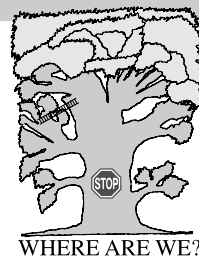


Chapter 4

EXACT SOLUTIONS – OUR BEACONS



Where are we?

We are in the middle of the TREE trunk.

An example

Two chlorine atoms stay together – they form the molecule Cl_2 . If we want to know its main mechanical properties, it would very quickly be seen that the two atoms have an equilibrium distance and any attempt to change this (in either direction) would be accompanied by work to be done. It looks like the two atoms are coupled together by a sort of spring. If one assumes that the spring satisfies Hooke's law,¹ the system is equivalent to a harmonic oscillator. If we require that no rotation in space of such a system is allowed, *the corresponding Schrödinger equation has the exact² analytical solution.*

What is it all about

Free particle (Δ)	p. 144
Particle in a box (Δ)	p. 145
• Box with ends	
• Cyclic box	
• Comparison of two boxes: hexatriene and benzene	
Tunnelling effect ($\Delta\boxtimes$)	p. 153
• A single barrier	
• The magic of two barriers ...	
The harmonic oscillator (Δ)	p. 164
Morse oscillator (Δ)	p. 169
• Morse potential	
• Solution	
• Comparison with the harmonic oscillator	
• The isotope effect	
• Bond weakening effect	
• Examples	
Rigid rotator (Δ)	p. 176

¹And if we limit ourselves to small displacements, see p. 239.

²Exact means ideal, i.e. without any approximation.

Hydrogen-like atom (Δ)	p. 178
Harmonic helium atom (harmonium) (Δ)	p. 185
What do all these problems have in common? (Δ)	p. 188
Beacons and pearls of physics (Δ)	p. 189

Short descriptions of exact solutions to the Schrödinger equations for the above model systems will be given.

Why is this important?

The Schrödinger equation is nowadays quite easy to solve with a *desired accuracy* for many systems. There are only a few systems for which the *exact* solutions are possible. These problems and solutions play an extremely important role in physics, since they represent kind of beacons for our navigation in science, when we deal with complex systems. Real systems may often be approximated by those for which exact solutions exist. For example, a real diatomic molecule is an extremely complex system, difficult to describe in detail and certainly does not represent a harmonic oscillator. Nevertheless, the main properties of diatomics follow from the simple harmonic oscillator model. When a chemist or physicist has to describe a complex system, he always first tries to simplify the problem,³ to make it similar to one of the simple problems described in the present chapter. Thus, from the beginning *we know the (idealized) solution*. This is of prime importance when discussing the (usually complex) solution to a higher level of accuracy. If this higher level description differs dramatically from that of the idealized one, most often this indicates that there is an error in our calculations and nothing is more urgent than to find and correct it.

What is needed?

- The postulates of quantum mechanics (Chapter 1, necessary).
- Separation of the centre of mass motion (Appendix I on p. 971, necessary).
- Operator algebra (Appendix B on p. 895, necessary).

In the present textbook we assume that the reader knows most of the problems described in the present chapter from a basic course in quantum chemistry. This is why the problems are given in short – only the most important results, without derivation, are reported. On the other hand, such a presentation, in most cases, will be sufficient for our goals.

Classical works

The hydrogen atom problem was solved by Werner Heisenberg in “*Über quantentheoretischen Umdeutung kinematischer und mechanischer Beziehungen*” published in *Zeitschrift für Physik*, 33 (1925) 879. ★ Erwin Schrödinger arrived at an equivalent picture within his wave mechanics in “*Quantisierung als Eigenwertproblem. I.*” published in *Annalen der Physik*, 79 (1926) 361. Schrödinger also gave the solution for the harmonic oscillator in a paper (under almost same title) which appeared in *Annalen der Physik*, 79 (1926) 489. ★ The Morse

³One of the cardinal strategies of science, when we have to explain a strange phenomenon, is first to simplify the system and create a model or series of models (more and more simplified descriptions) that still exhibit the phenomenon. The first model to study should be as simple as possible, because it will shed light on the main machinery.

oscillator problem was solved by Philip McCord Morse in “*Diatomic Molecules According to the Wave Mechanics. II. Vibrational Levels*” in *Physical Review*, 34 (1929) 57.⁴ ★ The tunnelling effect was first considered by Friedrich Hund in “*Zur Deutung der Molekelspektren*” published in *Zeitschrift für Physik*, 40 (1927) 742. ★ The Schrödinger equation for the harmonic⁵ was first solved by Sabre Kais, Dudley R. Herschbach and Raphael David Levine in “*Dimensional Scaling as a Symmetry Operation*”, which appeared in the *Journal of Chemical Physics*, 91 (1989) 7791.

4.1 FREE PARTICLE

The potential energy for a free particle is a constant (taken arbitrarily as zero): $V = 0$ and, therefore, energy E represents the kinetic energy only. The Schrödinger equation takes the form

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} = E\Psi$$

or in other words

$$\frac{d^2\Psi}{dx^2} + \kappa^2\Psi = 0$$

with $\kappa^2 = \frac{2mE}{\hbar^2}$. The constant κ in *this situation*⁶ is a real number.

The special solutions to this equation are $\exp(i\kappa x)$ and $\exp(-i\kappa x)$. Their linear combination with arbitrary complex coefficients A' and B' represents the general solution:

$$\Psi = A' \exp(i\kappa x) + B' \exp(-i\kappa x). \quad (4.1)$$

This is a de Broglie wave of wave length $\lambda = \frac{2\pi}{\kappa}$. Function $\exp(i\kappa x)$ represents the eigenfunction of the momentum operator:

$$\hat{p}_x \exp(i\kappa x) = -i\hbar \frac{d}{dx} \exp(i\kappa x) = -i\hbar i\kappa \exp(i\kappa x) = \kappa\hbar \exp(i\kappa x).$$

For eigenvalue $\hbar\kappa > 0$ the eigenfunction $\exp(i\kappa x)$ describes a particle moving towards $+\infty$. Similarly, $\exp(-i\kappa x)$ corresponds to a particle of the same energy, but moving in the opposite direction. The function $\Psi = A' \exp(i\kappa x) + B' \exp(-i\kappa x)$ is a superposition of these two states. A measurement of the momentum can give only two values: $\kappa\hbar$ with probability proportional to $|A'|^2$ or $-\kappa\hbar$ with probability proportional to $|B'|^2$.

⁴Note the spectacular speed at which the scholars worked.

⁵A harmonic model of the helium atom.

⁶The kinetic energy is always positive.

4.2 PARTICLE IN A BOX

4.2.1 BOX WITH ENDS

The problem pertains to a single particle in a potential (Fig. 4.1.a)

$$V(x) = 0 \quad \text{for } 0 \leq x \leq L,$$

$$V(x) = \infty \quad \text{for other } x.$$

Just because the particle will never go outside the section $0 \leq x \leq L$, therefore, the value of the wave function outside the section is equal to 0. It remains to find the function in $0 \leq x \leq L$.

Let us write down the Schrödinger equation for $0 \leq x \leq L$ with the Hamiltonian containing the kinetic energy only (since $V = 0$, one has $E \geq 0$)

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} = E\Psi. \quad (4.2)$$

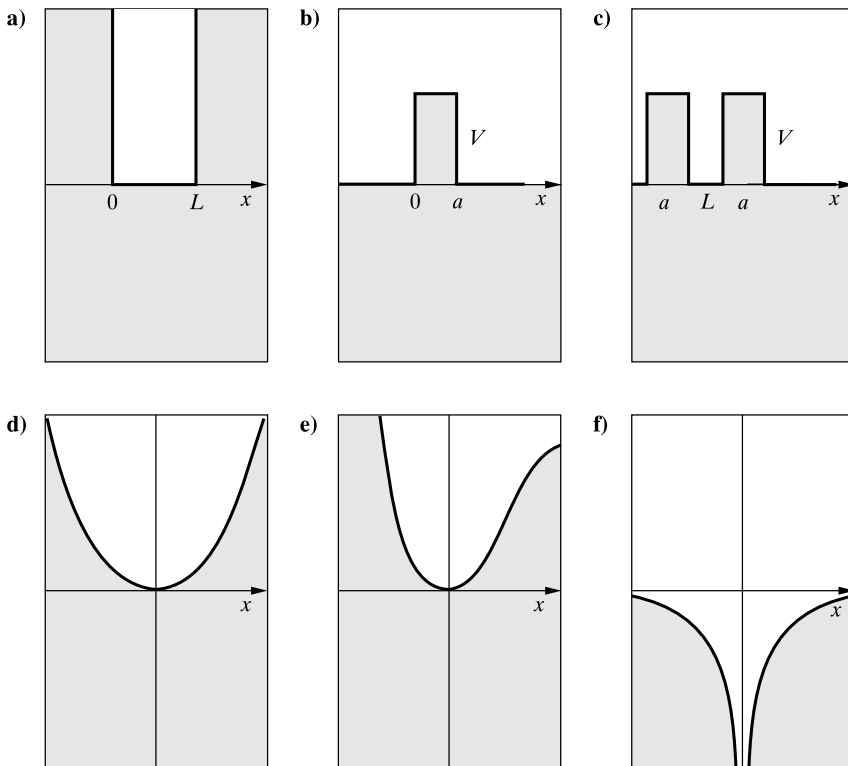


Fig. 4.1. The potential energy functions for a) particle in a box, b) single barrier, c) double barrier, d) harmonic oscillator, e) Morse oscillator, f) hydrogen atom.

The solution to this equation is given by (4.1), which may also be written as

$$\Psi = A \sin \kappa x + B \cos \kappa x \quad (4.3)$$

with

$$\kappa^2 = \frac{2mE}{\hbar^2}. \quad (4.4)$$

Now, the key is to recall (p. 74, Fig. 2.5), that the wave function has to be continuous and, therefore, two conditions have to be fulfilled: 1) $\Psi = 0$ for $x = 0$ and 2) $\Psi = 0$ for $x = L$. The first condition immediately gives $B = 0$, the second in this situation is equivalent to $\kappa L = n\pi$, for $n = 0, 1, \dots$. From this follows energy quantization, because κ contains energy E . One obtains, therefore, the following solution (a standing wave⁷):

$$E_n = \frac{n^2 \hbar^2}{8mL^2}, \quad n = 1, 2, 3, \dots, \quad (4.5)$$

$$\Psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x, \quad n = 1, 2, 3, \dots, \quad (4.6)$$

because $n = 0$ has to be excluded as leading to the wave function equal to zero everywhere, while $n < 0$ may be safely excluded as leading to the same wave functions as⁸ $n > 0$. Fig. 4.2 shows the wave functions for $n = 1, 2, 3$.

2D rectangular box

Let us consider a rectangular box (Fig. 4.3) with sides L_1 and L_2 and $V = 0$ inside and $V = \infty$ outside. We very easily obtain the solution to the Schrödinger equation after a straightforward separation of variables x and y leading to the two 1D Schrödinger equations.

The energy eigenvalue is equal to the sum of the energies for the 1D problems

$$E_n = \frac{\hbar^2}{8m} \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} \right), \quad (4.7)$$

while the wave function has form of the product

$$\Psi_{n_1 n_2} = 2 \sqrt{\frac{1}{L_1 L_2}} \sin \frac{n_1 \pi}{L_1} x \cdot \sin \frac{n_2 \pi}{L_2} y, \quad (4.8)$$

where $n_1, n_2 = 1, 2, \dots$

⁷Recall that any stationary state has a trivial time-dependence through the factor $\exp(-i\frac{E}{\hbar}t)$. A standing wave at any time t has a standing-still pattern of the nodes i.e. the points x with $\Psi = 0$.

⁸With the opposite sign, but it does not matter.

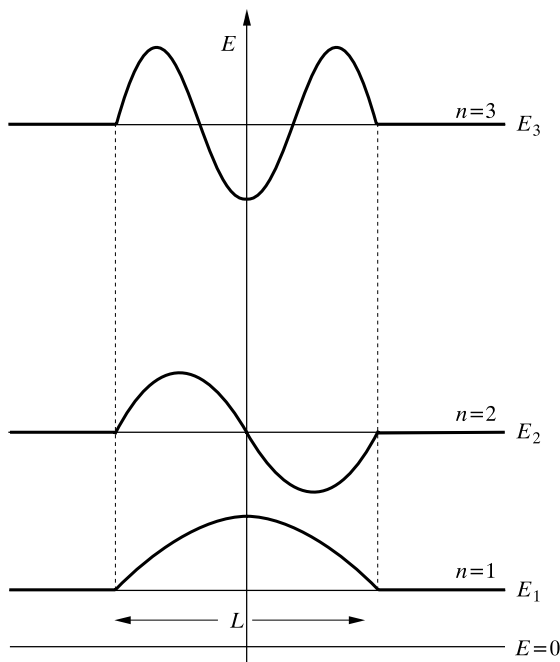


Fig. 4.2. The wave functions for the particle in a box corresponding to $n = 1, 2, 3$. Note the increasing number of nodes, when the energy E_i of the stationary state increases.

Example 1. *Butadiene naively*

The particle-in-box problem has more to do with chemistry than would appear at first glance.

In organic chemistry, we consider some molecules with conjugate double and single bonds, one of the simplest is butadiene: $= - =$.

What does this molecule have to do with the particle in a box? It seems nothing. First, we have not a single particle but 40 particles (10 nuclei and 30 electrons), second, where is this constant potential for the motion of the particle? Nowhere. Third, a molecule does not represent a one-dimensional but a three-dimensional object, and in addition, a curved one instead of a beautiful section of the x axis. It would seem that any attempt to apply such a primitive theory to our molecule is ridiculous and yet in such a difficult situation we will see the power of the exact solutions reported in the present chapter. All above objections are perfectly justified, but let us try to simplify our system a little.

In the molecule under study the CC bonds are “averaged”, which facilitates the motion of the π electrons along the system (this notion will become clear in Chapter 8; the π electrons are loosely bound to the molecule, we may assume that other electrons are always rigidly bound and will therefore be ignored).

If

- we removed the π electrons from the molecule (and put them temporarily into a safe), and then
- “ground up” the remaining (positively charged) molecular core and distributed the ground mass uniformly along the x axis within a section of length L equal to

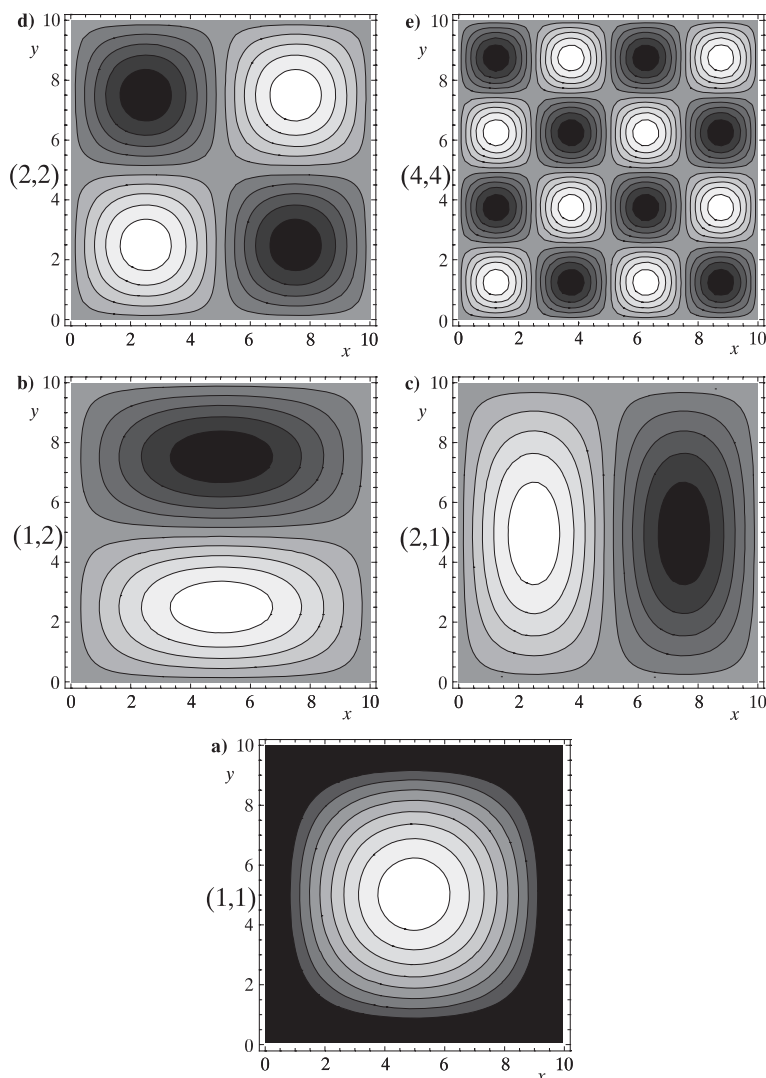


Fig. 4.3. Examples of the wave functions for a particle in a square box, the quantum numbers (n_1, n_2) correspond to: a) $(1, 1)$; b) $(1, 2)$; c) $(2, 1)$; d) $(2, 2)$; e) $(4, 4)$. The background colour corresponds to zero. In the case shown the higher the energy the more nodes in the wave function. This rule is not generally true. For example, in a rectangular box with $L_1 \gg L_2$ even a large increase of n_1 does not raise the energy too much, while introducing a lot of nodes. On the other hand, increasing n_2 by 1 raises the energy much more, while introducing only one extra node. A reader acquainted with hydrogen atom orbitals will easily recognize the resemblance of the above figures to some of them (cf. pp. 180–185), because of the rule mentioned above.

the length of the molecule (averaging the potential energy for a charged particle)
to construct a highway for the π electrons

- added the first π electron from the safe, then

this single electron would represent something similar to a particle in a box.⁹ Assuming this simplified model we know all the details of the electron distribution, including the ground-state and excited-state wave functions (in the one-particle case called the orbitals). If we now took all the π electrons from the safe, added them one by one to the system, assuming that they would not see one another,¹⁰ then taking into account the Pauli exclusion principle (described in more detail in Chapter 8) we would obtain information about the electron density distribution in the molecule. The idea we are describing is called the Free Electron Molecular Orbitals (FEMO) method.

FEMO method

In our example, the total electron density distribution (normalized to four π electrons, i.e. giving 4 after integration over x) is given as¹¹

$$\rho(x) = 2\psi_1^2 + 2\psi_2^2 = 2\frac{2}{L}\sin^2\frac{\pi}{L}x + 2\frac{2}{L}\sin^2\frac{2\pi}{L}x = \frac{4}{L}\left(\sin^2\frac{\pi}{L}x + \sin^2\frac{2\pi}{L}x\right).$$

The function $\rho(x)$ is shown in Fig. 4.4.a.

It is seen that:

1. $\rho(x)$ is the largest on the outermost bonds in the molecule, exactly where chemists put their two little lines to symbolize a double bond.
2. π -electron density, i.e. $\rho(x)$ is non-zero in the centre. This means that the bond over there is not strictly a single bond.

This key information about the butadiene molecule has been obtained at practically no cost from the simple FEMO model.

Of course, we cannot expect the description to reflect all the details of the charge distribution in the butadiene molecule, but one may expect this approach to be able to reflect at least some rough features of the π electron distribution. *If the results of more advanced calculations contradict the rough particle-in-box results, then we should take a closer look at them and search for an error.* This is the strength of the simple exact model systems. They play the role of the beacons – points of reference.

