České vysoké učení technické v Praze
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Katedra fyziky
Studijní program: Kvantové technologie

Kvantově-mechanický popis mnohaelektronového souboru v kulových nanočásticích

Quantum-Mechanical Description of Many-Electron System in Spherical Nanoparticles

DIPLOMOVÁ PRÁCE

Vypracoval:	Bc. Michael Píro
Vedoucí práce:	Mgr. Jaroslav Hamrle, Ph.D.
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FAKULTA JADERNÁ A FYZIKÁLNĚ INŽENÝRSKÁ
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ZADÁNÍ DIPLOMOVÉ PRÁCE

Akademický rok: 2022/2023

Student:	Bc. Michael Píro
Studijní program:	Kvantové technologie
Název práce: (česky)	Kvantově-mechanický popis mnohaelektronového souboru v kulových nanočásticích
Název práce: (anglicky)	Quantum-mechanical description of many-electron system in spherical nanoparticle
Jazyk práce:	Angličtina

Pokyny pro vypracování:

Kvantová hydrodynamika popisuje mnoha-elektronový systému blízko základního stavu, tj. stavu s nejnižší energií. Tento formalismus se typicky používá k popisu chování nerovnovážných volných elektronů v kovových nanočásticích, obsahujících řádově tisíce atomů, kde obecný DFT přístup již nelze použít pro výpočetní obtížnost problému. Na druhou stranu, současný tvar aproximací použitých v rovnicích kvantové hydrodynamiky je odvozený pro krystaly a jejich přesnost pro výpočet elektronového stavu nanočástic je nejasná, obvzláště pro povrchy nanočástic.

Cíle diplomové práce jsou následující:

1) Výpočet základního stavu elektronové hustoty pro kulovou kovovou nanočástici pomocí mnohaelektronového přístupu, s určením vlnových funkcí jednotlivých elektronů.

2) Analýza základního stavu elektronové struktury, jako určení radiálního profilu elektronové hustoty a jednotlivých energetických příspěvků. Tyto energetické profily budou porovnány s profily energií určenými z kvantově-hydrodynamických rovnic. Tato analýza poslouží ke kontrole a případnému vylepšení současného tvaru kvantově hydrodynamických rovnic.

Doporučená literatura:

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[2] Mats G. Larson, Fredrik Bengzon, The Finite Element Method: Theory, Implementation, and Applications, Springer (2013)

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[4] M. Bonitz et al, Quantum hydrodynamics for plasmas—Quo vadis?, Phys. Plasmas 26, 090601 (2019)

Jméno a pracoviště vedoucího diplomové práce:

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Datum zadání diplomové práce: 20.10.2022

Termín odevzdání diplomové práce: 03.05.2023

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V Praze dne 20.10.2022

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prohlašuji, že jsem diplomovou práci s názvem:

Kvantově-mechanický popis mnohaelektronového souboru v kulových nanočásticích

vypracoval samostatně a uvedl veškeré použité informační zdroje v souladu s Metodickým pokynem o dodržování etických principů při přípravě vysokoškolských závěrečných prací.

V Praze dne 3. 5. 2023

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podpis

Poděkování

Tímto bych chtěl poděkovat svému vedoucímu Mgr. Jaroslavu Hamrlemu, Ph.D. za vstřícný přístup, cenné podněty a především za velkou ochotu v průběhu vytváření této práce.

Bc. Michael Píro

Název práce:

Kvantově-mechanický popis mnohaelektronového souboru v kulových nanočásticích

Autor:	Bc. Michael Píro
Studijní program:	Kvantové technologie
Druh práce:	Diplomová práce
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Abstrakt: Tato diplomová práce se zabývá chováním elektronů v kulových nanočásticích. Cílem bylo vytvořit ucelenou představu o elektronové struktuře nanočástic modelovaných jako pevné koule s rovnoměrně rozloženým kladným nábojem. Pro tento účel je nejprve provedeno detailní odvození obecného řešení Schrödingerovy rovnice pro sféricky symetrické potenciály, konkrétně vodíkový a tzv. soft-core Coulombův modelující konečně rozměrné jádro. Čtenář je následně seznámen s obecným přístupem k mnohaelektronovým problémům vedoucím na tzv. Hartreeho-Fockovy rovnice. Nakonec je představena numerická maticová metoda efektivně řešící Hartreeho-Fockovy rovnice. Teoretická část práce je doplněna o konkrétní řešení elektronové struktury nanočástic o rozměrech do jednoho nanometru.

Klíčová slova: nanočástice, elektronová struktura, Hartreeho-Fockova aproximace, maticová metoda

Title:

Quantum-Mechanical Description of Many-Electron System in Spherical Nanoparticles

Author: Bc. Michael Píro

Abstract: This master thesis deals with the behaviour of electrons in spherical nanoparticles. The aim was to develop a comprehensive picture of the electronic structure of nanoparticles modelled as solid spheres with a uniformly distributed positive charge. For this purpose, a detailed derivation of the general solution of the Schrödinger equation for spherically symmetric potentials, namely the hydrogen and the soft-core Coulomb modelling a finite nucleus, is first performed. The reader is then introduced to a general approach to many-electron problems leading to the so-called Hartree-Fock equations. Finally, a numerical matrix method which is efficiently solving the Hartree-Fock equations is presented. The theoretical part of the work is complemented by concrete solutions of the electronic structure of nanoparticles with a diameter of up to one nanometer.

Key words: nanoparticle, electron structure, Hartree-Fock approximation, matrix method

Contents

Introduction

Nanotechnology and nanomaterials have been an important part of science and industrial research for several decades. The wide range of applications of nanoparticles includes, among others, the production of electronics and superconductors, imaging technology, cleaning agents, or the development of drugs with very efficient transport properties [1].

One of the important areas of study is the optical properties of the nanoparticles. Many studies have revealed interesting phenomena significantly differing from the known in the same bulk materials [2, 3]. To be able to describe these properties better theoretically, we need to know the exact electronic structure of the particles. Yet due to their size, this problem is difficult to solve. On the one hand, a classical description may overlook some interesting physical effects; on the other hand, a fully quantum description is infeasible given the complexity of the problem. It is therefore obvious that several approximations have to be made. One possible way is using the so-called quantum hydrodynamic formalism (QHD), where the nanoparticle consists of a solid ionic core with uniformly distributed charge and an electron shell [4]. For small particles, however, this model turns out to be insufficient.

In this work, we have chosen to solve the problem as a multi-electron system in the potential given by the ionic core. To get a good idea of the resulting wave functions, we first solve the one-electron problem. To do this, we review the general solution of the spherically symmetric potential in the first chapter. Next, we look at the solution of the hydrogen atom with a point-like nucleus. We will then extend our idea of the final functions with an interesting solution of the so-called soft-core Coulomb potential, representing a finite nucleus. In the third chapter, we show a detailed revision of the multi-electron problem resulting in the Hartree-Fock equations. We then introduce a modern approach to solving these equations using matrix calculus and we perform the calculations for multiple cases with a diameter within one nanometer.

Although the referred procedures are general and can be applied to different types of nanoparticles, we have limited ourselves to gold nanoparticles where each atom contributes one electron to the total electron shell. To simplify our analysis and calculations, we will also use Hartree atomic units throughout the whole text.

Chapter 1

Schrödinger Equation for Spherically Symmetric Potentials

The goal of this thesis is to determine the shape of the electron density function of a spherical nanoparticle. Although the complexity of the system does not allow us to have a precise quantum mechanical description, thanks to spherical symmetry for the one-electron problem, at least an exact angular dependence can be obtained. In this chapter, we derive a set of three equations describing any spherically symmetric potential. We then determine possible values of the angular momentum operators and find a general solution to the angular part of the equations.

1.1 Separation of the Schrödinger Equation

The general form of the time-independent Schrödinger equation for a problem in three dimensions is

$$\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r}), \tag{1.1}$$

with the Hamiltonian

$$\hat{H} = -\frac{1}{2}\Delta + V(\mathbf{r}). \tag{1.2}$$

To take advantage of the symmetry of the system, we transform the Schrödinger equation into spherical coordinates, using the following transformation:

$$x = r\sin\theta\cos\phi, \tag{1.3}$$

$$y = r\sin\theta\sin\phi, \tag{1.4}$$

$$z = r\cos\theta, \tag{1.5}$$

where $r \in \langle 0, +\infty)$, $\theta \in \langle 0, \pi\rangle$ and $\phi \in \langle 0, 2\pi)$. The Laplace operator is given by the expression

$$\Delta = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{1.6}$$

and we assume a central potential, i.e. V depends solely on r. To proceed, we use the angular momentum operator $\hat{\boldsymbol{L}}$ whose j-th component is defined as

$$\hat{L}_j = \epsilon_{jkl}\hat{X}_k\hat{P}_l = -i\epsilon_{jkl}x_k\frac{\partial}{\partial x_l}. \tag{1.7}$$

Rewritten in spherical coordinates

$$\hat{L}_1 = i\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right), \tag{1.8}$$

$$\hat{L}_2 = i\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right), \tag{1.9}$$

$$\hat{L}_3 = -i\frac{\partial}{\partial\phi}. \tag{1.10}$$

From here we have

$$\hat{\boldsymbol{L}}^2 = -\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right), \tag{1.11}$$

which exactly corresponds to the angular part of the Laplacian multiplied by the factor $-r^2$. Thus, we can write

$$\hat{H} = -\frac{1}{2r}\frac{\partial^2}{\partial r^2}r + \frac{\hat{\boldsymbol{L}}^2}{2r^2} + V(r). \tag{1.12}$$

Very importantly, the operator $\hat{\boldsymbol{L}}^2$ commutes with all the components $\hat{L}_j$ and with the Hamiltonian $\hat{H}$, since it depends only on the angles θ, ϕ and the angular part of $\hat{H}$ is the operator $\hat{\boldsymbol{L}}^2$ itself. But that means, that any $\hat{L}_j$ also commutes with $\hat{H}$. Taken together, we see that $\{\hat{H}, \hat{\boldsymbol{L}}^2, \hat{L}_j\}$ forms a set of compatible observables. This property ensures, that these three operators have the same eigenfunctions. For simplicity, we choose $\hat{L}_3$ for $\hat{L}_j$. This brings us to the following set of equations for $\psi(\mathbf{r})$:

$$\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r}), \tag{1.13}$$

$$\hat{\boldsymbol{L}}^2\psi(\mathbf{r}) = \lambda\psi(\mathbf{r}), \tag{1.14}$$

$$\hat{L}_3\psi(\mathbf{r}) = m\psi(\mathbf{r}). \tag{1.15}$$

Finally, let us substitute for the operators $\hat{H}$, $\hat{\boldsymbol{L}}^2$ and $\hat{L}_3$ and consider the eigenfunction in the separated form $\psi(\mathbf{r}) = R(r)f(\theta)g(\phi)$:

$$\left(-\frac{1}{2r}\frac{\partial^2}{\partial r^2}r + \frac{\lambda}{2r^2} + V(r)\right)R(r) = ER(r), \tag{1.16}$$

$$-\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)f(\theta)g(\phi) = \lambda f(\theta)g(\phi), \tag{1.17}$$

$$-i\frac{\partial}{\partial\phi}g(\phi) = mg(\phi). \tag{1.18}$$

We see, that we managed to simplify our initial problem by separating the Schrödinger equation into the radial and the angular part.

1.2 Angular Momentum Eigenvalues

We would like to find the possible eigenvalues of operators $\hat{\boldsymbol{L}}^2$ and $\hat{L}_3$. Let us start by defining yet another set of useful operators, the so-called ladder operators:

$$\hat{L}_+ = \hat{L}_1 + i\hat{L}_2, \tag{1.19}$$
$$\hat{L}_- = \hat{L}_1 - i\hat{L}_2. \tag{1.20}$$

It is easy to show, that they satisfy the following commutation relations:

$$[\hat{L}_3, \hat{L}_+] = \hat{L}_+, \tag{1.21}$$
$$[\hat{L}_3, \hat{L}_-] = -\hat{L}_-. \tag{1.22}$$

Using these and the equation 1.15, we get

$$\hat{L}_3(\hat{L}_+\psi) = \hat{L}_+(\hat{L}_3\psi) + \hat{L}_+\psi = (m+1)\hat{L}_+\psi, \tag{1.23}$$
$$\hat{L}_3(\hat{L}_-\psi) = \hat{L}_-(\hat{L}_3\psi) - \hat{L}_-\psi = (m-1)\hat{L}_-\psi. \tag{1.24}$$

We see, that using $\hat{L}_+(\hat{L}_-)$ creates another eigenfunction of $\hat{L}_3$ with the eigenvalue increased (decreased) by one. Hence the name ladder operators. But this does not go on forever. Since the components of $\hat{\boldsymbol{L}}$ are hermitian, i.e. $\hat{L}_j^\dagger = \hat{L}_j$,

$$\langle\psi|(\hat{\boldsymbol{L}}^2 - \hat{L}_3^2)\psi\rangle = \langle\psi|(\hat{L}_1^2 + \hat{L}_2^2)\psi\rangle = ||\hat{L}_1\psi||^2 + ||\hat{L}_2\psi||^2 \geq 0, \tag{1.25}$$
$$\langle\psi|(\hat{\boldsymbol{L}}^2 - \hat{L}_3^2)\psi\rangle = (\lambda - m^2)||\psi||^2 \tag{1.26}$$

and we see that $m \in \left\langle -\sqrt{\lambda}, \sqrt{\lambda} \right\rangle$. This means, that there are eigenstates ψ_{max}, ψ_{min} with corresponding eigenvalues m_{max}, m_{min}, such that

$$\hat{L}_+\psi_{max} = 0, \tag{1.27}$$
$$\hat{L}_-\psi_{min} = 0. \tag{1.28}$$

Next, we use another two important identities satisfied by the ladder operators:

$$\hat{L}_-\hat{L}_+ = \hat{L}_1^2 + \hat{L}_2^2 + [\hat{L}_1, \hat{L}_2] = \hat{\boldsymbol{L}}^2 - \hat{L}_3^2 - \hat{L}_3, \tag{1.29}$$
$$\hat{L}_+\hat{L}_- = \hat{L}_1^2 + \hat{L}_2^2 - [\hat{L}_1, \hat{L}_2] = \hat{\boldsymbol{L}}^2 - \hat{L}_3^2 + \hat{L}_3. \tag{1.30}$$

Joining relations 1.27, 1.29 allows us to write

$$(\hat{\boldsymbol{L}}^2 - \hat{L}_3^2 - \hat{L}_3)\psi_{max} = 0, \tag{1.31}$$

which leads to the relation

$$\hat{\boldsymbol{L}}^2\psi_{max} = m_{max}(m_{max}+1)\psi_{max}. \tag{1.32}$$

Similarly for m_{min} we get

$$\hat{\boldsymbol{L}}^2\psi_{min} = m_{min}(m_{min}-1)\psi_{min}. \tag{1.33}$$

If we now apply the operator $\hat{L}_-$ on equation 1.32 and use the fact, that it commutes with $\hat{\boldsymbol{L}}^2$, we see that the relation is independent of m and holds for any eigenfunction ψ. This also means, that

$$m_{max}(m_{max}+1) = m_{min}(m_{min}-1), \tag{1.34}$$

which is true for $m_{min} = -m_{max}$ and $m_{min} = m_{max}+1$, but only the former is a valid solution, since $m_{max} \geq m_{min}$. This together with the fact, that m_{max} and m_{min} must be separated by an interval of integer length implies, that m_{max} must be from the set $\{0, \frac{1}{2}, 1, \frac{3}{2}, ...\}$. Finally, we rename m_{max} to l and we conclude, that the spectral values of $\hat{\boldsymbol{L}}^2$ and $\hat{L}_3$ must be of the form

$$\lambda = l(l+1), \quad l \in \left\{0, \frac{1}{2}, 1, \frac{3}{2}, ...\right\}, \tag{1.35}$$

$$m \in \{-l, -l+1, ..., l-1, l\}. \tag{1.36}$$

This result is valid for a general angular momentum $\hat{\boldsymbol{J}}$ and is completely given by its defining property $[\hat{J}_j, \hat{J}_k] = i\epsilon_{jkl}\hat{J}_l$. However, in the following section, we show that there is an additional constraint on the eigenvalues of the orbital angular momentum $\hat{\boldsymbol{L}}^2$.

1.3 Spherical Harmonics

Since the equations 1.17 and 1.18 for the angular part do not depend on the potential, they can be solved in general and their solution is the same for any central potential. Denoting their common eigenfunction $Y_l^m(\theta,\phi) = F_l^m(\theta)G^m(\phi)$, we get

$$-\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)F_l^m(\theta)G^m(\phi) = l(l+1)F_l^m(\theta)G^m(\phi), \tag{1.37}$$

$$-i\frac{\partial}{\partial\phi}G^m(\phi) = mG^m(\phi). \tag{1.38}$$

The second equation can be solved immediately using the separation of variables yielding the solution

$$G^m(\phi) = e^{im\phi}. \tag{1.39}$$

In order to make this a valid solution, we require the periodic boundary condition

$$\lim_{\phi\to 2\pi} G^m(\phi) = G^m(0) \tag{1.40}$$

to hold. This can be only satisfied if m is an integer. But that is only true, if the values of l are integers. So the possible eigenvalues for the operator $\hat{\boldsymbol{L}}^2$ are

$$\lambda = l(l+1), \quad l \in \{0, 1, 2, ...\}. \tag{1.41}$$

We substitute for $G^m(\phi)$ in 1.37 to arrive at an equation for $F_l^m(\theta)$:

$$-\left(\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right) - \frac{m^2}{\sin^2\theta}\right)F_l^m(\theta) = l(l+1)F_l^m(\theta). \tag{1.42}$$

Now we use the following transformation:

$$t = \cos\theta, \tag{1.43}$$
$$P_l^m(t) = F_l^m(\theta). \tag{1.44}$$

Using the fact that

$$\sin\theta = \sqrt{1-t^2}, \tag{1.45}$$
$$\frac{d}{d\theta} = -\sqrt{1-t^2}\frac{d}{dt}, \tag{1.46}$$

we obtain

$$\left((1-t^2)\frac{d^2}{dt^2} - 2t\frac{d}{dt} + l(l+1) - \frac{m^2}{1-t^2}\right) P_l^m(t) = 0. \tag{1.47}$$

Let's first solve this equation for $m = 0$. We assume, that the solution can be found in the form of a series:

$$P_l^0(t) = \sum_{q=0}^{+\infty} c_q t^q. \tag{1.48}$$

Substituting into 1.47 leads to the equation

$$\sum_{q=0}^{+\infty} c_q \left[q(q-1)t^{q-2} + \Big(l(l+1) - q(q+1)\Big)t^q\right] = 0. \tag{1.49}$$

In order to make a series equal to zero for any t, one must ensure that all coefficients of the series are zero. In our case, this condition gives us a recurrence relation for c_q:

$$c_{q+2} = \frac{q(q+1) - l(l+1)}{(q+2)(q+1)} c_q. \tag{1.50}$$

From here, we can see multiple things. First, we can write our solution as

$$P_l^0(t) = \sum_{k=0}^{+\infty} c_{2k} t^{2k} + \sum_{k=0}^{+\infty} c_{2k+1} t^{2k+1} \tag{1.51}$$

and it can be characterized only by the coefficients c_0 and c_1 and the relation 1.50. Secondly, we see that one of these series terminates after l terms, since $c_{l+2} = 0$. Moreover, it can be shown (similarly as in [5]) that the other series must have a finite number of terms as well in order for the solution to be normalizable. But that can be achieved only by setting the first coefficient to zero. So we end up with polynomials containing either only odd or only even powers of t. These solutions are called the *Legendre polynomials* and can be rewritten in the following useful form:

$$P_l(t) = P_l^0(t) = \frac{d^l}{dt^l}(t^2-1)^l. \tag{1.52}$$

Indeed, using the fact, that

$$\begin{aligned}(t^2-1)^l &= \sum_{k=0}^{l}(-1)^{l-k}\frac{l!}{k!(l-k)!}t^{2k},\\ \frac{d^l}{dt^l}t^{2k} &= \frac{(2k)!}{(2k-l)!}t^{2k-l},\end{aligned} \tag{1.53}$$

we can write

$$P_l^0(t) = \sum_{k=0}^{l} a_{2k-l} t^{2k-l} = \sum_{k=0}^{l} (-1)^{l-k} \frac{l!(2k)!}{k!(l-k)!(2k-l)!} t^{2k-l}. \tag{1.54}$$

The coefficients a_{2k-l} satisfy

$$\begin{aligned} a_{2k-l+2} &= (-1)^{l-k-1} \frac{l!(2k+2)!}{(k+1)!(l-k-1)!(2k+2-l)!} = \\ &= -\frac{(l-k)(2k+2)(2k+1)}{(k+1)(2k+2-l)(2k+1-l)} a_{2k-l} = \frac{(2k-2l)(2k+1)}{(2k-l+2)(2k-l+1)} a_{2k-l}, \end{aligned} \tag{1.55}$$

which is exactly the relation 1.50 for $q = 2k - l$.

To solve 1.47 for $m \neq 0$ we suppose the solution of the form

$$P_l^m(t) = (1-t^2)^{\frac{m}{2}} Q_l^m(t). \tag{1.56}$$

Plugging this into 1.47 gives us

$$\left((1-t^2)\frac{d^2}{dt^2} - 2(m+1)t\frac{d}{dt} + l(l+1) - m(m+1) \right) Q_l^m(t) = 0. \tag{1.57}$$

If we now differentiate this equation, we get

$$\left((1-t^2)\frac{d^2}{dt^2} - 2(m+2)t\frac{d}{dt} + l(l+1) - (m+1)(m+2) \right) \frac{d}{dt} Q_l^m(t) = 0. \tag{1.58}$$

By simple comparison, we see that

$$Q_l^{m+1}(t) = \frac{d}{dt} Q_l^m(t). \tag{1.59}$$

Together with the fact that the equation 1.57 yields

$$Q_l^0(t) = P_l^0(t), \tag{1.60}$$

we can conclude, that P_l^m, the so-called *associated Legendre functions*, are of the form

$$P_l^m(t) = (1-t^2)^{\frac{m}{2}} \frac{d^m}{dt^m} P_l^0(t) = (1-t^2)^{\frac{m}{2}} \frac{d^{l+m}}{dt^{l+m}} (t^2-1)^l. \tag{1.61}$$

Finally, we can write the solution of the angular part of the Schrödinger equation in the following compact form:

$$Y_l^m(\theta, \phi) = P_l^m(\cos\theta) e^{im\phi}. \tag{1.62}$$

These functions are called spherical harmonics.

