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Lecture-26

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T. 9.1: Ipotesi di Bohr.

Bohr Hypothesis — I

Multiplying by h both sides of Balmer's law yields $(m > n)$

$$h\nu_{nm} = h\nu_R \left(\frac{1}{n^2} - \frac{1}{m^2}\right) = \left(-\frac{h\nu_R}{m^2}\right) - \left(-\frac{h\nu_R}{n^2}\right).$$

As the left hand side is now interpreted as the energy of the emitted photon, the terms on right hand side can be recast as

$$E_m = -\frac{h\nu_R}{m^2}, \qquad E_n = -\frac{h\nu_R}{n^2}, \qquad E_n < E_m < 0.$$

If E_m (E_n) is interpreted as the atom's energy before (after) emitting the photon, Balmer's law becomes the expression of energy conservation. From this, the "emission rule" of Ritz is easily explained:

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$$\nu_{nm} = \nu_{nk} + \nu_{km} \iff E_m - E_n = (E_m - E_k) + (E_k - E_n).$$

intermediate energy level

According to the Bohr hypothesis:

- ▷ The energy variations of the atoms are due to the electrons.
- ▷ The total energy of a non-radiative state is quantized $E_n = -h\nu_R/n^2$, $n = 1, 2, \ldots$
- ▷ The total energy can vary only between the quantized values by exchanging a photon of energy $\nu_{nm} = (E_m - E_n)/h$.

Q) If the Energy is quantized, what happens to remaining Dynamical quantities like velocity, Momentum, position, Radius of the orbit ....?

Ans from applying Quantized energy to the planetary model.

T. 9.2: Quantizzazione delle grandezze dinamiche conseguente all'ipotesi di Bohr.

Bohr Hypothesis — II

The quantization of the other dynamical quantities follows from that of energy. Taking by way of example the planetary model with circular orbit:

$$E = T + V = -V/2 + V = V/2 = -q^2/(8\pi\varepsilon_0 r)\,,$$

$$r = r_n = -\frac{q^2}{8\pi\varepsilon_0 E_n} = \frac{q^2}{8\pi\varepsilon_0}\frac{n^2}{h\nu_R}\,.$$

quantized energy

In particular, for the ground state $n = 1$ it is $r_1 \simeq 0.5$ Å $\sim r_a$.
The velocity is quantized from $T = -V/2 = -E$:

$$\frac{1}{2}mu^2 = \frac{h\nu_R}{n^2} \quad\Longrightarrow\quad u = u_n = \sqrt{\frac{2h\nu_R}{mn^2}}\,.$$

The largest velocity is found with $n = 1$, $m = m_0$. As $u_1 \simeq 7\times10^{-3}\,c$, a bound electron is non relativistic ($m = m_0$). Finally, for the angular momentum $M = rp = rmu$:

$$M = M_n = \frac{q^2n^2}{8\pi\varepsilon_0 h\nu_R}\,m\sqrt{\frac{2h\nu_R}{mn^2}} = \frac{1}{2\pi}\left[\frac{q^2}{\varepsilon_0}\sqrt{\frac{m}{8h\nu_R}}\right]n\,.$$

'h' plank's Constant

The quantity in brackets turns out to be h. It follows $2\pi M = nh$ (generalized by the Sommerfeld rule $\oint p_i\,\mathrm{d}q_i = n_i h$).

