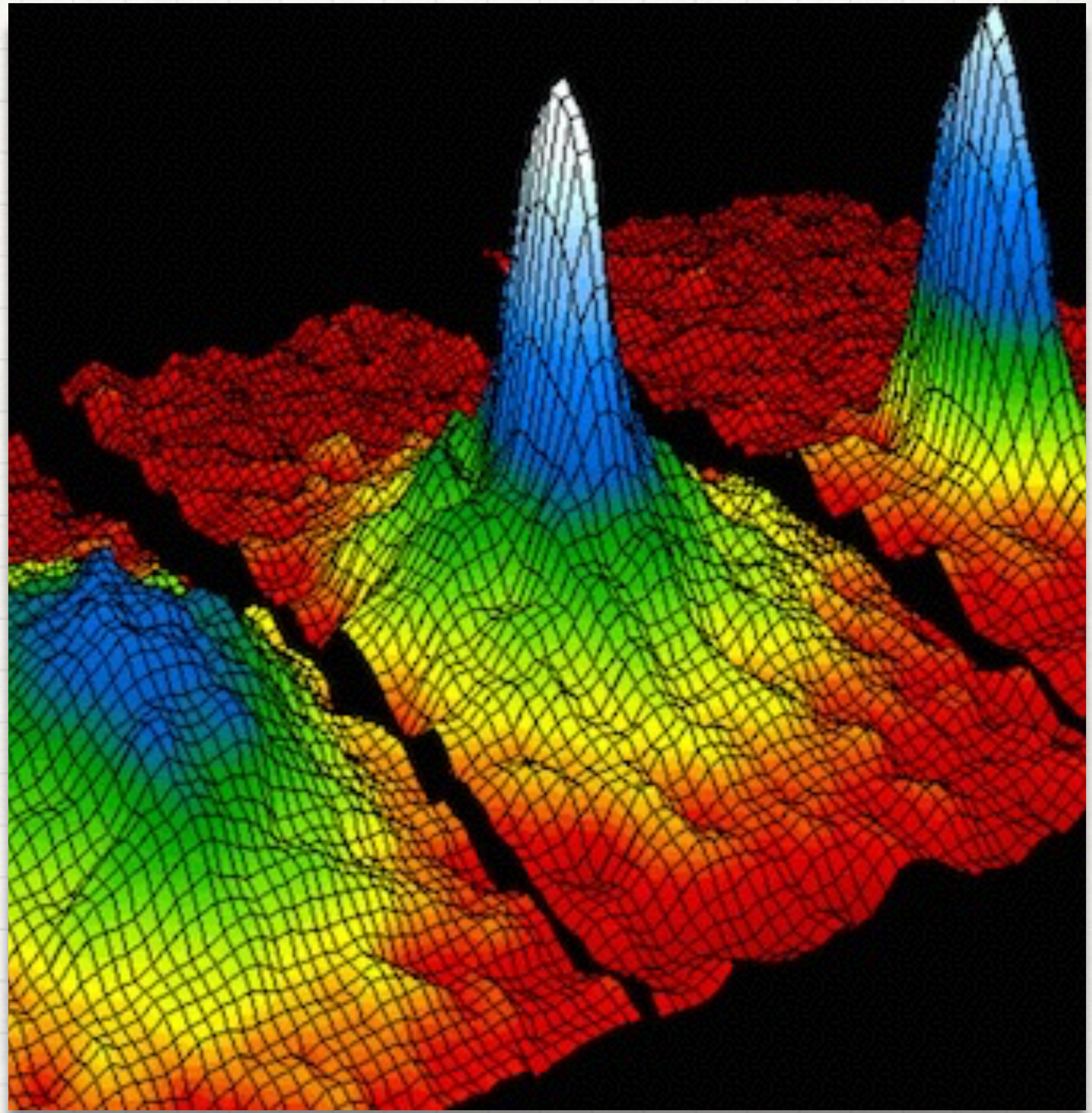
CHAPTER 3

WAVES OF MATTER



WAVE-FUNCTION

From our analysis of the double-slit gedanken experiment we have learnt:

1) The probability of an event in an ideal experiment is given by the square of the absolute value of a complex number ϕ which is called the probability amplitude:

$$P = \text{probability},$$
$$\phi = \text{probability amplitude},$$
$$P = |\phi|^2.$$

(2) The propagation through space in time of the amplitude ϕ(x,t) resamples <u>some</u> properties of waves (namely <u>interference</u>). For this reason it is called the **WAVE-FUNCTION**

How can we compute the wave function?

