The Schrödinger Equation with Coulomb Potential Admits no Exact Solutions

2019

Ilia Toli

University of Central Florida

Find similar works at: https://stars.library.ucf.edu/etd

University of Central Florida Libraries http://library.ucf.edu

Part of the Chemistry Commons

STARS Citation

https://stars.library.ucf.edu/etd/6585

This Doctoral Dissertation (Open Access) is brought to you for free and open access by STARS. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of STARS. For more information, please contact lee.dotson@ucf.edu.
ABSTRACT

We prove that the Schrödinger equation with the electrostatic potential energy expressed by the Coulomb potential does not admit exact solutions for three or more bodies. It follows that the exact solutions proposed by Fock [1–3] are flawed. The Coulomb potential is the problem. Based on the classical (non-quantum) principle of superposition, the Coulomb potential of a system of many particles is assumed to be the sum of all the pairwise Coulomb potentials. We prove that this is not accurate. The Coulomb potential being a hyperbolic (not linear) function, the superposition principle does not apply.

The Schrödinger equation as studied in this PhD dissertation is a linear partial differential equation with variable coefficients. The only exception is the Schrödinger equation for the hydrogen atom, which is a linear ordinary differential equation with variable coefficients. No account is kept of the spin or the effects of the relativity.

New electrostatic potentials are proposed for which the exact solutions of the Schrödinger equation exist. These new potentials obviate the need for the three-body force [4] interpretations of the electrostatic potential.

Novel methods for finding the exact solutions of the differential equations are proposed. Novel proof techniques are proposed for the nonexistence of the exact solutions of the differential equations, be they ordinary or partial, with constant or variable coefficients. Few novel applications of the established approximate methods of the quantum chemistry are reported. They are simple from the viewpoint of the quantum chemistry, but have some important aerospace engineering applications.
ACKNOWLEDGMENTS

This PhD dissertation would have never come into being, let alone become this good, without the help of few special people. I am grateful to the professors Shengli Zou, Andrés Dobal Campiglia, and Florencio Eloy Hernández for all of their help starting with my undergraduate studies in chemistry at UCF, and continuing all the way to the end of the graduate studies.

Professors James Kimball Harper, Emily Corinne Heider, Alfons Friedrich Schulte, Gang Chen, and Pedro Patiño Marin helped me numerous times during my studies at UCF, both undergraduate and graduate. They make the UCF the awesome place that it is, for study and research.

Professor Yongho “mother nature” Sohn of the Department of Materials Science and Engineering greatly helped me on several occasions during my undergraduate studies in aerospace engineering. “When it lights up, it lights up like a Christmas tree.”

Throughout my lifelong career as a professional learner, I have sometimes been the nightmare of the administrative assistants in six countries. Erica Walsh stands out with her awesomeness, talent, and professionalism.
# TABLE OF CONTENTS

LIST OF FIGURES ................................................................. viii

CHAPTER 1: INTRODUCTION ....................................................... 1

Quantum chemistry ............................................................... 1

The nonexistence of the exact solutions of the Schrödinger equation .... 4

The history of the existence results ............................................. 5

The Schrödinger equation for $n$ bodies ..................................... 8

The time-independent part in explicit form .................................. 12

CHAPTER 2: APPROXIMATE METHODS AND THEORIES .................. 14

The valence bond theory and the molecular orbital theory ............... 14

The linear combination of the atomic orbitals .............................. 17

The density functional theory .................................................. 18

Some applications of the density functional theory in the aerospace engineering ........................................... 19

The stable high-energy allotropes of the carbon .......................... 21

A zeolite-catalyzed Haber-Bosch process .................................. 24
LIST OF FIGURES

Figure 1.1: The IR spectrum of bromomethane. Here IR spectroscopy is used to identify the molecule through its unique IR spectrum. Reprinted courtesy of the National Institute of Standards and Technology, U.S. Department of Commerce. Not copyrightable in the United States. ........................................ 2

Figure 1.2: Second order $^1$H NMR spectrum of 2-dimethylaminoethyl acetate. Reprinted courtesy of Reusch [5]. ............................................................... 3

Figure 1.3: The C-13 spectrum of a jet fuel in CDCl$_3$. Reprinted courtesy of the National Institute of Standards and Technology, U.S. Department of Commerce. Not copyrightable in the United States. ........................................ 4

Figure 2.1: Atomic s-orbitals forming $\sigma$-bond (bonding) and $\sigma^*$-bond (antibonding) molecular orbitals. Reprinted courtesy of Rice University [6]. ........................................ 15

Figure 2.2: Atomic p-orbitals forming $\pi$-bond (bonding) and $\pi^*$-bond (antibonding) molecular orbitals. Reprinted courtesy of Rice University [6]. ........................................ 16

Figure 2.3: The valence shell molecular orbital formation in Be$_2^+$. Reprinted courtesy of Rice University [6]. ................................................................. 17

Figure 2.4: N$_{20}$, the nitrogen buckyball. It is the most stable and most sterically relaxed of all the nitrogen allotropes after N$_2$. It would be an outstanding unary hypergolic solid rocket fuel. It burns with itself to produce N$_2$, which has a low heat capacity. It would have an $I_{sp} = 578$ s. ........................................ 20
Figure 2.5: $O_6$ would be liquid oxygen at room conditions. It would greatly simplify rocket design, and releases some 10% more heat than $O_2$. It can be easily converted to breathable oxygen by an exothermic reaction. It should be easy to store.

Figure 2.6: Our preliminary studies show that $C_6$ with this configuration is stable at standard conditions. It could be liquid or solid. It is a high-energy allotrope of carbon. It could be stored in relatively mild conditions, by aerospace engineering standards. Its geometry is a planar regular hexagon. One possible route of synthesis may be the progressive dehydrogenation of benzene.

Figure 2.7: Carbon can be combined into long chains of single and triple bonds. For added stability, the ends of the chains can be capped with hydrogen atoms. This material should be relatively stable in relatively mild conditions by aerospace engineering standards, and is high-energy. It should be solid. One possible route of synthesis may be the progressive dehydrogenation of the linear alkanes.

Figure 3.1: The hydrogen atom in the Cartesian coordinates. Reprinted courtesy of LibreTexts [7].

Figure 4.1: Hylleraas coordinates for the hydrogen atom.

Figure 5.1: Helium atom in Cartesian coordinates. Reprinted courtesy of LibreTexts [7].

Figure 5.2: Helium atom in Hylleraas coordinates.
Figure 5.3: The electrostatic potential energy between two particles is a hyperbole, like the function $y = 1/x$. It is approximately linear far away from the origin, but not nearby. The superposition principle reasonably applies in the far region, but not in the near region. The omission of this fact gives rise to the interpretation of the deviation from the superposition principle for three bodies as “the three-body force”. There is nothing to superpose with two bodies.
Quantum chemistry

Quantum chemistry is the branch of chemistry that applies quantum mechanics to chemistry. It is variously considered a branch of the physical chemistry, theoretical chemistry, quantum mechanics, computational chemistry, or several at once.

In 1838 Michael Faraday created a partial vacuum on a glass tube, then applied high voltage at both of its metallic ends. The strange light that was observed was explained as a flux of free electrons. Many researcher regard this as the birthdate of the quantum chemistry.

Balfour Stewart in 1858 and Gustav Robert Kirchhoff in 1859 independently studied what today is called the black-body radiation. That is, the radiation with wavelengths outside of the range of the human perception.

Ludwig Boltzmann suggested in 1877 that the energy states of a physical system could be discrete.

Max Planck suggested in 1900 that the energy is irradiated in integer amounts of an indivisible unit, which he called quant. This quant of energy is proportional to the frequency $\nu$. The proportionality constant is called the Planck constant.

Albert Einstein suggested in 1905 that the light itself is made of particles, which he later in 1926 called photons, after photos, a Greek word for light.

One application of the quantum chemistry is the spectroscopy. The vibration modes depend on the arrangement of the various atoms in a molecule. The absorption of the energy depends on the various vibration modes. The infrared spectroscopy exploits this in order to identify the products of
the reactions, as shown in the example in Figure 1.1 for bromomethane.

![IR Spectrum of Bromomethane](image)

**Figure 1.1**: The IR spectrum of bromomethane. Here IR spectroscopy is used to identify the molecule through its unique IR spectrum. Reprinted courtesy of the National Institute of Standards and Technology, U.S. Department of Commerce. Not copyrightable in the United States.

The nuclear magnetic resonance spectroscopy, NMR spectroscopy observes the local magnetic fields around the atoms and their interactions for the purpose of molecule identification. The most common examples are $^1$H NMR spectroscopy (Figure 1.2), and $^{13}$C NMR spectroscopy (Figure 1.3).

Schrödinger first proposed the Schrödinger equation [8] in 1926. Many researchers regard this as the birthday of quantum chemistry. Whether one shares this belief or not, this shows the prominence of the Schrödinger equation in the quantum chemistry.

Promptly the Schrödinger equation was solved for the hydrogen atom. This gave rise to the hydrogen model in quantum mechanics and chemistry, that is still today the only one in use, despite all of its shortcomings. The quantum numbers $n, \ell, m_\ell$ first appeared mathematically in the solution of the Schrödinger equation for the hydrogen atom. Then they were given a physical meaning, and were extended throughout the hydrogen model for many bodies. The quantum number $m_s$ was introduced independently to explain data from various physical experiments.
Figure 1.2: Second order $^1$H NMR spectrum of 2-dimethylaminoethyl acetate. Reprinted courtesy of Reusch [5].

The Schrödinger equation describes the changes of a many-particle system over time. Since its proposal, the exact solutions have been actively sought. Currently the exact solutions are only known for some simple cases like the hydrogen atom (two-body problem in general) with the Coulomb potential, the Hooke atom, the Morse oscillator, but not for three or more particles with the Coulomb potential. Coulomb potential is the most widely used potential. Many researchers, like Bing-Hau and Witek [9] believe that finding the exact solutions for the helium atom has the potential to unleash a new quantum theory. We share this belief. The Schrödinger equation for the $\text{H}_2^+$ hydrogen cation is simpler. We believe that nonetheless it holds the same potential.
The nonexistence of the exact solutions of the Schrödinger equation

The main result of this dissertation is that we prove the following theorem.

**Theorem 1.1** *(Toli and Zou)* If a function admits a Taylor expansion in at least one point, then it cannot be the exact solution of a Schrödinger equation with the Coulomb potential for a system of three or more free particles (atom, molecule).

**Corollary 1.1** The solutions proposed by Fock [3] as exact are flawed.

In fact, the Fock solutions have Taylor expansions at most points, for example at \((1, 1, 1)\).

In mathematics, a function is an exact solution of a differential equation if the function satisfies the differential equation. In other disciplines this definition is often more relaxed in various ways. This
can lead to misunderstandings among the researchers from different backgrounds about whether or not a given solution is exact.

In quantum chemistry the meaning of the exact mathematical value of the energy does not conflict with the principle of uncertainty. The exact value of the energy is the exact mean of infinitely many measurements. Even for the ground zero level, the measurements are distributed over an interval with center at the exact theoretical value, independently of the arbitrary accuracy and precision of the instrumentation.

The history of the existence results

Bartlett, Gibbons, and Dunn [10] claimed that they proved that there are no solutions of the form

\[ \psi(x, y, z) = \sum_{i,j,k=0}^{\infty} c_{ijk} x^i y^j z^k \]  

(1.1)

In page 680, the middle of the right column, they wrote the system

\[
\begin{cases}
  c_{101} = 0 \\
  2c_{100} + c_{000} = 0 \\
  5c_{101} - \frac{1}{2} c_{100} = 0 
\end{cases}
\]  

(1.2)

From here it promptly follows that \( c_{000} = c_{100} = c_{101} = 0 \). This notwithstanding, for unknown reasons they went on to assume that \( c_{000} = 1 \), promptly reaching the contradiction that ended the
flawed proof. The series in equation (1.1) is in fact the Taylor expansion of $\psi(x, y, z)$ at the point $(0, 0, 0)$. Our claim is wider, and our proof is sound.

Withers [11] proved that the Schrödinger equation for the helium atom does not have a Frobenius-type solution in the variables $r_1$, $r_2$, and $r_{12}$. Frobenius-type solutions are power series solutions with some constraints. While Withers’ work is consistent with ours, our work is much more general.

Morgan [2] proved that for every complex $E$ value of the energy, Schrödinger equation has infinitely many solutions, each of which has a convergent Fock expansion. All these solutions admit Taylor expansion at most points, for example at $(1, 1, 1)$. Therefore they cannot be exact solutions, although accurate. This choosing of the values of the energy then solving the equation is essentially reverse engineering of the problem. This is not how the Schrödinger equation was solved for the hydrogen atom. The energy cannot assume all the possible complex values. It would be desirable to calculate the energy by solving the Schrödinger equation rather than solving the Schrödinger equation given the experimental values of the energy. Even then, the solutions ought not be infinitely many for every value of $E$. We are not aware of any physical meaning of the complex values of the energy.

In 1937 Bartlett [12] proved that the solution for the helium atom in Hylleraas coordinates [13], if it exists, cannot be of the form

$$\psi = \sum_{p,k=0}^{\infty} s^{p+\gamma} a^{p,k}(\beta) \cos k\phi$$

where $\gamma$ is a constant and

$$s = \sqrt{r} = \sqrt{r_1^2 + r_2^2}$$
This is consistent with the results of this PhD dissertation. In fact, this function has a Taylor expansion at most points, including the point \((1, 1, 1)\).

Fock [1] proposed wavefunctions in Hylleraas coordinates that asymptotically approach the exact solutions of the Schrödinger equation. His wavefunctions admit Taylor series expansions in most points, including the point \((1, 1, 1)\). In view of the results of this dissertation, those solutions cannot be exact, although accurate to beyond 40 digits. Fock wavefunctions include logarithmic terms that describe the three-particle coalescence region particularly well. In light of the uncertainty principle, it is not clear what \textit{40 digits accuracy} actually means.

The term \textit{exact solution of the Schrödinger equation} has a clear mathematical meaning. It means that when the eigenvalues (mathematical term for the energy levels) and the corresponding eigenfunctions (mathematical term for the wavefunctions) are substituted in the Schrödinger equation, they prove the equation true. They also have a clear physical meaning. They are the statistical mean of infinitely many measurements of the energy at that level. By the uncertainty principle we do not expect all the measurements to correspond exactly to that value. Approximately half of them are smaller, and approximately half are greater than the exact value. This is not due to any shortcomings of the instrumentations, rather it is an intrinsic quantum mechanical phenomenon, the uncertainty principle.

Schwartz [14] included a good review of the history and the state of the art of the result pertaining helium. Including negative and half integer exponents dramatically improves accuracy. Nakatsuji and his research group [15, 16] pioneered a new groundbreaking numerical method that they call ICI (Iterative Complement Interaction), to study the chemistry of the excited and the ionized states. This method, combined with information from NMR and other sources, enabled them to construct accurate solutions starting from approximate solutions.

The failure so far of the exact methods has led to a proliferation of the approximate and numerical
methods [3, 17–23], as well as to exact methods that simplify the problem. One exact simplified approach is due to Hylleraas [13]. This approach is used for the rest of this dissertation. Hylleraas coordinates lend themselves for both the exact and approximate treatments of any molecule. In a series of two papers, Kinoshita [24, 25] used wavefunctions with some 80 terms to calculate the ground state of the helium atom with eight digits accuracy.

The Schrödinger equation for $n$ bodies

The time-dependent Schrödinger equation in SI units is

$$i\hbar \frac{\partial |\psi(x,t)\rangle}{\partial t} = \hat{H} |\psi(x,t)\rangle$$

where $i$ is the purely imaginary unit number, and $\hbar$ is the Planck constant. Schrödinger first proposed it in 1926 [8]. It describes the changes over time in a system where the quantum effects are not relevant. It is considered to be the quantum mechanical equivalent of the Newton’s second law $F = am$, inasmuch as there is equivalence. It gives the probability distribution of the position of a particle.

Let the Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x,t)$$

be time-independent. It means that the system does not exchange energy with the environment. It
also means that the kinetic and potential energies do not convert into each other. This is the case for the ground state energy levels. Then \( V(x, t) = V(x) \) and the Schrödinger equation is linear with respect to time. It becomes

\[
i\hbar \frac{\partial |\psi(x, t)\rangle}{\partial t} = \left( \frac{\hat{p}^2}{2m} + V(x) \right) |\psi(x, t)\rangle
\]

The separation of the variables can be used to solve it with respect to time. Let

\[
\psi(x, t) = \phi(x)f(t)
\]

Then

\[
\frac{\partial \psi}{\partial t} = \phi(x) \frac{df(t)}{dt} \quad \frac{\partial \psi}{\partial x} = f(t) \frac{d\phi(x)}{dx} \quad \frac{\partial \psi^2}{\partial x^2} = f(t) \frac{d^2\phi(x)}{dx^2}
\]

Substituting in equation (1.7)

\[
i\hbar \phi(x) \frac{df(t)}{dt} = -\frac{\hbar^2}{2m} f(t) \frac{d^2\phi(x)}{dx^2} + f(t)\phi(x)V(x)
\]

Dividing both sides by \( \phi(x)f(t) \)
\[
\frac{i\hbar}{f(t)} \frac{df(t)}{dt} = -\frac{\hbar^2}{2m\phi(x)} \frac{d^2\phi(x)}{dx^2} + V(x)
\]  \hspace{1cm} (1.11)

Both sides of the last equation being functions of different variables, they must be constant for the equation to have solutions. This constant is denoted by \(E\). Mathematically it is the eigenvalue associated with the eigenfunction that together are a solution to the differential equation. Physically it represents the energy of the ground state of the system associated with the given wavefunction.

These two equations can now be written as

\[
\frac{i\hbar}{f(t)} \frac{df(t)}{dt} = E
\]  \hspace{1cm} (1.12)

\[
-\frac{\hbar^2}{2m\phi(x)} \frac{d^2\phi(x)}{dx^2} + V(x) = E
\]  \hspace{1cm} (1.13)

Equation (1.12) is a linear ordinary differential equation with constant coefficients. Its solution is

\[
f(t) = f(0)e^{-i\frac{Et}{\hbar}}
\]  \hspace{1cm} (1.14)

Equation (1.13) is the time-independent Schrödinger equation. It is a linear ordinary differential equation with variable coefficients. It constitutes the subject of much of this PhD dissertation. As
seen from equation (1.8), a solution to this leads to a solution to the time-dependent Schrödinger equation. E is the eigenvalue, ψ is the associated eigenfunction.

