Scuola di Dottorato in Ingegneria Leonardo da Vinci – a.a. 2009/10

PROPRIETÀ MECCANICHE, OTTICHE, ELETTRONICHE DEI MATERIALI ALLE PICCOLE E PICCOLISSIME SCALE

Versione 1 – Settembre 2010 – http://www.df.unipi.it/~fuso/dida

Parte 2

Richiami su alcuni strumenti teorici (MQ) per lo studio della matera su scala piccola e piccolissima

Lu 13.09.10 10-13 aula DIC

Outlook

- Basics of *quantum mechanics*

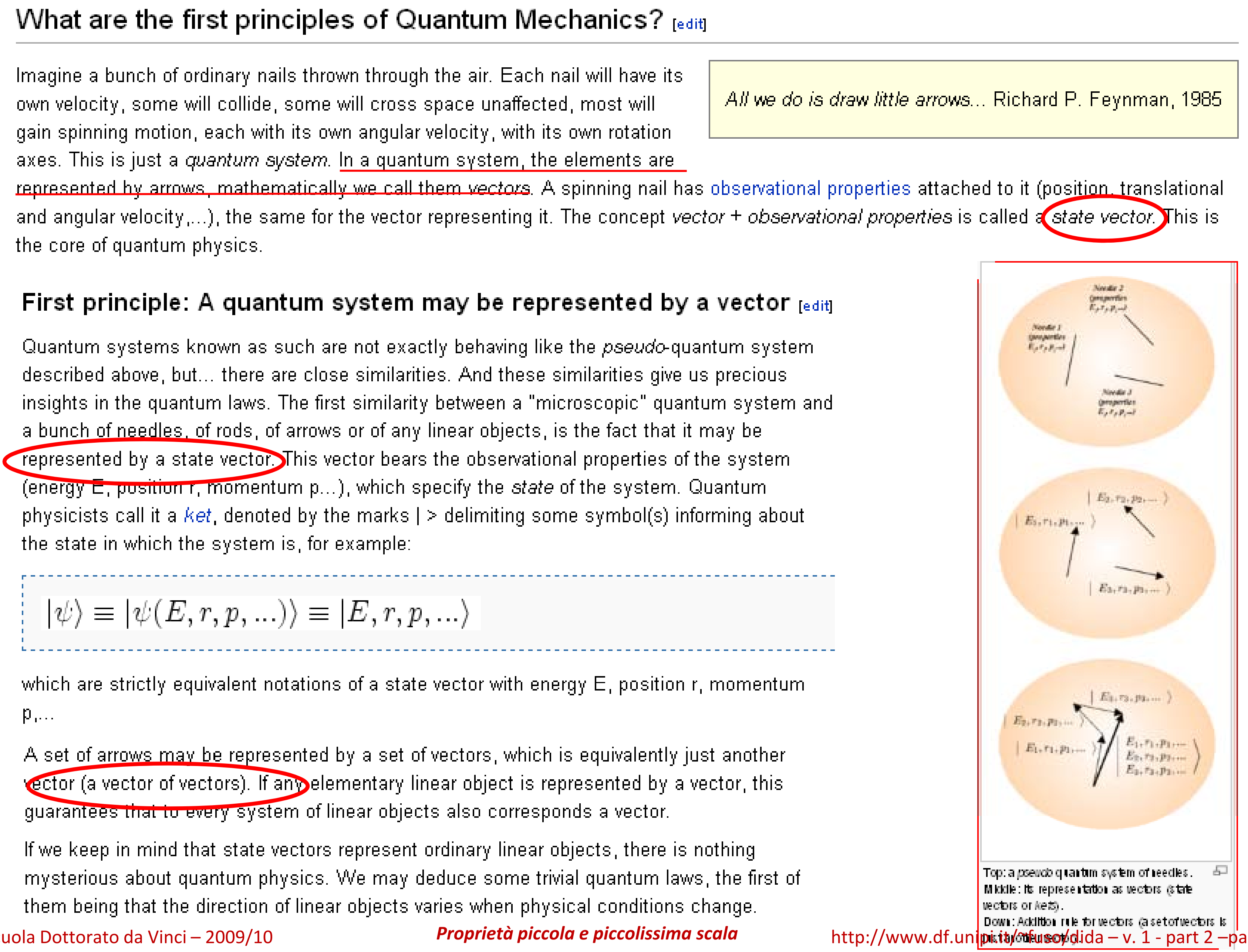
- The need for quantum description in *small-sized systems*

- A few *examples* of exercises and effects involving quantum physics:
  - *quantum box/quantum well*;
  - *free particle and duality principle;*
  - *step potential and tunneling;*
  - *harmonic oscillator*

- The quantum nature of the matter: *quantized levels* for the atom

Quantum nails (or arrows)

http://en.wikiversity.org/wiki/Making_sense_of_quantum_mechanics/Principles_of_Quantum_Mechanics



What are the first principles of Quantum Mechanics? [edit]

All we do is draw little arrows... Richard P. Feynman, 1985

Imagine a bunch of ordinary nails thrown through the air. Each nail will have its own velocity, some will collide, some will cross space unaffected, most will gain spinning motion, each with its own angular velocity, with its own rotation axes. This is just a *quantum system*. In a quantum system, the elements are represented by arrows, mathematically we call them *vectors*. A spinning nail has observational properties attached to it (position, translational and angular velocity,...), the same for the vector representing it. The concept *vector* + *observational properties* is called a *state vector*. This is the core of quantum physics.

First principle: A quantum system may be represented by a vector [edit]

Quantum systems known as such are not exactly behaving like the *pseudo*-quantum system described above, but... there are close similarities. And these similarities give us precious insights in the quantum laws. The first similarity between a "microscopic" quantum system and a bunch of needles, of rods, of arrows or of any linear objects, is the fact that it may be represented by a state vector. This vector bears the observational properties of the system (energy E, position r, momentum p...), which specify the *state* of the system. Quantum physicists call it a *ket*, denoted by the marks | > delimiting some symbol(s) informing about the state in which the system is, for example:

$$|\psi\rangle \equiv |\psi(E,r,p,...)\rangle \equiv |E,r,p,...\rangle$$

which are strictly equivalent notations of a state vector with energy E, position r, momentum p,...

A set of arrows may be represented by a set of vectors, which is equivalently just another vector (a vector of vectors). If any elementary linear object is represented by a vector, this guarantees that to every system of linear objects also corresponds a vector.

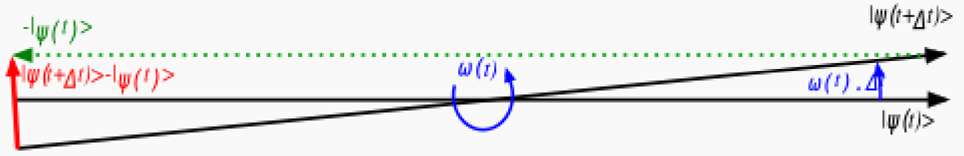
If we keep in mind that state vectors represent ordinary linear objects, there is nothing mysterious about quantum physics. We may deduce some trivial quantum laws, the first of them being that the direction of linear objects varies when physical conditions change.

Top: a *pseudo* quantum system of needles.
Middle: its representation as vectors (state vectors or *kets*).
Down: Addition rule for vectors (a set of vectors is just another vector).

Time evolution

Second principle: The orientation of the vector representing a quantum system evolves [edit]

Quantum evolution laws determine how the orientation of the state vector changes, given some modifications or perturbations of the physical conditions. For example, the time evolution law states that the vector difference of the vectors representing a needle at two infinitesimal close instants t and $t + dt$ is perpendicular to the vector at instant t and proportional to the angular velocity ω of the needle multiplied by the time difference (see Figure *Time evolution of a state vector*).



Time evolution of a state vector

An elegant way to represent changes of orientation of vectors is through Argand's method: multiplying by the complex factor $e^{i\theta}$, where θ is the rotation angle (also called the phase or phase angle). Perpendicularity between two equally normed vectors may therefore be seen as equality between one vector and the other vector multiplied by $e^{i\frac{\pi}{2}} = i$.

The vector equation pictured in figure "*Time evolution of a state vector*" therefore writes as:

$$|\psi(\omega,t+dt)>=e^{-i\omega dt}\,|\psi(\omega,t)>$$

$$\Rightarrow \frac{d\,|\psi(\omega,t)>}{dt}=\frac{|\psi(\omega,t+dt)>-|\psi(\omega,t)>}{dt}=$$

$$=\frac{d(e^{-i\omega dt}-1)}{dt}|\psi(\omega,t)>=-i\omega\,|\psi(\omega,t)>$$

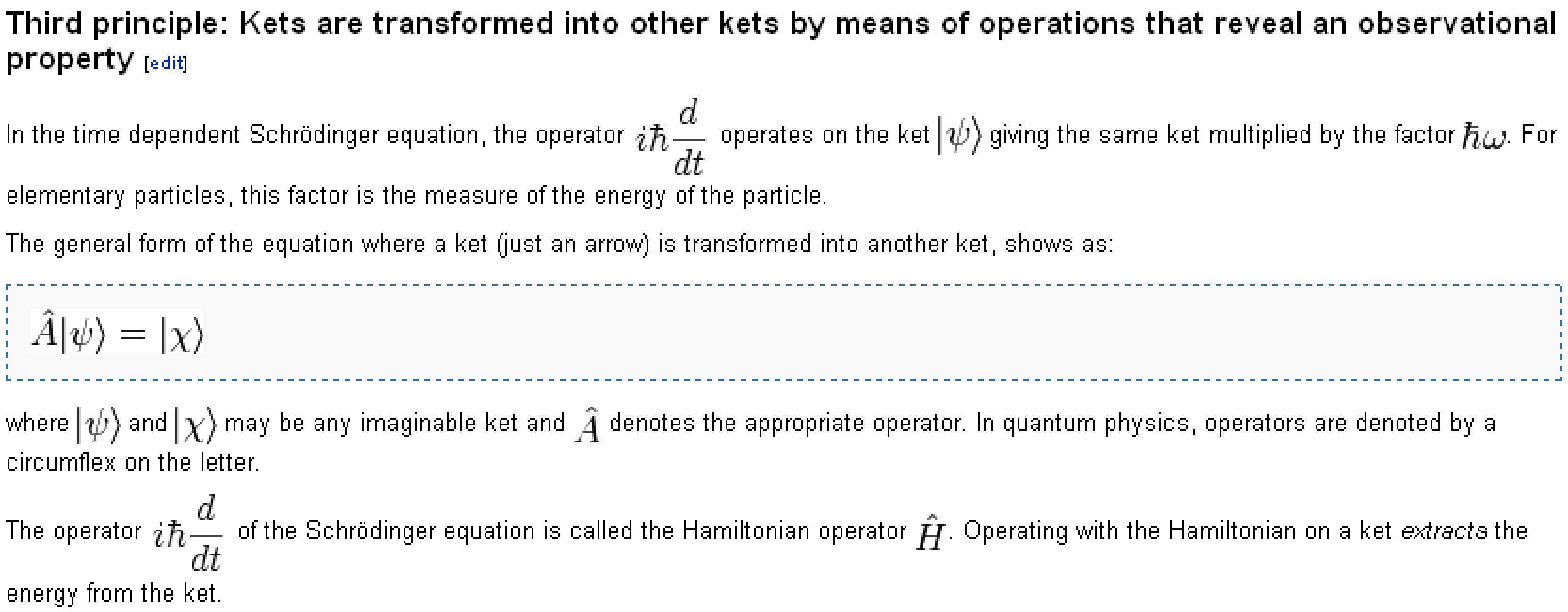
$$\frac{d|\psi(\omega,t)\rangle}{dt} = -i\omega|\psi(\omega,t)\rangle$$

if the time axis is set in the negative z-direction. This formula is a general deterministic law characterizing the time evolution of systems of linear objects, whether microscopic or macroscopic. For a system of fundamental particles, it usually appears with a factor $\hbar$ at both sides (and i at the left):

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

The factor $\hbar\omega$ multiplying the ket then represents the energy content of the system. This is Schrödinger's time-dependent equation. So we have a second close similarity between quantum systems and macroscopic linear objects: they both obey Schrödinger's equation.

Observable quantities



Third principle: Kets are transformed into other kets by means of operations that reveal an observational property [edit]

In the time dependent Schrödinger equation, the operator $i\hbar\frac{d}{dt}$ operates on the ket $|\psi\rangle$ giving the same ket multiplied by the factor $\hbar\omega$. For elementary particles, this factor is the measure of the energy of the particle.

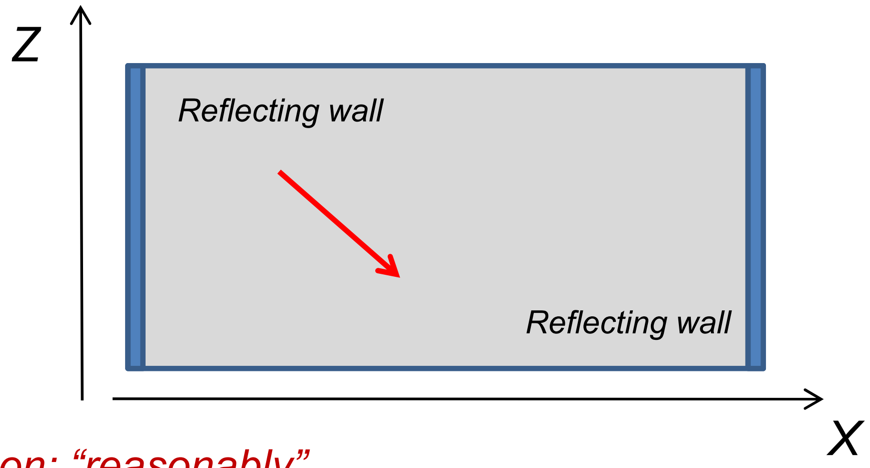
The general form of the equation where a ket (just an arrow) is transformed into another ket, shows as:

$$\hat{A}|\psi\rangle = |\chi\rangle$$

where $|\psi\rangle$ and $|\chi\rangle$ may be any imaginable ket and $\hat{A}$ denotes the appropriate operator. In quantum physics, operators are denoted by a circumflex on the letter.

