Molecular Physics

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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:

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

Clearly, $f_1(t)$ and $f_2(t)$ are solutions if $\omega^2 = \frac{k}{m}$. Neither of them is a good solution, 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:

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

So the final solution is:

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

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: $W^1_{AB} = W^2_{AB}$ and:

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

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

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

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

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:

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

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:

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

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

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

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:

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

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:

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

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:

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

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 $\hat{\mu}_x = +\mu_0$.

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 apliduteds, 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:

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

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:

$$E = \hbar\omega = h\nu$$

Protons propagate according to a wave equation:

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

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:

$$\phi(x,t) = Ae^{i(\vec{k}\vec{r}-\omega t)}$$

Then: $\frac{\partial^2}{\partial t^2}\phi = \omega^2\phi$ and $\nabla^2\phi = |\vec{k}|^2\phi$. So it is obtained that:

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

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

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

And not just to $|p|$.

3.1.3 Defining the 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:

$$\frac{\partial}{\partial t}e^{i(\vec{k}\vec{r}-\omega t)} = -i\omega e^{i(\vec{k}\vec{r}-\omega t)}$$

And:

$$\left(iA\frac{\partial}{\partial t} + B\nabla^2\right)\phi = 0 \Rightarrow \omega A - Bk^2 = 0$$

To obtain an energy $A = \hbar$, then:

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

The remaining constant is set by phenomenology:

$$i\hbar\frac{\partial}{\partial t}\phi = -\frac{\hbar^2}{2m}\nabla^2\phi$$

The right hand side represent a kinetic energy. For a free electron H equals the kinetic energy and is approximately the Hamiltonian. For an interacting electron:

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

So finally the Schröedinger equation:

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

3.1.3.1 Quantum Hamiltonian

Now the quantum Hamiltonian can be defines as:

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

The Schröedinger equation is then recast as:

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

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:

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

As a guess for the form of the solution and plugging it into the Schröedinger equation:

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

Which gives:

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

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:

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

So:

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_0 &= -\frac{\hbar^2}{2m}\mathcal{N}\frac{d}{dx}\left[-\frac{\alpha}{2}xe^{-\frac{\alpha x^2}{4}}\right. = \\ &= -\frac{\hbar^2}{2m}\left[-\frac{\alpha}{2}e^{-\frac{\alpha x^2}{4}} + \frac{\alpha^2}{4}x^2 e^{-\frac{\alpha x^2}{4}}\right]\mathcal{N} \end{aligned}$$

So:

$$\begin{aligned} \hat{H}\psi_0 &= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_0 + \frac{1}{2}m\omega^2 x^2\psi_0 = \\ &= \frac{\alpha}{4}\frac{\hbar^2}{m}\psi_0 - \frac{\hbar^2\alpha^2}{8m}x^2\psi_0 + \frac{1}{2}m\omega^2 x^2\psi_0 \end{aligned}$$

For ψ_0 to be an eigenstate $\hat{H}\psi_0 = const \cdot \psi_0$ so the dependence on x^2 must be cancelled:

$$-\frac{\hbar^2}{2m}\alpha^2\frac{1}{4}\cancel{x^2}\psi_0 + \frac{1}{2}m\omega^2\cancel{x^2}\psi_0 = 0$$

From this:

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

So:

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

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:

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

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:

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

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:

$$\begin{cases} \psi(x,y) = \psi_1(x)\psi_2(y) \\ H\psi = (E_1 + E_2(\psi)) \end{cases}$$

Where $H_1\psi_1 = E_1\psi_1$ and $H_2\psi_2 = E_2\psi_2$ So:

$$\begin{aligned} (H_1 + H_2)\psi_1(x)\psi_2(y) &= H_1\psi_1(x)\psi_2(y) + H_2\psi_1(x)\psi_2(y) = \\ &= \psi_2(y)\hat{H}_1\psi_1(x) + \psi_1(x0 + \psi)1(x)H_2\psi_2(y) = \\ &= \psi_2 E_1\psi_1 + \psi_1 E_2\psi_2 = \\ &= (E_1 + E_2)\psi_1\psi_2 \end{aligned}$$

So:

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

And $E_{n,m} = E_n + E_m$.

