Molecular Physics

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Part I

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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 is more and more 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

For 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 feature 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.

1.2 Classical mechanics

1.2.1 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:

$$\begin{aligned} f_1(t) = \sin(\omega t) \Rightarrow \frac{d^2}{dt^2}f)1(t) = -\omega^2 f_1(t) \\ f_2(t) = \cos(\omega t) \Rightarrow \frac{d^2}{dt^2}f)2(t) = -\omega^2 f_2(t) \end{aligned}$$

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

$$\begin{aligned} \frac{d}{dt}x(t) = -\sqrt{\frac{k}{m}}A\sin\sqrt{\frac{k}{m}}t + \sqrt{\frac{k}{m}}B\cos\sqrt{\frac{k}{m}}t \\ v_0 = \sqrt{\frac{k}{m}}B \Rightarrow B = \sqrt{\frac{m}{k}}v_0 \end{aligned}$$

So the final solution is:

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

1.2.2 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 an n-the order differential equation has exactly n solutions. Moreover, given n initial conditions there exists exactly one solution. Because of this trajectories in the phase space can never intersect. In this way future $x(t)$ and $v(t)$ can be unambiguously predicted. So classical mechanics is fully deterministic.

1.2.3 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:

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

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

1.2.4 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:

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

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

1.2.4.1 Conservative forces

For conservative forces the work from point A to point B does not depend on the path followed, in particular, for each paths 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:

$$U(r) - U(r_0) = -w_{x_0x} = -int_{x_0}^{x} dyF(y) \Rightarrow$$
$$-\frac{d}{dx}U(x) = F(x)$$

1.2.4.1.1 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:

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

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

1.2.5 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 if only conservative forces act on it. Energy conservation allow to solve Newton's equation 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.

1.2.5.1 Example

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

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

1.2.6 Angular momentum conservation

Let the angular momentum:

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

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:

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

Now considering:

$$\begin{aligned} \frac{d}{dt}\vec{L} &= \frac{d}{dt}(\vec{r} \times \vec{p} = \\ &= \underbrace{\frac{d\vec{r}}{dt}}_{=0} \times \vec{p} + \underbrace{\frac{d\vec{p}}{dt}}_{=F} \times \vec{r} = \\ &= \vec{r} \times \vec{F} \end{aligned}$$

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

1.3 Classical theory of the hydrogen atom

The classical theory of the hydrogen atom is defined by the classical Bohr model. The hydrogen atom if formed by a proton in the centre with an electron orbiting around it. Because $\frac{m_e}{M_p} \approx \frac{1}{2000}$, for the sake of simplicity an infinite proton mass $\frac{m_e}{M_p} = 0$ is assumed. Because $\frac{d}{dt}\vec{L} = 0$ (angular momentum conservation) electron's motion occurs on a plane and it is two dimensional

1.3.1 Mechanical energy in polar coordinates

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

The potential energy is derived from Coulomb's $F = -\hat{r}\frac{e^2}{r^2}$, so $U(|\vec{r}|) = -\frac{e^2}{|\vec{r}|}$

Now, 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 $v^2 = v_r^2 + v_\theta^2$:

$$\vec{v} = \hat{u}_\theta v_\theta + \hat{u}_r \underbrace{v_r}_{\frac{dr}{dt}} \Rightarrow v_2 = \left(\frac{dr}{dt}\right)^2 + v_\theta$$

Now, rewriting the angular momentum:

$$\begin{aligned} \vec{L} = m\vec{r} \times (\underbrace{\vec{v}_r}_{=0} + \vec{v}_\theta) = m\vec{r} \times \vec{v}_\theta \\ |L| = mrv_\theta \\ L^2 = m^2 r^2 v^2 \end{aligned}$$

Substituting this in the Hamiltonian:

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

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:

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

So using polar coordinate and angular momentum conservation the mechanical energy has been written in the form of that 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.

1.3.2 Case 1 - $E > 0$

The case that $E > 0$ 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.

1.3.3 Case 2 - $E < 0$

The case that $E < 0$ is the case of the bound orbit. The electron is trying to escape the proton. There are two inversion points

1.3.4 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.

1.4 Hamiltonian formulation of mechanics

In the Newtonian formulation the fundamental inspect is tat of the force:

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

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

1.4.1 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.

1.4.2 Hamilton's equations

From this point 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 becomes:

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

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:

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

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.

1.4.3 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:

$$\begin{aligned} \frac{p^2}{\omega^2} + q^2 &= q_0^2 \sin^2 \omega t + \frac{v_0^2}{\omega^2} \cos^2 \omega t - 2\frac{q_0 v_0}{\omega} \sin \omega t \cos \omega t + q_0^2 \cos^2 \omega t + \frac{v_0^2}{\omega_2} \sin^2 \omega t + 2\frac{q_0 v_0}{\omega} \sin \omega t \cos \omega t = \\ &= 2\left(q_0^2 + \frac{v_0^2}{\omega^2}\right) \end{aligned}$$

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.

Chapter 2

Breakdown of classical mechanics

2.1 The fall of determinism

2.1.1 Double slit experiment

Consider a gun shooting particle through a screen with two holes and a detection screen behind the first one.

2.1.1.1 Case 1 - particles are macroscopic bullets

If particles are bullets and macroscopic on the second detector a particle-like behaviour is detected. Bullets arrive one-by-one. First 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. 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:

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

2.1.1.2 Case 2 - macroscopic waves in a tank

In the case of macroscopic waves in a tank, can be seen that $P_{12} \neq P_1 + P_2$. This is because wave aptitudes are complex objects. So, deriving from wave theory:

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

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

$$\begin{aligned} A_{12} = A_1 + A_2 \to A_{12} = |A_1 + A_2|^2 = \\ = A_1^* A_1 + A_2^* A_2 + \underbrace{A_1^* A_2 + A_1 A_2^*}_{\text{interference}} \end{aligned}$$

Unlike bullets, wave hit the entire screen and not at a precise time. So a wave-like behaviour with de localization can be seen.

2.1.1.3 Case 3 - cathode as an electron gun

Finally considering a cathode to be an electron gun. If one hole is blocked electrons are detected one by one and have particle-like behaviour. If both holes are open quantum delocalization happens and an interference pattern can be seen ($P_{12} \neq P_1 + P_2$) and have wave-like behaviour. So detections reveals particle behaviour and the propagation wave-like behaviour in which the electron is everywhere like a wave. To see if he 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 apparatus never trigger together and the electron travels through one of the holes like a particle. Defining P_{A_1} 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. Counting all the events can be seen that the resulting pattern is $P_{A_1} + P_{A_2}$. In this case so $P_{A_1+A_2} = P_{A_1} + P_{A_2}$, delocalization is lost and the electron assumes ballistic behaviour. So can be seen that the measurement affects the nature of the electron and can change the state of the system.

2.1.1.4 Conclusions

The notion of trajectory looses 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 partile.

2.2 The photoelectric effect

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 woud 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 scale with the intensity.

2.2.2 Conclusions

This experiment determined that the energy transfer depends on the frequency ν of the electromagnetic radiation. Moreover electron 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 $E = \hbar\nu$, 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. So 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.

2.3.2 Finding

Performing this experiment has been found that only certain frequencies can be absorbed by the atoms.

2.3.3 Conclusion

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

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

Because of this finding classical mechanics can be seen is not a 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 detect those electron.

2.4.2 Finding

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 would be expected to find only $\mu_z = +\mu_0$. The final beam contains $\mu_z = \pm\mu_0$.

2.4.3 Conclusion

The act of measuring μ_x completely destroy the information about the state of μ_z. According to the uncertainty principle μ_x and μ_z cannot be simultaneously determined. Instead we find only two possible orientation 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 $\hat{\mu}_x = +\mu_0$.

2.5 Conclusions

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:

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

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

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

And:

$$\begin{aligned} \left(\frac{1}{v^2}\frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2}\right) &\begin{cases} f_>(x+vt) \\ f_<(x-vt) \end{cases} = 0 \\ \frac{1}{v^2}\frac{\partial}{\partial t}\left(\frac{\partial}{\partial t} f_>(x-vt)\right) &- \frac{\partial}{\partial x}\left(\frac{\partial}{\partial x} f_>(x+vt)\right) = \\ -\frac{1}{v}\frac{\partial}{\partial t}[f'_>(x-vt)] &= f''_>(x-vt) \\ f''_>(x-vt) &= f''_>(x-vt) \end{aligned}$$

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:

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

Considering that both the real and imaginary part oscillates:

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

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

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 Schröedinger equation is a modified wave equation to accomodate this:

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

2.5.1 Free particle Schröedinger 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 Schröedinger equation

It can be seen how the potential energy is more important than the forec:

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

Chapter 3

Waves of matter

3.1 The Shrödinger equation

Physical laws can never be demonstrated, but only inferred from experiment 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, so being $A(x, y)$ a wave, its intensity:

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

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

$$\begin{aligned} \psi(x,t) \to\ & Prob(x,t) \\ &= \psi^*(x,t)\psi(x,t) \\ &\equiv |\psi(x,t)|^2 \end{aligned}$$

3.1.2 Main assumption

Electrons behave exactly like photons: they both have a dual particle and wave nature. So for electron too is assumed that energy is proportional to frequency:

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

Protons propagate according to a wave equation:

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

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:

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

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:

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

And not just to $|p|$.

