Systematic physical chemistry

– theoretical chemistry –

Chapters envisaged:
- mathematics recap
- basics of quantum mechanics
- basis of quantum chemistry

Literature:
- David Z. Goodson, Mathematical Methods for Physical & Analytical Chemistry, Wiley, 2011
- Attila Szabo and Neil Ostlund, Modern Quantum Chemistry Dover, 1996

Homework: will be abbreviated as HW, letter G refers to the Goodson book, SzO refers to that of Szabo & Ostlund

Mathematics recap
– differential equations –

ordinary equation for unknown x :

$$f(x) = 2x + 3 = 0 \qquad \text{e.g.}$$

$x = -3/2$ solution for x

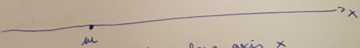
differential equation for unknown $f(x)$:

$$f'(x) = \frac{df}{dx} = \sin x \qquad \text{e.g.}$$

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

solution for $f(x)$ ⓐ

Description of the laws of nature involves lots of differential equations. E.g. Newtonian mechanics. In 1 dimension (1D):



point mass moving along axis x

we are interested in $x(t)$, where t stands for time

differential equation for unknown $x(t)$:

$F = m \cdot a$ Newton's equation

On Newton's equation in 1 D:

- $a = \frac{dv}{dt} = \frac{d^2x}{dt^2}$ acceleration

- $v = \frac{dx}{dt}$ speed, velocity

- $F = m \cdot a$ is an ordinary, second order differential equation (DE)

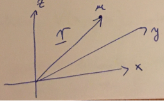
  ordinary : derivative of a 1D function is involved

  second order : second derivative is involved

- solution gives $x(t)$ when F and initial conditions are supplied; note the integration constant in ⊗ on page $\boxed{2}$

We usually work in 3D, What complications are brought about?

- point mass has 3 coordinates



$\underline{r}\,(x(t), y(t), z(t))$: position vector of point mass m in 3D; $x(t)$, $y(t)$ and $z(t)$ are the coordinates in the Cartesian system

$\underline{r}$ is an arrow possessing length & orientation

⊖ What else is a vector?

derivatives of $\underline{r}$: $\underline{v} = \frac{d\underline{r}}{dt} = \left(\frac{dx}{dt}, \frac{dy}{dt}, \frac{dz}{dt}\right)$

$$\underline{a} = \frac{d\underline{v}}{dt} = \ldots$$

the force : $\underline{F}\,(F_x, F_y, F_z)$

we speak of conservative force, when

$$F_x = -\frac{\partial}{\partial x} V(x,y,z)$$

$$F_y = -\frac{\partial}{\partial y} V(x,y,z)$$

$$F_z = \ldots$$

where $V(x,y,z)$: potential energy

note: partial derivative appears in the relation between $\underline{F}$ and V

relation between $\underline{F}$ and V in short notation:

$$\underline{F} = -\text{grad } V = -\hat{\underline{\nabla}} V$$

vector valued function of x, y, z

gradient

scalar valued function of x, y, z

$$\hat{\underline{\nabla}} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$$: nabla, a vector operator, converts a scalar field into a vector field

HW: take the example $V(x,y,z) = 5x^2 + \frac{3xz^3}{2y} - y$

and calculate $-\hat{\underline{\nabla}} V$

Newton's equation in 3D:

$$m \cdot \frac{d^2}{dt^2} \underline{r} = -\hat{\underline{\nabla}} V(x,y,z)$$

second order partial DE

Categorizing DE-s is an important thing, since it gives orientation in solution strategies.

Categorizing DE-s:

- ordinary or partial
- 1st order, 2nd order, etc
- linear or nonlinear

  ↑ involves the unknown function on the 1st power, the same applies to its derivatives
- homogeneous or inhomogeneous (applies to linear DE-s)

e.g. $f(x) + \frac{3}{2} f'(x) = 0$ homogeneous

$f(x) + \frac{3}{2} f'(x) = g(x)$ inhomogeneous

unknown function — inhomogeneous term, not depending on $f(x)$

HWs: G 14.2

Solving DE-s:

- involves constants of integration; we speak of initial conditions when $f(x_0)$, $f'(x_0)$, etc. are specified at a single x_0 value

  boundary conditions when $f(x_0)$, $f(x_1)$, $f'(x_0)$, etc. are specified, i.e. multiple x_0, x_1 values are involved
- general and particular solutions are to be distinguished

