# Computer Lab: Numerical Solution to the Radial Schrödinger Equation

## Part I: One-electron Systems

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## 1 Introduction

In this computer lab, we look at the time-independent Schrödinger equation for a single-electron in a central potential $V(r)$. We aim to solve the Schrödinger Equation in order to compute the radial equations and the corresponding energies. The one-electron problem handled in this part of the lab can be solved analytically, this allows us to develop our numerical method and compare with the analytical results. The numerical method can then be used to investigate many-electron systems, as will be done in the second part of this lab. This manual goes through the numerical methods to obtain solutions to the radial Schrödinger equation using the Cowell-Numerov's method as well as the Python implementation of this method. The improvement of the implementation that can be done by transforming to a logarithmic grid is also presented. The last section contains the exercises that you are asked to solve.

We focus on solving the radial Schrödinger equation numerically. The theoretical background of solving the Schrödinger equation analytically, which you have seen in the lectures, is presented in Appendix A. In this appendix is described how by expressing the equation in spherical coordinates (see Appendix A.1), the angular and radial parts of the equation can be separated. As the solutions to the angular part are the well-known spherical harmonics, we eventually obtain an equation governing the radial part of the wave function (see Appendices A.2 and A.3). For the special case of a Coulomb field, the radial Schrödinger equation can be solved analytically, and Appendices A.4 and A.5 discuss the exact solutions and some of their properties.

## 2 Numerical Solution to the Radial Equation

Our problem is to determine the *energy eigenvalues*, $E$, and the associated radial functions i.e. the eigenfunctions, $P_{n\ell}(r)$, in the case of a general potential $V(r)$.

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We use the Cowell-Numerov's method, described in the next section, to find solutions to the radial equation on a finite grid covering the region $r = 0$ to a practical infinity, $r_\infty$, a point determined by requiring that $P_{n\ell}(r)$ be negligible for $r > r_\infty$. The practical infinity depends on the eigenvalue $E$ and is typically chosen so that $\sqrt{2|E|} \cdot r_\infty \approx 40$.

Near the origin, there are two solutions to the radial Schrödinger equation, the desired solution which behaves as $r^{\ell+1}$, and an irregular solution, referred to as the complementary solution, which diverges as $r^{-\ell}$ as $r \to 0$. Numerical errors near $r = 0$ always introduce small admixtures of the complementary solution into the solution being sought. Integrating outward from the origin keeps such errors under control, since the complementary solution decreases in magnitude as $r$ increases. Continuing the integration toward the practical infinity, we will have admixtures of the irregular solution $e^{\sqrt{2|E|r}}$. Now, this solution will blow up and totally destroy our final result, i.e., the integration process is numerically unstable. Starting from the regular solution at the practical infinity, integrating inwards, we will, close to $r = 0$, have admixtures of the irregular solution $r^{-\ell}$, which in a similar way will blow up and destroy the solution.

To avoid the above problems, the general procedure to solve the radial equation is to integrate outward from the origin, using Cowell-Numerov's method, starting with solutions that are regular at the origin. The integration is continued to the outer classical turning point, the point beyond which classical motion in the potential

$$V(r) + \frac{\ell(\ell+1)}{2r^2} \tag{1}$$

is impossible (see Fig. 1). In the region beyond the classical turning point, the equation is integrated inwards, using Cowell-Numerov's method, starting from $r = r_\infty$ with an approximate solution obtained from the solution regular at the infinity. The solutions from the inward and outward integrations are matched at the classical outer turning point. The energy is, then, adjusted until the derivative of $P_{n\ell}(r)$ is continuous at the matching point. The resulting function $P_{n\ell}(r)$ is an eigenfunction and the corresponding energy $E$ is its eigenvalue. The radial function is, then, normalized to fulfill $\int_0^\infty P_{n\ell}(r)^2 \, dr = 1$.

## 3   The Cowell-Numerov's Method

We shall consider the Cowell-Numerov's method for solving equations of the form

$$y'' = f(x, y). \tag{2}$$

Introducing the notation $x_k = x_0 + kh$ for the uniformly spaced grid, where $h$ is the step and $y_k$ is the value of $y$ obtained at grid point $x_k$. The solution is given by the formula

$$y_{k+1} = 2y_k - y_{k-1} + \frac{h^2}{12}(f_{k+1} + 10f_k + f_{k-1}) \tag{3}$$
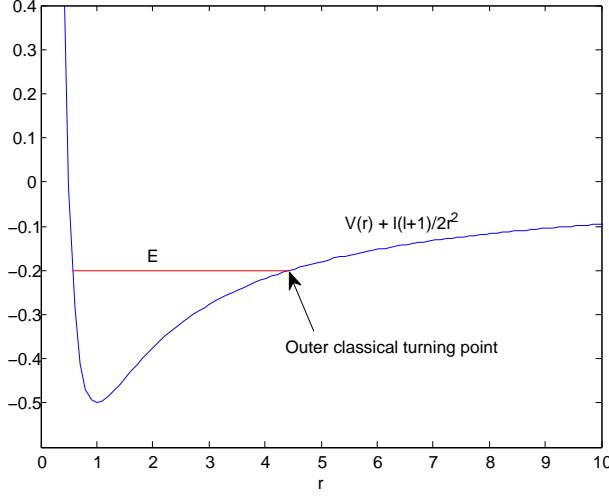
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Figur 1: *An electron with energy $E$ in a potential $V(r) + \frac{\ell(\ell+1)}{2r^2}$ is classically allowed to move only inside a certain region.*

