## **Albert Einstein (1905)**

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

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

photon\* = Lichtquantum in German

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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).

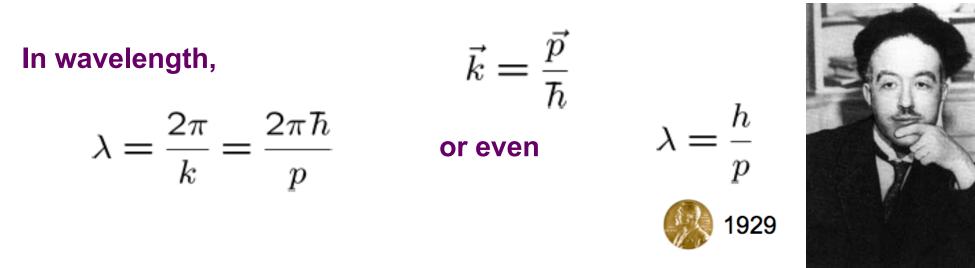
Does the duality still exist for particles of matter (electrons, etc.)?





## 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



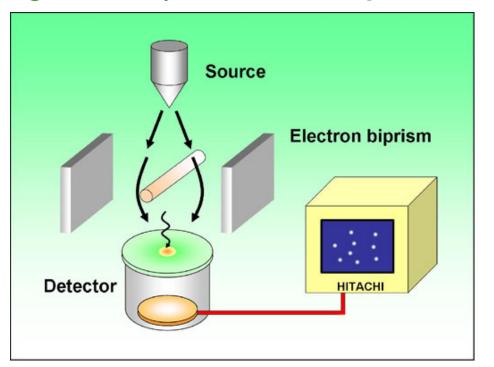
"The fact that, following Einstein's introduction of photons in light waves, one knew that light contains particles which are concentrations of energy incorporated into the wave, suggests that all particles, like the electron, must be transported by a wave into which it is incorporated..."

"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"

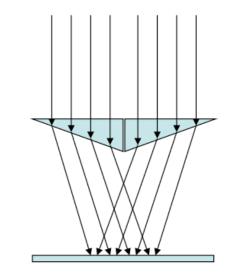


## **Double slit experiment with electrons**

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



Similar to Fresnel's biprism experiment

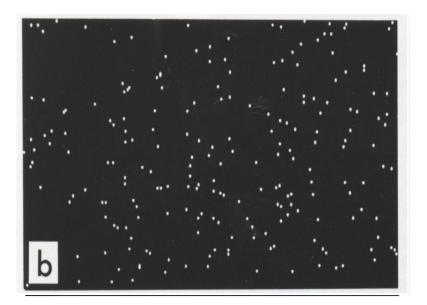


Although electrons are sent one by one, interference fringes could be observed. These interference fringes are formed only when electron waves pass through on both sides of the electron biprism at the same time but nothing other than this



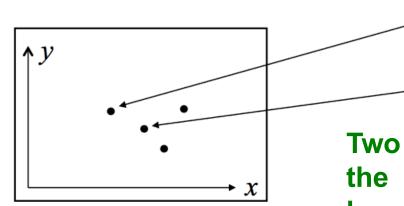
## **Double slit experiment with electrons**

 $(x_2, y_2)$ 



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 ??

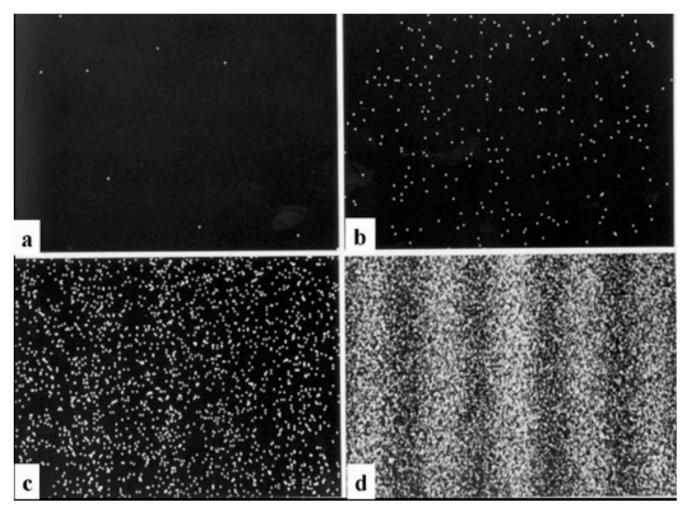


Two electrons identically prepared with the same initial conditions show however different impact points

 $(x_1, y_1)$ 



## **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)



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## The wave function

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

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

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

$$\psi(ec{r},t)$$
 probability amplitude  $|\psi(ec{r},t)|^2$  probability density

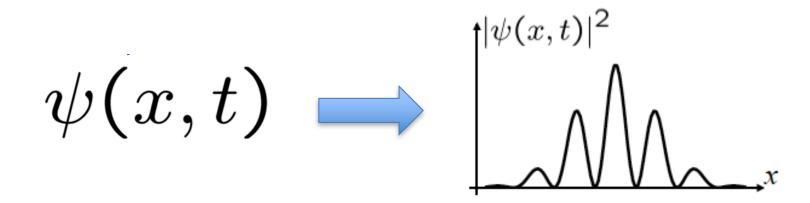
$$\int |\psi(\vec{r},t)|^2 d^3r = 1$$

#### **Normed function**



## **Probabilistic interpretation**

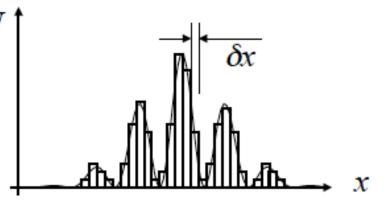
Assume N particles identically prepared in the same quantum state



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

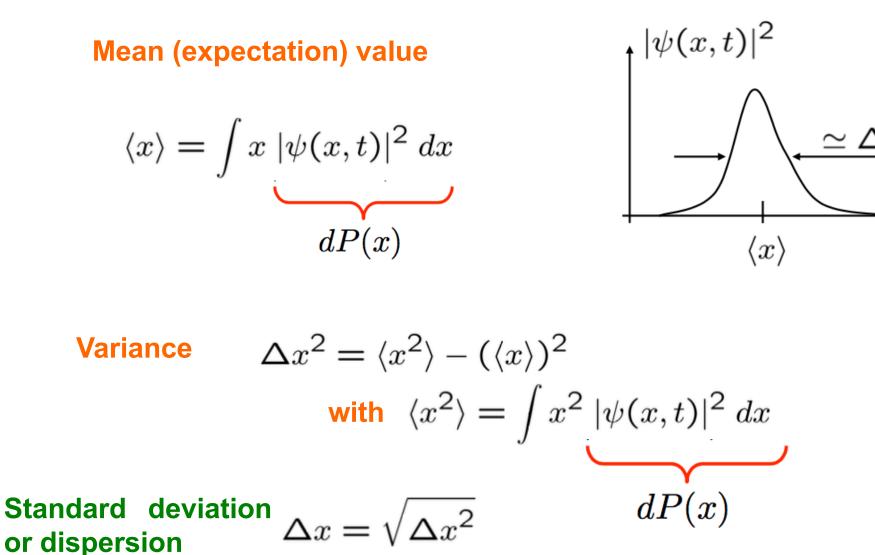
It is possible to retrieve  $|\psi(x,t)|^2$  with a good precision if and only if N >> 1

*n<sub>i</sub>: number of atoms detected in the i<sup>th</sup> channel* 





### Mean value and root mean square



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x

## Summary of the 1<sup>st</sup> 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

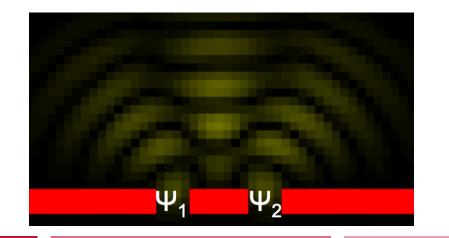
If  $\psi_1$  and  $\psi_2$  are wavefunctions with laws of probability $P_1 = |\psi_1|^2$  and  $P_2 = |\psi_2|^2$ 

$$\psi \propto \psi_1 + \psi_2$$

then,

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



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

#### **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  $\hat{A}$ 

ightarrow Each eigenvalue is element of the set of real numbers  $~\mathbb{R}$ 

ightarrow 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

$$\hat{H}\psi_E(x) = E \ \psi_E(x)$$

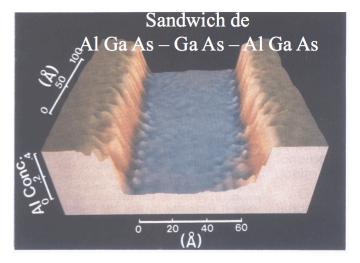
$$-\frac{\hbar^2}{2m} \ \frac{d^2\psi_E(x)}{dx^2} + V(x) \ \psi_E(x) = E \ \psi_E(x) \qquad \textbf{1}$$

#### Solutions usually not trivial ( $\rightarrow$ numerical analysis)

Some cases can be solved analytically

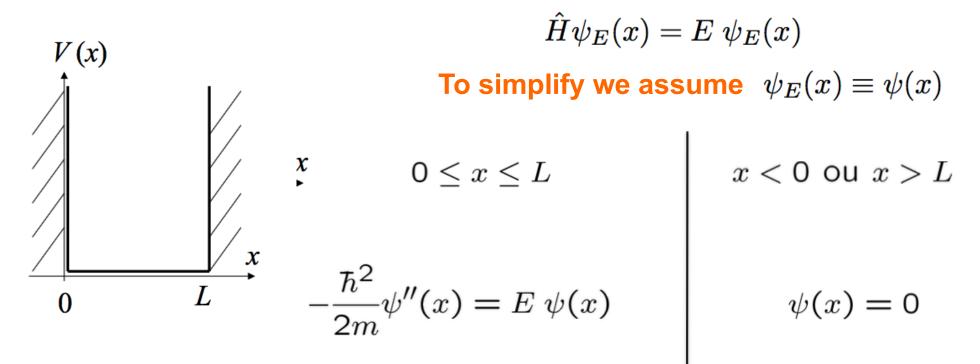
Harmonic potential 
$$V(x) = \frac{1}{2}m\omega^2 x^2$$
  
Coulomb potential  $V(r) = -\frac{q^2}{4\pi\epsilon_0 r}$ 

**Constant piecewise potentials** 





#### Particle in a box



Boundary conditions: The wave function is always continuous!