4.2.2 CYCLIC BOX

The 1D box described above is similar to a stick in which the particle can move. The butadiene molecule is rather similar to such a stick and, therefore, the 1D box models it quite well.

⁹Almost, because the potential is not quite constant (ends!). Also one might remove the particle from the box at the expense of a large but finite energy (ionization), which is not feasible for the particle in a box.

¹⁰As we will see in Chapter 8, this approximation is more realistic than it sounds.

¹¹The student “ i ” is characterized by a probability density distribution $\rho_i(x)$ of finding him at coordinate x (we limit ourselves to a single variable, measuring his position, say, on his way from the dormitory to the university). If all students moved independently, the sum of their individual probability densities at point x_0 , i.e. $\rho(x_0) = \sum_i \rho_i(x_0)$ would be proportional to the probability density of finding any student at x_0 . The same pertains to electrons, when assumed to be independent.

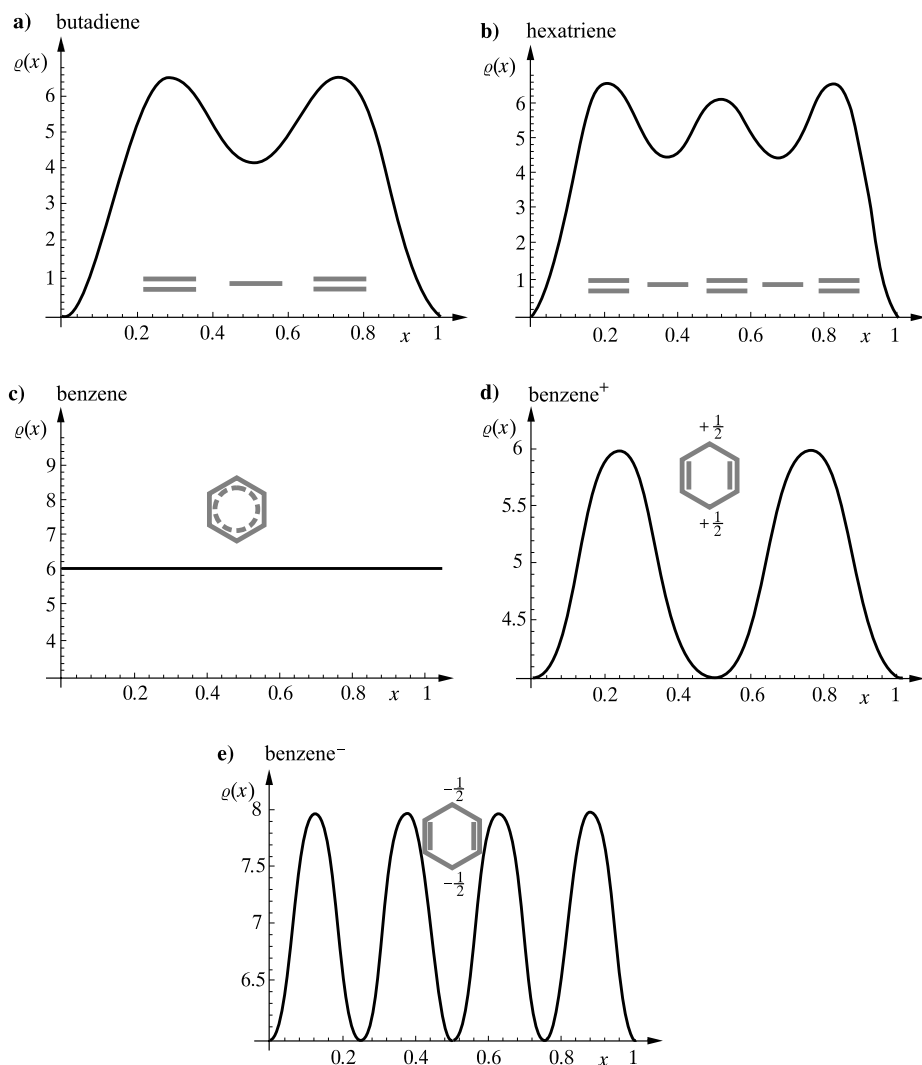


Fig. 4.4. π -electron density charge distributions for several molecules computed by the FEMO method. The length of each molecule L has been assumed to be equal 1. For other lengths the charge distributions are similar. The electron density for four electrons in butadiene (a) and of six electrons in hexatriene (b). The electron density maxima coincide with the positions chemists write as double bonds. The six electron density distribution in the benzene molecule is peculiar, because it is constant along the perimeter of the molecule (c). If we subtract an electron from benzene (d) or add an electron to it (e), then maxima and minima of the π electron density appear. If an electron is subtracted (d) there are two maxima (double bonds) and two π electron deficient regions denoted as having charge $+\frac{1}{2}$. After one electron π is added (e) then we obtain four maxima (two double bonds and two electron-rich regions denoted by charge $-\frac{1}{2}$).

And what can model the benzene molecule? In a crude approximation we may think of benzene as a stick with the two ends *joined* in such a way as to be unable to recognize where the union has taken place. Limiting ourselves to this effect,¹² we may use the solution given by (4.3) and impose appropriate boundary conditions. What could these boundary conditions be? The wave function at the two ends of the box has to be stitched together without leaving any trace of the seam. This is achieved by two boundary conditions: $\Psi(0) = \Psi(L)$ forcing the two wave function values to match and $\Psi'(0) = \Psi'(L)$ making the seam “invisible”. The two conditions mean:

$$\begin{aligned} A \sin \kappa 0 + B \cos \kappa 0 &= A \sin \kappa L + B \cos \kappa L, \\ A \kappa \cos \kappa 0 - B \kappa \sin \kappa 0 &= A \kappa \cos \kappa L - B \kappa \sin \kappa L \end{aligned}$$

or

$$\begin{aligned} B &= A \sin \kappa L + B \cos \kappa L, \\ A &= A \cos \kappa L - B \sin \kappa L. \end{aligned}$$

To find a non-trivial solution the determinant of the coefficients at the unknown quantities A and B has to vanish:¹³

$$\begin{vmatrix} \sin \kappa L & \cos \kappa L - 1 \\ \cos \kappa L - 1 & -\sin \kappa L \end{vmatrix} = 0,$$

which is equivalent to

$$\cos \kappa L = 1.$$

The last condition gives $\kappa L = 2\pi n$, $n = 0, \pm 1, \pm 2, \dots$. This immediately gives a formula for the energy very similar to that for the box with ends, but with the replacement $n \rightarrow 2n$:

$$E_n = \frac{(2n)^2 h^2}{8mL^2}, \quad (4.9)$$

where this time $n = 0, \pm 1, \pm 2, \dots$

The corresponding wave functions are

$$\begin{aligned} \psi_0 &= \sqrt{\frac{1}{L}} \quad \text{for } n = 0, \\ \psi_{n>0} &= A \sin \frac{2\pi n}{L} x + B \cos \frac{2\pi n}{L} x, \\ \psi_{n<0} &= -A \sin \frac{2\pi |n|}{L} x + B \cos \frac{2\pi |n|}{L} x. \end{aligned}$$

¹²And neglecting such effects as the particular shape of the benzene (curvature, etc.).

¹³This is a set of homogeneous linear equations.

Since $\psi_{n>0}$ and $\psi_{n<0}$ correspond to the same energy, any combination of them also represents an eigenfunction of the Schrödinger equation corresponding to the same energy (Appendix B on p. 895). Taking therefore as the new wave functions (for $n \neq 0$) the normalized sum and difference of the above wave functions, we finally obtain the solutions to the Schrödinger equation

$$\begin{aligned}\Psi_0 &\equiv \psi_0 = \sqrt{\frac{1}{L}} \quad \text{for } n = 0, \\ \Psi_{n>0} &= \sqrt{\frac{2}{L}} \sin \frac{2\pi n}{L} x \quad \text{for } n > 0, \\ \Psi_{n<0} &= \sqrt{\frac{2}{L}} \cos \frac{2\pi n}{L} x \quad \text{for } n < 0.\end{aligned}$$

4.2.3 COMPARISON OF TWO BOXES: HEXATRIENE AND BENZENE

Let us take an example of two molecules: hexatriene and benzene (i.e. the cyclohexatriene). Let us assume for simplicity that the length of the hexatriene L is equal to the perimeter of the benzene.¹⁴ Both molecules have 6 π electrons (any of them). The electrons doubly occupy (the Pauli exclusion principle) three one-electron wave functions corresponding to the lowest energies. Let us compute the sum of the electron energies¹⁵ (in the units $\frac{h^2}{8mL^2}$, to have the formulae as compact as possible):

- HEXATRIENE: $E_{\text{heks}} = 2 \times 1 + 2 \times 2^2 + 2 \times 3^2 = 28$,
- BENZENE: $E_{\text{benz}} = 2 \times 0 + 2 \times 2^2 + 2 \times 2^2 = 16$.

We conclude, that 6 π electrons in the benzene molecule correspond to lower energy (i.e. is more stable) than the 6 π electrons in the hexatriene molecule. Chemists find this experimentally: the benzene ring with its π electrons survives in many chemical reactions, whereas this rarely happens to the π -electron system of hexatriene.

Our simple theory predicts the benzene molecule is more stable than the hexatriene molecule.

And what about the electronic density in both cases? We obtain (Fig. 4.4.b,c)

- HEXATRIENE: $\rho(x) = 2 \times \frac{2}{L} [\sin^2 \frac{\pi}{L} x + \sin^2 \frac{2\pi}{L} x + \sin^2 \frac{3\pi}{L} x]$,
- BENZENE: $\rho(x) = 2 \times \frac{1}{L} + 2 \times \frac{2}{L} [\sin^2 \frac{2\pi}{L} x + \cos^2 \frac{2\pi}{L} x] = \frac{6}{L}$.

¹⁴This is to some extent an arbitrary assumption, which simplifies the final formulae nicely. In such cases we have to be careful that the conclusions are valid.

¹⁵As will be shown in Chapter 8, this method represents an approximation.

This is an extremely interesting result.

The π -electron density is constant along the perimeter of the benzene molecule.

No single and double bonds – *all CC bonds are equivalent* (Fig. 4.4.c). Chemical experience led chemists already long time ago to the conclusion that all the C–C bonds in benzene are equivalent. This is why they decided to write down the benzene formula in the form of a regular hexagon with a circle in the middle (i.e. not to give the single and double bonds). The FEMO method reflected that feature in a naive way. Don't the π electrons see where the carbon nuclei are? Of course they do. We will meet some more exact methods in further chapters of this textbook, which give a more detailed picture. The π -electron density would be larger, closer to the nuclei, but *all CC bonds would have the same density distribution*, similar to the solution given by the primitive FEMO method. From (4.9) and the form of the wave functions it follows that this will happen not only for benzene, but also for all the systems with $(4n+2)$ -electrons, $n = 1, 2, \dots$, because of a very simple (and, therefore, very beautiful) reason that $\sin^2 x + \cos^2 x = 1$.

The addition or subtraction of an electron makes the distribution non-uniform (Fig. 4.4.d,e). Also in six π electron hexatriene molecule, uniform electron density is out of the question (Fig. 4.4.b). Note that the maxima of the density coincide with the double bonds chemists like to write down. However, even in this molecule, there is still a certain equalization of bonds, since the π electrons are also where the chemists write a single bond (although the π electron density is smaller over there¹⁶).

Again important information has been obtained at almost no cost.

4.3 TUNNELLING EFFECT

Is it possible to pass through a barrier with less energy than the barrier height? Yes.

4.3.1 A SINGLE BARRIER

Let us imagine a rectangular potential energy barrier (Fig. 4.1.b) for the motion of a particle of mass m : $V(x) = V$ for $0 \leq x \leq a$, with $V(x) = 0$ for other values of x (V is the barrier height). Let us assume that the particles go from left to right and that their energy E is smaller than V . This assumption will make it possible to study the most interesting phenomenon – tunnelling through the barrier.¹⁷ In order to stress that $0 \leq E \leq V$ let us write:

$$E = V \sin^2 \beta. \quad (4.10)$$

¹⁶Where, in the classical picture, no π electron should be.

¹⁷Another interesting question would be what will happen if $E > V$. This question will be postponed for a moment.

The x axis will be divided in three parts:

- region 1 $-\infty < x < 0$,
 region 2 $0 \leq x \leq a$,
 region 3 $a < x < \infty$.

In each of these regions the Schrödinger equation will be solved, then the solutions will be stitched together in such a way as to make it smooth at any boundary. The general solution for each region has the form¹⁸ $\Psi(x) = Ae^{i\kappa x} + Be^{-i\kappa x}$, where A and B are the de Broglie wave amplitudes for motion to the right and to the left. The κ constant comes from the Schrödinger equation $\frac{\partial^2 \Psi}{\partial x^2} + \kappa^2 \Psi = 0$, where $\kappa^2 = \frac{2mE}{\hbar^2}$ for regions 1 and 3 and $\kappa^2 = \frac{2m(E-V)}{\hbar^2}$ for region 2. Therefore, the wave functions for each region is:

$$\Psi_1(x) = A_1 e^{\frac{ix\sqrt{2mE}}{\hbar}} + B_1 e^{-\frac{ix\sqrt{2mE}}{\hbar}}, \quad (4.11)$$

$$\Psi_2(x) = A_2 e^{\frac{-x \cot \beta \sqrt{2mE}}{\hbar}} + B_2 e^{\frac{x \cot \beta \sqrt{2mE}}{\hbar}}, \quad (4.12)$$

$$\Psi_3(x) = A_3 e^{\frac{ix\sqrt{2mE}}{\hbar}} + B_3 e^{-\frac{ix\sqrt{2mE}}{\hbar}}. \quad (4.13)$$

The second equation needs a little derivation, but using eq. (4.10) this is straightforward.

In regions 1 and 2 we may have the particle going right or left (reflection), hence in these regions A and B are non-zero. However, in region 3 we are sure that $B_3 = 0$, because there will be no returning particle (since no reflection is possible in region 3).

Now, the coefficients A and B are to be determined (with accuracy up to a multiplicative constant) in such a way as to ensure that the wave function sections match smoothly. This will be achieved by matching the function values and the first derivatives at each of the two boundaries.¹⁹

As the wave function has to be continuous for $x = 0$ and $x = a$, we obtain the following equations

$$\begin{aligned} A_1 + B_1 &= A_2 + B_2, \\ A_2 \exp\left(-\frac{a \cot \beta \sqrt{2mE}}{\hbar}\right) + B_2 \exp\left(+\frac{a \cot \beta \sqrt{2mE}}{\hbar}\right) \\ &= A_3 \exp\left(\frac{ia\sqrt{2mE}}{\hbar}\right). \end{aligned}$$

¹⁸This is the free particle wave function. The particle has the possibility (and, therefore, certain probability) of going left or right.

¹⁹The second derivative is discontinuous, because of the form of the potential function $V(x)$ introduced.

The continuity of the first derivative at $x = 0$ and $x = a$ gives:

$$\begin{aligned} i(A_1 - B_1) &= \cot(B_2 - A_2), \\ \cot \beta \left(-A_2 \exp\left(-\frac{a \cot \beta \sqrt{2mE}}{\hbar}\right) + B_2 \exp\left(+\frac{a \cot \beta \sqrt{2mE}}{\hbar}\right) \right) \\ &= iA_3 \exp\left(\frac{ia\sqrt{2mE}}{\hbar}\right). \end{aligned}$$

After introducing the abbreviations:

$$k = \exp\left(\frac{a \cot \beta \sqrt{2mE}}{\hbar}\right) \quad \text{and} \quad N = (1 - k^2) \cos 2\beta + i(1 + k^2) \sin 2\beta,$$

we obtain the following ratios of all the coefficients and coefficient A_1 :

$$\begin{aligned} \frac{B_1}{A_1} &= \frac{k^2 - 1}{N}, \quad \frac{A_2}{A_1} = \frac{k^2(1 - \exp(-2i\beta))}{N}, \\ \frac{B_2}{A_1} &= \frac{(\exp(2i\beta) - 1)}{N}, \quad \frac{A_3}{A_1} = \frac{2ik \sin 2\beta \exp(-\frac{ia\sqrt{2mE}}{\hbar})}{N}. \end{aligned}$$

A current in region 3 towards the positive direction of the x axis may be defined as the probability density $A_3^* A_3$ of the particle going right in region 3 times the velocity

$$\sqrt{\frac{2E}{m}} = \sqrt{\frac{2\frac{mv^2}{2}}{m}} = v$$

in this region. Therefore, the current passing through region 3 is equal to

current

$$A_3^* A_3 \sqrt{\frac{2E}{m}} = \frac{4k^2 A_1^* A_1 \sin^2 2\beta}{|N|^2} \sqrt{\frac{2E}{m}}. \quad (4.14)$$

Therefore, the ratio of the current going right in 3 to the current going right in 1 is equal to: $D_{\text{single}} = \frac{|A_3|^2}{|A_1|^2}$ (the *barrier transmission coefficient*, in our case equal to the probability of passing the barrier):

transmission
coefficient

$$D_{\text{single}} = \frac{4k^2 \sin^2(2\beta)}{NN^*} \quad (4.15)$$

- This result is exact (for $0 \leq E \leq V$). Despite its conciseness the formula for D_{single} as a function of E , V looks quite complicated. What does this formula tell us? Below are some questions:
- D_{single} should increase when the particle energy E increases, but is the function $D_{\text{single}}(E)$ monotonic? Maybe there are some “magic” energies at which passage through the barrier becomes easier? Maybe this is what those guys in the movies use, when they go through walls.

The answer is given in Figs. 4.5.a–f. It has been assumed that the particle has the mass of an electron (1 a.u.). From Figs. 4.5.a–c for three barrier heights (V), it follows that the function is monotonic, i.e. the faster the particle the easier it is to pass the barrier – quite a banal result. There are no magic energies.

- How does the function $D_{\text{single}}(V)$ look with other parameters fixed? For example, whether it is easier to pass a low or a high barrier with the same energy, or are there some magic barrier heights. Figs. 4.5.a–c tell us that at a fixed E it is easier to pass a lower barrier and the function is monotonic, e.g., for $E = 0.5$ a.u. $\cong 13.5$ eV the transmission coefficient D_{single} is about 80% for $V = 0.5$, 40% for $V = 1$, and 10% for $V = 2$. No magic barrier heights.
- How does the transmission coefficient depend on the barrier width? From Figs. 4.5.d–f we see that $D_{\text{single}}(a)$ is also monotonic (no magic barrier widths) and dramatically drops, when the barrier width a increases. On the other hand the larger the kinetic energy of the projectile heading towards the barrier the better the chance to cross the barrier. For example, at electron energies of the order of 0.5 a.u. (at fixed $V = 1$ and $m = 1$) the barrier of width 2 a.u. $\simeq 1$ Å allows 6% of the particles to pass, while at energy 0.75 a.u. 18%, and at energy 1 a.u. 30% pass.