Any nontrivial solution ψ of the Schrödinger equation that fulfills the following four criteria is called a wavefunction. Let \( w(x_1, \ldots, x_n) \) be a weight function.

1. ψ is everywhere smooth in the interval of interest \( I \). That is, it is continuous, and continuously differentiable. This is motivated by the shape of the Schrödinger equation for most physically meaningful potentials. By all current interpretations, the potential energy of a particle moving between two points changes smoothly, without singularities.

2. ψ is square integrable. That is, \( ψ \in L^2 \), or

\[
A = \langle ψ, ψ \rangle = \int_I |ψ(x_1, \ldots, x_n)|^2 w(x_1, \ldots, x_n) dx_1 \cdots dx_n < ∞ \quad (1.15)
\]

This is motivated by the Copenhagen interpretation of the wavefunction as a probability distribution.

3. Therefore, after normalization

\[
\langle ψ, ψ \rangle = \int_I |ψ(x_1, \ldots, x_n)|^2 w(x_1, \ldots, x_n) dx_1 \cdots dx_n = 1 \quad (1.16)
\]

4. Orthogonality. If \( ψ_1, ψ_2 \) are two eigenfunctions of different eigenvalues, then

\[
\langle ψ_1, ψ_2 \rangle = \int_I ψ_1(x_1, \ldots, x_n)^* ψ_2(x_1, \ldots, x_n) w(x_1, \ldots, x_n) dx_1 \cdots dx_n = 0 \quad (1.17)
\]
Most commonly, \( I = (0, \infty) \). The integral in equation (1.15) is some finite constant \( A \). Then

\[
\frac{\psi}{\sqrt{A}} \tag{1.18}
\]

is a wavefunction. This is the normalization of the solution \( \psi \), and \( \sqrt{A} \) is the normalization constant.

The time-independent part in explicit form

The Schrödinger equation turns out especially neat using \textit{atomic units} instead of the SI units. In atomic units, \( \hbar = m_e = e_e = 4\pi \epsilon_0 = 1 \), where

\[
\epsilon_0 = \frac{625000}{22468879468420441\pi} \ F/m \quad \text{exactly} \quad \approx 8.85418781762 \cdot 10^{-12} \ F/m \tag{1.19}
\]

is the permittivity of the vacuum, and \( e_e = 1.602176634 \cdot 10^{-19} \ C \) exactly is the charge of the electron. The \( e_e \) notation is used here for the charge of the electron in order to avoid confusion with the Euler constant \( e \approx 2.71828 \ldots \), which is also heavily used throughout this PhD dissertation, for example in equation (1.14).

Now in a more explicit form, the Schrödinger equation (1.13) is given below. Let there be given \( n' \) nuclei with masses \( m_i' \) and charges \( z_i \) each. Let there be given \( n \) electrons \( e_i \) with charges \(-1\) each. The primed indexes refer to the nuclei. This keeps the notation slightly lighter as there are more electrons than nuclei to be considered in general. Then the time-independent Schrödinger equation is given by
\[
\left(-\sum_{i'=1}^{n'} \frac{\Delta_{i'}}{2m_{i'}} - \sum_{i=1}^{n} \frac{\Delta_i}{2} - \sum_{i'=1}^{n'} \sum_{i=1}^{n} \frac{z_{i'}z_i}{r_{i'i}} + \sum_{i=1}^{n} \sum_{j=i+1}^{n-1} \frac{1}{r_{ij}} + \sum_{i'=1}^{n'-1} \sum_{j'=i'+1}^{n'} \frac{z_{i'}z_{j'}}{r_{i'j'}}\right) \psi = E \psi \quad (1.20)
\]

The first term expresses the kinetic energy of the nuclei. Setting it to zero is called the Born-Oppenheimer approximation. It assumes that the nuclei are stationary. Given that the mass of a proton is about 1836 times the mass of an electron, this is a fairly good assumption, even for hydrogen.

The second term expresses the kinetic energy of the electrons. The third term expresses the potential energy of the nucleus-electron Coulomb interactions. The fourth term expresses the potential energy of the electron-electron Coulomb interactions. The fifth term expresses the potential energy of the nucleus-nucleus Coulomb interactions. The prime index is used on nuclei. We work with the equation (1.20) and its variations for much of this PhD dissertation.
CHAPTER 2: APPROXIMATE METHODS AND THEORIES

What have we been solving until now?

Eduardo Mucciolo, UCF physics

This was in response to my claim that the Schrödinger equation does not have exact solutions (they do not exist) for three or more particles. “If they do not exist, what have we been finding?”.

“We” refers to the researchers working on solving the Schrödinger equation. “Until now” refers to the one century of Schrödinger equation, and the attempts to solve it.

The valence bond theory and the molecular orbital theory

The failure so far to find the exact solutions of the Schrödinger equation for other than the two-body problem has led to a proliferation of the approximate methods for solving the Schrödinger equation. Various theories have been advanced to explain the formation of the chemical bonds, as well as the physical and chemical properties of the matter. For the rest of this section we discuss the valence bond theory and the molecular orbital theory. Both of them are outgrowths of the hydrogen model.

The *valence bond theory* assumes that the electrons are localized. It satisfactorily explains bond formations and the integer (usually 1, 2, 3) bond orders between two atoms. Accomodations have been made to explain some other bond orders, like the 1.5 bond orders in the benzene. Nowadays the valence bond theory can be seen as a localized and complementary version of the molecular orbital theory. Figures 2.1 and 2.2 illustrate the formations of $\sigma$ and $\pi$ bonds the s-orbitals and p-orbitals according to the valence bond theory.
We think that in a way the valence bond theory is an approximation similar to the Born-Oppenheimer approximation. In the Born-Oppenheimer approximation the nuclei are assumed static because they move at velocities three orders of magnitude inferior to the velocities of the electrons. In the valence bond theory the electrons are assumed localized in regions where they actually spend the absolute majority of the time: the bond regions. This viewpoint can accommodate for any bond order within the valence bond theory. It seamlessly reconciles the valence bond theory with the molecular orbital theory.

The *molecular orbital theory* assumes that the electrons are delocalized. All electrons are distributed throughout the molecule. This theory satisfactorily explains the electrical conductivity of the graphite and the graphene. These materials have half-filled p-orbitals, where the electrons freely flow from p-orbital to p-orbital.

The orbitals describe the regions of the space where the electrons are more likely to be found. The bonding orbitals are those orbitals that contribute to the bond strength in the compound. The nonbonding orbitals are those orbitals that contribute to neither the strength nor the weakness of the bonds in the compound. The antibonding orbitals are those that contribute to the weakness of the bonds. These terms are illustrated in Figure 2.3.
Figure 2.2: Atomic p-orbitals forming $\pi$-bond (bonding) and $\pi^*$-bond (antibonding) molecular orbitals. Reprinted courtesy of Rice University [6].

The molecular orbital theory can easily accommodate for any bond order. An electron in a purely antibonding orbital can still contribute a little to bond strength, although most of its contribution goes to bond weakening. Similarly to the van der Waals forces, an electron situated in an antibonding orbital repeals the other electrons around it, thus increasing the electron density in the bonding and nonbonding orbitals. Thus it contributes to bond strength, although marginally. Similar considerations hold true for the bonding and nonbonding orbitals. These considerations can be made within the molecular orbital theory where the electrons are shared by the whole molecule, but not within the current valence bond theory where the electrons are localized.
The linear combination of the atomic orbitals

The linear combination of the atomic orbitals is a method for generating the molecular orbitals starting from the atomic orbitals. It is an approximation method, in the impossibility of the exact solutions for anything else but the two-body problem. Even the orbitals of the atoms other than the hydrogen have been generated by approximate methods. The atomic orbitals are assumed to be hydrogen-like. The molecular orbitals are calculated from these atomic orbitals by assigning a numerical value $c_{ri}$ to each atomic orbital.
The atomic orbitals are $\chi_r$, the $i$-th molecular orbital is $\psi_i$. They are the basis functions of the space of all the molecular orbitals. They are one-electron wavefunctions, not necessarily centered in a nucleus. The coefficients $c_{ri}$ are chosen so that the energy of the system reaches some local minimum. They are calculated by means of the Hartree-Fock procedure. This local minimum corresponds to a chemical bond. The molecular orbital is the weighted superposition (linear combination) of these atomic orbitals.

The density functional theory

The density functional theory (DFT) arose from the Thomas-Fermi model for the electronic structure of the materials. It has been popular among solid state physicists since the 1970ies. However, it is since the 1990ies that it became accurate enough to actually be useful in chemistry. With the DFT, the properties of many complex systems have been determined.

Ab initio is Latin for from scratch, from the beginning. In modern usage in computational chemistry it means using the basic principles of the quantum mechanics in order to calculate the properties of the matter, the configurations of the molecules, and solve other computational chemistry problems.

The DFT has a computational cost much lower than the other methods, like Hartree-Fock. Nonetheless, it has many limitations of its own. It is still not sufficiently good to deal with the van der Waals forces, the band gap calculations in solid matter, the charge transfer excitations, and a long list of other problems. As of now, a trend has been observed that the DFT methods are getting less and
less accurate with time, not better [26]. This is one more reason why the exact methods are strongly desirable, alongside with their potential to spur new quantum theories.

Some applications of the density functional theory in the aerospace engineering

As a matter of illustration we report some applications of the density functional theory in the aerospace engineering. By means of the density functional theory on Gaussian [27] we studied the existence and stability of the N\textsubscript{20} nitrogen buckyball, the O\textsubscript{6} oxygen 6-ring allotropes, and other compounds in an undergraduate research project that ended in Spring 2015.

Harada et al. [28] report failure to synthesize a 2-dimensional allotrope of nitrogen akin to graphene, which is theoretically known to exist. To our opinion, it is not clear whether they failed to form it, or it formed and then tore apart to become N\textsubscript{2} again in the process of the cooling. Routinely we see point defects in graphene sheets. Something similar must reasonably happen in a nitrogen sheet, with bigger likelihood due to increased steric strain. The problem is, the nitrogen sheet is already much less stable than the graphene. A point defect is the site where the tearing of the sheet starts, and it quickly propagates to everywhere. Besides, the geometry of a nitrogen sheet is not planar. Eventually the steric strain alone will grow to be sufficient to tear it apart. So, they in general will be possibly synthesized either in small sheets, or with regular undulated geometry, and without point defects. Still there is the problem of the border of the sheets. Double bonds N\textsubscript{2} occur that are further unstable, and further more strained.

The N\textsubscript{20} buckyball, shown in Figure 2.4, is also one of the smallest allotropes of nitrogen, which theoretically exists. The nitrogen atoms in N\textsubscript{20} are in relatively relaxed angles. It should be the most stable allotrope of nitrogen after N\textsubscript{2}, although a distant second. Being small in size, it should be comparably easy to synthesize buckyballs without defects. Those with defects tear, but those
without defects can be collected. It also lacks double bonds and borders. The \( \text{N}_{20} \) should be a single-propellant hypergolic, solid rocket fuel with high \( I_{sp} \). We have calculated that the \( I_{sp} = 578 \text{ s} \).

In aerospace engineering the \( I_{sp} \), the \textit{specific impulse} is a measure of the goodness of a propellant. It is measured in seconds. The higher the number, the better the propellant. The \( \text{N}_{20} \) may need to be stored in a cold temperature, yet mild by aerospace industry standards.

![Figure 2.4: N\textsubscript{20}, the nitrogen buckyball. It is the most stable and most sterically relaxed of all the nitrogen allotropes after N\textsubscript{2}. It would be an outstanding unary hypergolic solid rocket fuel. It burns with itself to produce N\textsubscript{2}, which has a low heat capacity. It would have an \( I_{sp} = 578 \text{ s} \).](image)

The liquid oxygen at room conditions, shown in Figure 2.5, would have a long list of applications in the aerospace industry, and elsewhere on Earth as it is in Heaven. It would have many applications in many other areas of engineering. Gadzhiev et al. [29] proved by ab initio methods that this allotrope exists. In an undergraduate research project we studied its thermodynamic properties. It would be a rather stable compound, yet less stable than O\textsubscript{2}. It would release some 10\% more heat than O\textsubscript{2} in the reactions. Given its molar mass, it should be liquid at room conditions. It can be easily converted into breathable oxygen O\textsubscript{2} by means of a slightly exothermic reaction. In view of the space exploration, Mars and Moon settlement, it would be convenient to carry a few kg of uncompressed liquid oxygen at room conditions over the shoulder, and gradually convert it into breathable oxygen. An average human consumes approximately 0.8 kg oxygen O\textsubscript{2} per day.

20
Figure 2.5: O₆ would be liquid oxygen at room conditions. It would greatly simplify rocket design, and releases some 10% more heat than O₂. It can be easily converted to breathable oxygen by an exothermic reaction. It should be easy to store.

In a paper published in a peer reviewed journal [30] as part of our undergraduate research project, we used density functional theory to construct a computer chip starting from a single sheet of fluorographene that is highly robust, and can store 100,000 times more data than the next best chip. The fluorographene is a graphene sheet with one fluorine atom attached to each carbon, some up and some down. The border carbon atoms have two fluorine atoms attached in order to make them too \( sp^3 \). These chips can be stacked, and the storage capability becomes practically infinite for most purposes. Reading and writing methods were proposed, and others have been found ever since.

To our opinion, a more appropriate name for fluorographene is fluorographane, that is, fluorinated graphane. Graphane is graphene with hydrogen atoms attached.

The stable high-energy allotropes of the carbon

Generally the engineers think that burning carbon with oxygen would have an \( I_{sp} \) of just above 200 s. By carbon the engineers mean the graphite allotrope. We made the following ab initio calculations with the atomic carbon allotrope. When burned with O₂ to yield CO₂ it has an \( I_{sp} = 742 \) s. If CO is formed, then \( I_{sp} = 827 \) s. If O₆ is burned with C to give CO₂, then \( I_{sp} = 749 \) s. When CO is formed, then \( I_{sp} = 832 \) s. These numbers compare favorably with the current \( I_{sp} \) of low 300 s for
most rocket fuels. The products of these reactions are CO or CO$_2$ or both, with low heat capacities. The engineers are especially fond of the water reaction because it is highly exothermic. The problem is, the product is water, which has a high heat capacity.

![Diagram of C$_6$](image)

Figure 2.6: Our preliminary studies show that C$_6$ with this configuration is stable at standard conditions. It could be liquid or solid. It is a high-energy allotrope of carbon. It could be stored in relatively mild conditions, by aerospace engineering standards. Its geometry is a planar regular hexagon. One possible route of synthesis may be the progressive dehydrogenation of benzene.

The atomic carbon is gaseous in standard conditions. It is high in energy, but unstable. It removes itself through autopolymerization. In cryogenic conditions it may be an option to be considered for rocket fuel. Its stability increases in cryogenic conditions. Alternatively, there exists a cornucopia of allotropes of carbon with the right combination of high energy levels, stability, and ease of fabrication. Figures 2.6 and 2.7 present just two examples of such high-energy allotropes.

$I_{sp} = 832$ s represents an upper bound of the goodness of the high-energy carbon allotropes as rocket fuels. Effectively, with good choices of the allotropes, any number less than that can be attained. Sometimes a lesser $I_{sp}$ may be preferred, in view of the choice of the materials for the design of the rocket engine.
Figure 2.7: Carbon can be combined into long chains of single and triple bonds. For added stability, the ends of the chains can be capped with hydrogen atoms. This material should be relatively stable in relatively mild conditions by aerospace engineering standards, and is high-energy. It should be solid. One possible route of synthesis may be the progressive dehydrogenation of the linear alkanes.

Most allotropes of carbon are solid, including most high-energy allotropes that we are interested in. This usually presents a problem in rocket design, including the issues usually associated with the solid fuels, and with the liquid-solid two-phase fuels. Among other, solid fuels present issues of control of combustion. Once ignited, they are currently impossible to stop. Their rate of combustion is variable, unstable, and little controllable. The combustion is approximately uniformized by means of complicated engineering configurations. One possible approach to solving these problems may be to store these fuels in the rocket tank woven into a single thread, if their mechanical properties and storage conditions allow for that. The thread is pulled into the combustion chamber as needed, and is cut and stopped when the combustion is needed to stop. The combustion can be restarted at any desired time.

Many more calculations about the $I_{sp}$ of the high-energy allotropes of carbon, the second-most stable allotrope of nitrogen $N_{20}$, the liquid oxygen at room conditions $O_6$ and others can be found in Toli et al. [31]. Designs for cheap high-altitude launch of spacecraft are included in the same paper. Fluorographene combined with graphene has big potential for constructing capacitors and other devices as well.
A zeolite-catalyzed Haber-Bosch process

The Haber-Bosch process for the production of ammonia from nitrogen from the air has been credited with providing food for one billion humans. The reaction itself

\[ \text{N}_2(g) + 3 \text{H}_2(g) \rightarrow 2 \text{NH}_3(g) \quad (2.2) \]

is exothermic, but \( \text{H}_2 \) is not freely available. The overall reaction including dihydrogen production is highly endothermic, that is, energy-consuming. But this is only one of the many problems with the Haber-Bosch process.

The reaction (2.2) takes place under extreme temperature and pressure conditions, with poor reaction yield at high cost. Higher temperatures are needed, else atomic hydrogen recombines with itself rather than with the nitrogen. This goes against the Le Chatelier principle for the exothermic final step reaction, hence the poor yield. A possible solution to all these ills may be using zeolites as catalysts. With their enormous surface area and stability, they would much more than make up for the low yield at milder temperatures. We have an ongoing project for the ab initio study of the various zeolites as catalysts for the Haber-Bosch process at room conditions.

The zeolites have a long list of advantages over the MOFs (metal-organic frameworks) and the currently used iron catalysts.

- Enormous catalytic surface area, around \( 800 \text{ m}^2/\text{g} \), unlike iron catalysts.
- Practically space-filling surfaces, more so than MOFs.
- More active sites than MOFs, more stable than MOFs.
• Can withstand the high temperatures intrinsic to the gas reactions, unlike MOFs.

• Already widely used as catalysts in oil industry.

• Cheaply mass-produced.

