \phi_2^{*\uparrow} \delta_2 \phi_1^\downarrow \phi_2^\uparrow \Big] d\vec{r_1} d\vec{r_2}$$

6.2.6.8.2 Action of an operator Now note that when the operator acts, e.g., on the electron 1, the remaining $\int \phi_2^{*\uparrow} \phi_2^\uparrow d\vec{r_2} = 1$

$$= \frac{1}{2} \int \phi_1^{*\uparrow} \phi_1^\uparrow \delta_1 \, d\vec{r_1} + \int \phi_2^{*\downarrow} \phi_2^\downarrow \delta_2 \, d\vec{r_2} - \int \phi_1^{*\uparrow} \phi_1^\downarrow d\vec{r_1} - \int \phi_2^{*\downarrow} \phi_2^\uparrow d\vec{r_2} - \int \phi_1^{*\downarrow} \phi_1^\uparrow d\vec{r_1} -$$

$$- \int \phi_2^{*\uparrow} \phi_2^\downarrow d\vec{r_2} + \int \phi_1^{*\downarrow} \phi_1^\downarrow \delta_1 \, d\vec{r_1} + \int \phi_2^{*\uparrow} \phi_2^\uparrow \delta_2 \, d\vec{r_2}$$

We can recall the fact that by construction $\phi_1^{*\uparrow} \phi_1^\uparrow = |\phi_1^\uparrow|^2$ and this $|\phi_1^\uparrow|^2$ corresponds to the probability of finding electron 1 with spin $\uparrow$ ($P^\uparrow(x)$). Same applies to electron 2.

$$= \frac{1}{2} \int |\phi_1^\uparrow|^2 \, \delta_1 \, d\vec{r_1} + \int |\phi_2^\downarrow|^2 \, \delta_2 \, d\vec{r_2} - \int \phi_1^{*\uparrow} \phi_1^\downarrow d\vec{r_1} - \int \phi_2^{*\downarrow} \phi_2^\uparrow d\vec{r_2} - \int \phi_1^{*\downarrow} \phi_1^\uparrow d\vec{r_1} -$$

$$- \int \phi_2^{*\uparrow} \phi_2^\downarrow d\vec{r_2} + \int |\phi_1^\downarrow|^2 \, \delta_1 \, d\vec{r_1} + \int |\phi_2^\uparrow|^2 \, \delta_2 \, d\vec{r_2}$$

6.2.6.8.3 Conclusion The integrals with an electron present with opposite spins $\int \phi_1^{*\uparrow} \phi_1^\downarrow d\vec{r_1}$ (the integrals with negative signs) represent the probability of finding the particle in state $\uparrow$ **and** $\downarrow$ that is zero, so they cancel. Mind that the contribution from the entanglement of the two states doesn't occur within observables so the inner product is zero. Fermions, though, must be entangled to give an antisymmetric wave function. By knowing that $\int dx \, g(x)\delta(x - x_0) = g(x_0)$ and by considering that there's no point in distinguishing the two electrons for anything but their spins (they have same mass and charge), we can say that:

- $P_1^\uparrow(x) = P_2^\uparrow(x) = P^\uparrow(x)$
- $P_1^\downarrow(x) = P_2^\downarrow(x) = P^\downarrow(x)$

Hence the probability density becomes

$$\langle\psi|\hat{\rho}(x)|\psi\rangle = \frac{1}{2}\left[P^\uparrow(x) + P^\uparrow(x) + P^\downarrow(x) + P^\downarrow(x)\right] = P^\uparrow(x) + P^\downarrow(x)$$

Either a particle is spin up or spin down in x.

Chapter 7

Molecular physics

7.1 The Born-Oppenheimer Approximation

Molecular physics explains the origin of chemical bonds and makes it possible to understand quantum chemistry calculations. Chemistry can be represented by an "unsolvable" Schrödinger equation:

$$\left[-\sum_{q=1}^{N_\alpha} \frac{\hbar^2}{2m_\alpha} \cdot \nabla_\alpha^2 - \sum_{i=0}^{N_e} \frac{\hbar^2}{2m_e} \cdot \nabla_i^2 + V[\{\vec{R}\}_\alpha, \{\vec{r_i}\}_i] \right] = E\psi[\{\vec{R}\}_\alpha, \{\vec{r}\}_i]$$

$$V[\{\vec{R}\}_\alpha, \{\vec{r_i}\}] = \left(\sum_{i<j} \frac{e^2}{|\vec{r_i} - \vec{r_j}|} + \sum_{\alpha<\beta} \frac{z_\alpha z_\beta e^2}{|\vec{R_\alpha} - \vec{R_\beta}|} - \sum_{i,\alpha} \frac{e^2 z_\alpha}{|\vec{r_i} - \vec{R_\alpha}|} \right)$$

In order, the different parts of the equation represent:

1. $-\sum_{q=1}^{N_\alpha} \frac{\hbar^2}{2m_\alpha} \cdot \nabla_\alpha^2$, Kinetics of nuclei.

2. $-\sum_{i=0}^{N_e} \frac{\hbar^2}{2m_e} \cdot \nabla_i^2$, Kinetics of electrons.

3. $\sum_{i<j} \frac{e^2}{|\vec{r_i} - \vec{r_j}|}$, Repulsive coulombic interaction between electrons

4. $\sum_{\alpha<\beta} \frac{z_\alpha z_\beta e^2}{|\vec{R_\alpha} - \vec{R_\beta}|}$, Repulsive coulombic inter-

    action between nuclei.

5. $-\sum_{i,\alpha} \frac{e^2 z_\alpha}{|\vec{r_i} - \vec{R_\alpha}|}$, Attractive coulombic interaction between nucleus and electrons.

6. Curly brackets represent the collection of all r and R.

This equation can be approximated by considering that protons are much bigger and slower than electrons, and therefore are fixed. The Born-Oppenheimer approximation divides these operations in two (**decoupling**).

7.1.1 Decoupling approach

We can implement a *divide et impera* approach.

7.1.1.1 Fixed nuclear configuration

First the electronic problem is studied at fixed nuclear configuration (i.e. ignoring the kinetic energy of the nuclei). The first fragment is ignored (no motion, no kinetic energy) and the coulombic repulsion becomes constant consequently. Nuclei bind only when they are close to each other.

$$\left[-\sum_{i=0}^{N_e} \frac{\hbar^2}{2m_e} \cdot \nabla_i^2 + \sum_{i<j} \frac{e^2}{|\vec{r_i} - \vec{r_j}|} - \sum_{i,\alpha} \frac{e^2 z_\alpha}{|\vec{r_i} - \vec{R_\alpha}|} \right] \cdot \psi[\{\vec{R}\}_\alpha, \{\vec{r}\}_i] = E[\{R_\alpha\}] \psi[\{\vec{R}\}_\alpha, \{\vec{r}\}_i]$$

Where $E[\{R_\alpha\}]$ is the energy of the system at a fixed nuclear position, R_α represents the contributions of the electrons to the potential energy. The energy eigenvalue describes the electron density around the nuclei at fixed nuclei positions. The fact that there are electrons moving increases the overall potential energy (repulsive interactions), electrons can lower their higher potential energy by tunneling to another nucleus with Pauli symmetry. This lowers the total energy of the system and creates bonds. Note that this is not a "charge-driven" attraction, but a phenomenon driven by quantum tunnelling and Pauli's symmetry.

7.1.1.2 Dynamics of the nuclei

The second step is to solve the dynamics of the nuclei based on their own coulombic interactions and electrons effect.

$$\left[-\sum_{q=1}^{N_\alpha} \frac{\hbar^2}{2m_\alpha} \cdot \nabla_\alpha^2 + \sum_{\alpha<\beta} \frac{z_\alpha z_\beta e^2}{|\vec{R_\alpha} - \vec{R_\beta}|} + E|\{R_\alpha\}| \right] \varphi(|R|) = \varepsilon \Phi(\{R\})$$

Note that ε is a value, not a function, it does not depend on any parameter. The quantum effect becomes weaker as the weight of the system increases.

7.1.2 Many-body systems

To describe a many-body system, I can replace this Schrödinger equation with a Newtonian equation.

$$M_\alpha \frac{d^2}{dt^2} R_\alpha(t) = -\nabla_\alpha (E(R) + E_t(R))$$

This equation is fine for describing **classical molecular simulations**. We loose the quantum effects of the nuclei (protonation - quantum tunneling of protons, chemical reactions, . . .), and often for molecules a classical formulation is enough.

7.2 The H$_2$ molecule

We are given two protons (a, b) and two electrons $(1, 2)$. Consider the structure of the electronic wave function as $\psi(\vec{r_1}, \vec{r_2}, s_1^z, s_2^z, (\vec{R_a}, \vec{R_b}))$ where $(\vec{R_a}, \vec{R_b})$ is a fixed external parameter because of the Born-Oppenheimer approximation and is the distance between nuclei. A schematic draw of the problem is depicted in figure 7.1.

7.2.1 Representation

The system can be firstly represented as two atoms at a large distance that approach slowly to each other, generating a linear combination of mean wave functions. The electrons are in a superposition of states when they start interacting, so the resulting H-H chemical bond is actually an entangled electron tunnelling.
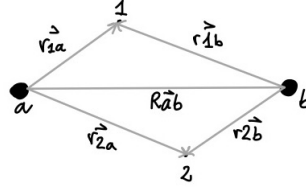
Figure 7.1: A representation of the H_2 molecule given the Born-Oppenheimer approximation.

$$\psi(\vec{r_1}, \vec{r_2}, s_1^z, s_2^z, (\vec{R_a}, \vec{R_b})) = \psi_{\text{spatial}}(\vec{r_1}, \vec{r_2}) \otimes \psi_{\text{spin}}(s_1^z, s_2^z) = \Phi \otimes \mathcal{X}$$

The wave-function can be factorized, as the Hamiltonian is separable (i.e. does not depend on the spin).

7.2.2 Spin

Spins can be $|\uparrow\uparrow\rangle$, $|\downarrow\downarrow\rangle$, $|\uparrow\downarrow\rangle$, and $|\downarrow\uparrow\rangle$. Since electrons are fermions, the two spins' product must be antisymmetric, hence one of the two spins must be antisymmetric and the other one must be symmetric (the two possibilities are spatial symmetry and spin antisymmetric or spatial antisymmetry and symmetric spin). Symmetry can be evaluated in entangled states, too.

- **Symmetric spin ($J = 1$)**: $|\uparrow\uparrow\rangle$, $|\downarrow\downarrow\rangle$, $\frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}}$ also called **triplet state** (quantum state of a system with a spin quantum number $s = 1$), molecule bends in Stern-Gerlach.

- Antisymmetric spin ($J = 0$): $\frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}$ also called **singlet state** (total spin angular moment $s = 0$), molecule doesn't bend in Stern-Gerlach.

The result is that a combination of two spin-$\frac{1}{2}$ particles can carry a total spin of 1 or 0, depending on whether they occupy a triplet or singlet state.

7.2.3 Model

Now we can generate now a model through a variational ansatz:

$$\psi = \Phi\mathcal{X} = \begin{cases} \psi_1 = \Phi_S \mathcal{X}_A = \frac{1}{\sqrt{2}}\big(\varphi_a(r_{1a})\varphi_b(r_{1b}) + \varphi_a(r_{2a})\varphi_b(r_{2b})\big) \otimes \frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}} \\ \psi_2 = \Phi_A \mathcal{X}_S = \frac{1}{\sqrt{2}}\big(\varphi_a(r_{1a})\varphi_b(r_{1b}) + \varphi_a(r_{2a})\varphi_b(r_{2b})\big) \otimes \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}} \end{cases}$$

The latter is a mean field model where E1 lives in P1 and E2 lives in P2. By the variational principle, the wavefunction with the lowest value of energy is the one that best approximates the H_2 atom.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_n^2 - \frac{\hbar^2}{2m}\nabla_e^2 - \frac{e^2}{|r_1a|} - \frac{e^2}{|r_1b|} - \frac{e^2}{|r_2a|} - \frac{e^2}{|r_2b|} - \frac{e^2}{|R_ab|}$$

Even if spin is not involved in the Hamiltonian and eventually results in $\left\langle \hat{S} \middle| \hat{S} \right\rangle = 1$, the sign of the expected value of the Hamiltonian depends on the spin symmetry, because spatial value and spin symmetry are entangled.

- $E_1 = \langle \psi_1 \,|\, \hat{H} \,|\, \psi_1 \rangle = \langle \Phi_S \,|\, \hat{H} \,|\, \Phi_S \rangle$

- $E_2 = \langle \psi_2 \,|\, \hat{H} \,|\, \psi_2 \rangle = \langle \Phi_A \,|\, \hat{H} \,|\, \Phi_A \rangle$

We must solve, then,

$$E_1 = \frac{1}{2} \int d\vec{r_1} \int d\vec{r_2} \left[\varphi(|\vec{r_1} - \vec{R_a}|)\varphi(|\vec{r_2} - \vec{R_b}|) + \varphi(|\vec{r_1} - \vec{R_b}|)\varphi(|\vec{r_2} - \vec{R_a}|) \right] (\hat{H})(\Phi_S)$$

And same for E_2. There are 6-dimensions functions in 6-dimensions integrals. Results are different whether the equations are solved for the first or second electron.