3.1.3 Defining the Shröedinger equation

So 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, to have $E \propto p^2$ one time derivative is tried. Then the equation to solve becomes:

$$\left(iC_1\frac{\partial}{\partial t}C_2\frac{\partial^2}{\partial x^2}\right)\psi = 0$$

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

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

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

$$\left(C_1\frac{i}{\hbar}E - C_2\big(-\frac{1}{\hbar^2}p^2\big)\right) = 0$$

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

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

Now:

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

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

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

So finally the Schröedinger equation:

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

3.1.3.1 Quantum Hamiltonian

Now the quantum Hamiltonian can be defined as:

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

Comparing it with a classical Hamiltonian there can be seen that $\frac{p^2}{2m} \xrightarrow{\text{quantization}} -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \Rightarrow p^2 \to \hbar^2\frac{\partial^2}{\partial x^2}$. Then because the forward propagating wave has a positive momentum $\hat{p} \to i\hbar\frac{\partial}{\partial x}$. 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 Schröedinger equation is then recast as:

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

So 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 Shröedinger equation

Assuming that the system conserves mechanical energy:

$$H(p,q,\cancel{t}) = \frac{p^2}{2m} + U(q,\cancel{t})$$

Considering the plane wave:

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

As a guess for the form of the solution and plugging it into the Schröedinger 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. So, from a discrete spectrum energy quantization is obtained and:

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

And:

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

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:

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

So:

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

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

$$-\frac{\hbar^2}{8m}\alpha^2\cancel{x^2\phi_0} + \frac{1}{2}m\omega^2\cancel{x^2\psi_0} = 0$$

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:

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

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

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

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

$$\begin{aligned}\hat{H}\phi_0 &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}(\mathcal{N}e^{-\alpha x^2}) = -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}(-2\alpha xe^{-\alpha x^2})\mathcal{N} = \\ &= -\frac{\hbar^2}{2m}(-2\alpha e^{-\alpha x^2} + 4\alpha xe^{-\alpha x^2})\mathcal{N} = \\ &= \frac{\hbar^2}{\cancel{2}m}\cancel{2}\alpha\phi_0 - \frac{\hbar^2}{2m}4\alpha^2x^2\phi_0 \\ \hat{H}\phi_0 &= \underbrace{\frac{\hbar^2}{m}\alpha\phi_0(x)}_{n\phi_0(x)} + \underbrace{\left(\frac{1}{2}m\omega^2 - \frac{\hbar^2}{m}\alpha^2\right)x^2\phi_0(x)}_{\text{depends on } x^2}\end{aligned}$$

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

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

So the Gaussian is a good solution:

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

3.3.2.1 Normalization evaluation

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

$$\begin{aligned} \mathcal{N}^2 &= \frac{1}{\int |\phi_0|^2 dx} = \frac{1}{(2\pi\sigma)^{\frac{1}{2}}} = \frac{1}{(2\pi\sqrt{\frac{\hbar}{2m\omega}})^{\frac{1}{2}}} \\ \mathcal{N} &= \frac{1}{(2\pi\sqrt{\frac{\hbar}{2m\omega}})^{\frac{1}{4}}} \end{aligned}$$

3.3.2.2 Compute the average value of kinetic and potential energy

Because this operations are stochastic the outcome cannot be predicted, only the probability or the average values can be computed. Let $\langle U \rangle$ be the average value of the potential energy, then:

$$\begin{aligned} \langle U \rangle &= \int P_0(x) U(x) dx = \frac{\int dx e^{-\frac{m\omega x^2}{\hbar}} \frac{1}{2} m\omega^2 x^2}{\int dx e^{-\frac{m\omega x^2}{\hbar}}} = \\ &= \frac{1}{2} m\omega^2 \underbrace{\langle x^2 \rangle}_{\text{variance } \sigma^2} = \frac{1}{2} \cancel{m}\omega^{\cancel{2}} \frac{\hbar^2}{2\cancel{m}\cancel{\omega}} = \\ &= \frac{1}{4}\hbar\omega \end{aligned}$$

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

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

To compute the kinetic energy, it needs to be considered 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:

$$
\begin{aligned}
O(\underbrace{\hat{p}}_{-i\hbar\vec{\nabla}}, \underbrace{\hat{q}}_{\vec{q}}) &\to \hat{O} \\
T = \frac{p^2}{2m} &\to \hat{T} = \frac{\hat{p}^2}{2m} = \frac{(-i\hbar\nabla)^2}{2m} = -\frac{\hbar^2\nabla^2}{2m} \\
U(q) &\to \hat{U}
\end{aligned}
$$

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:

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

Now considering $\langle\phi|O|\phi\rangle$ that specify the state and that is equivalent to $\langle O\rangle$, where:

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

Then:

$$
\begin{aligned}
\langle\phi|\hat{T}|\phi\rangle &= \frac{\int dx\phi^*(x)(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\phi(x))}{\int dx|\phi(x)|^2 = \frac{1}{4}\hbar^2} = \\
&= e^{-\alpha x^2}\frac{\partial^2}{\partial x^2}e^{-\alpha x^2} = e^{-\alpha x^2}\frac{\partial}{\partial x}(-2\alpha x e^{-\alpha x^2}) = \\
&= e^{-\alpha x^2}(-2\sigma w^{-\alpha x^2} + 4\alpha^2 x^2 e^{-\alpha x^2}) = \\
&= -2\alpha|\phi|^2 = 4\alpha^2 x^2|\phi|^2
\end{aligned}
$$

And so:

$$
\langle\phi|\hat{T}|\phi\rangle = \frac{-\frac{\hbar^2}{2m}\int|\phi(x)|^2 dx}{\int|\phi(x)|^2}2\alpha = -\frac{\hbar^2}{2m}4\alpha^2\frac{\int dx|\psi|^2 x^2}{\int dx|\psi|^2}
$$

3.4 Quantum particle in a one dimensional infinite square well

For the case of a quantum particle in a one dimensional infinite square well consider a particle constrained in a trap where interactions are so strong that it cannot escape and with two confining direction much narrower than the third. 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 Schröedinger equation is:

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

Mathematically the 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 equation 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:

$$\begin{aligned} k_1\frac{L}{2} &= \pm\frac{\pi}{2} \pm n\pi \Rightarrow \\ \Rightarrow k_1^{(n)} &= \pm\frac{\pi}{L}, \pm\frac{3\pi}{L}, \dots = \\ &= \pm 2(n-1)\frac{\pi}{L} \qquad n = \mathbb{N} \end{aligned}$$

So 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:

$$\begin{aligned} k_2\frac{L}{2} &= \pm\pi \pm n\pi \Rightarrow \\ \Rightarrow k_2^{(n)} &= \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \dots = \\ &= \pm 2n\frac{\pi}{L} \qquad n = \mathbb{N} \end{aligned}$$

So 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 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

To summarize 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:

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

3.4.2 Discussion

3.4.2.1 Quantized momenta

From the quantized energy:

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

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 $p = 0 \Rightarrow E = 0$. However 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 $\Delta p \sim L$ 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 $\Delta q = b$, hence there is a violation of the uncertainty principle:

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

.

3.4.2.3 Correspondence principle

Considering for $L \to \infty$ and $m \to \infty$ $E_0 = 0$, so there is no uncertainty in classical mechanics and $E_{n+1} - E_n \to 0$, so there is no quantization. So 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 dimension 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: $H(x,y) = H_1(x) + H_2(y)$.

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:

$$\begin{aligned} (H_1 + H_2)\phi_1(x)\phi_2(y) &= H_1\phi_1(x)\phi_2(y) + H_2\phi_1(x)\phi_2(y) = \\ &= \phi_2(y)\hat{H}_1\phi_1(x) + \phi_1(x0 + \phi)1(x)H_2\phi_2(y) = \\ &= \phi_2 E_1\phi_1 + \phi_1 E_2\phi_2 = \\ &= (E_1 + E_2)\phi_1\phi_2 \end{aligned}$$

So:

$$\phi_{n,m}(x,y) = \underbrace{\phi_n(x)}_{\text{solution of the 1D problem}} \phi_m(y)$$

And $E_{n,m} = E_n^x + E_m^y = -\frac{\hbar^2}{2m}\pi^2\left(\frac{n^2}{L_x^2} + \frac{m^2}{L_y^2}\right)$. 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 exploiting the connection between operators and matrices. A large but finite number of equally spaced possible position is used. The possible positions are $x = x_{\min} + \Delta x$, where $\Delta x = \frac{x_{\max} - x_{\min}}{N}$. Then the wave function is represented by a list $\psi(x) \to (\psi_1, \ldots, \psi_N)$. Thus the wave function becomes a vector and the Hamiltonian a matrix.

3.6.1 Discrete representation of 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:

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

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

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 a infinite dimensional vector space called the Hilbert space.

3.7 Time evolution operators

Consider the time-dependent Schröedinger 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 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:

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

So 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.

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.

4.3 Outcomes of measurement

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:

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

4.4 Expectation value

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

$$\langle \hat{O} \rangle = \frac{\langle \psi | \hat{O} | \psi \rangle}{\langle \psi | \psi \rangle}$$

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 Schröedinger 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:

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

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

Part II

Quantum chemistry

Chapter 5

Approximation methods

5.1 Truncated eigenstate expansion (Generalized Fourier)

An Hermitian operator $\hat{O}$ defined such as it is complete and orthonormal $\hat{O}^{+} = \hat{O}$ can be applied to a wave function $\hat{O}\Psi_n(x) = o_n \Psi_n(x)$ such as $\big(\Psi_n(x), \Psi_m(x)\big) = \delta_{mn}$
$\rightarrow$ If given $g(x) \in L^2$ I can write the projection of function onto a basis of functions

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

$\big(\Psi_n(n), g(n)\big)$ are coefficient of an inner product with $c_n \in \mathbb{C}$ I have a vector projected to its components.
$\vec{v} = v_1\hat{e}_1 + v_r\hat{e}_r$
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.
NOTE: $\hat{O} = \hat{P} \rightarrow$ eigenstates are represented by plane waves that are continuous. I can integrate:

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

This is an integral of a function over phase. The inner product represents a coefficient with a continuous label so it's a function of the label.