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:

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

Chapter 4

Quantum mechanics

4.1 State of a system

4.2 Observable quantities

4.3 Outcomes of measurement

4.4 Expectation value

4.5 Time evolution

Part II

Quantum chemistry

Chapter 5

Approximation methods

Chapter 6

Atomic physics

Chapter 7

Molecular physics

Appendices

Appendix A

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 $b = 0$.

A.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.

A.2 Operations

A.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:

$$z + w = (a + c) + (b + d)i$$

A.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:

$$z - w = (a - c) + (b - d)i$$

A.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:

$$\begin{aligned} z \cdot w &= (a + bi)(c + di) = \\ &= ac + adi + bci + bdi^2 = \\ &= ac + (ad + bc)i - bd = \\ &= (ac - bd) + (ad + bc)i \end{aligned}$$

A.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.

A.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:

$$\begin{aligned} \frac{z}{w} &= \frac{a + bi}{c + di} = \\ &= \frac{a + bi}{c + di}\frac{c - di}{c - di} = \\ &= \frac{ac - adi + bci + bd}{c^2 + d^2} = \\ &= \frac{(ac + bd) + (bc - ad)i}{c^2 + d^2} = \\ &= \frac{ac + bd}{c^2 + d^2} + \frac{bc - ad}{c^2 + d^2}i \end{aligned}$$

A.3 Polar form

A.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.

A.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 $2k\pi$, $\forall k \in \mathbb{Z}$.

A.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:

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

A.3.4 Operations

A.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:

$$zw = \rho_z\rho_q[\cos(\theta_z + \theta_w) + i\sin(\theta_z + \theta_w)]$$

A.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:

$$\frac{z}{w} = \frac{r_z}{r_w}[\cos(\theta_z - \theta_w) + i\sin(\theta_z - \theta_q)]$$

A.3.4.3 Power

According to the de Moivre theorem, for every $n \in \mathbb{N}$ positive integer and $z \in \mathbb{C}, z = \rho(\cos\theta+i\sin\theta)$:

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

A.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.

A.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.

A.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:

$$(f \pm g)'(x_0) = f'(x_0) + g'(x_0)$$

$$(fg)'(x_0) = f'(x_0)g(x_0) + f(x_0)g'(x_0)$$

$$\frac{f}{g}'(x_0) = \frac{f'(x_0)g(x_0) - f(x_0)g'(x_0)}{g^2(x_0)}$$

A.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 $a, b \neq 0$;

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

A.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 $z \in \mathbb{C}$, $\frac{de^z}{dz} = e^z$.

A.5.2 Roots of a complex number

The complex exponential allows to write the n roots of a complex number $z = r(\cos\theta + i \sin\theta)$ as:

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

Where $k \in \{0, 1, \ldots, n-1\}$.

Appendix B

Partial derivatives

B.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.

B.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.

B.1.2 Tangent plane

The tangent plane of $f(x, y)$ in the point (x_0, y_0) has the following form:

$$g(x, y) = f(x_0, y_0) + f_x(x_0, y_0)(x - x_0) + f_y(x_0, y_0)(y - y_0)$$

B.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.

B.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.

B.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 $\mathbb{R}^\kappa$ 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.

B.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.

Appendix C

Differential operators

C.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.

C.2 Properties

C.2.1 Sum and difference

Given two operators $\hat{A}$ and $\hat{B}$ acting on some function f:

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

C.2.2 Product

Given two operators $\hat{A}$ and $\hat{B}$ acting on some function f is their subsequent application:

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

C.2.3 Power

Given an operator $\hat{A}$

$$\hat{A}^n = \prod_{i=1}^{n} \hat{A}$$

C.2.4 Equality

Given two operators $\hat{A}$ and $\hat{B}$ acting on some function f, they are defined equal if:

$$\hat{A} = \hat{B} \Leftrightarrow \hat{A}f = \hat{B}f$$

C.2.5 Identity operator

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

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

C.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.