• Can be regenerated easily.

• Practically no loss of catalyst during the reactions.

Ferrierites, the FER structure, $(\text{Na,K})_2\text{Mg(Si,Al)}_{18}\text{O}_{36}(\text{OH}) \cdot 9\text{H}_2\text{O}$ are named after the Canadian mining engineer Walter Frederick Ferrier. Fe-FER is a variation where some 7-14% of the Al sites are replaced with Fe. These have already been studied for the cleanup of the nitrous oxide $\text{N}≡\text{N}–\text{O}$ pollutant by Jiša et al. [32], and show promise. The nitrous oxide attaches to the iron atom from the nitrogen side. This gives hope that it will work well to bind the dinitrogen molecule long enough and weak enough for the ammonia reaction to be initiated, with the dihydrogen molecule being attracted to the other nitrogen not attached to the iron atom. More DFT studies are needed in the topic for the various zeolites, and their variations.
CHAPTER 3: THE HYDROGEN ATOM

Introduction

With reference to Figure 3.1, the Coulomb potential between a proton and an electron in atomic units is

\[ V(r) = -\frac{1}{r} \]  \hspace{2cm} (3.1)

The reduced (or effective) mass of the system is

\[ \mu = \frac{mM}{m + M} \]  \hspace{2cm} (3.2)

where \( m \) is the mass of the electron and \( M \) is the mass of the proton. In atomic units,

\[ \mu = \frac{M}{M + 1} \approx 1 \]  \hspace{2cm} (3.3)
The mass of the proton is 1836 times the mass of the electron. For most practical purposes, \( \mu \approx 1 \) in atomic units. In general, the reduced mass \( \mu \) for a system of \( n \) bodies is given by the equation

\[
\frac{1}{\mu} = \sum_{i=1}^{n} \frac{1}{m_i}
\] (3.4)

The Hamiltonian for the hydrogen atom is

\[
\hat{H} = -\frac{1}{2\mu} \Delta - \frac{1}{r}
\] (3.5)

where \( \Delta = \nabla^2 \) is the Lagrangian operator. Expanding the \( \Delta \) and converting to the polar coordinates

\[
x = r \sin \theta \cos \phi \quad y = r \sin \theta \sin \phi \quad z = r \cos \theta
\] (3.6)
the Schrödinger equation becomes

\[-\frac{1}{2\mu} \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \frac{\partial}{\partial r} \right] + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left[ \sin \theta \frac{\partial}{\partial \theta} \right] + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) - \frac{1}{r} \psi = E \psi \tag{3.7} \]

\[\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left[ \sin \theta \frac{\partial}{\partial \theta} \right] + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + 2 \left( E + \frac{1}{r} \right) \psi = 0 \tag{3.8} \]

Either form of the last two equations will be used, as convenient. The radial variable can be separated from the two angular variables

\[\psi(r, \theta, \phi) = R(r)Y(\theta, \psi) \quad \rightarrow \quad \frac{\partial \psi}{\partial r} = Y \frac{dR}{dr} \tag{3.9} \]

\[\frac{Y}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{R}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left[ \sin \theta \frac{\partial Y}{\partial \theta} \right] + \frac{R}{r^2 \sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} + 2\mu (E + \frac{1}{r}) RY = 0 \tag{3.10} \]

Multiplying by \(r^2/RY\)

\[\frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2\mu r^2}{\hbar^2} \left( E + \frac{e^2}{4\pi\epsilon_0 r} \right) = -\frac{1}{Y} \frac{\partial}{\partial \theta} \left[ \sin \theta \frac{\partial Y}{\partial \theta} \right] - \frac{1}{Y \sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \tag{3.11} \]

The left hand side only depends on \(r\), the right hand side only depends on \(\theta\) and \(\phi\). This can only happen if both sides are constants as the variables vary. Denote this constant by \(A\). Then
\[
\frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + 2\mu r^2 \left( E + \frac{1}{r} - A \right) R = 0 \tag{3.12}
\]

\[
\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} + AY = 0 \tag{3.13}
\]

The first equation is called radial, the second angular. A and later B are called separation constants.

Set \( Y(\theta, \phi) = \Theta(\theta)\Phi(\phi) \), and substitute in the angular equation.

\[
\frac{\Phi}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \frac{\Theta}{\sin^2 \theta} \frac{\partial^2 \Phi}{\partial \phi^2} + A\Theta\Phi = 0 \tag{3.14}
\]

Multiply both sides by \( (\sin^2 \theta)/\Theta \Phi \)

\[
\frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + A\sin^2 \theta + \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} = 0 \tag{3.15}
\]

Again, the first two terms only depend on \( \theta \) and the last one only on \( \phi \). Denote by \( B \) this separation constant. Then

\[
\frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + A\sin^2 \theta - B = 0 \tag{3.16}
\]
\[
\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} + B = 0
\] (3.17)

The first equation is called polar, the second azimuthal. The original linear partial differential Schrödinger equation has been split into three linear ordinary differential equations. Of them all, the azimuthal is the simplest to solve. It is a second order linear ordinary differential equation with constant coefficients.

\[
\frac{\partial^2 \Phi}{\partial \phi^2} + B \Phi = 0 \quad \rightarrow \quad \Phi(\phi) = c_1 e^{i\sqrt{B}\phi} + c_2 e^{-i\sqrt{B}\phi}
\] (3.18)

The \( \sqrt{B} = m_\ell \) must be an integer, otherwise the values of the function at angles 0\(^\circ\) and 360\(^\circ\) would be different. The \( m_\ell \) is called the magnetic moment quantum number. Other constraints will be later imposed on the range of the values that it can assume. With a convenient choice of coordinates it can be assumed that \( c_2 = 0 \), without loss of generality. The azimuthal component of the wavefunction becomes

\[
\Phi(\phi) = c e^{i\sqrt{B}\phi}
\] (3.19)

The general solution is a product of the three solutions, and will be normalized. This means that the constant \( c \) in this solution can be altogether omitted. Now the solution of the azimuthal equation can be written as
\[ \Phi_{m\ell}(\phi) = e^{i\sqrt{B}\phi} = e^{im\ell\phi} \quad (3.20) \]

to emphasize the fact that there are as many solutions as allowable values of \( m\ell \).

Solving the angular polar equation

Now the angular polar equation becomes

\[ \sin \theta \frac{d}{d\Theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + A \sin^2 \theta - m^2_{\ell} = 0 \quad (3.21) \]

Multiply both sides by \( \Theta/\sin^2 \theta \) and rearrange

\[ \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \left( A - \frac{m^2_{\ell}}{\sin^2 \theta} \right) \Theta = 0 \quad (3.22) \]

Denote \( x = \cos \theta \) and \( P(x) = \Theta(\theta) \). Then \( \sin^2 \theta = 1 - x^2 \) and

\[ \frac{d}{d\theta} = \frac{dx}{d\theta} \frac{d}{dx} = -\sin \theta \frac{d}{dx} \quad (3.23) \]
\[
\frac{1}{\sin \theta} \left( - \sin \theta \right) \frac{d}{dx} \left( \sin \theta (- \sin \theta) \frac{dP}{dx} \right) + \left( A - \frac{m_\ell^2}{\sin^2 \theta} \right) P = 0 \quad (3.24)
\]

\[
\frac{d}{dx} \left( \sin^2 \theta \frac{dP}{dx} \right) + \left( A - \frac{m_\ell^2}{\sin^2 \theta} \right) P = 0 \quad (3.25)
\]

\[
\frac{d}{dx} \left( 1 - x^2 \right) \frac{dP}{dx} + \left( A - \frac{m_\ell^2}{1 - x^2} \right) P = 0 \quad (3.26)
\]

\[
(1 - x^2) \frac{d^2 P}{dx^2} - 2x \frac{dP}{dx} + \left( A - \frac{m_\ell^2}{1 - x^2} \right) P = 0 \quad (3.27)
\]

This is a linear ordinary differential equation, but with variable coefficients. With \( A = \ell(\ell + 1) \), this is the associated Legendre differential equation

\[
(1 - x^2) \frac{d^2 P^m_\ell}{dx^2} - 2x \frac{dP^m_\ell}{dx} + \left( \ell(\ell + 1) - \frac{m_\ell^2}{1 - x^2} \right) P^m_\ell(x) = 0 \quad (3.28)
\]

\[
\frac{d}{dx} \left( 1 - x^2 \right) \frac{dP^m_\ell}{dx} + \left( \ell(\ell + 1) - \frac{m_\ell^2}{1 - x^2} \right) P^m_\ell(x) = 0 \quad (3.29)
\]

Its solutions are the associated Legendre polynomials

\[
P^m_\ell(x) = (-1)^m_\ell (1 - x^2)^{m_\ell/2} \frac{d^{m_\ell}}{dx^{m_\ell}}(P_\ell(x)) \quad \text{with} \quad (3.30)
\]
$$P_\ell(x) = \frac{1}{2\ell \ell!} \frac{d^\ell}{dx^\ell} (x^2 - 1)^\ell$$  \hspace{1cm} \text{Rodrigues formula} (3.31)$$

for all integers \(0 \leq m_\ell \leq \ell\). For \(m_\ell = 0\) they become the Legendre polynomials. Thus, in a more explicit form

$$P_{m_\ell \ell}(x) = \frac{(-1)^{m_\ell}}{2\ell \ell!} (1 - x^2)^{m_\ell/2} \frac{d^{\ell + m_\ell}}{dx^{\ell + m_\ell}} (x^2 - 1)^\ell$$  \hspace{1cm} (3.32)$$

with \(-\ell \leq m_\ell \leq \ell\).

An alternative definition of the Legendre polynomials is recursive,

$$P_\ell^m = (1 - x^2)^{m/2} \left( a_0 \sum_{n=0}^\infty \frac{2n}{a_0} x^{2n} + a_1 \sum_{n=1}^\infty \frac{2n+1}{a_1} x^{2n+1} \right)$$  \hspace{1cm} (3.33)$$

where \(a_{n+2} = \frac{(n + m)(n + m + 1) - A}{(n + 1)(n + 2)} a_n\) (3.34)

The odd coefficients only depend on the \(A\) and \(a_1\). The even coefficients only depend on the \(A\) and \(a_0\). Again, \(A = \ell(\ell + 1)\). If \(\ell\) or \(m = m_\ell\) are not integers, the Legendre polynomials are called Legendre functions. The number \(\ell\) is called its degree, \(m\) its order. Wavefunctions must have finite integrals so that they can be normalized. So, only solutions that converge make physical sense and are accepted. In this case, the solution converges iff \(\ell\) is an integer.
Solving the radial equation

Now that $A = \ell(\ell + 1)$, the radial equation is rewritten as

$$
\frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + 2\mu r^2 \left( E + \frac{1}{r} \right) R - \ell(\ell + 1)R = 0 \tag{3.35}
$$

$$
\frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left[ 2\mu Er^2 + 2\mu r - \ell(\ell + 1) \right] R = 0 \tag{3.36}
$$

Substitute $y(r) = rR(r)$. Then

$$
\frac{d}{dr} \left( r^2 \frac{d}{dr} \right) R(r) = \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) \frac{1}{r} y(r) = \tag{3.37}
$$

$$
\frac{d}{dr} \left[ -r^{-2} y(r) + r^{-1} \frac{dy(r)}{dr} \right] = \frac{d}{dr} \left[ -y(r) + r \frac{dy(r)}{dr} \right] = \tag{3.38}
$$

$$
- \frac{dy}{dr} + \frac{dy}{dr} + r \frac{dy}{dr^2} = r \frac{d^2 y}{dr^2} \quad \text{and} \quad R(r) = \frac{y(r)}{r}
$$

Now equation (3.36) becomes

$$
r \frac{d^2 y}{dr^2} + \left[ 2\mu Er^2 + 2\mu r e^2 - \ell(\ell + 1) \right] \frac{y}{r} = 0 \tag{3.39}
$$
\[ \frac{d^2 y}{dr^2} + \left[ 2\mu E + \frac{2\mu}{r} - \frac{\ell(\ell + 1)}{r^2} \right] y = 0 \] (3.40)

Substitute

\[ \left( \frac{\epsilon}{2} \right)^2 = -2\mu E \] (3.41)

The negative sign is there to assure that the \( \epsilon \) is real valued. We are interested on the bound states, where \( E < 0 \). Now equation (3.40) becomes

\[ \frac{d^2 y}{dr^2} + \left[ \frac{2\mu}{r} - \frac{\epsilon^2}{4} - \frac{\ell(\ell + 1)}{r^2} \right] y = 0 \] (3.42)

The third and last substitution

\[ x = r\epsilon \quad \rightarrow \quad r = \frac{x}{\epsilon} \quad \rightarrow \quad dr = \frac{dx}{\epsilon} \] (3.43)

\[ \frac{d^2 y(r)}{dr^2} = \frac{d}{dr} \frac{dy(r)}{dr} = \epsilon \frac{d}{dx} \frac{dy(x)}{dx} = \epsilon^2 \frac{d^2 y(x)}{dx^2} \] (3.44)

Equation (3.42) now becomes
\[
\frac{\epsilon^2 d^2 y(x)}{dx^2} + \left[ \frac{2\mu}{x} - \frac{\epsilon^2}{4} - \frac{\epsilon^2 \ell(\ell + 1)}{x^2} \right] y(x) = 0
\] (3.45)

\[
\frac{d^2 y(x)}{dx^2} + \left[ -\frac{1}{4} + \frac{2\mu}{x\epsilon} - \frac{\ell(\ell + 1)}{x^2} \right] y(x) = 0
\] (3.46)

Set

\[
\ell(\ell + 1) = \frac{k^2 - 1}{4} \quad \quad \frac{2\mu}{\epsilon} = \frac{2j + k + 1}{2}
\] (3.47)

The equation now becomes

\[
y''(x) + \left( -\frac{1}{4} + \frac{2j + k + 1}{2x} - \frac{k^2 - 1}{4x^2} \right) y = 0
\] (3.48)

whose solutions are, for all integers \( j, k \),

\[
y_j^k(x) = e^{-x/2} x^{(k+1)/2} L_j^k(x)
\] (3.49)

with

36
\[ L_j^k(x) = (-1)^k \frac{d^k}{dx^k} L_{j+k}(x) \quad \text{and} \quad L_j(x) = e^x \frac{d^j}{dx^j} e^{-x} x^j \] (3.50)

The solution for the complete Schrödinger equation for the hydrogen is given by the product of the three solutions,

\[ \Psi(r, \phi, \theta) = N e^{-r\epsilon/2}(r\epsilon)^{(k+1)/2} L_j^k(r\epsilon) \cdot e^{i\sqrt{B}\phi} \cdot (-1)^m \frac{d^m}{2^m m!} (\sin^2 \theta)^{m/2} \frac{d^{\ell+m}}{d(\cos \theta)^{\ell+m}} (\sin^2 \theta)^\ell \] (3.51)

where \( N \) is the normalization constant. From the equations (3.41) and (3.47), the energy levels for hydrogen atom are

\[ -2\mu E = \left( \frac{4\mu}{2j + k + 1} \right)^2 \quad \rightarrow \quad E = -\frac{\mu}{n^2} \] (3.52)
CHAPTER 4: MATHEMATICAL AND COMPUTATIONAL BACKGROUND

In this chapter we introduce several mathematical concepts that we need in order to prove the main result of this PhD dissertation. We also give sufficient information on software to allow for the reproducibility of our results, as well as for further progress in this topic.

The mathematical induction

The mathematical induction is a standard and widespread proof technique throughout mathematics, throughout time. Its first documented usage goes back to 370 BC, with Plato’s Parmenides. Its modern formulation was done by Peano in the end of the 19th century. Conceptually we can think of it this way. We have an infinite row of dominos. We personally check that the first domino falls. Then we prove that if the first domino falls, the second domino falls as well. Because we checked that the first domino fell, we have proven that the second domino fell as well, without having to check this. Then we prove that if the second domino fell, the third fell as well. This is in good agreement with the discipline of the mathematical logic.

In general, we check that the first domino fell. Then we prove that if the domino number \( k \) fell, then the domino number \( k + 1 \) fell as well. With this we have proven that all dominos have fallen. More formalized, there are three steps to proving a proposition by induction.

1. **Base step.** Check that the proposition is true for \( n = 0 \).

2. **Inductive step.** Assume that the proposition is true for \( n = k \).

3. **Inductive proof.** Using the first two steps, prove that the proposition is true for \( n = k + 1 \).
Then the proposition is true for all the values of $n$.

**Example 4.1** *This is a classical example. Prove that*

\[ 0 + 1 + 2 + \cdots + n = \frac{n(n+1)}{2} \]  \hspace{1cm} (4.1)

**Base step.** *We check that for $n = 0$ identity (4.4) is true. In fact,*

\[ 0 = \frac{0 \cdot 1}{2} \]  \hspace{1cm} (4.2)

**Inductive step.** *We assume that the identity is true for $n = k$. That is, we assume that for some integer $k$ we have*

\[ 0 + 1 + 2 + \cdots + k = \frac{k(k+1)}{2} \]  \hspace{1cm} (4.3)

**Inductive proof.** *We need to prove the statement for $n = k + 1$. That is, we need to prove that*

\[ 0 + 1 + 2 + \cdots + k + (k + 1) = \frac{(k + 1)(k + 2)}{2} \]  \hspace{1cm} (4.4)

*We add $(k+1)$ to both sides of equation (4.3), then transform the right hand side to a suitable form.*
\[ 0 + 1 + 2 + \cdots + k + (k+1) = \frac{k(k+1)}{2} + (k+1) = \]

\[ \frac{k(k+1) + 2(k+1)}{2} = \frac{(k+1)(k+2)}{2} \]  

(4.5)

This ends the proof.

There exists a vast amount of variations in the techniques of the mathematical induction, fit for a variety of situations. There is induction on more than one indexes. In proving the main result of this PhD dissertation, Theorem 1.1, we use the mathematical induction on the two indexes \(i, j\) that are logically embedded in loops into each other. In a previous proof in a paper by Toli and Zou [33] we actually used three induction loops embedded into each other. We eventually found this much simpler proof with only two inductive loops. In Theorem 1.1 we want to prove that \(a_{ijk} = 0\) for all \(i, j, k\) integers. This is done by mathematical induction formulated as follows.

