Math Review

Before starting on quantum mechanics, it's helpful to review a few basic mathematical tools, such as:

i. vectors

ii. partial derivatives

iii. differential equations

Why are these topics important?

They are used in both classical and quantum equations of motion

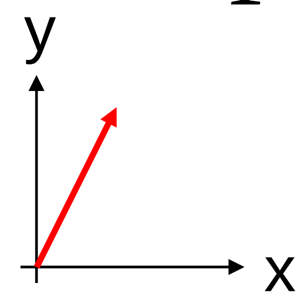
e.g., ***Newton's 2nd Law***

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

This is a vector equation. It is also a differential equation that often contains partial derivatives. (More on these shortly.)

Quick Review of Vectors

$\vec{F}$



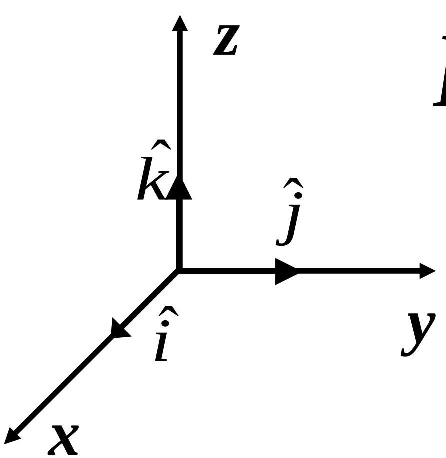
Vectors have both ***magnitude*** and ***direction***. Vector quantities include the velocity or acceleration of a particle or the force acting on it.

In contrast, scalar quantities have only magnitude.

In these notes, vectors will sometimes be represented in ***bold*** $\boldsymbol{F}$, $\boldsymbol{a}$, *etc.* (or by an arrow or hat on top)

Unit Vectors

Vectors are most often represented in terms of **unit vectors** lying along the axes of the coordinate system that have unit length.



$$\vec{F} = F_x\hat{i} + F_y\hat{j} + F_z\hat{k} \equiv (F_x, F_y, F_z)$$

F_x, F_y, F_z are scalars (magnitude only)

$\hat{i}, \hat{j}, \hat{k}$ are Cartesian unit vectors

Dot Product (or Scalar Product)

Consider two vectors given by:

$$\vec{a} = a_x\hat{i} + a_y\hat{j} + a_z\hat{k} \qquad \vec{b} = b_x\hat{i} + b_y\hat{j} + b_z\hat{k}$$

The dot product of $\vec{a}$ and $\vec{b}$ is defined as:

$$\vec{a} \bullet \vec{b} \;=\; a_x b_x + a_y b_y + a_z b_z \;=\; |a||b|\cos\theta$$

The dot product loosely gives an indication of the ‘overlap’ between two vectors.

The dot product between unit vectors is zero because they are ***orthogonal*** (*at right angles*) to one another.

$$\hat{i}\cdot\hat{j} = \hat{i}\cdot\hat{k} = \hat{j}\cdot\hat{k} = 0$$

Note that a dot product is not a vector, but a scalar. For this reason, the dot product is sometimes called the *scalar product*.

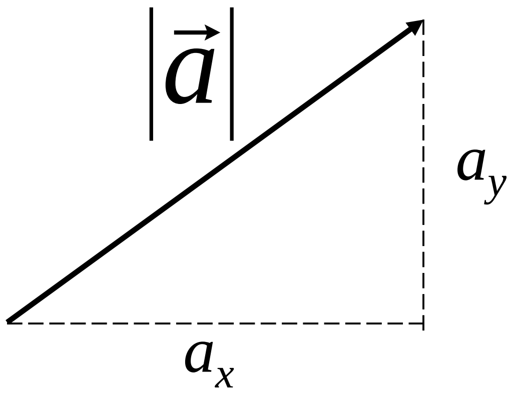
Magnitude (or Norm) of a Vector

The magnitude (or norm) of a vector is defined as:

$$\left|\vec{a}\right| \equiv \left\|\vec{a}\right\| = \sqrt{\vec{a} \bullet \vec{a}}$$

In 2 dimensions:

$$\left|\vec{a}\right| = \sqrt{a_x^2 + a_y^2}$$



In 3 dimensions it is:

$$\left|\vec{a}\right| = \sqrt{a_x^2 + a_y^2 + a_z^2}$$

In *n* dimensions it is:

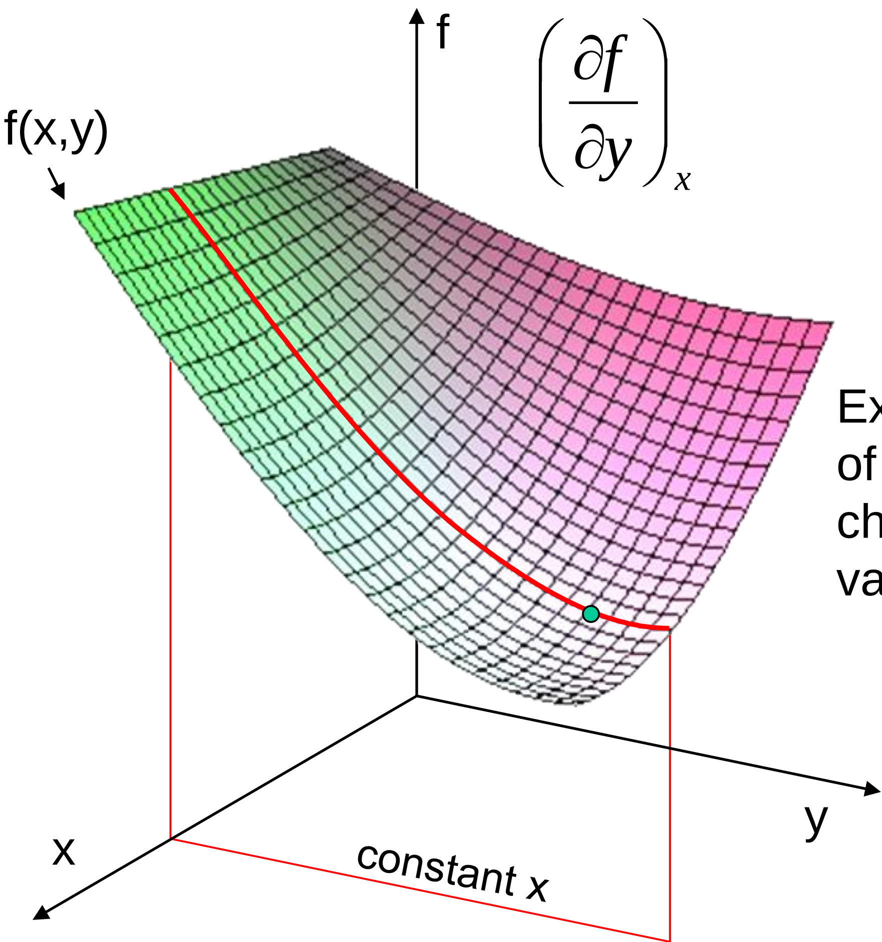
$$\left|\vec{a}\right| = \sqrt{a_{x_1}^2 + a_{x_2}^2 + a_{x_3}^2 + \ldots + a_{x_n}^2}$$

