# Lecture #4
# Quantum Mechanics: Mathematics

"If people do not believe that mathematics is simple, it is only because they do not realize how complicated life is." -- John von Neumann

- Topics
  - Linear vector spaces
  - Dirac Notation
  - Hilbert Space
  - Liouville Space
- Handouts and Reading assignments
  - van de Ven: Appendix A.
  - Miller, Chapter 4. (optional)
  - Ernst, Chapter 2, sections 2.1.3-2.1.4, pp 17-25 (optional).
  - Biographies: Hamilton, Dirac, Hilbert, Liouville.

# Review: Linear Algebra

- Solving sets of linear equations

$$\begin{aligned} x_1 + x_2 + x_3 &= 5 \\ 3x_1 + x_2 + 7x_3 &= 3 \\ x_1 + 2x_2 + 2x_3 &= 2 \end{aligned} \;\Rightarrow\; \begin{pmatrix} 1 & 1 & 1 \\ 3 & 1 & 7 \\ 1 & 2 & 2 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \begin{pmatrix} 5 \\ 3 \\ 2 \end{pmatrix} \;\Rightarrow\; \underline{A}x = y$$

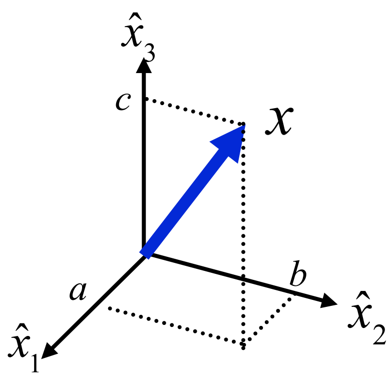
vectors

Matrix notation for this course

Analysis involves terms such as inverse, transpose, determinant, row and column spaces, eigen-vectors and values, etc.

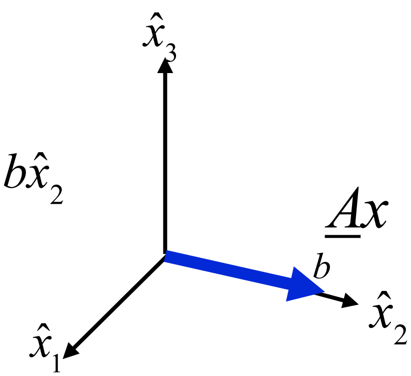
- Instead, consider an n x n matrix A as transforming a n-dimensional vector x into a new vector Ax.
- Linear transformations satisfy: $\underline{A}\left(ax + by\right) = a\left(\underline{A}x\right) + b\left(\underline{A}y\right)$ a, b scalars
- Matrices $\Longleftrightarrow$ Linear transformations

$$\underline{A} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$




$\hat{x}_1$, $\hat{x}_2$, and $\hat{x}_3$ are unit vectors along the three axes

$$\Rightarrow \quad \underline{A}x = \begin{pmatrix} 0 \\ b \\ 0 \end{pmatrix} = b\hat{x}_2$$




Projection of x along $\hat{x}_2$.

# Review: Wave Functions

- For the classical concept of a trajectory, we substitute the concept of the quantum state of a particle characterized by a *wave function*.
- Wavefunction $\psi(\vec{r},t)$

  generalized variable (position, angular momentum, spin, …)

  - contains all info possible to obtain about the particle
  - time evolution given by $\frac{\partial}{\partial t}\psi(\vec{r},t) = -\frac{i}{\hbar}H\psi(\vec{r},t)$
  - interpreted as a probability amplitude of the particle having state $\vec{r}$ with the probability density given by:

$$d\mathrm{P}(\vec{r},t) = C\left|\psi(\vec{r},t)\right|^2 d\vec{r}, \quad C \text{ constant.}$$

$$\int d\mathrm{P}(\vec{r},t) = 1 \Longrightarrow \frac{1}{C} = \int \left|\psi(\vec{r},t)\right|^2 d^3\vec{r} \quad << \infty$$

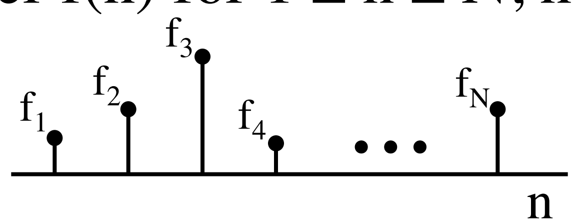
- Naturally leads us to the study of square-integrable functions.

