

Scuola di Dottorato Leonardo da Vinci – a.a. 2012/13

LASER: CARATTERISTICHE, PRINCIPI FISICI, APPLICAZIONI

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Part 3

A short primer of Quantum Mechanics

OUTLOOK

We have seen that:

- Purely classical approach cannot account for laser operation:
 - only absorption can be envisioned
 - conventional light sources (black-body) are by far different with respect to lasers
- Needed to move to a **semiclassical** approach (classical radiation + quantum matter):
 - wavefunctions, Schrodinger, quantum confinement
 - discrete energy levels

Final objective:

To show how (properly prepared) quantum matter can lead to light amplification

QUANTUM MECHANICS

Quantum effects are dominant in many systems (typically, involving small, fast particles)
They are essential to understand the light/matter interaction

Starting points of QM:

Wave-matter complementarity (or dualism), that means, e.g., an e.m. wave can be represented by particles (photons) and particles can be represented by waves

Basic QM tool (consequence of the dualism above):

Wavefunction $\Psi(r,t)$ to describe a quantum particle

→ **probabilistic approach**: $|\Psi(r,t)|^2$ represents the probability to find the particle in $r, r+dr$
→ the concept of trajectory does not apply any more!!

Indeed the **uncertainty principle** (a theorem, truly) states, e.g., in 1D case:

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

For instance, the more precisely the position of some particle is determined, the less precisely its momentum can be known, and vice versa.^[1] The original heuristic argument that such a limit should exist was given by **Werner Heisenberg** in 1927, after whom it is sometimes named the **Heisenberg principle**

THE WORKHORSE OF QM

Main problem of the mechanics:

- To predict $\mathbf{r}(t)$ e $\mathbf{v}(t)$ (trajectory) based on knowledge of forces $\mathbf{F}$
- Main tool: equation of motion (Newton) $\mathbf{a} = \mathbf{F}/m$

Main problem of QM:

- To determine $\Psi(\mathbf{r},t)$ starting from the knowledge of local potentials
- Main tool: Schroedinger's equation (non relativistic situations!):

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

with $\nabla^2\Psi(\vec{r},t) = (\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2})\Psi(\vec{r},t)$ (in cartesian coordinates)

$V(\mathbf{r},t)$ is the **potential**, typically depending on $\mathbf{r},t$, ruling the dynamics of the object

Note: classically potential and force are related through $\mathbf{F} = -\nabla U$

Schroedinger equation in the 1D case:

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

(partial derivatives equation)

CONCEPTUAL BASIS OF THE SCHROEDINGER'S EQ

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

$$\lambda = h/p \quad \text{and} \quad v = E/h$$

2. It must be consistent with the equation

$$E = p^2/2m + V \quad (5-9)$$

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

$$V(x,t) = V_0 \quad (5-10)$$

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 $v = E/h$, 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 v , we obtain

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

The equation “must be” as it is...

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

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

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.

EIGENSTATES AND EIGENFUNCTIONS

Many relevant physical situations offer for great simplifications of the mathematics

If V **does not** depend on time, $V(x)$ only, then:

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

and

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

Steady-state Schroedinger's equation

The wavefunction for steady state problems can factorized!!

$\psi(x)$: **eigenfunction (eigenstate)**
 E : **energy eigenvalue**

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*.

MATHEMATICS LEADING TO STEADY-STATE EQ

Substituting the assumed form of the solution, $\Psi(x,t) = \psi(x)\varphi(t)$, into the Schrodinger 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

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

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

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

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

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

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.

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

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

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

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

$$G = E \quad (5-42)$$

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

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

EXAMPLE 1 : THE FREE PARTICLE MOVING

A free particle (e.g., a photon!) which does not interact at all and moves along the X axis having a well defined impulse p

$$V = 0$$



A good solution of the
Schroedinger equation is:

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

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

with $p = \hbar k$
(*de Broglie wave*)

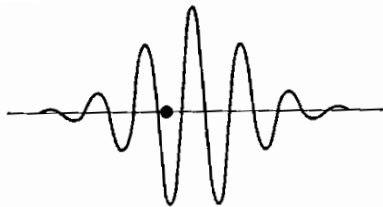
$$\text{de Broglie wavelength: } \lambda_{\text{dB}} = 2\pi/k = h/p$$

A “little” problem: it is $|\Psi|^2 = 1$ everywhere

→ the probability of finding the particle is always 1

→ the normalization factor $\int |\psi|^2 dx$ diverges!