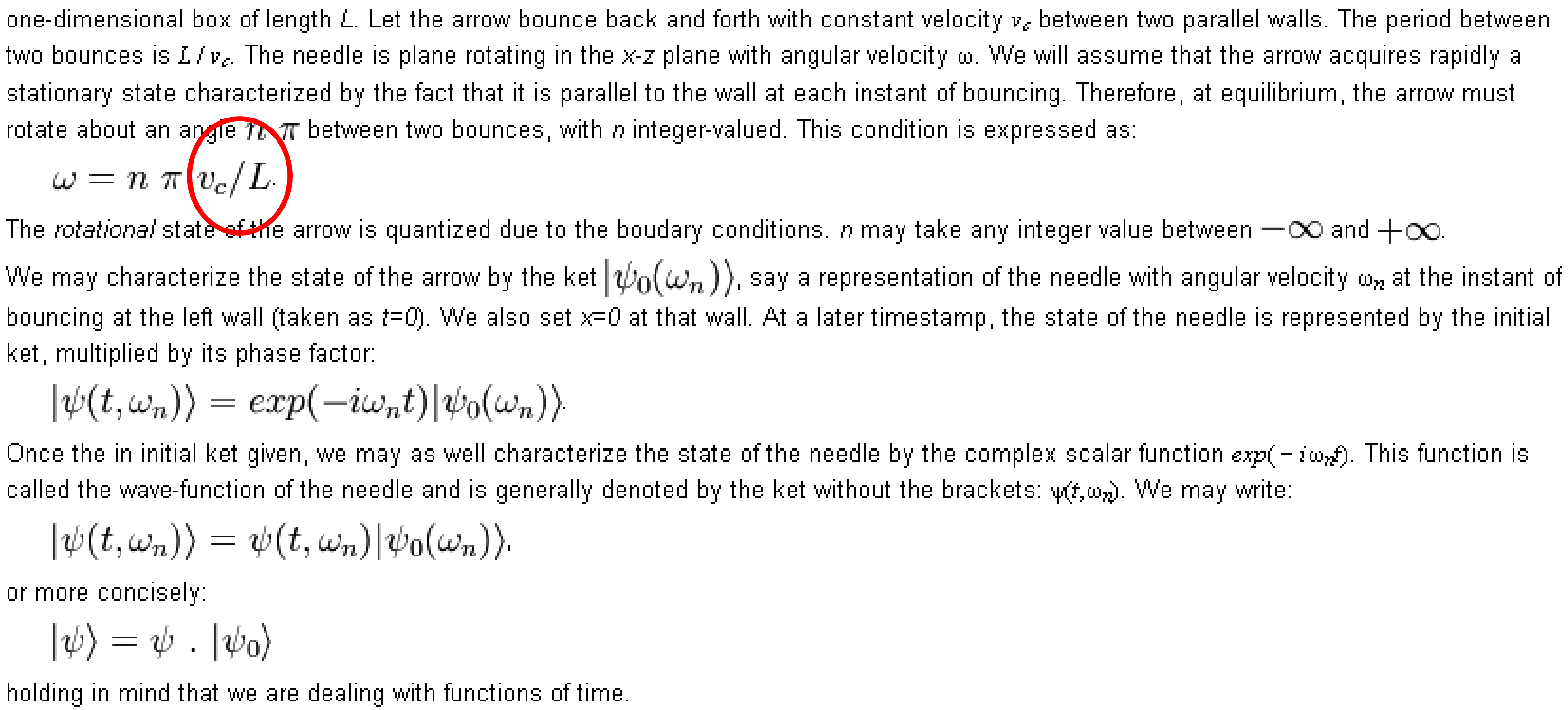
The operator $i\hbar\frac{d}{dt}$ of the Schrödinger equation is called the Hamiltonian operator $\hat{H}$. Operating with the Hamiltonian on a ket *extracts* the energy from the ket.

A famous, conventional application:
the quantum box



Boundary condition: "reasonably",
the arrow will be parallel to the reflecting wall when impinging on it

Quantum box



one-dimensional box of length L. Let the arrow bounce back and forth with constant velocity v_c between two parallel walls. The period between two bounces is L / v_c. The needle is plane rotating in the x-z plane with angular velocity ω. We will assume that the arrow acquires rapidly a stationary state characterized by the fact that it is parallel to the wall at each instant of bouncing. Therefore, at equilibrium, the arrow must rotate about an angle $n\ \pi$ between two bounces, with n integer-valued. This condition is expressed as:

$$\omega = n\ \pi\ v_c/L.$$

The *rotational* state of the arrow is quantized due to the boudary conditions. n may take any integer value between $-\infty$ and $+\infty$.

We may characterize the state of the arrow by the ket $|\psi_0(\omega_n)\rangle$, say a representation of the needle with angular velocity ω_n at the instant of bouncing at the left wall (taken as $t=0$). We also set $x=0$ at that wall. At a later timestamp, the state of the needle is represented by the initial ket, multiplied by its phase factor:

$$|\psi(t,\omega_n)\rangle = exp(-i\omega_n t)|\psi_0(\omega_n)\rangle.$$

Once the in initial ket given, we may as well characterize the state of the needle by the complex scalar function $exp(-i\omega_n t)$. This function is called the wave-function of the needle and is generally denoted by the ket without the brackets: $\psi(t,\omega_n)$. We may write:

$$|\psi(t,\omega_n)\rangle = \psi(t,\omega_n)|\psi_0(\omega_n)\rangle.$$

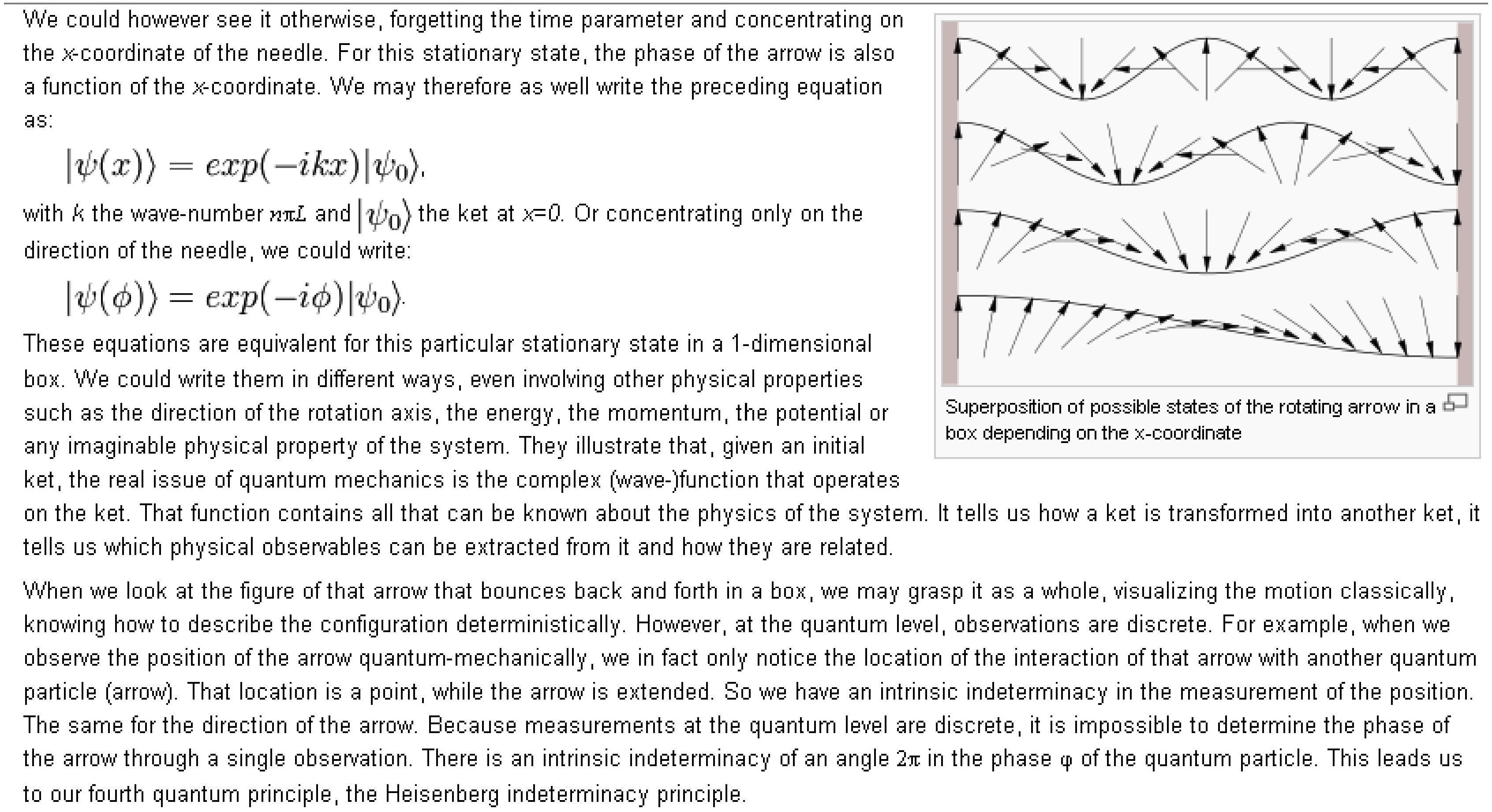
or more concisely:

$$|\psi\rangle = \psi\ .\ |\psi_0\rangle$$

holding in mind that we are dealing with functions of time.

Quantization (quantized energy, momentum, etc.) arises from boundary conditions

Standing waves in the box



We could however see it otherwise, forgetting the time parameter and concentrating on the *x*-coordinate of the needle. For this stationary state, the phase of the arrow is also a function of the *x*-coordinate. We may therefore as well write the preceding equation as:

$$|\psi(x)\rangle = exp(-ikx)|\psi_0\rangle.$$

with k the wave-number $n\pi L$ and $|\psi_0\rangle$ the ket at *x=0*. Or concentrating only on the direction of the needle, we could write:

$$|\psi(\phi)\rangle = exp(-i\phi)|\psi_0\rangle.$$

These equations are equivalent for this particular stationary state in a 1-dimensional box. We could write them in different ways, even involving other physical properties such as the direction of the rotation axis, the energy, the momentum, the potential or any imaginable physical property of the system. They illustrate that, given an initial ket, the real issue of quantum mechanics is the complex (wave-)function that operates on the ket. That function contains all that can be known about the physics of the system. It tells us how a ket is transformed into another ket, it tells us which physical observables can be extracted from it and how they are related.

Superposition of possible states of the rotating arrow in a box depending on the x-coordinate

When we look at the figure of that arrow that bounces back and forth in a box, we may grasp it as a whole, visualizing the motion classically, knowing how to describe the configuration deterministically. However, at the quantum level, observations are discrete. For example, when we observe the position of the arrow quantum-mechanically, we in fact only notice the location of the interaction of that arrow with another quantum particle (arrow). That location is a point, while the arrow is extended. So we have an intrinsic indeterminacy in the measurement of the position. The same for the direction of the arrow. Because measurements at the quantum level are discrete, it is impossible to determine the phase of the arrow through a single observation. There is an intrinsic indeterminacy of an angle 2π in the phase φ of the quantum particle. This leads us to our fourth quantum principle, the Heisenberg indeterminacy principle.

The state of a quantum system (the *vector*) can be naturally associated to a *wave*

Principles of MQ

Nel quantum box effetti quantistici diventano rilevanti (e predominanti) per *v/L* grande, cioè alta velocità e/o **piccole dimensioni**

Punto di partenza della MQ:
Complementarità (o dualismo) onda corpuscolo
(e.g., onda e.m. è rappresentabile con fotone e, viceversa, particella materiale deve poter essere rappresentata come onda)

Strumento fondamentale della MQ :
Funzione d'onda $\Psi(\mathbf{r},t)$ per descrivere una particella quantistica (e.g., elettrone, fotone, etc.)
→ approccio probabilistico: $|\Psi(\mathbf{r},t)|^2$ è la probabilità di trovare particella in $\mathbf{r}$, $\mathbf{r}+d\mathbf{r}$
→ decade il concetto di traiettoria

Infatti il principio di indeterminazione stabilisce, e.g., per un moto unidimensionale:

$$\Delta x \Delta p \geq \hbar/2$$

« non è possibile conoscere simultaneamente posizione e quantità di moto di un dato oggetto con precisione arbitraria »

Classical vs quantum

Problema fondamentale della meccanica classica (del punto):
- Determinare ***r****(t)* e ***v****(t)* (la traiettoria) a partire dalle forze ***F***
- Strumento principe: equazione del moto ***a* = *F****/m*

Problema fondamentale della meccanica quantistica:
-Determinare *Ψ(**r**,t)* e interpretarla probabilisticamente
-Strumento principe: equazione di Schroedinger (casi non relativistici!):

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r},t)+V(\vec{r},t)=i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t}$$

con $\nabla^2\Psi(\vec{r},t)=(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2})\Psi(\vec{r},t)$ (in coordinate cartesiane)