7.2.3.1 Distance of the atoms

This is the result that is obtained when the two atoms are infinitely far.

$$\left\langle \,|\, \hat{H} \,|\, \Big|\Big| \,|\, \hat{H} \,|\, \right\rangle_{S/A} = 2E_0 \pm \text{stuff}$$

Else, if the two atoms start to approach,

$$\left\langle \,|\, \hat{H} \,|\, \Big|\Big| \,|\, \hat{H} \,|\, \right\rangle_{S/A} = \frac{e^2}{R_{ab}} \pm \text{separated ground states}$$

7.2.4 Results

We obtain two different functions, depicted in figure 7.2:

- **Symmetric spatial function**: spin 0 state, has a lower energy value that corresponds to an optimal distance between the two nuclei $\bar{R}$. It allows different calculable energy levels, bond oscillations and strength. Important to notice is that

quantum symmetry (state $s = 0$) is key to the binding of atoms.

- **Antisymmetric spatial function**: goes against the variational approximation, but technically is a right solution from a quantum mechanical point of view.
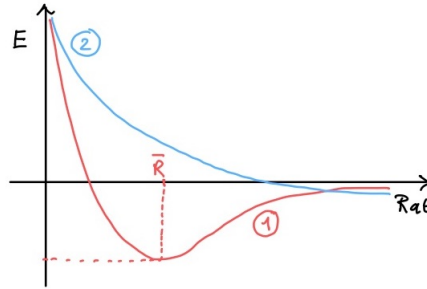
Figure 7.2: The total energy is: $|E\rangle = \langle \psi|H|\psi \rangle = 2E_0 + \frac{e^2}{R_{ab}} +$ other factors. E_0 corresponds tot the energy of two atoms infinitely far away from each others, while $\frac{e^2}{R_{ab}}$ acts when the two atoms start to approach.

7.3 Electronic structure calculation methods

When choosing the best method to describe an electronic structure, some evaluations have to be made regarding the accuracy of the calculation with respect to the computational cost of the operation. The first approximation to be chosen is always the most important, as it determines the further steps that need to be taken.
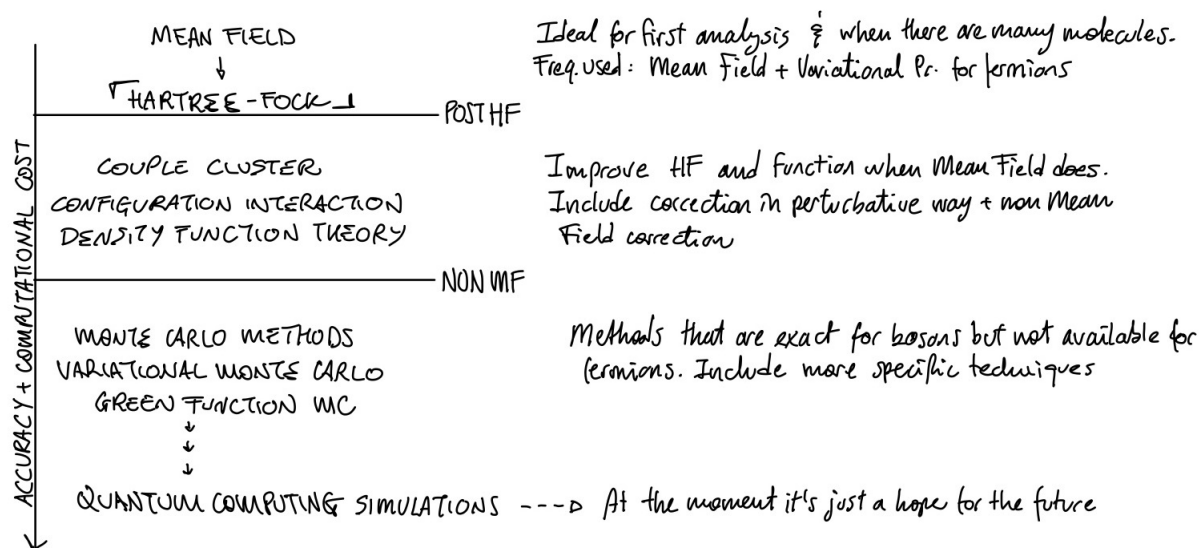
Figure 7.3: Cartoon representing the main types of calculations, divided based on the cost and accuracy. Exact diagonalization is not reported, since it's computationally extremely hard.

The **exact diagonalization** (truncated basis) technique that we encountered at the beginning of Chapter 5 is also used with very precise outcomes, but it can't be used with systems bearing more than 5 or 6 particles at the same time. For biological systems, chemical accuracy is important as long as the error is not dramatic (keep in mind that a slight change of temperature can drastically change the system). A simulation is acceptable when $K_B T < 1.5$ KJ/mol $\div$ 2.4 KJ/mol. For macromolecules in biology, very accurate DFT are today's state of the art, but they don't predict Van Der Waals dispersion forces, since they have a polynomial form. Instead, other methods are used (*i.e.*, Hartree-Fock). In practice, exact solutions for many-body systems are never found but excellent approximations are possible and this is the reason why DFT is the most commonly adopted scheme for electronic calculations in condensed matter physics and quantum chemistry. The general goal is using classical equations to predict quantum-mechanics-described movements. In figure 7.3 the main approaches are reported.

7.3.1 Hartree-Fock Method

We shall start the discussion about the Hartree-Fock method with the following observation: if the wave function is a sum of decoupled terms, then the wave function solution is a product of single particle wave functions:

$$H(x_1, .., x_n) = \sum_i \left(-\hbar^2 \frac{\nabla_i^2}{2m} + V(x_i) \right)$$

And the solution is in the form

$$\psi(x_1, ..., x_n) = \phi(x_1) \cdot ... \cdot \phi(x_n) \quad (*)$$

The Hartree method is a variational approach which yields the best solution to a quantum many-body problem in which the ground state trial wave function is in the factored form $(*)$ and Ritz variational principle is applied to determine the "best" single-particle orbitals $\phi(x)$. It combines Mean Field Approximation, Fermi symmetry, and the Variational Principle.

7.3.1.1 Slater matrix

Hartree Fock uses the Slater matrix's determinant to approximate a set of N fermions.

$$\psi(q_1 \cdots q_n) = \frac{1}{\sqrt{2}} \begin{pmatrix} \phi_1(q_1) & \cdots & \phi_n(q_1) \\ \cdots & & \cdots \\ \phi_1(q_m) & \cdots & \phi_n(q_m) \end{pmatrix}$$

Where q_i could contain the position and spin or just the position. Anyway, we do not expect to find $\psi(q_1 \cdots q_n)$. We can however consider it as the result of an equation and calculate the energy by using the Variational Principle with $E = \langle \psi \,|\, E \,|\, \psi \rangle$ and minimize E with respect to $\phi(q)$ (a single-particle function) under the constraint of normalization ($\langle \psi \,|\, \psi \rangle = 1$). Constraint minimization is operated with **Lagrange multipliers**: we consider a system of equations $f(x_1 ... x_n)$ where we can calculate the minimum and the maximum with the application of the gradient $\nabla f = 0$.

7.3.1.2 Hartree equation

We eventually obtain the **Hartree Equation**, representing **one electron interacting with a probability cloud**. It is a symmetric system (valid for bosons, since they have classical limits and can be represented as shown without further additions):

$$\left(-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Z}{r_i} \right) \Phi_\lambda(\vec{r_i}) + \sum_\mu \sum_{j \neq i} \int d^3 \vec{r_j} \left(\Phi_\mu^*(\vec{r_j}) \Phi_\mu(\vec{r_j}) \frac{1}{|r_i - r_j|} \Phi_\lambda(\vec{r_i}) \right) = E \Phi_\lambda(\vec{r_i})$$

In particular:

- $-\frac{Z}{r_i}$ is the coulombic attraction for a single nucleus (atomic physics version)

- $\Phi_\lambda(\vec{r_i})$ represents orbital position of the electron + spin. The number of electrons is the number of equations that need to be solved

- μ is the orbital index that changes the wave function

- $\Phi_\mu^*(r_j)\Phi_\mu(r_j) = \rho_\mu^{(i)}(r_j)$ is the electron density + density of charge around it (probability density) with sum of all electrons in all orbitals (μ)

7.3.1.3 Fock equation

The Fermi symmetry introduces the Slater determinant, that is also called **exchange term**, which is a repulsive term. (**Fock equation**). This introduction implies that two electrons with the same spin cannot exist in the same orbital. The wave function collapses to zero and we obtain a repulsion between the electrons (basically, it would cost infinite energy if the two spins happen to be the same).

$$\text{HARTREE EQN.} + \sum_{\mu} \sum_{j \neq i} \int d^3 \vec{r_j} \left(\Phi^*_{\mu}(\vec{r_j}) \Phi_{\lambda}(\vec{r_j}) \frac{1}{|r_i - r_j|} \Phi_{\mu}(\vec{r_i}) \right) = E \Phi_{\lambda}(\vec{r_i})$$

This implies that the electron density factor $(\varphi^{(1)}_{\mu}(r_j))$ of the Hartree equation is not present any more $(\varphi^{(2)}_{\mu\lambda}(r_j))$, the two particles are in a different state. At the same time, $\Phi_{\mu}(r_i)$ becomes Fock's generalization exchange term for fermions, generalizing the Hartree Fock to fermions. This equation though is non linear (Φ^3). However all N functions involve single particles, so we can simply the problem. The integral though is 3D, be we can apply nested methods. The basis cannot be expanded, diagonalized or transformed by other tricks previously used to simply problems.

7.3.1.4 Self consisted methods

Since we can't expand the equation on a different basis, we must use **self consisted methods**, which are **iterative** procedures operated until the function converges.

1. (Guess) $\Phi_{\lambda}(\vec{r})$

2. Compute $\rho^{(1)}_{\mu}(\vec{r})$ and $\rho^{(2)}_{\mu}(\vec{r})$, as they are numerical values

3. Insert $\rho^{(1)}_{\mu}(\vec{r})$ and $\rho^{(2)}_{\mu}(\vec{r})$ into the Hartree Fock equation, resulting in a conventional linear Schrödinger equation.

4. Solve the Hartree Fock equation and get a more accurate wave function $\Phi_{\lambda}(\vec{r})$

The obtained $\Phi_{\lambda}(\vec{r})$ is a better guess than the initial one, so it is used again for another iteration starting from point 1 and recomputing the density (this is why the first point of the list is in parenthesis). The algorithm will run until convergence is reached and usually a single minimum is present. Even with this approach, the computation of Hartree Fock is very expensive. For this reason, **semi-empirical methods** have been developed. Coefficients have been introduced in front of direct and exchange terms, that can weight the two terms in order to better match the experimental results. The Hartree Fock equation is usually employed to build the expansion of the eigenfunction or in quantum computing.

7.3.2 Density Function Theory (DFT)

DTF is a variational approximation which represents a significant improvement with respect to the Hartree Fock method, because in principle, it enables for the exact solution of the electronic problem. In practice, exact solution are never found. However excellent approximations are possible and this is the reason why DFT is the most commonly adopted scheme for electronic calculations in condensed matter and quantum chemistry. DTF reaches such excellent results because it fuels the density function (as we'll see later) with **heuristic** inputs.

7.3.2.1 Density function computation

This theory is not based on the wave function computation, but on the **density function computation**. Let the density operator:

$$\hat{\rho}(\vec{r}) = \sum_{i=1}^{N_0} \delta(\vec{r} - \vec{r_i})$$

Its expectation value, assuming $\langle \psi \,|\, \psi \rangle = 1$:

$$\langle \psi \,|\, \hat{\rho}(\vec{r}) \,|\, \psi \rangle = \sum_i \int d\vec{r_1}...d\vec{r}_{N_e} \left(\psi^*(\vec{r_1} - \vec{r}_{N_e})\delta(\vec{r} - \vec{r_i})\psi(\vec{r_1} - \vec{r}_{N_e}) \right) s = n(\vec{r})$$

Which is the probability of finding any electron at the point r. This concept is shown in picture 7.4.
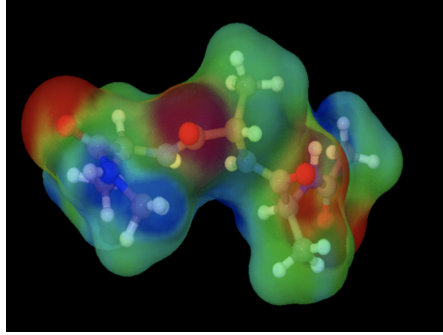
Figure 7.4: In this cartoon of a molecule, the parts with higher probability of finding the electrons are highlighted. Blue parts correspond to low electron density and the red ones to high electron density.

7.3.2.2 Single-body density

$n(\vec{r})$ is a so-called **single-body density**, it doesn't contain the same information of the full wave function (in fact $\hat{\rho}(\vec{r})$ reduces it when compared to ψ). For any Hamiltonian there is one and only single-body density.

7.3.2.3 Hochenberg and Kohn theorems

Hochenberg and Kohn have elaborated two theorems that show that the ground state and excited states' properties of a system (quantum many-body system) are entirely determined by the ground-state single body density $n(\vec{r})$. Mind that the quantum electronic structure calculation problem is:

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i^{N_e} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} + \sum_i^{N_e} V_{ext}(\vec{r_i})$$

The last term is the interaction between single electrons and nuclei. In the Born-Oppenheimer approximation, this was the external potential as nuclei were fixed.

7.3.2.3.1   First theorem   For any system of interacting particles, the external potential is determined uniquely by the ground state one-body density. There cannot be two external potentials which give the same ground-state density.

$$n_o(\vec{r}) = \langle \psi \,|\, \hat{\rho}(\vec{r}) \,|\, \psi \rangle$$

7.3.2.3.1.1   Corollary   All wavefunctions (ground state, first excited state and all eigenstates of $\hat{H}$) are fully determined by $n_0(\vec{r})$.