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



We assume the energy E > 0 and  $\in \mathbb{R}$   $k = \sqrt{2mE}/\hbar$   $E = \hbar^2 k^2/2m$  $-\frac{\hbar^2}{2m}\psi''(x) = E\psi(x)$   $\psi''(x) = -k^2\psi(x)$ 

General form of the solutions  $\psi(x) = \alpha \sin(kx) + \beta \cos(kx)$ 

**Boundary at** x = 0:  $\psi(0) = 0 \Rightarrow \beta = 0$ 

**Boundary at** x = L:  $\psi(L) = 0 \Rightarrow \alpha \sin(kL) = 0 \Rightarrow \sin(kL) = 0$ 

→ All wavevectors k can take only discrete values

$$k = k_n = \frac{n\pi}{L} \qquad n = 1, 2, \dots$$

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→ And all eigenvalues of the energy are quantized  $E_n = n^2 \frac{\hbar^2 \pi^2}{2m I^2}$ 



#### **Eigenfunctions of the Hamiltonian can be expressed as follows**

$$\psi_n(x) = \alpha \sin(k_n x)$$
 with  $k_n = \frac{n\pi}{L}$  and  $E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2mL^2}$   
Normalization  $\int_0^L |\psi_n(x)|^2 dx = 1 \Rightarrow \alpha = \sqrt{2/L}$ 

The set of functions  $\,\psi_n$  is an orthonormal base of functions such as

$$\psi(0) = \psi(L) = 0$$
  
Orthonormality  $\int_0^L \psi_n(x) \, \psi_\ell(x) \, dx = \delta_{n,\ell}$  (Kronecker delta)

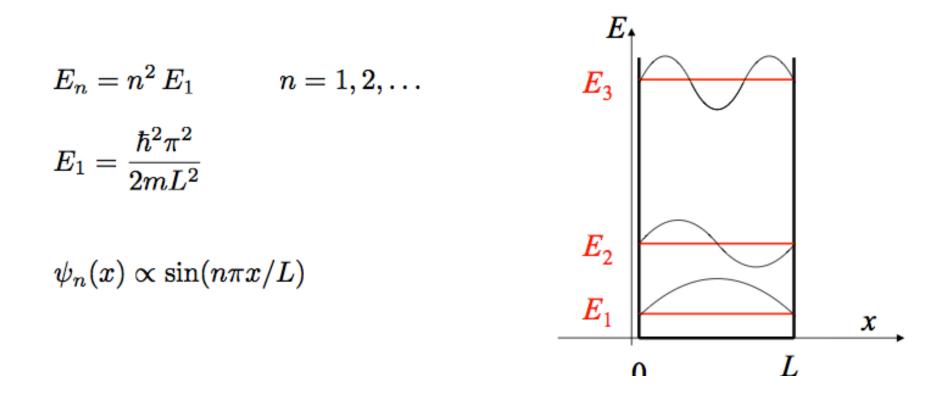
The wave function can be represented by the expansion

$$\psi(x) = \sum_{n=1}^{+\infty} C_n \,\psi_n(x) \qquad \qquad \sum_{n=1}^{+\infty} |C_n|^2 = 1$$

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



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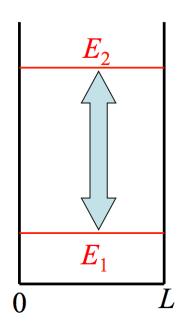
- → An electron in a quantum well of diameter L = 6 × 10<sup>-9</sup> m  $E_1=10$  meV
- → A nucleon (proton or neutron) in a nucleus of diameter L = 4 ×  $10^{-15}$  m E<sub>1</sub>=10 MeV

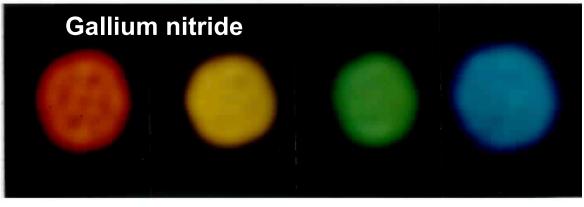
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## Light emission from a quantum well





L = 12 L Atomic layers

L = 6

#### Photon $hv = E_2 - E_1 = hc / \lambda$

$$E_2 - E_1 = (4 - 1) \times \frac{\hbar^2 \pi^2}{2mL^2}$$
  
=  $\frac{3\hbar^2 \pi^2}{2mL^2}$ 







The Nobel Prize in Physics 2014 Isamu Akasaki, Hiroshi Amano, Shuji Nakamura

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*"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**

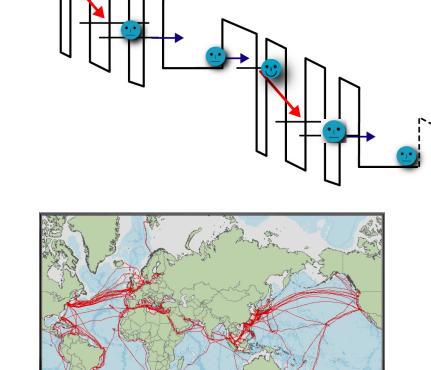
**Gas/molecule detection** 

- → Medical (breath analyses)
- → Environment (air pollution)
- → 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:**

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

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?**

$$\langle a \rangle = \int \psi^*(x) \left[ \hat{A} \psi(x) \right] dx \qquad \Delta a^2 = 0$$

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  $\langle a \rangle$ 

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



## Relationship between measured results and eigenvalues?

#### **Converse?**

$$\langle a \rangle = \int \psi^*(x) \left[ \hat{A} \psi(x) \right] dx \qquad \Delta a^2 = 0$$

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  $\langle a \rangle$ 

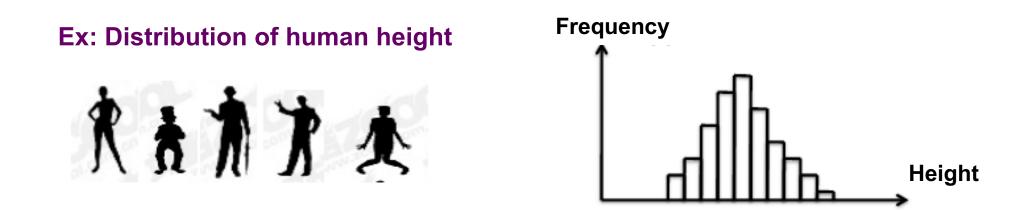
Conclusion: The measurement of A is predicted with certainty if and only if the state of the particle is an eigenstate of  $\hat{A}$ 

- $\rightarrow$  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



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)

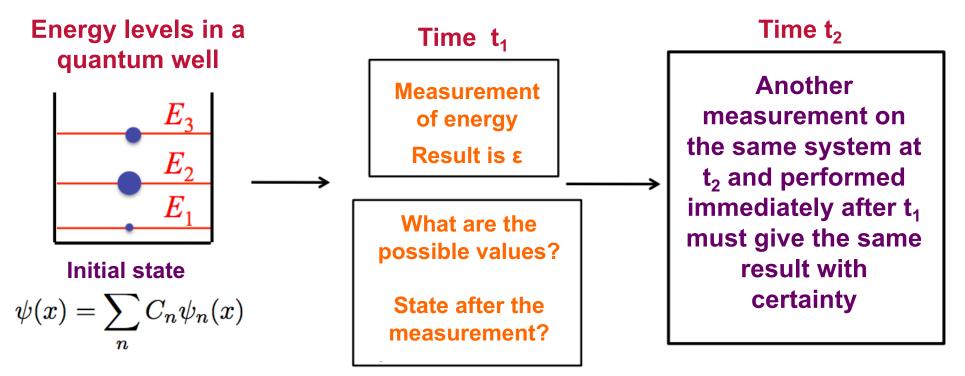
A short period of time means that the state of the system does not substantially evolve between two consecutive measurements (i.e. same experimental conditions)

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## Which state after the measurement?



The measurement performed at t<sub>2</sub> is predicted with certainty if and only if:

- (a) The energy  $\epsilon$  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 t<sub>2</sub>

Measurement at t<sub>1</sub>: 
$$\,\psi(x)\longrightarrow\psi_n(x)$$

## **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

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

Then the result is randomly an eigenvalue of the set of  $a_{\alpha}$ What is the corresponding probability law?