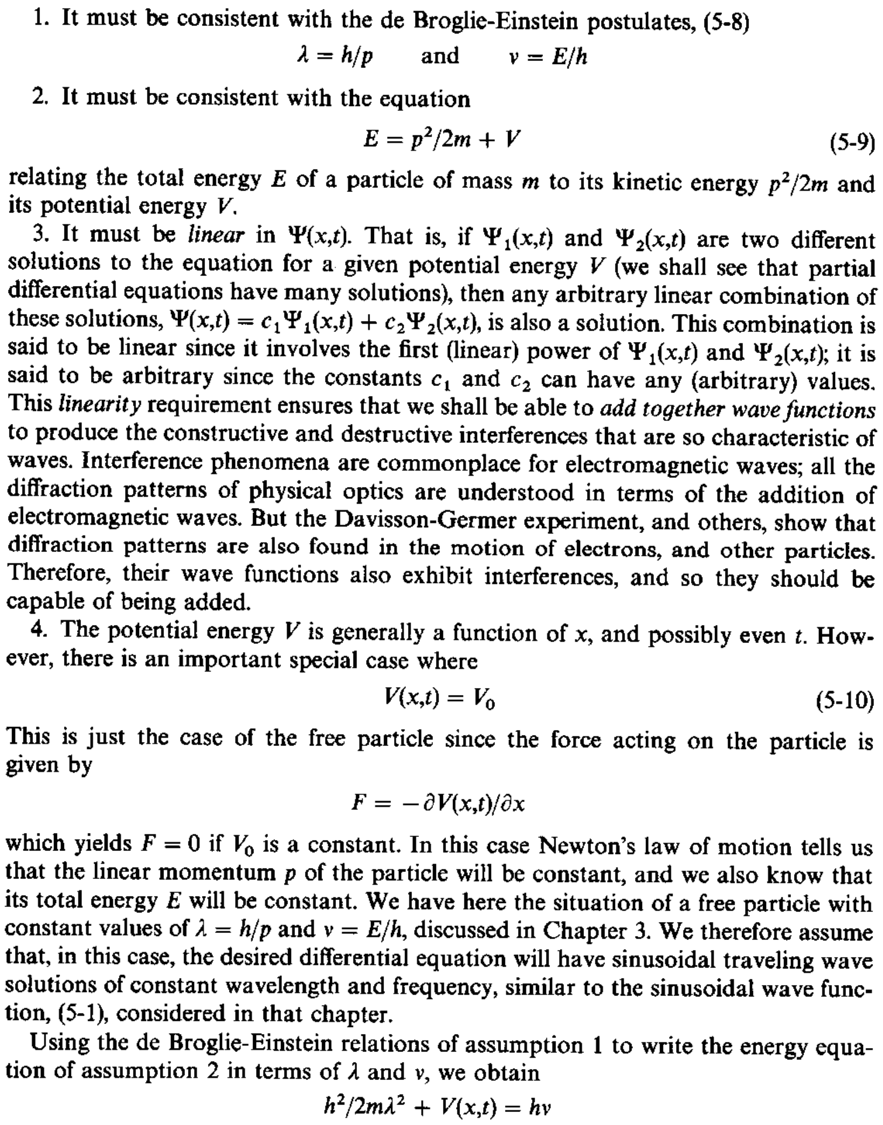
*V(**r**,t)* potenziale che controlla la dinamica del corpo), generciamente dipendente da ***r***,*t*

Equazione di Schroedinger nel caso unidimensionale:

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

Derivate parziali!

Formal requirements leading to Schroedinger



1. It must be consistent with the de Broglie-Einstein postulates, (5-8)

$$\lambda = h/p \qquad \text{and} \qquad \nu = E/h$$

2. It must be consistent with the equation

$$E = p^2/2m + V \tag{5-9}$$

relating the total energy E of a particle of mass m to its kinetic energy $p^2/2m$ and its potential energy V.

3. It must be *linear* in $\Psi(x,t)$. That is, if $\Psi_1(x,t)$ and $\Psi_2(x,t)$ are two different solutions to the equation for a given potential energy V (we shall see that partial differential equations have many solutions), then any arbitrary linear combination of these solutions, $\Psi(x,t) = c_1\Psi_1(x,t) + c_2\Psi_2(x,t)$, is also a solution. This combination is said to be linear since it involves the first (linear) power of $\Psi_1(x,t)$ and $\Psi_2(x,t)$; it is said to be arbitrary since the constants c_1 and c_2 can have any (arbitrary) values. This *linearity* requirement ensures that we shall be able to *add together wave functions* to produce the constructive and destructive interferences that are so characteristic of waves. Interference phenomena are commonplace for electromagnetic waves; all the diffraction patterns of physical optics are understood in terms of the addition of electromagnetic waves. But the Davisson-Germer experiment, and others, show that diffraction patterns are also found in the motion of electrons, and other particles. Therefore, their wave functions also exhibit interferences, and so they should be capable of being added.

4. The potential energy V is generally a function of x, and possibly even t. However, there is an important special case where

$$V(x,t) = V_0 \tag{5-10}$$

This is just the case of the free particle since the force acting on the particle is given by

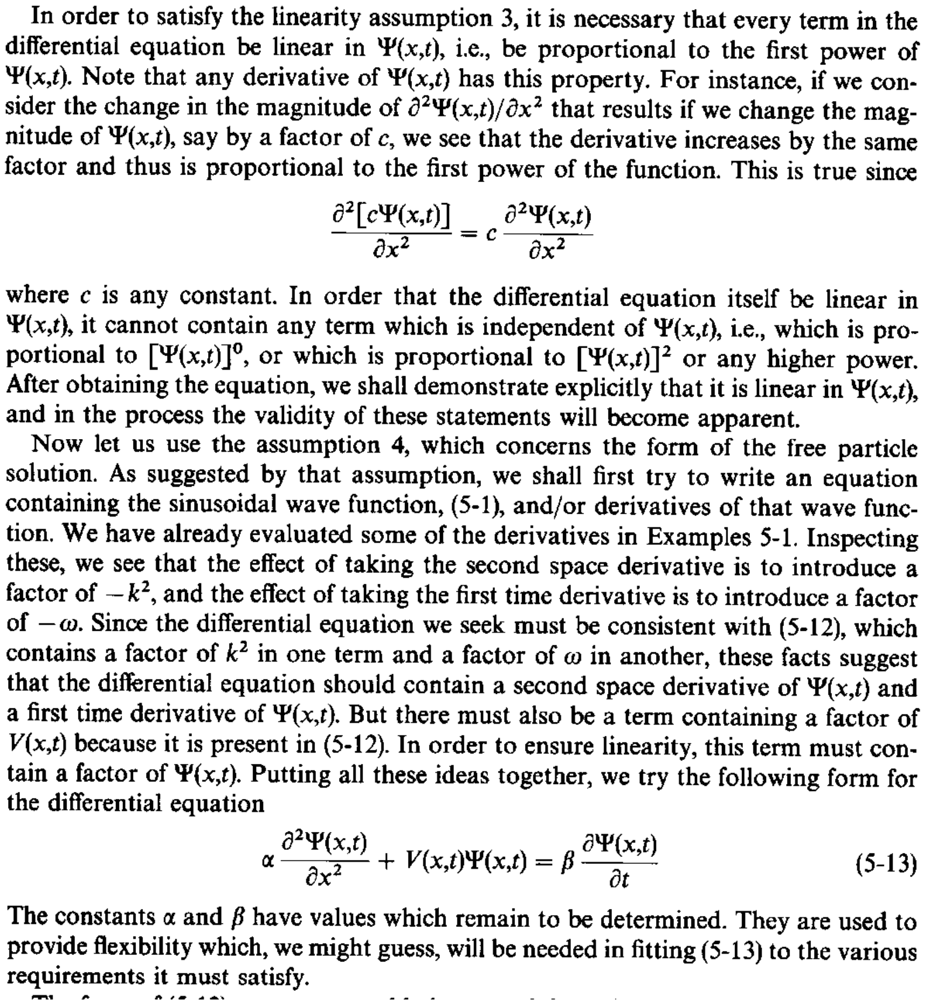
$$F = -\partial V(x,t)/\partial x$$

which yields $F = 0$ if V_0 is a constant. In this case Newton's law of motion tells us that the linear momentum p of the particle will be constant, and we also know that its total energy E will be constant. We have here the situation of a free particle with constant values of $\lambda = h/p$ and $\nu = E/h$, discussed in Chapter 3. We therefore assume that, in this case, the desired differential equation will have sinusoidal traveling wave solutions of constant wavelength and frequency, similar to the sinusoidal wave function, (5-1), considered in that chapter.

Using the de Broglie-Einstein relations of assumption 1 to write the energy equation of assumption 2 in terms of λ and ν, we obtain

$$h^2/2m\lambda^2 + V(x,t) = h\nu$$

Semplici ragionamenti generali conducono alla formulazione dell'equazione



In order to satisfy the linearity assumption 3, it is necessary that every term in the differential equation be linear in $\Psi(x,t)$, i.e., be proportional to the first power of $\Psi(x,t)$. Note that any derivative of $\Psi(x,t)$ has this property. For instance, if we consider the change in the magnitude of $\partial^2\Psi(x,t)/\partial x^2$ that results if we change the magnitude of $\Psi(x,t)$, say by a factor of c, we see that the derivative increases by the same factor and thus is proportional to the first power of the function. This is true since

$$\frac{\partial^2[c\Psi(x,t)]}{\partial x^2} = c\,\frac{\partial^2\Psi(x,t)}{\partial x^2}$$

where c is any constant. In order that the differential equation itself be linear in $\Psi(x,t)$, it cannot contain any term which is independent of $\Psi(x,t)$, i.e., which is proportional to $[\Psi(x,t)]^0$, or which is proportional to $[\Psi(x,t)]^2$ or any higher power. After obtaining the equation, we shall demonstrate explicitly that it is linear in $\Psi(x,t)$, and in the process the validity of these statements will become apparent.

Now let us use the assumption 4, which concerns the form of the free particle solution. As suggested by that assumption, we shall first try to write an equation containing the sinusoidal wave function, (5-1), and/or derivatives of that wave function. We have already evaluated some of the derivatives in Examples 5-1. Inspecting these, we see that the effect of taking the second space derivative is to introduce a factor of $-k^2$, and the effect of taking the first time derivative is to introduce a factor of $-\omega$. Since the differential equation we seek must be consistent with (5-12), which contains a factor of k^2 in one term and a factor of ω in another, these facts suggest that the differential equation should contain a second space derivative of $\Psi(x,t)$ and a first time derivative of $\Psi(x,t)$. But there must also be a term containing a factor of $V(x,t)$ because it is present in (5-12). In order to ensure linearity, this term must contain a factor of $\Psi(x,t)$. Putting all these ideas together, we try the following form for the differential equation

$$\alpha\,\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = \beta\,\frac{\partial\Psi(x,t)}{\partial t} \tag{5-13}$$

The constants α and β have values which remain to be determined. They are used to provide flexibility which, we might guess, will be needed in fitting (5-13) to the various requirements it must satisfy.

Eigenfunctions and eigenvalues

Soluzione dell’eq. di Schroedinger è in genere complicata (derivate parziali!)
Fortunatamente esistono casi in cui l’equazione è più semplice

Se *V* **non** dipende dal tempo, cioè è *V(x)*, allora:

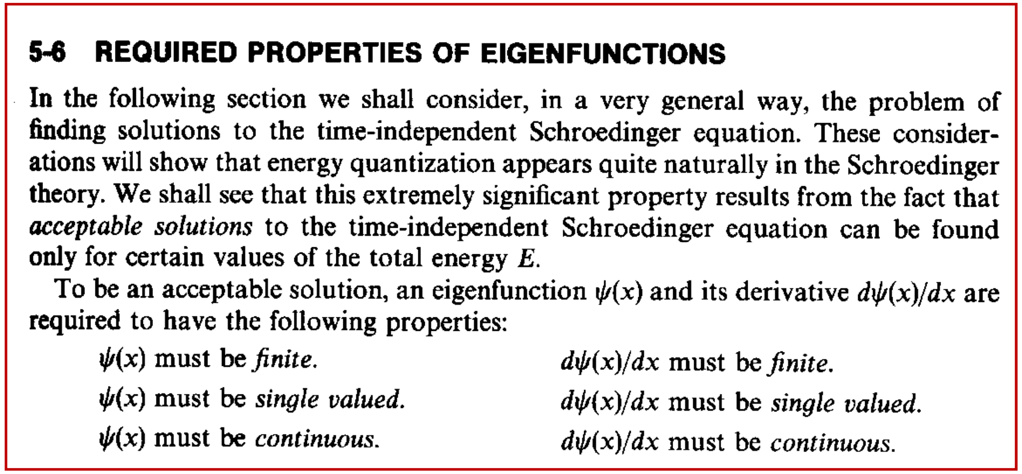
$$\Psi(x,t)=\psi(x)\varphi(t) \quad \text{con} \quad \varphi(t)=e^{-i\frac{E}{\hbar}t}$$

e

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)+V(x)=E\psi(x)$$

La f.ne d’onda degli stati stazionari è fattorizzabile

Ψ(x) : **autofunzione o autostato**
E : **autovalore dell’energia**



5-6 REQUIRED PROPERTIES OF EIGENFUNCTIONS

In the following section we shall consider, in a very general way, the problem of finding solutions to the time-independent Schroedinger equation. These considerations will show that energy quantization appears quite naturally in the Schroedinger theory. We shall see that this extremely significant property results from the fact that *acceptable solutions* to the time-independent Schroedinger equation can be found only for certain values of the total energy E.