7.3.2.3.2   Second theorem   An energy functional $E[n_0]$ can be defined such that the minimum of this functional with respect to $n_0(\vec{r})$ provides the exact $n_0(\vec{r})$ and E_0 (ground state energy).

7.3.2.3.2.1   Functionals   If a function $f(x) : x \to f(x)$ is such that x is a variable and $f(x)$ a number, a functional $E[f] : f(x) \to E[f]$ is such that $f(x)$ is a function of operators and $E[f]$ is a number. Examples of functionals are definite integrals or the expectation values of operators. Anyway, from Ritz Theorem we know that the minimum of the functional of the wave function (i.e., the expectation value of the Hamiltonian) is the exact ground state.

7.3.3   Building functionals

The challenge is therefore to build the energy functional. The HK theorems would have been relegated as useless curiosity if Kohn and Sham (KS) hadn't found a scheme to construct approximate functionals which turned out to work extremely well for a large class of electronic problems in condensed matter and molecular physics. The construction of such functionals stands on the so-called KS ansatz for $E[n]$ and is based on the following main assumption: *The ground state of the exact system can be found by minimising the Energy functional for an auxiliary non-interacting system with a local external potential:*

$$H_{aux.} = \sum_i \left(-\hbar^2 \frac{\nabla_i^2}{2m} + V_{aux.}(x_i) \right)$$

It is possible to define a functional such as the minimum of the functional is the exact value of the ground state energy. Differently from Ritz Theorem, here the functional is nor given or referred to the wave function. The one body density's functional's minimum is the exact ground state energy of the problem **for all** Hamiltonians.

7.3.4   Hybrid (QM-MM) Schemes

Hybrid QM-MM (Quantum Mechanics, Molecular Mechanics) schemes are used for large molecular models and chemical reactions studies like enzymatic reactions. Quantum mechanics is applied to the region of interest (so to have the computational effort only where needed), while classical molecular mechanics is applied elsewhere and an hybrid method is used at the border between the two regions. The difficulty is presented when considering thermodynamics. The more degrees of freedom, the more entropy. In figure 7.5 the main calculation methods we've seen are reported.
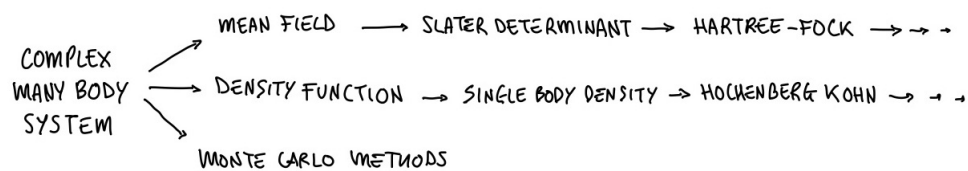
Figure 7.5: A visualization of the methods we've seen to deal with complex many body systems.

Part III

Quantum computing

Chapter 8

Quantum computing

8.1 Qubits

We can consider a quantum Hamiltonian $\hat{H}_0$ that describes a two-level system. We can represent it with the same mathematical representation of spin even if it's not spin.

- $|0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$

- $|1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

With: $\hat{H}_0 = -h\hat{\tau}_x$ and $\hat{\tau}_x$ Pauli matrix operator:

$$\hat{\tau}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

Then:

$$\hat{H}_0 = -h \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

8.1.1 State of the Hamiltonian

The objective is to find:

- $\left|\hat{\Omega}\right\rangle = \left|\text{Ground state of } \hat{H}_0\right\rangle$

- $\left|\hat{\Sigma}\right\rangle = \left|\text{First excited state of } \hat{H}_0\right\rangle$

To find the possible states of the Hamiltonian first $\hat{H}_0 |\phi\rangle = E |\phi\rangle$ is solved:

$$\det(H - \lambda \mathbb{1}) = 0$$
$$\det \begin{pmatrix} -\lambda & -h \\ -h & -\lambda \end{pmatrix} = 0$$
$$\lambda^2 - h^2 = 0 \rightarrow \lambda = \pm h$$

$-h$ and $+h$ are the two possible energy eigenvalues and correspond to the ground state and first excited state, respectively.

8.1.1.1   Ground state

The ground state is computed: $E_\Omega = -h$

$$|\Omega\rangle = \begin{pmatrix} a \\ b \end{pmatrix} \rightarrow -h \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = -h \begin{pmatrix} a \\ b \end{pmatrix}$$

This is a two-variables system and can be resolved as such:

$$\begin{cases} -ha = -ha \\ -hb = -hb \end{cases} \rightarrow a = 0 \,\text{and}\, b = 1 \,\text{or}\, a = 1 \,\text{and}\, b = 0$$

$|\Omega\rangle$ can be rewrited as:

$$|\Omega\rangle = \frac{1}{\sqrt{2}} |1\rangle + \frac{1}{\sqrt{2}} |0\rangle$$

And since $|1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$, the ket have to be normalized to get the $\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ that is the final result. $|\Omega\rangle$ is a quantum superposition of states.

8.1.1.2   First excited state

The first excited state: $E_\Sigma = +h$:

$$[|\Sigma\rangle = \begin{pmatrix} a \\ b \end{pmatrix} \rightarrow -h \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = +h \begin{pmatrix} a \\ b \end{pmatrix}$$

From this linear system we obtain the formulation for the first excited state.

$$|\Sigma\rangle = \frac{1}{\sqrt{2}} |1\rangle - \frac{1}{\sqrt{2}} |0\rangle$$

8.1.1.3   Conclusion

Each of these two quantum states, $|\Omega\rangle$ and $|\Sigma\rangle$, represent a **qubit** that is in a linear superposition of states.

8.1.2   Adiabatic Quantum Computing

Putting energy in the system changes the probability of the particle of being still in a ground state. The particle may be found in an excited state. This doesn't happen if the system is switched in a slow manner and becomes an adiabatic system. Doing so, according to the adiabatic system the system never ends up in an excited state and the transition is more likely to occur at time when ΔE is at its lowest.

8.1.2.1   Ground state of an arbitrary complex Hamiltonian

If $\hat{H}_f$ is complicated enough such that its ground state cannot be known, starting from $\hat{H}_0$ ground state and letting the system evolve in an adiabatic way to reach $\hat{H}_f$, $\hat{H}_f$ will reach the ground state spontaneously. Measuring the final state many times allows to discover the ground state of $\hat{H}_f$.

8.1.2.2 Final wave function through qubits

The final wavefunction can be obtained by means of qubits. Qubits are two level-systems that can thus have two levels of energy for which the two ground states are known.

The final solution can be computed by knowing the amount of values of $\alpha(t)$ and $\beta(t)$. The time needed for the computation depends on:

- Triviality of the problem.
- The number of qubits (n).

- The number of states (2^n).
- ΔE.

The time of computation depends on the function that regulated ΔE and corresponds to the clock of classical computers.

8.2 Two qubits system

Two qubits systems are interacting quantum systems.

8.2.1 Hamiltonian

The objective is to solve the Hamiltonian in the form:

$$\hat{H} = \mathbf{J}_{12}\hat{\tau_1^z}\hat{\tau_2^z} + h(\hat{\tau_1^z} + \hat{\tau_2^z})$$

This is a two-particles Hamiltonian that depends on the interaction of the two spins. If one of the two is down, $\hat{H}$ becomes negative and the energy is lowered. Hence I have a more favourable system. This can be obtained with a magnet that can properly align spins in order to have an overall negative energy. Implicitly, the Hamiltonian should be:

$$\hat{H} = \mathbf{J}_{12}\hat{\tau_1^z}\hat{\tau_2^z} + h(\hat{\tau_1^z}\hat{1\!\!1_z} + \hat{1\!\!1_z}\hat{\tau_2^z})$$

When using an operator on a particle, the other is multiplied by the identity matrix.

$$\hat{\tau_1^z} \otimes \hat{\tau_2^z} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} hat\tau_1^z \otimes \hat{1\!\!1_z} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \hat{1\!\!1^z} \otimes \hat{\tau_2^z} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

The Hamiltonian then becomes:

$$\hat{H} = \mathbf{J}_{12}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} + h\begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -2 \end{pmatrix} = \begin{pmatrix} \mathbf{J}_{12} + 2h & 0 & 0 & 0 \\ 0 & -\mathbf{J}_{12} & 0 & 0 \\ 0 & 0 & -\mathbf{J}_{12} & 0 \\ 0 & 0 & 0 & -2h + \mathbf{J}_{12} \end{pmatrix}$$

Each of the eigenvalues of the matrix can represent an eigenvector.

8.2.2 Quadratic unconstrained binary optimization problem

Suppose we have a function defined as a quadratic function of binary variables:

$$T = \sum_{i,j=1}^{N} O_{ij} x_i x_j + \sum_{i}^{N} U_i x_i \text{ with } x_i \in \{0,1\} \text{ and } O_{ij}, U_i \in \mathbb{R}$$

The problem is finding the configuration of binary variables that minimises T. This is a discrete optimization problem that is called **Quadratic Unconstrained Binary Optimization (QUBO)** problem. We can reduce the two-particle problem to a QUBO problem. By definition $\hat{\tau}_i^z = 2x_i - 1$. When

$$x_i = 0 \quad \hat{\tau}_i^z = -1$$
$$x_i = 1 \quad \hat{\tau}_i^z = +1$$

We can write the function T as

$$T = \sum_{i,j=1}^{N} \mathbf{J_{ij}} \tau_i^z \tau_j^z + \sum_{i}^{N} h_i \tau_i^z$$

That is similar to the original Hamiltonian. This is the total number of combination of 2^N. Values of T are encoded in the Hamiltonian. Results of finding the minimum of T and $\hat{H}$ are the same because the minimum value of the ground state corresponds to the ground eigenstate. The qubits corresponding to the ground eigenstate (eigenvectors) can be obtained from classical T but not as a superposition.

8.2.3 Entangled states

Entangled states can be created by imposing a different spin direction on the particles.

$$\hat{H} = \mathbf{J}_{12} \hat{\tau}_1^z \hat{\tau}_2^z + h(\hat{\tau}_1^x \hat{\mathbb{1}}_x + \hat{\mathbb{1}}_x \hat{\tau}_2^x)$$

$$\hat{\tau}_1^x \otimes \hat{\mathbb{1}}_x = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \quad \hat{\mathbb{1}}_x \otimes \hat{\tau}_2^x = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \quad \hat{H} = \begin{pmatrix} \mathbf{J}_{12} & h & h & 0 \\ h & -\mathbf{J}_{12} & 0 & h \\ h & 0 & -\mathbf{J}_{12} & h \\ 0 & h & h & \mathbf{J}_{12} \end{pmatrix}$$

The ground state is a vector correspondent to

$$\begin{pmatrix} 1 \\ 0 \\ -\frac{\sqrt{4h^2 + \mathbf{J}^2} + \mathbf{J}}{2h} \\ 1 \end{pmatrix} = |0\,0\rangle - \frac{\sqrt{4h^2 + \mathbf{J}^2} + \mathbf{J}}{2h} |1\,0\rangle + |1\,1\rangle$$

Where $c = \frac{\sqrt{4h^2 + \mathbf{J}^2} + \mathbf{J}}{2h}$. Let the normalization factor:

$$\frac{(1^2 + c^2 + 1^2)}{N} = 1 \rightarrow N = 2 + c^2$$

$$G.S. = \frac{1}{\sqrt{2 + c^2}}(|0\,0\rangle - c\,|1\,0\rangle + |1\,1\rangle)$$

Fix $c = 1$ so the ground state becomes:

$$G.S. = \frac{1}{\sqrt{3}}(|0\,0\rangle - |1\,0\rangle + |1\,1\rangle)$$

Compute the probability for $q_2 = 1$. q_2 can appear in two different states:

$$P_{11} = \frac{1}{3}(\langle 1\,1\,|\,0\,0|1\,1\,|\,0\,0\rangle - \langle 1\,1\,|\,1\,0|1\,1\,|\,1\,0\rangle + \langle 1\,1\,|\,1\,1|1\,1\,|\,1\,1\rangle)^2 = \left(\frac{1}{\sqrt{3}}\right)^2 = \frac{1}{3}$$

$$P_{01} = \frac{1}{3}(\langle 0\,1\,|\,0\,0|0\,1\,|\,0\,0\rangle - \langle 0\,1\,|\,1\,0|0\,1\,|\,1\,0\rangle + \langle 0\,1\,|\,1\,1|0\,1\,|\,1\,1\rangle)^2 = 0$$

This latter state never appears. The state is overall entangled because if $q_1 = 0$ the wave function collapses into $q_2 = 0$. If $q_1 = 1$, q_2 doesn't collapse because it can be either $q_2 = 0$ or $q_2 = 1$ with 50% probability. q_2 is in a linear superposition of states if $q_1 = 1$.

8.3 Quantum circuits

Quantum circuits are models for **quantum computation**, where a computation is a sequence of quantum gates, measurements, and initialization of qubits to known values. Circuits are written such as the horizontal axis is time and they are read from left to right. Horizontal lines represent qubits, doubled lines are classical bits. The items that connect the elements represents the operations performed on qubits.

8.3.1 Elementary logic gates

The elementary logic gates are model of computation or physical electronic devise that implements a boolean function on one or more binary input. They are irreversible: the input cannot be recovered from the output.