# Functions

- Important to be familiar with the concept of treating functions, e.g. $\psi_1(x,y,z)$ and $\psi_2(x,y,z)$, as elements in a vector space.

- Example: consider f(n) for $1 \le n \le N$, n integer.

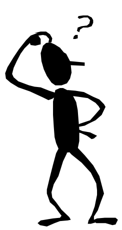
f(n) ⇨




⇨ $\vec{f} = \begin{pmatrix} f_1 \\ f_2 \\ \vdots \\ f_N \end{pmatrix}$

- We can also write $\vec{f}$ as a linear combination of vectors.

$$\vec{f} = f_1 \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} + f_2 \begin{pmatrix} 0 \\ 1 \\ \vdots \\ 0 \end{pmatrix} + \cdots f_N \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 1 \end{pmatrix} \quad \text{or} \quad \vec{f} = \tilde{f}_1 \begin{pmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{pmatrix} + \tilde{f}_2 \begin{pmatrix} 1 \\ \vdots \\ 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} + \cdots \tilde{f}_N \begin{pmatrix} 1 \\ \underline{0} \\ \vdots \\ \overline{1} \\ 0 \end{pmatrix}$$



What about f(n,m) or f(x) (x continuous)?

# Linear Vector Spaces

- The set of square-integrable functions belong to $L^2$
- Each wave function $\psi(\vec{r})$ is associated with an element of a <u>linear vector space</u> $F$ and is denoted as $|\psi\rangle$.

$$\psi(\vec{r}) \Leftrightarrow |\psi\rangle \in F$$

- Some properties:

$F \subset L^2$ (wave functions need to be sufficiently regular)

Linearity $\Rightarrow$ if $|\psi_1\rangle, |\psi_2\rangle \in F$, then

$$|\psi\rangle = \lambda_1 |\psi_1\rangle + \lambda_2 |\psi_2\rangle \in F$$

arbitrary complex numbers

Plus, other standard mathematical niceties

# Dirac Notation

- An element of $F$, denoted by $|\psi\rangle$ , is called a "ket".
- A <u>linear</u> <u>functional</u>, $\chi$, is an linear operation that associates a complex number with every ket $|\psi\rangle$.

$$\chi(|\psi\rangle) = number$$

- The set of all such linear functionals constitute a vector space $F^*$ called the <u>dual</u> <u>space</u> of $F$, and an element of $F^*$ is denoted as $\langle\chi|$ and called a "bra".

$$\chi(|\psi\rangle) = \langle\chi|\psi\rangle$$

<u>scalar</u> or <u>inner</u> <u>product</u>

"bra"+ "ket" = "bracket"

# Hilbert Space

- The scalar product satisfies:

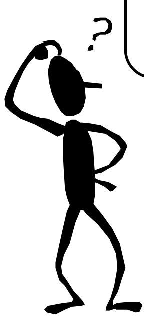
$$\langle \chi | \psi \rangle = \langle \psi | \chi \rangle^*$$

$$\langle \chi | \big( |\psi\rangle + |\xi\rangle \big) = \langle \chi | \psi \rangle + \langle \chi | \xi \rangle$$

$$\langle \chi | \lambda \psi \rangle = \lambda \langle \chi | \psi \rangle \quad \text{and} \quad \langle \lambda \chi | \psi \rangle = \lambda^* \langle \chi | \psi \rangle \qquad (\lambda \text{ scalar})$$

$$\langle \psi | \psi \rangle \geq 0 \quad (= 0 \text{ iff } |\psi\rangle = |0\rangle) \quad \Rightarrow \quad \text{norm: } \|\psi\| = \sqrt{\langle \psi | \psi \rangle}$$

- A linear vector space with a defined metric (in this case the scalar product) is called a <u>Hilbert Space</u>.