Review of Partial Derivatives

Partial derivatives occur when we discuss functions of more than one variable.

e.g. $f(x,y,z)$ or $P(n,V,T)$

A **partial derivative** can be defined as the slope of a function with respect to one of the variables, with all other variables held constant.



$$\left(\frac{\partial f}{\partial y}\right)_x$$

$$\frac{\partial}{\partial x}$$ ← symbol for partial derivative

Consider the function pressure, $P(n,V,T)$

Experimentally we may wish to vary only one of the variables, say temperature, to produce a change that is independent of the other variables (which are fixed).

$$\left(\frac{\partial P(n,V,T)}{\partial T}\right)_{n,V}$$

Review of Partial Derivatives

e.g. $$f(x,y,z) = x^2y^3 - 2xz^2$$

$$\frac{\partial f}{\partial x} = \left(\frac{\partial f}{\partial x}\right)_{y,z} =$$

$$\frac{\partial f}{\partial y} = \left(\frac{\partial f}{\partial y}\right)_{x,z}$$

Implies y and z are held constant when one differentiates with respect to x. (subscripts are usually omitted)

It is important to realize that <u>partial derivatives are themselves functions</u>! Thus, they can be differentiated again.

$$\left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial x}\right)_{y,z}\right)_{y,z} = \frac{\partial^2 f}{\partial x^2}$$

Mixed partial derivatives:

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_{y,z}\right)_{x,z} = \frac{\partial^2 f}{\partial y \partial x}$$

In general, the order does not matter, so we have

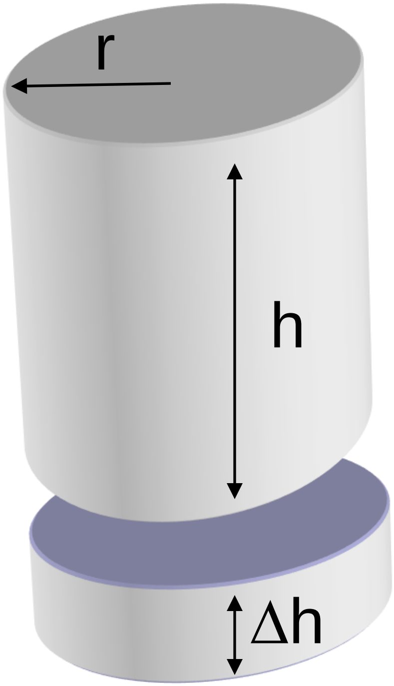
$$\boxed{\frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \partial y}}$$

A total derivative of a function can be obtained from its partial derivatives as:

$$\mathrm{d}f(x,y) = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y$$

$\mathbf{d}\boldsymbol{f}$ is called the **total differential** of the function $\boldsymbol{f}$ and can be thought of as 'what is the effect on $\boldsymbol{f}$ allowing all the variables to change'

Example. Consider the volume of a cylinder that is a function of the cylinder height and radius.



$$V = f(r,h) = \pi r^2 h$$

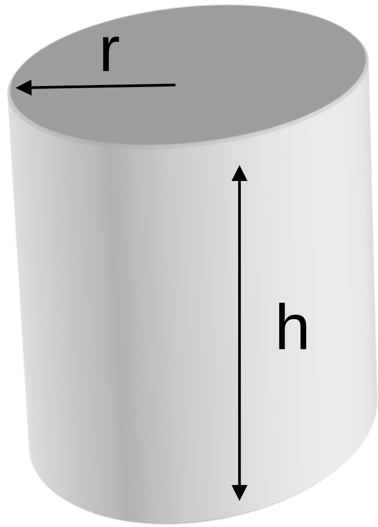
How does the volume change if the height is changed but the radius is held constant?

The procedure is:

$$\frac{\partial V}{\partial h} = \frac{\partial(\pi r^2 h)}{\partial h} = \pi r^2 \frac{\partial(h)}{\partial h} = \pi r^2$$

This result could probably be obtained by inspection. But for more complicated functions, it is not as obvious and partial derivatives are essential.

$$V = f(r,h) = \pi r^2 h$$



How does the volume change with as the radius changes with the height fixed?

This is given by the partial derivative:

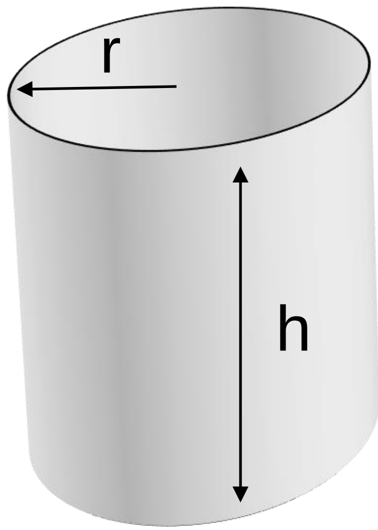
$$\frac{\partial V(r,h)}{\partial r} = \frac{\partial\left(\pi r^2 h\right)}{\partial r} = 2\pi r h$$