with a local truncation error $\mathcal{O}(h^6)$. The formula above is implicit but in the special case when $f(x, y) = g(x)y$, as for the radial equation, we get the following explicit formula for the outward integration

$$y_{k+1} = \frac{\beta_k y_k - \alpha_{k-1} y_{k-1}}{\alpha_{k+1}}, \tag{4}$$

where $\alpha_k = 1 - (h^2/12)\, g_k$ and $\beta_k = 2 + (5h^2/6)\, g_k$. After rearranging, we have

$$y_{k-1} = \frac{\beta_k y_k - \alpha_{k+1} y_{k+1}}{\alpha_{k-1}} \tag{5}$$

for the inward integration. To start the method, we need two values. These can be inferred from the regular solution at the origin and at the infinity, with additional corrective terms. For simplicity, we will drop higher-order terms.

## 4   General Numerical Procedure

For a given potential $V(r)$ and a given $\ell$, we obtain a solution $P_{n\ell}(r)$ to the radial equation with a specified number of nodes away from $r = 0$ by following the steps below:

1. Start with the lowest possible *energy eigenvalue $E = -Z^2/(2n^2)$*. Increase energy until the classical turning point is inside the grid (see Fig 1). This energy will be the starting point for further calculations.

2. Use the Cowell-Numerov's method with starting values from a low order series expansion $P_{n\ell}(r) \propto r^{\ell+1}\left(1 - \frac{Zr}{\ell+1}\right)$ of the regular solution to obtain values of the radial function at a number of grid points from $r = 0$ out to the classical turning point $r_c$ (outward solution).

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3. Use the Cowell-Numerov's method with starting values from the regular solution to obtain values of the radial function at a number of grid points from the practical infinity $r_\infty$ into the classical turning point $r_c$ (inward solution).

4. Multiply the wave function obtained in step 3 by a scale factor, which is chosen to make the wave function for $r < r_c$ from step 2 and that for $r > r_c$ from step 3 continuous at $r = r_c$.

Since we have guessed the energy $E$ in step 1, the solution may have too many *nodes* (initial energy too high) or too few *nodes* (initial energy too low). In the first case, we reduce the energy by multiplying with a factor of 1.1 and redo steps 2 – 4. In the second case, we increase the energy by multiplying with a factor 0.9 and redo steps 2 – 4 (remember that the energies of the bound states are negative). This process is continued until we have the desired number of *nodes*. In the routine, we keep track of the least upper bound on the energy $E_u$ (too many *nodes*) and the greatest lower bound $E_l$ (too few *nodes*) as the iteration proceeds. If increasing the energy at a particular step of the iteration would lead to $E > E_u$, then we simply replace $E$ by $(E + E_u)/2$, rather than following the above rules. Similarly, if decreasing $E$ would lead to $E < E_l$, then we replace $E$ by $(E + E_l)/2$.

Even if the solution after the steps above has the correct number of *nodes*, the derivative may still be discontinuous at the matching point. To achieve a wave function with a continuous derivative, we make further corrections to $E$ using a perturbative approach. If we let $P_1(r)$ and $P_1'(r)$ represent the radial wave function and its derivative at $E_1$, respectively, and let $P_2(r)$ and $P_2'(r)$ represent the same two quantities at $E_2$, then it follows from the radial Schrödinger equation that

$$2(E_1 - E_2)P_1 P_2 = \frac{d}{dr}\left(P_2' P_1 - P_2 P_1'\right).$$  (6)

From this equation, we find that

$$2(E_1 - E_2)\int_{r_c}^\infty P_1 P_2 \, dr = \left[P_2' P_1 - P_2 P_1'\right]_{r_c}^\infty = -\left(P_2' P_1 - P_2 P_1'\right)^+ \quad (7)$$

$$2(E_1 - E_2)\int_0^{r_c} P_1 P_2 \, dr = \left[P_2' P_1 - P_2 P_1'\right]_0^{r_c} = \left(P_2' P_1 - P_2 P_1'\right)^-, \quad (8)$$

where the superscripts $\pm$ indicate that the quantities in parentheses are to be evaluated just above or just below $r_c$. These equations are combined to give

$$E_1 - E_2 = \frac{(P_1'^+ - P_1'^-)P_2(r_c) + (P_2'^- - P_2'^+)P_1(r_c)}{2\int_0^\infty P_1 P_2 \, dr}.$$  (9)

Suppose that the derivative $P_1'$ is discontinuous at $r_c$. If we demand that $P_2'$ is continuous at $r_c$, then, the term $P_2'^- - P_2'^+$ in the numerator of (9) vanishes. Approximating $P_2$ by $P_1$ in this equation, we obtain

$$E_2 \approx E_1 + \frac{(P_1'^- - P_1'^+)P_1(r_c)}{2\int_0^\infty P_1^2 \, dr}.$$  (10)

as an approximation for the eigenenergy. We use this approximation iteratively until the discontinuity in $P'(r)$ at $r = r_c$ is reduced to an insignificant level.

In the last step, we normalize the solution and make sure that it has a positive slope at the origin.