(in agreement with uncertainty: $\Delta p = 0 \rightarrow \Delta x \rightarrow \infty$)



(we have already seen how wave packets, i.e., Fourier series, have to be used to solve this issue)

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.

EXAMPLE 2 : STEP POTENTIAL I

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 Schrodinger equation

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

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 Schrodinger equation which is almost as simple

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

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 Schrodinger equation for a free particle, we take for its *general* solution the traveling wave eigenfunction of (6-8). We write that eigenfunction as **incident** **reflected**

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

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

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

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

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

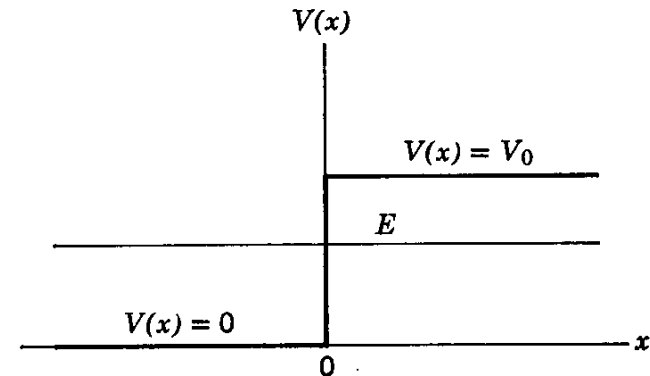
Then the substitution yields

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

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

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

If you bear in mind the relationship between potential and force, you can feel that this is very similar (classically) to a particle colliding with a rigid wall or, even better, to a particle climbing an inclined plane



Classically: for $E < V_0$ there is only reflection (no possibility to overcome the potential barrier)

In QM there reflection is accompanied by transmission (there is a non null probability for transmission to occur)

STEP POTENTIAL II

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

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

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

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

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

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 $x \rightarrow +\infty$. 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 $x \rightarrow +\infty$, 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

$$C = 0 \quad (6-19)$$

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

$$D = A + B \quad (6-20)$$

Continuity of the derivative of the two forms

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

and

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

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

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

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

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

Subtracting gives

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

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

$$\psi(x) = \frac{D}{2} (1 + ik_2/k_1)e^{ik_1x} + \frac{D}{2} (1 - ik_2/k_1)e^{-ik_1x} \quad x \leq 0$$

$$De^{-k_2x} \quad x \geq 0 \quad (6-24)$$

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.

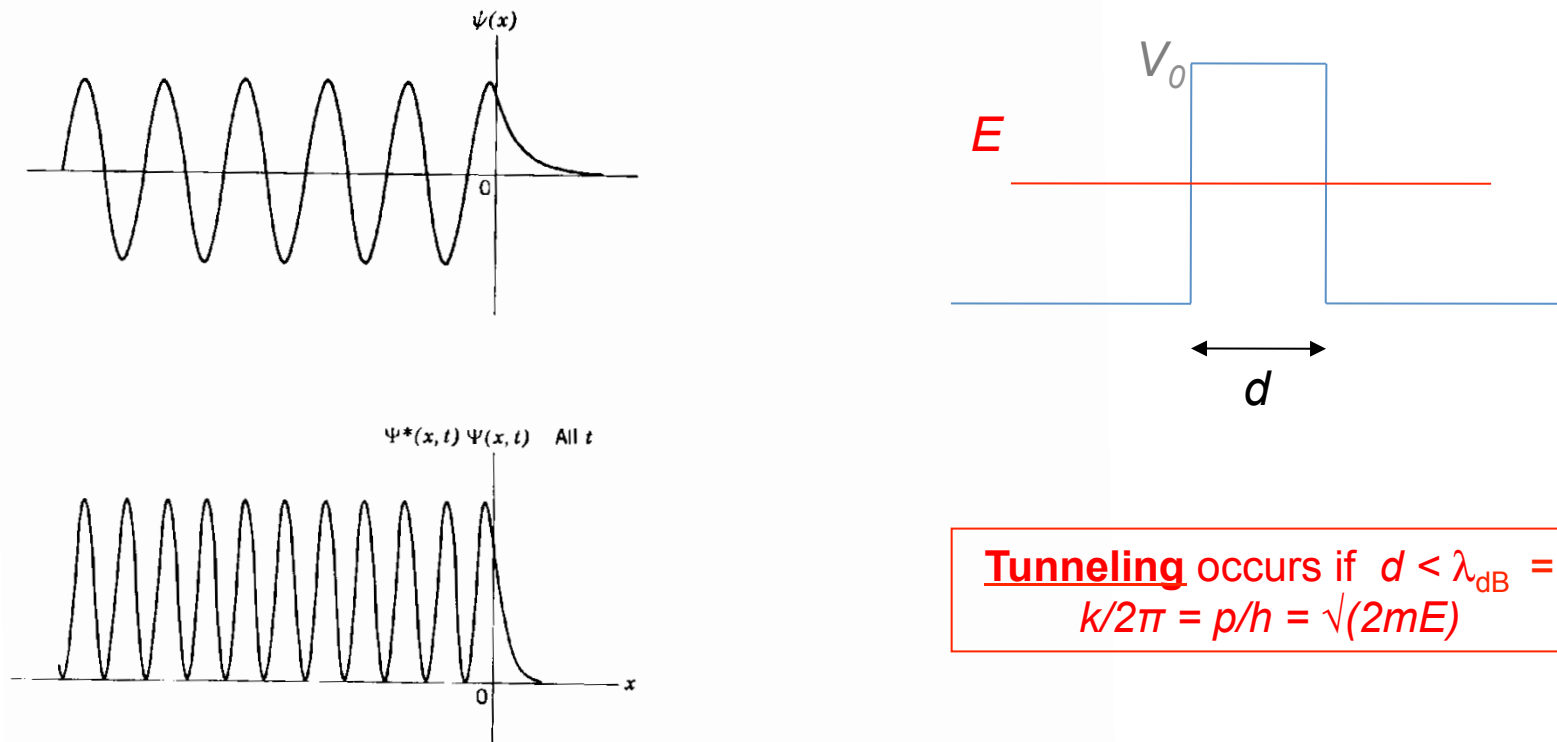
The wave function corresponding to the eigenfunction is

