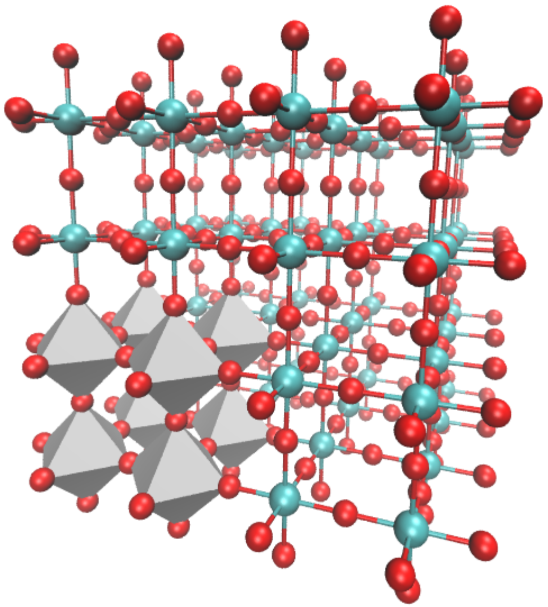
Calculus and Differential Equations



Prof. Lee M. Thompson

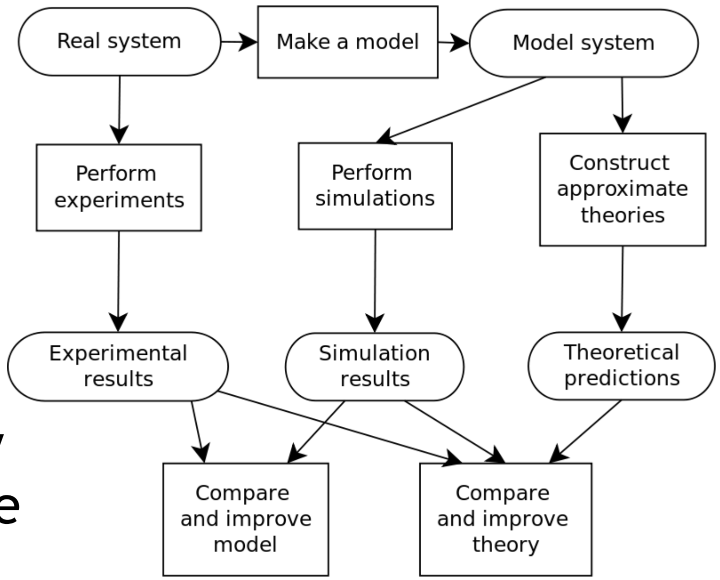
Introduction

Computers in chemistry

- Scientific understanding
  - Experiment
  - Theory
  - Simulation

- Theoretical chemistry
  - Apply math and physics to chemistry
  - Only one particle QM system solvable
  - Require numerical solutions

- Computational chemistry
  - Develop computer codes
  - Design efficient algorithms
  - Apply as a tool of investigation