T. 9.3: Fenomeni non spiegati dall'ipotesi di Bohr.

De Broglie Hypothesis — I

The Bohr hypothesis cannot account for a number of phenomena, e.g.,

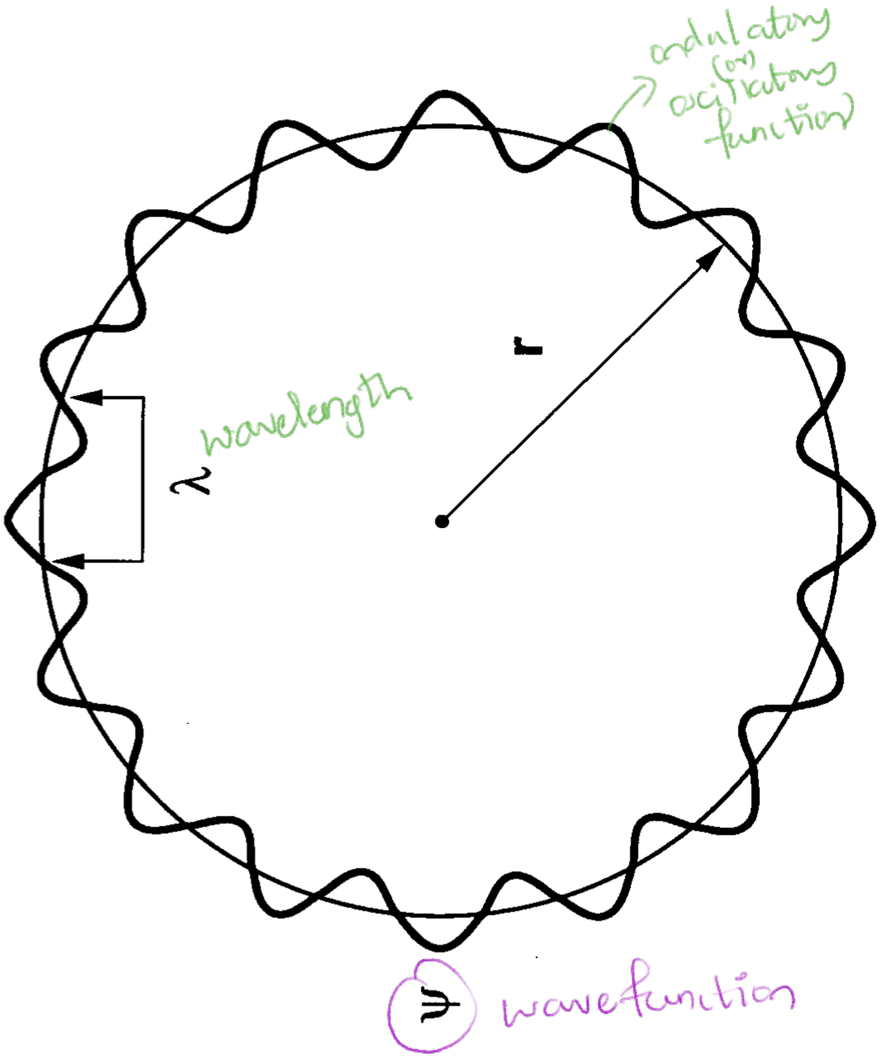
- ▷ The electron on an orbit of energy $E_n = -h\nu_R/n^2$ does not radiate.
- ▷ Excited atoms are unstable.

The experiments seem to suggest that an (osillatory) ondulatory process of some sort is associated to the motion of particles. Such process was introduced by De Broglie and called *wave function*, $\boxed{\psi = \psi(\mathbf{r}, t)}$. By way of example, a periodical function can be associated to a circular orbit so that

$$2\pi r = n\lambda ,$$

which holds to a good approximation if $r \gg \lambda$. The wavelength λ must somehow be related to the dynamical properties of the particle.

T. 9.4: Schematizzazione del processo ondulatorio associato all'orbita di un elettrone.



T. 9.5: Ipotesi di De Broglie — Funzione d'onda piana e monocromatica.

• Simpler case of motion in mechanics is linear particle motion in vacuum.

• Simplest odulatory process is Planar Monochromatic wave

De Broglie Hypothesis — II

In order to determine the form of the wave function, it is sensible to associate the simplest ondulatory function —the planar monochromatic wave, to the simplest dynamical case —the linear uniform motion. In complex form:

angular frequency

$$\psi = A \exp[j(\boldsymbol{k} \bullet \boldsymbol{r} - \omega t)]\,,$$

wave vector

where A is a complex constant, and the wave vector $\boldsymbol{k}$ identifies the direction of the particle motion. It is postulated that the parameters of the wave, ω and $k = |\boldsymbol{k}| = 2\pi/\lambda$, are given by the same relations that hold for the photons:

$$\boxed{\omega = 2\pi\nu = 2\pi \frac{E}{h} = \frac{E}{\hbar}}\,, \qquad \boxed{k = \frac{2\pi}{\lambda} = \frac{2\pi}{h/p} = \frac{p}{\hbar}\,, \qquad \boldsymbol{k} = \frac{\boldsymbol{p}}{\hbar}}\,.$$

As in the linear uniform motion $\boxed{H = p^2/(2m) = E}$, it follows

$$\boxed{\hbar\omega = \frac{1}{2m}\hbar^2 k^2} \qquad \Longrightarrow \qquad \boxed{\omega(\boldsymbol{k}) = \frac{\hbar}{2m} k^2}\,,$$

which is different from the e.m. case $\omega = ck$.