1.4 Normalization of the Wave Function

In quantum mechanics, the wave function expresses the probability amplitude of finding a particle at a certain point. Therefore, it is necessary to normalize this function so that we get a correctly defined probability density distribution. Written mathematically, we require the fulfilment of the relation

$$\int_{\mathbb{R}^3} |\psi(\mathbf{r})|^2 d\mathbf{r} = 1. \tag{1.63}$$

In spherical coordinates:

$$\int_0^{+\infty} r^2 |R(r)|^2 dr \int_0^{2\pi} \int_0^{\pi} |Y_l^m(\theta,\phi)|^2 \sin\theta d\theta d\phi = 1. \tag{1.64}$$

As we saw in the first section, the function $R(r)$ depends on the specific form of the potential, so we limit ourselves to normalizing the angular part only. For the spherical harmonics, we have the following:

$$\begin{aligned} \int_0^{2\pi} \int_0^{\pi} |Y_l^m(\theta,\phi)|^2 \sin\theta d\theta d\phi &= \int_0^{2\pi} d\phi \int_0^{\pi} P_l^m(\cos\theta) P_l^m(\cos\theta) \sin\theta d\theta = \\ &= 2\pi \int_{-1}^{1} P_l^m(t) P_l^m(t) dt. \end{aligned} \tag{1.65}$$

From 1.61 we have

$$N_l^m = \int_{-1}^{1} P_l^m(t) P_l^m(t) dt = \int_{-1}^{1} (1-t^2)^m \frac{d^{l+m}}{dt^{l+m}} (t^2-1)^l \frac{d^{l+m}}{dt^{l+m}} (t^2-1)^l dt. \tag{1.66}$$

Now we use the integration by parts $(l+m)$ times and expand the relation using the Leibniz rule:

$$\begin{aligned} N_l^m &= (-1)^{l+m} \int_{-1}^{1} (t^2-1)^l \frac{d^{l+m}}{dt^{l+m}} \left((1-t^2)^m \frac{d^{l+m}}{dt^{l+m}} (t^2-1)^l \right) dt = \\ &= (-1)^{l+m} \int_{-1}^{1} (t^2-1)^l \sum_{s=0}^{l+m} \binom{l+m}{s} \frac{d^s}{dt^s} (1-t^2)^m \frac{d^{2l+2m-s}}{dt^{2l+2m-s}} (t^2-1)^l dt. \end{aligned} \tag{1.67}$$

In order to get a non-zero number in the sum, two conditions must hold:

$$\begin{aligned} s &\le 2m, \\ 2l+2m-s &\le 2l. \end{aligned} \tag{1.68}$$

This is only true for $s = 2m$. Therefore, N_l^m simplifies to

$$\begin{aligned} N_l^m &= (-1)^{l+m} \binom{l+m}{2m} \int_{-1}^{1} (t^2-1)^l \frac{d^{2m}}{dt^{2m}} (1-t^2)^m \frac{d^{2l}}{dt^{2l}} (t^2-1)^l dt = \\ &= (-1)^{l+m} \binom{l+m}{2m} \int_{-1}^{1} (t^2-1)^l (-1)^m (2m)! (2l)! dt = \\ &= (-1)^l (2l)! \frac{(l+m)!}{(l-m)!} \int_{-1}^{1} (t^2-1)^l dt. \end{aligned} \tag{1.69}$$

The last integral can be evaluated using the change of variable $t = \cos\theta$:

$$\begin{aligned}\int_{-1}^{1}(t^2-1)^l dt &= (-1)^l\int_0^{\pi}(\sin\theta)^{2l+1}d\theta = (-1)^l 2l\int_0^{\pi}(\sin\theta)^{2l-1}\cos^2\theta d\theta = \\ &= 2l\left((-1)^l\int_0^{\pi}(\sin\theta)^{2l-1}d\theta - (-1)^l\int_0^{\pi}(\sin\theta)^{2l+1}d\theta\right) = \\ &= -2l\left(\int_{-1}^{1}(t^2-1)^{l-1}dt + \int_{-1}^{1}(t^2-1)^l dt\right) \qquad (1.70)\end{aligned}$$

where we used integration by parts in the second equality. From this we have

$$\begin{aligned}\int_{-1}^{1}(t^2-1)^l dt &= -\frac{2l}{2l+1}\int_{-1}^{1}(t^2-1)^{l-1}dt = (-1)^l\frac{2l}{2l+1}\frac{2(l-1)}{2l-1}...\frac{2}{3}\int_{-1}^{1}dt = \\ &= (-1)^l\frac{2^l l!}{(2l+1)!!}2 = (-1)^l\frac{2^{2l+1}(l!)^2}{(2l+1)!}. \qquad (1.71)\end{aligned}$$

Together with 1.69 we obtain the square of the norm of P_l^m:

$$N_l^m = \frac{2^{2l+1}(l!)^2}{2l+1}\frac{(l+m)!}{(l-m)!} \qquad (1.72)$$

We can now use this and the relation 1.65 to redefine Y_l^m as the normalized spherical harmonics:

$$Y_l^m(\theta,\phi) = \frac{1}{2^l l!}\sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)e^{im\phi}. \qquad (1.73)$$

Note, that the normalizing factor can differ in the literature since some authors include parts of the factor in the definition of P_l^m. Therefore it is always necessary to determine the exact form of the Legendre polynomials together with the functions $Y_l^m(\theta,\phi)$. Sometimes there is also a non-zero phase factor included in the definition, coming from the fact, that the normalization process can only determine the square of the norm.

Chapter 2

Nanoparticle Potential

2.1 Derivation of the Potential

For a given charge density distribution $n_I(\mathbf{r})$, we can calculate the electric potential $V(\mathbf{r})$ using the following formula:

$$V(\mathbf{r}) = -\int_{\mathbb{R}^3} \frac{n_I(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}'. \tag{2.1}$$

Let us now have a spherical nanoparticle with a radius R centred at the origin and let's assume, that its positive charge is uniformly distributed over the whole particle. Then for n_I we have

$$n_I(\mathbf{r}') = \begin{cases} n_I & |\mathbf{r}'| \leq R \\ 0 & |\mathbf{r}'| > R. \end{cases} \tag{2.2}$$

Thanks to spherical symmetry we know, that the potential will depend only on the distance $r = |\mathbf{r}|$ and not on the polar and azimuthal angles θ, ϕ. Without loss of generality, we can therefore orient the coordinate system so that the z axis is aligned with the position vector $\mathbf{r}$. Then for the distance of the vectors $\mathbf{r}'$, $\mathbf{r}$ in spherical coordinates we have

$$|\mathbf{r}' - \mathbf{r}| = \sqrt{r'^2 + r^2 - 2r'r\cos\theta'}, \tag{2.3}$$

where r', r are the lengths of the vectors $\mathbf{r}'$, $\mathbf{r}$, respectively. Now we can write

$$\begin{aligned} V(r) &= -\int_0^{2\pi} d\phi' \int_0^{\pi} \int_0^{R} \frac{n_I r'^2}{\sqrt{r'^2 + r^2 - 2r'r\cos\theta'}} dr' \sin\theta' d\theta' = \\ &= -\frac{2\pi n_I}{r} \int_0^R r' \int_{(r'-r)^2}^{(r'+r)^2} \frac{1}{2\sqrt{t}} dt dr' = -\frac{2\pi n_I}{r} \int_0^R r'(r' + r - |r' - r|) dr', \end{aligned} \tag{2.4}$$

where in the second equality we use the substitution $t = r'^2 + r^2 - 2r'r\cos\theta$. Now we have to distinguish two cases: $r \leq R$ and $r > R$. For the first one we get

$$V(r) = -\frac{2\pi n_I}{r} \Big(\int_0^r 2r'^2 dr' + \int_r^R 2r'r dr' \Big) = -\frac{2\pi n_I}{3}(3R^2 - r^2). \tag{2.5}$$

And for the second case,

$$V(r) = -\frac{2\pi n_I}{r}\int_0^R 2r'^2 dr' = -\frac{4}{3}\pi R^3 \frac{n_I}{r}. \tag{2.6}$$

Now we just use the fact, that the total charge of the particle $Q = \frac{4}{3}\pi R^3 n_I$ and we arrive at

$$V(r) = \begin{cases} \frac{Q}{2R^3}r^2 - \frac{3Q}{2R} & r \leq R \\ -\frac{Q}{r} & r > R. \end{cases} \tag{2.7}$$

Let us add two more notes on the general form of the potential. We see, that it is parameterized by the total charge Q and the radius of the nanoparticle R. The charge is given by

$$Q = N\nu, \tag{2.8}$$

where N is the number of atoms and ν is the number of electrons per atom, which are considered not bound to the nucleus. Secondly, since we assume, that the atoms of the particle are arranged in a crystal lattice, constants N and R are not independent, but related by the expression

$$R = r_s N^{1/3}, \tag{2.9}$$

where r_s is the so-called Wigner-Seitz radius. This means that for a given material, the potential can be described by only one parameter, usually the radius R. Putting it all together, we get the final form of the potential

$$V(r) = \begin{cases} \frac{\nu}{r_s^3}\frac{r^2-3R^2}{2} & r \leq R \\ -\frac{\nu}{r_s^3}\frac{R^3}{r} & r > R. \end{cases} \tag{2.10}$$

The particular shape of this potential for a gold nanoparticle is depicted in figure 2.1.

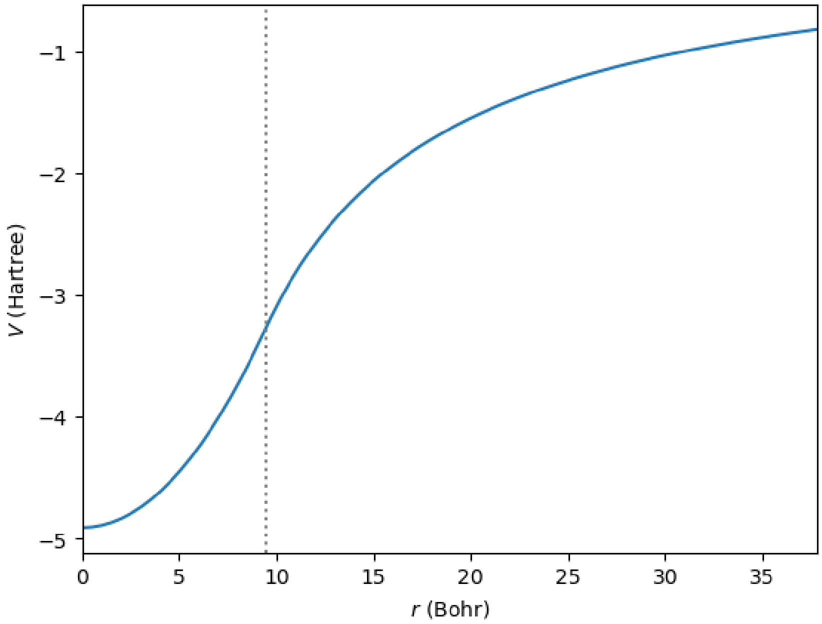


Figure 2.1: Potential V given by 2.10 for a gold nanoparticle with the parameters $R =$ 9.45 Bohr (0.5 nm), $r_s = 3.01$ Bohr and $\nu = 1$ ($Q = 30.945$). The dotted line shows the boundary of the nanoparticle.

2.2 Hydrogen Atom Solution

For a particle with a radius of the order of one nanometer, we have the number of electrons $N_e \sim 10^1 - 10^3$. Not only each electron changes the potential for other electrons, but they also interact with each other. This means that the system is very complex and obviously cannot be solved exactly analytically. Therefore, we have to use some simplifications and numerical methods to get a specific solution.

To gain a first insight into our problem, we will consider a particle consisting of only one point-like atom with $\nu = 1$. This is equivalent to the well-known equation for the hydrogen atom. The corresponding potential is

$$V(r) = -\frac{1}{r} \tag{2.11}$$

and by inserting into 1.16 we obtain the radial equation we need to solve:

$$\left(-\frac{1}{2r}\frac{d^2}{dr^2}r + \frac{l(l+1)}{2r^2} - \frac{1}{r}\right)R(r) = ER(r). \tag{2.12}$$

The last two terms on the left-hand side form together the so-called *effective potential*

$$V_{eff} = \frac{l(l+1)}{2r^2} - \frac{1}{r}. \tag{2.13}$$

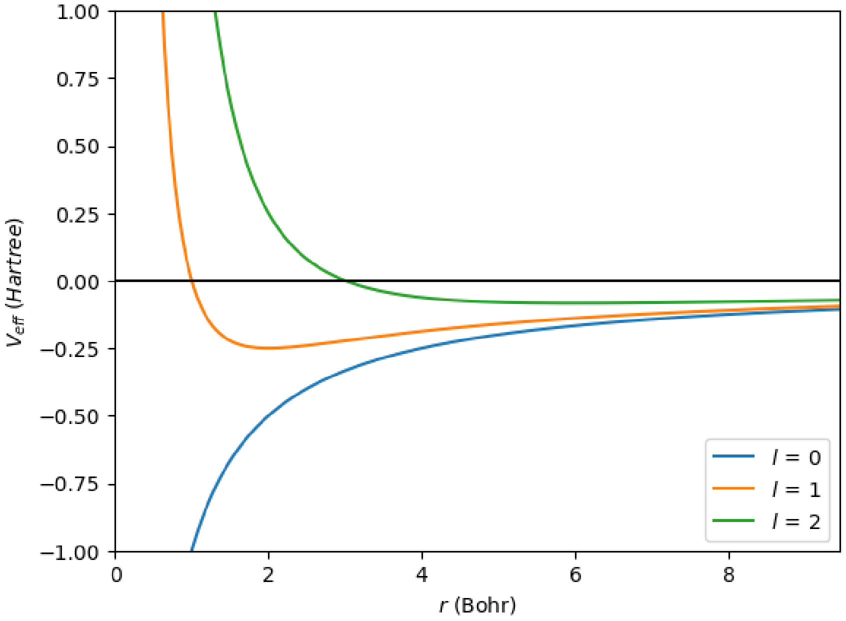


Figure 2.2: Effective potential of the hydrogen atom for the first three angular quantum numbers l.

You can see from figure 2.2 that all the bound states, which is what we are interested in, must have negative energies. We simplify 2.12 by substituting

$$u(r) = rR(r) \tag{2.14}$$

and multiplying by -2:

$$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{2}{r} + 2E\right)u(r) = 0. \tag{2.15}$$

In addition, to obtain a physically relevant solution we impose the following boundary conditions:

$$\begin{aligned} u(0) &= 0, \\ u(+\infty) &= 0. \end{aligned} \tag{2.16}$$

The next step is to look at the solution in the limit of large r. There, both terms of the effective potential are dominated by the energy term and we get a simple second-order linear differential equation

$$\left(\frac{d^2}{dr^2} + 2E\right)u(r) \approx 0 \tag{2.17}$$

with two fundamental solutions

$$u(r) \approx e^{\sqrt{-2E}r}, \quad u(r) \approx e^{-\sqrt{-2E}r}. \tag{2.18}$$

Thanks to the boundary condition, only the second solution is valid. This allows us to write

$$u(r) = v(r)e^{-\sqrt{-2E}r}. \tag{2.19}$$

After substituting into 2.15 we arrive at an equation for $v(r)$:

$$\left(\frac{d^2}{dr^2} - 2\sqrt{-2E}\frac{d}{dr} - \frac{l(l+1)}{r^2} + \frac{2}{r}\right)v(r) = 0. \tag{2.20}$$

Since each term contains either a division by r or a derivative with respect to r, it is again advantageous to assume a power series solution

$$v(r) = r^s \sum_{q=0}^{+\infty} c_q r^q = \sum_{q=0}^{+\infty} c_q r^{s+q}, \quad c_0 \neq 0. \tag{2.21}$$

This gives us an algebraic equation for the coefficients c_q:

$$\sum_{q=0}^{+\infty} c_q \Big(\big((s+q)(s+q-1) - l(l+1)\big)r^{s+q-2} + 2\big(1 - \sqrt{-2E}(s+q)\big)r^{s+q-1}\Big) = 0. \tag{2.22}$$

The only way a power series can equal zero for all r is if the coefficients in front of every power are zero. For these purposes, let us denote

$$A_q = (s+q)(s+q-1) - l(l+1), \tag{2.23}$$

$$B_q = 2\big(1 - \sqrt{-2E}(s+q)\big). \tag{2.24}$$

This leads to the following set of equations:

$$c_0 A_0 = 0, \tag{2.25}$$

$$c_q A_q + c_{q-1} B_{q-1} = 0, \quad q > 0. \tag{2.26}$$

Due to the condition $c_0 = 0$, the first relation gives us

$$s(s-1) - l(l+1) = 0, \tag{2.27}$$

which yields two solutions for s:

$$s = -l, \quad s = l+1. \tag{2.28}$$

To determine the correct expression, we need to return to the boundary condition at the origin. We know that $u(0) = 0$, which means that also $v(0) = 0$. This gives us

$$\sum_{q=0}^{+\infty} c_q r^{s+q} \Big|_{r=0} = 0, \tag{2.29}$$

which can be satisfied only for $s > 0$ and hence $s = l + 1$. Using this fact together with the set 2.26 we obtain a recurrence relation for the coefficients c_q:

$$c_q = \frac{2\Big(\sqrt{-2E}(l+q) - 1\Big)}{(l+q+1)(l+q) - l(l+1)} c_{q-1} = \frac{2\Big(\sqrt{-2E}(l+q) - 1\Big)}{q(q+2l+1)} c_{q-1}. \tag{2.30}$$

One should now determine, whether the series is finite or infinite, i.e. what is the asymptotic behaviour of the eigenfunctions. In [5] it is nicely shown that only a finite series gives a physically valid solution of the Schrödinger equation. This means that there is a number $k > 0$ such that $c_k = 0$. Our recurrence relation 2.30 gives us for such k an important equation for possible energy values:

$$\sqrt{-2E}(l+k) - 1 = 0 \tag{2.31}$$

with the solution parameterized by the numbers k and l

$$E_{kl} = -\frac{1}{2(k+l)^2}. \tag{2.32}$$

Let us turn our attention to the wave functions. We start by plugging the prescription for possible energy levels into 2.30. The recurrence relation for the coefficients c_q then reads

$$c_q = 2\frac{\frac{q+l}{k+l} - 1}{q(q+2l+1)} c_{q-1} = -\frac{2}{k+l}\frac{k-q}{q(2l+q+1)} c_{q-1}. \tag{2.33}$$

It is not difficult to see that by repeating this formula q-times we get the following explicit prescription for the coefficient c_q expressed in terms of c_0:

$$c_q = \left(-\frac{2}{k+l}\right)^q \frac{(k-1)!(2l+1)!}{(k-q-1)!q!(2l+q+1)!} c_0. \tag{2.34}$$

Using this result together with the relations 2.14, 2.19 and 2.21 we arrive at the

$$R_{kl}(r) = N r^l e^{-\frac{r}{k+l}} \sum_{q=0}^{k-1} \left(-\frac{2}{k+l}\right)^q \frac{(k-1)!(2l+1)!}{(k-q-1)!q!(2l+q+1)!} r^q, \tag{2.35}$$

where we included the coefficient c_0 in the normalization factor N.

Before we determine the normalization, we rewrite our result in a more compact way. For this, we will use the so-called *generalized (associated) Laguerre polynomials* L_n^m. We define them as follows:

$$L_n^m(x) = \frac{e^x x^{-m}}{n!}\frac{d^n}{dx^n}(e^{-x}x^{n+m}) = \frac{x^{-m}}{n!}\left(\frac{d}{dx}-1\right)^n x^{n+m}. \tag{2.36}$$

The term with the derivative can be written in the form of a series as

$$\left(\frac{d}{dx}-1\right)^n = \sum_{q=0}^{n}\binom{n}{q}(-1)^q\frac{d^{n-q}}{dx^{n-q}}. \tag{2.37}$$

This allows us to write

$$L_n^m(x) = \frac{x^{-m}}{n!}\sum_{q=0}^{n}\binom{n}{q}(-1)^q\frac{(n+m)!}{(m+q)!}x^{m+q} = \sum_{q=0}^{n}\frac{(n+m)!}{(n-q)!q!(m+q)!}(-x)^q. \tag{2.38}$$

If we now choose $n = k-1$, $m = 2l+1$ and substitute $x = \frac{2r}{k+l}$, we get

$$\begin{aligned} L_{k-1}^{2l+1}\left(\frac{2r}{k+l}\right) &= \sum_{q=0}^{k-1}\left(-\frac{2}{k+l}\right)^q\frac{(2l+k)!}{(k-q-1)!q!(2l+q+1)!}r^q = \\ &= \binom{2l+k}{2l+1}\sum_{q=0}^{k-1}\left(-\frac{2}{k+l}\right)^q\frac{(k-1)!(2l+1)!}{(k-q-1)!q!(2l+q+1)!}r^q. \end{aligned} \tag{2.39}$$

We see that the sum is exactly equal to the one we had in 2.35 and so we can write

$$R_{kl}(r) = N_{kl}r^l e^{-\frac{r}{k+l}}L_{k-1}^{2l+1}\left(\tfrac{2r}{k+l}\right), \tag{2.40}$$

where we included the binomial coefficient in the normalization factor N_{kl}.

