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Calculation of Electron Spectrum in Spherically Symmetric Potentials

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# 1 Introduction

An important problem in quantum mechanics is a behaviour of a particle in a spherically symmetric potential, which depends only on the distance between the particle and a defined center point. An electron in the potential derived from Coulomb's law is well-known example. The problem can be used to describe a hydrogen-like atom.

The spectrum of particle consists of all possible values of energy. The study of particle spectra allows us to see the global picture of particle behavior.

We are interested in finding a spectrum of electron in spherically symmetric potentials, such as: infinite and finite spherical potential well, quadratic potential, hydrogen-like atom; Woods-Saxon, Hulthen, Morse, Yukawa potentials and deuterium potential.

## 2 Theoretical part

### 2.1 Differential operators in spherical coordinates

Suppose we have 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 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  $Oxy$ .

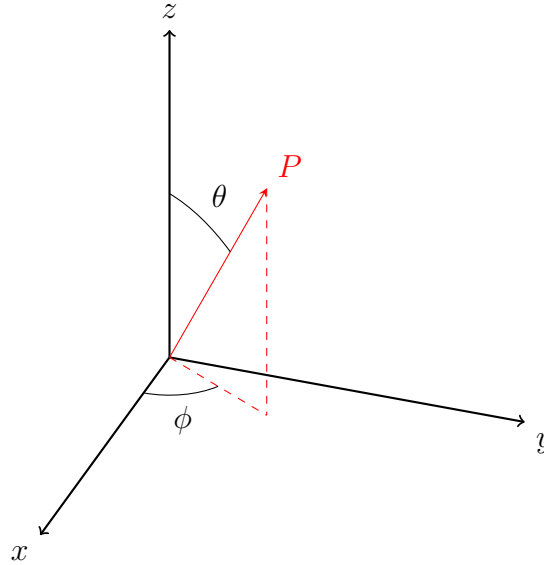


Fig. 1: Spherical coordinates

Cartesian coordinates to Spherical coordinates:

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

Laplacian is a differential operator given by the divergence of the gradient of a function on Euclidean space. 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 Laplasian 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.

## 2.2 Some necessary special functions

For working with Laplasian in spherical coordinates several special functions often appear. We will describe them in two following paragraphs.

### 2.2.1 Spherical functions

Spherical harmonics are the angular part of the family of orthogonal solutions of the Laplace equation written in 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 following form, called spherical garmonics of degree  $l$  and 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 Legendre Function, defined by:

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

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  $m$ :  $l = 0, 1, \dots, m = -l, -l+1, \dots, -1, 0, 1, \dots, l-1, l$ .

The general solution to Laplace's equation is linear combination of the spherical harmonic functions multiplied by the appropriate scale factor  $r^l$ :

$$f(r, \theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l f_l^m r^l Y_l^m(\theta, \phi).$$

where the  $f_l^m$  are constants.

### 2.2.2 Bessel functions

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 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  $y_n$ :