$$\Psi(x,t) = \frac{Ae^{ik_1x}e^{-iEt/\hbar} + Be^{-ik_1x}e^{-iEt/\hbar}}{De^{-k_2x}e^{-iEt/\hbar}} = Ae^{i(k_1x - Et/\hbar)} + Be^{i(-k_1x - Et/\hbar)} \quad x \leq 0$$

$$De^{-k_2x}e^{-iEt/\hbar} \quad x \geq 0 \quad (6-25)$$

The eigenfunction is completely determined by the potential value (but for a normalization coefficient)
→ Transmission coefficient can be derived

STEP POTENTIAL WITH A FINITE LENGTH



Tunneling occurs if $d < \lambda_{\text{dB}} = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$

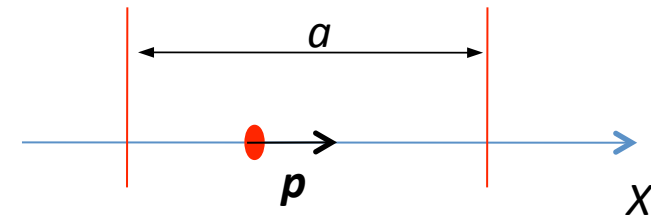
Figure 6-7 Top: The eigenfunction $\psi(x)$ for a particle incident upon a potential step at $x = 0$, with total energy less than the height of the step. Note the penetration of the eigenfunction into the classically excluded region $x > 0$. Bottom: The probability density $\Psi^* \Psi = \psi^* \psi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

Note: in the less interesting situation where $E < V_0$ the solution can be found following the same procedure, but the exponential behavior is no longer recovered

EXAMPLE 3 : POTENTIAL WELL (INFINITE) I

A free particle moves along the X axis and feels two (infinite) potential barriers at $x = -a/2$ and $x = a/2$

The potential reads:
$$V(x) = \begin{cases} 0 & 0 \leq x \leq a \\ \infty & x < 0; x > a \end{cases}$$



One can easily assume that the particle is **bound** to move within the two potential barriers defining the well

$\Psi(x,t)$ is given by superposition of a particle moving to the left and one moving to the right

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

Boundary conditions: $\psi = 0$ at $x = -a/2$ and $x = a/2$

$$A = B \quad \text{or} \quad A = -B$$

Note: the derivative of the wavefunction is here non continuous because $V \rightarrow \infty$

POTENTIAL WELL (INFINITE) II

The boundary conditions (and the related physics) are the same of the radiation (photons) in the box we have already seen!!