1. The base case is checked to hold true, the point \((0, 0, 0)\), \(a_{000} = 0\). There was no need, but we checked many more coefficients, and they are all zero.

2. The induction assumption is made for \(i\).

3. Within the scope of the induction assumption for \(i\), a base case is checked for the induction on \(j\).

4. The induction assumption for \(j\) is made.

5. The induction proof is made for \(j\).

6. This ends the induction proof for \(i\), and proves the theorem.
The Maple [34], Mathematica [35], MATLAB [36], and Singular [37] computational mathematics software were jointly and extensively used throughout this PhD dissertation to perform various mathematical calculations. Calculations with multivariate orthogonal polynomials and functions are performed with the package MOPS for Maple written by Dumitriu et al. [38]. The handbook of MOPS, plus a handy reference to many useful mathematical concepts is the paper by the same authors and title, Dumitriu et al. [38]. As of 2019, MOPS is the only package known to perform calculations with the multivariate orthogonal polynomials and functions.

The MOPS was last updated in 2001 by Dumitriu [39], with instructions for the Windows and Linux platforms of the time. It presents extra issues in 2019, on a Mac platform. Here is our workaround for Maple 2017, on Mac. The MOPS folder is placed inside the Maple 2017 folder. The current worksheet is placed inside the Help Files folder of the MOPS. All commands are executed from there. At the beginning of each work session, the following two commands are run

```maple
> libname := libname, "../MOPS.lib"

> with(MOPS)
```

It can now be checked whether it works properly by executing some MOPS command, as recommended by Dumitriu et al. [38]. Many thanks to Yogin of the Maple technical support for helping figure out MOPS on Mac. The synthax and examples for any of the thirty MOPS commands can be found in the Help Files folder of the MOPS.

Often we need to work with variable rather than constant parameters. This is not currently possible in the MOPS with the current state of the affairs. The workaround for this are various MATLAB programs, like the one in the appendix written by Koev [40], and reprinted with permission.
Various functions of the Mathematica were extensively used to generate all sorts of systems of polynomial equations.

Orthogonal functions in one and many variables

We need some definitions as itemized below from the topic of the orthogonal functions with argument matrices of many variables. These definitions and their in-depth treatment can be found in Dumitriu [39], Macdonald [41], and Muirhead [42]. For the matrices with real, complex, and quaternion entries respectively, $\beta = 1, 2, 4$, and $\alpha = 2/\beta$. We are only interested on the real and complex numbers, not on the quaternions. The wavefunctions are required to be orthogonal. The partitions of the integers are intrinsic to the orthogonal functions. In analogy with the quantum numbers for the hydrogen, the partitions must have a physical meaning to be discovered. It is quite appropriate to call “quantum partitions” the partitions associated to the respective wavefunctions.

- Partitions of integers, the length of a partition.
- Orderings of partitions and monomials, lexicographich ordering, total orderings, partial orderings.
- Dominance.
- Symmetric polynomials.
- Homogeneous polynomials.
- Jack polynomials.
- Binomial coefficients, generalized binomial coefficients.
- Gamma function, multivariate Gamma function.
• Shifted factorial, generalized shifted factorial. Generalized Pochhammer symbol.

• Generalized hypergeometric functions.

The Gröbner bases

The Gröbner bases were introduced by Buchberger [43]. They are in commutative algebra and algebraic geometry what the Gaussian elimination is in linear algebra. Theoretically, they solve the problem of whether a given element of a commutative ring belongs to an ideal or not. In practice, the complexity of the Buchberger algorithm [43] for calculating the Gröbner bases is most often prohibitive. Ideally, if the order of the variables is lexicographic, if there are enough independent equations (zero-dimensional ideal), if the complexity of the system is reasonably low, the Buchberger algorithm for the calculation of the Gröbner bases gives the solution to the system. Cox, Little, O’Shea [44] provide a wide and accessible introduction to the theory. In this PhD dissertation the terms ideal and system of equations are interchangeable.

Bruno Buchberger discovered the algorithm now named after him in 1965, in his PhD dissertation [43]. He named the bases that his algorithm produces after his professor, Wolfgang Gröbner. For the next 25 years the enormous importance of his algorithm will lay unnoticed, even to its own author. Had the computers not advanced the way they did, this theory might have been forgotten forever.

Nikolaj Maximowitsch Günther (Николай Максимович Гюнтер), a Russian mathematician of German origin, discovered what we now call Gröbner bases in a series of papers in 1910, 1913, and 1925, as reported by Renschuch et al. [45], some 80 years ahead of his time. The time gap becomes even more breathtaking if we keep into account that he did all this in a different geological era with respect to the computer development, in the obscurity, poverty, and the backwardness of a war-torn Russia.
The researchers first realized of the usefulness of the Gröbner bases in 1989, when Patrizia Gianni [46] and Michael Kalkbrenner [47] independently and at the same time discovered the Shape Lemma, also known as the Gianni-Kalkbrenner Lemma [48]. Their papers were published in the same number of the same journal, back to back. Even for a given order of variables, the Gröbner basis is not unique, but this is no limitation to its applications. The leading monomials of a Gröbner basis for a given monomial order are unique.

The real limitation of the Gröbner bases applicability is the complexity of the Buchberger algorithm. On a random system in \( n \) variables with the maximum occurring degree \( d \), the Buchberger algorithm requires \( d^n \) bit operations and \( d^n \) bit space to be successfully run. The worst case complexity is twice exponential in the number of variables \( n \), that is, a function that looks like \( f(n) = 2^{2^n} \). In fact, solving systems of nonlinear equations is a well known NP-complete problem, as proven by Fraenkel and Yesha [49]. The NP-completeness of many other problems is proven by reducing them to this problem in polynomial time. All this said, a vast amount of research and experience has arisen around Gröbner bases. Within our needs, they go far enough to be useful.

Calculating the Gröbner bases with a lexicographic order in practice proves to be the hardest of them all, despite them being practically the only useful in solving systems of nonlinear polynomial equations. Many algorithms exist that first calculate the Gröbner basis in another monomial order. Then, with this knowledge, the lexicographic Gröbner basis is calculated. One of the earliest and best known is the Traverso algorithm [50]. It first calculates the Gröbner basis in whichever monomial order is easiest, then calculates the Hilbert series of the ideal, then uses this series to render the complexity of the lexicographic Gröbner polynomial. Knowing any Gröbner basis makes it computationally easy to calculate the Hilbert series of an ideal. Practice has shown that the degree reverse lexicographic order is faster. The theoretical complexity boundaries for the Buchberger algorithm remain the same. The Traverso algorithm is implemented in all major mathematical software.
In the next section we use the Gröbner bases to illustrate a new method to find the exact solutions of the differential equations. There is nothing new in the results about the hydrogen, but the method is new. We calculate the radial part of the solution, but all parts can be calculated similarly. In an independent project we are using this method to find the exact solutions for the \( \text{H}_2^+ \) dihydrogen cation with a new, mathematically calculated potential representing the electrostatic potential, and with the Born-Oppenheimer approximation assumption.

The Hylleraas coordinates for the hydrogen atom

As described in the previous chapters, the exact solutions of the Schrödinger equation for the hydrogen atom are well known. For the purpose of the illustration of the method, the solutions are found again in this section. This method is supposed to also give the exact solutions for the Schrödinger equation with the correct electrostatic potential. This is an ongoing project. These solutions, with the quantum numbers present are more clearly given by Jones [51]. In page 11, equation (4.17), the radial part is given as

\[
R(r) = \frac{N}{an} \left( \frac{r}{an} \right)^\ell e^{-\frac{2r}{an}} L_{n-\ell-1}^{2\ell+1} \left( \frac{2r}{an} \right) \tag{4.6}
\]

\[
a = \frac{4\pi\varepsilon_0 \hbar^2}{me^2} \tag{4.7}
\]

where \( N \) is the normalization factor, \( n, \ell \) are the quantum numbers, \( r \) is the radius between nucleus and electron, \( a \) is the Bohr radius of the nucleus, \( e \) is the elementary charge, \( m \) is the rest mass of the electron, \( \varepsilon_0 \) is the permittivity of the free space.
In this section the Schrödinger equation is solved by our new method only for the purpose of the illustration of the method. The Schrödinger equation for the hydrogen atom in the atomic units is

\[
\left( -\frac{1}{2\mu} \Delta - \frac{1}{r} \right) \psi = E\psi \tag{4.8}
\]

\[
\left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} + \frac{2\mu}{r} + 2\mu E \right) \psi = 0 \tag{4.9}
\]

In the Hylleraas coordinates, with reference to Figure 4.1,

\[
\psi = \psi(r) \tag{4.10}
\]

\[
r = x^2 + y^2 + z^2 \tag{4.11}
\]

\[
rdr = xdx \tag{4.12}
\]
\[
x = \frac{dr}{dx}
\]  
\[
\frac{\partial \psi}{\partial x} = \frac{\partial \psi}{\partial r} \frac{dr}{dx} = x \frac{\partial \psi}{\partial r}
\]  
\[
\frac{\partial^2 \psi}{\partial x^2} = \frac{\partial}{\partial r} \left( \frac{x}{r} \frac{\partial \psi}{\partial r} \right) \frac{dr}{dx} = \frac{x^2 \partial^2 \psi}{r^2 \partial r^2} - \frac{x^2 \partial \psi}{r^3 \partial r}
\]  
Similarly,
\[
\frac{\partial^2 \psi}{\partial y^2} = \frac{y^2 \partial^2 \psi}{r^2 \partial r^2} - \frac{y^2 \partial \psi}{r^3 \partial r}
\]  
\[
\frac{\partial^2 \psi}{\partial z^2} = \frac{z^2 \partial^2 \psi}{r^2 \partial r^2} - \frac{z^2 \partial \psi}{r^3 \partial r}
\]  
Combining all of the above equations,
\[
\frac{\partial^2 \psi}{\partial r^2} - \frac{1}{r} \frac{\partial \psi}{\partial r} + \frac{2\mu}{r} \psi + 2\mu E \psi = 0
\]  
This is already a linear ordinary differential equation. Set \( \psi = R(r) \). Then
\[
R'' - \frac{1}{r} R' + 2 \left( \frac{\mu}{r} + \mu E \right) R = 0
\]  
\[
r R'' - R' + 2(\mu + \mu Er) R = 0
\]  
47
This equation is of the form

\[ xy'' - y' + (ax + b)y = 0 \]  \hspace{1cm} (4.20)

If \( y = e^{cnx} \) then \( y' = ncnx^{n-1}e^{xn} \) and \( y'' = n(n-1)cnx^{n-2}e^{xn} + n^2cn^2x^{2n-2}e^{xn} \). Substituting above, we have the following

\[ n(n-1)cnx^{n-1}e^{xn} + n^2cn^2x^{2n-1}e^{xn} - ncnx^{n-1}e^{xn} + (ax + b)e^{cnx} = 0 \]  \hspace{1cm} (4.21)
\[ n(n-1)cnx^{n-1} + n^2cn^2x^{2n-1} - ncnx^{n-1} + (ax + b) = 0 \]  \hspace{1cm} (4.22)

This equation must be identically 0, for all values of \( x \), yet the solution must be nontrivial. For this to happen, the highest degree must occur at least twice.

\[ n - 1 = 2n - 1 \rightarrow n = 0 \]  \hspace{1cm} (4.23)
\[ 2n - 1 = n - 1 \rightarrow n = 0 \]  \hspace{1cm} (4.24)
\[ 2n - 1 = 1 \rightarrow n = 1 \]  \hspace{1cm} (4.25)
\[ 2n - 1 = 0 \rightarrow n = \frac{1}{2} \]  \hspace{1cm} (4.26)

The first two choices are trivial. The last choice is not acceptable because maximum degree occurs elsewhere, only once. This is a lucky coincidence. Half integer \( n \) calls into play the Airy functions
and their derivatives, which are hard to work with. For the rest of the hydrogen atom considerations, $n = 1$ is settled. For $n = 1$ the equation above becomes

$$
\begin{align*}
    c^2 x - c + ax + b &= 0 \quad (4.27) \\
    (c^2 + a)x + (b - c) &= 0 \quad (4.28) \\
    c^2 + a &= 0 \quad \quad b = c \quad (4.29) \\
    b^2 + a &= 0 \quad (4.30) \\
    \mu^2 + \mu E &= 0 \quad (4.31) \\
    E &= -\mu \quad (4.32) \\
    c^2 + 2\mu E &= 0 \quad (4.33) \\
    c &= \pm \mu \sqrt{2} \quad (4.34)
\end{align*}
$$

Only the negative choice is accepted for $c$, as the integral of the wavefunction must be a finite number. The other energy levels are later found similarly. The non-normalized wavefunction is

$$
\psi(r) = e^{-\sqrt{2}\mu r} \quad (4.35)
$$

A solution of the form $\psi(r) = de^{cr}$ brings no new eigenvalues or eigenfunctions. For $\psi(r) = (d_1r + d_0)e^{cr}$ we have
\[
\psi(r)' = d_1 e^{cr} + c(d_1 r + d_0)e^{cr} \quad \psi(r)'' = 2d_1 e^{cr} + c^2(d_1 r + d_0)e^{cr} \quad (4.36)
\]

Substituting in this equation

\[
r R'' - R' + 2(\mu + \mu Er) R = 0 \quad (4.37)
\]

we obtain

\[
2d_1 c e^{cr} + c^2(d_1 r^2 + d_0 r)e^{cr} - d_1 e^{cr} - c(d_1 r + d_0)e^{cr} + 2(\mu + \mu E r)(d_1 r + d_0)e^{cr} = 0 \quad (4.38)
\]

\[
2d_1 c e^{cr} + c^2(d_1 r^2 + d_0 r) - d_1 - c(d_1 r + d_0) + 2(\mu + \mu E r)(d_1 r + d_0) = 0 \quad (4.39)
\]

\[
d_1 (c^2 + 2\mu E) r^2 + (2d_1 c + d_0 c^2 - cd_1 + 2\mu d_1 + 2\mu d_0 E)r + (2\mu d_0 - d_1 - cd_0) = 0 \quad (4.40)
\]

From here we get the system of the equations

\[
\begin{align*}
&c^2 + 2\mu E = 0 \\
&2d_1 c + d_0 c^2 - cd_1 + 2\mu d_1 + 2\mu d_0 E = 0 \\
&2\mu d_0 - d_1 - cd_0 = 0 
\end{align*}
\quad (4.41)
\]
One of the most efficiently implemented programs to calculate Gröbner bases is Singular [37]. In Singular for the lexicographical monomial order the syntax is

```
> ring r = 0, (v,a,r,i,A,b,l,e,s), lp;
> ideal i = equations, separated, by, commas;
> groebner(i);
```

The complexity of the calculations depends on the order of the variables, as well as the order of the monomials, but there are no easy tips in the topic. There exists a vast number of Singular commands and techniques, plus personal experience, that can help handle these systems in a more convenient way. Generally we are interested on solutions, not on their multiplicity. For this purpose, calculating the primary decomposition of the polynomial ideal is much faster than the Gröbner basis. In Singular this can be done with the command

```
> facstd(i);
```

For small systems, any program may be used. The lexicographical Gröbner basis of this ideal was calculated in Mathematica [35] with the command

```
GroebnerBasis[{poly1, poly2, ...}, {x1, x2, ...}]
```

In Maple the lexicographical Gröbner basis can be calculated for example with the following commands

```
> with(Groebner)
> B := [x^2+y^2-1, x+y+1]
> G := Basis(B, plex(x, y))
```
The Gröbner basis of system (4.41) is given in the first system below. In the simplifications in the second system, it is assumed that no parameter is 0. This is a happy assumptions as any parameter being 0 will give us the trivial solution.

Then \( d_0 \) and \( d_1 \) can be determined up to a constant factor. Numbers come simpler by setting \( d_0 = 1 \). We are not normalizing solutions anyway.

\[
\begin{align*}
2d_0d_1^2E + d_1^3 &= 0 \\
4d_0d_1\mu - d_1^2 &= 0 \\
d_1^3E + 2d_1^2\mu &= 0 \\
d_0E\mu + 2d_0\mu^2 &= 0 \\
d_1E\mu + 2d_1\mu^2 &= 0 \\
&\quad \rightarrow \begin{cases} 
2d_0E + d_1 = 0 \\
4d_0\mu - d_1 = 0 \\
E + 2\mu = 0 \\
cd_0 - 2d_0\mu + d_1 = 0 \\
c + 2\mu = 0 \\
c^2 + 2E\mu = 0 \\
c^2 + 2\mu E &= 0 
\end{cases}
\end{align*}
\]

(4.42)

The non-normalized wavefunction now is

\[
\psi(r) = (4\mu r + 1)e^{-2\mu r}
\]

(4.43)

Calculating the radial part is the simplest part, and is illustrated above. Calculating the other parts
can be done with this method as well. In fact, the Laguerre polynomial has been “silently” calculated once above. Now the idea is that more are calculated like this, for bigger \(n\) quantum numbers and nonzero constant part of the polynomial that multiplies the exponential function. This will make sure that the quantum number \(\ell = 0\). Once that a shape emerges from various values of \(n\), now two parts of the solution are known, and the \(x^\ell\) part is calculated. The other parts of the solution can be calculated similarly.

By this method, potentially all differential equations can be solved. Partial differential equations, ordinary differential equations with or without nonconstant coefficients, of higher orders and degrees can be reduced into solving systems of polynomial equations of higher degrees. This is a much simpler mathematical problem, which at least theoretically we know how to solve.

There is one strong requirement: the mathematical shape of the solution must be known. This requirement is strong at present, in the beginning of the method. If progress can be made by these means, progress is welcome. Also, as progress is made and as more and more researchers become acquainted with the method, the horizon of applicability enlarges more and more. More and more shapes of solutions become known and this becomes a positive feedback loop. The various mathematical shapes of the solutions of the various differential equations will be perlustrated, and the requirement of knowing the mathematical shape of the solution will not be considered a strong requirement. In the beginning we are working more by trial and error.