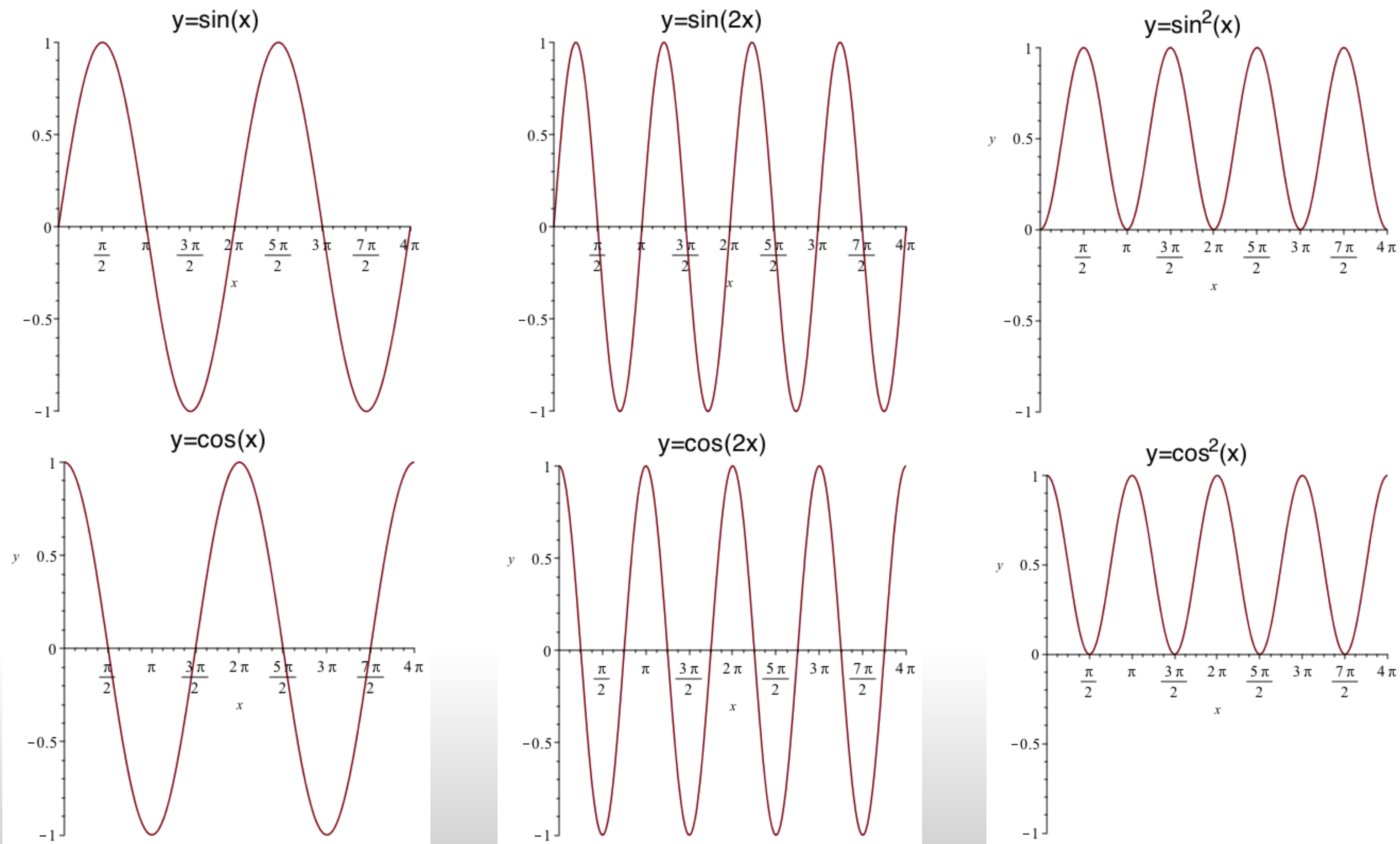
Introduction

Theoretical Chemistry

- Electronic structure theory
  - Motions of electrons in molecules
  - Properties of molecules
  - Potential energy surfaces
- Dynamics
  - Solve equations of motion of molecules
  - Use quantum or classical calculated surface
  - Obtain reaction rates
- Statistical Mechanics
  - Solve bulk properties of molecules
  - Use properties of individual molecules

Basics

Trigonometric functions



Basics

Trigonometric identities

$$\sin^2 x + \cos^2 x = 1$$

$$\sin(2x) = 2\sin(x)\cos(x)$$
$$\cos(2x) = 2\cos^2 x - 1$$

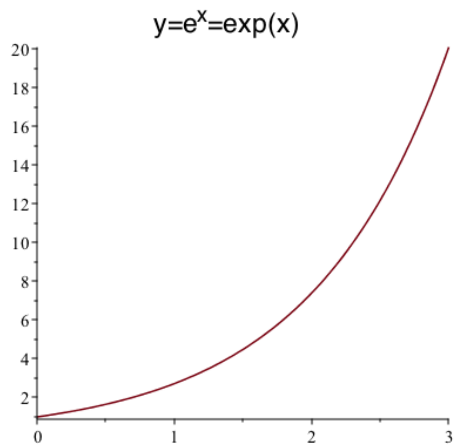
$$\sin^2 x = \frac{1}{2}(1 - \cos(2x))$$
$$\cos^2 x = \frac{1}{2}(1 + \cos(2x))$$

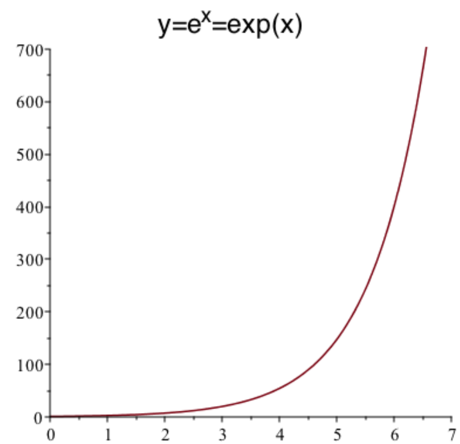
$$\frac{\sin(x)}{\sin(y)} \neq \frac{x}{y}$$
$$\sin(-x) = -\sin(x)$$
$$\cos(-x) = \cos(x)$$

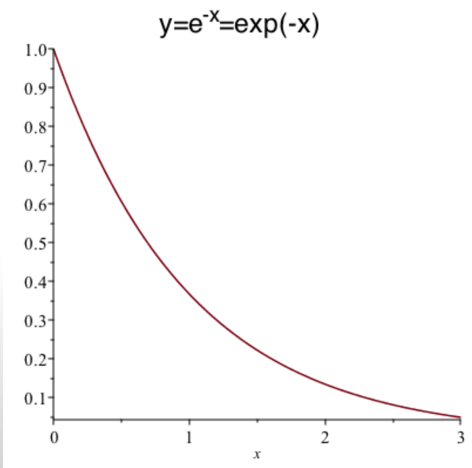
$$\tan(x) = \frac{\sin(x)}{\cos(x)}$$

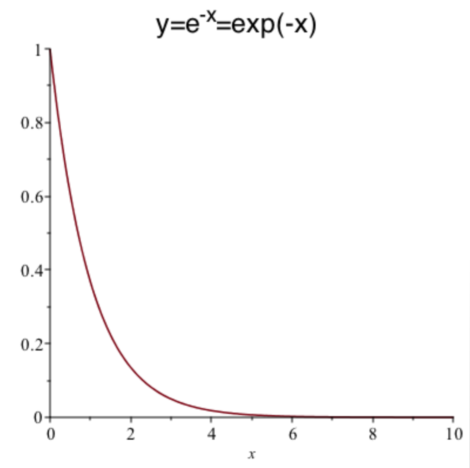
Basics

Exponential functions









sum notation

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!} = 1 + x + \frac{x^2}{2} + \ldots$$