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

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

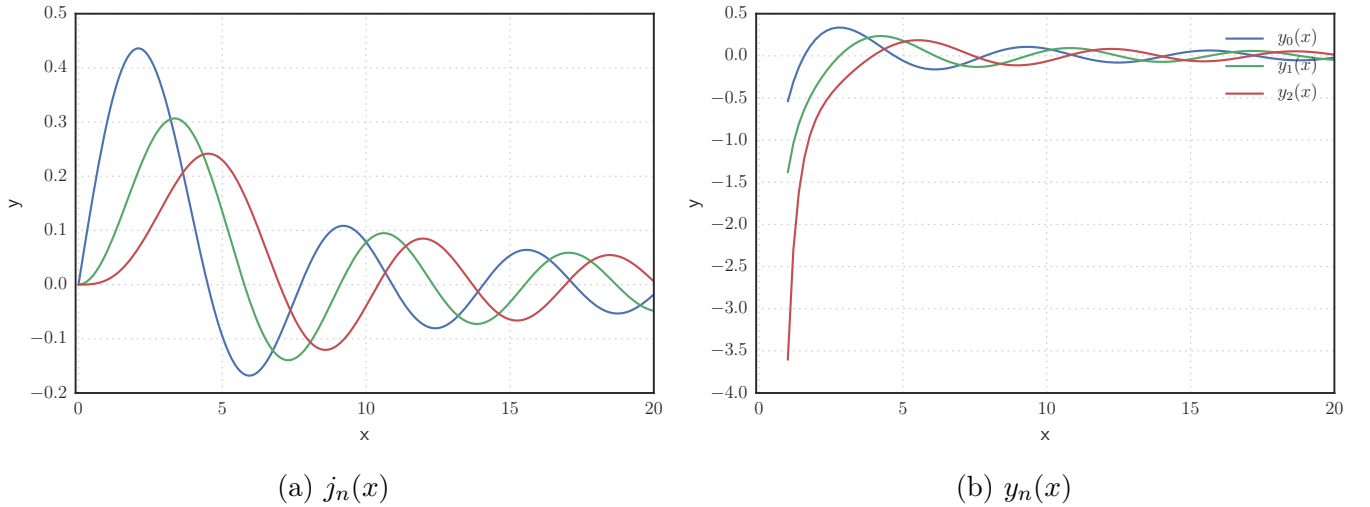


Fig. 2: Spherical Bessel functions

### 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:

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

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:  $\epsilon_{ijk}$  is 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 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. An 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 described by 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  $L$ .

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

The algebraic theory of spin is the same as theory for orbital angular momentum. So, there are 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 $\frac{1}{2}$

Important case is  $s = \frac{1}{2}$ , corresponds to, for example, 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: 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:

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

Hermitian inner product of spinors is following:

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

$|a_1|^2$  is a probability of having the particle with the spin  $\frac{1}{2}$ . The quantum mechanical operators associated with this spin observables are:

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

For particles with spin  $\frac{1}{2}$   $\sigma_x, \sigma_y, \sigma_z$  are three matrices, called 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 Pauli matrices are hermitian and unitary.

## 2.5 Perturbation theory

Perturbation theory is the method for the approximate solution of problems in theoretical physics in case when the problem has a small parameter, and for the problem without this parameter it is known an exact solution. Solutions have a form:

$$A = A^{(0)} + \epsilon A^{(1)} + \epsilon^2 A^{(2)} + \dots,$$

where  $A^{(0)}$  is solution of unperturbed problem,  $\epsilon$  is a small parameter, the coefficients  $A^{(n)}$  are found by successive approximations.

So, we can write Hamiltonian in form:

$$H = H^{(0)} + V,$$

where  $H^{(0)}$  is unperturbed Hamiltonian for which a solution is known,  $V$  is perturbation.

The problem is to find the eigenfunctions of the Hamiltonian (stationary states), and the corresponding energy levels. For this purpose Feynman-Hellman lemma is used, which claims:

**Lemma 1** Suppose a Hamiltonian  $H(\lambda)$ ,  $\lambda$  - parameter, and some normalized energy eigenstate  $|\psi_n(\lambda)\rangle$  with some energy  $E_n(\lambda)$ , then

$$\frac{dE_n(\lambda)}{d\lambda} = \langle \psi_n(\lambda) | \frac{dH(\lambda)}{d\lambda} | \psi_n(\lambda) \rangle$$

## 2.6 Numerical methods for the solution of the Schrodinger equation

In the general case, the dynamics of a particle are described by a Hamiltonian:

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

where  $\hbar$  - Planck constant,  $m$  - mass of particle,  $\nabla^2 = \frac{\partial^2}{\partial x^2}$  - Laplasian,  $V$  - potential .  
Schrodinger equation describes particle dynamics:

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

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

Bohr provided statistical interpretation of the wave function:  $|\Psi(x, t)|^2$  gives the probability of finding the particle at point  $x$ , at time  $t$ . 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 normalized wave function.

Suppose we are finding solutions in the following form:  $\Psi(x, t) = \psi(x)f(t)$  Time independent Schrodinger equation:

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

Notice, that general solution is a linear combination of the separable solutions:  $\Psi(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t}$  where  $\psi(x) = ce^{-iEt/\hbar}$ . The problem is to find a wave function, describing the dynamic of the particle. As it turns out, it is often impossible to solve a differential equation analytically. In this case it is used numerical methods: describe the main idea.

In the spherical summetry case we obtain the following equation, which is called 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)

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

The last equation explicitly hints at the search for eigenvalues of  $(\frac{d^2}{dr^2} - 2V)$ . To do this, we need to approximate the continuous expression discrete. Since the wave function is typically exponentially damped, we can assume that  $u(r) = 0$  for  $r \geq L$  for some sufficiently large  $L$ .

Thus, we obtain an eigenvalue problem with the boundary conditions  $u(0) = 0$  (since  $u(r) = rR(r)$ ) and  $u(L) = 0$ . We define the step  $h = LN^{-l}$ , where  $N$  is a natural (divide the segment  $[0, L]$  into  $N$



parts,  $h$  is the step),  $r_n = nh$  is the grid nodes.

