## Albert Einstein（1905）

Assuming a light of pulsation $\omega$ and momentum $k$ ，the quantum of particle named « photon＊» by Lewis in 1926 holds an energy and impulsion defined such as：

$$
E=\hbar \omega \quad \vec{p}=\hbar \vec{k} \quad|\vec{k}|=\frac{2 \pi}{\lambda}
$$

photon＊$=$ Lichtquantum in German
Einstein introduces the concept of light quantization

Is the photon granularity in contradiction with the standard wave equation which should be continuous（Maxwell）？

How to understand the duality nature of Light？（e．g．Light has both properties of wave and particle at the same time）．

Does the duality still exist for particles of matter（electrons，etc．）？

## Louis de Broglie (1923)

With every particle of matter with mass $m$ and velocity $v$, a real wave must be associated, related to the momentum by the equation

In wavelength,

$$
\vec{k}=\frac{\vec{p}}{\hbar}
$$

$$
\lambda=\frac{2 \pi}{k}=\frac{2 \pi \hbar}{p}
$$

or even

"The fact that, following Einstein's introduction of photons in light waves, one knew that light contains particles which are concentrations of energy incorporated into the wave, suggests that all particles, like the electron, must be transported by a wave into which it is incorporated..."
"My essential idea was to extend to all particles the coexistence of waves and particles discovered by Einstein in 1905 in the case of light and photons"

## Double slit experiment with electrons

Electrons are accelerated to 50 kV , with a speed of about $120,000 \mathrm{~km} / \mathrm{s}$ e.g. $0.4 \times$ c ( $\sim 10$ electrons per second)


Similar to Fresnel's biprism experiment


Although electrons are sent one by one, interference fringes could be observed. These interference fringes are formed only when electron waves pass through on both sides of the electron biprism at the same time but nothing other than this

## Double slit experiment with electrons



At the beginning, bright spots begin to appear here and there at random positions. Electrons are detected one by one as punctual particles

The electron impact point ( $x, y$ ) looks somewhat random ??


## Double slit experiment with electrons



Number of electrons accumulated: (a) 8; (b) 270; (c) 2,000; (d) 16,000. About 30 minutes is needed to reach stage (d)

## The wave function

First postulate: The state of a quantum mechanical system is completely specified by a wavefunction

$$
\psi(\vec{r}, t) \text { that depends on the spatial coordinates } \vec{r}=(x, y, z)
$$

The wavefunction or state function has the important property that is the probability that the particle lies in a volume element located at $\vec{r}$ and at time t

$$
d^{3} P=|\psi(\vec{r}, t)|^{2} d^{3} r
$$

The wavefunction must satisfy certain mathematical conditions because of this probabilistic interpretation

$$
\psi(\vec{r}, t) \text { probability amplitude } \quad \int|\psi(\vec{r}, t)|^{2} d^{3} r=1
$$

$$
|\psi(\vec{r}, t)|^{2} \text { probabilty density }
$$

Normed function

## Probabilistic interpretation

Assume N particles identically prepared in the same quantum state

For each particle, we measure the position with a detector having a spatial resolution $\delta x$, then we build-up an histogram of the results

It is possible to retrieve $|\psi(x, t)|^{2}$ with a good precision if and only if $N \gg 1$
$n_{i}$ : number of atoms detected in the $i^{i t h}$ channel


## Mean value and root mean square

Mean (expectation) value

$$
\langle x\rangle=\int x \underbrace{|\psi(x, t)|^{2} d x}_{d P(x)}
$$



Variance $\quad \Delta x^{2}=\left\langle x^{2}\right\rangle-(\langle x\rangle)^{2}$

$$
\begin{aligned}
& \text { with }\left\langle x^{2}\right\rangle=\int x^{2} \underbrace{|\psi(x, t)|^{2} d x}_{d P(x)} \\
& x=\sqrt{\Delta x^{2}}
\end{aligned}
$$

Standard deviation $\Delta x=\sqrt{\Delta x^{2}}$
or dispersion

## Summary of the $1^{\text {st }}$ postulate

The wave function contains all the information of the system e.g. there is nothing else in the quantum formalism that would allow to know, before doing a measurement where the particle will be detected

The probabilism character and randomness behavior does not result from a lack of knowledge of the initial conditions but is inherently included in the quantum formalism

No hidden variables, "God does not play dice with the Universe" (Einstein)
Experiment and theoretical proofs, Bell's theorem

## Superposition principle

The wavefunction is a complex-valued probability amplitude
If $\psi_{1}$ and $\psi_{2}$ are wavefunctions with laws of probability $P_{1}=\left|\psi_{1}\right|^{2}$ and $P_{2}=\left|\psi_{2}\right|^{2}$
then,

$$
\psi \propto \psi_{1}+\psi_{2}
$$

is also a possible wave function with the law of probability

$$
P=|\psi|^{2} \propto P_{1}+P_{2}+\psi_{1}^{*} \psi_{2}+\psi_{1} \psi_{2}^{*}
$$



Interferences
Superposition principle is a prerequisite for a structure of a vector space

## Second postulate

The wave function or state function of a system evolves in time according to the time-dependent Schrödinger equation


$$
i \hbar \frac{\partial \psi}{\partial t}=-\frac{\hbar^{2}}{2 m} \Delta \psi
$$

## Free particle without interaction

De Broglie's waves are solutions of Schrödinger equation

## Definition

An eigenfunction of an operator $\hat{A}$ defined on the wave function space is any non-zero function $\psi_{\alpha}(x)$ in that space that, when acted upon by $\hat{A}$ is only multiplied by some scaling factor called an eigenvalue $a_{\alpha}$

$$
\hat{A} \psi_{\alpha}(x)=a_{\alpha} \psi_{\alpha}(x)
$$

Spectral theorem: If the operator $\hat{A}$ is Hermitian, there exist an orthonormal basis of consisting of eigenvectors of $\hat{A}$
$\rightarrow$ Each eigenvalue is element of the set of real numbers $\mathbb{R}$
$\rightarrow$ The operator $\hat{A}$ is diagonalizable
Note the occurrence of some subtleties when moving to a complex space with an infinite-dimension! (see later on)

## Eigenfunctions of the Hamiltonian

Play a crucial role to describe the evolution of many quantum systems

$$
\begin{gathered}
\hat{H} \psi_{E}(x)=E \psi_{E}(x) \\
-\frac{\hbar^{2}}{2 m} \frac{d^{2} \psi_{E}(x)}{d x^{2}}+V(x) \psi_{E}(x)=E \psi_{E}(x)
\end{gathered}
$$

Solutions usually not trivial ( $\rightarrow$ numerical analysis)
Some cases can be solved analytically

Harmonic potential $\quad V(x)=\frac{1}{2} m \omega^{2} x^{2}$
Coulomb potential

$$
V(r)=-\frac{q^{2}}{4 \pi \epsilon_{0} r}
$$

Constant piecewise potentials


## Infinite well potential

## Particle in a box



$$
\begin{gathered}
\hat{H} \psi_{E}(x)=E \psi_{E}(x) \\
\text { To simplify we assume } \psi_{E}(x) \equiv \psi(x) \\
0 \leq x \leq L \\
-\frac{\hbar^{2}}{2 m} \psi^{\prime \prime}(x)=E \psi(x)
\end{gathered}
$$

Boundary conditions: The wave function is always continuous!

$$
\psi(0)=\psi(L)=0
$$

## Infinite well potential

We assume the energy $E>0$ and $\in \mathbb{R} k=\sqrt{2 m E} / \hbar \quad E=\hbar^{2} k^{2} / 2 m$

$$
-\frac{\hbar^{2}}{2 m} \psi^{\prime \prime}(x)=E \psi(x) \quad \square \psi^{\prime \prime}(x)=-k^{2} \psi(x)
$$