Examples for solving DE-s:

⊖ nth order ODE — when linear, its general solution involves n constants of integration

example: Newton's equation in 1D for a point mass attached to a spring

$$F = -\underset{\substack{\uparrow \\ \text{spring constant}}}{k}\, x$$

$$F = -\frac{dV}{dx} \quad ; \; V = \frac{1}{2} k x^2$$

{HW:} verify

equation: $m \dfrac{d^2x}{dt^2} = -kx$ harmonic oscillator in 1D in classical mechanics

{HW:} Is this DE linear?

solution: we guess the form of $x(t)$ as

$$x(t) = A \cdot \exp(i\omega t + \gamma)$$ ⊙

constants, i.e. independent on time

and check whether it can fulfill the DE

$$\frac{d^2x}{dt^2} = -A\omega^2 \exp(i\omega t + \gamma) = -\frac{k}{m} \cdot x$$

{HW:} verify

Newton's equation

Using the expression ⊙ on page 7 we see, that the DE is satisfied if

$$\frac{k}{m} = \omega^2$$

This is a famous result, telling that the frequency of oscillation is proportional to the square root of the spring constant.

Constants A and φ are the two constants of integration that must appear in the general solution.

HW: G 14.5

Another example for solving DE-s:

⊖ separation of variables of partial DE-s

example:

$$\frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2}$$

Fick's IInd law in 1D

$c(x,t)$: concentration at coordinate x at time t

D: empirical constant

separation step: $c(x,t) = X(x) \cdot T(t)$ a product form assumed for c

Now substitute the product form into $\boxed{1}$ on page $\boxed{8}$ to get

$$\frac{dT}{dt}\,X = D\,\frac{d^2X}{dx^2}\,T$$

$$\underbrace{\frac{1}{T}\frac{dT}{dt}}_{\text{function of } t \text{ only}} = \underbrace{\frac{D}{X}\frac{d^2X}{dx^2}}_{\text{function of } x \text{ only}}$$

$\Rightarrow$ both must be a constant depending on neither x nor t, say K

The product form hence leads to two ODE-s:

1) $\frac{1}{T}\frac{dT}{dt} = K$

2) $\frac{D}{X}\frac{d^2X}{dx^2} = K$

Further {HW}:

G 14.11

G 14.12

Solutions of 1) and 2):

1) $T(t) = T_0\, e^{-Kt}$

2) $X(x) = A \cos\left(\sqrt{\frac{K}{D}}\, x + \gamma\right)$

{HW}: verify that the the above $T(t)$ and $X(x)$ solve the appropriate DE-s

{HW}: verify that, the ~~given~~ function below is a solution of $\diamond$

$$c(x,t) = \sum_j A_j \cos\left(\sqrt{\frac{K_j}{D}}\, x + \gamma_j\right) e^{-K_j t} + Bx + C$$

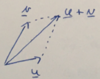
Mathematic recap
— linear algebra —

vector space : a set of elements (vectors), $\underline{u}, \underline{v}, \ldots$)
and two operations denoted + and ·
with the properties

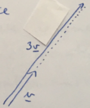
- $\underline{u} + \underline{v}$ does not leave the space
- $a \cdot \underline{v}$ — " —
- operations + and · behave as usual

(i.e. · is distributive, associative, has a unit element
+ has an inverse element)

example: vectors of 2D space



addition



multiplication by a number

Linear combination is an important concept in vector spaces

$\underline{u} = \sum \alpha_i \underline{v}_i$ is a linear combination

Note: due to the properties of vector space a linear combination does not leave the space

example: polynomials of degree N also form a vector space; take

$$u(x) = \sum_{i=1}^{N} u_j \, x^j$$

$$v(x) = \sum_{i=1}^{N} v_j \cdot x^j$$

HW: verify that $\left.\begin{array}{l} v(x) + u(x) \\ \alpha \cdot v(x) \end{array}\right\}$ are also polynomials of degree N

A more involved concept than vector space is

Hilbert space: a vector space augmented with one more operation, that is a multiplication among vectors, called inner product or scalar product denoted by $\langle \underline{u} | \underline{v} \rangle$

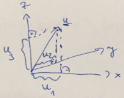
properties of the inner product:

- $\langle \underline{u} | \underline{v} \rangle = \langle \underline{v} | \underline{u} \rangle^*$ (star denotes complex conjugation)
- $\langle \underline{u} | \underline{v} + \underline{w} \rangle = \langle \underline{u} | \underline{v} \rangle + \langle \underline{u} | \underline{w} \rangle$
- $\langle \underline{u} | \alpha \underline{v} \rangle = \langle \underline{u} | \underline{v} \rangle \alpha$
- $\langle \underline{u} | \underline{u} \rangle \geq 0$ and $\langle \underline{u} | \underline{u} \rangle = 0 \Leftrightarrow \underline{u} = \underline{0}$

Note: multiplication denoted $\cdot$ multiplies a vector with a scalar, the result is a vector; multiplication denoted $\langle | \rangle$ multiplies two vectors, the result is a scalar (hence the name)

example: We are used to denoting vectors in 3D space as $\underline{u}\,(u_1, u_2, u_3)$
$\underline{v}\,(v_1, v_2, v_3)$

e.g.



and compute scalar product as

$$\langle \underline{u} | \underline{v} \rangle = \sum_{i=1}^{3} u_i^* v_i \, .$$

Does this fulfill the axioms of $\langle | \rangle$?

Let us see

$$\ominus \; \langle \underline{v} | \underline{u} \rangle^* = \left(\sum_{i=1}^{3} v_i^* u_i \right)^* = \sum_{i=1}^{3} v_i u_i^* = \langle \underline{u} | \underline{v} \rangle \quad \checkmark$$

$$\ominus \; \sum_{i=1}^{3} u_i^* (v_i + w_i) = \langle \underline{u} | \underline{v} + \underline{w} \rangle = \sum_{i=1}^{3} u_i^* v_i + \sum_{i=1}^{3} u_i^* w_i =$$

$$= \langle \underline{u} | \underline{v} \rangle + \langle \underline{u} + \underline{w} \rangle$$

{HW:} the rest of the properties at the bottom of page 11

example: $\langle \underline{v} | \underline{u} \rangle = \int_{-1}^{1} v^*(x)\, u(x)\, dx$ is an inner product for polynomials ~~up~~ on page 11

$\boxed{\text{HW:}}$ Check that this inner product fulfills the axioms at the bottom of page 11 with the two polynomials $u(x)$ and $v(x)$ on page 11

Things about inner products:

- length of a vector : $|\underline{v}| = \sqrt{\langle \underline{v} | \underline{v} \rangle}$

  e.g. $\underline{v}(v_1, v_2, v_3)$; $|\underline{v}| = \sqrt{\sum_i |v_i|^2}$ for 3D vectors

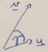
  $v(x) = 3 + 2x + 5x^2$; $|v(x)| = \sqrt{\int_{-1}^{1} (3 + 2x + 5x^2)^2 dx}$

  for polynomials

- angle of two vectors : $\cos\gamma = \dfrac{\langle \underline{u} | \underline{v} \rangle}{|\underline{u}|\ |\underline{v}|}$; γ is the angle

  (note: $|\underline{u}|$ and $|\underline{v}|$ should be nonzero)

remark:



$\langle \underline{u} | \underline{v} \rangle = |\underline{u}| \cdot |\underline{v}| \cdot \cos\gamma$

is the ordinary scalar product we learn for 3D vectors

but : you can also speak of the angle between polynomials...

$\boxed{\text{HW:}}$ find the angle between the two polynomials $\underline{v}(x) = x$

$\underline{u}(x) = (3x^2 - 1)/2$

important terminology : two elements of the Hilbert space are orthogonal, when $\langle \underline{u} | \underline{v} \rangle = 0$ since $\gamma = \pi/2$ is their angle

⊖ normalizing a vector

take $\underline{v}$ and form $\underline{v}_{norm} = \frac{1}{\sqrt{\langle \underline{v} | \underline{v} \rangle}} \underline{v}$

let us check the length of $\underline{v}_{norm}$:

$$\langle \underline{v}_{norm} | \underline{v}_{norm} \rangle = \left(\frac{1}{\sqrt{\langle \underline{v} | \underline{v} \rangle}} \right)^2 \langle \underline{v} | \underline{v} \rangle = 1$$

terminology: $\underline{v}_{norm}$ is the normalized form of $\underline{v}$

⊖ ortogonal and normal set of vectors (orthonormal in short ~~ON~~, or even ON):

$$\langle \underline{v}_i | \underline{v}_j \rangle = \emptyset \quad \text{for any } i \neq j$$

$$\langle \underline{v}_i | \underline{v}_i \rangle = 1 \quad \text{for any } i$$

handy notation: $\langle \underline{v}_i | \underline{v}_j \rangle = \delta_{ij}$ where