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

This 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).

Suppose I have a nucleus with an electron flying by. I need $|\Psi(x)|^2$, I can get it by solving Schrödinger equation. With scattering experiments I can measure $|\tilde{\boldsymbol{\Psi}}(\mathbf{p})|^{\mathbf{2}}$. This method is used in X-Ray Diffraction Crystallography, IR spectroscopy and so on.
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:

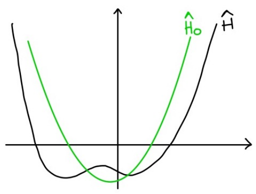
$$(g, g) = \sum_n c_n^* \cdot c_m \cdot 1 \rightarrow (g, g) = \sum_{n=0}^{\infty} |c_n|^2$$

that is the square module of Fourier coefficient.
If $g(x)$ is a wave function then $(g, g) = 1$, which is the probability of *always* finding the electron anywhere.

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.

We shall solve Schrödinger equation written as $\hat{H}\varphi_n = E_n\varphi_n$. We assume we can solve $\hat{H}_0\psi_n = \lambda_n\psi_n$ because it represents an harmonic oscillator.



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

since the Hamiltonian operator is a function it can be propagated through the equation. Right now I am expanding n and projecting it onto m.

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

We multiply both sides for an arbitrary wave function ψ_l (that we can supposedly solve).

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

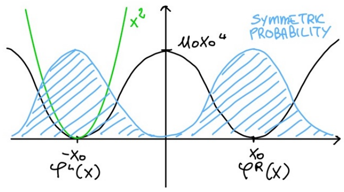
The inner product between two functions gives an integer.
$H_{lm} = H_{ml}^*$ is an hermitian matrix that can be diagonalized to get the eigenvalues.

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

I reduced a complex problem to a conventional matrix problem with a H_{lm} integral.

5.2 Quantum tunneling - The Landau problem

Wave function: $U(x) = U_0(x^2 - x_0^2)^2$
Hamiltonian for said wave function: $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U_0 \cdot (x^2 - x_0^2)^2$
This is a symmetric function, we can approximate the function with an harmonic oscillator. Considering the potential to its lowest points it can be approximated and then expanded.
I have two basis elements $\rightarrow$ two eigenstates $n = 0, 1$ (ground state and first excited state)



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

C_L and C_R are coefficients for each part of the function, one for each eigenstate.
I calculate the value of the matrices.

$$\begin{aligned} H_{RR} = (\psi_R, \hat{H}\,\psi_R) &= \int \psi_R^*(x)\, -\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2} + U_0 \cdot (x^2 - x_0^2)^2\right)\psi_R(x)\,dx \\ &= \int \psi_R^*(x)\, -\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 \cdot (x^2 - x_0^2)^2\right)\psi_R(x)\,dx \end{aligned}$$

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

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

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.

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

Now we can calculate the matrix

$$H_{mn} = \begin{pmatrix} \frac{1}{2}\hbar\omega & \varepsilon \\ \varepsilon & \frac{1}{2}\hbar\omega \end{pmatrix} = \begin{pmatrix} H_0 & \varepsilon \\ \varepsilon & H_0 \end{pmatrix} = \begin{pmatrix} \frac{H_0}{\varepsilon} & 1 \\ 1 & \frac{H_0}{\varepsilon} \end{pmatrix}$$

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

Ansatz 1: In the ground state I have 50% probability of finding the particle

$$\text{G.s.:} \begin{pmatrix} \frac{H_0}{\varepsilon} & 1 \\ 1 & \frac{H_0}{\varepsilon} \end{pmatrix}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 - \frac{\varepsilon}{E_0} \\ 1 - \frac{\varepsilon}{E_0} \end{pmatrix}$$

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

$$1^{st}\text{ ex. st.:} \begin{pmatrix} \frac{H_0}{\varepsilon} & 1 \\ 1 & \frac{H_0}{\varepsilon} \end{pmatrix}\begin{pmatrix} 1 \\ -1 \end{pmatrix} = \left(1 + \frac{\varepsilon}{E_0}\right) \cdot E_0 \cdot \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

N.B.: If the barrier is infinite the ground state is trivially degenerate. I then have two independent quantum systems. The particle cannot change its state.
If the barrier is finite (slightly determined end of the barrier at very high energies) there's a chance that two states interact between each other. This leads to **splitting states**. 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, I could expect to find the correspondance 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.

At $t = 0$, the particle is on the left $|\psi_0\rangle = |\psi_L\rangle$
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, $P_{R/L}(t) = |\,\langle\psi_{R/L}\,|\,\varphi(t)\rangle\,|^2$

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

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 small t. We perform the Taylor expansion of $e^{-\frac{i}{\hbar}\cdot t\hat{H}} = \hat{\mathbb{1}} - \frac{i}{\hbar}\cdot t\hat{H}$

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

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

but since $\frac{t\varepsilon}{\hbar} << 1$ we get $t << \frac{\hbar}{\varepsilon}$.
At little time the probability on the other side increases $\rightarrow$ Quantum Tunneling.
The rate of transitions is given by

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

which is an exponentially small amount.
There is an analogy between thermal kinetic activation and quantum tunneling, both happen because of <u>stochastic fluctuations</u>. ($K \propto e^{\frac{\Delta V}{K_B T}}$)
In quantum tunneling, 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 $\rightarrow$ 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).
... anyway,

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

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

By summing and dividing,

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

so we can substitute them:

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

where $e^{-\frac{it}{\hbar}\varepsilon}$ is the relative weight of quantum superposition.

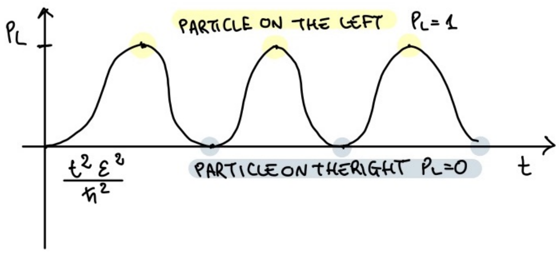
$$P_L = |\,\langle L\,|\,\psi(t)\rangle\,|^2 = \left|\,\langle L|\left(\frac{1}{\sqrt{2}}\,|0\rangle - \frac{1}{\sqrt{2}} \cdot e^{-\frac{it}{\hbar}\varepsilon}\,|1\rangle\right)\right|^2$$

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

$$= \left|\frac{1}{2} \cdot \frac{1}{\sqrt{2}} \cdot e^{-\frac{it}{\hbar}\varepsilon} \cdot \langle L\,|\,1\rangle\right|^2 = \left(\frac{1}{2} - \frac{1}{2} \cdot e^{-\frac{it}{\hbar}\varepsilon}\right)^2 = \left[\frac{1}{2} - \frac{1}{2}\left(\cos\frac{\varepsilon t}{\hbar} + i\sin\frac{\varepsilon t}{\hbar}\right)\right]^2$$

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

For $t = 0$, $P = 0$ then $\cos^2 x$ grows with a t^2 rate. There is an oscillation with a given period $T = \frac{\hbar}{2\varepsilon}$.



5.3 Ritz-Rayleigh variational principle

Suppose we want to solve the stationary Schrödinger equation for the ground state (E_0, energy and corresponding wave function).

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

I need to find any function approximating $\psi_0^{(x)}$, I also assume that the wave function is already normalized.

$$\frac{\langle \varphi \,|\, \hat{H} \,|\, \varphi \rangle}{(\langle \varphi \,|\, \varphi \rangle)} = \sum_{n,m} c_n^* c_m \langle \psi_n \,|\, \hat{H} \,|\, \psi_m \rangle = \sum_{n,m} c_n c_m E_m \delta_{nm} = \sum_n |c_n|^2 E_n$$

By assuming $c_n \geq 0$, the whole operation is $\geq E_0$ but this is true only if $\psi_n = \psi_0$.

TRIVIAL NOTE: if $\varphi(x) = \psi_0$ then we have a projection on a vector on itself:

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

Function 1 $\rightarrow$ Expected value E_0
Function 2 $\rightarrow$ Expected value E_1
$\rightarrow$ if $E_0 < E_1$ then E_0 is a better approximation of the wave function.

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.

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

I must find the minimum of the function (derivative = 0).

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

Find α such as E is the best approximation of E_0 and $\varphi_{\alpha min}(x)$ is the best approximation of ψ_0.
If I have multiple parameters: $\varphi_{\alpha \ldots \alpha_n(x)}$

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

I calculate the minimum of the multidimensional function:

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

I find a collection of energies and wavefunctions.
I am not always close to get the right solution because the probability of getting the right ground state is very low.

Hamiltonian equation for harmonic oscillator: $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$
1) Variational Ansatz: I use the normalized gaussian to best represent the harmonic oscillator: $\varphi_\alpha(x) = \left(\frac{1}{\sqrt{2\pi}\alpha}\right)^{1/2} e^{-\frac{x^2}{4\alpha^2}}$

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

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

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

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

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

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

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

I can also evaluate the harmonic oscillator's period.