To be an acceptable solution, an eigenfunction $\psi(x)$ and its derivative $d\psi(x)/dx$ are required to have the following properties:

$\psi(x)$ must be *finite.*	$d\psi(x)/dx$ must be *finite.*
$\psi(x)$ must be *single valued.*	$d\psi(x)/dx$ must be *single valued.*
$\psi(x)$ must be *continuous.*	$d\psi(x)/dx$ must be *continuous.*

Formal derivation of Schroedinger for eigenvalues

Substituting the assumed form of the solution, $\Psi(x,t) = \psi(x)\varphi(t)$, into the Schroedinger equation, and also restricting ourselves to time-independent potential energies that can be written as $V(x)$, we obtain

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

Now

$$\frac{\partial^2\psi(x)\varphi(t)}{\partial x^2} = \varphi(t)\frac{\partial^2\psi(x)}{\partial x^2} = \varphi(t)\frac{d^2\psi(x)}{dx^2}$$

the notation $\partial^2\psi(x)/\partial x^2$ being redundant with $d^2\psi(x)/dx^2$ since $\psi(x)$ is a function of x alone. Similarly

$$\frac{\partial\psi(x)\varphi(t)}{\partial t} = \psi(x)\frac{\partial\varphi(t)}{\partial t} = \psi(x)\frac{d\varphi(t)}{dt}$$

Therefore, we have

$$-\frac{\hbar^2}{2m}\varphi(t)\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\varphi(t) = i\hbar\psi(x)\frac{d\varphi(t)}{dt}$$

Dividing both sides of this equation by $\psi(x)\varphi(t)$, we obtain

$$\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\right] = i\hbar\frac{1}{\varphi(t)}\frac{d\varphi(t)}{dt} \tag{5-36}$$

Note that the right side of (5-36) does not depend on x, while the left side does not depend on t. Consequently, their common value cannot depend on either x or t. In other words, the common value must be a constant, which we shall call G. The result of this consideration is that (5-36) leads to two separate equations. One equation is obtained by setting the left side equal to the common value

$$\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\right] = G \tag{5-37}$$

The other equation is obtained by setting the right side equal to the common value

$$i\hbar\frac{1}{\varphi(t)}\frac{d\varphi(t)}{dt} = G \tag{5-38}$$

The constant G is called the *separation constant*, for the same reason that this technique for solving partial differential equations is called the separation of variables.

$$\frac{d\varphi(t)}{dt} = -\frac{iG}{\hbar}\varphi(t) \tag{5-39}$$

This differential equation tells us that the function $\varphi(t)$, which is its solution, has the property that its first derivative is proportional to the function itself. Anyone with much experience in differentiating would not have difficulty in guessing that $\varphi(t)$ must be an exponential function. Therefore, let us assume that the solution to the differential equation is of the form

$$\varphi(t) = e^{\alpha t}$$

where α is a constant that will be determined shortly. We verify this assumed solution by differentiating it, to obtain

$$\frac{d\varphi(t)}{dt} = \alpha e^{\alpha t} = \alpha\varphi(t)$$

which we then substitute into (5-39). This yields

$$\alpha\varphi(t) = -\frac{iG}{\hbar}\varphi(t)$$

If we set

$$\alpha = -\frac{iG}{\hbar}$$

the assumed solution obviously satisfies the equation. Therefore

$$\varphi(t) = e^{-iGt/\hbar} \tag{5-40}$$

is a solution to (5-38) or (5-39).

We see that $\varphi(t)$ is an oscillatory function of time of frequency $\nu = G/h$. But, according to the de Broglie-Einstein postulates of (5-8), the frequency must also be given by $\nu = E/h$, where E is the total energy of the particle associated with the wave function corresponding to $\varphi(t)$. The reason is, of course, that $\varphi(t)$ is the function that specifies the time dependence of the wave function. Comparing these expressions, we see that the separation constant must be equal to the total energy of the particle. That is

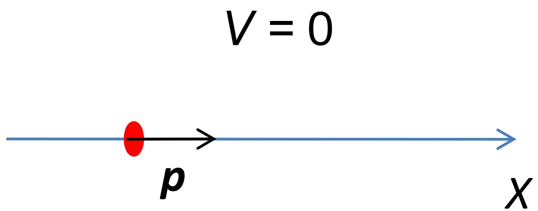
$$G = E \tag{5-42}$$

Using this value of G in the space equation, (5-37), that we obtained from the separation of variables, we have

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{5-43}$$

Example: free particle

Esempio: particella **libera** (cfr. fotone) che si muove lungo *X* avendo quantità di moto definita *p*



Secondo de Broglie si ha:

$$\Psi(x,t) \propto e^{ikx}e^{-i\omega t} = \psi(x)\varphi(t)$$

$$\psi(x) = e^{ikx}$$

con $p = \hbar k$

Lunghezza d'onda di de Broglie: $\lambda_{dB} = 2\pi/k = h/p$

Attenzione: la funzione d'onda di de Broglie ha $|\psi|^2 = 1$

→ la probabilità è sempre e ovunque unitaria

→ $\int |\psi|^2 \, dx$ (fattore di normalizzazione) diverge!

D'altra parte, per principio di indeterminazione: $\Delta p = 0 \rightarrow \Delta x \rightarrow \infty$

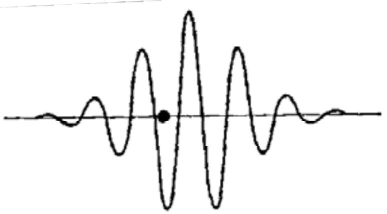
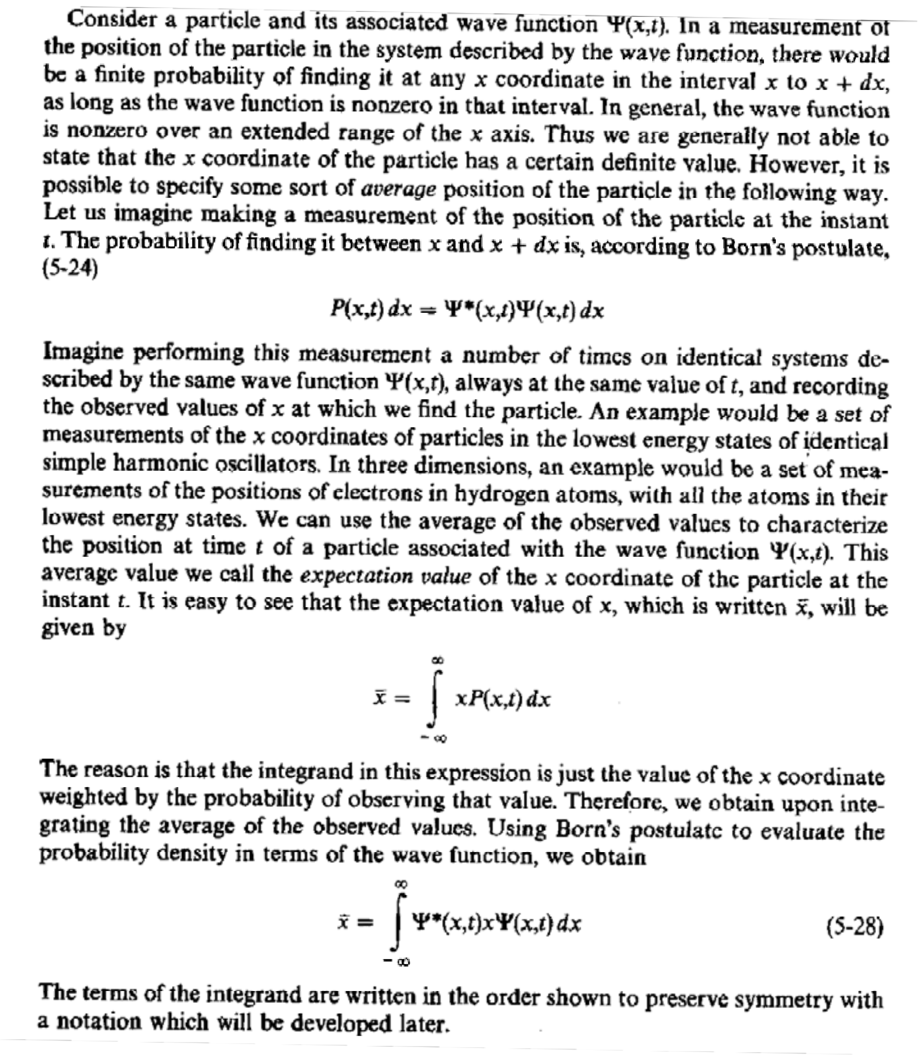


Figure 5-2 A very schematic picture of a wave function and its associated particle. The particle must be at some location where the wave function has an appreciable amplitude.

(realisticamente occorre pacchetto d'onda, cfr. serie di Fourier)

Expectation values and observable quantities



Consider a particle and its associated wave function $\Psi(x,t)$. In a measurement of the position of the particle in the system described by the wave function, there would be a finite probability of finding it at any x coordinate in the interval x to $x + dx$, as long as the wave function is nonzero in that interval. In general, the wave function is nonzero over an extended range of the x axis. Thus we are generally not able to state that the x coordinate of the particle has a certain definite value. However, it is possible to specify some sort of *average* position of the particle in the following way. Let us imagine making a measurement of the position of the particle at the instant t. The probability of finding it between x and $x + dx$ is, according to Born's postulate, (5-24)

$$P(x,t)\,dx = \Psi^*(x,t)\Psi(x,t)\,dx$$

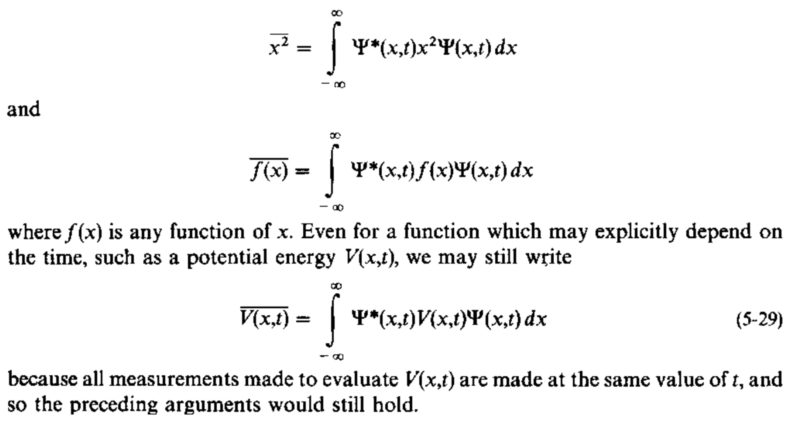
Imagine performing this measurement a number of times on identical systems described by the same wave function $\Psi(x,t)$, always at the same value of t, and recording the observed values of x at which we find the particle. An example would be a *set of* measurements of the x coordinates of particles in the lowest energy states of identical simple harmonic oscillators. In three dimensions, an example would be a set of measurements of the positions of electrons in hydrogen atoms, with all the atoms in their lowest energy states. We can use the average of the observed values to characterize the position at time t of a particle associated with the wave function $\Psi(x,t)$. This average value we call the *expectation value* of the x coordinate of the particle at the instant t. It is easy to see that the expectation value of x, which is written $\bar{x}$, will be given by

$$\bar{x} = \int_{-\infty}^{\infty} xP(x,t)\,dx$$

The reason is that the integrand in this expression is just the value of the x coordinate weighted by the probability of observing that value. Therefore, we obtain upon integrating the average of the observed values. Using Born's postulate to evaluate the probability density in terms of the wave function, we obtain

$$\bar{x} = \int_{-\infty}^{\infty} \Psi^*(x,t)x\Psi(x,t)\,dx \qquad (5\text{-}28)$$

The terms of the integrand are written in the order shown to preserve symmetry with a notation which will be developed later.



$$\overline{x^2} = \int_{-\infty}^{\infty} \Psi^*(x,t)x^2\Psi(x,t)\,dx$$

and

$$\overline{f(x)} = \int_{-\infty}^{\infty} \Psi^*(x,t)f(x)\Psi(x,t)\,dx$$

where $f(x)$ is any function of x. Even for a function which may explicitly depend on the time, such as a potential energy $V(x,t)$, we may still write

$$\overline{V(x,t)} = \int_{-\infty}^{\infty} \Psi^*(x,t)V(x,t)\Psi(x,t)\,dx \qquad (5\text{-}29)$$

because all measurements made to evaluate $V(x,t)$ are made at the same value of t, and so the preceding arguments would still hold.

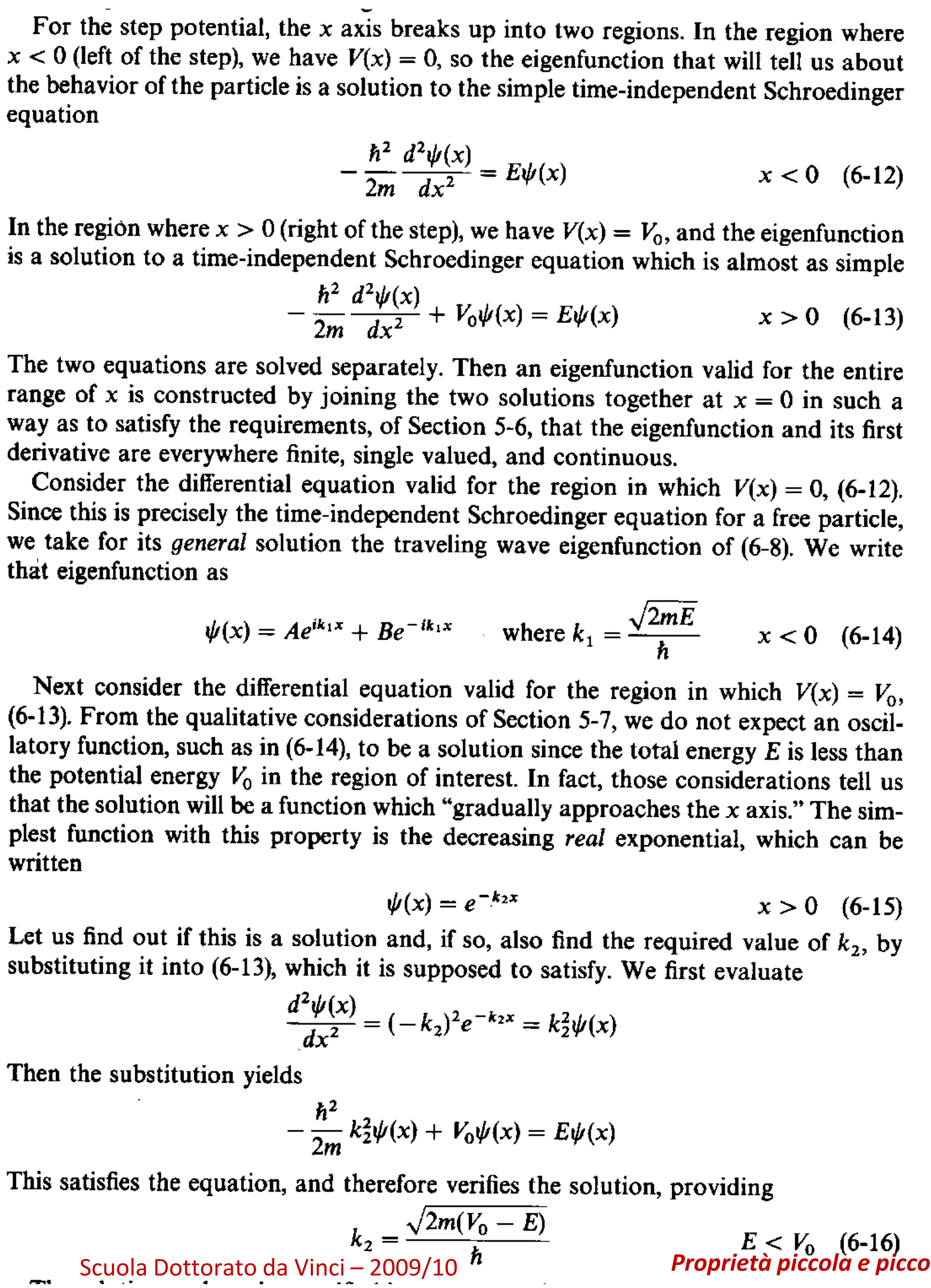
Il valore "medio" di una grandezza (misurabile) su un sistema quantistico è definito come

$$< f >= \int \Psi^*(\bar{r},t)\, f\, \Psi(\bar{r},t)\, d^3\bar{r} = <\Psi^* \mid f \mid \Psi >$$