δ_{ij}: Kronecker delta

$$\delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ \emptyset & \text{if } i \neq j \end{cases}$$

further notation: $\{\underline{v}_i\}_{i=1}^{N}$ is the set of vectors $\underline{v}_i$, N is the dimension of the set when $\underline{v}_i$ are ON

$\boxed{\text{HW:}}$ Do $v(x) = x$ and $u(x) = (3x^2 - 1)/2$ form an ON set? If not, can you ~~set~~ achieve that they become an ON set?

Important concept: expansion of a vector in terms of other vectors (c.f. linear combination).

Say that we have $\{\underline{v}_i\}_{i=1}^N$ an ON set and we seek $\omega_1, \omega_2, \dots, \omega_N$ linear combination coefficients to our vector $\underline{w}$, i.e

$$\underset{\substack{\uparrow \\ \text{we} \\ \text{know}}}{\underline{w}} = \sum_{i=1}^{N} \underset{\substack{\uparrow \\ \text{we} \\ \text{seek}}}{\omega_i} \, \underline{v}_i \quad \nwarrow \text{we know}$$

To find ω_j let us compute the scalar product

$$\langle \underline{v}_j | \underline{w} \rangle = \langle \underline{v}_j | \sum_{i=1}^{N} \omega_i \, \underline{v}_i \rangle =$$

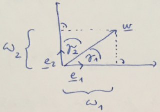
$$= \sum_{i=1}^{N} \underbrace{\langle \underline{v}_j | \underline{v}_i \rangle}_{\delta_{ij}} \omega_i = \omega_j$$

this is that we were looking for

Hence we have: $\omega_j = \langle \underline{v}_j | \underline{w} \rangle$

Terminology: ω_j are the coordinates of vector $\underline{w}$ ~~in the~~ corresponding to the ON set $\{\underline{v}_i\}_{i=1}^N$

example: $\underline{e}_1$ and $\underline{e}_2$ are the Cartesian basis vectors in 2D space and we seek coordinates of our vector $\underline{w}$



We see from the above figure that $\omega_i = |\underline{w}| \cos\gamma_i$

Now let us use the recipe from page 15

$$\omega_i = \langle \underline{e}_i \mid \underline{w} \rangle = \underbrace{|\underline{e}_i|}_{1}\, |\underline{w}| \cdot \cos\gamma_i$$

This gives the same, all right.

example with polynomials:

the ON set we take as
$$v_1(x) = 1/\sqrt{2}$$
$$v_2(x) = \sqrt{3}x/\sqrt{2}$$
$$v_3(x) = \sqrt{5}\,(3x^2 - 1)/(2\sqrt{2})$$

and we seek the coordinates of $w(x) = 1 + x + x^2$, i.e. we wish to represent $w(x)$ as

$$w(x) = \sum_{i=1}^{3} \omega_i\, v_i(x) \qquad (*)$$

again $\omega_i = \langle v_i \mid w \rangle$

In order to determine ω_1 for example we calculate

$$\omega_1 = \int_{-1}^{1} \left(\frac{1}{\sqrt{2}}\right)^* (1 + x + x^2)\, dx = \frac{1}{\sqrt{2}} \left(\underbrace{[x]_{-1}^{1}}_{2} + \frac{1}{2} \underbrace{[x^2]_{-1}^{1}}_{\emptyset} + \frac{1}{3} \underbrace{(x^3]_{-1}^{1}}_{2} \right) =$$

$$= \frac{1}{\sqrt{2}} \left(2 + \frac{2}{3}\right) = \frac{8}{\sqrt{2} \cdot 3}$$

{HW:} calculate ω_2, ω_3 and verify that ⊗ on page 16 indeed holds

Note: $\omega_1 \neq \sqrt{2}$ though you could have anticipated this, but be aware that $v_3(x)$ also involves a constant term

Some further concepts ~~with~~ about Hilbert spaces, that are often used:

basis: a set of vectors that can be used to represent any element of the space as the linear combination (i.e expansion) on page 15, ⊙