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

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

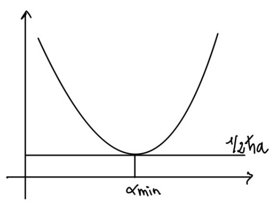
$$E(\alpha) = \frac{1}{\sqrt{2\pi}\alpha}\cdot\int dx\, e^{\frac{x^2}{2\alpha^2}}\left[\frac{\hbar^2}{4m\alpha}\left(1 - \frac{x^2}{2\alpha^2}\right) + \frac{1}{2}m\omega^2x^2\right] =$$

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

The integrand is called **gaussian variance** and it is equal to $\boldsymbol{\alpha^2}$. So

$$E(\alpha) = \left(\frac{1}{4} + \frac{1}{8}\right)\frac{\hbar^2}{m\alpha^2} + \frac{\alpha^2}{2}m\omega^2 = \frac{3}{8}\frac{\hbar^2}{m\alpha^2} + \frac{\alpha^2}{2}m\omega^2$$

The latter sum is a sum of two energy values. To find $\alpha_{min} \rightarrow \frac{\partial}{\partial\alpha}E(\alpha) = 0$



$$\frac{\partial}{\partial\alpha}E(\alpha) = -2\cdot\frac{3}{8}\frac{\hbar}{m}\alpha^{-3} + \alpha m\omega^2 = 0$$

Multiply by α^3 both sides:

$$\frac{\partial}{\partial\alpha}E(\alpha) = -\frac{\hbar}{m} + \alpha^4 m\omega^2 = 0$$

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

It's an intercept and it's valid for ground state only.

Chapter 6

Atomic physics

6.1 Quantum theory of the Hydrogen atom

6.1.1 Evaluation of conservation of energy

In classical mechanics I can write

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

that can be represented in quantum mechanics with the hamiltonian. The best evaluation of the hamiltonian for the quantum analysis of the hydrogen atom is obtained by using the **spherical coordinates**. Nabla 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 so 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**. Now I can consider the angular momentum in classical mechanics and quantum mechanics:

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

$$\rightarrow \hat{\vec{L}}^2 = \hat{L_x}\hat{L_x} + \hat{L_y}\hat{L_y} + \hat{L_z}\hat{L_z}$$

This is corresponding to the angular part of the hamiltonian that can be rewritten 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 invidual components of the angular momentum only commute with $\hat{L}^2$ but not with each other.

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

These are called **SPHERICAL HARMONICS**, they depend on two quantum numbers because they use two different operators and are only part of the angular part of the hamiltonian.

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

$\rightarrow$ QUANTIZATION OF $\hat{L}_j$ and $\hat{L}^2$.
The difference between l^2 and $l(l+1)$ is noticeable when l is small. For larger l you go back to the classical realm (correspondence principle).
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**, I obtain 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

I always use spherical coordinates and with these I can rewrite kinetic energy in a polar form.

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

$\hat{T}_r$ 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:

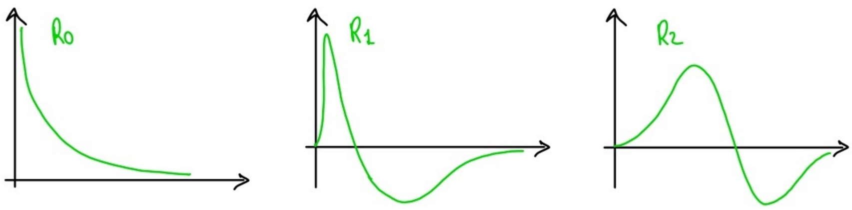
$$[\hat{T}_r\,,\,\hat{L}^2]=0\,,\;\;[\hat{V}\,,\,\hat{L}]=0\,,\;\;[\hat{L}^2\,,\,\hat{L}^2]=0$$

All these have common sets of eigenstates.

We can consider again one-dimensional Schrödinger equation:

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

$l=0\rightarrow$ **s-state**: $\frac{-\hbar^2}{2mr^2}\frac{\partial^2 r}{\partial r^2}R_n-\frac{e^2}{r}R_n=E_{n,l}R_n$
$l=1\rightarrow$ **p-state**: $\frac{-\hbar^2}{2mr^2}\frac{\partial^2 r}{\partial r^2}R_n+\frac{3\hbar^2}{2mr^2}R_n-\frac{e^2}{r}R_n=E_{n,m,l}R_n$
$l=2\rightarrow$ **d-state**: $\frac{-\hbar^2}{2mr^2}\frac{\partial^2 r}{\partial r^2}R_n+\frac{6\hbar^2}{2mr^2}R_n-\frac{e^2}{r}R_n=E_{n,m,l}R_n$
I get stronger repulsions between states as l grows. These function have specific graphs:
I want to calculate the probability of a particle to be at distance r.



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

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

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

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

Depending on the value of l I can get the probability of the electron depending on θ and φ. 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). There is no orbit on an atom, the concept of trajectory breaks down on a quantum level.

6.2 Relation 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.
Stern Gerlach experiments confirm the fact that electrons have a magnetic moment because they

can interact with a magnetic field. Generally, particles behave differently and may have different states of being.
I 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 fiels 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.

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

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

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

6.2.2 Spin-Statistics theorem

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.

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

$$\Psi(\vec{q_1}, \vec{q_2}, ..., \vec{q_n})$$

ANTISYMMETRIC WAVEFUNCTION: 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.

$$\Psi(\vec{q_1}, \vec{q_2}, ..., \vec{q_n}) = -\Psi(\vec{q_1}, \vec{q_2}, ..., \vec{q_n})$$

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

SYMMETRIC WAVEFUNCTION: 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.

$$\Psi(\vec{q_1}, \vec{q_2}, ..., \vec{q_n}) = \Psi(\vec{q_1}, \vec{q_2}, ..., \vec{q_n})$$

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

COROLLARY: 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.

A fermion once, a fermion forever

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

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 $\Psi = 0$. This is called **PAULI'S EXCLUSION PRINCIPLE**.

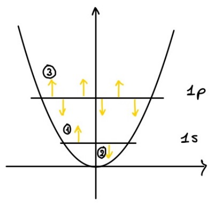
6.2.3 Mean Field Approximation

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

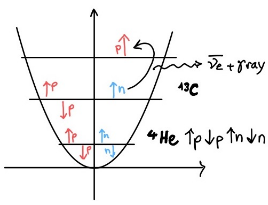
The solution to the eigenvalue problem that is also antisymmetric to the potential depends on the position.

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

Instead of keeping track of all the interactions of particles on one another, I consider the average of the whole many-body system e.g., mean coulombic repulsion. I calculate the interaction bertween single electron and average electron density. The larger symmetry is the ground state, for the H atom this is **1s**.



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. A nucleus is divided into two different nucleons. Nucleons can have two different states: spin up (protons) and spin down (neutrons). For each spin I can have an isospin up and an isospin down (isospin measures the charge).



Neutrons can decay into protons by going up to the next energy levels → PAULI BLOCK, not a spontaneous process.

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.

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

When $\hat{H}$ is separable into two parts, the wave function is the product of these two parts.
Consider N identical spin-0 bosons (simplest system that represents the sum of all possible permutations for N<2):

$$\Psi(r_1, ..., r_n) = \prod_K^n \varphi_n(r_i) = \varphi_1(r_1) \cdot ... \cdot \varphi_n(r_n)$$

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.

Consider 2 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 $\downarrow$. **The state of particle 2 is entangled to the state of particle 1**.
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 I carry on information in one single state out of two (either the gate is open or is closed, binary system). In quantum computers I have N states, I have 2_N states entangled with each other at the same time. I can store much more information in 2_N compared to 1.

entangled state: a two-particle state that cannot be expressed as the product of two one-particle states.

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

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

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

$\hat{S^2}$ doesn't have a classical correspondence, we cannot directly obtain a formula for $\hat{S^2}$ in classical mechanics. I must find objects that have two states.
Consider spin 1/2 only to build 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. The eigenstates of the z-components 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 $[\hat{S_x}\ ,\ \hat{S_y}] = i\hbar\hat{S_z}$.
Pauli matrices:

$$\hat{S_x} = \frac{\hbar}{2}\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix}\ \hat{S_y} = \frac{\hbar}{2}\begin{pmatrix}0 & -i\\i & 0\end{pmatrix}\ \hat{S_z} = \frac{\hbar}{2}\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}$$

The normalized eigenstates for the x-component are:

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

We can find the conditional probability of finding spin up with the condition of being in a state of spin left.

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

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

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

This latter is the mathematical formalism that represents the Stern Gerlach experiment.
I 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

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

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

6.2.5 Tensor product states

I have two vectors

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

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 et cetera.
I use tensor product to describe the *combination of two quantum states.*

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

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

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

These single quantum states represent qubits

The combination of the two states creates a wavefunction which amplitude corresponds to the observation of all the combinations of the particles.
I can build the basis for a vector product of two particles and with this I can describe four different states since $\mathbb{R}^2 \otimes \mathbb{R}^2 = \mathbb{R}^4$

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

Most general quantum mechanical state description of the EPR pair:

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

In this way I can carry on information about multiple state simultaneously.