The volume change is $\boldsymbol{2\pi r h}$ multiplied by the change in the radius:

$$\mathrm{d}V = 2\pi h r\,\mathrm{d}r \qquad (\text{constant } h)$$

In the language of differentials, an infinitesimal change in $\boldsymbol{r}$ given by $\mathbf{d}\boldsymbol{r}$ results in the infinitesimal volume change $\mathbf{d}\boldsymbol{V} = \mathbf{2}\boldsymbol{\pi h r}\mathbf{d}\boldsymbol{r}$.

$$V = f(r,h) = \pi r^2 h$$



Any change in either ***r*** or ***h*** will result in a change in the volume. This is given by the **total differential**:

$$\mathrm{d}V = \frac{\partial V(r,h)}{\partial r}\mathrm{d}r + \frac{\partial V(r,h)}{\partial h}\mathrm{d}h$$

$$\mathrm{d}V = 2\pi r h \mathrm{d}r + \pi r^2 \mathrm{d}h$$

$$\text{or:} \qquad \frac{\mathrm{d}V}{V} = 2\frac{\mathrm{d}r}{r} + \frac{\mathrm{d}h}{h}$$

The Gradient of a function is a Vector

The gradient **operator** ∇ is often used in science and engineering. It gives the "slope" of a function. **The negative gradient of a potential energy, for example, gives a force.**

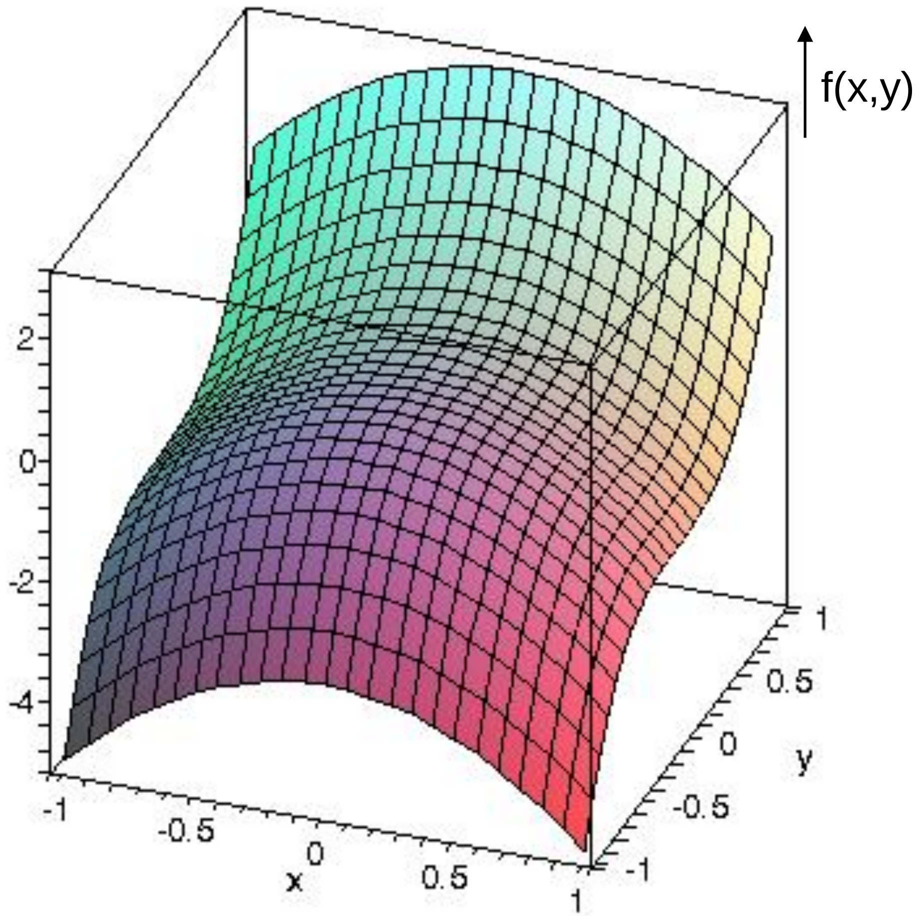
In three dimensions, the **gradient operator** is defined as:

$$\boxed{\vec{\nabla} = \hat{i}\,\frac{\partial}{\partial x} + \hat{j}\,\frac{\partial}{\partial y} + \hat{k}\,\frac{\partial}{\partial z}}$$

Example: What is the gradient of the following function?

$$f(x, y, z) = x^2 y^3 - 2xz^2$$

Consider the two dimensional function: $f(x,y) = -2x^2 + 3y^3$



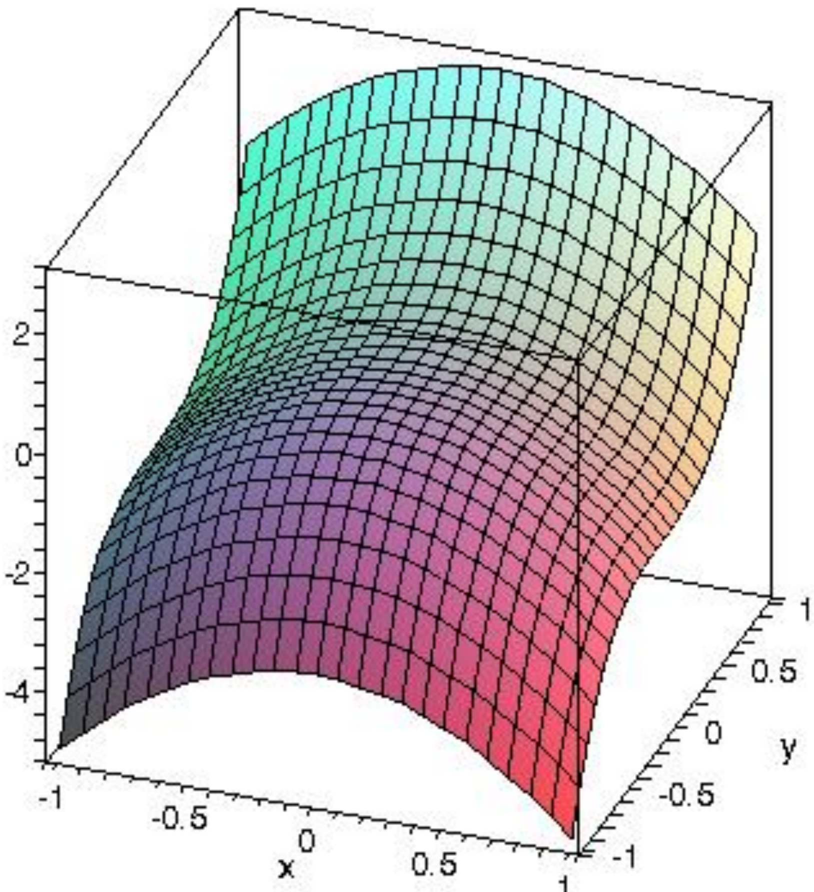
$$\vec{\nabla} f(x,y) = -4x\hat{i} + 9y^2\hat{j}$$

The gradient of this function gives the slope.