$$e = e^1 = \sum_{n=0} \frac{1}{n!} = 2.718\ldots$$

$$e^0 = 1$$

$$e^{-\infty} = 0$$

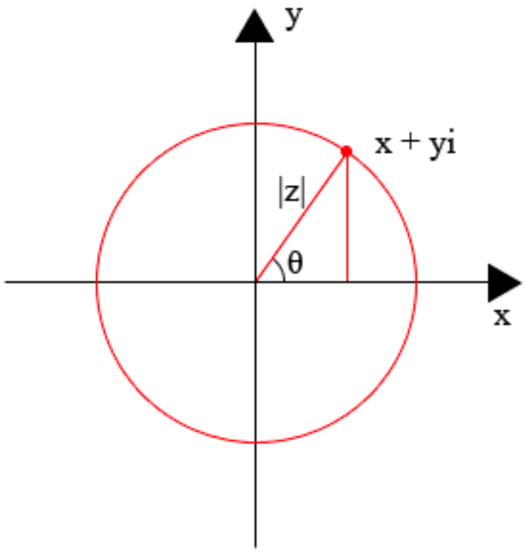
$$e^x e^y = e^{x+y}$$

$$(e^x)^y = e^{xy}$$

$$\ln(e^x) = x$$

Basics

Complex numbers



$$i^2 = -1$$

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

Euler's formula

$$(\cos(\theta) + i\sin(\theta))^n = \cos(n\theta) + i\sin(n\theta)$$

De Moivre's formula

$$z = x + iy = re^{i\theta}$$

$$x = Re(z)$$

$$y = Im(z)$$

$$z^* = x - iy$$

$$|z|^2 = zz^* = x^2 + y^2$$

$$abs(z) = |z| = r = \sqrt{x^2 + y^2}$$

$$z^{-1} = \frac{z^*}{|z|^2}$$

$$\tan(\theta) = \frac{y}{x}$$

Basics

Complex numbers

$$z = 3 + 4i$$

$$z^* = 3 - 4i$$

$$|z| = 5$$

$$z^{-1} = \frac{3 - 4i}{25}$$

$$z = 5e^{i\theta}$$

$$\tan(\theta) = 4/3$$

$$z = 2 + 3i$$

Basics

Complex numbers

$$i^* = -i$$

$$i^2 = -1$$

$$i^3 = -i$$

$$i^4 = 1$$

$$\frac{1}{i} = -i$$

$$\exp(i\pi) = -1$$

$$\exp\left(\frac{i\pi}{2}\right) = i$$

$$\exp\left(\frac{i\pi}{4}\right) = \frac{1}{\sqrt{2}}(1+i)$$

$$(i^2)^* =$$

$$i^5 =$$

$$\frac{1}{i^2} =$$

$$\frac{1}{i^3} =$$

$$\exp(-i\pi) =$$

$$\exp\left(\frac{-i\pi}{2}\right) =$$

$$\exp\left(\frac{-i3\pi}{4}\right) =$$

Basics

Complex numbers

$$i^* = -i$$

$$i^2 = -1$$

$$i^3 = -i$$

$$i^4 = 1$$

$$\frac{1}{i} = -i$$

$$\exp(i\pi) = -1$$

$$\exp\left(\frac{i\pi}{2}\right) = i$$

$$\exp\left(\frac{i\pi}{4}\right) = \frac{1}{\sqrt{2}}(1+i)$$

$$(i^2)^* = -1$$

$$i^5 = i$$

$$\frac{1}{i^2} = -1$$

$$\frac{1}{i^3} = i$$

$$\exp(-i\pi) = -1$$

$$\exp\left(\frac{-i\pi}{2}\right) = -i$$

$$\exp\left(\frac{-i3\pi}{4}\right) = -\frac{1}{\sqrt{2}} + i\frac{1}{\sqrt{2}}$$

Calculus

Differentiation

$$\frac{d}{dx}x^n = nx^{n-1}$$

$$\frac{d}{dx}\sin(x) = \cos(x)$$

$$\frac{d}{dx}\cos(x) = -\sin(x)$$

$$\frac{d}{dx}e^x = e^x$$

$$\frac{d}{dx}C = \frac{d}{dx}Cx^0 = 0$$

$$\frac{d}{dx}x = \frac{d}{dx}x^1 = 1$$

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

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

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

$$\frac{d}{dx}\sin(ax) = a\frac{d}{dax}\sin(ax) = a\cos(ax)$$

$$\frac{d}{dx}e^{ax} = a\frac{d}{dax}e^{ax} = ae^{ax}$$

Calculus

Product Rule

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

$$\frac{d}{dx}\sin(x)\cos(x) = \sin(x)\frac{d}{dx}\cos(x) + \cos(x)\frac{d}{dx}\sin(x)$$

