

Quantum Correlations in Frustrated Three-Body Systems

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BY
Chaitali Shah



Instrumentation and Applied Physics
Indian Institute of Science
Bangalore 560 012 (INDIA)

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Declaration

I hereby declare that the work presented in this report titled 'Quantum Correlations in Frustrated Three-Body Systems', is the result of the investigations carried out by me under the supervision of Prof. Apoorva Patel at the Centre for High Energy Physics, Indian Institute of Science, Bangalore, India, and that it has not been submitted elsewhere for the conferment of any degree or diploma of any Institute or University. Keeping with the general practice, due acknowledgements have been made wherever the work described is based on other investigations.

(Chaitali Shah)

July 2023

Department of Instrumentation and Applied Physics,
Indian Institute of Science,
Bangalore-560012,
India.

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Abstract

Many physical systems are not understood completely due to the presence of multi-body quantum correlations. The effort taken to simulate such systems on classical computers increases exponentially with the increase in the size of the system. In this project, the study of simple, yet non-trivial, three-body frustrated systems is undertaken in the hope of understanding the underlying quantum correlations. The systems chosen are - helium-like atoms, antiferromagnetic spin triangles and the hydrogen molecular ion. Quantum features like entanglement, degeneracy and tunnelling are investigated.

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Keywords

Quantum Correlations, Frustration, Entanglement, Variational method, Diagonalisation, Separation of Variables, Series Solution, Tunnelling.

Notation and Abbreviations

Atomic Units: a.u. stands for the Hartree atomic units, in which four fundamental physical constants - the reduced Planck's constant \hbar , elementary charge e , electron rest mass m and Coulomb constant k - are set to unity. The units of length then correspond to the Bohr radius $a_0 = \frac{\hbar^2}{kme^2}$ and the unit of energy is a Hartree $E_h = \frac{\hbar^2}{ma_0^2}$.

Pauli matrices: σ_x , σ_y and σ_z are the Pauli matrices. Their matrix representation is

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Chapter 1

Introduction

Many theoretically interesting and practically important physical systems have not been understood in their entirety despite the many leaps taken in the field of contemporary physics. Usually, such systems are studied using simulations and numerical computations on softwares that model their structure. Attempts that model real systems classically fail to explain many unique features exhibited by them. Deviations in the simulation results from experimental data are labelled as ‘anomalies’. These are not ‘anomalies’ but quantum mechanical features making their presence felt. Many systems have multi-body quantum correlations, and their modelling is essential to understand the ensuing properties in the system. In this project, we study three three-body systems and the nature of the quantum correlations that arise between their constituents under frustration.

Helium-like atoms are the first system studied. It is the simplest multi-electron system that can be used to understand the concept of quantum entanglement. We investigate the ground state wavefunction of the helium atom using the variational method. The variational method, an extremely useful technique in quantum mechanics, is employed to find the ground state energies of a system. It forms the basis for powerful quantum algorithms like Variational Quantum Eigensolvers, which can potentially solve many practical problems in quantum chemistry and biology [6, 9, 14]. The helium atom consists of a nucleus with two electrons. There is frustration in the system because there are two attractive coulombic forces (nuclei-electron) and one repulsive force (electron-electron). Numerous attempts have been made to obtain the ground state energy, and results of sufficient accuracy have been obtained by using various multi-parameter trial functions [19, 20, 28, 17, 30]. The aim of our study is better comprehension of the ground state which exhibits quantum entanglement.

The next subject of study is antiferromagnetic spin triangles. The antiferromagnetic Heisenberg model provides magnetic frustration in a triangular lattice, where every pair of neighbouring spins cannot align in opposite directions. The ground state of frustrated spin systems exhibits massive degeneracy, which enhances the role of quantum fluctuations. Strong quantum correlations in a material can prevent magnetic order and lead to exotic properties in substances [11]. This makes spin systems a very active area of research in quantum condensed matter physics.

The final system under investigation is the hydrogen molecular ion H_2^+ . It is the most elementary molecule, but the exact closed-form solution for its energy eigenstates and eigenvalues has not yet been discovered. It is the simplest system that can be studied to understand the nature of a chemical bond[13]. The Schrödinger equation for this system is separable [3], and there has been a lot of research in finding series solutions using various bases [8, 21, 31, 5, 4]. A more general approach to finding this system's ground state energy is using the variational method [26], with the ground state wavefunction of the molecule being chosen as a linear combination of atomic orbitals. In this project, the focus is the ground state wave function [24, 16] and the location of the electron in the bond rather than the solution to the energy eigenvalues. The understanding of this system can be extended to the concept of tunnelling and the formation of bonds in more complex systems.

Chapter 2

Helium-like Atoms

The helium atom is the simplest multi-electron system and consists of two electrons bound to a nucleus. The closed-form solution to this system's Schrödinger equation has not yet been discovered. Various approximations have been used to estimate its ground state energy and wavefunction.