# 5    Python Implementation

In the python file radial.py is the implementation of the general numerical procedure to solve the radial Schrödinger equation in a Coulomb potential $V(r) = -Z/r$. We target specific solutions by giving $n$ and $\ell$. The user has to supply the nuclear charge $Z$, together with the $n$ and $\ell$ quantum numbers. The starting energy is chosen to be the lowest possible for the given nuclear charge $Z$, based on Eq. (39).

In implementing the solution, we have prioritized simplicity rather than accuracy. To increase the numerical accuracy the starting values for the outward and inward integration should be improved by adding higher-order correction terms. Most importantly, we should have used a logarithmic grid rather than a uniform one. Paying attention to these things, an accuracy of parts in $10^{12}$ can be achieved with 500 grid points. However, for the present implementation, we use as many as 10 000 grid points to get a reasonable accuracy for $\ell = 0$.

# 6    Transformation to Logarithmic Grid

To achieve high numerical accuracy, it is essential that the gridpoints are densely spaced at the origin. Further away from the origin, the distance between the gridpoins can be larger. At the same time, numerical procedures become more simplified if the grid is equally spaced. To deal with both aspects, a transformation of the independent variable

$$\rho = \log(Zr) \rightarrow r = \frac{e^\rho}{Z} \tag{11}$$

and the dependent variable

$$\overline{P}(\rho) = \frac{P(r)}{\sqrt{r}} \tag{12}$$

has been suggested (Froese-Fischer, Brage and Jönsson, Computational Atomic Structure, p. 58). With this transformation the radial equation becomes

$$\frac{d^2\overline{P}_{n\ell}(\rho)}{d\rho^2} + \left(2r^2[E - V(r)] - \left(\ell + \frac{1}{2}\right)^2\right)\overline{P}_{n\ell}(\rho) = 0, \tag{13}$$

with the boundary conditions $\overline{P}_{n\ell}(\rho) \rightarrow 0$ as $\rho \rightarrow \pm\infty$. In order to avoid points at $-\infty$, it is customary to divide the range in $r$ in two regions $[0, r_1]$ and $[r_1, \infty[$ and transform only the latter to the $\rho$ variable. The value $r_1$ is sufficiently small so that a series expansion may be used for the solution near the origin.

Tests have shown that appropriate values are $\rho_1 = -10$ and $h = 1/48$. This gives the grid

$$\rho_i = -10 + (i-1)/48 \qquad \text{and} \qquad r_i = \frac{e^{\rho_i}}{Z}, \quad i = 1, 2, \ldots, M. \tag{14}$$

Near the origin, we use the series expansion

$$P_{n\ell}(r) \propto r^{\ell+1} \left( 1 - \frac{Zr}{\ell+1} \right). \tag{15}$$

The previous Python code can, with small modifications, be used also in this case. The accuracy is much better compared to that for a linear grid. The transformation implies a modification of the update formula for the energy, so that

```
DP_out = (P_out[i_c+1]-P_out[i_c-1])/(2*h)
DP_in = (P_in[i_c+1]-P_in[i_c-1])/(2*h)
dE = (DP_out-DP_in)*P[i_c]/(2*sum(r**2*P**2)*h) .
```

Also, the expressions for the normalization and radial expectation values, respectively, are

```
norm = math.sqrt(sum(P**2*r**2)*h)
```

and

```
r1 = sum(r**3*P**2)*h ,
```

where now `P` is $\overline{P}$. The program based on the logarithmic grid is found in the Python code radiallog.py.

# 7 References

The treatment is inspired by Walter R. Johnson, Atomic Structure Theory: Lectures on Atomic Physics, Springer Verlag, Berlin (ISBN 978-3-540-68010-9)

Part of the material can be found in C. Froese Fischer, T. Brage, and P. Jönsson, Computational Atomic Structure, IoP, Bristol (ISBN 0-7503-0466-9)

The interested reader should consult R. Cowan, The Theory of Atomic Structure and Spectra, Univ. of California Press, Berkely (ISBN 0-520-03821-5)

# 8 Preparatory question

Before the lab, read the lab manual and answer this preparatory question. The following numbered questions in this and the second part of the lab should be answered in the report.

1. Describe what spherical harmonics are, what do we use them to describe, and what does it mean that they are orthonormal?

# 9    Exercises

This is the lab work that will be done on the lab day. Use the functions in the Radial_fuctions.py code to test to plot different $P$ functions to get a feel for how they change for different orbitals and $Z$. By having the Radial_fuctions.py code in the same folder as your own code you can import the function into your code by

```
import Radial_functions as Rf
```

and then call the functions within it for a specific Z value and r array as f.ex

```
r = linspace(0,20,1000)
Z = 1
P = Rf.P1s(r,Z)
plot(r,P)
```

which plots the $1s$ orbital with $Z = 1$ for the range $r \in [0, 20]$

2. What is meant by the radial wave function $P(r)$. What is the radial density function $D(r)$ and how do you interpret it? Plot the radial density functions for $3s, 3p$, and $3d$ with $Z = 1$ in the same figure, comment on if the number of nodes is what is expected.

   In another plot, plot the effective potential $V(r) = -Z/r + \frac{\ell(\ell+1)}{2r^2}$ for $s$, $p$, and $d$ electrons (see also Fig. 1). Plot all the potentials in the same plot and test different intervals for $V$ and $r$ until the important features are clearly visible. It could be helpful to use the limit command to set the plot interval and to use a grid.

   How does the potential and the radial density function compare. What makes the potential of the $s$ orbital special and what result does this have on the density close to the nucleus?