What does the wave function of the tunnelling particle look like? The answer is in Fig. 4.6. We see that:

- The real as well as the imaginary parts of the wave function are non-zero in the barrier, i.e. the particle penetrates the barrier.
- Both (real and imaginary) parts decay very rapidly (exponentially) for large penetrations.
- Since the barrier has a finite width, the wave function does not vanish completely within the barrier range. Thus, after leaving the barrier region we again have a wave with the same frequency but with a smaller amplitude than that before the barrier range.²⁰ This means that there is a *non-zero probability that the particle*

²⁰The tunnelling of a particle is certainly a strange phenomenon and our imagination is too poor to figure out how this happens. However, as a matter of fact even in classical mechanics one may be taken by surprise. This happens when we have to do with the probability density distribution of configurations in an ensemble (as we often have to do in statistical thermodynamics and similarly in quantum mechanics). Then we may encounter the notion of “classical tunnelling” (J. Straub, “*New Developments in Theoretical Studies of Proteins*”, ed. R. Elber, World Scientific, 1996), since the mean value of the kinetic energy is lower than the barrier and yet the system overcomes the barrier. Let us put this problem aside.

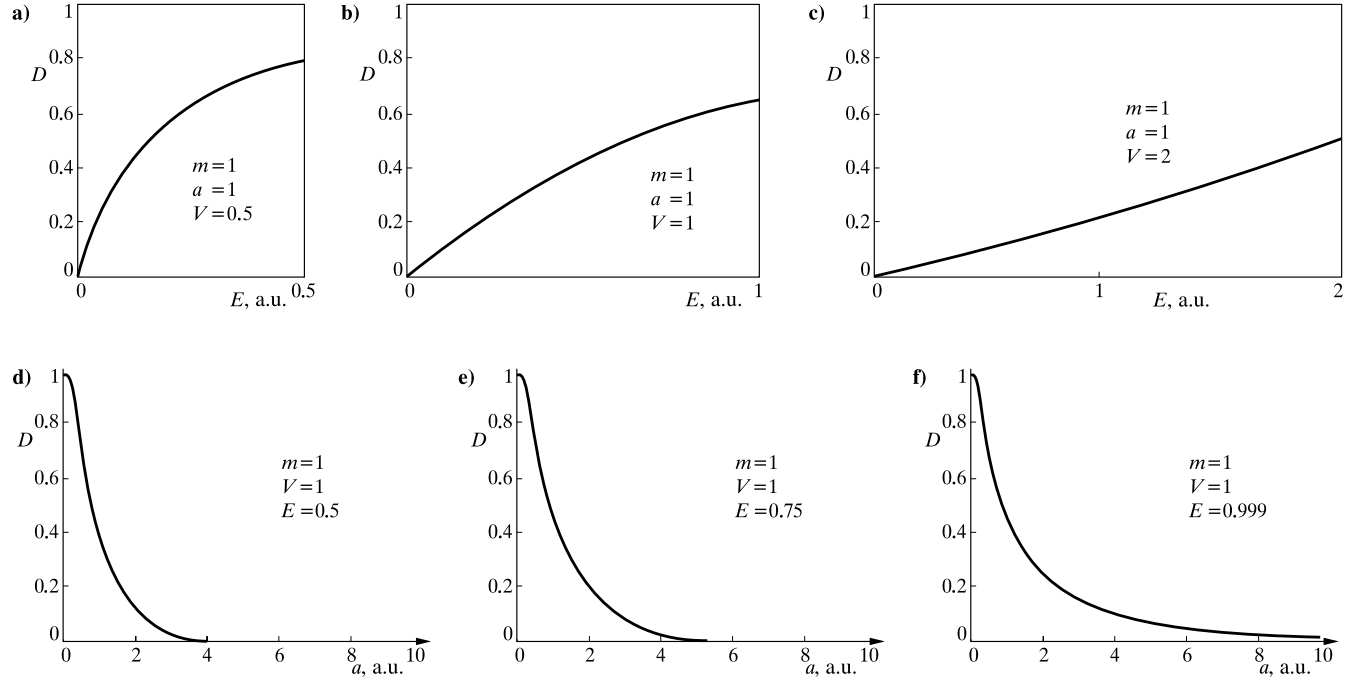


Fig. 4.5. A classical particle cannot tunnel through a barrier, while a quantum particle *can*. The figures show the transmission coefficient (tunnelling) of the electron having various energies (always lower than the barrier) and passing through a barrier of various heights and widths. Figs. a–c show, that the larger the energy the easier to tunnel, also the higher the barrier the harder to pass the barrier (at the same energy of the particle). Figs. d–f show the dependence of the transmission coefficient on the barrier width: the wider the barrier the harder to go through.

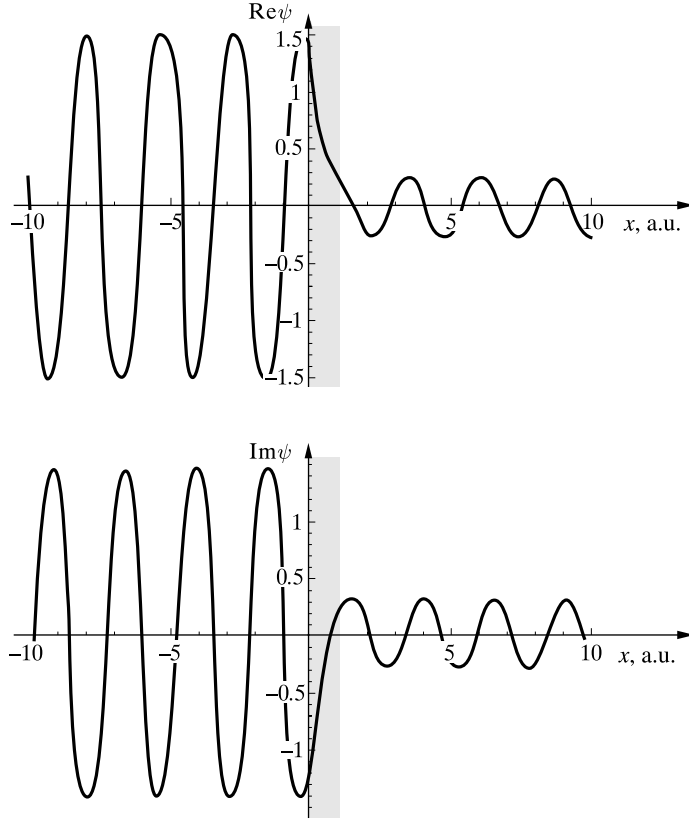


Fig. 4.6. Tunnelling of an electron ($m = 1$) with energy $E = 2.979$ a.u. through a single barrier of height $V = 5$ a.u., and width 1 a.u. The wave function plot (real and imaginary parts) corresponds to the following values of the coefficients $A_1 = 1$ (as a reference), $B_1 = 0.179 - 0.949i$, $A_2 = 1.166 - 0.973i$, $B_2 = 0.013 + 0.024i$, $A_3 = -0.163 - 0.200i$ and represents a wave.

*reflects from the barrier and a non-zero probability that the particle passes through the barrier.*²¹

4.3.2 THE MAGIC OF TWO BARRIERS...

Is there anything magic in life? Yes, there is. If we take *two* rectangular barriers of height V with a well between them (Fig. 4.1.c), then we have magic. This time we allow for any energy of the particle ($E > 0$).

How will the problem be solved?

We have five non-overlapping sections of the x axis. In each section the wave function will be assumed in the form $\Psi(x) = Ae^{i\kappa x} + Be^{-i\kappa x}$ with the corresponding

²¹This remains in general true even if $E > V$.

A and B coefficients, and with $\kappa^2 = \frac{2m(E-V)}{\hbar^2}$. In Section 5, however, the particle goes right and never left, hence $B_5 = 0$. Now, the other coefficients A and B will be determined by stitching the wave function nicely at each of the four boundaries in order to have it going smoothly through the boundary (the wave function values and the first derivative values have to be equal for the left and right section to meet at this boundary). In this way we obtain a set of eight linear equations with eight unknown ratios: $\frac{A_i}{A_1}$, $i = 2, 3, 4, 5$, and $\frac{B_i}{A_1}$, $i = 1, 2, 3, 4$. The most interesting ratio is A_5/A_1 , because this coefficient determines the transmission coefficient through the two barriers. Using the program Mathematica,²² we obtain an amazing result.

Transmission coefficient

Let us check how the transmission coefficient (in our case identical to the transmission probability) changes through two identical barriers of height $V = 5$, each of width $a = 1$, when increasing the impact energy E from 0 to $V = 5$. In general the transmission coefficient is very small. For example, for $E = 2$ the transmission coefficient through the *single* barrier (D_{single}) amounts to 0.028, that is the chance of transmission is about 3%, while the transmission coefficient through the double barrier (D_{double}) is equal to 0.00021, i.e. about 100 times smaller. It stands to reason, it is encouraging. It is fine that it is harder to cross two barriers than a single barrier.²³ And the story will certainly be repeated for other values of E . To be sure, let us scan the whole range $0 \leq E < V$. The result is shown in Fig. 4.7.

Magic energetic gates (resonance states)

There is something really exciting going on. In our case we have three energies $E \leq V$, at which the transmission coefficient D_{double} increases dramatically when compared to the neighbourhood. These are: 0.34, 1.364 and 2.979. Thus, there are three secret energetic gates for going through the double barrier! It is sufficient just to hit the right energy (resonance energy). Is the chance of passing two barriers large? Let us take a look. For all three resonances the transmission coefficient is equal to $D_{\text{double}} = 1$, but it drops down differently when going off resonance. Thus, there are three particle energies, for which the particle goes through the two barriers like a knife through butter, as if the barriers did not exist.²⁴ Moreover, as we can see for the third resonance, the transmission coefficient through the single barrier amounts to $D_{\text{single}} = 0.0669$ (i.e. only 7%), but through two barriers 100%! It looks as if it would be hard for a prisoner to pass through a single armoured prison door, but when the anxious prison governor built a second armoured door behind the first, the prisoner²⁵ disappeared through the two doors like a ghost.²⁶

resonance

²²See the Web Annex, the file Mathematica\ Dwiebar.ma.

²³This is even more encouraging for a prison governor. Of course, a double wall is better than a single one!

²⁴This news should be strictly confidential in penitentiary departments.

²⁵Educated in quantum mechanics.

²⁶There is experimental evidence for such resonance tunnelling through two energy barriers in semiconductors. One of the first reports on this topic was a paper by T.C.L.G. Sollner, W.D. Goodhue, P.E. Tannenwald, C.D. Parker, D.D. Peck, *Appl. Phys. Letters* 43 (1983) 588.

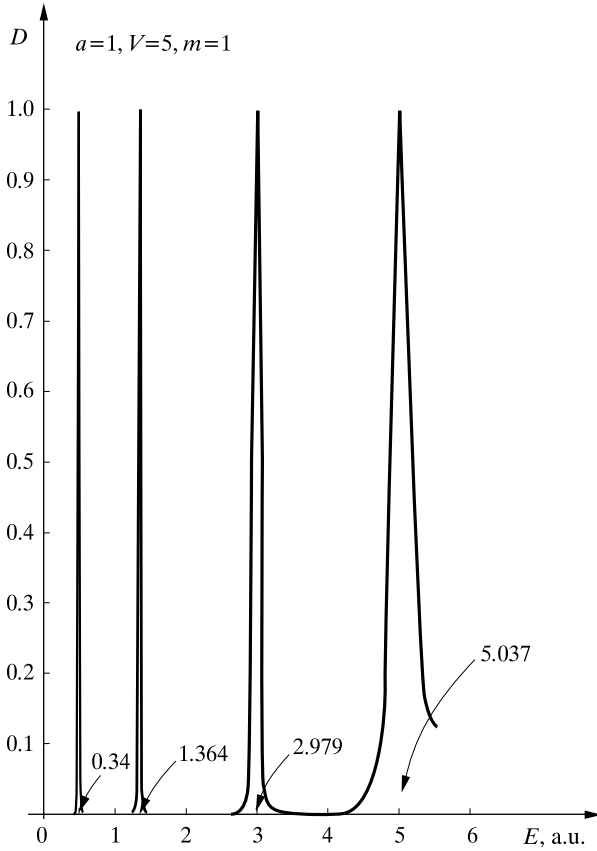


Fig. 4.7. The transmission coefficient (D) for a particle going through a potential double barrier (of height $V = 5$ a.u.) as a function of the particle impact energy E . We see some sudden increases of the transmission coefficient (resonance states).

What happens over there? Let us stress once more that the phenomenon is 100% of a quantum nature, because a classical particle would tunnel neither through the double nor through the single barrier. Why do we observe such dramatic changes in the transmission coefficient for the two barriers? We may have some suspicions. From the time the second barrier is created, a new situation appears: a well *between* the two barriers, something similar to the box discussed earlier.²⁷ A particle in a box has some peculiar energy values: the energies of the stationary states (cf. p. 146). In our situation all these states correspond to a continuum, but something magic might happen if the particle had just one of these energies. Let us calculate the stationary state energies *assuming* that $V = \infty$. Using the atomic units in the energy formula, we have $E_n = \frac{\hbar^2 n^2}{8m L^2} = \frac{\pi^2 n^2}{L^2 2}$. To simplify the formula even more let us take $L = \pi$. Finally, we have simply $E_n = \frac{n^2}{2}$. Hence, we might expect something strange for the energy E equal to $E_1 = \frac{1}{2}$, $E_2 = 2$, $E_3 = \frac{9}{2}$, $E_4 = 8$ a.u., etc. The last energy level, $E_4 = 8$, is already higher than the

²⁷Note, however, that the box has finite well depth and final width of the walls.

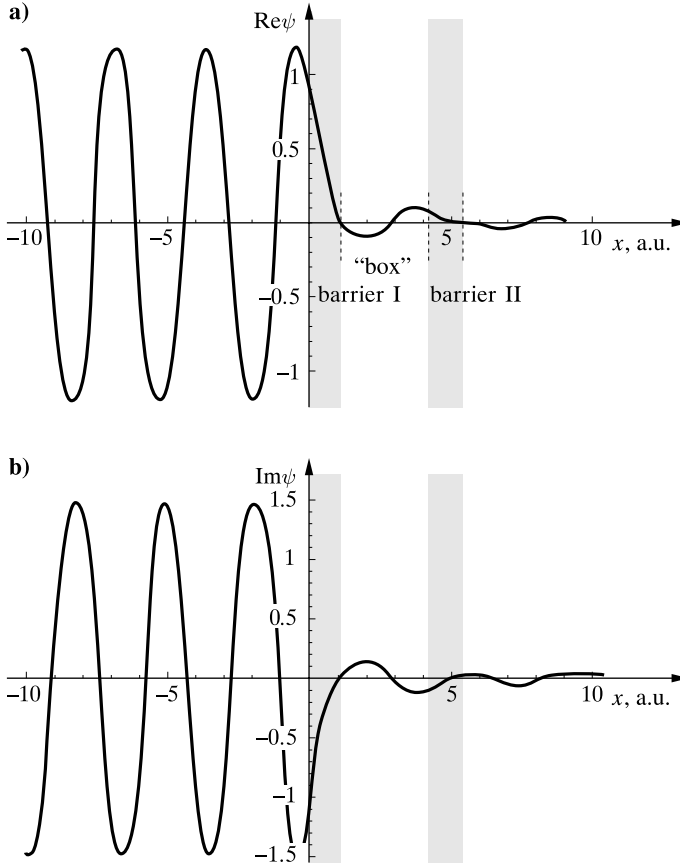


Fig. 4.8. Tunnelling of an electron with energy $E = 2$ a.u. through two barriers of height $V = 5$ and width $a = 1$, the barrier separation is $L = \pi$ (all quantities in a.u.). This is the off-resonance case. The real part of the wave function (a) oscillates before the first barrier, is reduced by an order of magnitude in the first barrier, between the barriers the function oscillates for ca. one period, decays in the second barrier and goes out of the barrier region with an amplitude representing about 5% of the starting amplitude. A similar picture follows from the imaginary part of the wave function (b).

barrier height. Note, however, that the resonance states obtained appear at quite different energies: 0.34, 1.364, 2.979.

Maybe this intuition nevertheless contains a grain of truth? Let us concentrate on E_1 , E_2 , E_3 . One may expect that the wave functions corresponding to these energies are similar to the ground-state (nodeless), the first (single node) and second (two nodes) excited states of the particle in a box. What then happens to the nodes of the wave function for the particle going through two barriers? Here are the plots for the off-resonance (Fig. 4.8) and resonance (of the highest energy, Fig. 4.9) cases.

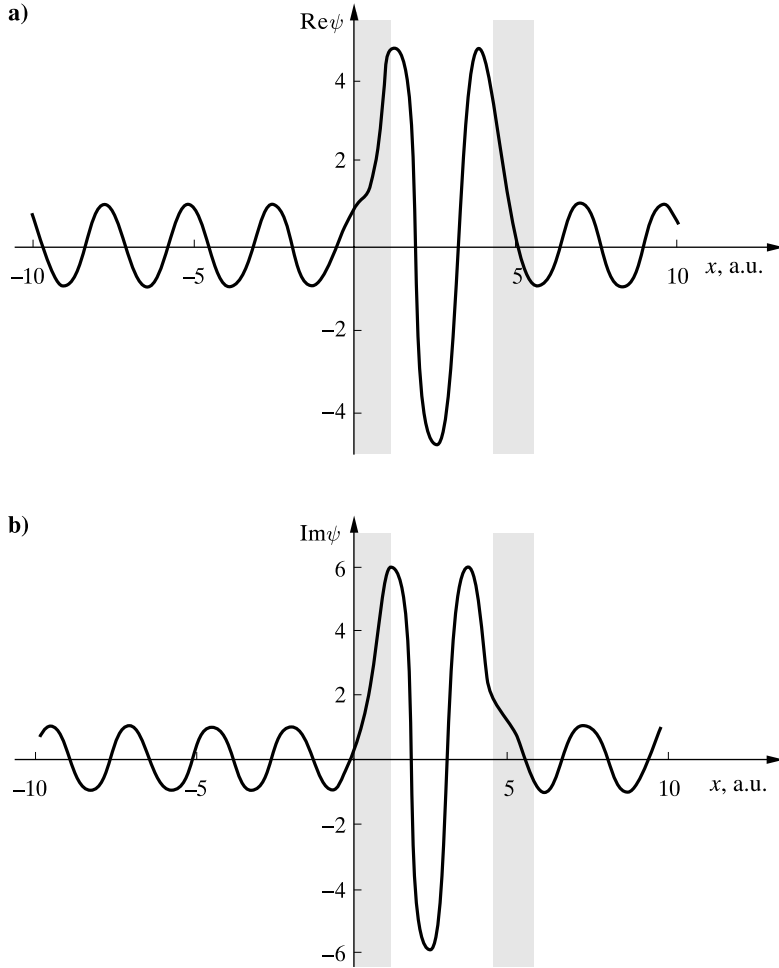


Fig. 4.9. Tunnelling of an electron with energy $E = 2.979$ a.u. through two barriers of height $V = 5$ and width $a = 1$, the barrier separation is $L = \pi$ (all quantities in a.u.). This is the resonance case. The real part of the wave function (a) oscillates before the first barrier with amplitude 1, *increases by a factor of about 3.5* within the first barrier, between the barriers the function makes slightly more than about one period, decays in the second barrier and goes out of the barrier region with an amplitude representing about 100% of the starting amplitude. A similar picture follows from the imaginary part of the wave function (b).

