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Calculation of Electron Spectrum in Spherically Symmetric Potentials

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## Abstract

An important problem in quantum mechanics is a behavior of a particle in a spherically symmetric potential, which depends only on the distance between a particle and a center point. The study of the particle spectrum allows to see the global picture of a particle behavior.

We have designed and implemented some numerical methods for investigation of the electron spectrum in spherically symmetric potentials such as the infinite spherical potential well and the finite spherical potential well, the spherical oscillator, the hydrogen-like atom; the Woods-Saxon, Hulthen, Morse, Yukawa potentials and the deuteron model.

## 1 Introduction

Solutions of the Shrodinger equation are of great interest in many fields of physics and chemistry. To find possible energy values of the particle in an exterior potential it is necessary to find eigenvalues of the radial part of the Hamiltonian. It is often impossible to solve this problem analytically in the three-dimension case.

We are interested in finding the particle possible energy values in some spherically symmetric potentials, which describes different types of interactions. For this purpose we construct the numerical scheme by discretizing the Laplace operator using the finite differences and solve corresponding eigenvalue problem.

As a result, we have obtained the numerical results for the following potentials: the infinite spherical potential well; finite spherical potential well; the spherical oscillator potential; the Coulomb potential; the Hulthen potential; the Morse potential; Woods-Saxon potential; Yukawa potential and the deuteron potential. We compared numerical results for all but Woods-Saxon and Yukawa potentials with known analytical solutions [2]. As for the Woods-Saxon potential, for which there is no analytical solution, our results were verified by comparing results of two numerical methods: the extrapolation method and the eigenvalue problem solving one. For the Yukawa potential also there is no exact analytical solution, but we used approximate analytical solution presented in [4].

## 2 Theoretical part

### 2.1 Differential operators in spherical coordinates

Suppose we have the standard three dimension axes. A spherical coordinate system is a coordinate system where the position of a point is specified by three quantities: the radial distance  $r$  of that point from the origin, its polar angle  $\theta$  measured between the polar axis (positive  $z$ -axis) and the line from the origin to the point, and the azimuth angle  $\phi$  between the positive  $x$ -axis and the line's from the origin to the point orthogonal projection on a reference plane  $Oxy$ .

Cartesian coordinates to spherical coordinates:

$$\begin{cases} x = r \sin \theta \cos \phi \\ y = r \sin \theta \sin \phi \\ z = r \cos \theta \end{cases} \quad (1)$$

The Laplacian is a differential operator given by the divergence of the gradient of a function in Euclidean space. The Laplace operator in Cartesian coordinates:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

So, using (1) we can find Laplacian in spherical coordinates:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial f}{\partial r}) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial f}{\partial \theta}) + \frac{1}{r^2 \sin^2 \theta} (\frac{\partial^2 f}{\partial \phi^2}) \quad (2)$$

Spherical coordinates are specially convenient in case when particle potential depends only on distance from some point.

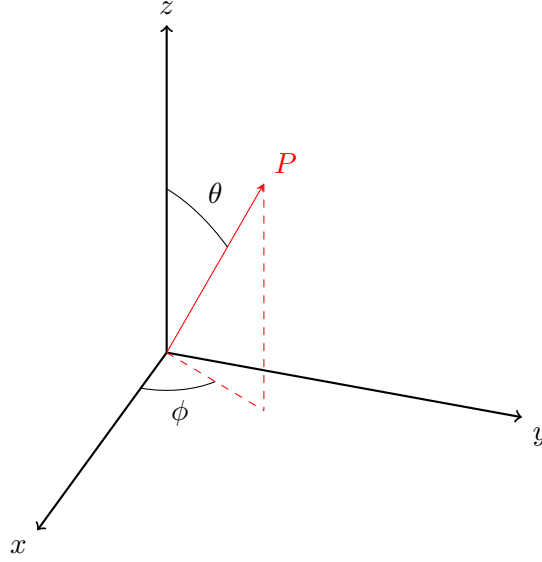


Fig. 1: Spherical coordinates

## 2.2 Some necessary special functions

With the Laplacian in the spherical coordinates several special functions often appear. We will describe them in the two following paragraphs.

### 2.2.1 Spherical functions

The spherical harmonics are the angular part of the family of orthogonal solutions of the Laplace equation written in the spherical coordinates (2):

$$\nabla^2 f = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial f}{\partial r}) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial f}{\partial \theta}) + \frac{1}{r^2 \sin^2 \theta} (\frac{\partial^2 f}{\partial \phi^2}) = 0$$

Suppose we can find solutions in the form

$$f(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

Separation of variables gives two differential equations:

$$\begin{aligned} \frac{1}{R} \frac{\partial}{\partial r} (r^2 \frac{dR}{dr}) &= \lambda \\ \frac{1}{Y} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial Y}{\partial \theta}) + \frac{1}{Y} \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} &= -\lambda \end{aligned} \quad (3)$$

The solution of (3) is represented in the following form, called the spherical harmonics of the degree  $l$  and the order  $m$ :

$$Y_l^m(\theta, \phi) = \varepsilon \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} e^{im\phi} P_l^m(\cos \theta), \quad (4)$$

where  $\varepsilon = (-1)^m$  for  $m \geq 0$  and  $\varepsilon = 1$  for  $m \leq 0$ ,  $-l \leq m \leq l$  and  $P_l^m$  is associated with the Legendre function defined by:

$$P_l^m(x) = (1-x^2)^{m/2} \frac{d^m}{dx^m} P_l(x),$$

where  $P_l(x)$  is Rodrigues formula:

$$P_l(x) = \frac{1}{2^l l!} \left( \frac{d}{dx} \right)^l (x^2 - 1)^l.$$

Notice that  $m$  and  $l$  are integers. For any given  $l$  there are  $(2l+1)$  possible values for  $m$ :  $l = 0, 1, \dots, m = -l, -l+1, \dots, -1, 0, 1, \dots, l-1, l$ .

### 2.2.2 Bessel functions

The Bessel functions are canonical solutions  $y(x)$  of following differential equation:

$$x^2 \frac{d^2 y}{dx^2} + x \frac{dy}{dx} + (x^2 - \alpha^2)y = 0, \quad (5)$$

where  $\alpha$  is an arbitrary complex number, called the order of the Bessel function.

The most important cases are for  $\alpha$  an integer or half-integer. Spherical Bessel functions with half-integer  $\alpha$  are obtained when the Helmholtz equation is solved in spherical coordinates:

$$\nabla^2 A + k^2 A = 0,$$

where  $k$  is a wave number and  $A$  is an amplitude.

When solving the Helmholtz equation in the spherical coordinates by separation of variables, the radial equation has the form:

$$x^2 \frac{d^2 y}{dx^2} + 2x \frac{dy}{dx} + [x^2 - n(n+1)]y = 0$$

The two linearly independent solutions to this equation are called the spherical Bessel functions  $j_n$  and  $y_n$ :

$$j_n(x) = (-x)^n \left( \frac{1}{x} \frac{d}{dx} \right)^n \frac{\sin x}{x} \quad (6)$$

$$y_n(x) = (-x)^n \left( \frac{1}{x} \frac{d}{dx} \right)^n \frac{\cos x}{x} \quad (7)$$