Study the program radial.py, test it to generate energies and radial functions for different orbitals. Similarly test the program radiallog.py. As with Radial_fuctions.py you can import the programs into your code. Running the functions creates output describing the iterations run by the program and gives the plot for the radial function and prints the number of iterations, the energy eigenvalue and the radial expectation value. The program returns the radial coordinate, the radial wave function and the energy expectation value.

```
import radial
l = 0
n = 1
Z = 1
r,P,E = radial.radial(l,n,Z)
```

3. Comment on what the difference between radial.py and radiallog.py is. Make a table containing the analytical $E_n = -\frac{Z^2}{2n^2}$ energies with those of radial.py and radiallog.py for the orbitals 1s, 2s, 3s, 6s and 9s. Add a

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column showing the number of grid points used by radiallog.py, radial.py uses 10000 points for all orbitals. Clearly show which method is more accurate and explain why is this the case considering the number of grid points used. Plot the radial wave function of the orbitals in the same plot and check that the number of nodes is correct. Note that for radiallog.py the radial wave function is given by $\frac{P}{\sqrt{r}}$ as defined in Eq. (12).

The radial expectation value is a measure of the orbital radius, it is given by

$$\langle r \rangle = \int_0^\infty r P_{n\ell}^2(r)\, dr\,. \tag{16}$$

This is given when running radial.py and radiallog.py. When using a linear grid, as when using radial.py and the functions in Radial_functions.py, on can calculate the radial expectation value using a Riemann integral as

```
dr = r[1] - r[0]
r_expectation_value = sum(r*P**2) * dr
```

4. For a few different orbitals compare the radial expectation values with the radial density functions by plotting them in the same plot, vertical lines showing the position of the expectation value can be ploted by using

```
vlines(r_expectation_value, top_value, bottom_value)
```
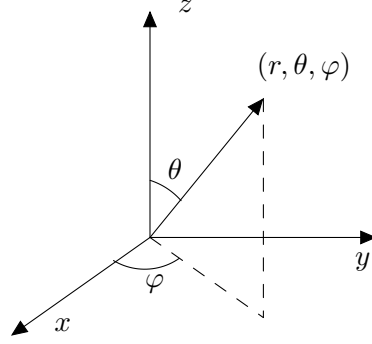
What is the meaning of the radial expectation value?

Compare the radial expectation values computed with radial or radiallog with the values that you get when integrating the analytical expressions.

# A  Theoretical Background on Solving the Schröding-er Equation

## A.1  Spherical coordinates

We start by reviewing the spherical coordinates $(r, \theta, \varphi)$, which are introduced in the figure below.



The definition is as follows,

$$\begin{cases} r = \sqrt{x^2 + y^2 + z^2} \\ \theta = \arctan(z/r) \\ \varphi = \arccos(z/r) \end{cases} \tag{17}$$

with $0 < r$, $0 \leq \theta < \pi$ and $0 \leq \varphi < 2\pi$.

Repeated use of the chain rule allows us to write the Laplacian operator

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{18}$$

as

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial}{\partial \varphi} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2}{\partial \varphi^2}. \tag{19}$$

In spherical coordinates, the integration over $\mathbf{R}^3$ is given by

$$\iiint f(r, \theta, \varphi) r^2 \sin(\theta) \, dr d\theta d\varphi. \tag{20}$$

## A.2  Schrödinger Equation

The Schrödinger equation for a single electron in a general central potential $V(r)$ can be written

$$H\phi(\mathbf{r}, \sigma) = E\phi(\mathbf{r}, \sigma), \tag{21}$$

where

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(r). \tag{22}$$

The solution $\phi(\mathbf{r}, \sigma)$ is referred to as a *spin-orbital*. When expressed in spherical coordinates $(r, \theta, \varphi)$, the equation becomes (for a detailed derivation see, e.g., Cowan, The Theory of Atomic Structure and Spectra, pages 39 – 41)

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\phi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\phi}{\partial\varphi}\right)$$
$$+ \frac{1}{r^2\sin^2\theta}\frac{\partial^2\phi}{\partial\varphi^2} + \frac{2m}{\hbar^2}\left(E - V(r)\right)\phi = 0. \quad (23)$$

We seek a solution of the form $\phi(\mathbf{r}, \sigma) = \frac{1}{r}P(r)Y(\theta, \varphi)\chi_{m_s}(\sigma)$.[3] Substituting this ansatz into equation (23), we obtain the following pair of equations for the functions $P(r)$ and $Y(\theta, \varphi)$ (see Appendix B for a full derivation)

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta, \varphi)}{\partial\varphi}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta, \varphi)}{\partial\varphi^2} + \lambda Y(\theta, \varphi) = 0 \quad (24)$$

$$\frac{d^2 P(r)}{dr^2} + \frac{2m}{\hbar^2}\left(E - V(r) - \frac{\lambda\hbar^2}{2mr^2}\right)P(r) = 0, \quad (25)$$

where $\lambda$ is a separation constant.