La grandezza misurata dipende dalla "sovrapposizione spaziale" delle funzioni che compaiono nell'integrazione (di volume)

Esempio: <*x*> = 0 per particella libera

Example 2: step function



For the step potential, the x axis breaks up into two regions. In the region where $x < 0$ (left of the step), we have $V(x) = 0$, so the eigenfunction that will tell us about the behavior of the particle is a solution to the simple time-independent Schroedinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \qquad x < 0 \quad (6\text{-}12)$$

In the region where $x > 0$ (right of the step), we have $V(x) = V_0$, and the eigenfunction is a solution to a time-independent Schroedinger equation which is almost as simple

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V_0\psi(x) = E\psi(x) \qquad x > 0 \quad (6\text{-}13)$$

The two equations are solved separately. Then an eigenfunction valid for the entire range of x is constructed by joining the two solutions together at $x = 0$ in such a way as to satisfy the requirements, of Section 5-6, that the eigenfunction and its first derivative are everywhere finite, single valued, and continuous.

Consider the differential equation valid for the region in which $V(x) = 0$, (6-12). Since this is precisely the time-independent Schroedinger equation for a free particle, we take for its *general* solution the traveling wave eigenfunction of (6-8). We write that eigenfunction as

$$\psi(x) = Ae^{ik_1x} + Be^{-ik_1x} \qquad \text{where } k_1 = \frac{\sqrt{2mE}}{\hbar} \qquad x < 0 \quad (6\text{-}14)$$

Next consider the differential equation valid for the region in which $V(x) = V_0$, (6-13). From the qualitative considerations of Section 5-7, we do not expect an oscillatory function, such as in (6-14), to be a solution since the total energy E is less than the potential energy V_0 in the region of interest. In fact, those considerations tell us that the solution will be a function which "gradually approaches the x axis." The simplest function with this property is the decreasing *real* exponential, which can be written

$$\psi(x) = e^{-k_2x} \qquad x > 0 \quad (6\text{-}15)$$

Let us find out if this is a solution and, if so, also find the required value of k_2, by substituting it into (6-13), which it is supposed to satisfy. We first evaluate

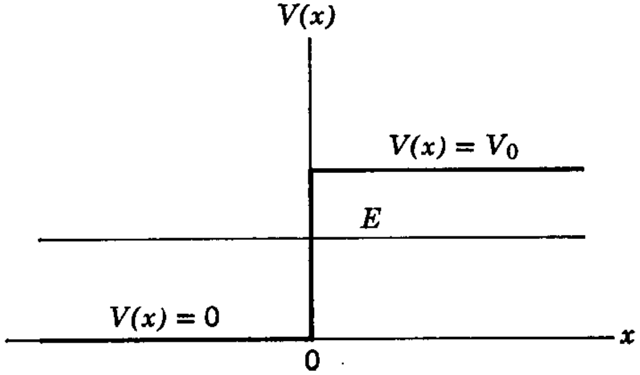
$$\frac{d^2\psi(x)}{dx^2} = (-k_2)^2e^{-k_2x} = k_2^2\psi(x)$$

Then the substitution yields

$$-\frac{\hbar^2}{2m}k_2^2\psi(x) + V_0\psi(x) = E\psi(x)$$

This satisfies the equation, and therefore verifies the solution, providing

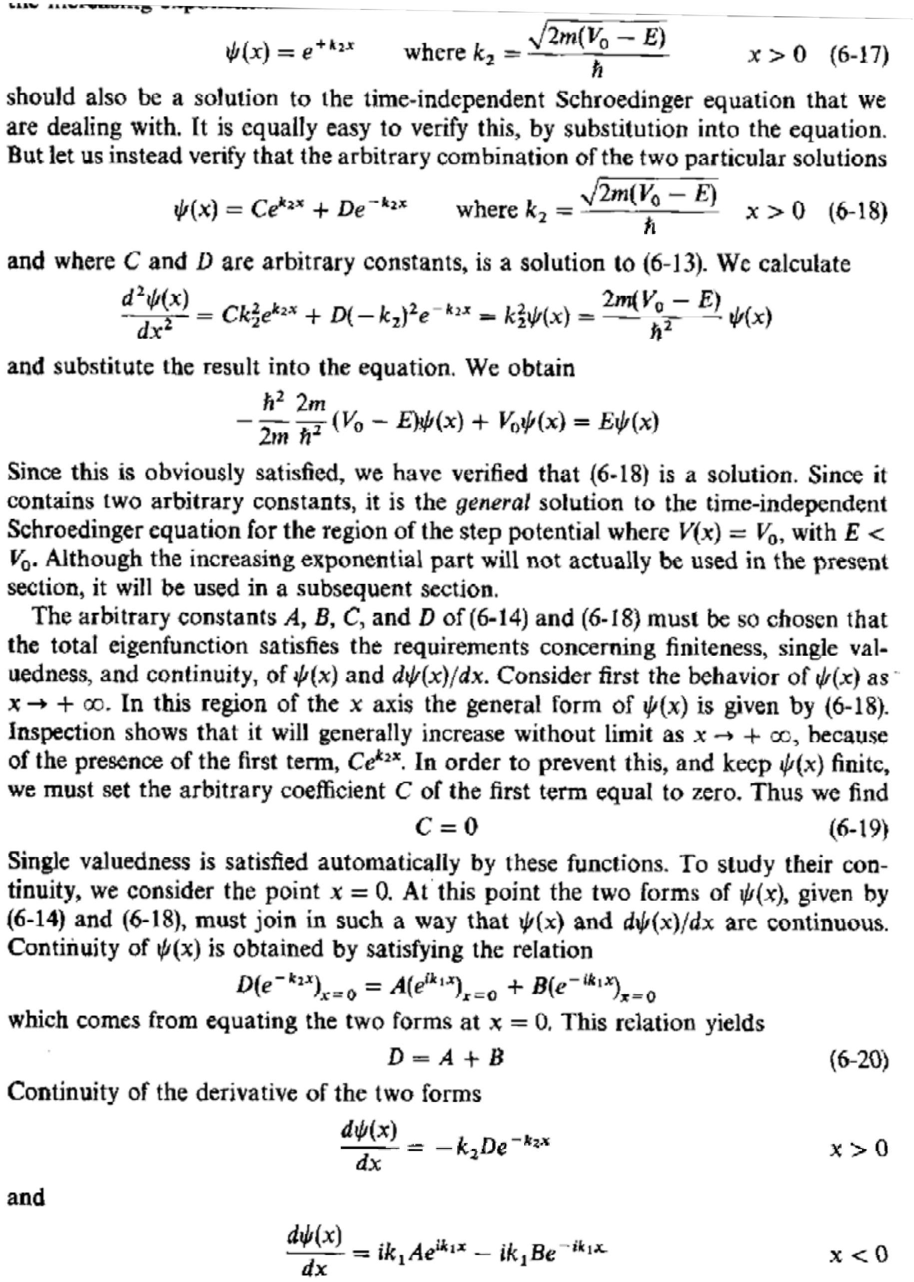
$$k_2 = \frac{\sqrt{2m(V_0 - E)}}{\hbar} \qquad E < V_0 \quad (6\text{-}16)$$



Classicamente: per $E<V_0$ ho solo riflessione sulla barriera (esempio: un piano inclinato che deve essere risalito da una particella)

Quantisticamente ho riflessione, ma anche trasmissione!!

Step potential II



$$\psi(x) = e^{+k_2x} \qquad \text{where } k_2 = \frac{\sqrt{2m(V_0 - E)}}{\hbar} \qquad x > 0 \quad (6\text{-}17)$$

should also be a solution to the time-independent Schroedinger equation that we are dealing with. It is equally easy to verify this, by substitution into the equation. But let us instead verify that the arbitrary combination of the two particular solutions

$$\psi(x) = Ce^{k_2x} + De^{-k_2x} \qquad \text{where } k_2 = \frac{\sqrt{2m(V_0 - E)}}{\hbar} \qquad x > 0 \quad (6\text{-}18)$$

and where C and D are arbitrary constants, is a solution to (6-13). We calculate

$$\frac{d^2\psi(x)}{dx^2} = Ck_2^2e^{k_2x} + D(-k_2)^2e^{-k_2x} = k_2^2\psi(x) = \frac{2m(V_0 - E)}{\hbar^2}\psi(x)$$

and substitute the result into the equation. We obtain

$$-\frac{\hbar^2}{2m}\frac{2m}{\hbar^2}(V_0 - E)\psi(x) + V_0\psi(x) = E\psi(x)$$

Since this is obviously satisfied, we have verified that (6-18) is a solution. Since it contains two arbitrary constants, it is the *general* solution to the time-independent Schroedinger equation for the region of the step potential where $V(x) = V_0$, with $E < V_0$. Although the increasing exponential part will not actually be used in the present section, it will be used in a subsequent section.

The arbitrary constants A, B, C, and D of (6-14) and (6-18) must be so chosen that the total eigenfunction satisfies the requirements concerning finiteness, single valuedness, and continuity, of $\psi(x)$ and $d\psi(x)/dx$. Consider first the behavior of $\psi(x)$ as $x \to +\infty$. In this region of the x axis the general form of $\psi(x)$ is given by (6-18). Inspection shows that it will generally increase without limit as $x \to +\infty$, because of the presence of the first term, Ce^{k_2x}. In order to prevent this, and keep $\psi(x)$ finite, we must set the arbitrary coefficient C of the first term equal to zero. Thus we find

$$C = 0 \qquad (6\text{-}19)$$

Single valuedness is satisfied automatically by these functions. To study their continuity, we consider the point $x = 0$. At this point the two forms of $\psi(x)$, given by (6-14) and (6-18), must join in such a way that $\psi(x)$ and $d\psi(x)/dx$ are continuous. Continuity of $\psi(x)$ is obtained by satisfying the relation

$$D(e^{-k_2x})_{x=0} = A(e^{ik_1x})_{x=0} + B(e^{-ik_1x})_{x=0}$$

which comes from equating the two forms at $x = 0$. This relation yields

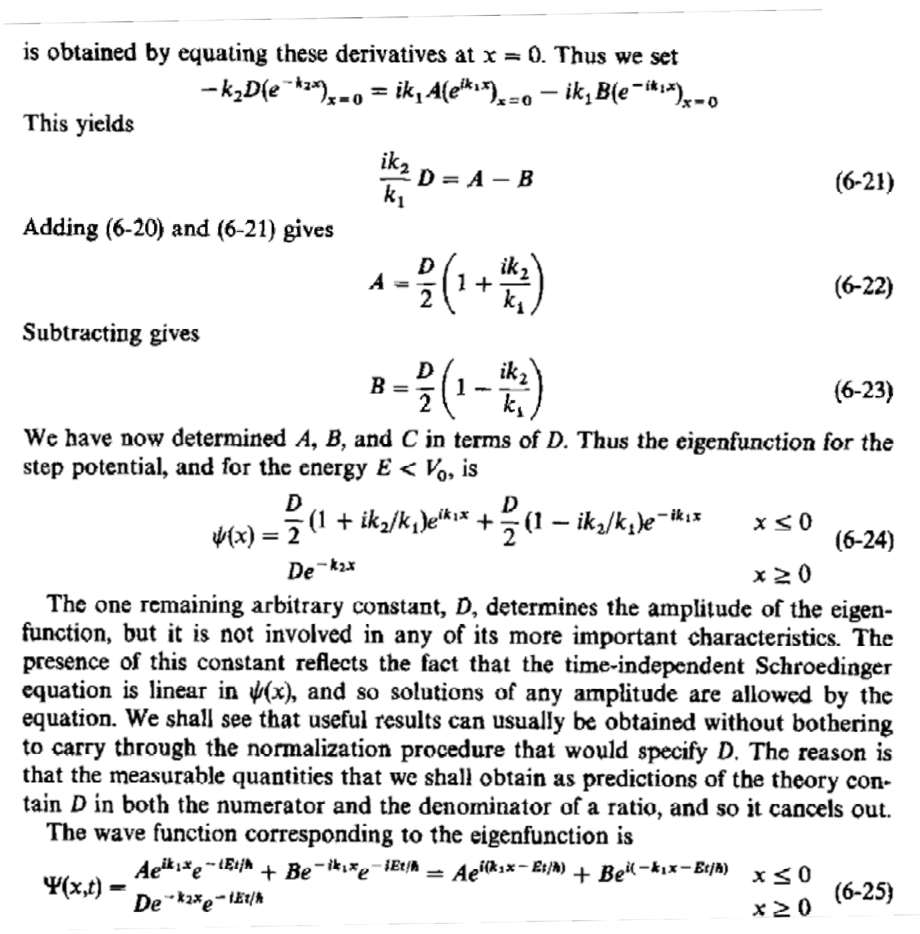
$$D = A + B \qquad (6\text{-}20)$$

Continuity of the derivative of the two forms

$$\frac{d\psi(x)}{dx} = -k_2De^{-k_2x} \qquad x > 0$$

and

$$\frac{d\psi(x)}{dx} = ik_1Ae^{ik_1x} - ik_1Be^{-ik_1x} \qquad x < 0$$



is obtained by equating these derivatives at $x = 0$. Thus we set

$$-k_2D(e^{-k_2x})_{x=0} = ik_1A(e^{ik_1x})_{x=0} - ik_1B(e^{-ik_1x})_{x=0}$$

This yields

$$\frac{ik_2}{k_1}D = A - B \qquad (6\text{-}21)$$

Adding (6-20) and (6-21) gives

$$A = \frac{D}{2}\left(1 + \frac{ik_2}{k_1}\right) \qquad (6\text{-}22)$$

Subtracting gives

$$B = \frac{D}{2}\left(1 - \frac{ik_2}{k_1}\right) \qquad (6\text{-}23)$$

We have now determined A, B, and C in terms of D. Thus the eigenfunction for the step potential, and for the energy $E < V_0$, is