These figures and similar figures for lower-energy resonances support the hypothesis: if an integer number of the half-waves of the wave function fit the region of the “box” between the barriers (“barrier-box-barrier”), in this case we may expect resonance – a secret gate to go through the barriers.²⁸ As we can see, in-

²⁸As one can see in this case, contrary to what happened with a single barrier, the wave function does not vanish exponentially within the barriers.

deed we have been quite close to guessing the reason for the resonances. On the other hand, it turned out that the box length should include not only the box itself but also the barrier widths. Maybe to obtain the right resonance energies we simply have to adjust the box length? Since, instead of resonance at $E_1 = \frac{1}{2}$ we have resonance at energy 0.34, then we may guess that it is sufficient to change the box width L to $L' = \sqrt{\frac{0.5}{0.34}}L = 1.21L$, to make the first resonance energies match. Then, instead of $E_1 = \frac{1}{2}$, we have exactly the first resonance energy equal to $E'_1 = 0.34$, an agreement forced on us. But later, instead of $E_2 = 2$ we obtain $E'_2 = 1.36$, which agrees very well with the second resonance energy 1.364. Then, instead of $E_3 = 4.5$, we obtain $E'_3 = 3.06$, a good approximation to 2.979, but evidently the closer the barrier energy the harder it is to obtain agreement.²⁹ The next resonance state is expected to occur at $E_4 = 8 \times 0.68 = 5.44$, but we have forgotten that this energy already exceeds the barrier height ($V = 5$ a.u.). We will come back to this state in a moment.

Close encounters of the third degree?

Let us consider the two barriers and an electron with *higher energy than the barrier* height V . What will happen? Well, we may say that this means the particle energy is sufficient to pass the barrier. Let us see.

Let us assume the barrier height $V = 5$ and the particle energy is equal to 5.5 a.u. We solve our equations and we obtain transmission coefficient equal to 0.138, hence the electron will bounce back with a probability of about 86%. How it did bounce off? Difficult to say.

Fig. 4.7 shows also the transmission coefficient also for energies higher than the barrier height. It turns out that at energy $E = 5.037$ a.u. (i.e. higher than the barrier height) another resonance state is hidden, which assures certainty (100%) of transmission (whereas the particle energies in the energetic neighbourhood lead to a considerable reflection rate as described above). We expected such behaviour for all $E > V$, but it turned out to be true for the resonance state. Let us recall that we have already predicted “by mistake” a box stationary state with energy $E_4 = 5.44$, higher than the barrier height V . This, and the number of the nodes within the barrier range seen in Fig. 4.10, tells us that indeed this is the state.³⁰

What makes the difference between the resonance and off-resonance states for $E > V$? The corresponding wave functions (real and imaginary parts) are given in Figs. 4.10 and 4.11.

Thus, resonance states may also hide in that part of the continuum which has energy higher than the barriers (with a short life time, because such resonances are

²⁹Note, please, that there is such a thing as resonance width, and that this width is different for each resonance. The most narrow resonance corresponds to the lowest energy, the widest to the highest energy. The width of resonances is related to the notion of the resonance life-time τ (τ is proportional to the inverse of the resonance width).

³⁰It corresponds to a lower energy than we predicted (similar to the case of E_3). No wonder that due to finite well depth, the states corresponding to the upper part of the well “feel” the box is longer.

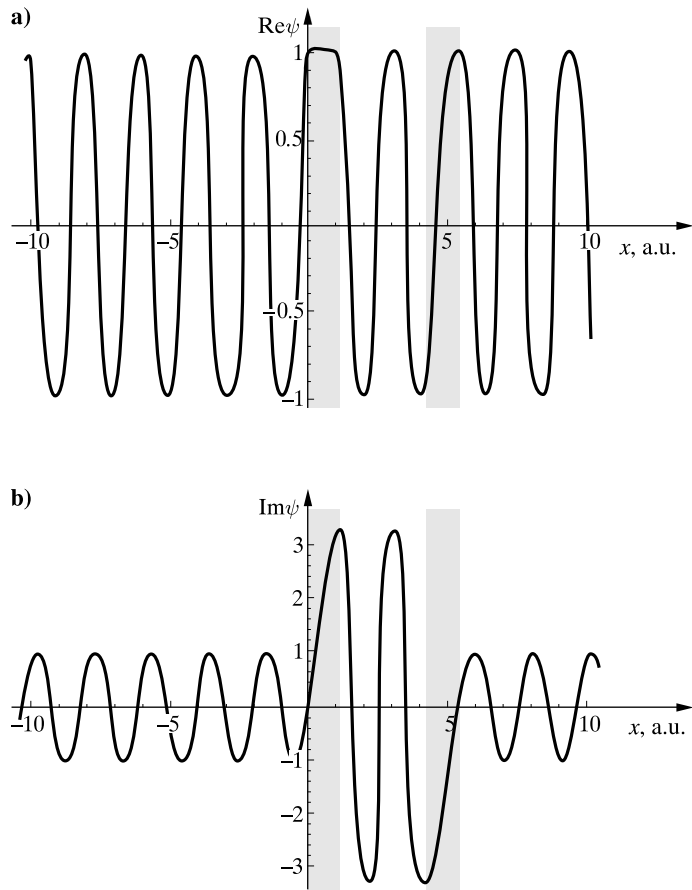


Fig. 4.10. The wave function for an electron with energy $E = 5.037$ a.u., i.e. *over the barrier* $V = 5$ (resonance case). As we can see the amplitude is nearly the same for the wave function before and after the barriers (this means the transmission coefficient of the order of 100%). The real part, and especially the imaginary part both wobble within the range of the barriers range, i.e. within section $(0, 5.14)$ (the imaginary part has a large amplitude). We may guess that the state is related to the three-node stationary state.

wide, cf. Fig. 4.7). They are also a reminder of the stationary states of the particle in a box longer than the separation of the barriers and infinite well depth.

4.4 THE HARMONIC OSCILLATOR

force constant
A one-dimensional harmonic oscillator is a particle of mass m , subject to force $-kx$, where the force constant $k > 0$, and x is the displacement of the particle from its equilibrium position ($x = 0$). This means the force pushes the particle

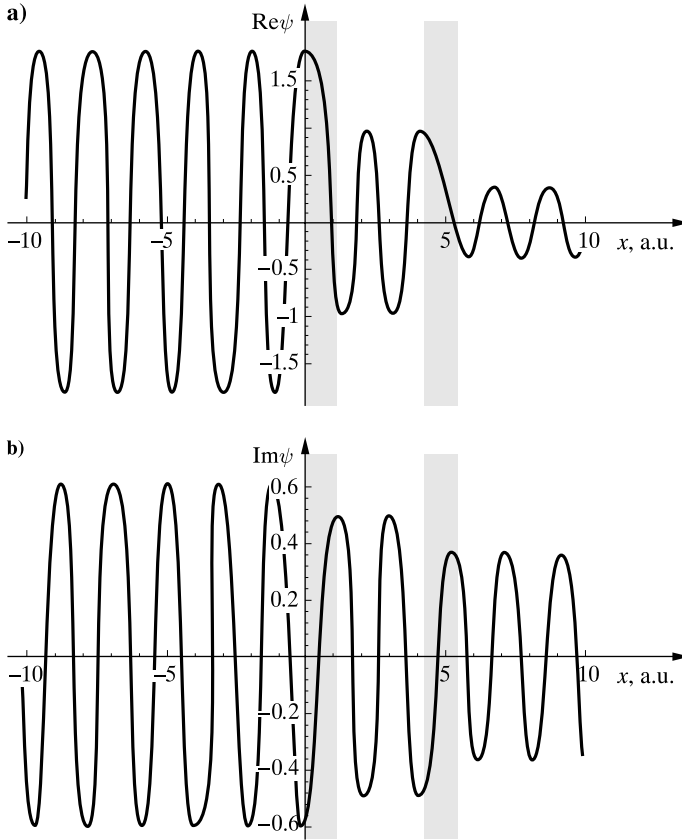


Fig. 4.11. The wave function for an electron in the off-resonance case ($E = 5.5$ a.u., i.e. over the barrier height $V = 5$). Despite the fact that $E > V$, the amplitude of the outgoing wave is considerably reduced after passing the range of the barriers (0, 5.14). This means that the particle flying over the barriers will reflect from them.

always towards the origin, because it has a negative (positive) component for $x > 0$ ($x < 0$). The potential energy is given as a parabola $V = \frac{1}{2}kx^2$, Fig. 4.1.d.

The Schrödinger equation has the following solutions of class Q :

$$\Psi_v(\xi) = N_v H_v(\xi) \exp\left(-\frac{\xi^2}{2}\right) \quad (4.16)$$

with energy

$$E_v = h\nu(v + 1/2), \quad (4.17)$$

vibrational
quantum
number

where h is the Planck constant, $v = 0, 1, 2, \dots$ is the *vibrational quantum number*, the variable ξ is proportional to the displacement x :

$$\xi = \sqrt{\alpha}x, \quad \alpha = \sqrt{\frac{km}{\hbar^2}}, \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

frequency

Hermite
polynomials

is the frequency of the classical vibration of a particle of mass m and a force constant k , H_v represent the Hermite polynomials³¹ (of degree v) defined as³²

$$H_v(\xi) = (-1)^v \exp(\xi^2) \frac{d^v \exp(-\xi^2)}{d\xi^v},$$

and N_v is the normalization constant, $N_v = \sqrt{(\frac{\alpha}{\pi})^{\frac{1}{2}} \frac{1}{2^v v!}}$.

The harmonic oscillator finger print: it has an infinite number of energy levels, all non-degenerate, with constant separation equal to $h\nu$.

Note, that the oscillator energy is never equal to zero.

Fig. 4.12 shows what the wave functions for the one-dimensional harmonic oscillator look like. Fig. 4.13 also shows the plots for a *two-dimensional* harmonic oscillator (we obtain the solution by a simple separation of variables, the wave function is a product of the two wave functions for the harmonic oscillators with x and y variables, respectively).

The harmonic oscillator is one of the most important and beautiful models in physics. When almost nothing is known, except that the particles are held by some

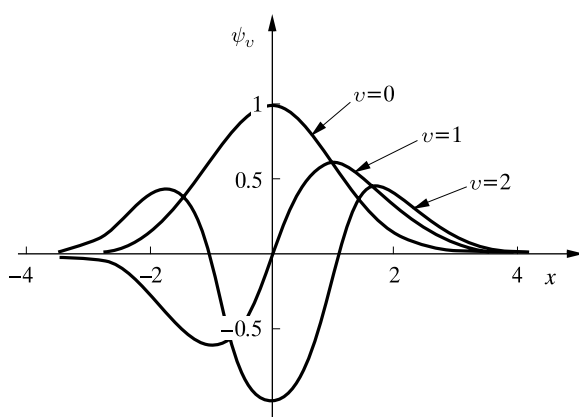


Fig. 4.12. Some of the wave functions Ψ_v for a one-dimensional oscillator. The number of nodes increases with the oscillation quantum number v .

³¹Charles Hermite was French mathematician (1822–1901), professor at the Sorbonne. The Hermite polynomials were defined half a century earlier by Pierre Laplace.

³² $H_0 = 1$, $H_1 = 2\xi$, $H_2 = 4\xi^2 - 2$, etc.

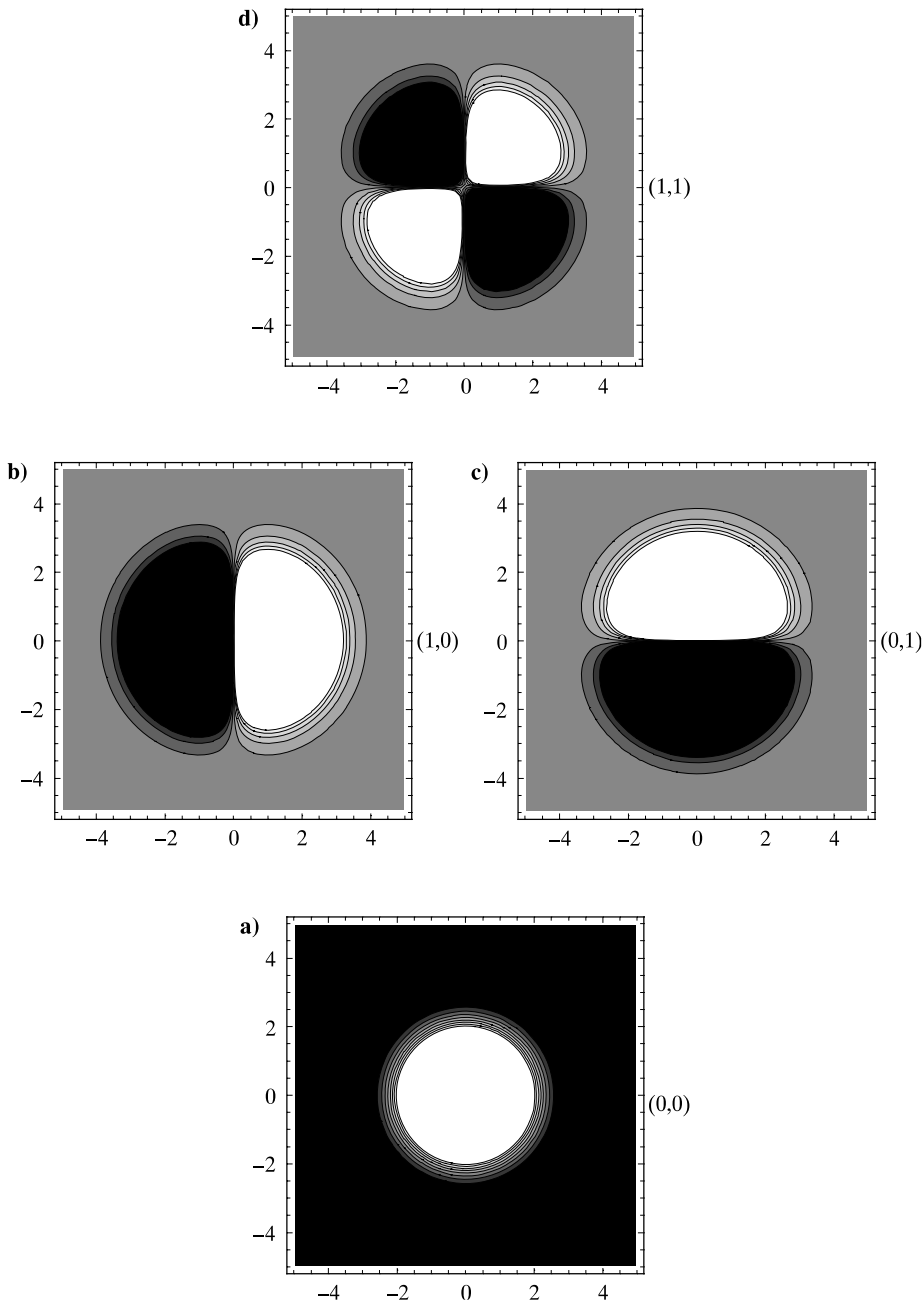


Fig. 4.13. A graphic representation of the 2D harmonic oscillator wave (isolines). The background colour corresponds to zero. Figs. a–i show the wave functions labelled by a pair of oscillation quantum numbers (v_1, v_2) . The higher the energy the larger the number of node planes. A reader acquainted with the wave functions of the hydrogen atom will easily recognize a striking resemblance between these figures and the orbitals.

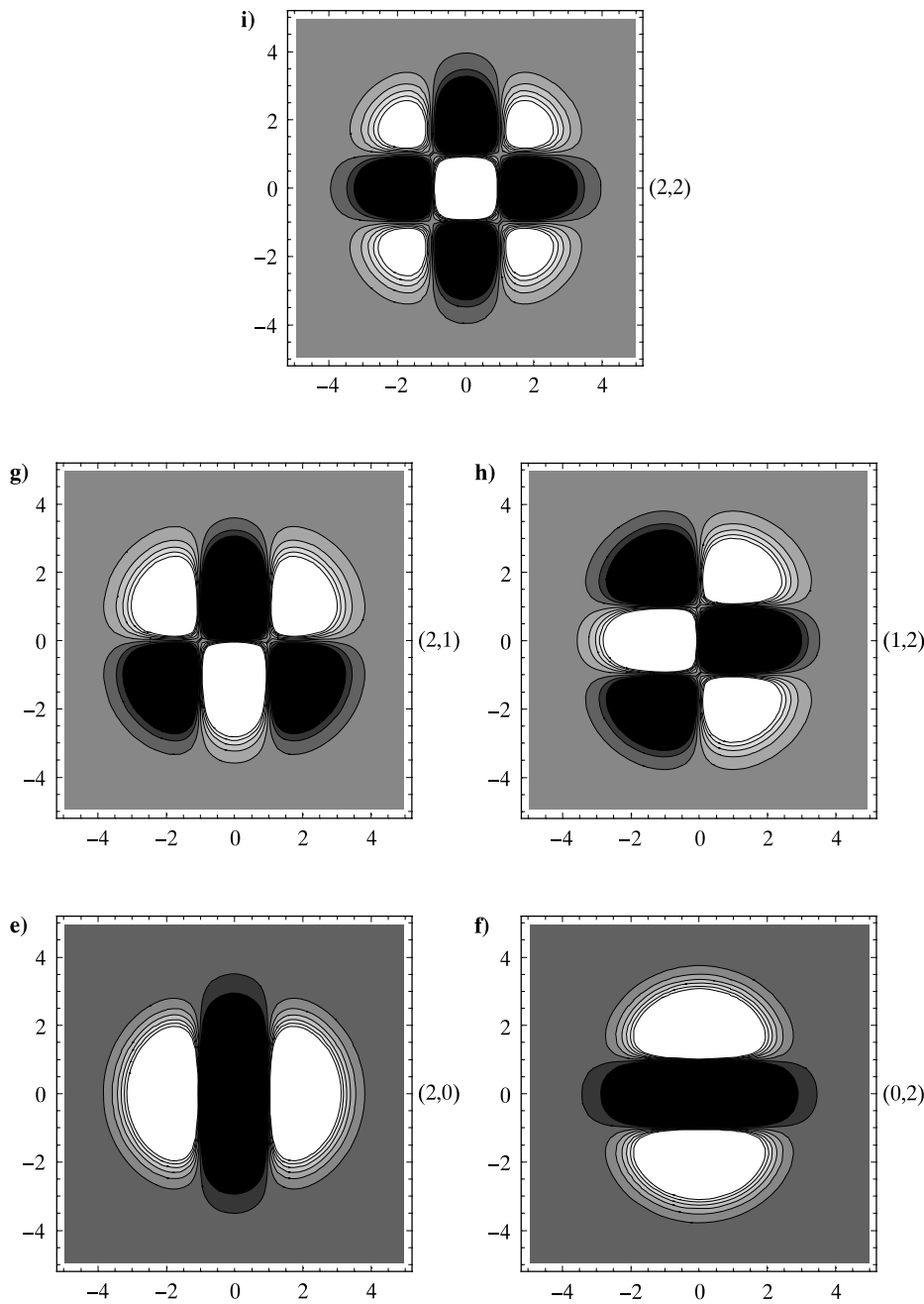


Fig. 4.13. Continued.

forces, then the first model to consider is the harmonic oscillator. This happened for the black body problem (Chapter 1), now it is the case with quantum dots,³³ string theory,³⁴ solvated electron,³⁵ and so on.