It can be shown that equation (24) has finite and single-valued solutions only for $\lambda = \ell(\ell + 1)$, $\ell = 0, 1, 2, \ldots$ . The solutions are given by the spherical harmonics $Y_{\ell m}(\theta, \varphi)$, $\ell = 0, 1, 2, \ldots$ where, for each $\ell$, the $m$ quantum numbers are given by $m = -\ell, -\ell + 1, \ldots, \ell$. The first few spherical harmonics are given below

$$
\begin{aligned}
Y_{00}(\theta, \varphi) &= \frac{1}{\sqrt{4\pi}} \\
Y_{1\pm 1}(\theta, \varphi) &= \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\varphi} \\
Y_{10}(\theta, \varphi) &= \sqrt{\frac{3}{4\pi}}\cos\theta \\
Y_{2\pm 2}(\theta, \varphi) &= \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm i2\varphi} \\
Y_{2\pm 1}(\theta, \varphi) &= \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\varphi} \\
Y_{20}(\theta, \varphi) &= \sqrt{\frac{5}{16\pi}}(2\cos^2\theta - \sin^2\theta).
\end{aligned}
$$

The spherical harmonics are orthonormal, meaning that

$$\iint Y_{lm}^*(\theta, \varphi)Y_{l'm'}(\theta, \varphi)\sin(\theta)\,d\theta d\varphi = \delta_{ll'}\delta_{mm'} \quad (26)$$

and make up a complete set with respect to the angular coordinates.

With the separation constant $\lambda = \ell(\ell + 1)$, the radial Schrödinger equation becomes

$$\frac{d^2 P(r)}{dr^2} + \frac{2m}{\hbar^2}\left(E - V(r) - \frac{\ell(\ell + 1)\hbar^2}{2mr^2}\right)P(r) = 0. \quad (27)$$

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[3]$\chi_{m_s}(\sigma)$ is the spin function. It is of importance when constructing wave functions for many-electron systems and when looking at relativistic corrections.

It is convenient to introduce <u>atomic units</u>. Atomic units are defined by requiring that the electron's mass $m$, the electron's charge $|e|/\sqrt{4\pi\epsilon_0}$, and Planck's constant $\hbar$, all have the value 1. The atomic unit of length is the Bohr radius $a_0 = 4\pi\epsilon_0\hbar^2/(me^2) = 0.529177$ Å and the atomic unit of energy is $me^4/(4\pi\epsilon_0\hbar)^2 = 27.2114$ eV. In atomic units, the radial equation is

$$\frac{d^2P(r)}{dr^2} + 2\left(E - V(r) - \frac{\ell(\ell+1)}{2r^2}\right)P(r) = 0. \tag{28}$$

We study bound state solutions to the radial Schrödinger equation (28) that satisfy the normalization condition

$$\int_0^\infty P^2(r)\,dr = 1. \tag{29}$$

Such bound state solutions exist only for certain discrete energy values $E < 0$, the *energy eigenvalues*. For general potentials $V(r)$ fulfilling the condition

$$\lim_{r\to 0} rV(r) = c, \tag{30}$$

where $c$ is a negative constant, and approaching zero at least as rapidly as $-1/r$ for $r \to \infty$, it can be shown that the different radial solutions belonging to these discrete *energy eigenvalues* can be distinguished by the value $\ell$ to which they correspond and by the number of zeros of the solutions away from the origin. A zero of the solution is often referred to as a *node*. For a given $\ell$, the solution belonging to the lowest energy has zero *nodes*, the solution belonging to the second lowest energy has one *node*, etc. It is customary to denote the orbital angular momentum with the spectroscopic notation

$$\begin{aligned}\ell =&0\ 1\ 2\ 3\ 4\ 5\ 6\ 7\ 8\ldots\\ &s\ p\ d\ f\ g\ h\ i\ k\ l\ldots\end{aligned} \tag{31}$$

and to use a principal quantum number $n$, which is defined by

$$n = \ell + \nu + 1, \tag{32}$$

where $\nu$ is the number of nodes of the radial function (not counting the zero at the origin). As an example, $P_{2s}(r)$ corresponds to an orbital angular quantum number $\ell = 0$ that has one *node* away from the origin, see Fig. 2. Since the solutions can be labeled by $n$ and $l$ then, for consistency, we also label the discrete energies by these quantum numbers, i.e., $E_{n\ell}$.

We end this section by looking at the limiting solutions of (28) at $r = 0$ and at the infinity. Near $r = 0$ we can neglect $E$ and $V(r)$ compared with $\ell(\ell+1)/r^2$ and the solutions take one of the following limiting forms

$$P_{nl}(r) = \begin{cases} r^{\ell+1} & \text{regular at the origin} \\ r^{-\ell} & \text{irregular at the origin.} \end{cases} \tag{33}$$
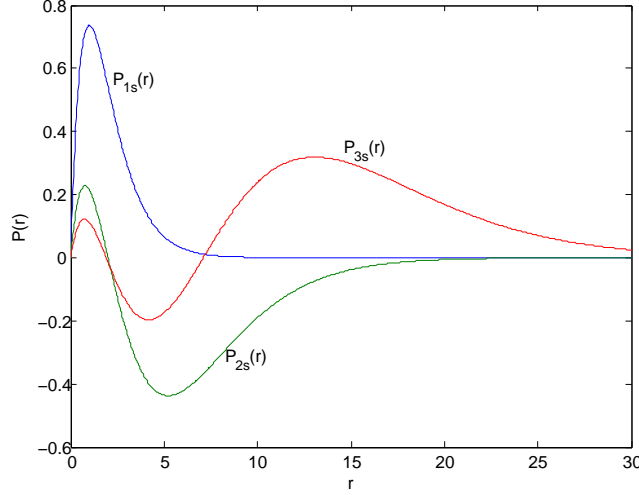
Figur 2: *Solutions with the same $\ell$ are distinguished by the number of nodes away from $r = 0$. $P_{1s}(r)$ has zero nodes, $P_{2s}(r)$ has one, $P_{3s}(r)$ has two, etc.*

Since we seek normalizable solutions, we must require that our solutions are of the first type, regular at the origin. Since the potential vanishes as $r \to \infty$, it follows that

$$P_{nl}(r) = \begin{cases} e^{-\sqrt{2|E|}\, r} & \text{regular at infinity} \\ e^{\sqrt{2|E|}\, r} & \text{irregular at infinity.} \end{cases} \tag{34}$$

Again, the normalizability constraint forces us to seek solutions of the first type, regular at infinity.