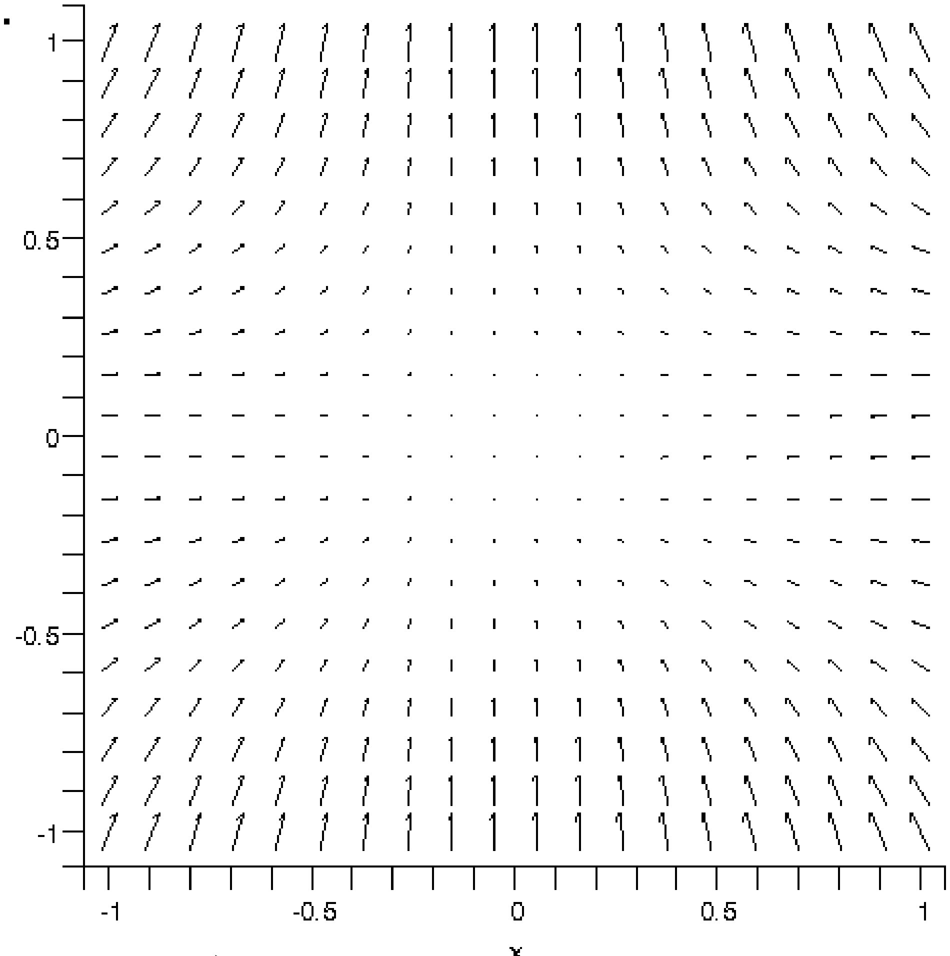
$f(x,y)$ is a scalar function. Associated with each point in (x,y) space, the function f gives a scalar.

$\nabla f(x,y)$, the gradient of f is a vector function. Associated with each point in (x,y) space is a vector.

The gradient, ∇, is often used in science and engineering since it gives the 'slope' of a multidimensional function.



$$f(x, y) = -2x^2 + 3y^3$$



$$\vec{\nabla} f(x, y) = (-4x, 9y^2)$$

For example, if $f(x,y)$ is a function that describes a hill, the negative gradient of $f(x,y)$ (downhill slope) will tell us in what direction a ball will roll if placed at the point (x,y) on the surface $f(x,y)$.