8.3.2 Universality

Quantum computers can achieve universality, the complete conversion of an input of an arbitrary set of items into a corresponding output. Usually in quantum computation the output is a rotation of the input, all the operations used to perform such rotation $f(x)$ on input x can be expressed as a single unitary matrix, for example

$$U = \sum_j |f(x)\rangle \langle x|$$

The ability to implement any unitary matrix would mean the achievement of universality in the sense of standard digital computers. A strictly physical example would be the simulation of the dynamics of a system, where the time evolution is the unitary matrix and the Hamiltonian is the associated hermitian matrix. Achieving any unitary matrix would therefore correspond to simulating any time evolution, and engineering the effects of any Hamiltonian.

8.3.3 Quantum logic gates

Quantum logic gates are reversible unitary transformations on at least one qubit.

8.3.3.1 Qubits

A qubit (the quantized version of classical n-bit space $\{0,1\}^n$) is the Hilbert space $H_{QB(n)} = L^2(\{0,1\}^2)$, that can be interpreted as a linear combination or superposition of classical bit strings. $H_{QB(n)}$ is a vector space over the complex numbers of dimension 2^n and elements of this vector space are possible state of n-qubits quantum registers. Quantum logic gates require a reversible function called unitary mapping which is linear transformation of a complex inner product space that preserves the Hermitian inner product.

8.3.4 Types of quantum circuits

There are three main types of quantum circuits:

- **Phase gate (S gate)**: single-qubit operation defined by the matrix $S = \begin{pmatrix} 1 & 0 \\ 0 & i \end{pmatrix}$, it represents a 90° rotation around the z-axis.

- **Hadamard gate**: single-qubit operation that maps the basis state $|0\rangle$ to $\frac{|0\rangle+|1\rangle}{\sqrt{2}}$ and $|1\rangle$ to $\frac{|0\rangle-|1\rangle}{\sqrt{2}}$ thus creates a superposition of the two basis states. It can be represented by the matrix $H = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$. It represents a 90° rotation around the y-axis followed by a 180° rotation around the x-axis.

- **CNOT gate**: two-qubit operation. The first qubit is the control qubit, the second qubit is the target qubit. This gate leaves the control qubit unchanged and performs a Pauli-X gate on the target qubit if control is $|1\rangle$. If control is $|0\rangle$ the target qubit is unchanged. The CNOT gate is represented by the matrix $C_{NOT} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$
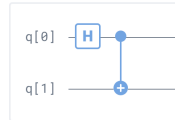
The figure represents the execution of Hadamard gate on qubit 0 to create a superposition state and then the execution of CNOT gate to create an entangled state of the two qubits.

8.3.5 Prove that Hadamard gate is the reverse of itself

$$H = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \ |0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \ |1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$H\,|0\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1+0 \\ 1+0 \end{pmatrix} = \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix}$$

$$H\,(H\,|0\rangle) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1/\sqrt{2}+1/\sqrt{2} \\ 1/\sqrt{2}-1/\sqrt{2} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 2/\sqrt{2} \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \ \text{Q.E.D.}$$

It's pointless to put two Hadamard gates in a row from a mathematical point of view. From a physical point of view it means that I am restoring the cat in an alive/dead definite state that is technically not possible.

8.3.6 Example of a HC_{NOT}

Application of the two gates on different entangled states of qubits $|0\rangle$ and $|1\rangle$.

$$C_{NOT}(H\,|0\,0\rangle) = C_{NOT}(H\,|0\rangle \otimes |0\rangle) = C_{NOT}\left(\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix}\right) =$$

$$= C_{NOT}\left(\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix}\right) =$$

$$= C_{NOT}\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \end{pmatrix} =$$

$$= \frac{1}{\sqrt{2}}\begin{pmatrix} 1+0+0+0 \\ 0+0+0+0 \\ 0+0+0+0 \\ 0+0+1+0 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ 0 \\ 1 \end{pmatrix} =$$

$$= \frac{|0\,0\rangle + |1\,1\rangle}{\sqrt{2}} = |\phi^+\rangle$$

As foreseen in the theory, the second qubit changes when the C_{NOT} gate is applied. The result is an entangled state of the two qubits called Bell state. All Bell states resulting from the combinations are orthogonal to each other.

$$\frac{|0\,0\rangle - |1\,1\rangle}{\sqrt{2}} = |\phi^-\rangle \quad \frac{|0\,1\rangle + |1\,0\rangle}{\sqrt{2}} = |\psi^+\rangle \quad \frac{|0\,1\rangle - |1\,0\rangle}{\sqrt{2}} = |\psi^-\rangle$$

$$\langle\psi^+|psi^-\rangle = 0$$

8.4 The Elitzur-Vaidman bomb tester

The Elitzur-Vaidman bomb tester is a quantum mechanics thought experiment that uses interaction-free mechanism to verify that a bomb is functional without having to detonate it. This experiment uses two characteristics of elementary particles: **nonlocality** and **wave-particle duality**. The fundamentals of this experiment can be explained with an example: if we have two closed boxes and we know that in one of the two there is an object, by opening one and finding it empty, we know that the object is in the other one without opening it. The particle, during the experiment, is in a superposition of states/locations, it can be anywhere in any moment. The particle's wave can be collapsed by observing it to obtain its local information. Information about previous positions of the particle can be obtained before the collapse and even in cases where the particle was never in those positions.
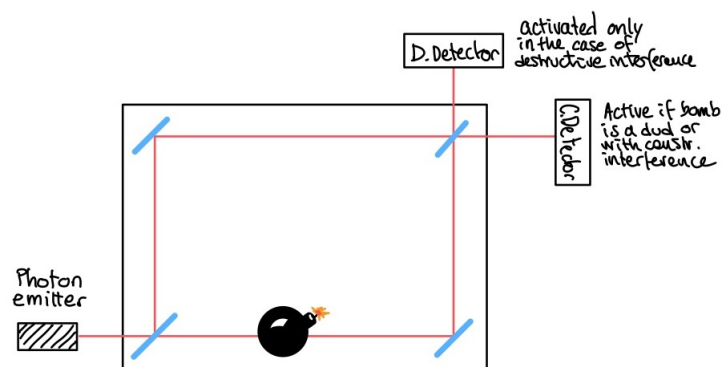
8.4.1 Bomb not inserted

When the photon is emitted and it reaches the first beam splitter, a superposition of states is created, the photon can either go to the upper path or to the lower path with a 50% probability each. The photon encounters two mirrors that reflect the beam and the two meet at a second beam splitter that directs the beam to two detectors with the same probability:

- C Detector: reached by the transmitted beam. Activated by the constructive interference of the two photons behaving as waves.

- D Detector: reached by the reflected beam. Never activated in normal conditions (destructive interference happens hence no signal)

8.4.2 Dud bomb

When the bomb is dud, C detector has a 100% probability of detecting a signal. The superposition of states created by the first beam splitter create a constructive interference that is detected by C. In D there is destructive interference so nothing is detected.

8.4.3 Bomb inserted and live

Three things may happen when the bomb is inserted and live:

- 50% the bomb explodes: The photon took the lower path and activated the bomb. The activation of the bomb can be considered as a collapse of the wave function, the photon never arrives at the detector and no signal is present.

- 25% photon detected at C: The photon took the upper way and was transmitted

by the second beam splitter.

- 25% photon detected at D: The photon took the upper way and was reflected by the second beam splitter. The presence of a signal at detector D is the only way to know whether the bomb is live without its explosion.

CHAPTER 8. QUANTUM COMPUTING 90

Part IV

Mathematical Background

Chapter 9

Complex numbers

A broad range of problems can be solved within real numbers, however it is easy to find some that are not solvable in $\mathbb{R}$. For example the equation $x^2 + 1 = 0$ has no solution in the real numbers. Because of this reason, the real number set is extended, trying to develop a coherent framework in which these problems can be solved. Following this procedure a new variable i is defined, such that:

$$i := \sqrt{-1} \notin \mathbb{R}$$

This quantity is called the imaginary unit and it is used to define a new kind of numbers or complex numbers, defined in standard form as:

$$z := \underbrace{a}_{\text{Real part, } \text{Re}\{z\}} + \underbrace{bi}_{\text{Imaginary part, } \text{Im}\{z\}}$$

Where $a \wedge b \in \mathbb{R}$. Thus we can define a new set of numbers $\mathbb{C}$ such that $z \in \mathbb{C}$ and $\mathbb{R} \subset \mathbb{C}$. In fact any real number is a complex number where $b = 0$.

9.1 Argand plane

Complex numbers can be seen as ordered pairs of reals and they can be naturally plotted on the complex or argand plane. The horizontal direction represents the real axis while the vertical one represents the imaginary one.

9.2 Operations

9.2.1 Addition

Let $z, w \in \mathbb{C}$ be two complex numbers such that $z = a + bi$ and $w = c + di$, where $a, b, c, d \in \mathbb{R}$. The addition is defined as:

$$z + w = (a + c) + (b + d)i$$

9.2.2 Subtraction

Let $z, w \in \mathbb{C}$ be two complex numbers such that $z = a + bi$ and $w = c + di$, where $a, b, c, d \in \mathbb{R}$. The subtraction is defined as:

$$z - w = (a - c) + (b - d)i$$

9.2.3 Multiplication

Let $z, w \in \mathbb{C}$ be two complex numbers such that $z = a + bi$ and $w = c + di$, where $a, b, c, d \in \mathbb{R}$. Remembering that $i^2 = -1$, the multiplication of two complex number is:

$$
\begin{aligned}
z \cdot w = (a + bi)(c + di) &= \\
&= ac + adi + bci + bdi^2 = \\
&= ac + (ad + bc)i - bd = \\
&= (ac - bd) + (ad + bc)i
\end{aligned}
$$

9.2.4 Complex conjugate

Let $z \in \mathbb{C}$ be a complex number such that $z = a + bi$, where $a, b \in \mathbb{R}$. The complex conjugate is defined as:

$$z^* = a - bi$$

So we take the opposite of the imaginary part.

9.2.5 Division

Let $z, w \in \mathbb{C}$ be two complex numbers such that $z = a + bi$ and $w = c + di$, where $a, b, c, d \in \mathbb{R}$. The complex conjugate can be used to define a division operation that brings the result in standard form. The operation is similar to the rationalization of a fraction: the nominator and the denominator are multiplied by the complex conjugate of the denominator. This is because the product of a complex number and its conjugate is always real. So the division is defined as:

$$
\begin{aligned}
\frac{z}{w} = \frac{a + bi}{c + di} &= \\
&= \frac{a + bi}{c + di} \frac{c - di}{c - di} = \\
&= \frac{ac - adi + bci + bd}{c^2 + d^2} = \\
&= \frac{(ac + bd) + (bc - ad)i}{c^2 + d^2} = \\
&= \frac{ac + bd}{c^2 + d^2} + \frac{bc - ad}{c^2 + d^2}i
\end{aligned}
$$

9.3 Polar form

9.3.1 Complex numbers as vectors

Complex numbers can be plotted as points in the Argand plane, using as coordinates the real and the imaginary parts. In this way a complex number can be seen as a vector of modulus:

$$\rho = |z| = \sqrt{a^2 + b^2}$$

Due to Pitagora's theorem. Complex number are added and subctrated as such.

9.3.2 Definition

The polar form is useful to have a simple interpretation of multiplication and division and it is defined as:

$$z := \rho(\cos\theta + i\sin\theta)$$

The variables used for this representation are the modulus ρ and the argument θ, the angle between the positive direction of the real axis and the vector itself. The modulus of a complex number is always positive. Complex numbers in polar form are periodic with the argument θ with periodicity $2k\pi$, $\forall k \in \mathbb{Z}$.

9.3.3 Conversion between polar form and standard form

Any complex number written in standard form can be written in polar form, where:

$$\begin{cases} \theta = \arctan\frac{b}{a} \\ \rho = \sqrt{a^2 + b^2} \end{cases}$$

Likewise, you can pass from polar form to standard form using:

$$\begin{cases} a = \rho\cos\theta \\ b = \rho\sin\theta \end{cases}$$

9.3.4 Operations

9.3.4.1 Multiplication

Let $z, w \in \mathbb{C}$ be two complex numbers such that $z = \rho_z(\cos\theta_z + i\sin\theta_z)$ and $w = \rho_w(\cos\theta_w + i\sin\theta_w)$. The multiplication between w and z is:

$$zw = \rho_z\rho_w(\cos\theta_z + i\sin\theta_z)(\cos\theta_w + i\sin\theta_w) =$$
$$= \rho_z\rho_w[\cos\theta_z\cos\theta_w - \sin\theta_z\sin\theta_w + i(\sin\theta_z\cos\theta_w + \cos\theta_z\sin\theta_w)]$$

Using now the addition formulas for cosine and sine:

$$zw = \rho_z\rho_q[\cos(\theta_z + \theta_w) + i\sin(\theta_z + \theta_w)]$$

9.3.4.2 Division

Let $z, w \in \mathbb{C}$ be two complex numbers such that $z = \rho_z(\cos\theta_z + i\sin\theta_z)$ and $w = \rho_w(\cos\theta_w + i\sin\theta_w)$. In a similar way as the multiplication, the division will be:

$$\frac{z}{w} = \frac{r_z}{r_w}[\cos(\theta_z - \theta_w) + i\sin(\theta_z - \theta_q)]$$

9.3.4.3 Power

According to the de Moivre theorem, for every $n \in \mathbb{N}$ positive integer and $z \in \mathbb{C}$, where $z = \rho(\cos\theta + i\sin\theta)$:

$$z^n = \rho^n(\cos n\theta + i\sin n\theta)$$

9.3.4.4 N-th root

For every $n \in \mathbb{N}$ positive integer and $z \in \mathbb{C}, z = \rho(\cos\theta + i\sin\theta)$:

$$\sqrt[n]{z} = \rho^{\frac{1}{n}}\left[\cos\left(\frac{\theta + 2k\pi}{n}\right) + i\sin\left(\frac{\theta + 2k\pi}{n}\right)\right]$$

Where k is an integer. Note that k and $k = k + n$ produce identical solutions, so k can be limited to the set $\{0, 1, \ldots, n-1\}$. In conclusion there are n distinct roots, each with modulus $r^{\frac{1}{n}}$, that when represented together on the Argand plane lie on the circle of radius ρ. The roots are equally spaced and they create a regular polygon when joined.