## A.3   Summary One-electron Systems

The bound state solutions to the Schrödinger equation for a single electron in a general central potential $V(r)$ are given by *spin-orbitals*. The *spin-orbitals* are characterized by the four quantum numbers $\alpha = n\ell m_\ell m_s$. Introducing the notation $\phi(\alpha, \mathbf{q})$ for the *spin-orbitals*, where $\mathbf{q} = (\mathbf{r}, \sigma)$ we have

$$\phi(\alpha, \mathbf{q}) = \frac{1}{r} P_{n\ell}(r) Y_{\ell m_\ell}(\theta, \varphi) \chi_{m_s}(\sigma). \tag{35}$$

The radial function $P_{n\ell}(r)$ is the solution to the radial equation

$$\frac{d^2 P_{n\ell}(r)}{dr^2} + 2 \left( E - V(r) - \frac{\ell(\ell+1)}{2r^2} \right) P_{n\ell}(r) = 0. \tag{36}$$

that has $\nu$ nodes away from zero, where

$$n = \ell + \nu + 1. \tag{37}$$

The corresponding energies depend on $n$ and $\ell$ and are labeled $E_{nl}$.

In the general case, the radial equation needs to be solved numerically. For the *spin-orbital* to be normalized, $P_{n\ell}(r)$ should satisfy

$$\int_0^\infty P_{n\ell}(r)^2 \, dr = 1. \tag{38}$$

Even for normalized *spin-orbitals* there is a trivial arbitrariness between $P_{n\ell}(r)$ and $-P_{n\ell}(r)$. To resolve this, we use the convention that radial functions should be positive near the origin.

## A.4  Analytical Solution to the Radial Equation

In a Coulomb field $V(r) = -Z/r$, the radial Schrödinger equation can be solved analytically. The energies depend only on the principal quantum number $n$, and not on the angular quantum number $\ell$, and are given by

$$E_n = -\frac{Z^2}{2n^2}, \quad n = 1, 2, 3, \ldots \tag{39}$$

The corresponding radial functions are products of the regular solutions at the origin and infinity and some polynomial in $r$. All details can be found in the book of Cowan pages, 70 – 71. Below, we give the expressions for some of the radial functions belonging to the lowest energies

$$
\begin{aligned}
P_{1s}(r) &= 2Z^{3/2} r e^{-Zr} \\
P_{2s}(r) &= \frac{1}{\sqrt{2}} Z^{3/2} r e^{-Zr/2} \left(1 - \frac{1}{2}Zr\right) \\
P_{2p}(r) &= \frac{1}{2\sqrt{6}} Z^{5/2} r^2 e^{-Zr/2} \\
P_{3s}(r) &= \frac{2}{3\sqrt{3}} Z^{3/2} r e^{-Zr/3} \left(1 - \frac{2}{3}Zr + \frac{2}{27}Z^2 r^2\right) \\
P_{3p}(r) &= \frac{8}{27\sqrt{6}} Z^{5/2} r^2 e^{-Zr/3} \left(1 - \frac{1}{6}Zr\right) \\
P_{3d}(r) &= \frac{4}{81\sqrt{30}} Z^{7/2} r^3 e^{-Zr/3}.
\end{aligned}
\tag{40}
$$

For hydrogen, the energies are degenerate, meaning that there are several states having the same energy. The states are often arranged in a diagram similar to the one shown in Fig. 3, with the energy on one axis and the quantum states arranged according to the quantum numbers on the other axis. Energies are relative to the ionization limit at which the electron is at rest at infinite distance from the nucleus.
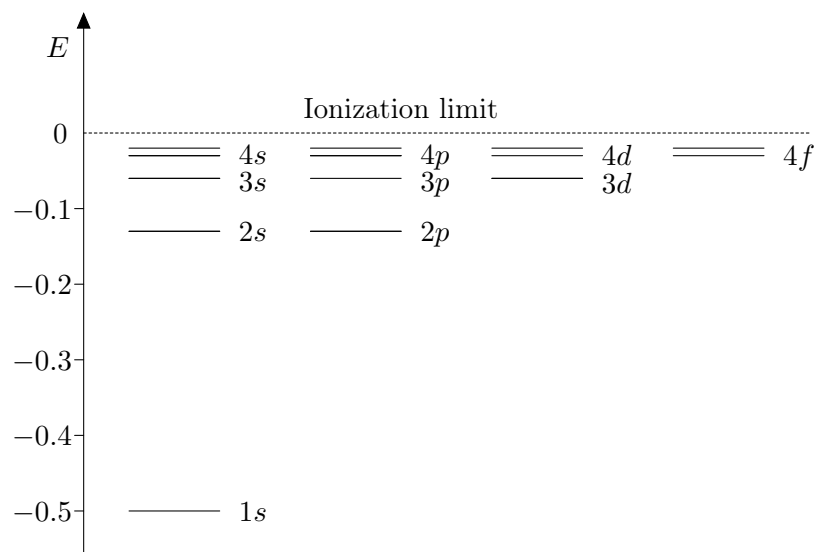
Figur 3: *Energy diagram for hydrogen. States are arranged according to the $\ell$ symmetry and energies are given relative to the ionization limit.*

