Mathematical Basics of Quantum Chemistry

5th Winter School of Computational Chemistry
Sharif University of Technology

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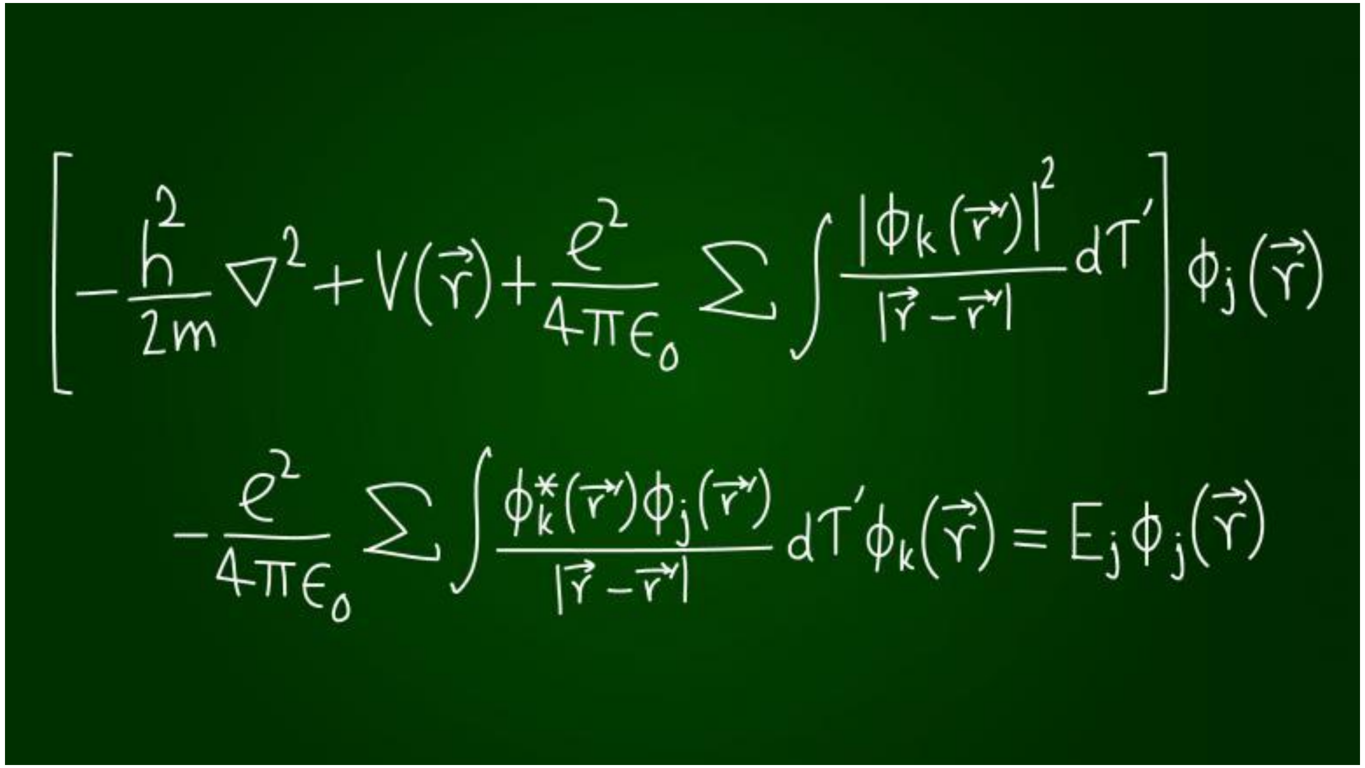
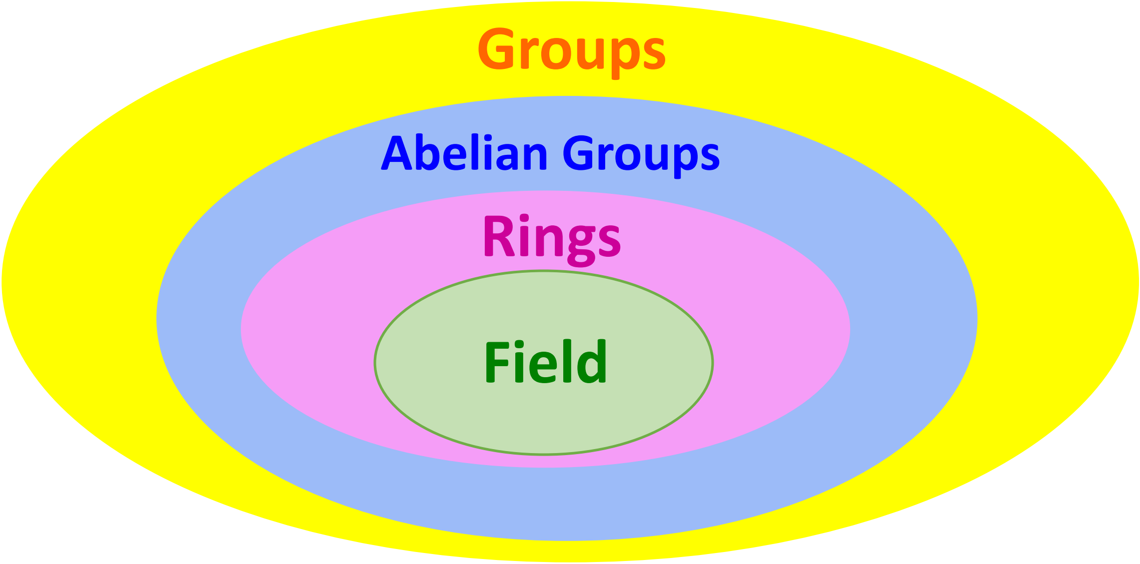
About the lecture

The aim of this lecture is to equip you with the necessary Linear Algebra, building on fundamental concepts of vectors and matrices in the context of quantum chemistry and quantum mechanics.





Ring → Field → Vector Space

Fraleigh, John B. A First Course in Abstract Algebra. 7th ed., Addison-Wesley, 2002.

Riabov VV. REVISING MATHEMATICAL FOUNDATIONS FOR COMPUTER SCIENCE COURSES. InSight: Rivier Academic Journal. 2018, 14(1).

Group: (G,+)   A group is defined as a set of elements together with an operation
which has to satisfy the following conditions:

1. $\forall g_1, g_2 \epsilon\, G;$ $\quad g_1 + g_2 \epsilon\, G$
2. $\exists\, 0 \in G\,;$ $\quad 0 + g = g + 0 = g,$ $\quad \forall g \in G$
3. $\forall g \in G,$ $\quad \exists\, (-g) \in G\,;$ $\quad g + (-g) = (-g) + g = 0$
4. $\forall\, g_1\,, g_2\,, g_3 \in G;$ $\quad (g_1+g_2)+g_3=g_1+(g_2+g_3)$

Niels Henrik Abel
(1802-1829)

G is commutative or abelian if:

$$\forall \boldsymbol{g_1}, \boldsymbol{g_2} \in \boldsymbol{G} \quad ; \qquad \boldsymbol{g_1} + \boldsymbol{g_2} = \boldsymbol{g_2} + \boldsymbol{g_1}$$

Otherwise, we say that G is non-commutative or non-abelian.