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

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

This latter matrix is called a **SPINOR**, which is a wavefunction that includes spin amplitude (usually wavefunction doesn't have information about spin of the particle).
Let's consider a <u>non-entangled state</u>.

$$|\Psi\rangle = \frac{1}{\sqrt{2}} \left|\uparrow\uparrow\right\rangle + \frac{1}{\sqrt{2}} \left|\uparrow\downarrow\right\rangle = |\alpha \uparrow\rangle$$

The two measures are independent of each other, I can find particle 2 with a probability which is independent of the measurement of particle 1.
Entangled state:

$$|\Psi\rangle = \frac{1}{\sqrt{2}}\big(\,|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\,\big)$$

I can generate an operator that generates entangled states

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

U is called **quantum gate** in quantum computing.
Quantum gates can be defined as a **time evolution operator** that acts on the function to solve time-dependent Schrödinger equation.
$\hat{U}(\Delta t) = e^{i\hat{H}\Delta t}$ 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.

Three-electrons system.

For this application we need two energy levels, I calculate the Slater determinant for a 3-particles-system:

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

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

Six-terms determinant, complicated to evaluate!

Application of the mean field approximation to calculate the density of electrons in a point

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:

$$\Psi(\vec{r_1}, \vec{r_2}, s_1^z, s_2^z) = \frac{1}{\sqrt{2}}\big(\phi_{\uparrow}(r_1)\phi_{\downarrow}(r_2) - \phi_{\downarrow}(r_1)\phi_{\uparrow}(r_2)\big)$$

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

This is a 6-dim integral

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

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

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

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.

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

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

The integrals with an electron present with opposite spins $\int \phi_1^{*\uparrow}\phi_1^{\downarrow} d\vec{r_1}$ (aka the integrals with negative signs) represent the probablity 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 wavefunction.
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

$$\langle \Psi \mid \hat{\rho}(x) \mid \Psi \rangle = \frac{1}{2}\Big[P^{\uparrow}(x) + P^{\uparrow}(x) + P^{\downarrow}(x) + P^{\downarrow}(x)\Big] = P^{\uparrow}(x) + P^{\downarrow}(x)$$

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

Chapter 7

Molecular physics

7.1 The Born-Oppenheimer Approximation

Molecular physics and 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. Kinetics of nuclei
2. Kinetics of electrons
3. Repulsive coulombic interaction between electrons
4. Repulsive coulombic interaction between nuclei
5. 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 electron. Born-Oppenheimer approximation divides these operations in two.

1 - Study the electronic problem at fixed nuclear configuration.
I ignore the first fragment (no motion, no kinetic energy) and the coulombic repulsion becomes constant consequently. Nuclei bind only when they are close to each other.

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

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.

2- Solve the dynamics of the nuclei based on their own coulombic interactions + electrons effect.

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

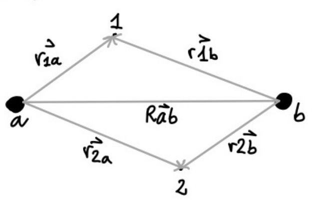
ε is a value, not a function, it does not depend on any parameter.
Quantum effect becomes weaker as the weight of the system increases. to describe a many-body system I can replace this Schrödinger equation with a newtonian equation.

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

This equation describes **CLASSICAL MOLECULAR SIMULATIONS**. I miss quantum effects of the nuclei (protonation - quantum tunneling of protons, chemical reactions...)

7.2 The H_2 molecule

I have 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 Born-Oppenheimer approximation (distance between nuclei).



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, the resulting H-H chemical bond is actually an entangled electron tunneling. *first reaction: shock*

$$\Psi(\vec{r_1},\vec{r_2},s_1^z,s_2^z,(\vec{R_a},\vec{R_b}))=\Psi_{\text{spatial}}(\vec{r_1},\vec{r_2})\otimes\Psi_{\text{spin}}(s_1^z,s_2^z)=\Phi\otimes\chi$$

I can factorialize the wave function because the hamiltonian is separable.
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. 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**, molecule bends in Stern-Gerlach.

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

$$\Psi = \Phi\chi = \begin{cases} \Psi_1 = \Phi_S\chi_A = \frac{\varphi_a^{r1a}\varphi_b^{r1b}+\varphi_a^{r2a}\varphi_b^{r2b}}{\sqrt{2}} \otimes \frac{|\uparrow\downarrow\rangle-|\downarrow\uparrow\rangle}{\sqrt{2}} \\ \Psi_2 = \Phi_A\chi_S = \frac{\varphi_a^{r1a}\varphi_b^{r1b}-\varphi_a^{r2a}\varphi_b^{r2b}}{\sqrt{2}} \otimes \frac{|\uparrow\downarrow\rangle+|\downarrow\uparrow\rangle}{\sqrt{2}} \end{cases}$$

This 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 $\langle\hat{S}\,|\,\hat{S}\rangle = 1$, the sign of the expected value of the hamiltonian depends on the spin symmetry because spatial value and spin symmetry are entangled.

$$E_1 = \langle\Psi_1\,|\,\hat{H}\,|\,\Psi_1\rangle = \langle\Phi_S\,|\,\hat{H}\,|\,\Phi_S\rangle$$

$$E_2 = \langle\Psi_2\,|\,\hat{H}\,|\,\Psi_2\rangle = \langle\Phi_A\,|\,\hat{H}\,|\,\Phi_A\rangle$$

I 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. I have two 6-dimensions functions in 6-dimensions integrals.
Results are different whether I solve for the first or second electron. This is the result that is obtained when the two atoms are infinitely far.

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

Else, if the two atoms start to approach,

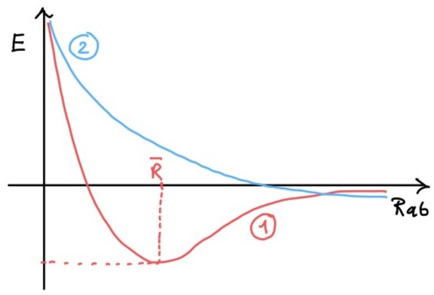
$$\langle\,|\,\hat{H}\,|\,\rangle_{S/A} = \frac{e^2}{R_{ab}} \pm \text{separated ground states}$$

I obtain two different functions:

- **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.
- **Antisymmetric spatial function**: goes against the variational approximation but technically is a right solution from a quantum mechanical point of view.

7.3 Electronic structure calculation methods

When choosing the best method to obtain an electronic structure, some evaluations have to be made regarding the accuracy of the calculation vs. the computational cost of the operation. The first approximation to be chosen is always the most important and it determines the further steps that need to be taken. It is very important then to consider strategic decisions in computational sciences.



MEAN FIELD ↓ HARTREE-FOCK — Ideal for first analysis & when there are many molecules. Freq. used: Mean Field + Variational Pr. for fermions

POST HF

COUPLE CLUSTER
CONFIGURATION INTERACTION
DENSITY FUNCTION THEORY

Improve HF and function when Mean Field does. Include correction in perturbative way + non Mean Field correction

NON MF

MONTE CARLO METHODS
VARIATIONAL MONTE CARLO
GREEN FUNCTION MC

Methods that are exact for bosons but not available for fermions. Include more specific techniques

↓
↓
↓

QUANTUM COMPUTING SIMULATIONS ---▷ At the moment it's just a hope for the future

ACCURACY + COMPUTATIONAL COST

I also have **EXACT DIAGONALIZATION (TRUNCATED BASIS)** that is very precise but can't be used with system with more than 5 or 6 particles at the same time.
For biological system, chemical accuracy is important as long as the error is not dramatic (slightly change of temperature can dramatically 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 performed. The problem is that it's very difficult to predict Van Der Waals forces since they are polynomial and DFT uses exponentials.
General goal is using classical equations to predict quantum-mechanics-descripted movements.

7.3.0.1 Hartree-Fock Method

Hartree-Fock method is a method of approximation for the determination of the wave function and the energy of a quantum many-body system in a stationary state that combines Mean Field Approximation, Fermi symmetry, and the Variational Principle.
The method uses the Slater matrix's determinant to approximate a set of N fermions.

$$\Psi(q_1...q_n) = \frac{1}{\sqrt{2}} \begin{pmatrix} \phi_1(r_1) & ... & \phi_n(r_1) \\ ... & & ... \\ \phi_1(r_m) & ... & \phi_n(r_m) \end{pmatrix}$$

I do not expect to find $\Psi(q_1...q_n)$, I can say it is the result of an equation and so calculate the energy by using the Variational Principle with $E = \langle \Psi \mid E \mid \Psi \rangle$ and minimize E with respect to$\psi(q)$ (a single-particle function) under the costraint of normalization ($\langle \psi \mid \psi \rangle = 1$)
Costraint minimization is operated with **Lagrange multipliers**: I consider a system of equations $f(x_1...x_n)$ where I can calculate the minimum and the maximum with the application of the gradient $\nabla f = 0$.

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

Fermi symmetry introduces Slater determinant that is also called **exchange term** (**Fock equation**). This introduction implies that I cannot bring two electrons with the same spin in the same orbital. The wave function collapses to zero and I have repulsion between the electrons.

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

This implies that the electron density factor of Hartree equation is not present anymore, the two particles are in a different state. At the same time $\Phi_\mu(r_i)$ becomes Fock's generalization exchange term for fermions.

This equation though is non linear (Φ^3) so many quantum mechanics properties can't be applied to HF.
The computational cost doesn't change over the introduction of the exchange term even if it has a three-dimensional integral.
I can't expand the equation on a different basis, I must use SELF CONSISTED METHODS/APPROACHES that 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 HF equation, resulting in a conventional linear Schrödinger equation.
4. Solve HF 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 I use the latter obtained again for point 1. and recompute the density. I continue until I converge. Usually I have a single minimum.
I can use SELF CONSISTENT FIELDS to compute HF equation but they are computationally expensive, they can be used for parallel computing.