4.5 MORSE OSCILLATOR

4.5.1 MORSE POTENTIAL

Diatomic molecules differ from harmonic oscillators mainly in that they may dissociate. If we pull a diatomic molecule with internuclear distance R equal to the equilibrium distance R_e , then at the beginning, displacement $x = R - R_e$ is indeed proportional to the force applied, but afterwards the pulling becomes easier and easier. Finally, the molecule dissociates, i.e. we separate the two parts without any effort at all. This fundamental difference with respect to the harmonic oscillator is qualitatively captured by the potential proposed by Morse (parameter $\alpha > 0$):³⁶

$$V(x) = De^{-\alpha x}(e^{-\alpha x} - 2). \quad (4.18)$$

As we can see (Fig. 4.14), D represents the well depth and, the parameter α decides its width. When the displacement $x = 0$, then the function attains the minimum $V = -D$, and when $x \rightarrow \infty$, then $V \rightarrow 0$.

The Morse oscillator will serve as a model of a diatomic molecule. In such a case $x = R - R_e$, where R_e means the length of the molecule which corresponds to the potential energy minimum. Besides the above mentioned advantage, the Morse oscillator differs from real diatomics mainly by two qualitative features. First, for $R = 0$ we obtain a *finite* potential energy for the Morse oscillator, second, the asymptotic behaviour of the Morse oscillator for $x \rightarrow \infty$ means exponential asymptotics, while the atomic and molecular systems at large distances interact as $\frac{1}{R^n}$.

The second derivative of $V(x)$ calculated at the minimum of the well represents the force constant k of the oscillator

$$k = 2\alpha^2 D. \quad (4.19)$$

Parabola $-D + \frac{1}{2}kx^2$ best approximates $V(x)$ close to $x = 0$ and represents the harmonic oscillator potential energy (with the force constant k). The Morse

³³A part of the “nanotechnology”: some atomic clusters are placed (*quantum dots*) on a solid surface, lines of such atoms (*nanowires*), etc. Such systems may exhibit unusual properties.

³⁴Quarks interact through exchange of gluons. An attempt at separating two quarks leads to such a distortion of the gluon bond (string) that the string breaks down and separates into two strings with new quarks at their ends created from the distortion energy.

³⁵Many polar molecules may lower their energy in a liquid by facing an extra electron with their positive pole of the dipole. This is the *solvated electron*.

³⁶Philip McCord Morse (1903–1985) was American theoretical physicist.

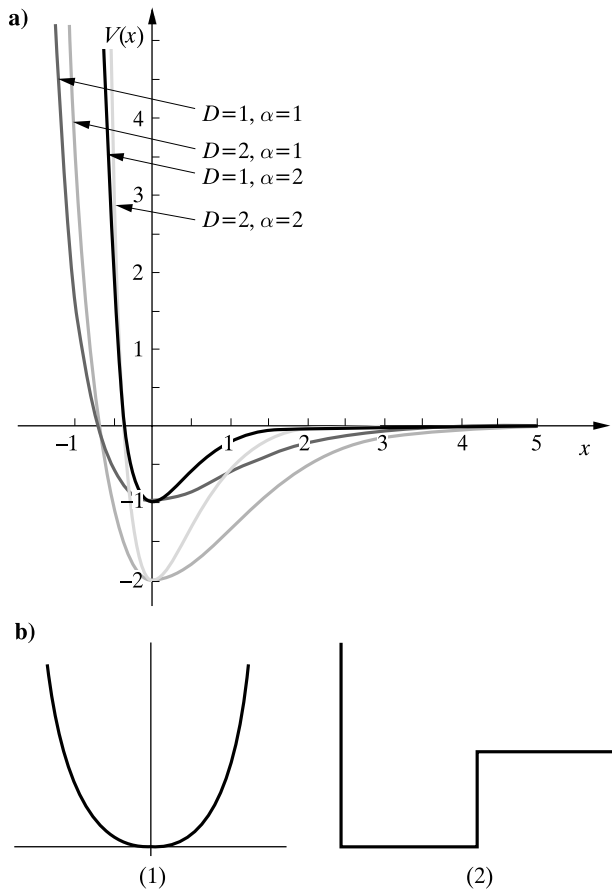


Fig. 4.14. (a) The Morse potential energy curves have the shape of a hook. How does the shape depend on the Morse parameters? The figures show the curves for $D = 1, 2$ and $\alpha = 1, 2$. As we can see D controls the well depth and α its width. (b) the Morse oscillator is a kind of compromise between the harmonic oscillator (b1) and a rectangular well (b2). Both potentials correspond to exact solutions of the Schrödinger equation. Model b2 gives the discrete spectrum as well as the continuum and the resonance states. The later ones are only very rarely considered for the Morse oscillator, but they play an important role in scattering phenomena (primarily in reactive collisions).

oscillator is hard to squeeze – the potential energy goes up faster than that of the harmonic oscillator with the same force constant k .

4.5.2 SOLUTION

One had to have courage to presume that analytical solution with such a potential energy exists. The solution was found by Morse. It represents a rare example of an exact solution to a non-linear problem. Exact solutions exist not only for the ground (vibrational quantum number $v = 0$) but also for all the excited states ($v = 1, 2, \dots, v_{\max}$) belonging to the discrete spectrum. The energy levels are non-degenerate and are given by the formula:

$$E_v = -D + h\nu\left(v + \frac{1}{2}\right) - h\nu\left(v + \frac{1}{2}\right)^2 \beta, \quad v = 1, 2, \dots, v_{\max}, \quad (4.20)$$

where using atomic units we obtain

$$h\nu = 2\alpha \left(\frac{D}{2\mu} \right)^{\frac{1}{2}}. \quad (4.21)$$

This formula follows from the parabolic approximation of the Morse potential (valid for small displacements x),³⁷ while

$$\beta = \alpha \left(\frac{1}{8\mu D} \right)^{\frac{1}{2}}, \quad (4.22)$$

where μ is the mass of the oscillating particle. When the Morse oscillator serves as a model of a diatomic molecule, μ stands for the reduced mass of both nuclei $\mu = (1/m_1 + 1/m_2)^{-1}$ (Appendix I on p. 971). As we can see, the energy of the oscillator never equals zero (similar to the harmonic oscillator) and that

the separation between consecutive energy levels decreases.

The wave functions are slightly more complicated than those for the harmonic oscillator and are given by the formula:

$$\psi_v = N_v e^{-\frac{z}{2}} z^{b_v} L_v^{2b_v}(z), \quad (4.23)$$

where the normalization coefficient

$$N_v = \sqrt{\frac{2b_v v!}{\Gamma(2b_v + v + 1)}} \quad \text{with } \Gamma(z) = \int_0^\infty e^{-t} t^{z-1} dt,$$

z is a real number related to displacement x by the formula $z = 2ae^{-\alpha x}$, while

$$a = \frac{\sqrt{2\mu D}}{\alpha}, \quad (4.24)$$

$$b_v = a - \frac{1}{2} - v > 0. \quad (4.25)$$

The above condition gives maximum $v = v_{\max}$ and, therefore, $v_{\max} + 1$ is the number of eigenfunctions. Thus, we always have a finite number of energy levels.

³⁷Let us recall that, for the harmonic oscillator $2\pi\nu = \sqrt{\frac{k}{\mu}}$, therefore, from (4.19) $h\nu = \hbar\alpha\sqrt{\frac{2D}{\mu}}$, while $\hbar = 1$ a.u.

L stands for the polynomial given by the formula

$$L_n^c(x) = \frac{1}{n!} e^x x^{-c} \frac{d^n}{dx^n} (e^{-x} x^{n+c}), \quad (4.26)$$

where $n = 0, 1, 2, \dots$ is the polynomial degree.³⁸ A short exercise gives

$$\begin{aligned} L_0^c(x) &= 1, \\ L_1^c(x) &= (c+1) - x, \\ L_2^c(x) &= \frac{1}{2}x^2 - (c+2)x + \frac{1}{2}(c+1)(c+2), \\ &\dots \end{aligned}$$

This means the number of nodes in a wave function is equal to v (as in the harmonic oscillator). The lowest energy level is, therefore, nodeless.

4.5.3 COMPARISON WITH THE HARMONIC OSCILLATOR

For very large well depths (D), the parameter β of eq. (4.22) becomes very small. This results in E_v approaching the corresponding formula for the harmonic oscillator $-D + h\nu(v + 1/2)$, and the energy levels become equidistant with the nearest neighbour separation equal to $h\nu$. The potential is highly anharmonic (of the “hook-type”), but the energy levels would be equidistant as in the harmonic oscillator. Is it possible? Yes, it is. The key is that, for small values of v , the term $-h\nu(v + 1/2)^2\beta$ does not yet enter into play and low-energy levels correspond to small amplitudes (x) of vibrations. For small x , the potential is close to parabolic³⁹ – as for the harmonic oscillator with force constant k .

4.5.4 THE ISOTOPE EFFECT

As we can see from eq. (4.21), $h\nu$ is large for narrow (large α) and deep (large D) wells, and for light oscillators (small μ). In particular, when we consider the ground states of two molecules that differ by an isotope substitution, the molecule with the heavier isotope (larger μ), would have lower energy than that corresponding to the light-isotope. This may be seen from the approximate formula for the energy $-D + \frac{1}{2}h\nu$ (zero-vibration energy).⁴⁰

This effect was also present in the harmonic oscillator. When β becomes larger this picture is modified. The larger ν , the larger the modification of the energies of the stationary states (see the last term in the formula for E_v).

Fig. 4.15 shows three different Morse curves and the calculated energy levels.

³⁸Indeed, n -time derivation gives $e^{-x} x^{n+c}$ as a term with the highest power of x . Multiplication by $e^x x^{-c}$ gives x^n .

³⁹As witnessed by a Taylor expansion of $V(x)$ for $x = 0$.

⁴⁰We have to stress that V is almost identical for both molecules, as will be explained in Chapter 6. The energy difference comes, therefore, mainly from the zero-vibration (i.e. $v = 0$) energy difference.

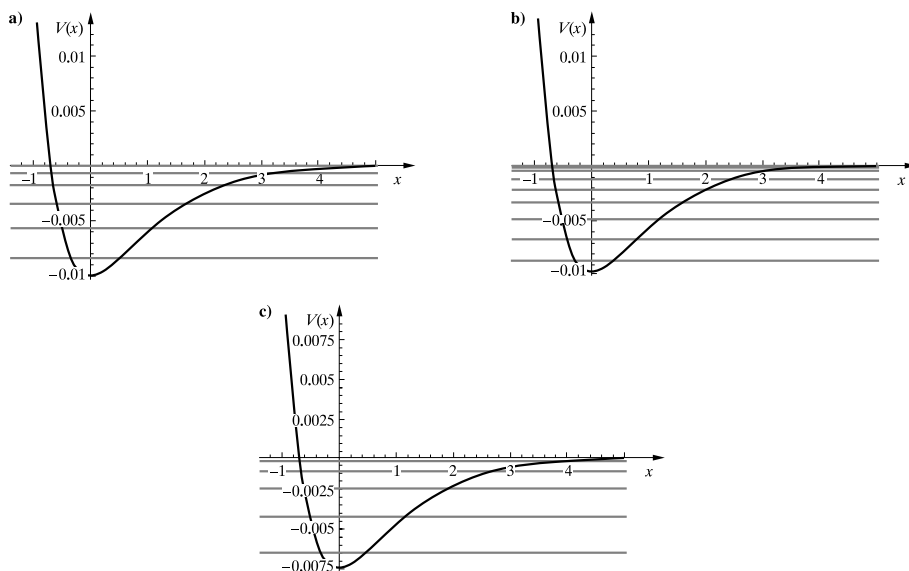


Fig. 4.15. The isotope effect and the effect of bond weakening. The Morse curve (a) corresponds to $D = 0.01$ a.u. and $\alpha = 1$. The calculated energy levels correspond to a proton mass $\mu = 1840$ a.u. The Morse curve (b) is identical, but an isotope substitution (deuteron instead of the proton) has been made. As a result we obtain a larger number of vibrational levels, the levels are closer each other and the system becomes more stable. The Morse curve (c) corresponds to $D = 0.008$ a.u., i.e. it is less deep by 20% with respect to curve (a). As we can see, the number of stationary states has diminished.

The two first curves are identical (Fig. 4.15 a and b) and illustrate the isotope effect. When calculating the energy levels in case of a (or b), the reduced mass of the proton (or deuteron) has been taken.⁴¹ As we can see in the deuteron case, the number of energy levels has increased (from 6 to 9), the levels lowered and have become closer, when compared to the proton case.

ISOTOPE EFFECT (after substitution by a heavy isotope)
results mainly in decreasing the zero-vibration energy, as well as in lowering and condensing higher energy levels.

Eq. (4.21) shows that the ratio of the OD bond frequency to the OH bond frequency is equal to the square root of the inverse reduced masses of D-substituted

⁴¹Why these masses? Let us imagine that the oscillators are the molecules OH and OD. The reduced masses for these two cases are equal to 0.94 and 1.78 of the proton mass, respectively, which is *close* to the proton and deuteron masses, respectively (these have been used in the example). In the system of two nuclei (the heavy oxygen and the light hydrogen) the light atom (hydrogen) is mainly responsible for the oscillatory motion, which justifies the choice made.

and H-substituted compounds, which may be approximated as:⁴²

$$\frac{\nu_{OD}}{\nu_{OH}} \cong \sqrt{\frac{m_H}{m_D}} \cong 0.7. \quad (4.27)$$

The red shift ($\nu_{OD} < \nu_{OH}$) in the IR spectrum represents one of the main characteristics of deuteration. The effect is used in spectroscopy to check whether a band is indeed the OH band. In such a case, the substance is dissolved in heavy water, and after a while the OH functional groups are replaced by OD functional groups. If the IR spectrum is registered again and compared with the previous one showing a red shift in agreement with (4.27), this proves that indeed we were concerned with an OH band.

4.5.5 BOND WEAKENING EFFECT

The condition $b_v > 0$ determines the number of vibrational levels, which may be accommodated by a potential well. This number is always finite. The key number, b_v , depends on a , whereas a is determined by μ , D and α . First of all, we can see that we may have a beautiful well which is unable to accommodate even a single vibrational energy level. This may happen if $b_0 < 0$, which, as seen from (4.25), requires $a \leq \frac{1}{2}$. Such a condition may be fulfilled because of a too shallow well (small D), or too light nuclei (small μ) or a too narrow well (large α). Even if in such a case there is no stationary vibrational state, such a shallow potential energy well may be detected in scattering experiments through the appearance of some resonance states. Such states are called *encounter complexes*.

The third curve (Fig. 4.15.c) differs only by reducing the binding energy (D) with respect to the first curve, which in real situations is similar to a bond weakening. As we can see, the number of stationary states has decreased to 5. We may imagine that, in the extreme, the curve may become very shallow and unable to accommodate any vibrational level. In such a case, even if the binding energy (i.e. the well depth) is non-zero, the molecule will sooner or later dissociate.

4.5.6 EXAMPLES

Example 2. Hydrogen molecule

The hydrogen molecule has been investigated in detail. As will be seen in Chapters 6 and 10 the theory challenges some very subtle experiments. Let us approximate the most accurate theoretical potential energy curve⁴³ (as a function of the internuclear distance R) by a Morse curve.

Is such an approximation reasonable? Let us see. From Wolniewicz's calculations we may take the parameter $D = 109.52 \text{ kcal/mol} = 38293 \text{ cm}^{-1}$, while the

⁴²In our example from Fig. 4.15 the ratio equals 0.73, while simply taking the masses instead of the reduced masses, gives this ratio equal 0.71.

⁴³L. Wolniewicz, *J. Chem. Phys.* 103 (1995) 1792.

parameter α is chosen in such a way as to reproduce the theoretical binding energy for $R = R_e + 0.4$ a.u.,⁴⁴ where $R_e = 1.4$ a.u. is the position of the minimum binding energy. It turns out that, say, “by chance” this corresponds to $\alpha = 1$. From eq. (4.24) and eq. (4.25) we obtain $a = 17.917$ and the allowed v are those satisfying the inequality $b_v = 17.417 - v > 0$. We expect, therefore, 18 energy levels with $v = 0, 1, \dots, 17$ for H_2 and 25 energy levels for T_2 (in the last case $b_v = 24.838 - v > 0$). Accurate calculations of Wolniewicz give 14 vibrational levels for H_2 , and 25 levels for T_2 . Moreover, from eq. (4.21) we obtain for H_2 : $h\nu = 0.019476$ a.u. = 4274 cm^{-1} , while from eq. (4.22) we have $\beta = 0.0279$. From these data one may calculate the energetic gap between the ground ($v = 0$) and the first excited state ($v = 1$) for H_2 , $\Delta E_{0 \rightarrow 1}$, as well as between the first and the second excited states, $\Delta E_{1 \rightarrow 2}$. We get:

$$\Delta E_{0 \rightarrow 1} = h\nu - h\nu[(1 + 1/2)^2 - (0 + 1/2)^2]\beta = h\nu(1 - 2\beta),$$

$$\Delta E_{1 \rightarrow 2} = h\nu - h\nu[(2 + 1/2)^2 - (1 + 1/2)^2]\beta = h\nu(1 - 4\beta).$$

Inserting the calculated $h\nu$ and β gives $\Delta E_{0 \rightarrow 1} = 4155 \text{ cm}^{-1}$ and $\Delta E_{1 \rightarrow 2} = 3797 \text{ cm}^{-1}$. The first value agrees very well with the experimental value⁴⁵ 4161 cm^{-1} . Comparison of the second value with the measured value 3926 cm^{-1} is a little bit worse, although it is still not bad for our simple theory. The quantity D represents the *binding energy*, i.e. the energy difference between the well bottom and the energy of the dissociated atoms. In order to obtain the dissociation energy we have to consider that the system does not start from the energy corresponding to the bottom of the curve, but from the level with $v = 0$ and energy $\frac{1}{2}h\nu$, hence our estimation of the *dissociation energy* is $E_{\text{diss}} = D - \frac{1}{2}h\nu = 36156 \text{ cm}^{-1}$, while the experimental value amounts to 36118 cm^{-1} .

binding energy

dissociation
energy

Example 3. Two water molecules

The above example pertains to a chemical bond. Let us take, in the same way, a quite different situation where we have relatively weak intermolecular interactions, namely the hydrogen bond between two water molecules. The binding energy in such a case is of the order of $D = 6 \text{ kcal/mol} = 0.00956 \text{ a.u.} = 2097 \text{ cm}^{-1}$, i.e. about twenty times smaller as before. To stay within a single oscillator model, let us treat each water molecule as a point-like mass. Then, $\mu = 16560$ a.u. Let us stay with the same value of $\alpha = 1$. We obtain (p. 171) $a = 17.794$ and hence $b_0 = 17.294$, $b_1 = 16.294$, \dots , $b_{17} = 0.294$, $b_{n>17} < 0$. Thus, (accidentally) we also have 18 vibrational levels.

This time from (4.21), we have $h\nu = 0.001074 \text{ a.u.} = 235 \text{ cm}^{-1}$, and $\beta = 0.02810 \text{ a.u.}$, therefore $\Delta E_{0 \rightarrow 1} = 222 \text{ cm}^{-1}$ and $\Delta E_{1 \rightarrow 2} = 209 \text{ cm}^{-1}$. These numbers have the same order of magnitude as those appearing in the experiments (cf. p. 303).

⁴⁴This choice is of course arbitrary.

⁴⁵I. Dabrowski, *Can. J. Phys.* 62 (1984) 1639.

