
The Stark effect in hydrogen

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Abstract

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In the report the Stark effect for the ground state of a hydrogen atom is studied using perturbation theory. First parabolic coordinates are introduced for the hydrogen atom without an external electric field and the Schrödinger equation for movement of the electron in three and two dimensions respectively is solved analytically to find the energy and the eigenstates. Then the Schrödinger equation for the Stark effect is solved using perturbation theory. First the calculations are made for three and two dimensions. This is then generalised to non-integer dimension between 2 and 3 in order to describe a more realistic confinement of an electron in a nanostructure. A series for the energy as a function of the dimension and the applied electric field is found. The series is seen to be divergent which is explained by the tunnelling effect which leads to an ionisation of the atom. The eigenfunctions are used to plot the probability density which shows an expected asymmetry due to the electric field. Far away from the nucleus in the opposite direction of the applied field, large increases of the probability density are seen which are interpreted as a consequence of the tunnelling effect.



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I rapporten undersøges Stark effekten for grundtilstanden i et hydrogenatom vha. perturbationsteori. Først introduceres paraboliske koordinater for et hydrogenatom uden et ydre elektrisk felt, og Schrödingerligningen for en elektron, hvis bevægelse er begrænset til henholdsvis tre og to dimensioner, løses analytisk for at finde energierne og egentilstandene. Dernæst løses Schrödingerligningen for Stark effekten med perturbationsteori. Beregningerne udføres først for tre og to dimensioner. Dette generaliseres herefter til ikke-heltals dimensioner mellem 2 og 3 for at opnå en mere realistisk beskrivelse af restriktionerne for en elektron i en nanostruktur. For energien findes en rækkeudvikling som funktion af dimensionen og det elektriske felt. Rækken ses at være divergent, hvilket forklares med tunneleffekten, der fører til, at atomet ioniseres. Egenfunktionerne bruges til at plote sandsynlighedstætheden, og denne viser en asymmetri grundet det elektriske felt. Langt fra kernen i den modsatte retning af det ydre elektriske felt ses store stigninger i sandsynlighedstætheden, og dette tolkes som en konsekvens af tunneleffekten.

Preface

This report is a master's thesis written by a FYS10 student at Aalborg University. In the report the Stark effect for a hydrogen atom is studied theoretically using perturbation theory. The aim is to find the energy and wave function of the electron in the ground state where the electron can move in N dimensions where $2 \leq N \leq 3$.

Readers of the report are assumed to have some basic knowledge of quantum mechanics, calculus and analysis.

Citations are referred to using the Harvard method where a reference is denoted by the name of one or two of the authors followed by the publishing year, like [Privman, 1980] or [Bransden and Joachain, 2003]. All calculations and illustrations are made using MATLAB R2015b.

The report is followed by three appendixes: In appendix A and B derivations of some of the mathematics used in the report can be found and in appendix C the script used to produce all the main results in the report is presented.

Aalborg University, January 8, 2016

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Chapter 1

Introduction

When a static electric field is applied to an atom, the spectral lines will split up and this effect is known as the Stark effect. Historically, the effect was first successfully observed in 1913 by the German physicist Johannes Stark. At this time wave mechanics and matrix formalism was yet to be developed but with the use of parabolic coordinates and a classical description of the atom combined with quantum condition ideas by Sommerfeld, Paul Epstein and Karl Schwarzschild each created models in agreement with Stark's observations. This was done in 1916. After 1926 when Heisenberg and Schrödinger developed their theories, new calculations were made using the matrix approach and wave equations. These could reproduce Epstein and Schwarzschild's results and since then, various quantum mechanical approaches has been made to describe different aspects of the Stark effect, [Kox, 2013].

In this report the Stark effect will be studied using perturbation theory. More specifically we will study the effect on the wave function and the energy for the ground state of the electron in a hydrogen atom. Furthermore, the effect of confining the electron in lower dimensions will be studied. This quantum-confined Stark effect has direct applications in for example optics where it can be used in modulators and switches, [Saleh and Teich, 2007].

The report consists of two parts. In chapter 2 the Schrödinger equation for the hydrogen atom without an external electric field is solved analytically. Here parabolic coordinates are introduced and the eigenfunctions and energies are found for an electron that is free to move in three and two dimensions respectively. In chapter 3 an external field is applied to the atom. After introducing our method for the perturbation calculations, these calculations are carried out for three and two dimensions respectively. In the hope to get a more realistic description of actual nanostructures - that are too thin to be considered bulk materials and yet not ideal two dimensional structures - we generalise the results to non-integer dimensions in the next part of the chapter. Lastly, the results for the energy and the eigenfunction are discussed.

Chapter 2

The hydrogen atom in parabolic coordinates

2.1 Introduction

When working with the Stark effect, it turns out that the mathematics can be simplified by using parabolic coordinates. To ease into the equations that arise when working in these coordinates, we start by looking at the simplest case: the hydrogen atom without any external field. The aim in this chapter is to study a hydrogen atom where the electron can move in three and two dimensions respectively. We will show that the Schrödinger equation can be separated in parabolic coordinates and we will use this to find the wave functions for the electron and the energy levels for the bound states.

With no external forces, only the Coulomb potential is present and the Hamiltonian for the system with just one electron is

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r}. \quad (2.1)$$

Here and henceforward Hartree's atomic units have been used. In this system of units the mass of the electron, the elementary charge, \hbar and $1/(4\pi\epsilon_0)$ have been set to unity, [Burkhardt and Leventhal, 2006]. That is

$$m_e = 1, \quad e = 1, \quad \hbar = 1 \quad \text{and} \quad \frac{1}{4\pi\epsilon_0} = 1. \quad (2.2)$$

2.2 The hydrogen atom in three dimensions

At first we look at a hydrogen atom where the electron can move in all directions. In this three-dimensional case the parabolic coordinates (ξ, η, ϕ) are defined through the following relations to the Cartesian coordinates (x, y, z) , [Bransden and Joachain, 2003]

$$x = \sqrt{\xi\eta} \cos \phi, \quad y = \sqrt{\xi\eta} \sin \phi, \quad z = \frac{1}{2} (\xi - \eta), \quad (2.3)$$

where $0 \leq \xi < \infty, 0 \leq \eta < \infty$ and $0 \leq \phi \leq 2\pi$. Rewriting these equations shows that surfaces with constant ξ or constant η are paraboloids of revolution about the z -axis with a maximum or a minimum respectively. Further details are given in appendix A where it is also shown that the parabolic system of coordinates is orthogonal. Simple calculations show that

$$r = \frac{1}{2} (\xi + \eta), \quad \xi = r + z, \quad \eta = r - z. \quad (2.4)$$

2.2.1 Separation in parabolic coordinates

Using the parabolic coordinates, the Schrödinger equation for the hydrogen atom described by Ψ with the Hamiltonian given in equation (2.1) can be expressed

$$\left(-\frac{1}{2} \nabla^2 - \frac{2Z}{\xi + \eta} \right) \Psi(\xi, \eta, \phi) = E \Psi(\xi, \eta, \phi), \quad (2.5)$$

As shown in appendix A in equation (A.17), the Laplacian operator can be expressed

$$\nabla^2 = \frac{4}{\xi + \eta} \left[\frac{\partial}{\partial \xi} \left(\xi \frac{\partial}{\partial \xi} \right) + \frac{\partial}{\partial \eta} \left(\eta \frac{\partial}{\partial \eta} \right) \right] + \frac{1}{\xi\eta} \frac{\partial^2}{\partial \phi^2}. \quad (2.6)$$

We now assume that the solution is of the form

$$\Psi(\xi, \eta, \phi) = u_1(\xi) u_2(\eta) f(\phi), \quad (2.7)$$

and substitute this into equation (2.5) and multiply by $-2\xi\eta/\Psi$ to get

$$\frac{4\xi\eta}{\xi + \eta} \left[\frac{1}{u_1} \frac{d}{d\xi} \left(\xi \frac{du_1}{d\xi} \right) + \frac{1}{u_2} \frac{d}{d\eta} \left(\eta \frac{du_2}{d\eta} \right) \right] + \frac{4Z\xi\eta}{\xi + \eta} + 2E\xi\eta = -\frac{1}{f} \frac{d^2 f}{d\phi^2}. \quad (2.8)$$

Since only the right hand side depends on ϕ , we set it to a constant m^2 . This gives us the differential equation

$$\frac{d^2 f}{d\phi^2} = -m^2 f. \quad (2.9)$$

The normalised solutions are of the form

$$f_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \dots \quad (2.10)$$

where m , defined as the magnetic quantum number, is an integer to ensure that the function has the same value for $\phi = 0$ and $\phi = 2\pi$, [Bransden and Joachain, 2003].

To solve the left hand side of equation (2.8), the two separation constants Z_1 and Z_2 are introduced such that

$$Z = Z_1 + Z_2. \quad (2.11)$$

Using these constants and the solution in equation (2.10), equation (2.8) becomes

$$\frac{1}{u_1} \frac{d}{d\xi} \left(\xi \frac{du_1}{d\xi} \right) + \frac{E\xi}{2} - \frac{m^2}{4\xi} + Z_1 + \frac{1}{u_2} \frac{d}{d\eta} \left(\eta \frac{du_2}{d\eta} \right) + \frac{E\eta}{2} - \frac{m^2}{4\eta} + Z_2 = 0. \quad (2.12)$$

This can be separated into an equation for $u_1(\xi)$

$$\frac{d}{d\xi} \left(\xi \frac{du_1}{d\xi} \right) + \left(\frac{E\xi}{2} - \frac{m^2}{4\xi} + Z_1 \right) u_1 = 0, \quad (2.13)$$

and an equivalent equation for $u_2(\eta)$ that only differ by having the constant term Z_2 instead of Z_1 . So the Schrödinger equation in three dimensions without any external fields has now been separated in parabolic coordinates.

2.2.2 Eigenfunctions of the bound states

In the following we only look at bound states where $E < 0$. To find the eigenfunctions for these states, we solve the part related to ξ by setting, [Bransden and Joachain, 2003]

$$\beta = \sqrt{-2E}, \quad \rho_1 = \beta\xi, \quad \text{and} \quad \lambda_1 = \frac{Z_1}{\beta}. \quad (2.14)$$

With this change of variables, equation (2.13) becomes

$$\frac{d^2 u_1}{d\rho_1^2} + \frac{1}{u_1} \frac{du_1}{d\rho_1} + \left(-\frac{1}{4} + \frac{\lambda_1}{\rho_1} - \frac{m^2}{4\rho_1} \right) = 0. \quad (2.15)$$

Looking at the asymptotic behaviour as $\rho_1 \rightarrow \infty$, this equation reduces to

$$\frac{d^2 u_1}{d\rho_1^2} - \frac{1}{4} u_1 = 0. \quad (2.16)$$

Since $u_1(\rho_1)$ has to be bounded everywhere, the physically acceptable solution in the limit is of the form

$$u_1(\rho_1) \underset{\rho_1 \rightarrow \infty}{\approx} e^{-\frac{1}{2}\rho_1}. \quad (2.17)$$

From this we conclude that the solution to equation (2.15) must be of the form

$$u_1(\rho_1) = U_1(\rho_1) e^{-\frac{1}{2}\rho_1}, \quad (2.18)$$

where $U_1(\rho_1)$ is some function to be determined. When this is inserted in equation (2.15), the equation can be reduced to

$$\frac{d^2 U_1}{d\rho_1^2} - \frac{dU_1}{d\rho_1} + \frac{1}{\rho_1} \left(\frac{dU_1}{d\rho_1} - \frac{1}{2} U_1 \right) + \frac{\lambda_1}{\rho_1} U_1 - \frac{m^2}{4\rho_1^2} U_1 = 0. \quad (2.19)$$

In order to solve this we use the method described in [Bethe and Salpeter, 1957] where we expand $U_1(\rho_1)$ in the power series

$$U_1(\rho_1) = \rho_1^c \sum_{k=0}^{\infty} a_k \rho_1^k, \quad a_0 \neq 0. \quad (2.20)$$

Differentiating this and substituting the result back into equation (2.19) gives us

$$\sum_{k=0}^{\infty} a_k \left\{ \rho_1^{k+c-2} \left[(k+c)^2 - \frac{m^2}{4} \right] + \rho_1^{k+c-1} \left[-(k+c) - \frac{1}{2} + \lambda_1 \right] \right\} = 0. \quad (2.21)$$

For this equation to hold, the coefficients of each power must vanish. Shifting of the indexes leads to

$$\sum_{k=-1}^{\infty} a_{k+1} \rho_1^{k+c-1} \left[(k+c+1)^2 - \frac{m^2}{4} \right] = \sum_{k=0}^{\infty} a_k \rho_1^{k+c-1} \left[(k+c) + \frac{1}{2} - \lambda_1 \right], \quad (2.22)$$

and for the coefficients we therefore get the recurrence relation

$$a_{k+1} = - \frac{(k+c) + \frac{1}{2} - \lambda_1}{(k+c+1)^2 - \frac{m^2}{4}} a_k. \quad (2.23)$$

Now assume that the power series for $U_1(\rho_1)$ does not terminate. Then for large k , we have

$$\frac{a_{k+1}}{a_k} \underset{k \rightarrow \infty}{\approx} \frac{1}{k}. \quad (2.24)$$

To see the implication of this, notice that by the definition of the exponential function, for some b we can write

$$x^b e^x = \sum_{k=0}^{\infty} \frac{x^{b+k}}{k!}, \quad (2.25)$$

where the ratio between the coefficients in this series as $k \rightarrow \infty$ is the same as in equation (2.24). From this we deduce that a power series that does not terminate, leads to a solution with the following asymptotic behaviour as $\rho_1 \rightarrow \infty$:

$$u_1(\rho_1) \underset{\rho_1 \rightarrow \infty}{\approx} \rho_1^c e^{\rho_1} e^{-\frac{1}{2}\rho_1} = \rho_1^c e^{\frac{1}{2}\rho_1}. \quad (2.26)$$

This solution goes to infinity as ρ_1 goes to infinity. Thus it is not valid and the power series for $U_1(\rho_1)$ has to terminate. If we assume that the highest power is n_1 , then a_{n_1+1} has to be zero. Inserted in the recurrence relation in equation (2.23), this gives the requirement that

$$n_1 = \lambda_1 - \frac{1}{2} - c. \quad (2.27)$$

Here c can be found using the fact that the coefficients of each power in equation (2.21) should still vanish. Setting the lowest power of ρ to zero, we get

$$c = \pm \frac{1}{2} |m|, \quad (2.28)$$

where only the positive solution ensures that $U_1(\rho)$ remains finite at the origin. So equation (2.27) can be rewritten as

$$n_1 = \lambda_1 - \frac{1}{2} (1 + |m|), \quad (2.29)$$

and to recap the asymptotic behaviour of the solution as $\rho_1 \rightarrow 0$ is

$$U_1(\rho_1) \underset{\rho_1 \rightarrow 0}{\approx} \rho_1^{\frac{1}{2}|m|}. \quad (2.30)$$

Combining this asymptotic result with the result as $\rho_1 \rightarrow \infty$ in equation (2.18), we see that the solution must be of the form

$$u_1(\rho_1) = e^{-\frac{1}{2}\rho_1} \rho_1^{\frac{1}{2}|m|} \nu(\rho_1), \quad (2.31)$$

where $\nu(\rho_1)$ is a function to be determined. To do this, $u_1(\rho_1)$ is used in the original equation that the function should solve, equation (2.15). Here the first and second order differentiation yields three and nine terms respectively. However, in the total equation several terms cancel out and the equation is reduced to, [Bethe and Salpeter, 1957]

$$\left[\rho_1 \frac{d^2}{d\rho_1^2} + (|m| + 1 - \rho_1) \frac{d}{d\rho_1} + \lambda_1 - \frac{1}{2} (|m| + 1) \right] \nu(\rho_1) = 0. \quad (2.32)$$

This equation is equivalent to the Kummer-Laplace differential equation which has the general form, [Bransden and Joachain, 2003]

$$\left[x \frac{d^2}{dx^2} + (c - x) \frac{d}{dx} - a \right] f(x) = 0. \quad (2.33)$$

In appendix B, section B.1 it is shown that the confluent hypergeometric function

$${}_1F_1(a, c, x) = \sum_{k=0}^{\infty} \frac{(a)_k}{(c)_k} \frac{x^k}{k!} \quad \text{where} \quad \begin{cases} (b)_k = b(b+1)\dots(b+k-1) \\ (b)_0 = 1 \end{cases} \quad (2.34)$$

is a solution to equation (2.33). From the arguments earlier, a physically acceptable solution still requires that the series terminate, leading to a polynomial of degree n_1 . In appendix B, theorem B.5 it is shown that a confluent hypergeometric function of degree $n - p$ is proportional to the associated Laguerre polynomials defined by

$$L_n^p(x) = \frac{d^p}{dx^p} L_n(x) \quad \text{with} \quad L_n(x) = e^x \frac{d^n}{dx^n} (x^n e^{-x}), \quad (2.35)$$

where $L_n(x)$ is the Laguerre polynomial. In theorem B.4 in the appendix it is shown that $L_n^p(x)$ satisfies

$$\left[x \frac{d^2}{dx^2} + (p+1-x) \frac{d}{dx} + (q-p) \right] L_n^p(x) = 0. \quad (2.36)$$

For equation (2.32) this implies that the following is a solution

$$u_1(\rho_1) = C_1 e^{-\frac{1}{2}\rho_1} \rho_1^{\frac{1}{2}|m|} L_{n_1+|m|}^{|m|}(\rho_1), \quad (2.37)$$

where C_1 is some constant. With similar calculations, the solution for the equation for η equivalent to equation (2.13) is found to be

$$u_2(\rho_2) = C_2 e^{-\frac{1}{2}\rho_2} \rho_2^{\frac{1}{2}|m|} L_{n_2+|m|}^{|m|}(\rho_2), \quad (2.38)$$

where $\rho_2 = \beta\eta$ and $n_2 = \lambda_2 - \frac{1}{2}(1 + |m|)$. We now define the principal quantum number n as, [Bransden and Joachain, 2003]

$$n = \lambda_1 + \lambda_2 = n_1 + n_2 + |m| + 1. \quad (2.39)$$

The numbers n_1 and n_2 are related specifically to ξ and η respectively and are named parabolic quantum numbers. Since these are non-negative integers it follows that $n = 0, 1, 2, \dots$

We can now express the eigenfunctions by combining the three solutions found and in total it depends on the three quantum numbers n_1 , n_2 and m , [Bethe and Salpeter, 1957]

$$\Psi_{n_1 n_2 m}(\xi, \eta, \phi) = c u_{1n_1|m|}(\rho_1) u_{2n_2|m|}(\rho_2) \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad (2.40)$$

where $\rho_1 = \beta\xi$, $\rho_2 = \beta\eta$, $\beta = Z/n$ and

$$u_i(\rho_i) = e^{-\frac{1}{2}\rho_i} \rho_i^{\frac{1}{2}|m|} L_{n_i+|m|}^{|m|}(\rho_i), \quad i = 1, 2. \quad (2.41)$$

The constant c is a normalisation constant which is found by requiring that

$$\int |\Psi_{n_1 n_2 m}|^2 dr = \int_0^\infty d\xi \int_0^\infty d\eta \int_0^{2\pi} d\phi |\Psi_{n_1 n_2 m}|^2 \frac{1}{4} (\xi + \eta) = 1. \quad (2.42)$$

Here the volume element in the parabolic coordinates have been calculated in appendix A. In appendix B, calculations of integrals involving the associated Laguerre functions are shown and using the results in equation (B.58), we find that

$$\int_0^\infty e^{-\rho_2} \rho_2^{|m|} [L_{n_2+|m|}^{(|m|)}(\rho_2)]^2 d\eta \int_0^\infty \xi e^{-\rho_1} \rho_1^{|m|} [L_{n_1+|m|}^{(|m|)}(\rho_1)]^2 d\xi = \frac{1}{\beta^3} \frac{(n_1 + |m|)!^3 (n_2 + |m|)!^3}{n_1! n_2!} (2n_1 + |m| + 1). \quad (2.43)$$

Using symmetry for the part multiplied with η and recalling that $n = n_1 + n_2 + |m| + 1$, it is seen that

$$c = \sqrt{2n} \left[\frac{n_1! n_2!}{(n_1 + |m|)!^3 (n_2 + |m|)!^3} \right]^{\frac{1}{2}} \left(\frac{Z}{n} \right)^{3/2}. \quad (2.44)$$

Using this result, the eigenfunctions are

$$\Psi_{n_1 n_2 m}(\xi, \eta, \phi) = \frac{1}{\sqrt{\pi n}} e^{im\phi} c_0 e^{-\frac{1}{2}\beta(\xi+\eta)} (\xi\eta)^{\frac{1}{2}|m|} L_{n_1+|m|}^{(|m|)}(\beta\xi) L_{n_2+|m|}^{(|m|)}(\beta\eta), \quad (2.45)$$

where

$$c_0 = \left[\frac{n_1! n_2!}{[(n_1 + |m|)! (n_2 + |m|)!]^3} \right]^{\frac{1}{2}} \beta^{|m| + \frac{3}{2}}. \quad (2.46)$$

With the parabolic quantum numbers, a characteristic of these eigenfunctions is that they are asymmetrical with respect to the plane $z = 0$, [Bethe and Salpeter, 1957]. To illustrate this we look at Ψ for an electron far away from the nucleus. For large arguments of the associated Laguerre function, the term with highest order has the most influence, and we can approximate $L_n^p(x) \approx x^{n-p}$, [Bethe and Salpeter, 1957]. So far away from the nucleus we have

$$\Psi_{n_1 n_2 m} \approx e^{im\phi} e^{-\frac{1}{2}(\xi+\eta)} \xi^{n_1 + \frac{1}{2}|m|} \eta^{n_2 + \frac{1}{2}|m|}. \quad (2.47)$$

Using this to calculate the probability density function for the electron and changing back to Cartesian coordinates gives

$$|\Psi_{n_1 n_2 m}|^2 \approx e^{-2r} (r+z)^{(n_1 + \frac{1}{2}|m|)} (r-z)^{(n_2 + \frac{1}{2}|m|)}. \quad (2.48)$$

First we notice that the probability is independent of ϕ , so it is cylindrically symmetric about the z -axis. Secondly, it is clear that for $n_1 > n_2$, the probability of having the electron with $z > 0$ is greater than the probability of finding it with $z < 0$, and vice versa for $n_2 > n_1$, [Bethe and Salpeter, 1957]. So for the hydrogen atom in parabolic coordinates the eigenfunctions can have permanent electric dipole moments and this asymmetry in the z -coordinate is what makes parabolic coordinates suitable in situations where one direction is of particular interest, [Burkhardt and Leventhal, 2006].