We know that 
$$\langle a \rangle = \int \psi^*[\hat{A}\psi] \, dx = \ldots = \sum_{\alpha} |C_{\alpha}|^2 \, a_{\alpha}$$
  
 $\langle a^n \rangle = \int \psi^*[\hat{A}^n \psi] \, dx = \ldots = \sum_{\alpha} |C_{\alpha}|^2 \, a_{\alpha}^n$   
leading to the probability law  $a_{\alpha} \colon p_{\alpha} = |C_{\alpha}|^2$ 



## 3<sup>rd</sup> 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  $a_{\alpha}$ Figure (non-degenerate)

$$\hat{A}\psi_{lpha}(x) = a_{lpha}\,\psi_{lpha}(x)$$
  $\psi_{lpha}(x)$  Orthonormal eigenfunctions

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Before the measurement:  $\psi(x) = \sum_{\alpha} C_{\alpha} \psi_{\alpha}(x)$  with  $\sum_{\alpha} |C_{\alpha}|^2 = 1$ 

(a) If the system is in an eigenstate of  $\hat{A}$  with eigenvalue  $a_{\alpha}$  then any measurement of the quantity will yield  $a_{\alpha}$ 

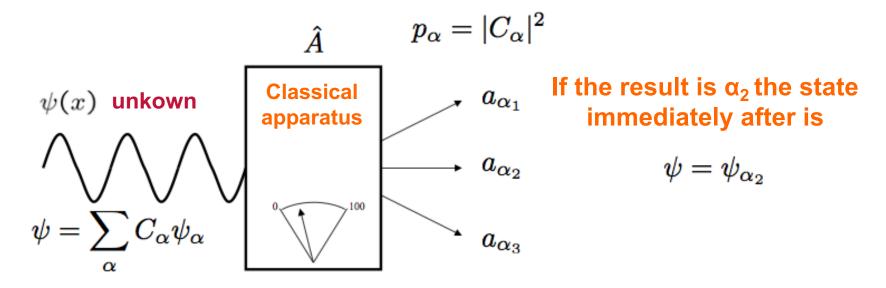
(b) The probability that eigenvalue  $a_{\alpha}$  will occur -- it is the absolute value squared of the coefficient,  $p_{\alpha}=|C_{\alpha}|^2$ 

(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



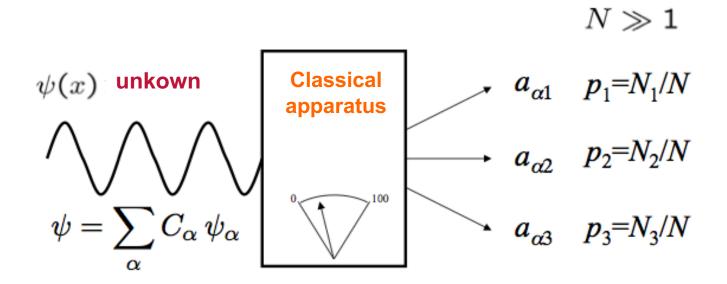
From this single measurement, we cannot retrieve the state  $\psi(x)$ We only know that  $p_{\alpha 2}$  is not zero

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 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



From  $p_{\alpha} = |C_{\alpha}|^2$  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  $C_n = \int \psi_n^*(x)\psi(x,0)dx$   
Wave function at time t:  $\psi(x,t) = \sum_{n} C_n \psi_n(x) e^{-iE_n t/\hbar}$ 

Proof

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

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



## **Eigenstates of the Hamiltonian**

Consider the particle in the initial state at t=0  $\psi(x,0) = \psi_n(x)$  Wave packet collapse

Then, the solutions of the Schrödinger equation at time t is given by

$$\psi(x,t) = \psi_n(x) e^{-iE_n t/\hbar}$$

The eigenstates of the Hamiltonian are stationary states

→ the probability density is time independent  $|\psi(x,t)|^2 = |\psi_n(x)|^2$ Also valid for all expected values associated to any physical quantities

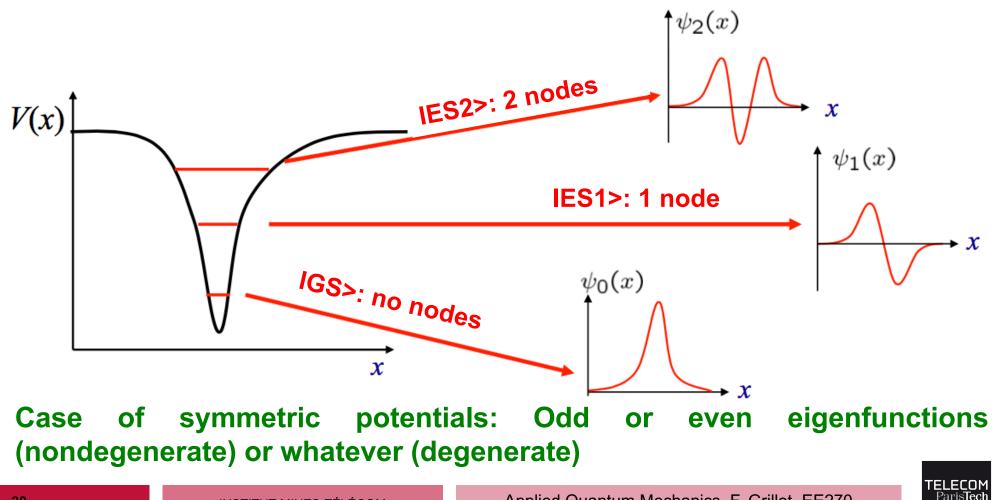
$$egin{aligned} \langle a 
angle(t) &= \int \psi^*(x,t) [\hat{A} \psi(x,t)] \; dx \ &= \int \psi^*_n(x) [\hat{A} \psi_n(x)] \; dx & {f No time \ dependence!} \end{aligned}$$



## **Steady-state solutions**

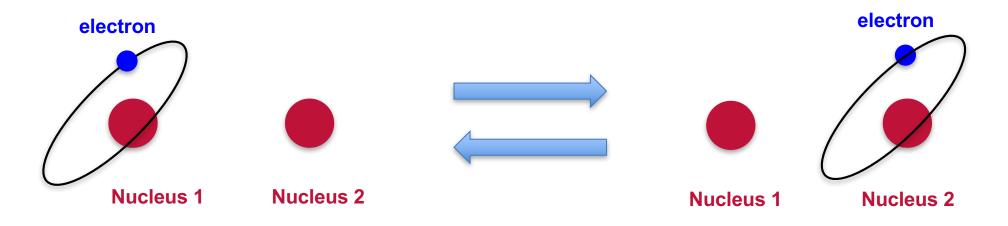
Sturm-Liouville theorem (real wave functions): As we change to a higher energy level, the index n grows, and we have more nodes (points where the sign changes) of the wave function

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



## How to explain the chemical bond?

#### 2 nuclei and 1 electron (Dihydrogen cation i.e. ion H<sub>2</sub><sup>+</sup>)



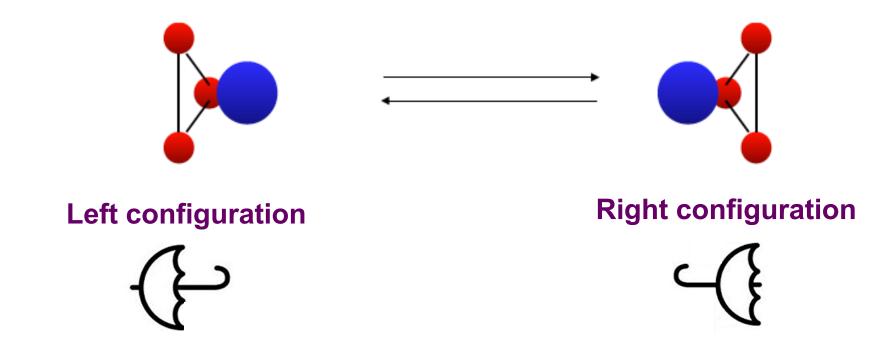
We will show that the tunneling jump of the electron from orbit 1 to orbit 2 lowers the energy. This effect is enhanced when the two nuclei are located relatively close to each other

Attraction between atoms explains the chemical bond



## Ammonia (NH<sub>3</sub>)

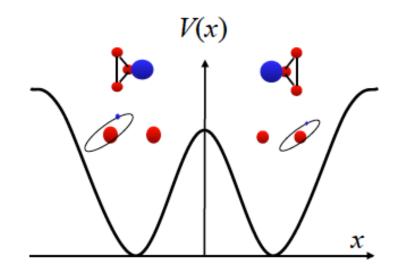
Under the right conditions, ammonia molecules can be flipped. Imagine you are looking at an open umbrella from the side. A strong wind comes along and turns the umbrella inside out!

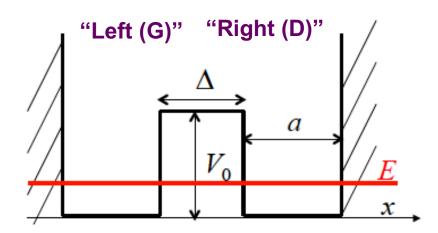


The fundamental state of the molecule is in a superposition of two configurations « Left » and « Right », hence quantum oscillations take place between the two states through tunneling effect



## **Double well potential**





Consider the energy levels such as E<V<sub>0</sub>

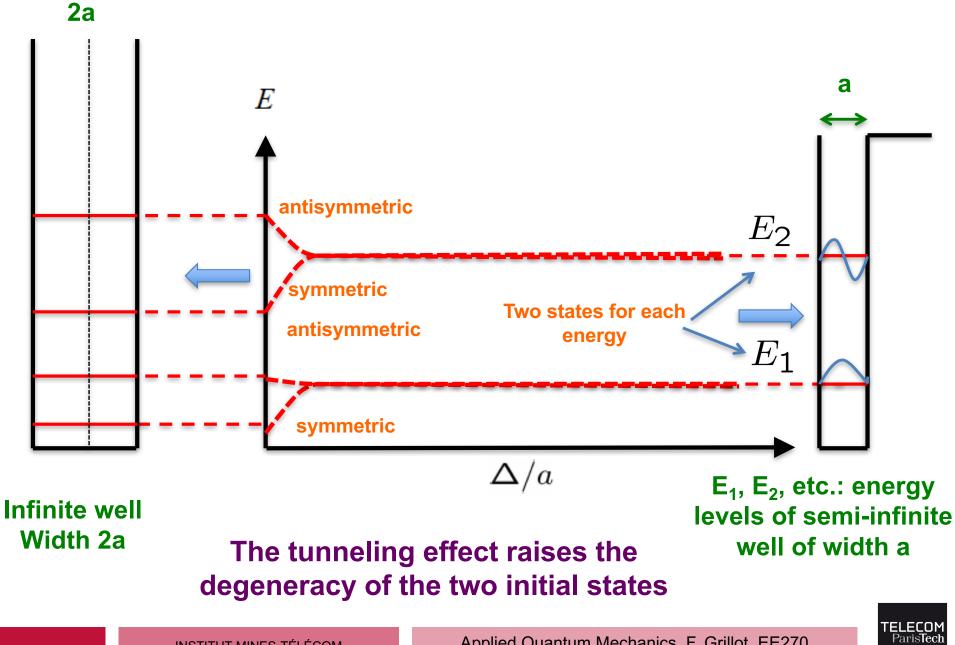
What is the role of the tunneling effect across the barrier ?

