Quantum Mechanics for NMR (I)

Frank Eisenmenger

Department of Structural Biology
Leibniz-Institut für Molekulare Pharmakologie (FMP)
Robert-Rössle-Str. 10, 13125 Berlin

eisenmenger@fmp-berlin.de

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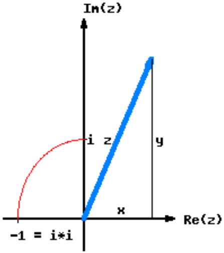
Outline

- Complex numbers
- Circular motion
- Cartesian vectors
- 2×2 matrices
- Pauli matrices
- Quantum operators
- Measurements and Quantum states
- Average of physical quantities
- $AB \neq BA$
- Density operator

Complex Numbers

$$
\begin{aligned}
z &= x + \mathrm{i}\ y && x, y \in \mathbb{R} \\
z^* &= x - \mathrm{i}\ y && \text{conjugate} \\
z\ z^* &= x^2 + y^2 = |z|^2 && 0 \le |z| \ \text{ module}
\end{aligned}
$$



Polar representation: $x = r\cos\theta$

$(r = |z|, \theta)$ $\quad y = r\sin\theta$

$$z = r(\cos\theta + \mathrm{i}\sin\theta) = re^{\mathrm{i}\theta} \ \text{(L. Euler 1748)}$$

Rotate z by ϕ with $w = e^{\mathrm{i}\phi}$: $\quad w \cdot z = e^{\mathrm{i}\phi} \cdot re^{\mathrm{i}\theta} = re^{\mathrm{i}(\theta+\phi)}$

Exercise

Prove:

$$i^{\,4} z = z$$

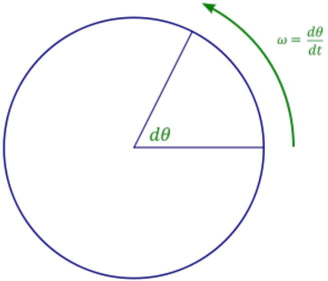
$$e^{i\pi} + 1 = 0$$

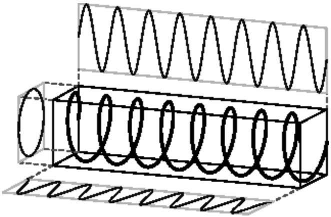
Circular Motion

Rotation in Gaussian plane with **constant** angular speed

$$\omega = \frac{\theta}{t} = \frac{2\pi}{T} \quad \longrightarrow \quad \theta = \omega t$$

$$x(t) = r e^{\mathrm{i}(\theta+\theta_0)} = (r e^{\mathrm{i}\theta_0}) e^{\mathrm{i}\omega t}$$





$$x(t) = a e^{\mathrm{i}\omega t} = a(\cos\omega t + \mathrm{i}\sin\omega t)$$

$$\begin{aligned} \cos\omega t &= \frac{e^{\mathrm{i}\omega t} + e^{-\mathrm{i}\omega t}}{2} \\ \sin\omega t &= \frac{e^{\mathrm{i}\omega t} - e^{-\mathrm{i}\omega t}}{2\mathrm{i}} \end{aligned}$$

Real oscillations consist of equal contributions of positive and negative frequency components.

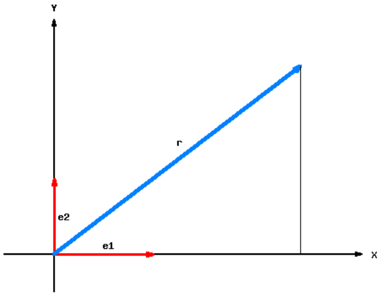
Cartesian Vectors

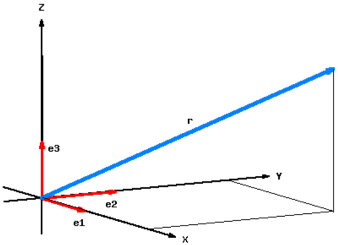
In 2D

$$\mathbf{r} = \begin{pmatrix} r_1 \\ r_2 \end{pmatrix} = r_1 \hat{\mathbf{e}}_1 + r_2 \hat{\mathbf{e}}_2$$

$$= r_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix} + r_2 \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$r_1 = \mathbf{r}^{\mathrm{T}} \hat{\mathbf{e}}_1 = (r_1 \ \ r_2) \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \ r_2 = \mathbf{r}^{\mathrm{T}} \hat{\mathbf{e}}_2$$