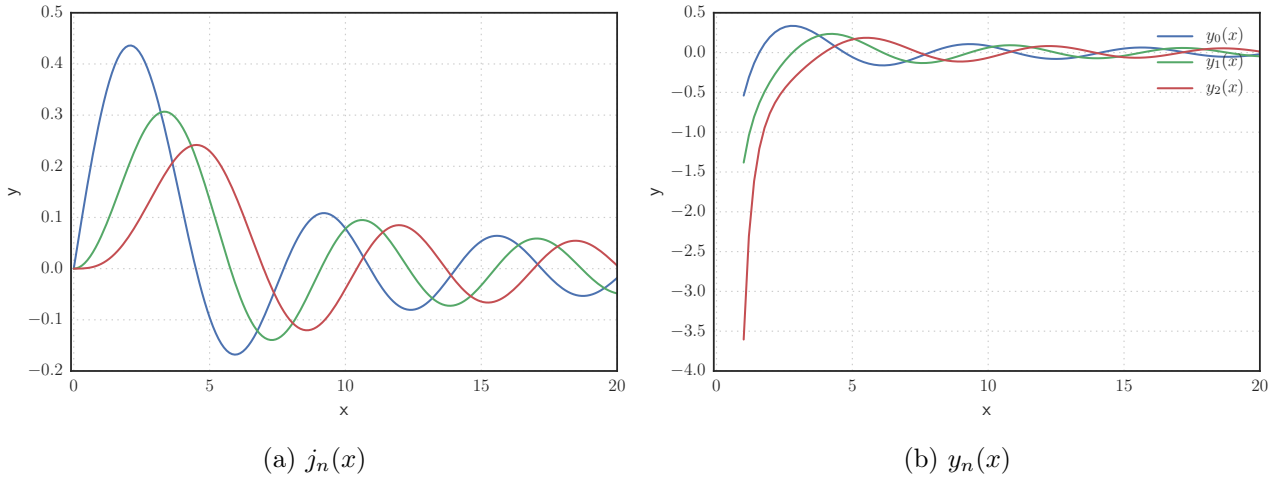


Fig. 2: Spherical Bessel functions

### 2.3 Angular momentum

The angular momentum  $L$  of a material point relative to a reference point is determined by the cross product of particle's position vector  $r$  (relative to some origin) and its momentum vector  $p$ :

$$\mathbf{L} = \mathbf{r} \times \mathbf{p},$$

which is to say,

$$\mathbf{L} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

This definition can be carried over to quantum mechanics, by reinterpreting  $r$  as the quantum position operator  $\hat{x} = x$  and  $p$  as the quantum momentum operator  $\hat{p} = \frac{\hbar}{i} \nabla$ :

$$\mathbf{L} = \frac{\hbar}{i} \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{vmatrix}$$

Writing this in coordinates, we obtain:

$$L_x = \frac{\hbar}{i} \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right), \quad L_y = \frac{\hbar}{i} \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right), \quad L_z = \frac{\hbar}{i} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

In the next section we will consider the eigenvalues and eigenfunctions of these operators.

### 2.3.1 Eigenvalues and eigenfunctions

We have the angular momentum operator  $\hat{L} = (\hat{L}_x, \hat{L}_y, \hat{L}_z)$  and these components satisfy the following commutation relations:

$$[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k, \quad i, j, k = 1, 2, 3 \quad (8)$$

where  $\epsilon_{ijk}$  is Levi-Civita symbol. The definition in three dimension is the following:  $\epsilon_{ijk}$  is equal to 1 if  $(i, j, k)$  is an even permutation of  $(1, 2, 3)$ , -1 if it is an odd permutation, and 0 if any index is repeated.

And

$$[\hat{L}_i, \hat{\mathbf{L}}^2] = 0,$$

where  $\hat{\mathbf{L}}^2 = \hat{\mathbf{L}}_x^2 + \hat{\mathbf{L}}_y^2 + \hat{\mathbf{L}}_z^2$ .

The angular momentum operators are commonly used in the solution of spherical symmetry problems. Then the momentum in the spherical coordinates:

$$-\frac{1}{\hbar^2}L^2 = \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} (\sin\theta \frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2}.$$

The eigenvalues and eigenfunctions are the following:

$$L^2 f_l^m = \hbar^2 l(l+1) f_l^m,$$

$$L_z f_l^m = \hbar m f_l^m,$$

where  $f_l^m = Y_l^m$  - spherical harmonics, defined in (4).

## 2.4 Spin

In classical mechanics, an object's rotation around a fixed axis is described by two kinds of angular momentum: orbital ( $L = r \times p$ ) associated with the motion of the center of mass and spin ( $S = I\omega$ ), associated with motion about the center of mass. Analogous things take place in quantum mechanics: in addition to orbital angular momentum associated with the motion of electron around the nucleus (in case of hydrogen) and which is described by the spherical harmonics, but electron also carries another form of angular momentum, which has nothing to do with motion in space, but which is somewhat analogous to classical spin. Notice that electron is a structureless point particle, and its spin angular momentum cannot be decomposed into orbital one of constituent parts. So elementary particles have intrinsic angular momentum  $S$  and "extrinsic" angular momentum  $L$ . ([3])

The existence of the spin angular momentum was proven in experiments, for instance the Stern-Gerlach experiment.

The algebraic theory of the spin is the same as the theory for the orbital angular momentum. So there are the fundamental commutation relations as (8). But these time the eigenvectors are not spherical harmonics (they are not functions of  $\theta$  and  $\phi$ ), so there is no reason to exclude half-integers values of  $s$  and  $m$ :

$$s = 0, \frac{1}{2}, 1, \dots; \quad m = -s, -s+1, \dots, s-1, s.$$

### 2.4.1 Spin $\frac{1}{2}$

An important case is  $s = \frac{1}{2}$ , corresponds to, for example, the electron. There are two eigenstates:  $\left| \frac{1}{2} \frac{1}{2} \right\rangle$  and  $\left| \frac{1}{2} -\frac{1}{2} \right\rangle$ . Let's add the following discrete variable: the spin quantum number  $\sigma$ . Then the particle's wave function becomes:  $\Psi = \Psi(x, y, z, \sigma, t)$ , and normalization condition becomes  $\sum_i \iint |\Psi_{\sigma_i}(x, y, z, \sigma, t)|^2 dV = 1$ . For electrons with  $s = \frac{1}{2}$ :  $\sigma_1 = \frac{1}{2}$  and  $\sigma_2 = -\frac{1}{2}$ . Then the spin wave function is

$$\phi(t) = \begin{pmatrix} \chi_{1/2}(t) \\ \chi_{-1/2}(t) \end{pmatrix} = \begin{pmatrix} \chi_1(t) \\ \chi_2(t) \end{pmatrix} - \text{spinor}.$$

The normalisation condition is

$$|\chi_1|^2 + |\chi_2|^2 = 1.$$

The hermitian inner product of spinors is the following:

$$\phi_1 = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}, \phi_2 = \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} \Rightarrow \langle \phi_1 | \phi_2 \rangle = a_1^* b_1 + a_2^* b_2.$$

The quantum mechanical operators associated with this spin observables are:

$$\hat{S} = \frac{\hbar}{2} \hat{\sigma},$$

For particles with spin  $\frac{1}{2}$   $\sigma_x, \sigma_y, \sigma_z$  there are three matrices called the Pauli matrices given by:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$S_x, S_y$  and  $S_z$  satisfy canonical momentum commutation relations. It is easy to check, that the Pauli matrices are hermitian and unitary.

## 2.5 Time dependent Schrodinger equation

In one-dimensional case, the total energy of a particle is described by the Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(x), \quad (9)$$

where  $\hbar$  is the Planck constant,  $m$  is mass of the particle,  $\nabla^2 = \frac{\partial^2}{\partial x^2}$  is the Laplasian,  $V$  - the potential

The Schrodinger equation describes a particle dynamics:

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = H \Psi(x, t), \quad (10)$$

where  $\Psi(x, t)$  is the wave function,  $H$  is the Hamiltonian.

Bohr provided the statistical interpretation of the wave function:  $|\Psi(x, t)|^2$  gives the probability density in coordinate space. Then  $|\Psi(x, t)|^2 dx$  gives probability of finding the particle at point  $(x + dx)$  at time  $t$ .

It follows that

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

Such function is called the normalized wave function.