As the Hamiltonian H(x) is invariant i.e. H(-x) = H(x), the eigenstates of the Hamiltonian can be described through a linear combination of even (symmetric) and odd (antisymmetric) functions

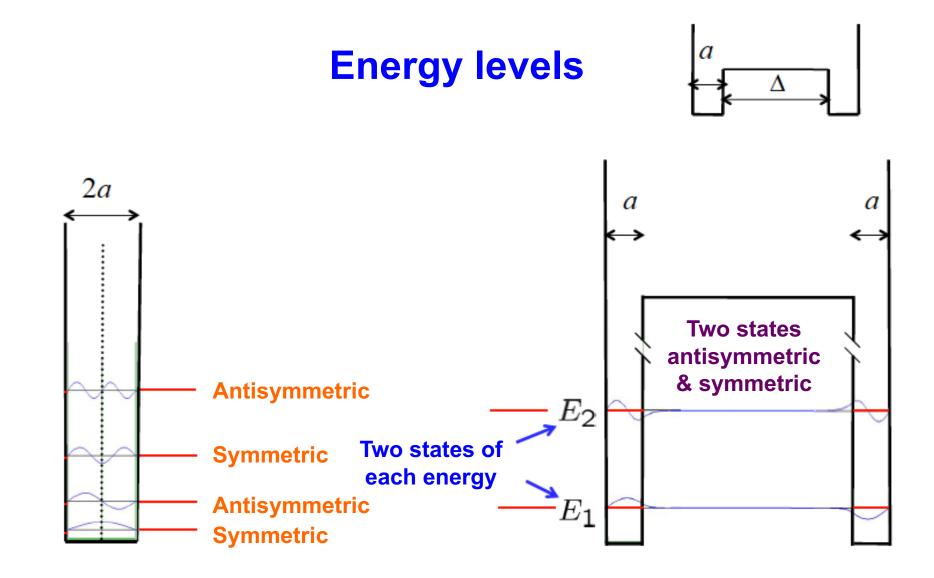
$$\psi(x) = \psi(-x)$$
  $\psi(x) = -\psi(-x)$ 



## **Energy levels**

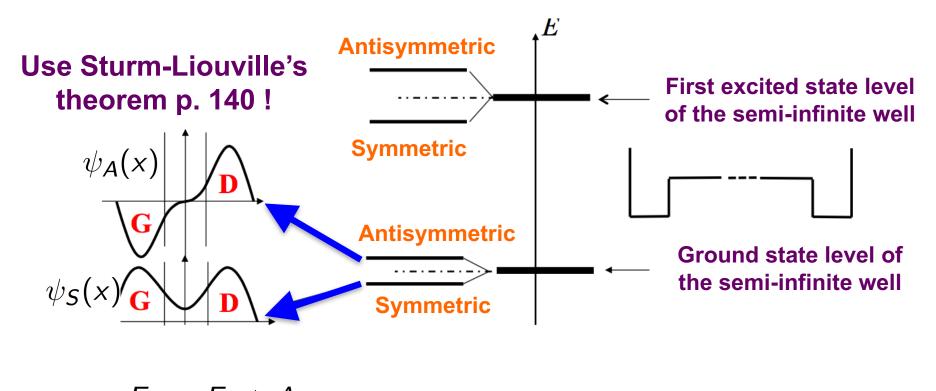


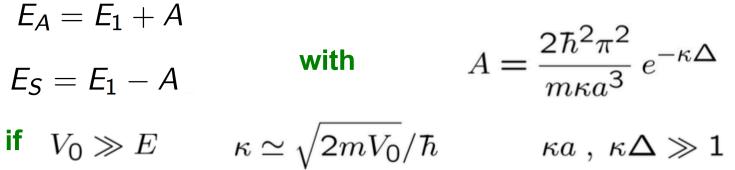
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The molecule appears in a superposition of two configurations « Left » and « Right », with quantum oscillations taking place between the two states through tunneling effect

# **Summary**

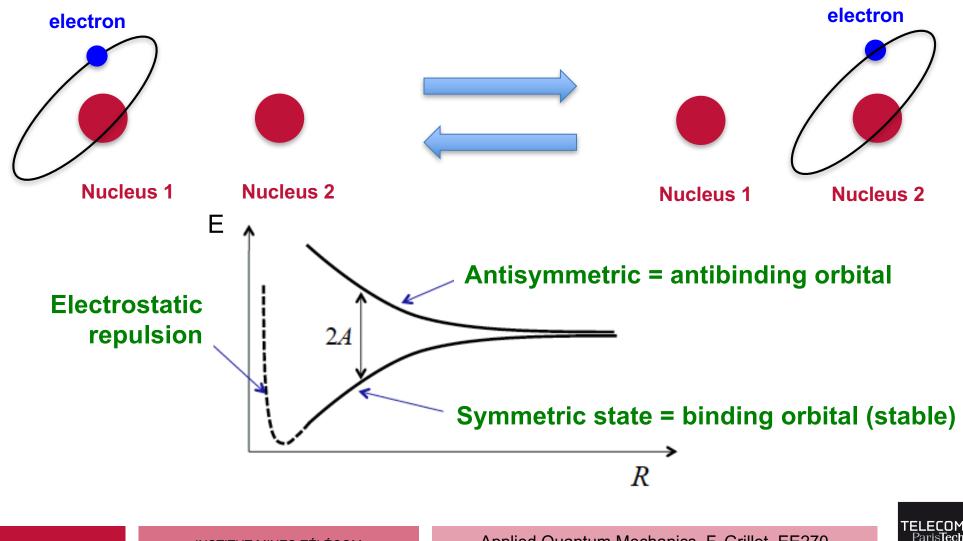




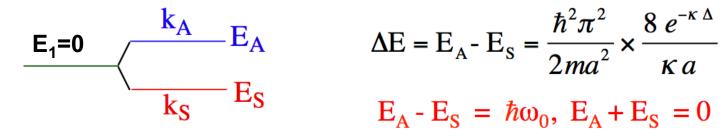


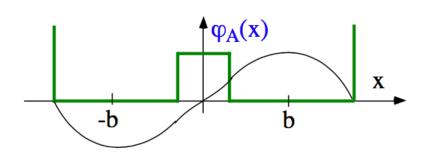
# **Chemical bond**

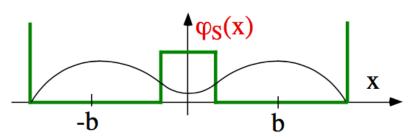
#### The cleavage 2A depends on the distance R between the two nuclei



Consider the ammonia inversion doublet with the lowest energy level







For both eigenstates

$$\psi_{A,S}(x,t) = \varphi_{A,S}(x)e^{-iE_{A,S}t/\hbar}$$

$$|\psi_{A,S}(x,t)|^2 = |\varphi_{A,S}(x)|^2$$

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



$$\hat{A} = \left( \begin{array}{cc} a & b+ic \\ b-ic & d \end{array} \right)$$

general expression with a, b, c, and d real numbers

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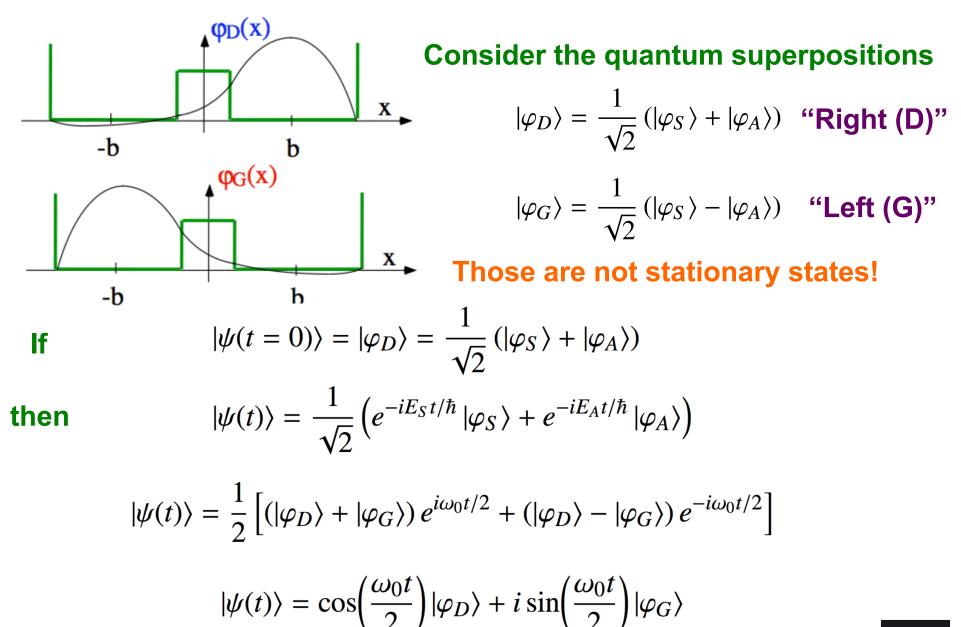
The Hamiltonian in the basis is  $(|\varphi_A\rangle, |\varphi_S\rangle)$  diagonal