In 3D

$$\mathbf{r} = \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix} = r_1 \hat{\mathbf{e}}_1 + r_2 \hat{\mathbf{e}}_2 + r_3 \hat{\mathbf{e}}_3$$

$$= r_1 \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} + r_2 \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} + r_3 \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

2×2 Matrices

$$\mathbf{a}\mathbf{b}^{\mathrm{T}} = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} (b_1 \;\; b_2) = \begin{pmatrix} a_1 b_1 & a_1 b_2 \\ a_2 b_1 & a_2 b_2 \end{pmatrix}$$

$$\mathbf{A}\mathbf{b} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = \begin{pmatrix} a_{11} b_1 + a_{12} b_2 \\ a_{21} b_1 + a_{22} b_2 \end{pmatrix}$$

$$\mathbf{b}^{\mathrm{T}}\mathbf{A} = (a_{11} b_1 + a_{21} b_2 \;\; a_{12} b_1 + a_{22} b_2)$$

$$\mathbf{A}\mathbf{B} = \begin{pmatrix} a_{11} b_{11} + a_{12} b_{21} & a_{11} b_{12} + a_{12} b_{22} \\ a_{21} b_{11} + a_{22} b_{21} & a_{21} b_{12} + a_{22} b_{22} \end{pmatrix}$$

Determinant: $\det(\mathbf{A}) = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11} a_{22} - a_{12} a_{21}$

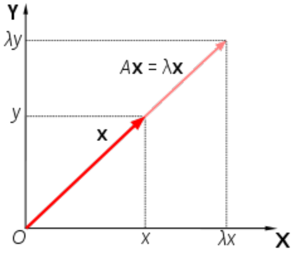
Inverse: $\mathbf{A}^{-1} = \dfrac{1}{\det(\mathbf{A})} \begin{pmatrix} a_{22} & -a_{12} \\ -a_{21} & a_{11} \end{pmatrix} \quad \det(\mathbf{A}) \neq 0$

2×2 Matrices (2)

Solve

$$\mathbf{A}\mathbf{x} = \lambda \mathbf{x}$$

for linear independent eigenvectors $\mathbf{x} \neq \mathbf{0}$ and eigenvalues λ:



$$\det(\mathbf{A} - \lambda \mathbf{I}) = 0$$

Characteristic polynomial for 2×2 matrix **A**

$$(\lambda - a_{11})(\lambda - a_{22}) - a_{12}a_{21} = 0$$

Exercise

Find eigenvalues for

$$\begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}$$

Hint: use $\sqrt{-1} = i$

Pauli matrices

W. Pauli (1924): two-valued quantum degree of freedom

Represent $\mathbf{r} = \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix}$ by $\begin{pmatrix} r_3 & r_1 - \mathrm{i} r_2 \\ r_1 + \mathrm{i} r_2 & -r_3 \end{pmatrix}$

Accordingly, standard basis vectors $\hat{\mathbf{e}}_i \in \mathbb{R}^3$ are related to Pauli matrices:

$$\boldsymbol{\sigma}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \ \boldsymbol{\sigma}_2 = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \ \boldsymbol{\sigma}_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Any $\mathbf{r} \in \mathbb{R}^3$ can hence be represented as $\boldsymbol{\sigma} = \sum_{i=1}^{3} r_i \boldsymbol{\sigma}_i, \quad \boldsymbol{\sigma} \in \mathbb{C}^2.$