2.2.3 Energy levels of the bound states

Finally we find the energy levels of the bound states. Recalling that $Z_i = \beta\lambda_i$ for $i = 1, 2$, the relation $Z = Z_1 + Z_2$ and using the definition of n , it is seen that

$$\beta = \frac{Z}{n}. \quad (2.49)$$

Combined with the definition of β as $\sqrt{-2E}$, we see that this leads to discrete energy levels that depend on n

$$E_n = -\frac{1}{2} \frac{Z^2}{n^2}, \quad (2.50)$$

which can also be expressed

$$E_{n_1 n_2 m} = -\frac{1}{2} \frac{Z^2}{(n_1 + n_2 + m + 1)^2}. \quad (2.51)$$

For the hydrogen atom, $Z = 1$ and hence, the energy levels depend only on the quantum number n . From the definition in equation (2.39), it is clear that various combinations of the parabolic quantum numbers and the magnetic quantum number can give the same n and therefore the energies are degenerate. Recall that $n_i \geq 0$ for $i = 1, 2$ and so $|m|$ can take integer values from 0 up to $n - 1$. If $m = 0$, there are n ways to choose the pair (n_1, n_2) and for $|m| > 0$ there are $n - |m|$ possible pairs of (n_1, n_2) , meaning that the total degeneracy of E_n is

$$n + 2 \sum_{|m|=1}^{n-1} (n - |m|) = n + 2 \left[(n-1)n - \frac{n(n-1)}{2} \right] = n^2, \quad (2.52)$$

where the formula for a triangular number has been used in the summation over $|m|$.

For later comparison we also notice that the energy level for the ground state with $n_1 = n_2 = m = 0$ is

$$E_{\text{ground}} = -\frac{1}{2}. \quad (2.53)$$

2.3 The hydrogen atom in two dimensions

Now we look at a hydrogen atom where the movement of the electron is assumed to be restricted to the xz -plane. In this section there will be equations similar to those in three dimensions and this will briefly be commented throughout the section.

2.3.1 Separation in parabolic coordinates

In the two-dimensional case, the parabolic coordinates are defined through the relations, [Alliluev and Popov, 1993]

$$x = \sqrt{\xi\eta}, \quad z = \frac{1}{2}(\xi - \eta), \quad (2.54)$$

where $0 \leq \xi < \infty$ and $0 \leq \eta < \infty$. We find the exact same relations as in equation (2.4) so the Schrödinger equation given in equation (2.1) differs only from the three-dimensional case in the Laplacian operator. In appendix A this is shown to be

$$\nabla^2 = \frac{4}{\xi + \eta} \left[\xi^{\frac{1}{2}} \frac{\partial}{\partial \xi} \left(\xi^{\frac{1}{2}} \frac{\partial}{\partial \xi} \right) + \eta^{\frac{1}{2}} \frac{\partial}{\partial \eta} \left(\eta^{\frac{1}{2}} \frac{\partial}{\partial \eta} \right) \right]. \quad (2.55)$$

In the Schrödinger equation we assume a solution of the form

$$\Psi(\xi, \eta) = u_1(\xi) u_2(\eta), \quad (2.56)$$

and by introducing the separation constants Z_1 and Z_2 , satisfying $Z = Z_1 + Z_2$ like before, we arrive at the following equation for $u_1(\xi)$:

$$\xi^{\frac{1}{2}} \frac{d}{d\xi} \left(\xi^{\frac{1}{2}} \frac{d}{d\xi} \right) + \left(\frac{E\xi}{2} + Z_1 \right) u_1(\xi) = 0. \quad (2.57)$$

For $u_2(\eta)$ the equation only differs by having the constant term Z_2 instead of Z_1 .

2.3.2 Eigenfunctions of the bound states

To find the eigenfunctions of the bound states we proceed as in the three-dimensional case and we use the same scaled variables β, ρ_1 and λ_1 . Then equation (2.57) becomes

$$\xi^{\frac{1}{2}} \frac{d}{d\xi} \left(\xi^{\frac{1}{2}} \frac{d}{d\xi} \right) + \left(\frac{\lambda_1}{\rho_1} - \frac{1}{4} \rho_1 \right) = 0. \quad (2.58)$$

Looking at the asymptotic behaviour as $\rho_1 \rightarrow \infty$, we see that the solution has to be of the form

$$u_1(\rho_1) = e^{-\frac{1}{2}\rho_1} U_1(\rho_1), \quad (2.59)$$

Inserting this in equation (2.58), reduces the equation to

$$\left[\rho_1 \frac{d^2}{d\rho_1^2} + \left(\frac{1}{2} - \rho_1 \right) \frac{d}{d\rho_1} + \frac{\lambda_1}{\beta} - \frac{1}{4} \right] U_1 = 0. \quad (2.60)$$

We recognize this as the differential equation for the associated Laguerre polynomials, see equation (2.36), and hence, the solution can be expressed

$$u_1(\rho_1) = C_1 e^{-\frac{1}{2}\rho_1} L_{n_1 - \frac{1}{2}}^{-\frac{1}{2}}(\rho_1), \quad (2.61)$$

where C_1 is some constant determined by normalisation and where

$$n_1 = \frac{\lambda_1}{\beta} - \frac{1}{4}, \quad (2.62)$$

is the first parabolic quantum number. As in the three-dimensional case, n_1 is a non-negative integer that determines the highest order of the polynomial. Repeating the calculations for the equation for η , we find a similar solution for $u_2(\rho_2)$ where n_1 is replaced by the second parabolic quantum number n_2 , satisfying $n_2 = \frac{\lambda_2}{\beta} - \frac{1}{4}$.

In total we have eigenfunctions of the form

$$\Psi_{n_1 n_2}(\xi, \eta) = c e^{-\frac{1}{2}\beta(\xi+\eta)} L_{n_1-\frac{1}{2}}^{-\frac{1}{2}}(\beta\xi) L_{n_2-\frac{1}{2}}^{-\frac{1}{2}}(\beta\eta), \quad (2.63)$$

where c is a normalisation constant. The calculation of this constant requires a generalisation of the integrals in appendix B for the associated Laguerre functions for non-integer upper indexes. This generalisation has been omitted in this report but the integrals needed for the normalisation can be found for instance in [Nieto, 1979]. We notice that the eigenfunctions in the three-dimensional case in equation (2.45) look similar to the solution in equation (2.63). We can write

$$\Psi_{n_1 n_2 m} \propto e^{-\frac{1}{2}\beta(\xi+\eta)} (\xi\eta)^{\frac{1}{2}|m|} L_{n_1+|m|-\frac{N-3}{2}}^{|m|-\frac{N-3}{2}}(\beta\xi) L_{n_2+|m|-\frac{N-3}{2}}^{|m|-\frac{N-3}{2}}(\beta\eta), \quad (2.64)$$

where N denotes the dimension, i.e. $N = 2, 3$, and where the magnetic quantum number m vanishes, i.e. is set to zero, in the two-dimensional case with no angle dependence. Furthermore, from equation (2.29) and (2.62) we see that the parabolic quantum numbers can be generalised

$$n_i = \frac{\lambda_i}{\beta} - \frac{1}{2} \left(|m| + \frac{N-1}{2} \right), \quad i = 1, 2. \quad (2.65)$$

2.3.3 Energy levels of the bound states

We are now ready to find the energy levels of the eigenfunctions. We used the same scaling as in the three-dimensional case and as in section 2.2.3, we have that the principal quantum number is $n = \lambda_1 + \lambda_2$, which gives us

$$n = n_1 + n_2 + \frac{1}{2}. \quad (2.66)$$

With this we can express the energy levels in terms on the parabolic quantum numbers

$$E_{n_1, n_2} = -\frac{1}{2} \frac{Z}{\left(n_1 + n_2 + \frac{1}{2} \right)^2}. \quad (2.67)$$

It is obvious that various combinations of the parabolic quantum numbers will give the same energy and thus the energies are degenerate like in the three-dimensional case. Another thing to notice is that for the ground state with $n_1 = n_2 = 0$, we have that

$$E_{\text{ground}} = -2. \quad (2.68)$$

This is four times lower than the ground state energy where the electron can move in three directions. So the restriction of the movement makes the electron bound tighter. Lastly we notice that equation (2.65) can be used to generalise the energy levels for $N = 2, 3$ such that

$$E_{n_1 n_2 m} = -\frac{1}{2} \frac{Z}{\left(n_1 + n_2 + |m| + \frac{N-1}{2}\right)^2}. \quad (2.69)$$

This result matches the ground state energies found in [Alliluev and Popov, 1993].

2.4 Conclusion of the hydrogen atom in parabolic coordinates

In this chapter we have used an analytical approach to solve the Schrödinger equation for the hydrogen atom in the cases where the electron can move three and two dimensions. After separating the Schrödinger equation in parabolic coordinates, the eigenfunctions for the bound states are seen to be proportional to

$$\Psi_{n_1 n_2 m} \propto e^{-\frac{1}{2}\beta(\xi+\eta)} (\xi\eta)^{\frac{1}{2}|m|} L_{n_1+|m|-\frac{N-3}{2}}^{|m|-\frac{N-3}{2}}(\beta\xi) L_{n_2+|m|-\frac{N-3}{2}}^{|m|-\frac{N-3}{2}}(\beta\eta), \quad (2.70)$$

where $N = 2, 3$ denotes the dimensions of the system and where m vanishes for $N = 2$ as there is no angle dependence for movement in the plane. For the ground state this reduces to

$$\Psi_{\text{ground}} \propto e^{-\frac{1}{2}\beta(\xi+\eta)} = e^{-\beta r}. \quad (2.71)$$

The energies for the bound states have been found to be

$$E_{n_1 n_2 m} = -\frac{1}{2} \frac{Z}{\left(n_1 + n_2 + |m| + \frac{N-1}{2}\right)^2}. \quad (2.72)$$

Furthermore, we have seen that by using parabolic coordinates, the eigenfunctions become asymmetrical with respect to the plane $z = 0$ which is that makes this system of coordinates useful in situations where especially one direction is of relevance.

Chapter 3

The Stark effect in a hydrogen atom

3.1 Introduction

After having considered the hydrogen atom with no external fields, we will now move on to the main part of the report: a study of the Stark effect in a hydrogen atom. The aim of the chapter is to solve the Schrödinger equation and find the eigenstates and the energy of the electron when a static electric field is applied to the atom. Unlike the analytical approach used until now, perturbation theory will be used in this chapter and after introducing the Schrödinger equation for the Stark effect, the perturbation theory method is presented.

This method is first applied to the cases where the electron is free to move in three and two dimensions. In addition to this, we will also look at the non-integer dimensions in between and find solutions of the wave function and energy of the electron that depends on both the strength of the applied electric field and the dimension of the system. The results are discussed in the end of the chapter.

3.2 The Schrödinger equation for the Stark effect

The perturbation of the Hamiltonian when a uniform static electric field of strength ε is applied to the atom in the positive z -direction is, [Privman, 1980]

$$\hat{H}' = \varepsilon z. \tag{3.1}$$

So the Schrödinger equation with the external field now becomes

$$\left[-\frac{1}{2}\nabla^2 - \frac{Z}{r} + \varepsilon z \right] \Psi = E\Psi, \quad (3.2)$$

which in parabolic coordinates is equivalent to

$$\left[-\frac{1}{2}\nabla^2 - \frac{2Z}{\xi + \eta} + \frac{1}{2}\varepsilon(\xi - \eta) \right] \Psi = E\Psi. \quad (3.3)$$

Before moving on with the perturbation theory, let us briefly look at these equations. In figure 3.1 the potential field due to both the Coulomb potential and the electric field are illustrated and the sum of the two is shown with the full line. The lowering of the potential on the negative z axis is in good agreement with how we would expect the electron of the hydrogen atom to move in the opposite direction of the applied field. It is exactly this effect that rest of the report aims to study to find out what happens with the wave function and the energy of the electron in further details. As mentioned, specifically the dependence on the applied field and the dimensions of the system will be our main interest.

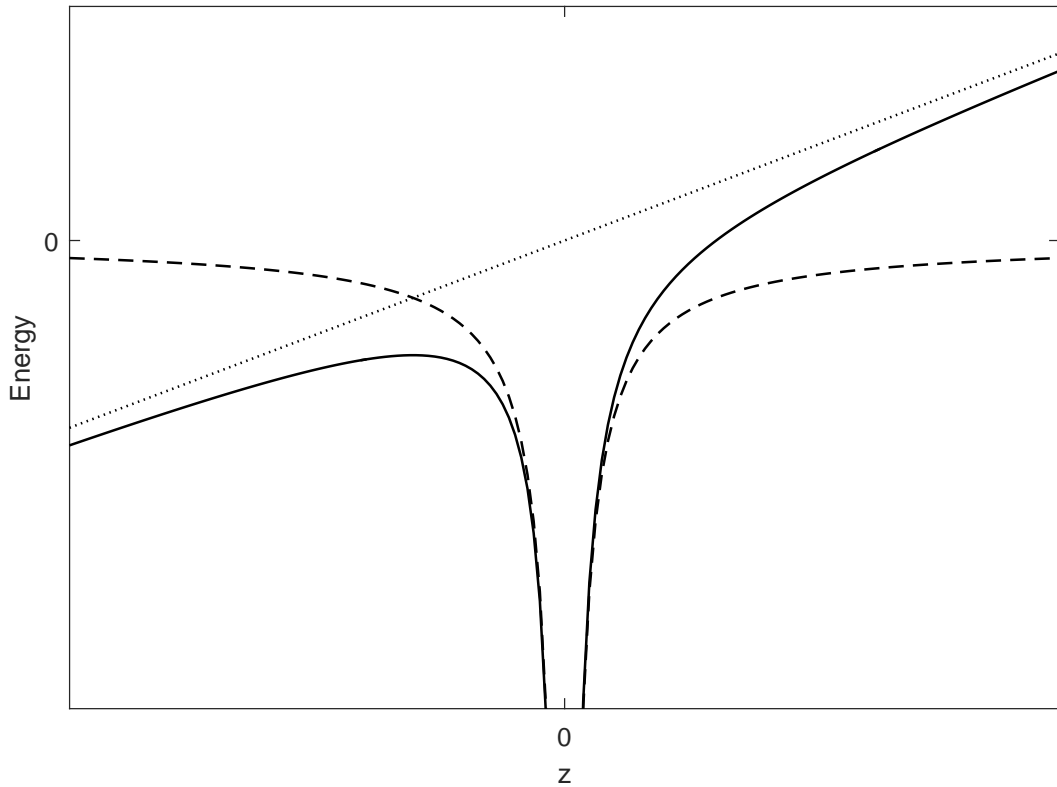


Figure 3.1: Illustration of the potential energies with arbitrary units. The dashed line is the Coulomb potential, the dotted line is the electric potential and the full is the total potential.

3.3 Outline of the perturbation theory method

To be able to solve the Schrödinger equation, we restrict ourselves to looking at electric fields that are small in comparison to the Coulomb field due the nucleus. This way perturbation theory can be applied. The approach for the calculations will be similar to the time independent perturbation theory taught in basic quantum mechanics courses in the sense that we will make expansions of the perturbation of the Hamiltonian and that an equation for each power of these expansions needs to be solved. However, instead of making the usual direct expansions of the wave function and the energy, we will go about it slightly different to simplify the mathematics. We make expansions of Z_1 and Z_2 which will then be turned into an expansion of the energy. Regarding the wave function we will make an expansion of the logarithmic derivative instead of the wave function directly.

In further details, we will use the same perturbation theory method as in [Privman, 1980]. Here the overall idea is to make the perturbation expansion in three steps. Just like in the study of the hydrogen atom with no external fields, we will define β such that $E = -\beta^2/2$ and as in equation (2.39) and (2.49), β will be related to the two separation constants Z_1 and Z_2 . This motivates the following procedure, [Privman, 1980].

- Step 1: Make an expansion of Z_1/β and Z_2/β in powers of the field ε .
- Step 2: Using that $(Z_1 + Z_2)/\beta = 1/\beta$ for the hydrogen atom, make an expansion of $1/\beta$ in powers of the field.
- Step 3: Use the result above to make an expansion of the energy in powers of the field.

Whether the electron is free to move in two or three dimensions will explicitly affect the calculations in step 1, while it will only implicitly affect the results in step 2 and 3. Besides, in step 1 it will become obvious that the calculations enable us to make an expansion of the wave function in powers of ε .

A last comment concerning the perturbation theory, is that we will use the ground state solution for the unperturbed Hamiltonian, [Privman, 1980], i.e. m , n_1 and n_2 from chapter 2 are all set to zero. So all our results will be ground state perturbation expansions.

3.4 Step 0: Setting up the differential equations

The Schrödinger equation depends on the two variables ξ and η and to simplify things we will reduce this to two one-variable differential equations.