Question: What is $\langle \chi | \psi \rangle$ equivalent to in terms of $\psi(\vec{r})$ and $\chi(\vec{r})$?

Answer:

$$\langle \chi | \psi \rangle = \int_{\vec{r}} \psi(\vec{r}) \chi^*(\vec{r})\, d\vec{r}$$

or

$$= \sum_{n=1}^{N} \psi(n) \chi^*(n) \qquad \text{(discrete case)}$$

# Basis

- If it follows that: $\sum_{i=1}^{N} c_i |f_i\rangle = 0$ implies $c_i = 0$ for all $i$

  then the kets $|f_i\rangle$ are called <u>linearly independent</u>.

- If $n$ is the maximum number of linearly independent kets in a vector space $F$, then $F$ is call <u>$n$-dimensional</u>.

- In an $n$-dimensional vector space, $n$ linearly independent kets constitute a <u>basis</u>, and every element $|\psi\rangle$ in $F$ can be written as

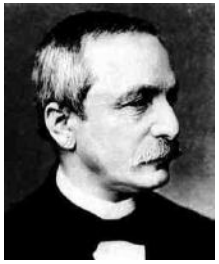
$$|\psi\rangle = \sum_{i=1}^{n} \psi_i |f_i\rangle$$ where $\psi_i$ is the coefficient of the ket $|f_i\rangle$.

# Orthonormal Basis

- If the basis kets $|f_i\rangle$ are normalized (i.e. $\langle f_i | f_i \rangle = 1$) and

$$\langle f_i | f_j \rangle = \delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases}$$

Kronecker delta function



then they constitute an orthonormal basis.

- The following identity (known as closure) also holds:

$$|\psi\rangle = \sum_{i=1}^{n} \langle f_i | \psi \rangle |f_i\rangle = \sum_{i=1}^{n} |f_i\rangle \langle f_i | \psi \rangle$$

Simply states that a vector is equal to the sum of its projections.

# Operators

- An operator, $\hat{O}$, generates one ket from another: $\hat{O}|\psi\rangle = |\xi\rangle$

  linear operators: $\hat{O}\big(\lambda|\psi\rangle + \mu|\xi\rangle\big) = \lambda\hat{O}|\psi\rangle + \mu\hat{O}|\xi\rangle$

  scalars

- A vector space $F$ is <u>closed</u> under $\hat{O}$ if

$$|\psi\rangle \in F \text{ and } \hat{O}|\psi\rangle = |\xi\rangle \text{ implies } |\xi\rangle \in F$$

- The <u>adjoint</u> of $\hat{O}$ is denoted $\hat{O}^\dagger$ as defined as

$$\left(\hat{O}|\psi\rangle\right)^\dagger = \langle\psi|\hat{O}^\dagger \quad \text{note}: \ \langle\psi|\hat{O}|\xi\rangle = \langle\xi|\hat{O}^\dagger|\psi\rangle^*$$

- $\hat{O}$ is <u>Hermitian</u> if $\hat{O} = \hat{O}^\dagger$

# Projection Operators

- Example linear operator: Projection onto ket $|\psi\rangle$: $\hat{P}_\psi = |\psi\rangle\langle\psi|$

$$\hat{P}_\psi|\xi\rangle = |\psi\rangle\underbrace{\langle\psi|\xi\rangle}_{\text{scalar}} = \lambda|\psi\rangle$$