$$\psi(x) = \begin{array}{ll} \frac{D}{2}(1 + ik_2/k_1)e^{ik_1x} + \frac{D}{2}(1 - ik_2/k_1)e^{-ik_1x} & x \leq 0 \\ De^{-k_2x} & x \geq 0 \end{array} \qquad (6\text{-}24)$$

The one remaining arbitrary constant, D, determines the amplitude of the eigenfunction, but it is not involved in any of its more important characteristics. The presence of this constant reflects the fact that the time-independent Schroedinger equation is linear in $\psi(x)$, and so solutions of any amplitude are allowed by the equation. We shall see that useful results can usually be obtained without bothering to carry through the normalization procedure that would specify D. The reason is that the measurable quantities that we shall obtain as predictions of the theory contain D in both the numerator and the denominator of a ratio, and so it cancels out.

The wave function corresponding to the eigenfunction is

$$\Psi(x,t) = \begin{array}{ll} Ae^{ik_1x}e^{-iEt/\hbar} + Be^{-ik_1x}e^{-iEt/\hbar} = Ae^{i(k_1x - Et/\hbar)} + Be^{i(-k_1x - Et/\hbar)} & x \leq 0 \\ De^{-k_2x}e^{-iEt/\hbar} & x \geq 0 \end{array} \qquad (6\text{-}25)$$

Autofunzione determinata completamente dalla continuità a parte un coefficiente di normalizzazione

Step potential and tunneling

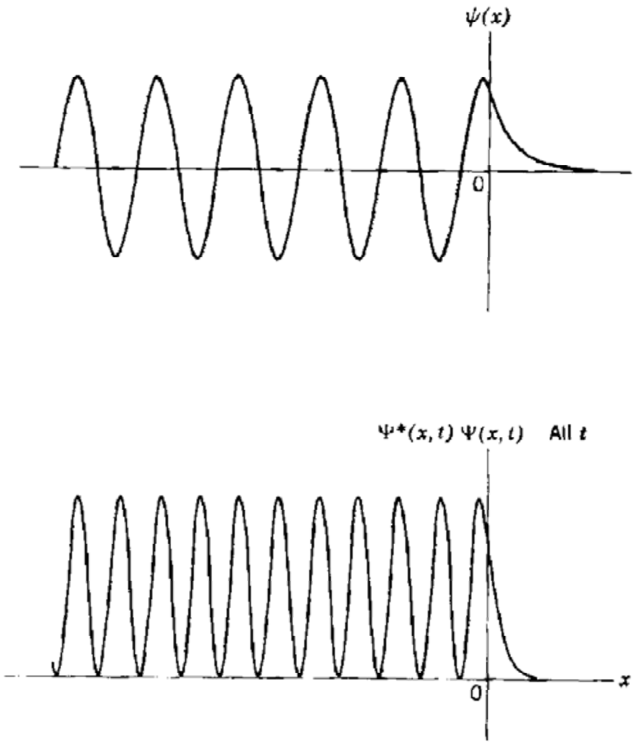
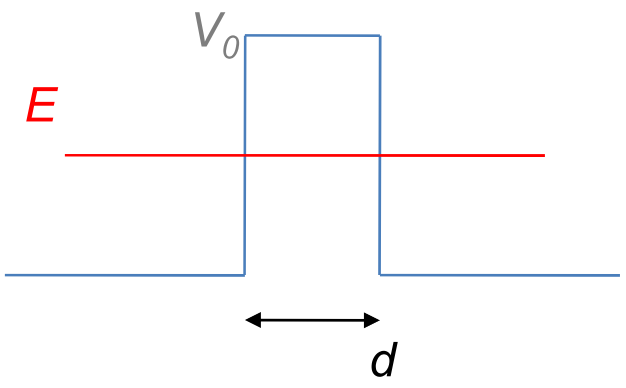


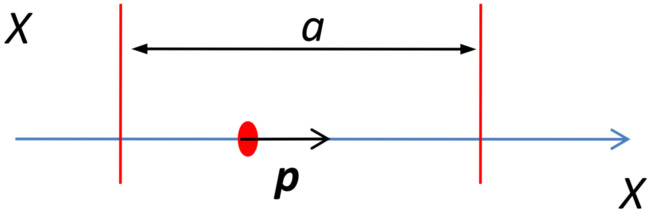
Figure 6-7 *Top:* The eigenfunction $\psi(x)$ for a particle incident upon a potential step at $x = 0$, with total energy less than the height of the step. Note the penetration of the eigenfunction into the classically excluded region $x > 0$. *Bottom:* The probability density $\Psi^*\Psi = \psi^*\psi = \psi^2$ corresponding to this eigenfunction. The spacing between the peaks of ψ^2 is twice as close as the spacing between the peaks of ψ.



Nota: la particella può “tunnellare” se il gradino termina dopo $d < \lambda_{dB}$

Nota: nel caso (meno interessante) in cui $E<V_0$ la soluzione si trova con procedimento simile, ma manca l’andamento esponenziale decrescente

Example 3: quantum well (infinite)



Esempio: particella libera (elettrone) che si muove lungo *X* essendo confinata in intervallo *–a/2, a/2* da potenziale

$$V(x) = \begin{cases} 0 & 0 \le x \le a \\ \infty & x < 0;\ x > a \end{cases}$$

Suppongo, ragionevolmente, che la particella sia costretta a stare nella buca

⇩

$\Psi(x,t)$ sarà sovrapposizione di particella/onda che si muove vs dx e verso sin

$$\Psi(x,t) = Ae^{i(kx-\omega t)} + Be^{i(-kx-\omega t)} \quad \text{con} \quad \omega = \frac{E}{\hbar}$$

Condizioni al bordo: $\Psi = 0$ per $x = 0$ e $x = a$

⇩

$A = B$ oppure $A = -B$

Nota: qui non vale continuità della derivata a causa di $V \rightarrow \infty$

Infinte quantum well II

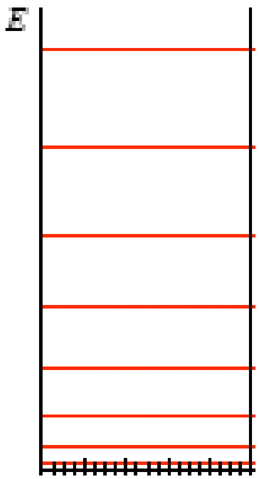
Le condizioni al contorno sono le stesse della radiazione nella cavità (scatola)

Si era ottenuto: $k_n = n\frac{\pi}{a}$

Essendo la particella libera l'energia è solo cinetica:

$$E_n = \frac{p_n^2}{2m} = \frac{\hbar^2 k^2}{2m} = n^2 \frac{\hbar^2 \pi^2}{2ma^2}$$

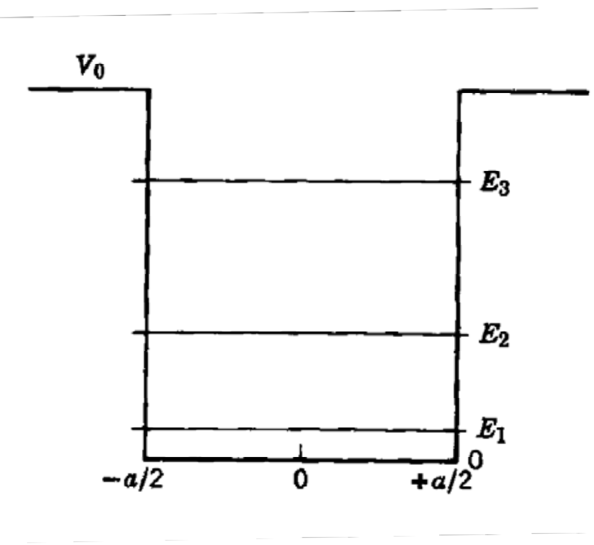
Sistema con livelli discreti (quantizzati) di energia



Nota: $n \neq 0$
Energia stato fondamentale non è nulla

Esempio: pallina $m = 0.1$ kg in scatola $a = 10$ cm → $E_1 \sim 10^{-64}$ J !!
Elettrone $m \sim 10^{-30}$ kg in scatola $a = 1$ nm → → $E_1 \sim 5 \times 10^{-20}$ J ~ 0.5 eV
(valore significativo se paragonato alle scale di energia tipiche nei sistemi materiali)

Quantum well (finite)



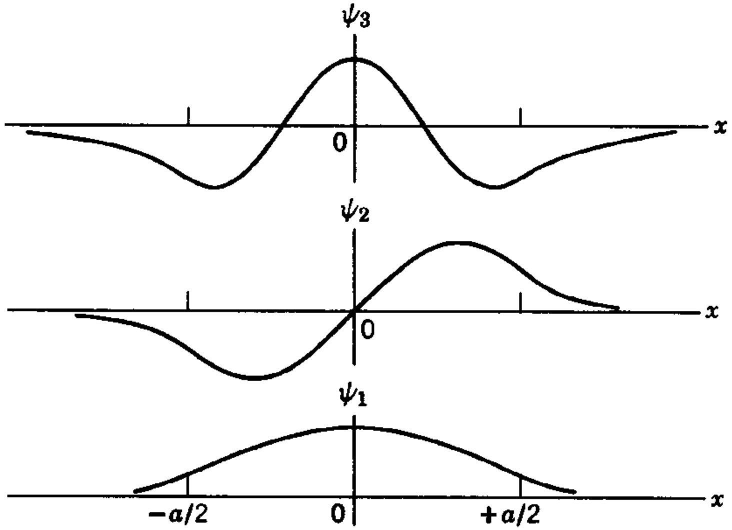


Figure 6-26 The three bound eigenfunctions for the square well of Figure 6-25.

Le condizioni al contorno non impongono più $\Psi = 0$

- La funzione d’onda “deborda” esponenzialmente dalla buca
- Il numero di livelli possibili è limitato

<u>In ogni caso</u>: confinamento spaziale ←→ quantizzazione livelli

Example 4: quantum harmonic oscillator

$V(x)=(C/2)x^2$

Soluzione autofunzioni oscillatore armonico più complicata
Sempre autofunzioni confinate spazialmente (decadono esponenzialmente oltre i punti di inversione)

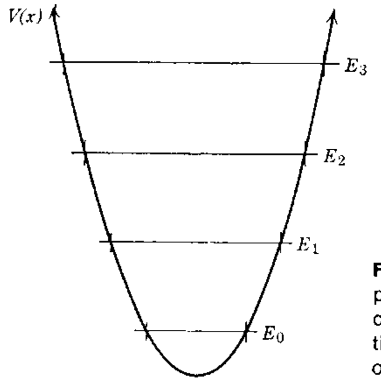
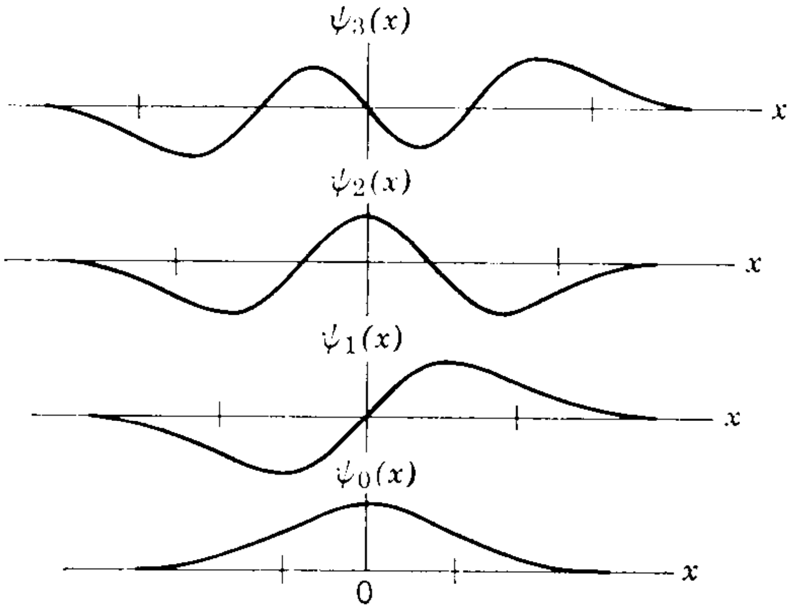


Figure 6-35 The first few eigenvalues of the simple harmonic oscillator potential. Note that the classically allowed regions (between the intersections of $V(x)$ and E_n) expand with increasing values of E_n.