The number of Hylleraas coordinates

Assume that a system of \(n\) bodies is to be studied. Then the number of the Coulomb potentials involved is
\[
\binom{n-1}{2}
\tag{4.44}
\]

The number of the Cartesian coordinates needed to specify the system is \(3(n - 1)\). Setting these two numbers equal, we have

\[
\frac{n(n - 1)}{2} = 3(n - 1) \quad \rightarrow \quad n = 6
\tag{4.45}
\]

For \(n \leq 5\), the system is underspecified in the Hylleraas coordinates. This means that the Hylleraas coordinates alone do not suffice, but still plenty of information can be obtained, as Hylleraas did with helium, for \(n = 3\). For \(n > 6\) there are more Hylleraas than Cartesian coordinates. This does not necessarily mean that the system is overspecified without loss of information. A redundant system of coordinates can be used for the sake of the simplicity of the presentation, and for the conservation of the various symmetries, as shown by Ruiz Ruiz [13].

The Taylor expansion of functions

The Taylor expansion of a function \(f(x)\) at a point \(x = a\) is the power series

\[
f(x) = f(a) + \frac{f'(a)}{1!}(x-a) + \frac{f''(a)}{2!}(x-a) + \frac{f'''(a)}{3!}(x-a) + \cdots
\tag{4.46}
\]
In a more succinct way this can be written as

$$f(x) = \sum_{n=0}^{\infty} \frac{f^{(n)}(a)}{n!} (x - a)^n$$  \hspace{1cm} (4.47)

The \((n)\) is the \(n\)-th derivative. For the Taylor expansion to exist at a point, all the derivatives of the function \(f(x)\), that is \(f^{(n)}(a)\) must exist \(\forall n\). A similar concept exists for the functions in many variables \(f(x_1, \ldots, x_d)\).

$$f(x_1, \ldots, x_d) = \sum_{n_1=0}^{\infty} \cdots \sum_{n_d=0}^{\infty} \frac{(x_1 - a_1)^{n_1} \cdots (x_d - a_d)^{n_d}}{n_1! \cdots n_d!} \left( \frac{\partial^{n_1 + \cdots + n_d} f}{\partial x_1^{n_1} \cdots \partial x_d^{n_d}} \right)(a_1, \ldots, a_d)$$  \hspace{1cm} (4.48)

Again, all the derivatives at the point \((a_1, \ldots, a_d)\) must exist for the Taylor expansion at that point to exist. This seems like a harsh condition, but for example all the current wavefunctions, exact and approximate alike, fulfill this requirement. The Taylor expansions are important in our work because they take a generic function, and turn it into a power series. So we have a way to study the properties of the function. In this PhD dissertation we prove the nonexistence of the exact solutions of the Schrödinger equation with the Coulomb potential by using the generic Taylor expansion of the potential wavefunctions. Thus we prove that only the trivial wavefunction exists, the one with all the coefficients \(a_{ijk} = 0 \forall i, j, k\). The proof technique is two embedded loops of mathematical inductions. This is enabled by the Taylor expansion of the wavefunctions.
The Coulomb law and the Coulomb electrostatic potential

The Coulomb force $F(r)$ is the electrostatic force engendered by the stationary particles interacting with each other. The Coulomb law quantifies this force. In its scalar form for two particles, the Coulomb law is

$$F(r) = k_e \frac{q_1 q_2}{r^2}$$  \hspace{1cm} (4.49)

where $k_e = 8987551787.3681764 \text{Nm}^2/C^2$ exactly is the Coulomb constant, $r$ is the scalar distance between the two charges, and the $q_i$ are the signed charges of the two particles. By applying the principle of the superposition, the Coulomb force of a system of more than two particles is widely assumed to be the sum of all the pairwise forces. We dissent. For some reason, the principle of the superposition does not apply in this context.

The Coulomb potential $V(r)$ is the electrostatic potential engendered by the electrostatic interactions of two charged particles.

$$V(r) = k_e \frac{q_1 q_2}{r}$$  \hspace{1cm} (4.50)

In atomic units, $k_e = 1$. Therefore
\[ V(r) = \frac{q_1 q_2}{r} \]  

(4.51)

Again, it is widely assumed that the potential of a system with more than two particles is the sum of all the pairwise potentials. As seen in Chapter 4, it is the major result of this PhD dissertation, this does not appear to be correct, although it works fine for most purposes.
CHAPTER 5: THE 3-BODY PROBLEM WITH COULOMB POTENTIAL

There is a story about the famous organic chemist August Kekule, who supposedly wrote that the paper he had reviewed comprised assertions which were true and new but what was true was not new and what was new was not true.

Sadly, this statement perfectly characterizes the present manuscript. It is true that the expansion (4) does not exist but this fact has been shown 83 years ago by Bartlett. The new claim in the paper is that the nonexistence of such an expansion implies nonexistence of an exact (closed-form?) solution of the Schrodinger equation. This is obviously false. In fact, if one admits solutions in form of infinite series then the Fock expansion (which the authors mention!) is the exact solution.

The paper is not publishable in any reputable journal.

Unsung reviewer

This is the feedback from an unsung reviewer of Toli and Zou [33] in a different, reputable journal. For the ironically challenged ones, a major result of this PhD dissertation is that we prove that the solutions proposed by Fock [1–3] are not exact, although accurate for most purposes. The proof of Bartlett, Gibbons, and Dunn [10] (wrongly attributed to Bartlett alone) is obviously flawed, as shown in Chapter 1. Our proof is sound, and our claim is much wider.

“This is obviously false” is obviously false.
The helium atom in Hylleraas coordinates

Following Hylleraas [52] and with reference to Figure 5.1 and Figure 5.2, for helium with nucleus \( Z = 2 \) and center of coordinates in the nucleus, the Schrödinger equation in the atomic units becomes

\[
\Delta_1 \psi + \Delta_2 \psi + \left( \frac{\lambda}{4} + \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{2r_{12}} \right) \psi = 0 \tag{5.1}
\]

written explicitly as

\[
\left[ \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} + \left( \frac{\lambda}{4} + \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{2r_{12}} \right) \right] \psi = 0 \tag{5.2}
\]
The variables \( r_1, r_2, r_{12} \) depend on the original Cartesian variables. They are chosen as the independent variables, and the equation is written in their function. These are called the Hylleraas coordinates [52]. It is pronounced *heegeros*, like Spanish *jigueros*. This also doubles as a projection from the space of functions in the variables \( x_1, y_1, z_1, x_2, y_2, z_2 \) to the space of the functions in the variables \( r_1, r_2, r_{12} \). In the new space there are only three variables instead of the six needed to fully specify the system in a bijection form. Some information is lost and it is not possible to obtain the original equation from the new equation. Nonetheless, solving the new equation gives the most information about the 3-body system. Now

\[
\psi = \psi(r_1, r_2, r_{12}) \quad \quad r_1^2 = x_1^2 + y_1^2 + z_1^2 \quad \quad r_2^2 = x_2^2 + y_2^2 + z_2^2 \tag{5.3}
\]

\[
r_{12}^2 = (x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2 \quad \quad r_1 dr_1 = x_1 dx_1 \tag{5.4}
\]

\[
r_{12} dr_{12} = (x_1 - x_2) dx_1 \quad \quad \frac{x_1}{r_1} = \frac{dr_1}{dx_1} \quad \quad \frac{x_1 - x_2}{r_{12}} = \frac{dr_{12}}{dx_1} \tag{5.5}
\]

\[
\frac{\partial \psi}{\partial x_1} = \frac{\partial \psi}{\partial r_1} \frac{dr_1}{dx_1} + \frac{\partial \psi}{\partial r_{12}} \frac{dr_{12}}{dx_1} + \frac{\partial \psi}{\partial r_2} \frac{dr_2}{dx_1} = \frac{x_1}{r_1} \frac{\partial \psi}{\partial r_1} + \frac{x_1 - x_2}{r_{12}} \frac{\partial \psi}{\partial r_{12}} \tag{5.6}
\]

Similarly for the second derivative with respect to \( x_1 \).
\[
\frac{\partial^2 \psi}{\partial x_1^2} = \frac{\partial}{\partial r_1} \left( \frac{x_1}{r_1} \frac{\partial \psi}{\partial r_1} + \frac{x_1 - x_2}{r_1^2} \frac{\partial \psi}{\partial r_{12}} \right) \frac{dr_1}{dx_1} + \frac{\partial}{\partial r_{12}} \left( \frac{x_1}{r_1} \frac{\partial \psi}{\partial r_1} + \frac{x_1 - x_2}{r_1^2} \frac{\partial \psi}{\partial r_{12}} \right) \frac{dr_{12}}{dx_1} =
\]

\[
= \frac{x_1^2}{r_1^2} \frac{\partial^2 \psi}{\partial r_1^2} + \frac{x_1(x_1 - x_2)}{r_1 r_{12}} \frac{\partial^2 \psi}{\partial r_1 \partial r_{12}} + \frac{\partial^2 \psi}{\partial r_{12}^2} \left( \frac{x_1}{r_1} + \frac{x_1 - x_2}{r_{12}} \right) \frac{dr_1}{dr_{12}} + \frac{\partial^2 \psi}{\partial r_{12}^3} \left( \frac{x_1}{r_1} + \frac{x_1 - x_2}{r_{12}} \right) \frac{dr_1}{dr_{12}} \frac{dr_{12}}{dx_1} \frac{dr_{12}}{dr_{12}}
\]

\[
= \frac{x_1^2}{r_1^2} \frac{\partial^2 \psi}{\partial r_1^2} + \frac{1}{r_1} \frac{x_1^2}{r_1^2} \frac{\partial \psi}{\partial r_1} + \frac{(x_1 - x_2)^2}{r_{12}^2} \frac{\partial^2 \psi}{\partial r_{12}^2}
\]

\[
+ \left( \frac{1}{r_{12}} - \frac{(x_1 - x_2)^2}{r_{12}^3} \right) \frac{\partial \psi}{\partial r_{12}} + 2 \frac{x_1(x_1 - x_2)}{r_1 r_{12}} \frac{\partial^2 \psi}{\partial r_1 \partial r_{12}}
\]

Similarly for the second derivatives with respect to the variables \(y_1, z_1, x_2, y_2, z_2\)

\[
\frac{\partial^2 \psi}{\partial y_1^2} = \frac{y_1^2}{r_1^2} \frac{\partial^2 \psi}{\partial r_1^2} + \left( \frac{1}{r_1} - \frac{y_1^2}{r_1^2} \right) \frac{\partial \psi}{\partial r_1} + \frac{(y_1 - y_2)^2}{r_{12}^2} \frac{\partial^2 \psi}{\partial r_{12}^2}
\]

\[
+ \left( \frac{1}{r_{12}} - \frac{(y_1 - y_2)^2}{r_{12}^3} \right) \frac{\partial \psi}{\partial r_{12}} + 2 \frac{x_1(y_1 - y_2)}{r_1 r_{12}} \frac{\partial^2 \psi}{\partial r_1 \partial r_{12}}
\]
\[
\frac{\partial^2 \psi}{\partial z_1^2} = \frac{x_1^2 \partial^2 \psi}{r_1^2 \partial r_1^2} + \left( \frac{1}{r_1} - \frac{z_1^2}{r_1^3} \right) \frac{\partial \psi}{\partial r_1} + \frac{(z_1 - z_2)^2 \partial^2 \psi}{r_{12}^2 \partial r_{12}^2} \tag{5.9}
\]

\[
+ \left( \frac{1}{r_{12}} - \frac{(z_1 - z_2)^2}{r_{12}^3} \right) \frac{\partial \psi}{\partial r_{12}} + 2 \frac{z_1(z_1 - z_2)}{r_{12} r_{12} r_{12} \partial r_{12} \partial r_{12}}
\]

\[
\frac{\partial^2 \psi}{\partial x_2^2} = \frac{x_2^2 \partial^2 \psi}{r_2^2 \partial r_2^2} + \left( \frac{1}{r_2} - \frac{x_2^2}{r_2^3} \right) \frac{\partial \psi}{\partial r_2} + \frac{(x_2 - x_1)^2 \partial^2 \psi}{r_{12}^2 \partial r_{12}^2} \tag{5.10}
\]

\[
+ \left( \frac{1}{r_{12}} - \frac{(x_2 - x_1)^2}{r_{12}^3} \right) \frac{\partial \psi}{\partial r_{12}} + 2 \frac{x_2(x_2 - x_1)}{r_{12} r_{12} \partial r_{12} \partial r_{12}}
\]

\[
\frac{\partial^2 \psi}{\partial y_2^2} = \frac{y_2^2 \partial^2 \psi}{r_2^2 \partial r_2^2} + \left( \frac{1}{r_2} - \frac{y_2^2}{r_2^3} \right) \frac{\partial \psi}{\partial r_2} + \frac{(y_2 - y_1)^2 \partial^2 \psi}{r_{12}^2 \partial r_{12}^2} \tag{5.11}
\]

\[
+ \left( \frac{1}{r_{12}} - \frac{(y_2 - y_1)^2}{r_{12}^3} \right) \frac{\partial \psi}{\partial r_{12}} + 2 \frac{y_2(y_2 - y_1)}{r_{12} r_{12} \partial r_{12} \partial r_{12}}
\]

\[
\frac{\partial^2 \psi}{\partial z_2^2} = \frac{z_2^2 \partial^2 \psi}{r_2^2 \partial r_2^2} + \left( \frac{1}{r_2} - \frac{z_2^2}{r_2^3} \right) \frac{\partial \psi}{\partial r_2} + \frac{(z_2 - z_1)^2 \partial^2 \psi}{r_{12}^2 \partial r_{12}^2} \tag{5.12}
\]

\[
+ \left( \frac{1}{r_{12}} - \frac{(z_2 - z_1)^2}{r_{12}^3} \right) \frac{\partial \psi}{\partial r_{12}} + 2 \frac{z_2(z_2 - z_1)}{r_{12} r_{12} \partial r_{12} \partial r_{12}}
\]

The eigenvalue problem for the radial terms is written in the following. There is a typo in equation (5) in the Hylleraas’ original German paper, carried over in the Hettema’s English translation [53]. It is corrected here below in equation (5.13). In the original paper both partial derivatives in the seventh and eighth terms are with respect to the \( r_1, r_{12} \). Obviously, the equation is symmetric with respect to the \( r_1, r_2 \). The equation is obtained by substituting the second derivatives in the
Schrödinger equation with the equations above. Equation (5.13) is obtained from equation (5.2) by substituting in equation (5.2) all of the equations between them, and setting \( \lambda/4 = E \).

\[
\frac{\partial^2 \psi}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial \psi}{\partial r_1} + \frac{\partial^2 \psi}{\partial r_2^2} + \frac{2}{r_2} \frac{\partial \psi}{\partial r_2} + \frac{4}{r_{12}} \frac{\partial \psi}{\partial r_{12}} + \frac{r_1^2 - r_2^2 + r_{12}^2}{r_1 r_{12}} \frac{\partial^2 \psi}{\partial r_1 \partial r_{12}} + \frac{r_2^2 - r_1^2 + r_{12}^2}{r_2 r_{12}} \frac{\partial^2 \psi}{\partial r_2 \partial r_{12}} + \left( E + \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{2r_{12}} \right) \psi = 0
\]  

\( (5.13) \)

\[
2r_1 r_2 r_{12} \frac{\partial^2 \psi}{\partial r_1^2} + 4r_2 r_{12} \frac{\partial \psi}{\partial r_1} + 2r_1 r_2 r_{12} \frac{\partial^2 \psi}{\partial r_2^2} + 4r_1 r_{12} \frac{\partial \psi}{\partial r_2} + 4r_1 r_2 r_{12} \frac{\partial^2 \psi}{\partial r_{12}^2} + 8r_1 r_2 \frac{\partial \psi}{\partial r_{12}} + 2 \left( r_1^2 r_2 - r_2^3 + r_{12}^2 \right) \frac{\partial^2 \psi}{\partial r_1 \partial r_{12}} + 2 \left( r_1 r_2^2 - r_1^3 + r_{12}^2 \right) \frac{\partial^2 \psi}{\partial r_2 \partial r_{12}}
\]

\[
+ 2E r_1 r_2 r_{12} \psi + 2r_2 r_{12} \psi + 2r_1 r_{12} \psi - r_1 r_2 \psi = 0
\]  

\( (5.14) \)

The potential energy of a system of more than two bodies is described by the sum of the pairwise potentials. As proven in the remainder of this chapter, the Schrödinger equation with the Coulomb potential admits no exact solutions. This is the proof that this description of the potential energy for more than two bodies is not correct. Alternatively, if this is correct, then the Schrödinger equation must not be correct.

Since Schrödinger equation was first proposed in 1926 [8], the exact solutions are actively sought. As of present, only the case of a two-particle system has been solved by exact (also known as analytical, closed-form) methods.
The failure so far of the exact methods has led to a proliferation of approximate, numerical methods [54–62], as well as to exact methods that simplify the problem. One of these exact simplified approaches is due to Hylleraas [13]. Hylleraas sheds the angular components of the equation, and only keeps the radial ones. This representation is still a Schrödinger equation, just with a “wandering” coordinate system.

Here we prove that in the most generic case, indeed even with three particles, the exact solutions do not exist. This implies that the exact solutions for the Schrödinger equation in the Cartesian coordinates do not exist as well.

“Has no exact solutions” does not necessarily mean “bad”. It may mean some or all of the following.

- The physical model is wrong, but it can still be useful. The experimental data fit sufficiently well for most purposes.

- It is futile to commit further efforts to find the exact solutions, as shown by Jacoby [26].

- Intrinsic of the nonexistence of exact solutions, the approximate solutions can only go so far, and no farther, as shown by Jacoby [26]. If excessive accuracy is tried with the approximate solutions with one parameter, all the other parameters will become excessively inaccurate. This is the situation at present [26]. This paper explains why, and why it is futile to continue without changing the Coulomb potential in a system of three or more bodies.

- Change the potential energy terms in the Schrödinger equation if better match between the mathematical solutions and the experimental data is desired. This is sometimes done in the perturbation theory.

The Schrödinger equation itself as used here only keeps into account quantum numbers \( n, \ell, m = m_\ell \), omitting spin quantum number \( m_s \). The Hylleraas coordinates omit \( m \) as well. No account is kept
of the effects of the relativity.

The two-electron system

In the next section we consider a nucleus-electron-electron three-particle system. One nucleus-electron interaction is omitted. This is similar to the three-particle system where the electron-electron interaction is omitted, but unstable. It may be argued that it is physically unstable, therefore it has no solutions. This point is rendered moot in this section by considering the two-electron system, even more unstable. It has mathematical solutions, but those solutions do not qualify as wavefunctions.