General solution of the time dependent Schrodinger equation is

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t / \hbar},$$

where stationary states  $\psi_n(x)$  are solutions of time independent Schrodinger equation:

$$H\psi = E\psi, \quad (11)$$

and the coefficients  $c_n$  are determined in order to fit the initial conditions. As it turns out, it is often impossible to solve even stationary Schrodinger equation analytically. In this case numerical methods are used. In the following sections the main ideas of this methods are described.

## 2.6 Finite difference and eigenvalue problem

In the spherical symmetry case we obtain the following equation, which is called the radial (see section 3):

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + [V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}]u = Eu,$$

where  $u(r) = rR(r)$ .

If  $l = 0$  the equation says:

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + Vu &= Eu, \\ -\frac{\hbar^2}{2m} u'' + Vu &= Eu. \end{aligned}$$

If we let  $\hbar = 1, m = 1$  (atomic units):

$$\begin{aligned} -\frac{u''}{2} + Vu &= Eu, \\ u'' + (-2V)u &= -2Eu, \\ (\frac{d^2}{dr^2} - 2V)u &= -2Eu. \end{aligned}$$

The last equation says  $-2E$  is the eigenvalue of  $(\frac{d^2}{dr^2} - 2V)$  operator. To find this value, we have to approximate the continuous expressions by the discrete ones. Also we need boundary conditions. Since the wave function is typically exponentially damped, we can assume that  $u(r) = 0$  for  $r \geq L$  for some sufficiently large  $L$  (so called effective infinity).

Thus we obtain the eigenvalue problem with the boundary conditions  $u(0) = 0$  (since  $u(r) = rR(r)$ ) and  $u(L) = 0$ . We define the step  $h = LN^{-1}$ , where  $N$  is positive integer (divide the segment  $[0, L]$  into  $N$  parts),  $r_n = nh$  is the grid nodes.

The first derivative is

$$u'_n = \frac{u_{n+1} - u_n}{h}.$$

The second derivative is given by the following relation :

$$u''_n = \frac{u_{n+1} - 2u_n + u_{n-1}}{h^2}.$$

Then  $u''_n \rightarrow u''(r_n)$  and

$$\begin{bmatrix} u''_1 \\ u''_2 \\ u''_3 \\ \vdots \\ u''_n \end{bmatrix} = -\frac{1}{h^2} \begin{bmatrix} -2 & 1 & 0 & 0 & 0 & \cdots & 0 \\ 1 & -2 & 1 & 0 & 0 & \cdots & 0 \\ 0 & 1 & -2 & 1 & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & -2 & 1 \\ 0 & 0 & 0 & 0 & \cdots & 1 & -2 \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ \vdots \\ u_n \end{bmatrix}$$

Note that the resulting matrix has a tridiagonal form.

Now we need to approximate  $-2V(r_n)u(r_n)$ :

$$-2V(r_n)u(r_n) = \begin{bmatrix} -2V(r_1) & 0 & 0 & 0 & 0 & \cdots & 0 \\ 0 & -2V(r_2) & 0 & 0 & 0 & \cdots & 0 \\ 0 & 0 & -2V(r_3) & 0 & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & 0 & -2V(r_{n-1}) \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ \vdots \\ u_n \end{bmatrix}$$



It is easy to check that  $\|u_n'' - u''(r_n)\| \sim O(h^2)$ .

Thus our problem is to find the eigenvalues for the sum of the matrices presented.

## 2.7 Richardson method

Let's use some ideas from the Richardson extrapolation method to find the spectrum. We discretize the uniform grid  $[0, L]$  into  $N$  and  $2N$  parts with the step  $2h$  and  $h$  correspondingly. Suppose we have the residual of the order  $h^2$ , then

$$\begin{aligned} E_N - E &= C(2h)^2, \\ E_{2N} - E &= Ch^2, \end{aligned}$$

where  $E$  is the exact energy value,  $C$  is some constant. We obtain

$$E = \frac{4E_N - E_{2N}}{3}. \quad (12)$$

This equation can be used to 'predict' the energy value if the exact solution is unknown.

## 3 Electron in spherically symmetric potentials

In this section we will try to solve some problems with concrete potentials. But, firstly, we are going to consider some principles for solving Schrodinger equation in three dimensions.

Using results from paragraph 2.1 and the Laplacian in the spherical coordinates (2) we find time-independent Schrodinger equation in the form:

$$-\frac{\hbar^2}{2m} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial \psi}{\partial r}) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial \psi}{\partial \theta}) + \frac{1}{r^2 \sin^2 \theta} (\frac{\partial^2 \psi}{\partial \phi^2}) \right] + V\psi = E\psi \quad (13)$$

We are looking for solutions that are separable into products:

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi),$$

putting this in (13) and using results from previous sections, we get:

$$\frac{1}{R} \frac{\partial}{\partial r} (r^2 \frac{\partial R}{\partial r}) - \frac{2mr^2}{\hbar^2} [V(r) - E] = l(l+1), \quad (14)$$

$$\frac{1}{Y} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial Y}{\partial \theta}) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} = -l(l+1). \quad (15)$$

The equation (15) is the angular part of the wave function, (16) is the radial part of the wave function. Notice, that the angular part is the same for all spherically symmetric potentials, but for our purposes it is important to investigate the radial part, because spherically symmetric potentials depend only on  $r$ .

Let  $u(r) = rR(r)$ , so:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 u}{\partial r^2} + [V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}]u = Eu \quad (16)$$

It is so called radial equation. Normalization condition becomes

$$\int_0^\infty |u|^2 dr = 1$$

### 3.1 Spherically potential well

#### 3.1.1 Infinite spherical well

For the infinite spherical well with the radius  $a$  the potential is

$$V(r) = \begin{cases} 0, & \text{if } r \leq a \\ \infty, & \text{if } r > a \end{cases}$$

Then, inside the well the radial equation (16) says

$$\frac{d^2 u}{dr^2} = \left[ \frac{l(l+1)}{r^2} - k^2 \right] u, \quad (17)$$

where

$$k = \frac{\sqrt{2mE}}{\hbar}$$

We need to solve this equation using the boundary condition  $u(a) = 0$ . Suppose  $l = 0$ :

$$\frac{d^2 u}{dr^2} = -k^2 u \Rightarrow u(r) = A \sin(kr) + B \cos(kr)$$

This case is easy. But notice, the actual radial wave function is  $R(r) = u(r)/r$ , and  $(\cos(kr))/r$  blows up as  $r \rightarrow 0$ . Thus  $B = 0$ . Then it requires  $\sin(ka) = 0$ , and hence  $ka = n\pi$ , for some integer  $n$ . The allowed energies are

$$E_{n0} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}, \quad n = 1, 2, \dots$$

To solve the equation in all cases define a new variable  $z = kr$ , and let  $u = z^{1/2} \phi z$ . Then (17) takes the following form:

$$\frac{d^2 \phi}{dz^2} + \frac{1}{z} \frac{d\phi}{dz} + \left[ 1 - \frac{(l + \frac{1}{2})^2}{z^2} \right] \phi = 0.$$

This is Bessel's differential equation (5). So, general solution is

$$u(r) = A r j_l(kr) + B n_l(kr),$$

where  $j_l(x)$  and  $n_l(x)$  are the spherical Bessel functions (6), (6) of an order  $l$ . Notice, that (6) blow up at the origin. So we must have  $B_l = 0$ , and hence

$$R(r) = A j_l(kr).$$

The boundary condition says  $R(a) = 0$ , which implies  $k$  must be chosen such that

$$j_l(kr) = 0.$$

This means, that  $ka$  is zero of the  $l^{th}$ -order spherical Bessel function, but they are not located in good points, such as  $n$  or  $\pi n$ . The boundary condition requires

$$k = \frac{1}{a} \beta_{nl},$$

where  $\beta_{nl}$  is the  $n^{th}$  zero of the  $l^{th}$  spherical Bessel function. The allowed energies are defines by

$$E_{nl} = \frac{\hbar^2}{2ma^2} \beta_{nl}^2, \quad (18)$$

and the wave functions are

$$\psi_{nlm}(r, \theta, \phi) = A_{nl} j_l(\beta_{nl} r/a) Y_l^m(\theta, \phi),$$

where  $A_{nl}$  is a constant determined by normalization,  $Y_l^m(\theta, \phi)$  is spherical harmonics (4). We assume atomic units, so  $\hbar = 1, m = 1$ . As an example we consider finite spherical well with  $a = 5$  a.u. Results are presented in the table 3.