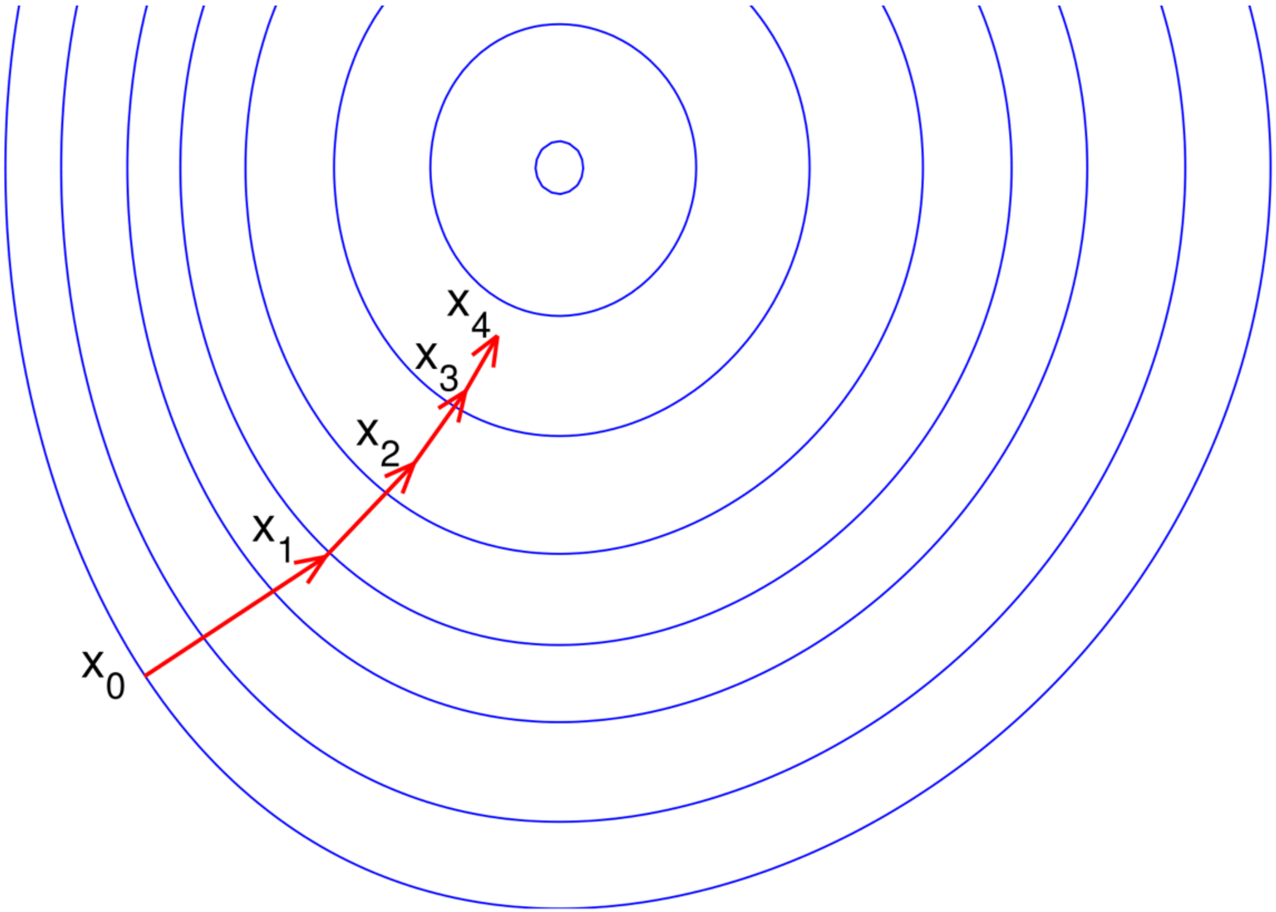
Consider the same function:

$$f(x,y) = -2x^2 + 3y^3$$

What is the gradient of the function *f*(*x*,*y*) at the point (1,2)?

$$\vec{\nabla} f(x,y) = (-4x, 9y^2)$$

Application: Optimization (Finding the Maximum) Value of Multivariable Functions by the **Method of Steepest Ascent (or Descent)**



The Laplacian Operator

One operator we will use frequently is the Laplacian **operator**. It is defined in Cartesian coordinates (x, y, z) as:

$$\boxed{\nabla^2 = \vec{\nabla} \bullet \vec{\nabla} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}}$$

The Laplacian operator, ∇^2, is often pronounced ‘del squared’ and it returns a **scalar** quantity, not a vector like the gradient operator.

$$\nabla^2 f = \nabla^2 (x^2 y^3 - 2xz^2)$$

$$= 2y^3 + 6x^2 y - 4x$$

Differential Equations

Definition: *A Differential Equation is an equation containing a function of one or more variables, its n-th derivatives, and independent variables.*

Example:

unknown function, $f(x)$

$$\underbrace{\frac{df(x)}{dx}}_{\text{derivative of unknown function}} = af(x)$$

Differential equations are used in many areas of science and engineering, especially mathematics, physics and chemistry.

They frequently occur in both classical mechanics and quantum mechanics.

Consider the **first-order rate equation** where the rate of a chemical reaction is dependent on the concentration of one species:

$$-\frac{d[A]}{dt} = k[A]$$

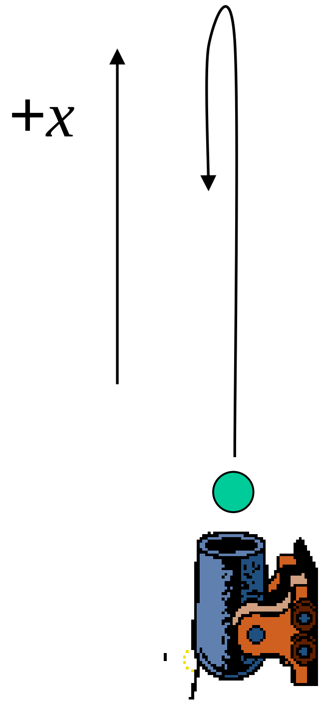
Consider the **equation of motion** of a body under the influence of gravity in one dimension:

$$F_x = ma_x$$

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

using $F = -mg$

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



The Solution of a Differential Equation is a Function

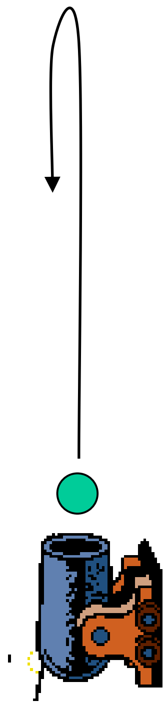
The solution of a differential equation is a function rather than a number.

Solutions of differential equations are the functions, which do not contain derivatives, that satisfy the differential equation.

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

Here the solution is the function $x(t)$ the ‘trajectory’ of the ball.

$$x(t) = -\frac{g}{2}t^2 + C_1 t + C_2$$



$$-\frac{d[A]}{dt} = k[A]$$

Here the solution is the concentration [A] as a function of time [A](t)

$$[A](t) = [A]_o e^{-kt}$$

The general solutions often contain unknown constants. When describing a physical system, the unknown constants are determined by **initial conditions** or **boundary conditions**.

Differential Equations Often Have Many Valid Solutions

Differential equations will often have more than one solution. Many that we will encounter will have a whole family of solutions (infinite in number!).

$$\frac{d}{dx} f(x) = a f(x)$$

$$f(x) = 0 \longleftarrow$$

trivial solution - mathematically valid, but typically has little physical meaning.

$$f(x) = e^{ax}$$

Confirm that both are valid solutions to the differential equation (also a constant times e^{ax})

Terminology of Differential equations

The **order** of a DE is given by the highest derivative in the equation. For example, two and one, respectively, for:

$$-g = \frac{d^2x(t)}{dt^2} \qquad\qquad -\frac{d[A]}{dt} = k[A]$$

Linear Differential Equations

A special kind of differential equation that we will use is the **linear differential** equation. A linear DE is simply one that can be put in the following form:

$$A_o(x)f(x) + A_1(x)\frac{df(x)}{dx} + A_2(x)\frac{d^2f(x)}{dx^2} + ... + A_n(x)\frac{d^{(n)}f(x)}{dx^{(n)}} = g(x)$$

$A_n(x)$'s and $g(x)$ are functions of x and some can be constants or zero.