General form of the solutions $\quad \psi(x)=\alpha \sin (k x)+\beta \cos (k x)$
Boundary at $x=0: \psi(0)=0 \Rightarrow \beta=0$
Boundary at $x=L: \psi(L)=0 \Rightarrow \alpha \sin (k L)=0 \Rightarrow \sin (k L)=0$
$\rightarrow$ All wavevectors k can take only discrete values

$$
k=k_{n}=\frac{n \pi}{L} \quad n=1,2, \ldots
$$

$\rightarrow$ And all eigenvalues of the energy are quantized $E_{n}=n^{2} \frac{\hbar^{2} \pi^{2}}{2 m L^{2}}$

## Infinite well potential

Eigenfunctions of the Hamiltonian can be expressed as follows
$\psi_{n}(x)=\alpha \sin \left(k_{n} x\right) \quad$ with $\quad k_{n}=\frac{n \pi}{L} \quad$ and $\quad E_{n}=\frac{\hbar^{2} k_{n}^{2}}{2 m}=\frac{\hbar^{2} n^{2} \pi^{2}}{2 m L^{2}}$
Normalization $\quad \int_{0}^{L}\left|\psi_{n}(x)\right|^{2} d x=1 \quad \Rightarrow \quad \alpha=\sqrt{2 / L}$
The set of functions $\psi_{n}$ is an orthonormal base of functions such as

$$
\psi(0)=\psi(L)=0
$$

Orthonormality $\quad \int_{0}^{L} \psi_{n}(x) \psi_{\ell}(x) d x=\delta_{n, \ell} \quad$ (Kronecker delta)
The wave function can be represented by the expansion

$$
\psi(x)=\sum_{n=1}^{+\infty} C_{n} \psi_{n}(x) \quad \sum_{n=1}^{+\infty}\left|C_{n}\right|^{2}=1
$$

Similar to a Fourier series expansion Similar to a decomposition in a vector subspace

## Infinite well potential

$$
\begin{aligned}
& E_{n}=n^{2} E_{1} \quad n=1,2, \ldots \\
& E_{1}=\frac{\hbar^{2} \pi^{2}}{2 m L^{2}} \\
& \psi_{n}(x) \propto \sin (n \pi x / L)
\end{aligned}
$$


$\rightarrow$ An electron in a quantum well of diameter $L=6 \times 10^{-9} \mathrm{~m}$

$$
E_{1}=10 \mathrm{meV}
$$

$\rightarrow$ A nucleon (proton or neutron) in a nucleus of diameter $L=4 \times 10^{-15} \mathrm{~m}$ $\mathrm{E}_{1}=10 \mathrm{MeV}$

## Light emission from a quantum well


Gallium nitride

Photon $\mathrm{h} v=E_{2}-E_{1}=\mathrm{hc} / \lambda$

$$
\begin{aligned}
E_{2}-E_{1} & =(4-1) \times \frac{\hbar^{2} \pi^{2}}{2 m L^{2}} \\
& =\frac{3 \hbar^{2} \pi^{2}}{2 m L^{2}}
\end{aligned}
$$


The Nobel Prize in Physics 2014
Isamu Akasaki, Hiroshi Amano, Shuji Nakamura
"for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources"

## A key application: Semiconductor lasers

Optical communications
Gas/molecule detection
$\rightarrow$ Medical (breath analyses)
$\rightarrow$ Environment (air pollution)
$\rightarrow$ Security (explosive detectio।
Countermeasures
Atmospheric communications


Diode lasers and quantum cascade lasers can produce stimulated light from near infrared to THz range!

## Relationship between measured results and eigenvalues?

We want to measure a physical quantity $A$ of a particle prepared in the quantum state $\psi(x)$
The result of the measurement of $A$ is predicted with certainty if and only if the state $\psi(x)$ is an eigenstate of observable $\hat{A}$

Proof:

$$
\begin{aligned}
& \text { If } \psi(x)=\psi_{\alpha}(x) \text { the measure of } A \text { is predicted with certainty } \\
& \langle a\rangle=\int \psi_{\alpha}^{*}(x)\left[\hat{A} \psi_{\alpha}(x)\right] d x=\int \psi_{\alpha}^{*}(x)\left[a_{\alpha} \psi_{\alpha}(x)\right] d x=a_{\alpha} \quad \text { QED } \\
& \left\langle a^{2}\right\rangle=\int \psi_{\alpha}^{*}(x)\left[\hat{A}^{2} \psi_{\alpha}(x)\right] d x=a_{\alpha}^{2} \quad \Rightarrow \Delta a^{2}=\left\langle a^{2}\right\rangle-(\langle a\rangle)^{2}=0
\end{aligned}
$$

Example: we found that an eigenstate of the Hamiltonian corresponds to an energy level of the quantum well (particle in a box)

## Relationship between measured results and eigenvalues?

Converse?

$$
\langle a\rangle=\int \psi^{*}(x)[\hat{A} \psi(x)] d x \quad \Delta a^{2}=0
$$

We assume the system in the state $\psi(x)$ in such way that the physical quantity $A$ is well defined (no fluctuations among the measured results)
Then, $\psi(x)$ is an eigenstate of $\hat{A}$ with the corresponding eigenvalue $\langle a\rangle$

$$
\begin{aligned}
\text { Proof } \quad 0 & =\int \psi^{*}(x)\left[(\hat{A}-\langle a\rangle)^{2} \psi(x)\right] d x \\
& =\int[(\hat{A}-\langle a\rangle) \psi(x)]^{*}[(\hat{A}-\langle a\rangle) \psi(x)] d x \\
(\hat{A}-\langle a\rangle) \psi(x) & =0 \quad \Rightarrow \hat{A} \psi(x)=\langle a\rangle \psi(x) \quad \text { QED }
\end{aligned}
$$

## Relationship between measured results and eigenvalues?

Converse?

$$
\langle a\rangle=\int \psi^{*}(x)[\hat{A} \psi(x)] d x \quad \Delta a^{2}=0
$$

We assume the system in the state $\psi(x)$ in such way that the physical quantity $A$ is well defined (no fluctuations among the measured results)

Then, $\psi(x)$ is an eigenstate of $\hat{A}$ with the corresponding eigenvalue $\langle a\rangle$

Conclusion: The measurement of $A$ is predicted with certainty if and only if the state of the particle is an eigenstate of $\hat{A}$
$\rightarrow$ The result is the associated eigenvalue (must be a real number )
$\rightarrow$ An eigenstate is basically a state without dispersion

## What to expect from a measurement?

The measurement of a physical quantity gives a number (or a set of numbers) which brings information on the system under study

Ex: Distribution of human height


The result is trustable if and only if the measurement of a physical quantity done over a short period of time gives the same numbers (repeatability)
A short period of time means that the state of the system does not substantially evolve between two consecutive measurements (i.e. same experimental conditions)

## Which state after the measurement?

Energy levels in a quantum well


Initial state

$$
\psi(x)=\sum_{n} C_{n} \psi_{n}(x)
$$



The measurement performed at $\mathrm{t}_{2}$ is predicted with certainty if and only if:
(a) The energy $\varepsilon$ must be an eigenvalue of the energy operator i.e. is an element of the set of the eigenvalues $E_{n}$
(b) The system has to be in an eigenstate of the energy operator at $\mathrm{t}_{2}$

$$
\text { Measurement at } \mathrm{t}_{1}: \psi(x) \longrightarrow \psi_{n}(x)
$$

## Possible results?

In any measurement of the observable $A$ associated with operator $\hat{A}$, the only values that will ever be observed are the eigenvalues of $\hat{A}$

If the particle, before the measurement, is in an eigenstate $\psi_{\alpha}(x)$ of $\hat{A}$ then the result is with certainty the eigenvalue $a_{\alpha}$
If the particle, before the measurement, is in whatever state

$$
\psi(x)=\sum_{\alpha} C_{\alpha} \psi_{\alpha}(x) \quad \text { with } \quad \sum_{\alpha}\left|C_{\alpha}\right|^{2}=1
$$