2.1 Formulation of the Problem

The non-relativistic time-independent Schrödinger equation of helium-like atoms is given by,

$$\mathcal{H}\psi(r_1, r_2) = E\psi(r_1, r_2) \quad (2.1)$$

The Hamiltonian \mathcal{H} can be written by separating out the centre-of-mass motion as follows.

$$\mathcal{H} = -\frac{\hbar^2}{2\mu}\nabla_{r_1}^2 - \frac{\hbar^2}{2\mu}\nabla_{r_2}^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} - \frac{\hbar^2}{M}\nabla_{r_1}\cdot\nabla_{r_2} + \frac{e^2}{r_{12}}$$

where $\mu = \frac{mM}{m+M}$ is the reduced mass of an electron with respect to the nucleus with m and M specifying the mass of the electron and nucleus respectively, Z is the atomic number, \vec{r}_1 and \vec{r}_2 are the distance vectors between the electrons and the nucleus, and $r_{12} = |\vec{r}_1 - \vec{r}_2|$.

Since the mass of the nucleus is much larger than that of the electrons (the mass of a proton or neutron is about 1840 times that of an electron), the nucleus can be considered to be infinitely heavy ($M \rightarrow \infty$, $\mu \rightarrow m$) and the Hamiltonian simplifies to

$$\mathcal{H} = -\frac{\hbar^2}{2m}\nabla_{r_1}^2 - \frac{\hbar^2}{2m}\nabla_{r_2}^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \quad (2.2)$$

The Hamiltonian can be written as the following, in atomic units,

$$\mathcal{H} = -\frac{1}{2}\nabla_{r_1}^2 - \frac{1}{2}\nabla_{r_2}^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad (2.3)$$

The first two terms indicate the kinetic energies of the two electrons, and the other terms comprise the potential energy from coulombic interactions between the three bodies. The electron-electron repulsion term (the last term in the Hamiltonian) makes the separation of variables inapplicable to solve this eigenvalue equation. Hence, we resort to approximation techniques to obtain the ground state energy of the system.

2.2 The Variational Method

The Variational Method is extremely useful in finding approximate estimation of the ground state energy of systems.

2.2.1 Upper Bound on the Ground State energy

The Rayleigh-Ritz variational principle states that for any normalised wavefunction ψ [15],

$$\langle \mathcal{H} \rangle \geq E_0 \quad (2.4)$$

where E_0 is the ground state energy of the system described by the Hamiltonian \mathcal{H} and $\langle \mathcal{H} \rangle$ is the expectation value of the Hamiltonian.

For an unnormalised wavefunction, the modified inequality is [29],

$$\frac{\langle \psi | \mathcal{H} | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_0 \quad (2.5)$$

2.2.2 Lower Bound on the Ground State energy

The lower bound on the ground state energy can be derived from the expectation value and variance of the Hamiltonian \mathcal{H} , to be the following [23].

$$\langle \mathcal{H} \rangle - \langle \mathcal{H}^2 - \langle \mathcal{H} \rangle^2 \rangle^{\frac{1}{2}} \leq E_0 \quad (2.6)$$

if $\langle \mathcal{H} \rangle$ is closer to E_0 than to any other level.

In the variational method, the right-hand sides of the inequalities (2.5) and (2.6) are evaluated using a trial function, or a *variational ansatz*, $\tilde{\psi}$ which depends on a number of parameters. The bounds on the ground state energy are then obtained by varying the parameters

until the minimum value of the expectation is obtained for the upper bound, and the maximum value of the quantity on the right-hand side of inequality (2.6) is obtained for the lower bound.

For $|\psi\rangle = \sum_i c_i |i\rangle$, where $|i\rangle$ are the eigenstates of the Hamiltonian, $\langle f(\mathcal{H}) \rangle = \sum_i |c_i|^2 f(E_i)$. It follows that for small deviations from the ground state, $|\psi\rangle = |\psi_0\rangle + O(\epsilon)$, the upper bound is $\langle \mathcal{H} \rangle = E_0 + O(\epsilon^2)$, and the lower bound is $\langle \mathcal{H} \rangle - \sqrt{\langle \mathcal{H}^2 - \langle \mathcal{H} \rangle^2 \rangle} = E_0 - O(\epsilon)$. Thus, to be useful, the lower bound requires a more accurate variational ansatz than the upper bound. In the following sections, the variational method is performed for various ansatzes for Z=1,2 and 3. For reference, the experimentally obtained values of the ground state energy are given below:

- For Z=1, $E_0 = -0.5255$ Hartrees.
- For Z=2, $E_0 = -2.9037$ Hartrees.
- For Z=3, $E_0 = -7.2796$ Hartrees.

2.3 Choosing the Variational Ansatz

The choice of the variational ansatz affects the estimates of the ground state energy - the better the ansatz, the closer the bound to the actual value. The inequalities in (2.5) and (2.6) reduce to equality if the ansatz chosen is the actual ground state.