According to the uncertainty principle. being able to predict ϕ(x,t) is all we can hope to achieve!!!

CRUSH COURSE ON WAVES

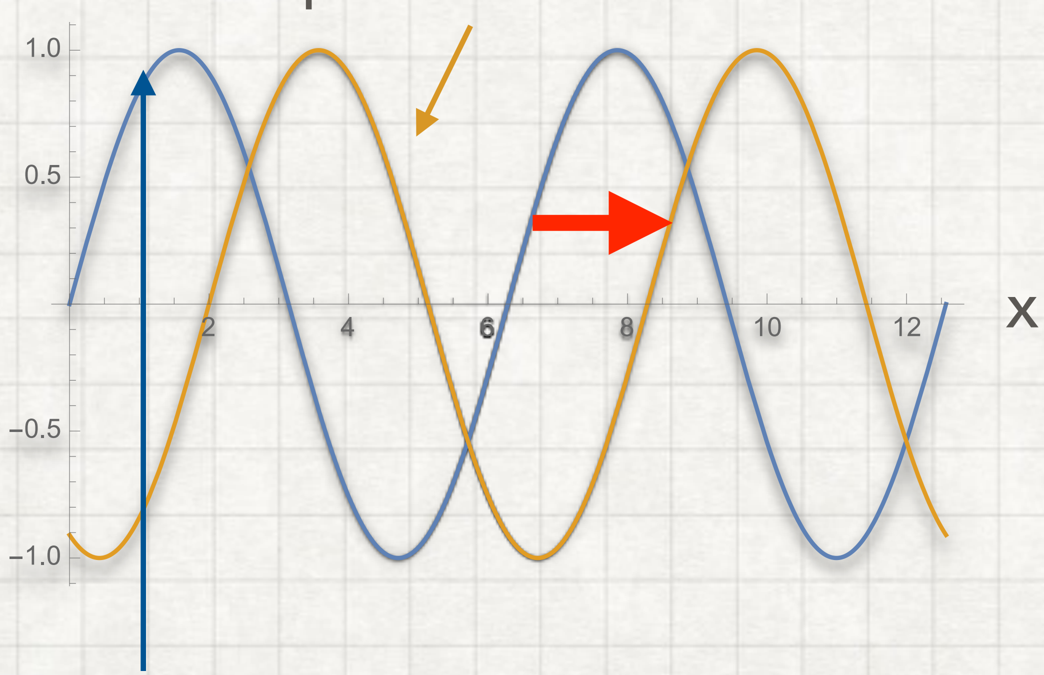
To compute the wave-function the first question we need to ask is: what is a wave?

A **traveling wave** is function which keeps its shape while moving in space, i.e.

$$f(x,t) = g_f(x - vt) + g_b(x + vt)$$

where v is the velocity of the wave

is the same as the height at position x+vt at time t…



the height at x at time t=0…

It is immediate to show that this type of function obeys the so-called **WAVE EQUATION:**

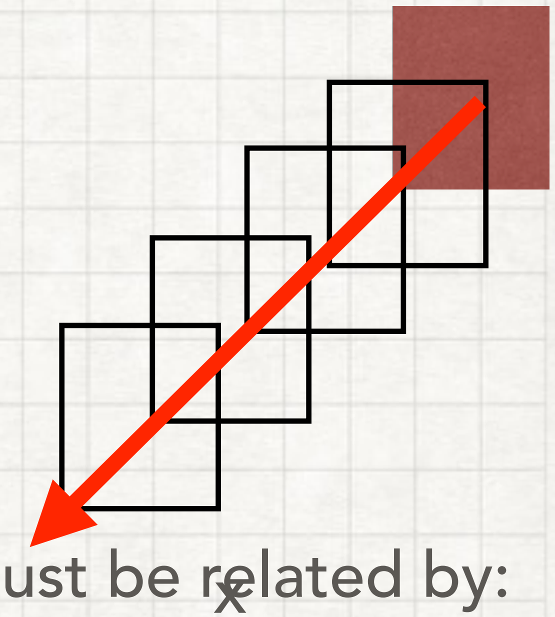
$$\frac{1}{v^2}\frac{\partial^2}{\partial t^2} f(x,t) = \frac{\partial^2}{\partial x^2} f(x,t)$$

Indeed fluid-dynamics equations or Maxwell's equations are in this form!