The last step in deriving the radial function is to determine N_{kl}. Since we already normalized the angular part of our wave function, we only need to satisfy the identity

$$\int_0^{+\infty} r^2|R_{kl}(r)|^2 dr = 1. \tag{2.41}$$

For our solution we have

$$\begin{aligned} \frac{1}{|N_{kl}|^2} &= \int_0^{+\infty} r^{2l+2}e^{-\frac{2r}{k+l}}\left[L_{k-1}^{2l+1}\left(\tfrac{2r}{k+l}\right)\right]^2 dr = \\ &= \left(\frac{k+l}{2}\right)^{2l+3}\int_0^{+\infty} x^{2l+2}e^{-x}\left(L_{k-1}^{2l+1}(x)\right)^2 dx = \\ &= \left(\frac{k+l}{2}\right)^{2l+3}\int_0^{+\infty} x^{m+1}e^{-x}\left(L_n^m(x)\right)^2 dx\Big|_{\substack{n=k-1\\ m=2l+1}} \end{aligned} \tag{2.42}$$

To evaluate the last integral we will use a useful formula called the *generating function for the generalized Laguerre polynomials*:

$$g(x,u) = \sum_{n=0}^{+\infty} L_n^m(x)u^n = \frac{e^{-\frac{ux}{1-u}}}{(1-u)^{m+1}}. \tag{2.43}$$

Sometimes, it is this expression which is used as a defining relation for the Laguerre polynomials. To see that it is equivalent to 2.39 we recommend the work of Rainville [6]. We first rewrite the following integral in the language of L_n^m:

$$\int_0^{+\infty} x^{m+1}e^{-x}g(x,u)g(x,v)dx = \int_0^{+\infty} x^{m+1}e^{-x}\sum_{s=0}^{+\infty} L_s^m(x)u^s \sum_{t=0}^{+\infty} L_t^m(x)v^t dx = \\ = \sum_{s=0}^{+\infty}\sum_{t=0}^{+\infty}\int_0^{+\infty} x^{m+1}e^{-x}L_s^m(x)L_t^m(x)dx\, u^s v^t. \quad (2.44)$$

On the other hand from 2.43 we have

$$\int_0^{+\infty} x^{m+1}e^{-x}g(x,u)g(x,v)dx = \\ = \frac{1}{(1-u)^{m+1}(1-v)^{m+1}}\int_0^{+\infty} x^{m+1}\exp\Big[-x\Big(1+\frac{u}{1-u}+\frac{v}{1-v}\Big)\Big] = \\ = \frac{1}{(1-u)^{m+1}(1-v)^{m+1}}\frac{(m+1)!(1-u)^{m+2}(1-v)^{m+2}}{(1-uv)^{m+2}} = \\ = \sum_s^{+\infty}(m+1)!(1-u-v+uv)\tbinom{m+1+s}{s}(uv)^s, \quad (2.45)$$

where we used the identities

$$\int_0^{+\infty} x^n e^{-\alpha x}dx = \frac{n!}{\alpha^{n+1}}, \quad (2.46)$$

$$1+\frac{u}{1-u}+\frac{v}{1-v} = \frac{1-uv}{(1-u)(1-v)}, \quad (2.47)$$

$$(1+x)^{-n} = \sum_i^{+\infty}\tbinom{n+i-1}{i}(-x)^i. \quad (2.48)$$

We see that we can retrieve the required integral by comparing the coefficients of the series at the term $(uv)^n$:

$$\int_0^{+\infty} x^{m+1}e^{-x}\Big(L_n^m(x)\Big)^2 dx = (m+1)!\left[\tbinom{n+m+1}{n}+\tbinom{n+m}{n-1}\right] = \\ = (m+1)!\left(\frac{(n+m+1)!}{n!(m+1)!}+\frac{(n+m)!}{(n-1)!(m+1)!}\right) = \\ = \frac{(n+m)!}{n!}(2n+m+1). \quad (2.49)$$

Together with 2.42 we get the normalization factor

$$N_{kl} = \frac{2^{l+1}}{(k+l)^{l+2}}\sqrt{\frac{(k-1)!}{(k+2l)!}}. \quad (2.50)$$

Now we have everything to write the complete prescription for the radial part of the wave function of our first-degree approximation - the hydrogen atom:

$$R_{kl}(r) = \frac{2^{l+1}}{(k+l)^{l+2}}\sqrt{\frac{(k-1)!}{(k+2l)!}}r^l e^{-\frac{r}{k+l}}L_{k-1}^{2l+1}\left(\tfrac{2r}{k+l}\right). \quad (2.51)$$

Again, it is important to remember that the hydrogen atom eigenfunctions should always be stated together with the particular prescription for the Laguerre polynomials since there are unfortunately many different definitions in the scientific literature. Instead of the number k, it is also a common practice to use the so-called *principal quantum number* n, which we define as $n = k + l$. Using this notation we get

$$R_{nl}(r) = \frac{2^{l+1}}{n^{l+2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}} r^l e^{-\frac{r}{n}} L_{n-l-1}^{2l+1}\left(\tfrac{2r}{n}\right) \tag{2.52}$$

with the energy levels

$$E_n = -\frac{1}{2n^2}. \tag{2.53}$$

In the case of our nanoparticle, we would like to use the approximation of a point nucleus, but carrying a general charge Q. This is reflected by the change of the potential V to

$$V(r) = -\frac{Q}{r}, \tag{2.54}$$

where Q is given by

$$Q = \nu \left(\frac{R}{r_s}\right)^3. \tag{2.55}$$

This slight variation changes the problem just a little and the entire solution derivation process demonstrated in this section can be repeated without any significant changes. In particular, after denoting

$$\tilde{r} = Qr, \tag{2.56}$$

$$\tilde{E} = \frac{E}{Q^2} \tag{2.57}$$

we retrieve an equation of the same shape as 2.15. The resulting radial wave functions are

$$R_{nl}(r) = \frac{2^{l+1}}{n^{l+2}} Q^{l+\frac{3}{2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}} r^l e^{-\frac{Q}{n}r} L_{n-l-1}^{2l+1}\left(\tfrac{2Q}{n}r\right) \tag{2.58}$$

with the corresponding energies

$$E_n = -\frac{Q^2}{2n^2}. \tag{2.59}$$

Knowing the radial wave functions enables us to determine both the radial probability density distribution P_{nl} and the radial electron density distribution n_{nl}. The probability distribution is given by the relation

$$P_{nlm}(r, \theta, \phi) = r^2 \sin\theta |R_{nl}(r)|^2 |Y_l^m(\theta, \phi)|^2. \tag{2.60}$$

We see that P_{nlm} does not depend on the angle ϕ since the functions Y_l^m appear only as modules. To get the radial distribution we integrate over the angles θ, ϕ. Thanks to the normalization of the angular part the probability simplifies to

$$P_{nl}(r) = r^2|R_{nl}(r)|^2. \tag{2.61}$$

This relation describes how much negative charge is in an infinitesimal shell of radius r and as we see it no longer depends on the quantum number m. The electron density can be in general obtained as the module of the wave function, i.e.

$$n_{nlm}(\mathbf{r}) = |\psi_{nlm}(\mathbf{r})|^2 \tag{2.62}$$

For spherically symmetric wave functions ($l = 0$) is n_{nlm} constant for all angles θ, ϕ and it is equal to the probability distribution divided by the area of the shell of radius r, that is

$$n_{nl}(r) = \frac{P_{nl}(r)}{4\pi r^2}. \tag{2.63}$$

We can also use this relation to define the mean radial electron density for electron wave functions depending on the angle ($l > 0$):

$$\bar{n}_{nl}(r) = \frac{P_{nl}(r)}{4\pi r^2} = \frac{1}{4\pi}|R_{nl}(r)|^2. \tag{2.64}$$

The radial probability distribution and electron density functions of the first three electrons are shown in figures 2.3, 2.4, respectively.

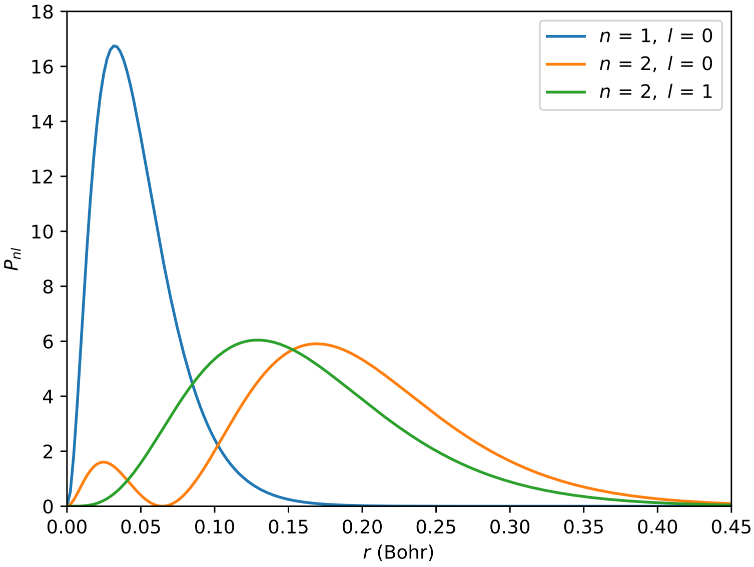


Figure 2.3: Radial probability density functions P_{nl} of the first three electrons for the parameters $R = 9.45$ Bohr, $r_s = 3.01$ Bohr and $\nu = 1$.

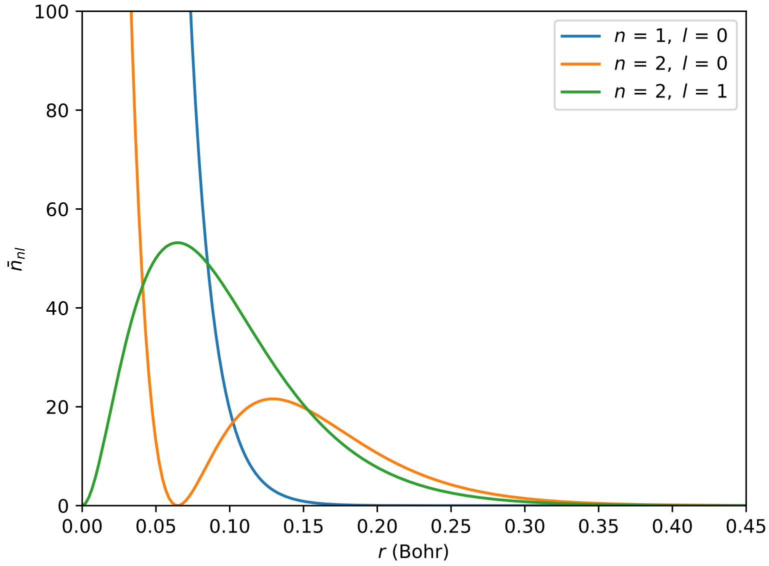


Figure 2.4: Radial electron density functions $\bar{n}_{nl}$ of the first three electrons for the parameters $R = 9.45$ Bohr, $r_s = 3.01$ Bohr and $\nu = 1$.

2.3 Soft-Core Coulomb Potential Solution

The first step in improving our view of the electron wave functions described in the previous section is to consider a finite-size nucleus. One can try to solve this task using the perturbation theory. Here we look for a solution for the potential

$$V(r) = V_0(r) + V_P(r), \tag{2.65}$$

where

$$V_0(r) = -\frac{\nu R^3}{r_s^3 r} \tag{2.66}$$

and

$$V_P(r) = \begin{cases} \frac{\nu}{r_s^3} \frac{r^3 - 3R^2 r + 2R^3}{2r} & r \leq R \\ 0 & r > R. \end{cases} \tag{2.67}$$

The calculation is pretty straightforward and shows, that the ground state energy increases compared to the point-like nucleus case. Nevertheless, this approximation is only valid for very small nuclei. Another possibility, which works for arbitrary large nuclei, is to approximate the nanoparticle potential V (2.10) with the so-called *soft core Coulomb potential*. In its general form it can be written as

$$\tilde{V}(r) = -\frac{a}{\sqrt{b^2 + r^2}}, \quad a, b \geq 0. \tag{2.68}$$

There are several reasonable ways how to choose the coefficients a, b so that $\tilde{V}$ fits our potential well. One of the constants can be fixed by satisfying the boundary condition of V at the origin:

$$\tilde{V}(0) = -\frac{3\nu R^2}{2r_s^3}. \tag{2.69}$$

Since the second boundary condition

$$\lim_{r\to+\infty} \tilde{V}(r) = 0 \tag{2.70}$$

is automatically true for all constants a, b, we require a stronger constraint:

$$\tilde{V}(r) \underset{r\to+\infty}{\sim} -\frac{\nu R^3}{r_s^3 r}. \tag{2.71}$$

These conditions give us the set of equations

$$\frac{a}{b} = \frac{3\nu R^2}{2r_s^3}, \tag{2.72}$$

$$\frac{a}{r} = \frac{\nu R^3}{r_s^3 r} \tag{2.73}$$

with the solution

$$a = \nu \left(\frac{R}{r_s}\right)^3, \quad b = \frac{2}{3}R \tag{2.74}$$

and we come to the form of the potential $\tilde{V}$ parameterized solely by the nucleus radius R:

$$\tilde{V}(r) = -\frac{3\nu}{\sqrt{4R^2 + 9r^2}} \left(\frac{R}{r_s}\right)^3. \tag{2.75}$$

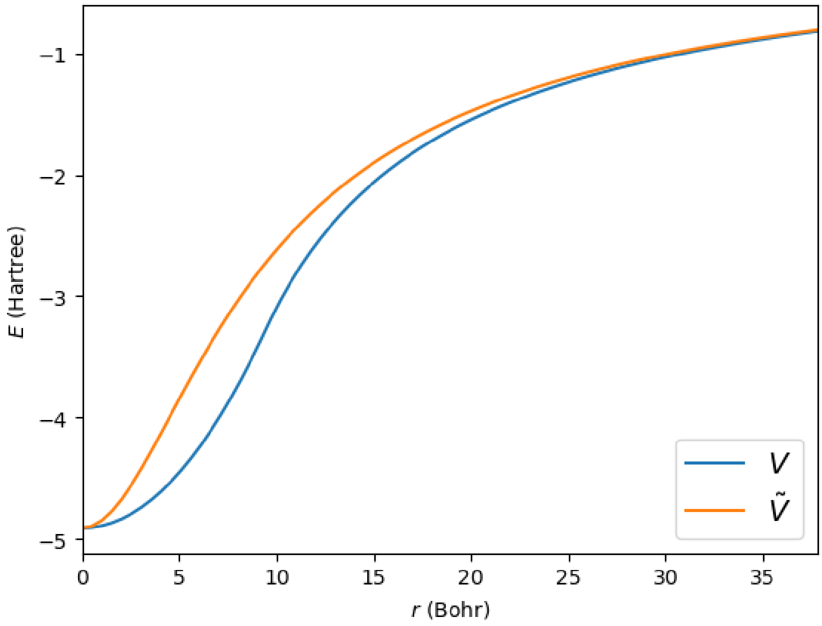


Figure 2.5: Comparison of the two potentials V (2.10) and $\tilde{V}$ (2.75) for the parameters $R = 9.45$ Bohr, $r_s = 3.01$ Bohr and $\nu = 1$.

We compare this with the precise potential V for our nanoparticle in figure 2.5. For simplicity, however, the following calculations will be performed with the general form of $\tilde{V}$. The goal is to find the ground state of an electron in this potential. To do this we will use the approach proposed by Li [7], which shows an analytical solution of this problem. From 1.16 we have the Schrödinger equation for the radial function R

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} - \frac{a}{\sqrt{b^2+r^2}}\right)R(r) = ER(r). \tag{2.76}$$

Since the hydrogen atom ground state radial function, given by the formula 2.52 for $n = 1$, $l = 0$ is of the form

$$R_{10}(r) = 2e^{-r}, \tag{2.77}$$

it is sensible to use the ansatz

$$R(r) = e^{u(r)}. \tag{2.78}$$

This yields the equation

$$\frac{d^2u}{dr^2} + \left(\frac{du}{dr}\right) + \frac{2}{r}\frac{du}{dr} + \frac{2a}{\sqrt{b^2+r^2}} + 2E = 0. \tag{2.79}$$

The next step is to change the independent variable so that there are no terms with the square root. This can be achieved by applying the substitution

$$\rho = \sqrt{b^2+r^2}, \tag{2.80}$$

$$v(\rho) = u(r), \tag{2.81}$$

where $\rho \in \langle b, +\infty)$. Using this we get the derivatives

$$\frac{du}{dr} = \sqrt{1-\frac{b^2}{\rho^2}}\frac{dv}{d\rho}, \tag{2.82}$$

$$\frac{d^2u}{dr^2} = \left(1-\frac{b^2}{\rho^2}\right)\frac{d^2v}{d\rho^2} + \frac{b^2}{\rho^2}\frac{dv}{d\rho} \tag{2.83}$$

and therefore the equation 2.79 simplifies to

$$\left(1-\frac{b^2}{\rho^2}\right)\frac{d^2v}{d\rho^2} + \left(1-\frac{b^2}{\rho^2}\right)\left(\frac{dv}{d\rho}\right)^2 + \left(\frac{b^2}{\rho^3}+\frac{2}{\rho}\right)\frac{dv}{d\rho} + \frac{2a}{\rho} + 2E = 0. \tag{2.84}$$

The order of this differential equation can be easily reduced by considering

$$w(\rho) = \frac{dv}{d\rho}(\rho). \tag{2.85}$$

To simplify this even more we use another change of variables:

$$z = 1 - \frac{b}{\rho}, \tag{2.86}$$

$$h(z) = w(\rho) \tag{2.87}$$

with $z \in \langle 0, 1)$. This gives the derivative

$$\frac{dw}{d\rho} = \frac{(1-z)^2}{b}\frac{dh}{dz} \tag{2.88}$$

and allows us to write

$$f_0(z)\frac{dh}{dz}(z) + f_1(z)h^2(z) + f_2(z)h(z) + f_3(z) = E, \tag{2.89}$$

where

$$f_0(z) = \frac{z(z-1)^2(z-2)}{b}, \tag{2.90}$$

$$f_1(z) = \frac{z(z-2)}{2}, \tag{2.91}$$

$$f_2(z) = \frac{2(z-1)+(z-1)^3}{2b}, \tag{2.92}$$

$$f_3(z) = \frac{a(z-1)}{b}. \tag{2.93}$$

Now we assume

$$\lim_{z\to 0,1} f_0(z)\frac{dh}{dz}(z) = 0. \tag{2.94}$$

This assumption is understandable since it is true if we start with the Hydrogen atom ground state 2.77, and together with equation 2.89 provides the boundary conditions for $h(z)$:

$$f_2(0)h(0) + f_3(0) = E, \tag{2.95}$$

$$f_1(1)h^2(1) = E. \tag{2.96}$$

We continue by expanding $h(z)$ into a Taylor series at $z = 0$:

$$h(z) = \sum_{k=0}^{+\infty} h_k z^k, \quad h_k = \frac{h^{(k)}(0)}{k!}. \tag{2.97}$$

Hence, we can write

$$f_1(1)\left(\sum_{k=0}^{+\infty} h_k\right)^2 = E. \tag{2.98}$$

h_0 is already given by the boundary condition 2.95. To find the remaining coefficients we take the k-th derivative of equation 2.89, set $z = 0$ and solve for h_k. The resulting relations read

$$h_0 = \frac{E - f_{30}}{f_{20}}, \tag{2.99}$$

$$h_k = -\frac{1}{kf_{01}+f_{20}}\left(\sum_{l=0}^{k-1} f_{1(k-l)} \sum_{m=0}^{l} h_{l-m}h_m + \right.$$
$$\left. + \sum_{l=0}^{k-1} f_{2(k-l)}h_l + \sum_{l=1}^{k-1} l f_{0(k-l+1)}h_l + f_{3k}\right), \quad k \geq 1,$$

where we denoted

$$f_{ij} = \frac{f_i^{(j)}(0)}{j!} \tag{2.100}$$

for all $i \in \{0, \dots, 3\}$. Substituting for h_k in 2.98 gives us an algebraic equation for the ground state energy E. However, the solution cannot be obtained directly, since the equation consists of terms of arbitrary large powers of E. The correct way is to solve 2.98 for finitely many terms and then find a convergent sequence while increasing the number of h_k included. Such a sequence is guaranteed to exist and to be unique.

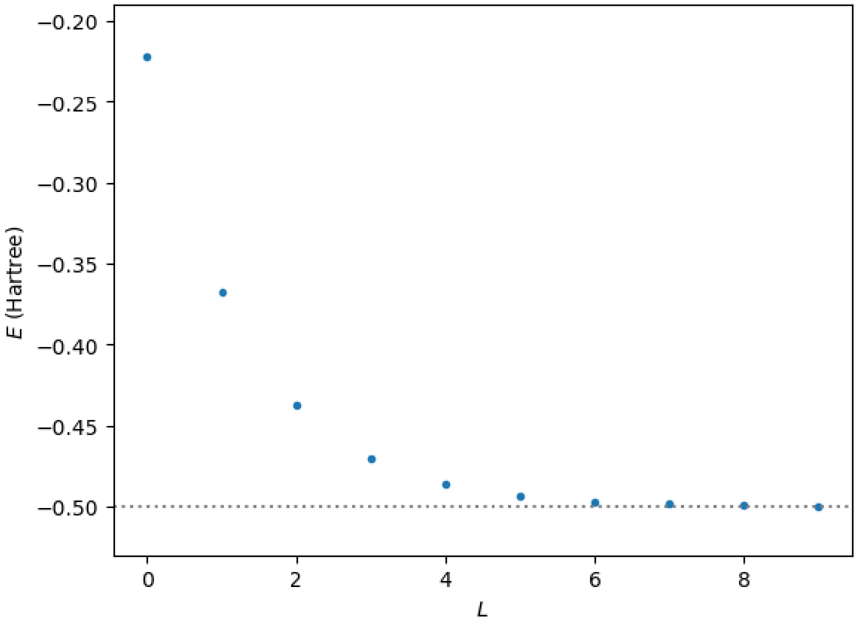


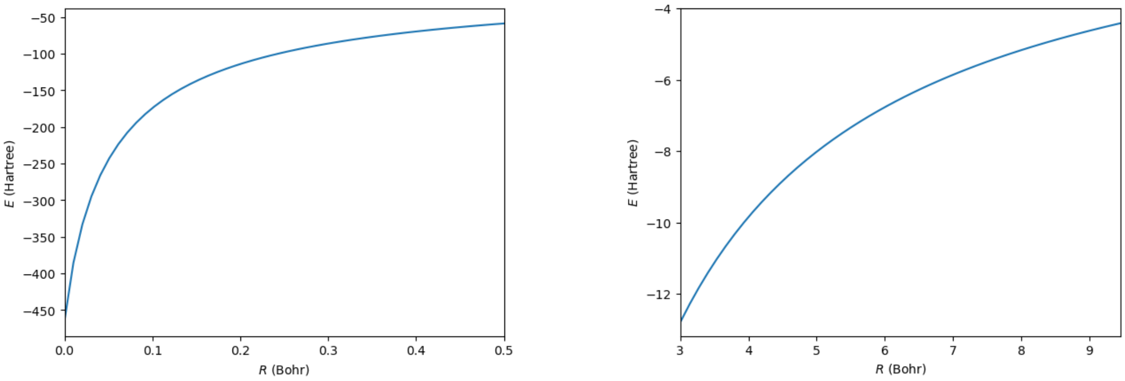
Figure 2.6: Convergence of the hydrogen atom ground state energy ($a = 1$, $b = 0$) computed from 2.98 using only the first $L + 1$ coefficients h_k.

