# Quantum Mechanics
# and
# Quantum Chemistry

## Part 1: Intro & Mathematics

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# Preamble

These notes are specifically designed for the people **who want to know.** If you don't – this may be too much for you.

**If you do** - my goal is to help you to get started and give some general (sometimes a bit philosophical) and more specialized guidance in the topic of quantum mechanics.

This course is a bare minimum anyone who **wants to study quantum mechanics seriously** needs to know.
If your ultimate goals are different, you don't have to dive into each detail.

These notes were originally created for the first undergraduate Q Chem class I taught and have been extended further. This set **will be used** in the following years, although not all topics will be required for the general class or will be taught in a simplified form, but this document **is not for the Q Chem class only!**

This smaller text (and maybe annotations) are for the online reader, not if you look at the presentation in class.

This document will be **constantly updated**, but all the version should be available at the GitHub

# The Resources

## Lecture notes: **learn to create your own conspectus!**

Even though you now have this document, one point of the class is for you to learn to comprehend and compile new information, organize it, assess the relative importance of different points, find out the connections and take your own notes on how you understand the topic

## Books: **no reading – no progress!**

You may be familiar with the "no pain – no gain" concept. Reading books may be hard, especially these days, but this is an ultimate source of your knowledge. No one but you can make a qualitative change in your mind that is called the "understanding". For the qualitative changes to occur, it is important to have

## Office hours: **make sure you understand!**

The point of the office hour is for you to make sure you correctly understand the concepts and to help you to overcome some barriers

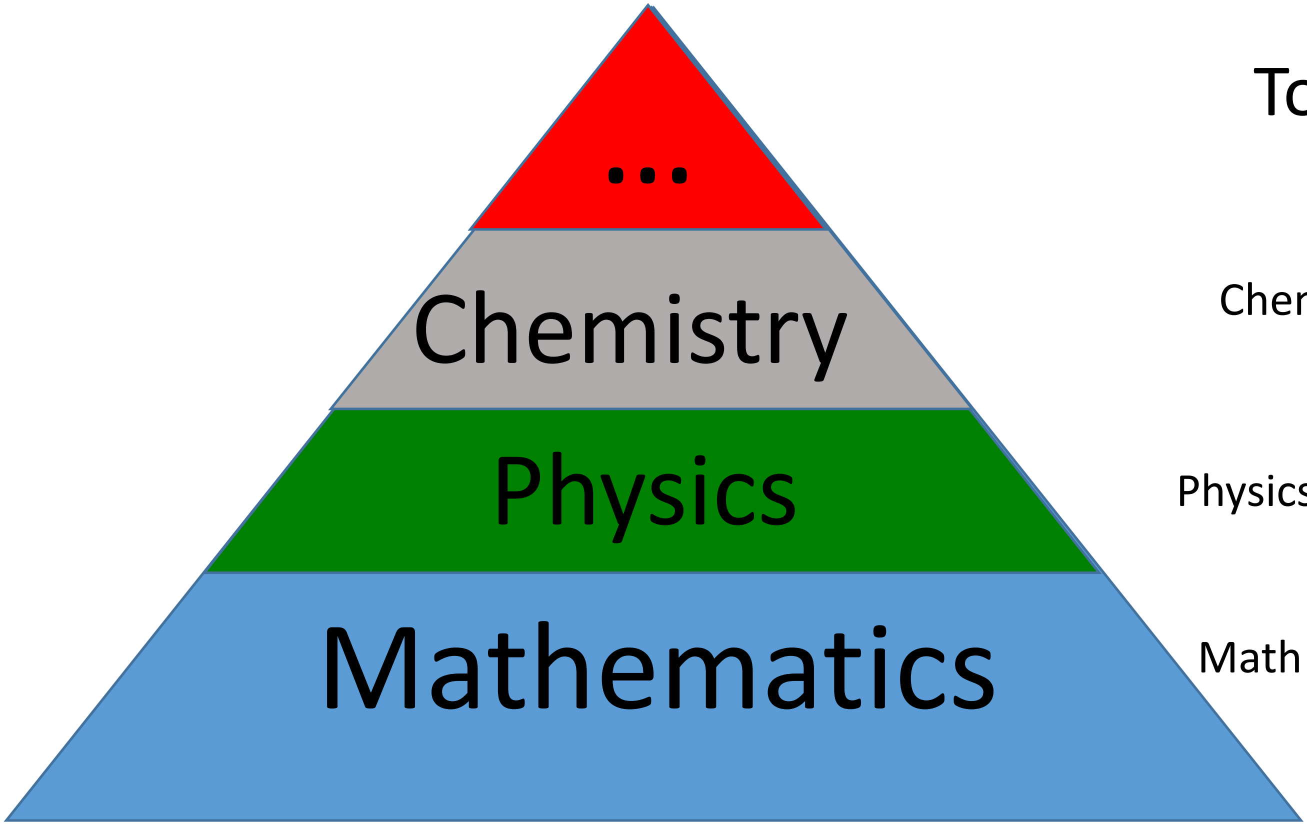
## My notes:

- Derivatory https://github.com/alexvakimov/Derivatory
- Universal notes https://github.com/alexvakimov/Universal_Lecture_Notes

## YouTube: check out my Live sessions (requests are considered)

https://www.youtube.com/channel/UCMYtg3EQNsVZK4qah6rhXTQ

# Math revision




## Tools hierarchy

Chemistry rules the world ☺

Physics is a tool in chemists' hands

Math is a tool in physicists' hands

Why do we need mathematics?
Mathematics helps to operate with physics constructions and concepts (not to understand physics!)

Physics (from the Greek, meaning "Nature") is what really happens. This is where the actual understanding is needed.

Chemistry can not be fully understood without Physics. Well, one can stay at the myphological/alchemical, intuitive or simply pragmatic level, but the modern Chemistry is not possible without Physics. By the way, knowing that molecular orbitals exist being able to use them to rationalize chemistry, but not knowing what they actually are and what one can do with them and how to obtain them is still an alchemical level of understanding. IMHO.

# Derivatives $\frac{d}{dx}$

*This little cute sign is the differential sign.*

*It is quite useful. It is a pure pleasure to compute*

*You can differentiate practically any function without efforts – the formulae are easy to remember and will save **you** many times.*

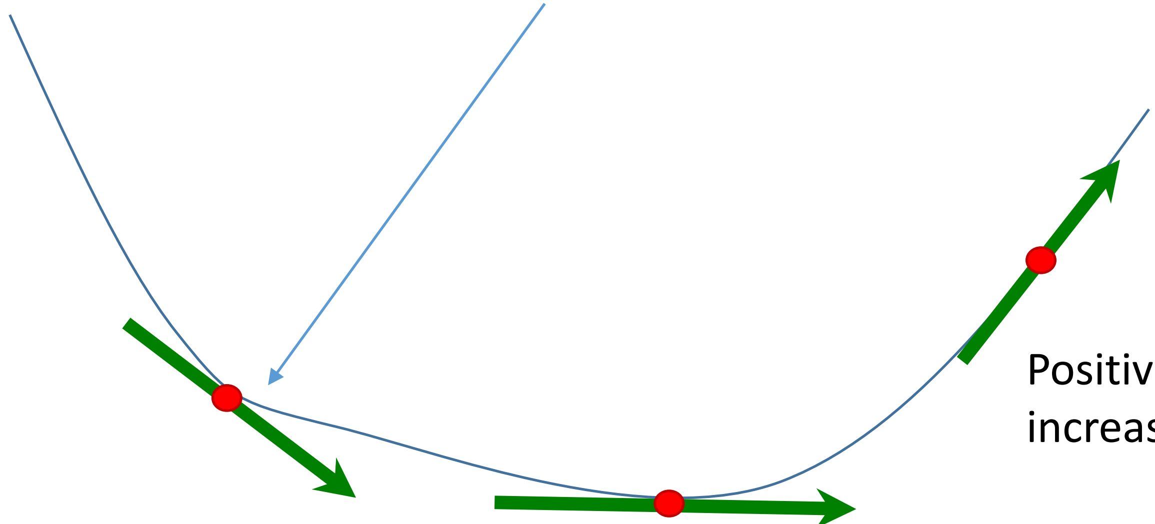
*Definitely, **the differential is your bro**.*

# Derivatives: Geometric Meaning

$$f'(x) = \frac{df}{dx} = \frac{d}{dx} f \equiv \lim_{\Delta x \to 0} \frac{f(x+\Delta x) - f(x)}{\Delta x}$$

Meaning: slope
How fast the function changes in a given point

You find derivative in a point



Positive: function increases

Negative: function is decreasing

Zero: function doesn't change constant

# Derivatives: Basic formulas

F1. $C' = 0$, where $C = const$ is a constant. Note: this can still be a function, but depending on a different argument (e.g. y).