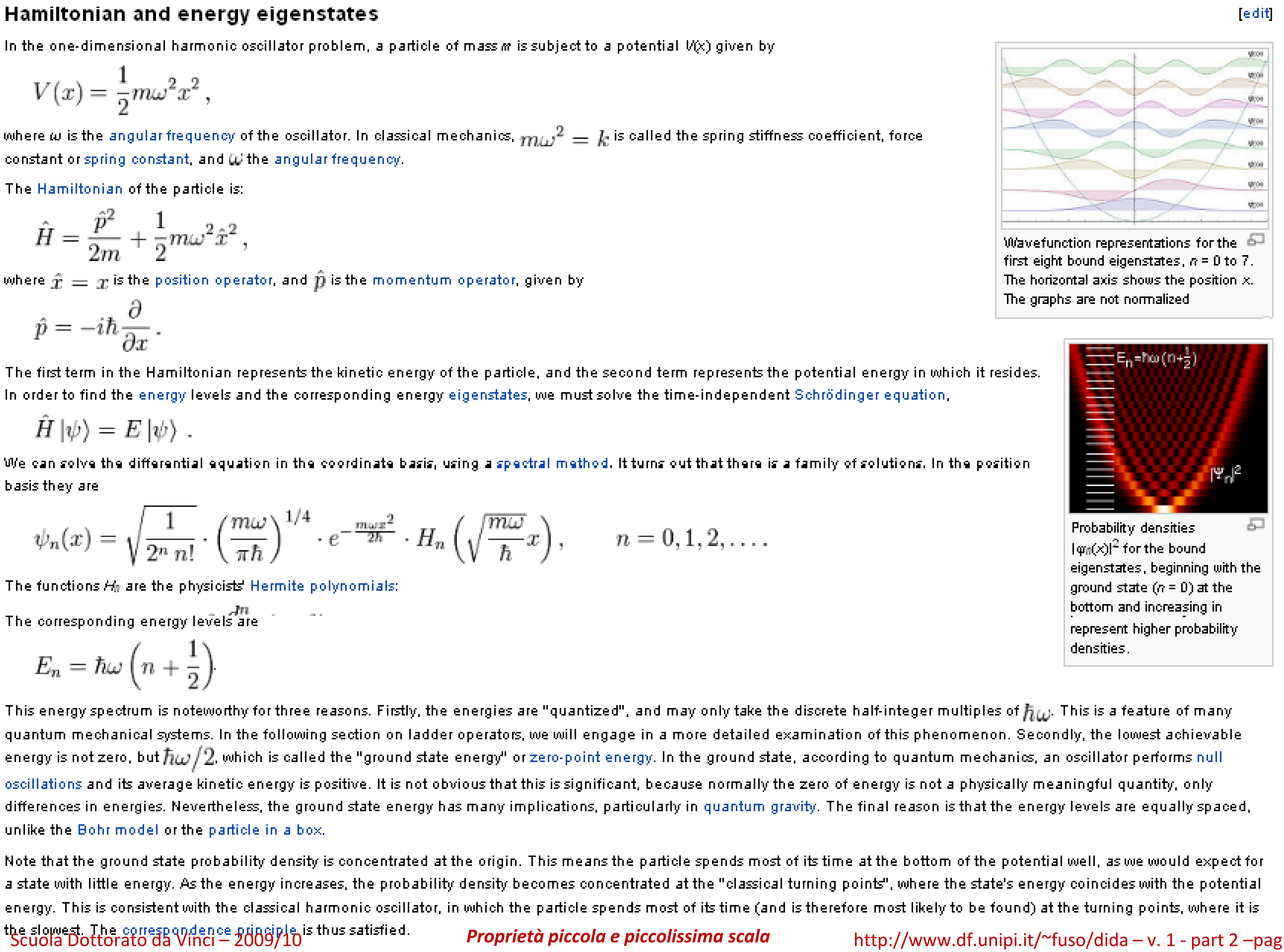
Table 6-1 Some Eigenfunctions $\psi(u)$ for the Simple Harmonic Oscillator Potential, where u is Related to the Coordinate x by the Equation $u = [(Cm)^{1/4}/\hbar^{1/2}]x$

Quantum Number	Eigenfunctions
0	$\psi_0 = A_0 e^{-u^2/2}$
1	$\psi_1 = A_1 u e^{-u^2/2}$
2	$\psi_2 = A_2(1 - 2u^2)e^{-u^2/2}$
3	$\psi_3 = A_3(3u - 2u^3)e^{-u^2/2}$
4	$\psi_4 = A_4(3 - 12u^2 + 4u^4)e^{-u^2/2}$
5	$\psi_5 = A_5(15u - 20u^3 + 4u^5)e^{-u^2/2}$



Livelli equispaziati
Autovalori: $E_n = (n+1/2)h\nu$
(cfr. **energia fotoni**, che sono autofunzioni di oscillatore armonico di radiazione)

Eigenfunctions and eigenvalues for QHO



Hamiltonian and energy eigenstates

In the one-dimensional harmonic oscillator problem, a particle of mass *m* is subject to a potential *V*(*x*) given by

$$V(x) = \frac{1}{2}m\omega^2 x^2\,,$$

where *ω* is the angular frequency of the oscillator. In classical mechanics, $m\omega^2 = k$ is called the spring stiffness coefficient, force constant or spring constant, and ω the angular frequency.

The Hamiltonian of the particle is:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2\,,$$

where $\hat{x} = x$ is the position operator, and $\hat{p}$ is the momentum operator, given by

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}\,.$$

The first term in the Hamiltonian represents the kinetic energy of the particle, and the second term represents the potential energy in which it resides. In order to find the energy levels and the corresponding energy eigenstates, we must solve the time-independent Schrödinger equation,

$$\hat{H}\left|\psi\right\rangle = E\left|\psi\right\rangle\,.$$

We can solve the differential equation in the coordinate basis, using a spectral method. It turns out that there is a family of solutions. In the position basis they are

$$\psi_n(x) = \sqrt{\frac{1}{2^n\,n!}}\cdot\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\cdot e^{-\frac{m\omega x^2}{2\hbar}}\cdot H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right),\qquad n = 0,1,2,\ldots.$$

The functions *H*

The functions H_n are the physicists' Hermite polynomials:

The corresponding energy levels are

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right).$$

This energy spectrum is noteworthy for three reasons. Firstly, the energies are "quantized", and may only take the discrete half-integer multiples of $\hbar\omega$. This is a feature of many quantum mechanical systems. In the following section on ladder operators, we will engage in a more detailed examination of this phenomenon. Secondly, the lowest achievable energy is not zero, but $\hbar\omega/2$, which is called the "ground state energy" or zero-point energy. In the ground state, according to quantum mechanics, an oscillator performs null oscillations and its average kinetic energy is positive. It is not obvious that this is significant, because normally the zero of energy is not a physically meaningful quantity, only differences in energies. Nevertheless, the ground state energy has many implications, particularly in quantum gravity. The final reason is that the energy levels are equally spaced, unlike the Bohr model or the particle in a box.

Note that the ground state probability density is concentrated at the origin. This means the particle spends most of its time at the bottom of the potential well, as we would expect for a state with little energy. As the energy increases, the probability density becomes concentrated at the "classical turning points", where the state's energy coincides with the potential energy. This is consistent with the classical harmonic oscillator, in which the particle spends most of its time (and is therefore most likely to be found) at the turning points, where it is the slowest. The correspondence principle is thus satisfied.

Wavefunction representations for the first eight bound eigenstates, *n* = 0 to 7. The horizontal axis shows the position *x*. The graphs are not normalized

Probability densities $|\psi_n(x)|^2$ for the bound eigenstates, beginning with the ground state (*n* = 0) at the bottom and increasing in energy to the top. The horizontal axis shows the position *x*, and brighter colors represent higher probability densities.

Summary

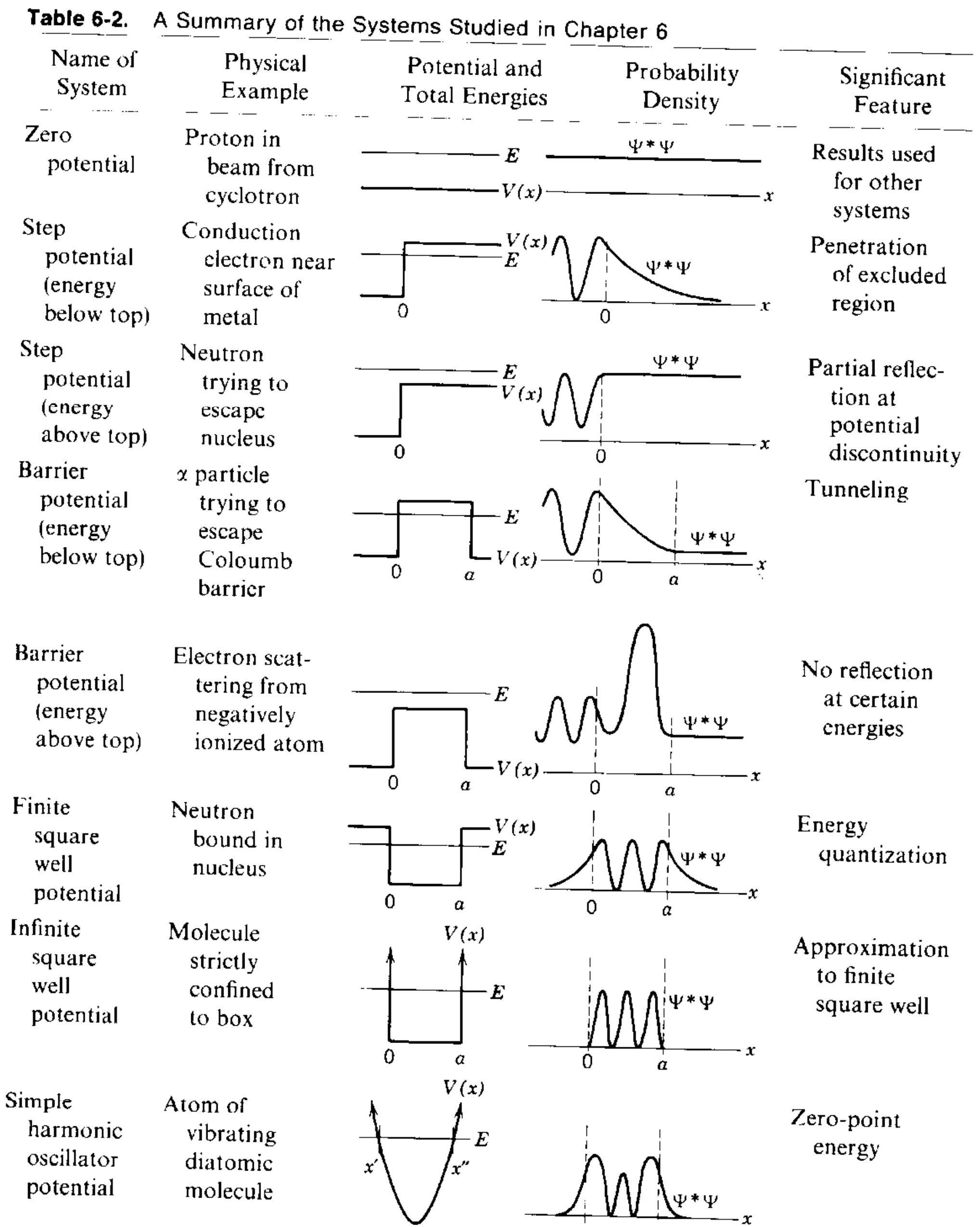


Table 6-2. A Summary of the Systems Studied in Chapter 6

Name of System	Physical Example	Potential and Total Energies	Probability Density	Significant Feature
Zero potential	Proton in beam from cyclotron			Results used for other systems
Step potential (energy below top)	Conduction electron near surface of metal			Penetration of excluded region
Step potential (energy above top)	Neutron trying to escape nucleus			Partial reflection at potential discontinuity
Barrier potential (energy below top)	α particle trying to escape Coloumb barrier			Tunneling
Barrier potential (energy above top)	Electron scattering from negatively ionized atom			No reflection at certain energies
Finite square well potential	Neutron bound in nucleus			Energy quantization
Infinite square well potential	Molecule strictly confined to box			Approximation to finite square well
Simple harmonic oscillator potential	Atom of vibrating diatomic molecule			Zero-point energy

Quantum matter: single atom

La descrizione quantistica della materia è essenziale per interpretare correttamente l’interazione radiazione/materia, con approcci sia semiclassici (radiazione come onda) che quantistici (radiazione come fotoni)

Paradiigma della materia è l’atomo, anzi il più semplice tra gli atomi: idrogeno

Modello planetario dell’atomo (classico):

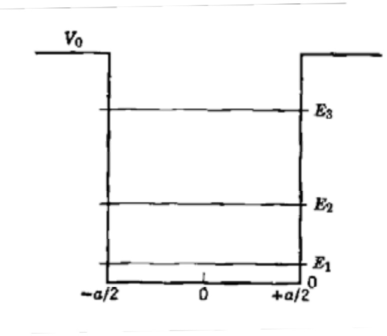
- Equilibrio (forza Coulomb dà acc. centr.)