4.6 RIGID ROTATOR

A rigid rotator is a system of two point-like masses, m_1 and m_2 , with a constant distance R between them. The Schrödinger equation may be easily separated giving two equations, one for the centre-of-mass motion and the other for the relative motion of the two masses (see Appendix I on p. 971). We are interested only in the second equation, which describes the motion of a particle of mass equal to the reduced mass of the two particles μ , and position in space given by the spherical coordinates R, θ, ϕ , where $0 \leq R < \infty$, $0 \leq \theta \leq \pi$, $0 \leq \phi \leq 2\pi$. The kinetic energy operator is equal to $-\frac{\hbar^2}{2\mu}\Delta$, where the Laplacian Δ represented in the spherical coordinates is given in Appendix H on p. 969. Since R is a constant, the part of the Laplacian which depends on the differentiation with respect to R is absent.⁴⁶ In this way we obtain the equation (equivalent to the Schrödinger equation) for the motion of a particle on a sphere:

$$-\frac{\hbar^2}{2\mu R^2} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{(\sin \theta)^2} \frac{\partial^2}{\partial \phi^2} \right\} Y = EY, \quad (4.28)$$

where $Y(\theta, \phi)$ is the wave function to be found, and E represents the energy. This equation may be rewritten as (Y is also an eigenfunction of \hat{J}^2):

$$\hat{J}^2 Y = 2\mu R^2 EY, \quad (4.29)$$

where \hat{J}^2 is the square of the angular momentum operator.

Eq. (4.28) may be also written as

$$\frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{(\sin \theta)^2} \frac{\partial^2 Y}{\partial \phi^2} \right\} = \lambda,$$

where $\lambda = -\frac{2\mu R^2}{\hbar^2}E$. The solution of the equation is known in mathematics as a *spherical harmonic*,⁴⁷ it exists if $\lambda = -J(J+1)$, $J = 0, 1, 2, \dots$:

$$Y_J^M(\theta, \phi) = N_{JM} \cdot P_J^{|M|}(\cos \theta) \cdot \frac{1}{2\pi} \exp(iM\phi) \quad (4.30)$$

⁴⁶This reasoning has a heuristic character, but the conclusions are correct. Removing an operator is a subtle matter. In the correct solution to this problem we have to consider the two masses with a variable distance R with the full kinetic energy operator and potential energy in the form of the Dirac delta function (see Appendix E on p. 951) $-\delta(R - R_0)$.

⁴⁷There are a few definitions of the spherical harmonics in the literature (see E.O. Steinborn, K. Ruedenberg, *Advan. Quantum Chem.* 7 (1973) 1). The Condon–Shortley convention often is used, and is related to the definition given above in the following way: $Y_J^M = \varepsilon_M [Y_J^M]_{CS}$, $Y_J^J = (-1)^J [Y_J^J]_{CS}$, where $\varepsilon_M = i^{|M|+M}$.

where $N_{JM} = \sqrt{\frac{(2J+1)}{2} \frac{(J-|M|)!}{(J+|M|)!}}$ is the normalization coefficient, and P is the *associated Legendre polynomial*⁴⁸ defined as

associated
Legendre
polynomials

$$P_J^{|M|}(x) = (1-x^2)^{\frac{|M|}{2}} \frac{d^{|M|}}{dx^{|M|}} P_J(x) \quad (4.31)$$

with the *Legendre polynomial*

Legendre
polynomial

$$P_J(x) = \frac{1}{2^J J!} \frac{d^J}{dx^J} (x^2 - 1)^J. \quad (4.32)$$

From the uniqueness of the solution (Fig. 2.5.g,h) it follows that M has to be an integer.⁴⁹ The solution exists if $J = 0, 1, 2, 3, \dots$, and from the analysis of the associated Legendre polynomials, it follows that M cannot exceed⁵⁰ J , because otherwise $Y = 0$. The energetic levels are given by

quantum
number M

$$E_J = J(J+1) \frac{\hbar^2}{2\mu R^2} \quad \text{for } J = 0, 1, 2, \dots \quad (4.33)$$

It is seen that the lowest energy level ($J = 0$) corresponds to $Y_0^0 = \text{const}$ (the function is, of course, nodeless, Fig. 4.16.a). This means that all orientations of the rotator are of equal probability. The first excited state corresponds to $J = 1$ and is triply degenerate, since $M = 0, \pm 1$. The corresponding wave functions are: $Y_1^0 = \cos \theta$, $Y_1^1 = \sin \theta \exp(i\phi)$, $Y_1^{-1} = \sin \theta \exp(-i\phi)$. The first function, being real, may be easily plotted (Fig. 4.16.b), while the second and the third are not (they are complex). Since they both correspond to the same eigenvalue of the Hamiltonian, their arbitrary linear combination is an equally good eigenfunction of this operator. We may take, therefore, Y_1^1 and Y_1^{-1} as $\psi_1 = \frac{1}{2}(Y_1^1 + Y_1^{-1}) = \sin \theta \cos \phi$ and $\psi_2 = \frac{1}{2i}(Y_1^1 - Y_1^{-1}) = \sin \theta \sin \phi$. Both functions are real, they are shown in Fig. 4.16.c,d. Note, that again we have the usual situation: the ground state is nodeless, the first excited state has a single node, etc.

quantum
number J

Y_J^M is not only the eigenfunction of the Hamiltonian \hat{H} and of the square of the angular momentum \hat{J}^2 (with the eigenvalue $J(J+1)\hbar^2$) but also of the z component of the angular momentum operator:

$$\hat{J}_z Y_J^M = M \hbar Y_J^M. \quad (4.34)$$

⁴⁸Adrien Legendre (1752–1833), French mathematician, professor at the Ecole Normale Supérieure – an elite school of France founded by Napoleon Bonaparte.

⁴⁹Indeed, since ϕ is an angle, we have $\exp(iM\phi) = \exp[iM(\phi + 2\pi)]$. Hence, $\exp(iM2\pi) = 1$, and, therefore, $\cos(2\pi M) = 1$ and $\sin(2\pi M) = 0$. This is fulfilled only if M is an integer.

⁵⁰ $P_J(x)$ is a polynomial of J -th degree, while $\frac{d^{|M|}}{dx^{|M|}} P_J^{|M|}(x)$ decreases the degree by M . If $|M|$ exceeds J , then $P_J^{|M|}(x)$ automatically becomes equal to zero.

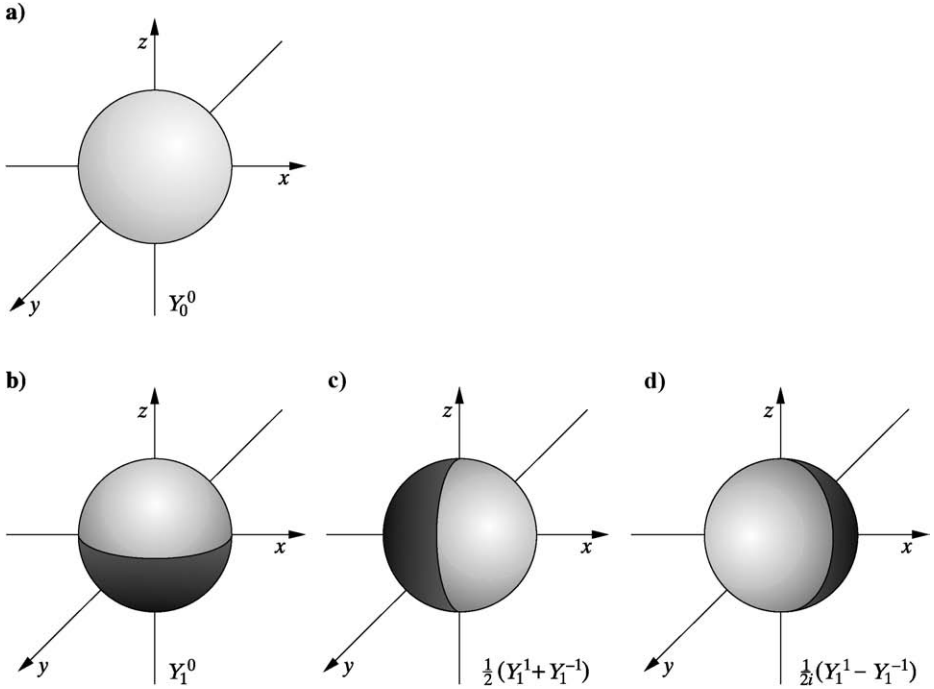


Fig. 4.16. A schematic representation of the nodes for rigid rotator wave functions: (a) ground state (nodeless), $J = 0$ (b) triply degenerate first excited state (single node), $J = 1$.

4.7 HYDROGEN-LIKE ATOM

We have two particles: an electron of mass m and charge $-e$ and a nucleus of mass M and charge $+Ze$. The Hamiltonian contains two kinetic energy operators and the Coulombic interaction $-Ze^2/r$, where r is the electron–nucleus separation. We have, therefore, 6 coordinates. In Appendix I on p. 971, it is shown how the centre-of-mass motion can be separated (we are not interested in this motion). There remain three coordinates, x, y, z , showing where the electron is with respect to the nucleus. The resulting Schrödinger equation contains a single kinetic energy operator of a particle of reduced mass μ (almost equal to the electron mass) with coordinates x, y, z , and Coulombic interaction of the electron and the nucleus (as before). Now, instead of x, y, z , we introduce the spherical coordinates r, θ, ϕ . Then, as in the class Q solution, we obtain

$$\psi_{nlm}(r, \theta, \phi) = N_{nl} R_{nl}(r) Y_l^m(\theta, \phi) \quad (4.35)$$

where Y_l^m is identical to the solution (4.30) of a rigid rotator of length r , and the

function R_{nl} has the following form in a.u. (N_{nl} is the normalization constant)

$$R_{nl}(r) = r^l L_{n+l}^{2l+1} \left(\frac{2Zr}{na_0} \right) \exp \left(-\frac{Zr}{na_0} \right), \quad (4.36)$$

where the *Bohr first orbit radius*

Bohr first orbit
radius

$$a_0 = \frac{1}{\mu} \simeq 1 \text{ a.u.}, \quad (4.37)$$

where

principal quantum number $n = 1, 2, 3, \dots$,
azimuthal quantum number $l = 0, 1, 2, \dots, n-1$,
magnetic quantum number $m = -l, -l+1, \dots, 0, \dots, +l$.

and the *associated Laguerre polynomial* $L_{\alpha}^{\beta}(x)$ is defined as

associated
Laguerre
polynomial

$$L_{\alpha}^{\beta}(x) = \frac{d^{\beta}}{dx^{\beta}} L_{\alpha}(x), \quad (4.38)$$

while the *Laguerre polynomial* is given by⁵¹

$$L_{\alpha}(x) = \exp(x) \frac{d^{\alpha}}{dx^{\alpha}} [x^{\alpha} \exp(-x)]. \quad (4.39)$$

The one-electron wave functions (orbitals) of the hydrogen atom with $l = 0$ are traditionally denoted as ns: $\psi_{100} = 1s$, $\psi_{200} = 2s, \dots$, with $l = 1$ as np, with $l = 2, 3, \dots$ as nd, nf, \dots

The wave functions ψ_{nlm} can be plotted in several ways. For example, the function $(nlm) = (100)$ or $1s$ given by the formula

$$\psi_{100}(r, \theta, \phi) = \sqrt{\frac{Z^3}{\pi}} \exp(-Zr), \quad (4.40)$$

and can be visualized in several alternative forms shown in Fig. 4.17.

We see that what the electron likes most is to sit on the nucleus. Indeed, if we chopped the space into tiny cubes, then computed the value of $(1s)^2$ in each cube (the function is real, therefore, the modulus is irrelevant), and multiplied

⁵¹Both $L_{\alpha}^{\beta}(x)$ and L_{α} are indeed polynomials of $\alpha - \beta$ degree. If $\beta > \alpha$, from (4.38) it follows that $L_{\alpha}^{\beta} = 0$.

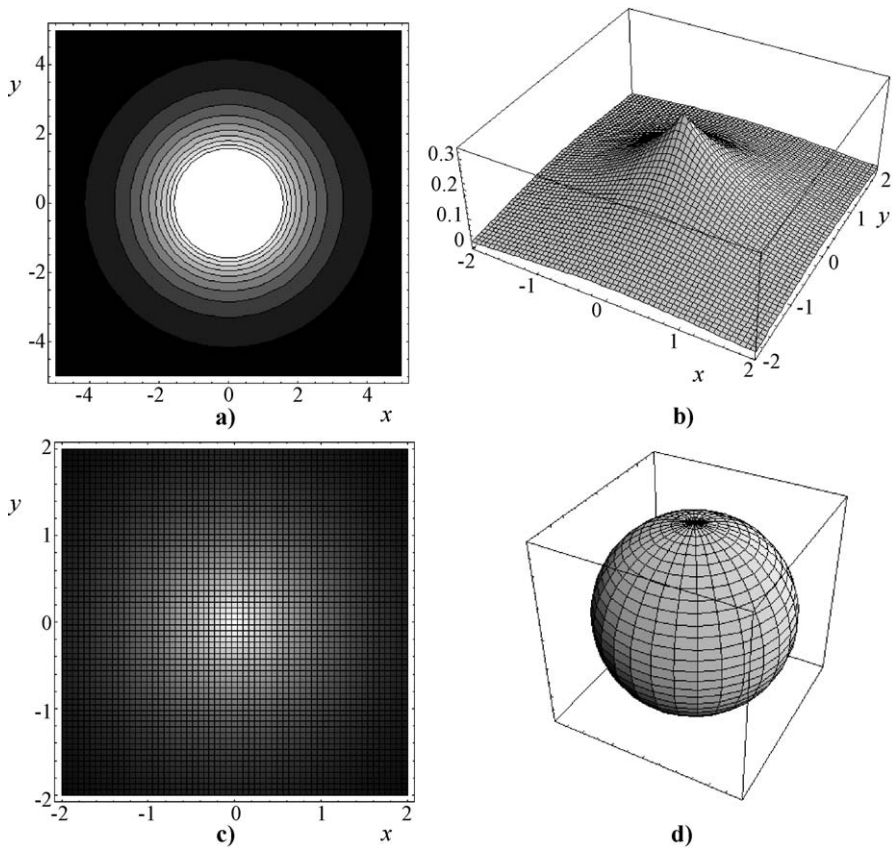


Fig. 4.17. Various ways of visualization the 1s hydrogen orbital, which is a function of electron position in 3D space (coordinates in Figs. (a)–(c) in a.u.). (a) Isolines of the $z = 0$ section of the wave function (going through the nucleus). Background colour means the value zero, white colour means a high value. This is a map of a mountain. The centre of Fig. (a) shows a large white plateau, which represents, however, an artifact. In fact (b), the section of the 1s orbital as a function of r represents a mountain with a sharp summit (a discontinuity of the first derivative). Fig. (c) is similar to (a), but instead of isolines we have a white mist with the highest concentration in the centre, disappearing exponentially with increasing distance r . Fig. (d) shows a spherically symmetric isosurface of the wave function.

the number obtained by the volume of the cube, the resulting number in each cube would have a meaning of the probability of finding the electron in a particular cube. Evidently, this number will be largest for the cube that contains the nucleus (the origin). We were told about the Bohr model⁵² in school, about the orbits, and about the first Bohr orbit (corresponding to the atom ground state).

⁵²Nobody is perfect. Geniuses also... Here is a story by John Slater: "... Brillouin delivered an interesting lecture concerning his relations. When he finished, Bohr stood up and attacked him with an inhuman fury. I have never heard any adult to scold another person in public with such an emotional engagement without any reason whatsoever. After this show I have decided that my antipathy with respect to Bohr dating since 1924 continues to be justified."

Do we relegate all this to fairy-tales? Not completely. If we changed the question: what is the *distance* at which the electron is most likely to be found, then the answer should indeed be as we were taught in school: the first Bohr orbit. This is easy to show by computing the *radial probability density* of finding the electron (i.e. integrating over all orientations, leaving the dependence on the distance): $\rho(r) = \int d\theta d\phi r^2 \sin \theta |\psi_{100}|^2 = 4Z^3 r^2 \exp -2Zr$, i.e. such a function computed for a given $r = r_0$ and multiplied by the volume $4\pi r_0^2 dr$ confined between two concentric spheres, one with radius r_0 , the other with radius $r_0 + dr$, gives the probability of finding the electron exactly between these spheres. The maximum of $\rho(r)$ corresponds exactly to $r = 1$ a.u. or the first Bohr orbit radius.⁵³

Since the Hamiltonian commutes with the square of the total angular momentum operator \hat{J}^2 and with the operator of \hat{J}_z (cf. Chapter 2 and Appendix F on p. 955), then the functions ψ_{nlm} are also the eigenfunctions of these two operators:

$$\hat{H}\psi_{nlm} = E_n\psi_{nlm}, \quad (4.41)$$

$$\hat{J}^2\psi_{nlm} = l(l+1)\hbar^2\psi_{nlm}, \quad (4.42)$$

$$\hat{J}_z\psi_{nlm} = m\hbar\psi_{nlm}, \quad (4.43)$$

where in a.u.

$$E_n = -\frac{Z^2}{2n^2} \left(\frac{1}{1 + \frac{1}{M_p}} \right), \quad (4.44)$$

with M_p representing the proton mass (in a.u.), i.e. about 1840. The content of the parenthesis in the last equation works out as 0.999457, almost 1, which would be obtained for an infinite mass of the nucleus.

Each of the energy levels is n^2 -fold degenerate. Note, that the hydrogen atom energy depends solely on the principal quantum number n . The fact that the energy does not depend on the projection of the angular momentum $m\hbar$ is natural, because the space is isotropic and no direction is privileged. However, the fact that it does not depend on the length of the angular momentum $\sqrt{l(l+1)}\hbar$, is at first sight strange. The secret is in the Coulombic potential $\frac{1}{r}$ produced by the *point-like* nucleus and is connected with the notion of dynamic symmetry mentioned on p. 76. If we considered a non-point-like nucleus or were interested in the orbital 2s of such a quasi-hydrogen atom as lithium,⁵⁴ then the energy would depend on the quantum number l , e.g., would be different for orbitals 2s and 2p.

The 2s orbital ($n = 2, l = 0, m = 0$) reads as (Fig. 4.18)

$$\psi_{2s}(r, \theta, \phi) = N_{2s}(Zr - 2) \exp(-Zr/2) \quad (4.45)$$

⁵³The computed maximum position does not coincide with the mean value of r (cf. Appendix H on p. 969) $\langle r \rangle = \langle \psi_{100} | r | \psi_{100} \rangle = \int_0^\infty dr r \rho(r) = \frac{3}{2}$ a.u.

⁵⁴In which the nucleus is screened by a cloud of two 1s electrons. The 2s electron thinks it is in a hydrogen atom with a spacious nucleus of the size of the 1s orbital and an effective charge $+1$.