$$= -\sin^2(x) + \cos^2(x)$$

$$\frac{d}{dx}\sin(x)e^{ax} = \sin(x)\frac{d}{dx}e^{ax} + e^{ax}\frac{d}{dx}\sin(x)$$

$$= e^{ax}(a\sin(x) + \cos(x))$$

Calculus

Chain Rule

$$\frac{d}{dx}f(g(x)) = \frac{df}{dg}\frac{dg}{dx}$$

$$\frac{d}{dx}\sin^2(x) = \frac{d}{d\sin(x)}\sin^2(x)\frac{d}{dx}\sin(x) = 2\sin(x)\cos(x)$$

$$\frac{d}{dx}\exp(-2x^2) = \frac{d}{d(-2x^2)}\exp(-2x^2)\frac{d}{dx}(-2x^2) = -4x\exp(-2x^2)$$

Quotient Rule

$$\frac{d}{dx}\frac{f(x)}{g(x)} = \frac{g(x)\frac{df(x)}{dx} - f(x)\frac{dg(x)}{dx}}{g(x)^2}$$

$$\frac{d}{dx}\frac{\sin^2(x)}{2x} = \frac{4x\sin(x)\cos(x) - 2\sin^2(x)}{4x^2} = \frac{\sin(x)\cos(x)}{x} - \frac{\sin^2(x)}{2x^2}$$

Calculus

Practice

$$\frac{d}{dx}\exp(i2x) =$$

$$\frac{d}{dx}\cos(\pi x)\exp(i2x) =$$

$$\frac{d}{dx}\cos(3\pi x) =$$

$$\frac{d}{d\theta}\cos(\pi\sin(\pi\theta)) =$$

$$\frac{d}{dx}\cos^2(\pi x) =$$

$$\frac{d}{dx}\frac{e^{2x}}{ix} =$$

Calculus

Practice

$$\frac{d}{dx}\exp(i2x) = e^{i2x} \times i2$$

$$\frac{d}{dx}\cos(\pi x)\exp(i2x) =$$
$$\cos(\pi x)\exp(i2x)i2 - \sin(\pi x)\pi\exp(i2x)$$

$$\frac{d}{dx}\cos(3\pi x) = -\sin(3\pi x) \times 3\pi$$

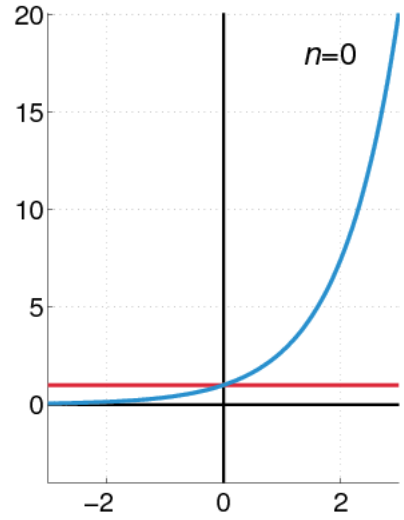
$$\frac{d}{d\theta}\cos(\pi\sin(\pi\theta)) =$$
$$-\sin(\pi\sin(\pi\theta)) \times \pi\cos(\pi\theta) \times \pi$$

$$\frac{d}{dx}\cos^2(\pi x) =$$
$$2\cos(\pi x) \times -\sin(\pi x) \times \pi$$

$$\frac{d}{dx}\frac{e^{2x}}{ix} = \frac{ie^{2x}}{x^2}(1 - 2x)$$

Calculus

Taylor series



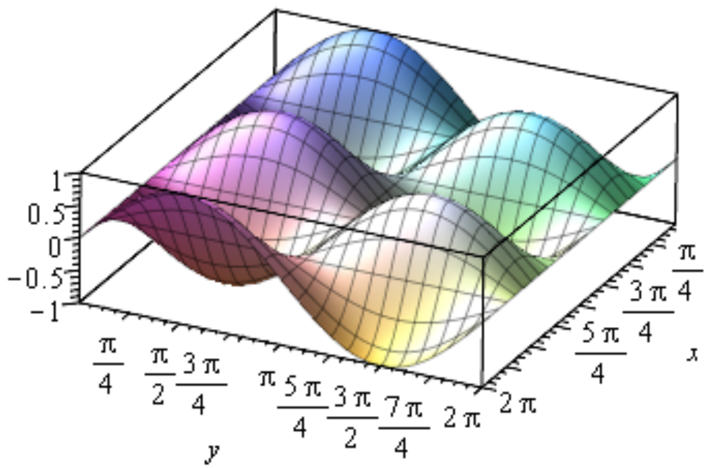
$$f(x) = f(a) + \frac{1}{1!}\frac{d}{dx}f(a)(x-a) + \frac{1}{2!}\frac{d^2}{dx^2}f(a)(x-a)^2 + \frac{1}{3!}\frac{d^3}{dx^3}f(a)(x-a)^3 + \cdots$$

$$f(x) = \sum_{n=0}^{\infty} \frac{1}{n!}\frac{d^n}{dx^n}f(a)(x-a)^n$$

$$\frac{d^n}{dx^n} = \frac{d}{dx}\frac{d}{dx}\frac{d}{dx}\ldots\text{n times}$$

Calculus

Partial differentiation



$$\frac{\partial}{\partial x} f(x,y)$$

$$\frac{\partial}{\partial x}\sin(x)\cos(y) = \left(\frac{d}{dx}\sin(x)\right)\cos(y) = \cos(x)\cos(y)$$

$$\frac{\partial}{\partial x} x\sin(xy) = \left(\frac{d}{dx}x\right)\sin(xy) + x\left(\frac{d}{dx}\sin(xy)\right) = \sin(xy) + xy\cos(xy)$$