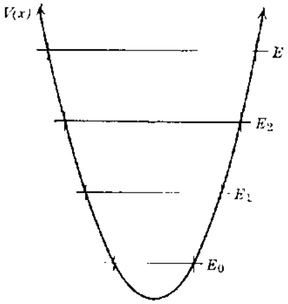
$$m\frac{v^2}{r}=\frac{Ze^2}{4\pi\varepsilon_o r^2}$$

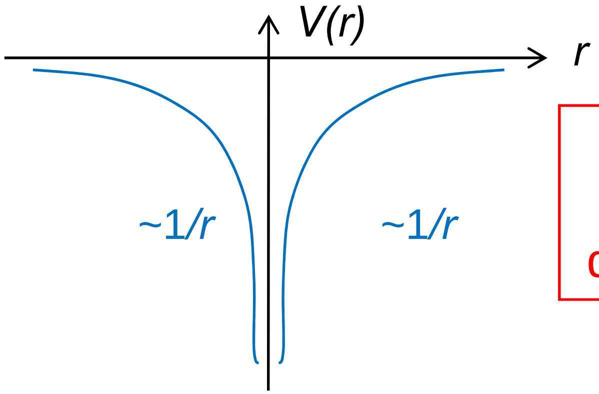
- Energia (elettrostatica + cinetica)

$$E=\frac{1}{2}mv^2-\frac{Ze^2}{4\pi\varepsilon_o r}$$

$$E=\frac{1}{2}\frac{Ze^2}{4\pi\varepsilon_o r}-\frac{Ze^2}{4\pi\varepsilon_o r}=-\frac{1}{2}\frac{Ze^2}{4\pi\varepsilon_o r}$$







Confinamento

→

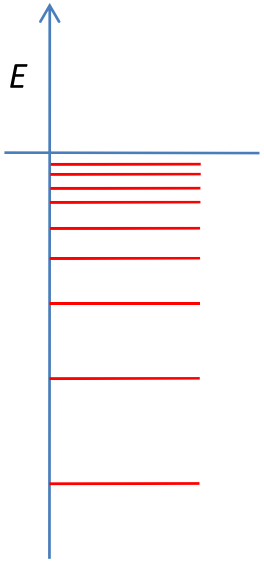
quantizzazione

Bohr atom (old MQ)

Ipotesi di Bohr (quantistica): $L = mvr = n\frac{h}{2\pi}$

Quantizzazione raggio orbitale: $r_n = \frac{n^2 h^2 \varepsilon_o}{\pi m Z e^2}$

Quantizzazione energia: $E_n = -\frac{mZ^2e^4}{8\varepsilon_o^2 h^2}\frac{1}{n^2}$ $E_n = -13.6\frac{Z^2}{n^2}\quad eV$



Sistema con livelli discreti (quantizzati) di energia

Esistono orbite stabili con momento angolare quantizzato
→ energia quantizzata
→ possibilità di transizioni tra livelli discreti (spiegazione spettri sperimentali)

Schroedinger atom (hydrogen)

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(r,\theta,\varphi) + V(r)\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \qquad (7\text{-}12)$$

where

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} \qquad (7\text{-}13)$$

is the Laplacian operator in the spherical polar coordinates r, θ, φ. For the details of the coordinate transformation leading to (7-12) and (7-13), the student should consult Appendix M. A comparison of the forms of the Laplacian operator in rectangular and spherical polar coordinates, (7-8) and (7-13), shows that we have simplified the expression of the potential energy function at the expense of considerably complicating the expression of the Laplacian operator in the time-independent Schroedinger equation that must be solved.

Nevertheless, the change of coordinates is worthwhile because it will allow us to find solutions to the time-independent Schroedinger equation of the form

$$\psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi) \qquad (7\text{-}14)$$

That is, we shall show that there are solutions $\psi(r,\theta,\varphi)$ to (7-12) that split into products of three functions, $R(r)$, $\Theta(\theta)$, and $\Phi(\varphi)$, each of which depends on only one of the coordinates. The advantage lies in the fact that these three functions can be found by solving *ordinary* differential equations. We show this by substituting the product form, $\psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi)$, into the time-independent Schroedinger equation obtained by evaluating the Laplacian operator in (7-12) from (7-13). This yields

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R\Theta\Phi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial R\Theta\Phi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 R\Theta\Phi}{\partial\varphi^2}\right] + V(r)R\Theta\Phi = ER\Theta\Phi$$

Carrying out the partial differentiations, we have

$$-\frac{\hbar^2}{2\mu}\left[\frac{\Theta\Phi}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{R\Phi}{r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{R\Theta}{r^2\sin^2\theta}\frac{d^2\Phi}{d\varphi^2}\right]$$

In this equation we have written the partial derivative $\partial R/\partial r$ as the total derivative dR/dr since the two are equivalent because R is a function of r alone. The same comment applies to the other derivatives. If we now multiply through by $-2\mu r^2\sin^2\theta/R\Theta\Phi\hbar^2$, and transpose, we obtain

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2} = -\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{2\mu}{\hbar^2}r^2\sin^2\theta[E - V(r)]$$

As the left side of this equation does not depend on r or θ, whereas the right side does not depend on φ, their common value cannot depend on any of these variables. The common value must therefore be a constant, which we shall find it convenient to designate as $-m_l^2$. Thus we obtain two equations by setting each side equal to this constant

$$\frac{d^2\Phi}{d\varphi^2} = -m_l^2\Phi \qquad (7\text{-}15)$$

and

$$-\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{2\mu}{\hbar^2}r^2[E - V(r)] = -\frac{m_l^2}{\sin^2\theta}$$

By transposing, we can rewrite the second equation as

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}[E - V(r)] = \frac{m_l^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)$$

Since we have here an equation whose left side does not depend on one of the variables and whose right side does not depend on the other, we conclude again that both sides must equal a constant. It is convenient to designate this constant as $l(l+1)$. Thus we obtain, by setting each side equal to $l(l+1)$, two more equations

$$-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{m_l^2\Theta}{\sin^2\theta} = l(l+1)\Theta \qquad (7\text{-}16)$$

and

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}[E - V(r)]R = l(l+1)\frac{R}{r^2} \qquad (7\text{-}17)$$

We see that the assumed product form of the solution, $\psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi)$, is valid because it works! We also see that the problem has been reduced to that of solving the ordinary differential equations, (7-15), (7-16), and (7-17), for $\Phi(\varphi)$, $\Theta(\theta)$, and $R(r)$.

In solving these equations, we shall find that the equation for $\Phi(\varphi)$ has *acceptable* solutions only for *certain values of* m_l. Using these values of m_l in the equation for $\Theta(\theta)$, it turns out that this equation has *acceptable* solutions only for *certain values of* l. With these values of l in the equation for $R(r)$, this equation is found to have *acceptable* solutions only for *certain values of the total energy* E; that is, the energy of the atom is quantized.

Ricerca autofunzioni complicata da simmetria sferica
(coordinate sferiche)

Hydrogen atom II

7-5 EIGENVALUES, QUANTUM NUMBERS, AND DEGENERACY

One of the important results of the Schroedinger theory of the one-electron atom is the prediction of (7-22) for the allowed values of total energy of the bound states of the atom. Comparing this prediction for the eigenvalues

$$E_n = -\frac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} = -\frac{13.6\text{ eV}}{n^2}$$

with the predictions of the Bohr model (see (4-18)), we find that *identical* allowed energies are predicted by these treatments. Both predictions are in excellent agreement with experiment. Schroedinger's derivation of (7-22) provided the first convincing verification of his theory of quantum mechanics. Figure 7-3 illustrates the Coulomb potential $V(r)$ for the one-electron atom, and its *eigenvalues* E_n.

What is the relation between the Coulomb potential and its eigenvalues, and the potentials studied in Chapter 6 and their eigenvalues? One obvious difference is that the quantum mechanical calculations leading to the eigenvalues of the Coulomb potential are appreciably more complicated. But the Coulomb potential is an exact description of a real three-dimensional system. The potentials previously treated are approximate descriptions of idealized one-dimensional systems, which are designed to simplify the calculations. Part of the complication for the Coulomb potential is also due to its spherical symmetry, which forces the use of spherical polar coordinates instead of rectangular coordinates.

The similarities are much more fundamental than the differences. For the Coulomb potential, as for any other binding potential, the allowed total energies of a particle bound to the potential are *discretely quantized*. Figure 7-4 makes a comparison between the allowed energies for a Coulomb potential and for several one-dimensional binding potentials. In this figure the Coulomb potential is represented on a crosscut along a diameter through the one-electron atom. Note that all the binding potentials have a *zero-point energy*. That is, in all cases the lowest allowed value of total energy lies above the minimum value of the potential energy. Associated with its zero-point energy, the one-electron atom has a zero-point motion like other systems described by binding potentials. In the following section we shall see that this phenomenon can give us a basic explanation of the stability of the ground state of the atom.

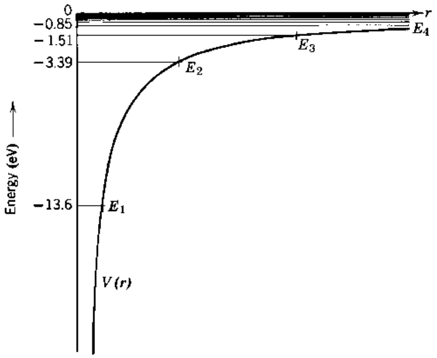


Figure 7-3 The Coulomb potential $V(r)$ and its eigenvalues E_n. For large values of n the eigenvalues become very closely spaced in energy since E_n approaches zero as n approaches infinity. Note that the intersection of $V(r)$ and E_n, which defines the location of one end of the classically allowed region, moves out as n increases. Not shown in this figure is the continuum of eigenvalues at positive energies corresponding to unbound states.

Table 7-2 Some Eigenfunctions for the One-Electron Atom

Quantum Numbers			
n	l	m_l	Eigenfunctions
1	0	0	$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	0	$\psi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$
2	1	0	$\psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos\theta$
2	1	±1	$\psi_{21\pm1} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin\theta\, e^{\pm i\varphi}$
3	0	0	$\psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(27 - 18\frac{Zr}{a_0} + 2\frac{Z^2r^2}{a_0^2}\right) e^{-Zr/3a_0}$
3	1	0	$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6 - \frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0} \cos\theta$
3	1	±1	$\psi_{31\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6 - \frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0} \sin\theta\, e^{\pm i\varphi}$
3	2	0	$\psi_{320} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}(3\cos^2\theta - 1)$
3	2	±1	$\psi_{32\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \sin\theta\cos\theta\, e^{\pm i\varphi}$
3	2	±2	$\psi_{32\pm2} = \frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \sin^2\theta\, e^{\pm 2i\varphi}$

Autovalori simili a Bohr
Autofunzioni con “armoniche sferiche”

Hydrogen atom III

Autofunzioni dipendenti da ***r***

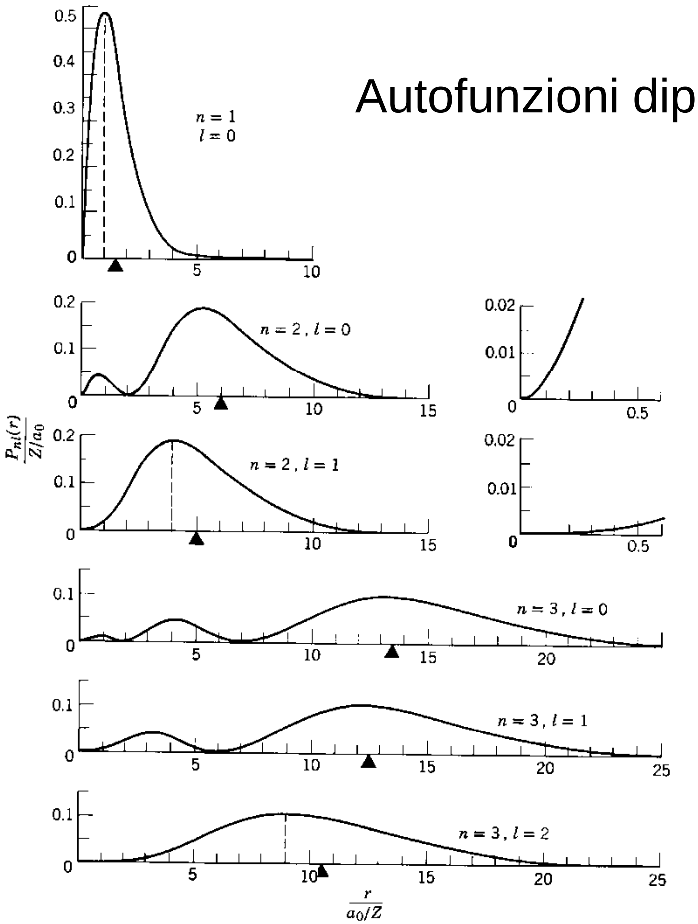


Figure 7-5 The radial probability density for the electron in a one-electron atom for $n = 1, 2, 3$ and the values of l shown. The triangle on each abscissa indicates the value of $\overline{r_{nl}}$ as given by (7-29). For $n = 2$ the plots are redrawn with abscissa and ordinate scales expanded by a factor of 10 to show the behavior of $P_{nl}(r)$ near the origin. Note that in the three cases for which $l = l_{max} = n - 1$ the maximum of $P_{nl}(r)$ occurs at $r_{Bohr} = n^2 a_0/Z$,

Risolvendo atomo di idrogeno con Schroedinger si trovano stati stazionari

Esistono livelli stabili con energia quantizzata

Applicabile anche ad altri atomi (con maggiori difficoltà)

Esistono “degenerazioni” dei livelli (scompaiono per altri atomi e scompaiono in parte anche per idrogeno in trattazione relativistica)

Conclusions

- Quantum mechanics required to interpret *matter at the local* (ultra-small) scale
- Some *words (concepts) of MQ* are: state vectors, observables, wavefunctions, energy levels, …
- Confinement, i.e., boundary conditions, leads to quantuized levels
- "Isolated" material systems (e.g., atoms, but also molecules and small clusters) show quantized levels thanks to Bohr or Schroedinger
- Also quantum boxes (wells) and *harmonic oscillators* have quantum properties
- *Tunneling* is a possibility according to MQ (classically impossible)
- We will now move to the quantum description of a more complicated system, able to depict solid state matter