The second derivative is given by the following relation (from the Taylor series):

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

Then  $(u''(r))_n \rightarrow u_n''(r)$ :

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

We note that the resulting matrix has a tridiagonal form.

Now we need approximate  $(-2Vu)(r_n)$ :

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

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

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

### 3 Electron in spherically symmetric potentials

In this section we will try 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 Laplacian in spherical coordinates (2), we find time-independent Schrodinger equation in the form:

$$-\frac{\hbar^2}{2m} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial \psi}{\partial r}) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial \psi}{\partial \theta}) + \frac{1}{r^2 \sin^2 \theta} (\frac{\partial^2 \psi}{\partial \phi^2}) \right] + V\psi = E\psi \quad (12)$$

We are looking for solutions that are separable into products:

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

putting this in (12) and using results from previous sections, we get:

$$\frac{1}{R} \frac{\partial}{\partial r} (r^2 \frac{\partial R}{\partial r}) - \frac{2mr^2}{\hbar^2} [V(r) - E] = l(l+1), \quad (13)$$

$$\frac{1}{Y} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial Y}{\partial \theta}) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} = -l(l+1). \quad (14)$$

The equation (14) is the angular part of wave function, (15) is radial part of 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 potential. Let  $u(r) = rR(r)$ , so:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 u}{\partial r^2} + [V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}]u = Eu \quad (15)$$

It is so called radial equation. Normalization condition becomes

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

### 3.1 Spherically symmetric potential well

#### 3.1.1 Infinite spherical well

For infinite spherical well with radius  $a$  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 (15) says

$$\frac{d^2 u}{dr^2} = \left[ \frac{l(l+1)}{r^2} - k^2 \right] u, \quad (16)$$

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 (16) 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 spherical Bessel functions (6), (6) of 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

$$E_{nl} = \frac{\hbar^2}{2ma^2} \beta_{nl}^2, \quad (17)$$

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 following table:

	$n = 1$	$n = 2$	$n = 3$	$n = 4$
$l = 0$	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 finite spherical well 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:

$$\frac{d^2u}{dr^2} + [k^2 - \frac{l(l+1)}{r^2}]u = 0 \quad (18)$$

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

The solution of the quation (18) is a spherical Bessel function (with the boundary conftion  $u(0) = 0$ ):

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

To find the solutions of (19) 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 quation (19) 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:

$$Aj_l(kR) = Bh_l(i\kappa R). \quad (20)$$

Second match the first derivative:

$$Ak \left[ \frac{dj_l(\rho)}{d\rho} \right]_{\rho=kR} = Ai\kappa \left[ \frac{dh_l(\rho)}{d\rho} \right]_{\rho=i\kappa R}. \quad (21)$$

Now divide (21) by (20), 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  $\rho$ :

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

$$k \text{ctg}(kR) = -\kappa. \quad (22)$$

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 (22) with the notations  $kR = x$ ,  $k_0R = x_0$ ,  $\frac{k}{k_0} = \xi$ ,  $\kappa R = \sqrt{1 - \xi^2}$ :

$$\text{tg}(x_0\xi) = f_l(x_0\xi), \quad (23)$$

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  $l = 0$  (23) takes the form (22). In the further analysis we assume atomic units, so  $\hbar = 1, m = 1$ . By substituting values of  $k_0, k$  and  $\kappa$  to the (22) we obtain:

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

As an example we consider finite spherical well with  $a = 5$  a.u.,  $V_0 = 10$  a.u. We solved the equation (22) using Newton's method. The resulting energies are given in the Figure 4b.

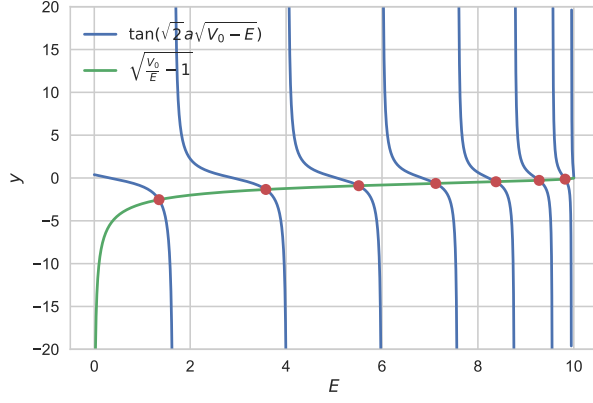
### 3.2 Isotropic Harmonic Oscillator

For isotropic harmonic oscillator potential is defined as:

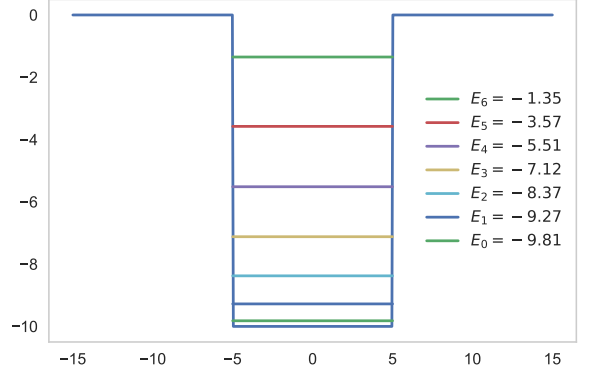
$$V(r) = \frac{1}{2}m\omega^2 r^2$$

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  $x, y, \text{and } z$  directions. The Hamiltonian then takes the form:

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



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



(b) Energy levels (a.u.)

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

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

The spectrum for this quantum mechanical system has degeneracies, that are explained by the existence of some hidden symmetry. Thus in some ways this quantum 3D oscillator is a lot more symmetric than the infinite spherical well.

For analytical solution we use the standard separation variables procedure, then the radial equation (15) takes the form:

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

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:

$$E_{nl} = \hbar \omega \left( 2n_r + l + \frac{3}{2} \right), \quad n_r = 0, 1, 2, \dots \quad (24)$$

Results are the following:

$n$	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)  $l = 0$

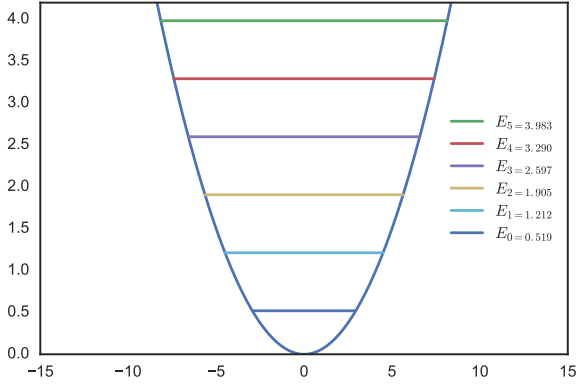
$n$	Numerical	Analytical
0	0.866016	0.866025
1	1.558807	1.558846
2	2.251574	2.251666
3	2.944318	2.944486
4	3.637037	3.637307
5	4.329732	4.330127

(b)  $l = 1$

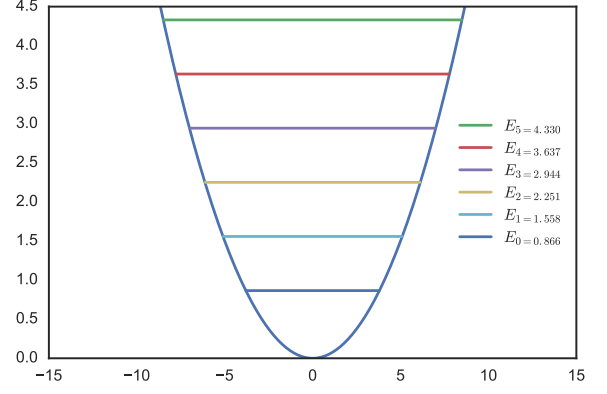
Fig. 5:  $E_{nl}$  in a.u. for harmonic oscillator

For more detailed information about numerical experiment see Appendix. For larger  $l$  convergence is the same.

Illustration of energy levels given in Figure 6:



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



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

Fig. 6: Isotropic Harmonic Oscillator

### 3.3 The Hydrogen Atom

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

$$V(r) = -\frac{1}{r}, \quad (25)$$

and the radial equation (15) 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:

$$E_n = -\frac{1}{2n^2} \quad (26)$$

Notice, that the hydrogen's spectrum depends only on the energy level  $n$ . The reason that the energy level depends only on  $n$  is that for just one electron the only force acting on it is the coulomb force between the nucleus and the electron. As such this is the only force that dictates the potential energy term in the Schrodinger equation. In this case the strength of the coulomb force between the hydrogen nucleus and the electron only depends on the distance between the two and the charge involved ( $2q$  in this case). The force is spherically symmetric (aka rotationally invariant) so it doesn't matter where around the hydrogen nucleus an electron is. As long as the distance between the two is constant the strength of the force is constant. Hence, the energy is constant.