F2. $\frac{d}{dx}\left[x^n\right] = nx^{n-1}$

- Hey, function, I'll differentiate you
- I am exp(x)
- But, I'm d/dy, ha-ha

F3a. $\frac{d}{dx}\left[a^x\right] = a^x \ln a$; F3b. $\frac{d}{dx}\left[e^x\right] = e^x$

F4a. $\frac{d}{dx}\left[\log_a(x)\right] = \frac{\log_a e}{x}$; F4b. $\frac{d}{dx}\left[\ln(x)\right] = \frac{1}{x}$

F5a. $\frac{d}{dx}\left[\sin(x)\right] = \cos(x)$; F5b. $\frac{d}{dx}\left[sh(x)\right] = ch(x)$

F6a. $\frac{d}{dx}\left[\cos(x)\right] = -\sin(x)$; F6b. $\frac{d}{dx}\left[ch(x)\right] = sh(x)$

You have to **memorize** these results

F7. $\frac{d}{dx}\left[\arcsin(x)\right] = \frac{1}{\sqrt{1-x^2}}$

Can you derive some of these results?

F8. $\frac{d}{dx}\left[\arccos(x)\right] = -\frac{1}{\sqrt{1-x^2}}$

F9. $\frac{d}{dx}\left[\arctan(x)\right] = \frac{1}{1+x^2}$ F10. $\frac{d}{dx}\left[arcctg(x)\right] = -\frac{1}{1+x^2}$

# Derivatives: Rules

R1. $\frac{d}{dx}[u+v] = u' + v'$

R2a. $\frac{d}{dx}[u \cdot v] = u'v + v'u$ ; R2b. $\frac{d}{dx}[C \cdot u] = C \cdot u'$

R3. $\frac{d}{dx}\left[\frac{u}{v}\right] = \frac{u'v - v'u}{v^2}$

R4. $\frac{d}{dx}[u(v(x))] = \frac{du}{dv}(v(x)) \cdot \frac{dv}{dx}(x)$ (chain rule)

Practice with the last

# Examples

Ex #1: Compute approximately ln(1.001) using the rules of differentiation and involving the geometric meaning of the derivative.

Solution:

$$\ln(1.001) = \ln\left(\frac{1001}{1000}\right) = \ln(1001) - \ln(1000) = \frac{\ln(1001) - \ln(1000)}{1}$$

Since 1 is much smaller than 1000, it can be considered an infinitesimally small value (small and large are not the absolute concepts – they are always with respect to something). That is we have

$$\lim_{dx\to 0}\frac{f(x+dx)-f(x)}{dx} \qquad \text{with} \qquad x = 1000, dx = 1, f(x) = \ln(x)$$

So we find that our expression above is the approximate derivative of $\ln(x)$

in the point $x = 1000$ so, $\dfrac{\ln(1001) - \ln(1000)}{1} \approx \dfrac{1}{1000}$

A direct calculation gives: ln(1.001) = 0.0009995 so our approximation is pretty good

# Derivatives: Where we use them

Taylor series:

$$f\left(x_0+x\right)=f\left(x_0\right)+f'\left(x_0\right)\cdot x+\frac{1}{2!}f''\left(x_0\right)\cdot x^2+\ldots+\frac{1}{n!}f^{(n)}\left(x_0\right)\cdot x^n+\ldots$$

It is said that the function f is expanded in the Taylor series around the point $x_0$

## Functions approximation

(Note: here we expand the square root function around $x_0 = 1$)

E.g. $$(x_0+dx)^{\frac{1}{2}} \approx (x_0)^{\frac{1}{2}} + \frac{1}{2}(x_0)^{-\frac{1}{2}}dx + \cdots$$

$$\sqrt{1.01} \approx 1^{\frac{1}{2}} + \frac{1}{2*1^{\frac{1}{2}}}0.01 + \cdots = 1 + 0.005 = 1.005$$

Explicit calculations give: $\sqrt{1.01} = 1.0049875 \ldots$

## Analysis of function properties

Whether the function is increasing or decreasing, maxima and minima, etc.

# Integrals $\int \cdot \, dx$

*This concentrated evil, right from the middle of hell,*
*will troll you all your life.*

*The calculations will take priceless years of your life and kilometers of paper.*