I can further use HF equation with SEMI EMPIRICAL METHODS with coefficients in front of direct and exchange terms that can weight the two terms in order to better match the experiment. I usually use HF to build the expansion of the eigenfunction or in quantum computing.

7.3.1 Density Function Theory (DFT)

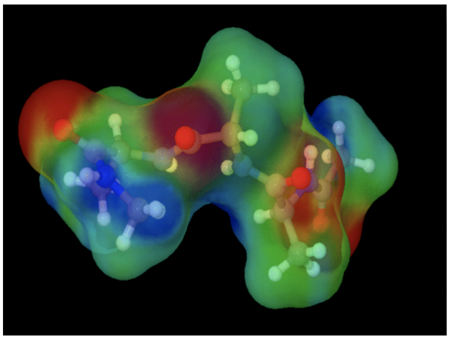
Variational scheme that in principle can yield the exact result, in practice it needs heuristic input/approximation. Over the made assumptions, I can have excellent results. I need simple inputs for the perfect compromise between accuracy and computational cost.
This theory is not based on the wave function computation but on the **density function computation**.

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

Expectation value, assuming $\langle\Psi\mid\Psi\rangle = 1$: $\langle\Psi\mid\hat{\rho}(\vec{r})\mid\Psi\rangle = \sum_i\int d\vec{r_1}...d\vec{r_{N_e}}\left(\Psi^*(\vec{r_1}-\vec{r_{N_e}})\delta(\vec{r}-\vec{r_i})\Psi(\vec{r_1}-\vec{r_{N_e}})\right)$

$$\langle\Psi\mid\hat{\rho}(\vec{r})\mid\Psi\rangle = n(\vec{r})$$

which is the probability of finding any electron at the point r. This concept is shown in the following picture, blue is low electron density, red is high electron density.



OBS: $n(\vec{r})$ is a so-called **SINGLE-BODY DENSITY**, it doesn't tell me the same information of the 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.

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

*determined by some sort of *quantum magic*, cit.*

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

Last term is the interaction between single electrons and nuclei. IN BO approximation this was the external potential because nuclei were fixed.

THEOREM 1) For any system of interacting particles, the external potential is determined uniquely by the ground state one-body density.

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

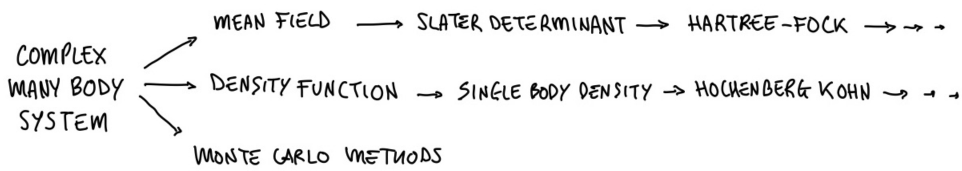
$\rightarrow$ Corollary: All wavefunctions (ground state, first excited state, all eigenstates of $\hat{H}$) are fully determined by $n_0(\vec{r})$

THEOREM 2) A 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).

OBS: A function: $f : x \rightarrow f(x)$ (x is a variable, $f(x)$ is a number)
A functional: $E[f] : f(x) \rightarrow E[f]$ ($f(x)$ is a function of operators, $E[f]$ is a number). Examples of functionals are definite integrals or 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.

I can define/is it 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 not given and not referred to the wave function. One body density's functional's minimum is the exact ground state energy of the problem ∀ Hamiltonians.

These two are existent theorems, they do not provide any solution, usually they are complemented with ways to build the right functional to solve the problem.



7.3.2 QM-MM Schemes

QM-MM = Quantum Mechanics, Molecular Mechanics. These schemes are used for large molecular models and chemical reactions studies (e.g., enzymatic reactions).
QM is applied to the region of interest so to have the computational effort only where needed, classical molecular mechanics is applied elsewhere and an hybrid method is used at the threshold of the two regions.
The difficulty is presented when considering thermodynamics. The more degrees of freedom, the more entropy.

Part III

Quantum computing

Chapter 8

Quantum computing

Not for the exam but perfect to read before going to bed!

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.

$$|0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} ;\ |1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \text{ with } \hat{H}_0 = -h\hat{\tau_x},\ \hat{\tau_x} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \text{Pauli matrix operator}$$

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

Questions, find:

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

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

$$\det(H - \lambda\mathbb{1}) = 0$$

$$\det \begin{pmatrix} -\lambda & -h \\ -h & -\lambda \end{pmatrix} = 0$$

$$\lambda^2 - h^2 = 0 \rightarrow \lambda = \pm h$$

$-h$ and $+h$ are the two possible energy eigenvalues and correspond to the ground state and first excited state, respectively.
Let's compute the ground state: $E_\Omega = -h$

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

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

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

We can rewrite $|\Omega\rangle$ as

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

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

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

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

8.1.1 Adiabatic Quantum Computing

Putting energy in the system chenges the probability of the particle of being still in a ground state. I may find the particle in an excited state. This doesn't happen if I switch the system in a slow manner (adiabatic system). I can never end up in an excited state → ADIABATIC THEOREM.
The transition is more likely to occur at the time when ΔE is at its lowest.
If $\hat{H}_f$ is complicated enough such as I can't know its ground state I can start from $\hat{H}_0$ ground state and let the system evoke in an adiabatic way to reach $\hat{H}_f$ ground state spontaneously and measure the final state many times.
I can obtain the final wavefunction by means of qubits. where qubits are two level-systems that can thus have two levels of energy. I know the two ground states.
I can compute the final solution by knowing the amount of values of $\alpha(t)$ and $\beta(t)$.

Time needed depends on the triviality of the problem, the larger number of qubits (n), the larger number of states (2^n) and ΔE, the most time, unless I have uncertainty. This depends on the function that "regulates" the ΔE. The function corresponds to the *clock* on classical computers that is how often registers are updated.

8.2 Two qubits system

Interacting quantum systems. 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. I can obtain this with a magnet that can properly align spins in order to have an overall negative energy. Implicitally, the Hamiltonian should be:

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

When you use an operator on a particle, you multiply the other by the identity matrix.

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

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.

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

$$\begin{aligned} x_i = 0 \quad \hat{\tau_i^z} = -1 \\ x_i = 1 \quad \hat{\tau_i^z} = +1 \end{aligned}$$

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. I have a 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.
I can create entangled states by imposing a different spin direction on the particles.

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

$$\hat{\tau_1^x} \otimes \hat{\nVdash}_x = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \quad \hat{\nVdash}_x \otimes \hat{\tau_2^x} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \quad \hat{H} = \begin{pmatrix} \mathbf{J}_{12} & h & h & 0 \\ h & -\mathbf{J}_{12} & 0 & h \\ h & 0 & -\mathbf{J}_{12} & h \\ 0 & h & h & \mathbf{J}_{12} \end{pmatrix}$$

The ground state is a vector correspondant 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 $c = \frac{\sqrt{4h^2+\mathbf{J}^2}+\mathbf{J}}{2h}$
Normalization factor:

$$\frac{(1^2 + c^2 + 1^2)}{N} = 1 \to N = 2 + c^2$$

$$G.S. = \frac{1}{\sqrt{2+c^2}}(|0\,0\rangle - c\,|1\,0\rangle + |1\,1\rangle)$$

Let's fix $c = 1$ so the ground state becomes:

$$G.S. = \frac{1}{\sqrt{3}}(|0\,0\rangle - |1\,0\rangle + |1\,1\rangle)$$

Let's calculate the probability for $q_2 = 1$. q_2 can appear in two different states:

$$P_{11} = \frac{1}{3}(\langle 1\,1\,|\,0\,0\rangle - \langle 1\,1\,|\,1\,0\rangle + \langle 1\,1\,|\,1\,1\rangle)^2 = \left(\frac{1}{\sqrt{3}}\right)^2 = \frac{1}{3}$$

$$P_{01} = \frac{1}{3}(\langle 0\,1\,|\,0\,0\rangle - \langle 0\,1\,|\,1\,0\rangle + \langle 0\,1\,|\,1\,1\rangle)^2 = 0$$

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 et cetera. Circuits are written such as horizontal axis is time, 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.

This divulgative fragment is from Wikipedia, Quantum Inspire, Qiskit

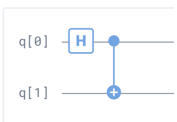
Most **elementary logic gates** (= model of computation or physical electronic device that implements a boolean function on one or more binary inputs) are **irreversible**, this means that if I have a *AND gate* applied on two bits, I cannot recover these two bits from the result.
Quantum computers can achieve **universality**, i.e., 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, I can express all the operations used to perform such rotation $f(x)$ on input x 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, the time evolution is the unitary, the Hamiltonian is the associated hermitian matrix. Achieving any unitary would therefore correspond to simulating any time evolution, and engineering the effects of any Hamiltonian.

Quantum logic gates are reversible unitary transformations on at least one qubit. We must first define 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 combinations/superpositions of classical bit strings. $H_{QB(n)}$ is a vector space over the complex numbers of dimension 2^n, the elements of this vector space are the possible state of n-qubits quantum registers. Quantum logic gates require a reversible function called unitary mapping (linear transformation of a complex inner product space that preserves the Hermitian inner product).
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-degree 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.

Exercise 1 - 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 aline/dear definite state that is technically not possible.

Exercise 2 - Example of a HC_{NOT} quantum circuit

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.