We got: $k_n = n \frac{\pi}{a}$

Being the particle free, the energy is only kinetic:

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

**Confinement → energy quantization
(set of discrete energies is allowed)**

Note: $n \neq 0$

The energy of the ground state cannot be zero

Example: a ball with $m = 0.1$ kg in a box with $a = 10$ cm → $E_1 \sim 10^{-64}$ J !!
An electron with $m \sim 10^{-30}$ kg in a box with $a = 1$ nm → $E_1 \sim 5 \times 10^{-20}$ J ~ 0.5 eV



POTENTIAL WELL (FINITE)

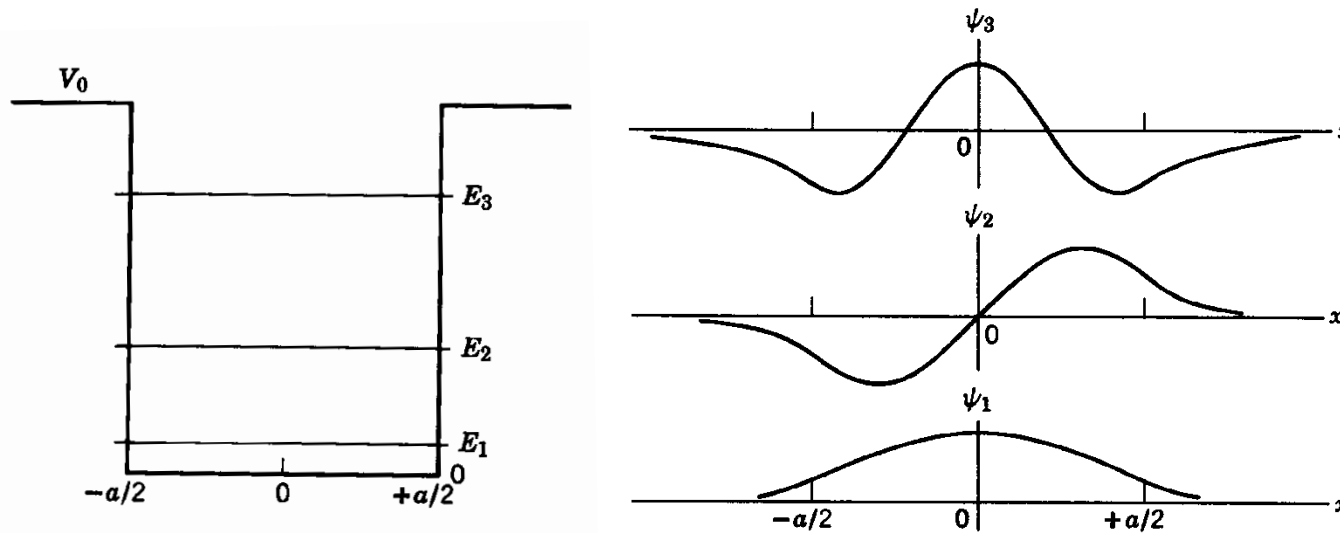


Figure 6-26 The three bound eigenfunctions for the square well of Figure 6-25.

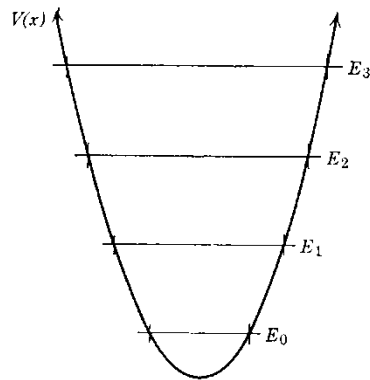
Boundary conditions do not lead anymore to $\Psi = 0$ outside the well



- there is a finite probability for the particle to tunnel outside the well
- there is a “leakage” of the wavefunction outside the well
- (the number of allowed energy levels is limited)

In any case: spatial confinement $\leftarrow$ quantized energy levels

HARMONIC OSCILLATOR (A FEW WORDS)