2.3.1 Ansatz 1 : $\tilde{\psi}_1$

For helium-like atoms, we choose the trial function based on the information we have about the ground state of the hydrogen atom. The Hamiltonian (in a.u.) for the hydrogen atom is,

$$\mathcal{H} = -\frac{1}{2}\nabla_r^2 - \frac{Z}{r} \quad (2.7)$$

The exact solution for the ground state wavefunction of the hydrogen atom has been found analytically. The ground state wavefunction (in a.u.) is [15]

$$\psi_g(r) = \left(\frac{Z^3}{\pi}\right)^{\frac{1}{2}} e^{-Zr} \quad (2.8)$$

Comparing the Hamiltonians in (2.3) and (2.7), it can be seen that if the electron-electron interaction terms were absent from the helium atom Hamiltonian in (2.3), then it would appear like the sum of two hamiltonians of the hydrogen atom. Ignoring the electron repulsion, the

ground wavefunction of the Helium atom would be the product of two normalized hydrogenic wave functions.

$$\psi(r_1, r_2) = \psi_g(r_1) \times \psi_g(r_2) = \frac{Z^3}{\pi} e^{-Z(r_1+r_2)} \quad (2.9)$$

with $Z=2$ for the Helium atom. We choose this as the variational ansatz by making Z the parameter to be varied. Changing notation for clarity, the choice for the normalised variational ansatz is,

$$\tilde{\psi}_1(r_1, r_2) = \frac{\alpha^3}{\pi} e^{-\alpha(r_1+r_2)} \quad (2.10)$$

with α as the variational parameter.

2.3.1.1 Upper Bound

The expectation value of the Hamiltonian for the ansatz $\tilde{\psi}_1$ is computed as shown.

$$\langle \mathcal{H} \rangle = \langle \tilde{\psi}_1 | \mathcal{H} | \tilde{\psi}_1 \rangle = E_1 + E_2 + E_3 + E_4 + E_5$$

where

$$\begin{aligned} E_1 &= \langle \tilde{\psi}_1 | \left(-\frac{1}{2} \nabla_{r_1}^2 \right) | \tilde{\psi}_1 \rangle = \frac{\alpha^2}{2} \\ E_2 &= \langle \tilde{\psi}_1 | \left(-\frac{1}{2} \nabla_{r_2}^2 \right) | \tilde{\psi}_1 \rangle = \frac{\alpha^2}{2} \\ E_3 &= \langle \tilde{\psi}_1 | \left(-\frac{Z}{r_1} \right) | \tilde{\psi}_1 \rangle = -Z\alpha \\ E_4 &= \langle \tilde{\psi}_1 | \left(-\frac{Z}{r_2} \right) | \tilde{\psi}_1 \rangle = -Z\alpha \\ E_5 &= \langle \tilde{\psi}_1 | \left(\frac{1}{r_{12}} \right) | \tilde{\psi}_1 \rangle = \frac{5}{8}\alpha \end{aligned}$$

Therefore, the expectation value is [29, 27],

$$\langle \mathcal{H} \rangle = \sum_{i=1}^5 E_i = \alpha^2 - 2Z\alpha + \frac{5}{8}\alpha \quad (2.11)$$

We set the first derivative of the expectation value, obtained in (2.11), with respect to the

parameter α to zero to find the value of α at which it is minimum.

$$\frac{d\langle \mathcal{H} \rangle}{d\alpha} = 2\alpha - 2Z + \frac{5}{8} = 0$$

$$\alpha_{min} = Z - \frac{5}{16} \quad (2.12)$$

The approximate ground state energy is then given by substituting α_{min} from (2.12) in (2.11).

$$\langle \mathcal{H} \rangle |_{\alpha=\alpha_{min}} = \tilde{E}_0 = -\frac{1}{2} \left(Z - \frac{5}{16} \right)^2$$

For $Z = 1$ (H⁻ ion), $\tilde{E}_0 = -0.47265625$ Hartree.

For $Z = 2$ (He atom), $\tilde{E}_0 = -2.84765625$ Hartree.

For $Z = 3$ (Li⁺ ion), $\tilde{E}_0 = -7.22265625$ Hartree.

2.3.1.2 Variance and the Lower Bound

We begin by calculating the value of $\langle \mathcal{H}^2 \rangle$ with the ansatz $\tilde{\psi}_1$. We simplify the square of the Hamiltonian by grouping similar terms and calculate the resulting integrals.