In the three- and two-dimensional case, we have already seen the corresponding Laplacian operator in equation (2.6) and (2.55) respectively:

$$\nabla_{3D}^2 = \frac{4}{\xi + \eta} \left[\frac{\partial}{\partial \xi} \left(\xi \frac{\partial}{\partial \xi} \right) + \frac{\partial}{\partial \eta} \left(\eta \frac{\partial}{\partial \eta} \right) \right] + \frac{1}{\xi \eta} \frac{\partial^2}{\partial \phi^2}, \quad (3.4)$$

$$\nabla_{2D}^2 = \frac{4}{\xi + \eta} \left[\xi^{\frac{1}{2}} \frac{\partial}{\partial \xi} \left(\xi^{\frac{1}{2}} \frac{\partial}{\partial \xi} \right) + \eta^{\frac{1}{2}} \frac{\partial}{\partial \eta} \left(\eta^{\frac{1}{2}} \frac{\partial}{\partial \eta} \right) \right], \quad (3.5)$$

As mentioned we will only look at perturbation expansions for the ground state which means that the states will have no angular dependence. It is then easy to see that the Laplacian operator can be generalised to N dimensions for $N = 2, 3$ as

$$\nabla_{ND}^2 = \frac{4}{\xi + \eta} \left[\xi^{-\frac{N-3}{2}} \frac{\partial}{\partial \xi} \left(\xi^{\frac{N-1}{2}} \frac{\partial}{\partial \xi} \right) + \eta^{-\frac{N-3}{2}} \frac{\partial}{\partial \eta} \left(\eta^{\frac{N-1}{2}} \frac{\partial}{\partial \eta} \right) \right]. \quad (3.6)$$

We use this in the Schrödinger equation and look for solutions of the form

$$\Psi(\xi, \eta, \phi) = u_1(\xi) u_2(\eta), \quad (3.7)$$

to get the differential equation

$$\begin{aligned} & \frac{2}{\xi + \eta} \left[\xi^{-\frac{N-3}{2}} \frac{\partial}{\partial \xi} \left(\xi^{\frac{N-1}{2}} \frac{\partial}{\partial \xi} \right) + \eta^{-\frac{N-3}{2}} \frac{\partial}{\partial \eta} \left(\eta^{\frac{N-1}{2}} \frac{\partial}{\partial \eta} \right) \right. \\ & \left. + \frac{2Z}{\xi + \eta} - \frac{\varepsilon}{2}(\xi - \eta) + E \right] u_1 u_2 = 0. \end{aligned} \quad (3.8)$$

As in section 2.2 and 2.3, we introduce the two separation constants Z_1 and Z_2 such that

$$Z_1 + Z_2 = 1, \quad (3.9)$$

where we from now on use that $Z = 1$ for the hydrogen atom to make the notation lighter. Multiplying equation (3.8) by $-(\xi + \eta)/2$ it can be separated into an equation for $u_1(\xi)$ and $u_2(\eta)$ such that

$$\left[\xi^{-\frac{N-3}{2}} \frac{d}{d\xi} \left(\xi^{\frac{N-1}{2}} \frac{d}{d\xi} \right) + Z_1 + \frac{E}{2}\xi - \frac{\varepsilon}{4}\xi^2 \right] u_1 = 0, \quad (3.10)$$

$$\left[\eta^{-\frac{N-3}{2}} \frac{d}{d\eta} \left(\eta^{\frac{N-1}{2}} \frac{d}{d\eta} \right) + Z_2 + \frac{E}{2}\eta + \frac{\varepsilon}{4}\eta^2 \right] u_2 = 0. \quad (3.11)$$

3.4.1 The potential for u_1 and u_2

Before simplifying this further, we will look at the implications of these two equations. Aside from Z_1 and Z_2 , we notice that the only difference between the two is the sign of the term proportional to the strength of the field. If we multiply by -1 to get slightly closer to the form of the Schrödinger equation, we see that the equation for

U_1 has a term similar to the harmonic oscillator, that is $+\varepsilon\xi^2/4$. This indicates that ξ -coordinate of the electron experiences a restoring force, $F = -\varepsilon\xi/4$, that will pull it back towards the centre of the nucleus. For U_2 on the other hand, the term with opposite sign indicates that η -coordinate of the electron will experience a repelling force, $F = +\varepsilon\eta/4$, that will push the electron away from the centre of the nucleus.

Since equation (3.10) and (3.11) are not fully of the same form as a one-dimensional Schrödinger equation, these interpreted terms are not fully correct potentials. But with a few calculations we can get a more precise interpretation. Using the same approach as in [Bransden and Joachain, 2003] for N dimensions, we briefly introduce G_1 and G_2 satisfying that

$$u_1 = \xi^{-\frac{N-1}{4}} G_1, \quad \text{and} \quad u_2 = \eta^{-\frac{N-1}{4}} G_2. \quad (3.12)$$

This makes us able to rewrite equation (3.10) and (3.11) such that

$$-\frac{1}{2} \frac{d^2}{d\xi^2} G_1 + \left[\frac{1}{2} \left(\frac{N^2}{16} - \frac{3N}{8} + \frac{5}{16} \right) \frac{1}{\xi^2} - \frac{Z_1}{2\xi} + \frac{\varepsilon}{8} \xi \right] G_1 = \frac{E}{4} G_1, \quad (3.13)$$

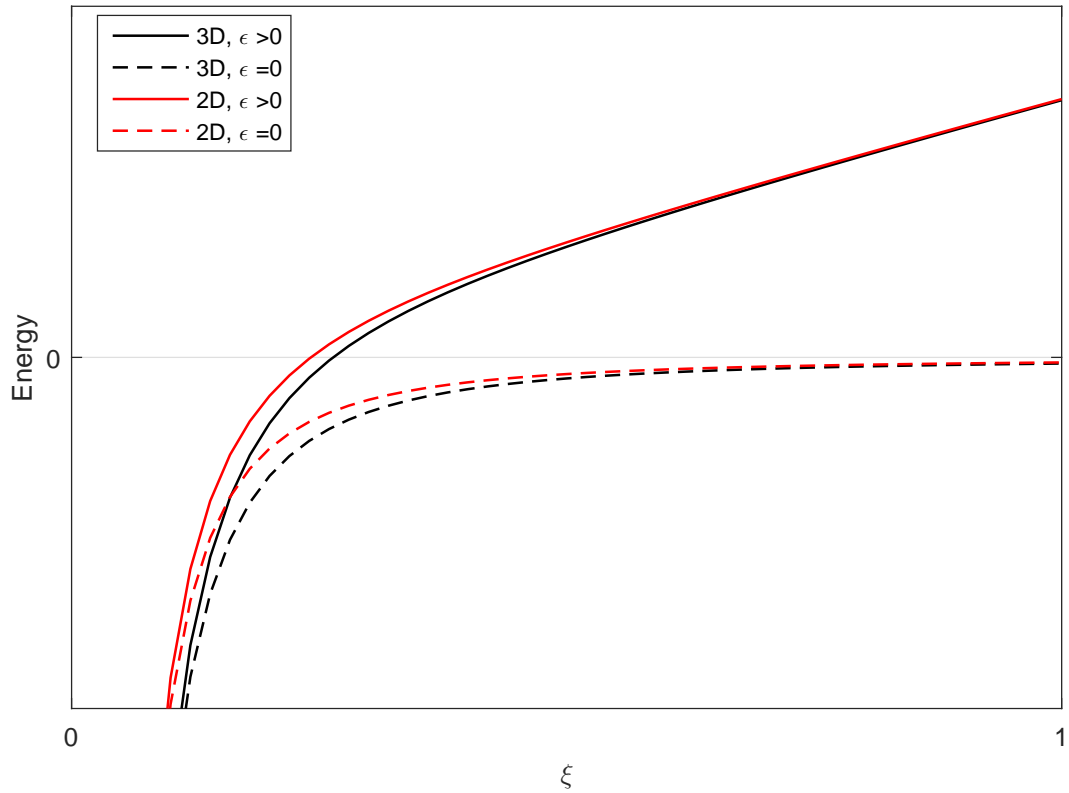
$$-\frac{1}{2} \frac{d^2}{d\eta^2} G_2 + \left[\frac{1}{2} \left(\frac{N^2}{16} - \frac{3N}{8} + \frac{5}{16} \right) \frac{1}{\eta^2} - \frac{Z_2}{2\eta} - \frac{\varepsilon}{8} \eta \right] G_2 = \frac{E}{4} G_2. \quad (3.14)$$

In three-dimensional case this matches the result in [Bransden and Joachain, 2003]. Now these equations are of the same form as the Schrödinger equation where $E/4$ is the new energy for G_1 and G_2 . So here we can identify the potentials for G_1 and for G_2 as the terms inside the square brackets. In figure 3.2a and 3.2b the two potentials have been plotted for two and three dimensions for $G_1(\xi)$ and $G_2(\eta)$ respectively. We have not solved the equation and found Z_1 and Z_2 yet, so these are just set to a value to illustrate the shape of the functions. The dashed lines represent the potentials with no external field. Naturally there is no asymmetry and as we would expect, it looks similar to the Coulomb potential for both ξ and η . The full lines represent the potentials with an arbitrary positive electric field. Comparing with figure 3.1 we recognize the shape of the potentials where the effect has been split up to two coordinates. For the ξ -coordinate of the electron, the potential continues to grow larger for $\xi \rightarrow \infty$ which will stop $G_1(\xi)$ from going to large values of ξ . But for the η -coordinate the potential has a finite maximum. Hence, it would not be unlikely to find $G_2(\eta)$ at large values of η if the electron can penetrate the potential barrier. This will be commented again later.

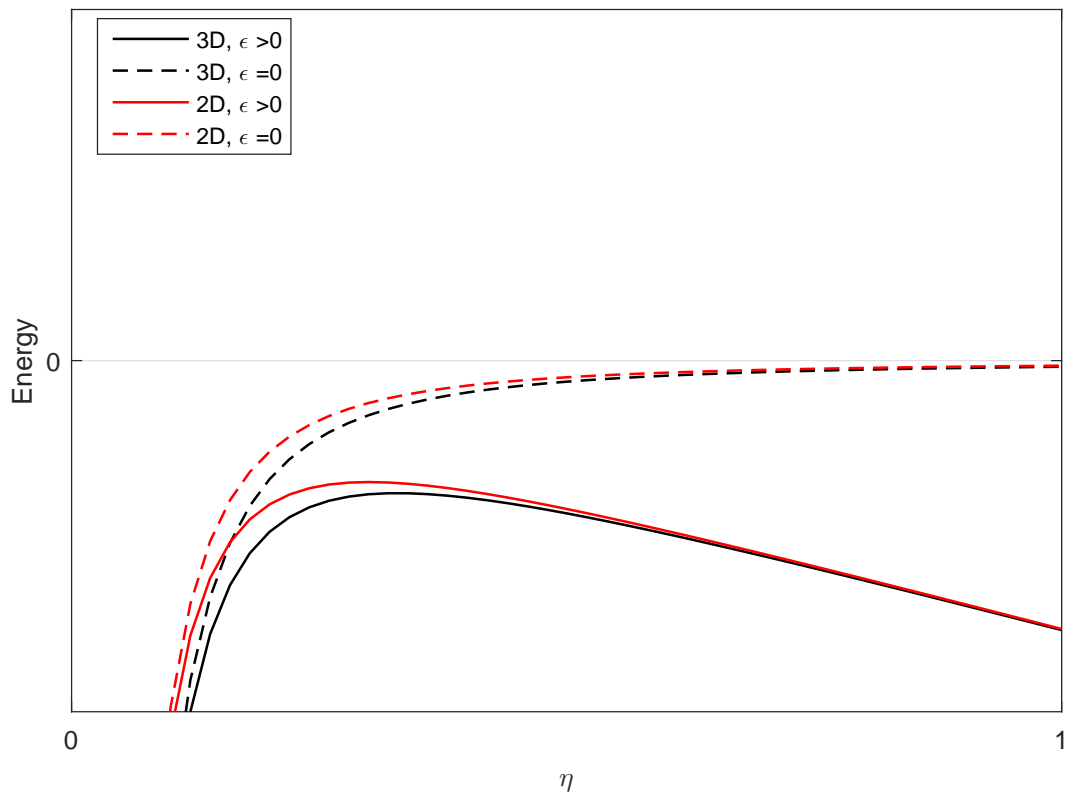
3.4.2 Preparing for the perturbation theory method

We return to the differential equations for $u_1(\xi)$ and $u_2(\xi)$ found in equation (3.10) and (3.11). Before we apply our perturbation theory method, we define

$$\beta = \sqrt{-2E}, \quad \rho_1 = \beta\xi, \quad \text{and} \quad \rho_2 = \beta\eta, \quad (3.15)$$



(a)



(b)

Figure 3.2: (a) Illustration of the potential for $G_1(\xi)$ with arbitrary units. Values for Z_1 and the strength of the electric field have been chosen to visibly show the tendencies. The black and red line are for the three- and two-dimensional case respectively with the same values for Z_1 and ϵ . The dashed line shows the potential without an external field, and the full line is for $\epsilon > 0$. (b) The same illustration as (a) but with the potential for $G_2(\eta)$.

like before in section 2.2.2 and 2.3.2. Using the change of variables and dividing by β , equation (3.10) becomes, [Privman, 1980]

$$\left(\rho_1 \frac{d^2}{d\rho_1^2} + \frac{N-1}{2} \frac{d}{d\rho_1} + B - \frac{1}{4}\rho_1 - F\rho_1^2 \right) u_1 = 0. \quad (3.16)$$

Here B and F defined as

$$B = \frac{Z_1}{\beta} \quad \text{and} \quad F = \frac{\varepsilon}{4\beta^3}, \quad (3.17)$$

have been introduced to simplify the notation. Regarding the three perturbation steps, it should be noticed that some of our expansions of the field will be through F . The equation for u_2 takes the same form, except from the sign of F . Later it will become clear that we only need to focus on the part of the wavefunction for ξ as the results for the part related to η can be found from these results with only a few arguments. So with equation (3.16), we are ready to proceed with the perturbation steps.

3.5 Step 1: Expansion of $B(F)$

In the first perturbation theory step, we make an expansion of B in terms of F . To do this we need equation (3.16) and we simplify this by using the logarithmic derivative as in [Privman, 1980]. We define

$$v = \frac{u'_1}{u_1}, \quad (3.18)$$

and differentiation of $v(\rho_1)$ with respect to ρ_1 leads to the relation

$$v' + v^2 = \frac{u''_1}{u_1}. \quad (3.19)$$

Using this, equation (3.16) becomes

$$\rho_1 (v' + v^2) + \frac{N-1}{2}v + B - \frac{1}{4}\rho_1 - F\rho_1^2 = 0. \quad (3.20)$$

Now we are ready to use perturbation theory expansions and we substitute both

$$B = \sum_{n=0}^{\infty} b_n F^n \quad (3.21)$$

$$v(\rho_1) = \sum_{n=0}^{\infty} v_n(\rho_1) F^n, \quad (3.22)$$

into equation (3.20). The coefficient of each power of F must be zero and hence, we are left with a differential equation for each power of F .

3.5.1 Solution without an electric field, F^0

When no external field is applied, the equation is

$$\rho_1 (v'_0 + v_0^2) + \frac{N-1}{2}v_0 + b_0 - \frac{1}{4}\rho_1 = 0. \quad (3.23)$$

In this case the situation is just the same as in chapter 2 and for the ground state, the solutions for $u_1(\rho_1)$ found in equation (2.41) and (2.61) for three and two dimensions are both proportional to $e^{-\rho_1/2}$. This implies that $v_0 = -1/2$. It is easily verified that this solution indeed solves equation (3.23) when $b_0 = (N-1)/4$.

3.5.2 Solution for the first order equation, F^1

To find the coefficient for F^1 , it is first easily seen that

$$v^2 = v_0^2 + \sum_{k=1}^{\infty} \left[2v_0v_k + \sum_{n=1}^{k-1} v_nv_{k-n} \right] F^k. \quad (3.24)$$

Using this and the value for v_0 in equation (3.20), we get the following first-order equation

$$v'_1 + \left(\frac{N-1}{2\rho_1} - 1 \right) v_1 = \rho_1 - \frac{b_1}{\rho_1}, \quad (3.25)$$

after dividing by ρ_1 . This is a differential equation of the form

$$f'(\rho_1) + P(\rho_1)f(\rho_1) = Q(\rho_1), \quad (3.26)$$

where $f = v_1$, $P = (N-1)/(2\rho_1) - 1$ and $Q = \rho_1 - b_1/\rho_1$. We solve this type of linear differential equation by multiplying with some function g called the integrating factor, satisfying $g' = gP$, to get, [Hyslop et al., 1970]

$$(fg)' = gQ. \quad (3.27)$$

Separation of variables gives us $g = e^{\int P d\rho_1}$ and integrating equation (3.27) gives the solution

$$f' = e^{-\int P d\rho_1} \int e^{\int P} Q d\rho_1 + c, \quad (3.28)$$

where c is some integration constant determined by the initial conditions, [Hyslop et al., 1970]. For equation (3.25) the integrating factor is

$$e^{\int \left(\frac{N-1}{2\rho_1} - 1 \right) d\rho_1} = e^{(N-1)\ln(\rho_1)/2 - \rho_1} = \rho_1^{(N-1)/2} e^{-\rho_1}, \quad (3.29)$$

and we find the solution

$$v_1 = e^{\rho_1} \rho_1^{-\frac{N-1}{2}} \int \left(\rho_1' - \frac{b_1}{\rho_1'} \right) \rho_1'^{\frac{N-1}{2}} e^{-\rho_1'} d\rho_1'. \quad (3.30)$$

Due to the electric field, the electron should not be localised infinitely far out on the positive z -axis. Recalling the potential in figure 3.2a, we see that this is equivalent to requiring $v_1(\infty) = 0$ when we work in parabolic coordinates. We use this to make a definite integral where the integration constant is no longer needed. We then have

$$-v_1 = e^{\rho_1} \rho_1^{-\frac{N-1}{2}} \int_{\rho_1}^{\infty} \left(\rho_1' - \frac{b_1}{\rho_1'} \right) \rho_1'^{\frac{N-1}{2}} e^{-\rho_1'} d\rho_1'. \quad (3.31)$$

The way to solve this equation can depend on the value of N . The integral takes the simplest form for $N = 3$ so we will look at this case first.

Solution for the first order equation in 3D

In the three-dimensional case, equation (3.31) simplifies to

$$-v_{1,3D} = \frac{e^{\rho_1}}{\rho_1} \int_{\rho_1}^{\infty} \left(\rho_1'^2 - b_{1,3D} \right) e^{-\rho_1'} d\rho_1'. \quad (3.32)$$

Here we notice two things. First, using integration by parts n times, it is easily found that

$$\int_x^{\infty} x'^n e^{-x'} dx' = \left(x^n + nx^{n-1} + \dots + n! \right) e^{-x} = \left(\sum_{k=0}^n \frac{n!}{(n-k)!} x^{n-k} \right) e^{-x}. \quad (3.33)$$

This means that the integral over $\rho_1'^2 e^{-\rho_1'}$ will contain one term with a constant coefficient of e^{ρ_1} . Second, we notice that if the full integral in equation (3.32) consists of a term that is only proportional to e^{ρ_1} , i.e. the coefficient does not include ρ_1 , the solution v_1 will not be regular at $\rho_1 = 0$. Therefore, to ensure regularity, the coefficient $b_{1,3D}$ must be chosen such that the integral over $-b_{1,3D} e^{-\rho_1'}$ cancels out with the term with a constant coefficient. Using equation (3.33) it is seen that the term with constant coefficient in the sum can be found by setting the lower limit to zero. So we must have that

$$b_{1,3D} = \int_0^{\infty} \rho_1'^2 e^{-\rho_1'} d\rho_1' = 2. \quad (3.34)$$

Using this in equation (3.32) we find that

$$-v_{1,3D} = \rho_1 + 2. \quad (3.35)$$

Solution for the first order equation in 2D

In the two-dimensional case, things are slightly more complicated. Equation (3.31) becomes

$$-v_{1,2D} = e^{2\rho_1} \frac{1}{\sqrt{\rho_1}} \int_{\rho_1}^{\infty} \left(\rho_1'^{3/2} - b_{1,2D} \rho_1'^{-1/2} \right) e^{-\rho_1'} d\rho_1'. \quad (3.36)$$

To solve this integral we need the error function and the complementary error function which are defined, [Oldham et al., 2009]

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt, \quad \text{and} \quad \operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^{\infty} e^{-t^2} dt. \quad (3.37)$$

These functions have the property that $\operatorname{erf}(x) + \operatorname{erfc}(x) = 1$. The error function is also related to the confluent hypergeometric function:

$$\operatorname{erf}(x) = \frac{2x}{\sqrt{\pi}} e^{-x^2} {}_1F_1\left(1, \frac{3}{2}, x^2\right). \quad (3.38)$$

Recalling the definition in equation (2.34), we see that this implies that the complementary error function expressed using the hypergeometric function includes a term that is simply 1 and is hence not proportional to x to any power.