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

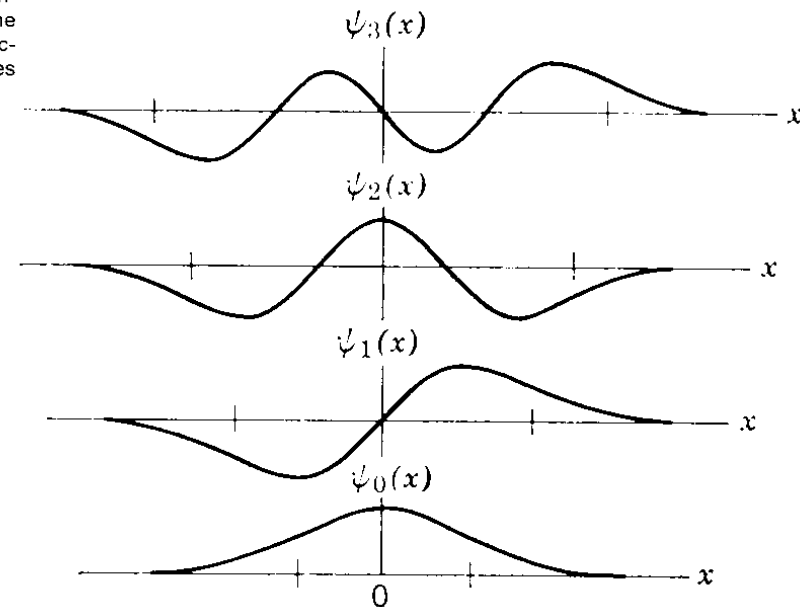
More complicated mathematics

Interesting to note that also in this case one gets discrete energy levels

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	$\psi_5 = A_5 (15u - 20u^3 + 4u^5) e^{-u^2/2}$



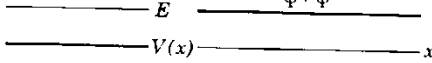
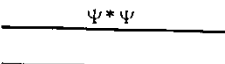
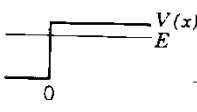
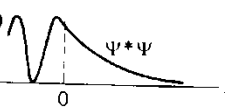
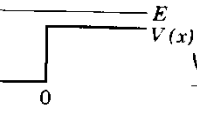
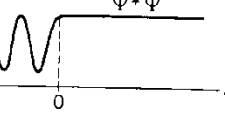
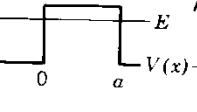
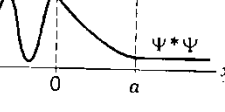
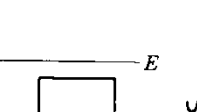
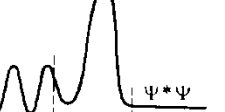
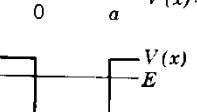
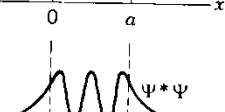
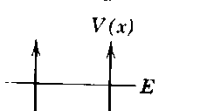
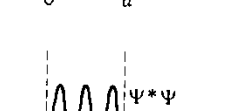
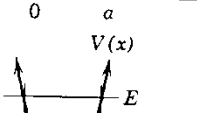
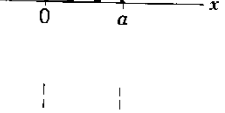
Discrete energy levels (equispaced, here)

$$\text{Eigenvalues: } E_n = (n+1/2)\hbar\omega$$

(cfr. **photon energy**, the photon can be seen as a solution of an harmonic oscillator problem)

SUMMARY OF EIGENFUNCTIONS/EIGENVALUES

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

Let's now go back to our initial problem: how to correctly describe the matter in quantum mechanical terms, in order to provide with a simple, yet effective, light/matter interaction picture

The simplest matter (paradigmatic): the hydrogen atom

Very classical picture of the atom: the planetary model

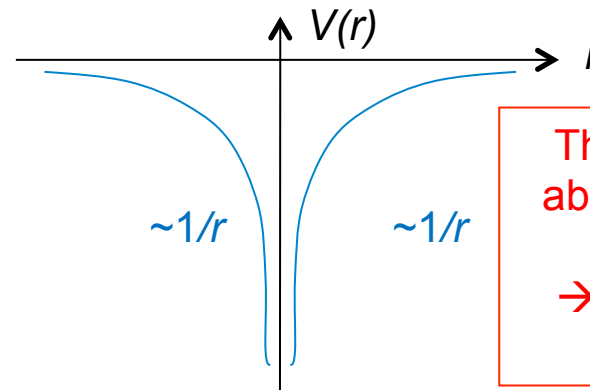
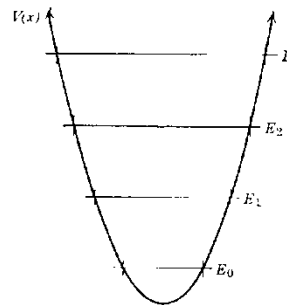
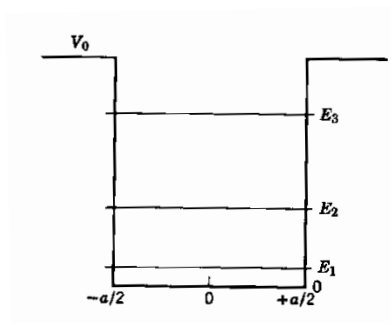
- Coulomb attraction provides with centripetal acceleration