Then the result is randomly an eigenvalue of the set of $a_{\alpha}$
What is the corresponding probability law?
We know that $\langle a\rangle=\int \psi^{*}[\hat{A} \psi] d x=\ldots=\sum_{\alpha}\left|C_{\alpha}\right|^{2} a_{\alpha}$

$$
\left\langle a^{n}\right\rangle=\int \psi^{*}\left[\hat{A}^{n} \psi\right] d x=\ldots=\sum_{\alpha}^{\alpha}\left|C_{\alpha}\right|^{2} a_{\alpha}^{n}
$$

leading to the probability law $a_{\alpha}: p_{\alpha}=\left|C_{\alpha}\right|^{2^{\alpha}}$

## $3^{\text {rd }}$ postulate (strong version)

In any measurement of the observable $A$ associated with operator $\hat{A}$, the only values that will ever be observed are the eigenvalues, which satisfy the eigenvalue equation

$$
\hat{A} \psi_{\alpha}(x)=a_{\alpha} \psi_{\alpha}(x) \quad \psi_{\alpha}(x) \text { Orthonormal eigenfunctions }
$$

Before the measurement: $\psi(x)=\sum_{\alpha} C_{\alpha} \psi_{\alpha}(x) \quad$ with $\quad \sum_{\alpha}\left|C_{\alpha}\right|^{2}=1$
(a) If the system is in an eigenstate of $\hat{A}$ with eigenvalue $a_{\alpha}$ then any measurement of the quantity will yield $a_{\alpha}$
(b) The probability that eigenvalue $a_{\alpha}$ will occur -- it is the absolute value squared of the coefficient, $p_{\alpha}=\left|C_{\alpha}\right|^{2}$
(c) After measurement of $\psi(x)$ yields some eigenvalue $a_{\alpha}$, the wave function immediately collapses into the corresponding eigenstate $\psi_{\alpha}(x)$. In the case that is degenerate, $\psi(x)$ becomes the projection of $\psi(x)$ onto the degenerate subspace associated to the eigenvalue $a_{\alpha}$

## What to learn from a measurement?

A single measurement performed on a single particle reveals information on the state of the quantum system after the measurement


From this single measurement, we cannot retrieve the state $\psi(x)$
We only know that $p_{\mathrm{a} 2}$ is not zero
The wave function is modified in an irreversible way by the measurement
Wave function collapse e.g. quantum decoherence

## What to learn from a measurement?

If we prepare $\mathbf{N}$ particles in the same quantum state (unknown), it is possible to determine the probabilities $p_{\alpha}$. This would require to perform only a single measurement of $A$ on each particle

|  | $N \gg 1$ |
| ---: | :--- |
| $\psi=\sum_{\alpha} C_{\alpha} \psi_{\alpha}$ |  | | $a_{\alpha 1}$ | $p_{1}=N_{1} / N$ |
| :--- | :--- |
| $a_{\alpha 2}$ | $p_{2}=N_{2} / N$ |
| $a_{\alpha 3}$ | $p_{3}=N_{3} / N$ |

From $p_{\alpha}=\left|C_{\alpha}\right|^{2}$ it is possible to retrieve at least partially $\psi(x)$

## Evolution of an eigenstate

We determine the eigenstates of the Hamiltonian $\hat{H} \psi_{n}(x)=E_{n} \psi_{n}(x)$ The set of functions $\psi_{n}$ is an orthonormal basis of wave functions

Initial wave function: $\psi(x, 0)=\sum_{n} C_{n} \psi_{n}(x)$ with $C_{n}=\int \psi_{n}^{*}(x) \psi(x, 0) d x$
Wave function at time t: $\quad \psi(x, t)=\sum_{n} C_{n} \psi_{n}(x) e^{-i E_{n} t / \hbar}$
Proof

$$
i \hbar \frac{\partial \psi}{\partial t}=\hat{H} \psi(x, t)
$$

$i \hbar \frac{\partial \psi}{\partial t}=i \hbar \sum_{n} C_{n} \psi_{n}(x)\left(\frac{-i E_{n}}{\hbar}\right) e^{-i E_{n} t / \hbar}=\sum_{n} C_{n} E_{n} \psi_{n}(x) e^{-i E_{n} t / \hbar}$
$\hat{H} \psi(x, t)=\sum_{n} C_{n} \hat{H} \psi_{n}(x) e^{-i E_{n} t / \hbar}=\sum_{n} C_{n} E_{n} \psi_{n}(x) e^{-i E_{n} t / \hbar}$

## Eigenstates of the Hamiltonian

Consider the particle in the initial state at t=0 $\quad \psi(x, 0)=\psi_{n}(x) \begin{gathered}\text { Wave packet } \\ \text { collapse }\end{gathered}$
Then, the solutions of the Schrödinger equation at time $t$ is given by

$$
\psi(x, t)=\psi_{n}(x) e^{-i E_{n} t / \hbar}
$$

The eigenstates of the Hamiltonian are stationary states
$\rightarrow$ the probability density is time independent $|\psi(x, t)|^{2}=\left|\psi_{n}(x)\right|^{2}$
Also valid for all expected values associated to any physical quantities

$$
\begin{array}{rlr}
\langle a\rangle(t) & =\int \psi^{*}(x, t)[\hat{A} \psi(x, t)] d x \\
& =\int \psi_{n}^{*}(x)\left[\hat{A} \psi_{n}(x)\right] d x \quad \text { No time } & \text { dependence! }
\end{array}
$$

## Steady-state solutions

Sturm-Liouville theorem (real wave functions): As we change to a higher energy level, the index n grows, and we have more nodes (points where the sign changes) of the wave function

Further readings: Arfken and Weber, Mathematical Methods for Physicists, Academic Press, Wiley


Case of symmetric potentials: Odd or even eigenfunctions (nondegenerate) or whatever (degenerate)

## How to explain the chemical bond?

2 nuclei and 1 electron (Dihydrogen cation i.e. ion $\mathrm{H}_{2}{ }^{+}$)


Nucleus 1


Nucleus 2


Nucleus 1


Nucleus 2

We will show that the tunneling jump of the electron from orbit 1 to orbit 2 lowers the energy. This effect is enhanced when the two nuclei are located relatively close to each other

Attraction between atoms explains the chemical bond

## Ammonia ( $\mathrm{NH}_{3}$ )

Under the right conditions, ammonia molecules can be flipped. Imagine you are looking at an open umbrella from the side. A strong wind comes along and turns the umbrella inside out!


Left configuration



Right configuration


The fundamental state of the molecule is in a superposition of two configurations « Left » and « Right », hence quantum oscillations take place between the two states through tunneling effect

## Double well potential



Consider the energy levels such as $\mathrm{E}<\mathrm{V}_{0}$
What is the role of the tunneling effect across the barrier ?
As the Hamiltonian $\mathrm{H}(\mathrm{x})$ is invariant i.e. $\mathrm{H}(-\mathrm{x})=\mathrm{H}(\mathrm{x})$, the eigenstates of the Hamiltonian can be described through a linear combination of even (symmetric) and odd (antisymmetric) functions

$$
\psi(x)=\psi(-x) \quad \psi(x)=-\psi(-x)
$$

## Energy levels



## Energy levels



The molecule appears in a superposition of two configurations «Left » and «Right»，with quantum oscillations taking place between the two states through tunneling effect

## Summary

Use Sturm-Liouville's theorem p. 140 !