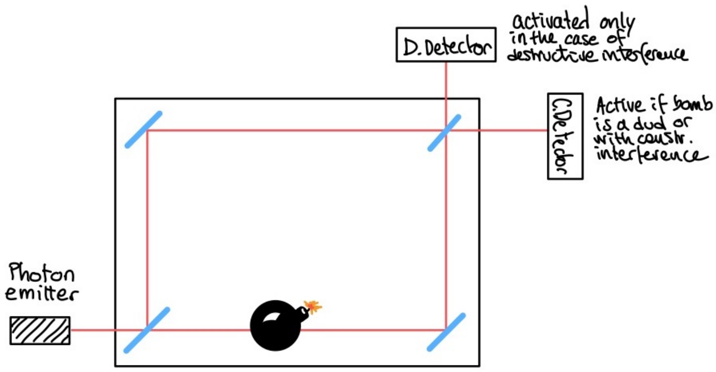
$$\frac{|0\,0\rangle - |1\,1\rangle}{\sqrt{2}} = |\phi^-\rangle \quad \frac{|0\,1\rangle + |1\,0\rangle}{\sqrt{2}} = |\psi^+\rangle \quad \frac{|0\,1\rangle - |1\,0\rangle}{\sqrt{2}} = |\psi^-\rangle$$

$$\langle\psi^+\,|\,\psi^-\rangle = 0$$

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. I

can obtain information about previous positions of the particle before the collapse and even in cases where the particle was never in those positions.



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)

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 (I have destructive interference in D so nothing is detected).
With this being said, 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.

Part IV

Appendices

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 number. Because of this the real number set is extended, trying to develop a coherent framework in which this problems can be treated. 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:

$$z := \underbrace{a}_{\text{Real part, } \Re z} + \underbrace{bi}_{\text{Imaginary part, } \Im z}$$

Where $a \wedge b \in \mathbb{R}$. This create 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 represente the real axis and on the vertical 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 id 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 variable used for this repreesntation 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 writtein in standard form can be writtein in polar form, where:

$$\begin{cases} \theta = \arctan \frac{b}{a} \\ \rho = \sqrt{a^2 + b^2} \end{cases}$$

And the invers operation:

$$\begin{cases} a = \rho\cos\theta \\ b = \rho\sin\theta \end{cases}$$

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:

$$\begin{aligned} zw &= \rho_z\rho_w(\cos\theta_z + i\sin\theta_z)(\cos\theta_w + i\sin\theta_w) = \\ &= \rho_z\rho_w[\cos\theta_z\cos\theta_w - \sin\theta_z\sin\theta_w + i(\sin\theta_z\cos\theta_w + \cos\theta_z\sin\theta_w)] \end{aligned}$$

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 $z \in \mathbb{C}, z = \rho(\cos\theta + i\sin\theta)$:

$$z^n - \rho^n(\cos n\theta + i\sin n\theta)$$

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 solutiion, 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 lie on the circle of radius equal to the modulus equally spaced on the Argand plane, creating a regular polygon.

9.4 Complex valued functions

Real function can be extended to complex valued function. Taken f from an interval $A \subset \mathbb{R}$ to $\mathbb{C}$ the function can be written as:

$$f(x) = u(x) + v(x)i$$

Where u and v are reale valued functions. The limit of a complex valued function exists if the limits of the real and the complex component exist.

9.4.1 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, as 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 $a, b \neq 0$;

$$\begin{aligned} e^{a+bi} &= e^a e^{bi} = \\ &= e^a(\cos b + i \sin b) \end{aligned}$$

9.5.1 Properties

Not only the product of two complex exponentials meets the classical properties of the real exponentials, also the derivatives maintains them. Let $t \in \mathbb{R}$ adn $y(t) = e^{(a+bi)t} = e^{at}(\cos tb + i \sin b)$, its derivative with respecto to t is:

$$\begin{aligned} \frac{dy(t)}{dt} &= \frac{de^{(a+bi)t}}{dt} = \\ &= (a+bi)e^{(a+bi)t} \end{aligned}$$

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:

$$w_k = r^{\frac{1}{n}} e^{i\frac{\theta+2k\pi}{n}}$$

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 function of $n \geq 2$ variables. Let $f : \mathbb{R}^2 \supseteq A \to \mathbb{R}$, where A is an open set of $\mathbb{R}^2$ 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 derivative 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 $f(x,y)$ exists 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 exists the tangent plane in that point.

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:

$$\begin{array}{ll} \frac{\partial^2 f}{\partial x^2} : \frac{\partial}{\partial x} g = \frac{\partial}{\partial x}\frac{\partial f}{\partial x} & \frac{\partial^2 f}{\partial y \partial x} : \frac{\partial}{\partial y} g = \frac{\partial}{\partial y}\frac{\partial f}{\partial x} \\ \frac{\partial^2 f}{\partial x \partial y} : \frac{\partial}{\partial x} h = \frac{\partial}{\partial x}\frac{\partial f}{\partial y} & \frac{\partial^2 f}{\partial y^2} : \frac{\partial}{\partial y} h = \frac{\partial}{\partial y}\frac{\partial f}{\partial y} \end{array}$$

When the partial derivative is taken two times in the same direction the second partial derivatives are named pures, when is 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 form many reasons, one of which the fact that if the four order mixed partial derivatives are continuous at (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 involve 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 equation: 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 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 is defined as come 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 is their subsequent application:

$$(\hat{A}\hat{B})f = \hat{A}(\hat{B}f)$$

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 $\hat{1}$ is an operator such that:

$$\hat{1}f = f$$

11.2.6 Commutability

Two operatore 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 C^2 functions.

11.2.7 Linearity

Linear operator are operators which respect the property of linearity: given $\hat{A}$ an operator acting on f and g and c a constant multiplier:

$$\hat{A}(f \pm g) = \hat{A}f \pm \hat{A}g$$
$$\hat{A}(cf) = c\hat{A}f$$

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 function 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 $\mathbb{R}^2$, a function of three variables $f(x, y, z)$. Be the function derivable. The gradient of f in Cartesian coordinates is defined by:

$$gradf = \nabla f := \frac{\partial f(x,y,z)}{\partial x}\hat{i} + \frac{\partial f(x,y,z)}{\partial y}\hat{j} + \frac{partial f(x,y,z)}{\partial z}\hat{k}$$

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 axis 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 its has a magnitude equal to the maximum rate of increase at the point.

11.3.3.1 Directional derivatives

Directional derivatives for C^1 functions can be written as a 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 an open set of $\mathbb{R}^3$. This vectorial field is defined by means of its components along the axis directions: $\vec{V} = v_1\hat{i} + v_2\hat{j} + v_3\hat{k}$. It 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 defined as nabla acting on a vector field via the scalar product This gives informations on where a vectorial fields has source or sink, or, when the vectorial field represent 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 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 if the field rotates around a point and 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 the last operator and it is defines 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 second partial derivatives can be build to study functions from $\mathbb{R}^n$ to $\mathbb{R}$. The presence of possible extrema at one point is linked to the one of a null gradient in that point. 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 $\nabla f = \vec{0}$. 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 $f \in C^2$, where c^2 meaning that all partial second 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 $f \in C^2$ and (x_0, y_0) 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 variable $f = (f_1(x, y), f_2(x, y))$ for whigh all the derivatives exist ant 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. Also the Jacobian determinant makes possible to consistently define the change of volume in 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 that are differentiable function 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 relation there is a need to compute:

$$
\begin{aligned}
\frac{\partial\rho}{\partial x} &= \frac{\partial\sqrt{x^2+y^2}}{\partial x} = \frac{1}{2}\frac{2x}{\sqrt{x^2y^2}} = \frac{x}{\sqrt{x^2+y^2}} = \frac{\rho\cos\theta}{\rho} = \cos\theta \\
\frac{\partial\rho}{\partial y} &= \frac{\partial\sqrt{x^2+y^2}}{\partial y} = \frac{1}{2}\frac{2y}{\sqrt{x^2y^2}} = \frac{y}{\sqrt{x^2+y^2}} = \frac{\rho\sin\theta}{\rho} = \sin\theta \\
\frac{\partial\theta}{\partial x} &= \frac{\partial\arctan\frac{y}{x}}{\partial x} = -\frac{y}{x^2+y^2} = -\frac{\rho\sin\theta}{\rho^2} = -\frac{\sin\theta}{\rho} \\
\frac{\partial\theta}{\partial y} &= \frac{\partial\arctan\frac{y}{x}}{\partial y} = \frac{x}{x^2+y^2} = \frac{\rho\cos\theta}{\rho^2} = \frac{\cos\theta}{\rho}
\end{aligned}
$$

So:

$$
\frac{\partial g}{\partial x} = \frac{\partial f}{\partial\rho}\cos\theta + \frac{\partial f}{\partial\theta}\frac{-\sin\theta}{\rho} \qquad \frac{\partial g}{\partial y} = \frac{\partial f}{\partial\rho}\sin\theta + \frac{\partial f}{\partial\theta}\frac{\cos\theta}{\rho}
$$