$$\langle \mathcal{H}^2 \rangle = \langle \tilde{\psi}_1 | \mathcal{H}^2 | \tilde{\psi}_1 \rangle = E_1 + E_2 + E_3 + E_4 + E_5 + E_6 + E_7$$

where

$$E_1 = \langle \tilde{\psi}_1 | (\alpha^4) | \tilde{\psi}_1 \rangle = \alpha^4$$

$$E_2 = \langle \tilde{\psi}_1 | \left(-4\alpha^2 \frac{(\alpha - Z)}{r_1} \right) | \tilde{\psi}_1 \rangle = 4(Z - \alpha)\alpha^3$$

$$E_3 = \langle \tilde{\psi}_1 | \left(2 \frac{(\alpha - Z)^2}{r_1^2} \right) | \tilde{\psi}_1 \rangle = 4(Z - \alpha)^2\alpha^2$$

$$E_4 = \langle \tilde{\psi}_1 | \left(2 \frac{(\alpha - Z)^2}{r_1 r_2} \right) | \tilde{\psi}_1 \rangle = 2(Z - \alpha)^2\alpha^2$$

$$E_5 = \langle \tilde{\psi}_1 | \left(-\frac{2\alpha^2}{r_1} \right) | \tilde{\psi}_1 \rangle = -\frac{5}{4}\alpha^3$$

$$E_6 = \langle \tilde{\psi}_1 | \left(4 \frac{(\alpha - Z)}{r_1^2} \right) | \tilde{\psi}_1 \rangle = 3(\alpha - Z)\alpha^2$$

$$E_7 = \langle \tilde{\psi}_1 | \left(\frac{1}{r_{12}} \right) | \tilde{\psi}_1 \rangle = \frac{2}{3}\alpha^2$$

The expectation value of \mathcal{H}^2 is evaluated to be,

$$\langle \mathcal{H}^2 \rangle = \sum_{i=1}^7 E_i = \frac{1}{12} \alpha^2 (36\alpha^2 + \alpha(21 - 96Z) + 72Z^2 - 36Z + 8) \quad (2.13)$$

The variance of \mathcal{H} is,

$$\langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2 = \frac{1}{192} \alpha^2 (384\alpha^2 + 96\alpha(1 - 8Z) + 384Z^2 - 96Z + 53)$$

On observing equations (2.5) and (2.6), we can see that the variance represents the gap between the bounds and reduces to zero when the variational ansatz is the actual ground state wavefunction. Therefore, we try to estimate the ground state energy by two approaches: (i) minimising the variance, (ii) maximising the right-hand side of equation (2.6) (in other words, the difference of the expectation value and the standard deviation). By definition, the second approach gives the better estimate.

The numerical calculations for Z=1,2,3 are presented in the following sections.

Z = 1: H⁻ ion The plots in Figure 2.1 show the dependence of variance and the lower bound function on the variational parameter α for the H⁻ ion.

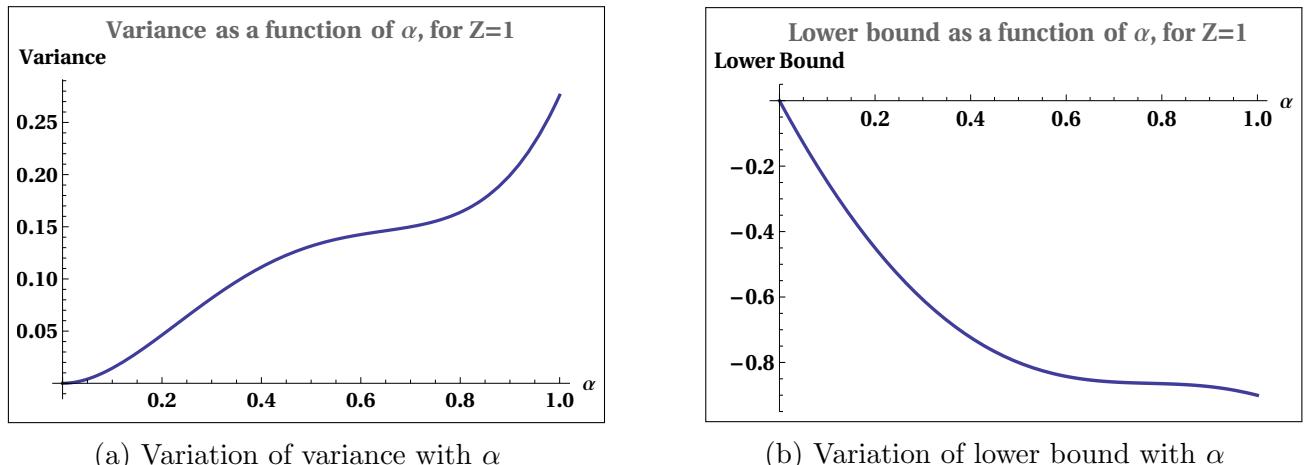
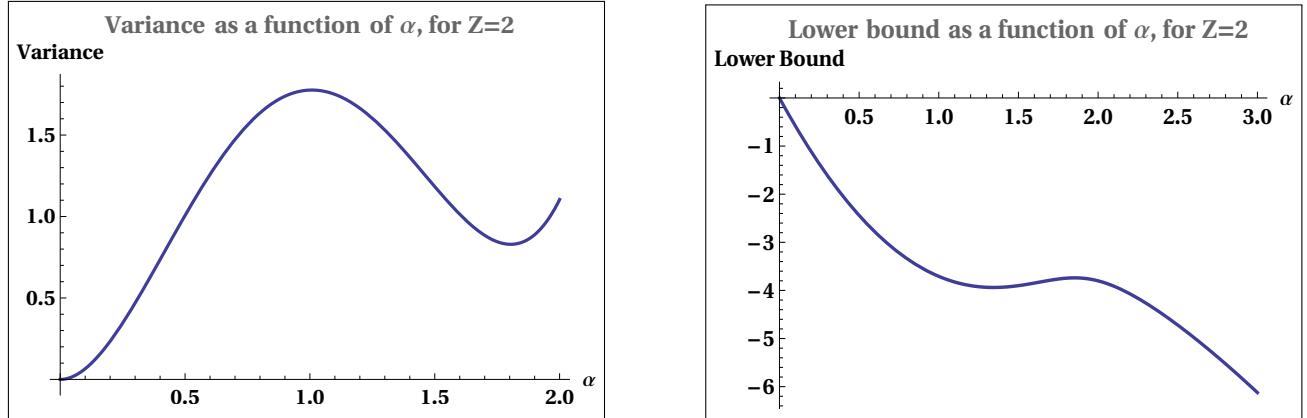