First excited state level of the semi-infinite well

Ground state level of the semi-infinite well

$$
\begin{array}{ccc}
E_{A}=E_{1}+A & & \text { with } \\
E_{S}=E_{1}-A & A=\frac{2 \hbar^{2} \pi^{2}}{m \kappa a^{3}} e^{-\kappa \Delta} \\
\text { if } \quad V_{0} \gg E & \kappa \simeq \sqrt{2 m V_{0}} / \hbar & \kappa a, \kappa \Delta \gg 1
\end{array}
$$

## Chemical bond

## The cleavage 2A depends on the distance $R$ between the two nuclei



Nucleus 1

Nucleus 2


Nucleus 2


Nucleus 1


## Ammonia inversion

Consider the ammonia inversion doublet with the lowest energy level


$$
\begin{aligned}
& \Delta \mathrm{E}=\mathrm{E}_{\mathrm{A}}-\mathrm{E}_{\mathrm{S}}=\frac{\hbar^{2} \pi^{2}}{2 m a^{2}} \times \frac{8 e^{-\kappa \Delta}}{\kappa a} \\
& \mathrm{E}_{\mathrm{A}}-\mathrm{E}_{\mathrm{S}}=\hbar \omega_{0}, \mathrm{E}_{\mathrm{A}}+\mathrm{E}_{\mathrm{S}}=0
\end{aligned}
$$



For both eigenstates

$$
\begin{gathered}
\psi_{A, S}(x, t)=\varphi_{A, S}(x) e^{-i E_{A, S} t / \hbar} \\
\left|\psi_{A, S}(x, t)\right|^{2}=\left|\varphi_{A, S}(x)\right|^{2}
\end{gathered}
$$



Probability densities are symmetric and time independent (i.e. stationary states) with values of $1 / 2$ for each state

## Ammonia inversion

$$
\hat{A}=\left(\begin{array}{cc}
a & b+i c \\
b-i c & d
\end{array}\right) \quad \begin{gathered}
\text { general expression with } \\
\mathbf{a}, \mathbf{b}, \mathbf{c}, \text { and d real numbers }
\end{gathered}
$$

The Hamiltonian in the basis is $\left(\left|\varphi_{A}\right\rangle,\left|\varphi_{S}\right\rangle\right)$ diagonal

$$
\left(\left|\varphi_{A}\right\rangle,\left|\varphi_{S}\right\rangle\right) \text { are eigenstates of the } \hat{H}_{N H_{3}}
$$

with eigenvalues $\quad E_{A}=E_{1}+A=\frac{\hbar \omega_{0}}{2}$
(Taking $\mathrm{E}_{1}=0$ )

$$
E_{S}=E_{1}-A=-\frac{\hbar \omega_{0}}{2}
$$

then

$$
\hat{H}_{N H_{3}}=\left(\begin{array}{cc}
E_{A} & 0 \\
0 & E_{S}
\end{array}\right)=\frac{\hbar}{2}\left(\begin{array}{cc}
\omega_{0} & 0 \\
0 & -\omega_{0}
\end{array}\right)
$$

## Ammonia inversion



Consider the quantum superpositions

$$
\left|\varphi_{D}\right\rangle=\frac{1}{\sqrt{2}}\left(\left|\varphi_{S}\right\rangle+\left|\varphi_{A}\right\rangle\right) \quad \text { "Right (D)" }
$$



$$
\left|\varphi_{G}\right\rangle=\frac{1}{\sqrt{2}}\left(\left|\varphi_{S}\right\rangle-\left|\varphi_{A}\right\rangle\right) \quad \text { "Left (G)" }
$$

Those are not stationary states!
If
then

$$
\begin{gathered}
|\psi(t)\rangle=\frac{1}{\sqrt{2}}\left(e^{-i E_{S} t / \hbar}\left|\varphi_{S}\right\rangle+e^{-i E_{A} t / \hbar}\left|\varphi_{A}\right\rangle\right) \\
|\psi(t)\rangle=\frac{1}{2}\left[\left(\left|\varphi_{D}\right\rangle+\left|\varphi_{G}\right\rangle\right) e^{i \omega_{0} t / 2}+\left(\left|\varphi_{D}\right\rangle-\left|\varphi_{G}\right\rangle\right) e^{-i \omega_{0} t / 2}\right] \\
|\psi(t)\rangle=\cos \left(\frac{\omega_{0} t}{2}\right)\left|\varphi_{D}\right\rangle+i \sin \left(\frac{\omega_{0} t}{2}\right)\left|\varphi_{G}\right\rangle
\end{gathered}
$$

## Ammonia inversion


Consider the quantum superpositions


$$
\left|\varphi_{G}\right\rangle=\frac{1}{\sqrt{2}}\left(\left|\varphi_{S}\right\rangle-\left|\varphi_{A}\right\rangle\right) \quad \text { "Left (G)" }
$$

$$
\text { If } \quad|\psi(t)\rangle=\cos \left(\frac{\omega_{0} t}{2}\right)\left|\varphi_{D}\right\rangle+i \sin \left(\frac{\omega_{0} t}{2}\right)\left|\varphi_{G}\right\rangle
$$

If the molecule is initially prepared to be in the "Right" configuration, over time, the molecule will be oscillating at frequency $\omega_{0}$ between "Right" and "Left" dispositions

Nitrogen inversion $\rightarrow$ oscillating dipole $\rightarrow$ radiation at frequency

## Ammonia inversion





$$
\left|\varphi_{G}\right\rangle=\frac{1}{\sqrt{2}}\left(\left|\varphi_{S}\right\rangle-\left|\varphi_{A}\right\rangle\right) \quad \text { "Left (G)" }
$$

$$
\begin{aligned}
& \nu_{0}=\omega_{0} /(2 \pi)=24 \mathrm{GHz} \\
& 0.10 \mathrm{meV} \hat{\imath} \frac{\left|\psi_{2}\right\rangle \equiv\left|\psi_{A}\right\rangle}{\frac{\cdots-\cdots----}{\left|\psi_{1}\right\rangle \equiv\left|\psi_{S}\right\rangle}} \\
& \lambda_{0}=c / \nu_{0}=1.25 \mathrm{~cm}
\end{aligned}
$$

## Interference \& measurement

Suppose we start with an energy eigenstate $\left|\varphi_{S}\right\rangle$

$$
\left|\varphi_{S}\right\rangle=\frac{1}{\sqrt{2}}\left(\left|\varphi_{D}\right\rangle+\left|\varphi_{G}\right\rangle\right)
$$

If we measure $X$, we can find $\pm \mathrm{X}_{0}$ with probabilities $1 / 2$
Suppose the measurement has given the result $+\mathrm{x}_{0}$; the state right after the measurement is then

$$
\left|\varphi_{D}\right\rangle=\frac{1}{\sqrt{2}}\left(\left|\varphi_{S}\right\rangle+\left|\varphi_{A}\right\rangle\right)
$$

If we measure $\mathbf{X}$ again immediately afterwards, before the oscillation is appreciable, we find $+x_{0}$ with probability 1; the state after the measurement is $\left|\varphi_{D}\right\rangle$

## Interference \& measurement

Now, suppose that, on this new state $\left|\varphi_{D}\right\rangle$ we measure not $X$ but the energy E which we are sure was $\mathrm{E}=\mathrm{E}_{\mathrm{S}}$ when we started. We know that that we do not always find $\mathrm{E}_{\mathrm{S}}$ but the two possibilities $\mathrm{E}_{\mathrm{S}}$ and $\mathrm{E}_{\mathrm{A}}$, each with a probability of $\mathbf{1 / 2}$
$\rightarrow$ We see in this case how the measurement has perturbed the system
At the beginning, the state was $\left|\varphi_{S}\right\rangle$
At the end it is a mixture of $\left|\varphi_{S}\right\rangle$ and $\left|\varphi_{A}\right\rangle$ in interference, for which <E> = $\left(E_{S}+E_{A}\right) / 2$
All of this results from the superposition principle on one hand and the filtering of which a measurement consists
$\rightarrow$ A position measurement implies a minimum energy exchange with the system. Here, on the average, the exchange of energy is equal to $A$