To solve equation (3.36), we look at the two terms in the integral separately. To solve the integral multiplied by $b_{1,2D}$, we substitute $\rho_1 = t^2$ to find

$$\int_{\rho_1}^{\infty} \rho_1'^{-1/2} e^{-\rho_1'} d\rho_1' = \sqrt{\pi} \operatorname{erfc}(\sqrt{\rho_1}). \quad (3.39)$$

To solve the other part of the equation, we need to integrate an expression of the form $x^{n/2}e^{-x}$, where n is an odd positive integer. Using integration by parts $(n-1)/2$ times, it is found that

$$\begin{aligned} \int_x^{\infty} y^{n/2} e^{-y} dy &= e^{-x} \left[x^{n/2} + \frac{n}{2} x^{n/2-1} + \frac{n}{2} \left(\frac{n}{2} - 1 \right) x^{n/2-2} + \dots \right. \\ &\quad \left. + \frac{n}{2} \left(\frac{n}{2} - 1 \right) \dots \left(\frac{3}{2} \right) x^{1/2} \right] \\ &\quad + \frac{n}{2} \left(\frac{n}{2} - 1 \right) \dots \left(\frac{1}{2} \right) \int_x^{\infty} y^{-1/2} e^{-y} dy. \end{aligned} \quad (3.40)$$

Introducing the notation $(n)_{-1,k} = n(n-1)(n-2)\dots(n-k+1)$ with $n_{-1,0} = 1$, we can simplify the expression

$$\int_x^{\infty} y^{n/2} e^{-y} dy = e^{-x} \sum_{k=0}^{\frac{n-1}{2}} \binom{n}{2}_{-1,k} x^{n/2-k} + \binom{n}{2}_{-1, \frac{n+1}{2}} \sqrt{\pi} \operatorname{erfc}(\sqrt{x}). \quad (3.41)$$

where the result from equation (3.39) has been used for the last term. We now use this result for $n = 3$ and combine it with the result in equation (3.39) to find $v_{1,2D}$ from equation (3.36). We get

$$-v_{1,2D} = e^{2\rho_1} \frac{1}{\sqrt{\rho_1}} \left[e^{-\rho_1} \left(\rho_1^{3/2} + \frac{3}{2} \rho_1^{1/2} \right) + \sqrt{\pi} \operatorname{erfc}(\sqrt{\rho_1}) \left(\frac{3}{4} - b_{1,2D} \right) \right]. \quad (3.42)$$

Since the complementary error function contains a term proportional to 1, the only way to ensure regularity at $\rho_1 = 0$ is to make the coefficient of $\operatorname{erfc}(\sqrt{\rho_1})$ zero. This implies that $b_{1,2D} = 3/4$. Since $\operatorname{erfc}(0) = 1$ this can also be found by using (3.41) in the following way

$$b_{1,2D} = \sqrt{\frac{1}{\pi}} \int_0^\infty y^{3/2} e^{-y} dy = \frac{3}{4}. \quad (3.43)$$

With this result, v_1 in equation (3.42) becomes

$$-v_{1,2D} = \rho_1^{1/2} + \frac{3}{2}. \quad (3.44)$$

3.5.3 Solution for the k 'th order equation, F^k

Now that v_0 and v_1 have been found, we combine equation (3.20) and (3.24) to find the coefficient for F^k , where $k > 1$. Using the boundary conditions, we get

$$v_k = e^{\rho_1} \rho_1^{-\frac{N-1}{2}} \int_{\rho_1}^\infty \left(\frac{b_k}{\rho_1'} + \sum_{n=1}^{k-1} v_n v_{k-n} \right) e^{-\rho_1'} \rho_1'^{\frac{N-1}{2}} d\rho_1', \quad k > 1. \quad (3.45)$$

For both the three- and two-dimensional case, the solution v_1 ensures that the integral for all $k > 1$ remains in a form such that the formulas for integration by parts in equation (3.33) and (3.41) still apply. In both cases b_k is found by ensuring regularity.

For the three-dimensional case, v_1 is a polynomial with integer coefficients, and it then follows that the summation in equation (3.45) will give a polynomial with integer coefficients for all $k > 1$ as well. From the regularity argument we have that

$$b_{k,3D} = - \int_0^\infty \rho_1' e^{-\rho_1'} \sum_{n=1}^{k-1} v_n v_{k-n} d\rho_1', \quad k > 1, \quad (3.46)$$

from which it is clear b_k will be integers for all k . Both v_k and b_k has been found using MATLAB and the first ten values for b_k can be seen in table 3.1a. All these are in agreement with the results in [Privman, 1980]. The algorithm used to find these coefficients and the rest of the values found in the remaining perturbation steps can be found in appendix C.

For the two-dimensional case, v_1 is a sum of power functions with rational coefficients and exponents. Again this implies that all v_k for $k > 1$ will be the same type of function. The regularity argument gives us

$$b_k = -\sqrt{\frac{1}{\pi}} \int_0^\infty \rho_1^{1/2} e^{-\rho_1} \sum_{n=1}^{k-1} v_n v_{k-n} d\rho_1', \quad k > 1, \quad (3.47)$$

and b_k is a rational number for all k . The first ten values for b_k can be found in table 3.1b.

Table 3.1: The first ten coefficients in the expansion $B(F) = \sum_{n=0}^\infty b_n F^n$ for two and three dimensions.

(a) Three dimensions		(b) Two dimensions	
n	$b_{n,3D}$	n	$b_{n,2d}$
0	1/2	0	1/4
1	2	1	3/4
2	-18	2	-21/4
3	356	3	333/4
4	-10026	4	-30885/16
5	353004	5	916731/16
6	-14648676	6	-65518401/32
7	693735432	7	2723294673/32
8	-36761448858	8	-1030495099053/256
9	2151195801980	9	54626982511455/256

3.5.4 Solutions for the differential equation for η

Based on the differential equation for ξ we have now found the coefficients in our expansions of B and $v(\rho_1)$. Recall that $v(\rho_1)$ is related to the ξ -part of the original wavefunction, $\Psi(\xi, \eta) = u_1(\xi) u_2(\eta)$ by equation (3.18). To be able to find the eigenfunctions later, we also need to know the behaviour of the part of the wavefunction related to η . By comparing equation (3.10) and (3.11) we will now find the solutions for the second part of the wavefunction using the same type of expansions as in equation (3.21) and (3.22).

Let us first rewrite equation (3.11) using the scale of variables and logarithmic derivative. To clarify that it is the second part of the wavefunction, a slightly heavier notation is used where $B_\eta = Z_2/\beta$ and $v_\eta = u_2'/u_2$. The equation is

$$\rho_2 (v_\eta' + v_\eta^2) + \frac{N-1}{2} v_\eta + B_\eta - \frac{1}{4} \rho_2 + F \rho_2^2 = 0. \quad (3.48)$$

Comparing this to the equivalent equation related to ξ , (3.20)

$$\rho_1 \left(v'_\xi + v_\xi^2 \right) + \frac{N-1}{2} v_\xi + B_\xi - \frac{1}{4} \rho_1 - F \rho_1^2 = 0, \quad (3.49)$$

where the index ξ has been added to avoid confusion, we see that the equation when no field is applied is exactly the same. Hence, $v_{\eta,0} = v_{\xi,0} = -1/2$ and $b_{\eta,0} = b_{\xi,0} = (N-1)/4$. This is in agreement with the result in chapter 2 where the ground state solution with no field is proportional to $e^{-(\rho_1+\rho_2)/2}$.

This implies that the integrating factor used when solving equation (3.48) takes the same form as it does for equation (3.49). For the first order equation it is easy to see that the opposite sign of the last squared term leads to solutions for $v_{\eta,1}$ and $b_{\eta,1}$ of the same form but with opposite signs. So $b_{1,\eta} = -b_{1,\xi}$ and

$$v_{\eta,1,3D} = \rho_2 + 2, \quad \text{and} \quad v_{\eta,1,2D} = \frac{1}{2} \rho_1^{1/2} + \frac{3}{8}, \quad (3.50)$$

which is in comparison to

$$v_{\xi,1,3D} = -(\rho_2 + 2), \quad \text{and} \quad v_{\xi,1,2D} = -\left(\frac{1}{2} \rho_1^{1/2} + \frac{3}{8} \right). \quad (3.51)$$

Moving on to the k 'th order equation, we see that the structure of the formula for the equation for η is the same as for ξ in equation (3.45). Clearly the opposite sign of b_1 does not influence the calculations. But in the summation $\sum_{n=1}^{k-1} v_n v_{k-n}$ it only takes a few simple calculations to see that the opposite sign of $v_{\eta,1}$ means that $v_{\eta,k}$ will be of the opposite sign for all odd k . So each v_k will have the same structure for ξ and η while the sign alternates. Thus the results found for v_ξ can be used to find the expansion of v_η . To summarize, we let v_n be the functions we have already found for ξ and we can write

$$v_\xi(\rho_1) = \sum_{n=0}^{\infty} v_n F^n, \quad \text{and} \quad v_\eta(\rho_2) = \sum_{n=0}^{\infty} (-1)^n v_n F^n. \quad (3.52)$$

where the variable is of course changed from ρ_1 to ρ_2 in the expansion for v_η . In the expansions for B_ξ and B_η , the absolute values for b_η will remain the same as they are still found by regularity requirements. From equation (3.52) it follows that $b_{\eta,k} = b_{\xi,k}$ for k even and $b_{\eta,k} = -b_{\xi,k}$ for k odd.

3.6 Step 2: Expansion of $1/\beta$

Having found the coefficients in the expansion for $B = Z_1/\beta$, we are ready for the second step of the perturbation theory. Here we make an expansion of $1/\beta$ in terms of the applied electric field. To find the expansion, recall equation (3.9): $Z_1 + Z_2 = 1$.

Dividing by β and substituting the expansions of B related to each coordinate, we get that, [Privman, 1980]

$$\frac{1}{\beta} = B_{\xi}(F) + B_{\eta}(F) = \sum_{n=0}^{\infty} b_n F^n + \sum_{n=0}^{\infty} (-1)^n b_n F^n. \quad (3.53)$$

Simplifying and using equation (3.17), this becomes

$$\frac{1}{\beta} = \sum_{n=0}^{\infty} 2b_{2n} \left(\frac{\varepsilon}{4}\right)^{2n} \left(\frac{1}{\beta^3}\right)^{2n}. \quad (3.54)$$

From this we see that the expansion of $1/\beta$ will be of the form

$$\frac{1}{\beta} = \sum_{n=0}^{\infty} c_{2n} \varepsilon^{2n}. \quad (3.55)$$

When this is substituted into equation (3.54), c_{2n} is found by setting the coefficients of each power of ε equal. Here we see how to find the first three coefficients:

$$\begin{aligned} c_0 + c_2 \varepsilon^2 + c_4 \varepsilon^4 + O(\varepsilon^6) &= 2b_0 + \frac{2b_2}{4^2} \varepsilon^2 \left[c_0 + c_2 \varepsilon^2 + O(\varepsilon^4) \right]^6 + \frac{2b_4}{4^2} \varepsilon^4 \left[c_0 + O(\varepsilon^2) \right]^{12} \\ &= 2b_0 + \left(\frac{2b_2}{4^2} c_0^6 \right) \varepsilon^2 + \left(\frac{2b_2}{4^2} 6c_0^5 c_2 + \frac{2b_4}{4^4} c_0^{12} \right) \varepsilon^4 + O(\varepsilon^6). \end{aligned} \quad (3.56)$$

Using the value for b_0 , we get c_0 and with this and the value for b_2 , c_2 can be found and so on. The first six values of c_{2n} for the three-dimensional case are shown in table 3.2a and the first six values for the two-dimensional case are shown in table 3.2b. The algorithm used to find these can be found in appendix C.

Table 3.2: The first six coefficients in the expansion $1/\beta(\varepsilon) = \sum_{n=0}^{\infty} c_{2n} \varepsilon^{2n}$ for two and three dimensions.

(a) Three dimensions		(b) Two dimensions	
n	$c_{2n,3D}$	n	$c_{2n,2D}$
0	1	0	1
1	-9/4	1	-21/1024
2	-3069/64	2	-20301/4194304
3	-2335389/512	3	-45947829/8589934592
4	-12426906909/16384	4	-774387617277/70368744177664
5	-24717664942335/131072	5	-5112273432973143/144115188075855872

3.7 Step 3: Expansion of the energy

In the last step of the perturbation theory, we are finally able to make an expansion of the energy as a function of the electric field. From the relations in equation (3.15), we have that

$$E = -\frac{1}{2}\beta^2. \quad (3.57)$$

Using the expansion of $1/\beta$ it is seen that

$$\beta^2 = \frac{1}{(c_0 + c_2\varepsilon^2 + c_4\varepsilon^4 + \dots)^2} = \frac{1}{c_0^2 + 2c_0c_2\varepsilon^2 + (2c_0c_4 + c_2^2)\varepsilon^4 + \dots}, \quad (3.58)$$

which is a function of the form $1/(a+x)$. The terms in x get smaller for each power of ε and we approximate the expression by its Taylor series around zero:

$$\frac{1}{a+x} \approx \frac{1}{a} - \frac{1}{a^2}x + \frac{1}{a^3}x^2 - \frac{1}{a^4}x^3 + \dots = \sum_{n=0}^{\infty} \frac{(-1)^n}{a^{n+1}}x^n. \quad (3.59)$$

Writing the energy as

$$E = \sum_{n=0}^{\infty} e_{2n}\varepsilon^{2n}, \quad (3.60)$$

and combining this with equation (3.57), we again find e_{2n} by equating the coefficients for each power of ε on each side. To show the principle we illustrate how to find the first three coefficients.

$$e_0 + e_2\varepsilon^2 + e_4\varepsilon^4 + O(\varepsilon^6) = -\frac{1}{2} \left[\frac{1}{c_0^2} - \frac{2c_0c_2}{c_0^4}\varepsilon^2 + \left(\frac{4c_0^2c_2^2}{c_0^6} - \frac{c_2^2 + 2c_0c_4}{c_0^4} \right) \varepsilon^4 + O(\varepsilon^6) \right] \quad (3.61)$$

Hence, using the coefficients in the expansion of $1/\beta$ we can find the perturbation expansion for the energy. The first six values for the coefficients are presented in table 3.3a for the three-dimensional case and in table 3.3b for the two-dimensional case. As previously, the algorithm used to make the calculations can be found in appendix C. We notice that the results in table 3.3a matches the results in [Privman, 1980]. Furthermore, the first four results in table 3.3b are in agreement with [Yang et al., 1991], where only the first four values are explicitly mentioned.

3.8 The Stark effect for non-integer dimensions

Already now there are several results worth commenting. However, before doing so we will venture one step deeper into the solution of the Schrödinger equation for the Stark effect.

Table 3.3: The first six coefficients in the expansion $E(\varepsilon) = \sum_{n=0}^{\infty} e_{2n} \varepsilon^{2n}$ for two and three dimensions.

(a) Three dimensions		(b) Two dimensions	
n	$e_{2n,3D}$	n	$e_{2n,2D}$
0	$-1/2$	0	-2
1	$-9/4$	1	$-21/256$
2	$-3555/64$	2	$-22947/1048576$
3	$-2512779/512$	3	$-48653931/2147483648$
4	$-13012777803/16384$	4	$-800908686795/17592186044416$
5	$-25497693122265/131072$	5	$-5223462120917049/36028797018963968$

So far we have studied the cases where the electron is free to move specifically in two and three dimensions. Mathematically, this way of describing it is what might be intuitively easiest to understand and plot, etc. But looking at it from the physical point of view, creating for instance a material that is purely flat with no depth, or creating an environment where the electron is fully confined only in the plane, is not that realistic. From other areas of physics, we know that the properties of materials differ when we look at a bulk material and a quantum well or quantum wire, [Saleh and Teich, 2007]. So just assuming that the not perfectly two-dimensional confinement is equivalent to a bulk material might be too coarse an assumption. Now imagine that we treat the problem as for example a 2.1- or 2.2-dimensional case instead. If we can accept the abstract idea of not only having the usual one, two and three spatial dimensions, it seems intuitively possible that the 2.1 or 2.2 dimension could lead to theoretical results that match experimental results better than the mathematics based on integer dimensions.

This line of thinking motivates the idea of generalising our solutions to the Schrödinger equation to non-integer dimensions, both the result for the wavefunction $\Psi = u_1 u_2$ and the expansion for the energy. So we will now solve the Schrödinger equation for N dimensions. Since some complications arise for the Coulomb potential in one dimension, [Raff and Palma, 2006] and since it is not immediately clear what it means for an electron to move in four dimensions, we only let N take the value of any number between 2 and 3, i.e. $2 \leq N \leq 3$. With this restriction all results can also be verified in the lower and upper limit with the calculations made so far.

3.8.1 Perturbation theory for N dimensions

We will solve the Schrödinger equation using the same perturbation theory method presented so far. When we restrict ourselves to perturbation expansions for the ground state, we already found a generalised formula for the Laplacian operator for $N = 2, 3$ in section 3.4. Our interpolation of this to formula to the non-integers in between

will follow the very simple approach described in [Andrew and Supplee, 1990], where we just allow N to take the value of the real numbers between the two integers. This approach makes both the differential equation (3.16) and (3.20) valid for non-integer dimensions as well. So we can easily go to the first step of our perturbation theory method.

Step 1: Expansion of $B(F)$

In the first step of the perturbation theory recall that we used expansions of B and $v = u'_1/u_1$ and found the coefficients by solving the equation for each power of F . For the equation with no applied electric field, we found $v_0 = -1/2$ and $b_0 = (N - 1)/4$ and these solutions still apply for the non-integer case.

For the first order equation a bit more calculations are required. Here we need a solution for non-integer values of N to the integral in equation (3.31):

$$-v_1 = e^{\rho_1} \rho_1^{-\frac{N-1}{2}} \int_{\rho_1}^{\infty} \left(\rho'_1 - \frac{b_1}{\rho'_1} \right) \rho_1^{\prime \frac{N-1}{2}} e^{-\rho'_1} d\rho'_1. \quad (3.62)$$

For this type of integral, the incomplete gamma function which is defined, [Oldham et al., 2009]

$$\Gamma(a, x) = \int_x^{\infty} t^{a-1} e^{-t} dt, \quad (3.63)$$

will be useful. This function has the important recursive property that

$$\Gamma(a + 1, x) = a\Gamma(a, x) + x^a e^{-x}. \quad (3.64)$$

For $a > 0$ we have that $\Gamma(a, 0) = \Gamma(a)$, where $\Gamma(a)$ is the gamma function which only depends on a and reduces to the factorial $(a - 1)!$ for integer values of a , [Oldham et al., 2009].

To solve equation (3.62), we will look at each term in the integral. For the part multiplied by b_1 , we use the definition of incomplete gamma function to find

$$\int_{\rho_1}^{\infty} \frac{b_1}{\rho'_1} \rho_1^{\prime \frac{N-1}{2}} d\rho'_1 = b_1 \Gamma\left(\frac{N-1}{2}, \rho_1\right). \quad (3.65)$$

To solve the second part of equation (3.62), we notice that this is an integral of the form

$$\int_{\rho_1}^{\infty} \rho_1^{\prime P} e^{-\rho'_1} \rho_1^{\prime \frac{N-1}{2}} d\rho'_1 = \Gamma\left(\frac{N-1}{2} + P + 1, \rho_1\right), \quad (3.66)$$

where P is zero or is some integer. We now use the recursive property from equation (3.64) $P + 1$ times in total to get

$$\int_{\rho_1}^{\infty} \rho_1'^P e^{-\rho_1'} \rho_1'^{\frac{N-1}{2}} d\rho_1' = e^{-\rho_1} \left[\sum_{k=0}^P \left(\frac{N-1}{2} + P \right)_{-1,k} \rho_1^{\frac{N-1}{2} + P - k} \right] + \left(\frac{N-1}{2} + P \right)_{-1, P+1} \Gamma \left(\frac{N-1}{2}, \rho_1 \right), \quad (3.67)$$

where the following notation is introduced

$$(n)_{-1,k} = n(n-1)(n-2)\dots(n-k+1) \quad \text{and} \quad n_{-1,0} = 1. \quad (3.68)$$

Using this result for $P = 1$ and combining it with equation (3.65) in equation (3.62) for v_1 , we get

$$-v_1 = e^{\rho_1} \rho_1^{-\frac{N-1}{2}} \left\{ -e^{-\rho_1} \left[\rho_1^{\frac{N-1}{2}+1} + \left(\frac{N-1}{2} + 1 \right) \rho_1^{\frac{N-1}{2}} \right] + \Gamma \left(\frac{N-1}{2}, \rho_1 \right) \left[\left(\frac{N-1}{2} + 1 \right) \left(\frac{N-1}{2} \right) - b_1 \right] \right\}. \quad (3.69)$$

Just like in the two and three dimensional case, our wavefunction and hence v_1 should be regular at $\rho_1 = 0$. Recall that $\Gamma \left(\frac{N-1}{2}, 0 \right)$ is independent on ρ_1 and due to the term with ρ_1 outside the brackets, the coefficient of $\Gamma \left(\frac{N-1}{2}, \rho_1 \right)$ has to be zero. This implies that $b_1 = \left(\frac{N-1}{2} + 1 \right) \left(\frac{N-1}{2} \right)$ which could also have been found by changing the lower limit in equation (3.67) as such

$$b_1 = \int_0^{\infty} \rho_1' e^{\rho_1'} \rho_1'^{\frac{N-1}{2}} d\rho_1' = \left(\frac{N-1}{2} + 1 \right) \left(\frac{N-1}{2} \right). \quad (3.70)$$

So now b_1 for $2 \leq N \leq 3$ has been found and v_1 in equation (3.69) becomes

$$-v_1 = \rho_1 + \frac{N+1}{2}. \quad (3.71)$$

When we substitute both v_0 and v_1 back into equation (3.20), we see that the equation for F^k for $k > 1$ is exactly the same as found earlier in equation (3.45). The structure of v_1 ensures that all integrals can be found using the formulas found in equation (3.65) and (3.67). Regarding b_k , the regularity arguments are similar to before and we have that

$$b_k = - \int_{\rho_1}^{\infty} e^{-\rho_1'} \rho_1'^{\frac{N-1}{2}} \sum_{n=1}^{k-1} v_n v_{k-n}, \quad k > 1. \quad (3.72)$$

Later, the expansions for $v(F)$ will be of importance and the first few coefficients for this expansion are found in table 3.4. The first few coefficients for the expansion

of $B(F)$ are presented in table 3.5. Like previously, the algorithm used for the calculations for the values in both tables can be found in appendix C.