*The sign looks like a torture tool, which it is.*

*Run away from it in fear* ***– it is not your bro****.*

*But still, don't be afraid.*

# Integrals

Essentially – an inverse of the differential

if

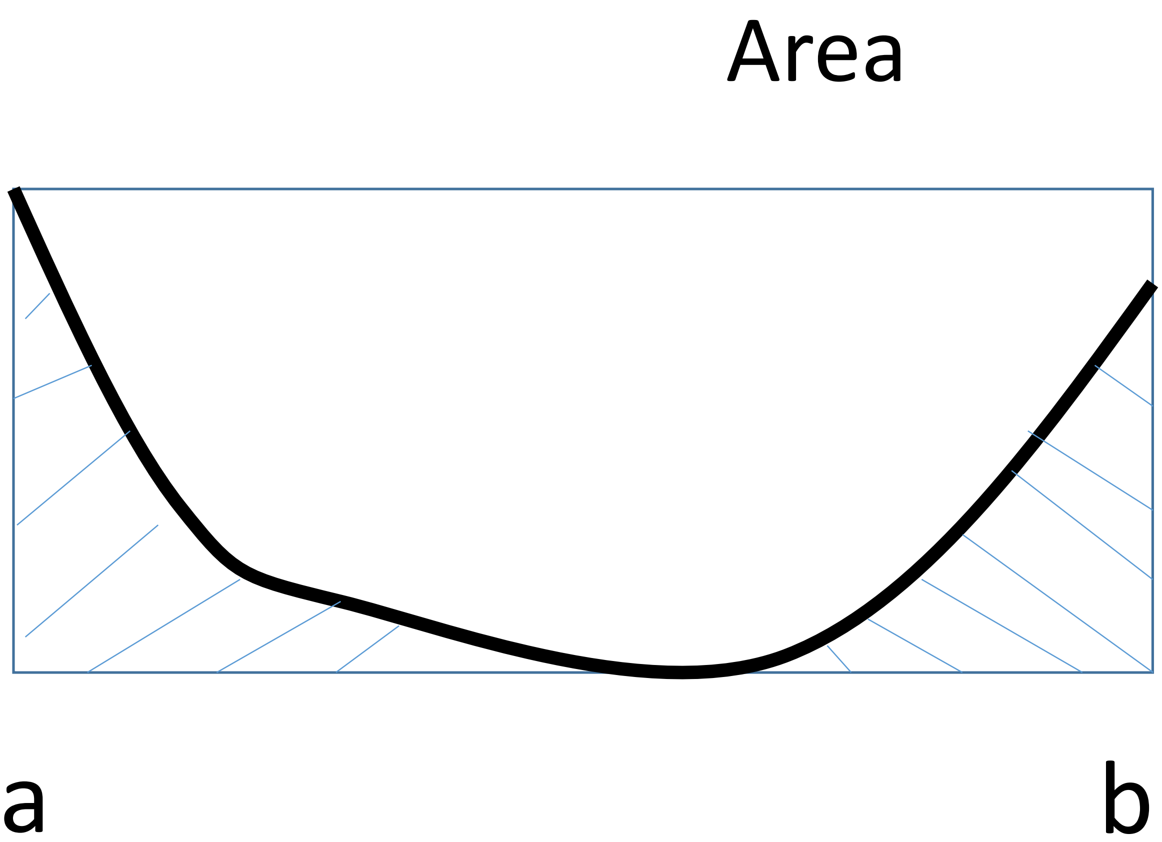
$$F'(x) = f(x), \forall x \in I$$

then

$$\int f(x)dx = \{F(x) + C\}$$

*Indefinite integral*

# Integrals: Meaning




$$\int_a^b f(x)dx = F(b) - F(a)$$

*definite integral*

# Integrals: Basic formulas

F1. $\int 0dx = C$

F2. $\int x^n dx = \frac{x^{n+1}}{n+1} + C$, $n \in Z, n \neq -1$

F3. $\int \frac{dx}{x} = \ln|x| + C$, $\forall x \in R \setminus \{0\}$

F4a. $\int \cos(x)dx = \sin(x) + C$

F4b. $\int \sin(x)dx = -\cos(x) + C$

F5a. $\int \frac{dx}{\cos^2(x)} = tg(x) + C$

F5b. $\int \frac{dx}{\sin^2(x)} = -ctg(x) + C$

F6a. $\int e^x dx = e^x + C$

F6b. $\int a^x dx = \frac{a^x}{\ln a} + C$

F7a. $\int ch(x)dx = sh(x) + C$

F7b. $\int sh(x)dx = ch(x) + C$

F8a. $\int \frac{dx}{ch^2(x)} = th(x) + C$

F8b. $\int \frac{dx}{sh^2(x)} = -cth(x) + C$

F9. $\int \frac{dx}{x^2 + a^2} = \frac{1}{a} arctg\left(\frac{x}{a}\right) + C$

F10. $\int \frac{dx}{x^2 - a^2} = \frac{1}{2a} \ln\left|\frac{x-a}{x+a}\right| + C$, $a \neq 0$ ("high" logarithm)

F11. $\int \frac{dx}{\sqrt{a^2 - x^2}} = \arcsin\left(\frac{x}{a}\right) + C$

F12. $\int \frac{dx}{\sqrt{x^2 \pm a^2}} = \ln\left|x + \sqrt{x^2 \pm a^2}\right| + C$ ("long" logarithm)

Again,

**memorize these**

Hint: in principle, if you remember derivatives, these formula can be recalled

# Integrals: Rules

R1. $\int [u(x)+v(x)]dx = \int u(x)dx + \int v(x)dx$

R2. $\int Cu(x)dx = C\int u(x)dx$

R3. If $\int u(x)dx = U(x)+C$, then $\int u(ax)dx = \frac{1}{a}U(ax)+C$

R4. If $\int u(x)dx = U(x)+C$, then $\int u(x+b)dx = U(x+b)+C$

R5. (integration by part) $\int u \cdot dv = u \cdot v - \int v \cdot du$

Practice with the last

# Methods of integration

## Change of variables

$$I = \int \sqrt{\sin(x)}\cos(x)dx \qquad I = \int \frac{xdx}{1+x^4} \qquad I = \int \frac{arctg(x)dx}{1+x^2}$$

This is why you need
to remember the basic
differentiation formula

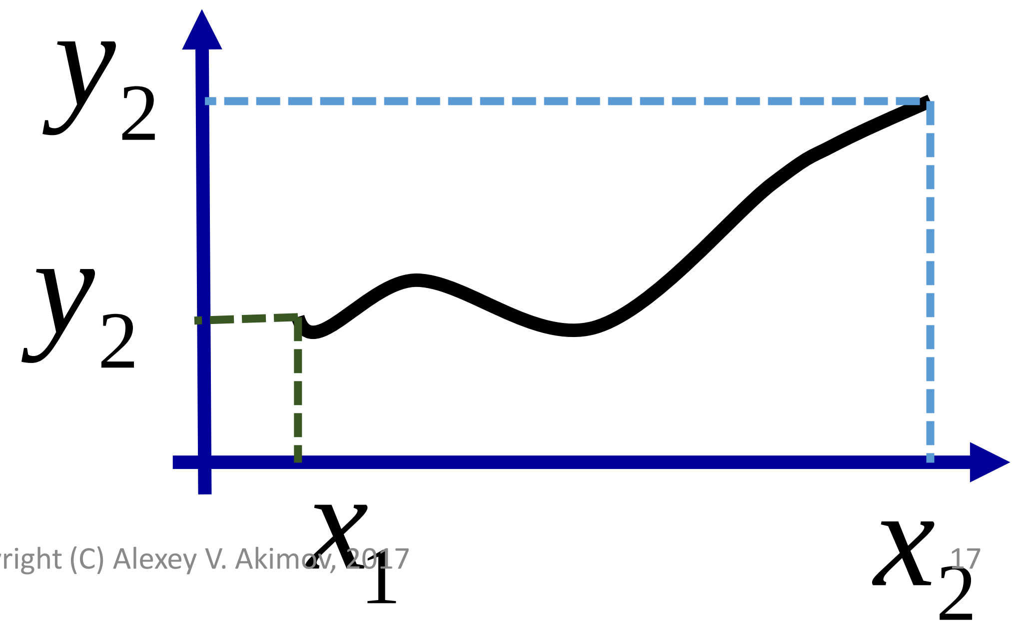
# Where we need it: Solving ODE

Homogeneous ODE, formal solution. Trivial case

$$\frac{dy}{dx} = f(x) \Rightarrow dy = f(x)dx \Rightarrow \int dy = \int f(x)dx$$

**Important!!!: limits of integration**

$$\int_{y(x_1)}^{y(x_2)} dy = \int_{x_1}^{x_2} f(x)dx$$



# Types of limits

**Boundary conditions**

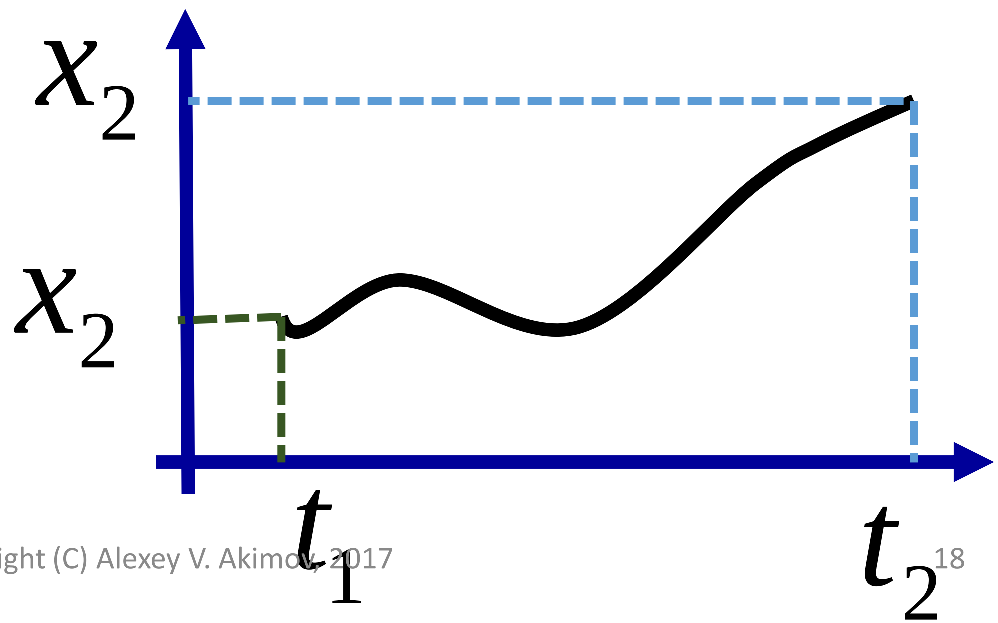
$$\frac{dy}{dx} = f\left(x\right)$$

**Initial conditions**

$$\frac{dx}{dt} = f\left(t\right)$$

How X changes in time

Solve EOM ODE = integrate EOM



# Homogeneous ODE: separation of variables

$$\frac{dy}{dx} + By(x) = 0 \Rightarrow \frac{dy}{y(x)} + Bdx = 0 \Rightarrow \int \frac{dy}{y(x)} + \int Bdx = \int 0$$

$$\int d \ln y + \int Bdx = \int 0 \Rightarrow \ln y + Bx = C \Rightarrow y = e^{C-Bx} = \tilde{C}e^{-Bx}$$

# Nonhomogeneous ODE: Variation of integration constant

$$\frac{dy}{dx} + By(x) = C$$

$$\frac{dy}{dx} + By(x) = 0$$

First solve homogeneous ODE

$$y = Ae^{-Bx}$$

A – is the integration constant

Then assume A – is not constant A = A(x)

$$y(x) = A(x)e^{-Bx}$$

and…

# Second order homogeneous ODE: Characteristic polynomial

$$ay''+by'+cy=0, a \neq 0$$

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

$$a\lambda^2 + b\lambda + c = 0$$

Two roots: $\lambda_{1,2}$ Two specific solutions: $y_i = e^{\lambda_i x}$

General solution = superposition $y = C_1 e^{\lambda_1 x} + C_2 e^{\lambda_2 x}$

Think about: Particle in the box (or general SE)