## Scanning tunneling microscopy



Binning \& Rohrer (IBM) 1981-85 Nobel prize winners 1986


Nickel surface, (D. Eigler, IBM)
Electron : $V_{0}-E=1 \mathrm{eV}, a=5$ Angströms : $T \sim 6 \times 10^{-3}$

$$
a=6 \text { Angströms : } T \sim 2 \times 10^{-3}
$$

The tunneling current changes very quickly with the distance (due to the exponential term in the transmission coefficient)

## Moving atoms one by one

Nanomanipulation：The STM tip is used to lift and put down the atomic units


1
2 3

4
A set of STM images showing formation of a quantum coral from 48 Fe atoms adsorbed on the surface of $\mathrm{Cu}(111)$

## Moving atoms one by one

Carbon monoxide man (IBM)


Stadium coral: Iron atoms on a copper surface (IBM)

## Ket vector

Introduced by . P. A. MDirac in 1926


The ket is a normed vector that is an element of an abstract complex vector space e.g. the infinite-dimensional vector space of square integrable wavefunctions

## Hilbert space

A Hilbert space $\mathcal{E}_{H}$ is a linear vector space whose elements are functions or vectors $|\psi\rangle$ with a positive-definite scalar product
The dimensionality of the Hilbert space is the number of linearly independent vectors/states needed to span it (may be finite or infinite)

## Properties

(1) Linearity: if $|\psi\rangle$ and $|\phi\rangle$ are elements of $\mathcal{E}_{H}$ so is $a \psi+b \phi$.
(2) Inner product: $\langle\psi \mid \phi\rangle$ exists and $\langle\psi \mid \phi\rangle=\langle\phi \mid \psi\rangle^{*}$.
(3) Every element $|\psi\rangle$ has a norm/length $\|\psi\|$ such that $\langle\psi \mid \psi\rangle=\|\psi\|^{2}$.
(1) Completeness: every Cauchy series of functions in $\mathcal{E}_{H}$ converges to an element in $\mathcal{E}_{H}$

## Hilbert space

The Hillbert space $\mathcal{L}_{2}(a, b)$ is the set of all square-integrable functions $\mathrm{f}(\mathrm{x})$ on the interval [a,b], i.e., $\mathrm{f}(\mathrm{x})$ such that

$$
\int_{a}^{b} f^{*}(x) f(x) d x<\infty
$$

Inner product in

$$
\langle\psi \mid \phi\rangle=\int_{a}^{b} \psi^{*}(x) \phi(x) d x
$$

Note the infinite dimensionality of the Hilbert spaces (evidenced by the infinite number of energy eigenfunctions, which comprise possible bases for these spaces)

$$
\mathcal{L}_{2}(-\infty, \infty)
$$

Free particle

$$
\mathcal{L}_{2}(0, a)
$$

Infinite square well

## Generalization of the $1^{\text {st }}$ postulate

Every physical system can be represented by a unique Hilbert's space $\mathcal{E}_{H}$
The state of a given physical system is described by a single vector state (normed vector) of unit length in the system's Hilbert space

$$
|\psi(t)\rangle
$$

## The Hilbert's space satisfies the principle of superposition

Existence of Hilbert's basis composed of eigenstates

$$
|\psi(t)\rangle \longleftrightarrow\left(\begin{array}{c}
C_{0}(t) \\
C_{1}(t) \\
\vdots
\end{array}\right)
$$

## Inner product

The inner product is defined using the braket notation

$$
\left\langle\psi_{b} \mid \psi_{a}\right\rangle
$$

$\rightarrow$ linear with the second argument, anti-linear with the first argument
$\left|\psi_{a}\right\rangle=\left(\begin{array}{c}C_{0} \\ C_{1} \\ \vdots\end{array}\right) \quad\left|\psi_{b}\right\rangle=\left(\begin{array}{c}D_{0} \\ D_{1} \\ \vdots\end{array}\right) \quad$ then $\quad\left\langle\psi_{b} \mid \psi_{a}\right\rangle=\sum_{n} D_{n}^{*} C_{n}$
All acceptable vectors for a complete description of the quantum system must be normalized

$$
\sum_{n}\left|C_{n}\right|^{2}=1
$$

## Bra vector

The bra labeled vector is obtained by forming the row vector and complex conjugating the entries

$$
\left|\psi_{b}\right\rangle=\left(\begin{array}{c}
D_{0} \\
D_{1} \\
\vdots
\end{array}\right) \quad \square\left\langle\psi_{b}\right|=\left(D_{0}^{*}, D_{1}^{*}, \ldots\right)
$$

Inner product

$$
\begin{gathered}
\left\langle\psi_{b} \mid \psi_{a}\right\rangle=\sum_{n} D_{n}^{*} C_{n} \\
\left\langle\psi_{b} \mid \psi_{a}\right\rangle=\left(D_{0}^{*}, D_{1}^{*}, \ldots\right)\left(\begin{array}{c}
C_{0} \\
C_{1} \\
\vdots
\end{array}\right)
\end{gathered}
$$

Braket $=$ complex number

## Matrix mechanics

An operator $\widehat{A}$ is described by a matrix $\left[A_{p, n}\right]$ acting in the Hilbert's space basis $\left|\phi_{n}\right\rangle$

$$
\left.A_{p, n}=\left\langle\phi_{p}\right| \underset{\substack{\text { Row } \\ \text { vector }}}{\left(\hat{A}\left|\phi_{n}\right\rangle\right)} \underset{\substack{\text { Square } \\ \text { matrix }}}{\substack{\text { Column } \\ \text { vector }}}|\hat{A}| \phi_{n}\right\rangle
$$

Operators are Hermitian (or self-adjoints) if and only if

$$
\left[\hat{A}^{\dagger}\right]_{p, n}=\left([\widehat{A}]_{n, p}\right)^{*} \square \hat{A}=\hat{A}^{\dagger}
$$

## Matrix mechanics

Examples of Hermitian operators

$$
\widehat{x}, \widehat{p}_{x}, \quad \hat{A}=\left(\begin{array}{lr}
5 & 2+3 i \\
2-3 i & -1
\end{array}\right)
$$

Spectral theorem：a Hermitian matrix is diagonalizable and as a consequence it is possible to find a Hilbert＇s basis composed of eigenvectors

$$
\widehat{A}\left|\psi_{n}\right\rangle=a_{n}\left|\psi_{n}\right\rangle \quad \text { such as } \quad\left\langle\psi_{p} \mid \psi_{n}\right\rangle=\delta_{p, n}
$$

All eigenvalues of Hermitian operators are real．Therefore，（by postulate）， all operators for physical observables are Hermitian（because measured quantities are real numbers）．Some subtleties persist with Hilbert＇s space with infinite dimensional case

## The Hamiltonian

Physical quantity：energy $E \longrightarrow$ Energy operator：Hamiltonian $\hat{H}$ hermitien

As in classical physics，possible values for the energy will depend on the physical configuration of the problem
$\Rightarrow$ Particle of mass $m$ in a potential $\hat{H}=\frac{\hat{p}^{2}}{2 m}+V(\hat{x})$
$\Rightarrow$ Dipole in an external electric field（E）

$$
\hat{H}=-\hat{\vec{D}} \cdot \vec{E}
$$

$\Rightarrow$ Dipole in an external magnetic field（B）
Potential energy of Interaction

$$
\hat{H}=-\hat{\vec{\mu}} \cdot \vec{B}
$$

## Projection operator

$\Rightarrow P_{n}=\left|\psi_{n}\right\rangle\left\langle\psi_{n}\right|$ is an operator (not closed braket)
$\Rightarrow P_{n}=\left|\psi_{n}\right\rangle\left\langle\psi_{n}\right|$ is a projector

$$
P_{n}^{2}=\left(\left|\psi_{n}\right\rangle\left\langle\psi_{n}\right|\right)^{2}=\left|\psi_{n}\right\rangle\left\langle\psi_{n} \mid \psi_{n}\right\rangle\left\langle\psi_{n}\right|=\left|\psi_{n}\right\rangle\left\langle\psi_{n}\right|=P_{n}
$$

$$
P_{n}=\left|\psi_{n}\right\rangle\left\langle\psi_{n}\right| \text { is a projector on state }|\psi\rangle
$$

$$
\begin{aligned}
P_{n}|\psi\rangle & =\left(\left|\psi_{n}\right\rangle\left\langle\psi_{n}\right|\right)|\psi\rangle \\
& =\left(\left\langle\psi_{n} \mid \psi\right\rangle\right)\left|\psi_{n}\right\rangle
\end{aligned}
$$