For the b_n coefficients, inserting $N = 2$ and $N = 3$ gives the same values as found previously for the integer dimensions in table 3.1. This is exactly what we want and of course the reason lies in the fact that our integrals in equation (3.65) and (3.67) are generalisations of the corresponding integrals in (3.33) and (3.41) for three and two dimensions respectively. In the three dimensional case, it is clear that substituting $P + 1$ with n in equation (3.67), we get equation (3.33). From the recurrence relation in (3.64), we also see that $\Gamma(1, x) = e^{-x}$ which reduces equation (3.65) to the corresponding equation in three dimensions. In the two dimensional case, it can be shown that $\Gamma(1/2, x) = \sqrt{\pi} \operatorname{erfc}(x)$, [Oldham et al., 2009] and this combined with a substitution of $2P + 1$ with n in equation (3.67), gives us equation (3.41).

Table 3.4: The first eight coefficients in the expansion $v(F) = \sum_{n=0}^{\infty} v_n F^n$ for N dimensions.

n	v_n
0	$-1/2$
1	$-(N + 1)/2 - \rho_1$
2	$N^2 + (5N + 3)/2 + \rho_1(3N + 5)/2 + \rho_1^2$
3	$-4N^3 - (35N^2 + 25)/2 - 26N + \rho_1[-6N^2 - 22(N - 1)] - \rho_1^2(5N + 11) - 2\rho_1^3$
4	$21N^4 + (1101N^3 + 2833N^2 + 3319N + 1419)/8 + \rho_1[32N^3 + (761N^2 + 1301)/4 + (825N)/2] + \rho_1^2[30N^2 + (279N + 361)/2] + \rho_1^3[(35N + 93)/2] + 5\rho_1^4$
5	$-128N^5 - (9205N^4 + 28767)/8 - (17581N^3 + 36147N)/4 - (17627N^2)/2 - \rho_1(198N^4 + 1676N^3 + 5828N^2 + 9846N + 6762) - \rho_1^2(200N^3 + 1464N^2 + 3967N + 3969) - \rho_1^3(140N^2 + 772N + 1188) - \rho_1^4(63N + 193) - 14\rho_1^5$
6	$858N^6 + (159921N^5 + 831615N^4 + 4012649N + 1519623)/16 + (1226715N^3 + 2130517N^2)/8 + \rho_1[1344N^5 + (120387N^4 + 1451075)/8 + (147729N^3 + 578737N)/2 + (793401N^2)/4] + \rho_1^2[1430N^4 + (29135N^3 + 256689N)/2 + 61676N^2 + 110012] + \rho_1^3(1120N^3 + 9579N^2 + 30406N + 35695) + \rho_1^4(630N^2 + 3965N + 6955) + \rho_1^5(231N + 793) + 42\rho_1^6$
7	$-6144N^7 - (1426299N^6 + 38087095N^4 + 152801321N^2 + 49451685)/16 - (2387737N^5 + 33882891N)/4 - 6036599N^3 - \rho_1[9724N^6 + (549211N^5 + 3541139N^4 + 40637911N + 23844255)/4 + (6664143N^3 + 15351151N^2)/2] - \rho_1^2[10752N^5 + (569127N^4 + 14761401)/4 - (1666307N^3 + 9559153N)/2 + 2693646N^2] - \rho_1^3(9100N^4 + 106990N^3 + 524026N^2 + 1263410N + 1256774) - \rho_1^4(5880N^3 + 56905N^2 + 204200N + 270615) - \rho_1^5(2772N^2 + 19428N + 37860) - \rho_1^6(858N + 3238) - 132\rho_1^7$

Table 3.5: The first eight coefficients in the expansion $B(F) = \sum_{n=0}^{\infty} b_n F^n$ for N dimensions.

n	b_n
0	$N/4 - 1/4$
1	$N^2/4 - 1/4$
2	$-N^3/2 - (3N^2)/4 + N/2 + 3/4$
3	$2N^4 + (27N^3)/4 + (17N^2)/4 - (27N)/4 - 25/4$
4	$(475N)/4 - (243N^2)/8 - (433N^3)/4 - (933N^4)/16 - (21N^5)/2 + 1419/16$
5	$64N^6 + (8181N^5)/16 + (25957N^4)/16 + (17673N^3)/8 + (893N^2)/8 - (43527N)/16 - 28767/16$
6	$-429N^7 - (146193N^6)/32 - (335847N^5)/16 - (1621815N^4)/32 - (451901N^3)/8 + (248385N^2)/32 + (1246513N)/16 + 1519623/32$
7	$3072N^8 + (1327995N^7)/32 + (8124649N^6)/32 + (28536147N^5)/32 + (58498489N^4)/32 + (56215737N^3)/32 - (17269757N^2)/32 - (86079879N)/32 - 49451685/32$

Step 2 and 3: Expansion of $1/\beta$ and the energy

For the remaining two steps of the perturbation theory, we notice that the dimension only influences the calculations in section 3.6 and 3.7 implicitly through the values of b_n . So no generalising mathematics is necessary and we go directly to the results for the expansion of the energy in N dimensions in table 3.6. As the coefficients for the $B(F)$ expansion are in agreement with the two and three dimensional case, the results in table 3.6 are naturally in agreement with the earlier results in table 3.3.

3.9 Discussion of the results

We now have several results for both the two-, three- and non-integer-dimensional Stark effect. In this section we will look closer at the expansion for the energy and the development of the coefficients and lastly, the eigenfunctions will be discussed.

3.9.1 The perturbation expansion of the energy

Let us first look at the ground state energy for N dimensions: $E = -2/(N-1)^2$. This solutions matches the ground state energies found with the analytical solutions in chapter 2, and the formula is in agreement with [Alliluev and Popov, 1993]. As noticed earlier, the ground state energy is four times lower when the movement of the electron is restricted to the plane compared to a free movement in three directions.

Table 3.6: The first eight coefficients in the expansion $E(\varepsilon) = \sum_{n=0}^{\infty} e_{2n}\varepsilon^{2n}$ for N dimensions.

n	e_n
0	$-2/(N-1)^2$
1	$-[(N-1)^4(2N^2+5N+3)]/256$
2	$-[(N-1)^{10}(96N^4+741N^3+2167N^2+2779N+1257)]/1048576$
3	$-[(N-1)^{16}(5888N^6+85461N^5+533445N^4+1815650N^3+3501194N^2+3538889N+1399473)]/2147483648$
4	$-[(N-1)^{22}(2031616N^8+45636589N^7+467275091N^6+2834146381N^5+11052956155N^4+28075072847N^3+44654970977N^2+39701144183N+14478766161)]/17592186044416$
5	$-[(N-1)^{28}(209584128N^{10}+6569927583N^9+97047334259N^8+886867029116N^7+5526252189596N^6+24372392773538N^5+76378415949962N^4+166038976419596N^3+235957856688140N^2+193460326650167N+66805351053915)]/36028797018963968$
6	$-[(N-1)^{34}(48297410560N^{12}+1981579244145N^{11}+39140443865451N^{10}+491213722785395N^9+4348021676743233N^8+28462743869658906N^7+140437410204395518N^6+522350350662665046N^5+1440515114369870610N^4+2840475733219725573N^3+3745537527786901191N^2+2901994475633920935N+962899235908813437)]/147573952589676412928$
7	$-[(N-1)^{40}(5999515664384N^{14}+308431571536637N^{13}+7748364187468901N^{12}+125922847163921830N^{11}+1475369862574341886N^{10}+13135206627232730335N^9+91205775101297288207N^8+498920164409459983940N^7+2146498909529725493492N^6+7173746674085743949739N^5+18173479445366378535411N^4+33481787184916263893046N^3+41816586142886697650094N^2+31049007639215299984473N+9987469703422359557625)]/302231454903657293676544$

Since we are working in units where the ionisation energy is zero this implies that the electron is bound tighter as the dimension decreases.

A second thing we notice is that all odd powers of the electric field do not appear in the expansion of the energy. Mathematically, this is a consequence of the opposite sign of F in the differential equation for ξ and η in equation (3.48) and (3.49) which cancelled out all odd powers in equation (3.53) already. Physically, we can understand this from the charge distribution of the ground state of the electron. The s-orbital has spherical symmetry, [Phillips, 2003] and hence, the changes in the energy when the electric field is applied do not depend on the direction of the field.

Changing the direction of the field from the positive z -direction to the negative z -direction, results in the exact same energy expansion when only the odd powers of ε are present and so our expectation holds.

Another implication of only the even powers being present in the expansion for ground state, is that there is no linear Stark effect. From classical electrostatics we know that a system with an electric dipole moment D in an external electric field ε will have the energy shifted by $E = -D\varepsilon$, [Bransden and Joachain, 2003]. As this effect is linear in ε , we conclude that the ground state for the electron in a hydrogen atom cannot possess a permanent electric dipole moment, [Bransden and Joachain, 2003].

3.9.2 The behaviour of the expansion of the energy as $n \rightarrow \infty$

Now we will move on from looking at the overall shape of the function for the expansion of the energy to a study of the actual behaviour as a function of N and ε . In table 3.6 it is seen that the first eight coefficients have a negative value for all $2 \leq N \leq 3$. In the algorithm in MATLAB the first 15 coefficients have been found and for all of these, the value is still negative. So already now we see that the ground state energy is lowered when the external field is present. This is just what we would expect, as the electric field will drag the electron in the negative z -direction and thus taking it further apart from the nucleus. But let us look at this closer.

In figure 3.3 the absolute value of the coefficients have been plotted for two to three dimensions for each 0.1 increment in N . The red line is for $N = 2$ and the full black line is for $N = 3$. For three dimensions and dimensions close to three we see that the coefficients continuously become greater. For the lower dimensions, the first few coefficients decrease in absolute value, however for $n > 3$ they start growing, although not as fast as for the higher dimensions. This slower increase for the lowest dimensions is explained by the lower ground state energy. As the electron is initially bound tighter to the nucleus, the external field has a smaller effect, [Yang et al., 1991]. In theory our expansion for the energy is an infinite sum and a natural question is whether the series is convergent for a range of ε or if it diverges. From the first glance, the coefficients in figure 3.3 could appear to be growing exponentially in which case a convergence radius might be found. However, in the upper plot in figure 3.4 the logarithm of the coefficients for the two- and three-dimensional case have been found and the values are seen to grow faster than an exponential function. In [Ivanov, 1997] a factorial growth is mentioned and in the lower plot in figure 3.4, the coefficients have been divided by $(2n)!$ before the logarithm is found. Here the new data shows a more proper exponential growth. From the definition of $F = \varepsilon / (4\beta^3)$ in the expansion of B , a factor for 4^{2n} will also appear in the coefficients for the energy. Multiplying the coefficients in the lower plot in figure 3.4 by this factor and doing a linear regression using Curve Fitting Toolbox in MATLAB, we find the following

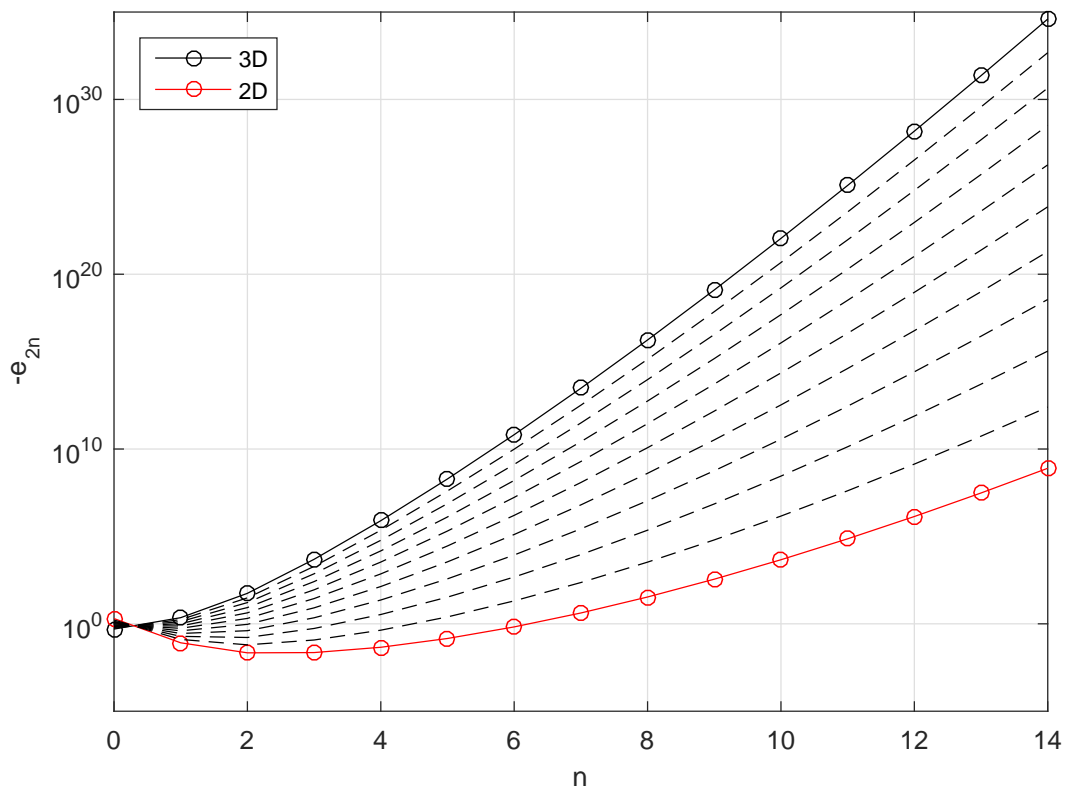


Figure 3.3: The absolute value of the coefficients in the expansion of the energy. The red line is for $N = 2$, the dashed lines are for 2.1, 2.2, \dots , 2.9 dimensions and the full black line is for $N = 3$.

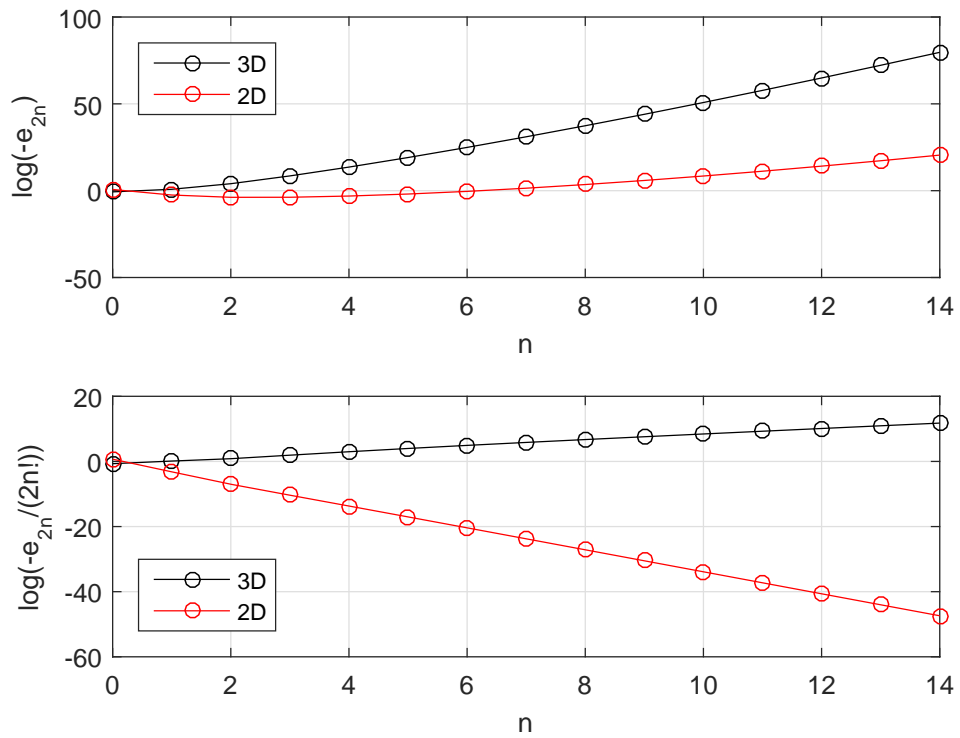


Figure 3.4: The logarithm of the absolute value of the coefficients of the expansion of the energy and the absolute value divided by $(2n)!$ respectively in the upper and lower plot. The red line is for $N = 2$, and the black line is for $N = 3$.

formulas for the expansions in two and three dimensions:

$$E_{2D} = -2 \sum_{n=0}^{\infty} \frac{(2n)!}{4^{2n}} (0.4758) e^{-0.6056n} \varepsilon^{2n}, \quad (3.73)$$

$$E_{3D} = -\frac{1}{2} \sum_{n=0}^{\infty} \frac{(2n)!}{4^{2n}} (3.079) e^{3.587n} \varepsilon^{2n}. \quad (3.74)$$

To improve accuracy the linear regression is based on the first 30 coefficients. In figure 3.5 the values for each coefficient found using these formulas have been plotted with the actual values and the agreement between the data sets is clear. Furthermore, for $n \rightarrow \infty$ equation (3.74) has approximately the same form as the expansion in [Ivanov, 1997]. Now let us see if these power series for the energies converge for any

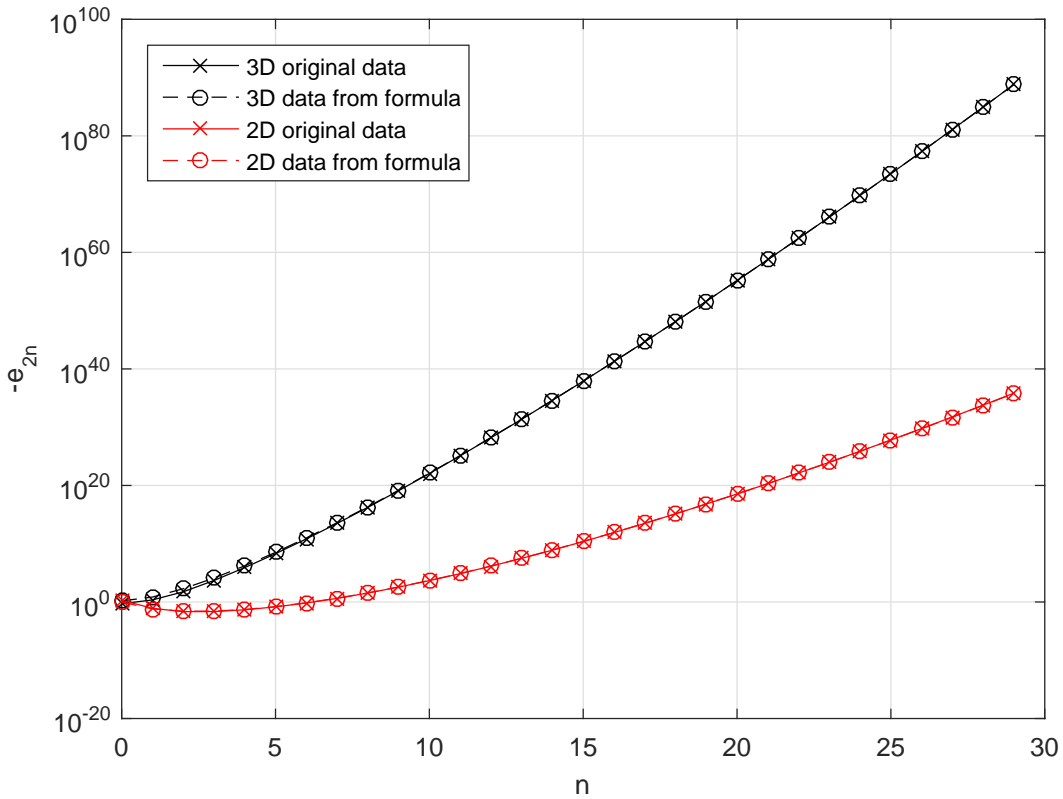


Figure 3.5: A comparison of the origin coefficients and the coefficients from the formulas in equation (3.73) and (3.74). Crosses indicate the original values, circles indicates values using the formula, $N = 2$ is the red line and $N = 3$ is the black line.

ε . Using the ratio test on a series of the form

$$f(x) = \sum_{n=0}^{\infty} (2n)! a e^{bn} x^n, \quad (3.75)$$

we find the radius of convergence R to be zero, [Wade, 1995]

$$R = \lim_{n \rightarrow \infty} \frac{|a(2n)!e^{bn}|}{|a(2(n+1))!e^{b(n+1)}|} = \lim_{n \rightarrow \infty} \left| e^b \frac{1}{(2n+1)(2n+2)} \right| = 0. \quad (3.76)$$

So both the expansion for E_{2D} and E_{3D} are divergent. As the case with two and three dimensions are upper and lower bound of our calculations for non-integer dimensions, these two divergent results are considered to be enough argument that the factor $(2n)!$ will appear in the expansion for non-integer N as well. Hence, the expansion of the energy is divergent for all $2 \leq N \leq 3$.