Ring: (M, + , .) A ring is a special type of group endowed with two operations that can be considered as generalizations of addition and multiplication. which has to satisfy the following conditions:

1. $(M,+)$ $\rightarrow$ Abelian group

2. $\forall\, m_1, m_2, m_3$ $\qquad m_1.(m_2+m_3) = m_1.m_2 + m_1.m_3$

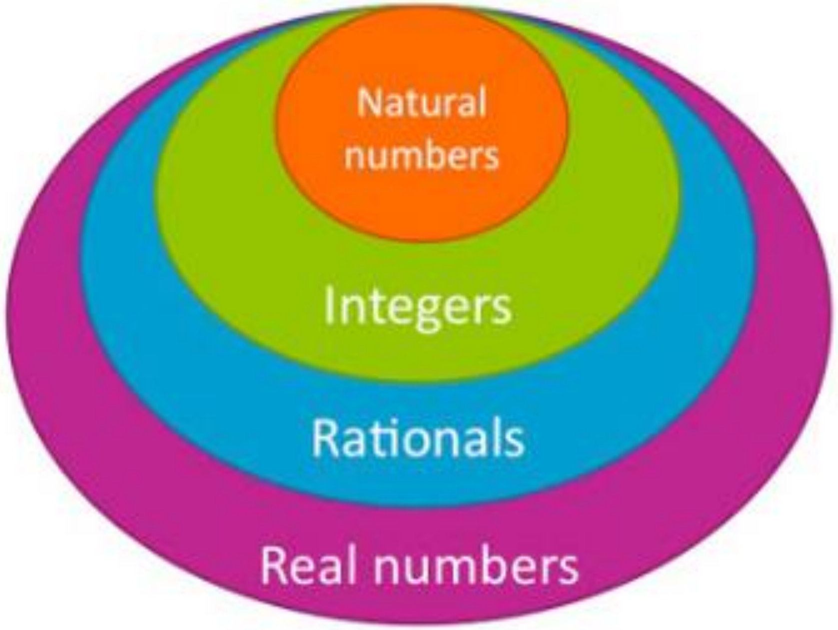
3. $\forall\, m_1, m_2, m_3$ $\qquad m_1.(m_2\,.\,m_3) = (m_1.m_2)\,.\,m_3$

Definition: A ring with identity is a ring M that contains a multiplicative identity element 1 which:

$$\forall \boldsymbol{m} \in \boldsymbol{M};\, \mathbf{1}.\boldsymbol{m} = \boldsymbol{m}.\mathbf{1} = \boldsymbol{m}$$

Field: it is a commutative ring with identity where every non-zero element has a multiplicative inverse; essentially, a ring where division (except by zero) is always possible.

$\forall\, \boldsymbol{m} \in \boldsymbol{M}\,;\ \exists\, \boldsymbol{m}^{-1} \in \boldsymbol{M}$ $\quad$ $\boldsymbol{m}.\boldsymbol{m}^{-1} = \boldsymbol{m}^{-1}.\mathbf{m} = \mathbf{1}\, \epsilon\, \boldsymbol{M}$



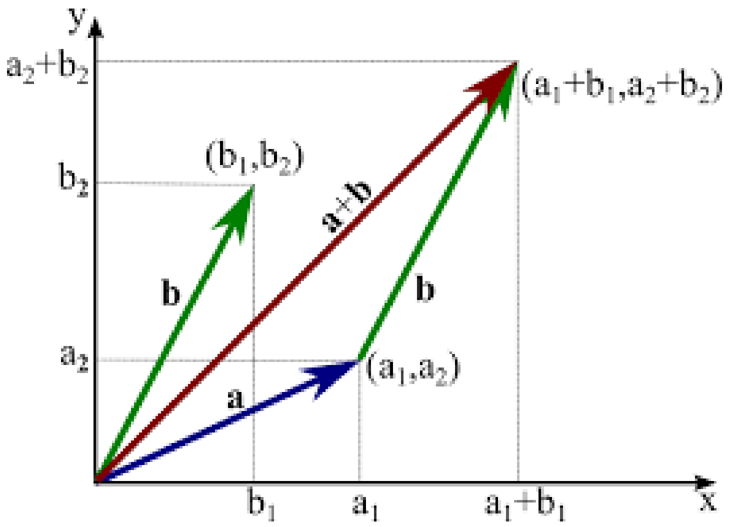
Vector Space: V, F

A vector space is a collection of objects, called vectors, for which **addition** and **scalar multiplication** are defined such that :

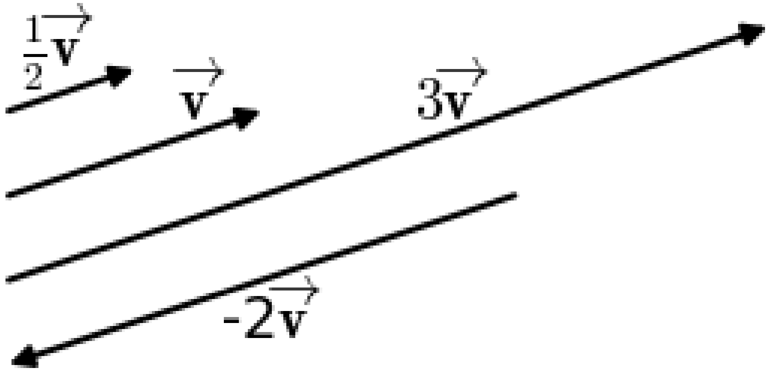
$$(V, +, .) \quad \begin{cases} +: \boldsymbol{V} \times \boldsymbol{V} \rightarrow \boldsymbol{V} \\ .: \boldsymbol{F} \times \boldsymbol{V} \rightarrow \boldsymbol{V} \end{cases}$$

$$\text{if } \vec{u} \text{ and } \vec{v} \in V \quad then \quad \vec{u} + \vec{v} \in V$$

$$\text{if } \vec{u} \in V$$
$$\forall c \in F \; (c \text{ is a scalar}) \quad then \quad c\vec{u} \in V$$



Closure under addition



Closure under scalar multiplication

In order to be a vector space those operation along the vectors have to satisfy the following properties:

Closure under addition

$\vec{u} + \vec{v} = \vec{v} + \vec{u}$ Commutivity

$(\vec{u} + \vec{v}) + \vec{w} = \vec{u} + (\vec{v} + \vec{w})$ Associativity

$\vec{u} + \vec{0} = \vec{0} + \vec{u} = \vec{u}$

$\vec{u} + (-\vec{u}) = 0$

Closure under scalar multiplication

$c.(\vec{u} + \vec{v}) = c.\vec{u} + c.\vec{v}$

$(c+c').\vec{u} = c.\vec{u} + c'.\vec{u}$

$(c.c').\vec{u} = c.(c'.\vec{u})$

$\forall c \in F$ so:
$1 \in F \quad 1.\vec{u} = \vec{u}$

(V,+) is an Abelian Group

Examples of Vector Space

1. $(R^n, +, .)$ $\quad n \in N$ $\qquad$ n=3 $\qquad \vec{u} = u_x\vec{i} + u_y\vec{j} + u_z\vec{k}$