Here the operator projects a vector onto the $n^{\text {th }}$ eigenstate


## Projection operator

$$
\begin{gathered}
\left\langle\psi_{n}\right|=\left(\begin{array}{lllllll}
0 & \ldots & 0(1) & 0 & \ldots & 0
\end{array}\right) \\
\left|\psi_{n}\right\rangle=\left(\begin{array}{c}
0 \\
\vdots \\
0 \\
1 \\
0 \\
0 \\
\vdots \\
0
\end{array}\right) \quad\left|\psi_{n}\right\rangle\left\langle\psi_{n}\right|=\left(\begin{array}{cccccc}
0 & & & & & \\
& \ddots & & 0 & & \\
& & 0 & & & \\
\\
& & & 1 & & \\
\\
0 & & & & & \\
& & & & & \\
& & & & & \\
0
\end{array}\right)
\end{gathered}
$$

## Completeness relationship

If we sum over a complete set of states, like the eigenstates of a Hermitian operator, we obtain the (useful) resolution of identity

$$
\begin{aligned}
& \sum_{n}\left|\psi_{n}\right\rangle\left\langle\psi_{n}\right|=\left(\begin{array}{cccccc}
1 & & & & & \\
& \ddots & & & 0 & \\
& & 1 & & & \\
& & & 1 & & \\
\\
& & & & 1 & \\
I & & & & \ddots & \\
& & & & & 1
\end{array}\right)=\hat{I} \\
&|\psi\rangle=\sum_{n}\left|\psi_{n}\right\rangle\left\langle\psi_{n}\right| \\
&
\end{aligned}
$$

## Completeness relationship

If we sum over a complete set of states，like the eigenstates of a Hermitian operator，we obtain the（useful）resolution of identity

$$
\sum_{n}\left|\psi_{n}\right\rangle\left\langle\psi_{n}\right|=\left(\begin{array}{ccccccc}
1 & & & & & & \\
& \ddots & & & \mathbf{0} & & \\
& & 1 & & & & \\
& & & 1 & & & \\
\mathbf{0} & & & & & \ddots & \\
& & & & & & 1
\end{array}\right)=\hat{I}
$$

If the eigenvalues indexed by $n$ range over a continuous set of values， the summation becomes an integration

$$
\hat{I}=\int\left|\psi_{n}\right\rangle\left\langle\psi_{n}\right| d n
$$

## Generalization of the $3^{\text {rd }}$ postulate

In any measurement of the observable $A$ associated with operator $\hat{A}$, the only values that will ever be observed are the eigenvalues, which satisfy the eigenvalue equation

$$
\hat{A}\left|\psi_{n}\right\rangle=a_{n}\left|\psi_{n}\right\rangle \quad\left\langle\psi_{p} \mid \psi_{n}\right\rangle=\delta_{p, n}
$$

The result of a measurement is one of the set of eigenvalues $\left(\mathrm{a}_{\mathrm{n}}\right)$ of $\hat{A}$
The probability of measuring eigenvalue $\left(a_{n}\right)$ is given by

$$
\mathcal{P}\left(a_{n}\right)=\left|\left\langle\psi_{n} \mid \psi\right\rangle\right|^{2} \quad \text { Non degenerate }
$$

Right after the measurement with result $\left(a_{n}\right)$, the system is projected onto the vector subspace $\left|\psi_{n}\right\rangle$
This means that a second measurement performed immediately after will produce the same result ( $\mathrm{a}_{\mathrm{n}}$ )

## Generalization of the $3^{\text {rd }}$ postulate

In case of degenerate eigenvalues the dimension of the Hilbert space is

$$
\left(a_{n}\right)=g_{n} \geq 2
$$

$$
\hat{A}\left|\psi_{n, r_{n}}\right\rangle=a_{n}\left|\psi_{n, r_{n}}\right\rangle \quad \text { with } \quad r_{n}=1, \ldots, g_{n}
$$

The result of a measurement is one of the set of eigenvalues $\left(\mathrm{a}_{\mathrm{n}}\right)$ of $\hat{A}$
The probability of measuring eigenvalue $\left(a_{n}\right)$ is given by

After the measurement

$$
\frac{\hat{P}_{n}|\psi\rangle}{\| \hat{P}_{n}|\psi\rangle \|}
$$

## Infinite dimensional case

$\longrightarrow A$ "good operator": Hamiltonian of the harmonic oscillator

$$
\hat{H}=-\frac{\hbar^{2}}{2 m} \frac{d^{2}}{d x^{2}}+\frac{1}{2} m \omega^{2} x^{2} \quad \text { Discrete spectrum }: E_{n}=\hbar \omega(n+1 / 2)
$$

Eigenfunctions (Hermite polynomials) $\mathrm{e}^{-x^{2} / 2 a^{2}}, x \mathrm{e}^{-x^{2} / 2 a^{2}}, \ldots a=\sqrt{\hbar / m \omega}$
Included in Hilbert space of square-integrable functions
$\longrightarrow A$ "delicate operator": the momentum
$\hat{p}_{x}=\frac{\hbar}{i} \frac{d}{d x} \quad$ Continuous spectrum $\hbar k \quad \rightarrow$ Set of real numbers

$$
\text { Eigenfunctions }: e^{i k x}
$$

Not included in Hilbert space of square-integrable functions

## Position and momentum space

As the position and momentum eigenfunctions are not square-integrable (and hence technically outside the Hilbert space), they are orthonormal in the Dirac sense. This is generally the case for operators whose eigenvalues are continuous.

To use these states as basis functions, we write a general state $\psi$ as

$$
\begin{aligned}
|\psi\rangle & =\int d x|x\rangle\langle x \mid \psi\rangle \\
& =\int d p|p\rangle\langle p \mid \psi\rangle
\end{aligned}
$$

Note that because we are dealing with a continuous rather than discrete range of eigenvalues, we integrate rather than sum over all possible eingenvalues

## Position and momentum space

$$
|\psi\rangle=\int d x|x\rangle\langle x \mid \psi\rangle=\int d p|p\rangle\langle p \mid \psi\rangle
$$

$\langle x \mid \psi\rangle=\psi(x) \quad$ is the value of the wave function at position x is simply the projection of the state $|\psi\rangle$ onto an eigenstate $|x\rangle$
$|\langle x \mid \psi\rangle|^{2} \quad$ Probability of measurement of x
$\psi(p)=\langle p \mid \psi\rangle \quad$ Probability amplitude for measurement of p
Inner product
$\langle\phi \mid \psi\rangle=\left\langle\phi \mid\left(\int|x\rangle\langle x| d x\right) \psi\right\rangle=\int\langle\phi \mid x\rangle\langle x \mid \psi\rangle d x=\int \phi^{*}(x) \psi(x) d x$

## Position and momentum space

Conversion between $\psi(x)$ and $\psi(p)$ :

$$
\begin{aligned}
\psi(p)=\langle p \mid \psi\rangle & =\int\langle p \mid x\rangle\langle x \mid \psi\rangle d x \\
& =\int e^{-i p x / \hbar} \psi(x) \frac{d x}{\sqrt{2 \pi \hbar}}
\end{aligned}
$$