3.9.3 Interpretation of the asymptotic series

The divergent expansion means that the energy, when all the infinite terms in our expansion is taken into consideration, goes to $-\infty$ whenever an electric field is applied. We notice that is regardless of the strength of the electric field as long as it is just different from zero. This is a breakdown of the perturbation expansion, [Yang et al., 1991], and we can explain it by recalling the illustration of the potential both in figure 3.1 and 3.2. For large negative z , the potential with an applied field goes to minus infinity. But before this happens, there is a maximum in the potential on the negative z -axis. Recalling that the force is the negative of the slope of the potential, we see that this maximum must be where the applied and internal electric field cancel each other. This maximum creates a potential barrier between the two minima of the potential: the minimum at the nucleus and the minimum at the large negative z . Through the tunnel effect an electron that is initially in a bound state therefore has a probability of penetrating this barrier. Electrons that have tunneled through the barrier will now accelerate in the field and hereby the hydrogen atom is ionised, [Bransden and Joachain, 2003]. So it is because of the finite probability of tunnelling, and hence ionisation, that the expansion of the energy goes to minus infinity.

A relevant question is then if our perturbation approach is useful for anything practical when even the smallest field gives us a series for the energy representing that the electron is ionised. However, the probability that the electron can tunnel through a barrier of width d is approximately proportional to e^{-d} , [Phillips, 2003]. From the illustration of the potential in figure 3.3, it is clear that the barrier increases as the applied field decreases, [Bethe and Salpeter, 1957]. So for small electric fields, the tunnelling takes so much time that it can be neglected in practical experiments: In other words the ground state is stable for a long enough time to make the first terms of the expansion useful when comparing with experiments, [Bransden and Joachain, 2003]. It turns out that for a given electric field, there is an optimal number of terms in the expansion of the energy which gives results that matches the actual energies, [Yang et al., 1991].

3.9.4 Eigenfunctions of the bound states

From the results in our perturbation theory we are able to construct eigenfunctions for the bound states. In the light of the asymptotic series for the energy just discussed, it should be mentioned that because of the tunnelling effect we do not mean bound states in the strict sense. To find the eigenfunctions recall that our expansion of $v(\rho_1)$ is related to the ξ -part of the original wavefunction $\Psi = u_1(\xi)u_2(\eta)$ by equation (3.18): $v = u'_1/u_1$. Using the expansion for v and the corresponding expansion for the part related to η , we are therefore able to find the ground state eigenfunction for the Schrödinger equation with the applied electric field.

From the definition of v , it is clear that we can find u_1 by

$$u_1(\rho_1) = e^{\int v d\rho_1}, \quad (3.77)$$

and the unnormalised wavefunction can be found using

$$\Psi(\rho_1, \rho_2) = \exp^{\int v_\xi(\rho_1) d\rho_1 + \int v_\eta(\rho_2) d\rho_2}, \quad (3.78)$$

where $v_\xi(\rho_1)$ and $v_\eta(\rho_2)$ are from equation (3.52) which is to be combined with the results in table 3.4. For an easier interpretation we use this to find the probability density

$$|\Psi(\rho_1, \rho_2)|^2 = \exp^{2(\int v_\xi(\rho_1) d\rho_1 + \int v_\eta(\rho_2) d\rho_2)}. \quad (3.79)$$

As the wave function is not normalised, the result above is only correct up to a constant factor. However, in a moment we will see that the breakdown of the perturbation theory makes this less relevant. Ψ is a function of our scaled parabolic coordinates $\rho_1 = \beta\xi$ and $\rho_2 = \beta\eta$ and if the x - and y -coordinates are kept constant, the relation between the two coordinate systems implies that we can make the substitutions $\rho_1 = \beta(|z| + z)$ and $\rho_2 = \beta(|z| - z)$. Lastly, recall that β is a function of the energy for the eigenfunction $\beta = \sqrt{-2E}$. As the expansion of the energy is asymptotic, we will here choose to calculate the energy up to the same order as the order of the expansions used in v in the eigenfunctions. For example, if v for ξ and η are calculated up to the fourth order, F^4 , these results also give us enough information to find the energy to the fourth order, ε^4 .

In figure 3.6a the probability density for the case where the electron can move in all three dimensions can be seen where the expansions are up to the second order. The applied electric field varies from $\varepsilon = 0$ to $\varepsilon = 0.9$. When no electric field is applied, we notice that the probability density is symmetric around the nucleus at $z = 0$ just like it is expected to be. For the lines with an applied electric field let us first focus on the interval where $z > 0$. Here we clearly see that the greater the strength of the field is, the more $|\Psi|^2$ is pushed towards the nucleus. So the area under the curve for positive z decreases, as the external field increases which implies that the probability

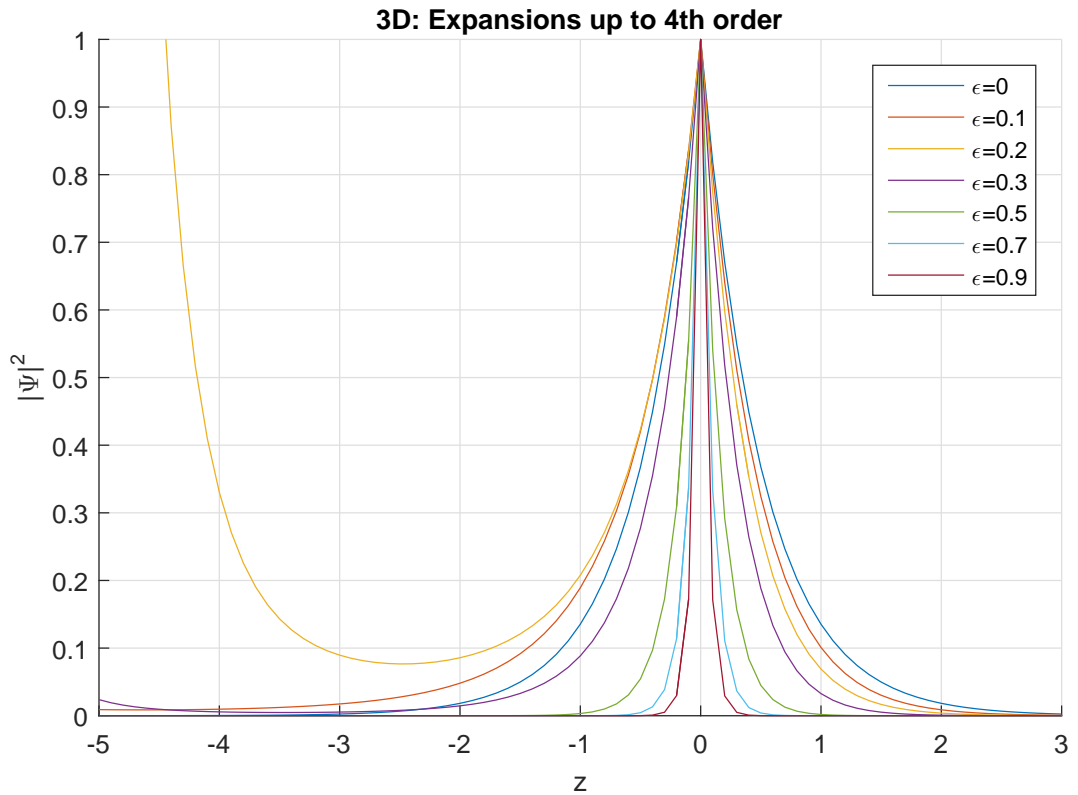
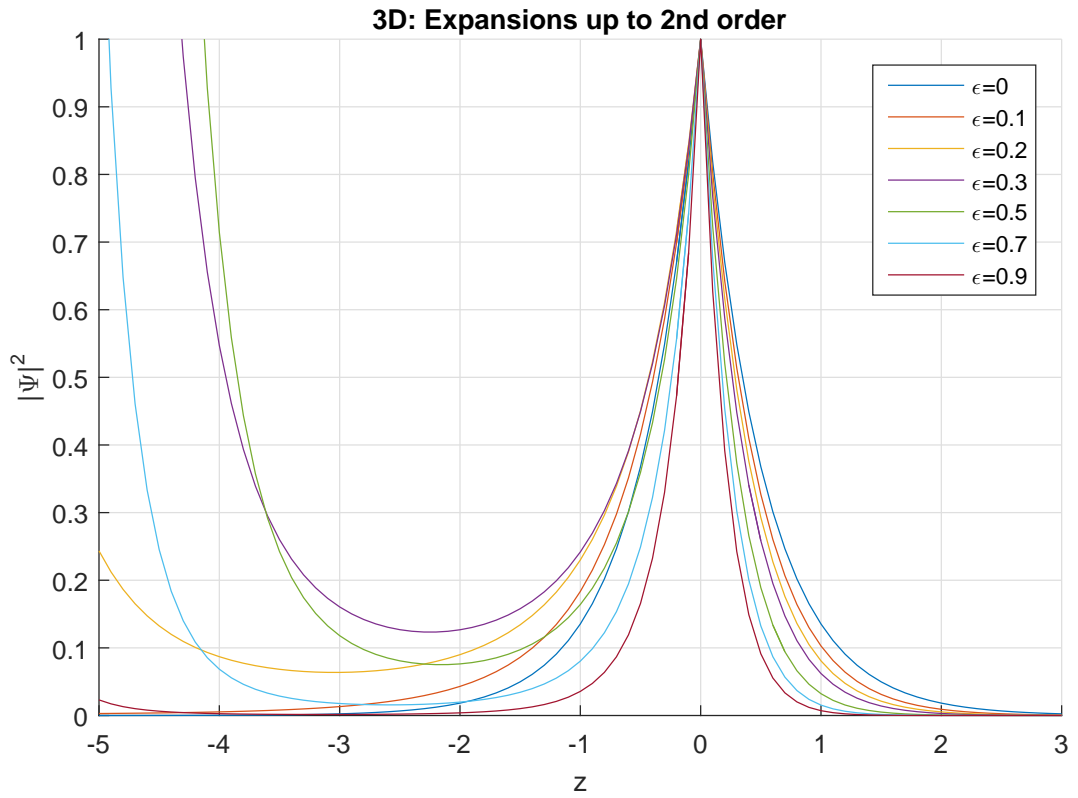


Figure 3.6: (a) The probability density as a function of z for the unnormalised eigenfunction for three dimensions up to the second order. Each line represents the function for a different electric field. (b) The same illustration as (a) but where expansions up to the fourth order are used.

of finding the electron on the positive z axis becomes smaller - like we expect. The same tendency is seen in figure 3.6b which shows a similar plot for three dimensions but where the expansions are up to the fourth order. In figure 3.7 the electric field is held constant at $\varepsilon = 0.2$ and the dimensions is varied in steps of 0.2 from $N = 2$ to $N = 3$ and here we see this same tendency for $z > 0$ for all N as well.

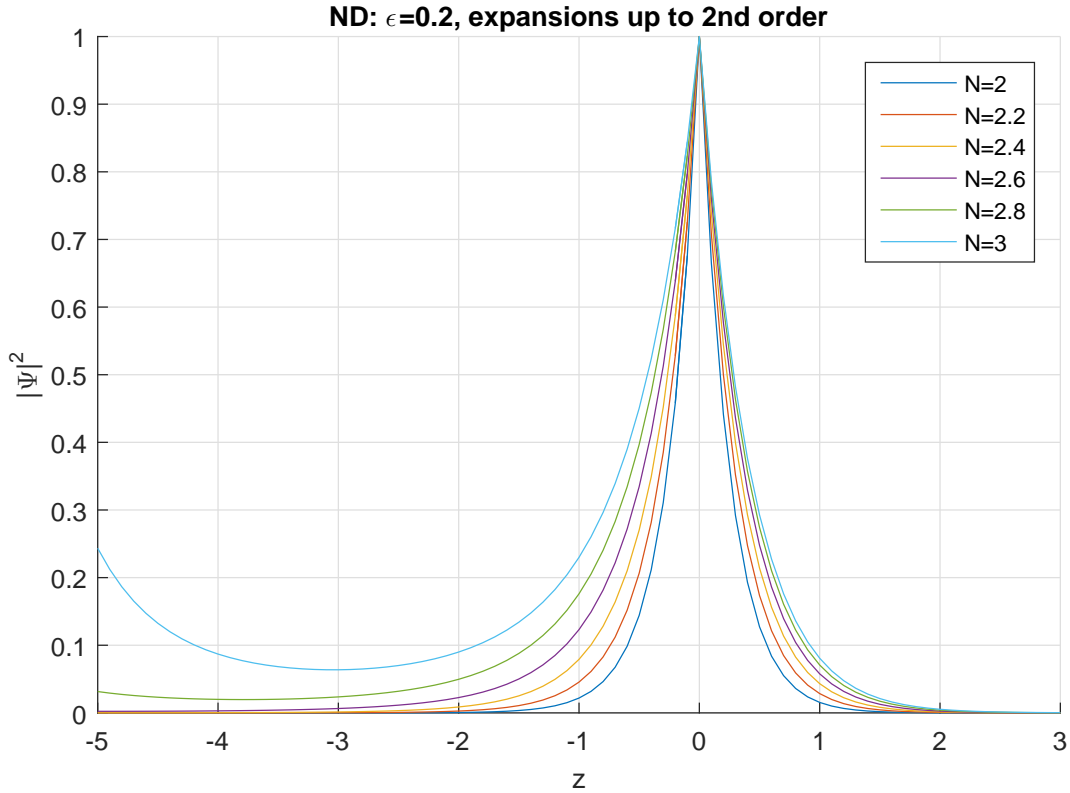


Figure 3.7: The probability density as a function of z for the unnormalised eigenfunction for N dimensions up to second order. The electric field is held constant at $\varepsilon = 0.2$.

Going back to figure 3.6a, let us now focus on $-2 < z < 2$. For all the eigenfunctions where $\varepsilon > 0$ we see that the decrease in the probability density is slower for negative z such that the probability of finding the electron here is greater than for positive z . The asymmetry increases for large ε which makes sense as these fields should have a larger impact on the electron. The same is also seen in figure 3.7 for other dimensions. But when we look at $z < -2$ in figure 3.6a we start to see the effect of the asymptotic series for the energy. Even for a field of strength $\varepsilon = 0.3$ and for $\varepsilon = 0.2$ with an expansion to the fourth order in figure 3.6b, we see the probability density increasing dramatically. This illustrates the consequence of the tunnelling effect leading to ionisation of the hydrogen atom.

We notice that for the small electric field $\varepsilon = 0.1$, this increase happens much further

out on the negative z -axis than for larger fields. At the same time we see that for the very large fields with $\varepsilon = 0.8$ and $\varepsilon = 0.9$ the increase again takes place further away from the nucleus. This could indicate that these electric fields are too large for the perturbation theory to be applicable.

Figure 3.6b illustrates the effect of increasing the order in the perturbation expansions when calculating $|\Psi|^2$. For small electric fields we still see an asymmetry but everything is pushed closer to the nucleus. When expansions of even higher orders are included, the probability density is still just pushed closer to the nucleus. For large electric fields we also notice that the asymmetry becomes less apparent. The line for $\varepsilon = 0.2$ stands out a bit, as both the line for $\varepsilon = 0.1$ and $\varepsilon = 0.3$ does not increase until much further out on the negative z -axis. Why this is the case, and if it has something to do with how the optimal number of terms in the expansion depends on the electric field, as mentioned in section 3.9.3, is a question that could be interesting to study further.

Finally, figure 3.7 shows the dependence on the dimension. The lower the dimension, the closer the lines are to the nucleus which illustrates how restrictions in the movement of the electron makes it bound tighter in agreement with earlier results. In continuation of this, the asymmetry becomes more and more apparent as N increases which shows how the increasing dimension makes the electric field have more influence on the electron.

3.10 Conclusions of the Stark effect in a hydrogen atom

In this chapter we have solved the Schrödinger equation for the Stark effect in a hydrogen atom where the electron is free to move in three dimensions and where the motion of the electron is restricted to the plane. By allowing the dimension N to take on the real values between 2 and 3, the results are generalised for non-integer dimensions between two and three dimensions as well. The solutions are found using perturbation theory on the ground state based on an expansion of the logarithmic derivative of the wave function and expansions of the charge related to each coordinate – all as functions of the applied electric field ε and the dimension.

For the energy this leads to a power series in ε in which the coefficients for each power grow factorially. Thus, the series has a convergence radius of zero and for all applied electric fields, the energy diverges to minus infinity. This result is explained by the tunnelling effect in which the electron has a finite probability of penetrating the potential barrier that is created by applying the electric field. Ionisation matches this divergent energy. In relation to the dimensions, we see that for lower dimensions the electron is initially bound tighter to the nucleus and hence it has a slower response to the applied field.

The expansions for the eigenfunctions are used to plot the probability density as a function of the electric field and the dimension. An asymmetry with respect to $z = 0$ shows the expected increased probability of finding the electron on the negative z -axis. Dramatic increases for large negative z for certain applied fields, depending on the order of the perturbation expansions included, is seen as a consequence of the tunnelling effect leading to ionisation of the atom. The lower the dimension is, the more the probability density is squeezed towards the centre with the nucleus which matches the results seen for the energy.

Especially two limitations regarding all results should be noticed. The first thing is to recall that the perturbation theory is based on the solution for the ground state. If further studies were to be made, it could be interesting to see if a similar perturbation theory method could be used for excited states. Secondly, the tunnelling effect and ionisation has only been qualitative interpretations of the asymptotic expansion for the energy and plots of the potentials and probability density. Solving the Schrödinger equation for the Stark effect using other approximation methods than perturbation theory, more quantitative results for the tunnelling effect and ionisation can be found, [Bethe and Salpeter, 1957].

Chapter 4

Conclusion

In this report the Stark effect has been studied for the ground state of an electron free to move in N dimensions in a hydrogen atom, where $2 \leq N \leq 3$. To do this we initially looked at a hydrogen atom with no external forces. The Schrödinger equation was separated in parabolic coordinates and solved analytically for the case where the electron can move in the plane and in three dimensions respectively. The wave functions and corresponding energies were found and for the ground state the wave function is proportional to e^{-r} , where r is the distance to the nucleus, and the ground state energy is inversely proportional to $-(N - 1)^2 / 2$.

Then the Schrödinger equation with an external electric field ε was solved using perturbation theory based on the ground state solution with no field applied. Our method included expansions of the charge related to each of two parabolic coordinates leading to a series for the energy and expansions of the logarithmic derivative of the wave function. The calculations were made for two and three dimensions before being generalised to non-integer dimensions.

A power series in ε for the energy was found as a function of N and in the two limits of $N = 2, 3$ the radius of convergence was found to be zero. This divergence is seen as a consequence of the tunnelling effect leading to ionisation. The energy expansion also showed that the lower the dimension is, the tighter the electron is bound to the nucleus.

The expansion found for the logarithmic derivative of the wave function was used to calculate the probability density as a function of ε and N . An expected asymmetry with respect to the axis on which the electric field is applied was observed. Far away from the nucleus in the opposite direction of the applied field, dramatic increases were found for certain values of ε , depending on the order of the perturbation expansions included. Like the divergent energy, this was interpreted as consequence of the tunnelling effect.

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Appendix A

Parabolic coordinates

In this appendix the calculations behind the used formula for the volume element and Laplacian operator for parabolic coordinates are presented.

A.1 Orthogonal curvilinear coordinates

First some general properties of curvilinear coordinate systems are described in this section which is based on [Adams and Essex, 2009]

The Cartesian coordinates (x, y, z) can be transformed to the curvilinear coordinates (q_1, q_2, q_3) using continuously differentiable and locally invertible functions

$$x = x(q_1, q_2, q_3), \quad y = y(q_1, q_2, q_3), \quad z = z(q_1, q_2, q_3). \quad (\text{A.1})$$

The position vector r can now be expressed

$$r = x(q_1, q_2, q_3) \hat{x} + y(q_1, q_2, q_3) \hat{y} + z(q_1, q_2, q_3) \hat{z}, \quad (\text{A.2})$$

where \hat{x}, \hat{y} and \hat{z} are the Cartesian unit vectors. For an orthogonal curvilinear coordinate system, the unit vectors

$$\hat{q}_i = \frac{\partial r}{\partial q_i} \left| \frac{\partial r}{\partial q_i} \right|^{-1} \quad \text{for } i = 1, 2, 3, \quad (\text{A.3})$$

satisfy $\hat{q}_i \cdot \hat{q}_j = \delta_{ij}$ where δ_{ij} . The length of the unit vectors are also called scale factors and are denoted by

$$h_{q_i} = \left| \frac{\partial r}{\partial q_i} \right| \quad \text{for } i = 1, 2, 3. \quad (\text{A.4})$$

For an orthogonal curvilinear coordinate system, the volume element is spanned by the vectors $\frac{\partial r}{\partial q_i}$, $i = 1, 2, 3$. Thus it is given by

$$dV = h_{q_1} h_{q_2} h_{q_3} dq_1 dq_2 dq_3 . \quad (\text{A.5})$$

Combining calculations for the gradient and the divergence in curvilinear coordinates, the following expression for the Laplacian operator is

$$\nabla^2 = \frac{1}{h_{q_1} h_{q_2} h_{q_3}} \left[\frac{\partial}{\partial q_1} \left(\frac{h_{q_2} h_{q_3}}{h_{q_1}} \frac{\partial}{\partial q_1} \right) + \frac{\partial}{\partial q_2} \left(\frac{h_{q_3} h_{q_1}}{h_{q_2}} \frac{\partial}{\partial q_2} \right) + \frac{\partial}{\partial q_3} \left(\frac{h_{q_1} h_{q_2}}{h_{q_3}} \frac{\partial}{\partial q_3} \right) \right] . \quad (\text{A.6})$$

A.2 Parabolic coordinates

It is now shown that the parabolic coordinates form an orthogonal curvilinear coordinate system and the general expressions for the orthogonal curvilinear coordinates are calculated for parabolic coordinates. The section is based on [Bethe and Salpeter, 1957].

