An historical introduction to Quantum Mechanics

Serena Cenatiempo - GSSI

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GSSI PhD Program in Mathematics A.Y. 2020/21

An invitation to Quantum Statistical Mechanics

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Plan of the class

- Week 1
  Historical introduction & Formulation of the theory
- Weeks 2-3 - Solvable (one particle) models
  - free particle
  - harmonic oscillator
  - hydrogen atom
- Week 4 - Many particle Quantum Mechanics
- Tutorial classes: Linear operators in Hilbert spaces

Reference book for weeks 1-3:
Alessandro Teta, A Mathematical Primer on Quantum Mechanics

Quantum Mechanics: why ?

http://scivenue.com/2018/03/08/quantum-physics-applications/

The triumph of Classical Mechanics

At the end of the 19th century Classical Mechanics and Classical Statistical Mechanics are very well established, and have lead to an incredible series of successes and amazing technology developments:

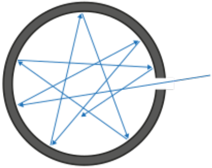
- Newton theory
- Thermodynamics and kinetic theories
- Electromagnetic theory and Maxwell equations
- geometrical and physical optics understood in terms of electromagnetic waves

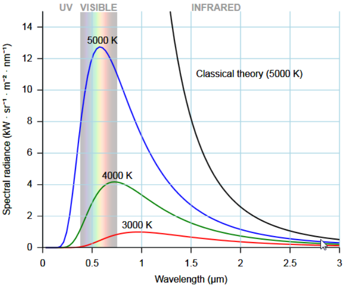
But ...

Classical Physics happens be inadequate to describe some phenomena related to emission and absorption of light.

The black body radiation & the “quantum” assumption

Phenomenon: in a black body (=body that absorbs all the incident radiation) the electromagnetic radiation reaches an equilibrium condition with the internal walls, depending only on T





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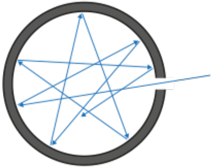

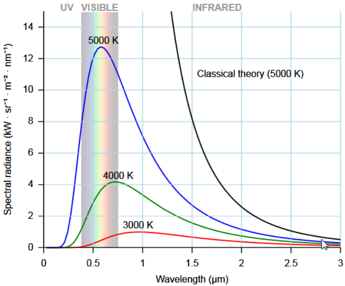

Classical model: the atoms of the wall are described as charged harmonic oscillators in equilibrium with electromagnetic radiation.

Electromagnetism + classical statistical mechanics lead to:

$$u(\nu, T) \propto \nu^2 T$$

with $u(\nu, T)$ the energy density of the radiation at temperature T.

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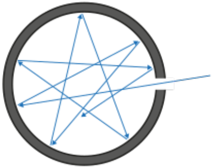

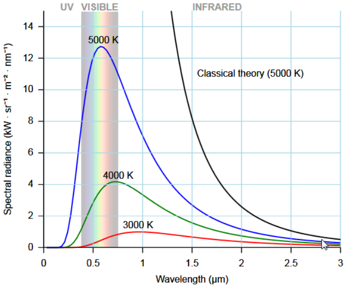

Planck hypothesis (1900): the exchanged energy between electromagnetic wave and matter must be of the form

$$\Delta E = n\, h\nu \qquad h = \text{Planck constant} \sim 10^{-27}\text{Joule/s}$$

$$\nu = \text{frequency}, \qquad n \in \mathbb{N}$$

Physical units: $[h]$ = Energy × Time (Action) and $[\nu] = 1/\text{Time}$.

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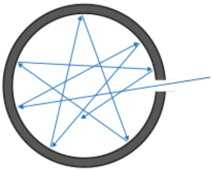

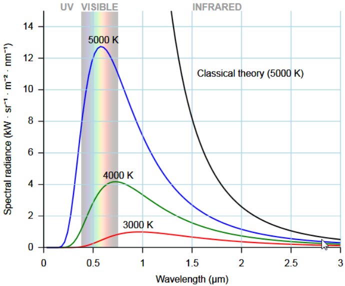

Planck hypothesis (1900): the exchanged energy between electromagnetic wave and matter must be of the form $\longrightarrow$ existence of a new physical constant.