To simplify our calculations and properly perform the limit $b \to 0$, we normalize the coefficients f_{ij}. This is achieved simply by multiplying them by the factor $2b$. Using the fact that the functions f_i are polynomials, hence there are finitely many nontrivial derivatives, we can write the nontrivial normalized coefficients $F_{ij} = 2bf_{ij}$ in the following matrix:

$$\mathbb{F} = \begin{pmatrix} 0 & -4 & 10 & -8 & 2 \\ 0 & -2b & b & 0 & 0 \\ -3 & 5 & -3 & 1 & 0 \\ -2a & 2a & 0 & 0 & 0 \end{pmatrix} \tag{2.101}$$

The set of equations for h_k then changes to

$$\begin{aligned} h_0 &= \frac{2bE - F_{30}}{F_{20}}, \\ h_k &= -\frac{1}{kF_{01} + F_{20}} \left(\sum_{l=0}^{k-1} F_{1(k-l)} \sum_{m=0}^{l} h_{l-m} h_m + \right. \\ &\qquad \left. + \sum_{l=0}^{k-1} F_{2(k-l)} h_l + \sum_{l=1}^{k-1} l F_{0(k-l+1)} h_l + F_{3k} \right), \quad k \geq 1. \end{aligned} \tag{2.102}$$



(a) (b)

Figure 2.7: Dependence of the ground state energy on the size of the nanoparticle radius for a constant charge ($a = 30.945$).

We see that if $b = 0$, all coefficients are independent of E and therefore the limiting procedure is simplified to a plain limit. Figure 2.6 shows how quickly E approaches the value of the hydrogen atom ground state energy for increasing number of h_k. Figures 2.7a, 2.7b and 2.8 then depict the behaviour of E depending on the parameter b (radius R). Using this procedure, we obtain the ground state energy value of -4.414 Hartree for the case of our gold nanoparticle.

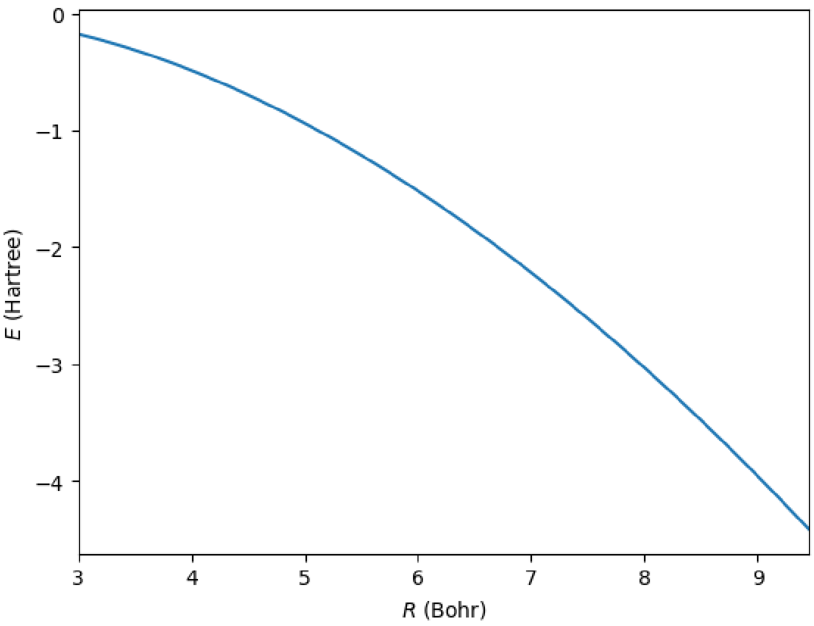


Figure 2.8: Dependence of the ground state energy on the nanoparticle radius for a charge depending on R. Parameters a and b are given by 2.74 ($r_s = 3.01$ Bohr, $\nu = 1$).

Next, we would like to find the corresponding shape of the radial wave function R. This simply means going back over all substitutions and changes of variables we used in the previous process of solving the ground state energy. From the now known values of h_k we get the function h and hence from 2.85-2.87 we can write

$$\begin{aligned}
v(\rho) &= \int_{\rho_0}^{1-\frac{b}{\rho}} \frac{b}{(1-z)^2} h(z) dz = b \sum_{k=0}^{\infty} h_k \int_{\rho_0}^{1-\frac{b}{\rho}} \frac{z^k}{(1-z)^2} dz = \\
&= b \sum_{k=0}^{\infty} h_k \int_{t_0}^{-\frac{b}{\rho}} \frac{(t+1)^k}{t^2} dt = \\
&= b \sum_{k=0}^{\infty} h_k \left(\int_{t_0}^{-\frac{b}{\rho}} \frac{1}{t^2} dt + \int_{t_0}^{-\frac{b}{\rho}} \frac{k}{t} dt + \int_{t_0}^{-\frac{b}{\rho}} \sum_{l=0}^{k-2} \tbinom{k}{l+2} t^l dt \right) = \\
&= \sum_{k=0}^{\infty} h_k \rho - b \sum_{k=1}^{\infty} k h_k \ln \rho + b \sum_{k=2}^{\infty} h_k \sum_{l=1}^{k-1} \frac{1}{l} \tbinom{k}{l+1} \left(-\tfrac{b}{\rho}\right)^l = \\
&= \alpha \rho + \beta \ln \rho + G\left(-\tfrac{b}{\rho}\right), \qquad (2.103)
\end{aligned}$$

where we omitted the constant term, since it will be determined by the normalization, and we denoted

$$\alpha = \sum_{k=0}^{\infty} h_k, \qquad (2.104)$$

$$\beta = -b \sum_{k=1}^{\infty} k h_k, \qquad (2.105)$$

$$G(x) = b \sum_{k=2}^{\infty} h_k \sum_{l=1}^{k-1} \frac{1}{l} \tbinom{k}{l+1} x^l. \qquad (2.106)$$

To find the constants α, β we look at the derivatives of v for $\rho \to +\infty$. It's not hard to see that

$$\frac{dv}{d\rho} = \alpha + \frac{\beta}{\rho} + \mathcal{O}\left(\frac{1}{\rho^2}\right), \qquad (2.107)$$

$$\frac{d^2 v}{d\rho^2} = \mathcal{O}\left(\frac{1}{\rho^2}\right) \qquad (2.108)$$

Inserting these into 2.84 and comparing terms of the same order of ρ than yields

$$\alpha = -\sqrt{-2E}, \quad \beta = \frac{a}{\sqrt{-2E}} - 1. \qquad (2.109)$$

Now, using the change of variables 2.80, 2.81 and the ansatz $R(r) = e^{u(r)}$ we started with we arrive at the total form of the radial wave function:

$$R(r) = N \left(b^2 + r^2\right)^{\frac{\beta}{2}} e^{\alpha\sqrt{b^2+r^2} + G\left(-\frac{b}{\sqrt{b^2+r^2}}\right)}. \qquad (2.110)$$

Here, N is again the normalization factor which is to be calculated numerically. One can easily check that in the limit $b \to 0$ R takes the shape of the hydrogen atom ground state function R_{10}, as β equals zero. Finally, we substitute for a, b to find the desired form of R approximating our nanoparticle ground state wave function:

$$R(r) = N \left(4R^2 + 9r^2\right)^{\frac{\nu}{2\sqrt{-2E}}\left(\frac{R}{r_s}\right)^3 - \frac{1}{2}} e^{-\sqrt{-\frac{2}{9}E(4R^2+9r^2)} + G\left(-\frac{2R}{\sqrt{4R^2+9r^2}}\right)}. \qquad (2.111)$$

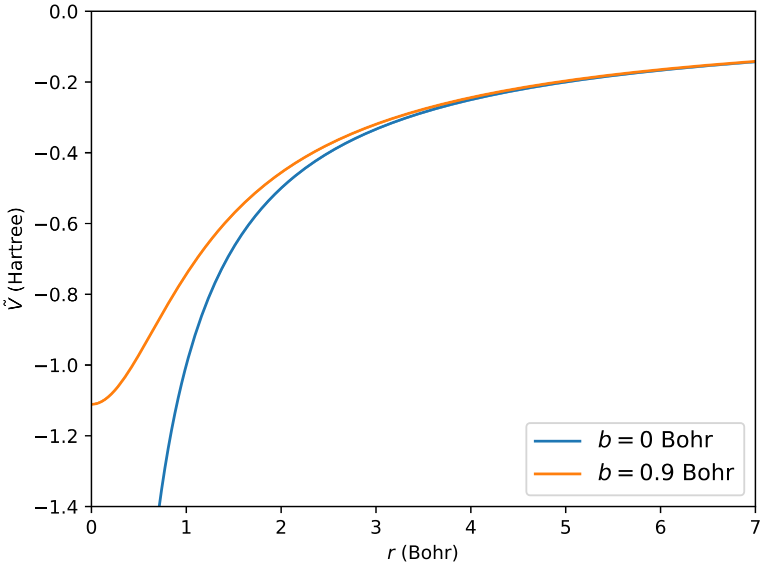


Figure 2.9: Potential $\tilde{V}$ for fixed parameter $a = 1$ and two different values of b.

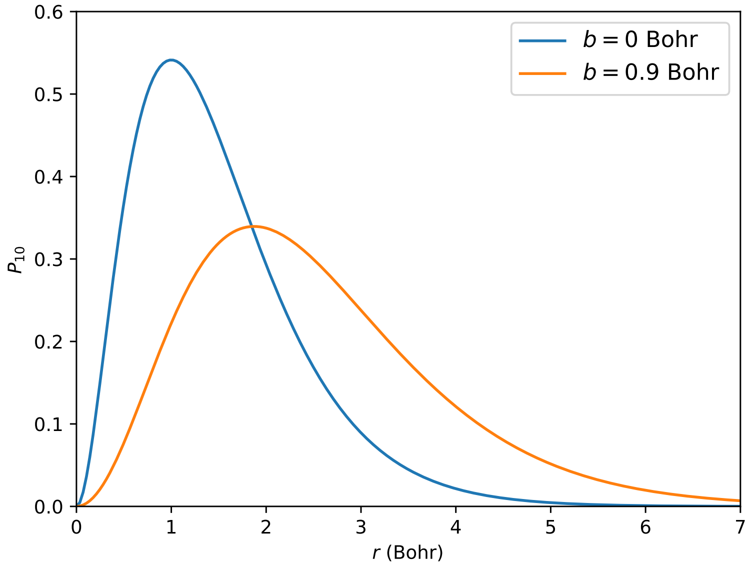


Figure 2.10: Comparison of the ground state radial probability density function for the point-like nucleus hydrogen atom ($b = 0$) and the finite nucleus particle ($b = 0.9$) for the same charge ($a = 1$).

Radial probability density P_{10} and radial electron density n_{10} for two different values of b are depicted in figures 2.10 and 2.11, respectively. It shows how the densities change when one considers a finite nucleus. In the article [7] it was shown that for large parameters a, b approximate formulae for the energy can be derived. Moreover, it is also possible to use this approach for higher excited states. To do that, one only changes the initial ansatz to the corresponding shape of the hydrogen excited state.

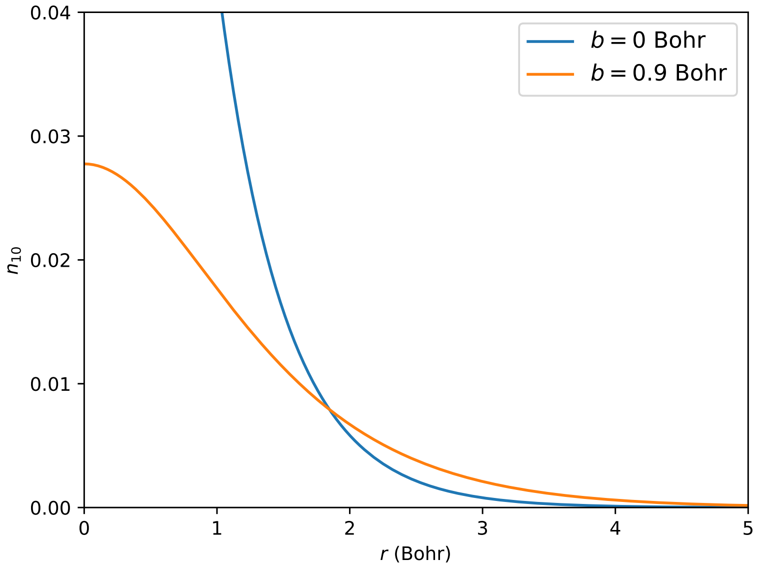


Figure 2.11: Comparison of the ground state radial electron density function for the point-like nucleus hydrogen atom ($b = 0$) and the finite nucleus particle ($b = 0.9$) for the same charge ($a = 1$).

Chapter 3

Many-Electron Systems

So far we considered a single electron moving in the nanoparticle's potential V. However, to obtain the resulting electron density, a multi-electron system must be described. That would mean solving a 3N-dimensional Hamiltonian which contains the interactions of all particles not only with the nucleus but also with each other. This is not possible in practice. Therefore several approximations must be made.

3.1 Non-Interacting Electrons

The easiest, but not very accurate way of solving the many-electron problem is to consider the motion of N non-interacting electrons in the potential V. This approach no longer needs any additional computations and the solution can be fully determined from the previous one-electron wave functions. Namely, the solution of the Schrödinger equation with the Hamiltonian of the form

$$\hat{H}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_{i=1}^{N} \Big(-\frac{\Delta_{\mathbf{r}_i}}{2} + V(\mathbf{r}_i) \Big) \tag{3.1}$$

can be assumed in a separate form

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \ldots \psi_N(\mathbf{r}_N) \tag{3.2}$$

and thus leads to a set of N identical one-electron equations. Furthermore, we use the fact that electrons have a spin (with two possible values, either up or down), and must fulfil the so-called *Pauli exclusion principle*. This will provide us with a prescription for how to choose individual wave functions and thereby retrieve the resulting electron distribution that minimizes the total eigenenergy. That is obtained by a simple sum of the respective one-electron eigenenergies.

Since our primary goal is to determine the overall charge distribution of the nanoparticle, let us now show how to determine the electron density n_e of a many-particle system. Let's start by calculating the multi-electron probability:

$$P(\mathbf{r}_1, \ldots, \mathbf{r}_N) = |\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)|^2 = |\psi_1(\mathbf{r}_1)|^2 \ldots |\psi_N(\mathbf{r}_N)|^2. \tag{3.3}$$

The probability distribution of a single electron is the marginal probability function, that is

$$P_i(\mathbf{r}_i) = \int_{\mathbb{R}^{3(N-1)}} P(\mathbf{r}_1, \dots, \mathbf{r}_N) d\mathbf{r}_1 \dots d\mathbf{r}_{i-1} d\mathbf{r}_{i+1} \dots d\mathbf{r}_N = \\ = |\psi_i(\mathbf{r}_i)|^2 \prod_{\substack{j=1 \\ j \neq i}}^{N} \int_{\mathbb{R}^3} |\psi_j(\mathbf{r}_j)|^2 d\mathbf{r}_j = |\psi_i(\mathbf{r}_i)|^2, \tag{3.4}$$

where in the last equality we used the fact that every one-electron wave function is normalized. The total electron density function is then a simple sum of the single-electron densities:

$$n_e(\mathbf{r}) = \sum_{i=1}^{N} n_i(\mathbf{r}) = \sum_{i=1}^{N} P_i(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2. \tag{3.5}$$

Even though this model can help us to understand the basic features of our problem and to create a primitive view of the final electron density distribution, it is not sufficiently accurate and therefore needs to be improved. To do so, we need to include the electron-electron interactions in our calculations. This can be done in general by adding an extra potential V_{ee} to the total Hamiltonian:

$$\hat{H} = \hat{T} + V + V_{ee}. \tag{3.6}$$

Usually, V_{ee} is chosen to represent all the two-electron Coulomb interactions, i.e.

$$V_{ee}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{\substack{i,j=1 \\ i<j}}^{N} V_2(\mathbf{r}_i, \mathbf{r}_j) = \sum_{\substack{i,j=1 \\ i<j}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{3.7}$$

with $\mathbf{r}_i$ being the position of the i-th electron. In the following sections, we will learn concretely how this extended Hamiltonian can be solved.

3.2 Hartree Approximation

First way how to approach the many-interacting-electron problem is to presume that the eigenfunction $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ of the Hamiltonian $\hat{H}$ can be expressed as a product of one-electron functions $\psi_i(\mathbf{r}_i)$, that is

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \dots \psi_N(\mathbf{r}_N). \tag{3.8}$$

The total Hamiltonian described as acting on all the one-electron functions ψ_i has then the form

$$\hat{H}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i=1}^{N} \hat{H}_1(\mathbf{r}_i) + \sum_{\substack{i,j=1 \\ i<j}}^{N} V_2(\mathbf{r}_i, \mathbf{r}_j) = \\ = \sum_{i=1}^{N} \Bigg(- \frac{\Delta_{\mathbf{r}_i}}{2} + V(\mathbf{r}_i) + \sum_{\substack{j=2 \\ i<j}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \Bigg), \tag{3.9}$$

where $\hat{H}_1$ is the one-electron Hamiltonian, V_2 is the two-electron interaction potential and V is the nanoparticle potential 2.10 for $r = |\mathbf{r}_i|$.

We would now like to find the ground state energy of our system. Let's assume we have a Hamiltonian operator $\hat{H}$ with the eigenvalues E_i and the corresponding normalized eigenstates u_i which form a complete set. Next, let Ψ be an arbitrary normalized wave function. Using the completeness of the eigenstates we can write

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_i \alpha_i u_i(\mathbf{r}_1, \ldots, \mathbf{r}_N). \tag{3.10}$$

The expectation value of the Hamiltonian is then

$$\langle \Psi | \hat{H} \Psi \rangle = \sum_{i,j} \alpha_i^* \alpha_j \langle u_i | \hat{H} u_j \rangle = \sum_{i,j} \alpha_i^* \alpha_j E_j \delta_{ij} = \sum_i |\alpha_i|^2 E_i. \tag{3.11}$$

Since

$$\langle \Psi | \Psi \rangle = \sum_{i,j} \alpha_i^* \alpha_j \langle u_i | u_j \rangle = \sum_{i,j} \alpha_i^* \alpha_j \delta_{ij} = \sum_i |\alpha_i|^2 = 1, \tag{3.12}$$

holds due to the normalization of ψ, expression 3.11 can be further expanded as

$$\langle \Psi | \hat{H} \Psi \rangle = E_0 + \sum_i |\alpha_i|^2 (E_i - E_0), \tag{3.13}$$

where E_0 denotes the ground state energy. We see that for any eigenstate Ψ, the expectation value of the Hamiltonian $\hat{H}$ is always greater than or equal to E_0. Finding E_0 is thus equivalent to finding such Ψ that minimizes $\langle \Psi | \hat{H} \Psi \rangle$ while keeping Ψ normalized. According to the variational principle, the desired function must then satisfy the equation

$$\delta \left[\langle \Psi | \hat{H} \Psi \rangle - \sum_{i=1}^{N} \epsilon_i \Big(\langle \psi_i | \psi_i \rangle - 1 \Big) \right] = 0, \tag{3.14}$$

where the second term expresses the normalization constraint of all one-electron wave functions. Clearly, the Lagrange multipliers ϵ_i have the dimension of energy. Applying the variation on the individual terms gives us

$$\begin{aligned} \delta \langle \Psi | \hat{H} \Psi \rangle &= \langle \delta \Psi | \hat{H} \Psi \rangle + \langle \hat{H} \Psi | \delta \Psi \rangle = \\ &= \langle \delta \Psi | \hat{H} \Psi \rangle + \langle \delta \Psi | \hat{H} \Psi \rangle^* = 2 \operatorname{Re} \Big(\langle \delta \Psi | \hat{H} \Psi \rangle \Big) \end{aligned} \tag{3.15}$$

and

$$\begin{aligned} \delta \langle \psi_i | \psi_i \rangle &= \langle \delta \psi_i | \psi_i \rangle + \langle \psi_i | \delta \psi_i \rangle = \\ &= \langle \delta \psi_i | \psi_i \rangle + \langle \delta \psi_i | \psi_i \rangle^* = 2 \operatorname{Re} \Big(\langle \delta \psi_i | \psi_i \rangle \Big), \end{aligned} \tag{3.16}$$

where we used the fact that $\hat{H}$ is hermitian. In order to see how to write the expectation value of the total Hamiltonian in the language of ψ_i we explicitly break down the scalar product $\langle\Psi|\hat{H}\Psi\rangle$:

$$\begin{aligned}\langle\Psi|\hat{H}\Psi\rangle &= \int_{\mathbb{R}^{3N}} \Psi^*(\mathbf{r}_1\ldots\mathbf{r}_N)\hat{H}\Psi(\mathbf{r}_1\ldots\mathbf{r}_N)d\mathbf{r}_1\ldots d\mathbf{r}_N = \\ &= \sum_{i=1}^{N}\int_{\mathbb{R}^{3N}} \psi_1^*(\mathbf{r}_1)\ldots\psi_N^*(\mathbf{r}_N)\hat{H}\psi_1(\mathbf{r}_1)\ldots\psi_N(\mathbf{r}_N)d\mathbf{r}_1\ldots d\mathbf{r}_N = \\ &= \sum_{i=1}^{N}\int_{\mathbb{R}^{6}} \psi_i^*(\mathbf{r}_i)\left(-\frac{\Delta_{\mathbf{r}_i}}{2}+V(\mathbf{r}_i)\right)\psi_i(\mathbf{r}_i)d\mathbf{r}_i + \\ &\qquad + \sum_{\substack{i,j=1\\ i<j}}^{N}\int_{\mathbb{R}^{6}} \psi_i^*(\mathbf{r}_i)\psi_j^*(\mathbf{r}_j)V_2(\mathbf{r}_i,\mathbf{r}_j)\psi_i(\mathbf{r}_i)\psi_j(\mathbf{r}_j)d\mathbf{r}_i d\mathbf{r}_j = \\ &= \sum_{i=1}^{N}\langle\psi_i|\hat{H}_1\psi_i\rangle + \sum_{\substack{i,j=1\\ i<j}}^{N}\langle\psi_i|\langle\psi_j|V_2\psi_j\rangle\psi_i\rangle. \end{aligned} \tag{3.17}$$

This relation allows us to rewrite the expression 3.15 using the variations $\delta\psi_i$:

$$\begin{aligned}\delta\langle\Psi|\hat{H}\Psi\rangle &= 2\,\mathrm{Re}\left(\sum_{i=1}^{N}\langle\delta\psi_i|\hat{H}_1\psi_i\rangle + 2\sum_{\substack{i,j=1\\ i<j}}^{N}\langle\delta\psi_i|\langle\psi_j|V_2\psi_j\rangle\psi_i\rangle.\right) = \\ &= 2\,\mathrm{Re}\left(\sum_{i=1}^{N}\langle\delta\psi_i|\hat{H}_1\psi_i\rangle + \sum_{\substack{i,j=1\\ i\neq j}}^{N}\langle\delta\psi_i|\langle\psi_j|V_2\psi_j\rangle\psi_i\rangle.\right)\end{aligned} \tag{3.18}$$

The factor of 2 in the first equation was obtained by using the Leibniz rule for variations and interchanging the indices $i \leftrightarrow j$ in the second term. Due to the symmetry of the interaction, it was replaced in the second equation by including terms with the indices $i > j$ in the sum, as well. Putting everything together then yields

$$\sum_{i=1}^{N}\mathrm{Re}\left(\langle\delta\psi_i|\hat{H}_1\psi_i + \sum_{\substack{j=1\\ j\neq i}}^{N}\langle\psi_j|V_2\psi_j\rangle\psi_i - \epsilon_i\psi_i\rangle\right) = 0. \tag{3.19}$$

Since every variation $\delta\psi_i$ (and for the complex conjugate part the variations $\delta\psi_i^*$) can be arbitrary, we arrive at a set of N equations for the one-electron wave functions ψ_i:

$$\hat{H}_1\psi_i + \sum_{\substack{j=1\\ j\neq i}}^{N}\langle\psi_j|V_2\psi_j\rangle\psi_i - \epsilon_i\psi_i = 0 \tag{3.20}$$

or explicitly

$$\begin{aligned}&\epsilon_i\psi_i(\mathbf{r}_i) = \\ &= \Big(-\frac{\Delta_{\mathbf{r}_i}}{2}+V(\mathbf{r}_i)\Big)\psi_i(\mathbf{r}_i) + \sum_{\substack{j=1\\ j\neq i}}^{N}\int_{\mathbb{R}^3}\psi_j^*(\mathbf{r})V_2(\mathbf{r}_i,\mathbf{r})\psi_j(\mathbf{r})\psi_i(\mathbf{r}_i)d\mathbf{r},\end{aligned} \tag{3.21}$$

where the unknowns are not only the functions ψ_i, but also the Lagrange multipliers ϵ_i. These equations are called the *Hartree equations* and usually, they are solved iteratively in the following way:

1. Calculate the interaction term from an initial guess of the functions ψ_i (typically the non-interacting electron solution).
2. Solve the remaining N differential equation for all ψ_i and ϵ_i as an eigenvalue problem.
3. Repeat steps 1 and 2 until the difference between two consecutive solutions is zero.