Calculus

Partial differentiation

$$\frac{\partial}{\partial x}\cos(2\pi x + 3\pi y) =$$

$$\frac{\partial}{\partial y}\exp(-i\pi x y) =$$

Calculus

Partial differentiation

$$\frac{\partial}{\partial x}\cos(2\pi x+3\pi y)=-\sin(2\pi x+3\pi y)\times 2\pi$$

$$\frac{\partial}{\partial y}\exp(-i\pi xy)=\exp(-i\pi xy)\times -i\pi x$$

Calculus

Indefinite integrals

$$\int x^n dx = \frac{1}{n+1} x^{n+1}$$

$$\int dx = x \qquad \int x dx = \frac{1}{2} x^2$$

$$\int \sin(x) dx = -\cos(x) \qquad \int \cos(x) dx = \sin(x) \qquad \int \exp(x) dx = \exp(x)$$

$$\int \sin(ax) dx = -\frac{1}{a}\cos(ax) \qquad \int \cos(ax) dx = \frac{1}{a}\sin(ax)$$

$$\int \exp(ax) dx = \frac{1}{a}\exp(ax)$$

Calculus

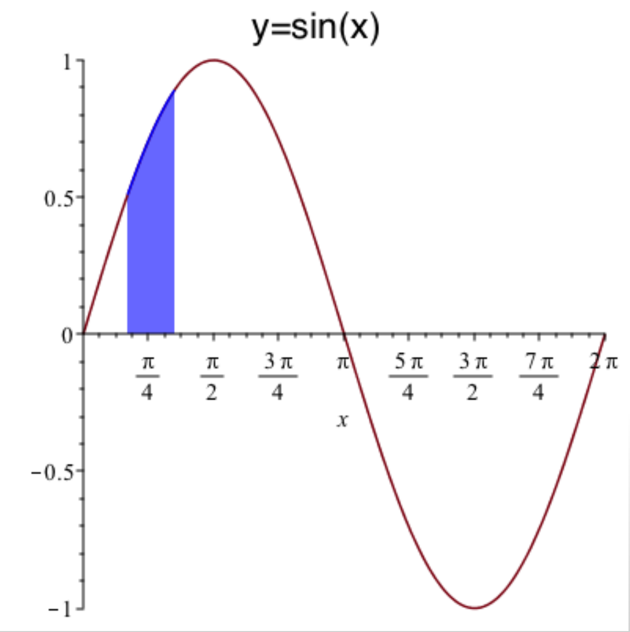
Definite integrals

$$\int_a^b f(x)dx = \left[\int f(x)dx\right]_{x=b} - \left[\int f(x)dx\right]_{x=a}$$

$$\int_a^b \sin(x)dx = \left[\int \sin(x)dx\right]_{x=b} - \left[\int \sin(x)dx\right]_{x=a}$$

$$= \left[-\cos(x)\right]_{x=b} - \left[-\cos(x)\right]_{x=a}$$

$$= \cos(a) - \cos(b)$$



Calculus

Definite integrals

$$\int_a^b \sin(\pi x)dx =$$

$$\int_a^b \exp(-i\pi x)dx =$$

$$\int_0^\infty \exp(-x)dx =$$

$$\int_0^1 \sin(2\pi\theta)d\theta =$$

Calculus

Definite integrals

$$\int_a^b \sin(\pi x)dx = \left[\frac{-\cos(\pi x)}{\pi}\right]_a^b$$

$$\int_a^b \exp(-i\pi x)dx = \left[\frac{\exp(i\pi x)}{-i\pi}\right]_a^b$$

$$\int_0^\infty \exp(-x)dx = \left[\frac{\exp(-x)}{-1}\right]_0^\infty = 0-(-1) = 1$$

$$\int_0^1 \sin(2\pi\theta)d\theta = \left[\frac{-\cos(2\pi\theta)}{2\pi}\right]_0^1 = -\frac{1}{2\pi} - \left(-\frac{1}{2\pi}\right) = 0$$

Calculus

Integration by partial fractions

$$I = \int \frac{1}{x^2 + x} dx = \int \frac{1}{x(x+1)} dx = \int \left(\frac{1}{x} - \frac{1}{x+1} \right) dx$$

$$= \ln x - \ln(x+1) + C = \ln\left(\frac{x}{x+1} \right) + C$$

$$\frac{1}{x(x+1)} = \frac{A}{x} + \frac{B}{x+1}$$

$$1 = \frac{Ax(x+1)}{x} + \frac{Bx(x+1)}{x+1}$$

$$1 = A(x+1) + Bx$$

$$x = 0; A = 1$$

$$x = -1; B = -1$$

Integration by substitution

$$I = \int \frac{1}{\sqrt{1 - x^2}} dx \qquad x = \sin(u) \Rightarrow dx = \cos(u) du$$

$$I = \int \frac{1}{\sqrt{1 - \sin^2(u)}} \cos(u) du = \int \frac{1}{\sqrt{\cos^2(u)}} \cos(u) du = \int du = u + C$$