One notices that for the circular orbit the relation $2\pi\, r = n\lambda$ is consistent with the Bohr quantization condition $2\pi\, rp = nh$.

Linear uniform motion $\Rightarrow H = \dfrac{p^2}{2m} = E$

$E = \hbar \omega$

$P = \hbar K$

$$\Rightarrow \frac{(\hbar K)^2}{2m} = \hbar \omega$$

$$\Rightarrow \boxed{\omega(K) = \frac{\hbar K^2}{2m}}$$

This is different from EM case $\omega = cK$

* The above approximation of wave functions works only for linear motion of particles.

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T. 9.6: Funzione d'onda monocromatica.

De Broglie Hypothesis — III

From Hamilton's equations

$$u_i = \dot{x}_i = \frac{\partial H}{\partial p_i} = \frac{1}{\hbar}\frac{\partial H}{\partial k_i} = \frac{\partial \omega}{\partial k_i} = \frac{\hbar k_i}{m} = \frac{p_i}{m}.$$

The group velocity thus proves consistent with the dynamical relations. In contrast, the phase velocity turns out to be

$$u_f = \frac{\omega}{k} = \frac{E/\hbar}{p/\hbar} = \frac{p^2/(2m)}{p} = \frac{p}{2m} = \frac{u}{2} \neq u\,.$$

A straightforward generalization of the planar monochromatic wave is the monochromatic wave

Spatial part of wave function.

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$$\boxed{\psi = w(\boldsymbol{r}) \exp(-j\omega t)\,.}$$

The above is postulated to be the wavefunction associated with the motion of a particle at constant energy $E = \hbar\omega$. The function w is called *spatial part* of ψ, and reduces to $A\exp(j\boldsymbol{k} \bullet \boldsymbol{r})$ for the linear uniform motion.

T. 9.7: Interpretazione statistica della funzione d'onda.

Statistical Interpretation of the Wave Function

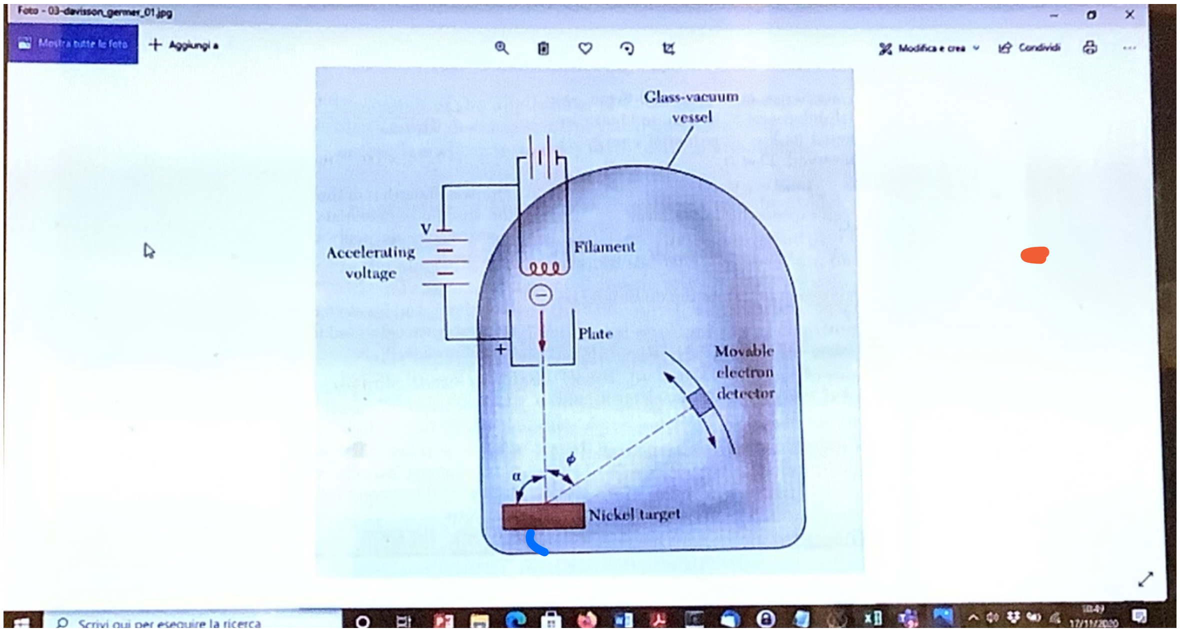
By using the optical analogy to interpret the Davisson and Germer experiment, it is possible to infer the wavelength λ from the distance between the interference fringes. The corresponding momentum $p = h/\lambda$ agrees with that derived from the initial energy $E = p^2/(2m)$. This suggests that the energy is conserved in the experiment, while the direction of momentum is changed.