9.4 Complex valued functions

Real functions can be extended to complex valued functions. Taken f from an interval $A \subset \mathbb{R}$ to $\mathbb{C}$, the function can then be written as:

$$f(x) = u(x) + v(x)i$$

Where u and v are real valued functions. The limit of a complex valued function exists if the limits of the real and the complex component exist.

9.4.1 Complex conjugate

The complex conjugate of a composite function propagates through each of the components, meaning you have to change the sign before each imaginary unit i. For example:

$$(\sin(ix) + ie^{3x+2i})^* = (\sin(ix))^* + (ie^{3x+2i})^* = \sin(-ix) - ie^{3x-2i}$$

9.4.2 Derivative

The derivative of a complex valued function is obtained differentiating its real and imaginary parts:

$$f'(x) = u'(x) + v'(x)$$

The properties of the derivatives can be extended to this case: if f and g are two complex valued functions differentiable at some point x_0 in the domain of both functions, $f \pm g$, fg and $\frac{f}{g}$ $(g(x_0) \neq 0)$ are differentiable and the values of these functions are, just like in the real case:

$$(f \pm g)'(x_0) = f'(x_0) + g'(x_0)$$

$$(fg)'(x_0) = f'(x_0)g(x_0) + f(x_0)g'(x_0)$$

$$\frac{f}{g}'(x_0) = \frac{f'(x_0)g(x_0) - f(x_0)g'(x_0)}{g^2(x_0)}$$

9.5 Complex exponential

Due to its properties and applications it is desirable to extend the exponential function to the complex field. A complex exponential function is in the form e^{a+bi}. From the case $a = 0$:

$$e^{ti} = \cos t + i \sin t$$

If $a, b \neq 0$;

$$e^{a+bi} = e^a e^{bi} =$$
$$= e^a(\cos b + i \sin b)$$

9.5.1 Properties

Not only the product of two complex exponentials meets the classical properties of the real exponentials, the derivatives maintains them too. Let $t \in \mathbb{R}$ and $y(t) = e^{(a+bi)t} = e^{at}(\cos tb + i \sin b)$, its derivative with respecto to t is:

$$\frac{dy(t)}{dt} = \frac{de^{(a+bi)t}}{dt} =$$
$$= (a + bi)e^{(a+bi)t}$$

It can be demonstrated that given $z \in \mathbb{C}$, $\frac{de^z}{dz} = e^z$.

9.5.2 Roots of a complex number

The complex exponential allows to write the n roots of a complex number $z = r(\cos \theta + i \sin \theta)$ as:

$$w_k = r^{\frac{1}{n}} e^{i\frac{\theta + 2kn}{n}}$$

Where $k \in \{0, 1, \ldots, n-1\}$.

Chapter 10

Partial derivatives

10.1 First order derivatives

The concept of derivative can be used to explore functions of $n \geq 2$ variables. Let $f : \mathbb{R}^2 \supseteq A \to \mathbb{R}$, where A is an open set of $\mathbb{R}^2$, be a function of two variables: $f(x, y)$. The partial derivative of $f(x, y)$ with respect to x in the point (x_0, y_0) is defined as:

$$\frac{\partial f(x_0, y_0)}{\partial x} := \lim_{h \to 0} \frac{f(x_0 + h, y_0) - f(x_0, y_0)}{h}$$

With $h \in \mathbb{R}$ when the limit exists. Equivalently the partial derivative of $f(x, y)$ with respect to y in (x_0, y_0) is:

$$\frac{\partial f(x_0, y_0)}{\partial y} := \lim_{h \to 0} \frac{f(x_0, y_0 + h) - f(x_0, y_0)}{h}$$

With $h \in \mathbb{R}$ when the limit exists. That is, the derivative of $f(x, y)$ with respect to a variable is computed as if other variables are held constant. The existence of the partial derivative with respect to one variable does not imply the existence of the partial derivatives along any other direction. The derivative along a general direction $\vec{v}$ is called directional derivative and is defined as:

$$D_{\vec{v}} f(x_0, y_0) := \lim_{t \to 0} \frac{f((x_0, y_0) + t\vec{v}) - f(x_0, y_0)}{t}$$

With $t \in \mathbb{R}$ where the limit exists.

10.1.1 Differentiability

The concept of differentiability is introduced because the existence of the derivative along one direction does not imply the existence of directional derivatives along different directions. Let $\mathbb{R}^2 \supseteq A \to \mathbb{R}$, with A an open set of $\mathbb{R}^2$; a function of two variables $f(x, y)$ is differentiable if the partial derivatives exist in (x_0, y_0) and:

$$\lim_{(h,k) \to (0,0)} \frac{f(x_0 + h, y_0 + k) - f_x(x_0, y_0)h - f_y(x_0, y_0)k}{\sqrt{h^2 + k^2}} = 0$$

Where f_x and f_y are the partial derivatives with respect to x or y.

10.1.2 Tangent plane

The tangent plane of $f(x, y)$ in the point (x_0, y_0) has the following form:

$$g(x, y) = f(x_0, y_0) + f_x(x_0, y_0)(x - x_0) + f_y(x_0, y_0)(y - y_0)$$

10.1.3 Determine if a function is differentiable

A function if differentiable in a point if the following condition holds true. Let $f : \mathbb{R}^2 \supseteq A \to \mathbb{R}$ with A an open set of $\mathbb{R}^2$. If in a neighbourhood of (x_o, y_0) all the partial derivatives of $f(x, y)$ exist and are continuous in (x_0, y_0) then $f(x, y)$ are differentiable in (x_0, y_0). If a function has all the partial derivatives in a point and they are continuous, the function is differentiable. That means that the tangent plane in that point exists.

10.2 Higher order derivatives

Let $f : \mathbb{R}^2 \supseteq A \to \mathbb{R}$, with A an open set of $\mathbb{R}^2$, a function of two variables $f(x, y)$. Supposing that the partial derivatives exist in a neighbourhood I of (x_0, y_0), the two functions $g(x, y) = \frac{\partial f(x, y)}{dx}$: $\mathbb{R}^2 \supseteq I \to \mathbb{R}$ and $h(x, y) = \frac{\partial f(x, y)}{dy} : \mathbb{R}^2 \supseteq I \to \mathbb{R}$ can be seen as the analogous of f and there is a possibility of taking the partial derivatives of g and h in a point (x_0, y_0). This means applying the g and h the operators $\frac{\partial}{\partial x}$ and $\frac{\partial}{\partial y}$. The second order derivatives are defined as:

$$\frac{\partial^2 f}{\partial x^2} : \frac{\partial}{\partial x} g = \frac{\partial}{\partial x} \frac{\partial f}{\partial x} \qquad \frac{\partial^2 f}{\partial y \partial x} : \frac{\partial}{\partial y} g = \frac{\partial}{\partial y} \frac{\partial f}{\partial x}$$
$$\frac{\partial^2 f}{\partial x \partial y} : \frac{\partial}{\partial x} h = \frac{\partial}{\partial x} \frac{\partial f}{\partial y} \qquad \frac{\partial^2 f}{\partial y^2} : \frac{\partial}{\partial y} h = \frac{\partial}{\partial y} \frac{\partial f}{\partial y}$$

When the partial derivative is taken two times in the same direction the second partial derivatives are named pures, when they are taken along a different direction with respect to the first time they are named mixed.

10.2.1 Schwartz's theorem

Let $f(x, y)$ be a function defined in $\mathbb{R}^2$ and I a neighbourhood of (x_0, y_0) and $\partial x \partial y f$ and $\partial y \partial x f$ be continuous in I, then:

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$$

All of this can be extended to higher order partial derivatives and to functions from $\mathbb{R}^\ltimes$ to $\mathbb{R}$ with an increasing number of combinations of derivatives. This theorem is useful for many reasons, one of which is the fact that if the fourth order mixed partial derivatives are continuous in (x_0, y_0) the order of the first order partial derivatives can be rearranged as preferred.

10.3 Differential equation

A differential equation is a relation between an unknown function $f(\vec{x})$ and its arbitrary-order derivatives valid for every point $\vec{x}$ of the domain under consideration. The general solutions of differential equations involves several arbitrary constants, depending on the type of the equation

and on the order of the derivatives involved. The general solution of a partial differential equation involves an infinite set of unknown constants. Obtaining a particolar solution involves the addition of boundary or initial condition. There are two types of differential equations: linear and non-linear. The Schroedinger equation is a differential equation of the first order in time and second order in coordinates and a linear partial differential equation.

Chapter 11

Differential operators

11.1 Definition

An operator is a mapping of a certain set of structured objects such as a functions onto itself:

$$\hat{A} \cdot f = g$$

Operators can map functions to function or vectors to vectors. These two cases are conceptually the same, because functions are elements of a vector space called the Hilbert space. A differential operator is an operator which acts on functions and it is defined as some combination of differentiation operations.

11.2 Properties

11.2.1 Sum and difference

Given two operators $\hat{A}$ and $\hat{B}$ acting on some function f:

$$(\hat{A} \pm \hat{B})f = \hat{A}f \pm \hat{B}f$$

11.2.2 Product

Given two operators $\hat{A}$ and $\hat{B}$ acting on some function f:

$$(\hat{A}\hat{B})f = \hat{A}(\hat{B}f)$$

Basically you apply the operators in subsequent order.

11.2.3 Power

Given an operator $\hat{A}$

$$\hat{A}^n = \prod_{i=1}^{n} \hat{A}$$

11.2.4 Equality

Given two operators $\hat{A}$ and $\hat{B}$ acting on some function f, they are defined equal if:

$$\hat{A} = \hat{B} \Leftrightarrow \hat{A}f = \hat{B}f$$

11.2.5 Identity operator

The identity operator $\hat{\mathbb{1}}$ is an operator such that:

$$\hat{\mathbb{1}}f = f$$

11.2.6 Commutability

Two operators are said to commute when the order of their consecutive application does not matter:

$$\hat{A}\hat{B} = \hat{B}\hat{A}$$

If this is the case their commutator is zero:

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0$$

Note that:

$$\forall \hat{A}, \hat{B} : [\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$$

Two partial derivatives commute for $\mathbb{C}^2$ functions.

11.2.7 Linearity

Linear operators are operators which respect the property of linearity: given an operator $\hat{A}$ acting on f and g, and given a constant multiplier c:

$$\hat{A}(f \pm g) = \hat{A}f \pm \hat{A}g$$
$$\hat{A}(cf) = c\hat{A}f$$

11.3 Gradient, divergence and curl

11.3.1 Nabla operator

The nabla operator defined in the $3D$ cartesian coordinate system is the 3-component vector of partial derivatives over each axis:

$$\vec{\nabla} = \begin{pmatrix} \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{pmatrix}$$

The nabla operator is a linear differential operator which acts on functions and works as a $3D$ vector in space.

11.3.2 Scalar fields and vector fields

Single-valued functions of coordinate $f(\vec{x})$ are called scalar fields. They may represent a distribution of some density or the distribution of electrostatic charge in spece. $3D$ vectors which depend on coordinates, for example 3-valued functions of coordinates $\vec{f}(\vec{x})$ are called vector fields. They can represent quantities such as currents flow in a fluid, or the electric and magnetic fields in space.

11.3.3 Gradient

Let $f : \mathbb{R}^3 \supseteq A \to \mathbb{R}$, with A an open set of $\mathbb{R}^3$, a function of three variables $f(x, y, z)$. Be the function derivable. The gradient of f in Cartesian coordinates is defined as:

$$grad(f) = \nabla f := \frac{\partial f(x, y, z)}{\partial x}\hat{i} + \frac{\partial f(x, y, z)}{\partial y}\hat{j} + \frac{\partial f(x, y, z)}{\partial z}\hat{k}$$

The gradient of a scalar function is defined as nabla acting on it and producing a vector field of its derivatives. The gradient is then the vector that takes as components along the axes directions the first order partial derivatives. The gradient is the vector of major increment of the function with respect to the variations in the variables and it has magnitude equal to the maximum rate of increase at the point.

11.3.3.1 Directional derivatives

Directional derivatives for $\mathbb{C}^1$ functions can be written as the scalar product of the gradient of the function and the vector $\vec{v}$:

$$\vec{\nabla}_{\vec{v}} f(\vec{x}) = \vec{v}\vec{\nabla} f(\vec{x})$$

11.3.4 Divergence

Suppose now to have a derivable vectorial field $\vec{V} : \mathbb{R}^3 \supseteq A \to \mathbb{R}^3$, with A being an open set of $\mathbb{R}^3$. This vectorial field is defined by means of its components along the axes directions: $\vec{V} = v_1\hat{i} + v_2\hat{j} + v_3\hat{k}$. Basically, the vectorial field associates a vector to each point of A. The gradient, if it exists and if it is derivable, is a vectorial field. The divergence of $\vec{V}$ in Cartesian coordinates is:

$$div\vec{V} = \nabla \cdot \vec{V} := \frac{\partial v_1(x, y, z)}{\partial x} + \frac{\partial v_2(x, y, z)}{\partial y} + \frac{\partial v_3(x, y, z)}{\partial z}$$

It is thus defined as nabla acting on a vector field via the scalar product. This gives information on where a vectorial field has source or sink or, when the vectorial field represents a fluid flux, if the fluid is incompressible or solenoidal.