# Linear algebra

Why bother? Quantum mechanics **IS** linear algebra

In principle, QM can be formulated as an abstract mathematical theory

Born-**Heisenberg**-Jordan ("matrix mechanics")

New way of thinking: **a bit like religion**

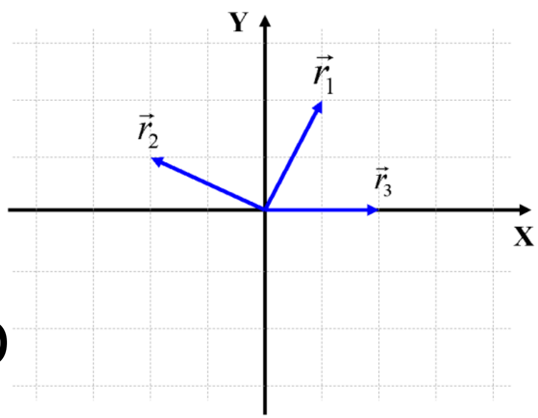
# Vectors

Vector (mathematics) = list (programming) =

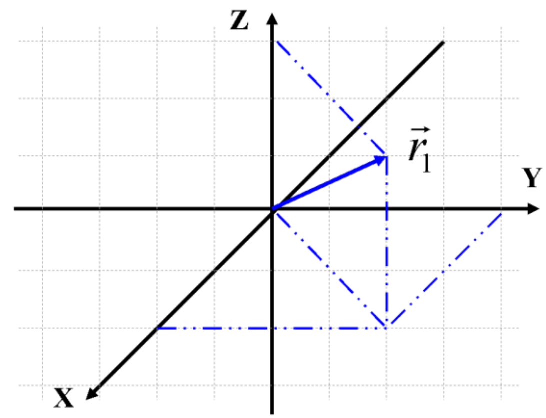
ordered set of numbers

$$\vec{a} = \begin{pmatrix} a_1 \\ a_2 \\ \ldots \\ a_N \end{pmatrix}$$

projections (components)



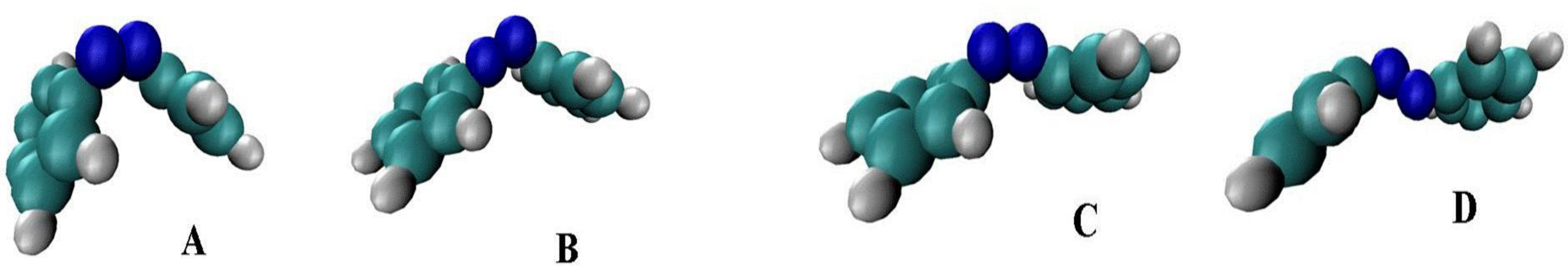

2D




3D

# Multidimensional vectors

$$\vec{R} = \begin{pmatrix} \vec{r}_1 \\ \vec{r}_2 \\ \ldots \\ \vec{r}_N \end{pmatrix} = \begin{pmatrix} x_1 & y_1 & z_1 & \ldots & x_N & y_N & z_N \end{pmatrix}^T$$



# Vector spaces

All vectors + vector addition + scalar multiplication = **vector space**

Examples:

$$R^3 \quad C^n \quad C[a,b] \quad \{\hat{A}\} \quad \{A_n\} \quad \{P_n\}$$

# Linear dependence

$\vec{a}, \vec{b}, \vec{c}, \ldots$ linearly independent if

$$\alpha \cdot \vec{a} + \beta \cdot \vec{b} + \gamma \cdot \vec{c} + \ldots = 0$$

only if

$$\alpha = \beta = \gamma = \ldots = 0$$

# Basis, dimensionality

Dimensionality of a vector space =
# of linearly-independent vectors

Basis vectors

Important:

- Basis vectors can be arbitrarily chosen (transformations)
- Other vectors of the linear space can be expressed as:

**superposition** $f = \sum_{i=1}^{n} c_i e_i$

If any = linear space is **complete**

# Euclidian spaces

$$(\cdot,\cdot): V \times V \to R(C)$$

**Scalar product (metric)**

$$(x, y) = (y, x)^*$$

$$(x + y, z) = (x, z) + (y, z)$$

$$(\alpha \cdot x, y) = \alpha^* \cdot (x, y)$$

$$(x, x) \geq 0 \qquad (x, x) = 0 \Leftrightarrow x = 0$$

Examples:

$$(x, y) = x_1^* y_1 + x_2^* y_2 + x_3^* y_3 + \ldots$$

$$(f, g) = \int_a^b f^*(x) g(x) dx$$

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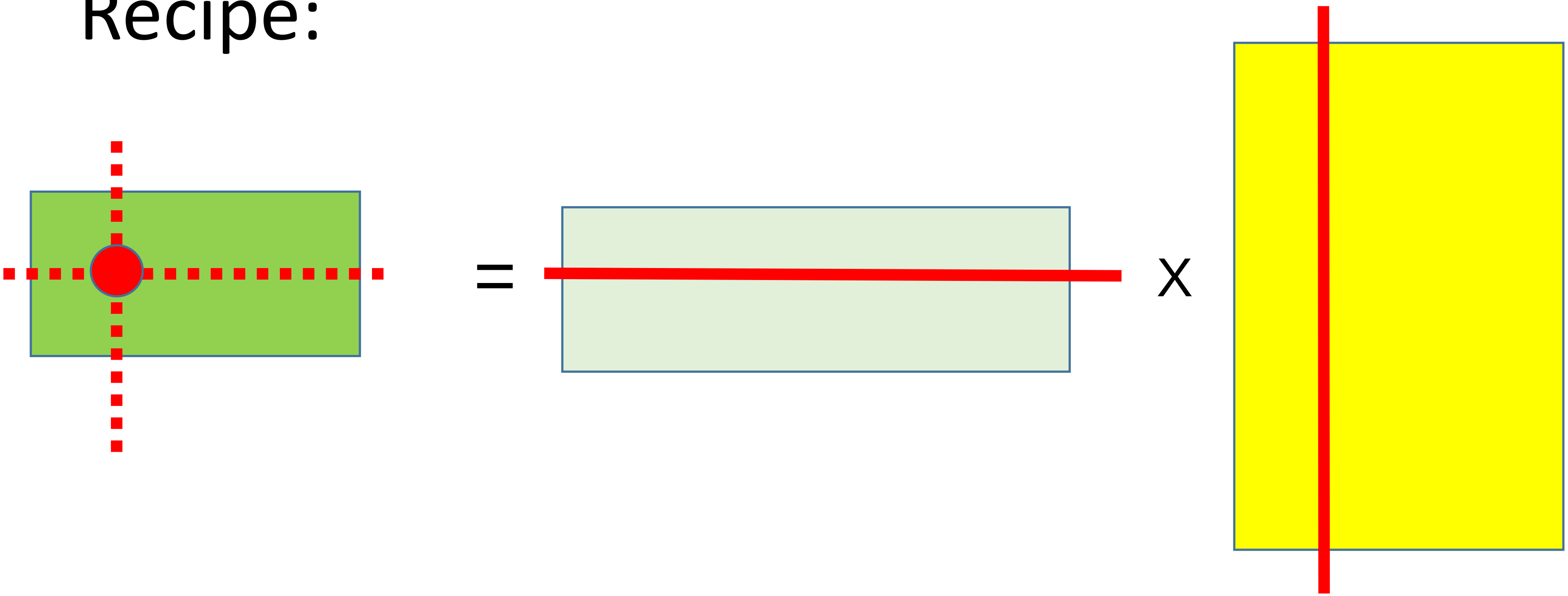
$$\|x\| = \sqrt{(x, x)}$$