Calculus

Integration by parts

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

Product rule

$$f(x)g(x) = \int f(x)\frac{d}{dx}g(x)dx + \int g(x)\frac{d}{dx}f(x)dx$$

$$\int f(x)\frac{d}{dx}g(x)dx = f(x)g(x) - \int g(x)\frac{d}{dx}f(x)dx$$

$f(x)$ | $\frac{d}{dx}g(x)$

I	L	A	T	E
n	o	l	r	x
v	g	g	i	p
e	a	e	g	o
r	r	b	o	t
s	i	r	n	n
e	t	a	o	e
	h		m	n
	m		e	t
			t	i
			r	a
			i	l
			c	

$$I = \int x\sin(x)dx \qquad f(x) = x \qquad \frac{d}{dx}g(x) = \sin(x)$$

$$\frac{d}{dx}f(x) = 1 \qquad g(x) = -\cos(x)$$

$$I = -x\cos(x) + \int \cos(x)dx = -x\cos(x) + \sin(x) + C$$

Calculus

Lagrange undetermined multipliers

Want to find the solutions of a function subject to one (or more) constraints

e.g. what is the minimum value of the function

$$f(x,y,z) = (x-2)^2 + (y+4)^2 + (z-4)^2$$

subject to the constraint

$$x^2 + y^2 + z^2 = 1$$

Define a new function

$$\varphi(x,y,z) = f(x,y,z) + \lambda g(x,y,z)$$

Determine set of simultaneous equations by differentiating wrt x, y, z, λ

$$\frac{\partial \varphi(x)}{\partial x} = \frac{\partial f(x)}{\partial x} + \lambda \frac{\partial g(x)}{\partial x} = 0$$

from which we obtain

$$x = \frac{2}{(\lambda+1)} \qquad y = \frac{-4}{(\lambda+1)} = -2x \qquad z = \frac{4}{(\lambda+1)} = 2x$$

and plugging into the constraint and solving gives

$$x = 1/3 \qquad y = -2/3 \qquad z = 2/3$$

Differential Equations

Differential equations

- Group of equations that contain derivatives
- Describe the relation between derivatives of dependent variable (y) and independent variable (x)
- Solutions are functions of x
- A simple example:

$$y = x^3 \qquad y = x^3 + C \qquad y = x^3 + Ax + C$$

$$\frac{dy}{dx} = 3x^2 \qquad \frac{dy}{dx} = 3x^2 \qquad \frac{dy}{dx} = 3x^2 + A$$

$$\frac{d^2y}{dx^2} = 6x \qquad \frac{d^2y}{dx^2} = 6x$$

- **General solution** is most general that satisfies equation
- Contains constants of integration which can be determined through boundary conditions to give **particular solution**

Differential Equations

Order and Degree

- Differential equations can be grouped according to **order**
  - The highest derivative contained in an equation
  - n^{th} order differential equation has n arbitrary constants of integration
- Each order can be further classified according to **degree**
  - The highest power to which a derivative is raised after rationalization of the power

$$\frac{d^3y}{dx^3} + x\left(\frac{dy}{dx}\right)^{3/2} + x^2y = 0$$

First Order Ordinary Differential Equations

- Ordinary differential equations contain only full derivatives (no partial derivatives)

$$\frac{dy}{dx} = F(x,y) \qquad A(x,y)dx + B(x,y)dy = 0 \qquad F(x,y) = -\frac{A(x,y)}{B(x,y)}$$

- Classifications: **exact**, **separable**, **linear**, homogeneous, others

Differential Equations

Separable First Order ODEs

- Has the form

$$\frac{dy}{dx} = F(x, y) \qquad F(x, y) = f(x)g(y)$$

- Can rearrange to separate variables on both sides and integrate

$$\int \frac{1}{g(y)} dy = \int f(x) dx$$

- Example:

$$\frac{dy}{dx} = x + xy \longrightarrow \frac{dy}{dx} = (1 + y)x$$

$$\downarrow$$

$$\int \frac{1}{(1 + y)} dy = \int x dx$$

$$\downarrow$$

$$\ln(1 + y) = \frac{x^2}{2} + C \longrightarrow y = A \exp\left(\frac{x^2}{2}\right) - 1$$

Differential Equations

Exact First Order ODEs

- Has the form

$$F(x,y) = df(x,y) = \frac{\partial f(x,y)}{\partial x}dx + \frac{\partial f(x,y)}{\partial y}dy = A(x,y)dx + B(x,y)dy$$

$$\frac{\partial f(x,y)}{\partial x} = A(x,y) \qquad \frac{\partial f(x,y)}{\partial y} = B(x,y)$$