Similarly $\quad \psi(x)=\int e^{i p x / \hbar} \psi(p) \frac{d p}{\sqrt{2 \pi \hbar}}$.
The conversion between position and momentum space is mathematically a Fourier transform because

$$
\langle x \mid p\rangle=\frac{1}{\sqrt{2 \pi \hbar}} \exp (i p x / \hbar)
$$

## Discrete vs continuous

$\hat{A}\left|a_{n}\right\rangle=a_{n}\left|a_{n}\right\rangle$ with discrete eigenvalues $a_{n}$ $\hat{B}\left|b_{n}\right\rangle=b_{n}\left|b_{n}\right\rangle \quad$ with continuous eigenvalues $b_{n}$

| Discrete | Continuous |
| :---: | :---: |
| $\left\langle a_{m} \mid a_{n}\right\rangle=\delta_{m n}$ | $\left\langle b_{m} \mid b_{n}\right\rangle=\delta\left(b_{m}-b_{n}\right)$ |
| $\sum_{m}\left\|a_{m}\right\rangle\left\langle a_{m}\right\|=1$ | $\int d b_{m}\left\|b_{m}\right\rangle\left\langle b_{m}\right\|=1$ |
| $\|\alpha\rangle=\sum_{m}\left\|a_{m}\right\rangle\left\langle a_{m} \mid \alpha\right\rangle$ | $\|\beta\rangle=\int d b_{m}\left\|b_{m}\right\rangle\left\langle b_{m} \mid \beta\right\rangle$ |
| $\sum_{m}\left\|\left\langle a_{m} \mid \alpha\right\rangle\right\|^{2}=1$ | $\int d b_{m}\left\|\left\langle b_{m} \mid \beta\right\rangle\right\|^{2}=1$ |
| $\left\langle a_{m}\right\| A\left\|a_{n}\right\rangle=a_{n} \delta_{m n}$ | $\left\langle b_{m}\right\| B\left\|b_{n}\right\rangle=b_{n} \delta\left(b_{m}-b_{n}\right)$ |

$\delta_{m n} \quad$ Kronecker delta function $\quad \delta\left(b_{m}-b_{n}\right)$ Dirac delta function

## Commutators

Commutators between two operators are defined as

$$
\begin{gathered}
{[\hat{A}, \hat{B}]=\hat{A} \hat{B}-\hat{B} \hat{A}} \\
{[\hat{A}, \hat{B}]=-[\hat{B}, \hat{A}]}
\end{gathered}
$$

Two operators commute (or are compatible) if $[\hat{A}, \hat{B}]=0$


Heisenberg

To figure out commutation relations, apply the operators on a test function and look at the end result (sans test function)

$$
\text { Example: the canonical commutation relation }[\hat{x}, \hat{p}]=i \hbar
$$

Note that if two operators commute, it becomes possible that the same state will be an eigenfunction of both operators. Then the two corresponding observables can be simultaneously specified for that state. The eigenvalues of the observables are basically "good quantum numbers" of the state

## Time evolution

Evolution of the state vector $|\psi(t)\rangle$

$$
i \hbar \frac{d|\psi(t)\rangle}{d t}=\hat{H}|\psi(t)\rangle
$$

If eigenstates of the Hamiltonian $\hat{H}$ are known (not time dependent)

$$
\hat{H}\left|\psi_{n}\right\rangle=E_{n}\left|\psi_{n}\right\rangle
$$

We can write the following decomposition

$$
\begin{gathered}
|\psi(t)\rangle=\sum_{n} c_{n}(t)\left|\psi_{n}\right\rangle \\
|\psi(t)\rangle=\sum_{n}\left\langle\psi_{n} \mid \psi\left(t_{0}\right)\right\rangle e^{-i \frac{E_{n}\left(t-t_{0}\right)}{\hbar}}\left|\psi_{n}\right\rangle \quad \text { with } \quad c_{n}\left(t_{0}\right)=\left\langle\psi_{n} \mid \psi\left(t_{0}\right)\right\rangle
\end{gathered}
$$

## The EPR argument


A. Einstein

B. Podolsky

N. Rosen

N. Bohr

PHYSICAL REVIEW
Can Quantum-Mechanical Description of Physical Reality Be Considered Complete?
A. Einstein, B. Podolsky and N. Rosen, Institute for Advanced Study, Princeton, New Jersey
(Received March 25, 1935)
In 1935, EPR said the quantum theory is not complete pointing out the existence of possible hidden variables in the formalism
Einstein discovered that the formalism of quantum mechanics contains the existence of particular states named entangled states

$$
|\Psi\rangle=\frac{1}{\sqrt{2}}[|++\rangle+|--\rangle]
$$

"If, without in any way disturbing a system, we can predict with certainty the value of a physical quantity, then there exists an element of physical reality corresponding to this physical quantity"

## The EPR argument


A. Einstein

B. Podolsky

N. Rosen

N. Bohr

PHYSICAL REVIEW
VOLUME 4.7
Can Quantum-Mechanical Description of Physical Reality Be Considered Complete?
A. Einstein, B. Podolsky and N. Rosen, Institute for Advanced Study, Princeton, New Jersey
(Received March 25, 1935)
In 1935, Niels Bohr answered EPR by saying that the quantum theory is complete i.e. there are no hidden variables

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Can Quantum-Mechanical Description of Physical Reality be Considered Complete?
N. Bohr, Institute for Theoretical Physics, University, Copenhagen
(Received July 13, 1935)
In 1964, John Bells introduced an inequality that has further led to the experimental evidence that quantum mechanics is indeed complete

## Tensor product of two Hilbert spaces

Consider a quantum system (a) represented by an Hillbert space $\mathcal{E}_{a}$ with basis $\left\{\left|\alpha_{m}\right\rangle\right\}$
Consider a quantum system (b) represented lby an Hillbert space $\mathcal{E}_{b}$ with basis $\left\{\left|\beta_{n}\right\rangle\right\}$

If (a) is in state $\left|\alpha_{m}\right\rangle$ and (b) $\left|\beta_{n}\right\rangle$ then the state of the total quantum system is

$$
\begin{aligned}
& \left|\alpha_{m}\right\rangle \underset{\uparrow}{\text { Tensor product }}
\end{aligned}
$$

$$
\left\langle\alpha_{m}\right| \otimes\left\langle\beta_{n}\right|=\left\langle\alpha_{m}\right|\left\langle\beta_{n}\right|=\left\langle\alpha_{m}, \beta_{n}\right|=\langle m, n|
$$

Tensor product vector space $\quad \mathcal{E}_{a} \otimes \mathcal{E}_{b}$

## Entangled state

An entangled system is defined to be one whose quantum state cannot be factored as a product of states of its local constituents; that is to say, they are not individual particles but are an inseparable whole

Let us consider two vectors $\left|\psi_{1}\right\rangle=\sum_{n} a_{n}\left|\phi_{n}^{(1)}\right\rangle$ et $\left|\psi_{2}\right\rangle=\sum_{p} b_{p}\left|\phi_{p}^{(2)}\right\rangle$ then

$$
\begin{aligned}
|\psi\rangle=\left|\psi_{1}\right\rangle \otimes\left|\psi_{2}\right\rangle=\sum_{n, p} a_{n} b_{p}\left|\phi_{n}^{(1)}\right\rangle \otimes\left|\phi_{p}^{(2)}\right\rangle & \text { is a vector of the total Hilbert } \\
& \text { space } \mathcal{H}_{1}^{M} \otimes \mathcal{H}_{2}^{N}
\end{aligned}
$$

However the reverse statement is wrong i.e. there exists non separable states of the Hilbert Space that can not be expressed as

$$
|\psi\rangle=\sum_{n, p} c_{n, p}\left|\phi_{n}^{(1)}\right\rangle \otimes\left|\phi_{p}^{(2)}\right\rangle \neq\left|\psi_{1}\right\rangle \otimes\left|\psi_{2}\right\rangle=\sum_{n, p} a_{n} b_{p}\left|\phi_{n}^{(1)}\right\rangle \otimes\left|\phi_{p}^{(2)}\right\rangle
$$