 $(|\varphi_A\rangle, |\varphi_S\rangle)$  are eigenstates of the  $\hat{H}_{NH_3}$ 

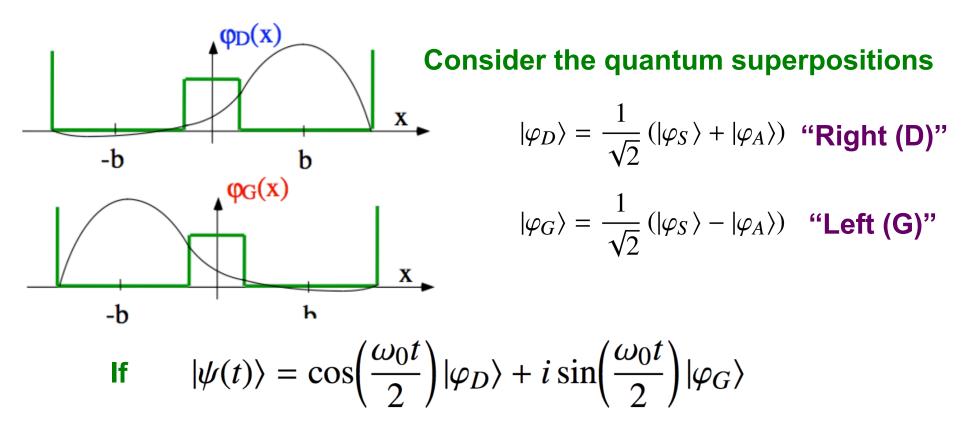
with eigenvalues 
$$E_A = E_1 + A = \frac{\hbar\omega_0}{2}$$
 (Taking E<sub>1</sub>=0)  
 $E_S = E_1 - A = -\frac{\hbar\omega_0}{2}$ 

then 
$$\hat{H}_{NH_3} = \begin{pmatrix} E_A & 0\\ 0 & E_S \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} \omega_0 & 0\\ 0 & -\omega_0 \end{pmatrix}$$

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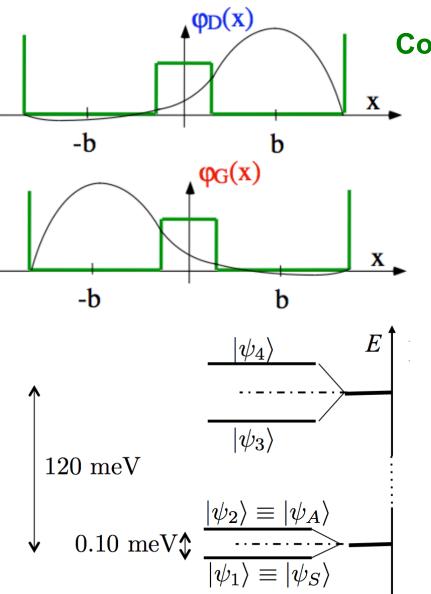




If the molecule is initially prepared to be in the "Right" configuration, over time, the molecule will be oscillating at frequency  $\omega_0$  between "Right" and "Left" dispositions

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





**Consider the quantum superpositions** 

$$|\varphi_D\rangle = \frac{1}{\sqrt{2}} (|\varphi_S\rangle + |\varphi_A\rangle)$$
 "Right (D)"

$$|\varphi_G\rangle = \frac{1}{\sqrt{2}} (|\varphi_S\rangle - |\varphi_A\rangle)$$
 "Left (G)"

**Frequency and wavelength** 

$$\nu_0 = \omega_0/(2\pi) = 24 \text{ GHz}$$

$$\lambda_0 = c/\nu_0 = 1.25 \text{ cm}$$

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## **Interference & measurement**

Suppose we start with an energy eigenstate  $|\varphi_S
angle$ 

$$|\varphi_S\rangle = \frac{1}{\sqrt{2}} \left(|\varphi_D\rangle + |\varphi_G\rangle\right)$$

If we measure X, we can find  $\pm x_0$  with probabilities 1/2

Suppose the measurement has given the result  $+x_0$ ; the state right after the measurement is then

$$|\varphi_D\rangle = \frac{1}{\sqrt{2}} \left( |\varphi_S\rangle + |\varphi_A\rangle \right)$$

If we measure X again immediately afterwards, before the oscillation is appreciable, we find  $+x_0$  with probability 1; the state after the measurement is  $|\varphi_D\rangle$ 



# **Interference & measurement**

Now, suppose that, on this new state  $|\varphi_D\rangle$  we measure not X but the energy E which we are sure was  $E = E_s$  when we started. We know that that we do not always find  $E_s$  but the two possibilities  $E_s$  and  $E_A$ , each with a probability of 1/2

→ We see in this case how the measurement has perturbed the system

At the beginning, the state was  $|arphi_S
angle$ 

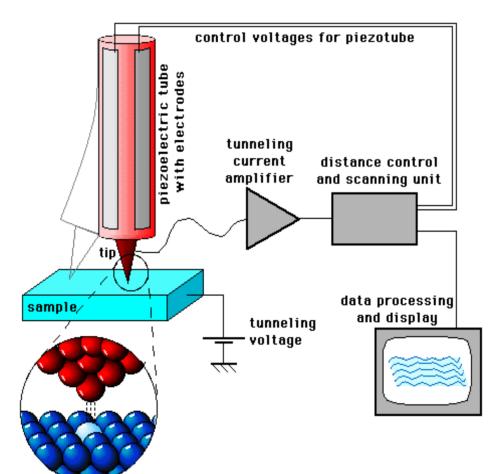
At the end it is a mixture of  $|\varphi_S\rangle$  and  $|\varphi_A\rangle$  in interference, for which <E> = (E<sub>s</sub> + E<sub>A</sub>)/2

All of this results from the superposition principle on one hand and the filtering of which a measurement consists

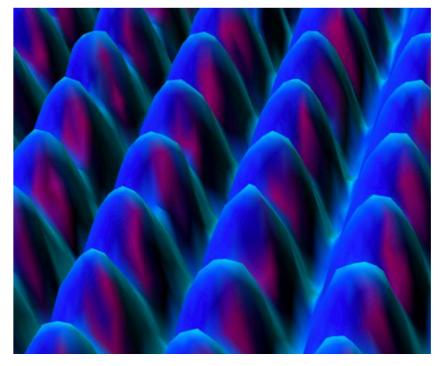
 $\rightarrow$ A position measurement implies a minimum energy exchange with the system. Here, on the average, the exchange of energy is equal to A



# **Scanning tunneling microscopy**



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



Nickel surface, (D. Eigler, IBM)

Electron :  $V_0$ -E = 1 eV, a = 5 Angströms :  $T \sim 6 \times 10^{-3}$ a = 6 Angströms :  $T \sim 2 \times 10^{-3}$ 

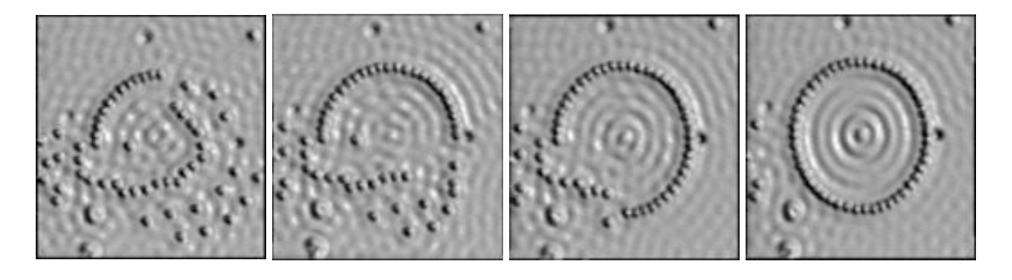
The tunneling current changes very quickly with the distance (due to the exponential term in the transmission coefficient)



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# Moving atoms one by one

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



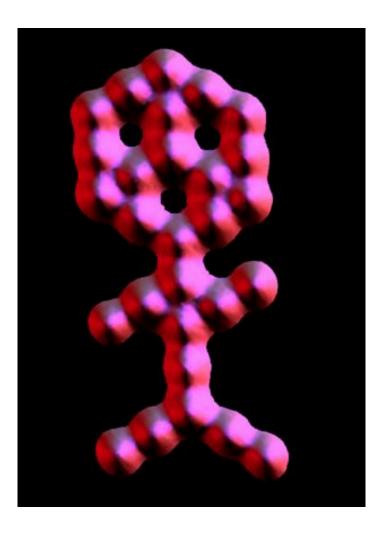
A set of STM images showing formation of a quantum coral from 48 Fe atoms adsorbed on the surface of Cu(111)

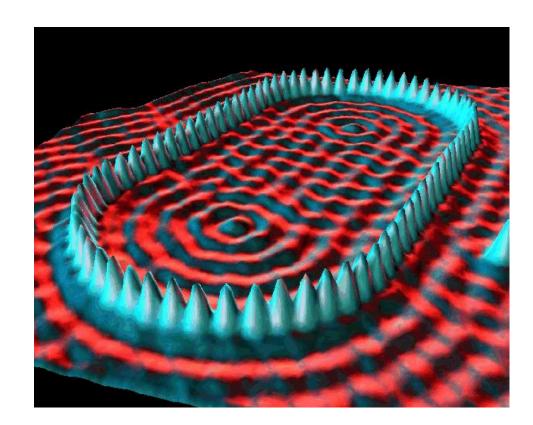


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# Moving atoms one by one

#### Carbon monoxide man (IBM)

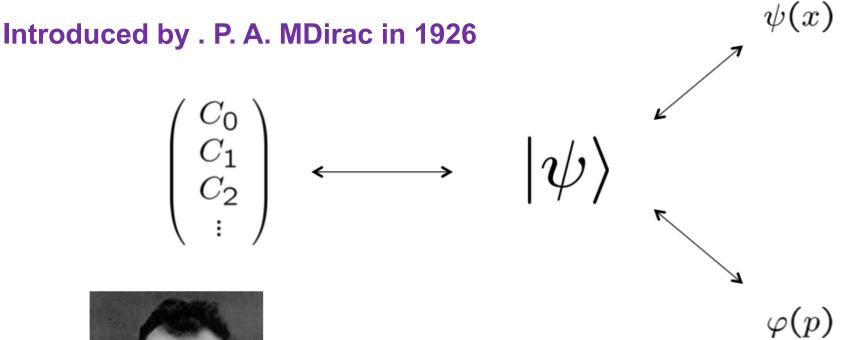


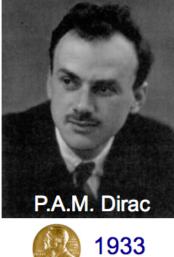


# Stadium coral: Iron atoms on a copper surface (IBM)



# **Ket vector**





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  $|\psi
angle$  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**