**Norm**

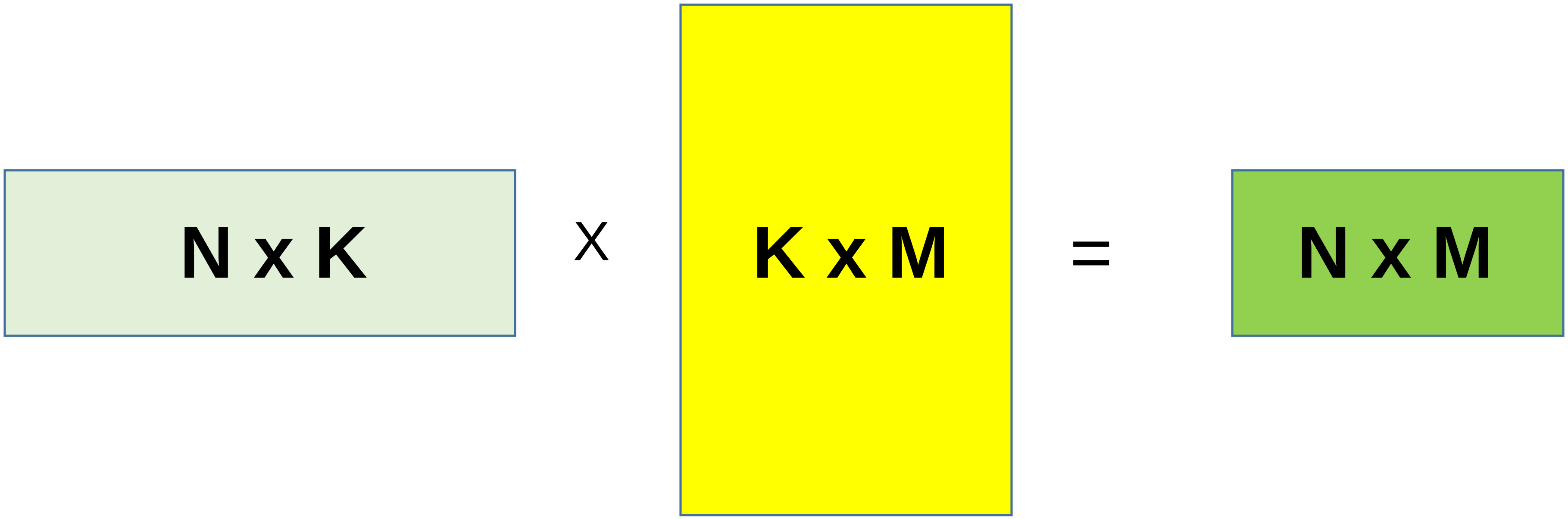
# Matrices

$$X = AB \Leftrightarrow X_{ij} = \sum_k A_{ik} B_{kj}$$

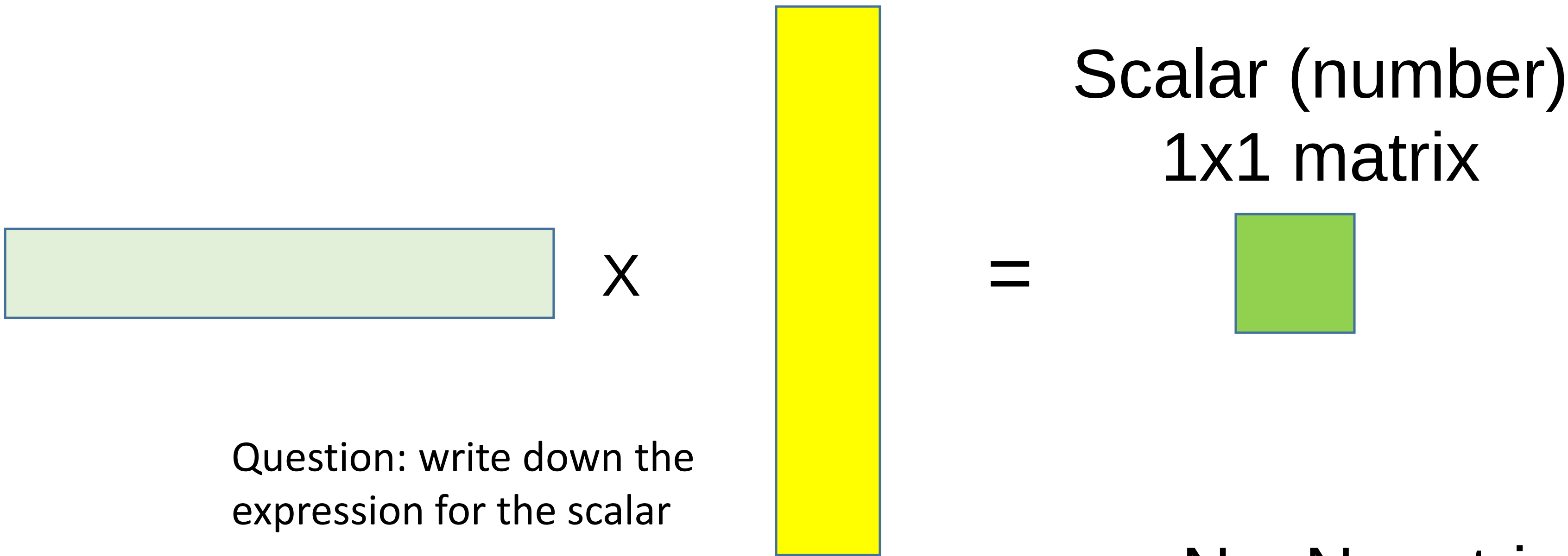
Recipe:



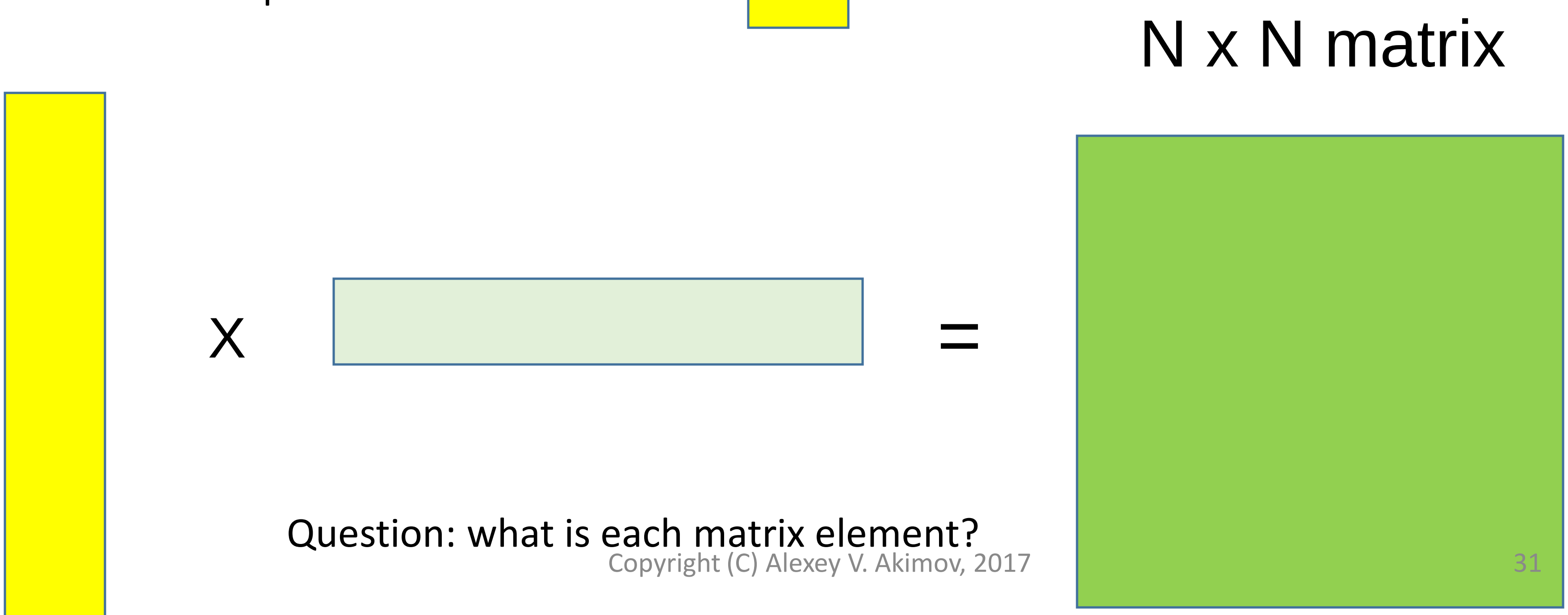
# Matrix multiplication



# Matrix multiplication




Question: write down the expression for the scalar




Question: what is each matrix element?