- Order of derivations should not matter so $\frac{\partial^2 f(x,y)}{\partial x \partial y} = \frac{\partial^2 f(x,y)}{\partial y \partial x}$

$$\frac{\partial A}{\partial y} = \frac{\partial B}{\partial x} \qquad A(x,y)dx + B(x,y)dy = 0 \qquad df(x,y) = 0 \Rightarrow f(x,y) = C$$

$$\partial f(x,y) = A(x,y)\partial x \Rightarrow f(x,y) = \int A(x,y)dx + g(y)$$

$$\frac{\partial f(x,y)}{\partial y} = \frac{\partial}{\partial y}\left(\int A(x,y)dx + g(y)\right) = B(x,y)$$

Differential Equations

Exact First Order ODEs

- Example:

$$x\frac{dy}{dx}+3x+y=0 \longrightarrow (3x+y)dx+xdy=0 \longrightarrow A(x,y)=3x+y \Rightarrow \frac{\partial A(x,y)}{\partial y}=1$$

$$B(x,y)=x \Rightarrow \frac{\partial B(x,y)}{\partial x}=1$$

Equal!

$$f(x,y)=\int(3x+y)dx+g(y)=C_1 \Rightarrow \frac{3x^2}{2}+yx+g(y)=C_1$$

$$\frac{\partial}{\partial y}\left(\frac{3x^2}{2}+yx+g(y)\right)=x+\frac{\partial g(y)}{\partial y}=B(x,y)=x \Rightarrow \frac{\partial g(y)}{\partial y}=0 \Rightarrow g(y)=C_2$$

$$f(x,y)=\frac{3x^2}{2}+yx=C \qquad C=C_1-C_2$$

Differential Equations

Inexact First Order ODEs

- Has the form

$$A(x,y)dx + B(x,y)dy = 0 \qquad \frac{\partial A}{\partial y} \neq \frac{\partial B}{\partial x}$$

- Can always be made exact with an integrating factor

$$\frac{\partial\{\mu(x,y)A(x,y)\}}{\partial y} = \frac{\partial\{\mu(x,y)B(x,y)\}}{\partial x}$$

- General method for finding integrating factor only exists when integrating factor is function of one variable

$$\mu(x)\frac{\partial A(x,y)}{\partial y} = \mu(x)\frac{\partial B(x,y)}{\partial x} + B(x,y)\frac{d\mu(x)}{\partial x}$$

$$\frac{1}{\mu(x)}d\mu(x) = \frac{1}{B(x,y)}\left(\frac{\partial A(x,y)}{\partial y} - \frac{\partial B(x,y)}{\partial x}\right)dx = f(x)dx$$

$$\mu(x) = \exp\left(\int f(x)dx\right)$$

Differential Equations

Inexact First Order ODEs

- Example:

$$\frac{dy}{dx} = -\frac{2}{y} - \frac{3y}{2x} \longrightarrow (4x + 3y^2)dx + 2xydy = 0 \longrightarrow A(x,y) = 4x + 3y^2 \Rightarrow \frac{\partial A(x,y)}{\partial y} = 6y$$

$$B(x,y) = 2xy \Rightarrow \frac{\partial B(x,y)}{\partial x} = 2y$$

Not equal!

$$\frac{1}{B(x,y)}\left(\frac{\partial A(x,y)}{\partial y} - \frac{\partial B(x,y)}{\partial x}\right) = \frac{2}{x}$$

$$\mu(x) = \exp\left(2\int \frac{1}{x}dx\right) = \exp(2\ln x) = x^2$$

Function of x only!

$$(4x^3 + 3x^2y^2)dx + 2x^3ydy = 0 \longrightarrow A(x,y) = 4x^3 + 3x^2y^2 \Rightarrow \frac{\partial A(x,y)}{\partial y} = 6x^2y$$

$$B(x,y) = 2x^3y \Rightarrow \frac{\partial B(x,y)}{\partial x} = 6x^2y$$

Equal!

Differential Equations

Inexact First Order ODEs

- Example:

$$A(x,y) = 4x^3 + 3x^2y^2 \Rightarrow \frac{\partial A(x,y)}{\partial y} = 6x^2y$$

$$(4x^3 + 3x^2y^2)dx + 2x^3y\,dy = 0 \qquad B(x,y) = 2x^3y \Rightarrow \frac{\partial B(x,y)}{\partial x} = 6x^2y$$

$$\downarrow$$

$$f(x,y) = \int (4x^3 + 3x^2y^2)dx + g(y) = C_1 \Rightarrow x^4 + x^3y^2 + g(y) = C_1$$

$$\downarrow$$

$$\frac{\partial}{\partial y}\left(x^4 + x^3y^2 + g(y)\right) = 2x^3y + \frac{\partial g(y)}{\partial y} = B(x,y) = 2x^3y$$