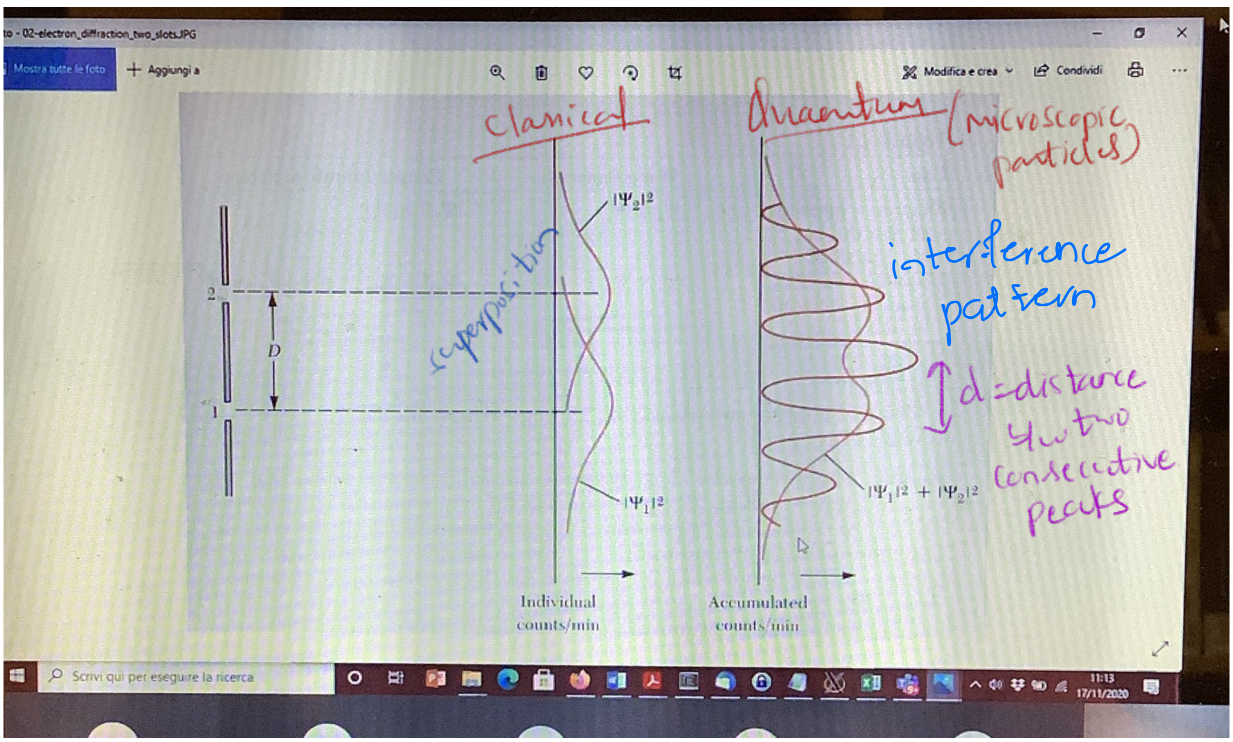
Also, the intensity of the fringes is a measure of the number of electrons impinging upon each area $\Delta x \, \Delta y$ of the screen, hence of the number of electrons that, just before impinging onto the screen, have a position belonging to the volume $\tau = \Delta x \, \Delta y \, \Delta z$ adjacent to the screen. It is sensible to admit that ψ must provide such information, specifically, that some function $f(\psi)$ must exist such that $\int_\tau f(\psi) \, d\tau$ predicts the number of these electrons. The analogy with the e.m. case, corroborated by experiments, yields $f(\psi) = |\psi|^2$, whence