	$n = 1$	$n = 2$	$n = 3$	$n = 4$
$l = 0$	0.197443	0.789522	1.776613	3.158087
$l = 1$	0.403741	1.193512	2.377944	3.957047
$l = 2$	0.664243	1.654381	3.037127	4.814305
$l = 3$	0.976643	2.170278	3.752704	5.728436
$l = 4$	1.339230	2.740140	4.524032	6.698532

Fig. 3:  $E_{nl}$  in a.u. of an electron in an infinite spherical well of radius  $a = 5$  a.u.

### 3.1.2 Finite spherical well

For the finite spherical well the potential is defined as

$$V(r) = \begin{cases} -V_0, & \text{if } r < R \\ 0, & \text{if } r > R \end{cases}$$

Let

$$\frac{2m|E|}{\hbar^2} = \kappa^2, \quad \frac{2mV_0}{\hbar^2} = k_0^2, \quad \frac{2m(V_0 - |E|)}{\hbar^2} = k^2,$$

then the radial equation inside of the well and outside are correspondently:

$$\frac{d^2u}{dr^2} + \left[k^2 - \frac{l(l+1)}{r^2}\right]u = 0 \quad (19)$$

$$\frac{d^2u}{dr^2} + \left[-\kappa^2 - \frac{l(l+1)}{r^2}\right]u = 0 \quad (20)$$

The solution of the equation (19) is a spherical Bessel function (with the boundary condition  $u(0) = 0$ ):

$$ru(r) = Aj_l(kr), \quad r < R.$$

To find the solutions of the equation (20) we need to define spherical Hankel functions:

$$h_l(x) = j_l(x) + in_l(x),$$

$$h_l^*(x) = j_l(x) - in_l(x),$$

where  $j_l(x)$  and  $n_l(x)$  are spherical Bessel functions (6), (7).

As  $r \rightarrow \infty$

$$h_l(x) \rightarrow \frac{e^{[ix - \pi(l+1)/2]}}{x}$$

$$h_l^*(x) \rightarrow \frac{e^{-[ix - \pi(l+1)/2]}}{x}$$

The solution of the equation (20) is a spherical Hankel function of an imaginary argument:

$$ru(r) = Bh_l^{(1)}(i\kappa r), \quad r > R.$$

We are interested in finding constants  $A$  and  $B$  from continuity and normalization condition. First match the wavefunction:

$$Aj_l(kR) = Bh_l(i\kappa R). \quad (21)$$

Second match the first derivative:

$$Ak \left[ \frac{dj_l(\rho)}{d\rho} \right]_{\rho=kR} = Ai\kappa \left[ \frac{dh_l(\rho)}{d\rho} \right]_{\rho=i\kappa R}. \quad (22)$$

Now divide (22) by (21), then the constants cancel out. This trick is called logarithmic derivative:

$$k \left[ \frac{\frac{dj_l(\rho)}{d\rho}}{j_l(\rho)} \right]_{\rho=kR} = i\kappa \left[ \frac{\frac{dh_l(\rho)}{d\rho}}{h_l(\rho)} \right]_{\rho=i\kappa R}$$

Then, the solution of the problem depends on the value of  $l$ . Let  $l = 0$ , the boundary condition becomes

$$k \left[ \frac{\frac{\cos \rho}{\rho} - \frac{\sin \rho}{\rho^2}}{\frac{\sin \rho}{\rho}} \right]_{\rho=kR} = i\kappa \left[ \frac{\frac{ie^{i\rho}}{i\rho} - \frac{e^{i\rho}}{i\rho^2}}{\frac{e^{i\rho}}{i\rho}} \right]_{\rho=i\kappa R},$$

divide and substitute for  $\rho$ :

$$k \left( \text{ctg}(kR) - \frac{1}{kR} \right) = i\kappa \left( i - \frac{1}{i\kappa R} \right),$$

$$k \text{ctg}(kR) = -\kappa. \quad (23)$$

This is transcendental equation, but we can solve it numerically for  $k$ , for which  $k_0^2 - \kappa^2 = k^2$ . Also, it is possible that there can be no solution. For instance, we can solve this equation graphically, but remember, it is only for case  $l = 0$ . We are interested in more general cases.

For finding numerical solutions of our problem (our problem is to calculate the possible values of the electron energy) not only for  $l = 0$  it is convenient to use the following form of (23) with the notations  $kR = x$ ,  $k_0R = x_0$ ,  $\frac{k}{k_0} = \xi$ ,  $\kappa R = \sqrt{1 - \xi^2}$ :

$$\tan(x_0\xi) = f_l(x_0\xi), \quad (24)$$

where

$$f_0(x_0, \xi) = -\frac{\xi}{\sqrt{1 - \xi^2}},$$

$$f_1(x_0, \xi) = \frac{x_0\xi}{1 + \frac{\xi^2}{1 - \xi^2}(1 + x_0\sqrt{1 - \xi^2})}.$$

It can be easily seen that in case  $l = 0$  (24) takes the form (23). In the further analysis we assume atomic units, so  $\hbar = 1, m = 1$ . By substituting values of  $k_0, k$  and  $\kappa$  to the (23) we obtain:

$$\tan(\sqrt{2}a\sqrt{V_0 - E}) = -\sqrt{\frac{V_0}{E} - 1}$$

As an example we consider finite spherical well with  $a = 5$  a.u.,  $V_0 = 10$  a.u. We solved the equation (23) using Newton's method. The resulting energies are given in the Figure 5b. For  $l = 1$  we have the

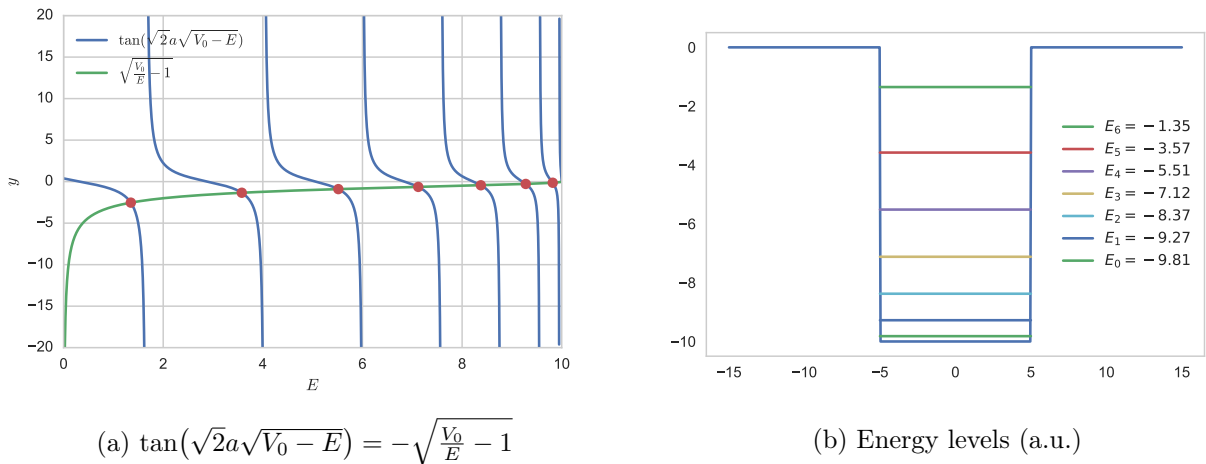
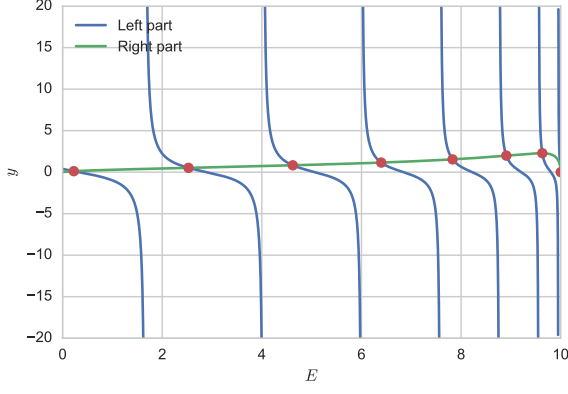


Fig. 4: Finite spherical well  $V_0 = 10$  a.u.,  $a = 5.0$  a.u.