Exercise

Show $\boldsymbol{\sigma}_i^2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$

Pauli matrices (2)

Eigenvalues $\det(\boldsymbol{\sigma}_i - \lambda \mathbf{I}) = 0 \quad \rightarrow \quad \lambda = \pm 1$

Eigenvectors $\boldsymbol{\sigma}_i \mathbf{x} = \lambda \mathbf{x}$

	$\lambda = 1 \rightarrow \mathbf{x}_1$	$\lambda = -1 \rightarrow \mathbf{x}_2$
$\boldsymbol{\sigma}_3$:	$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \equiv \lvert\alpha\rangle$	$\begin{pmatrix} 0 \\ 1 \end{pmatrix} \equiv \lvert\beta\rangle$
$\boldsymbol{\sigma}_1$:	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} (\lvert\alpha\rangle + \lvert\beta\rangle)$	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} = \frac{1}{\sqrt{2}} (\lvert\alpha\rangle - \lvert\beta\rangle)$
$\boldsymbol{\sigma}_2$:	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \mathrm{i} \end{pmatrix} = \frac{1}{\sqrt{2}} (\lvert\alpha\rangle + \mathrm{i}\,\lvert\beta\rangle)$	$\frac{1}{\sqrt{2}} \begin{pmatrix} \mathrm{i} \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} (\mathrm{i}\,\lvert\alpha\rangle + \lvert\beta\rangle)$

with $\langle\varphi_m|\cdot|\varphi_n\rangle \equiv \langle\varphi_m|\,\varphi_n\rangle = (x^*_{m_1}\ x^*_{m_2}\ ..) \begin{pmatrix} x_{n_1} \\ x_{n_2} \\ .. \end{pmatrix} = \begin{cases} 1, & m = n \\ 0, & m \neq n \end{cases}$

Quantum Operators

Postulate

In quantum mechanics physical quantities (observables) are represented by linear, Hermitean operators $Q = Q^\dagger$ ($\dagger$ - conjugate transpose).

Pauli matrices - projections of moment of electrons, protons etc. in three perpendicular reference directions:

spin angular momentum $\mathbf{S} = \frac{\hbar}{2}\sum_{i=1}^{3}\boldsymbol{\sigma}_i \quad \hbar \simeq 1.0546 \cdot 10^{-27}\ \frac{g \cdot cm^2}{s}$

spin magnetic moment $\boldsymbol{\mu} = \mu\sum_{i=1}^{3}\boldsymbol{\sigma}_i \quad \mu_p \simeq 1.4 \cdot 10^{-23}\ \frac{g \cdot cm^2}{s^2 \cdot gauss}$

Measurements and Quantum States

Postulate

In any measurement of an observable only eigenvalues ε_n of its associated operator Q may be observed.

State of quantum (micro) system prepared for measurement of Q

$$|\Psi\rangle = \sum_n c_n |\varphi_n\rangle$$

$|\varphi_n\rangle$ - eigenstate of Q

$c_n \in \mathbb{C}$ - probability amplitude

$$\langle\Psi|\Psi\rangle = \sum_m \sum_n c_m^* c_n \langle\varphi_m|\varphi_n\rangle = \sum_n |c_n|^2 = 1$$

Measurement: $|\psi\rangle \to |\varphi_n\rangle$ with probability $p_n = |c_n|^2$ yielding $Q = \varepsilon_n$.

Exercise

Show state $e^{i\theta}|\Psi\rangle$ to be indistinguishable from $|\Psi\rangle$.