Figure 2.1: Variance and Lower Bound plots for Z=1: H⁻ ion

It can be seen in figures 2.1a and 2.1b that the variance has no minimum and the lower bound function has no maximum at a positive value of α . The lower bound equation (2.6) fails to confirm a bound state for the negative hydrogen ion.

Z = 2 : He atom The plots in Figure 2.2 show the dependence of variance and the lower bound function on the variational parameter α for the Helium atom.



(a) Variation of variance with α

(b) Variation of lower bound with α

Figure 2.2: Variance and Lower Bound plots for Z=2: He atom

From the figure 2.2a (and also using numerical calculations), it is found that the variance has a minimum at $\alpha_{min} = 1.804406$. The ground state energy estimate at this value of α is,

$$\tilde{E}_0 = -3.744738 \text{ Hartree}$$

From the figure 2.2b (and numerical calculations), the maximum in the lower bound function is found to be at $\alpha_{max} = 1.852947$. The ground state energy estimate at this value of α is,

$$\tilde{E}_0 = -3.738875 \text{ Hartree}$$

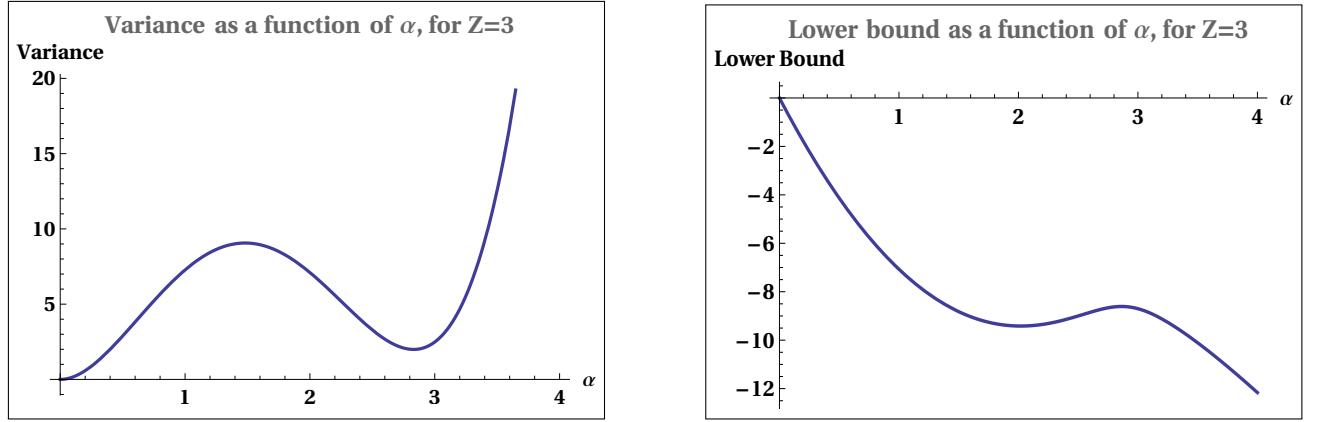
Z = 3 : Li⁺ ion The plots in Figure 2.3 show the dependence of variance and the lower bound function on the variational parameter α for the Li⁺ ion.

Figure 2.3a (and also using numerical calculations) shows that the variance is minimal at $\alpha_{min} = 2.83109$. The ground state energy estimate at this value of α is,

$$\tilde{E}_0 = -8.613751 \text{ Hartree}$$

From the figure 2.3b (and numerical calculations), the maximum in the lower bound function is found to be at $\alpha_{max} = 2.862443$. The ground state energy estimate at this value of α is,

$$\tilde{E}_0 = -8.609197 \text{ Hartree}$$



(a) Variation of variance with α

(b) Variation of lower bound with α

Figure 2.3: Variance and Lower Bound plots for $Z = 3$: Li^+ ion

2.3.2 Ansatz 2 : $\tilde{\psi}_2$

The estimates evaluated by the variational method can be improved by increasing the number of parameters. We improve on the ansatz $\tilde{\psi}_1$ by adding an additional parameter while imposing the system's symmetry on the wavefunction. Electrons are identical particles, so their spatial wavefunction must be symmetrized with respect to interchange. The spin state is evidently anti-symmetric for this system.