- Linearity: if  $|\psi\rangle$  and  $|\phi\rangle$  are elements of  $\mathcal{E}_H$  so is  $a\psi + b\phi$ .
- 2 Inner product:  $\langle \psi | \phi \rangle$  exists and  $\langle \psi | \phi \rangle = \langle \phi | \psi \rangle^*$ .
- 3 Every element  $|\psi\rangle$  has a norm/length  $||\psi||$  such that  $\langle \psi|\psi\rangle = ||\psi||^2$ .
- ④ Completeness: every Cauchy series of functions in  $\mathcal{E}_H$  converges to an element in  $\mathcal{E}_H$



#### **Hilbert space**

The Hilbert space  $\mathcal{L}_2(a, b)$  is the set of all square-integrable functions f(x) on the interval [a,b], i.e., f(x) such that

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

Inner product in

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

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

FI FCOI

# **Generalization of the 1<sup>st</sup> 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

 $|\psi(t)
angle$ 

The Hilbert's space satisfies the principle of superposition

**Existence of Hilbert's basis composed of eigenstates** 

$$|\psi(t)\rangle \iff \begin{pmatrix} C_0(t) \\ C_1(t) \\ \vdots \end{pmatrix}$$



# **Inner product**

#### The inner product is defined using the braket notation

 $\langle \psi_b | \psi_a \rangle$ 

→ linear with the second argument, anti-linear with the first argument

$$|\psi_a\rangle = \begin{pmatrix} C_0 \\ C_1 \\ \vdots \end{pmatrix} \qquad |\psi_b\rangle = \begin{pmatrix} D_0 \\ D_1 \\ \vdots \end{pmatrix} \quad \text{then} \qquad \langle \psi_b | \psi_a \rangle = \sum_n D_n^* C_n$$

All acceptable vectors for a complete description of the quantum system must be normalized

$$\sum_{n} |C_n|^2 = 1$$

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### **Bra vector**

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

$$|\psi_b\rangle = \begin{pmatrix} D_0 \\ D_1 \\ \vdots \end{pmatrix} \qquad (\psi_b) = (D_0^*, D_1^*, \ldots)$$

**Inner product** 

$$\langle \psi_b | \psi_a \rangle = \sum_n D_n^* C_n$$
$$\langle \psi_b | \psi_a \rangle = (D_0^*, D_1^*, \ldots) \begin{pmatrix} C_0 \\ C_1 \\ \vdots \end{pmatrix}$$

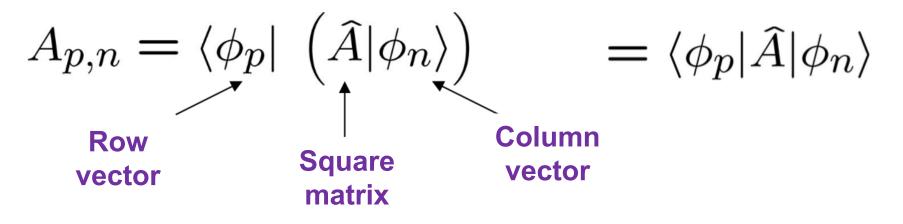
**Braket = complex number** 



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## **Matrix mechanics**

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



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

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



## **Matrix mechanics**

**Examples of Hermitian operators** 

$$\hat{x}, \hat{p}_x, \quad \hat{A} = \begin{pmatrix} 5 & 2+3i \\ 2-3i & -1 \end{pmatrix}$$

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

$$\widehat{A}|\psi_n
angle=a_n|\psi_n
angle$$
 such as  $\langle\psi_p|\psi_n
angle=\delta_{p,n}$ 

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

Particle of mass m in a potential

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$$

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Dipole in an external electric field (E)

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

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

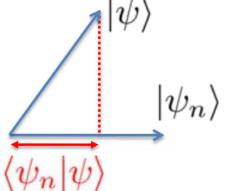
Dipole in an external magnetic field (B)

Potential energyof Interaction

# **Projection operator**

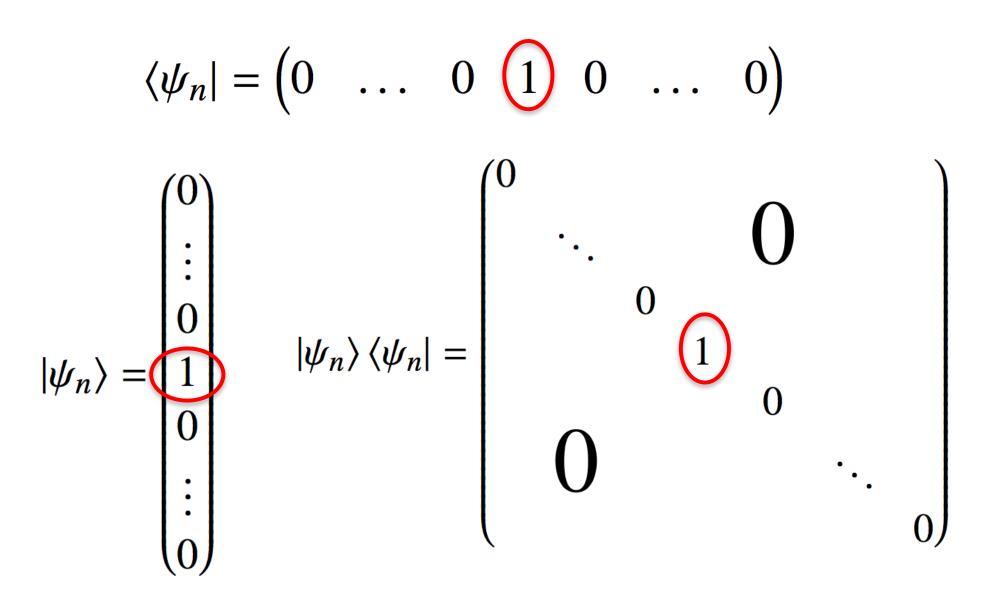
 $\Rightarrow P_n = |\psi_n\rangle \langle \psi_n|$  is an operator (not closed braket)  $\Rightarrow P_n = |\psi_n\rangle \langle \psi_n|$  is a projector  $P_n^2 = (|\psi_n\rangle \langle \psi_n|)^2 = |\psi_n\rangle \langle \psi_n|\psi_n\rangle \langle \psi_n| = |\psi_n\rangle \langle \psi_n| = P_n$  $\Rightarrow P_n = |\psi_n\rangle \langle \psi_n|$  is a projector on state  $|\psi\rangle$  $P_n |\psi\rangle = (|\psi_n\rangle \langle \psi_n|) |\psi\rangle$  $= (\langle \psi_n | \psi \rangle) | \psi_n \rangle$  $|\psi_n\rangle$ 

Here the operator projects a vector onto the n<sup>th</sup> eigenstate





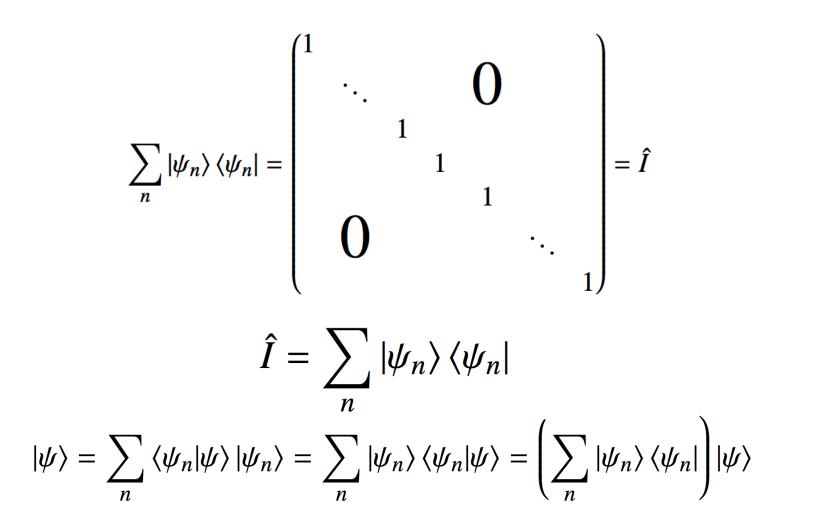
# **Projection operator**





#### **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





## **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

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

$$\hat{I} = \int |\psi_n\rangle \langle \psi_n| \, dn$$



# **Generalization of the 3rd 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

$$\hat{A}|\psi_{n}
angle = a_{n} |\psi_{n}
angle \qquad \langle \psi_{p}|\psi_{n}
angle = \delta_{p,n}$$