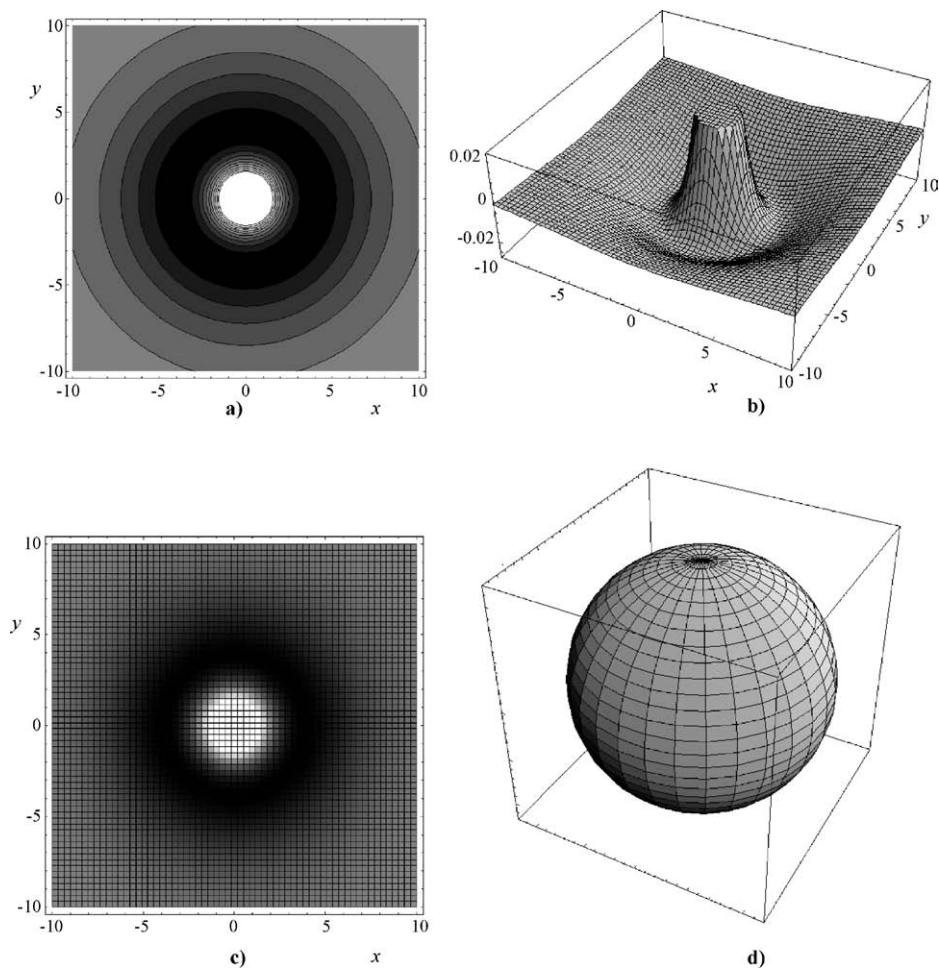


Fig. 4.18. Various graphical representations of the hydrogen 2s orbital (coordinates in Figs. (a)–(c) in a.u.). (a) Isolines of $z = 0$ section of the orbital. Gray means the value zero, white a high value, black a negative value. Note, that gray is not only at peripheries, but also around the centre. This means that 2s orbital exhibits a nodal sphere of radius 2 a.u. (see eq. (4.45)), that contains a little more than 5% of the electronic density (whereas for the 1s orbital such a sphere contains about 75% of electron cloud). The centre of the figure shows a quite large white plateau, which represents, however, an artifact. In fact, (b) showing the section of 2s orbital as a function of r represents a mountain with a sharp peak (a discontinuity of the first derivative is shown incorrectly on the figure, instead a sharp summit one has an artifact plateau) with a depression at its base. Fig. (c) is similar to (a), but instead of isolines one has a white mist with the largest concentration in the centre, then taking the negative values (black mist) and finally disappearing exponentially with increasing distance r . Fig. (d) shows a spherically symmetric isosurface of the wave function (the sphere was shown as larger than 1s orbital, because 2s orbital decays more slowly than 1s).

with the normalization constant $N_{2s} = \frac{Z^3}{4\sqrt{2\pi}}$. A sphere of radius $2/Z$ (representing the nodal sphere) contains⁵⁵ only a little more than 5% of the total electronic density (independently of Z).⁵⁶

The wave functions (orbitals) with $m \neq 0$ are difficult to draw, because they are complex. We may, however, plot the real part of ψ_{nlm} ($\text{Re } \psi_{nlm}$) by taking the sum of ψ_{nlm} and ψ_{nl-m} , i.e. $2\text{Re } \psi_{nlm}$ and the imaginary part of ψ_{nlm} ($\text{Im } \psi_{nlm}$) from the difference of ψ_{nlm} and ψ_{nl-m} equal to $2i \text{Im } \psi_{nlm}$. These functions are already real and can be easily plotted. In this way we obtain the orbitals $2p_x$ and $2p_y$ from the functions 211 and 21-1. The orbital 210 is identical to $2p_z$:

$$2p_x = N_{2p}x \exp(-Zr/2),$$

$$2p_y = N_{2p}y \exp(-Zr/2),$$

$$2p_z = N_{2p}z \exp(-Zr/2),$$

where an easy calculation (just five lines) gives the normalization constant $N_{2p} = ZN_{2s}$. The $2p$ orbitals are shown in Fig. 4.19.

Note, please, that a linear combination of eigenfunctions is not necessarily an eigenfunction. It does, if the functions mixed, correspond to the same eigenvalue. This is why $2p_x$ and $2p_y$ are the eigenfunctions of the Hamiltonian, of the square of the angular momentum operator, but are not eigenfunctions of \hat{J}_z .

Similarly we obtain the five real $3d$ orbitals. They can be easily obtained from eq. (4.35) and subsequently making them real by choosing $\text{Re } \psi_{nlm}$ and $\text{Im } \psi_{nlm}$.

As a result we have the following normalized $3d$ orbitals ($N_{3d} = \frac{Z^3}{81} \sqrt{\frac{2}{\pi}}$)

$$3d_{xy} = N_{3d}xy \exp(-Zr/3),$$

$$3d_{xz} = N_{3d}xz \exp(-Zr/3),$$

$$3d_{yz} = N_{3d}yz \exp(-Zr/3),$$

$$3d_{x^2-y^2} = \frac{1}{2}N_{3d}(x^2 - y^2) \exp(-Zr/3),$$

$$3d_{3z^2-r^2} = \frac{1}{2\sqrt{3}}N_{3d}(3z^2 - r^2) \exp(-Zr/3).$$

The $3d$ orbitals are shown in Figs. 4.20 and 4.21. A summary of the hydrogen atomic orbitals is shown in Fig. 4.22.⁵⁷

⁵⁵See the Mathematica files for Chapter 4 in the Web Annex.

⁵⁶A sphere of the same radius encloses about 75% of the electron density for the $1s$ orbital.

⁵⁷A night bus ride might enrich us with some unexpected impressions. Of all atomic orbitals you may most easily “see” is the orbital $1s$. Just look through the condensation on a bus window at a single street lamp. You will see a gleam that decays to black night. You may also quite easily find a double lamp that will offer you a $2p$ orbital and sometimes have the chance to see some of the $3d$ orbitals. Once I have

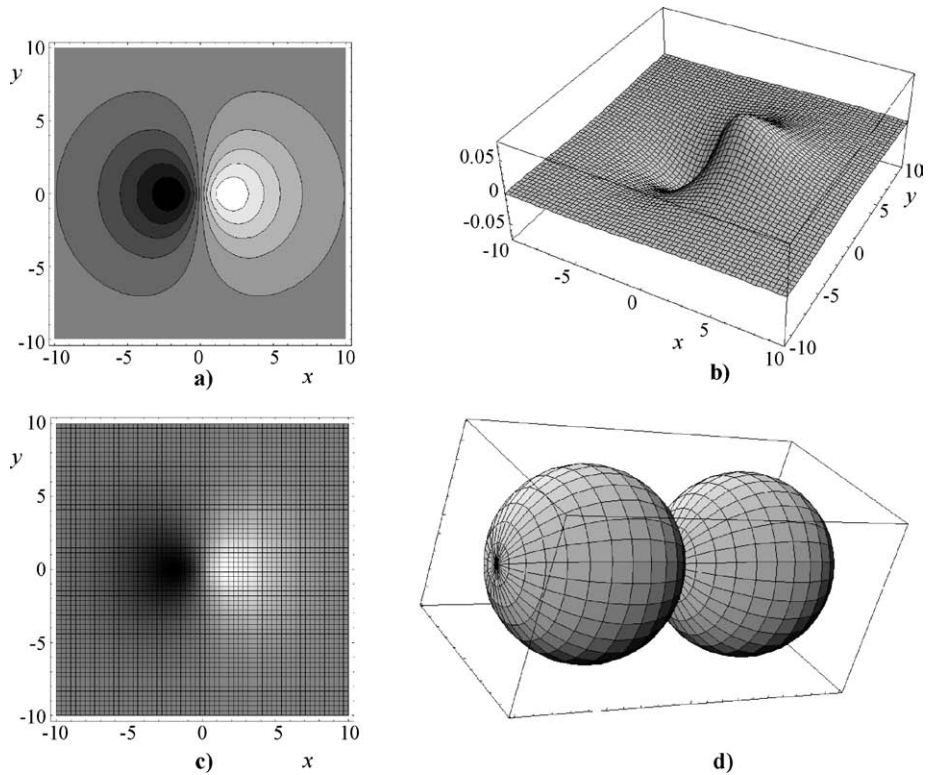


Fig. 4.19. Various graphical representations of the hydrogen $2p_x$ orbital (coordinates in Figs. (a)–(c) in a.u.). The two other $2p$ orbitals: $2p_y$, $2p_z$ look the same as $2p_x$, but are oriented along axes y and z . Note that for the hydrogen atom all four orbitals $2s$, $2p_x$, $2p_y$, $2p_z$ correspond to the same energy, and all have a single nodal surface. For $2s$ the surface (Fig. 4.18) is a sphere of radius 2, for the $2p_x$, $2p_y$ and $2p_z$ orbitals the nodal surfaces are the planes x , y , $z = 0$. (a) Isolines of the $z = 0$ section of the orbital. Gray means zero, white means a high value, black means a negative value. Note (Figs. (a), (b)), that the right-hand side of the orbital is positive, the left-hand side is negative. The maximum (minimum) value of the orbital is at $x = 2$ ($x = -2$) a.u. Fig. (c) is similar to (a), but instead of isolines we have a mist with the largest concentration (white) on the right and the smallest (and negative, black) concentration on the left. The orbital finally disappears exponentially with increasing distance r from the nucleus. Fig. (d) shows an isosurface of the absolute value of the angular part of the wave function $|Y_1^0|$. As for Y_1^0 itself, one of the lobes takes negative, the other positive values and they touch each other at the position of the nucleus. To obtain the orbital, we have to multiply this angular function by a spherically symmetric function of r . This means that an isosurface of the absolute value of the wave function will also have two lobes (for the wave function itself, one will be positive, the other negative), but they will not touch each other in full accordance with Fig. (a).

even found the $2s$ orbital, but I do not understand how it was possible. I was looking at a single lamp, which made an intense gleam in the centre, which gradually decayed and then again an annular gleam appeared that finally vanished. This is what the square of the $2s$ orbital looks like.

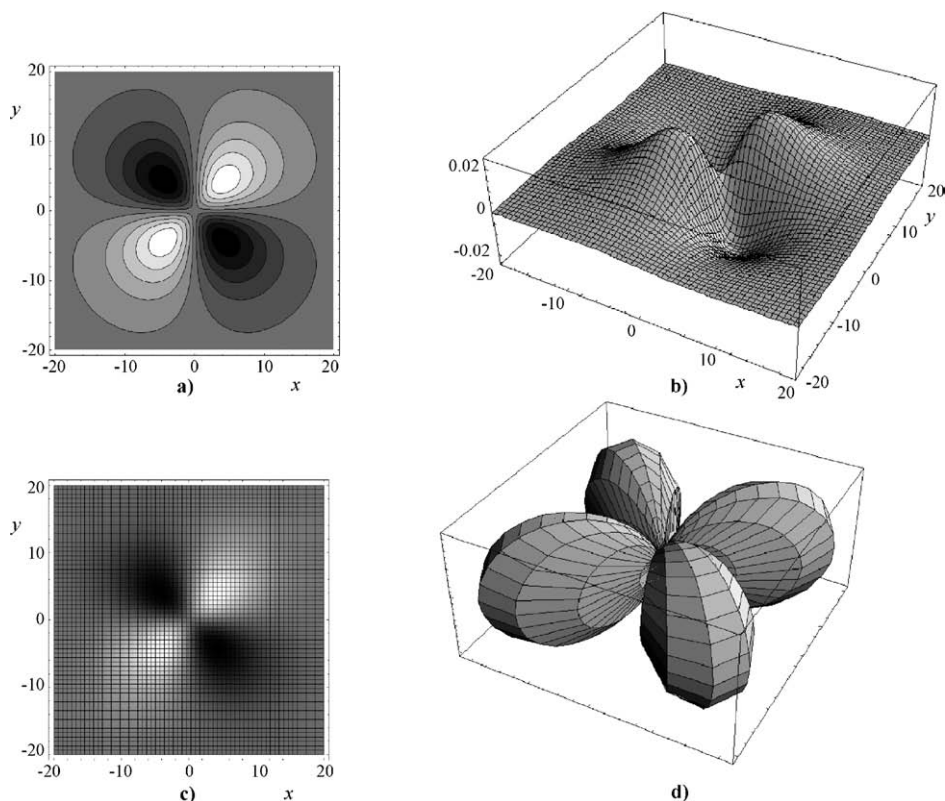


Fig. 4.20. Various graphical representations of the hydrogen $3d_{xy}$ orbital (coordinates in Figs. (a)–(c) in a.u.). The three other $3d$ orbitals: $3d_{yz}$, $3d_{xz}$ and $3d_{x^2-y^2}$ look the same as $3d_{xy}$, but are oriented in space according to their indices (in the last case along x and y axes). (a) Isolines of $z = 0$ section of the orbital. Gray means zero, white means a positive value, black means a negative value. Note (Figs. (a), (b)), that $3d$ orbitals are symmetric with respect to inversion. One may imagine the $z = 0$ section of $3d_{xy}$ as two hills and two valleys (b). Fig. (c) is similar to (a), but instead of isolines one has a white mist with the highest concentration on the North-East line and the smallest (and negative) concentration on the North-West line (black mist). The orbital finally disappears exponentially with increasing distance r from nucleus. Fig. (d) shows an isosurface of the absolute value of the angular part of the wave function: $|Y_2^2 - Y_2^{-2}|$. As for $Y_2^2 - Y_2^{-2}$ itself two of the lobes take the negative, the other two take positive values, they touch each other at nucleus. To obtain the orbital one has to multiply this angular function by a spherically symmetric function of r . This means that an isosurface of the absolute value of the wave function will have also four lobes (for the wave function itself two will be positive, the other two negative), but they will not touch in full accordance with Fig. (a).

4.8 HARMONIC HELIUM ATOM (HARMONIUM)

Two-electron systems already represent a serious problem for quantum chemistry, because the mutual correlation of electron motions must be carefully taken into account. As we will see in further chapters, such calculations are feasible, but the

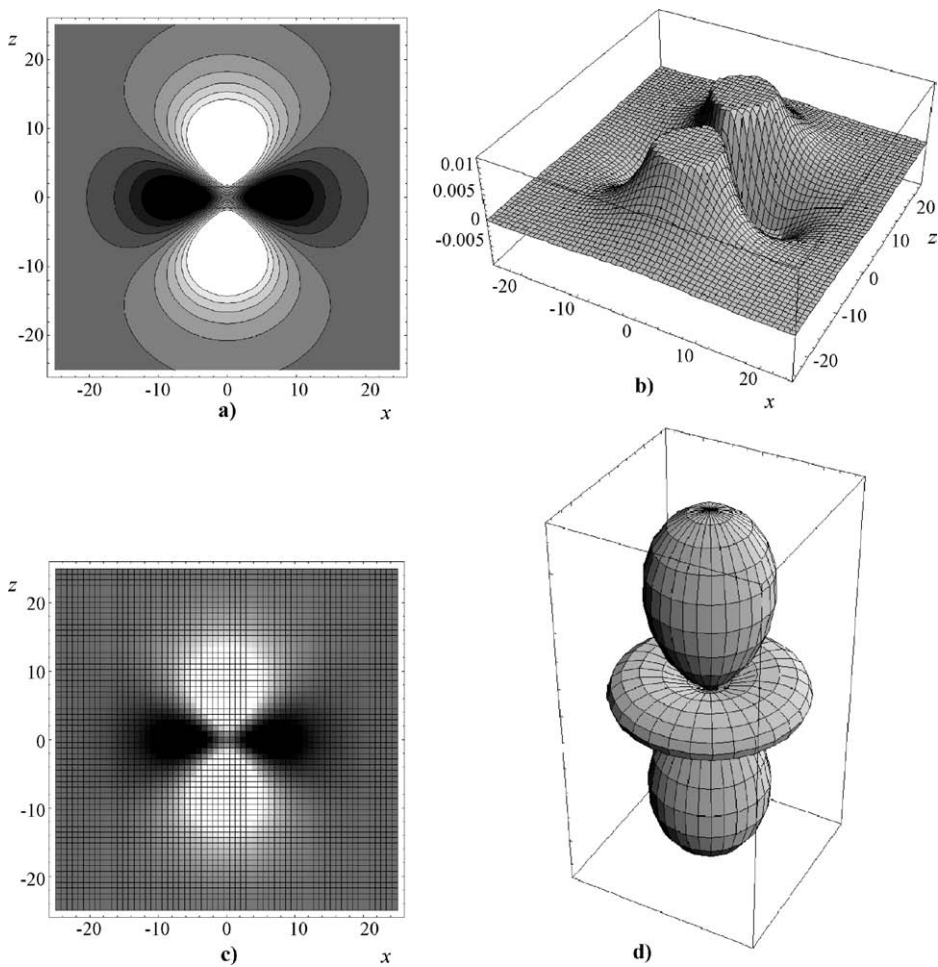


Fig. 4.21. Various graphical representations of the hydrogen $3d_{3z^2-r^2}$ orbital (coordinates in Figs. (a)–(c) in a.u.). The z axis is vertical, x axis is horizontal. (a) Isolines of the xz section of the orbital. Gray means zero, white means a high positive value, black means a negative value. Note (Figs. (a), (b)), that $3d_{3z^2-r^2}$ orbitals are symmetric with respect to inversion. We may imagine xz section of the $3d_{3z^2-r^2}$ as two hills and two valleys (b), the hills are higher than the depth of the valleys (the plateaus in Fig. (b) are artificial). Fig. (c) is similar to (a), but instead of isolines one has a mist with the highest concentration (white) on the North-South line and the smallest (and negative, black mist) concentration on the East-West line. The orbital finally disappears exponentially with increasing distance r from the nucleus. Fig. (d) shows an isosurface of the absolute value of the angular part of the wave function ($|Y_2^0|$). As for Y_2^0 itself there are two positive lobes and a negative ring, they touch each other at nucleus. To obtain the orbital, we have to multiply this angular function by a spherically symmetric function of r . This means that an isosurface of the absolute value of the wave function will have also two lobes along the z axis as well as the ring, but they will not touch in accordance with Fig. (a). The lobes along the z axis are positive, the ring is negative.