PLANE WAVES

$$f_+(x,t) = A \times e^{i(xk-\omega t)}$$ forward propagating

$$f_-(x,t) = A \times e^{i(xk+\omega t)}$$ backward propagating



To obey the wave equation, **k** (wave vector) and **ω** (frequency) must be related by:

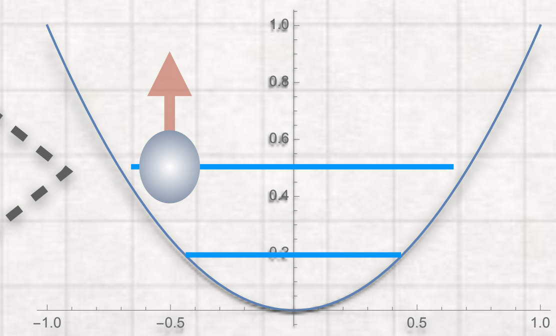
$$c^2k^2 = \omega^2$$ (dispersion relation)

We recall that , the wave vector is proportional to the **momentum** carried by the wave!

Not quite what we need. Indeed we know

Energy of a quantum particle is proportional to the frequency of the associated wave

$h\nu$ ⇨



$$E_k = \hbar\omega$$

$$E_k = \frac{p^2}{2m}$$

⇨ $\omega \propto k^2$

WAVES OF FREELY TRAVELING MATTER:

Plane traveling waves are also solutions of a slightly different type of equation

$$i\frac{\partial}{\partial t}\phi(x,t) = -C\frac{\partial^2}{\partial x^2}\phi(x,t) \qquad \textbf{(*)}$$

This time the dispersion relation is $\omega = Ck^2$ just what we need!!!

We need to determine C:

$$E_k = \hbar\omega$$

$$E_k = \frac{p^2}{2m}$$

$$\begin{aligned}\phi(x,t) &= A\, e^{i(\omega t \pm kx)} \\ &= A\, e^{\frac{i}{\hbar}(\hbar\omega t \pm \hbar kx)} \\ &= A\, e^{\frac{i}{\hbar}\left(\frac{p^2}{2m}t \pm \hbar kx\right)}\end{aligned}$$

The equation (*) is satisfied if: $C = \frac{\hbar}{2m}$ $\quad k = \frac{1}{\hbar}p$

We then obtain:

$$i\hbar\frac{\partial}{\partial t}\phi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\phi(x,t)$$

(FREE PARTICLE) SCHRÖDINGER EQUATION

A freely propagating quantum particle with **fixed momentum** is described by

$$\phi(x,t) = A_+\ e^{\frac{i}{\hbar}\left(\frac{p^2}{2m}t-px\right)} + A_-\ e^{\frac{i}{\hbar}\left(\frac{p^2}{2m}t+px\right)}$$

Matter wave

Traveling wave function have fixed velocity (momentum)! Position is unspecified!!

$$|\phi(x,t)|^2 = \text{uniform in space}$$

Heisemberg's principle is safe!!!!!

WAVE-FUNCTION IN MOMENTUM REPRESENTATION

Suppose we are interested in knowing the probability of observing the particle with a certain momentum Prob(p,t) (typical in scattering problems)

QUESTION: How can we calculate it from the wave function **φ**(x,t) ?

STATEMENT (not proven here): one needs to compute the Fourier Transform of **φ**(x,t):

wave function in momentum representation ←

$$\tilde{\phi}(p,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx\; e^{\frac{i}{\hbar} p \cdot x}\; \phi(x,t)$$

Then in analogy with the probability in position representation

$$\mathcal{P}(p,t) = |\tilde{\phi}(p,t)|^2$$

To convince ourselves this is the right thing to do, let's recall Heisemberg's uncertainty principle: increased information on x implies decreased info on p

$$\phi(x,t_0) = \frac{1}{\lambda^{\frac{1}{2}}\ \pi^{\frac{1}{4}}} e^{-\frac{x^2}{2\lambda^2}}$$