11.3.5 Curl

Suppose now to have a derivable vectorial field $\vec{V} : \mathbb{R}^3 \supseteq A \to \mathbb{R}^3$, with A an open set of $\mathbb{R}^3$. The application of the curl to $\vec{V}$ is:

$$rot\vec{V} = \nabla \times \vec{V} := \left(\frac{\partial v_3}{\partial y} - \frac{\partial v_2}{\partial z}\right)\hat{i} + \left(\frac{\partial v_1}{\partial z} - \frac{\partial v_3}{\partial x}\right)\hat{j} + \left(\frac{\partial v_2}{\partial x} - \frac{\partial v_1}{\partial y}\right)\hat{k}$$

It is thus defined as nabla acting on a vector field via the vector or cross product. The application of the curl to a vectorial field gives information on whether the field rotates around a point and on

the verse of that rotation. The output of the curl is the modulus of the rotation, and the direction is linked by means of the right hand rule to the verse of rotation.

11.3.6 Properties

- $\nabla \times \nabla f = \vec{0}$
- $\nabla \cdot \nabla \times \vec{V} = 0$
- $\nabla \cdot f = \nabla^2 f$

11.3.7 Laplacian

The Laplacian is an operator defined as:

$$\Delta f = \nabla^2 f = \frac{\partial^2}{\partial x^2} f + \frac{\partial^2}{\partial y^2} f + \frac{\partial^2}{\partial z^2} f$$

It is the scalar product of two nabla operators. In spherical coordinates:

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

11.4 Hessian matrix: maxima and minima

A matrix of n order partial derivatives can be built to study functions from $\mathbb{R}^n$ to $\mathbb{R}$. We will only consider Hessian matrices where $n = 2$ Let $f : \mathbb{R}^2 \supseteq A \to R$, with A an open set of $\mathbb{R}^2$ a function $f(x, y)$. If (x_0, y_0) is a local extremum if exists $\nabla f = \vec{0}$ (the point is a local extremum is the gradient of the function in that point is null). To find local extrema are considered points in which $\nabla f = \vec{0}$. Let $f : \mathbb{R}^2 \supseteq A \to R$, with A an open set of $\mathbb{R}^2$ and $f \in \mathbb{C}^2$, where $\mathbb{C}^2$ means that all second order partial derivatives exist and are continuous. Then the Hessian matrix is defined as:

$$H_f(x_0, y_0) = \begin{pmatrix} \partial_{xx} f(x_0, y_0) & \partial_{yx} f(x_0, y_0) \\ \partial_{xy} f(x_0, y_0) & \partial_{yy} f(x_0, y_0) \end{pmatrix}$$

This matrix is useful to determine the nature of the extrema. Let $f \in \mathbb{C}^2$ and (x_0, y_0) be a critical point of f, then:

- If the determinant of $H_f(x_0, y_0) > 0$ and $\partial_{xx} f(x_0, y_0) > 0$ then (x_0, y_0) is a minimum.

- If the determinant of $H_f(x_0, y_0) > 0$ and $\partial_{xx} f(x_0, y_0) < 0$ then (x_0, y_0) is a maximum.

- If the determinant of $H_f(x_0, y_0) < 0$ then (x_0, y_0) is a saddle point.

- If the determinant of $H_f(x_0, y_0) = 0$ further analysis is necessary.

11.5 Jacobian matrix

With a vectorial function the concept of gradient can be extended and applied to each component of the function. Let $f : \mathbb{R}^2 \supseteq A \to \mathbb{R}^2$ be a function of two variables $f = (f_1(x, y), f_2(x, y))$ for which all the derivatives exist and are continuous. The jacobian matrix is defined as:

$$J_f = \begin{pmatrix} \partial_x f_1 & \partial_y f_1 \\ \partial_x f_2 & \partial_y f_2 \end{pmatrix} = \begin{pmatrix} \nabla f_1 \\ \nabla f_2 \end{pmatrix}$$

Due to the fact that we have a function that takes as input two variables and gives as output two variables, this can be thought as a change of coordinates:

$$f = (f_1(x,y), f_2(x,y)) = (u,w) \qquad (x,y) \to (u,w)$$

The Jacobian matrix allows to determine the domain of the transformation. The change of variables is $1 \leftrightarrow 1$ (a bijective function) only if the determinant of the Jacobian matrix is not null. The Jacobian determinant also allows to consistently define the change of volume while changing the coordinates. Given a transformation from (x,y) to (u,v) the change in the expression of the area with respect to the coordinates is:

$$dA = dxdy = \left| det \frac{\partial(x,y)}{\partial(u,v)} \right| dudv$$

Where dx, dy, du, dv are small coordinates intervals.

11.6 Chain rule

Let $u(x,y)$ be a differentiable function of two variables which are differentiable functions of two variables each $x(s,t)$ and $y(s,t)$, then the composite function is differentiable and the partial derivatives are:

$$\frac{\partial u}{\partial s} = \frac{\partial u}{\partial x}\frac{\partial x}{\partial s} + \frac{\partial u}{\partial y}\frac{\partial y}{\partial s} \qquad \frac{\partial u}{\partial t} = \frac{\partial u}{\partial x}\frac{\partial x}{\partial t} + \frac{\partial u}{\partial y}\frac{\partial y}{\partial t}$$

11.6.1 Gradient in polar coordinates

Suppose to have $g(x,y)$, a function of two variables in Cartesian coordinates. If (ρ, θ) are the usual polar coordinates related to (x,y) by $x = \rho\cos\theta$ and $y = \rho\sin\theta$, then by substituting these for x and y, g becomes a function of ρ and θ:

$$g(x,y) = f(\rho(x,y), \theta(x,y))$$

With $\rho(x,y) = \sqrt{x^2 + y^2}$ and $\theta(x,y) = \arctan\frac{y}{x}$. The objective is to compute the gradient $\nabla g(x,y)$ and express it in terms of ρ and θ. The chain rule can be used to compute the partial derivatives of g with respect to x and y:

$$\frac{\partial g}{\partial x} = \frac{\partial f}{\partial \rho}\frac{\partial \rho}{\partial x} + \frac{\partial f}{\partial \theta}\frac{\partial \theta}{\partial x} \qquad \frac{\partial g}{\partial y} = \frac{\partial f}{\partial \rho}\frac{\partial \rho}{\partial y} + \frac{\partial f}{\partial \theta}\frac{\partial \theta}{\partial y}$$

To fill these relations one must compute:

$$\frac{\partial \rho}{\partial x} = \frac{\partial \sqrt{x^2 + y^2}}{\partial x} = \frac{1}{2}\frac{2x}{\sqrt{x^2 y^2}} = \frac{x}{\sqrt{x^2 + y^2}} = \frac{\rho \cos \theta}{\rho} = \cos \theta$$

$$\frac{\partial \rho}{\partial y} = \frac{\partial \sqrt{x^2 + y^2}}{\partial y} = \frac{1}{2}\frac{2y}{\sqrt{x^2 y^2}} = \frac{y}{\sqrt{x^2 + y^2}} = \frac{\rho \sin \theta}{\rho} = \sin \theta$$

$$\frac{\partial \theta}{\partial x} = \frac{\partial \arctan \frac{y}{x}}{\partial x} = -\frac{y}{x^2 + y^2} = -\frac{\rho \sin \theta}{\rho^2} = -\frac{\sin \theta}{\rho}$$

$$\frac{\partial \theta}{\partial y} = \frac{\partial \arctan \frac{y}{x}}{\partial y} = \frac{x}{x^2 + y^2} = \frac{\rho \cos \theta}{\rho^2} = \frac{\cos \theta}{\rho}$$

Hence:

$$\frac{\partial g}{\partial x} = \frac{\partial f}{\partial \rho}\cos \theta + \frac{\partial f}{\partial \theta}\frac{-\sin \theta}{\rho} \qquad \frac{\partial g}{\partial y} = \frac{\partial f}{\partial \rho}\sin \theta + \frac{\partial f}{\partial \theta}\frac{\cos \theta}{\rho}$$

The gradient of g using Cartesian versors will be:

$$\nabla g = g_x \hat{e}_x + g_y \hat{e}_y = \left(\frac{\partial f}{\partial \rho}\cos \theta + \frac{\partial f}{\partial \theta}\frac{-\sin \theta}{\rho}\right)\hat{e}_x + \left(\frac{\partial f}{\partial \rho}\sin \theta + \frac{\partial f}{\partial \theta}\frac{\cos \theta}{\rho}\right)\hat{e}_y =$$

$$= \left(\frac{\partial f}{\partial \rho}\cos \theta\right)\hat{e}_x + \left(\frac{\partial f}{\partial \theta}\frac{-\sin \theta}{\rho}\right)\hat{e}_x + \left(\frac{\partial f}{\partial \rho}\sin \theta\right)\hat{e}_y + \left(\frac{\partial f}{\partial \theta}\frac{\cos \theta}{\rho}\right)\hat{e}_y =$$

$$= \frac{\partial f}{\partial \rho}(\cos \theta \hat{e}_x + \sin \theta \hat{e}_y) + \frac{1}{\rho}\frac{\partial f}{\partial \theta}(-\sin \theta \hat{e}_x + \cos \theta \hat{e}_y)$$

The unit versors $\hat{e}_\rho$ and $\hat{e}_\theta$ are introduced. They have unitary modulus and direction that change from point to point. In particolar for polar coordinates they have the components $\hat{e}_\rho = (\cos \theta, \sin \theta)$ and $\hat{e}_\theta = (-\sin \theta, \cos \theta)$. So finally the explicit gradient in polar coordinates is:

$$\nabla g = f_\rho \hat{e}_\rho + \frac{f_\theta}{\rho}\hat{e}_\theta$$

Chapter 12

Spherical coordinates

12.1 Definition

An important change of coordinates is the one that takes the cartesian coordinates and maps them into the spherical ones (ρ, θ, ϕ). This transformation allows to simplify working on systems with spherical symmetry. The relationship between cartesian and spherical coordinates can be defined as:

- $x = x_0 + \rho \cos\theta \sin\phi$
- $y = y_0 + \rho \sin\theta \sin\phi$
- $z = z_0 + \rho \cos\phi$

With the following conditions:

- $0 \leq \rho \leq \infty$
- $0 \leq \theta \leq 2\pi$
- $0 \leq \phi \leq \pi$

Computing all the first order partial derivatives, we obtain the following jacobian matrix:

$$J_f = \begin{pmatrix} \nabla(x(\rho,\theta,\phi)) \\ \nabla(t(\rho,\theta,\phi)) \\ \nabla(z(\rho,\theta,\phi)) \end{pmatrix} = \begin{pmatrix} x_\rho & x_\theta & x_\phi \\ y_\rho & y_\theta & y_\phi \\ z_\rho & z_\theta & z_\phi \end{pmatrix} =$$

$$= \begin{pmatrix} \cos\theta\sin\phi & -\rho\sin\theta\cos\phi & \rho\cos\theta\cos\phi \\ \sin\theta\sin\phi & \rho\sin\theta\cos\phi & \rho\sin\theta\cos\phi \\ \cos\phi & 0 & -\rho\sin\phi \end{pmatrix}$$

With the jacobian determinant $-\rho^2 \sin\phi$. So for spherical coordinates:

$$dV = dxdydz = \left| det \frac{\partial(x,y,z)}{\partial(\rho,\theta,\phi)} \right| d\rho d\theta d\phi = \rho^2 \sin\phi d\rho d\theta d\phi$$

12.2 The sphere volume

To compute the volume of a ball B with radius $\rho \leq R$, the simplest way is to rewrite the problem in spherical coordinates with the following conditions:

- $0 \leq \rho \leq R$
- $0 \leq \theta \leq 2\pi$
- $0 \leq \phi \leq \pi$

So that the integral to compute is:

$$Vol(B) = \int\limits_0^\pi \int\limits_0^{2\pi} \int\limits_0^R \rho^2 \sin\phi d\rho d\theta d\phi =$$

$$= \int\limits_0^\pi \int\limits_0^{2\pi} \left[\frac{\rho^3}{3}\right]_0^R \sin\phi d\theta d\phi = \int\limits_0^\pi \int\limits_0^{2\pi} \frac{R^3}{3} \sin\phi d\theta d\phi =$$

$$= \int\limits_0^\pi [\theta]_0^{2\pi} \frac{R^3}{3} \sin\phi d\phi = \int\limits_0^\pi \frac{2\pi R^3}{3} \sin\phi d\phi =$$

$$= [-\cos\phi]_0^\pi \frac{2\pi R^3}{3} =$$

$$= \frac{4\pi R^3}{3}$$

Chapter 13

Multidimensional integrals

When working in multiple dimensions, the domain can have a shape that can produce effects on the integration procedure. Another difficulty introduced by solving integrals in many dimensions is the choice of the order of integration.