We can conclude that we have converted our N-dimensional problem to an iterative solution of N Schrödinger equations with total Hamiltonians

$$\hat{H}^{(1)} = \hat{H}_1 + V_C \tag{3.22}$$

where

$$V_C(\mathbf{r}_i) = \sum_{\substack{j=1 \\ j \neq i}}^{N} \int_{\mathbb{R}^3} \psi_j^*(\mathbf{r}) V_2(\mathbf{r}_i, \mathbf{r}) \psi_j(\mathbf{r}) d\mathbf{r} \tag{3.23}$$

expresses the Coulomb mean field created by all the other electrons and is computed from the wave functions from the previous iteration.

The last thing we will mention in this section is the calculation of the total electron density n_e. Since we started with the wave function in the product form

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\ldots\psi_N(\mathbf{r}_N), \tag{3.24}$$

we arrive at the same relation as we had in the case of non-interacting electrons, i.e.

$$n_e(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2. \tag{3.25}$$

3.3 Hartree-Fock Approximation

The Hartree approximation is good to show the wave function decomposition and the variational principle, but does not take into account the very nature of the electrons - they are fermions. To fix this, we need to impose another condition on the wave function, namely, it must be antisymmetric under the exchange of any two particles:

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_j, \ldots, \mathbf{r}_N) = -\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_j, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_N), \tag{3.26}$$

In practice, this is usually solved by extending our previous factorization 3.8 with all permutations of the positions $\mathbf{r}_i$, including the sign of the permutation. This model can be easily rewritten using the so-called *Slater determinant*:

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_2(\mathbf{r}_1) & \dots & \psi_N(\mathbf{r}_1) \\ \psi_1(\mathbf{r}_2) & \psi_2(\mathbf{r}_2) & \dots & \psi_N(\mathbf{r}_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(\mathbf{r}_N) & \psi_2(\mathbf{r}_N) & \dots & \psi_N(\mathbf{r}_N) \end{vmatrix}, \tag{3.27}$$

where the factor $\frac{1}{\sqrt{N!}}$ is necessary due to normalization. The rest of the derivation process is identical to the procedure in the previous section. Therefore, we again need to determine the expectation values of the Hamiltonian. For easier manipulation, we start by rewriting Ψ using the permutation operator P_π:

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \sum_{\pi \in S_N} \operatorname{sgn} \pi P_\pi(\psi_1 \dots \psi_N), \tag{3.28}$$

where S_N is the set of all permutations over N, $\operatorname{sgn} \pi$ is the sign of the permutation and P_π is defined as follows:

$$P_\pi(\psi_1 \dots \psi_N) = \psi_1(\mathbf{r}_{\pi(1)}) \dots \psi_N(\mathbf{r}_{\pi(N)}). \tag{3.29}$$

The non-interaction Hamiltonian expectation value is then

$$\begin{aligned}
&\langle \Psi | \hat{H}_1 \Psi \rangle = \\
&\quad = \frac{1}{N!} \sum_{\pi, \pi' \in S_N} \operatorname{sgn}(\pi \circ \pi') \int_{\mathbb{R}^{3N}} P_\pi(\psi_1^* \dots \psi_N^*) \hat{H}_1 P_{\pi'}(\psi_1 \dots \psi_N) d\mathbf{r}_1 \dots d\mathbf{r}_N = \\
&\quad = \frac{1}{N!} \sum_{\pi, \pi' \in S_N} \operatorname{sgn} \sigma P_\pi \int_{\mathbb{R}^{3N}} \psi_1^*(\mathbf{r}_1) \dots \psi_N^*(\mathbf{r}_N) \hat{H}_1 P_\sigma(\psi_1 \dots \psi_N) d\mathbf{r}_1 \dots d\mathbf{r}_N = \\
&\quad = \sum_{\sigma \in S_N} \operatorname{sgn} \sigma \int_{\mathbb{R}^{3N}} \psi_1^*(\mathbf{r}_1) \dots \psi_N^*(\mathbf{r}_N) \hat{H}_1 P_\sigma(\psi_1 \dots \psi_N) d\mathbf{r}_1 \dots d\mathbf{r}_N = \\
&\quad = \sum_{\sigma \in S_N} \operatorname{sgn} \sigma \int_{\mathbb{R}^3} \psi_i^*(\mathbf{r}_i) \hat{H}_1 \psi_i(\mathbf{r}_{\sigma(i)}) \delta^1_{\sigma(1)} \dots \delta^{i-1}_{\sigma(i-1)} \delta^{i+1}_{\sigma(i+1)} \dots \delta^N_{\sigma(N)} d\mathbf{r}_i = \\
&\quad = \int_{\mathbb{R}^3} \psi_i^*(\mathbf{r}_i) \hat{H}_1 \psi_i(\mathbf{r}_i) d\mathbf{r}_i = \langle \psi_i | \hat{H}_1 \psi_i \rangle,
\end{aligned} \tag{3.30}$$

where $\sigma = \pi \circ \pi'$. Similarly for the interaction term

$$\begin{aligned}
&\langle \Psi | V_2 \Psi \rangle = \\
&= \frac{1}{N!} \sum_{\pi, \pi' \in S_N} \operatorname{sgn}(\pi \circ \pi') \int_{\mathbb{R}^{3N}} P_\pi(\psi_1^* \dots \psi_N^*) V_2 P_{\pi'}(\psi_1 \dots \psi_N) d\mathbf{r}_1 \dots d\mathbf{r}_N = \\
&= \frac{1}{N!} \sum_{\pi, \pi' \in S_N} \operatorname{sgn} \sigma P_\pi \int_{\mathbb{R}^{3N}} \psi_1^*(\mathbf{r}_1) \dots \psi_N^*(\mathbf{r}_N) V_2 P_\sigma(\psi_1 \dots \psi_N) d\mathbf{r}_1 \dots d\mathbf{r}_N = \\
&= \sum_{\sigma \in S_N} \operatorname{sgn} \sigma \int_{\mathbb{R}^{3N}} \psi_1^*(\mathbf{r}_1) \dots \psi_N^*(\mathbf{r}_N) V_2 P_\sigma(\psi_1 \dots \psi_N) d\mathbf{r}_1 \dots d\mathbf{r}_N = \\
&= \sum_{\sigma \in S_N} \operatorname{sgn} \sigma \int_{\mathbb{R}^6} \psi_i^*(\mathbf{r}_i) \psi_j^*(\mathbf{r}_j) V_2(\mathbf{r}_i, \mathbf{r}_j) \psi_i(\mathbf{r}_{\sigma(i)}) \psi_j(\mathbf{r}_{\sigma(j)}) d\mathbf{r}_i d\mathbf{r}_j \cdot \\
&\qquad\qquad \cdot \delta^1_{\sigma(1)} \dots \delta^{i-1}_{\sigma(i-1)} \delta^{i+1}_{\sigma(i+1)} \dots \delta^{j-1}_{\sigma(j-1)} \delta^{j+1}_{\sigma(j+1)} \dots \delta^N_{\sigma(N)} = \\
&= \int_{\mathbb{R}^6} \psi_i^*(\mathbf{r}_i) \psi_j^*(\mathbf{r}_j) V_2(\mathbf{r}_i, \mathbf{r}_j) \psi_i(\mathbf{r}_i) \psi_j(\mathbf{r}_j) d\mathbf{r}_i d\mathbf{r}_j - \\
&\qquad\qquad - \int_{\mathbb{R}^6} \psi_i^*(\mathbf{r}_i) \psi_j^*(\mathbf{r}_j) V_2(\mathbf{r}_i, \mathbf{r}_j) \psi_i(\mathbf{r}_j) \psi_j(\mathbf{r}_i) d\mathbf{r}_i d\mathbf{r}_j.
\end{aligned} \tag{3.31}$$

By applying the variational principle we arrive at the *Hartree-Fock equations*:

$$\begin{aligned}
\epsilon_i \psi_i(\mathbf{r}_i) = \Big(- \frac{\Delta_{\mathbf{r}_i}}{2} + V(\mathbf{r}_i) \Big) \psi_i(\mathbf{r}_i) &+ \\
&+ \sum_{\substack{j=1 \\ j \neq i}}^{N} \int_{\mathbb{R}^3} \psi_j^*(\mathbf{r}) V_2(\mathbf{r}_i, \mathbf{r}) \psi_j(\mathbf{r}) \psi_i(\mathbf{r}_i) d\mathbf{r} - \\
&- \sum_{\substack{j=1 \\ j \neq i}}^{N} \int_{\mathbb{R}^3} \psi_j^*(\mathbf{r}) V_2(\mathbf{r}_i, \mathbf{r}) \psi_j(\mathbf{r}_i) \psi_i(\mathbf{r}) d\mathbf{r}.
\end{aligned} \tag{3.32}$$

We see that, in contrast to the Hartree equations, there is an additional potential

$$\hat{V}_{ex}(\mathbf{r}_i) \psi_i(\mathbf{r}_i) = - \sum_{\substack{j=1 \\ j \neq i}}^{N} \int_{\mathbb{R}^3} \psi_j^*(\mathbf{r}) V_2(\mathbf{r}_i, \mathbf{r}) \psi_j(\mathbf{r}_i) \psi_i(\mathbf{r}) d\mathbf{r}. \tag{3.33}$$

V_{ex} is the so-called *exchange potential* and it decreases the energy of the electron-electron mean field. Again, these equations are usually solved iteratively in the same manner as in the previous section. The only change is the corresponding total one-particle Hamiltonians which take the form

$$\hat{H}^{(1)} = \hat{H}_1 + V_C + \hat{V}_{ex}. \tag{3.34}$$

So far, we have only considered the antisymmetry of the wave functions with respect to position interchange. For a more precise description, however, the electron spin must also be included in the considerations. In the case of a single electron, the Hamiltonian was independent of spin and it was sufficient to describe the particle only with the position vector. Nevertheless, by adding more electrons and interactions between them, spin acquires a crucial role. Therefore, the one-electron wave function should be of the form:

$$\psi_i(x_i) = \psi_i(\mathbf{r}_i, s_i), \tag{3.35}$$

where s_i takes on values of $\pm\frac{1}{2}$ (or equivalently ↑ and ↓) expressing the spin basis states. Again, the fully antisymmetric function can be obtained using the Slater determinant

$$\Psi(x_1, \ldots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(x_1) & \psi_2(x_1) & \ldots & \psi_N(x_1) \\ \psi_1(x_2) & \psi_2(x_2) & \ldots & \psi_N(x_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(x_N) & \psi_2(x_N) & \ldots & \psi_N(x_N) \end{vmatrix}. \tag{3.36}$$

To proceed with the variational principle we need to extend our definition of the scalar product for functions with spin. Having the functions normalized, we can write

$$\langle f|g\rangle = \sum_s \int_{\mathbb{R}^3} f^*(\mathbf{r}, s) g(\mathbf{r}, s) \tag{3.37}$$

All steps of deriving the Hartree-Fock equations can therefore be repeated with only a single interchange:

$$\int_{\mathbb{R}^3} d\mathbf{r} \longleftrightarrow \sum_s \int_{\mathbb{R}^3} d\mathbf{r}, \tag{3.38}$$

The spin Hartree-Fock equations have then the form

$$\begin{aligned} \epsilon_i \psi_i(\mathbf{r}_i, s_i) = \Big(-\frac{\Delta_{\mathbf{r}_i}}{2} + V(\mathbf{r}_i)\Big)\psi_i(\mathbf{r}_i, s_i) + &\\ + \sum_{\substack{j=1 \\ j\neq i}}^{N} \sum_s \int_{\mathbb{R}^3} \psi_j^*(\mathbf{r}, s) V_2(\mathbf{r}_i, \mathbf{r}) \psi_j(\mathbf{r}, s) \psi_i(\mathbf{r}_i, s_i) d\mathbf{r} - &\\ - \sum_{\substack{j=1 \\ j\neq i}}^{N} \sum_s \int_{\mathbb{R}^3} \psi_j^*(\mathbf{r}, s) V_2(\mathbf{r}_i, \mathbf{r}) \psi_j(\mathbf{r}_i, s_i) \psi_i(\mathbf{r}, s) d\mathbf{r}. & \end{aligned} \tag{3.39}$$

It is important to note that the functions ψ_i are again orthonormal, but this time with respect to the extended definition of the scalar product, i.e.

$$\langle \psi_i|\psi_j\rangle = \sum_s \int_{\mathbb{R}^3} \psi_i^*(\mathbf{r}, s)\psi_j(\mathbf{r}, s) d\mathbf{r} = \delta_{ij}. \tag{3.40}$$

In order to simplify the resulting equations into a form suitable for practical calculations, let us now assume the one-electron wave functions in the separated form

$$\psi_i(\mathbf{r}, s) = \varphi_i(\mathbf{r})\sigma_i(s). \tag{3.41}$$

Although the spin functions σ_i can in general represent any direction of the spin, we will further assume that the electron is either in the spin up state ($s = \frac{1}{2}$) or the spin down state ($s = -\frac{1}{2}$). This in particular means, that if an electron is in the spin up state, its corresponding spin function σ_i will be defined as

$$\sigma_i(s) = \begin{cases} 1 & s = \frac{1}{2} \\ 0 & s = -\frac{1}{2} \end{cases} \tag{3.42}$$

and similarly, if it's in the spin down state

$$\sigma_i(s) = \begin{cases} 0 & s = \frac{1}{2} \\ 1 & s = -\frac{1}{2}. \end{cases} \tag{3.43}$$

Plugging the decomposition 3.41 with σ_i defined as above into the Hartree-Fock equations 3.39 gives

$$\begin{aligned} \epsilon_i \varphi_i(\mathbf{r}_i)\sigma_i(s_i) = \Big(-\frac{\Delta_{\mathbf{r}_i}}{2} + V(\mathbf{r}_i)\Big)\varphi_i(\mathbf{r}_i)\sigma_i(s_i) + {} \\ + \sum_{\substack{j=1 \\ j\neq i}}^{N} \int_{\mathbb{R}^3} \varphi_j^*(\mathbf{r}) V_2(\mathbf{r}_i, \mathbf{r}) \varphi_j(\mathbf{r}) \varphi_i(\mathbf{r}_i) d\mathbf{r}\, \sigma_i(s_i) - {} \\ - \sum_{\substack{j=1 \\ j\neq i}}^{N} \sum_{s} \sigma_j^*(s)\sigma_j(s_i)\sigma_i(s) \int_{\mathbb{R}^3} \varphi_j^*(\mathbf{r}) V_2(\mathbf{r}_i, \mathbf{r}) \varphi_j(\mathbf{r}_i) \varphi_i(\mathbf{r}) d\mathbf{r}, \end{aligned} \tag{3.44}$$

which in our case of only spin up or spin down simplifies to

$$\begin{aligned} \epsilon_i \varphi_i(\mathbf{r}_i) = \Big(-\frac{\Delta_{\mathbf{r}_i}}{2} + V(\mathbf{r}_i)\Big)\varphi_i(\mathbf{r}_i) + \sum_{\substack{j=1 \\ j\neq i}}^{N} \int_{\mathbb{R}^3} \varphi_j^*(\mathbf{r}) V_2(\mathbf{r}_i, \mathbf{r}) \varphi_j(\mathbf{r}) \varphi_i(\mathbf{r}_i) d\mathbf{r} - {} \\ - \sum_{\substack{j=1 \\ j\neq i}}^{N} \delta_{\sigma_j \sigma_i} \int_{\mathbb{R}^3} \varphi_j^*(\mathbf{r}) V_2(\mathbf{r}_i, \mathbf{r}) \varphi_j(\mathbf{r}_i) \varphi_i(\mathbf{r}) d\mathbf{r}, \end{aligned} \tag{3.45}$$

where

$$\delta_{\sigma_i \sigma_j} = \begin{cases} 1 & \sigma_i = \sigma_j \\ 0 & \text{otherwise.} \end{cases} \tag{3.46}$$

This means that the exchange term is non-trivial only for electrons which are in the same spin state.

It is important to note that the magnitudes of energies ϵ_i express the energy required to tear a given electron out of the system. Since these energies change after each extraction, we cannot get the total energy of the system by simply summing ϵ_i over all the electrons. Instead, we can obtain it as the expected value of the total Hamiltonian:

$$\begin{aligned} \langle \Psi | \hat{H} \Psi \rangle = \sum_{i=1}^{N} \Big(\langle \psi_i | \hat{H}_1 \psi_i \rangle + \sum_{\substack{i,j=1 \\ j>i}}^{N} \langle \psi_i | \langle \psi_j | V_2 \psi_j \rangle \psi_i \rangle - \sum_{\substack{i,j=1 \\ j>i}}^{N} \langle \psi_j | \langle \psi_i | V_2 \psi_j \rangle \psi_i \rangle \Big) = {} \\ = \sum_{i=1}^{N} \Big\langle \psi_i \Big| \hat{H}_1 + \frac{1}{2}\Big(V_C + \hat{V}_{ex}\Big) \psi_i \Big\rangle = \sum_{i=1}^{N} \Big(\langle \psi_i | \hat{H}_1 \psi_i \rangle + \frac{1}{2} \langle \psi_i | (V_C + \hat{V}_{ex}) \psi_i \rangle \Big). \end{aligned} \tag{3.47}$$

Finally, let us determine the total electron density n_e. Again, this can be calculated as the sum of one-electron densities given by the marginal probabilities n_i, that is

$$n_e(\mathbf{r}) = \sum_{i=1}^{N} \int_{\mathbb{R}^{3(N-1)}} P(\mathbf{r}_1, \ldots, \mathbf{r}_N) d\mathbf{r}_1 \ldots d\mathbf{r}_{i-1} d\mathbf{r}_{i+1} \ldots d\mathbf{r}_N \Big|_{\mathbf{r}_i = \mathbf{r}}. \tag{3.48}$$

Here

$$P(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_s |\Psi(x_1, \ldots, x_N)|^2. \tag{3.49}$$

Using the definition of Ψ and the normalization of every ψ_i we get the total density as

$$\begin{aligned} n_e(\mathbf{r}) = \sum_{i=1}^{N} \int_{\mathbb{R}^{3(N-1)}} \sum_s \frac{1}{N!} \sum_{\pi, \pi' \in S_N} \operatorname{sgn}(\pi \circ \pi') \psi_1^*(x_{\pi(1)}) \ldots \psi_N^*(x_{\pi(N)}) \cdot \\ \cdot \psi_1(x_{\pi'(1)}) \ldots \psi_N(x_{\pi'(N)}) d\mathbf{r}_1 \ldots d\mathbf{r}_{i-1} d\mathbf{r}_{i+1} \ldots d\mathbf{r}_N \Big|_{\mathbf{r}_i = \mathbf{r}} = \\ = \sum_{i=1}^{N} \sum_s |\psi_i(\mathbf{r}, s)|^2 = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2, \end{aligned} \tag{3.50}$$

where we used the fact that after the integration and summing over the spins, only terms where $\pi = \pi'$ are non-zero (see 3.40) and summing over the permutation gives $N!$ identical terms. We see that the result is the same as for the non-interacting electrons and the Hartree approximation (except the spin part which could be included in those approximations in the same manner as in the Hartree-Fock theory).

Chapter 4

Numerical Solution - Matrix Method

As mentioned earlier, there are no exact analytical solutions for such complex systems as our nanoparticle. Fortunately, over the years, a number of numerical methods have been developed that are used to solve these types of problems and whose results correspond very well to experiments. To find the nanoparticle ground state energy and the corresponding wave functions we decided to use the so-called *Matrix method* recently introduced by Gomez et. al in [8]. This method is based on the Hartree-Fock equations where both the differential and the integral parts are expressed by some matrices.