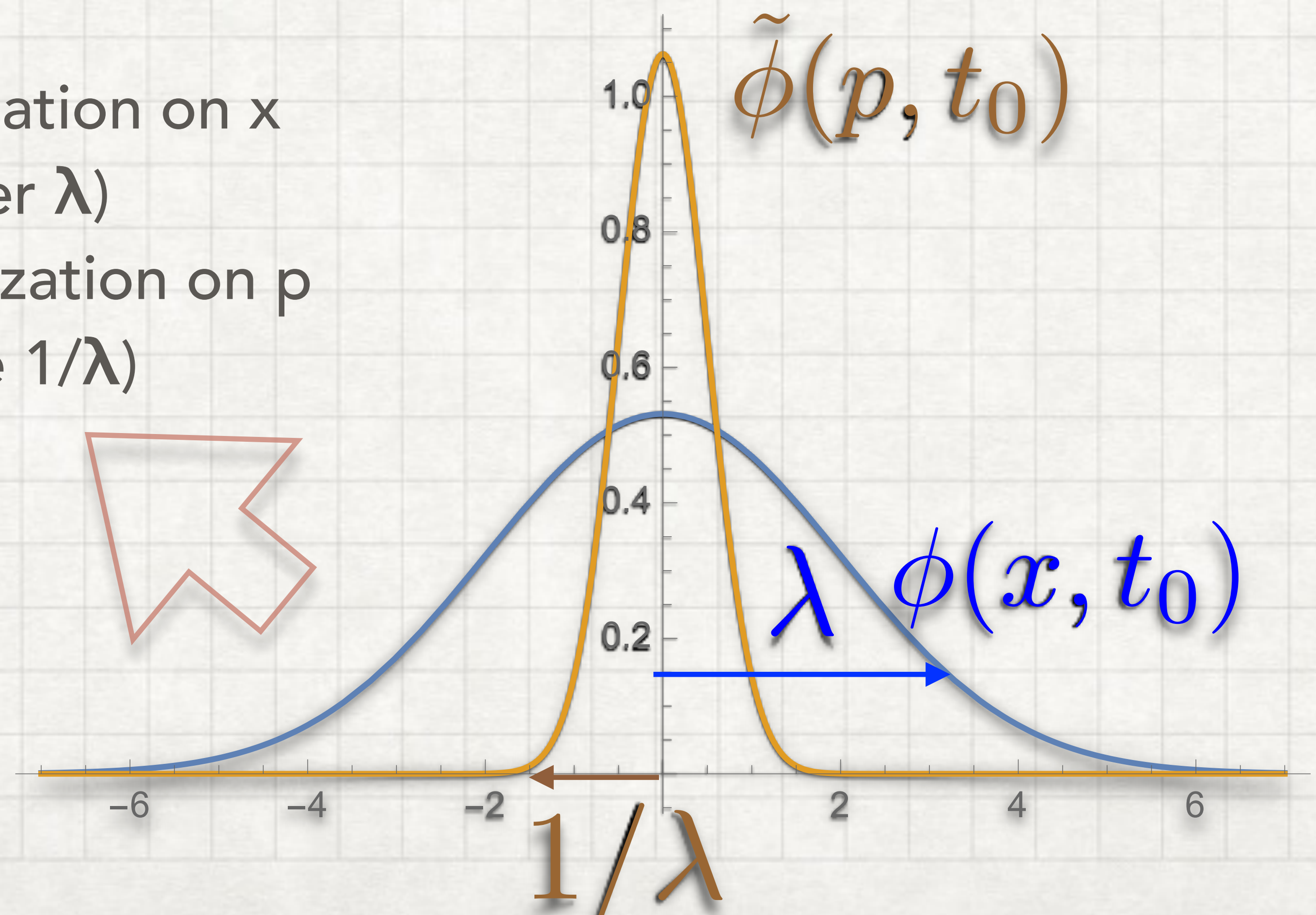
normalization

$$\int_{-\infty}^{\infty} dx |\phi(x,t_0)|^2 = 1$$

$$\int_{-\infty}^{\infty} dp |\tilde{\phi}(p,t_0)|^2 = 1$$

$$\tilde{\phi}(p,t_0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx e^{ipx}\ \phi(x,t_0) = \sqrt{2\lambda}\ \pi^{-\frac{1}{4}}\ e^{-\frac{1}{2}\lambda^2 p^2}$$

more localisation on x
(larger **λ**)
=> less localization on p
(smalle 1/**λ**)



Frequency representation

We can Fourier transform also time!

$$\tilde{\phi}(p, E) = \int_{\infty}^{\infty} \frac{dt}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{dx}{\sqrt{2\pi}} e^{\frac{i}{\hbar}(Et - p \cdot x)} \; \phi(x, t)$$

$|\tilde{\phi}(p, E)|^2$ Amplitude to find the particle with momentum p and energy E

By the same argument of p, x:

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

One more uncertainty relationship!