Average of Physical Quantities

Postulate

The average value for observable Q obtained by measurements in state $|\Psi\rangle$ is $\langle Q\rangle = \langle\Psi| Q |\Psi\rangle$.

$$\langle Q\rangle = \sum_m \sum_n c_m^* c_n \langle\varphi_m| Q |\varphi_n\rangle = \sum_m \sum_n c_m^* c_n Q_{mn}$$

$$\Delta Q = \sqrt{\langle Q^2\rangle - \langle Q\rangle^2} \qquad \text{(uncertainty)}$$

For Pauli matrices it can be shown: $\quad \langle\boldsymbol{\sigma}_1\rangle^2 + \langle\boldsymbol{\sigma}_2\rangle^2 + \langle\boldsymbol{\sigma}_3\rangle^2 \leq 1$

Exercise

Compute $\langle\boldsymbol{\sigma}_3\rangle$ for $|\Psi\rangle = \frac{1}{\sqrt{5}}(|\alpha\rangle + 2|\beta\rangle)$.
Provide $\langle\boldsymbol{\sigma}_1\rangle$, $\langle\boldsymbol{\sigma}_2\rangle$ for given $\langle\boldsymbol{\sigma}_3\rangle = -1$.

$AB \neq BA$

W.Heisenberg, P. Jordan, M. Born (1925)

$$[P, Q] \equiv PQ - QP = \mathrm{i}\hbar \quad \rightarrow \quad \Delta P \Delta Q \geq \frac{\hbar}{2}$$

Pauli-Matrices

$$[\boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2] = 2\mathrm{i}\boldsymbol{\sigma}_3 \quad [\boldsymbol{\sigma}_2, \boldsymbol{\sigma}_3] = 2\mathrm{i}\boldsymbol{\sigma}_1 \quad [\boldsymbol{\sigma}_3, \boldsymbol{\sigma}_1] = 2\mathrm{i}\boldsymbol{\sigma}_2$$

Proposition

For two physical quantities to be simultaneously measured with arbitrary accuracy, their operators must commute: $[A, B] = 0$.

Consider

$$\boldsymbol{\sigma}^2 = (\lambda_1\boldsymbol{\sigma}_1 + \lambda_2\boldsymbol{\sigma}_2 + \lambda_3\boldsymbol{\sigma}_2)^2 = (\lambda_1^2 + \lambda_2^2 + \lambda_3^2)\mathbf{I} \rightarrow \left[\boldsymbol{\sigma}^2, \boldsymbol{\sigma}_i\right] = 0$$

Eigenvalues of $\boldsymbol{\sigma}_i$: $\lambda = \pm 1 \quad \rightarrow \quad$ eigenvalue of $\boldsymbol{\sigma}^2$: 3

Density Operator

Given ensemble of states $|\Psi_j\rangle$ each prepared with probability $\tilde{p}_j$.

Probability to measure eigenvalue ε_n of observable Q:

$$p_n = \sum_j \tilde{p}_j c_n^* c_n = \sum_j \tilde{p}_j \langle\varphi_n|\,\Psi_j\rangle\langle\Psi_j|\,\varphi_n\rangle = \langle\varphi_n|\,\rho\,|\varphi_n\rangle$$

Density operator $\rho \equiv \sum_j \tilde{p}_j |\Psi_j\rangle\langle\Psi_j|$

$$\sum_n p_n = \sum_n \langle\varphi_n|\,\rho\,|\varphi_n\rangle = Tr(\rho) = 1$$

$$\begin{aligned}\langle\overline{Q}\rangle &= \sum_j \tilde{p}_j \langle Q_j\rangle = \sum_j \tilde{p}_j \langle\Psi_j|\,Q\,|\Psi_j\rangle = \left|\text{use: } \sum_n |\varphi_n\rangle\langle\varphi_n| = \mathbf{1}\right| \\ &= \sum_n \sum_j \langle\Psi_j|\,Q\,|\varphi_n\rangle\langle\varphi_n|\,\Psi_j\rangle = \sum_n \sum_j \langle\varphi_n|\,\Psi_j\rangle\langle\Psi_j|\,Q\,|\varphi_n\rangle \\ &= \sum_n \langle\varphi_n|\,\rho Q\,|\varphi_n\rangle = Tr(\rho Q)\end{aligned}$$