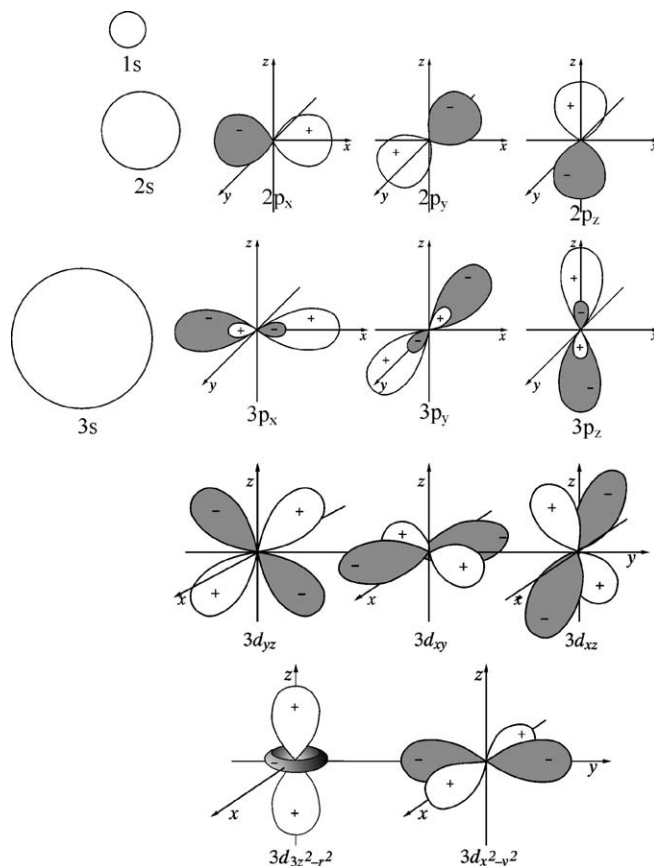


Fig. 4.22. Summary: schematic representation of $1s$, $2s$, $2p$, $3s$, $3p$, $3d$ orbitals of the hydrogen atom. $1s$, $2s$, $3s$ orbitals are spherically symmetric and increase in size; $1s$ has no node, $2s$ has one nodal sphere (not shown), $3s$ has two nodal spheres (not shown). The shadowed area corresponds to the “minus” sign of the orbital. The $2p$ orbitals have a single nodal plane (perpendicular to the orbital shape). $3p$ orbitals are larger than $2p$, and have a more complex nodal structure. Note that among $3d$ orbitals all except $3d_{3z^2-r^2}$ have identical shape, but differ by orientation in space. A peculiar form of $3d_{3z^2-r^2}$ becomes more familiar when one realizes that it simply represents a sum of two “usual” $3d$ orbitals. Indeed, $3d_{3z^2-r^2} \propto [2z^2 - (x^2 + y^2)]\exp(-Zr/3) \propto [(z^2 - x^2) + (z^2 - y^2)]\exp(-Zr/3) \propto (3d_{z^2-x^2} + 3d_{z^2-y^2})$.

wave functions are very complicated, e.g., may represent linear combinations of thousands of terms and still only be *approximations* to the exact solution to the Schrödinger equation. This is why people were surprised when Kais et al. showed that a two electron system has an *exact analytical solution*.⁵⁸

Unfortunately, this wonderful two-electron system is (at least partially) non-physical. It represents a strange helium atom, in which the two electrons (their distance denoted by r_{12}) interact through the Coulombic potential, but each is at-

⁵⁸S. Kais, D.R. Herschbach, N.C. Handy, C.W. Murray, G.J. Laming, *J. Chem. Phys.* 99 (1993) 417.

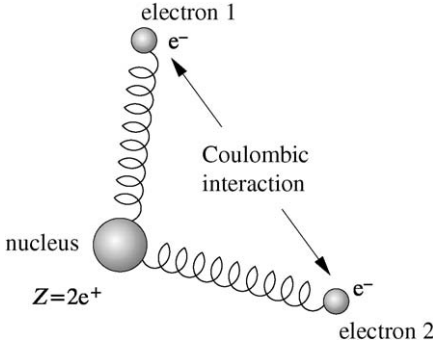


Fig. 4.23. The harmonic helium atom. The electrons repel by Coulombic forces and are attracted by the nucleus by a harmonic (non-Coulombic) force.

tracted to the nucleus by a harmonic spring (of equilibrium length 0 and force constant k , with electron–nucleus distances denoted by r_1 and r_2), Fig. 4.23.

The Hamiltonian of this problem (the adiabatic approximation and atomic units are used) has the form:

$$\hat{H} = -\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 + \frac{1}{2}k(r_1^2 + r_2^2) + \frac{1}{r_{12}}.$$

It is amazing in itself that the Schrödinger equation for this system has an analytical solution (for $k = \frac{1}{4}$), but it could be an extremely complicated analytical formula. It is a sensation that the solution is dazzlingly beautiful and simple

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = N \left(1 + \frac{1}{2}r_{12} \right) \exp \left[-\frac{1}{4}(r_1^2 + r_2^2) \right],$$

where

$$|N|^2 = \frac{\pi^{\frac{3}{2}}}{8 + 5\sqrt{\pi}}.$$

The wave function represents the product of the two harmonic oscillator wave functions (Gaussian functions), but also an additional extremely simple correlation factor $(1 + \frac{1}{2}r_{12})$. As we will see in Chapter 13, exactly such a factor is required for the ideal solution. In this exact function there is nothing else, just what is needed.⁵⁹

4.9 WHAT DO ALL THESE SOLUTIONS HAVE IN COMMON?

- In all the systems considered (except the tunnelling effect, where the wave function is non-normalizable), the stationary states are similar, the number of their nodes increasing with their energy (the nodeless function corresponds to the lowest energy).

⁵⁹We might have millions of complicated terms.

- If the potential energy is a *constant* (particle in a box, rigid rotator), then the energy level (nearest-neighbour) distance *increases* with the energy.⁶⁰ The energy levels get closer for larger boxes, longer rotators, etc.
- A *parabolic* potential energy well (harmonic oscillator) reduces this tendency and the energy levels are *equidistant*. The distance decreases if the parabola gets wider (less restrictive).
- The Morse potential energy curve may be seen as a function that may be approximated (as the energy increases) by wider and wider parabolic sections. No wonder, therefore, that the energy level distance *decreases*. The number of energy levels is finite.⁶¹
- The Coulomb potential, such as that for the hydrogen atom, resembles vaguely the Morse curve. Yet its form is a little similar to the Morse potential (dissociation limit, but infinite depth). We expect, therefore, that the energy levels for the hydrogen-like atom will become closer and closer when the energy increases, and we are right. Is the number of these energy levels finite as for the Morse potential? This is a more subtle question. Whether the number is finite or not is decided by the asymptotics (the behaviour at infinity). The Coulomb potential makes the number infinite.

4.10 BEACONS AND PEARLS OF PHYSICS

Sometimes students, fascinated by handy computers available nowadays, tend to treat the simple systems described in this chapter as primitive and out of date. A Professor has taken them from the attic and after dusting off shows them to a class, whilst outside sophisticated computers, splendid programs and colourful graphs await. This is wrong. The simple systems considered in this chapter correspond to extremely rare *exact solutions of Schrödinger equation* and are, therefore, precious pearls of physics by themselves. Nobody will give a better solution, the conclusions are hundred percent sure. It is true that they all (except for the hydrogen atom) correspond to some idealized systems.⁶² There is no such a thing as an unbreakable spring (e.g., harmonic oscillator) or a rotator, that does not change its length, etc. And yet these problems represent our firm ground or the beacons of our native land. After reading the present chapter we will be preparing our ship for a long voyage. When confronted with the surprises of new lands and trying to understand them

⁶⁰In both cases the distance goes as the square of the quantum number.

⁶¹Such type of reasoning prepares us for confronting real situations. Practically, we will never deal with the abstract cases described in the present chapter, and yet in later years we may say something like this: “look, this potential energy function is similar to case *X* in Chapter 4 of that thick boring book we have been forced to study. So the distribution of energy levels and wave functions has to be similar to those given there”.

⁶²Like Platonic ideal solids.

the *only* points of reference or the beacons which tell us about *terra firma* will be the problems for which analytical solutions have been found.

Summary

Exact analytical solutions⁶³ to the Schrödinger equation play an important role as an organizer of our quantum mechanical experience. Such solutions have only been possible for some idealized objects. This is of great importance for the interpretation of approximate solutions for real systems. Another great feature of exact solutions is that they have an extremely wide range of applications: they are useful independently of whether we concentrate on an electron in an atom, in molecule, a nucleon in a nucleus or a molecule as an entity, etc.

The main features of the solutions are:

- **Free particle.** The particle may be described as the superposition of the state $\exp(i\kappa x)$, corresponding to the particle moving right (positive values of x), and the state $\exp(-i\kappa x)$, that corresponds to the particle moving left. Both states correspond to the same energy (and opposite momenta).
- **Particle in a box.** We consider first a particle in a 1D box, i.e. the particle is confined to section $[0, L]$ with potential energy (for a particle of mass m and coordinate x) equal to zero and ∞ outside the section. Such a potential forces the wave function to be non-zero only within the section $[0, L]$. We solve the elementary Schrödinger equation and obtain $\Psi = A \sin \kappa x + \cos \kappa x$, where $\kappa^2 = \frac{2mE}{\hbar^2}$. Quantization appears in a natural way from the condition of continuity for the wave function at the boundaries: $\Psi(0) = 0$ and $\Psi(L) = 0$. These two conditions give the expression for the energy levels $E_n = \frac{n^2 \hbar^2}{8mL^2}$ and for the wave functions $\Psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x$ with quantum number $n = 1, 2, \dots$. Conclusion: the successive energy levels are more and more distant and the wave function is simply a section of the sine function (with 0 value at the ends).
- **Tunnelling effect.** We have a particle of mass m and a rectangular barrier (section $[0, a]$, width a and height V). Beyond this section the potential energy is zero. The particle comes from the negative x values and has energy $E < V$. A classical particle would be reflected from the barrier. However, for the quantum particle:
 - the transmission coefficient is non-zero,
 - the passage of a large energy particle is easier,
 - a narrower barrier means larger transmission coefficient,
 - the higher the barrier the smaller transmission coefficient.

The first feature is the most sensational, the others are intuitively quite acceptable. This is not the case for a particle tunnelling through two consecutive barriers. It turns out that (for a given interbarrier distance) *there are some “magic” energies of the particle (resonance energies), at which the transmission coefficient is particularly large*. The magic energies correspond to the stationary states that would be for a particle in a box a little longer than the interbarrier distance. The resonance states exist also for energies greater than barrier

⁶³To distinguish from accurate solutions (i.e. received with a desired accuracy).

and have a transmission coefficients equal to 100%, whereas other energies may lead to reflection of the particle, even if they are larger than the barrier energy.

- **Harmonic oscillator.** A single particle of mass m attached to a harmonic spring (with force constant k) corresponds to potential energy $V = \frac{kx^2}{2}$. We obtain quantization of the energy: $E_v = h\nu(v + \frac{1}{2})$, where the vibrational quantum number $v = 0, 1, 2, \dots$, and the angular frequency $\omega = 2\pi\nu = \sqrt{\frac{k}{m}}$. We see that *the energy levels are equidistant*, and their distance is larger for a larger force constant and smaller mass. The wave function⁶⁴ has the form of a Gaussian factor and a polynomial of degree v . The polynomial assures the proper number of nodes, while the Gaussian factor damps the plot to zero for large displacements from the particle equilibrium position. The harmonic oscillator may be viewed (Chapter 6) as equivalent (for small displacements) to two masses bound by a spring.
- **Morse oscillator.** The harmonic oscillator does not allow for the breaking of the spring connecting two particles, while the Morse oscillator admits dissociation. This is extremely important, because real diatomic molecules resemble the Morse rather than the harmonic oscillator. The solution for the Morse oscillator has the following features:
 - energy levels are non-degenerate,
 - their number is finite,
 - for large well depths the low energy levels tend to the energy levels of the harmonic oscillator (the levels are equidistant),
 - the higher the energy level the larger the displacement from the equidistant situation (the energy levels get closer),
 - the wave functions, especially those corresponding to deep-lying levels, are very similar to the corresponding ones of the harmonic oscillator,⁶⁵ but they do not exhibit the symmetry.⁶⁶
- **Rigid rotator.** This is a system of two masses m_1 and m_2 that keeps their distance R fixed. After separating the centre-of-mass motion (Appendix I on p. 971) we obtain an equation of motion for a single particle of mass equal to the reduced mass μ moving on a sphere of radius R (position given by angles θ and ϕ). The energy is determined by the quantum number $J = 0, 1, 2, \dots$ and is equal to $E_J = J(J+1)\frac{\hbar^2}{2\mu R^2}$. As we can see:
 - there is an infinite number of energy levels,
 - the separation of the energy levels increases with the energy (similar to the particle in a box problem),
 - the separation is smaller for larger masses,
 - the separation is smaller for longer rotators.
 The wave functions are the spherical harmonics $Y_J^M(\theta, \phi)$, which for low J are very simple, and for large J complicated trigonometric functions. The integer quantum number M satisfies the relation $|M| \leq J$. The energy levels are, therefore, $(2J+1)$ -tuply degenerate.
- **Hydrogen-like atom.** We have an electron and a nucleus of charges $-e$ and $+Ze$, respectively, or -1 and $+Z$ in a.u. The wave function is labelled by three quantum numbers: principal $n = 1, 2, \dots$, azimuthal $l = 0, 1, \dots, (n-1)$ and magnetic $m = -l, (-l+1, \dots, l-1, l)$.

⁶⁴The energy levels are non-degenerate.

⁶⁵Despite the fact, that the formula itself is very different.

⁶⁶The wave functions for the harmonic oscillator are either even or odd with respect to the inversion operation ($x \rightarrow -x$).

$1), \dots, 0, \dots, l$. The energy in a.u. is given by the formula⁶⁷ $E_n = -Z^2/(2n^2)$. The wave function represents the product of a polynomial (of r), an exponential function decreasing with r and a spherical harmonic $Y_l^m(\theta, \phi)$, where r, θ, ϕ are the spherical coordinates of the electron, and the nucleus is at the origin. The wave functions that correspond to low energies are denoted by the symbols nl_m (with s for $l = 0$, p for $l = 1$, etc.): $1s, 2s, 2p_0, 2p_1, 2p_{-1}, \dots$. The degeneracy of the n -th level is equal to n^2 .

- **Harmonic helium atom.** In this peculiar helium atom the electrons are attracted to the nucleus by harmonic springs (of equal strength) of equilibrium length equal to zero. For $k = \frac{1}{4}$ an exact analytical solution exists. The exact wave function is a product of two Gaussian functions and a simple factor: $(1 + \frac{1}{2}r_{12})$ that correlates the motions of the two electrons.

Main concepts, new terms

free particle (p. 144)

particle in a box (p. 145)

box with ends (p. 145)

FEMO (p. 149)

cyclic box (p. 149)

tunnelling effect (p. 153)

current (p. 155)

transmission coefficient (p. 155)

resonance state (p. 155)

harmonic oscillator (p. 166)

Hermite polynomials (p. 166)

Morse oscillator (p. 169)

isotope effect (p. 172)

encounter complex (p. 174)

binding energy (p. 175)

dissociation energy (p. 175)

rigid rotator (p. 176)

spherical harmonics (p. 176)

Legendre polynomials (p. 176)

associated Legendre polynomials (p. 176)

hydrogen-like atom (p. 178)

Laguerre polynomials (p. 178)

associated Laguerre polynomials (p. 178)

correlation factors (p. 188)

From the research front

A field like that discussed in the present chapter seems to be definitely closed. We have been lucky enough to solve some simple problems, that could be solved, but others are just too complicated. This is not true. For several decades it has been possible to solve a series of non-linear problems, thought in the past to be hopeless. What decides success is: choice of the problem, quality of researchers, courage, etc.⁶⁸ It is worth noting that there are also attempts at a systematic search for promising systems to solve.

Ad futurum...

It seems that the number of exactly solvable problems will continue to increase, although the pace of such research will be low. If exactly solvable problems were closer and closer to practise of physics, it would be of great importance.

Additional literature

J. Dvořák and L. Skála, "Analytical Solutions of the Schrödinger Equation. Ground State Energies and Wave Functions", Collect. Czech. Chem. Commun., 63 (1998) 1161.

⁶⁷An infinite number of levels.

⁶⁸Already the Morse potential looks very difficult to manage, to say nothing about the harmonic helium atom.

Very interesting article with the character of a review. Many potentials,⁶⁹ leading to exactly solvable problems are presented in a uniform theoretical approach. The authors give also their own two generalizations.

Questions

- Particle in a box. After doubling the box length the energy of the levels will:
 - stay the same;
 - decrease four times;
 - increase twice;
 - decrease twice.
- Tunnelling of a particle through a system of two rectangular barriers of height V . $E > 0$ is the particle energy. The transmission coefficient as a function of E :
 - does not depend on E ;
 - increases with E ;
 - has maxima;
 - vanishes exponentially when E decreases.
- Harmonic oscillator. The energy E of the lowest vibrational level of the H_2 molecule is equal to A , of the DH molecule is equal to B , of the TH molecule is equal to C . The following inequality holds:
 - $A > B > C$;
 - $C > A > B$;
 - $B < C < A$;
 - $A < B < C$.
- Morse oscillator. The number of vibrational levels:
 - is always larger than 1;
 - does not depend on the well width, and depends on its depth;
 - may be equal to zero for a non-zero well depth;
 - may be equal to ∞ .
- Rigid rotator. The separation between neighbouring levels with quantum numbers J and $J + 1$:
 - increases linearly with J ;
 - increases with $J(J + 1)$;
 - decreases proportionally to $2J + 1$;
 - is constant.
- The following spherical harmonics Y_J^M have the correct indices:
 - $Y_{-1}^0, Y_1^2, Y_2^{-1}$;
 - Y_2^1, Y_1^0, Y_1^5 ;
 - Y_0^0, Y_0^1, Y_2^2 ;
 - Y_3^3, Y_3^2, Y_3^{-2} .
- In the ground-state hydrogen atom:
 - the probability of finding the electron in a cube with its centre on the nucleus is equal to 0;
 - the maximum probability density for finding the electron is on the nucleus;
 - the probability density for finding the electron on the nucleus is equal to 0;
 - the radial probability density has its maximum on the nucleus.
- The following linear combination of the hydrogen atom orbitals (\hat{H} is the Hamiltonian, \hat{j}^2 is the operator of the square of the angular momentum, \hat{j}_z is the operator of the z -component of the angular momentum):
 - $2s + 3 \cdot (2p_{-1})$ is an eigenfunction of \hat{H} and \hat{j}_z ;
 - $3s - 1/3 \cdot 2p_z$ is an eigenfunction of \hat{j}_z ;
 - $2p_0 + 3p_{-1}$ is an eigenfunction of \hat{H} and \hat{j}^2 ;
 - $2s - 3s$ is an eigenfunction of \hat{H} .
- Please choose the acceptable hydrogen atom orbitals ψ_{nlm} :
 - $\psi_{200}, \psi_{100}, \psi_{220}$;
 - $\psi_{100}, \psi_{2-10}, \psi_{211}$;
 - $\psi_{320}, \psi_{52-1}, \psi_{210}$;
 - $\psi_{-200}, \psi_{010}, \psi_{210}$.

⁶⁹Among them six not discussed in the present textbook.

10. Harmonic helium atom. In this system the electrons:
- a) attract themselves harmonically, but interact by Coulombic force with the nucleus;
 - b) interact harmonically with themselves and with the nucleus;
 - c) oscillate between two positions;
 - d) repel each other by Coulombic forces and are attracted harmonically by the nucleus.

Answers

1b, 2c, 3a, 4c, 5a, 6d, 7b, 8b, 9c, 10d