Notice that the function f and its derivatives are not squared, cubed, etc., but only appear raised to the power one (i.e., "linear" in f)

Complex Numbers

Complex numbers frequently occur in quantum mechanics and in many branches of mathematics.

They naturally arise in the quadratic equation, solutions of higher order polynomials, and solutions to differential equations.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Complex numbers involve the imaginary quantity "***i***" defined as:

$$i = \sqrt{-1} \quad \text{or} \quad i^2 = -1$$

We generally write complex numbers as:

$$z = x + yi$$

x is the **REAL component** and ***y*** is the **IMAGINARY component** of the complex number.

$$x = \mathrm{Re}(z) \qquad y = \mathrm{Im}(z)$$

e.g.

$$z = 2 + 9i$$

$$z = 3.73i$$

$$z = -1.3 + 5i$$

Addition/Subtraction of Complex Numbers

Simply add/subtract the **Re** and **Im** parts separately.

$$(2+4\mathrm{i}) + (6 - 3\mathrm{i}) = (2+6) + (4 - 3)\mathrm{i}$$

$$= 8 + \mathrm{i}$$

Multiplication of Complex Numbers

When we multiply two complex numbers, we simply multiply them like binomials and use the fact that $\boldsymbol{i}^2 = -1$.

$$z_1 = 2 - \boldsymbol{i} \qquad z_2 = -3 + 2\boldsymbol{i}$$

$$\begin{aligned} z_1 \cdot z_2 &= (2 - \boldsymbol{i})(-3 + 2\boldsymbol{i}) \\ &= -6 + 3\boldsymbol{i} + 4\boldsymbol{i} - 2\boldsymbol{i}^2 \\ &= -6 + 3\boldsymbol{i} + 4\boldsymbol{i} - 2(-1) \\ &= -4 + 7\boldsymbol{i} \end{aligned}$$

Division of Complex Numbers

Division of complex numbers is simple:

$$z_1 = 2 - i \qquad z_2 = -3 + 2i$$

$$z_1 \,/\, z_2 = \frac{z_1}{z_2}$$

We can simply leave it as:

$$= \frac{(2 - i)}{(-3 + 2i)}$$

Complex Conjugate of Complex Numbers

The complex conjugate is used frequently in quantum mechanics.

The complex conjugate of a complex number is obtained by replacing all instances of $\boldsymbol{i}$ with $-\boldsymbol{i}$.

For example if:

$$z = x + y\boldsymbol{i}$$

the complex conjugate is:

$$z^* = x - y\boldsymbol{i}$$

The short-hand notation the complex conjugate of a number $\boldsymbol{z}$ is $\boldsymbol{z^*}$.

e.g.

$$z = 2 - 3\boldsymbol{i} \quad \Rightarrow \quad z^* = 2 + 3\boldsymbol{i}$$

What is the complex conjugate of z = 54?

A number multiplied by its complex conjugate is ALWAYS a real, positive number!

$$z \cdot z^* = A$$

A is **real and positive**

$$\boxed{z \cdot z^* = x^2 + y^2}$$

e.g.

$$z = 2 - 3\boldsymbol{i}$$

$$z \cdot z^* = (2 - 3\mathrm{i})(2+3\mathrm{i}) = (2)^2 + (-3)^2$$

$$= 4 + 6\mathrm{i} - 6\mathrm{i} - 9\mathrm{i}^2$$

$$= 4 - (9)(-1) = 13$$

We'll see that $z{\cdot}z^*$ is related to the 'magnitude' of a complex number.

$$z = \frac{(2-i)}{(-3+2i)}$$

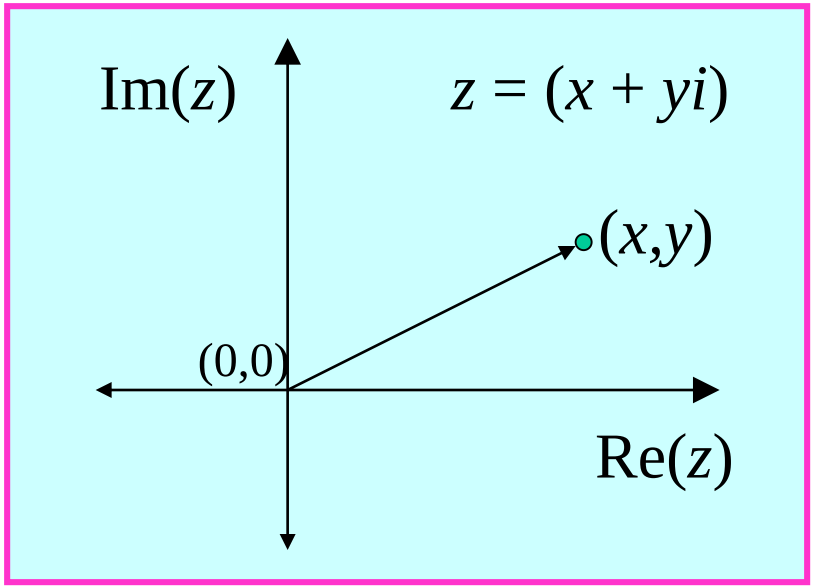
In the division of complex numbers, we can use the complex conjugate to simplify our answers by multiplying the numerator and denominator by the complex conjugate of the denominator.

$$z = \frac{(2-i)}{(-3+2i)} \cdot \frac{(-3-2i)}{(-3-2i)}$$

$$= \frac{(2-i)(-3-2i)}{(-3)^2 + (-2)^2}$$

$$= \frac{-6+3i-4i-2}{9+4} = \frac{-8-i}{13}$$

Complex numbers can be represented as a point in a 2-D coordinate system.



