Molecular Physics

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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:

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

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 $\mathbb{R}^{\ltimes}$ 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.

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:

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

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:

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

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:

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

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

Appendix F

Hilbert spaces

F.1 From vector to hilbert spaces

F.1.1 Definition

F.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:

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

F.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:

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

F.1.2 Complete orthonormal bases

F.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 $\{e_k\}_{k=1,\ldots,N}$.

F.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.

F.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:

$$\vec{w} = \hat{O}\vec{v} \to \vec{e}_j \cdot \vec{w} = \sum_{i=1}^{N}(\vec{e}_i \cdot \vec{v})\vec{e}_j \cdot \hat{O}\vec{e}_i = \sum_{i=1}^{N} O_{ji}v_j$$

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.

F.1.3.1 Multiplicative operator

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

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

.

F.1.3.2 Derivative operator

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

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

F.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.

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

F.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.

F.2.3 Corollaries

F.2.3.1 First corollary

Hermitian matrices are such that:

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

F.2.3.2 Second corollary

Hermitian matrices in real vector spaces are symmetric.

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

F.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.