13.1 Definition

The integral of a function $f(x, y)$ in two dimensions is the volume under the surface $z = f(x, y)$. Supposing that the function is defined over a rectangular domain $(a, b) \times (c, d)$, the domain can be divided in many smaller rectangles with dimension $\Delta x \times \Delta y$. The sum of all these subdomains covers the whole original domain. In each subdomain we can define the infimum and the supremum. The infimum of the function is the greatest element of $\mathbb{R}$ that is less than or equal to all elements of the function in the corresponding subdomain. The supremum is the least element of $\mathbb{R}$ that is greater than or equal to all elements of the function in the corresponding subdomain. A specific division of the domain is denoted as P. The Darboux sums are defined as:

$$L(f, P) = \sum_{\Delta x_k \times \Delta y_k} \sup_{[\Delta x_k \times \Delta y_k]} f(x, y)(\Delta x_k \times \Delta y_k)$$

$$U(f, P) = \sum_{\Delta x_k \times \Delta y_k} \inf_{[\Delta x_k \times \Delta y_k]} f(x, y)(\Delta x_k \times \Delta y_k)$$

Where the sum is over all the subdomains labelled by k. The function $f(x, y)$ is Riemann-integrable if:

$$\sup L(f, P) = \inf U(f, P) = I$$

when varying the partition; furthermore we can write that:

$$I = \int_c^d \int_a^b f(x, y) dx dy$$

This relation implies several properties.

13.2 Properties

13.2.1 Integrability

Let $f(x, y)$ be a continuous function from $(a, b) \times (c, d)$, then the function is integrable. This lemma states the integrability requirements for a small subset of functions, but the result can be extended to different kind of integrals and to more than two dimensions.

13.2.2 Order of integration

If $f(x, y)$ is continuous on $(a, b) \times (c, d)$ then:

$$\int\limits_c^d \left(\int\limits_a^b f(x, y) dx \right) dy = \int\limits_a^b \left(\int\limits_c^d f(x, y) dy \right) dx$$

Basically you can choose the order of integration as you see fit.

13.2.3 x-simple and y-simple domains

In some cases the domain of the function is not defined over a rectangular domain. One case of easy integration is when the domain is x-simple or y-simple. In the case of a y-simple domain, the function is bounded on the x axis by two numerical values and on the y axis by two continuous function $y = g_1(x)$ and $y = g_2(x)$. The case of a x-simple domain is the symmetric of the y-simple one. Let $f(x, y)$ be a continuous function defined on an x-simple domain Ω:

$$\Omega = \{(x, y) \in \mathbb{R}, c \leq y \leq d, h_1(y) \leq x \leq h_2(y)\}$$

The integral can be computed as:

$$\iint\limits_\Omega f = \int\limits_c^d dy \left(\int\limits_{h_1(y)}^{h_2(y)} f(x, y) dx \right)$$

In the same way for a y-simple domain:

$$\Omega = \{(x, y) \in \mathbb{R}, g_1(x) \leq y \leq g_2(x), a \leq x \leq b\}$$

$$\iint\limits_\Omega f = \int\limits_a^b dx \left(\int\limits_{g_1(x)}^{g_2(x)} f(x, y) dy \right)$$

13.2.4 Change of variables

The absolute value of the jacobian determinant gives the change in the volume element when passing from a set of coordinates to another. In two dimension, given $f(x, y)$ defined on Ω and supposing to change the integral variables from x and y to u and v:

$$\iint\limits_\Omega f(x, y) dx dy = \iint\limits_{\Omega^*} f(x(u, v), y(u, v)) |J| du dv$$

Where Ω^* is the new region of integration in the (u, v) plane.

Chapter 14

Wave equations

14.1 Definition

In mathematical physics, a propagating wave is described by a function retaining its shape while shifting in time and space. In one dimension this is formalized as:

$$f(x,t) \doteq \begin{cases} f_+(x - vt) & \text{forward propagating} \\ f_-(x + vt) & \text{backward propagating} \end{cases}$$

The functions $f_\pm$ are solutions of:

$$\frac{\partial^2}{\partial t^2} f_\pm(x \pm vt) = v^2 f''(x \pm vt)$$

$$\frac{\partial^2}{\partial x^2} f_\pm(x \pm vt) = k^2 f''(x \pm vt)$$

Hence the wave equation becomes:

$$\left(\underbrace{\frac{1}{v^2}}_{\text{speed of the wave}} -\frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2} \right) f_\pm = 0$$

14.1.1 Three-dimensional case

To get the corresponding form for a wave in three dimensions, note that a function $f(kx + \omega t)$ is still a function of (x, t) in the form $x + vt$:

$$f(kx + \omega t) = f\left(k\left(x + \underbrace{\frac{\omega}{k}}_{=v} t \right) \right)$$

Consequently, $f(kx \pm \omega t)$ satisfies as a wave equation:

$$\frac{\partial^2}{\partial t^2} f(kx + \omega t) = \omega^2 f(kx + \omega t)$$

$$\frac{\partial^2}{\partial x^2} f(kx + vt) = k^2 f(kx + \omega t)$$

And:

$$\left(\frac{1}{vr^2} \frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2} \right) f = 0$$

If $\frac{\omega^2}{v^2} = k \Rightarrow |k| = \frac{\omega}{v} \Rightarrow \omega = |k|v$. To generalize to three dimensions:

- $k \to \vec{k}$

- $x \to \vec{r} = (x, y, z)$

- $\frac{\partial^2}{\partial x^2} \to \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \equiv \nabla^2$

So the three dimensional wave equation becomes:

$$\left(\nabla^2 - \frac{1}{v^2} \frac{\partial^2}{\partial t^2} \right) f(\vec{r}, t) = 0$$

14.2 Plane waves

Plane waves are oscillatory waves in the form:

$$f(\vec{k}\vec{x} \pm \omega t) = A_{\pm} e^{i(\overbrace{\vec{k}}^{\text{wave vector}} \vec{x} \pm \overbrace{\omega}^{\text{pulsation}} t)}$$

Fixing $t = 0$ in one dimension:

$$f(kx) = Ae^{ikx} = A(\cos kx + i \sin kx)$$

Fixing $x = 0$:

$$f(\omega t) = Ae^{i\omega t} = A(\cos \omega t + i \sin \omega t)$$

Where $\nu = \frac{\omega}{2\pi} = \frac{1}{T}$. In a plane wave the amplitude is constant throughout a plane perpendicular to $\vec{k}$. Assuming $\vec{k} = k_0 \hat{z}$ and $\vec{r}\vec{k} = z \cdot k$:

$$f_{\pm}(\vec{r} \cdot \vec{k} \pm \omega t) = f(zk \pm \omega t)$$

So it does not depend on x nor y. Any wave can be locally approximated by a plane wave.

Chapter 15

Hilbert spaces

15.1 From vector to hilbert spaces

15.1.1 Definition

15.1.1.1 Classical mechanics

In classical mechanics the instantaneous state of a single particle is specified by the vector position $\vec{r}(t)$ and its momentum $\vec{p}(t)$ in the real vector spaces. In these vector spaces linearity holds: any linear combination of elements arbitrarily chosen inside the vector space $\mathcal{V}$ is still an element of the same vector space:

$$\forall \vec{v}, \vec{w} \in \mathcal{V} \wedge \forall a, b \in \mathbb{R} : a\vec{v} + b\vec{w} \in \mathcal{V}$$

Imposing that $a, b \in \mathbb{R}$ restricts the discussion to real vector spaces. These have an operation called inner or scalar product that takes as input two vectors and gives as output a scalar. This is a real number for real vector spaces:

$$(\vec{v}, \vec{w}) \equiv \vec{v} \cdot \vec{w} = \vec{w} \cdot \vec{v} \in \mathbb{R}$$

This operation is bi-linear:

$$(a_1 \vec{v}_1 + a_2 \vec{v}_2) \cdot (b_1 \vec{w}_1 + b_2 \vec{w}_2) = \sum_{i,k=1}^{2} a_i b_k \vec{v}_i \vec{w}_k$$

15.1.1.2 Quantum mechanics

In quantum mechanics the instantaneous state of a particle is described by a quantum state $|\psi(t)\rangle$ that belongs to a hilbert space or $\mathcal{H}$, which provides a suitable generalization for the notion of vector spaces. In a hilbert space any linear combination of quantum states is still inside the hilbert space:

$$\forall |\psi\rangle, |\phi\rangle \in \mathcal{H} \wedge \alpha, \beta \in \mathbb{C} : \alpha |\psi\rangle + \beta |\phi\rangle \in \mathcal{H}$$

A scalar product can be then defined as:

$$\langle \psi | \phi \rangle = (\langle \phi | \psi \rangle)^* \in \mathbb{C}$$

In hilbert spaces, reversing the order of the elements of an inner product leads to the complex conjugate result. The inner product is bi-linear:

$$\begin{cases} |\xi\rangle \equiv \alpha_1|\psi_1\rangle + \alpha_2|\psi_2\rangle \\ |\omega\rangle \equiv \beta_1|\phi_1\rangle + \beta_2|\phi_2\rangle \end{cases} \Rightarrow \langle\xi|\omega\rangle = \sum_{i=1}^{2} \alpha_i^*\beta_i\langle\psi_i|\phi_i\rangle$$

15.1.2 Complete orthonormal bases

15.1.2.1 Standard vector spaces

When talking about standard vector spaces, orthonormal basis vectors are a set form of elements which are mutually orthogonal and have unitary norm:

$$\vec{e}_i \cdot \vec{e}_j = \delta_{ij}$$

Where δ_{ij} is the Kronecker-Delta and it is defined as:

$$\delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases}$$

It also has the property that:

$$\sum_j \delta_{ij}A_j = A_i$$

A set of N versors is said to form a complete orthonormal basis of the vector space $\mathcal{V}$ if, for any vector $\vec{v} \in \mathcal{V}$, there exists a unique set of N real coefficient $\lambda_1, \ldots, \lambda_N$ which enables to express $\vec{v}$ as a linear combination of the vectors of the basis:

$$\vec{v} = \sum_{k=1}^{N} \lambda_k \vec{e}_k$$

N is the dimension of the vector space. The set of coefficients is refferred to as coordinates of the vector $\vec{v}$ in the given complete orthonormal basis $\{e_k\}_{k=1,\ldots,N}$.

15.1.2.2 Hilbert space

A set of quantum states is said to be a complete orthonormal basis of a Hilbert space $\mathcal{H}$ if:

- They are mutually orthogonal.

- They have unit norm.

- Any quantum state belonging to the Hilbert space can be written as linear combination of them.

The elements of a complete orthonormal basis of a Hilbert space may form an infinite and dense set. Let's consider the set of position quantum states $|x\rangle$. Clearly two position can differ by an infinitesimal amount, therefore a continuous index x is needed to label them. Two position states are said to obey the orthonormally condition if the following equality holds:

$$\langle\vec{x}|\vec{y}\rangle = \delta(\vec{x} - \vec{y})$$

$\delta(\vec{x} - \vec{y})$ denotes the Dirac-delta, defined as:

$$\int d^3\vec{y} A(y)\delta(\vec{x} - \vec{y}) = A(\vec{x})$$

The fact that position states form a basis of $\mathcal{H}$ expresses the fact that any quantum state in the Hilbert space can be obtained from a linear combination of the position states:

$$|\psi\rangle = \int d^3\vec{x}\phi(\vec{x})|\vec{x}\rangle \qquad \phi(\vec{x}) \in \mathbb{C}$$

The complex function $\phi(x)$ is called the wave function and can be regarded as a dense and infinite set of complex coefficients. Therefore Hilbert spaces are infinite dimension vector spaces.

15.1.3 Operators

Operators are defined by their action on the elements of the vector space:

$$\vec{w} = \hat{O}\vec{v}$$

In particular $\hat{O}$ is linear if:

$$\hat{O}(\alpha_1\vec{v}_1 + \alpha_2\vec{v}_2) = \alpha_1\hat{O}\vec{v}_1 + \alpha_2\hat{O}\vec{v}_2$$

Once a basis of an N-dimensional real vector space is defined, then to each linear operator can be assigned an $N \times N$ matrix, through the representation of the operator in the specific basis:

$$\vec{w} = \hat{O}\vec{v} \rightarrow \vec{e}_j \cdot \vec{w} = \sum_{i=1}^{N}(\vec{e}_i \cdot \vec{v})\vec{e}_j \cdot \hat{O}\vec{e}_i = \sum_{i=1}^{N} O_{ji}v_j$$

Where $v_i = \vec{e}_i \cdot \vec{v}$ and $O_{ij} = \vec{e}_i \cdot \hat{O}\vec{e}_j$. In a complete analogy, a linear operator $\hat{O}$ defined in an hilbert space $\mathcal{H}$ linearly maps a quantum state into another:

$$|w\rangle = \hat{O}|v\rangle \qquad \hat{O}(\alpha_1|v_1\rangle + \alpha_2|v_2\rangle) = \alpha_1\hat{O}|v_1\rangle + \alpha_2\hat{O}|v_2\rangle$$

Just like what happens for real vector spaces, operators in hilbert spaces can be represented in a given orthonormal basis, like the position state basis, through a projection procedure:

$$|\omega\rangle = \hat{O}|\psi\rangle \Rightarrow \omega(\vec{x} = \langle\vec{x}|w\rangle) = \int d^3\vec{y}\langle\vec{y}|\psi\rangle\langle\vec{x}|\hat{O}|\vec{y}\rangle = \int d^3\vec{y}O(\vec{x},\vec{y})\psi(\vec{y})$$

Where $\omega(\vec{x})$ and $\psi(\vec{x})$ denote the wave functions associated to the states $|\omega\rangle$ and $|\psi\rangle$ respectively. In most cases $O(\vec{x},\vec{y})$ is a nearly local operator.