A.2.1 An orthogonal curvilinear coordinate system

The parabolic coordinates (ξ, η, ϕ) are related to the Cartesian coordinates (x, y, z) through the equations

$$x = \sqrt{\xi\eta} \cos \phi, \quad y = \sqrt{\xi\eta} \sin \phi, \quad z = \frac{1}{2} (\xi - \eta) , \quad (\text{A.7})$$

where $0 \leq \xi < \infty$, $0 \leq \eta < \infty$ and $0 \leq \phi \leq 2\pi$. Clearly, this is a transition that defines curvilinear coordinates. To see that the coordinates are orthogonal, r is defined as in equation (A.2) and the unit vectors are calculated. First we find $\hat{\xi}$ to be

$$\hat{\xi} = \frac{1}{h_\xi} \left(\frac{1}{2} \frac{\sqrt{\eta}}{\sqrt{\xi}} \cos \phi \hat{x} + \frac{1}{2} \frac{\sqrt{\eta}}{\sqrt{\xi}} \sin \phi \hat{y} + \frac{1}{2} \hat{z} \right) , \quad (\text{A.8})$$

where

$$\begin{aligned} h_\xi &= \sqrt{\left(\frac{1}{2} \frac{\sqrt{\eta}}{\sqrt{\xi}} \cos \phi \right)^2 \hat{x} \cdot \hat{x} + \left(\frac{1}{2} \frac{\sqrt{\eta}}{\sqrt{\xi}} \sin \phi \right)^2 \hat{y} \cdot \hat{y} + \left(\frac{1}{2} \right)^2 \hat{z} \cdot \hat{z}} \\ &= \frac{1}{2} \sqrt{\frac{\eta}{\xi} + 1} . \end{aligned} \quad (\text{A.9})$$

From symmetry and similar arguments, the other unit vectors are found to be

$$\hat{\eta} = \frac{1}{h_\eta} \left(\frac{1}{2} \frac{\sqrt{\xi}}{\sqrt{\eta}} \cos \phi \hat{x} + \frac{1}{2} \frac{\sqrt{\xi}}{\sqrt{\eta}} \sin \phi \hat{y} - \frac{1}{2} \hat{z} \right) \quad (\text{A.10})$$

$$\hat{\phi} = \frac{1}{h_\phi} \left(-\sqrt{\xi\eta} \sin \phi \hat{x} + \sqrt{\xi\eta} \cos \phi \hat{y} \right) \quad (\text{A.11})$$

with

$$h_\eta = \frac{1}{2} \sqrt{\frac{\xi}{\eta} + 1} \quad \text{and} \quad h_\phi = \sqrt{\xi\eta}. \quad (\text{A.12})$$

Obviously, all the unit vectors have unit length and the next step to verify orthogonality is to calculate the dot product between different unit vectors. This leads to

$$\hat{\xi} \cdot \hat{\eta} = \frac{1}{h_\xi h_\eta} \left(\frac{1}{4} \cos^2 \phi + \frac{1}{4} \sin^2 \phi - \frac{1}{4} \right) = 0, \quad (\text{A.13})$$

$$\hat{\xi} \cdot \hat{\phi} = \frac{1}{h_\xi h_\phi} \left(-\frac{1}{2} \eta \cos \phi \sin \phi + \frac{1}{2} \eta \cos \phi \sin \phi \right) = 0. \quad (\text{A.14})$$

The last dot product $\hat{\eta} \cdot \hat{\phi} = 0$ follows by symmetry and the parabolic coordinates are hereby seen to form an orthogonal curvilinear coordinate system.

A.3 The volume element and Laplacian operator

For the orthogonal coordinate system, equation (A.5) can be used to calculate the volume element. This yields

$$dV = \frac{1}{4} \sqrt{\left(\frac{\eta}{\xi} + 1 \right) \left(\frac{\xi}{\eta} + 1 \right)} \xi \eta d\xi d\eta d\phi = \frac{1}{4} (\xi + \eta) d\xi d\eta d\phi. \quad (\text{A.15})$$

Using the scale factors in equations (A.9) and (A.12), it is found that

$$\frac{h_\eta h_\phi}{h_\xi} = \xi, \quad \frac{h_\phi h_\xi}{h_\eta} = \eta \quad \text{and} \quad \frac{h_\xi h_\eta}{h_\phi} = \frac{1}{4\xi\eta} (\xi + \eta). \quad (\text{A.16})$$

When we insert this in equation A.6, the Laplacian in parabolic coordinates can be expressed

$$\nabla^2 = \frac{4}{\xi + \eta} \left[\frac{\partial}{\partial \xi} \left(\xi \frac{\partial}{\partial \xi} \right) + \frac{\partial}{\partial \eta} \left(\eta \frac{\partial}{\partial \eta} \right) \right] + \frac{1}{\xi\eta} \frac{\partial^2}{\partial \phi^2}. \quad (\text{A.17})$$

A.4 Parabolic coordinates in two dimensions

The two dimensional parabolic coordinates (ξ, η) are related to the Cartesian coordinates through the equations

$$x = \sqrt{\xi\eta}, \quad z = \frac{1}{2}(\xi - \eta), \quad (\text{A.18})$$

where $0 \leq \xi, \eta < \infty$. The following relations are easily found

$$r = \frac{1}{2}(\xi + \eta), \quad \eta = r + z, \quad \xi = r - z. \quad (\text{A.19})$$

As in the three dimensional case, both the volume element and the Laplacian operator will be of interest. We first find the scale factors to be similar to the case in three dimensions, that is

$$h_\xi = \frac{1}{2}\sqrt{\frac{\eta}{\xi} + 1}, \quad h_\eta = \frac{1}{2}\sqrt{\frac{\xi}{\eta} + 1}. \quad (\text{A.20})$$

Using the two dimensional versions of the formulas for the volume element and the Laplacian operator in equation (A.5) and (A.6), and using that

$$\frac{h_\xi}{h_\eta} = \sqrt{\frac{\eta}{\xi}}, \quad \frac{h_\eta}{h_\xi} = \sqrt{\frac{\xi}{\eta}}, \quad (\text{A.21})$$

we calculate the volume element and Laplacian operator respectively as

$$dV = \frac{1}{4\sqrt{\xi\eta}}(\xi + \eta) d\xi d\eta, \quad (\text{A.22})$$

and

$$\nabla^2 = \frac{4}{\xi + \eta} \left[\xi^{-\frac{1}{2}} \frac{\partial}{\partial \xi} \left(\xi^{\frac{1}{2}} \frac{\partial}{\partial \xi} \right) + \eta^{-\frac{1}{2}} \frac{\partial}{\partial \eta} \left(\eta^{\frac{1}{2}} \frac{\partial}{\partial \eta} \right) \right]. \quad (\text{A.23})$$

Appendix B

Laguerre functions

The Laguerre functions form the basis for the solution of the Kummer-Laplace differential equation that arises when working with the Schrödinger equation in parabolic coordinates. Starting with a definition of the confluent hypergeometric function, the aim of this appendix is to define the Laguerre and associated Laguerre polynomials and to derive some properties and finally showing the strategy to integrate over the Laguerre functions. Where nothing else is specified, the appendix is based on [Bethe and Salpeter, 1957] and [Bransden and Joachain, 2003].

B.1 The Kummer-Laplace differential equation and the confluent hypergeometric function

The Kummer-Laplace differential equation is a second order differential equation of the form

$$x \frac{d^2 w}{dx^2} + (c - x) \frac{dw}{dx} - ax = 0, \quad (\text{B.1})$$

where w is a function of a variable x . A solution to this is the confluent hypergeometric function which is defined as

$${}_1F_1(a, c, x) = 1 + \frac{a}{c}x + \frac{a(a+1)}{c(c+1)2}x^2 + \dots = \sum_{k=0}^{\infty} \frac{(a)_k}{(c)_k} \frac{x^k}{k!}, \quad (\text{B.2})$$

where $(b)_k = b(b+1)\dots(b+k-1)$ and $(b)_0 = 1$. To see that this indeed solves the Kummer-Laplace differential equation, two relations involving the derivative of ${}_1F_1$

with respect to x are useful. First simple differentiation with respect to x shows that

$$\begin{aligned} \frac{d_1 F_1(a, c, x)}{dx} &= \frac{a}{c} \left[1 + \frac{a+1}{c+1}x + \frac{(a+1)(a+2)}{(c+1)(c+2)}x^2 + \dots \right] \\ &= \frac{a}{c} {}_1F_1(a+1, c+1, x). \end{aligned} \quad (\text{B.3})$$

Using this result and the relations

$$k(a+1)(a+2)\cdots(a+k-1) = k(a+1)_{k-1} \quad (\text{B.4})$$

$$k(a+1)_{k-1} + (a)_k = k(a+1)_{k-1} + a(a+1)_{k-1} = (a+1)_k, \quad (\text{B.5})$$

a few calculations show that

$$\begin{aligned} x \frac{d_1 F_1(a, c, x)}{dx} + a {}_1F_1(a, c, x) &= a \left\{ 1 + \sum_{k=1}^{\infty} x^k \left[\frac{(a+1)_{k-1}}{(c)_k (k-1)!} + \frac{(a)_k}{(c)_k k!} \right] \right\} \\ &= a {}_1F_1(a+1, c, x). \end{aligned} \quad (\text{B.6})$$

Substituting equation (B.3) and (B.6) back into the Kummer-Laplace differential equation, we get

$$\begin{aligned} &x \frac{a(a+1)}{c(c+1)} {}_1F_1(a+2, c+2, x) + a {}_1F_1(a+1, c+1, x) - a {}_1F_1(a+1, c, x) \\ &= \sum_{k=0}^{\infty} x^k \left[\frac{k(a)_{k+1}}{k!(c)_{k+1}} + \frac{(a)_{k+1}}{k!(c+1)_k} - \frac{(a)_{k+1}}{k!(c)_k} \right] \\ &= \sum_{k=0}^{\infty} x^k \left[\frac{k(a)_{k+1}}{k!(c)_{k+1}} + \frac{c(a)_{k+1}}{k!(c)_{k+1}} - \frac{(c+k)(a)_{k+1}}{k!(c)_{k+1}} \right] = 0, \end{aligned} \quad (\text{B.7})$$

verifying that the confluent hypergeometric function is indeed a solution.

B.2 Laguerre Polynomials

The Laguerre polynomial is defined

$$L_n(x) = e^x \frac{d^n}{dx^n} (x^n e^{-x}). \quad (\text{B.8})$$

Using the Leibniz Rule

$$\frac{d^n}{dx^n} (fg) = \sum_{k=0}^n \binom{n}{k} \frac{d^k}{dx^k} f \frac{d^{n-k}}{dx^{n-k}} g, \quad (\text{B.9})$$

the Laguerre polynomial can also be expressed in the closed form

$$L_n(x) = \sum_{k=0}^n \binom{n}{k} (-1)^k \frac{n!}{k!} x^k. \quad (\text{B.10})$$

The Laguerre polynomial can also be found from the generating function

$$\frac{1}{1-s} \exp\left(-\frac{xs}{1-s}\right) = \sum_{n=0}^{\infty} \frac{L_n(x)}{n!} s^n, \quad |s| < 1, \quad (\text{B.11})$$

which can be verified using Cauchy's integral formula for derivatives. Using the definition of the Laguerre function in equation (B.8), the right hand side of equation (B.11) can be rewritten to

$$\begin{aligned} e^x \sum_{n=0}^{\infty} \frac{1}{n!} \frac{d^n}{dx^n} [e^{-x} (sx)^n] &= e^x \frac{1}{2\pi i} \sum_{n=0}^{\infty} \left[\int_{\gamma} \frac{e^{-\xi} (s\xi)^n}{(\xi-x)^{n+1}} d\xi \right] \\ &= e^x \frac{1}{2\pi i} \int_{\gamma} e^{-\xi} \sum_{n=0}^{\infty} \left[\frac{(s\xi)^n}{(\xi-x)^{n+1}} \right] d\xi, \end{aligned} \quad (\text{B.12})$$

where the equality holds when γ is a simple, closed positively orientated contour. The sum is rewritten using the properties of the geometric series where s and ξ are chosen such that $s\xi < \xi - x$:

$$e^x \frac{1}{2\pi i} \int_{\gamma} e^{-\xi} \sum_{n=0}^{\infty} \left[\frac{(s\xi)^n}{(\xi-x)^{n+1}} \right] d\xi = e^x \frac{1}{2\pi i} \int_{\gamma} \frac{e^{-\xi}}{(1-s)\xi-x} d\xi. \quad (\text{B.13})$$

The integral is now solved by making the substitution $\alpha = (1-s)\xi$ which gives us

$$e^x \frac{1}{2\pi i} \int_{\gamma} \frac{e^{-\xi}}{(1-s)\xi-x} d\xi = e^x \frac{1}{2\pi i} \int_{\gamma} \frac{e^{-\frac{\alpha}{1-s}} / (1-s)}{\alpha-x} d\alpha. \quad (\text{B.14})$$

Now using Cauchy's integral formula once again, this is seen to be equal to the left hand side of equation (B.11).

Theorem B.1 (Recurrence relation 1): *The Laguerre polynomials satisfy the relation*

$$L_{n+1}(x) + (x-1-2n)L_n(x) + n^2 L_{n-1}(x) = 0. \quad (\text{B.15})$$

◇

Proof. This is shown rewriting the generating function as

$$\exp\left(-\frac{xs}{1-s}\right) = (1-s) \sum_{n=0}^{\infty} \frac{L_n(x)}{n!} s^n, \quad |s| < 1, \quad (\text{B.16})$$

and differentiating with respect to s to get

$$-\frac{x}{(1-s)^2} \exp\left(-\frac{xs}{1-s}\right) = -\sum_{n=0}^{\infty} \frac{L_n(x)}{n!} s^n + (1-s) \sum_{n=0}^{\infty} \frac{L_n(x)}{(n-1)!} s^{n-1}. \quad (\text{B.17})$$

Inserting the generating function, equation (B.16) and multiplying with $(1-s)$ we get

$$x \underbrace{\sum_{n=0}^{\infty} \frac{L_n(x)}{n!} s^n}_{\alpha} + (s-1) \underbrace{\sum_{n=0}^{\infty} \frac{L_n(x)}{n!} s^n}_{\beta} + (1-s)^2 \underbrace{\sum_{n=0}^{\infty} \frac{L_n(x)}{(n-1)!} s^{n-1}}_{\gamma} = 0. \quad (\text{B.18})$$

For this to be true, the coefficient of s^n for each n has to be zero. In each term denoted α , β and γ , the coefficient of s^n is found to be

$$\text{Coefficient of } s^n \text{ for } \alpha: x \frac{L_n(x)}{n!} \quad (\text{B.19})$$

$$\text{Coefficient of } s^n \text{ for } \beta: \frac{L_{n-1}(x)}{(n-1)!} - \frac{L_n(x)}{n!} \quad (\text{B.20})$$

$$\text{Coefficient of } s^n \text{ for } \gamma: \frac{L_{n+1}(x)}{n!} - 2 \frac{L_n(x)}{(n-1)!} + \frac{L_{n-1}(x)}{(n-2)!} \quad (\text{B.21})$$

The relation in equation (B.15) then follows by adding the coefficients and setting the sum to be zero. \square

Theorem B.2 (Recurrence relation 2): *The Laguerre polynomials satisfy the differential equation*

$$\frac{d}{dx} L_n(x) - n \frac{d}{dx} L_{n-1}(x) + n L_{n-1}(x) = 0. \quad (\text{B.22})$$

\diamond

Proof. The strategy of the proof is similar to the one in the proof of theorem B.1. The generating function in equation (B.16) is differentiated with respect to x yielding

$$s \sum_{n=0}^{\infty} \frac{L_n(x)}{n!} s^n + \sum_{n=0}^{\infty} \frac{d}{dx} L_n(x) \frac{1}{n!} s^n - \sum_{n=0}^{\infty} \frac{d}{dx} L_n(x) \frac{1}{n!} s^{n+1} = 0. \quad (\text{B.23})$$

For the equation to hold, the coefficient of s^n for each n has to be zero. This is satisfied when

$$\frac{L_{n-1}(x)}{(n-1)!} + \frac{d}{dx} \frac{L_n(x)}{n!} - \frac{d}{dx} \frac{L_{n-1}(x)}{(n-1)!} = 0, \quad (\text{B.24})$$

which multiplied by $n!$ gives equation (B.22). \square

Theorem B.3 (Differential equation): *The lowest order differential equation involving only $L_n(x)$ is*

$$\left[x \frac{d^2}{dx^2} + (1-x) \frac{d}{dx} + n \right] L_n(x) = 0. \quad (\text{B.25})$$

\diamond

Proof. Using the differential equation in theorem B.2 with $n = n' + 1$ and the same equation differentiated with respect to x for $n = n' + 1$ and $n = n' + 2$, the three expressions are obtained:

$$\frac{d}{dx}L_{n'+1} = (n' + 1) \left[\frac{d}{dx}L_{n'} - L_{n'} \right] \quad (\text{B.26})$$

$$\frac{d^2}{dx^2}L_{n'+1} = (n' + 1) \left[\frac{d^2}{dx^2}L_{n'} - \frac{d}{dx}L_{n'} \right] \quad (\text{B.27})$$

$$\frac{d^2}{dx^2}L_{n'+2} = (n' + 2)(n' + 1) \left[\frac{d^2}{dx^2}L_{n'} - 2\frac{d}{dx}L_{n'} + L_{n'} \right] \quad (\text{B.28})$$

Now differentiating the recurrence relation in theorem B.1 with respect to x twice and using $n = n' + 1$, we get

$$\frac{d^2}{dx^2}L_{n'+2} + (x - 3 - 2n') \frac{d^2}{dx^2}L_{n'+1} + 2\frac{d}{dx}L_{n'+1} + (n' + 1)^2 \frac{d^2}{dx^2}L_{n'} = 0. \quad (\text{B.29})$$

Substituting equation (B.26) to (B.28) into this equation gives equation (B.25). \square

B.3 Associated Laguerre polynomials

The associated Laguerre polynomial is defined

$$L_n^\mu(x) = \frac{d^\mu}{dx^\mu}L_n(x) \quad (\text{B.30})$$

Theorem B.4 (Differential equation): *The associated Laguerre polynomials satisfy the differential equation:*

$$\left[x \frac{d^2}{dx^2} + (\mu + 1 - x) \frac{d}{dx} + (n - \mu) \right] L_n^\mu(x) = 0. \quad (\text{B.31})$$

\diamond

Proof. It is easily seen that

$$\frac{d^\mu}{dx^\mu} \left[x \frac{d^2}{dx^2}L_n(x) \right] = x \frac{d^2}{dx^2}L_n^\mu(x) + \mu \frac{d}{dx}L_n^\mu(x), \quad (\text{B.32})$$

$$\frac{d^\mu}{dx^\mu} \left[(1 - x) \frac{d}{dx}L_n(x) \right] = (1 - x) \frac{d}{dx}L_n^\mu(x) - \mu L_n^\mu(x). \quad (\text{B.33})$$

Differentiating equation (B.25) μ times with respect to x and using the above results now gives the desired differential equation. \square

Theorem B.5: *The associated Laguerre polynomials can be expressed in the closed form*

$$L_n^\mu(x) = (-1)^\mu n! \sum_{k=0}^{n-\mu} \binom{n}{\mu+k} \frac{(-x)^k}{k!}, \quad (\text{B.34})$$

and its relation to the confluent hypergeometric function is

$$L_n^\mu(x) = (-1)^\mu n! \binom{n}{\mu} {}_1F_1(- (n - \mu), \mu + 1, x). \quad (\text{B.35})$$

◇

Proof. To prove the closed form, recall the closed form of the Laguerre polynomials in equation (B.10). With this, the associated Laguerre polynomial can be written

$$L_n^\mu = \frac{d^\mu}{dx^\mu} \left[\sum_{k=0}^n \binom{n}{k} (-1)^k \frac{n!}{k!} x^k \right]. \quad (\text{B.36})$$

Each time we differentiate with respect to x , the exponent is lowered by one and the new coefficient clearly corresponds to the ones given in equation (B.34) where the $(-1)^\mu$ factor comes into play as the term with the lowest exponent is lost with each differentiation.