In general, fermions are anti-symmetric and are described by *Slater determinants*, which can be calculated in $O(n^3)$ effort using Gaussian elimination. Bosons are symmetric and require *Permanents* for their description. The effort to calculate permanents increases exponentially with the input size (the problem is categorized as belonging to the complexity class #P [1]). The search for a more efficient algorithm for permanent calculations is among the motives for studying frustrated systems wherein such features are exhibited.

The unnormalised variational ansatz is hence of the form [10],

$$\tilde{\psi}_2(r_1, r_2) = e^{-(\alpha r_1 + \beta r_2)} + e^{-(\alpha r_2 + \beta r_1)}$$

with α and β as the variational parameters.

2.3.2.1 Upper Bound

The expectation value of the Hamiltonian with the ansatz $\tilde{\psi}_2$ is calculated.

$$\langle \mathcal{H} \rangle = \langle \tilde{\psi}_2 | \mathcal{H} | \tilde{\psi}_2 \rangle = E_a + E_b + E_c$$

where E_a , E_b and E_c correspond to integrals involving $\tilde{\psi}_{2a} = e^{-(\alpha r_1 + \beta r_2)}$, $\tilde{\psi}_{2b} = e^{-(\alpha r_2 + \beta r_1)}$ and $\tilde{\psi}_{2c} = e^{-(\alpha + \beta)(r_1 + r_2)}$ respectively, post simplification.

$$\begin{aligned}
E_a &= \langle \tilde{\psi}_{2a} | \left(-\frac{\alpha^2 + \beta^2}{2} + \frac{\alpha - Z}{r_1} + \frac{\beta - Z}{r_2} + \frac{1}{r_{12}} \right) | \tilde{\psi}_{2a} \rangle \\
&= \int dr_1^3 dr_2^3 e^{-2(\alpha r_1 + \beta r_2)} \left(-\frac{\alpha^2 + \beta^2}{2} + \frac{\alpha - Z}{r_1} + \frac{\beta - Z}{r_2} + \frac{1}{r_{12}} \right) \\
&= \pi^2 \left(\frac{\alpha - Z}{\alpha^2 \beta^3} + \frac{\beta - Z}{\alpha^3 \beta^2} - \frac{\alpha^2 + \beta^2}{2\alpha^3 \beta^3} + \frac{\alpha^2 + 3\alpha\beta}{\alpha^2 \beta^2 (\alpha + \beta)^3} \right) \\
E_b &= \langle \tilde{\psi}_{2b} | \left(-\frac{1}{2} \nabla_{r_2}^2 \right) | \tilde{\psi}_{2b} \rangle \\
&= E_a \text{ (wavefunction is symmetric under exchange of } \alpha \text{ and } \beta) \\
&= \pi^2 \left(\frac{\alpha - Z}{\alpha^2 \beta^3} + \frac{\beta - Z}{\alpha^3 \beta^2} - \frac{\alpha^2 + \beta^2}{2\alpha^3 \beta^3} + \frac{\alpha^2 + 3\alpha\beta}{\alpha^2 \beta^2 (\alpha + \beta)^3} \right) \\
E_c &= \langle \tilde{\psi}_{2c} | \left(-(\alpha^2 + \beta^2) + \frac{\alpha + \beta - 2Z}{r_1} + \frac{\alpha + \beta - 2Z}{r_2} + \frac{2}{r_{12}} \right) | \tilde{\psi}_{2c} \rangle \\
&= \int dr_1^3 dr_2^3 e^{-(\alpha + \beta)(r_1 + r_2)} \left(-\frac{\alpha^2 + \beta^2}{2} + \frac{\alpha - Z}{r_1} + \frac{\beta - Z}{r_2} + \frac{1}{r_{12}} \right) \\
&= \pi^2 \left(\frac{64(\alpha + \beta - 2Z) + 40}{(\alpha + \beta)^6} - \frac{64(\alpha^2 + \beta^2)}{(\alpha + \beta)^6} \right)
\end{aligned}$$

The normalisation constant for the expectation value is found to be

$$\langle \tilde{\psi}_2 | \tilde{\psi}_2 \rangle = 16\pi^2 \left(\frac{1}{8\alpha^3 \beta^3} + \frac{8}{(\alpha + \beta)^6} \right) \quad (2.14)$$