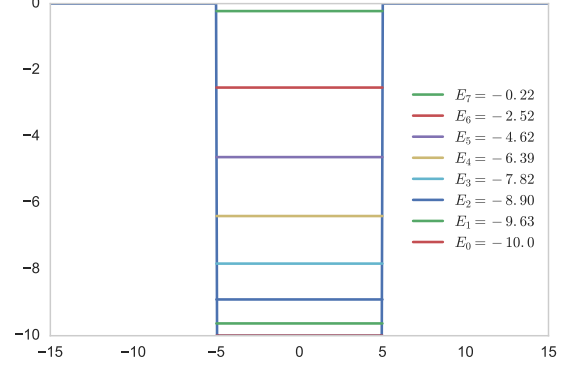
formula:

$$\tan(\sqrt{2}a\sqrt{V_0 - E}) = \frac{aE\sqrt{2(V_0 - E)}}{V_0 + aV_0\sqrt{2E} - a\sqrt{2E}^{3/2}}.$$

The resulting energies are given in the Figure 5



$$(a) \tan(\sqrt{2}a\sqrt{V_0 - E}) = -\sqrt{\frac{|E|}{V_0}} - 1$$



(b) Energy levels (a.u.)

Fig. 5: Finite spherical well in case  $l = 1$   $V_0 = 10$  a.u.,  $a = 5.0$  a.u.

### 3.2 Isotropic Harmonic Oscillator

For the isotropic harmonic oscillator the potential is defined as

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

Isotropy means that the frequencies for independent  $x, y, z$  oscillations are the same. So for the oscillator in 3 dimensions we can use creation and annihilation operators  $\hat{a}_x^\dagger, \hat{a}_y^\dagger, \hat{a}_z^\dagger$  and  $\hat{a}_x, \hat{a}_y, \hat{a}_z$  associated with 1D oscillators in the  $x, y,$  and  $z$  directions. The Hamiltonian then takes the form:

$$H = \hbar\omega(\hat{N}_1 + \hat{N}_2 + \hat{N}_3 + \frac{3}{2}) = \hbar\omega(\hat{N} + \frac{3}{2}),$$

where  $\hat{N} = \hat{N}_1 + \hat{N}_2 + \hat{N}_3$ .

For analytical solution we use the standard separation variables procedure, then the radial equation (16) takes the form:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 u}{\partial r^2} + [\frac{1}{2}m\omega^2 r^2 + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}]u = Eu$$

However, a 3D oscillator spectrum finding procedure is complicated, due to this reason we used the numerical methods, described in subsection 2.6, for solving the problem and compared it with the known formula:

$$E_{nl} = \hbar\omega(2n_r + l + \frac{3}{2}), \quad n_r = 0, 1, 2, \dots \quad (25)$$

Results are represented in the Figure 6 and 7. For more detailed information about numerical experiment see Appendix.

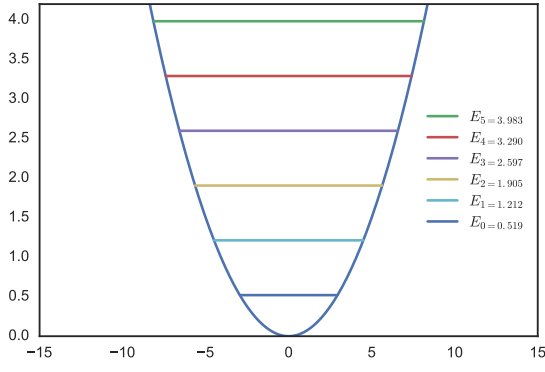
$n$	Numerical	Analytical
0	0.519608	0.519615
1	1.212398	1.212436
2	1.905165	1.905256
3	2.597907	2.598076
4	3.290626	3.290897
5	3.983320	3.983717

(a)  $l = 0$

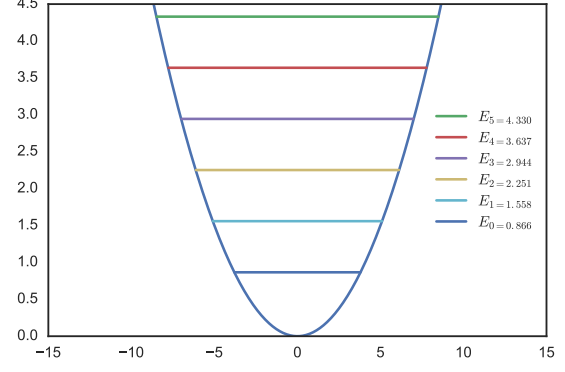
$n$	Numerical	Analytical
0	0.866016	0.866025
1	1.558807	1.558846
2	2.251574	2.251666
3	2.944318	2.944486
4	3.637037	3.637307
5	4.329732	4.330127

(b)  $l = 1$

Fig. 6:  $E_{nl}$  in a.u. for harmonic oscillator



(a) Spectrum in case  $l = 0$  (a.u.)



(b) Spectrum in case  $l = 1$  (a.u.)

Fig. 7: Isotropic Harmonic Oscillator

### 3.3 Hydrogen Atom

From the Coulomb's law, the potential energy (in a.u.) is

$$V(r) = -\frac{1}{r}, \quad (26)$$

and the radial equation (16) says

$$-\frac{1}{2} \frac{d^2 u}{dr^2} + \left[ -\frac{1}{r} + \frac{1}{2} \frac{l(l+1)}{r^2} \right] u = Eu.$$

The analytical solution is known:

$$E_n = -\frac{1}{2n^2} \quad (27)$$

Notice, that the hydrogen's spectrum depends only on the energy level  $n$ .

We used the numerical methods from the section 2.6, and results are represented in the Figure 8.

$n$	Numerical	Analytical
1	-0.499911	-0.500000
2	-0.124994	-0.125000
3	-0.055554	-0.055556
4	-0.031250	-0.031250
5	-0.020000	-0.020000

Fig. 8:  $E_{nl}$  in a.u. of The Hydrogen Atom

We have some problems with the convergence, because the potential (26) is singular at point 0. Graphical illustration of the spectrum is given in Figure 9.

### 3.4 Woods-Saxon potential

The Woods-Saxon potential describes the interaction of the protons and neutrons with the heavy nucleus inside the atomic nucleus:

$$V(r) = -\frac{V_0}{1 + e^{\frac{r-R}{a}}}, \quad (28)$$

where  $a \ll R$ .

$R$  is a the nuclear radius,  $a$  is the parameter that characterizes the thickness of a surface layer within which the potential falls from  $V = 0$  outside the nuclear to  $V = -V_0$  inside one. If let  $a = 0$ , we obtain

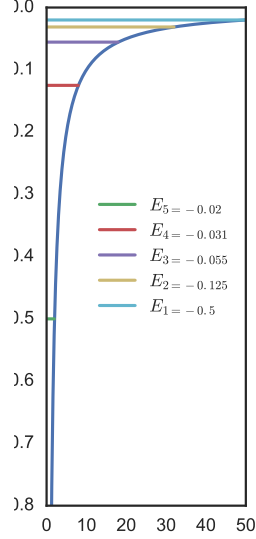


Fig. 9: The Hydrogen Atom Spectrum (in a.u.)

a potential well with a potential jump at the nuclear surface.