To prove the relation to the confluent hypergeometric function, we use the closed form that was just found. Showing that equation (B.34) is equal to equation (B.35) is equivalent to showing

$$\sum_{k=0}^{n-\mu} \binom{n}{\mu+k} \frac{(-x)^k}{k!} = \binom{n}{\mu} \sum_{k=0}^{\infty} \frac{(-(n-\mu))_k}{(\mu+1)_k} \frac{x^k}{k!}. \quad (\text{B.37})$$

First it is noticed that the series on the right hand side terminates when $k = n - \mu + 1$ since

$$(-(n-\mu))_{n-\mu+1} = -(n-\mu)(-(n-\mu)+1)\cdots(-(n-\mu)+n-\mu) = 0. \quad (\text{B.38})$$

Secondly it is noticed that

$$\begin{aligned} \binom{n}{\mu} \frac{(-(n-\mu))_k}{(\mu+1)_k} &= \frac{n!}{(n-\mu)! \mu!} \frac{(-1)^k (n-\mu)(n-\mu-1)\cdots(n-\mu-(k+1))}{(\mu+1)(\mu+2)\cdots(\mu+k-1)(\mu+k)} \\ &= (-1)^k \frac{n!}{(n-\mu-k)! (\mu+k)!}, \end{aligned} \quad (\text{B.39})$$

which proves equation (B.37). □

B.3.1 Integrals over Laguerre functions

We will now see how to calculate integrals over Laguerre functions. We denote

$$J_{n\mu}^{(\sigma)} = \frac{1}{n!^2} \int_0^\infty e^{-x} x^{\mu+\sigma} [L_n^\mu(x)]^2 dx. \quad (\text{B.40})$$

Using the definition of the associated Laguerre polynomial, we get

$$n!^2 J_{n\mu}^{(\sigma)} = \int_0^\infty e^{-x} x^{\mu+\sigma} L_n^\mu(x) \frac{d^\mu}{dx^\mu} \left[e^x \frac{d^n}{dx^n} (x^n e^{-x}) \right] dx, \quad (\text{B.41})$$

and integration by parts gives

$$\begin{aligned} n!^2 J_{n\mu}^{(\sigma)} &= e^{-x} x^{\mu+\sigma} L_n^\mu(x) \frac{d^{\mu-1}}{dx^{\mu-1}} \left[e^x \frac{d^n}{dx^n} (x^n e^{-x}) \right] \Big|_0^\infty \\ &\quad - \int_0^\infty \frac{d^{\mu-1}}{dx^{\mu-1}} \left[e^x \frac{d^n}{dx^n} (x^n e^{-x}) \right] \frac{d}{dx} \left[e^{-x} x^{\mu+\sigma} L_n^\mu(x) \right] dx. \end{aligned} \quad (\text{B.42})$$

Repeating this μ times, we get

$$\begin{aligned} n!^2 J_{n\mu}^{(\sigma)} &= \sum_{k=0}^{\mu-1} (-1)^k \frac{d^{\mu-k-1}}{dx^{\mu-k-1}} \left[e^x \frac{d^n}{dx^n} (x^n e^{-x}) \right] \frac{d^k}{dx^k} \left[e^{-x} x^{\mu+\sigma} L_n^\mu(x) \right] \Big|_0^\infty \\ &\quad + (-1)^\mu \int_0^\infty e^x \frac{d^n}{dx^n} (x^n e^{-x}) \frac{d^\mu}{dx^\mu} \left[e^{-x} x^{\mu+\sigma} L_n^\mu(x) \right] dx. \end{aligned} \quad (\text{B.43})$$

We will now evaluate this expression for the case where σ is non-negative as this is what will be needed in the report.

When σ is non-negative:

Then the terms in the sum in equation (B.43) are seen to be proportional to

$$x^\sigma e^{-x}. \quad (\text{B.44})$$

which goes to zero in both limits: In the lower limit due to the x^σ term and due to the exponential term in the upper limit.

To evaluate the remaining integral in equation (B.43), we replace the Laguerre function by its closed form given in equation (B.34). Using the Leibniz rule from equation (B.9) we get

$$\begin{aligned} \frac{d^\mu}{dx^\mu} \left[e^{-x} x^{\mu+\sigma} L_n^\mu(x) \right] &= \frac{d^\mu}{dx^\mu} \left[e^{-x} x^{\mu+\sigma} (-1)^\mu n! \sum_{k=0}^{n-\mu} \binom{n}{\mu+k} \frac{(-x)^k}{k!} \right] \\ &= (-1)^\mu n! \sum_{k=0}^{n-\mu} \binom{n}{\mu+k} \frac{(-1)^k}{k!} \\ &\quad \times \sum_{\gamma=0}^{\mu} \binom{\mu}{\gamma} (-1)^\gamma e^{-x} \frac{(\mu+\sigma+k)!}{(\gamma+\sigma+k)!} x^{\gamma+\sigma+k}. \end{aligned} \quad (\text{B.45})$$

Substituting this back into equation (B.43) we get

$$J_{n\mu}^{(\sigma)} = \frac{1}{n!} \int_0^\infty \frac{d^n}{dx^n} (x^n e^{-x}) \sum_{k=0}^{n-\mu} \binom{n}{\mu+k} \frac{(-1)^k}{k!} \sum_{\gamma=0}^{\mu} \binom{\mu}{\gamma} (-1)^\gamma \frac{(\mu+\sigma+k)!}{(\gamma+\sigma+k)!} x^{\gamma+\sigma+k} dx. \quad (\text{B.46})$$

Integrating by parts n times gives

$$J_{n\mu}^{(\sigma)} = \frac{1}{n!} \sum_{\beta=0}^{n-1} \left[(-1)^\beta U(x) \frac{d^{n-\beta-1}}{dx^{n-\beta-1}} (x^n e^{-x}) \right]_0^\infty + (-1)^n \frac{1}{n!} \int_0^\infty x^n e^{-x} \times \sum_{k=0}^{n-\mu} \binom{n}{\mu+k} \frac{(-1)^k}{k!} \sum_{\gamma=0}^{\mu} (-1)^\gamma \binom{\mu}{\gamma} \frac{(\mu+\sigma+k)!}{(\gamma+\sigma+k-n)!} x^{\gamma+\sigma+k-n} dx, \quad (\text{B.47})$$

where

$$U(x) = \sum_{k=0}^{n-\mu} \binom{n}{\mu+k} \frac{(-1)^k}{k!} \sum_{\gamma=0}^{\mu} (-1)^\gamma \binom{\mu}{\gamma} \frac{(\mu+\sigma+k)!}{(\gamma+\sigma+k-\beta)!} x^{\gamma+\sigma+k-\beta}. \quad (\text{B.48})$$

Following the same argument as earlier, the terms in the sum vanish in both limits due to the $x^n e^{-x}$ term where $n > 0$. In the integral in equation (B.47), recall that the part with $x^{\gamma+\sigma+k-n}$ comes from differentiating n times. We notice that for $n = \gamma + \sigma + k$, the expression to differentiate is just $x^0 = 1$ and hence, for all n greater than this, or equivalently $\gamma < n - \sigma - k$ we just get zero. Using this and multiplying and dividing by $(\mu + \sigma)!$, we get

$$J_{n\mu}^{(\sigma)} = (-1)^n \frac{(\mu + \sigma)!}{n!} \int_0^\infty x^n e^{-x} \sum_{k=0}^{n-\mu} (-1)^k \binom{\mu + \sigma + k}{k} \binom{n}{\mu + k} \times \sum_{\gamma=n-\sigma-k}^{\mu} (-1)^\gamma \binom{\mu}{\gamma} \frac{x^{\gamma+\sigma+k-n}}{(\gamma + \sigma + k - n)!} dx, \quad (\text{B.49})$$

and with rewriting this becomes

$$J_{n\mu}^{(\sigma)} = (-1)^n \frac{(\mu + \sigma)!}{n!} \sum_{k=0}^{n-\mu} (-1)^k \binom{\mu + \sigma + k}{k} \binom{n}{\mu + k} \times \sum_{\gamma=n-\sigma-k}^{\mu} (-1)^\gamma \binom{\mu}{\gamma} \frac{1}{(\gamma + \sigma + k - n)!} \int_0^\infty e^{-x} x^{\gamma+\sigma+k} dx. \quad (\text{B.50})$$

Integrating by parts $\gamma + \sigma + k$ more times and using the same argument for a vanishing summation as before regarding equation (B.47), we get

$$\int_0^\infty e^{-x} x^{\gamma+\sigma+k} dx = (\gamma + \sigma + k)! \int_0^\infty e^{-x} dx = (\gamma + \sigma + k)!. \quad (\text{B.51})$$

Inserting this result in equation (B.50) gives

$$J_{n\mu}^{(\sigma)} = (-1)^n (\mu + \sigma)! \sum_{k=0}^{n-\mu} (-1)^k \binom{\mu + \sigma + k}{k} \binom{n}{\mu + k} \\ \times \sum_{\gamma=n-\sigma-k}^{\mu} (-1)^\gamma \binom{\mu}{\gamma} \binom{\gamma + \sigma + k}{n}. \quad (\text{B.52})$$

Here the summation over γ can be simplified using the properties of the binomial coefficients. Denoting the summation $g(\gamma)$ and using that, [Oldham et al., 2009]

$$\binom{a}{b} = \binom{a}{a-b}, \quad \text{and} \quad \binom{a}{b} = (-1)^b \binom{b-a-1}{b}, \quad (\text{B.53})$$

we see that

$$g(\gamma) = \sum_{\gamma=n-\sigma-k}^{\mu} (-1)^{\sigma+k-n} \binom{\mu}{\mu-\gamma} \binom{-n-1}{\gamma + \sigma + k - n}. \quad (\text{B.54})$$

Substituting with $\gamma' = \gamma + \sigma + k - n$ and using, [Oldham et al., 2009]

$$\sum_{k=0}^b \binom{m}{b-k} \binom{n}{b-k} = \binom{m+n}{b}, \quad (\text{B.55})$$

we get

$$g(\gamma) = (-1)^{\sigma+k-n} \sum_{\gamma'=0}^{\mu+\sigma+k-n} \binom{\mu}{\mu + \sigma + k - n - \gamma'} \binom{-n-1}{\gamma'} \\ = (-1)^{\sigma+k-n} \binom{\mu - n - 1}{\mu + \sigma + k - n} = (-1)^\mu \binom{\sigma + k}{n - \mu}, \quad (\text{B.56})$$

where the two properties in equation (B.53) has been used to arrive at the last expression. When is inserted in equation (B.52) and we substitute with $\beta = k + \mu + \sigma - n$ and multiply and divide by $\sigma!$, we see that the integral over the associated Laguerre polynomial with $\sigma > 0$ is

$$J_{n\mu}^{(\sigma)} = (-1)^{-\sigma} \frac{n!}{(n-\mu)!} \sum_{\beta=0}^{\sigma} (-1)^\beta \binom{\sigma}{\beta} \binom{n+\beta}{\sigma} \binom{n+\beta-\mu}{\sigma}. \quad (\text{B.57})$$

For calculations related to the one-electron atom without an external field, two special cases for σ equal to zero and one will be of importance. In these cases it is easily found that

$$J_{n\mu}^{(0)} = \frac{n!}{(n-\mu)!}, \quad \text{and} \quad J_{n\mu}^{(1)} = \frac{n!}{(n-\mu)!} (2n+1-\mu). \quad (\text{B.58})$$

Appendix C

Scripts in MATLAB

In this appendix the algorithm used to calculate the coefficients for the expansions found in the three perturbation steps is inserted. The algorithm is written in MATLAB R2015B. The main script is seen in code C.1. In this script a function for calculating the product of two polynomials up to a specific degree is used to make the script run faster and this is shown in code C.2. Furthermore a function to implement the notation used in equation (3.68) is used and this can be seen in code C.3.

```
1 %% The Stark effect in N dimensions
2 clc;
3 clear all;
4 close all;
5 format rat;
6
7 %% Parameters to adjust
8 syms N % or N = some number between 2 and 3
9 order = 10; % an even number divisible by 5
10 automatic = 0; % 0 or 1
11
12 % N is the dimension. N can be either a symbol or the
13 % specific dimension can be calculated.
14
15 % order:
16 % The order*2 is number of b_k coefficients and v_k
    polynomials.
17 % order is the number of c_k and e_k coefficients different
    from zero.
18
19 % automatic:
```

```

20 % When automatic=0, the sub-function has been used to
21 % evaluate coefficients for 1/beta and the energy. This
22 % is done in a rather manual way. However, this ensures
23 % that Matlab works with symbolic numbers which
24 % increases the accuracy. Due to manual implementation,
25 % the algorithm is currently only able to calculate a
26 % maximum of 20 coefficients (order = 20).
27 % When automatic=1, the eval-function is used to
28 % evaluate the coefficients for 1/beta and the energy
29 % in a more "automatic" way. However, the use of this
30 % function means working with less decimals which limits
31 % the accuracy of the output. F.x. when working with more
32 % than 7 coefficients (order = 7) for N = 3, this
33 % inaccuracy starts to show. To reproduce coefficients
34 % in the report, automatic should be set to zero.
35
36 %% Step 1: Expansion of B(F), calculating b_k and v_k
37
38 max = order*2+2;
39 syms x
40 b = sym(zeros(1,max)); % b_k coefficients
41 y = sym(zeros(max,max)); % v_k polynomials
42 b(1) = (N-1)/4; % b_0
43 b(2) = ((N-1)/2+1)*((N-1)/2); % b_1
44 y(1,1) = -1/2; % v_0
45 y(2,1:2) = [ -((N-1)/2+1), -1]; % v_1 = x - ((N-1)/2+1);
46 % y(k,1:k) denotes v_k in such a way that
47 % y(k,1:k) = [a1,a2,...,ak] = a1+a2*x+...+ak*x^(k-1)
48
49 for kk = 3:max
50     z = 0;
51     for j = 2:kk-1;
52         z = z+simplify( product(y(j,:),y(kk+1-j,:),0) );
53     end
54     res = sym(zeros(1,kk));
55     btemp = sym(zeros(1));
56     for j = 1:kk
57         p = j-1;
58         if p == 0;
59             res(j) = res(j)+z(j);
60             btemp = btemp+z(j)*((N-1)/2);
61         else
62             for k = 0:p

```

```

63         res(k+1) = res(k+1)+z(j)*simplify( poch((N
64             -1)/2+p,p-k) );
65         end
66         btemp = btemp+z(j)*simplify( poch((N-1)/2+p,p+1)
67             );
68     end
69     y(kk,1:length(res)) = simplify( res );
70     b(kk) = -simplify( btemp );
71 end
72 %% Step 2: Expansion of 1/beta, calculating c_k
73
74 stepsize = 1;
75 n = stepsize;
76 nmax = max/2;
77 counter = 1;
78
79 while n < nmax
80     % Generating 1/beta
81     c = sym(zeros(1,n));
82     for k = 1:n
83         c(k) = sym(sprintf('c%d',k));
84     end
85     bi = 2*b(1);
86     for k = 1:n
87         bi = bi+c(k)*x^(2*k);
88     end
89     bi = subs(bi);
90
91     % Calculating 1/beta^3 up to O( x^(n+1) )
92     f = coeffs(bi,x); % 1/beta
93     g = f;
94     for kk = 1:2
95         g = product(f,g,n+1);
96     end
97
98     f = g; % 1/beta^3
99     bi2 = 2*b(1);
100    % Generating 1/beta from the sum over F
101    for kk = 1:n
102        % Calculating 1/(beta^(3))^(2*kk) up to O( x^(n+1) )
103        if kk == 1

```

```

104         g = simplify( product(f,g,n+1) );
105         adding = poly2sym( fliplr(g),x);
106         bi2 = bi2+2*b(2*kk+1)*4^(-2*kk)*adding*x^(kk);
107     end
108     if kk > 1
109         for ii = 1:2
110             g = simplify( product(f,g,n+1) );
111         end
112         adding = poly2sym( fliplr(g),x);
113         bi2 = bi2+2*b(2*kk+1)*4^(-2*kk)*adding*x^(kk);
114     end
115 end
116 % Calculating coefficients of each power
117 C = coeffs(bi2,x);
118 C = C(1:n+1);
119 if automatic == 0
120     if n == 1*stepsize
121         c1 = simplify(C(2));
122     end
123     if n == 2*stepsize
124         c2 = simplify(C(3));
125     end
126     if n == 3*stepsize
127         c3 = simplify(C(4));
128     end
129     if n == 4*stepsize
130         c4 = simplify(C(5));
131     end
132     if n == 5*stepsize
133         c5 = simplify(C(6));
134     end
135     if n == 6*stepsize
136         c6 = simplify(C(7));
137     end
138     if n == 7*stepsize
139         c7 = simplify(C(8));
140     end
141     if n == 8*stepsize
142         c8 = simplify(C(9));
143     end
144     if n == 9*stepsize
145         c9 = simplify(C(10));
146     end

```



```
147     if n == 10*stepsize
148         c10 = simplify(C(11));
149     end
150     if n == 11*stepsize
151         c11 = simplify(C(12));
152     end
153     if n == 12*stepsize
154         c12 = simplify(C(13));
155     end
156     if n == 13*stepsize
157         c13 = simplify(C(14));
158     end
159     if n == 14*stepsize
160         c14 = simplify(C(15));
161     end
162     if n == 15*stepsize
163         c15 = simplify(C(16));
164     end
165     if n == 16*stepsize
166         c16 = simplify(C(17));
167     end
168     if n == 17*stepsize
169         c17 = simplify(C(18));
170     end
171     if n == 18*stepsize
172         c18 = simplify(C(19));
173     end
174     if n == 19*stepsize
175         c19 = simplify(C(20));
176     end
177     if n == 20*stepsize
178         c20 = simplify(C(21));
179     end
180 end
181     if automatic == 1
182         for i = counter:n
183             eval(sprintf('c%d = [sym(C(i))]', i-1));
184             C(i+1) = eval(C(i+1));
185         end
186         counter = counter+5;
187     end
188     n = n+stepsize
189 end
```

```

190
191 if automatic == 1
192     eval(sprintf('c%d = [sym(C(n-stepsize+1))]', n-stepsize)
193           );
194     C(n-stepsize+1) = eval(C(n-stepsize+1));
195 end
196 % If automatic = 0, c_k is found in c1, c2, ...
197 % If automatic = 1, c_k is found in C(1), C(2), ...
198
199 %% Step 3: Expansion of the energy, calculating e_k
200
201 if automatic == 0
202     energy0 = subs(-1/2*(1/(bi))^2);
203 end
204
205 if automatic == 1
206     energy0 = eval(-1/2*(1/(bi))^2);
207 end
208
209 energy = taylor(energy0, 'order', 30) ;
210 e = coeffs(energy, x); % e_k

```

Code C.1: The algorithm used to find the coefficients of the expansions in the perturbation theory.

```

1 function y = product(f,g,n)
2 % This function calculates the product y(x) of two
3 % polynomials, f(x) and g(x) up to the order O(x^n).
4
5 % Explanation of input and output:
6 % f, g and y are polynomials as vectors with the
7 % coefficient of lowest power first.
8 % e.g. 3+x+4x^2 = [3 1 4]
9 % n is a parameter for the order. So it only
10 % calculates the product up to O(x^n).
11 % If n = 0, the full product will be calculated.
12
13 y = sym([zeros(1, length(f)-1+length(g)-1+1)]);
14 for i = 1:length(f)
15     d = [f(i).*g];
16     if i > 1
17         dd = sym(zeros(1, i-1));
18         d = [dd, d];
19     end

```

```

20     if n == 0
21         for j = 1:length(d)
22             y(j) = y(j)+d(j);
23         end
24     else
25         for j = 1:n
26             y(j) = y(j)+d(j);
27         end
28     end
29 end

```

Code C.2: A function for calculating the product of two polynomials up to a specific degree.

```

1 function y = poch(a,n)
2 syms k
3 if n==0;
4     y=sym(1);
5 else
6     y=symprod(a-k,k,0,n-1);
7 end

```

Code C.3: A function for $(a)_{-1,n}$.