The Schrödinger equation in the Hylleraas coordinates for a two-electron system is

\[
-\frac{\partial^2 \psi}{\partial z^2} - \frac{2}{z} \frac{\partial \psi}{\partial z} + \frac{1}{z} \psi = E \psi 
\]  

(5.15)

\[
z \frac{\partial^2 \psi}{\partial z^2} + 2 \frac{\partial \psi}{\partial z} - \psi + Ez \psi = 0
\]  

(5.16)

All the exact solutions of this equation are given below.

\[
\psi(z) = c_2 e^{-\sqrt{-E}z} \mathbf{1}_F \left(1 + \frac{1}{2\sqrt{-E}}, 2; 2\sqrt{-E}z\right)
\]  

(5.17)
\[ +c_1 e^{-\sqrt{-E}z} U \left( 1 + \frac{1}{2\sqrt{-E}}, 2, 2\sqrt{-E}z \right) \]

\( U \) is the Tricomi’s confluent hypergeometric function, \( _1F_1 \) is the Kummer’s function. Both solutions have no physical meaning. Take for example

\[
\psi(z) = ce^{-\sqrt{-E}z} _1F_1 \left( 1 + \frac{1}{2\sqrt{-E}}, 2; 2\sqrt{-E}z \right)
\] (5.18)

with \( c \) any (normalizing) constant. For any \( n \) natural, setting

\[
1 + \frac{1}{2\sqrt{-E_n}} = -n
\] (5.19)

in any of the two basis solutions, we get

\[
-\frac{1}{2(n+1)} = \sqrt{-E_n}
\] (5.20)

with \( n \) an integer. Substituting this back in the solution in equation (5.17), we obtain that the area under the function is infinite. Therefore it is not eligible for wavefunction. So, the physical instability of a system does not imply that the differential equation does not have mathematical solutions. This is the case for the three-particle system with one omitted nucleus-electron interaction. We only treat this here because it is simpler and mathematically makes the same point. For further
convincing, the complete helium atom is treated later in this chapter. Although physically stable, it
does not admit exact mathematical solutions, with or without physical meaning.

The wavefunction for two variables $x$ and $z$

In the following we assume that one electron does not interact with the nucleus. That is, the
interactions are nucleus-electron-electron. This simplifies the Hylleraas equation for the helium as
follows

$$\frac{-1}{2} \frac{\partial^2 \psi}{\partial x^2} - \frac{1}{x} \frac{\partial \psi}{\partial x} - \frac{2}{x} \psi - \frac{\partial^2 \psi}{\partial z^2} - \frac{2}{z} \frac{\partial \psi}{\partial z} + \frac{1}{z} \psi - \frac{1}{2} \frac{x^2 + z^2}{xz} \frac{\partial^2 \psi}{\partial x \partial z} = E \psi$$  \hspace{1cm} (5.21)

Simplifying fractions

$$xz \frac{\partial^2 \psi}{\partial x^2} + 2z \frac{\partial \psi}{\partial x} + 4xz \frac{\partial^2 \psi}{\partial z^2} + 4x \frac{\partial \psi}{\partial z} - 2x \psi + (x^2 + z^2) \frac{\partial^2 \psi}{\partial x \partial z} + 2xz E \psi = 0$$  \hspace{1cm} (5.22)

Let the mathematical solution be

$$\psi(x, z) = \sum_{i,j=0}^{\infty} a_{i,j} x^i z^j$$  \hspace{1cm} (5.23)

Obviously $a_{ij} = 0$ if $i < 0$ or $j < 0$. Substituting $\psi(x, z)$ in equation 5.22, we have
\[ \begin{align*}
&\sum_{i,j=0}^{i,j=\infty} i(i-1)a_{i,j}x^{i-2}z^j + 2z \sum_{i,j=0}^{i,j=\infty} ia_{i,j}x^{i-1}z^j + 4z \sum_{i,j=0}^{i,j=\infty} a_{i,j}x^{i}z^j \\
&\quad + 2xz \sum_{i,j=0}^{i,j=\infty} j(j-1)a_{i,j}x^{i}z^{j-2} + 4x \sum_{i,j=0}^{i,j=\infty} ja_{i,j}x^{i}z^{j-1} \\
&\quad + (x^2 + z^2) \sum_{i,j=0}^{i,j=\infty} ij a_{i,j}x^{i-1}z^{j-1} - 2x \sum_{i,j=0}^{i,j=\infty} a_{i,j}x^{i}z^j + 2xz E \sum_{i,j=0}^{i,j=\infty} a_{i,j}x^{i}z^j = 0
\end{align*} \] (5.24)

Multiplying by the coefficients in front of the power series, we have

\[ \begin{align*}
&\sum_{i,j=0}^{i,j=\infty} i(i-1)a_{i,j}x^{i-1}z^{j+1} + \sum_{i,j=0}^{i,j=\infty} 2ia_{i,j}x^{i-1}z^{j+1} + \sum_{i,j=0}^{i,j=\infty} 4a_{i,j}x^{i}z^{j+1} \\
&\quad + \sum_{i,j=0}^{i,j=\infty} 2j(j-1)a_{i,j}x^{i+1}z^{j-1} + \sum_{i,j=0}^{i,j=\infty} 4ja_{i,j}x^{i+1}z^{j-1} - \sum_{i,j=0}^{i,j=\infty} 2a_{i,j}x^{i+1}z^j \\
&\quad + \sum_{i,j=0}^{i,j=\infty} ij a_{i,j}x^{i+1}z^{j-1} + \sum_{i,j=0}^{i,j=\infty} ij a_{i,j}x^{i-1}z^{j+1} + \sum_{i,j=0}^{i,j=\infty} 2Ea_{i,j}x^{i+1}z^{j+1} = 0
\end{align*} \] (5.25)

Combining the like terms, we have

\[ \begin{align*}
&\sum_{i,j=0}^{i,j=\infty} (i^2 + i + ij)a_{i,j}x^{i-1}z^{j+1} + \sum_{i,j=0}^{i,j=\infty} 4a_{i,j}x^{i}z^{j+1} - \sum_{i,j=0}^{i,j=\infty} 2a_{i,j}x^{i+1}z^{j+1} = 0
\end{align*} \]
\[
+ \sum_{i,j=0}^{i,j=\infty} (2j^2 + 2j + ij)a_{i,j}x^{i+1}z^{j+1} + \sum_{i,j=0}^{i,j=\infty} 2Ea_{i,j}x^{i+1}z^{j+1} = 0 \tag{5.26}
\]

Aligning the indexes, we get

\[
+ \sum_{i=-1, j=1}^{i,j=\infty} (i^2 + 2i + ij + j + 1)a_{i+1,j-1}x^iz^j + \sum_{i=0, j=1}^{i,j=\infty} 4a_{i,j-1}x^iz^j
\]

\[- \sum_{i=1, j=0}^{i,j=\infty} 2a_{i-1,j}x^iz^j + \sum_{i=1, j=-1}^{i,j=\infty} (2j^2 + 5j + ij + i + 3)a_{i-1,j+1}x^iz^j
\]

\[+ \sum_{i,j=1}^{i,j=\infty} 2Ea_{i-1,j-1}x^iz^j = 0 \tag{5.27}
\]

The set \( \{x^mz^n\}_{0}^{\infty} \) for all \( m, n \geq 0 \) is a basis of the local ring of all the functions analytical at the origin. All the coefficients of all the \( x^mz^n \) must be zero for \( \psi(x, z) \) to be the solution. The coefficient of \( x^iz^j \) is

\[
(i + 1)(i + j + 1)a_{i+1,j-1} + 4a_{i,j-1} - 2a_{i-1,j} + (j + 1)(2j + i + 3)a_{i-1,j+1} + 2Ea_{i-1,j-1} = 0 \tag{5.28}
\]

It can be checked that \( a_{0,0} = a_{0,1} = a_{1,0} = a_{1,1} = 0 \) by direct observation of the system of equations.

By substituting \( j = 0 \) above, we have \( a_{i-1,0} = 0 \) for all \( i \).
We prove by mathematical induction on $i + j$ that $a_{ij} = 0$ for all $i, j$. The statement is true for $i, j = 0, 1$, therefore for $n = 0, 1$. We checked it for a few bigger $i, j$ values.

Assume it true for all couples of integers $i, j$ with $i + j < n$, and prove it for $i + j = n$. By the induction assumption, equation (5.28) becomes

$$
(i + 1)(i + j + 1)a_{i+1,j-1} + (j + 1)(2j + i + 3)a_{i-1,j+1} = 0
$$

(5.29)

For $j = 0, i = n$, we have $a_{n-1,1} = 0$. For $j = 2, i = n - 2$, we have $a_{n-3,3} = 0$, and so on. The $n$ is a finite number, there is no need to cover all the combinations $i + j = n$ by induction, but it can still be done by considering that if $i < 0$ or $j < 0$, then $a_{ij} = 0$. Thus, by induction for $j = 2k$, we can prove that $a_{n-2k-1,2k+1} = 0$. If $n$ is odd, by doing the same argument on $i$, we have proven that $a_{i,j} = 0$ for $i + j = n$. This ends the induction for odd $n$.

The following argument holds for both $n$ odd and even, but we use it here to prove the final part of the statement, that $a_{n-2k,2k} = 0$ for all $k$, for even $n$. From the above, we already have for $n$ even and all $k$

$$
a_{n-2k-1,2k+1} = 0
$$

(5.30)

For $k = 0, \ldots n/2$, we have
\[ a_{n-2k,2k} = \frac{(n + 1)^k n(n - 2) \ldots [n - 2(k - 1)]}{(-1)^k 2^{k!} (n + 4) \ldots [n + 2(k + 1)]} a_{n,0} \quad (5.31) \]

But we have already proven that \( a_{n,0} = 0 \). Therefore, \( a_{n-2k,2k} = 0 \) for all \( k \). This finishes the induction.

The Schrödinger equation for the helium atom in the Hylleraas coordinates

The Schrödinger equation for the helium atom with the Coulomb potential in the Hylleraas coordinates is equation (5.32). In the rest of this chapter the terms are occasionally moved around for esthetical reasons.

\[
-\frac{1}{2} \frac{\partial^2 \psi}{\partial r_1^2} - \frac{1}{r_1} \frac{\partial \psi}{\partial r_1} - \frac{2}{r_1} \psi - \frac{1}{2} \frac{\partial^2 \psi}{\partial r_2^2} - \frac{1}{r_2} \frac{\partial \psi}{\partial r_2} - \frac{2}{r_2} \frac{\partial \psi}{\partial r_{12}} + \frac{1}{r_{12}} \psi - \frac{2}{r_2} \psi
\]

\[
-\frac{1}{2} \frac{r_1^2 - r_2^2 + r_{12}^2}{r_1 r_{12}} \frac{\partial^2 \psi}{\partial r_1 \partial r_{12}} - \frac{\partial^2 \psi}{\partial r_{12}^2} - \frac{1}{2} \frac{r_1^2 - r_2^2 + r_{12}^2}{r_2 r_{12}} \frac{\partial^2 \psi}{\partial r_2 \partial r_{12}} = E\psi \quad (5.32)
\]

For simplicity, we set \( r_1 = x, r_2 = y, r_{12} = z \).

\[
-\frac{1}{2} \frac{\partial^2 \psi}{\partial x^2} - \frac{1}{x} \frac{\partial \psi}{\partial x} - \frac{2}{x} \psi - \frac{1}{2} \frac{\partial^2 \psi}{\partial y^2} - \frac{1}{y} \frac{\partial \psi}{\partial y} - \frac{2}{y} \psi - \frac{2}{z} \frac{\partial \psi}{\partial z} + \frac{1}{z} \psi
\]

\[
-\frac{1}{2} \frac{x^2 - y^2 + z^2}{x z} \frac{\partial^2 \psi}{\partial x \partial z} - \frac{\partial^2 \psi}{\partial z^2} - \frac{1}{2} \frac{y^2 - x^2 + z^2}{y z} \frac{\partial^2 \psi}{\partial y \partial z} = E\psi \quad (5.33)
\]
We multiply by $-2xyz$ to simplify fractions. Now we have the following

$$0 = 2xyz E\psi + xyz \frac{\partial^2 \psi}{\partial x^2} + 2yz \frac{\partial \psi}{\partial x} + xz \frac{\partial^2 \psi}{\partial y^2} + 2x \frac{\partial \psi}{\partial y} + 4xz \psi + 2xyz \frac{\partial^2 \psi}{\partial z^2}
$$

$$+ 4xy \frac{\partial \psi}{\partial z} - 2xy \psi + (x^2 y - y^3 + yz^2) \frac{\partial^2 \psi}{\partial x \partial z} + (xy^2 - x^3 + xz^2) \frac{\partial^2 \psi}{\partial y \partial z} + 4yz \psi \quad (5.34)$$

The Taylor expansion of the wavefunction at some arbitrary point

This section lays the ground work for the proof of Theorem 1. Let $\psi(x, y, z)$ be the solution of equation (5.34). Let equation (5.35) be the Taylor expansion of $\psi(x, y, z)$ at the point $(0, 0, 0)$.

$$\psi(x, y, z) = \sum_{i, j, k=0}^{\infty} a_{i,j,k} x^i y^j z^k \quad (5.35)$$

Substituting equation (5.35) in equation (5.34), we obtain the following relations of the various coefficients. All the coefficients with some negative index are zero.

$$xyz \sum_{i,j,k=0}^{\infty} i(i - 1) a_{i,j,k} x^{i-2} y^j z^k + 2yz \sum_{i,j,k=0}^{\infty} ia_{i,j,k} x^{i-1} y^j z^k
$$

$$+ 4yz \sum_{i,j,k=0}^{\infty} a_{i,j,k} x^i y^j z^k + xyz \sum_{i,j,k=0}^{\infty} j(j - 1) a_{i,j,k} x^i y^{j-2} z^k$$

72
\[+2xz \sum_{i,j,k=0}^{\infty} j a_{i,j,k} x^i y^{j-1} z^k + (xy^2 - x^3 + xz^2) \sum_{i,j,k=0}^{\infty} jk a_{i,j,k} x^i y^{j-1} z^{k-1}\]

\[+2xyz \sum_{i,j,k=0}^{\infty} k(k-1) a_{i,j,k} x^i y^j z^{k-2} + 4xy \sum_{i,j,k=0}^{\infty} k a_{i,j,k} x^i y^j z^{k-1}\]

\[-2xy \sum_{i,j,k=0}^{\infty} a_{i,j,k} x^i y^j z^k + (x^2y - y^3 + yz^2) \sum_{i,j,k=0}^{\infty} ika_{i,j,k} x^{i-1} y^j z^{k-1}\]

\[+2xyz E \sum_{i,j,k=0}^{\infty} a_{i,j,k} x^i y^j z^k + 4xz \sum_{i,j,k=0}^{\infty} a_{i,j,k} x^i y^j z^k = 0 \quad (5.36)\]

By simplifying the coefficients, we derive

\[\sum_{i,j,k=0}^{\infty} i(i-1) a_{i,j,k} x^{i-1} y^{j+1} z^{k+1} + \sum_{i,j,k=0}^{\infty} 2ia_{i,j,k} x^{i-1} y^{j+1} z^{k+1}\]

\[+ \sum_{i,j,k=0}^{\infty} 4a_{i,j,k} x^i y^{j+1} z^{k+1} + \sum_{i,j,k=0}^{\infty} j(j-1) a_{i,j,k} x^{i+1} y^{j-1} z^{k+1}\]

\[+ \sum_{i,j,k=0}^{\infty} 2j a_{i,j,k} x^{i+1} y^{j-1} z^{k+1} + \sum_{i,j,k=0}^{\infty} 4a_{i,j,k} x^{i+1} y^{j} z^{k+1}\]

\[+ \sum_{i,j,k=0}^{\infty} 2k(k-1) a_{i,j,k} x^{i+1} y^{j+1} z^{k-1} + \sum_{i,j,k=0}^{\infty} 4ka_{i,j,k} x^{i+1} y^{j+1} z^{k-1}\]

\[- \sum_{i,j,k=0}^{\infty} 2a_{i,j,k} x^{i+1} y^{j+1} z^{k} + \sum_{i,j,k=0}^{\infty} ika_{i,j,k} x^{i+1} y^{j+1} z^{k} - 1\]

\[- \sum_{i,j,k=0}^{\infty} ika_{i,j,k} x^{i-1} y^{j+3} z^{k-1} + \sum_{i,j,k=0}^{\infty} ika_{i,j,k} x^{i-1} y^{j+1} z^{k+1}\]
\[ + \sum_{i,j,k=0}^{\infty} jka_{i,j,k}x^{i+1}y^{j+1}z^{k-1} - \sum_{i,j,k=0}^{\infty} jka_{i,j,k}x^{i+3}y^{j-1}z^{k-1} \]

\[ + \sum_{i,j,k=0}^{\infty} jka_{i,j,k}x^{i+1}y^{j-1}z^{k+1} + \sum_{i,j,k=0}^{\infty} 2Ea_{i,j,k}x^{i+1}y^{j+1}z^{k+1} = 0 \] (5.37)

By aligning the indexes, equation (5.37) becomes

\[ \sum_{i=-1;j,k=1}^{\infty} i(i + 1)a_{i+1,j-1,k-1}x^i y^j z^k + \sum_{i=-1;j,k=1}^{\infty} 2(i + 1)a_{i+1,j-1,k-1}x^i y^j z^k \]

\[ + \sum_{i,k=1;j=-1}^{\infty} j(j + 1)a_{i-1,j+1,k-1}x^i y^j z^k + \sum_{i,k=1;j=-1}^{\infty} 2(j + 1)a_{i-1,j+1,k-1}x^i y^j z^k \]

\[ + \sum_{i,j=1;k=-1}^{\infty} 2k(k + 1)a_{i-1,j-1,k+1}x^i y^j z^k + \sum_{i,j=1;k=-1}^{\infty} 4(k + 1)a_{i-1,j-1,k+1}x^i y^j z^k \]

\[ + \sum_{i=0;j,k=1}^{\infty} 4a_{i,j-1,k-1}x^i y^j z^k + \sum_{i,j,k=1}^{\infty} (i - 1)(k + 1)a_{i-1,j-1,k+1}x^i y^j z^k \]

\[ + \sum_{i,k=1;j=0}^{\infty} 4a_{i,j,k-1}x^i y^j z^k - \sum_{i,k=-1;j=3}^{\infty} (i + 1)(k + 1)a_{i+1,j-3,k+1}x^i y^j z^k \]

\[ - \sum_{i,j,k=1}^{\infty} 2a_{i-1,j-1,k}x^i y^j z^k + \sum_{i=-1;j,k=1}^{\infty} (i + 1)(k - 1)a_{i+1,j-1,k-1}x^i y^j z^k \]

\[ + \sum_{i,j,k=-1}^{\infty} 2Ea_{i-1,j-1,k-1}x^i y^j z^k + \sum_{i,j=1;k=-1}^{\infty} (j - 1)(k + 1)a_{i-1,j-1,k+1}x^i y^j z^k \]

\[ - \sum_{i=3;j,k=-1}^{\infty} (j + 1)(k + 1)a_{i-3,j+1,k+1}x^i y^j z^k \]
\[ + \sum_{i,k=1;j=-1}^{\infty} (j + 1)(k - 1)a_{i-1,j+1,k-1}x^i y^j z^k = 0 \]  