The radial equation (16) says:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 u}{\partial r^2} + \left[ -\frac{V_0}{1 + e^{\frac{r-R}{a}}} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu.$$

When using the Schrodinger equation to find the spectrum of nucleons subjected to the Woods-Saxon potential, it is impossible to find the analytical solution. Numerical method results are shown in the Figure 10.

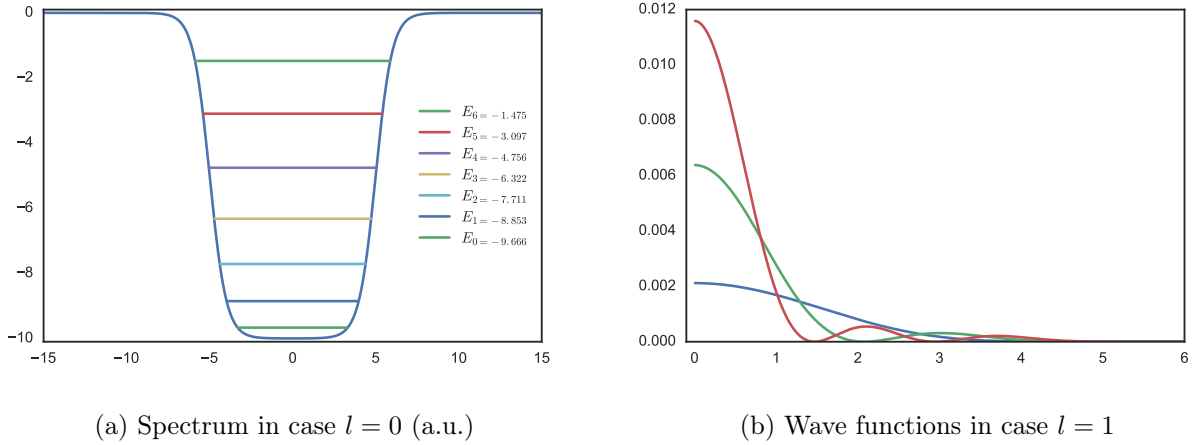


Fig. 10: Woods-Saxon potential

### 3.5 Hulthen Potential

The Hulthen potential is given by

$$V(r) = -V_0 \frac{e^{-\frac{r}{a}}}{1 - e^{-\frac{r}{a}}}. \quad (29)$$

Our problem to find the spectrum in case  $l = 0$ .

The radial part (16) of the Schrodinger equation in a.u. says:

$$-\frac{1}{2} \frac{\partial^2 u}{\partial r^2} + \left[ -V_0 \frac{e^{-\frac{r}{a}}}{1 - e^{-\frac{r}{a}}} + \frac{1}{2} \frac{l(l+1)}{r^2} \right] u = Eu.$$

The analytical solution is known:

$$E_n = -V_0 \left( \frac{\beta^2 - n^2}{2n\beta} \right)^2, \quad (30)$$

$$\beta^2 > n^2, \quad (31)$$

where  $\beta^2 = \frac{2mV_0}{\hbar^2} a^2 > 0$ .

If we rewrite (30) in the atomic units:

$$E_n = -V_0 \left( \frac{2V_0 a^2 - n^2}{2na\sqrt{2V_0}} \right)^2,$$

and compare it with the numerical methods from section 2.6. The resulting table is shown in Figure 11.

$n$	Numerical	Analytical
1	-7.99988128221	-8.0
2	-0.124924678667	-0.125

Fig. 11:  $E_{n0}$  in a.u. for the Hulthen Potential

In our calculation we let  $V_0 = 10a.u.$ ,  $a = 0.5$ , so from the condition 31:  $2.5 > n^2$ , we obtain only two energy levels.

Notice, that the Hulthen potential behaves like a Coloumb potential at small values of  $r$ :

$$V_c = -\frac{V_0 a}{r},$$

and for large values of  $r$  it decreases exponentially so that its "capacity" for bound states is smaller than that of  $V_c$ .

### 3.6 Morse potential

The Morse potential describes the vibrations of a two-atomic molecule:

$$V(r) = D(e^{-2\alpha x} - 2e^{-\alpha x}), \quad (32)$$

$$x = \frac{r - r_0}{r_0}.$$

This formula is used to model the atom-surface interaction, and  $r$  is the coordinate perpendicular to the surface,  $r_0$  is the equilibrium bond distance,  $D$  is the well depth and  $\alpha$  controls the 'width' of the potential (the smaller  $\alpha$  is, the larger the well).

The parameters  $D$ ,  $\alpha$  and  $r_0$  are known for some typical molecules such as  $H_2$  or  $HCl$  from experiments. We will research the hydrogen atom, for more detailed information about parameters see Appendix. The problem is to find the spectrum for  $l = 0$  bond states.

The radial equation in a. u. says:

$$-\frac{1}{2m} \frac{\partial^2 u}{\partial r^2} + [D(e^{-2\alpha x} - 2e^{-\alpha x}) + \frac{1}{2m}] u = Eu.$$

The analytical solution is known:

$$E_n = -D + \hbar\omega \left[ \left( n + \frac{1}{2} \right) - \frac{1}{\xi} \left( n + \frac{1}{2} \right)^2 \right],$$



$n$	Numerical	Analytical
0	-0.706884	-0.707390
1	-0.686828	-0.688970
2	-0.667061	-0.671669
3	-0.647583	-0.655489
4	-0.628393	-0.640428
5	-0.609493	-0.626487
6	-0.590881	-0.613665
7	-0.572558	-0.601964
8	-0.554524	-0.591382
9	-0.536779	-0.581920

Fig. 12:  $E_{n0}$  in a.u. for the Morse potential

where  $\xi = \frac{2\gamma}{\alpha}$ ,  $\gamma^2 = \frac{2MDr_0^2}{\hbar^2}$ , and  $\omega$  can be found from the following equation:  $\hbar\omega = \frac{\hbar^2}{2Mr_0^2}$ .

We used the numerical method from section 2.6. Results are presented in the Figure 12. Notice, that at large distances the potential corresponds to the attraction forces, it comes to a minimum  $-D$  at  $x = 0$  or  $r = r_0$ , but produces a strong repulsion if the two nuclei approach even closer.

Around  $x = 0$  it may be expanded into a series:

$$V(r) = D(-1 + \alpha^2 x^2 + \dots) = -D + \frac{1}{2}M\omega^2(r - r_0)^2 + \dots, \quad (33)$$

where  $\omega^2 = \frac{2D\alpha^2}{Mr_0^2}$ .

Thus, for low vibrational levels, a spectrum not deviating very much from that of a harmonic oscillator:

$$E(\nu) = -D + \hbar\omega(\nu + \frac{1}{2}), \quad \nu = 0, 1, 2, \dots,$$

with  $\nu$  the vibrational quantum number, the almost equidistant terms becoming increasingly denser with increasing energy, in consequence of the anharmonicity neglected in 33.

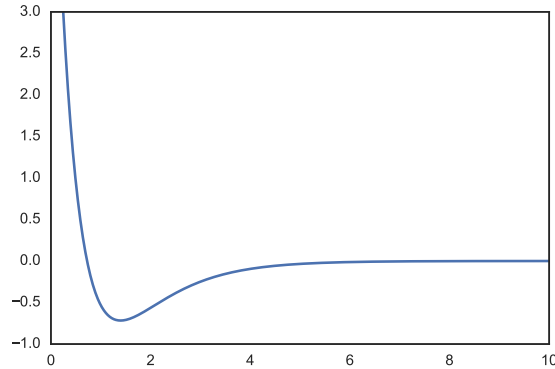


Fig. 13: Morse potential

### 3.7 Yukawa Potential

The Yukawa potential is used to describe the nuclear attraction between two particles (for example, nucleons), it is often used to compute the spectrum of neutral atoms.