- For the orthonormal basis kets $|f_k\rangle$

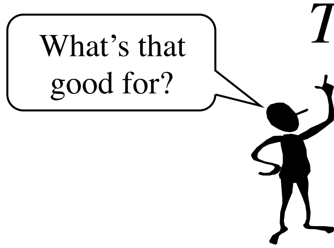
$$\hat{P}_k = |f_k\rangle\langle f_k|$$

$$\sum_k \hat{P}_k = \sum_k |f_k\rangle\langle f_k| = \hat{E} \qquad \text{(closure)}$$

identity operator

- Another common operator is the <u>transition</u> operator.

$$\hat{T}_{kl} = |f_k\rangle\langle f_l|$$



# More About Operators

- The product $\hat{O}_1\hat{O}_2$ means first $\hat{O}_2$ is applied to a ket and then $\hat{O}_1$ is applied to the result.

$$\hat{O}_1\hat{O}_2|\psi\rangle = \hat{O}_1\left(\hat{O}_2|\psi\rangle\right)$$

- In general, $\hat{O}_1\hat{O}_2 \neq \hat{O}_2\hat{O}_1$, and a quantity used frequently in QM is the <u>commutator</u> defined as:

$$\left[\hat{O}_1,\hat{O}_2\right] = \hat{O}_1\hat{O}_2 - \hat{O}_2\hat{O}_1$$

- A function of an operator is defined via the corresponding polynomial expansion.

e.g. $$e^{\hat{O}} = \hat{E} + \hat{O} + \frac{1}{2!}\hat{O}\hat{O} + \frac{1}{3!}\hat{O}\hat{O}\hat{O} + \ldots$$

identity operator

# Vector and Matrix Representations

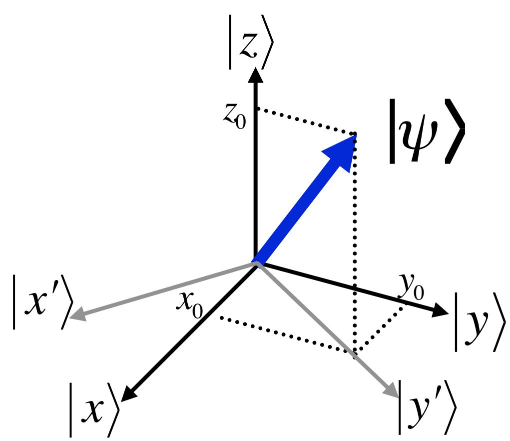
- When a ket, $|\psi\rangle$, is expressed as a linear combination of basis kets, $|f_i\rangle$, then a corresponding column vector, $\vec{\psi}$, can be constructed.

$$|\psi\rangle = \sum_{i=1}^{N} \psi_i |f_i\rangle \;\Rightarrow\; \vec{\psi} = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_n \end{pmatrix} \qquad \langle\psi| \;\Rightarrow\; \vec{\psi}^{\dagger} = \left(\psi_1^{*}, \psi_2^{*}, \ldots, \psi_n^{*}\right)$$

- Similarly, operators have matrix representations.

$|x\rangle = \hat{O}|y\rangle \;\Rightarrow\; \vec{x} = \underline{O}\vec{y}$ where $\underline{O}$ is a $n$ x $n$ matrix with elements: $O_{ij} = \langle f_i|\hat{O}|f_j\rangle$

Remember: vector and matrix representations depends on the basis set!




$$|\psi\rangle \;\Rightarrow\; \vec{\psi} = \begin{pmatrix} x_0 \\ y_0 \\ z_0 \end{pmatrix} \qquad \vec{\psi} = \begin{pmatrix} 0 \\ \sqrt{x_0^2 + y_0^2} \\ z_0 \end{pmatrix}$$

basis: $\{|x\rangle, |y\rangle, |z\rangle\}$ $\{|x'\rangle, |y'\rangle, |z\rangle\}$