2. $(M_{m\times n}(C), +, .)$

3. $(C^k[a,b], +, .) \longrightarrow f(x) = \sum_{n=1}^{n} c_{n-1}x^{n-1}$

Examples of Vector Space

$$f(x) = \sum_{n=1}^{n} c_{n-1}x^{n-1}$$

$f(x) + g(x) =$

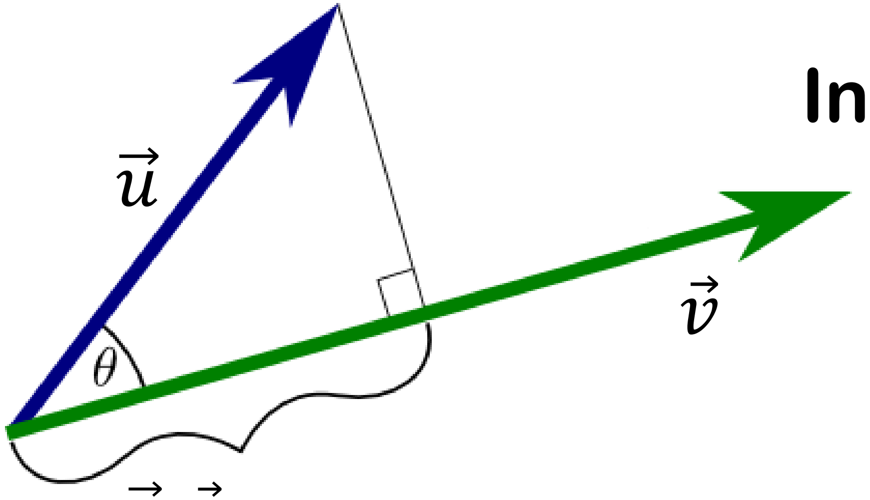
$$(c_0 + c_1x + c_2x^2 + \cdots + c_{n-1}x^{n-1}) + (c'_0 + c'_1x + c'_2x^2 + \cdots + c'_{n-1}x^{n-1}) =$$

$$(c_0 + c'_0) + (c_1 + c'_1)x + (c_2 + c'_2)x^2 + \ldots + (c_{n-1} + c'_{n-1})x^{n-1}$$

$Cf(x) =$

$c(c_0 + c_1x + c_2x^2 + \cdots + c_{n-1}x^{n-1}) = (cc_0) + (cc_1)x + (cc_2)x^2 + \ldots + (cc_{n-1})x^{n-1}$

Inner Product Spaces



$$\frac{\vec{u}.\vec{v}}{|\vec{v}|} = |\vec{u}|\, cos\theta$$

Dot Product between two three dimensional vectors :

$$\vec{u}.\vec{v} = |\vec{u}|\, |\vec{v}|\, cos\theta$$

Inner product (.) :
$\boldsymbol{V} \times \boldsymbol{V} \;\rightarrow \boldsymbol{c}\;(\boldsymbol{c} \in \boldsymbol{F})$

Inner product vector space

Properties:

$$1:\;\; (\vec{v}, \vec{u}) = (\vec{u}, \vec{v})^*$$

$$2:\;\; (a\vec{u} + b\vec{v}, \vec{w}) = a^*(\vec{u}, \vec{w}) + b^*(\vec{v}, \vec{w})$$

$$\boxed{3:}\; (\vec{u}, \vec{u}) \geq 0; \text{ proof: } (\vec{u}, \vec{u}) = \textstyle\sum_i u_i^* u_i = \sum_i |u_i|^2 \geq 0.$$

length of a vector $|\vec{u}|$ (norm of a vector)

$$|\vec{u}| \;\; = \;\; \sqrt{(\vec{u}, \vec{u})} = \sqrt{u_x^2 + u_y^2 + u_z^2}$$

If $(\vec{u}, \vec{u}) = 1$, then $\vec{u}$ is normalized to unity

Inner product spaces: Euclidean vector space

In an n-dimensional space:

$\vec{u}, \vec{u} \epsilon C^n$

$$\left\{ \begin{array}{rcl} \vec{u} & = & (u_1, u_2, \ldots, u_n) \\ \vec{v} & = & (v_1, v_2, \ldots, v_n), \end{array} \right.$$

the scalar product is defined as

$$(\vec{u}, \vec{v}) = \sum_{i=1}^{n} u_i \, v_i \qquad \text{if } u_i, v_i \text{ are real}$$

$$(\vec{u}, \vec{v}) = \sum_{i=1}^{n} u_i^* \, v_i \qquad \text{if } u_i, v_i \text{ are complex.}$$

From the definition,

$$(\vec{v}, \vec{u}) = (\vec{u}, \vec{v}) \qquad \text{for real space}$$

$$(\vec{v}, \vec{u}) = (\vec{u}, \vec{v})^* \qquad \text{for complex space.}$$

Linear Independence, Bases, and Dimensionality

$$c_1 v_1 + c_2 v_2 + \ldots + c_n v_n = \sum_{i=1}^{n} c_i v_i = \vec{u}$$

A set of n vectors $\{ v_i \}$ in a vector space V is said to be linearly independent if and only if:

$$c_1 v_1 + c_2 v_2 + \ldots + c_n v_n = 0$$

Implies that:

$$c_1 = c_2 = \ldots = c_n = 0$$

Dimension of Vector Space (Linear Space)

$$\boldsymbol{n_{max}} < \infty$$

Orthonormality and Complete Sets

In the 3D rectangular (Cartesian) coordinate system the basis is

$$\{\vec{i}, \vec{j}, \vec{k}\}, \text{ where } \vec{i} = (1,0,0), \quad \vec{j} = (0,1,0), \quad \vec{k} = (0,0,1),$$

The basis vectors are *orthogonal*

$$(\vec{i}, \vec{j}) = |\vec{i}|\,|\vec{j}|\,\cos\theta_{ij} = (1)(1)\cos 90^\circ = 0.$$

For any $\vec{v}$ in this space,

$$\vec{v} = v_x\vec{i} + v_y\vec{j} + v_z\vec{k}.$$

Taking the inner product

$$(\vec{i}, \vec{v}) = \underbrace{v_x(\vec{i}, \vec{i})}_{=1} + \underbrace{v_y(\vec{i}, \vec{j})}_{=0} + \underbrace{v_z(\vec{i}, \vec{k})}_{=0} = v_x$$

i.e. the components (coordinates) of a vector are projections of that vector onto the basis set vectors.

- $\vec{u}, \vec{v}$ are <u>*orthogonal*</u> if $(\vec{u}, \vec{v}) = 0$.