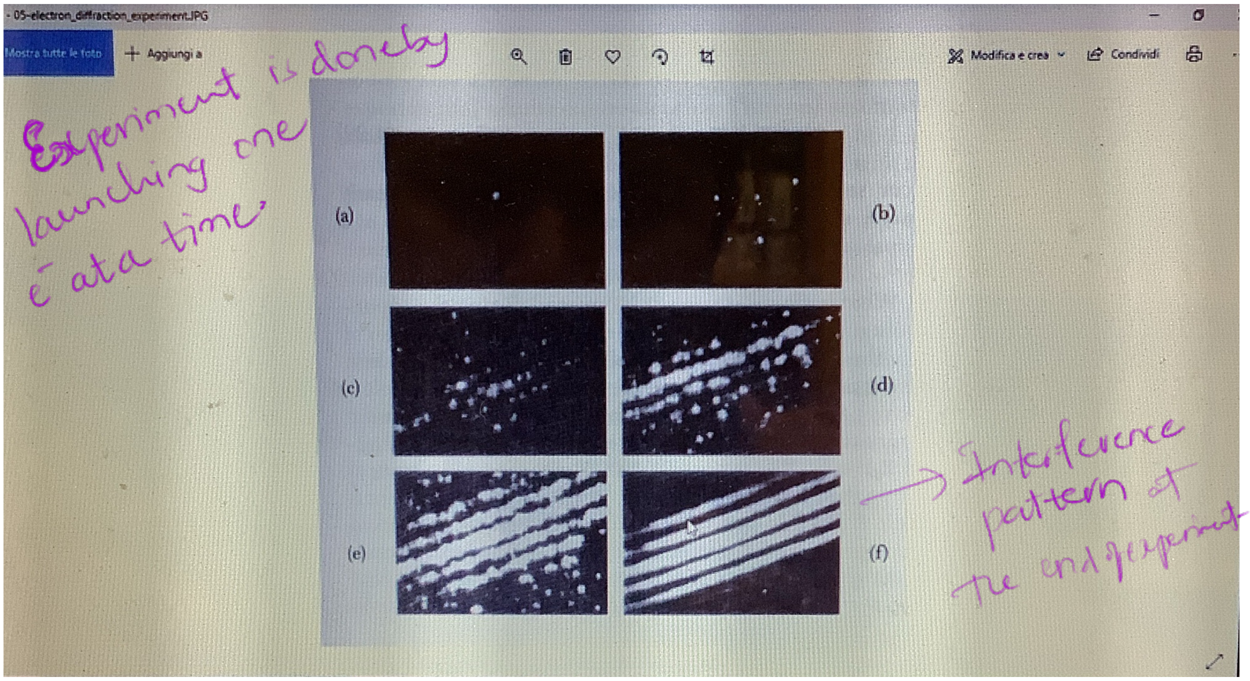
$$\int_\tau |\psi|^2 \, d\tau$$

provides the number of electrons that would be found within τ if a measurement were performed.

Davison & Germer experiment







** • wave function simply is a Mathematic function attached to the mechanical motion of an electron.

• May be WF can be exploited to find out statistical distribution of these electrons of the experiment. and it would be helpful to describe general statistical distribution.

→ $\tau = \Delta x \, \Delta y \, \Delta z$ adjacent to the screen

'ψ' even though a complex function

There should exist $f(\psi)$ s.t

$$\int_{\tau} f(\psi) \, d\tau$$ predicts the no. of electrons

(i) This can be done by simply repeating the experiments.

(ii) 2nd way is the analogy w.r.to EMF case

(i.e oscillatory properties of EMF when we studied about photons, when we consider the EMF the basic quantities are the EF & MF so then we have something that is the intensity of the Radiation, it is the Square Modulus of the EMF. WF

Square Modulus of wave function ∴ $\int_{\tau} |\psi|^2 d\tau$ $f(\psi) = |\psi|^2$

provides the no. of e^- that belong to the volume at particular time 't'

∴ Statistical interpretation of The Wave function is this. We take WF at a particular instant of time then we take Square Modulus over a Volume This gives a no. of e^-s that belong to the volume at time e.g. t

- The units of $|\psi|^2$ is that of Inverse of Volume because

$$\int_\tau |\psi|^2 d\tau$$

is a Number

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T. 9.8: Interpretazione probabilistica della funzione d'onda.