The simplified equation for the upper bound is,

$$\begin{aligned}
\frac{\langle \tilde{\psi}_2 | \mathcal{H} | \tilde{\psi}_2 \rangle}{\langle \tilde{\psi}_2 | \tilde{\psi}_2 \rangle} &= \frac{8(5\alpha + 5\beta + 16\alpha\beta - 16Z(\alpha + \beta))}{16(\alpha + \beta)^6 \left(\frac{1}{8\alpha^3 \beta^3} + \frac{8}{(\alpha + \beta)^6} \right)} + \frac{(\alpha + \beta)^3(\alpha^5 + 3\alpha^4\beta + \beta^5 - 2Z(\alpha + \beta)^4)}{16\alpha^3 \beta^3 (\alpha + \beta)^6 \left(\frac{1}{8\alpha^3 \beta^3} + \frac{8}{(\alpha + \beta)^6} \right)} \\
&\quad + \frac{((\alpha + \beta)^3(2\alpha^3\beta(1 + 2\beta) + 2\alpha^2\beta^2(3 + 2\beta) + \alpha\beta^3(2 + 3\beta)))}{16\alpha^3 \beta^3 (\alpha + \beta)^6 \left(\frac{1}{8\alpha^3 \beta^3} + \frac{8}{(\alpha + \beta)^6} \right)}
\end{aligned} \quad (2.15)$$

Numerical methods are used to compute the values of α and β at which (2.15) is minimum for various Z . The plots in Figure 2.15 show the dependence of the upper bound function on the variational parameter α and β for the H^- ion, Helium atom and Li^+ ion.

It can be seen that the plots are symmetric about $\alpha = \beta$. A double well structure is formed, and the minima do not lie on the $\alpha = \beta$ line. If $\alpha = \beta$, the permanent structure would van-

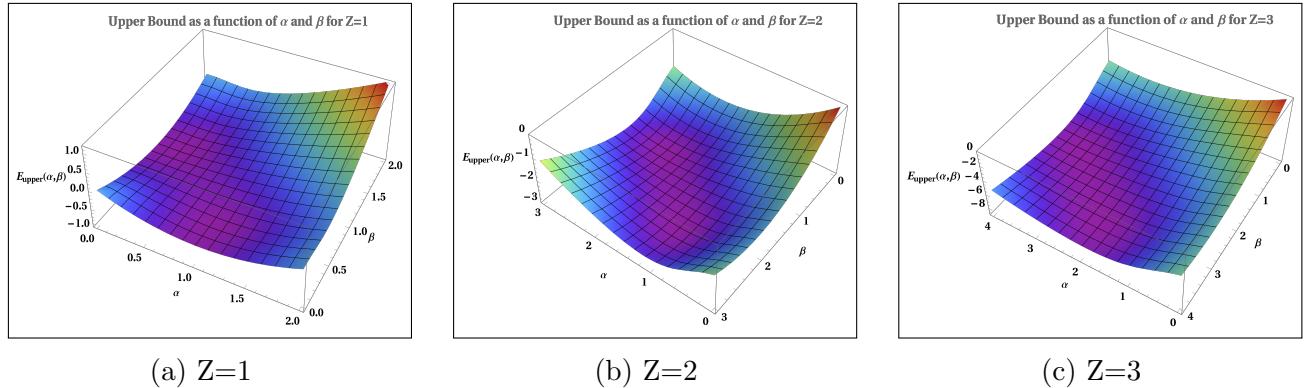


Figure 2.4: Variation of upper bound with α and β

ish, and the ansatz $\tilde{\psi}_2$ would reduce to $\tilde{\psi}_1$ with a multiplicative factor.

The values of parameters and ground state energy estimate are found numerically and tabulated in Table 2.1.

Atomic Number, Z	α_{\min}	β_{\min}	\tilde{E}_0 (in Hartrees)
1	0.2832	1.0392	-0.5133
2	2.1832	1.1885	-2.8757
3	3.2949	2.0790	-7.2487

Table 2.1: The value of parameters α_{min} and β_{min} with the energy minima \tilde{E}_0 for Z=1,2,3 for the upper bound. (upto four decimal places)

2.3.2.2 Variance and the Lower Bound

The integrals for the variance and lower bound are evaluated for the ansatz $\tilde{\psi}_2$ in a manner similar to that of $\tilde{\psi}_1$ in Section 2.3.1.2.

The plots in Figure 2.5 show the dependence of the variance on the variational parameter α and β for the H^- ion, Helium atom and Li^+ ion.

- It can be seen in Figure 2.5a for Z=1, that the variance function has no minimum for non-zero α and β . Hence, the ground state energy for the H⁻ ion cannot be estimated.
 - For Z=2, the minimum in Figure 2.5b occurs at $\alpha_{min} \sim 2$ and $\beta_{min} \sim 0$. This represents to the ionisation of the Helium atom with energy ~ 2 Hartree.
 - In Figure 2.5c for Z=3, the variance plot has a minimum representing the ionisation of Li⁺ ion at $\alpha_{min} \sim 3$ and $\beta_{min} \sim 0$, corresponding to energy ~ 3 Hartree.