## A.5   Graphical Representation of Charge Densities

According to the statistical interpretation of quantum mechanics, the electron density, which equals the spin-independent probability density, is given by

$$|R_{n\ell}(r)Y_{\ell m_\ell}(\theta, \varphi)|^2. \tag{41}$$

Using the formulas for the spherical harmonics, it is seen that this quantity is independent of the azimuthal angle $\varphi$, and that there is a rotational symmetry around the $z$-axis. In Fig. 4, we display the charge density in the $xz$-plane for a few electron states in hydrogen.
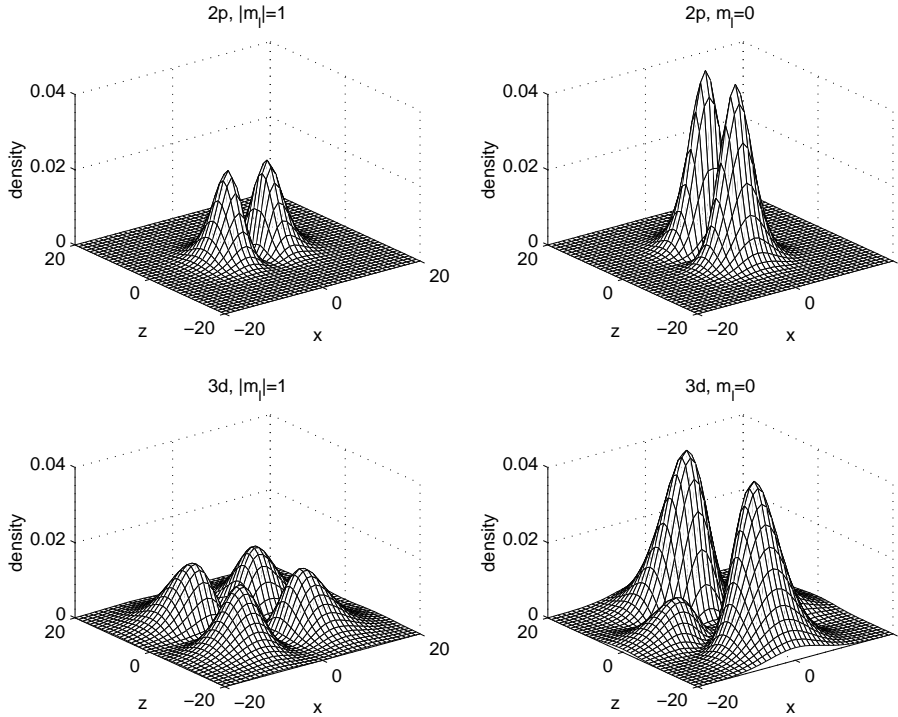


Figur 4: Charge densities in the $xz$-plane for the $2p$, $m_l = \pm 1, 0$ and $3d$, $m_l = \pm 1, 0$ states in hydrogen. There is a rotational symmetry around the $z$-axis.

Another important measure of the charge density is the *radial density function $D(r)$*, which gives the probability per unit length of finding the electron at distance $r$ from the nucleus. The *radial density function* is obtained by integrating the charge density over the angular coordinates

$$D(r) = R_{n\ell}^2(r)r^2 \iint |Y_{lm_l}(\theta, \varphi)|^2 \sin\theta \; d\theta d\varphi. \tag{42}$$

Since the angular integral equals one, this expression simplifies to

$$D(r) = R_{nl}^2(r)r^2 = P_{nl}^2(r). \tag{43}$$

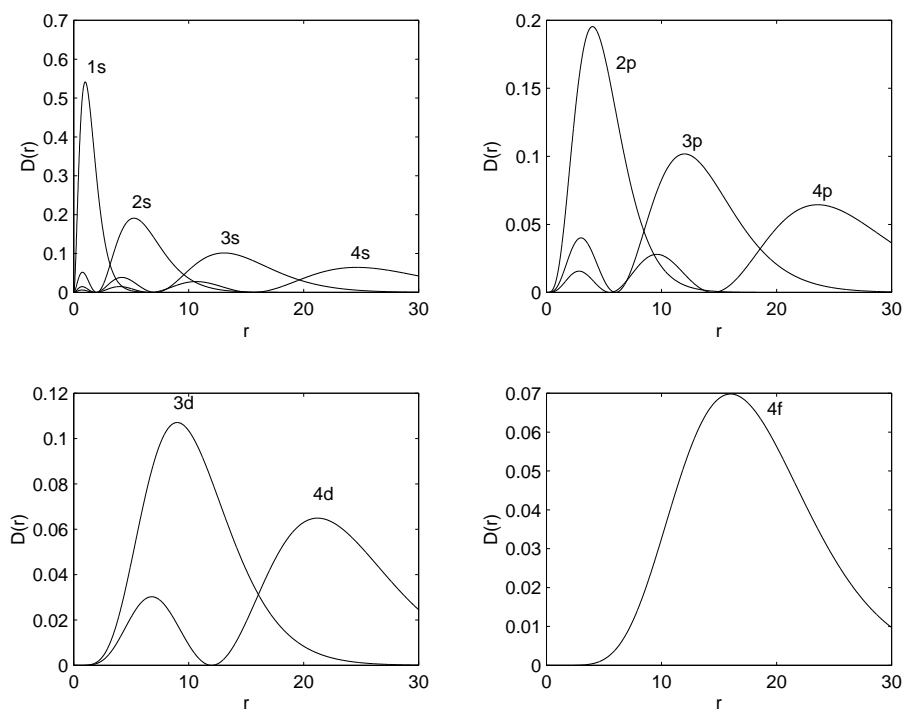Some of the radial densities for hydrogen are depicted in Fig. 5 below.