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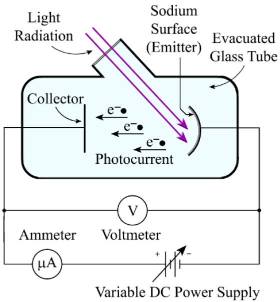
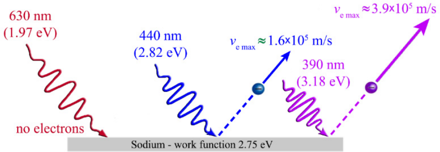
Planck hypothesis & the Photoelectric Effect

Phenomenon: emission of electrons when the surface of a conductor is illuminated by a beam of light



(a)



(b)

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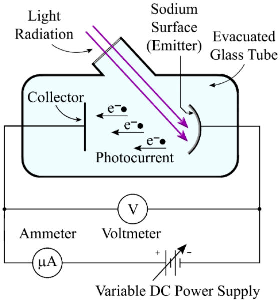

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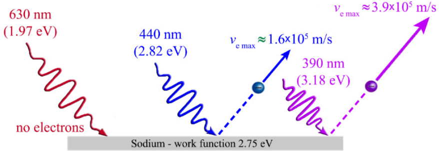

(b)

Observations:

- electrons emitted only if light frequency is larger than a threshold value;
- the kinetic energy of the emitted electrons has a maximum;
- number of emitted electrons/second proportional to the beam intensity

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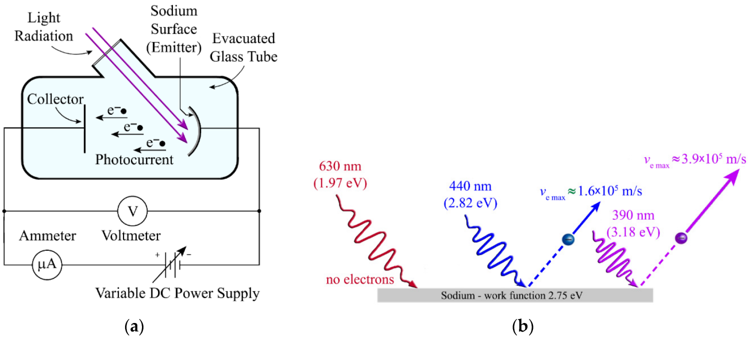

Einstein idea (1905): the extraction of an electron results from the interaction between a single quantum of radiation and a single atom of the metal.

Planck hypothesis & the Photoelectric Effect

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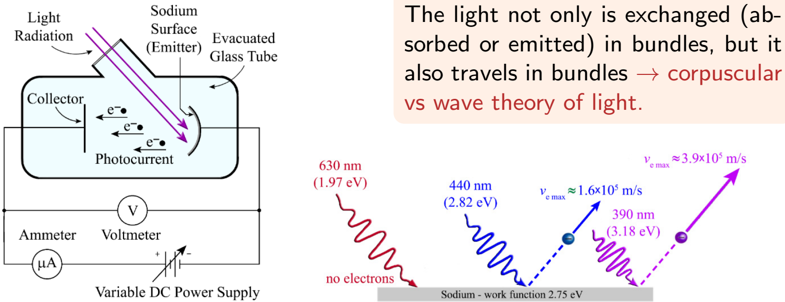
The light not only is exchanged (absorbed or emitted) in bundles, but it also travels in bundles → corpuscular vs wave theory of light.



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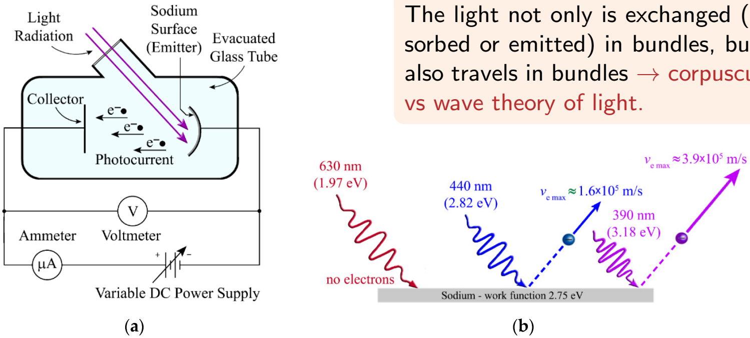