# Matrix operations

$A^T$ transpose $\left(A^T\right)_{ij} = A_{ji}$

$A^*$ complex conjugate $\left(A^*\right)_{ij} = \left(A_{ij}\right)^*$

$A^+ = \left(A^T\right)^* = \left(A^*\right)^T$ adjoint = Hermitian conjugate

$$\left(AB\right)^{-1} = B^{-1}A^{-1} \qquad \left(AB\right)^T = B^T A^T$$

# Product of sums

$$\left(\sum_i a_i\right)\cdot\left(\sum_i b_i\right) = ? \qquad \left(\sum_i a_i b_i\right) = ? \qquad \left(\sum_{i,i} a_i b_i\right) = ?$$

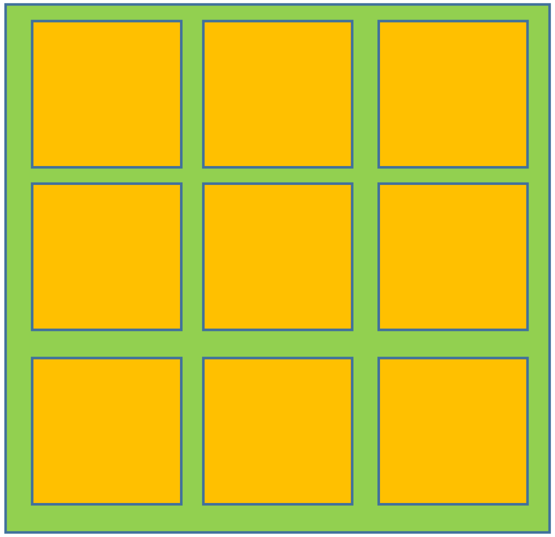
For example:

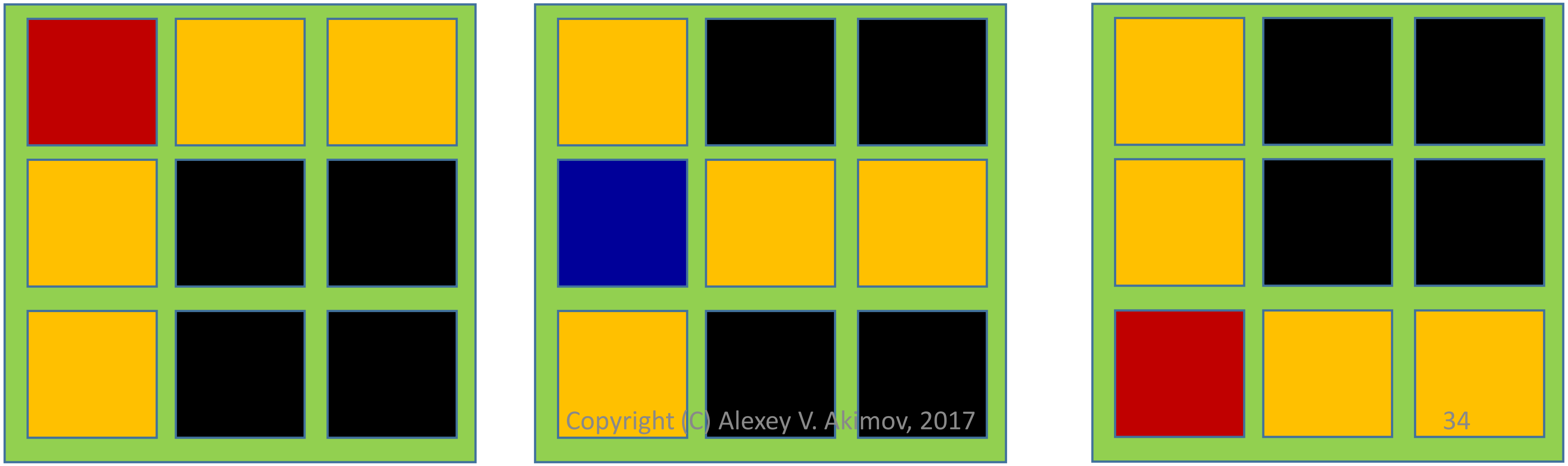
$$(a_1 + a_2 + a_3)\cdot(b_1 + b_2 + b_3) =$$
$$= a_1b_1 + a_1b_2 + a_1b_3 + a_2b_1 + a_2b_2 + a_2b_3 + a_3b_1 + a_3b_2 + a_3b_3$$

$$\left(\sum_i a_i\right)\cdot\left(\sum_i b_i\right) = \left(\sum_i a_i\right)\cdot\left(\sum_j b_j\right) = \sum_{i,j} a_i b_j$$

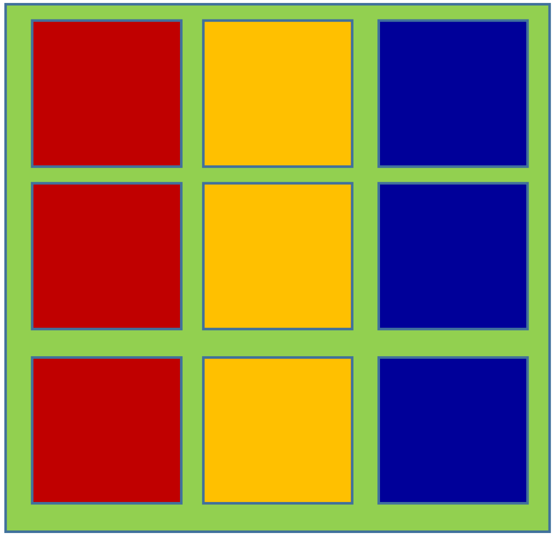
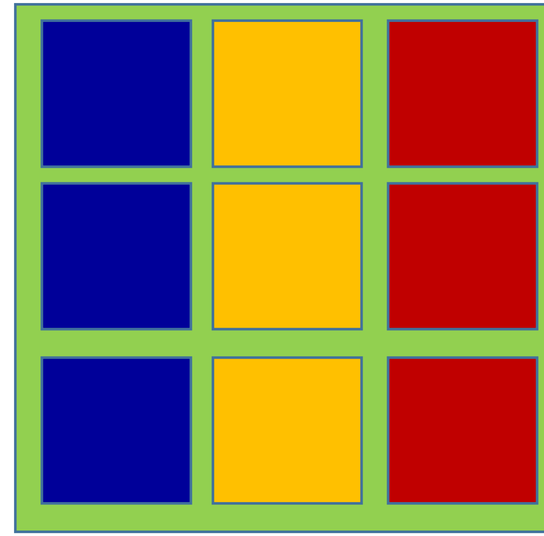
This indices are independent

# Matrix Determinant

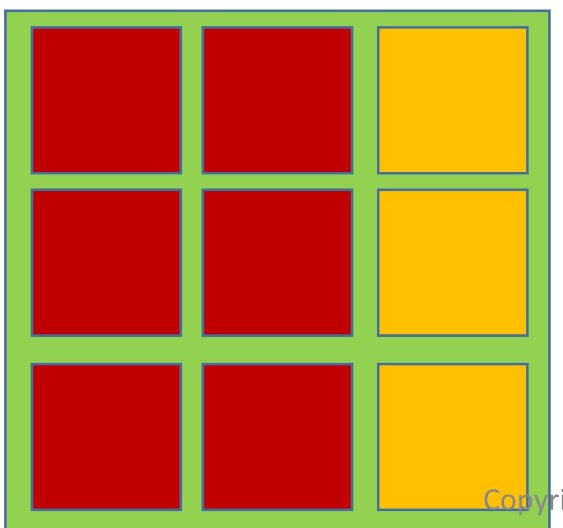
det  =



# Properties Determinant

det  = – det 

As a consequence:

det  = 0

Think about:

Slater determinant

Pauli exclusion principle

# Other properties

$$\det(A) = \sum_P (-1)^{[P]} \prod_{i=1}^{N} A_{i,P_i}$$

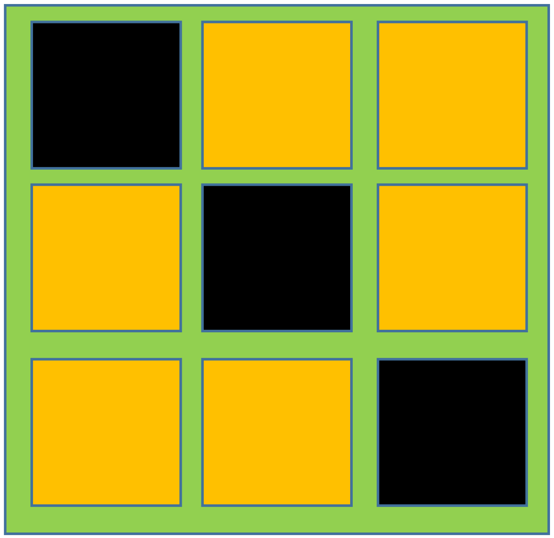
P = permutation of [1, 2, 3, …, N]. Total, there are N!

[P] = parity of the permutation

$$\det(AB) = \det(A) \cdot \det(B)$$
$$\det(A^T) = \det(A)$$

Think about: Hartree-Fock theory

# Matrix Trace



$$Tr(A) = \sum_i A_{ii}$$

$$Tr\left(A^T B\right) = \sum_{i,j} A_{ij} B_{ij}$$

Prove this: using indexing conventions

Cyclic permutations

$$Tr(ABCD) = Tr(BCDA) = Tr(CDAB) = Tr(DABC)$$

# Elements of field theory

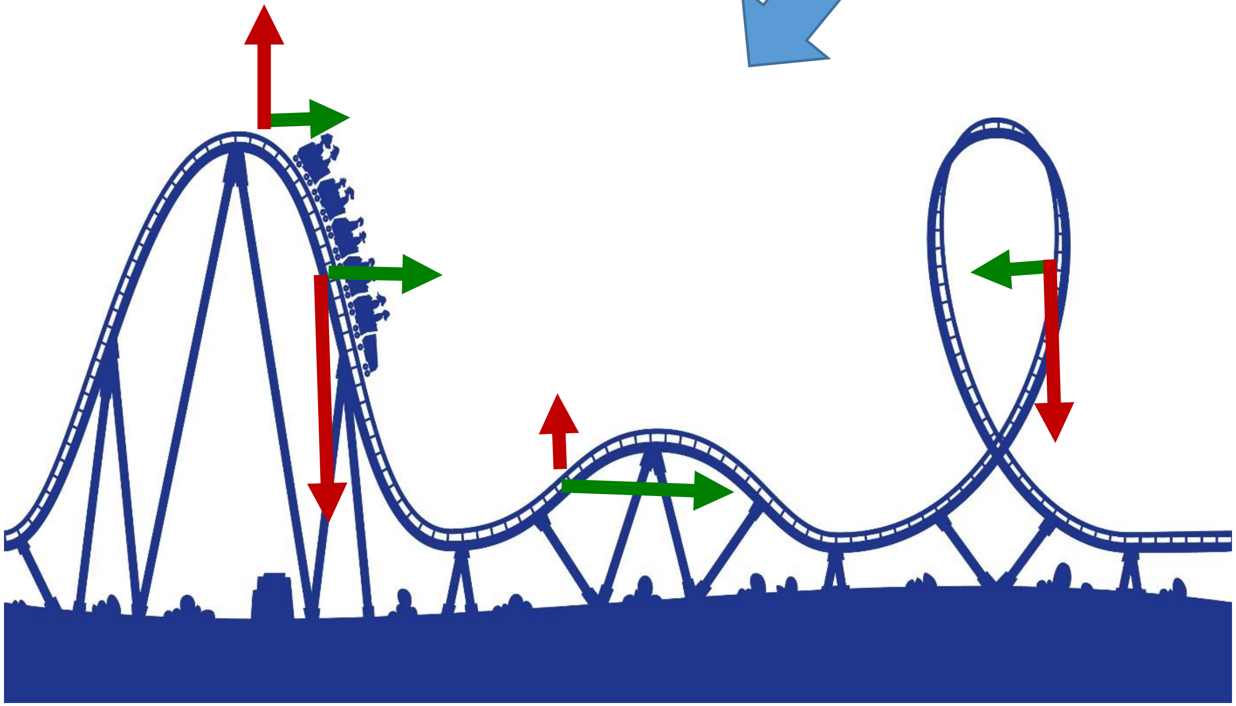
Scalar field

$$u = u(x, y, z)$$

???

Vector field

$$\vec{a} = \left(a_x(x, y, z), a_y(x, y, z), a_z(x, y, z)\right)^T$$



# Gradient

$$grad(u) = \vec{\nabla} u = \begin{pmatrix} \dfrac{\partial u}{\partial x} \\ \dfrac{\partial u}{\partial y} \\ \dfrac{\partial u}{\partial z} \end{pmatrix}$$

$$\vec{\nabla} = \begin{pmatrix} \dfrac{\partial}{\partial x} \\ \dfrac{\partial}{\partial y} \\ \dfrac{\partial}{\partial z} \end{pmatrix}$$

Think about: Newton's equations of motion

QM operators, e.g. momentum operator

# Divergence

$$div(\vec{a}) = (\vec{\nabla}, \vec{a}) = \frac{\partial a_x}{\partial x} + \frac{\partial a_y}{\partial y} + \frac{\partial a_z}{\partial z}$$

This is just a scalar product of two "vectors". Show

Think about: Kinetic energy operator in QM

# Laplacian

$$\Delta = \left(\vec{\nabla}, \vec{\nabla}\right) = \begin{pmatrix} \dfrac{\partial}{\partial x} & \dfrac{\partial}{\partial y} & \dfrac{\partial}{\partial z} \end{pmatrix} \begin{pmatrix} \dfrac{\partial}{\partial x} \\ \dfrac{\partial}{\partial y} \\ \dfrac{\partial}{\partial z} \end{pmatrix} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

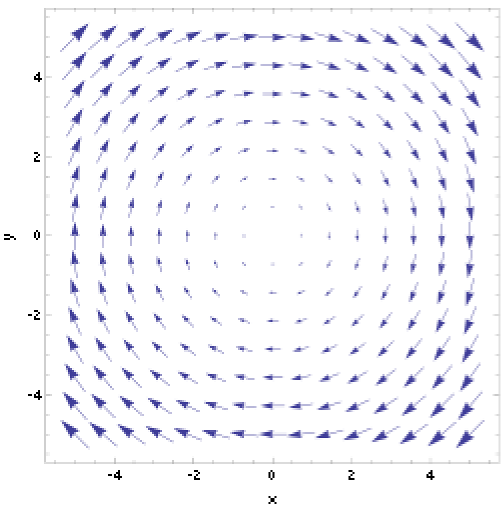
This is just a scalar product of two “vectors”

Think about: Kinetic energy operator in QM

# Rotor (Curl)

$$rot(\vec{a}) = \vec{\nabla} \times \vec{a} = \begin{vmatrix} \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ a_x & a_y & a_z \\ i & j & k \end{vmatrix}$$

Just a vector (cross) product of two "vectors"




$$\vec{a} = \begin{pmatrix} y \\ -x \\ 0 \end{pmatrix}$$

$$\begin{vmatrix} \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ y & -x & 0 \\ i & j & k \end{vmatrix} = \begin{pmatrix} 0 \\ 0 \\ -2 \end{pmatrix}$$