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Probabilistic Interpretation of the Wave Function

The meaning of $\int_\tau |\psi|^2 \, d\tau$ should also hold when ψ refers to one particle at the time. Actually, ψ was originally introduced in relation to a single particle. In view of this, the probabilistic interpretation introduced by Born states that

$$\int_\tau |\psi(\boldsymbol{r}, t)|^2 \, d^3 r$$

is proportional to the probability that a measuring process finds the particle within τ at the time t.

When $\tau \to \infty$ the integral above may, or may not, converge. In the first case, ψ is called *normalizeable*, and can be multiplied by a suitable real constant $\sigma > 0$, namely, $\psi \leftarrow \psi' \doteq \sigma\psi$, to obtain a probability:

$$\int_\tau |\psi'|^2 \, d^3 r \leq 1 \, , \qquad \sigma^{-2} \doteq \int_\infty |\psi|^2 \, d^3 r \, .$$

In the second case ψ is not normalizeable (a typical example is $\psi = A \exp[j(\boldsymbol{k} \bullet \boldsymbol{r} - \omega t)]$), but it is still possible to give the meaning of probability ratio to

$$\int_{\tau_1} |\psi|^2 \, d^3 r \left(\int_{\tau_2} |\psi|^2 \, d^3 r \right)^{-1} .$$

→ The probabilistic Interpretation of Wave function introduced by Born.

- When we consider a single particle the integral of the square Modulus of the W.F at an instant of time 't' integrated over a volume is proportional to the probability that if we measure the position of the particle, we can find the particle within the volume 'τ' at time 't'.
This interpretation is only Mathematical, not measured.

- Here also we say proportional to the probability than equal to the probability. Because if you extend volume to ∞ you expect the probability should be equal to 1. (i.e the particle should exist somewhere)

- But the point is there is a WF's whose integral over infinity diverges & the typical example is exactly the WF associated to the Uniform motion.

De Broglie Hypothesis - II

→ If we take $\psi = A \exp(j(k \cdot r - \omega t))$

$A \rightarrow$ is a complex constant

$K \rightarrow$ Wave vector identifies the direction of motion of Particle.

It is postulated that parameters of the Wave

ω & $k = |K| = 2\pi/\lambda$ are given by the same relations that hold for Photons

$$\omega = 2\pi\nu = 2\pi \frac{E}{h} \Rightarrow \frac{E}{\hbar}$$

$$\hbar = h/2\pi$$

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

For the above WF and take the square Modulus we will get ONE, then if we integrate the Quantity over a finite volume offcourse you will find finite value. But, if we integrate over Infinity we will get Infinity.

So, the simplest possible WF turns out to be Non integrable in space (in this case we can not talk about probability, because Integral Diverges)

Note: Before making 'τ' go to infinity we must check whether the wave function is integrable in Square Modulus. Then we can call it Normalizable

$$\int_\tau |\psi(\boldsymbol{r},t)|^2\,\mathrm{d}^3\boldsymbol{r}$$

is proportional to the probability that a measuring process finds the particle within τ at the time t.

When $\tau \to \infty$ the integral above may, or may not, converge. In (i) the first case, ψ is called normalizeable, and can be multiplied by a suitable real constant $\sigma > 0$, namely, $\psi \leftarrow \psi' \doteq \sigma\psi$, to obtain a probability:

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(ii) In the second case ψ is not normalizeable (a typical example is $\psi = A\exp[j(\boldsymbol{k}\bullet\boldsymbol{r} - \omega t)]$), but it is still possible to give the meaning of probability ratio to

$$\int_{\tau_1} |\psi|^2\,\mathrm{d}^3\boldsymbol{r}\left(\int_{\tau_2} |\psi|^2\,\mathrm{d}^3\boldsymbol{r}\right)^{-1}.$$

ratio of two integrals.

Q) Can we Normalize WF at will?

Ans YES, ∵ The WF is a solution to a Differential equation that is Homogeneous

& B.C also Homogeneous.