$$\frac{\partial g(y)}{\partial y} = 2x^3y - 2x^3y \Rightarrow g(y) = C_2$$

$$\downarrow$$

$$f(x,y) = x^4 + x^3y^2 = C \qquad C = C_1 - C_2$$

Differential Equations

Linear First Order ODEs

- Has the form

$$\frac{dy}{dx} + P(x)y = Q(x)$$

- Can be made exact and always integrating factor of one variable

$$\mu(x)\frac{dy}{dx} + \mu(x)P(x)y = \mu(x)Q(x)$$

Assume that

$$\frac{d\mu(x)}{dx} = \mu(x)P(x)$$

$$\mu(x)\frac{dy}{dx} + \frac{d\mu(x)}{dx}y = \mu(x)Q(x)$$

Reverse product rule

$$\frac{d}{dx}\mu(x)y = \mu(x)Q(x)$$

$$\int \frac{d}{dx}\mu(x)y\,dx = \int \mu(x)Q(x)dx \Rightarrow \mu(x)y + C_1 = \int \mu(x)Q(x)dx \qquad y = \frac{\int \mu(x)Q(x)dx - C_1}{\mu(x)}$$

$$\int \frac{1}{\mu(x)}d\mu(x) = \int P(x)dx \Rightarrow \ln(\mu(x)) = \int P(x)dx + C_2 \Rightarrow \mu(x) = \exp\left(\int P(x)dx + C_2\right)$$

Differential Equations

Linear First Order ODEs

- Example:

$$\frac{dy}{dx} + 2xy = 4x \longrightarrow \begin{array}{c} P(x) = 2x \\ Q(x) = 4x \end{array} \longrightarrow \mu(x) = \exp\left(\int 2x dx + C_2\right) = \exp\left(x^2\right)$$

$$y = \frac{\int e^{x^2} 4x dx - C_1}{e^{x^2}}$$

$$\int e^{x^2} 4x dx = 4\int e^u \sqrt{u} \frac{1}{2\sqrt{u}} du = 2\int e^u du = 2e^u + C = 2e^{x^2} + C$$

$$x = \sqrt{u} \Rightarrow dx = \frac{1}{2\sqrt{u}} du$$

Solve by substitution

$$y = \frac{2e^{x^2} + C_2 - C_1}{e^{x^2}} = 2 + Ce^{-x^2}$$

Differential Equations

Second Order Ordinary Differential Equations

- Much harder to solve in general that first order differential equations
- Example:

$$\frac{d^2y}{dx^2} = ky$$

- Models behavior of mass on spring to Schrödinger's equation for single particle in one dimensional box
- Can try to solve by thinking of function which is proportion to it's second derivative

$$y = e^{\lambda x}$$

$$\frac{d^2}{dx^2}e^{\lambda x} = \lambda^2 e^{\lambda x}$$

$$\lambda = \pm\sqrt{k}$$

- Because multiplying a function by a constant has the effect of multiplying its derivative by the same constant

$$y = Ae^{\sqrt{k}x} + Be^{-\sqrt{k}x}$$

is also a solution, where A and B are the constants of integration determined by two boundary conditions

Differential Equations

Second Order Ordinary Differential Equations

- Solve the following equation subject to the boundary conditions y=0 and dy/dx=4 when x=0:

$$\frac{d^2}{dx^2}y = 4y$$

Determine the **general solution**

$$y = Ae^{2x} + Be^{-2x} \qquad \lambda = \sqrt{k} = \sqrt{4} = 2$$

Differentiate y

$$\frac{d}{dx}y = 2Ae^{2x} - 2Be^{-2x}$$

At x=0

$$y(0) = A + B = 0 \qquad \frac{dy}{dx}(0) = 2A - 2B = 4$$

Solve the simultaneous equations for A and B

$$A = 1$$

$$B = -1$$

Substitute in to obtain the **particular solution**

$$y = e^{2x} - e^{-2x}$$

Differential Equations

Second Order Ordinary Differential Equations

- What about where k is negative?
- Example:

$$\frac{d^2y}{dx^2} = -y$$

- We obtain the general solution

$$y = Ae^{ix} + Be^{-ix}$$

- Using

$$e^{\pm i\theta} = \cos\theta \pm i\sin\theta$$

$$y = A(\cos x + i\sin x) + B(\cos x - i\sin x)$$

$$y = (A + B)\cos x + (A - B)i\sin x$$

- Can simplify equation further by introducing new arbitrary constants of integration

$$y = C\cos x + D\sin x$$

- Gives the general solution

$$y = C\cos(\sqrt{|k|}x) + D\sin(\sqrt{|k|}x)$$

Differential Equations

Second Order Ordinary Differential Equations

- Solve the following equation subject to the boundary conditions y=0 and dy/dx=8 when x=0:

$$\frac{d^2}{dx^2}y = -4y$$

Determine the **general solution**

$$y = C\cos(2x) + D\sin(2x) \qquad \lambda = \sqrt{|k|} = \sqrt{|-4|} = 2$$

Differentiate y

$$\frac{d}{dx}y = -2C\sin(2x) + 2D\cos(2x)$$

At x=0

$$y(0) = C = 0 \qquad \frac{dy}{dx}(0) = 2D = 8$$

Solve the simultaneous equations for A and B

$$C = 0$$

$$D = 4$$

Substitute in to obtain the **particular solution**

$$y = 4\sin(2x)$$

Summary

- Introduction to computational chemistry
- Basic mathematics
  - Trigonometry
  - Exponentials and logarithms
  - Complex numbers
- Calculus
  - Differentiation
  - Taylor Series
  - Partial differentiation
  - Integration
  - Lagrange multipliers
- Differential Equations
  - First order ordinary differential equations
  - Second order ordinary differential equations