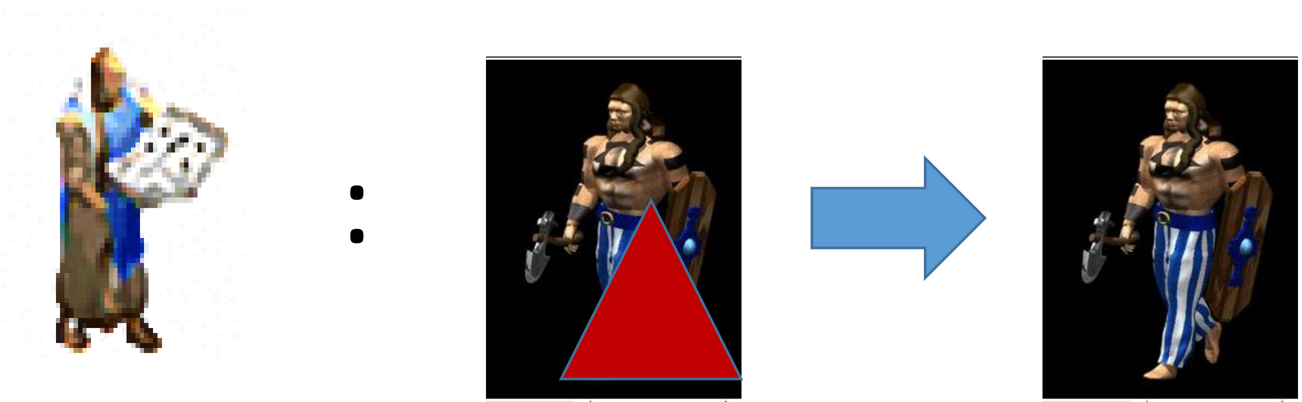
Think about: Angular momentum operators in QM

# Operators

$$\hat{F} : X \rightarrow X'$$

A generic recipe (mapping)
to convert
something into something else

A “monk” operator (AOE)



enemy friend

# Operators: classification

$$f\left(x\right): x \to y = x^2$$

Function =
Scalar (number) to scalar

$$F\left[f\right]: f \to y = \int_0^L f\left(x\right)dx$$

Functional =
Function to scalar

$$U\left\lfloor \hat{H} \right\rfloor: \hat{H} \to \hat{Y} = \exp\left(-i\hat{H} \cdot t\right)$$

Super operator =
Operator to operator

# Linear Operators

$$\hat{F}\left(c_1\psi_1 + c_2\psi_2\right) = c_1\hat{F}\left(\psi_1\right) + c_2\hat{F}\left(\psi_2\right)$$

$$\psi_1, \psi_2 \in X; c_1, c_2 \in R(C)$$

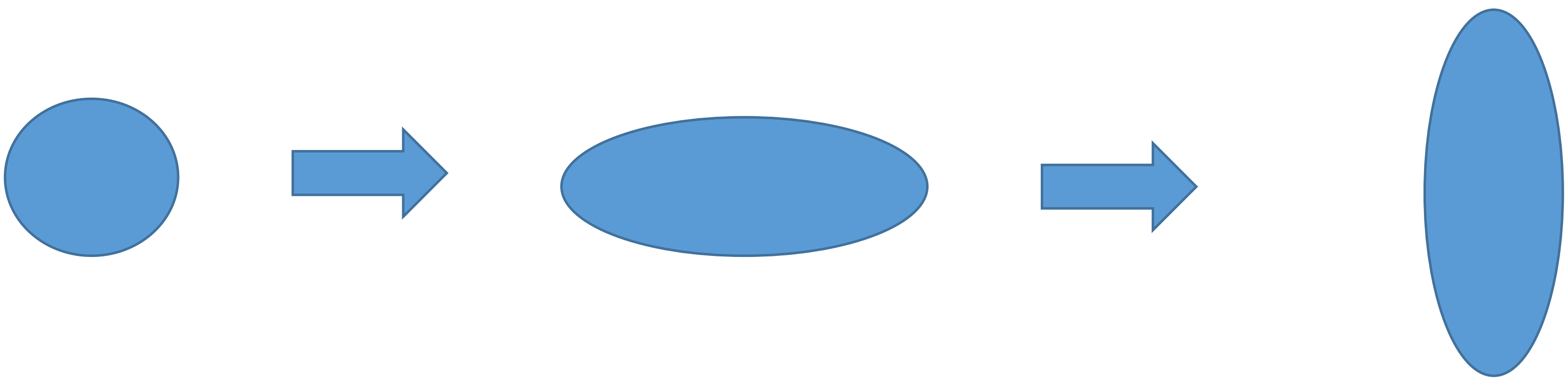
$$\left(\hat{F} + \hat{G}\right)\psi = \hat{F}\psi + \hat{G}\psi$$

$$\left(c\hat{F}\right)\psi = c\left(\hat{F}\psi\right)$$

$$\left(\hat{F}\hat{G}\right)\psi = \hat{F}\left(\hat{G}\psi\right)$$

# The meaning of $\left(\hat{F}\hat{G}\right)\psi = \hat{F}\left(\hat{G}\psi\right)$

$\hat{G} = \text{deform in x}$ $\qquad$ $\hat{F} = \text{rotate by 90 deg}$

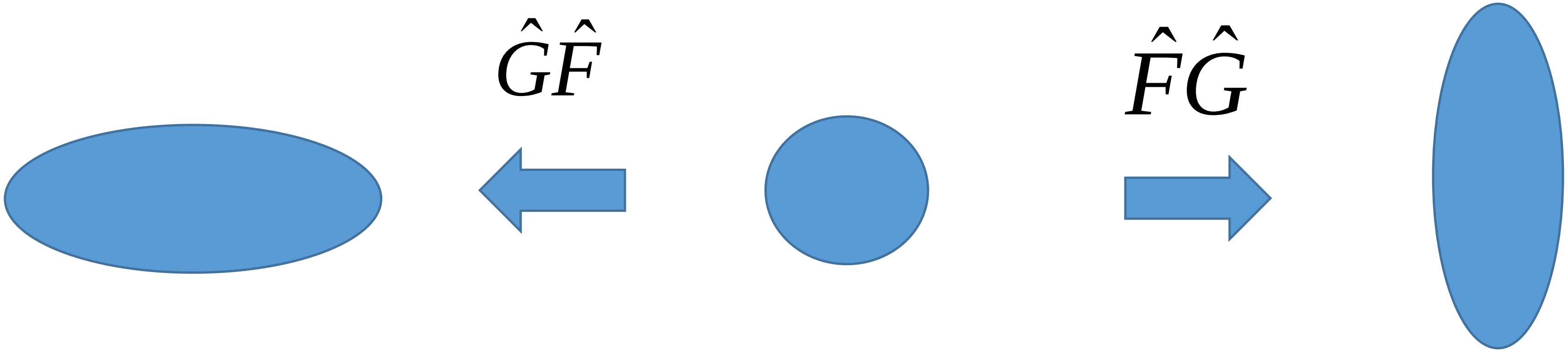


$\hat{x} : f \to xf$ $\qquad$ $\dfrac{d}{dx} : f \to f'$

Think about: Theorem about the commuting operators

# Commutation

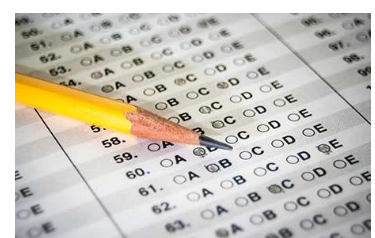
$$\hat{F}\hat{G} \neq \hat{G}\hat{F}$$




## Another example:

$\hat{G} = \text{study}$

$\hat{F} = \text{take an exam}$



# Commutator and anti-commutator

$$\left[\hat{F},\hat{G}\right]=\hat{F}\hat{G}-\hat{G}\hat{F} \qquad \left[\hat{F},\hat{G}\right]_+=\hat{F}\hat{G}+\hat{G}\hat{F}$$

How to compute: Need an auxiliary function

$$\hat{G}=x\frac{d}{dx}$$

$$\hat{G}^2 f=\left(\hat{G}\hat{G}\right)f=\hat{G}\left(\hat{G}f\right)=\hat{G}\left(x\frac{d}{dx}f\right)=\hat{G}\left(x\frac{df}{dx}\right)=x\frac{d}{dx}\left(x\frac{df}{dx}\right)=x\left(x'f'+xf''\right)=$$

$$=\left(xx'f'+x^2f''\right)=\left(x\frac{d}{dx}+x^2\frac{d^2}{dx^2}\right)f$$

$$\hat{G}^2=\left(x\frac{d}{dx}+x^2\frac{d^2}{dx^2}\right)=\hat{G}+x^2\frac{d^2}{dx^2}$$

**NOT** $\left(x^2\frac{d^2}{dx^2}\right)$