(5.38)

After combining the like terms, we obtain

\[ i(i + 1)a_{i+1,j-1,k-1} + 2(i + 1)a_{i+1,j-1,k-1} + 4a_{i,j-1,k-1} + j(j + 1)a_{i-1,j+1,k-1} \]
\[ + 2(j + 1)a_{i-1,j+1,k-1} + 4a_{i-1,j,k-1} + 2k(k + 1)a_{i-1,j-1,k+1} + 4(k + 1)a_{i-1,j-1,k+1} \]
\[ - 2a_{i-1,j-1,k} + (i - 1)(k + 1)a_{i-1,j-1,k+1} - (i + 1)(k + 1)a_{i+1,j-3,k+1} \]
\[ + (i + 1)(k - 1)a_{i+1,j-1,k-1} + (j - 1)(k + 1)a_{i-1,j-1,k+1} \]
\[ + 2Ea_{i-1,j-1,k-1} - (j + 1)(k + 1)a_{i-3,j+1,k+1} + (j + 1)(k - 1)a_{i-1,j+1,k-1} = 0 \]  

(5.39)

Subsequently, equation (5.39) is brought in the final form by further combining the like terms

\[ 2Ea_{i-1,j-1,k-1} + (1 + i)(1 + i + k)a_{i+1,j-1,k-1} + (1 + j)(1 + j + k)a_{i-1,j+1,k-1} \]
\[ + 4a_{i-1,j,k-1} - 2a_{i-1,j-1,k} + (1 + k)(2 + i + j + 2k)a_{i-1,j-1,k+1} \]
\[ + 4a_{i,j-1,k-1} - (i + 1)(k + 1)a_{i+1,j-3,k+1} - (j + 1)(k + 1)a_{i-3,j+1,k+1} = 0 \]  

(5.40)

The proof of the theorem

We prove by mathematical induction on \(i\) that \(a_{i,j,k} = 0 \forall i, j, k \geq 0\). We checked that \(a_{i0,k} = 0\) for \(i, j, k = 0, 1\). Assume it true for \(i = i_0\). That is, assume that \(a_{i0,j,k} = 0 \forall i \leq i_0\). We prove it for \(i = i_0 + 1\). That is, we prove that \(a_{i0+1,j,k} = 0 \forall j, k\). Replacing \(i = i_0\), equation (5.40) becomes
\[(1 + i_0 + k)a_{i_0+1,j-1,k-1} - (k + 1)a_{i_0+1,j-3,k+1} = 0\]  
(5.41)

All the other terms are 0 by the assumption of the induction. For \(j = 1\) we obtain that \(a_{i_0+1,0,k} = 0 \forall k\). For \(j = 2\) we have \(a_{i_0+1,1,k} = 0 \forall k\). For \(j = 3\) we have

\[(1 + i_0 + k)a_{i_0+1,2,k-1} - (k + 1)a_{i_0+1,0,k+1} = 0\]  
(5.42)

The second term is 0 from the above. Therefore \(a_{i_0+1,2,k} = 0 \forall k\). By induction on \(j\) we can now prove that \(a_{i_0+1,j,k} = 0 \forall j, k\). In fact, assume this true for \(j \leq j_0\). That is, \(a_{i_0+1,j,k} = 0 \forall j \leq j_0\). Then for \(j = j_0 + 2\) we have

\[(1 + i_0 + k)a_{i_0+1,j_0+1,k-1} - (k + 1)a_{i_0+1,j_0-1,k+1} = 0\]  
(5.43)

The second term is 0 by the induction assumption. Whence \(a_{i_0+1,j_0+1,k} = 0 \forall k\). This ends the proof of the theorem.

Discussion

It may be argued that the situation is created by the Hylleraas coordinates. The Hylleraas coordinates are nothing but a system of coordinates that runs after the nucleus. The Schrödinger equation in
those coordinates is still a Schrödinger equation. The existence of the solutions is independent of
the system of the coordinates.

It may be argued that the power series only gave one solution, the trivial one, and that the other
solutions exist but are just hidden somehow. The power series captures all the solutions analytical at
that point, at once. For example, in the hydrogen case in the Hylleraas coordinates, the equation
becomes

\[
- \frac{1}{2} \frac{\partial^2 \psi}{\partial x^2} - \frac{1}{x} \frac{\partial \psi}{\partial x} - \frac{2}{x} \psi = E \psi
\]  

(5.44)

\[
x \frac{\partial^2 \psi}{\partial x^2} + 2 \frac{\partial \psi}{\partial x} + 4 \psi + 2x E \psi = 0
\]  

(5.45)

The generic analytical solution is \( \psi(x) = \sum_{i=0}^{\infty} a_i x^i \). Substituting this in the equation, we have

\[
x \sum_{i=0}^{\infty} i(i-1)a_i x^{i-2} + 2 \sum_{i=0}^{\infty} i a_i x^{i-1} + 4 \sum_{i=0}^{\infty} a_i x^i + 2x E \sum_{i=0}^{\infty} a_i x^i = 0
\]  

(5.46)

\[
\sum_{i=0}^{\infty} i(i-1)a_i x^{i-1} + \sum_{i=0}^{\infty} 2ia_i x^{i-1} + \sum_{i=0}^{\infty} 4a_i x^i + \sum_{i=0}^{\infty} 2E a_i x^{i+1} = 0
\]  

(5.47)
\[ \sum_{i=-1}^{\infty} i(i+1)a_{i+1}x^i + \sum_{i=-1}^{\infty} 2(i+1)a_{i+1}x^i + \sum_{i=0}^{\infty} 4a_ix^i + \sum_{i=1}^{\infty} 2Ea_{i-1}x^i = 0 \] (5.48)

The generic coefficient is

\[ i(i+1)a_{i+1} + 2(i+1)a_{i+1} + 4a_i + 2Ea_{i-1} = 0 \] (5.49)

Combining the like terms we get

\[ (i^2 + 3i + 2)a_{i+1} + 4a_i + 2Ea_{i-1} = 0 \] (5.50)

Writing the equations for \( i = 0, 1, 2 \ldots \), we have

\[
\begin{cases}
2a_1 + 4a_0 = 0 & i = 0 \\
6a_2 + 4a_1 + 2Ea_0 = 0 & i = 1 \\
12a_3 + 4a_2 + 2Ea_1 = 0 & i = 2 \\
\vdots & \vdots
\end{cases}
\] (5.51)

The first equation of this system has two variables, and is linear. All the others have four, all are
quadratic. $E$ is one of the variables. Every new equation adds one new variable. The system is infinite, and underdefined. It is certainly impossible to solve, but it admits all the known solutions for the hydrogen atom, at once. This is not the case with the previous system, which is possible to solve, and only admits the trivial solution.

It may be argued that elsewhere but in the origin the situation is different. In this proof we used the Taylor expansion at $(0, 0, 0)$. The same argument, verbatim, can be made with the Taylor expansion at any point $(x_0, y_0, z_0)$. It suffices to do the calculations in the basis $\{(x-x_0)^i(y-y_0)^j(z-z_0)^k\}_0^\infty$. All the coefficients in this basis have to be zero as well. By comparison, the Taylor expansion for the hydrogen atom at $(0, 0, 0)$ presents no problems. In fact, for our proof we only need that the Taylor expansion exists in at least one point. The same arguments can be made for the molecules as well as for the atoms. In fact, only some coefficients change in the whole series expansion. This proof is valid for any three-body system with Coulomb potential.

It may be argued that the theorem has been proven only for three particles, and that the situation is different for more than three particles. If a nontrivial solution existed for more than three particles, then it must project to a nontrivial solution in a three-particle system in a variety of ways. Because we proved that such a nontrivial projection does not exist, this proves that the solution does not exist for more particles as well.

If constraints are placed on a physical system, the exact solutions with the Coulomb potential may still exist.

The quantum numbers $n$ (principal), $\ell$ (azimuthal), $m_\ell$ (magnetic) first appeared mathematically in the solutions of the Schrödinger equation for the hydrogen atom. Thereafter they were given a physical meaning, which is appropriate for the hydrogen atom. The $m_s$ spin quantum number was introduced to accomodate for unrelated physical experimental observations. Later on, the Schrödinger equation was modified to accomodate for the $m_s$ spin quantum number. By extension,
all these quantum numbers are used in systems of more than two bodies, in the so-called *hydrogen model*, that is, the entirety of the quantum mechanics, quantum physics, quantum chemistry.

The hydrogen model is not sufficiently satisfactory for more than two bodies. We propose the partitions of the integers as the extension of the quantum numbers to many bodies. We call them quantum partitions. The partitions of the integers are intrinsically associated with the sets of the orthogonal functions in many variables. Whatever the sets of the wavefunctions might be, they have to be functions in many variables, all pairwise orthogonal. Therefore the partitions of the integers are intrinsically involved.

In the long run this could prove useful. For a nanoparticle or a bulk material, the respective partitions have statistical shapes that can be easily studied. The theory about the statistical shapes of the partitions of the integers is already established and relatively mature in mathematics. Connections may be eventually established between these statistical shapes, and the various physical properties of the matter. This could be used to design materials with desired properties.

In an ongoing project beyond this PhD dissertation, we are working to find the exact solutions of the Schrödinger equation for the $H_2^+$ dihydrogen cation with new, mathematically determined electrostatic potentials, with the Born-Oppenheimer approximation. We believe that this case contains all the breakthrough information needed to solve the Schrödinger equation in the most generic cases, without any assumptions or simplifications. The new mathematically-determined electrostatic potentials as we understand them now are reported in this dissertation.

The mathematical choice of the electrostatic potential is not unique. The unique, natural electrostatic potential must come from physics after our mathematical input, but this is irrelevant. The mathematical shape of the solutions is the same. Should we succeed in solving the Schrödinger equation with our mathematically determined electrostatic potentials, it will be easy from there to find the exact solutions of the Schrödinger equation for the $H_2^+$ with the new physically determined,
mathematically aided electrostatic potential.

Potential potentials

With the hindsight, the nonexistence of the exact solutions of the Schrödinger equation was to be expected. The electrostatic potential for many particles is still at present assumed to be the sum of the pairwise electrostatic potentials. This is known in classical physics as the superposition principle. This principle only applies to functions that are linear. The Coulomb potential is not linear, it is hyperbolic. For most of its range though, it can be safely approximated by linear functions. More so at farther distances among the particles. But most interesting things happen when the particles are in the proximity of each other, where the principle of superposition fails best.

The existence of the exact solutions would not imply that the Schrödinger equation is correct, nor that the Coulomb potential is correct. That is, it is possible that both the Schrödinger equation and the Coulomb potential (or only one of the two) were wrong, and the exact solutions still exist. The nonexistence of the exact solutions proves that one or more things are wrong. It is open for interpretation what is wrong. A more plausible interpretation is the one that deviates the least from the current understanding of the facts. In this dissertation we have assumed that the Schrödinger equation is correct, and the Coulomb potential for many bodies is not correct.

It can be formally proven that the exact solutions of the Schrödinger equation exist if the electrostatic potential in the case of $\text{H}_2^+$ with the Born-Oppenheimer assumption is

$$V = \frac{a_1}{r_1} + \frac{a_2}{r_2} + \frac{a_3}{r_1 r_2}$$ (5.52)

81
This potential is not the unique one for which the solutions exist. The correlation between the $a_i$ and the charges of the particles is neither obvious nor straightforward. Nor does the existence of the exact mathematical solutions imply anything about the fitness or correctness of the physical model. But this choice of the electrostatic potential is in some way algebraically minimalist. For this reason among others, this is the choice for which we are trying to find the exact solutions of the Schrödinger equation in an ongoing project beyond this dissertation. The physical meaning could be given afterwards, or things could be reconsidered to make it assume a physical meaning.

In equation (5.52), the smaller the $r_1, r_2$, the more important the third term becomes. The bigger they are, the less important it becomes, and the more the new potential behaves like the classical Coulomb potential.

In the case of the helium atom in the Hylleraas coordinates, an algebraic equivalent electrostatic potential for which the exact solutions exist is

$$V = \frac{a_1}{r_1} + \frac{a_2}{r_2} + \frac{a_3}{r_3} + \frac{a_4}{r_1 r_2} + \frac{a_5}{r_1 r_3} + \frac{a_6}{r_2 r_3} + \frac{a_7}{r_1 r_2 r_3}$$  \hspace{1cm} (5.53)

The Hamming weight of a 01 string is the number of ones in it. For example, the Hamming weight of $\tau$ below is 5.

At this stage it is not yet clear whether $a_7 \neq 0$ or not. It appears like the exact solutions exist for both $a_7 = 0$ and $a_7 \neq 0$. On deeper considerations on algebraic varieties, it appears that we must have $a_7 \neq 0$. Either way, it appears like the actual contribution of terms with higher Hamming weight is minimal, and can be ignored.

In the most generic case, let us have $n$ particles. Then the number of the Hylleraas coordinates is
Let $S = \{0, 1\}^m$ be the set of all 01 strings of length $m$. Let $r_1, \ldots, r_m$ be the various Hylleraas coordinates. For $\tau \in S$, let $r_\tau$ be the product of the various Hylleraas coordinates above, where $r_i$ is present iff $\tau$ contains 1 in the $i$-th position. E.g., let $\tau = 00011001011$. Then $r_\tau = r_4 r_5 r_8 r_{10} r_{11}$. Only accounting for $\tau$ with Hamming weight 1 we obtain the classical Coulomb potential.

Now the new electrostatic potential is

$$V = \sum_{\tau \in S} \frac{a_\tau}{r_\tau}$$

(5.55)

If we have for example $n = 15$ particles, then $m = 105$. This means that only writing down the potential requires $2^{105}$ terms. For $n = 10$, we have $m = 45$. That is $2^{45}$ terms. Thus for 10 or more particles the Schrödinger equation with the new electrostatic potential energy function cannot even be explicitly written down, let alone solved. In a more formal complexity theory language, the space complexity of explicitly writing down the new electrostatic potential energy is $O(2^{n^2})$. This means that advancement in computer technology brings no hope of increasing $n$.

In practice the situation may not be as helpless as it appears now. It is possible that the solution wavefunctions have mathematical shapes that can be exactly explicitly written, even though the potential itself cannot be explicitly written. This will be clarified as the exact solutions may be calculated for bigger $n$, as far as we can computationally afford. Now we are still working on $n = 3$, the $H_2^+$ case with fixed nuclei (Born-Oppenheimer approximation).
Another possibility is some sort of truncation and approximation of the electrostatic potential, ignoring the least relevant terms, similar to the Born-Oppenheimer approximation. That is, only those terms of the potential are kept that have some small, predetermined Hamming weight. Alternatively, the terms of the potential energy with the biggest Hamming weight may matter the most when the particles are in proximity of each other. This is for most purposes the most interesting case. Thus, another possibility of truncation is keeping only the terms with Hamming weight bigger than some predetermined limit. As said for the helium case, at this stage it is not yet clear whether the real, natural, physical potential contains terms with Hamming weight greater than 2.

Yet another approach is to statistically study the various aspects of the wavefunctions with the new electrostatic potentials.

This situation of the nonexistence of the solutions is not unique to the Schrödinger equation or quantum mechanics. It has analogues in the celestial bodies and many other fields. Should a physically meaningful solution be found with this approach, it will have ramifications in many other fields. One such example is the Newton law of the universal gravitation for three or more bodies.

Although it is easy to prove that the exact solutions exist for the potentials proposed above, we are open to the consideration of other potentials. Yukawa potential [63] suffers from the same mathematical shortcomings as Coulomb potential. The fix could be similar.

In physics there exists the concept of the three-body force, a force that does not exist when two bodies interact, but appears when three bodies interact. There is experimental evidence of this, including the interactions of the elementary particles; protons, electrons, neutrons, as reported by Loiseau and Nogami [4] and many others. We dissent. The three-body force does not exist. It is just that the two-body forces are not linear functions, and the principle of superposition does not apply in the near regions, although it is satisfactorily accurate in the far regions.
Figure 5.3: The electrostatic potential energy between two particles is a hyperbole, like the function \( y = 1/x \). It is approximately linear far away from the origin, but not nearby. The superposition principle reasonably applies in the far region, but not in the near region. The omission of this fact gives rise to the interpretation of the deviation from the superposition principle for three bodies as "the three-body force". There is nothing to superpose with two bodies.

By the same measure, there ought to exist a four-body force, five-body force, and so on. They might not have been yet observed because it is harder to have four or more bodies in proximity, where the effect (the deviation from the superposition principle) would become observable. The solution to this situation is similar to that of the electrostatic potential problem. There must exist some mathematical model that describes the force for \( n \) bodies, and the two-body force is just a trivial case of it, like the electrostatic potentials proposed in this section. This obviates the superposition principle in this context, and the need for artifices like the specific three-body or \( n \)-body forces.
Conclusions

We formally, mathematically proved that the Schrödinger equation for the elements and the molecules made of three or more particles do not admit nontrivial exact solutions if the potential energy is expressed by means of the Coulomb potential. One important corollary is that the exact solutions proposed by Fock [2, 3] are not exact, although accurate, because they admit Taylor expansion at most points, for example at \((1, 1, 1)\).