# Change of Basis

- If the kets $|f_k\rangle$ constitute one orthonormal basis and the kets $|g_k\rangle$ constitute another, then a change of basis (also called basis transformation) is accomplished by:

$$O_{kl} = \langle f_k|\hat{O}|f_l\rangle = \sum_i \sum_j \langle f_k|g_i\rangle\langle g_i|\hat{O}|g_j\rangle\langle g_j|f_l\rangle$$

- Defining the unitary transformation matrix $\underline{U}$ as $U_{ij} = \langle f_i|g_j\rangle$ ,

$$\underline{O_f} = \underline{U}\,\underline{O_g}\,\underline{U^\dagger}$$

where $\underline{O_f}$ and $\underline{O_g}$ represent the operator matrices of $\hat{O}$ with respect to the basis $|f_k\rangle$ and $|g_k\rangle$.

# Eigenkets and Eigenvalues

- If $\hat{O}|\psi\rangle = \underset{\text{scalar}}{\lambda}|\psi\rangle$

  then $|\psi\rangle$ is called an eigenket of $\hat{O}$ with eigenvalue λ.

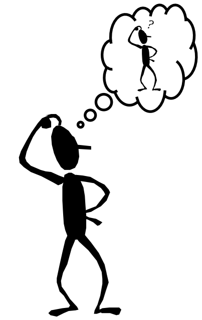
- The trace of a matrix is defined at the sum of the diagonal elements:

$$\mathrm{Tr}(\underline{O}) = \sum_i O_{ii}$$

- Since the trace of a matrix is invariant under a change of basis (see Problem Set 2), we can talk about the trace of the corresponding operator.

$$\mathrm{Tr}(\hat{O}) = \sum_i \lambda_i \quad \text{where } \lambda_i \text{ are the eigenvalues of } \hat{O}$$

# Liouville Space



- Operators defined on an $n$-dimensional Hilbert space, are themselves elements of an $n^2$-dimensional vector space known as <u>Liouville space</u> (sometimes called operator space or, more generally, an <u>algebra</u>).
- The metric in Liouville space is defined as: $\left(\hat{A}\,|\,\hat{B}\right) = \mathrm{Tr}\left(\hat{A}^{\dagger}\hat{B}\right)$
- In contrast to Hilbert space, the <u>product</u> of two Liouville Space elements is defined.

$$\hat{A},\hat{B} \in \mathcal{L} \quad \Rightarrow \quad \hat{A}\hat{B} = \hat{C} \in \mathcal{L}$$

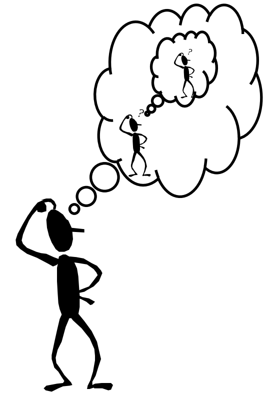
a Liouville space

Product is associative, but not necessarily commutative.

In general, $\hat{A}\hat{B} \neq \hat{B}\hat{A}$

For experts only. What are the remaining digits in this famous number 0.110001000000000000000001000…?

# Superoperators



- Operators that work on elements of a Liouville space are called <u>superoperators</u>.

$$\hat{\hat{A}}\hat{O}_1 = \hat{O}_2$$

superoperator denoted by double hat

- We will primarily deal with just one superoperator, namely the commutator:

$$\hat{\hat{A}}\hat{B} \equiv \left[\hat{A},\hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

- de Graaf text, unlike van de Ven, doesn't use superoperators, but I think the notation and concept makes things easier. Another good reference for superoperators and Liouville space:

  R. Ernst, G. Bodenhausen, and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, Clarendon Press, 1987.

# Fun with Superoperators

- Cyclic Commutators: Let $\left[\hat{A},\hat{B}\right]=\hat{C}$.

$\hat{A}$ and $\hat{B}$ are said to commute cyclically if $\left[\hat{A},\hat{C}\right]=\hat{B}$.