C.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:

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

C.3 Gradient, divergence and curl

C.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.

C.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.

C.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.

C.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 $\vec{v}$:

$$\vec{\nabla}_{\vec{v}} f(\vec{x}) = \vec{v}\vec{\nabla} f(\vec{x})$$

C.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.

C.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.

C.3.6 Properties

- $\nabla \times \nabla f = \vec{0}$
- $\nabla \cdot \nabla \times \vec{V} = 0$
- $\nabla \cdot f = \nabla^2 f$

C.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:

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

C.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.

C.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.

C.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:

$$\frac{\partial u}{\partial s} = \frac{\partial u}{\partial x}\frac{\partial x}{\partial s} + \frac{\partial u}{\partial y}\frac{\partial y}{\partial s} \qquad \frac{\partial u}{\partial t} = \frac{\partial u}{\partial x}\frac{\partial x}{\partial t} + \frac{\partial u}{\partial y}\frac{\partial y}{\partial t}$$

C.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:

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

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:

$$\nabla g = f_\rho\hat{e}_\rho + \frac{f_\theta}{\rho}\hat{e}_\theta$$

Appendix D

Spherical coordinates

D.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:

$$dV = dxdydz = \left| det \frac{\partial(x,y,z)}{\partial(\rho,\theta,\phi)} \right| d\rho d\theta d\phi = \rho^2 \sin\phi d\rho d\theta d\phi$$

D.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:

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

Appendix E

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.

E.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

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

E.2 Properties

E.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.

E.2.2 Order of integration

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

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

E.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:

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

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

E.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:

$$\iint_\Omega f(x,y)dxdy = \iint_{\Omega^*} f(x(u,v), y(u,v))|J|dudv$$

Where Ω^* is the new region of integration in the (u, v) plane.

Appendix F

Wave equations

F.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:

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

F.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:

$$\left(\nabla^2 - \frac{1}{v^2}\frac{\partial^2}{\partial t^2}\right) f(\vec{r}, t) = 0$$

F.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.

Appendix G

Hilbert spaces

G.1 From vector to hilbert spaces

G.1.1 Definition

G.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:

$$(a_1\vec{v}_1 + a_2\vec{v}_2) \cdot (b_1\vec{w}_1 + b_2\vec{w}_2) = \sum_{i,k=1}^{2} a_i b_k \vec{v}_i \vec{w}_k$$

G.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:

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

G.1.2 Complete orthonormal bases

G.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 $\lambda_1, \ldots, \lambda_N$ 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 de dimension of the vector spece. The set of coefficients is called the coordinates of the vector $\vec{v}$ in the given complete orthonormal basis $\{e_k\}_{k=1,\ldots,N}$.

G.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 dens 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:

$$|\psi\rangle = \int d^3\vec{x}\phi(\vec{(x)})|vecx\rangle \qquad \phi(\vec{x}) \in \mathbb{C}$$

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.

G.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.

G.1.3.1 Multiplicative operator

A multiplicative operator is the potential energy operator: $U(\vec{x},\vec{y} = \delta(\vec{x}-\vec{y})u(y)$:

$$\int d^3\vec{y}U(\vec{x},\vec{y})\psi(\vec{y}) = u(\vec{x})\psi(\vec{x})$$

.

G.1.3.2 Derivative operator

A derivative operator is the kinetic energy operator: $T(\vec{x},\vec{y}) = -\frac{\hbar^2}{2m}\delta(\vec{x}-\vec{y})\nabla^2_{\vec{x}}$:

$$\int d^3\vec{y} T(\vec{x},\vec{y})\psi(\vec{y}) = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{x})$$

G.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.

G.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 $\hat{U}^\dagger\hat{U} = 1$.

G.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.

G.2.3 Corollaries

G.2.3.1 First corollary

Hermitian matrices are such that:

$$(O^T)^* = O$$

G.2.3.2 Second corollary

Hermitian matrices in real vector spaces are symmetric.

G.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 $\hat{O}$, $\{|o_n\rangle\}$.

G.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.