New potentials that are more physically meaningful should be sought for future efforts in seeking the exact solution of the equation. This topic constitutes the subject of an ongoing project by the authors, where substitutions for the Coulomb potential are sought. The new potential energy function is derived mathematically rather than physically. The mathematically acceptable potential is not unique, but it serves as a template for the physicists to narrow down to physically acceptable electrostatic potentials. In the last section we have already proposed some substitutes. The exact solutions for the Schrödinger equation for the \(H_2^+\) hydrogen cation are being investigated.
APPENDIX A: THE GENERALIZED HYPERGEOMETRIC FUNCTIONS
By theoretical definition, the wavefunctions for more than two particles ought to be multivariate orthogonal functions. The multivariate orthogonal functions are of paramount importance in the research topic of finding the exact solutions of the differential equations by commutative computational algebraic means. Their implementation is hard to find. With adequate choices of the parameters, the multivariate orthogonal functions can be found among the generalized multivariate hypergeometric functions. In this appendix we report the implementation of the generalized multivariate hypergeometric functions in MATLAB by Plamen Koev. Reprinted with permission. Two minor issues fixed by me. Save the text below in a file hg.m in the folder MATLAB, and run

\[
\text{>> } \text{hg(\text{MAX, } \text{alpha}, p, q, x, y, lambda)}
\]

The MAX needs to be an integer. It is the maximum degree occurring in the output polynomial, a portion of the infinite series. For our purposes, \(\text{alpha} = 2\). That is, we are working with real numbers. If working with complex numbers, \(\text{alpha} = 1\). If working with quaternions, \(\text{alpha} = 1/2\). The alpha can assume any value in the half-interval \((0, 2]\), but the other values than these three have no prompt useful mathematical interpretation.

If symbolic calculations need to be performed, the Symbolic Math Toolbox add-in of MATLAB is required. For our needs, all the other parameters are real, and symbolic. The two most useful commands look like

\[
\text{>> syms a1 a2 a3 a4 a5 a6 a7 real}
\]

\[
\text{>> hg(9, 2, [a1 a2], [a3 a4], [a7 a6])}
\]

The program hg.m below is slightly different from the original one by Plamen Koev. Minor changes were done by Raymond Kan and me. For those variables that need to be symbolic, find their first
occurrence, and redefine it. For example,

\[ x_n = \text{ones}(n, \text{MAX}+1) \quad \text{becomes} \quad x_n = \text{sym(ones}(n, \text{MAX}+1)) \]

Program indentation is sometimes sacrificed for the sake of typesetting requirements.
function \([s, ss]=hg(MAX, alpha, p, q, x, y, lambda)\)
% computes the truncated hypergeometric function
% \(pFq^\alpha(p; q; x; y)\) of two matrix arguments
% The sum is only over \(|\kappa|\leq MAX(1)\) and \(\kappa(i)\leq MAX(2)\)
% if \(size(MAX)=[1,1]\), then \(MAX(2)\) is by default equal to \(MAX(1)\)
% (and optionally \(\kappa\leq lambda\))
% \(p, q, x, y\) are arrays,
% so \(hg(6, 9, [3 4], [5 6 7], [1, 2], [8 9], [4 3])\) is
% \(2F3^9([3 4]; [5 6 7]; [1 2]; [8, 9])\)
% with the sum over all partitions
% \(\kappa\leq(4, 3)\) and \(|\kappa|\leq6\)
% \(y\) and \(lambda\) may be omitted
%
% by Plamen Koev, February 2004, May 22, 2004
%
% May 19, 2007:
% 1) Raymond Kan introduced faster Q_kappa
% and beta_kappa_lambda updates
% 2) removed all recursions
% 3) only storing Jacks for partitions of size \(\leq n-1\) now
% 4) returning the partial sums in \(ss\)

function \([s, ss]=hg(MAX, alpha, p, q, x, y, lam)\)
    if length(MAX)==2
        K=MAX(2);
        MAX=MAX(1);
    end

91
else
    K=MAX;
end

% ss are the partial sums

% XY=1 means we have two arguments x AND y;
% XY=0 means we only have x;

n=length(x);
lambda=floor(MAX./(1:n));
if nargin==7
    lambda=min(lam,lambda(1:length(lam)));
    MAX=min(sum(lambda),MAX);
end
Lp=length(lambda);
while lambda(Lp)==0
    Lp=Lp-1;
end % number of parts in l
lambda=lambda(1:Lp);

% figure out number of partitions lambda with |lambda|<=MAX
% and number of parts less than or equal to Lp
Lp1=min(Lp,n-1);
if nargin==7
    f=fn(lambda(1:Lp1));
else
f=1:MAX+1;
for i=2:Lp1
    for j=i+1:MAX+1
        f(j)=f(j)+f(j-i);
    end
end
f=f(end);

% only need to allocate space for partitions of <=n-1 parts
end

XY=0;
if nargin>5&&~isempty(y), XY=1; end

% Let N(kappa) be the index for partition kappa
% D(N(kappa)) stores N((kappa,1))
% Sx(i,1:n) stores various jack functions of X
% with the first entry J_kappa(x_1), second entry
% J_kappa(x_1,x_2), and so on, where i=N(kappa).
% Note that we do not store J in lexicographic
% order because it helps us to identify the location
% of mu<kappa by using the D vector.
% Sy is similar to Sx but it is for Y.
%
    D=zeros(f,1);
    Sx=sym(zeros(f,n));
    Sx(1,:)=1;

% xn(i,j)=x(i)^(j-1), yn(i,j)=y(i)^(j-1)
xn = sym(ones(n, MAX+1));
if size(x,2)>1, x=x'; end
for i=2:MAX+1
    xn(:,i)=xn(:,i-1).*x;
end
prodx = cumprod(x);
prodxn = prodx(n);

if XY
    Sy=Sx;
    yn=ones(n, MAX+1);
    if size(y,2)>1, y=y'; end
    for i=2:MAX+1
        yn(:,i)=yn(:,i-1).*y;
    end
    prody = cumprod(y);
    prodxn = prodxn*prody(n);
end

l = zeros(1, Lp);
z = sym(ones(1, Lp));
kt = -(1:Lp);
% kt(i)=alpha*l(i)-i,
% it is updated instead of recomputed every time
cc1 = 0;
ss = sym(zeros(1, MAX+1)); % these are the partial sums
ss(1)=1;

sl=1;

% sl=sum(l), it is updated instead of recomputed every time

%
% Note that h is the number of nonzero parts of l,
% w is N(l), i.e., the index for partition l.
% heap tells us where next block of memory is available after the current l(h)=1,..,m is stored,
% where m=max(lambda(h),l(h-1)) is the number of % possible elements for l(h).
%

h=1;

ww=ones(1,Lp1+1);

heap=lambda(1)+2;

d = zeros(1,Lp);

% d=1-[l(2:Lp) 0], it is the places we will be adding boxes

while h>0

if (l(h)<lambda(h)) && ((h==1 & l(1)<K) || (h>1 && l(h)<l(h-1))) && (MAX>=sl) && (z(h)~=0)

  l(h)=l(h)+1;

% Update Q

  c=(1-h)/alpha+l(h)-1;
  zn=prod(p+c)*alpha;
  dn=prod(q+c)*(kt(h)+h+1);

end

end
if XY
    zn=zn*alpha*l(h);
    dn=dn*(n+alpha*c);
    for j=1:h-1
        delta=kt(j)-kt(h);
        zn=zn*delta;
        dn=dn*(delta-1);
    end
end

kt(h)=kt(h)+alpha;
for j=1:h-1
    delta=kt(j)-kt(h);
    zn=zn*delta;
    dn=dn*(delta+1);
end

z(h)=z(h)*zn/dn;
sl=sl+1;
%
% Only need to do work when number of nonzero
% parts in l is less than n.

if h<n
    if l(h)==1&&h>1
        D(ww(h))=heap;
        ww(h)=heap;
        m=min(lambda(h),MAX-sl+2);
    end
end
heap = heap + min(m, l(h-1));
else
    ww(h) = ww(h) + 1;
end
w = ww(h);
if h > 1
    d(h-1) = d(h-1) - 1;
end
d(h) = l(h);
cc = prod(h+1-alpha+kt(1:h))/prod(h+kt(1:h));

% pp is the index of l-ones(1, Lp)
pp = l(1);
k = 2;
while k <= length(l) && l(k) > 1
    pp = D(pp) + l(k) - 2;
    k = k + 1;
end
Sx(w, h) = cc * prodx(h) * Sx(pp, h);
if XY
    Sy(w, h) = cc * prody(h) * Sy(pp, h);
end
%
% For example, when l = [3 2 1]; then d = [3 2 1] - [2 1 0] = [1 1 1],
% so we can create mu by subtracting 0 or 1 at the first index
% of l, subtracting 0 or 1 at the second index of l,
% and subtracting 0 or 1 at the third index of l.
So there are altogether 8 possible \( \mu \)'s which are horizontal strips of \( l \).

\[
g = \text{find}(d(1:h)>0);
\]
% g are the indices of places we will be adding

\[
lg = \text{length}(g);
\]

\[
slm = 1;
\]
% this is sum\((l - \mu) + 1\) which we will be updating

\[
nhstrip = \text{prod}(d(g)+1)-1;
\]
% number of \( \mu \) that are horizontal strips of \( l \), other than \( l \)

\[
mu = 1;
\]
\[
mt = kt; \quad \% mt(i) = \alpha \cdot \mu(i) - i
\]
\[
blm = \text{ones}(1,lg);
\]
% This is a vector to store the beta_{\(\lambda, \mu\)} update

\[
lmd = l(g) - d(g); \quad \% \text{This gives us the lower bound of } \mu
\]
for \( i = 1 : nhstrip 

\[
j = lg;
\]
\[
gz = g(lg);
\]

while \( \mu(gz) == lmd(j) 

\[
mu(gz) = l(gz);
\]
\[
mt(gz) = kt(gz);
\]
\[
slm = slm - d(gz);
\]
\[
j = j - 1;
\]
\[
gz = g(j);
\]
end
\[ t = k_t(gz) - m_t(gz); \]
\[ blm(j) = blm(j) \times (1 + t); \]
\[ dn = (t + \alpha); \]

for \( r = 1:gz-1 \)
\[
q1 = m_t(r) - m_t(gz);
q2 = k_t(r) - m_t(gz);
blm(j) = blm(j) \times (q1 + \alpha - 1) \times (1 + q2);
dn = dn \times q1 \times (\alpha + q2);
\]
end

blm(j) = blm(j) / dn;
mu(gz) = mu(gz) - 1;
mt(gz) = mt(gz) - \alpha;
slm = slm + 1;

% Push blm(j) all the way to the end because subsequent % partitions of mu will be smaller than the current one.

if \( j < lg \)
    blm(j+1:end) = blm(j);
end

% Find out the index for partition mu.

nmu = mu(1) + 1;
for \( k = 2:h-(mu(h) == 0) \)
    nmu = D(nmu) + mu(k) - 1;
end
for k=h+1:n
Sx(w,k) = Sx(w,k) + blm(j) * Sx(nmu,k-1) * xn(k,slm);
end
if XY
    for k=h+1:n
        Sy(w,k) = Sy(w,k) + blm(j) * Sy(nmu,k-1) * yn(k,slm);
    end
end
for k=h+1:n
    Sx(w,k) = Sx(w,k) + Sx(w,k-1);
end
if XY
    for k=h+1:n
        Sy(w,k) = Sy(w,k) + Sy(w,k-1);
    end
    ss(sl) = ss(sl) + z(h) * Sx(w,n) * Sy(w,n);
else
    ss(sl) = ss(sl) + z(h) * Sx(w,n);
end
else % of "if h<n", i.e., the case h=n
    % pp is the index of l-l(n)*ones(1,Lp)
    pp = l(1) + l-1(n);
    k = 2;
    while k<=n-1&&l(k)>l(n)
pp = D(pp) + l(k) - 1 - l(n);
k = k + 1;
end
k = (l(n) == 1); cc1 = k + (1 - k) * cc1;
% The above line executes:
% "if l(n)==1, cc1=1; end" but does not use "if"

if XY
    cc1 = cc1 * prodxn * (prod(1 + kt(1:n-1) - kt(n)) * (1/alpha + l(n) - 1) ... 
        / (prod(alpha + kt(1:n-1) - kt(n)) * l(n)))^2;
    ss(sl) = ss(sl) + z(n) * cc1 * Sx(pp, n) * Sy(pp, n);
else
    cc1 = cc1 * prodxn * prod(1 + kt(1:n-1) - kt(n)) * (1/alpha + l(n) - 1) / ... 
        (prod(alpha + kt(1:n-1) - kt(n)) * l(n));
    ss(sl) = ss(sl) + z(n) * cc1 * Sx(pp, n);
end
end

if h < Lp % increase length of partition if possible
    z(h+1) = z(h); % carry over Q_kappa and index pointer
    h = h + 1;
    ww(h) = w;
end
else
    sl = sl - l(h);
    l(h) = 0;
    kt(h) = -h;
function p = fn(kappa)

    n = length(kappa);
    s = sum(kappa == kappa(1));
    p = nchoosek(kappa(1) + n, n);
    if s < n
        f = zeros(1, n);
        f(n) = kappa(n) + 1;
        sn = 1;
        c = kappa(n-1) + 1;
        d = 1;
        kt = kappa(1:n);
        for i = n-1:-1:s+2
            if kappa(i) == kappa(i+1)
                % sn keeps track of the number of repeated elements at the
                % beginning of the subvector kappa(i:n)
                % c and d are the first term and the last term in the
                % recursive relation, they are updated when sn>1.
                sn = 1;
                c = kappa(n-1) + 1;
                d = 1;
                kt = kappa(1:n);
                for i = n-1:-1:s+2
                    if kappa(i) == kappa(i+1)
                        % sn keeps track of the number of repeated elements at the
                        % beginning of the subvector kappa(i:n)
                        % c and d are the first term and the last term in the
                        % recursive relation, they are updated when sn>1.
                        sn = 1;
                        c = kappa(n-1) + 1;
                        d = 1;
                        kt = kappa(1:n);
                        for i = n-1:-1:s+2
                            if kappa(i) == kappa(i+1)
                                % sn keeps track of the number of repeated elements at the
                                % beginning of the subvector kappa(i:n)
                                % c and d are the first term and the last term in the
                                % recursive relation, they are updated when sn>1.
                                sn = 1;
                                c = kappa(n-1) + 1;
                                d = 1;
                                kt = kappa(1:n);
                                for i = n-1:-1:s+2
                                    if kappa(i) == kappa(i+1)
                                        % sn keeps track of the number of repeated elements at the
                                        % beginning of the subvector kappa(i:n)
                                        % c and d are the first term and the last term in the
                                        % recursive relation, they are updated when sn>1.
                                        sn = 1;
                                        c = kappa(n-1) + 1;
                                        d = 1;
                                        kt = kappa(1:n);
                                        for i = n-1:-1:s+2
                                            if kappa(i) == kappa(i+1)
                                                % sn keeps track of the number of repeated elements at the
                                                % beginning of the subvector kappa(i:n)
                                                % c and d are the first term and the last term in the
                                                % recursive relation, they are updated when sn>1.
                                                sn = 1;
                                                c = kappa(n-1) + 1;
                                                d = 1;
                                                kt = kappa(1:n);
                                                for i = n-1:-1:s+2
                                                    if kappa(i) == kappa(i+1)
                                                        % sn keeps track of the number of repeated elements at the
                                                        % beginning of the subvector kappa(i:n)
                                                        % c and d are the first term and the last term in the
                                                        % recursive relation, they are updated when sn>1.
                                                        sn = 1;
                                                        c = kappa(n-1) + 1;
                                                        d = 1;
                                                        kt = kappa(1:n);
                                                        for i = n-1:-1:s+2
                                                            if kappa(i) == kappa(i+1)
                                                                % sn keeps track of the number of repeated elements at the
                                                                % beginning of the subvector kappa(i:n)
                                                                % c and d are the first term and the last term in the
                                                                % recursive relation, they are updated when sn>1.
                                                                sn = 1;
                                                                c = kappa(n-1) + 1;
                                                                d = 1;
                                                                kt = kappa(1:n);
                                                                for i = n-1:-1:s+2
                                                                    if kappa(i) == kappa(i+1)
                                                                        % sn keeps track of the number of repeated elements at the
                                                                        % beginning of the subvector kappa(i:n)
                                                                        % c and d are the first term and the last term in the
                                                                        % recursive relation, they are updated when sn>1.
                                                                        sn = 1;
                                                                        c = kappa(n-1) + 1;
                                                                        d = 1;
                                                                        kt = kappa(1:n);
                                                                        for i = n-1:-1:s+2
                                                                            if kappa(i) == kappa(i+1)
sn=sn+1;
c=c*(n+1+kt(i))/(n+1-i);
if kappa(i)>kappa(n)
    d=d*(kt(i)-kt(n))/(n+1-i);
else
    d=0;
end
else
    sn=1;
c=nchoosek(n+1+kt(i),n+1-i);
d=nchoosek(kt(i)-kt(n),n+1-i);
end
f(i)=c-d;
for j=sn+i:n-1
    f(i)=f(i)-nchoosek(kt(i)-kt(j),j-i+1)*f(j+1);
end
end
for i=s+1:n-1
    p=p-nchoosek(kt(1)-kt(i),i)*f(i+1);
end
p=p-nchoosek(kt(1)-kt(n),n);
end
INDEX

$e_e$, electron charge, 12
atomic unit, 12
black-body radiation, 1
Born-Oppenheimer approximation, 13
classical principle of superposition, iii
Coulomb potential, iii
dominance, 40
effective mass, 24
exact solution of the Schrödinger equation, 7
generalized binomial coefficient, 40
generalized hypergeometric function, 41
generalized Pochhammer symbol, 41
generalized shifted factorial, 41
Hamming weight, 80
homogeneous polynomial, 40
Hylleraas coordinates, 58
ideal, 41
Jack polynomial, 40
Legendre differential equation, 30
Legendre function, 31
lexicographical ordering, 40
Molecular orbital theory, 15
multivariate Gamma function, 40
Nikolaj Maximowitsch Günther, 41
partition, 40
photon, 1
Planck constant, 1
reduced mass, 24
Schrödinger equation, iii
specific impulse, 20
symmetric polynomial, 40
system of equations, 41
three-body force, 82
valence bond theory, 14
Yukawa potential, 82
LIST OF REFERENCES