∴ The solution (WF) multiplied by a constant is also a solution to the D.E

So it is legitimate to multiply Normalizable W.F by an constant.

→

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T. 9.9: Contrazione della funzione d'onda — I due casi limite della f. d'onda.

Simple Examples of Wave Function

- The process of measuring the particle's position improves the information about the localization; e.g., if the position measurement lasts from t to t', it is

$$\psi(\boldsymbol{r}, t) \neq 0 \ \forall \boldsymbol{r} \in \tau\,, \qquad \psi(\boldsymbol{r}, t') \neq 0 \ \forall \boldsymbol{r} \in \tau'\,, \qquad \tau' \subset \tau\,,$$

which is referred to as *contraction* of the wave function. If $t' - t \to 0$ the wave function becomes discontinuous in time.
From the meaning of $\int_\tau |\psi|^2 \, \mathrm{d}^3 r$ it follows that $|\psi|^2 \, \mathrm{d}^3 r$ is proportional to an infinitesimal probability, and $|\psi|^2$ to a probability density.

- By way of example, the $\boxed{\text{wave function } \psi = A \exp[j(\boldsymbol{k} \bullet \boldsymbol{r} - \omega t)]}$ associated to the motion of a free particle provides full information about the momentum ($\boldsymbol{p} = \hbar \boldsymbol{k}$), but no information about the position as $|\psi|^2 = |A|^2 = \text{const}$. It also provides information about the particle energy ($E = \hbar\omega$) for the special reason that in the linear uniform motion it is $E = p^2/(2m)$.

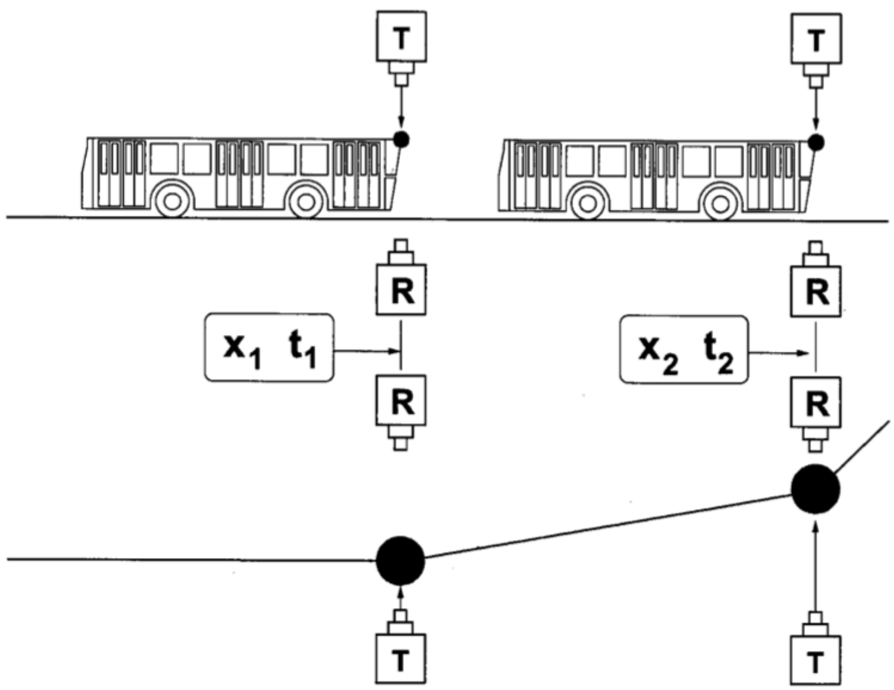
- If an exact measurement of position localizes the particle in $\boldsymbol{r}_0$ at t', it is $\psi(\boldsymbol{r}, t') = \delta(\boldsymbol{r} - \boldsymbol{r}_0)$, still non normalizeable. The information about $\boldsymbol{p}$ is lost. ↳ Diract delta function.

$$\psi = A \exp\left[j\left(k \cdot r - \omega t\right)\right]$$

$$\psi(r, t') = \delta(r - r_0)$$

$\delta(r)$ & $\exp\left(j\left(k \cdot r - \omega t\right)\right)$

are F.T of each other. We will see the reason later!



T. 9.10: Schematizzazione dell'effetto di una misura di velocità.

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