4.1 One-Electron System

To introduce the matrix method and to show its possible precision we start with the hydrogen atom which was already solved analytically in 2.2. We know that thanks to the spherical symmetry of this system the wave function can be decomposed into its angular and radial parts:

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_l^m(\theta,\phi). \tag{4.1}$$

Here, we are concerned with solving the radial part. The corresponding Schrödinger equation is then

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{1}{r}\right)u_{nl}(r) = E_{nl}u_{nl}(r), \tag{4.2}$$

where

$$u_{nl}(r) = rR_{nl}(r). \tag{4.3}$$

To solve this equation numerically we need to approximate the derivative with finite differences. Using the centre-point difference expression for the first derivative

$$\frac{df}{dr}(r) \approx \frac{f(r+\frac{\Delta r}{2}) - f(r-\frac{\Delta r}{2})}{\Delta r} \tag{4.4}$$

we can write the second derivative as

$$\frac{d^2 f}{dr^2}(r) \approx \frac{f(r+\Delta r) - 2f(r) + f(r-\Delta r)}{(\Delta r)^2}. \tag{4.5}$$

Next, we add another approximation. We will consider that there is a maximal $r = r_m$ after which the wave function is effectively zero. This assumption makes sense given the fact that for a wave function to be normalizable, it must rapidly decay to zero from a certain point towards infinity. In our case, we already know the analytical form of the functions, so determining the appropriate r_m is straightforward. However, in an unknown problem, some prior ideas about the shape of the solution must be used. The difference Δr is then given by

$$\Delta r = \frac{r_m}{M}, \tag{4.6}$$

where M is another user parameter determining the accuracy of the solution. If we now denote $r_i = i\Delta r$, $i \in \{1, 2, \ldots, M\}$, and express the wave function as a vector of its values at the points r_i, i. e.

$$\mathbf{u}_{nl} \equiv \begin{pmatrix} u_{nl}(r_1) \\ u_{nl}(r_2) \\ \vdots \\ u_{nl}(r_m) \end{pmatrix}, \tag{4.7}$$

we can rewrite the kinetic term of 4.2 using 4.5 in the following matrix form:

$$-\frac{1}{2}\frac{d^2 u_{nl}}{dr^2} \equiv \mathbb{T}\mathbf{u}_{nl} = \frac{1}{2(\Delta r)^2} \begin{pmatrix} 2 & -1 & 0 & \ldots & 0 \\ -1 & 2 & -1 & \ldots & 0 \\ 0 & -1 & 2 & \ldots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \ldots & 2 \end{pmatrix} \begin{pmatrix} u_{nl}(r_1) \\ u_{nl}(r_2) \\ u_{nl}(r_3) \\ \vdots \\ u_{nl}(r_m) \end{pmatrix}. \tag{4.8}$$

Since the potential term of the Hamiltonian expresses just multiplication by the potential, the matrix form corresponding to the effective potential

$$V_{eff} = \frac{l(l+1)}{2r^2} - \frac{1}{r} \tag{4.9}$$

is simply

$$V_{eff} u_{nl} \equiv \mathbb{V}\mathbf{u}_{nl} = \begin{pmatrix} V_{eff}(r_1) & 0 & 0 & \ldots & 0 \\ 0 & V_{eff}(r_2) & 0 & \ldots & 0 \\ 0 & 0 & V_{eff}(r_3) & \ldots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \ldots & V_{eff}(r_m) \end{pmatrix} \begin{pmatrix} u_{nl}(r_1) \\ u_{nl}(r_2) \\ u_{nl}(r_3) \\ \vdots \\ u_{nl}(r_m) \end{pmatrix}. \tag{4.10}$$

We see that we transformed the original Schrödinger equation 4.2 in a matrix eigenvalue problem

$$\mathbb{H}\mathbf{u}_{nl} = E\mathbf{u}_{nl}, \tag{4.11}$$

where

$$\mathbb{H} = \frac{1}{2(\Delta r)^2}\begin{pmatrix} 2 & -1 & 0 & \dots & 0 \\ -1 & 2 & -1 & \dots & 0 \\ 0 & -1 & 2 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & 2 \end{pmatrix} + \\ + \begin{pmatrix} V_{eff}(r_1) & 0 & 0 & \dots & 0 \\ 0 & V_{eff}(r_2) & 0 & \dots & 0 \\ 0 & 0 & V_{eff}(r_3) & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & V_{eff}(r_m) \end{pmatrix}. \tag{4.12}$$

It is important to mention that since we started directly from the Schrodinger equation, this way we get the whole spectrum of the hydrogen atom, not just the ground state. Tables 4.1 and 4.2 show the accuracy of the matrix method compared to the exact solution and the dependence of the energy values on the parameters Δr and r_m.

	n = 1	n = 2	n = 3	n = 4
$\Delta r = 0.2$	-0.49510	-0.12469	-0.05549	-0.03119
$\Delta r = 0.1$	-0.49876	-0.12492	-0.05554	-0.03120
$\Delta r = 0.05$	-0.49969	-0.12498	-0.05555	-0.03120
Exact	-0.50000	-0.12500	-0.05556	-0.03125

Table 4.1: First four energy levels of the hydrogen atom computed for various values of Δr with a fixed parameter $r_m = 50$ Bohr compared to the exact solution.

	n = 1	n = 2	n = 3	n = 4
$r_m = 25$	-0.49510	-0.12469	-0.05459	-0.01386
$r_m = 50$	-0.49510	-0.12469	-0.05549	-0.03119
$r_m = 100$	-0.49510	-0.12469	-0.05549	-0.03123
Exact	-0.50000	-0.12500	-0.05556	-0.03125

Table 4.2: First four energy levels of the hydrogen atom computed for various values of r_m with a fixed parameter $\Delta r = 0.2$ Bohr compared to the exact solution.

We see that to get some useful accuracy for higher energy levels we need to increase the parameter r_m. This makes sense given that the corresponding electrons have the peak of the probability density further away from the nucleus. On the other hand, we see that beyond a certain value, there is no purpose in further increasing r_m

and to achieve better accuracy the step Δr needs to be reduced. It is also good to mention that higher energy levels are more precise for larger l. How well this method approximates the wave functions (and thus the probability density distributions) is shown in 4.1.

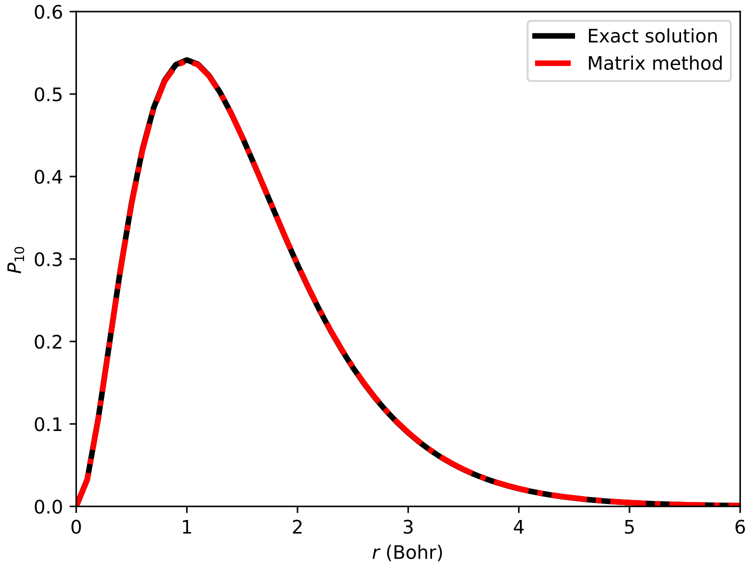


Figure 4.1: Comparison of the ground state radial probability density function of the hydrogen atom for the exact solution and the matrix method approximation with $\Delta r = 0.2$ Bohr and $r_m = 20$ Bohr.

Let us now turn our attention to other potentials. The whole procedure remains the same except for the change of the effective potential V_{eff}. We start with the soft-core Coulomb potential:

$$V_{eff} = \frac{l(l+1)}{2r^2} - \frac{a}{\sqrt{b^2 + r^2}}, \tag{4.13}$$

where

$$a = \nu \left(\frac{R}{r_s}\right)^3, \quad b = \frac{2}{3}R. \tag{4.14}$$

In section 2.3 (specifically in figure 2.10) we saw that increasing the size of the nucleus (reflected in parameter b) flattens and stretches the wave functions. We will use this to estimate the adequate value of r_m. Furthermore, it should be noted that in this case, the energies may already depend on both the principal quantum number n and the angular momentum quantum number l. In this case, we will number the energies as follows: For each number $l = 0, 1, \ldots$ we will create an increasing sequence of energies, which we will number using $n = l+1, l+2, \ldots$ For a point nucleus, this method corresponds to the previous meaning of numbers n and l. However, the number n can no longer be used to compare energies overall. Therefore, energies and corresponding wave functions were computed for different values of n and l, as shown in the table 4.3. From there we can see that the lowest four energy levels are E_{10}, E_{21}, E_{20} and E_{32}. We can also check that the ground

	n = 1	n = 2	n = 3	n = 4
$l = 0$	-4.41774	-3.84237	-3.35454	-2.94095
$l = 1$		-4.11002	-3.58112	-3.13283
$l = 2$			-3.81930	-3.33420
$l = 3$				-3.54523

Table 4.3: Energy levels of the soft-core Coulomb potential for the first four quantum numbers n and all the corresponding quantum numbers l (nanoparticle parameters $R = 9.45$ Bohr, $r_s = 3.01$ Bohr and computation parameters $\Delta r = 0.05$ Bohr, $r_m = 50$ Bohr).

state energy matches well with the value computed in section 2.3 ($E_{10} = -4.414$ Hartree). The corresponding probability density functions are depicted in figure 4.2.

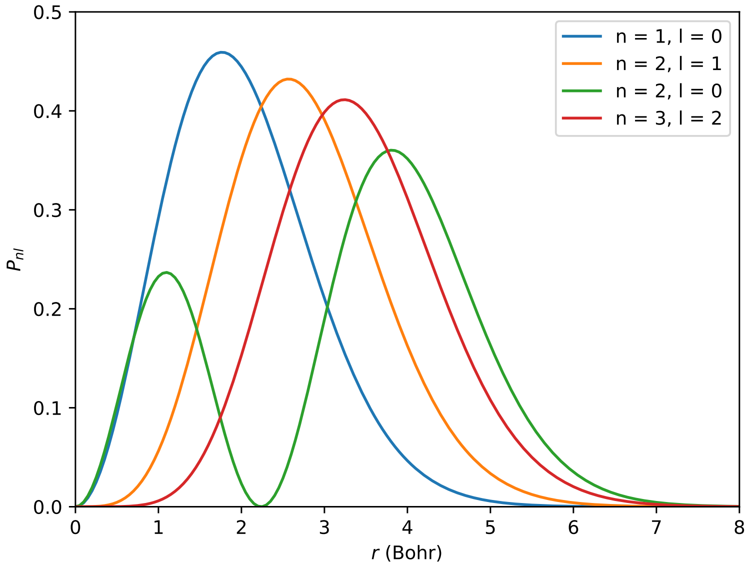


Figure 4.2: Radial probability density functions of the ground state and the first three excited states of the soft-core Coulomb potential (nanoparticle parameters $R = 9.45$ Bohr, $r_s = 3.01$ Bohr and computation parameters $\Delta r = 0.05$ Bohr, $r_m = 50$ Bohr).

The last case we will discuss in this section is our nanoparticle potential

$$V(r) = \begin{cases} \frac{\nu}{r_s^3}\frac{r^2-3R^2}{2} & r \leq R \\ -\frac{\nu}{r_s^3}\frac{R^3}{r} & r > R. \end{cases} \tag{4.15}$$

Thanks to its similarity to the soft-core potential, we can use the insight gained in the previous calculation and compute the energies and wave functions for the same parameters Δr, r_m. Again, table 4.4 shows the energies for various quantum numbers n and l.

	n = 1	n = 2	n = 3	n = 4
$l = 0$	-4.62474	-4.24182	-3.85896	-3.47654
$l = 1$		-4.43326	-4.05033	-3.66754
$l = 2$			-4.24176	-3.85884
$l = 3$				-4.05027

Table 4.4: Energy levels of the nanoparticle potential for the first four quantum numbers n and all the corresponding quantum numbers l (nanoparticle parameters $R = 9.45$ Bohr, $r_s = 3.01$ Bohr and computation parameters $\Delta r = 0.05$ Bohr, $r_m = 50$ Bohr).

We see that the energy sequence starts the same way as for the soft-core Coulomb potential, i.e. E_{10}, E_{21}, E_{20} and E_{32}, but at first sight there appears to be a degeneracy of the energy states considering the computation precision. Namely

$$E_{nl} \approx E_{n-1,l-2}. \tag{4.16}$$

Further analysis would be needed to confirm or refute this relation. Corresponding probability density functions of the first four energies are shown in figure 4.3.

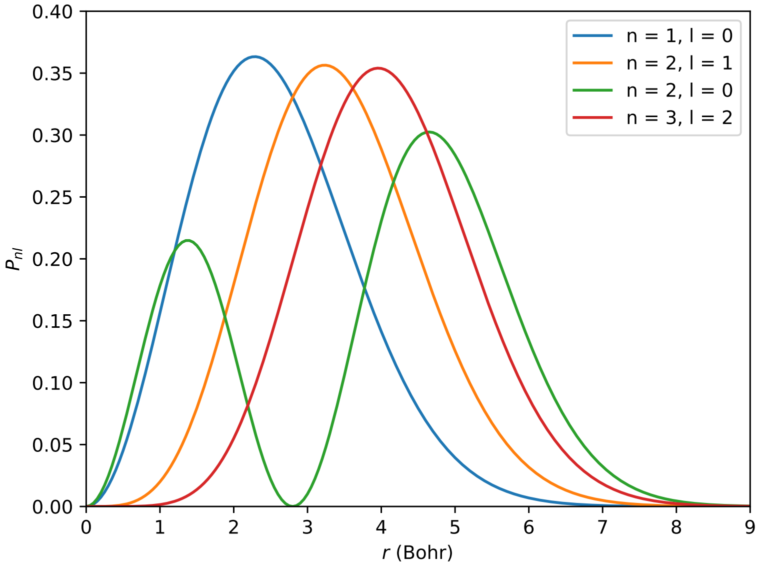


Figure 4.3: Radial probability density functions of the ground state and the first three excited states of the nanoparticle potential (nanoparticle parameters $R = 9.45$ Bohr, $r_s = 3.01$ Bohr and computation parameters $\Delta r = 0.05$ Bohr, $r_m = 50$ Bohr).

4.2 Non-Interacting Electrons

In order to describe a nanoparticle as a neutral object made up of N_i positively charged ions and $N_e = \nu N_i$ negatively charged electrons, we need to add another constraint to our particle, specifically its radius R. We require the particle to have only such size that corresponds to an integer charge Q. The gold particle ($r_s = 3.01$

Bohr, $\nu = 1$), which we have considered so far, has for the radius $R = 9.45$ Bohr (0.5 nm) a charge $Q = 30.945$. Therefore, we now start by choosing the closest integer charge and then we calculate the corresponding radius of the particle. For $Q = 31$ we get $R = 9.46$ Bohr (0.5004 nm).

Next, we would like to use the theory of non-interacting electrons described in section 3.1 expanded by spin. This can be easily done in the same way as shown in the Hartree-Fock approximation. In particular, we assume that the single-electron wave functions depend on the spin s and that they can be decomposed in the positional and spin functions:

$$\psi_i(\mathbf{r}, s) = \varphi_i(\mathbf{r})\sigma_i(s), \tag{4.17}$$

where σ_i represents the electron being in either the spin state up or the spin state down. The total electron density function n_e is then

$$n_e(\mathbf{r}) = \sum_i^N |\varphi_i(\mathbf{r})|^2. \tag{4.18}$$

Furthermore, thanks to the spherical symmetry of the non-interaction system we can express the positional functions φ_i in spherical coordinates as a product of radial and angular functions:

$$\varphi_{nlms}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi). \tag{4.19}$$

Here, we renumbered the wave functions using the quantum numbers n, l, m introduced in the sections devoted to the single-electron solution and the spin quantum number s. The sought electron density function has then the form

$$\begin{aligned} n_e(r, \theta) &= \sum_{n,l,m,s} |R_{nl}(r)|^2 |Y_l^m(\theta, \phi)|^2 = \sum_{n,l,m,s} \frac{1}{r^2} |u_{nl}(r)|^2 |Y_l^m(\theta, \phi)|^2 = \\ &= \sum_{n,l,m,s} n_{nlm}(r, \theta), \end{aligned} \tag{4.20}$$

where n_{nlm} are the one-electron density functions which can be calculated using the procedure described in the previous section. In general, n_e depends on r and θ (dependence on ϕ disappears due to the module of Y_l^m). If we want a density function depending solely on the coordinate r, we can either calculate n_e for specific angles θ, ϕ or we can average n_e over these angles, that is first integrate with respect to $\sin\theta d\theta d\phi$ and then divide by the solid angle 4π. The later approach defines the mean radial electron density function $\bar{n}_e$. The resulting relation for $\bar{n}_e$ is then

$$\begin{aligned} \bar{n}_e(r) &= \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \sum_{n,l,m,s} n_{nlm}(r, \theta) \sin\theta d\theta d\phi = \frac{1}{4\pi} \sum_{n,l,m,s} |R_{nl}(r)|^2 = \\ &= \sum_{n,l,m,s} \bar{n}_{nl}(r), \end{aligned} \tag{4.21}$$

where we used the normalization of the spherical harmonics and the relation 2.64. For electron configurations where every energy shell is filled, $n_e(r, \theta)$ does not depend on the angle θ and is equal to $\bar{n}_e(r)$. To determine the total probability density distribution P_e we average all the one-electron probabilities over the number of electrons N. This allows us to relate the probability distribution and the electron density:

$$P_e(r,\theta,\phi) = \frac{1}{N}\sum_{n,l,m,s} P_{nlm}(r,\theta,\phi) = \frac{1}{N}\sum_{n,l,m,s} r^2 \sin\theta |R_{nl}(r)|^2 |Y_l^m(\theta,\phi)|^2 =$$

$$= \frac{4\pi}{N} r^2 \sin\theta\, n_e(r,\theta). \tag{4.22}$$

Integrating over the angles gives us the radial probability distribution, this time related to the mean electron density:

$$P_e(r) = \frac{4\pi}{N} r^2\, \bar{n}_e(r). \tag{4.23}$$

Inspired by the hydrogen atom we can now define a new parameter R_e as the distance at which P_e is maximal, i.e.

$$R_e = \arg\max_r P_e(r). \tag{4.24}$$

We will call this parameter the effective electron radius of the nanoparticle.

In order to calculate the electron density function of our nanoparticle with the charge $Q = 31$, we need to determine the arrangement of energy levels that the electrons will gradually fill. To do that, we first calculate the necessary number of energy sequences for individual quantum numbers l. From them, we create a final sequence of energy levels, which we will fill in as follows: Each level will be occupied by $2l+1$ pairs of electrons with opposite spins. The last level is filled with the remaining electrons. The energy sequence together with the maximal number of electrons that can be in a certain energy state is given by table 4.5. We see that we need six different energy levels and the last one will be occupied by only five electrons. The total ground state energy is given by simply summing over all one-electron energies, i.e.

	E_{10}	E_{21}	E_{20}	E_{32}	E_{31}	E_{43}
energy	-4.63052	-4.43903	-4.24759	-4.24754	-4.05611	-4.05604
N_{max}	2	6	2	10	6	14

Table 4.5: First six energy levels of the nanoparticle potential ($Q = 31$, $r_s = 3.01$ Bohr) and corresponding maximal numbers of electrons at these levels for computation parameters $\Delta r = 0.05$ Bohr, $r_m = 50$ Bohr.

$$E = \sum_{n,l,m,s} E_{nl} \doteq -\,131.48 \text{ Hartree}. \tag{4.25}$$

Figure 4.4 shows the one-electron probability densities n_{nl}. We can see that there is a large overlap of the individual functions. It is therefore obvious that the resulting density will be very inaccurate. However, the obtained functions will be useful as an initial guess for the Hartree-Fock method. The total radial probability distribution is depicted in figure 4.5.

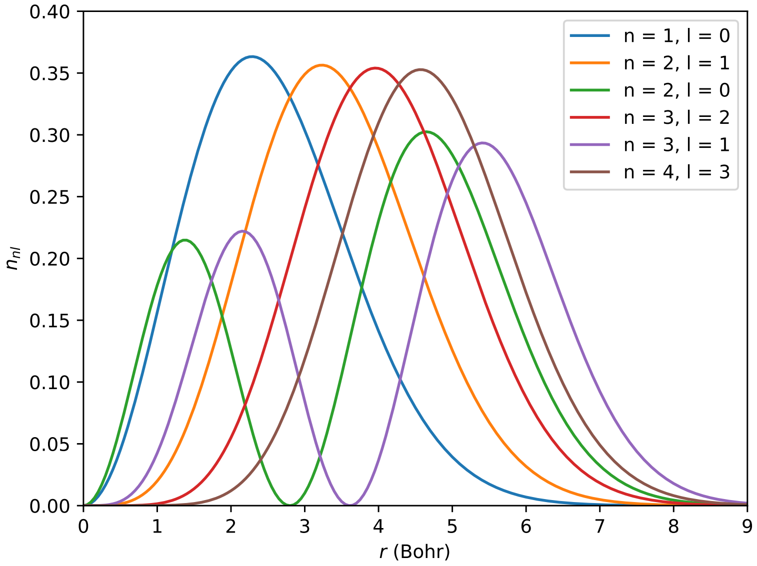


Figure 4.4: First six one-electron radial probability density functions of the gold nanoparticle ($Q = 31$, $r_s = 3.01$ Bohr) computed using $\Delta r = 0.05$ Bohr, $r_m = 50$ Bohr.

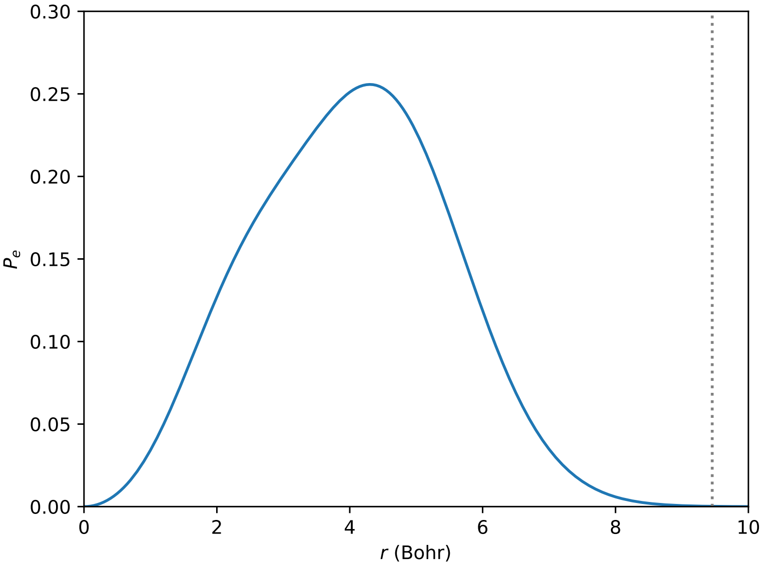


Figure 4.5: Radial probability density function of the non-interacting-electron model of the gold nanoparticle ($Q = 31$, $r_s = 3.01$ Bohr). The grey dotted line shows the boundary of the particle.