Orthonormal basis

- vectors $\{\vec{v}_1, \ldots, \vec{v}_n\}$ form an *orthonormal* (orthogonal and normalized to unity) set if

$$\boxed{(\vec{v}_i, \vec{v}_j) = \delta_{ij} = \begin{cases} 0 \text{ if } i \neq j \\ 1 \text{ if } i = j \end{cases}}$$

δ_{ij} defined above is the Kronecker delta.

The Gram-Schmidt method of orthogonalization

Basis set vectors $\{\vec{v}_1, \vec{v}_2, \ldots, \vec{v}_n\}$ in $\mathcal{V}$ are neither normalized nor orthogonal. A normalized basis $\{\vec{u}_1, \vec{u}_2, \ldots, \vec{u}_n\}$ may be obtained as follows:

Take $\boxed{\vec{u}_1 = \vec{v}_1}$. $\dfrac{\overrightarrow{v_1}}{\|v_1\|}$

Define $\vec{u}_2 = \vec{v}_2 + k\vec{u}_1$ with k such that $(\vec{u}_2, \vec{u}_1) = 0$.

$$
\begin{aligned}
(\vec{u}_2, \vec{u}_1) = (\vec{v}_2 + k\vec{u}_1, \vec{u}_1) &= 0 \\
(\vec{v}_2, \vec{u}_1) + k^*(\vec{u}_1, \vec{u}_1) &= 0
\end{aligned}
$$

$$
\begin{aligned}
k^* &= -\frac{(\vec{v}_2, \vec{u}_1)}{(\vec{u}_1, \vec{u}_1)} = -\frac{(\vec{v}_2, \vec{u}_1)}{|\vec{u}_1|^2} \\
k &= -\frac{(\vec{v}_2, \vec{u}_1)^*}{(\vec{u}_1, \vec{u}_1)} = -\frac{(\vec{u}_1, \vec{v}_2)}{|\vec{u}_1|^2}
\end{aligned}
$$

$$
\boxed{\vec{u}_2 = \vec{v}_2 - \frac{(\vec{u}_1, \vec{v}_2)\overrightarrow{u_1}}{|\vec{u}_1|^2}}
$$

Define the third vector $\vec{u}_3 = \vec{v}_3 + k_1\vec{u}_1 + k_2\vec{u}_2$ with k_1, k_2 such that (a) $(\vec{u}_3, \vec{u}_1) = 0$ and (b) $(\vec{u}_3, \vec{u}_2) = 0$.

$$
\begin{aligned}
(a) \qquad 0 = (\vec{u}_3, \vec{u}_1) &= (\vec{v}_3, \vec{u}_1) + k_1^*(\vec{u}_1, \vec{u}_1) + k_2^* \underbrace{(\vec{u}_2, \vec{u}_1)}_{=0\,!} \\
&= (\vec{v}_3, \vec{u}_1) + k_1^*|\vec{u}_1|^2 \\
k_1^* &= -\frac{(\vec{v}_3, \vec{u}_1)}{|\vec{u}_1|^2} \\
k_1 &= -\frac{(\vec{u}_1, \vec{v}_3)}{|\vec{u}_1|^2}
\end{aligned}
$$

$$
\begin{aligned}
(b) \qquad 0 = (\vec{u}_3, \vec{u}_2) &= (\vec{v}_3, \vec{u}_2) + k_1^* \underbrace{(\vec{u}_1, \vec{u}_2)}_{=0\,!} + k_2^*(\vec{u}_2, \vec{u}_2) \\
&= (\vec{v}_3, \vec{u}_2) + k_2^*|\vec{u}_2|^2 \\
k_2^* &= -\frac{(\vec{v}_3, \vec{u}_2)}{|\vec{u}_2|^2} \\
k_2 &= -\frac{(\vec{u}_2, \vec{v}_3)}{|\vec{u}_2|^2}
\end{aligned}
$$

$$
\boxed{\vec{u}_3 = \vec{v}_3 - \frac{(\vec{u}_1, \vec{v}_3)}{|\vec{u}_1|^2}\vec{u}_1 - \frac{(\vec{u}_2, \vec{v}_3)}{|\vec{u}_2|^2}\vec{u}_2}
$$

and the process may be continued for the remaining vectors. The general formula is

$$\vec{u}_i = \vec{v}_i - \sum_{j=1}^{i=1} \frac{(\vec{u}_j, \vec{v}_i)}{|\vec{u}_j|^2} \vec{u}_j$$

$$V: \{e_1, e_1, \dots, e_n\}$$

$\text{Any } \vec{u} \text{ vector in an } n - \text{dimensional space } V,$
$\text{spanned by an orthonormal basis } \{\vec{e_i}\}\text{: as projections on the basis set vectors}$

$$\vec{u} = \sum_{i=1}^{n} c_i \vec{e_i} \quad = \sum_{i=1}^{n} (\vec{e_i}, \vec{u})\, \vec{e_i}$$

$$(\vec{e_k}\ , \vec{u}\,) = \left(\vec{e_k}\ , \sum_{i=1}^{n} c_i \vec{e_i}\right) = \sum_{i=1}^{n} c_i\, (\vec{e_k}\,, \vec{e_i}\,) = \sum_{i=1}^{n} c_i\, \delta_{ki} = c_k$$

Linear Operator: $\hat{A}$

$$\hat{A}\vec{v} = \vec{u}$$

$$\hat{A}\,(\alpha\,\overrightarrow{v_1} + \beta\,\overrightarrow{v_2}) = \alpha\,\hat{A}\,\overrightarrow{v_1} + \beta\,\hat{A}\,\overrightarrow{v_2}$$

$$\forall\, \alpha\,,\beta \in C$$
$$\forall\, \overrightarrow{v_1}\,,\overrightarrow{v_2}\ \in V$$

<u>Examples:</u>

(a) $\hat{D} = d/dx$:
(1°) $\hat{D}[f(x) + g(x)] = \hat{D}f(x) + \hat{D}g(x)$;
(2°) $\hat{D}[cf(x)] = c[\hat{D}f(x)]$

(b) $\hat{S} = \sqrt{\ }$
(1°) $\hat{S}[f(x) + g(x)] \neq \hat{S}f(x) + \hat{S}g(x)$.