The result of a measurement is one of the set of eigenvalues (a<sub>n</sub>) of  $\hat{A}$ The probability of measuring eigenvalue (a<sub>n</sub>) is given by

$$\mathcal{P}(a_n) = |\langle \psi_n | \psi 
angle|^2$$
 Non degenerate

Right after the measurement with result (a\_n), the system is projected onto the vector subspace  $|\psi_n\rangle$ 

This means that a second measurement performed immediately after will produce the same result (a<sub>n</sub>)



### Generalization of the 3<sup>rd</sup> postulate

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

$$(a_n) = g_n \ge 2$$

$$\hat{A} |\psi_{n,r_n}\rangle = a_n |\psi_{n,r_n}\rangle$$
 with  $r_n = 1, \dots, g_n$ 

The result of a measurement is one of the set of eigenvalues ( $a_n$ ) of AThe probability of measuring eigenvalue  $(a_n)$  is given by

# **Infinite dimensional case**

#### A "good operator": Hamiltonian of the harmonic oscillator

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 \qquad \text{Discrete spectrum} : \quad E_n = \hbar\omega \left(n + 1/2\right)$$
$$n \in \mathbb{N}$$

**Eigenfunctions (Hermite polynomials)**  $e^{-x^2/2a^2}$ ,  $x e^{-x^2/2a^2}$ ,  $\dots a = \sqrt{\hbar / m\omega}$ 

#### Included in Hilbert space of square-integrable functions

$$\hat{p}_x = \frac{\hbar}{i} \frac{d}{dx}$$
 Continuous spectrum  $\hbar k \rightarrow$  Set of real numbers  
Eigenfunctions :  $e^{ikx}$ 

#### 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

$$\begin{aligned} |\psi\rangle &= \int dx \, |x\rangle \, \langle x|\psi\rangle \\ &= \int dp \, |p\rangle \, \langle p|\psi\rangle \end{aligned}$$

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**

$$\left|\psi\right\rangle = \int dx \left|x\right\rangle \left\langle x |\psi\right\rangle = \int dp \left|p\right\rangle \left\langle p |\psi\right\rangle$$

 $\begin{array}{l} \langle x|\psi\rangle=\psi(x) & \mbox{is the value of the wave function at position x is} \\ \mbox{simply the projection of the state } |\psi\rangle \mbox{ onto an} \\ \mbox{eigenstate } |x\rangle \end{array} \end{array}$ 

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 $|\langle x|\psi
angle|^2$  Probability of measurement of x

 $\psi(p) = \langle p | \psi 
angle$  Probability amplitude for measurement of p

$$\langle \phi | \psi \rangle = \langle \phi | (\int |x\rangle \langle x| \, dx) \psi \rangle = \int \langle \phi | x\rangle \langle x| \psi \rangle \, dx = \int \phi^*(x) \psi(x) \, dx$$



#### **Position and momentum space**

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

$$\begin{split} \psi(p) &= \langle p | \psi \rangle = \int \langle p | x \rangle \, \langle x | \psi \rangle \, dx \\ &= \int e^{-ipx/\hbar} \psi(x) \frac{dx}{\sqrt{2\pi\hbar}} \end{split}$$

Similarly 
$$\psi(x) = \int e^{ipx/\hbar} \psi(p) \frac{dp}{\sqrt{2\pi\hbar}}.$$

The conversion between position and momentum space is mathematically a Fourier transform because

$$\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}} \exp(ipx/\hbar).$$



## **Discrete vs continuous**

 $\hat{A} |a_n\rangle = a_n |a_n\rangle$  with discrete eigenvalues  $a_n$  $\hat{B} |b_n\rangle = b_n |b_n\rangle$  with continuous eigenvalues  $b_n$ 

Discrete	Continuous
$\langle a_m   a_n \rangle = \delta_{mn}$	$\langle b_m   b_n \rangle = \delta(b_m - b_n)$
$\sum_{m}  a_{m}\rangle \langle a_{m}  = 1$	$\int db_m \left  b_m \right\rangle \left\langle b_m \right  = 1$
$ \alpha\rangle = \sum_{m}  a_{m}\rangle \langle a_{m} \alpha\rangle$	$\ket{eta} = \int db_m \ket{b_m} raket{b_m} eta$
$\sum_{m}  \langle a_{m}   \alpha \rangle ^{2} = 1$	$\int db_m  \langle b_m  \beta \rangle  ^2 = 1$
$\langle a_m   A   a_n \rangle = a_n \delta_{mn}$	$\langle b_m   B   b_n \rangle = b_n \delta(b_m - b_n)$

 $\delta_{mn}$  Kronecker delta function

 $\delta(b_m-b_n)~$  Dirac delta function

# Commutators

#### **Commutators between two operators are defined as**

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



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

Heisenberg

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

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  $|\psi(t)
angle$ 

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

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

$$\widehat{H}|\psi_n\rangle = E_n|\psi_n\rangle$$

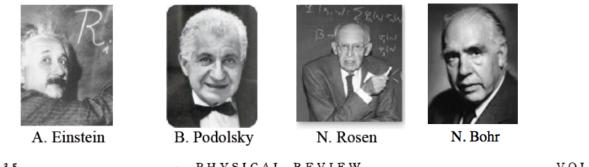
We can write the following decomposition

$$|\psi(t)\rangle = \sum_{n} c_{n}(t) |\psi_{n}\rangle$$

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



# The EPR argument



MAY 15, 1935

PHYSICAL REVIEW

VOLUME 47

#### 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

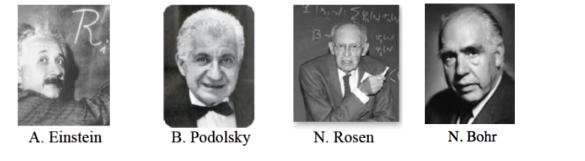
Einstein discovered that the formalism of quantum mechanics contains the existence of particular states named entangled states

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

*"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



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# In 1935, Niels Bohr answered EPR by saying that the quantum theory is complete i.e. there are no hidden variables

OCTOBER 15, 1935

PHYSICAL REVIEW

VOLUME 48

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 Hilbert space  $\mathcal{E}_a$  with basis  $\{|lpha_m
angle\}$ 

Consider a quantum system (b) represented by an Hilbert space  $\mathcal{E}_b$  with basis  $\{|\beta_n\rangle\}$ 

If (a) is in state  $|\alpha_m\rangle$  and (b)  $|\beta_n\rangle$  then the state of the total quantum system is

$$\begin{array}{c} |\alpha_m\rangle \otimes |\beta_n\rangle = |\alpha_m\rangle |\beta_n\rangle \\ \uparrow \\ \text{Tensor product} \end{array}$$

 $\langle \alpha_m | \otimes \langle \beta_n | = \langle \alpha_m | \langle \beta_n | = \langle \alpha_m, \beta_n | = \langle m, n |$ 

Tensor product vector space  $~~ \mathcal{E}_a \otimes \mathcal{E}_b$ 



#### **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  $|\psi_1
angle = \sum_n a_n |\phi_n^{(1)}
angle$  et  $|\psi_2
angle = \sum_p b_p |\phi_p^{(2)}
angle$  then

 $|\psi\rangle = |\psi_1\rangle \otimes |\psi_2\rangle = \sum_{n,p} a_n b_p |\phi_n^{(1)}\rangle \otimes |\phi_p^{(2)}\rangle$  is a vector of the total Hilbert space  $\mathcal{H}_1^M \otimes \mathcal{H}_2^N$ 

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

$$|\psi
angle = \sum_{n,p} c_{n,p} |\phi_n^{(1)}
angle \otimes |\phi_p^{(2)}
angle \ 
eq \ |\psi_1
angle \otimes |\psi_2
angle = \sum_{n,p} a_n \ b_p \ |\phi_n^{(1)}
angle \otimes |\phi_p^{(2)}
angle$$

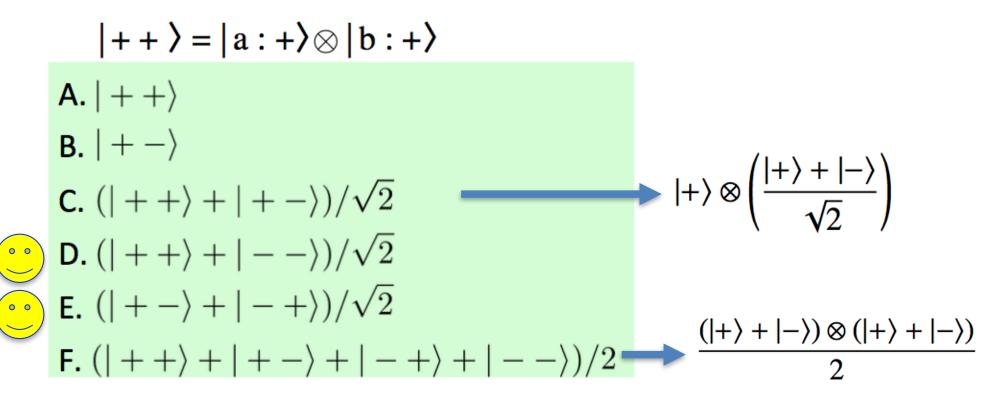
Such a general state  $\Psi$  which cannot be written in the form of a tensor product is called an entangled state



# 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?





#### **Photon polarization**

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

$$|\psi\rangle = \alpha |\mathbf{v}\rangle + \beta |\mathbf{h}\rangle$$
  
 $|\alpha|^2 + |\beta|^2 = 1$ 

#### $(\alpha, \beta)$ real coefficients: linear polarizations $(\alpha, \beta)$ complex coefficients: elliptic and circular polarizations