The Yukawa potential is given by

$$V(r) = -V_0 \frac{e^{-ar}}{r}, \quad (34)$$

where  $V_0 = \alpha Z$  and  $Z$  is the atomic number,  $\alpha = \frac{1}{137}$  is the fine-structure constant and  $a$  is the screening parameter. Our problem is to find the spectrum. The radial part (16) of the Schrodinger equation in a.u. becomes:

$$-\frac{1}{2} \frac{\partial^2 u}{\partial r^2} + [-V_0 \frac{e^{ar}}{r} + \frac{1}{2} \frac{l(l+1)}{r^2}]u = Eu.$$

No exact analytical solution was found, however some approximate analytical solution was obtained using Nikiforof-Uvarov method in the [4]:

$$E_{nl} = -\frac{a^2}{2m} \frac{(\frac{mV_0}{a} - (n+1)^2 - l(2n+l+2))^2}{(n+l+1)^2} \quad (35)$$

Compare results of numerical method from the section 2.6 and formula (35) if  $l = 0$ . Results are shown in the Figure 14.

n	Numerical	App. Analytical
0	-0.096186	-0.097882
1	-0.024362	-0.024470
2	-0.010854	-0.010876
3	-0.006111	-0.006118
4	-0.003912	-0.003915
5	-0.002717	-0.002719
6	-0.001997	-0.001997
7	-0.001529	-0.001529
8	-0.001208	-0.001208
9	-0.000978	-0.000979

Fig. 14:  $E_{n0}$  in a.u. for the Yukawa Potential

Accordingly to [4], if the screening parameter  $a \rightarrow 0$ , the potential (34) becomes the Coulomb potential. Hence, the eigenvalues of (35) become the spectrum of pure Coulomb potential:

$$E_{nl}^{Coulomb} = -\frac{1}{2}m \frac{V_0^2}{n'^2},$$

where  $n' = n + l + 1$ .

### 3.8 Central-force model of deuteron

The neutron-proton interaction in the idealized situation is described by the following potential:

$$V(r) = -Ae^{-r/a}$$

Our problem is to solve the Schrodinger equation for the bound state with  $l = 0$  (deuteron). As it was determined by experiment there exists only one bound state (see [3]):

$$E = -2.23 \text{ MeV} \quad (36)$$

The following results are obtained in [3].

#### 3.8.1 Exact solution

For  $l = 0$  we obtain the following radial Schrodinger equation (16):

$$\frac{d^2 u}{dr^2} + \frac{2m^*}{\hbar^2} (E + Ae^{-r/a})u = 0, \quad (37)$$

where  $m^* = \frac{1}{2}$ , because we let masses of both nucleons equal. Use of the new variable:

$$y = e^{-r/2a} \quad (38)$$

we obtain:

$$\frac{d^2u}{dy^2} + \frac{1}{y} \frac{du}{dy} + (c^2 - \frac{q^2}{y^2})u = 0, \quad (39)$$

where

$$c^2 = \frac{8m^*}{\hbar^2} Aa^2, \quad q^2 = -\frac{8m^*}{\hbar^2} Ea^2 > 0 \quad (40)$$

The equation (39) is Bessel's differential equation (5) with the general solution:

$$u = C_1 J_q(cy) + C_2 J_{-q}(cy).$$

On the one hand,  $r$  blows up if  $y = 0$  where  $u$  must vanish. Therefore  $C_2 = 0$  :

$$u = \frac{C_1}{r} J_q(ce^{-r/2a}) \quad (41)$$

On the other hand,  $y = 1$  corresponds to  $r = 0$  where  $u$  must be finite so that the Bessel function in bound to vanish ([3]):

$$J_q(c) = 0.$$

### 3.8.2 Approximate solution

The wave function

$$\tilde{u} = \frac{C}{r} (e^{-\frac{qr}{2a}} - e^{-\frac{qr}{a}})$$

has a finite value

$$u(0) = C \frac{q}{2a}$$

at  $r = 0$ , and decreases, for large  $r$ , exponentially with the correct decay length:

$$\exp\left(-\frac{qr}{2a}\right) = \exp\left(-r\sqrt{\frac{2m^*|E|}{\hbar^2}}\right).$$

The normalization constant  $C$  can be obtained from

$$4\pi \int_0^\infty dr r^2 \tilde{u}(r)^2 = 1; \quad (42)$$

$$C = \sqrt{\frac{3q}{2\pi a}}.$$

By putting the exact solution (40) in the formula (42) we obtain the exact answer for  $E$ . By using approximation  $\tilde{u}$  we obtain an approximation for the energy:

$$E = 4\pi \int_0^\infty dr r^2 \left[ \frac{\hbar^2}{2m^*} (du/dr)^2 - Ae^{-r/a} u^2 \right] \quad (43)$$

Using the equation (40) for  $u$  the formula (42) yields the exact eigenvalue  $E$ . Using instead the approximate function  $\tilde{u}$ , we find the approximate eigenvalue  $\tilde{E}$ .

The evaluation of (43) with (41) has the following form:

$$E = \frac{\hbar^2}{4m^*a^2} q^2 - 6A \left[ \frac{1}{1 + \frac{1}{q}} - \frac{1}{\frac{3}{2} + \frac{1}{q}} + \frac{1}{2 + \frac{1}{q}} \right] \quad (44)$$

Some numerical results:  $\tilde{E} = -2.18$  MeV if  $a = 2.18$  fm and  $A = 32.7$  MeV. The correct value  $E = -2.23$  MeV (from [3]).

### 3.9 Convergence analysis

As an example of choosing  $h$  we also investigated the convergence rate corresponding to the grid size for the hydrogen atom. Results are presented in the Figure 15. We observed the quadratic convergence. For more detailed information see the section 5.

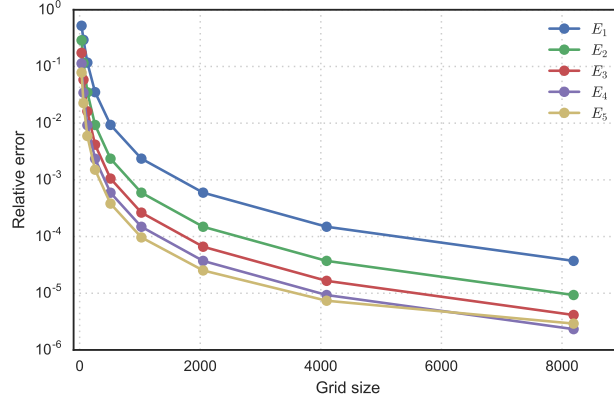


Fig. 15: Convergence for the hydrogen atom

## 4 Conclusion

In this work we have investigated the spectrum problem for an electron in several spherically symmetric potentials by constructing the numerical scheme of solving the eigenvalue problem. We used the second-order discretization scheme for the Hamiltonian operator and solved corresponding eigenvalue problems by various methods. Numerical results obtained by numerical methods were compared with the analytical ones if the latter existed. If analytical solutions for a potential did not exist we compared results obtained from various numerical or approximate methods.

Developed software tools will be used in educational process for students of 'Materials, devices and nanotechnology' master's programme.

## 5 Appendix

The purpose of this section is to expand on some of the techniques and values used in numerical computations. All programs were written in Python 3 using `numpy` and `scipy` libraries, see [1].

### Infinite spherical well

The potential is defined by

$$E_{nl} = \frac{\hbar^2}{2ma^2} \beta_{nl}^2,$$

where  $\beta_{nl}$  -  $n^{th}$  zero of the  $l^{th}$  spherical Bessel function  $j_n(x) = (-x)^n \left( \frac{1}{x} \frac{d}{dx} \right)^n \frac{\sin x}{x}$ . To find zeros we used the Newton method. Results are summarized in the Table 16.