Superoperator notation $\Longrightarrow$ $\left[\hat{A},\hat{C}\right]=\left[\hat{A},\left[\hat{A},\hat{B}\right]\right]=\hat{\hat{A}}\hat{\hat{A}}\hat{B}=\hat{B}$

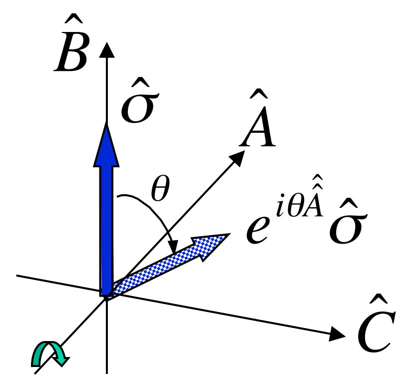
- Rotations: Given $\hat{A}$ and $\hat{B}$ cyclically commute, solve: $e^{i\theta\hat{\hat{A}}}\hat{B}=?$

$$e^{i\theta\hat{\hat{A}}}\hat{B}=\left(1+i\theta\hat{\hat{A}}+\tfrac{1}{2!}(i\theta\hat{\hat{A}})^2+\tfrac{1}{3!}(i\theta\hat{\hat{A}})^3+\cdots\right)\hat{B}$$

$$=\hat{B}+i\theta[\hat{A},\hat{B}]+\frac{(i\theta)^2}{2!}\hat{B}+\frac{(i\theta)^3}{3!}[\hat{A},\hat{B}]+\cdots=\overbrace{\hat{B}\cos\theta}^{\text{odd terms}}+\overbrace{i\hat{C}\sin\theta}^{\text{even terms}}$$

<u>Geometric interpretation</u>

Superoperator exponential $e^{i\theta\hat{\hat{A}}}\hat{B}$ produces a rotation in $\hat{B}\times[\hat{A},\hat{B}]$ plane of operator space!




Rotation is about $\hat{A}$ axis.

$$\underbrace{e^{i\theta\hat{\hat{A}}}}_{\text{We' ll stick with this notation.}}\equiv\hat{\hat{R}}_{\theta\hat{A}}$$ Rotation superoperator

# Summary of Vector Spaces

Hilbert Space $\mathcal{H}$

$$\{|\psi_i\rangle\}, i = 1, \ldots, n$$

$\downarrow$

Liouville Space $\mathcal{L}$

(operator algebra)

$$\{\hat{O}_i\}, i = 1, \ldots, n^2$$

$\downarrow$

Superoperator Algebra $S$

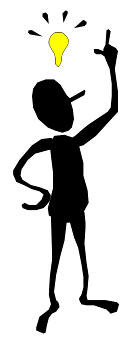
$$\{\hat{\hat{S}}_i\}, i = 1, \ldots, n^4$$

$\leftarrow$ We'll first describe QM followed by NMR in Hilbert space ...

$\leftarrow$ …then in Liouville space.

**<u>Key Concept</u>**

NMR is easiest to understand in Liouville space!



# Next Lecture: Basic Postulates of QM

# Biography: Paul Dirac

(born Aug. 8, 1902, Bristol, Gloucestershire, Eng. — died Oct. 20, 1984, Tallahassee, Fla., U.S.) English mathematician and theoretical physicist. His first major contribution (1925 – 26) was a general and logically simple form of quantum mechanics. About the same time, he developed ideas of Enrico Fermi, which led to the Fermi-Dirac statistics. He then applied Albert Einstein's special theory of relativity to the quantum mechanics of the electron and showed that the electron must have spin of 1/2. Dirac's theory also revealed new states later identified with the positron. He shared the 1933 Nobel Prize for Physics with Erwin Schrödinger. In 1932 Dirac was appointed Lucasian Professor of Mathematics at the University of Cambridge, a chair once occupied by Isaac Newton. Dirac retired from Cambridge in 1969 and held a professorship at Florida State University from 1971 until his death.