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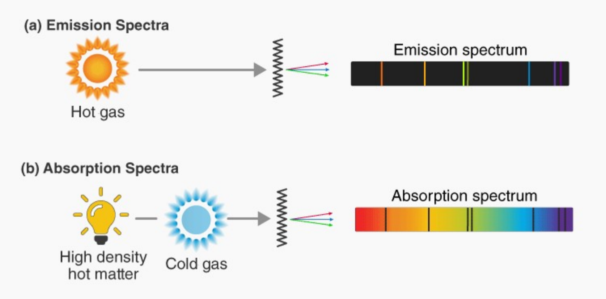
Atomic structure of matter

Emission and Absorption Spectra

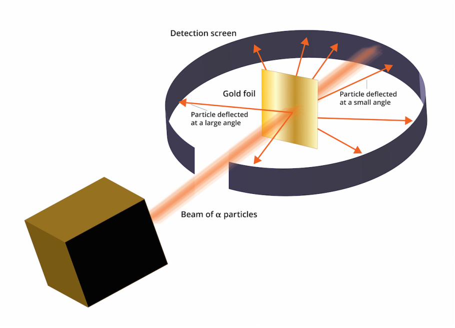


Balmer formula: the frequencies λ_n of the emission and absorption spectra of the hydrogen atom are given by:

$$\frac{1}{\lambda_n} = R\left(\frac{1}{4} - \frac{1}{n^2}\right)$$

Atomic structure of matter

Rutherford experiment (1911)



The atom is a structure with lots of free space: its mass is concentrated in a very small nucleus (nucleus radius $\sim 10^{-13} cm$), surrounded by electrons moving around far apart (atom radius $\sim 10^{-8} cm$).

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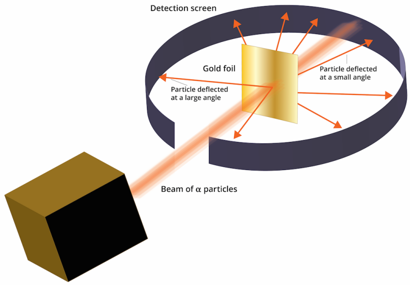

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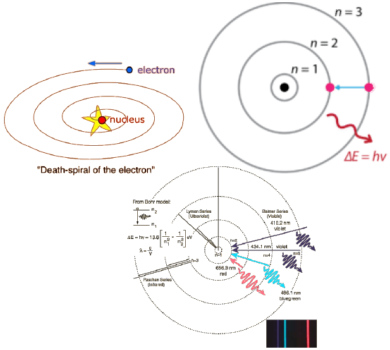
Problems:

- Why do atoms of the same species (ex. hydrogen) have the same radius?
- Electric charges in movement radiate according to Maxwell equations... how can the atom be stable?

Bohr model-atom (1913)



Bohr assumptions:

- For most of the time there is no emission and classical mechanics holds;
- For a very short period of time there is emission of electromagnetic radiation with frequency

$$\nu = \frac{E_{in} - E_{fin}}{h}$$

- The electron can have only discrete energies given by

$$E_n = -\frac{1}{2} n h \nu_e$$

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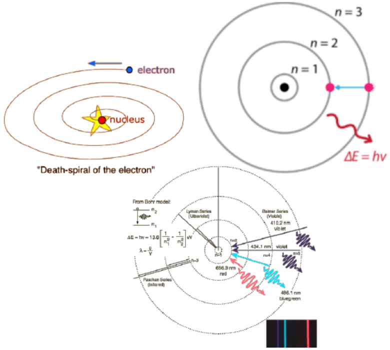

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An attempt to use the old theory with new ideas, but **it predicts well** both energy levels and the amplitude of the electron orbits (a_n = major semi axis)

$$E_n = -\frac{2\pi^2 e^4 m}{h^2 n^2}, \qquad a_n = \frac{h^2 n^2}{4\pi^2 e^2 m} \quad n = 1, 2, 3, \ldots$$

A long story made short

1913-24 Old quantum theory (Born, Sommerfield)

Predictions: atoms subject to electric fields (Stark effect) or magnetic fields (Zeeman effects)

Limitations: only bounded orbits, difficulties with multielectron atoms, lack of internal coherence

1925-26 The new theory

- Matrix Mechanics: Heisenberg (1925), Born, Jordan, Dirac

  Idea: **focus on the observables**, which for an atom are amplitudes and frequencies of the emitted radiation: $(A_{nm}, \nu_{nm}) \rightarrow$ infinite matrices (non commutative algebra!)