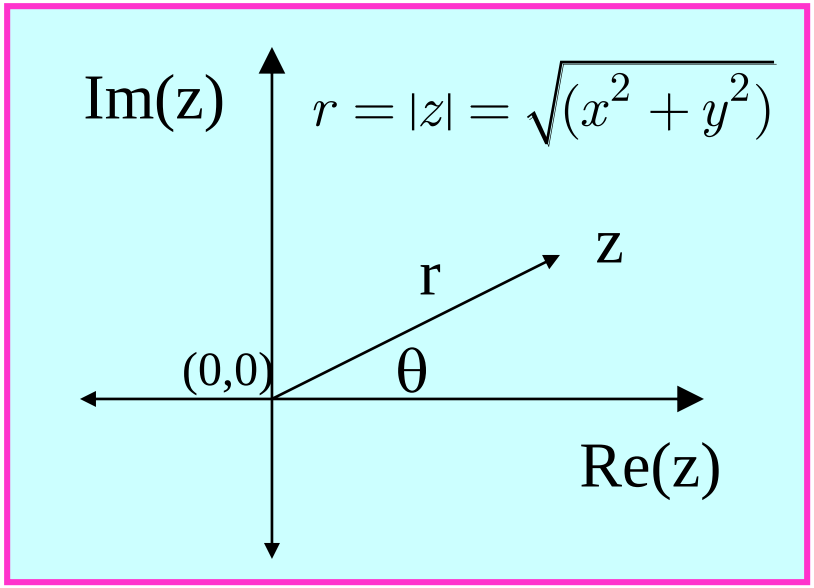
By convention, the real part is plotted along the horizontal (x) axis and the imaginary part of z is plotted along the y-axis.

The above figure is a representation of the **complex-plane**.

Notice that the above representation of z is that of a vector, with a magnitude given by:

$$|z| = \left(z \cdot z^*\right)^{\frac{1}{2}} = \sqrt{x^2 + y^2}$$

It is often very useful to express the complex number in polar form.



θ is the angle z makes with the real (x) axis. θ is often called the phase factor.

It can be shown that we can alternatively express a complex number in what is termed exponential form:

$$\boxed{z = (x + yi) = r \cdot e^{i\theta}} = r\cos\theta + ir\sin\theta$$

A very useful relationship linking the two representations of complex numbers is **Euler's formula**:

$$\boxed{e^{i\theta} = \underbrace{\cos\theta}_{} + \underbrace{i\sin\theta}_{}}$$

$$z = (x + yi)$$

Given $e^{i\theta} = \cos\theta + i\sin\theta$

a) what is $e^{2i\theta}$?

b) what is $e^{-i\theta}$?

We will often be working with the exponential form of complex numbers.

multiplication

$$z_1 \times z_2 = r_1 e^{iq_1} \cdot r_2 e^{iq_2} \;= r_1 r_2 e^{i\theta_1 + i\theta_2} = r_1 r_2 e^{i(\theta_1 + \theta_2)}$$

division

$$z_1 \,/\, z_2 = \frac{r_1 e^{i\theta_1}}{r_2 e^{i\theta_2}} = \frac{r_1}{r_2} e^{i(\theta_1 - \theta_2)}$$

$$z^{-1} = \frac{1}{re^{i\theta}} = \frac{1}{r} e^{-i\theta}$$

Complex Functions

Many of the functions we will work with will contain complex numbers.

e.g. $$f(x) = x \cdot e^{-ix}$$

One just has to treat '$\boldsymbol{i}$' as a constant and use the algebra rules presented above.

Differentiation and Integration with complex numbers

Calculus of functions with '$\boldsymbol{i}$' is simple - we just treat '$\boldsymbol{i}$' as a constant.

a) $$\frac{d}{dx} \; i \sin(2x)$$

b) $$\frac{d}{dx} \; x \cdot e^{-ix}$$

c) $$\frac{d\left(x^{i}\right)}{dx}$$

Some Differential Equations Have *Oscillatory* Solutions

For a possible solution of the ordinary differential equation

$$\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} + y(x) = 0 \qquad \text{try} \qquad y(x) = \mathrm{e}^{\alpha x}$$

Then

$$\frac{\mathrm{d}y}{\mathrm{d}x} = \frac{\mathrm{d}\mathrm{e}^{\alpha x}}{\mathrm{d}x} = \alpha \mathrm{e}^{\alpha x} \qquad \text{and} \qquad \frac{\mathrm{d}^2 y}{\mathrm{d}x^2} = \frac{\mathrm{d}}{\mathrm{d}x}\frac{\mathrm{d}y}{\mathrm{d}x} = \frac{\mathrm{d}}{\mathrm{d}x}\left(\alpha \mathrm{e}^{\alpha x}\right) = \alpha^2 \mathrm{e}^{\alpha x}$$

Substituting $y(x) = \mathrm{e}^{\alpha x}$ back in the original differential equation:

$$\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} + y(x) = 0 = \alpha^2 \mathrm{e}^{\alpha x} + \mathrm{e}^{\alpha x} \qquad \text{So} \qquad \boldsymbol{\alpha^2 + 1 = 0}$$

Possible values of $e^{\alpha x}$ are

$$\alpha^2 + 1 = 0$$

$$\alpha^2 = -1$$

$$\alpha = \pm\sqrt{-1} = \pm i$$

e^{ix} and e^{-ix}

This gives solutions to the differential equation of the form (c_1 and c_2 are constants)