# Biography: Sir William Hamilton

Irish mathematician (1805–1865) Hamilton was a child prodigy, and not just in mathematics; he also managed to learn an extraordinary number of languages, some of them very obscure. In 1823 he entered Trinity College in his native city of Dublin, and four years later at the age of 22 was appointed professor of astronomy and Astronomer Royal for Ireland; these posts were given to him in order that he could continue to research unhampered by teaching commitments.

In 1827 he produced his first original work, in the theory of optics, expounded in his paper A Theory of Systems of Rays. In 1832 he did further theoretical work on rays, and predicted conical refraction under certain conditions in biaxial crystals. This was soon confirmed experimentally. In dynamics he introduced Hamilton's equations – a set of equations (similar to equations of Joseph Lagrange) describing the positions and momenta of a collection of particles. The equations involve the Hamiltonian function, which is used extensively in quantum mechanics. Hamilton's principle is the principle that the integral with respect to time of the kinetic energy minus the potential energy of a system is a minimum.

One of Hamilton's most famous discoveries was that of quaternions. These are a generalization of complex numbers with the property that the commutative law does not hold for them (i.e., A × B does not equal B × A). Hamilton's discovery of such an algebraic system was important for the development of abstract algebra; for instance, the introduction of matrices. Hamilton spent the last 20 years of his life trying to apply quaternions to problems in applied mathematics, although the more limited theory of vector analysis of Josiah Willard Gibbs was eventually preferred. Toward the end of his life Hamilton drank increasingly, eventually dying of gout.

# Biography: Joseph Liouville

(March 24, 1809 – September 8, 1882) was a French mathematician. Liouville graduated from the École Polytechnique in 1827. After some years as an assistant at various institutions including the Ecole Centrale Paris, he was appointed as professor at the École Polytechnique in 1838. He obtained a chair in mathematics at the Collège de France in 1850 and a chair in mechanics at the Faculté des Sciences in 1857.

Besides his academic achievements, he was very talented in organisatorial matters. Liouville founded the Journal de Mathématiques Pures et Appliquées which retains its high reputation up to today, in order to promote other mathematicians' work. He was the first to read, and to recognize the importance of the unpublished work of Évariste Galois which appeared in his journal in 1846. Liouville was also involved in politics for some time, and he became member of the Constituting Assembly in 1848. However, after the defeat in the Assembly elections in 1849, he turned away from politics.

Liouville worked in a number of different fields in mathematics, including number theory, complex analysis, differential geometry and topology, but also mathematical physics and even astronomy. He is remembered particularly for Liouville's theorem, a nowadays rather basic result in complex analysis. In number theory, he was the first to prove the existence of transcendental numbers by a construction using continued fractions (Liouville numbers). In mathematical physics, Liouville made two fundamental contributions: the Sturm–Liouville theory, which was joint work with Charles François Sturm, and is now a standard procedure to solve certain types of integral equations by developing into eigenfunctions, and the fact (also known as Liouville's theorem) that time evolution is measure preserving for a Hamiltonian system. In Hamiltonian dynamics, Liouville also introduced the notion of action-angle variables as a description of completely integrable systems. The modern formulation of this is sometimes called the Liouville-Arnold theorem, and the underlying concept of integrability is referred to as Liouville integrability.

In 1851, he was elected a foreign member of the Royal Swedish Academy of Sciences.
The crater Liouville on the Moon is named after him.

# Biography: David Hilbert

(born Jan. 23, 1862, Königsberg, Prussia — died Feb. 14, 1943, Göttingen, Ger.) German mathematician whose work aimed at establishing the formalistic foundations of mathematics. He finished his Ph.D. at the University of Königsberg (1884) and moved to the University of Göttingen in 1895. In 1900 at the International Mathematical Congress in Paris, he laid out 23 research problems as a challenge to the 20th century. Many have since been solved, in each case to great fanfare. Hilbert's name is prominently attached to an infinite-dimensional space called a Hilbert space, a concept useful in mathematical analysis and quantum mechanics.