We used the numerical methods from section 2.6, and results are the following: We have some

$n$	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. 7:  $E_{nl}$  in a.u. of The Hydrogen Atom

problems with the convergence, because the potential (25) is singular at point 0. Graphical illustration of the spectrum is the following:

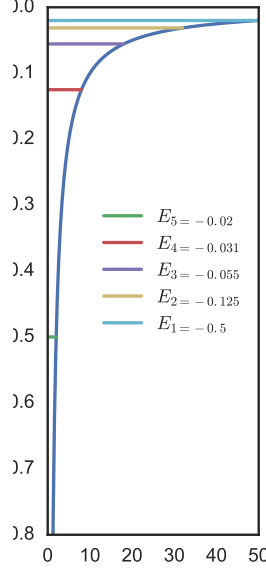


Fig. 8: The Hydrogen Atom Spectrum (in a.u.)

### 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:

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

where  $a \ll R$ .

$R$  is 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 a potential well with a potential jump at the nuclear surface.

The radial equation (15) 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 an analytical solution. Numerical method results are the following:

It is also possible to solve this problem using the Nikiforov-Uvarov method.

### 3.5 Hulthen Potential

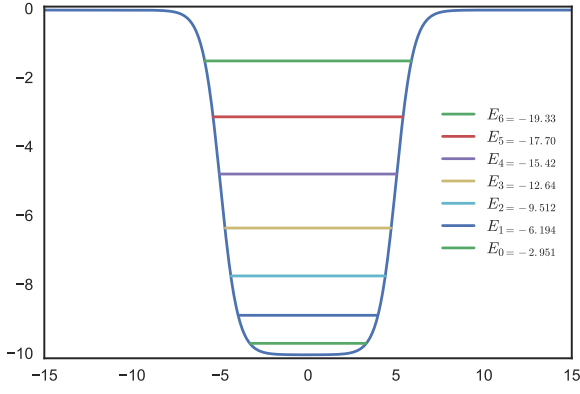
The Hulthen potential is given by

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

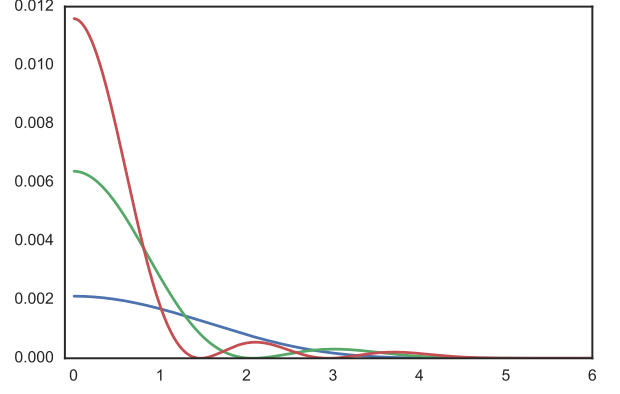
Our problem to find the spectrum in case  $l = 0$ .

The radial part (15) of the Schrodinger equation in a.u. says:

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



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



(b) Wave functions in case  $l = 1$

Fig. 9: Woods-Saxon potential

The analytical solution is known:

$$E_n = -V_0 \left( \frac{\beta^2 - n^2}{2n\beta} \right)^2, \quad (27)$$

$$\beta^2 > n^2, \quad (28)$$

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

Rewrite (27) in the atomic units:

$$E_n = -V_0 \left( \frac{2V_0a^2 - n^2}{2na\sqrt{2V_0}} \right)^2,$$

and compare it with the numerical methods from section 2.6:

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

Fig. 10:  $E_{n0}$  in a.u. for the Hulthen Potential

In our calculation we let  $V_0 = 10a.u.$ ,  $a = 0.5$ , so from the condition 28:  $2.5 > n^2$ , we obtain only two energy levels.

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

$$V_c = -\frac{V_0a}{r},$$

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:

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



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

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 parametres  $D$ ,  $\alpha$  and  $r_0$  are known for some typical molecules such as  $H_2$  or  $HCl$  from experiments. We will research the hydrogen atom with the following parametres:  $D = 38292cm^{-1}$ ,  $\alpha = 1440$ ,  $r_0 = 0,13984$ . The problem is to find the spetrum 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:

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

where  $\xi = \frac{a}{b}$