Note: several vector sets can serve as basis, a basis is not unique

dimension of the basis: the smallest number of vectors that can be collected into a set forming a basis overlap : the scalar product of basis vectors $\{\underline{v}_i\}_{i=1}^{N}$ is often called the overlap

$\langle \underline{v}_i | \underline{v}_j \rangle$: the overlap of vectors $\underline{v}_i$ and $\underline{v}_j$

this is a terminology mostly used for function spaces, see later

overlap matrix : overlap values are sometimes arranged into a table, called overlap matrix

$$\begin{pmatrix} \langle \underline{v}_1 | \underline{v}_1 \rangle & \langle \underline{v}_1 | \underline{v}_2 \rangle & \cdots \\ \langle \underline{v}_2 | \underline{v}_1 \rangle & \langle \underline{v}_2 | \underline{v}_2 \rangle & \ddots \\ \vdots & & \end{pmatrix}$$

HW: Prove, that the overlap matrix of the ON set $\{\underline{v}_i\}_{i=1}^{N}$ is the unit $N \times N$ matrix

Remark: we will see more of matrices in the next lecture linear dependence: $\{\underline{v}_i\}_{i=1}^{N}$ forms a linearly independent set if ω_i in ⊙ are all zero if and only if

$$\underline{w} = \underline{0}$$

remark: an alternative statement for linear dependence is that $\{\underline{v}_i\}_{i=1}^{N}$ is linearly dependent when the elements of the set are expressible with each other

let us check this and suppose

$$\underline{0} = \underline{w} = \sum_{i=1}^{N} \omega_i \underline{v}$$ and there are nonzero ω_i

(with this we contradict the statement on the top of the page)

express now $\underline{v}_1$ from the above to get

$$\underline{v}_1 = -\frac{1}{\omega_1} \sum_{i=2}^{N} \omega_i \underline{v}_i$$

provided that $\omega_1 = \phi$ and some $\omega_i \neq 0$ also for $i \geqslant 2$ we see $\underline{v}_1$ expressed with the others

HW: Show that an ON set, i.e. $\langle \underline{v}_i | \underline{v}_j \rangle = \delta_{ij}$ can not be linearly dependent.
Hint: start from the assumption $\underline{v}_1 = \sum_{i=2}^{N} \omega_i \underline{v}_i$

and determine ω_i based on ⊙ on page 15

HW: G 16.2 and G 16.4

A further thing on Hilbert spaces :
compleness is a property applying to them ;
it means that when a series of their elements
converges than the limit is also element of
the space

One more example for the concepts introduced.
Hilbert space of so-called square integrable
functions

$L^2(a,b)$: contains functions $f(x)$ that are
piecewise continuous on the interval
$a \leq x \leq b$ and $\langle f|f\rangle = \int_a^b f^*(x) f(x)\,dx$
is finite

inner product in $L^2(a,b)$: $\langle f|g\rangle = \int_a^b f^*(x)\, g(x)\,dx$

Function resolution in $L^2(a,b)$ means constructing
the approximation to function $g(x)$

$$g(x) \approx \sum_i \omega_i f_i(x) \qquad \boxed{\cdot}$$

where $\{f_i(x)\}_{i=1}^{N}$ is an ON set. The approximate
nature of $\boxed{\cdot}$ stems from the ON set being finite
while the space is of infite ~~dimens~~ dimension

How to determine ω_i in ▣ on page 19?

As usual:
$$\omega_i = \int_a^b f_i^*(x)\, g(x)\, dx$$

Important ON sets in $L^2(a,b)$ space:

- so-called orthogonal polynomials ◈
- Fourier basis $f_i = \frac{1}{\sqrt{2\pi}} e^{ikx}$, $k \in \mathbb{Z}$
  $a = 0$; $b = 2\pi$; i is the imaginary unit

{home study: { example 17.4 on page 273 in Goodson's book

A little more complicated set:

- spherical harmonics : see Table 17.4 on page 277 in Goodson's book

→ we have 2 variables and a more complicated scalar product
$$\langle f|g\rangle = \int_0^{2\pi} d\varphi \int_0^{\pi} d\vartheta\, f^*(\vartheta,\varphi)\, g(\vartheta,\varphi) \sin\vartheta$$
weight function

→ note: they involve single variable orthogonal polinomials, c.f. ◈, named after Legendre

Note: ON sets in Hilbert spaces have to do with DE-s, since they are solutions of PDE-s usually, c.f. Eq. (17.58) on page 278 in Goodson's book