The effective electron radius is approximately 4.30 Bohr, which is less than half of the nanoparticle radius R. By considering the interaction between electrons, the resulting probability density can be expected to flatten and stretch. Figures 4.6, 4.7 show the mean radial density $\bar{n}_e$ and a comparison of the total electron density for different values of θ.

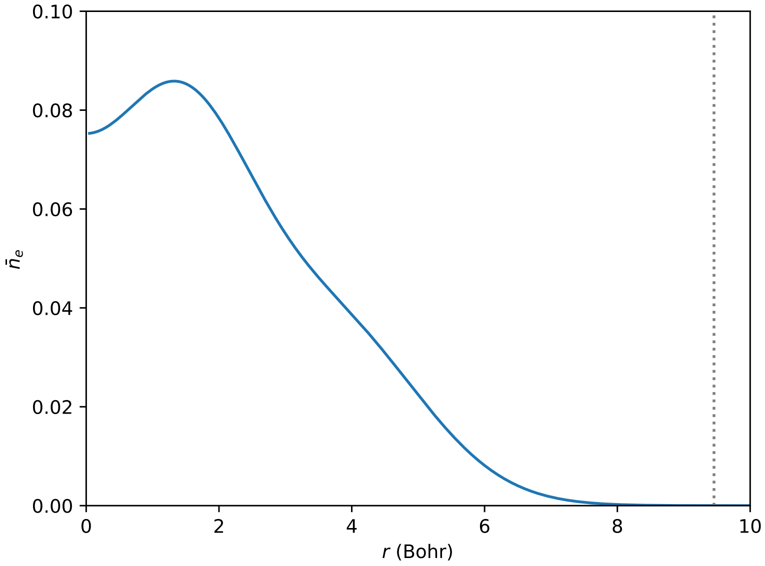


Figure 4.6: Mean radial electron density function of the non-interacting-electron model of the gold nanoparticle ($Q = 31$, $r_s = 3.01$ Bohr). The grey dotted line shows the boundary of the particle.

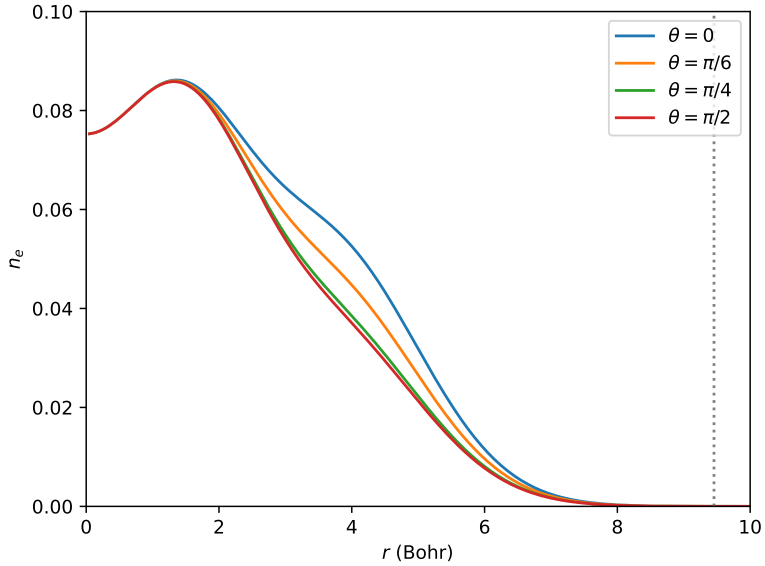


Figure 4.7: Comparison of the total electron density of the gold nanoparticle ($Q = 31$, $r_s = 3.01$ Bohr) at four different values of θ. The grey dotted line shows the boundary of the particle.

4.3 Hartree-Fock Approximation

As we have seen in the previous section, the non-interacting electron model cannot well describe the total electron density because of the large overlap of the individual electrons. To fix this issue, we need to include the electron-electron interaction in our numerical calculations. For this, we will need to further simplify our task. First, we will use the Hartree-Fock approximation described in the chapter 3.3. Next, although we lose the spherical symmetry due to the interaction between electrons, we will continue to use the decomposition of the wave functions into the radial and angular parts. Since we want to solve the Hartree-Fock equations only in radial coordinates, it will be necessary to express the potentials V_C and V_{ex} in a suitable form. Finally, we convert these again into a matrix form using the finite step approximation.

We begin by expressing the two-particle Coulomb potential in spherical coordinates using the so-called *generating function of Legendre polynomials*:

$$V_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\vartheta}} = \sum_{l=0}^{+\infty} \frac{1}{2^l l!} P_l(\cos\vartheta) \frac{r_<^l}{r_>^{l+1}}, \tag{4.26}$$

where $r_i = |\mathbf{r}_i|$, ϑ is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$, $r_< = \min(r_1, r_2)$ and $r_> = \max(r_1, r_2)$. Note that the factor $\frac{1}{2^l l!}$ is present due to our definition of the Legendre polynomials (1.52) and is usually absent in the formula. Next, we rewrite the polynomials P_l with the help of the *addition theorem of spherical harmonics* ([9]):

$$P_l(\cos\vartheta) = 2^l l! \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y_l^{m*}(\theta_1, \phi_1) Y_l^m(\theta_2, \phi_2), \tag{4.27}$$

where θ_i, ϕ_i are the angles of $\mathbf{r}_i$ in their common spherical coordinates. Together, V_2 can be expressed as

$$V_2(\mathbf{r}_1, \mathbf{r}_2) = \sum_{l=0}^{+\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} Y_l^{m*}(\theta_1, \phi_1) Y_l^m(\theta_2, \phi_2) \frac{r_<^l}{r_>^{l+1}}. \tag{4.28}$$

Since the Coulomb mean field term and the exchange term of the Hartree-Fock equations contain integration of spherical harmonics multiplied by this potential, we will use another useful relation for the functions Y_l^m, namely

$$\begin{aligned} &\int_0^{2\pi} \int_0^{\pi} Y_{l_1}^{m_1*}(\theta, \phi) Y_{l_2}^{m_2}(\theta, \phi) Y_{l_3}^{m_3}(\theta, \phi) \sin\theta d\theta d\phi = \\ &\qquad = (-1)^{m_1} \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ -m_1 & m_2 & m_3 \end{pmatrix}, \end{aligned} \tag{4.29}$$

where $\begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix}$ denotes the *Wigner* 3-*j symbol*. This allows us to write

$$\begin{aligned}
V_C(\mathbf{r}_i) &= \sum_{\substack{j=1 \\ j\neq i}}^{N} \int_{\mathbb{R}^3} \varphi_j^*(\mathbf{r}) V_2(\mathbf{r}_i, \mathbf{r}) \varphi_j(\mathbf{r}) d\mathbf{r} = \\
&= \sum_{\substack{j=1 \\ j\neq i}}^{N} \sum_{l=0}^{+\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} Y_l^{m*}(\theta_i, \phi_i) \int_0^{+\infty} \frac{r_<^l}{r_>^{l+1}} |R_{n_j l_j}(r)|^2 r^2 dr \, \cdot \\
&\qquad\qquad \cdot \int_0^{2\pi} \int_0^{\pi} Y_l^m(\theta, \phi) |Y_{l_j}^{m_j}(\theta, \phi)|^2 \sin\theta d\theta d\phi = \\
&= \sum_{\substack{j=1 \\ j\neq i}}^{N} \sum_{l=0}^{+\infty} \sum_{m=-l}^{l} (-1)^{m_j} \sqrt{\frac{4\pi}{2l+1}} (2l_j + 1) \int_0^{+\infty} \frac{r_<^l}{r_>^{l+1}} |R_{n_j l_j}(r)|^2 r^2 dr \, \cdot \\
&\qquad\qquad \cdot \, Y_l^{m*}(\theta_i, \phi_i) \begin{pmatrix} l_j & l & l_j \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_j & l & l_j \\ -m_j & m & m_j \end{pmatrix}, \qquad (4.30)
\end{aligned}$$

where $r_< = \min(r, r_i)$ and $r_> = \max(r, r_i)$. There are several simplification we are going to carry out. First, we again use the substitution

$$u_{nl}(r) = r R_{nl}(r). \qquad (4.31)$$

Next we use the fact that the Wigner 3-j symbol $\begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix}$ is non-zero only if

$$d + e + f = 0. \qquad (4.32)$$

In our case, this means that the only non-zero term in the sum over m will be for $m = 0$. Finally, we would like the potential V_C to be independent of the angles θ_i, ϕ_i, as our goal is to obtain an equation for the radial part of the wave functions only. This can be achieved by integrating over the angles and then dividing by the total solid angle 4π. Since

$$\int_0^{2\pi} \int_0^{\pi} Y_l^m(\theta, \phi) \sin\theta d\theta d\phi = \sqrt{4\pi} \delta_{m0} \delta_{l0}, \qquad (4.33)$$

we see that only terms with $l = 0$ contribute to the result. Using the relation

$$\begin{pmatrix} l_j & 0 & l_j \\ -m_j & 0 & m_j \end{pmatrix} = (-1)^{l_j - m_j} \frac{1}{\sqrt{2l_j + 1}} \qquad (4.34)$$

we conclude that

$$\begin{aligned}
V_C(\mathbf{r}_i) \approx V_C(r_i) &= \sum_{\substack{j=1 \\ j\neq i}}^{N} \int_0^{+\infty} |u_{n_j l_j}(r)|^2 \frac{1}{r_>} dr = \\
&= \sum_{\substack{j=1 \\ j\neq i}}^{N} \left(\int_0^{r_i} |u_{n_j l_j}(r)|^2 \frac{1}{r_i} dr + \int_{r_i}^{+\infty} |u_{n_j l_j}(r)|^2 \frac{1}{r} dr \right). \qquad (4.35)
\end{aligned}$$

Using certain rules for the Wigner 3-j symbols, it can be shown that averaging over the quantum number $m_j \in \{-l_j, -l_j+1, \dots, l_j\}$ leads to the same result. This is an important finding. In our case, summing over m_j is represented by a part of the sum over j. Since the missing term for $j = i$ is up to the sign identical in both V_C and V_{ex}, its addition to these potentials does not change the Hartree-Fock equations. In such a case, we see that the result 4.35 is exact for configurations with fully filled orbitals. This is in agreement with the fact that such electron configurations are spherically symmetric and therefore cannot depend on the angles θ_i, ϕ_i.

In a similar way, we derive an analogical expression for the exchange term:

$$\begin{aligned}
&\hat{V}_{ex}(\mathbf{r}_i)\varphi_i(\mathbf{r}_i) = \hat{V}_{ex}(\mathbf{r}_i)R_{n_il_i}(r_i)Y_{l_i}^{m_i}(\theta_i,\phi_i) = \\
&\quad = -\sum_{\substack{j=1\\ j\neq i}}^{N} \delta_{\sigma_j\sigma_i} \int_{\mathbb{R}^3} \varphi_j^*(\mathbf{r})V_2(\mathbf{r}_i,\mathbf{r})\varphi_i(\mathbf{r})\varphi_j(\mathbf{r}_i)d\mathbf{r} = \\
&\quad = -\sum_{\substack{j=1\\ j\neq i}}^{N} \delta_{\sigma_j\sigma_i} \sum_{l=0}^{+\infty}\sum_{m=-l}^{l} \frac{4\pi}{2l+1} Y_l^{m*}(\theta_i,\phi_i) \int_0^{+\infty} \frac{r_<^l}{r_>^{l+1}} R_{n_jl_j}^*(r)R_{n_il_i}(r)r^2dr \;\cdot \\
&\qquad \cdot \int_0^{2\pi}\int_0^{\pi} Y_{l_j}^{m_j*}(\theta,\phi)Y_l^m(\theta,\phi)Y_{l_i}^{m_i}(\theta,\phi)\sin\theta d\theta d\phi\, R_{n_jl_j}(r_i)Y_{l_j}^{m_j}(\theta_i,\phi_i) = \\
&\quad = -\sum_{\substack{j=1\\ j\neq i}}^{N} \delta_{\sigma_j\sigma_i} \sum_{l=0}^{+\infty}\sum_{m=-l}^{l} \sqrt{\frac{4\pi(2l_j+1)(2l_i+1)}{2l+1}} \int_0^{+\infty} \frac{r_<^l}{r_>^{l+1}} R_{n_jl_j}^*(r)R_{n_il_i}(r)r^2dr \;\cdot \\
&\qquad \cdot\; R_{n_jl_j}(r_i)Y_l^{m*}(\theta_i,\phi_i)Y_{l_j}^{m_j}(\theta_i,\phi_i)(-1)^{m_j} \begin{pmatrix} l_j & l & l_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_j & l & l_i \\ -m_j & m & m_i \end{pmatrix}.
\end{aligned} \tag{4.36}$$

In fact, we do not need to sum over l to infinity. Thanks to the triangular inequalities for the Wigner 3-j symbols, there is a maximal number l_m for which the symbols are defined. This maximal value is given as

$$l_m = l_i + l_j. \tag{4.37}$$

In order to eliminate the dependence on angles θ_i, ϕ_i, this time we must first multiply the equation by the function $Y_{l_i}^{m_i*}$ and only then integrate. Using relations 4.29, 4.31 and 4.32, we arrive at the following approximate form of the exchange potential:

$$\begin{aligned}
&\hat{V}_{ex}(\mathbf{r}_i)\varphi_i(\mathbf{r}_i) \approx \hat{V}_{ex}(r_i)u_{n_il_i}(r_i) = \\
&\qquad = -\sum_{\substack{j=1\\ j\neq i}}^{N} \delta_{\sigma_j\sigma_i} \sum_{l=0}^{l_m} u_{n_jl_j}(r_i) \int_0^{+\infty} \frac{r_<^l}{r_>^{l+1}} u_{n_jl_j}^*(r)u_{n_il_i}(r)dr \;\cdot \\
&\qquad \cdot (2l_j+1)(2l_i+1) \begin{pmatrix} l_j & l & l_i \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} l_j & l & l_i \\ -m_j & m_j - m_i & m_i \end{pmatrix}^2.
\end{aligned} \tag{4.38}$$

As in the case of the potential V_C, we can further simplify this expression for electron configurations with fully filled orbitals by partially summing over j expressing the summation over all quantum numbers $m_j \in \{-l_j, -l_j+1, \dots, l_j\}$. Using the relation

$$\sum_{m_j=-l_j}^{l_j} \begin{pmatrix} l_j & l & l_i \\ -m_j & m_j - m_i & m_i \end{pmatrix}^2 = \frac{1}{(2l_i+1)} \tag{4.39}$$

and the fact that

$$(2l_j+1) = \sum_{m_j=-l_j}^{l_j} 1 \tag{4.40}$$

we get the final form of the exchange operator defined as

$$\hat{V}_{ex}(r_i) u_{n_i l_i}(r_i) = -\sum_{\substack{j=1 \\ j\neq i}}^{N} \delta_{\sigma_i \sigma_j} \sum_{l=0}^{l_m} \begin{pmatrix} l_j & l & l_i \\ 0 & 0 & 0 \end{pmatrix}^2 u_{n_j l_j}(r_i) \int_0^{+\infty} \frac{r_<^l}{r_>^{l+1}} u^*_{n_j l_j}(r) u_{n_i l_i}(r) dr. \tag{4.41}$$

In this case, if we use the notation where we add the term for $j = i$ to both V_C and V_{ex}, the condition on the spin functions simplifies to a factor of 1/2.

The question now is, how can we represent the potentials V_C and $\hat{V}_{ex}$ in a matrix form suitable for our numerical calculations? We start by considering $r_i \in \langle 0, r_m \rangle$, where again $r_m = M\Delta r$ is the point from which we consider the wave function to be zero, and by rewriting the integral in 4.35 using the transition:

$$r_i \longrightarrow k\Delta r, \quad k \in \{1, 2, \dots, M\},$$

$$\int_0^{k\Delta r} f(r) dr \longrightarrow \sum_{q=1}^{k} f(q\Delta r)\Delta r. \tag{4.42}$$

This leads to

$$\begin{aligned} V_C(k\Delta r) &= \sum_{\substack{j=1 \\ j\neq i}}^{N} \left(\int_0^{k\Delta r} |u_{n_j l_j}(r)|^2 \frac{1}{k\Delta r} dr + \int_{k\Delta r}^{+\infty} |u_{n_j l_j}(r)|^2 \frac{1}{r} dr \right) \approx \\ &\approx \sum_{\substack{j=1 \\ j\neq i}}^{N} \left(\sum_{q=1}^{k} |u_{n_j l_j}(q\Delta r)|^2 \frac{1}{k} + \sum_{q=k+1}^{M} |u_{n_j l_j}(q\Delta r)|^2 \frac{1}{q} \right), \end{aligned} \tag{4.43}$$

If we denote this approximation $\tilde{V}_C$, we can define the corresponding matrix operator as follows:

$$\mathbb{V}_C = \begin{pmatrix} \tilde{V}_C(\Delta r) & 0 & 0 & \dots & 0 \\ 0 & \tilde{V}_C(2\Delta r) & 0 & \dots & 0 \\ 0 & 0 & \tilde{V}_C(3\Delta r) & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & \tilde{V}_C(M\Delta r) \end{pmatrix}. \tag{4.44}$$

Similarly, for the exchange, we can write

$$\hat{V}_{ex}(k\Delta r)u_{n_il_i}(k\Delta r) \approx$$

$$\approx -\sum_{\substack{j=1\\ j\neq i}}^{N} \delta_{\sigma_i\sigma_j} \sum_{l=0}^{l_m} \begin{pmatrix} l_j & l & l_i \\ 0 & 0 & 0 \end{pmatrix}^2 u_{n_jl_j}(k\Delta r) \Bigg(\sum_{q=1}^{k} \frac{q^l}{k^{l+1}} u^*_{n_jl_j}(q\Delta r) u_{n_il_i}(q\Delta r) +$$

$$+ \sum_{q=k+1}^{M} \frac{k^l}{q^{l+1}} u^*_{n_jl_j}(q\Delta r) u_{n_il_i}(q\Delta r) \Bigg). \quad (4.45)$$

The resulting matrix operator is this time defined as

$$\mathbb{V}_{ex} = -\sum_{\substack{j=1\\ j\neq i}}^{N} \delta_{\sigma_i\sigma_j} \sum_{l=0}^{l_m} \begin{pmatrix} l_j & l & l_i \\ 0 & 0 & 0 \end{pmatrix}^2 \mathbb{V}^{jl}_{ex}, \quad (4.46)$$

where the matrices $\mathbb{V}^{jl}_{ex}$ are of the form

$$\begin{pmatrix} u_{n_jl_j}(\Delta r)u^*_{n_jl_j}(\Delta r) & u_{n_jl_j}(\Delta r)\frac{1}{2^{l+1}}u^*_{n_jl_j}(2\Delta r) & \dots & u_{n_jl_j}(\Delta r)\frac{1}{M^{l+1}}u^*_{n_jl_j}(M\Delta r) \\ u_{n_jl_j}(2\Delta r)\frac{1}{2^{l+1}}u^*_{n_jl_j}(\Delta r) & u_{n_jl_j}(2\Delta r)\frac{1}{2}u^*_{n_jl_j}(2\Delta r) & \dots & u_{n_jl_j}(2\Delta r)\frac{2^l}{M^{l+1}}u^*_{n_jl_j}(M\Delta r) \\ \vdots & \vdots & \ddots & \vdots \\ u_{n_jl_j}(M\Delta r)\frac{1}{M^{l+1}}u^*_{n_jl_j}(\Delta r) & u_{n_jl_j}(M\Delta r)\frac{2^l}{M^{l+1}}u^*_{n_jl_j}(2\Delta r) & \dots & u_{n_jl_j}(M\Delta r)\frac{1}{M}u^*_{n_jl_j}(M\Delta r) \end{pmatrix}. \quad (4.47)$$

With this, we managed to convert our task to a set of the following matrix eigenvalue problems for all the one-electron radial wave functions:

$$\mathbb{H}_i \mathbf{u}_{n_il_i} = \epsilon_i \mathbf{u}_{n_il_i}, \quad (4.48)$$

where

$$\mathbb{H}_i = \mathbb{T}_i + \mathbb{V}_i + \mathbb{V}_C + \mathbb{V}_{ex} \quad (4.49)$$

with $\mathbb{T}_i$ and $\mathbb{V}_i$ defined as in 4.8 and 4.10. Although we have N equations, there is no need to solve all of them. This is because the equations do not depend on the quantum numbers m and s. Therefore, for each wave function with quantum number l there are $4l + 2$ identical equations.

In the following text, we will solve the set of equations 4.49 for different nanoparticle sizes (and therefore different N). In order to achieve the best accuracy, we will perform the calculations only for full electron shells. We start with the simplest case of two electrons with opposite spins. In this case, the exchange term is zero, so we only need to calculate V_C in every iteration. This also allows us to work only with the probability functions as V_C depends solely on the module of the wave functions. Figure 4.8 shows that in this case to achieve good accuracy, it is sufficient to perform ten iterations. We see from figure 4.9a that the resulting probability distribution stretches and flattens compared to the non-interacting electron model. Also, the parameter R_e, expressing the distance from the origin where it is most likely to find the electron, shifted towards the particle boundary given by R.