The gradient of g using Cartesian versors will be:

$$
\begin{aligned}
\nabla g = g_x\hat{e}_x + g_y\hat{e}_y &= \left(\frac{\partial f}{\partial\rho}\cos\theta + \frac{\partial f}{\partial\theta}\frac{-\sin\theta}{\rho}\right)\hat{e}_x + \left(\frac{\partial f}{\partial\rho}\sin\theta + \frac{\partial f}{\partial\theta}\frac{\cos\theta}{\rho}\right)\hat{e}_y = \\
&= \left(\frac{\partial f}{\partial\rho}\cos\theta\right)\hat{e}_x + \left(\frac{\partial f}{\partial\theta}\frac{-\sin\theta}{\rho}\right)\hat{e}_x + \left(\frac{\partial f}{\partial\rho}\sin\theta\right)\hat{e}_y + \left(\frac{\partial f}{\partial\theta}\frac{\cos\theta}{\rho}\right)\hat{e}_y = \\
&= \frac{\partial f}{\partial\rho}(\cos\theta\hat{e}_x + \sin\theta\hat{e}_y) + \frac{1}{\rho}\frac{\partial f}{\partial\theta}(-\sin\theta\hat{e}_x + \cos\theta\hat{e}_y)
\end{aligned}
$$

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 the treatment of 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 conditions:

- $0 \leq \rho \leq \infty$
- $0 \leq \theta \leq 2\pi$
- $0 \leq \phi \leq \pi$

Computing all the first order partial derivatives the jacobian matrix is:

$$J_f = \begin{pmatrix} \nabla(x(\rho,\theta,\phi)) \\ \nabla(t(\rho,\theta,\phi)) \\ \nabla(z(\rho,\theta,\phi)) \end{pmatrix} = \begin{pmatrix} x_\rho & x_\theta & x_\phi \\ y_\rho & y_\theta & y_\phi \\ z_\rho & z_\theta & z_\phi \end{pmatrix} =$$
$$= \begin{pmatrix} \cos\theta\sin\phi & -\rho\sin\theta\cos\phi & \rho\cos\theta\cos\phi \\ \sin\theta\sin\phi & \rho\sin\theta\cos\phi & \rho\sin\theta\cos\phi \\ \cos\phi & 0 & -\rho\sin\phi \end{pmatrix}$$

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 most simple thing to do is to put it 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:

$$
\begin{aligned}
Vol(B) &= \int_0^{\pi}\int_0^{2\pi}\int_0^{R} \rho^2 \sin\phi d\rho d\theta d\phi = \\
&= \int_0^{\pi}\int_0^{2\pi}\left[\frac{\rho^3}{3}\right]_0^R \sin\phi d\theta d\phi = \int_0^{\pi}\int_0^{2\pi}\frac{R^3}{3}\sin\phi d\theta d\phi = \\
&= \int_0^{\pi}[\theta]_0^{2\pi}\frac{R^3}{3}\sin\phi d\phi = \int_0^{\pi}\frac{2\pi R^3}{3}\sin\phi d\phi = \\
&= [-\cos\phi]_0^{\pi}\frac{2\pi R^3}{3} = \\
&= \frac{4\pi R^3}{3}
\end{aligned}
$$

Chapter 13

Multidimensional integrals

In many dimension 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 order of integrations.

13.1 Definition

The integral of a function $f(x, y)$ in two dimension 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 $\Delta x \times \Delta y$. These subdomains cover the whole original domain. In each subdomain 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 on the corresponding subdomain. The supremum is the least element of $\mathbb{R}$ that is less than or equal to all elements of the function on 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 subdomain labelled by k. The function $f(x, y)$ is Riemann-integrable if:

$$\sup L(f, P) = \inf U(f, P) = I$$

Varying the partition, so

$$I = \int_c^d \int_a^b f(x, y) dx dy$$

13.2 Properties

13.2.1 Differentiability

Let $f(x, y)$ be a continuous function from $(a, b) \times (c, d)$ then the function is integrable. This result can be extended with different kind of integrals. Also this definition can be easily extended in more dimension.

13.2.2 Order of integration

If $f(x, y)$ is continuous on $(a, b) \times (c, d)$ then:

$$\int_c^d \left(\int_a^b f(x, y) dx \right) dy = \int_a^b \left(\int_c^d f(x, y) dy \right) dx$$

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:

$$\iint_\Omega f = \int_c^d dy \left(\int_{h_1(y)}^{h_2(y)} f(x, y) dx \right)$$

In the same way for an y-simple domain:

$$\Omega = \{(x, y) \in \mathbb{R}, g_1(x) \leq y \leq g_2(x), a \leq x \leq b\}$$

$$\iint_\Omega f = \int_a^b dx \left(\int_{g_1(x)}^{g_2(x)} f(x, y) dy \right)$$

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 coordinate 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:

$$\iint_\Omega f(x, y) dx dy = \iint_{\Omega^*} f(x(u, v), y(u, v)) |J| du dv$$

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 solution of:

$$\frac{\partial^2}{\partial t^2} f_\pm(x \pm vt) = v^2 f''(x \pm vt)$$

$$\frac{\partial^2}{\partial x^2} f_\pm(x \pm vt) = k^2 f''(x \pm vt)$$

So the wave equation is:

$$\Bigg(\underbrace{\frac{1}{v^2}}_{\text{speed of the wave}} - \frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2}\Bigg)] f_\pm = 0$$

14.1.1 Three-dimensional case

To get the corresponding form for a wave in three dimension 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 $\vec{k} = k_0 \hat{z}$: $\vec{r}\vec{k} = z \cdot k$ and:

$$f_{\pm}(\vec{r} \cdot \vec{k} \pm \omega t) = f(zk \pm \omega t)$$

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 $a, b \in \mathbb{R}$ the discussion is restricted 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 state of a particle is instantaneously 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 speces. 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 defined:

$$\langle\psi|\phi\rangle = (\langle\phi|\psi\rangle)^* \in \mathbb{C}$$

In hilbert spaces reversing the order of elements in the inner spaces leads to the complex conjugate result. The inner product is bi-linear:

$$\begin{cases} |\xi\rangle \equiv \alpha_1|\psi_1\rangle + \alpha_2|\psi_2\rangle \\ |\omega\rangle \equiv \beta_1|\phi_1\rangle + \beta_2|\phi_2 \end{cases} \Rightarrow \langle\xi|\omega\rangle = \sum_{i=1}^{2} \alpha_i^* \beta_i \langle\psi_i|\phi_i\rangle$$

15.1.2 Complete orthonormal bases

15.1.2.1 Standard vector spaces

In 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 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 $\lambda_1, \dots, \lambda_N$ which enable to express $\vec{v}$ as a linear combination 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 called the coordinates of the vector $\vec{v}$ in the given complete orthonormal basis $\{e_k\}_{k=1,\dots,N}$.

15.1.2.2 Hilbert space

A set of quantum states is defined to be a complete orthonormal basis of the Hilbert space $\mathcal{H}$ if:

- They are mutually orthogonal.
- They have unit norm.
- Any state 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 if holds:

$$\langle\vec{x}|\vec{y}\rangle = \delta(\vec{x} - \vec{y})$$

$\delta(\vec{x} - \vec{y})$ denotes the dirac-delta:

$$\int d^3\vec{y}A(y)\delta(\vec{x}-\vec{y}) = A(\vec{x})$$

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 a N-dimensional real vector space is defined, then each linear operator can be assigned a $N \times N$ 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:

$$|w\rangle = \hat{O}|v\rangle \qquad \hat{O}(\alpha_1|v_1\rangle + \alpha_2|v_2\rangle) = \alpha_1\hat{O}|v_1\rangle + \alpha_2\hat{O}|v_2\rangle$$

Like real vector space, 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 $\hat{A}$ an operator, then:

$$e^{\hat{A}} \equiv \not{\Bbbk} + \hat{A} + \frac{1}{2}\hat{A}^2 + \cdots = \sum_{n=0}^{\infty}\frac{1}{n!}\hat{A}^n$$

Not 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, or if it coincides with its hermitian conjugate: $\hat{O} = \hat{O}^\dagger$. Furthermore an operator $\hat{U}$ is called unitary if $\hat{U}^\dagger\hat{U} = \not{\Bbbk}$. Observables in quantum mechanics are associated to hermitian operators and the outcome of a measurement it's 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 exist 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 $\hat{O}$, $\{|o_n\rangle\}$.

15.3 Fourier transform

A special case of basis change is provided by the fourier transformation. Let $\phi(\vec{x})$ be the wave function in coordinate representation. The unitary transformation to the momentum basis is called direct fourier transform and is defined as:

$$\hat{F}[\phi(\vec{x})] = \tilde{\phi}(\vec{p}) = \int_{-\infty}^{\infty} d^3\vec{x} e^{\frac{i}{\hbar}\vec{p}\cdot\vec{x}} \phi(\vec{x})$$

The inverse transformation from the momentum basis to the position one is called the inverse fourier transform:

$$\hat{F}^{-1}[\tilde{\phi}(\vec{p})] = \phi(\vec{x}) = \int_{-\infty}^{\infty} \frac{d^3\vec{p}}{(2\pi)^3} e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{x}} \tilde{\phi}(\vec{p})$$

The term $(2\pi)^3$ is introduced conventionally to guarantee the preservation of the normalization condition. An important properties of the fourier transform is that:

$$\begin{aligned} F^{-1}[\vec{p}\tilde{\phi}(\vec{p})] &= \int_{-\infty}^{\infty} \frac{d^3\vec{p}}{(2\pi)^3} e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{x}} \vec{p}\tilde{\phi}(\vec{p}) = \\ &= \left(-i\hbar\frac{\partial}{\partial\vec{x}}\right) \int_{-\infty}^{\infty} \frac{d^3\vec{p}}{(2\pi)^3} e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{x}} \tilde{\phi}(\vec{p}) \\ &= \left(-i\hbar\frac{\partial}{\partial\vec{x}}\right) \phi(x) \end{aligned}$$

Where $\frac{\partial}{\partial\vec{x}}$ denotes the gradient operator.