$$y(x) = c_1 e^{ix} + c_2 e^{-ix}$$

Oscillatory ??? Yes, using

$$e^u = 1 + u + \frac{u^2}{2!} + \frac{u^3}{3!} + \frac{u^4}{4!} + \cdots$$

$$\cos(u) = 1 - \frac{u^2}{2!} + \frac{u^4}{4!} - \frac{u^6}{6!} + \cdots$$

$$\sin(u) = u - \frac{u^3}{3!} + \frac{u^5}{5!} - \frac{u^7}{7!} + \cdots$$

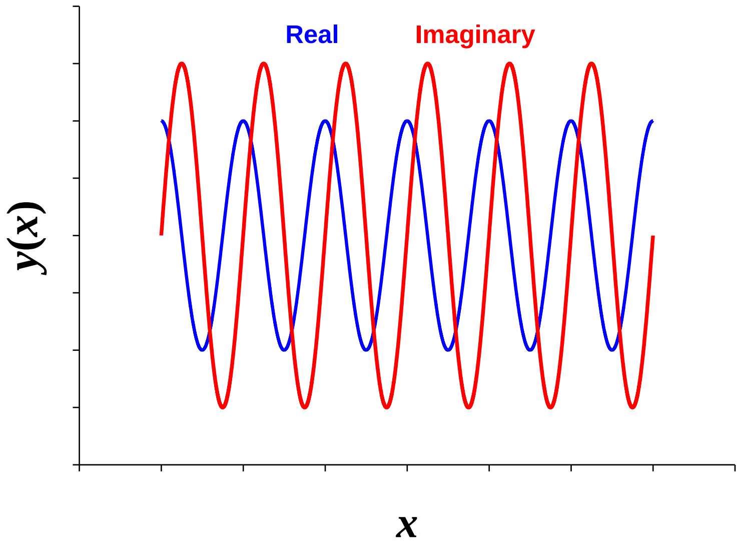
$$e^{\pm ix} = \cos(x) \pm i\sin(x)$$

gives

and

$$\begin{aligned} y(x) &= c_1 e^{ix} + c_2 e^{-ix} \\ &= c_1\left[\cos(x) + i\sin(x)\right] + c_2\left[\cos(x) - i\sin(x)\right] \\ &= (c_1 + c_2)\cos(x) + (c_1 - c_2)i\sin(x) \\ &= c_3\cos(x) + ic_4\sin(x) \end{aligned}$$

Standing Waves



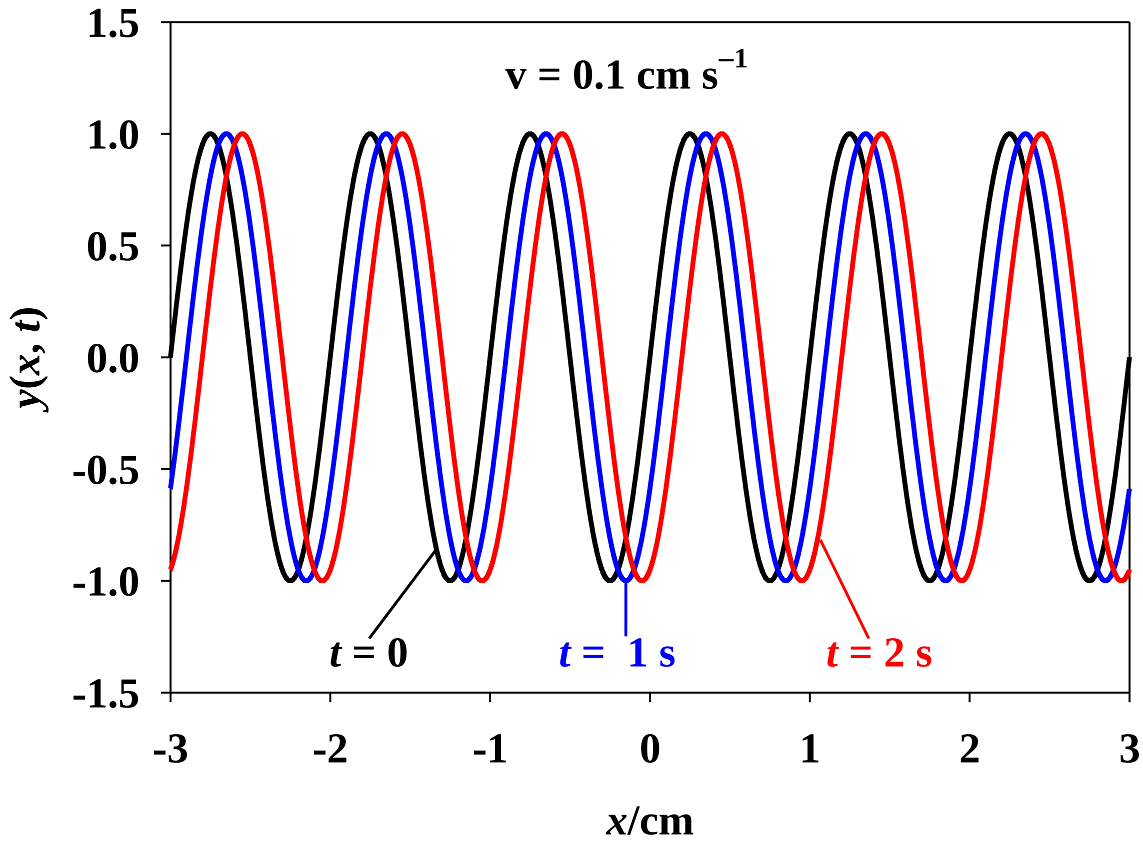
$c_3\cos(x)$

$c_4\sin(x)$

Traveling (Time-Dependent) Waves

sine wave moving to the right at speed v

$$y(x, t) = \sin[2\pi(x - \mathrm{v}t)]$$



It obeys the one-dimensional wave equation

$$\frac{\partial^2 y(x,t)}{\partial t^2} = \mathrm{v}^2 \frac{\partial^2 y(x,t)}{\partial x^2}$$

Wave equation in three dimensions:

$$\frac{\partial^2 u(x,y,z,t)}{\partial t^2} = \mathrm{v}^2 \nabla^2 u(x,y,z,t)$$

The wave velocity is v.

Complex functions are important in quantum mechanics. **Examples:**

a) Solving the **time-dependent Schrodinger equation** gives

wave function $$\Psi(x,y,z,t) \;=\; \psi(x,y,z)\mathrm{e}^{-i2\pi Et/h}$$

probability distribution function $$\Psi^*(x,y,z,t)\,\Psi(x,y,z,t)$$

b) The **2p orbitals** for the hydrogen atom are

$$\frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{5/2} r\,\mathrm{e}^{-r/2a_0}\sin\theta\,\mathrm{e}^{+i\phi}$$

$$\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{5/2} r\,\mathrm{e}^{-r/2a_0}\cos\theta$$

$$\frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{5/2} r\,\mathrm{e}^{-r/2a_0}\sin\theta\,\mathrm{e}^{-i\phi}$$