- The mechanical energy is given by the kinetic energy plus the interaction (electrostatic) energy

$$m \frac{v^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2}$$

$$E = \frac{1}{2}mv^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

$$E = \frac{1}{2} \frac{Ze^2}{4\pi\epsilon_0 r} - \frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{1}{2} \frac{Ze^2}{4\pi\epsilon_0 r}$$



The potential is again able to produce spatial confinement
→ quantization of the energy levels

THE BOHR'S ATOM ("OLD QUANTUM THEORY")

Bohr's hypothesis (quantized angular momentum):

$$L = mvr = n \frac{h}{2\pi}$$

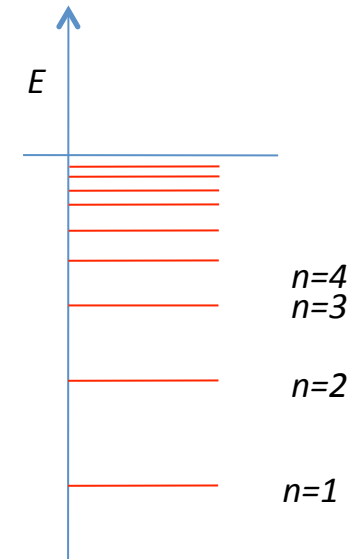
Quantized orbital radius:

$$r_n = \frac{n^2 h^2 \epsilon_0}{\pi m Z e^2}$$

Quantized energy:

$$E_n = -\frac{mZ^2 e^4}{8\epsilon_0^2 h^2} \frac{1}{n^2}$$

$$E_n = -13.6 \frac{Z^2}{n^2} \text{ eV}$$



The simple Bohr's model accounts for quantized energy levels in the matter

Bohr's statements:

- orbits are possible with certain values of the radius
- the energy is quantized
- the electron can jump from one orbit to another one (**transitions**)

SCHROEDINGER'S VIEW OF THE ATOM I

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

where

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

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 Schrodinger equation that must be solved.

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

$$\psi(r, \theta, \varphi) = R(r) \Theta(\theta) \Phi(\varphi) \quad (7-14)$$

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 Schrodinger equation obtained by evaluating the Laplacian operator in (7-12) from (7-13). This yields

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

Carrying out the partial differentiations, we have

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

Unfortunately, the mathematics is not trivial due to the need to express operators in spherical coordinates

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

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

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

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

and

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

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.

SCHROEDINGER'S VIEW OF THE ATOM II

7-5 EIGENVALUES, QUANTUM NUMBERS, AND DEGENERACY

One of the important results of the Schrodinger 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. Schrodinger'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.