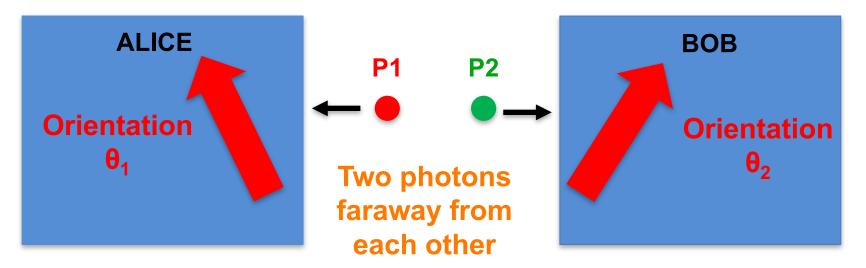
An individual photon can be described as having right or left circular polarization, or a superposition of the two. Equivalently, a photon can be described as having horizontal or vertical linear polarization, or a superposition of the two

→ 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

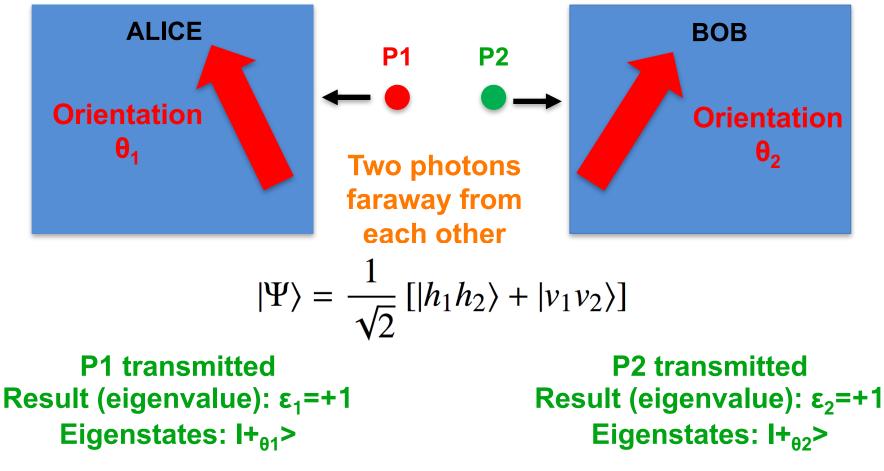
The Hilbert space of dimension 4

 $\dim \mathcal{E} = \dim \mathcal{E}_{P_1} \times \dim \mathcal{E}_{P_2}$ 

 $\mathcal{E} = \mathcal{E}_{P_1} \otimes \mathcal{E}_{P_2}$ 



#### **Measurement on an entangled state**

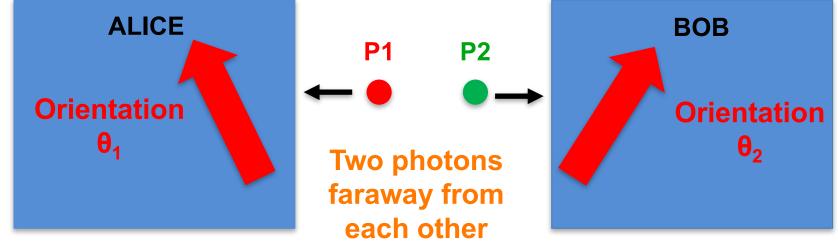


P1 reflected Result (eigenvalue): ε<sub>1</sub>=-1 Eigenstates: I-<sub>θ1</sub>> Eigenstates: I+<sub>θ2</sub>> P2 reflected Result (eigenvalue): ε<sub>1</sub>=-1

Eigenstates: I-<sub>02</sub>>



#### **Measurement on an entangled state**



$$P(+_{\theta_{1}}, +_{\theta_{2}}) = |\langle +_{\theta_{1}}, +_{\theta_{2}}|\Psi\rangle|^{2} = \frac{1}{2}\cos^{2}(\theta_{2} - \theta_{1})$$

$$P(-_{\theta_{1}}, -_{\theta_{2}}) = |\langle -_{\theta_{1}}, -_{\theta_{2}}|\Psi\rangle|^{2} = \frac{1}{2}\cos^{2}(\theta_{2} - \theta_{1})$$

$$P(+_{\theta_{1}}, -_{\theta_{2}}) = |\langle +_{\theta_{1}}, -_{\theta_{2}}|\Psi\rangle|^{2} = \frac{1}{2}\sin^{2}(\theta_{2} - \theta_{1})$$

$$P(-_{\theta_{1}}, +_{\theta_{2}}) = |\langle -_{\theta_{1}}, +_{\theta_{2}}|\Psi\rangle|^{2} = \frac{1}{2}\sin^{2}(\theta_{2} - \theta_{1})$$

What are the single probabilities for separated results?

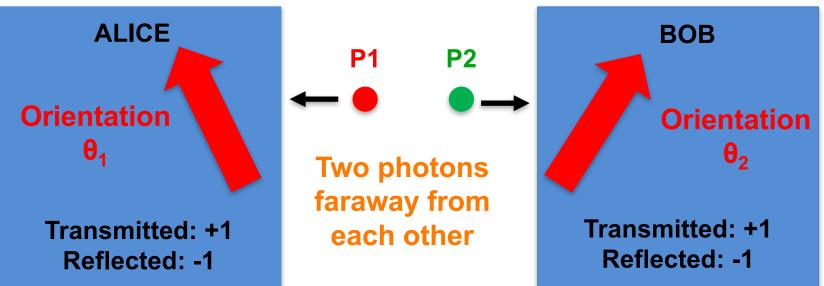
$$P(+_{\theta 1}) = P(+_{\theta 1}, +_{\theta 2}) + P(+_{\theta 1}, -_{\theta 2}) = \frac{1}{2}$$

$$P(-_{\theta 1}) = P(+_{\theta 2}) = P(-_{\theta 2}) = \frac{1}{2}$$

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



# **Bell inequality**



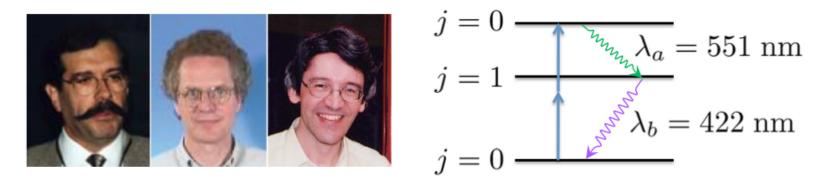
How to explain quantum correlations? Following the EPR argument, John Bell assumed that there exists hidden parameters  $\lambda$  that must determine the outcome of Alice and Bob measurements



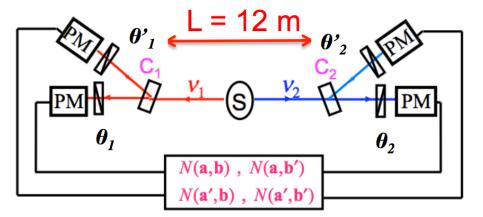
 $A(\theta_1, \lambda) = \pm 1$   $B(\theta_2, \lambda) = \pm 1$   $E(\theta_1, \theta_2) = \int A(\theta_1, \lambda) B(\theta_2, \lambda) \rho(\lambda) d\lambda$ J.S. Bell, Rev. Mod. Phys. 38, 447 (1966)



#### Aspect experiments (1981-82)



 $C_1$ ,  $C_2$  are optical switches redirecting photons towards polarizers with angles  $(\theta_1, \theta'_1)$  and  $(\theta_2, \theta'_2)$ . 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)



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#### **Aspect experiments (1981-82)**

#### Result in a perfect agreement with quantum theory $E(\theta_1, \theta_2) = \cos[2(\theta_2 - \theta_1)]$ $S = E(\theta_1, \theta_2) + E(\theta_1', \theta_2) + E(\theta_1', \theta_2') - E(\theta_1, \theta_2')$ .5 θ Ø 30 60 90 $S_{exp} = 2.697 \pm 0.015$ -.5

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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, L = 1.3 km in Delft, The Netherlands [3]

→ All results are in a perfect agreement with quantum theory
→ 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)

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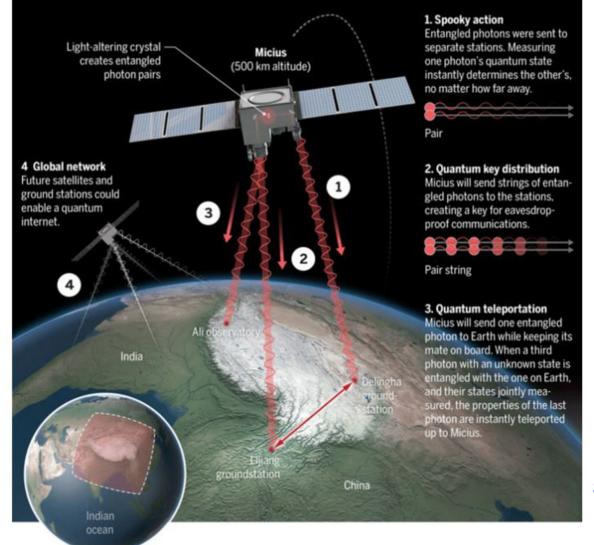
See also, https://physics.aps.org/articles/v8/123



### **Quantum teleportation**

#### Quantum leaps

China's Micius satellite, launched in August 2016, has now validated across a record 1200 kilometers the "spooky action" that Albert Einstein abhorred (1). The team is planning other quantum tricks (2–4).

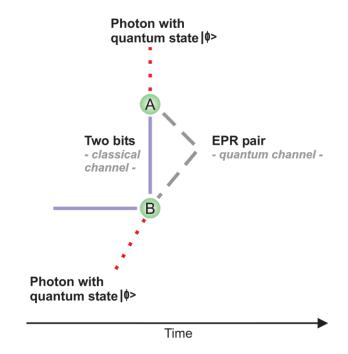


#### **RESEARCH ARTICLE**

#### **QUANTUM OPTICS**

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# Satellite-based entanglement distribution over 1200 kilometers



#### Science, Vol. 356, 6343, pp. 1140-1144, 2017