A mathematical relationship (directly from rules of integration by parts):

$$\int \frac{dx}{\sqrt{2\pi}} \int \frac{dt}{\sqrt{2\pi}} e^{-\frac{i}{\hbar}(Et-px)} i\hbar \frac{\partial}{\partial t}\phi(x,t) = E\tilde{\phi}(E,p)$$

$$\int \frac{dx}{\sqrt{2\pi}} \int \frac{dt}{\sqrt{2\pi}}\, e^{-\frac{i}{\hbar}(Et-px)} \left(-i\hbar\frac{\partial}{\partial x}\right)\phi(x,t) = p\tilde{\phi}(E,p)$$

This enables us to understand what the Schrödinger equation means!!

Indeed by Fourier transforming both terms:

$$i\hbar\frac{\partial}{\partial t}\phi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\phi(x,t)$$

$$\int \frac{dx}{\sqrt{2\pi}} \int \frac{dt}{\sqrt{2\pi}} e^{-\frac{i}{\hbar}(Et-px)} i\hbar\frac{\partial}{\partial t}\phi(x,t) = \int \frac{dx}{\sqrt{2\pi}} \int \frac{dt}{\sqrt{2\pi}}\, e^{-\frac{i}{\hbar}(Et-px)}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right)\phi(x,t)$$

We obtain find a sensible stament:

$$E\ \tilde{\phi}(p,E) = \frac{p^2}{2m}\tilde{\phi}(p,E)$$

The energy of a free particle is given by the kinetic energy!

FULL TIME-DEPENDENT SCHRÖDINGER EQUATION (i.e with interactions)

We have learnt that this term in the free SE accounts for the kinetic energy

$$i\hbar\frac{\partial}{\partial t}\phi(x,t) = -\frac{\hbar^2}{2m}\nabla^2\phi(x,t)$$

…then we are ready to guess the structure of the Schrödinger equation if the particle is subject to a potential V(x): just add it up to E_k!

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

(TSE)

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

Hamiltonian

(related to the total energy)

Summary

$$i\hbar\partial_t\phi(x,t) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(x)\right)\ \phi(x,t)$$

coord. rep. Schrödinger eq.

Fourier transf.

$$\phi(x,t) \equiv \langle x|\psi(t)\rangle$$

coord. rep. wave-function

Inverse Fourier transf.

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

quantum state

Fourier transf.

Inverse Fourier transf.

$$\tilde{\phi}(p,t) \equiv \langle p|\psi(t)\rangle$$

mom. rep. wave-function

$$i\hbar\partial_t\tilde{\phi}(p,t) = \frac{p^2}{2m}\tilde{\phi}(p,t) + \int \frac{dp'}{\sqrt{2\pi}}V(p-p')\tilde{\phi}(p',t)$$

mom. rep. Schrödinger eq.

TIME-INDEPENDENT SCHRÖDINGER EQUATION

The time-dependent Schrödinger equation (TSE) is a partial differential equation and is very difficult to solve, even numerically. The problem can be however strongly simplified by making an ansatz*:

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

$$\phi(x,t) = e^{\frac{i}{\hbar}Et}\psi(x)$$

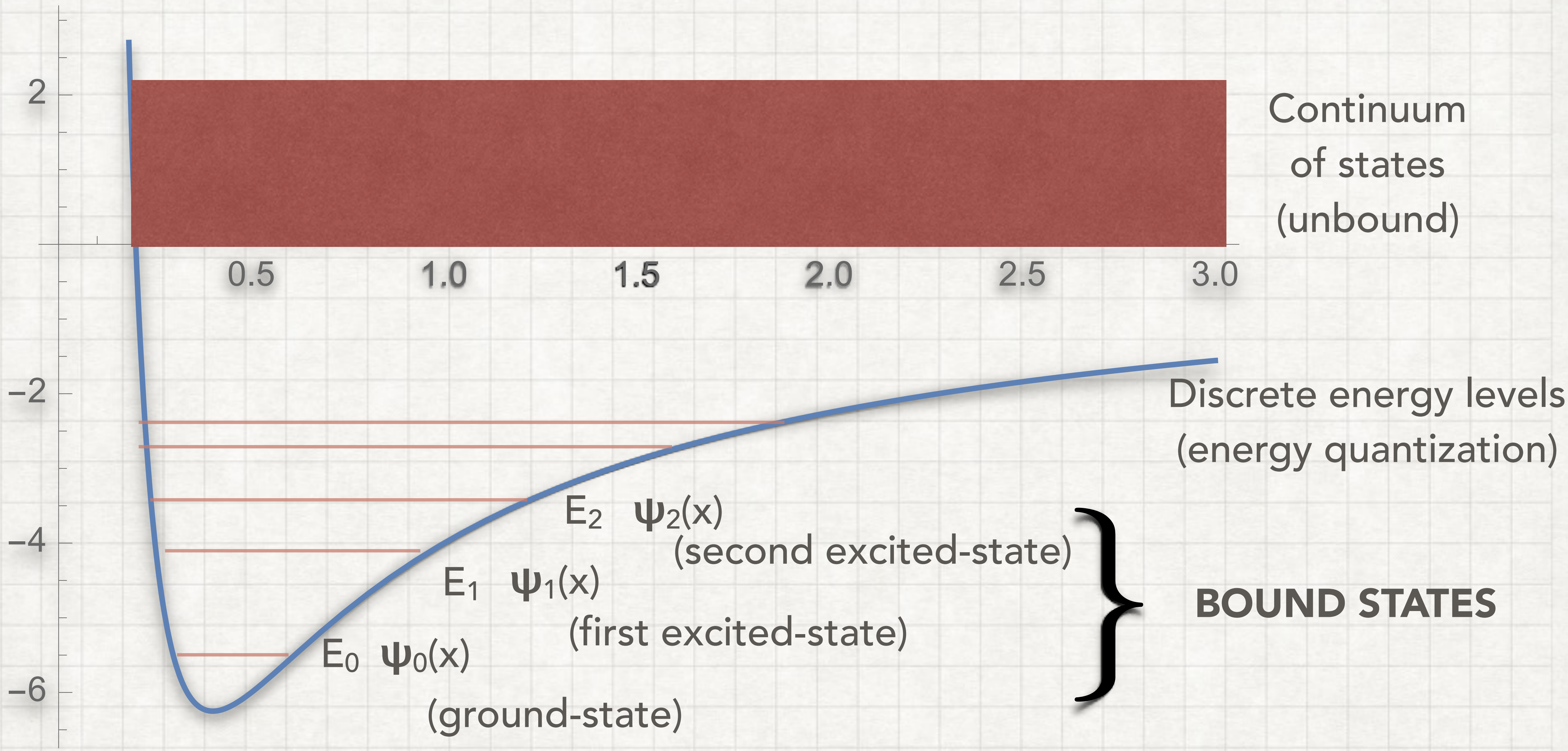
(TISE)

NB: (TISE) defines an **eigenvalue problem**, much easier to find numerical or analytical solutions

The solutions are called **Eigenstates of H**

A quantum particle can be found only in one of the eigenstates !!!

Energy Spectrum and States



the integer numbers which label the different states are called **QUANTUM NUMBERS**

Orbitals of chemistry are representations of the approximate elecronic wave-functions of different states $\psi_n(x)$

BOHR'S POSTULATE (Copenhagen Interpretation)

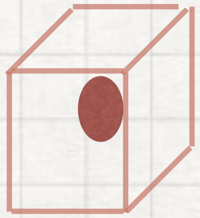
Consider a wave function for one particle in 3D: $\psi(x,y,z; t)$

Solution of the Schrödinger equation.

Then the quantity

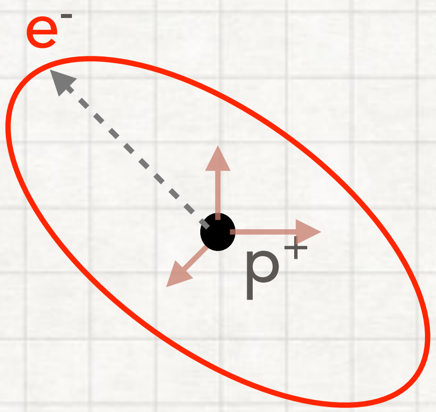
$$p(x,y,t) = |\psi(x,y,z;t)|^2 \; dx \; dy \; dz$$

Is to be interpreted as the probability to observe through a measurement at time t the particle in a small volume *dV=dx dy dz* centered at x,y,z