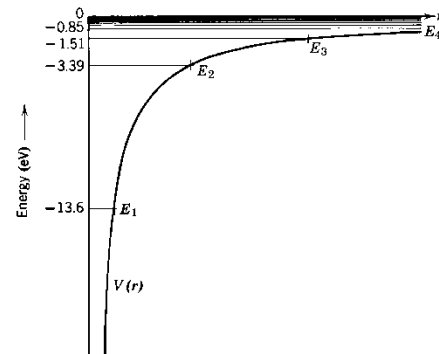


Figure 7-3 The Coulomb potential $V(r)$ and its eigenvalues E_n . For large values of n the eigenvalues become very closely spaced in energy since E_n approaches zero as n approaches infinity. Note that the intersection of $V(r)$ and E_n , which defines the location of one end of the classically allowed 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			Eigenfunctions
n	l	m_l	
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	$\psi_{21\pm 1} = \frac{1}{8\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin \theta e^{\pm i\varphi}$
3	0	0	$\psi_{300} = \frac{1}{81\sqrt{3\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(27 - 18\frac{Zr}{a_0} + 2\frac{Z^2 r^2}{a_0^2}\right) e^{-Zr/3a_0}$
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	$\psi_{31\pm 1} = \frac{1}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(6 - \frac{Zr}{a_0}\right) \frac{Zr}{a_0} e^{-Zr/3a_0} \sin \theta e^{\pm i\varphi}$
3	2	0	$\psi_{320} = \frac{1}{81\sqrt{6\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2 r^2}{a_0^2} e^{-Zr/3a_0} (3 \cos^2 \theta - 1)$
3	2	± 1	$\psi_{32\pm 1} = \frac{1}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2 r^2}{a_0^2} e^{-Zr/3a_0} \sin \theta \cos \theta e^{\pm i\varphi}$
3	2	± 2	$\psi_{32\pm 2} = \frac{1}{162\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2 r^2}{a_0^2} e^{-Zr/3a_0} \sin^2 \theta e^{\pm 2i\varphi}$

Practically the same eigenvalues than in the Bohr's atom are found
Eigenfunctions can be also obtained (cfr. "orbitals" in chemistry)

SCHROEDINGER'S VIEW OF THE ATOM III

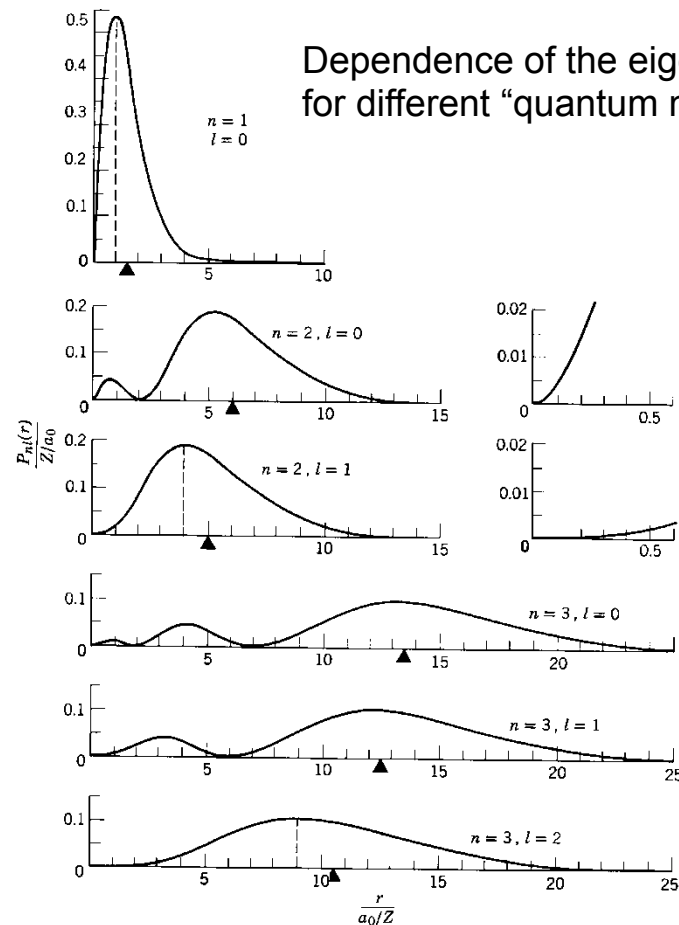


Figure 7-5 The radial probability density for the electron in a one-electron atom for $n = 1, 2, 3$ and the values of l shown. The triangle on each abscissa indicates the value of $\bar{r}_{nl}$ as given by (7-29). For $n = 2$ the plots are redrawn with abscissa and ordinate scales expanded by a factor 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 $r_{\text{Bohr}} = n^2 a_0/Z$, which is indicated by the triangle on the abscissa.

Basically, the simple Bohr's model is confirmed

Eigenfunctions (stationary states) and eigenvalues (energy levels) can be found analytically

Level degeneracy and specific symmetrical properties are found (they depend on the specific atom considered)

The approach holds for all atoms (and molecules, and, with suitable modifications/simplifications, solid and liquid matter), but the analytical solution is no longer possible

CONCLUSIONS

QM is a very powerful tool to explore the matter

QM shows, among others, that spatial confinement implies the occurrence of discrete energy levels (and states)

Roughly speaking, all the main aspects highlighted in the simple problems (potential well, harmonic oscillator, hydrogen atom) can be at some extent transferred to the matter

We have now all the ingredients to afford a description of light/matter interaction which will eventually lead to discover amplification of light!

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