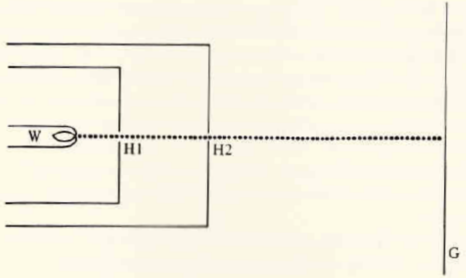
- Wave mechanics: De Broglie (1924), Schrödinger (1926)

  Idea: **The electron is described by a wave**, a scalar function $\psi(x, t)$ depending on position and time

The electron two slits experiment

Davisson and Germer (1927): W is a source of electrons, H1 and H2 holes. On the photographic plate G scintillations are observed (leaving black spots on the plate); they are naturally interpreted as electron impacts on the plate.

Fig. 1. Electron gun.



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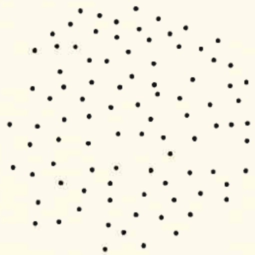


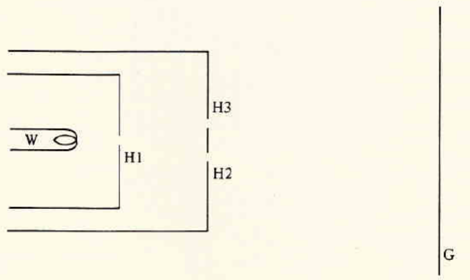
Fig. 2. Pattern built up by many pulses of electron gun of Fig. 1.

Above a typical output observed for small linear size of H2. The smaller is H2 the larger is the linear size of the region occupied by the spots.

The electron two slits experiment

The most stricking phenomenon is observed when the experiment is performed using two holes

Fig. 3. Electron gun with two holes in second screen.



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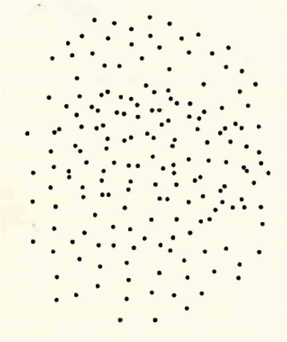

Guess on the basis of classical particle mechanics

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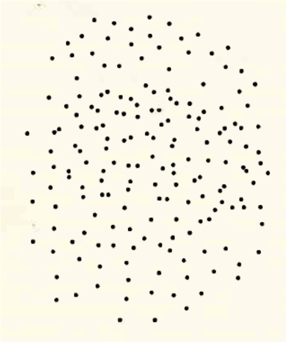

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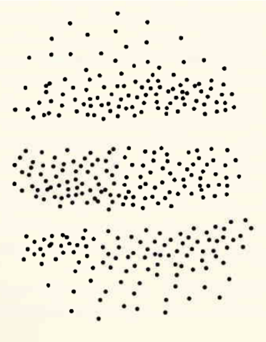
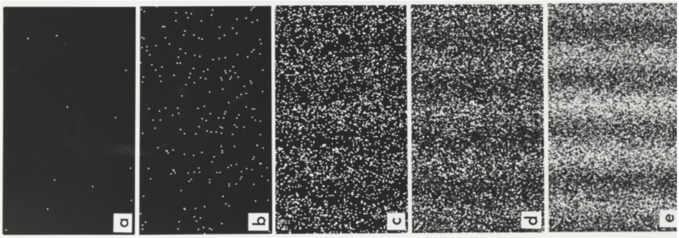


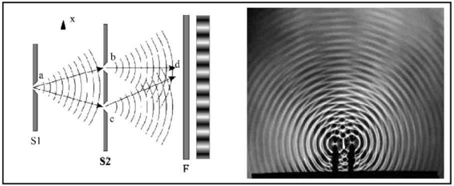
Actual pattern

The electron two slits experiment

Dynamics of the spot formation:



After a large number of identically prepared experiment, the overall scheme of spots looks like the interference patters in water waves (Young, 1801)



The electron two slits experiment

To sum up

- The distribution of impact positions, measured on a large number of identically prepared experiments is similar to the interference pattern generated by spherical waves emitted by two coherent almost point-like sources $\longrightarrow$ the electron has to be described by a wave

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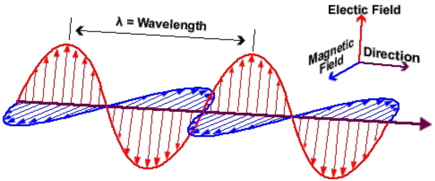
- The impact positions statistics differs qualitatively and quantitatively from the one observed when a single hole is open. Moreover it differs from the superposition of the two pattern observed when one or the other of the two holes are closed $\longrightarrow$ effect of measurement in Quantum Mechanics

The Schrödinger equation

following the line of thought of Wave Mechanics

- Which wave equation?
- Which physical meaning ?

Schrödinger equation: derivation by optical analogy



Wave equation in optics: the generic component of the electric field E in the scalar optics approximation evolves according to

$$\Delta u(x,t) - \frac{1}{v_f^2(x)}\frac{\partial^2 u(x,t)}{\partial t^2} = 0\,, \qquad v_f = \lambda\nu\,.$$

where $v_f(x) = n(x)/c$ is the phase velocity, $n(x)$ and c being the refraction index of the medium and the speed of sound respectively.

The monocromatic component of u satisfies

$$\Delta\tilde{u}(x,\nu) - \frac{4\pi^2\nu^2}{v_f^2(x)}\tilde{u}(x,\nu) = 0\,, \qquad \tilde{u}(x,\nu) = \int dt\, e^{i2\pi\nu t}u(x,t)$$

Schrödinger equation: derivation by optical analogy

Analogy between Geometrical Optics and Classical Mechanics: the trajectory of a point particle with mass m, energy E and subject to a potential $V(x)$ coincides with the trajectory of a light propagating in a medium with phase velocity

$$v_f(x) = \frac{E}{\sqrt{2m(E - V(x))}}$$

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Schrödinger equation: derivation by optical analogy

wave optics (Maxwell)

$$\Delta \tilde{u}(x,\nu) - 4\pi^2 \frac{\nu^2}{v_f^2(x)} \tilde{u}(x,\nu) = 0$$

$\lambda \to 0$

geometrical optics (Fermat)

$v_f(x) = c/n(x)$

wave mechanics (Schrödinger)

?

$h \to 0$

classical mechanics (Newton)

$m, E, V(x)$

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classical mechanics (Newton)

$m, E, V(x)$

$\longleftrightarrow$ $v_f(x) = \frac{E}{\sqrt{2m\,(E-V(x))}}$

Guiding idea: let us associate to the microscopic particle a wave with

phase velocity: $v_f(x) = \dfrac{E}{\sqrt{2m(E-V(x))}}$ (through optical analogy)

frequence: $\nu = E/h$ (Planck-Einstein relation)

and hence wave length $\lambda(x) = \frac{v_f(x)}{\nu} = \frac{h}{\sqrt{2m(E-V(x))}}$ (De Broglie hypothesis).

Schrödinger equation: derivation by optical analogy

wave optics (Maxwell)		wave mechanics (Schrödinger)
$\Delta\tilde{u}(x,\nu) - 4\pi^2 \frac{\nu^2}{v_f^2(x)}\tilde{u}(x,\nu) = 0$		$\Delta\tilde{\psi}(x,\nu) + 4\pi^2 \frac{2m(E-V(x))}{h^2}\tilde{\psi}(x,\nu) = 0$
↓ $\lambda \to 0$		↓ $h \to 0$
geometrical optics (Fermat) $v_f(x) = c/n(x)$	⟷ $v_f(x) = \frac{E}{\sqrt{2m(E-V(x))}}$	classical mechanics (Newton) $m, E, V(x)$

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The stationary Schrödinger equation:

By optical analogy we assumed that $\tilde{\psi}(x,\nu) = \int dte^{2\pi i\nu t}\psi(x,t)$ satisfies

$$\Delta\tilde{\psi}(x,\nu) + 4\pi^2 \frac{2m(E - V(x))}{h^2}\tilde{\psi}(x,\nu) = 0$$

Setting $\hbar = h/2\pi$, we obtain the stationary Schrödinger equation

$$-\frac{\hbar^2}{2m}\Delta\tilde{\psi}(x,\nu) + V(x)\tilde{\psi}(x,\nu) = E\tilde{\psi}(x,\nu)$$

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By multiplying the eq. above by $e^{-2\pi i\nu t}$, using $E = h\nu$ and integrating over ν:

$$\begin{aligned}
-\frac{\hbar^2}{2m}\Delta\psi(x,t) + V(x)\psi(x,t) &= \int e^{-2\pi i\nu t} h\nu\tilde{\psi}(x,\nu)d\nu \\
&= \frac{h}{-2\pi i}\int \frac{d}{dt}\left(e^{-2\pi i\nu t}\right)\tilde{\psi}(x,\nu)d\nu \\
&= i\hbar\frac{\partial}{\partial t}\psi(x,t)
\end{aligned}$$

The time dependent Schrödinger equation:

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\Delta\psi(x,t) + V(x)\psi(x,t) \qquad (*)$$

- We derived $(*)$ by an heuristic argument. From now on $(*)$ will be assumed;

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- $(*)$ contains the imaginary unit, hence $\psi(x,t)$ is a complex valued function.
  The wave function cannot have a direct physical meaning!

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- $(*)$ contains the imaginary unit, hence $\psi(x,t)$ is a complex valued function. The wave function cannot have a direct physical meaning!
- Conservation law: For ψ regular enough and decaying sufficiently fast for large x it is easy to check (Prop. 3.1, Teta's book)

$$\int_{\mathbb{R}^3} |\psi(x,t)|^2 dx = \int_{\mathbb{R}^3} |\psi(x,0)|^2 dx$$

The time dependent Schrödinger equation:

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\Delta\psi(x,t) + V(x)\psi(x,t) \qquad (*)$$

- We derived $(*)$ by an heuristic argument. From now on $(*)$ will be assumed;
- $(*)$ is a PDE, while in classical mechanics one solves ODEs;
- $(*)$ is linear, hence the sum of two solutions is a solution
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$\longrightarrow$ $L^2(\mathbb{R}^2)$ is a natural space for solutions of $(*)$, and $|\psi(x,t)|^2$ could be interpreted has a quantity with a physical meaning.

Interpretation of the Schrödinger equation

Schrödinger original idea: $\rho = e|\psi(x,t)|^2$ density of charge. But

- Except for special cases, solutions of $(*)$ spread in space as time goes by;
- a fraction of the electronic charge has been never observed.

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Statistical interpretation (Born, 1926)

$|\psi(x,t)|^2 =$ probability density to find the microscopic particle in x at time t

For any measurable set A

$$\int_A |\psi(x,t)|^2 dx = \text{probability to find the particle in } A \text{ at time } t$$

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Suppose to perform N experiments in identical conditions, and denote with $N_{A,t}$ the number of times the particle is found in A at time t. Then:

$$\frac{N_{A,t}}{N} \xrightarrow[N \text{ large}]{} \int_A |\psi(x,t)|^2 dx$$

Hence $\|\psi_t\|_{L^2(\mathbb{R}^3)} = \|\psi_{t=0}\|_{L^2(\mathbb{R}^3)}$ is a conservation of probability!

Interpretation of the Schrödinger equation

With the statistical interpretation Quantum Mechanics becomes a statistical theory. Even if I completely know the state $\psi(x, t)$ what I can predict in general is only the probability/statistical distribution of results.

Which is the meaning of this probability?

Might this probability be removed (hidden variables)
or is it intrinsic?

Is the wave function as real as physical fields are considered to be,
or just a mathematical expression of our inability to access the
microscopic world?

Is there a boundary among the classical and quantum description,
and how to identify it?

[Quantum Mechanics has] two powerful bodies of fact in its favour, and only one thing against it. First, in its favour are all the marvellous agreements that the theory has had with every experimental result to date. Second [...] it is a theory of astonishing and profound beauty. The only thing that can be said against it is that it makes absolutely no sense!

Roger Penrose