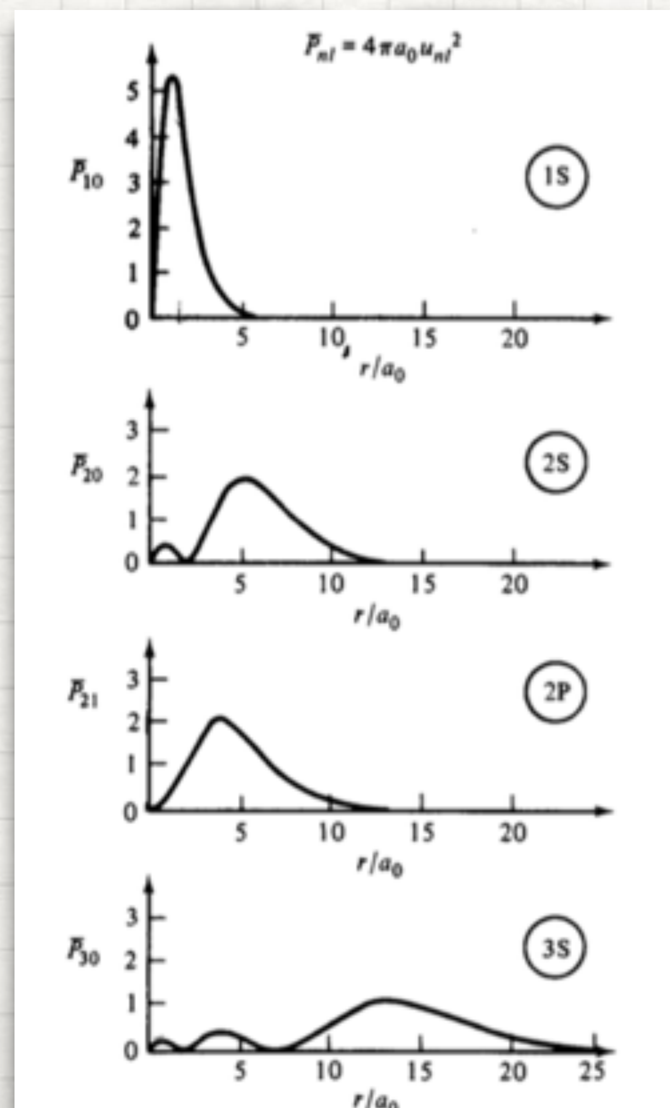
NB: Quantum mechanics does not give information about the position of the particle. It gives information about the result of measuring the position of the particle

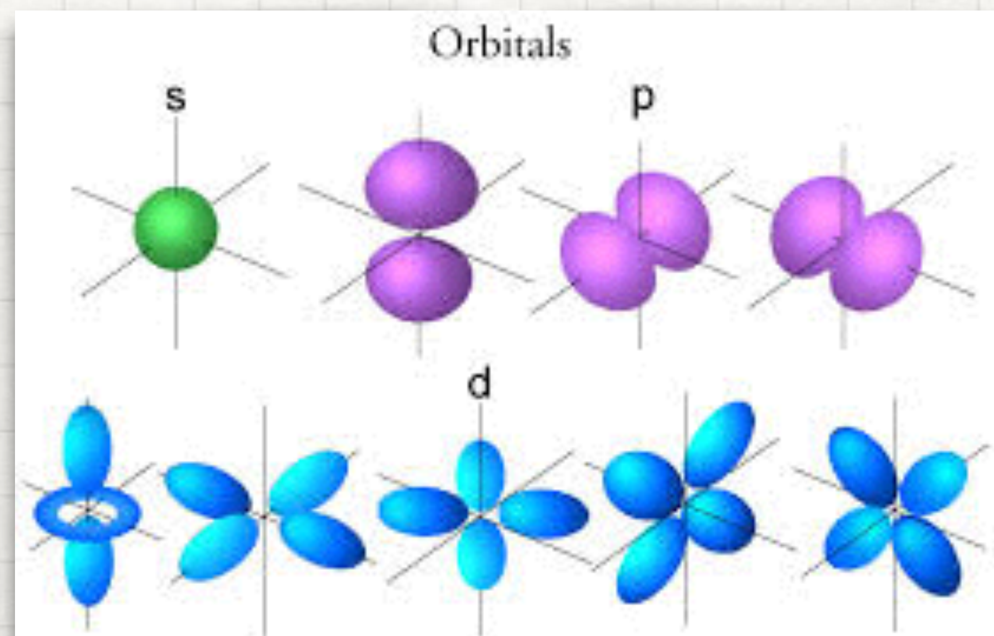
Electron's probability density in a hydrogen atom



$M_p >> m_e$:

$$\hat{H} = -\hbar^2 \frac{\nabla^2}{2m_e} - \frac{e^2}{r}$$





Counter-intuitive predictions:

In some excited states, the electron cannot be found at certain distances from the proton

EXERCIZES:

DISPERSING WAVE :

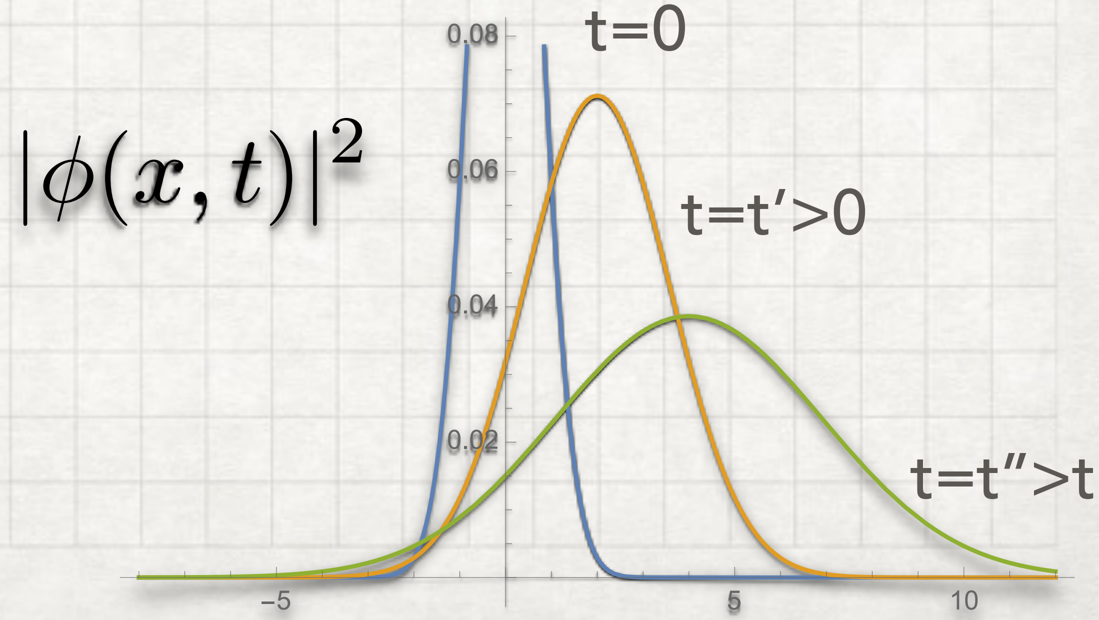
Traveling waves are not the only solutions of the Schrödinger equation.

Show that the wave function

$$\phi(x,t) = \left(\frac{\hbar^2}{2\pi(\lambda^2 + 2i\frac{\hbar^2 t}{m})} \right)^{1/2} e^{-\frac{x^2}{2(m\lambda^2 + 2it\hbar^2)}}$$

1) Discuss the degree of initial uncertainty on position as a function of the parameter **λ**…

2) Show that it satisfies the free Schrödinger equation at any time t



1-DIMENSIONAL SQUARE WELL POTENTIAL:

Consider a particle interacting with the potential

$$V = \begin{cases} 0 & |x| < L/2 \\ \infty & |x| > L/2 \end{cases}$$

1) Solve the stationary Schrödinger equation. Find spectrum of energy levels and corresponding stationary wave functions
2) Construct the correpsonding time-dependent wave-functions
3) Assume that a particle in this potential can perform transitions from eigenstates by absorbing or emitting photons, compute the spectrum frequency of the absorbed radiation

SPECTRUM OF THE HYDROGEN ATOM

Consider an electron in the Coulomb field generated by a proton (considered very heavy)

1) Write down the (3D) hamiltonian and the corresponding Schrödinger equation.

2) This equation has been solved exactly. The spectrum of energy levels is given by

$$E = E_0 \, \frac{1}{n'^2}$$

where E_0=-13.6 eV

(1 eV = 1.602×10-19 Joules)

Show that such an atom can absorb or emit only photons with energy given by the formula

$$E = E_0 \left(\frac{1}{n'^2} - \frac{1}{n^2} \right)$$

Show that the corresponding wavelength of the emitted photons obeys the rule

$$\frac{1}{\lambda} = R z^2 \left(\frac{1}{n'^2} - \frac{1}{n^2} \right)$$

$R = 1.097373 \times 10^7 \ m^{-1}$

(Rydberg Constant)

Identify the color of the first line (n=1, n′=2)