For further computation we assume the atomic units, so  $\hbar = 1$ ,  $m = 1$ :

$$E_{nl} = \frac{1}{2a^2} \beta_{nl}^2$$

As an example we consider infinite spherical well with  $a = 5$  a.u. The results are presented in the Figure 3.

### Finite spherical well

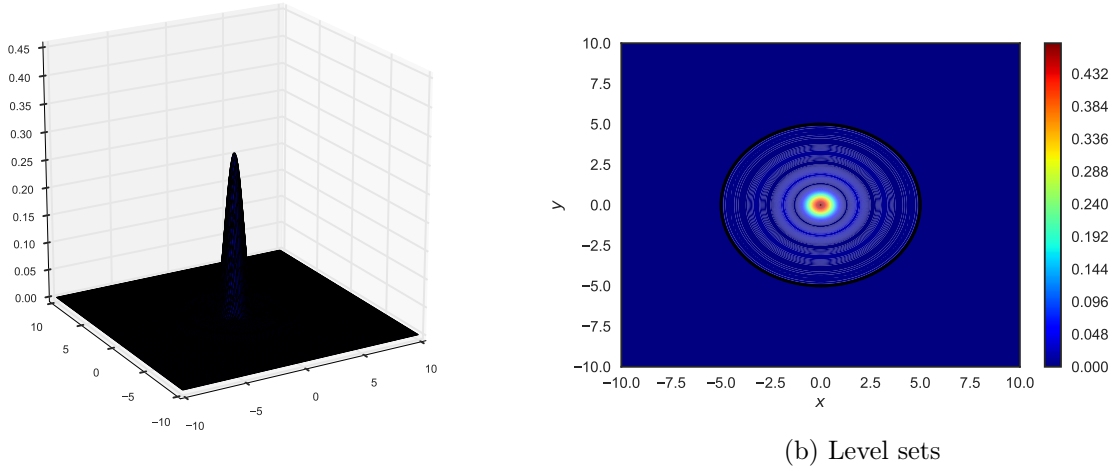
	$n = 1$	$n = 2$	$n = 3$	$n = 4$
$l = 0$	3.142	6.283	9.425	12.566
$l = 1$	4.493	7.725	10.904	14.066
$l = 2$	5.763	9.095	12.323	15.515
$l = 3$	6.988	10.417	13.698	16.924
$l = 4$	8.183	11.705	15.040	18.301

Fig. 16: Bessel Function Zeros

In case  $l = 0$  the particle spectrum is defined by the following formula (in the atomic units):

$$\tan\left(\sqrt{2}a\sqrt{V_0 - E}\right) = -\sqrt{\frac{V_0}{E}} - 1.$$

We solved this equation by using the Newton's method. As an example we consider finite spherical well with  $a = 5$  a.u.,  $V_0 = 10$  a.u. The results are shown in the Figure 5b. More illustrations for our finite spherical well



(a) Wave functions

Fig. 17: Finite spherical well in case  $l = 0$

In case  $l = 1$  we have the following expression (in the atomic units):

$$\tan\left(\sqrt{2}a\sqrt{V_0 - E}\right) = \frac{aE\sqrt{2(V_0 - E)}}{V_0 + aV_0\sqrt{2E} - a\sqrt{2}E^{3/2}}.$$

We also solved this equation by using the Newton's method with the same values of the parameters. The results are shown in the Figure 5.

### Isotropic Harmonic Oscillator

The analytical solution for the energies of the spherical oscillator is given by

$$E_{nl} = \hbar\omega\left(2n + l + \frac{3}{2}\right).$$

For the numerical method described in the Section 2.6 we assume the following values for  $\omega = \sqrt{0.12}$  and the grid size  $N = 2000$ . The results are illustrated in the Figures 6 and 7.

## Hydrogen Atom

The hydrogen atom spectrum are defined (in a. u.) by

$$E_n = -\frac{1}{2n^2}$$

Results of the numerical method are presented in the Figures 8 and 9. We investigated the convergence rate, and results are shown in the Figure 15. We get acceptable results by using the sufficiently large grid size  $N = 15000$  in comparison with, for example, the spherical oscillator. It can be explained by the singularity of the potential:

$$V(r) = -\frac{1}{r}.$$

The method convergence could be improved by a non-uniform grid around zero or by using a larger number of terms in the finite difference from the Section 2.6.

## Woods-Saxon potential

There is no analytical solution. So for investigation of the Woods-Saxon potential spectrum we use the numerical method from the section 2.6. The radial equation (16) in case  $l = 0$  says

$$-\frac{1}{2} \frac{\partial^2 u}{\partial r^2} - \frac{V_0}{1 + e^{\frac{r-R}{a}}} u = Eu.$$

For solving this eigenvalue problem we assume the following values for the grid size  $N = 3000$ ,  $V_0 = 10$  a. u.,  $R = 5.0$  a.u. Resulting energies and wave functions are shown in the Figure 10.

## Hulthen Potential

The Hulthen potential spectrum in the atomiv units is defined by

$$E_n = -V_0 \left( \frac{2V_0 a^2 - n^2}{2na\sqrt{2V_0}} \right)^2$$

and the the following condition

$$2V_0 a^2 > n^2.$$

In our calculations we let  $V_0 = 10$  a.u.,  $a = 0.5$  a. u and the grid size  $N = 3000$ . From the condition  $2.5 > n^2$ , we obtain two energy levels. Results are presented in the Figure 11.

## Morse potential

The vibrations of a two-atomic molecule are described by

$$V(r) = D(e^{-2\alpha x} - 2e^{-\alpha x}).$$

The analytical solution for the energies of the Morse potential with  $l = 0$  is given by

$$E_n = -D + \hbar\omega \left[ \left(n + \frac{1}{2}\right) - \frac{1}{\xi} \left(n + \frac{1}{2}\right)^2 \right],$$

where  $\xi = \frac{2\gamma}{\alpha}$ ,  $\gamma^2 = \frac{2MDr_0^2}{\hbar^2}$ , and  $\omega$  can be found from the following equation:  $\hbar\omega = \frac{\hbar^2}{2Mr_0^2}$ . We have investigated the hydrogen atom spectrum, and the special parametes for the potential formula were experimentally established such as  $\alpha = 1.440$ ,  $D = 0.71702$  a.u.,  $r_0 = 0,13984$  a.u. For numerical solution we let the grid size  $N = 8000$  and the molecule mass  $m = 3674.30535$  a.u.,  $\omega = 0.1$  a.u. Results are shown in the Figure 12.

## Yukawa potential

The Yukawa potential is given by

$$V(r) = -V_0 \frac{e^{ar}}{r}, \quad (45)$$

where  $V_0 = \alpha Z$  and  $Z$  is the atomic number,  $\alpha = \frac{1}{137}$  is the fine-structure constant and  $a$  is the screening parameter.

There is no exact analytical solution, however some approximate analytical solution is known:

$$E_{nl} = -\frac{a^2}{2m} \frac{\left(\frac{mV_0}{a} - (n+1)^2 - l(2n+l+2)\right)^2}{(n+l+1)^2}.$$

For the numerical method described in the Section 2.6 we assume the following values for  $V_0 = \frac{1}{137}$  (we investigate  $H_2$ ),  $a = 0.002V_0$ ,  $m = 3674.30535$  and the grid size  $N = 1000$ . The results are illustrated in the Figure 14.

## References

- [1] <https://github.com/elena-orlova/Potentials/blob/master/Potentials.ipynb>.
- [2] Siegfried Flügge. *Practical quantum mechanics*. Springer Science & Business Media, 2012.
- [3] David J Griffiths. *Introduction to quantum mechanics*. Cambridge University Press, 2016.
- [4] M Hamzavi, M Movahedi, K-E Thylwe, and AA Rajabi. Approximate analytical solution of the Yukawa potential with arbitrary angular momenta. *Chinese Physics Letters*, 29(8):080302, 2012.