Algebra of linear operators

Operations

- *sum*: $\hat{L}_1 + \hat{L}_2 = \hat{L} \Longrightarrow (\hat{L}_1 + \hat{L}_2) f(x) = \hat{L} f(x)$
  always associative and commutative

- *product*: $\hat{L}_1\ \hat{L}_2 = \hat{L} \Longrightarrow (\hat{L}_1\ \hat{L}_2) f(x) = \hat{L} f(x)$
  always associative, but not necessarily commutative; for example

$$
\begin{aligned}
\hat{D} &= d/dx, \qquad \hat{a} = x \\
\hat{A}\hat{D} f(x) &= x\frac{df}{dx} = \left(x\frac{d}{dx}\right) f(x) \\
\hat{D}\hat{A} f(x) &= \frac{d}{dx}(x f(x)) = \left(\frac{d}{dx}x\right) f(x) + x\left(\frac{df}{dx}\right) dx \\
&= f(x) + x\frac{df}{dx} = \left[1 + x\frac{d}{dx}\right] f(x) \\
\hat{A}\hat{D} &= x\frac{d}{dx} \\
\hat{D}\hat{A} &= 1 + x\frac{d}{dx} \\
\hat{A}\hat{D} &\neq \hat{D}\hat{A}
\end{aligned}
$$

- if $\hat{L}_1 \, \hat{L}_2 = \hat{L}_2 \, \hat{L}_1$, the operators *commute*
- if $\hat{L}_1 \, \hat{L}_2 \neq \hat{L}_2 \, \hat{L}_1$, the operators do not commute; commutator: $\left[\hat{L}_1, \hat{L}_2\right] = \hat{L}_1 \, \hat{L}_2 - \hat{L}_2 \, \hat{L}_1$

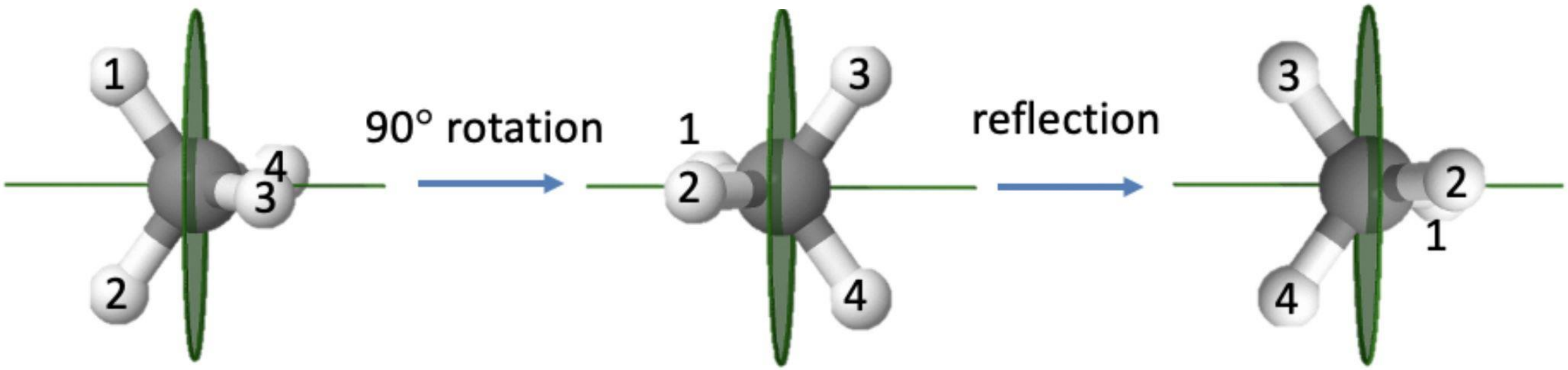
Functions of operators

1. $\hat{L}^2 = \hat{L} \, \hat{L}$; $\hat{L}^n = \underbrace{\hat{L} \, \hat{L} \, \ldots \, \hat{L}}_{n \ times}$
2. power series: $\hat{L}^0 + \hat{L}^1 + \hat{L}^2 + \cdots + \hat{L}^n + \cdots$; $f(\hat{L})$ may be expanded as a power series, e.g.

$$e^{\hat{L}} = \hat{L}^0 + \hat{L}^1 + \frac{1}{2!}\hat{L}^2 + \frac{1}{3!}\hat{L}^3 + \cdots$$

Examples of linear transformation

- Rotations
- Reflections
- Scaling along some axis
- Any combination of linear operations!



A symmetry operation can be described as a matrix

[New coordinates] = [Transformation Matrix] x [Old Coordinates]

Matrices

A matrix (plural: matrices) is just a rectangular array of quantities, usually inclosed in large parentheses, such as

To indicate a number in the array, we will write A_{ij} where i is the row number and j is the column number.

$$A = \begin{bmatrix} A_{11} & A_{12} & \cdots & A_{1n} \\ A_{21} & A_{22} & \cdots & A_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ A_{m1} & A_{m2} & \cdots & A_{mn} \end{bmatrix}$$

$$A \in \mathbb{F}^{m \times n}$$

mxn

#Columns

#Rows

- Vectors are also matrices!

$$\mathbf{x} \in \mathbb{F}^n = \mathbb{F}^{n \times 1}$$

Matrix-Matrix Product

$$AB = C \qquad C_{ij} = \sum_k A_{ik} B_{kj}$$

$$\begin{bmatrix} A_{11} & A_{12} & \cdots & A_{1n} \\ A_{21} & A_{22} & \cdots & A_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ A_{m1} & A_{m2} & \cdots & A_{mn} \end{bmatrix} \begin{bmatrix} B_{11} & B_{12} & \cdots & B_{1o} \\ B_{21} & B_{22} & \cdots & B_{2o} \\ \vdots & \vdots & \ddots & \vdots \\ B_{n1} & B_{n2} & \cdots & B_{no} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & \cdots & C_{1o} \\ C_{21} & C_{22} & \cdots & C_{2o} \\ \vdots & \vdots & \ddots & \vdots \\ C_{m1} & C_{m2} & \cdots & C_{mo} \end{bmatrix}$$

$m \times n$ $\qquad$ $n \times o$ $\qquad$ $m \times o$

Properties of Matrix multiplications

- $\underline{A}(\underline{B}\,\underline{C}) = (\underline{A}\,\underline{B})\underline{C}$ (associative)
- $\underline{A}(\underline{B} + \underline{C}) = \underline{A}\,\underline{B} + \underline{A}\,\underline{C}$ (distributive)
- not necessarily commutative:

$$\underline{A}\,\underline{B} = \underline{B}\,\underline{A} \quad \boxed{\text{matrices commute}}$$

$$\underline{A}\,\underline{B} \neq \underline{B}\,\underline{A} \quad \boxed{\text{do not commute}}$$

$$\begin{pmatrix} 1 & 0 \\ 0 & 2 \end{pmatrix}\begin{pmatrix} 3 & 0 \\ 0 & 4 \end{pmatrix}$$

$$\begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix}\begin{pmatrix} 5 & 6 \\ 7 & 8 \end{pmatrix}$$