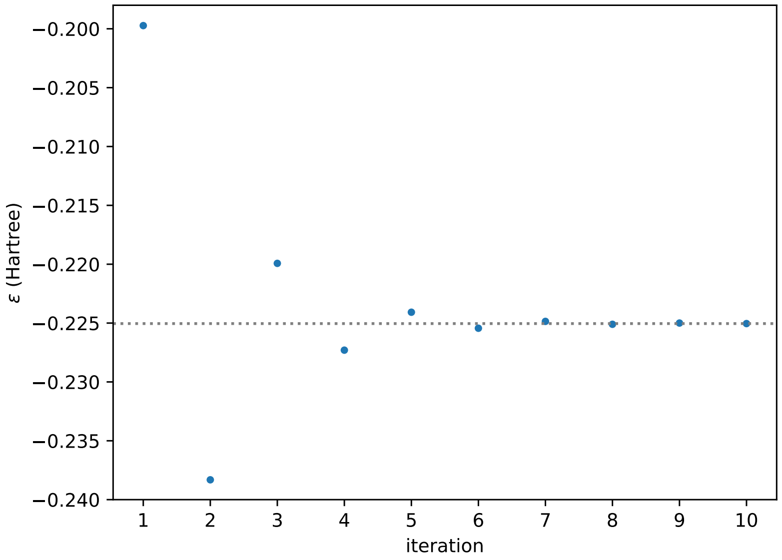
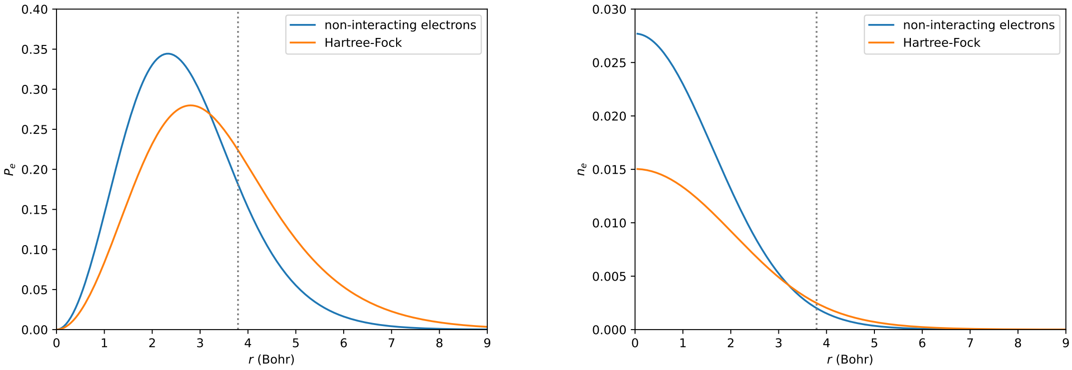


Figure 4.8: Convergence of the energy ϵ for $N = 2$. The grey line shows the last values of ϵ.



(a) **(b)**

Figure 4.9: Comparison of the total probability densities P_e (a) and the electron densities n_e (b) of the two computational models for $N = 2$. The grey dotted line shows the boundary of the particle.

To better describe the final result, we introduce the electron spill-out SO. It is defined as the proportion of the electron charge outside of the radius R, i.e.

$$SO = \int_R^\infty P_e(r). \tag{4.50}$$

For the two-electron case we have $SO = 35.1\%$. Lastly, figure 4.9b shows the comparison of the total electron density for the non-interacting electron and the Hartree-Fock models.

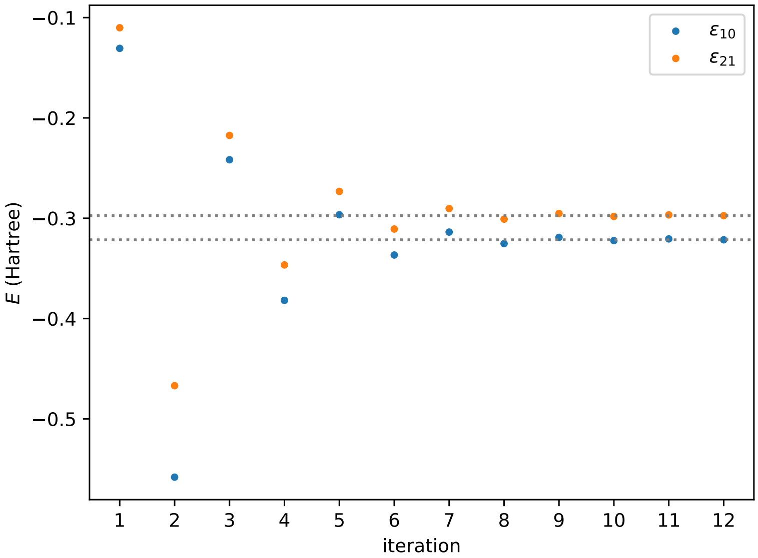
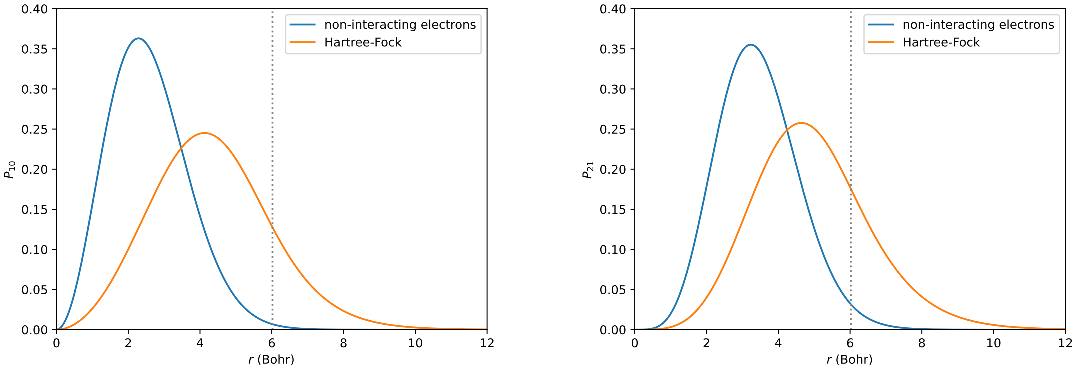


Figure 4.10: Convergence of the energies ϵ_{10} and ϵ_{21} for $N = 8$. The grey lines show the last values of ϵ_{10} and ϵ_{21}.

Next, we investigate the second case with fully filled orbitals. Since the energy levels follow the sequence 4.5, this time we will need to solve 4.49 for two radial wave functions R_{10} and R_{21} having eight electrons in total. The convergence of the energies ϵ_{nl} is depicted in figure 4.10 and we see that ten iterations are again sufficient. The shift of the corresponding probability densities can be seen in figures 4.11a, 4.11b. Clearly, it is of the same nature as in the two-electron case. Again, we also compare the total radial probability distributions and electron densities for both models, as shown in figures 4.12a, 4.12b. In addition, figure 4.13 displays the

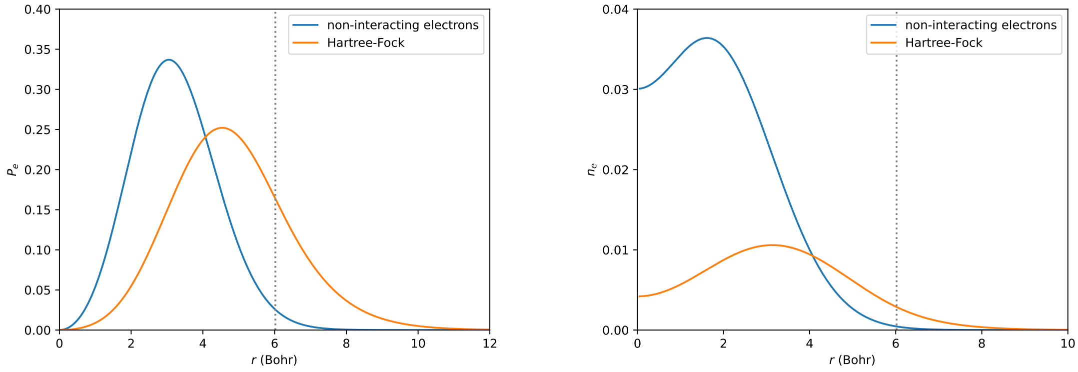


(a) **(b)**

Figure 4.11: Comparison of the probability distributions P_{10} (a) and P_{21} (b) of the two computational models for $N = 8$. The grey dotted line shows the boundary of the particle.

final charge density distribution n given as

$$n(r) = n_I(r) - n_e(r), \tag{4.51}$$



(a) **(b)**

Figure 4.12: Comparison of the total probability distribution P_e (a) and electron density n_e (b) of the two computational models for $N = 8$. The grey dotted line shows the boundary of the particle.

where

$$n_I(r) = \begin{cases} \frac{Q}{V} & r \leq R \\ 0 & r > R \end{cases} \tag{4.52}$$

is the positive charge density created by the gold ions. We see that there are oscillations between the positive and the negative charge inside of the particle which is in disagreement with the classical concept.

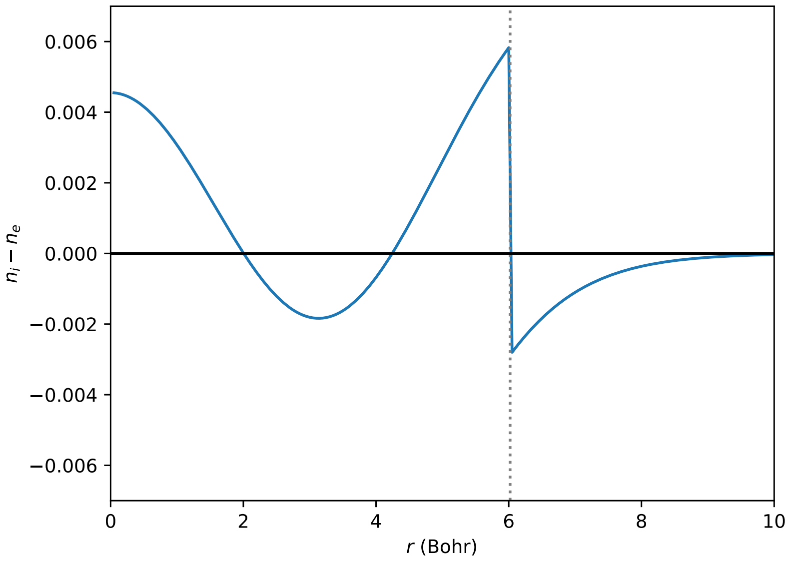


Figure 4.13: Total charge density distribution for $N = 8$. The grey dotted line shows the boundary of the particle.

As stated earlier, for our potential there appears to be a degeneracy of energy levels (see 4.16). Therefore, it is not obvious in what order the electrons will fill these levels. For this reason, we will compute both variants. First we consider the wave functions R_{10}, R_{21} and R_{20} ($N = 10$). Then we examine the case with R_{10}, R_{21} and R_{32} ($N = 18$). Combining these leads to the last system with $N = 20$. For all three problems, we show the final one-electron probability distributions (4.14a, 4.15a, 4.16a), total probability density functions (4.14b, 4.15b, 4.16b) and the total electron densities compared to the ion charge distributions (4.14c, 4.15c, 4.16c). Table 4.6 then gives a summary of the parameters R, R_e, SO, the one-electron energies ϵ_{nl} and the total energy E for all the discussed cases $N \in \{2, 8, 10, 18, 20\}$.

	R	R_e	$SO(\%)$	ϵ_{10}	ϵ_{21}	ϵ_{20}	ϵ_{32}	E
$N = 2$	3.79	2.80	35.1	-0.225				-0.720
$N = 8$	6.02	4.55	21.8	-0.321	-0.297			-6.981
$N = 10$	6.48	4.70	28.8	-0.448	-0.362	-0.103		-9.864
$N = 18$	7.89	6.20	19.5	-0.367	-0.378		-0.266	-25.969
$N = 20$	8.17	6.50	18.7	-0.779	-0.385	-0.143	-0.278	-31.124

Table 4.6: Parameters and energies of first five gold nanoparticles with fully filled orbitals.

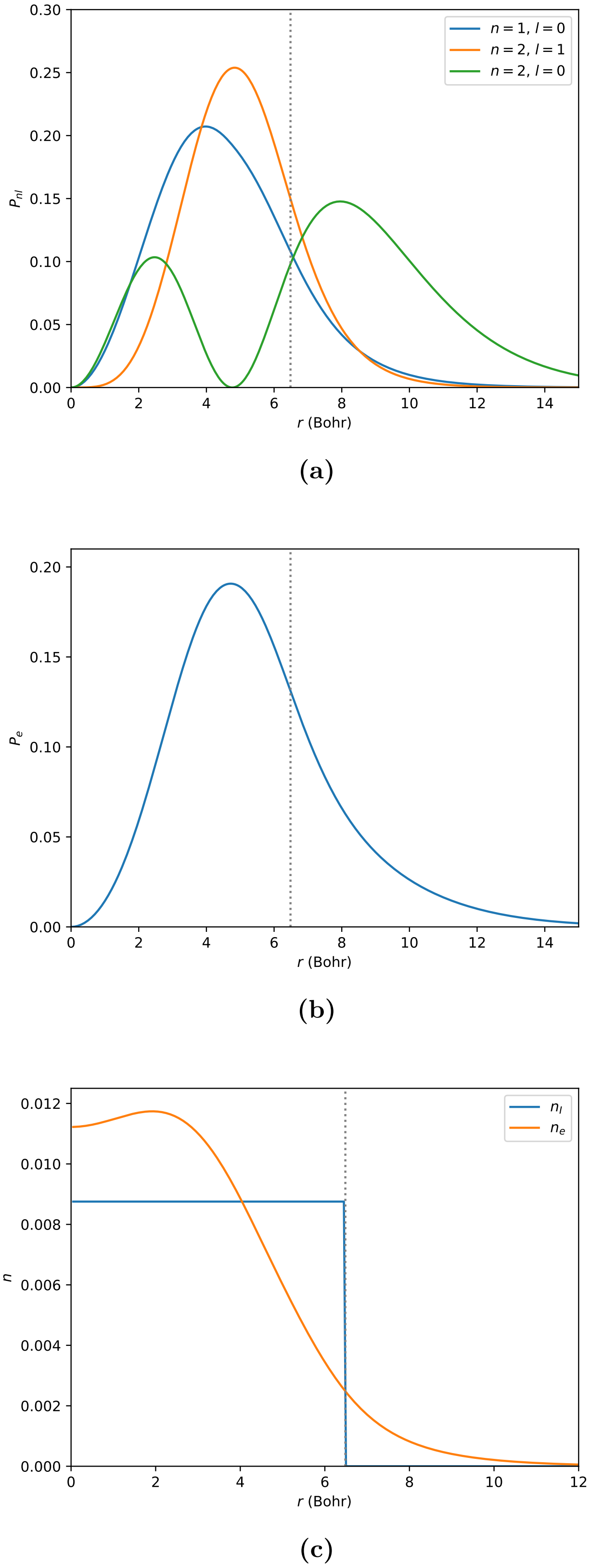
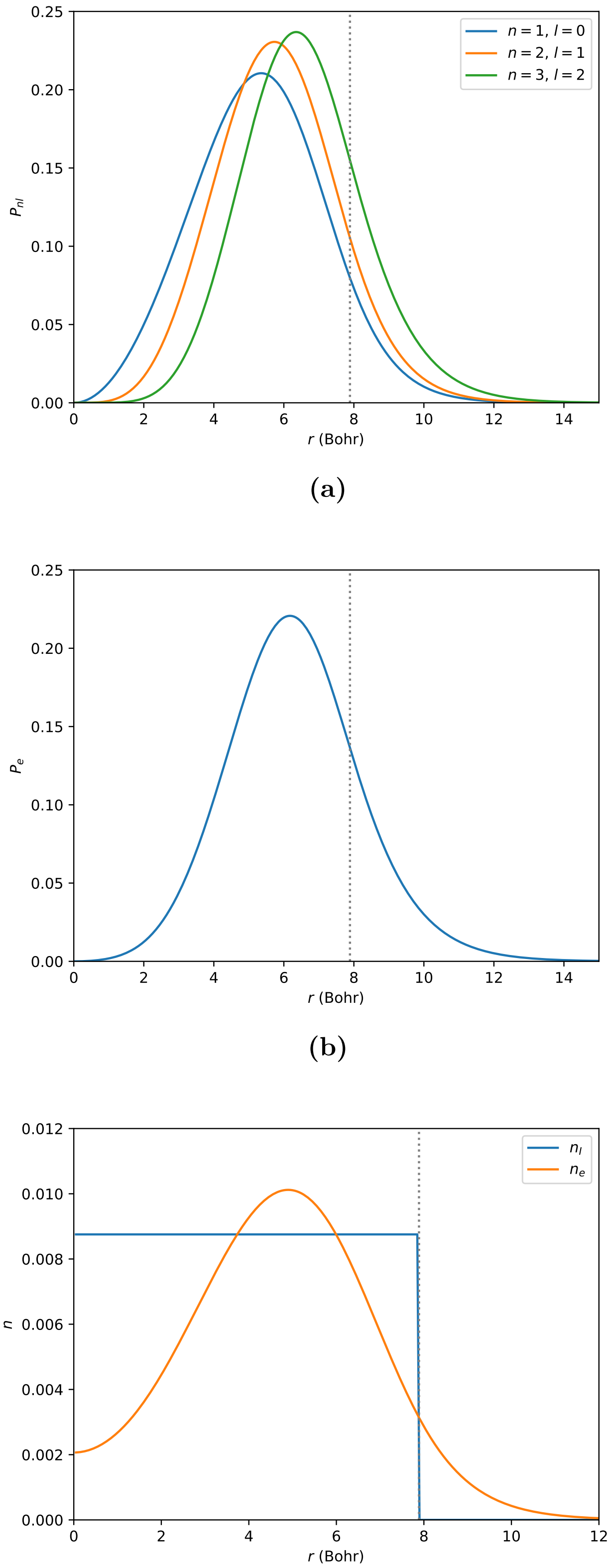


Figure 4.14: Probability distributions P_{nl} (a), total radial probability distribution P_e (b) and the comparison of the total radial electron density n_e and the radial ion density n_I for $N = 10$. The grey dotted lines show the boundary of the particle.



(a)

(b)

(c)

Figure 4.15: Probability distributions P_{nl} (a), total radial probability distribution P_e (b) and the comparison of the total radial electron density n_e and the radial ion density n_I for $N = 18$. The grey dotted lines show the boundary of the particle.

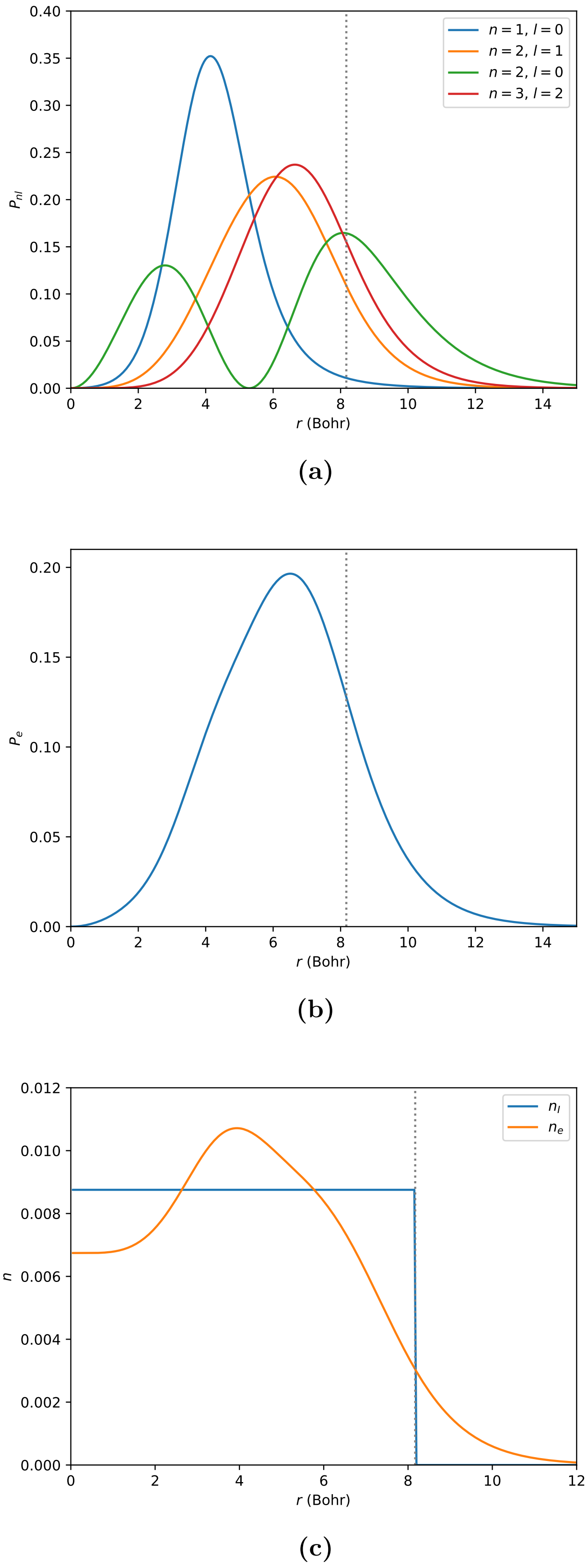


Figure 4.16: Probability distributions P_{nl} (a), total radial probability distribution P_e (b) and the comparison of the total radial electron density n_e and the radial ion density n_I for $N = 20$. The grey dotted lines show the boundary of the particle.

Conclusion

The aim of this thesis was to obtain a comprehensive understanding of the shape and properties of the charge density distribution of nanoparticles modelled as a sphere with an evenly distributed positive charge and a corresponding number of electrons. The first idea was obtained from the known solutions of the hydrogen atom. Since in our case the size of the ionic core cannot be neglected, it was necessary to extend this view with a finite nuclei model, which is provided by the so-called soft-core Coulomb potential. The radial wave functions, and hence the corresponding electron densities, flatten and broaden compared to those of hydrogen. The Hartree-Fock approximation, specifically the numerical matrix method introduced in Chapter 4, was then used to solve the multi-electron system with electron-electron interactions. The initial functions were chosen to be those calculated by the same computational method for the nanoparticle potential with non-interacting electrons (although some better guesses are used for more complex problems to achieve better convergence). From figures 4.12b, 4.14c, 4.15c and 4.16c, it can be seen that for all cases considered with $N > 2$, there is an oscillation of the electron density inside the particle and a sharp decrease outside the particle. This behaviour is contrary to classical ideas and to the conclusions predicted by quantum hydrodynamics [4]. Nevertheless, they correspond well to the results for nanolayers [10]. The electron spill-out is considerably big for small particles and generally decreases with increasing particle radius, even though this is not always the rule (cf. the cases $N = 8$ and $N = 10$ in 4.6). In all cases studied, the most likely location of an electron was inside the particle between $0.7R$ and $0.8R$.

A possible continuation of research in this area is to extend the procedure to particles with dimensions above 1 nm. However, this requires higher computational power, further approximations or other computational methods. On the other hand, one could get more precise solutions by removing some of the approximations using the perturbation calculus. Furthermore, the results can be used to improve the shape of the potential in QHD, which could be sufficient for larger particles.

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