15.1.3.1 Multiplicative operator

A multiplicative operator is the potential energy operator: $U(\vec{x},\vec{y}) = \delta(\vec{x} - \vec{y})u(y)$:

$$\int d^3\vec{y}U(\vec{x},\vec{y})\psi(\vec{y}) = u(\vec{x})\psi(\vec{x})$$

.

15.1.3.2 Derivative operator

A derivative operator is the kinetic energy operator: $T(\vec{x}, \vec{y}) = -\frac{\hbar^2}{2m}\delta(\vec{x} - \vec{y})\nabla^2_{\vec{x}}$:

$$\int d^3\vec{y}T(\vec{x}, \vec{y})\psi(\vec{y}) = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{x})$$

15.1.3.3 Exponential of an operator

Let $\hat{A}$ be an operator, then:

$$e^{\hat{A}} \equiv \hat{\mathbb{1}} + \hat{A} + \frac{1}{2}\hat{A}^2 + \cdots = \sum_{n=0}^{\infty}\frac{1}{n!}\hat{A}^n$$

Notice that:

$$e^{\hat{A}+\hat{B}} \neq e^{\hat{A}}e^{\hat{B}}$$

15.2 Spectral theorem

The spectral theorem is a fundamental result in the theory of linear operators in vector and hilbert spaces and specifies the general conditions under which operators can be diagonalized to yield a complete orthonormal basis. The spectral theorem of standard linear algebra follows as a special case of this fundamental result.

15.2.1 Adjoint

The adjoint or hermitian conjugate operator $O^\dagger$ of a generic linear operator $\hat{O}$ is defined as:

$$\langle \vec{v}\hat{O}^\dagger, \vec{w}\rangle = \langle \vec{v}, \hat{O}\vec{w}\rangle$$

An operator is called hermitian if it is self-adjoint, meaning that it coincides with its hermitian conjugate: $\hat{O} = \hat{O}^\dagger$. Furthermore an operator $\hat{U}$ is called unitary if $\hat{U}^\dagger\hat{U} = \hat{\mathbb{1}}$. Observables in quantum mechanics are associated to hermitian operators and the outcome of a measurement is one of its real eigenvalues. The expectation value of an observable O in any state ϕ is:

$$\frac{(\phi, O, \phi)}{(\phi, \phi)}$$

15.2.2 Statement of the spectral theorem

Let $\hat{O}$ be an hermitian operator defined on a hilbert space $\mathcal{H}$. Then there exists a complete orthonormal basis of $\mathcal{H}$ defined by the eigenstates of $\hat{O}$. Furthermore each eigenvalue is real.

15.2.3 Corollaries

15.2.3.1 First corollary

Hermitian matrices are such that:

$$(O^T)^* = O$$

15.2.3.2 Second corollary

Hermitian matrices in real vector spaces are symmetric.

15.2.3.3 Third corollary

Given a complete orthonormal basis of a hilbert space $\{|e_n\rangle\}$ possibly dense and a hermitian operator $\hat{O}$, it is possible to identify a unitary transformation which connects the $\{|e_n\rangle\}$ with the basis of eigenstates of $\hat{O}$, called $\{|o_n\rangle\}$.

15.3 Fourier transform

A special case of basis change is provided by the fourier transform. Let $\phi(\vec{x})$ be the wave function in coordinate representation. The unitary transformation to the momentum basis is called direct fourier transform and it is defined as:

$$\hat{F}[\phi(\vec{x})] = \tilde{\phi}(\vec{p}) = \int\limits_{-\infty}^{\infty} d^3\vec{x}\, e^{\frac{i}{\hbar}\vec{p}\cdot\vec{x}}\phi(\vec{x})$$

The inverse transformation from the momentum basis to the position one is called the inverse fourier transform:

$$\hat{F}^{-1}[\tilde{\phi}(\vec{p})] = \phi(\vec{x}) = \int\limits_{-\infty}^{\infty} \frac{d^3\vec{p}}{(2\pi)^3} e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{x}}\tilde{\phi}(\vec{p})$$

The term $(2\pi)^3$ is introduced conventionally to guarantee the preservation of the normalization condition. An important property of the fourier transform is that:

$$F^{-1}[\vec{p}\tilde{\phi}(\vec{p})] = \int\limits_{-\infty}^{\infty} \frac{d^3\vec{p}}{(2\pi)^3} e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{x}}\vec{p}\tilde{\phi}(\vec{p}) =$$

$$= \left(-i\hbar\frac{\partial}{\partial\vec{x}}\right) \int\limits_{-\infty}^{\infty} \frac{d^3\vec{p}}{(2\pi)^3} e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{x}}\tilde{\phi}(\vec{p})$$

$$= \left(-i\hbar\frac{\partial}{\partial\vec{x}}\right)\phi(x)$$

Where $\frac{\partial}{\partial\vec{x}}$ denotes the gradient operator.

Chapter 16

Dirac notation

In quantum mechanics, the state of a system can be represented by a vector $\left|\vec{L}(t)\right\rangle$ that "lives out there in Hilbert space" but can be expressed by means of any number of different bases. The wave function $\psi(x,t)$ is the coefficient in the expansion of $\left|\vec{L}\right\rangle$ in the basis of position eigenfunctions.

$$\psi(x,t) = \left\langle x\middle|\vec{L}\right\rangle$$

The momentum space wavefunction $\phi(p,t)$ is the expansion of $\left|\vec{L}\right\rangle$ in the basis of momentum eigenfunctions.

$$\phi(p,t) = \left\langle p\middle|\vec{L}\right\rangle$$

We can also expand the wave function $\left|\vec{L}\right\rangle$ with energy eigenfunctions (discrete spectrum)

$$c_n(t) = \left\langle n\middle|\vec{L}\right\rangle$$

The functions ψ, ϕ, and the set of coefficients c_n are the same way of describing the same vector:

$$\psi(x,t) = \int \psi(y,t)\delta(x-y)\,dy = \int \phi(p,t)\cdot\frac{1}{\sqrt{2\pi\hbar}}e^{\frac{ipx}{\hbar}}\,dp = \sum c_n \cdot e^{-\frac{iE_n t}{\hbar}}\psi_n(x)$$

Operators acting on observables are linear transformations and transform one vector into another $|\beta\rangle = \hat{O}|\alpha\rangle$ and can be represented with respect to a particular basis by their matrix elements.

$$\langle e_m|\hat{O}|e_n\rangle \equiv Q_{mn} \text{ so we can say } \sum_n b_n\,|e_n\rangle = \sum_n a_n\hat{O}\,|e_n\rangle$$

By considering the inner product $\sum_n b_n \langle e_m|e_n\rangle = \sum_n a_n \langle e_m|\hat{O}|e_n\rangle$

$$b_m = \sum_n Q_{mn}a_n$$

Where Q_{mn} is a matrix element that will determine how the components transform.
I might have a system that only admits a finite number of linearly independent states (usually two). $|L(t)\rangle$ lives in an N-dimensional vector space that can be represented with a column of N components. Operators take the form of a (NxM) matrix.
Anyway, for the inner product Dirac proposed the **braket notation** $\langle a|b\rangle$ where:

- $|b\rangle$ Ket = vector
- $\langle a|$ Bra = linear function of vector that, if it hits the ket, it gives the inner product of the two, a <u>number</u>

$$Operator + vector = vector$$

$$Bra + vector = number$$

Bra notation can be resembled as a function to integrate $\langle f| = \int f^*[...]dx$ in an infinite vector space. In a finite vector space, the bra represents a row complex vector such as

$$\langle a|b\rangle = \begin{pmatrix} a_1^* & a_2^* & ... & a_n^* \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \\ ... \\ b_n \end{pmatrix}$$

Collection of bras is another vector space, so there is a dual space.

16.1 Vector space representation

In vector space ($\mathbb{R}^3$), we can express each v as $v_i = \hat{e}_i \cdot \vec{v}$. $\hat{e}_1, \hat{e}_2, \hat{e}_3$ are orthogonal and orthonormal. The choice of the basis is key.

16.1.1 Inner product

$$(\bar{v}\bar{w}) = \sum_i v_i w_i$$

16.1.2 Operator

$$(\hat{e}_j; \vec{0}(\sum_i \hat{e}_i v_i)_1) = 0_{ji}$$

1. take each component of the vector

2. apply transformation

3. compute the product of the transformed components

$$(\hat{e}_{ij}(\hat{o}\bar{v})) = (\hat{e}_j, \sum_i \hat{o}\underbrace{\hat{e}_i v_i}_{v_i}) = \sum (\hat{e}_j, \hat{o}\hat{e}_i)\, v_i$$

As a result:

$$\hat{o}\bar{v} \to \Sigma_{ji} v_i = w_j$$

16.2 Hilbert space representation

The elements of the Hilbert space are represented as following: $|\psi\rangle, |\xi\rangle \in \mathcal{H}$

16.2.1   Inner product

The Dirac delta function can assume either 0 or 1 as a value.

$$\langle x|x \rangle = \delta(x, x')$$

We can compute $|\psi\rangle$ as the integral over the inner product with the position ($\langle x|\psi\rangle \in \mathbb{C}$) and the position vector itself.

$$|\psi\rangle = \int dx\, \langle x|\psi\rangle\, |x\rangle = \int dx\, \psi(x)\, |x\rangle$$

16.2.2   Operator

$$\langle x|\hat{p}|\psi\rangle = \int dx'\, \underbrace{\langle x|p|x'\rangle}_{\text{matrix}}\, \psi(x') = \int dx\, \delta(x, x')\left(-i\hbar\frac{d}{dx'}\right)\psi(x') = -i\hbar\frac{d}{dx}\psi(x)$$

Since

$$\int dx'\, \delta(x, x')\, g(x') = g(x)$$

In general, $\sum_j \delta_{ij} A_j = A_i$. In the case in which $i = 2$:

$$\underbrace{\delta_{21}A_1}_{0} + \underbrace{\delta_{22}A_2}_{1} + \underbrace{\delta_{23}A_3}_{0}$$

$|\psi(x)\rangle$ is called "ket" and $\langle\psi(x)|$ is called "bra"; together they form the norm of ψ, also known as "bracket".

16.2.2.1   Expectation value

$$\langle\psi|\hat{O}|\psi\rangle = \int dx\, \langle\psi|\hat{O}|\psi\rangle\, \psi(x) = \int dx'\, \psi^*(x)\, \langle x'|\hat{O}|x\rangle\, \psi(x)$$

16.2.2.2   SChröedinger equation

$$|\psi(t)\rangle \rightarrow i\hbar\frac{d}{dt}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle \overset{x\text{ space}}{\rightarrow} i\hbar\frac{d}{dt}\langle x|\psi(t)\rangle = \int dx'\, \langle x'|\hat{H}|x\rangle\, \langle x|\psi\rangle$$

16.3   two linearly independent states

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}\quad |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

The most general state is a normalized linear combination: $|L\rangle = a|1\rangle + b|2\rangle = \begin{pmatrix} a \\ b \end{pmatrix}$ with $|a|^2 + |b|^2 = 1$.

$$\text{Hamiltonian: } \hat{H} = \begin{pmatrix} h & g \\ g & h \end{pmatrix}, h, g \in \mathbb{R}$$

If the system at $t = 0$ is at $|1\rangle$, what state will it be at t?

1. Solve time independent Schrödinger equation $\hat{H}\ket{L} = E\ket{L}$ and find eigenvalues and eigenvectors.

$$\det \begin{pmatrix} h - E & g \\ g & h - E \end{pmatrix} = (h - E)^2 - g^2 = 0 \rightarrow h - E = \pm g \rightarrow E_\pm = h \pm g$$

There are two allowed energies.

2. Determine eigenvectors:

$$\begin{pmatrix} h & g \\ g & h \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = (h \pm g)\begin{pmatrix} \alpha \\ \beta \end{pmatrix} \rightarrow h\alpha + g\beta = (h \pm g)\alpha \rightarrow \beta = \pm\alpha$$

Normalized eigenvectors: $\ket{L_\pm} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}$

3. Expansion of the initial state as linear combination of eigenvectors of the hamiltonian (entanglement of the two states).

$$\ket{L(0)} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}}(\ket{L_+} + \ket{L_-})$$

4. We add the time-dependence $e^{-\frac{iE_n t}{\hbar}}$ to calculate the state at time t:

$$\begin{aligned}
\ket{L(t)} &= \frac{1}{\sqrt{2}}\left[e^{-\frac{i(g+h)t}{\hbar}}\ket{L_+} + e^{-\frac{i(h-g)t}{\hbar}}\ket{L_-} \right] = \\
&= \frac{1}{2}\left[e^{-\frac{i(g+h)t}{\hbar}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} + e^{-\frac{i(h-g)t}{\hbar}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \right] = \\
&= \frac{1}{2}e^{-\frac{iht}{\hbar}}\left[\begin{pmatrix} e^{-\frac{igt}{\hbar}} + e^{-\frac{igt}{\hbar}} \\ e^{-\frac{igt}{\hbar}} - e^{-\frac{igt}{\hbar}} \end{pmatrix} \right] = \\
&= e^{-\frac{iht}{\hbar}}\begin{pmatrix} \cos(gt/\hbar) \\ -i\sin(gt/\hbar) \end{pmatrix}
\end{aligned}$$

We can check this by observing that the result satisfies the time-dependent Schrödinger equation. It's a first raw model for neutrino oscillations.