Determinants

$$\text{for a matrix } \underline{A} = \begin{pmatrix} A_{11} & A_{12} & \dots & A_{1n} \\ A_{21} & A_{22} & \dots & A_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ A_{n1} & A_{n2} & \dots & A_{nn} \end{pmatrix}$$

$$\det \underline{A} = |\underline{A}| = \text{ a number}$$

Evaluation of a determinant by the Laplace method

$$|\underline{A}| = \sum_{i=1}^{n} A_{ij} \underbrace{|A_{ij}|}_{cofactor} = \sum_{i=1}^{n} A_{ij} \underbrace{(-1)^{i+j} \underbrace{|M_{ij}|}_{minor}}_{cofactor}$$

$$|\underline{A}| = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & \boxed{\begin{matrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{matrix}} \\ a_{31} & & \end{vmatrix} = a_{11} (-1)^{1+1} \begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} +$$

$$|\underline{A}| = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = a_{11}(-1)^{1+1}\begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} + a_{12}(-1)^{1+2}\begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} +$$

$$|\underline{A}| = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = a_{11}(-1)^{1+1}\begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} + a_{12}(-1)^{1+2}\begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} + a_{13}(-1)^{1+3}\begin{vmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{vmatrix}$$

$$\begin{aligned} &= a_{11}(a_{22}a_{33} - a_{23}a_{32}) - a_{12}(a_{21}a_{33} - a_{23}a_{31}) + \\ &\quad a_{13}(a_{21}a_{32} - a_{22}a_{31}) \\ &= a_{11}a_{22}a_{33} - a_{11}a_{23}a_{32} - a_{12}a_{21}a_{33} + \\ &\quad a_{12}a_{23}a_{31} - a_{13}a_{22}a_{31} + a_{13}a_{21}a_{32} \end{aligned}$$

Determinant of a Diagonal Matrix

$$\text{If } A = \begin{bmatrix} a_{11} & 0 & 0 & \cdots & 0 \\ 0 & a_{22} & 0 & \cdots & 0 \\ 0 & 0 & a_{33} & \cdots & 0 \\ \vdots & \vdots & \vdots & & \vdots \\ 0 & 0 & 0 & \cdots & a_{nn} \end{bmatrix} \text{, then}$$

$$\det A = a_{11} \cdot a_{22} \cdot a_{33} \cdot \cdots \cdot a_{nn}$$

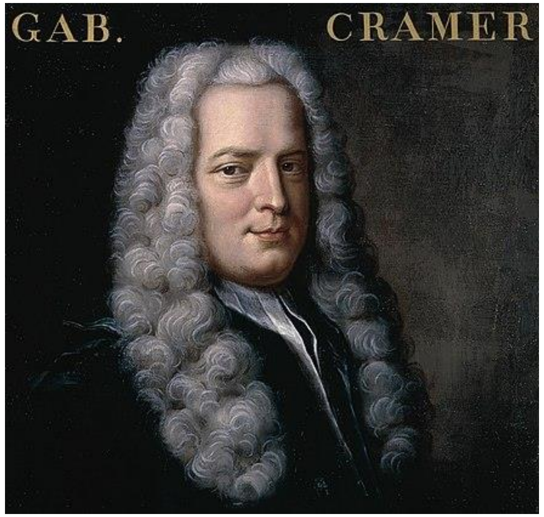
The computational challenges that arise with larger matrices

The Laplace expansion method, while straightforward for small matrices, becomes computationally impractical for larger ones due to its factorial time complexity. This inefficiency is a key reason why computational tools are employed in practice.

In practical applications, especially in computational quantum chemistry, leveraging programming languages like Python with libraries such as **NumPy** is common. NumPy provides efficient functions to compute determinants using optimized algorithms.

Python section

Determinants and systems of linear equations



Coefficient Matrix

$$\left.\begin{aligned} a_{11}\boxed{x_1} + a_{12}x_2 &= \boxed{b_1} \\ a_{21}x_1 + a_{22}x_2 &= b_2 \end{aligned}\right\} \Longrightarrow \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \begin{pmatrix} b_1 \\ b_2 \end{pmatrix}$$

Cramer's Rule

$$\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} = A$$

The ith component of the solution can be found by taking the determinant of the matrix with the i-th **column replaced by the constant terms.**

$$x_i = \frac{|A_i|}{|A|} \qquad x_1 = \frac{|A_1|}{|A|} \qquad A_1 = \begin{bmatrix} b_1 & a_{12} \\ b_2 & a_{22} \end{bmatrix} \quad \text{->}\ x_1 = \frac{\begin{vmatrix} b_1 & a_{12} \\ b_2 & a_{22} \end{vmatrix}}{\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}} \qquad x_2 = \frac{\begin{vmatrix} a_{11} & b_1 \\ a_{21} & b_2 \end{vmatrix}}{\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}}$$

Inverse Matrix

$$A\,A^{-1} = \mathbb{1} = \begin{bmatrix} 1 & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & 1 \end{bmatrix}$$

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix}^{-1} = \frac{1}{(ad - bc)} \begin{pmatrix} d & -b \\ -c & a \end{pmatrix}$$

Formula for $\underline{A}^{-1}$ is:

$$\boxed{\underline{A}^{-1} = \frac{1}{|\underline{A}|} \overbrace{\begin{pmatrix} |A_{11}| & |A_{21}| & \dots & |A_{n1}| \\ |A_{12}| & |A_{22}| & \dots & |A_{n2}| \\ \vdots & \vdots & \ddots & \vdots \\ |A_{1n}| & |A_{2n}| & \dots & |A_{nn}| \end{pmatrix}}^{C^T}}$$

- $\underline{A}$ must be non-singular ($|\underline{A}| \neq 0$)
- the matrix is built from cofactors, $|A_{ij}| = \underbrace{(-1)^{i+j}\, \underbrace{|M_{ij}|}_{minor}}_{cofactor}$

C

Example

$$\boxed{\underline{A} = \begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix} \qquad \underline{A}^{-1} = \frac{1}{|\underline{A}|} \begin{pmatrix} |A_{11}| & |A_{21}| \\ |A_{12}| & |A_{22}| \end{pmatrix}}$$

$$\begin{aligned} |\underline{A}| &= 4 - 6 = -2 \\ |A_{11}| &= (-1)^{1+1}\ 4 \qquad & |A_{21}| = (-1)^{2+1}\ 2 \\ |A_{12}| &= (-1)^{1+2}\ 3 \qquad & |A_{22}| = (-1)^{2+2}\ 1 \end{aligned}$$

$$\boxed{\underline{A}^{-1} = \frac{1}{-2} \begin{pmatrix} 4 & -2 \\ -3 & 1 \end{pmatrix} = \begin{pmatrix} -2 & 1 \\ 3/2 & -1/2 \end{pmatrix}}$$

Check:

$$\begin{aligned} \underline{A}\,\underline{A}^{-1} &= \begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix} \begin{pmatrix} -2 & 1 \\ 3/2 & -1/2 \end{pmatrix} = \begin{pmatrix} -2+3 & 1-1 \\ -6+6 & 3-2 \end{pmatrix} \\ &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \underline{I} \end{aligned}$$

Inverse of a Diagonal Matrix

$$\text{If } A = \begin{bmatrix} a_{11} & 0 & 0 & \cdots & 0 \\ 0 & a_{22} & 0 & \cdots & 0 \\ 0 & 0 & a_{33} & \cdots & 0 \\ \vdots & \vdots & \vdots & & \vdots \\ 0 & 0 & 0 & \cdots & a_{nn} \end{bmatrix} \text{, then}$$

$$A^{-1} = \begin{bmatrix} 1/a_{11} & 0 & 0 & \cdots & 0 \\ 0 & 1/a_{22} & 0 & \cdots & 0 \\ 0 & 0 & 1/a_{33} & \cdots & 0 \\ \vdots & \vdots & \vdots & & \vdots \\ 0 & 0 & 0 & \cdots & 1/a_{nn} \end{bmatrix}$$