Figur 5: *Radial charge densities for hydrogen. Note that only s electrons have finite charge densities at the origin and that other orbitals are kept away from the nucleus by the $\frac{\ell(\ell+1)}{2r^2}$ term in the radial part of the Schrödinger equation. Compare also with Exercise 3.*

Note that for any given $n$, the probability of finding the electron close to the nucleus is highest for states having low values of $\ell$. This is consistent with the semi-classical picture of the electron moving in an elliptic orbit that is eccentric for low $\ell$ and more circular for high $\ell$ (see Cowan pages 80 – 81).

# B  Separation of variables

The wave function is $\phi(\mathbf{r}, \sigma) = R(r)Y(\theta, \varphi)\chi_{m_s}(\sigma) = \frac{1}{r}P(r)Y(\theta, \varphi)\chi_{m_s}(\sigma)$. Inserting into equation (23) we get

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)Y(\theta, \varphi) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta, \varphi)}{\partial\varphi}\right)R(r)$$

$$+ \frac{1}{r^2\sin^2\theta}\frac{\partial^2 Y(\theta, \varphi)}{\partial\varphi^2}R(r) + \frac{2m}{\hbar^2}\left(E - V(r)\right)R(r)Y(\theta, \varphi) = 0. \quad (44)$$

Now multiply with $r^2$ and divide by $R(r)Y(\theta, \varphi)$

$$\frac{\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)}{R(r)} + \frac{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta, \varphi)}{\partial\varphi}\right)}{Y(\theta, \varphi)}$$

$$+ \frac{\frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta, \varphi)}{\partial\varphi^2}}{Y(\theta, \varphi)} + \frac{2m}{\hbar^2}\left(E - V(r)\right)r^2 = 0. \quad (45)$$

Rearrange so that we have all terms depending on $r$ to the left and all terms depending on $(\theta, \varphi)$ to the right

$$\frac{\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)}{R(r)} + \frac{2m}{\hbar^2}\left(E - V(r)\right)r^2 =$$

$$- \frac{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta, \varphi)}{\partial\varphi}\right)}{Y(\theta, \varphi)} - \frac{\frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta, \varphi)}{\partial\varphi^2}}{Y(\theta, \varphi)}. \quad (46)$$

Since the LHS depends only on $r$ and the RHS only on $(\theta, \varphi)$ both sides must be constant. We call the constant the separation constant and denote it by $\lambda$. Thus, we have two equations

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta, \varphi)}{\partial\varphi}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta, \varphi)}{\partial\varphi^2} + \lambda Y(\theta, \varphi) = 0 \quad (47)$$

and

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right) + \frac{2m}{\hbar^2}\left(E - V(r)\right)r^2 R(r) = \lambda R(r). \quad (48)$$

Now utilizing the fact that $R(r) = \frac{P(r)}{r}$, it is not difficult to show that the latter equation yields

$$\frac{d^2 P(r)}{dr^2} + \frac{2m}{\hbar^2}\left(E - V(r) - \frac{\lambda\hbar^2}{2mr^2}\right)P(r) = 0. \quad (49)$$

# C SymPy

**Example 1.** To take the derivative of the function

$$f(x) = (2x^5 + 3)\sin(2x)$$

Start python and type:

```
>>> from sympy import *
>>> x=symbols('x')
>>> diff((2*x**5+3)*sin(2*x),x)
10*x**4*sin(2*x) + 2*(2*x**5 + 3)*cos(2*x)
```

The `integrals` module in SymPy implements methods to calculate definite and indefinite integrals of expressions.

1. integrate(f, x) returns the indefinite integral $\int f(x)dx$

2. integrate(f, (x, a, b)) returns the definite integral $\int_a^b f(x)dx$

**Example 2.** To perform the integration

$$\int_0^\pi (2x^5 + 3)\sin(2x)\, dx$$

Type:

```
>>> from sympy import *
>>> x=symbols('x')
>>> integrate(2*x**5*sin(2*x),(x,0,pi))
-pi**5 - 15*pi/2 + 5*pi**3
```

**Example 3.** To perform the double integration

$$\int_0^2 \left( \int_0^\pi \left( (2y^5 + 3)\sin(2x) + y \right) dx \right) dy$$

Type:

```
>>> from sympy import *
>>> x,y=symbols('x y')
>>> f=(2*y**5+3)*sin(2*x)+y
>>> integrate(f,(x,0,pi),(y,0,2))
2*pi
```

Note, if you want the numerical value as output you can use N() as illustrated below,

```
>>> pi
pi
>>> N(pi)
3.14159265358979
```