Such a general state $\Psi$ which cannot be written in the form of a tensor product is called an entangled state

## Quiz 12

An entangled system is defined to be one whose quantum state cannot be factored as a product of states of its local constituents.
A non separable state is entangled
Find below which of the following quantum states are entangled?
A. $|++\rangle$
B. $|+-\rangle$
C. $(|++\rangle+|+-\rangle) / \sqrt{2}$
D. $(|++\rangle+|--\rangle) / \sqrt{2}$
E. $(|+-\rangle+|-+\rangle) / \sqrt{2}$
F. $(|++\rangle+|+-\rangle+|-+\rangle+|--\rangle) / 2$


## Photon polarization

The polarization of a single photon is described in an Hilbert space of dimension 2

$$
\begin{aligned}
& |\psi\rangle=\alpha|\mathrm{v}\rangle+\beta|\mathrm{h}\rangle \\
& |\alpha|^{2}+|\beta|^{2}=1
\end{aligned}
$$

$(\alpha, \beta)$ real coefficients: linear polarizations
$(\alpha, \beta)$ complex coefficients: elliptic and circular polarizations
An individual photon can be described as having right or left circular polarization, or a superposition of the two. Equivalently, a photon can be described as having horizontal or vertical linear polarization, or a superposition of the two
$\rightarrow$ It is a two-state quantum system called quantum bit or qbit
Applications: quantum cryptography \& quantum information

## Measurement on an entangled state



Consider the following entangled quantum configuration with two photons linearly polarized

$$
\begin{gathered}
|\Psi\rangle=\frac{1}{\sqrt{2}}\left[\left|P 1: h_{1}\right\rangle \otimes\left|P 2: h_{2}\right\rangle+\left|P 1: v_{1}\right\rangle \otimes\left|P 2: v_{2}\right\rangle\right] \\
|\Psi\rangle=\frac{1}{\sqrt{2}}\left[\left|h_{1} h_{2}\right\rangle+\left|v_{1} v_{2}\right\rangle\right] \longleftrightarrow \\
\mathcal{E}=\mathcal{E}_{P_{1}} \otimes \mathcal{E}_{P_{2}}
\end{gathered}
$$

The Hilbert space of dimension 4

$$
\operatorname{dim} \mathcal{E}=\operatorname{dim} \mathcal{E}_{P_{1}} \times \operatorname{dim} \mathcal{E}_{P_{2}}
$$

## Measurement on an entangled state



P1 transmitted
Result (eigenvalue): $\varepsilon_{1}=+1$
Eigenstates: $\mid+_{\theta 1}$ >
P1 reflected
Result (eigenvalue): $\varepsilon_{1}=-1$
Eigenstates: $\mathrm{I}_{-{ }_{01}>}$

P2 transmitted Result (eigenvalue): $\varepsilon_{2}=+1$

Eigenstates: $\mid+{ }_{\theta 2}>$
P2 reflected
Result (eigenvalue): $\varepsilon_{1}=-1$
Eigenstates: $\mathrm{I}_{-{ }_{\theta 2}>}$

## Measurement on an entangled state



$$
\begin{aligned}
& P\left(+_{\theta 1},+_{\theta 2}\right)=\left|\left\langle+_{\theta 1},+_{\theta 2} \mid \Psi\right\rangle\right|^{2}=1 / 2 \cos ^{2}\left(\theta_{2}-\theta_{1}\right) \\
& P\left(--_{\theta 1},-_{\theta 2}\right)=\left|\left\langle-_{\theta 1},-_{\theta 2} \mid \Psi\right\rangle\right|^{2}=1 / 2 \cos ^{2}\left(\theta_{2}-\theta_{1}\right) \\
& P\left(+_{\theta 1},-_{\theta 2}\right)=\left|\left\langle+_{\theta 1},-_{\theta 2} \mid \Psi\right\rangle\right|^{2}=1 / 2 \sin ^{2}\left(\theta_{2}-\theta_{1}\right) \\
& P\left(-_{\theta 1},+_{\theta 2}\right)=\left|\left\langle-_{\theta 1},+_{\theta 2} \mid \Psi\right\rangle\right|^{2}=1 / 2 \sin ^{2}\left(\theta_{2}-\theta_{1}\right)
\end{aligned}
$$

What are the single probabilities for separated results?

$$
\begin{aligned}
& P\left(+_{\theta 1}\right)=P\left(+_{\theta 1},+_{\theta 2}\right)+P\left(+_{\theta 1},--_{\theta 2}\right)=1 / 2 \\
& P\left(-{ }_{\theta 1}\right)=P\left(+_{\theta 2}\right)=P\left(-{ }_{\theta 2}\right)=1 / 2
\end{aligned}
$$

Randomness results not dependent on the polarizer angles. However those obtained by Alice and Bob together are strongly correlated

## Bell inequality



How to explain quantum correlations? Following the EPR argument, John Bell assumed that there exists hidden parameters $\boldsymbol{\lambda}$ that must determine the outcome of Alice and Bob measurements


$$
\begin{aligned}
& A\left(\theta_{1}, \lambda\right)= \pm 1 \quad \begin{array}{c}
\text { Statistic distribution } \\
\text { (normalized) }
\end{array} \\
& B\left(\theta_{2}, \lambda\right)= \pm 1 \quad \\
& E\left(\theta_{1}, \theta_{2}\right)=\int A\left(\theta_{1}, \lambda\right) B\left(\theta_{2}, \lambda\right) \rho(\lambda) d \lambda \\
& \text { J.S. Bell, Rev. Mod. Phys. 38, } 447(1966)
\end{aligned}
$$

## Aspect experiments (1981-82)


$\mathrm{C}_{1}, \mathrm{C}_{2}$ are optical switches redirecting photons towards polarizers with angles $\left(\theta_{1}, \theta^{\prime}{ }_{1}\right)$ and $\left(\theta_{2}, \theta^{\prime}{ }_{2}\right)$. Commutation was faster (10 ns) than propagation of light between polarizers ( 40 ns ) and even faster than time of flight of photons between the source and each switch ( 20 ns )

A. Aspect, P. Grangier, G. Roger, Phys. Rev. Lett. 49, 91 (1982)
A. Aspect, J. Dalibard, G. Roger, Phys. Rev. Lett. 49, 1804 (1982)

## Aspect experiments (1981-82)

## Result in a perfect agreement with quantum theory



FIG. 3. Correlation of polarizations as a function of the relative angle of the polarimeters. The indicated errors are $\pm 2$ standard deviations. The dotted curve is not a fit to the data, but quantum mechanical predictions for the actual experiment. For ideal polarizers, the curve would reach the values $\pm 1$.

## Others experiments

Aspect experiments were pioneered and showed (fairly) conclusively that quantum physics is non-local, and that the universe is much stranger than it appears, or than Einstein would've liked it to be

Others ultimate experiments have been done in 2015
Entangled photon pair, L=58 m in Vienna, Austria Vienne [1]
Entangled photon pair, L = 185 m in Boulder, USA [2]
Entangled spin pair, $\mathrm{L}=1.3 \mathrm{~km}$ in Delft, The Netherlands [3]
$\rightarrow$ All results are in a perfect agreement with quantum theory
$\rightarrow$ Closing the door on Einstein and Bohr's quantum debate!
[1] M. Giustina et al., Phys. Rev. Lett. 115, 250401 (2015)
[2] L. K. Shalm et al., Phys. Rev. Lett. 115, 250402 (2015)
[3] B. Hensen et al., Nature 526, 682 (2015)
See also, https://physics.aps.org/articles/v8/123

## Quantum teleportation



## RESEARCH ARTICLE

QUANTUM OPTICS

## Satellite-based entanglement distribution over 1200 kilometers



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