Special classes of matrices

1. $\underline{A}^t$: transpose of $\underline{A}$ – interchange rows and columns

$$\boxed{(\underline{A}^t)_{ij} = A_{ji}}$$

Examples:

$$\underline{A} = \begin{pmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{pmatrix}; \quad \underline{A}^t = \begin{pmatrix} 1 & 4 & 7 \\ 2 & 5 & 8 \\ 3 & 6 & 9 \end{pmatrix}$$

$$\underline{B} = (1\ 2\ 3); \quad \underline{B}^t = \begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix}$$

2. $\underline{A}^*$: complex conjugate of $\underline{A}$

$$\boxed{(\underline{A}^*)_{ij} = A^*_{ij}}$$

Example:

$$\underline{A} = \begin{pmatrix} 1 & -3i \\ 2+i & 3 \end{pmatrix}; \quad \underline{A}^* = \begin{pmatrix} 1 & 3i \\ 2-i & 3 \end{pmatrix}$$

3. $\underline{A}^\dagger$: adjoint of $\underline{A}$ – complex conjugate of transpose

$$\boxed{(\underline{A}^\dagger)_{ij} = A^*_{ji}}$$

If all A_{ij} are real, $\underline{A}^\dagger = \underline{A}^t$.

Trace of a Matrix

$$\underline{A} = \begin{pmatrix} A_{11} & A_{12} & \dots & A_{1n} \\ A_{21} & A_{22} & \dots & A_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ A_{n1} & A_{n2} & \dots & A_{nn} \end{pmatrix}$$

$$\mathrm{Tr}(A) = \sum_{i=1}^{n} A_{ii}$$

$$Tr\ (AB) = Tr\ (BA)$$

If	then $\underline{A}$ is called
$\underline{A}^* = \underline{A}$	real
$\underline{A}^t = \underline{A}$	symmetric
$\underline{A}^\dagger = \underline{A}$	hermitian
$\underline{A}^{-1} = \underline{A}^t$	orthogonal
$\underline{A}^{-1} = \underline{A}^\dagger$	unitary

$AA^\dagger = A^\dagger A$ Normal (A and $A^\dagger$ commute)

Matrix Eigenvalue Problem

$$H\,u = \lambda u$$

Eigen Vector

Eigen Value

$$\begin{pmatrix} H_{11} & H_{12} & \dots & H_{1n} \\ H_{21} & H_{22} & \dots & H_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} & H_{n2} & \dots & H_{nn} \end{pmatrix} \begin{pmatrix} u_1 \\ u_1 \\ \vdots \\ u_n \end{pmatrix} = \lambda \begin{pmatrix} u_1 \\ u_1 \\ \vdots \\ u_n \end{pmatrix}$$

These equations may be written as a homogeneous set of linear equations

$$(\underline{H} - \lambda \underline{I})\,\underline{u} = \underline{0}$$

non-trivial solutions to these equations exist if

$$|\underline{H} - \lambda \underline{I}\,| = 0,$$

or, writing the *secular determinant* explicitly,

$$\begin{vmatrix} H_{11} - \lambda & H_{12} & \dots & H_{1n} \\ H_{21} & H_{22} - \lambda & \dots & H_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} & H_{n2} & \dots & H_{nn} - \lambda \end{vmatrix} = 0.$$

Example

$$\underline{H} = \begin{pmatrix} 1 & 2 \\ 2 & 1 \end{pmatrix}$$

$$\left|\underline{H} - \lambda \underline{I}\right| = \begin{pmatrix} 1-\lambda & 2 \\ 2 & 1-\lambda \end{pmatrix} = (1-\lambda)^2 - 4 = \lambda^2 - 2\lambda - 3 = 0$$

$$\Longrightarrow \lambda_1 = -1, \qquad \lambda_2 = 3$$

To find eigenvectors, we substitute the eigenvalues into the secular equation, identifying the eigenvector associated with λ_i by the subscript i:

$$\begin{pmatrix} 1-\lambda_i & 2 \\ 2 & 1-\lambda_i \end{pmatrix} \begin{pmatrix} u_{1i} \\ u_{2i} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

(1) $\underline{\lambda_1 = -1}$: $\Longrightarrow 2u_{11} + 2u_{21} = 0 \Longrightarrow u_{11} = -u_{21}$

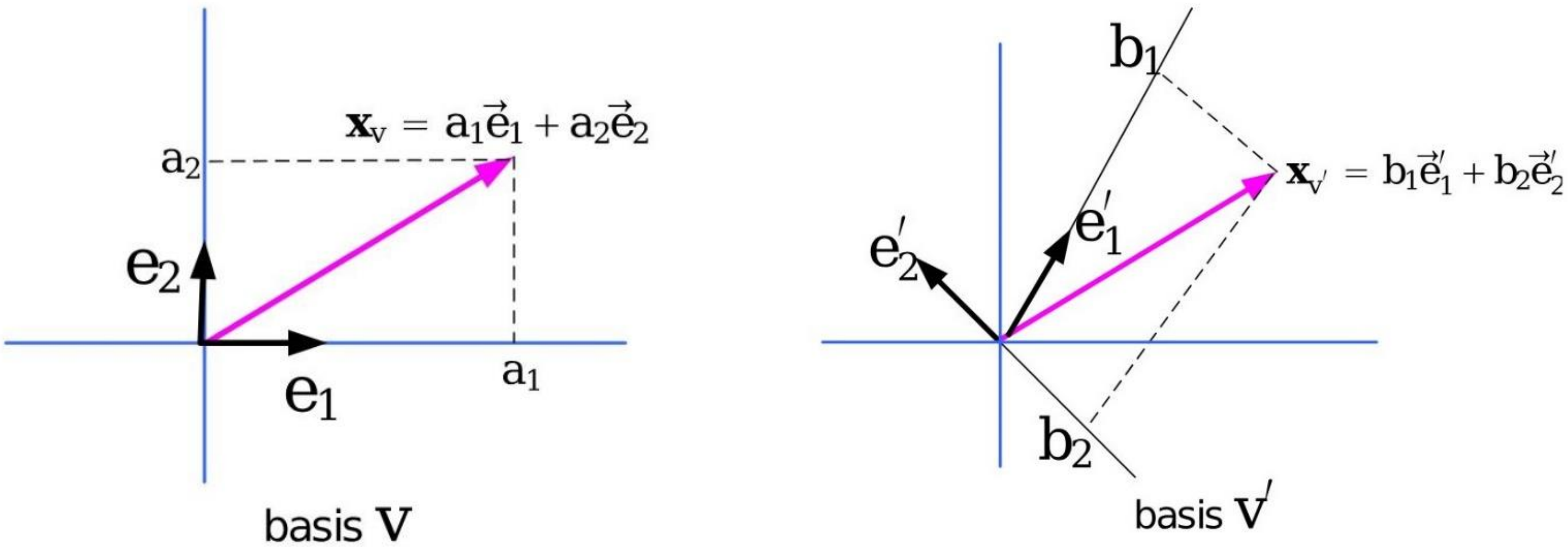
$$\begin{pmatrix} u_{11} \\ u_{21} \end{pmatrix} = c_1 \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

(2) $\underline{\lambda_1 = 3}$: $\Longrightarrow -2u_{12} + 2u_{22} = 0 \Longrightarrow u_{12} = u_{22}$

$$\begin{pmatrix} u_{12} \\ u_{22} \end{pmatrix} = c_2 \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

Application of Matrix eigenvalue Problem: Diagonalization of a matrix

Change of Basis and similarity transformation



Old basis **New basis**

$$\hat{X}\vec{V} = \vec{V'}$$

$$V = \hat{X}^{-1}\vec{V'}$$

$$\hat{X}\vec{V} = \overrightarrow{V'}$$

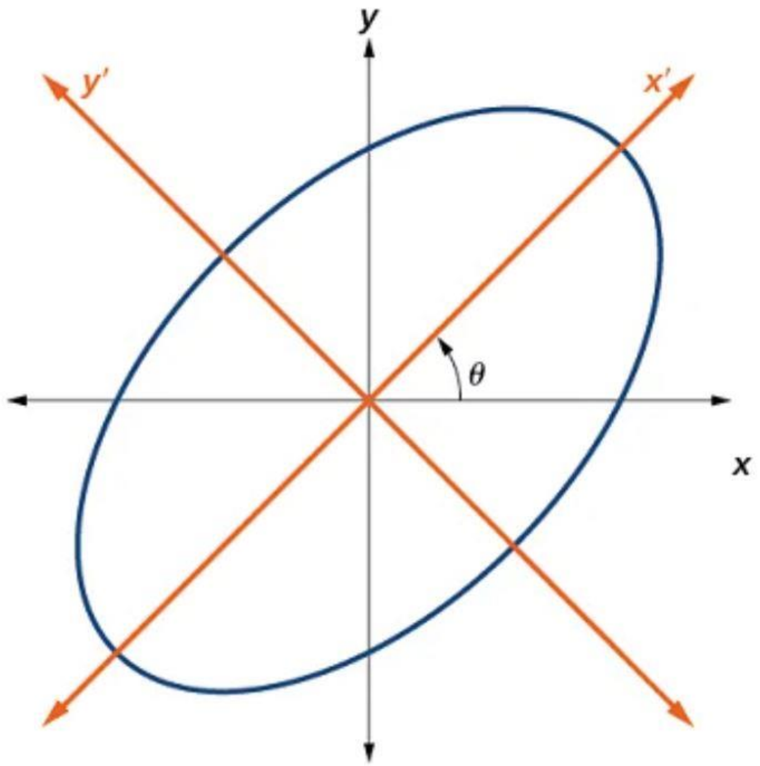
$$\hat{X}\hat{A}\vec{V} = ?$$

$$\hat{X}\hat{A}\mathbb{1}\vec{V} = \hat{X}\hat{A}\,\underbrace{\hat{X}^{-1}\,\hat{X}}\,\vec{V} = \hat{X}\hat{A}\,\hat{X}^{-1}\overrightarrow{V'}$$

$$\hat{A} \rightarrow \hat{X}\hat{A}\,\hat{X}^{-1}$$

Old basis **New basis**

Similarity Transformation



X-Y Coordinate:

$$\alpha x^2 + \beta y^2 + 2\gamma xy = 1$$

$$(x\ y)\begin{pmatrix} \alpha & \gamma \\ \gamma & \beta \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix} = 1$$

X'-Y' Coordinate:

$$\frac{x'^2}{a^2} + \frac{y'^2}{b^2} = 1$$

$$\boxed{(x'\ y')\begin{pmatrix} \frac{1}{a^2} & 0 \\ 0 & \frac{1}{b^2} \end{pmatrix}\begin{pmatrix} x' \\ y' \end{pmatrix} = 1}$$

Similarity Transformation for Diagonalization

Define the matrix P whose **columns** are the eigenvectors of A:

$$P = \begin{bmatrix} \mathbf{x}_1 & \mathbf{x}_2 & \dots & \mathbf{x}_n \end{bmatrix}$$

Since the eigenvectors are **linearly independent**, P is **invertible**, meaning P^{-1} exists.

$$AP = A \begin{bmatrix} \mathbf{x}_1 & \mathbf{x}_2 & \dots & \mathbf{x}_n \end{bmatrix}$$

$$AP = \begin{bmatrix} A\mathbf{x}_1 & A\mathbf{x}_2 & \dots & A\mathbf{x}_n \end{bmatrix} = \begin{bmatrix} \lambda_1\mathbf{x}_1 & \lambda_2\mathbf{x}_2 & \dots & \lambda_n\mathbf{x}_n \end{bmatrix}$$

Factoring out the eigenvalues:

$$AP = PD \qquad D = \begin{bmatrix} \lambda_1 & 0 & 0 & \dots & 0 \\ 0 & \lambda_2 & 0 & \dots & 0 \\ 0 & 0 & \lambda_3 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & \lambda_n \end{bmatrix}$$

From:

$$AP = PD$$

we **multiply both sides by P^{-1} from the left**:

$$P^{-1}AP = P^{-1}PD$$

Since $P^{-1}P = I$ (identity matrix), this simplifies to:

$$D = P^{-1}AP$$

P is Unitary $\boldsymbol{\hat{P}^{-1}} = \boldsymbol{\hat{P}^{\dagger}}$

$$\boxed{\boldsymbol{D} = \boldsymbol{\hat{P}}^{\dagger}\, A\, \boldsymbol{\hat{P}}}$$

Diagonalization of a matrix

$$H = \begin{pmatrix} 1 & 2 \\ 2 & 1 \end{pmatrix}$$

$$\lambda_1 = -1 \;\rightarrow\; u_1 = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$\lambda_2 = 3 \;\rightarrow\; u_2 = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

$$U = (\; \overrightarrow{u_1} \quad \overrightarrow{u_2} \;)$$

$$U^\dagger = \begin{pmatrix} \overrightarrow{u_1} \\ \overrightarrow{u_2} \end{pmatrix}$$

$$\hat{P}^\dagger \hat{H} \hat{P} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{-1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} \underbrace{\begin{pmatrix} 1 & 2 \\ 2 & 1 \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{-1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}}_{\begin{pmatrix} \frac{-1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{3}{\sqrt{2}} & \frac{3}{\sqrt{2}} \end{pmatrix}} = \begin{pmatrix} -1 & 0 \\ 0 & 3 \end{pmatrix}$$

Exercise

Illustrate diagonalizing a Hermitian matrix by a unitary similarity transformation

$$\mathrm{H} = \begin{pmatrix} 2 & 3-i \\ 3+i & -1 \end{pmatrix}.$$

Thanks For Your Attention