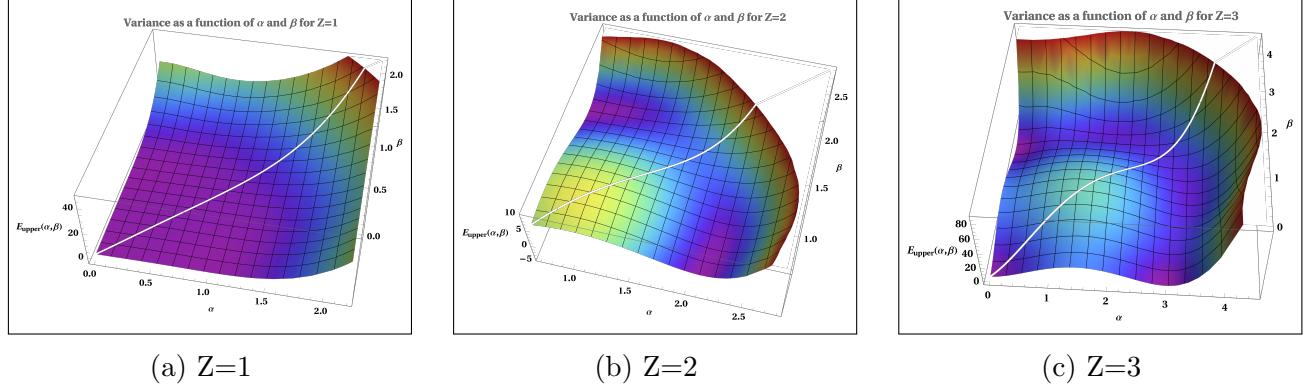


Figure 2.5: Variation of variance with α and β

- A local minimum is obtained at $\alpha_{min} = 3.36131$ and $\beta_{min} = 1.93085$. This is the ground state estimate of the Li^+ ion with $\tilde{E}_0 = -8.382328$ Hartree.

Since the expression for variance failed to have a minimum for the H⁻ ion and the Helium atom, we compute the energy values for the parameters from Table 2.1 to get an estimate of the lower bound. The results are displayed in Table 2.2.

Atomic Number, Z	α_{\min}	β_{\min}	\tilde{E}_0 (in Hartrees)
1	0.2832	1.0392	-0.7169
2	2.1832	1.1885	-3.5830
3	3.2949	2.0790	-8.4149

Table 2.2: The value of parameters α_{min} and β_{min} with the approximate ground state energy \tilde{E}_0 for Z=1,2,3 for the lower bound. (upto four decimal places)

2.3.3 Ansatz 3 : $\tilde{\psi}_3$

The variational ansatzes chosen in previous sub-sections ignore the electron-electron Coulombic repulsion. In an attempt to understand the contribution of this particular interaction, we now modify $\tilde{\psi}_1$ to include the r_{12} term (by approximation $e^{r_{12}} \approx (1 + r_{12})$).

$$\tilde{\psi}_3(r_1, r_2) = e^{-\alpha(r_1 + r_2)}(1 + cr_{12})$$

where α and c are the variational parameters.

It was observed in the previous sections that a better approximation of the ground state energy is found using the upper bound equation (2.5) than the lower bound equation (2.6). So we restrict ourselves to calculating the expectation value of the Hamiltonian for the upper bound hereafter.

2.3.3.1 Upper bound

The expectation value of the Hamiltonian with the ansatz $\tilde{\psi}_3$ is computed.

$$\begin{aligned}\langle \mathcal{H} \rangle &= \langle \tilde{\psi}_3 | \mathcal{H} | \tilde{\psi}_3 \rangle = \pi^2 \left(\frac{35c^2}{16\alpha^7} + \frac{2c}{\alpha^6} + \frac{5}{8\alpha^5} - \frac{3c^2}{\alpha^2} - \frac{35c}{8\alpha^5} - \frac{2(Z-\alpha)}{\alpha^5} \right) \\ &\quad + \pi^2 \left(\frac{9c^2(\alpha-Z)}{\alpha^2} - \frac{15c(\alpha-Z)}{2\alpha^6} - \frac{2c^2+\alpha^2}{\alpha^6} \right)\end{aligned}\quad (2.16)$$

The normalisation constant for the expectation value is found to be

$$\langle \tilde{\psi}_3 | \tilde{\psi}_3 \rangle = \pi^2 \left(\frac{6c^2}{\alpha^8} + \frac{35c}{8\alpha^7} + \frac{1}{\alpha^6} \right) \quad (2.17)$$

The upper bound estimate of ground state energy is given by the equation,

$$\frac{\langle \mathcal{H} \rangle}{\langle \tilde{\psi}_3 | \tilde{\psi}_3 \rangle} = \frac{\alpha(2\alpha^2(8\alpha - 16Z + 5) + 2c\alpha(25\alpha - 60Z + 16) + c^2(64\alpha - 144Z + 35))}{96c^2 + 70c\alpha + 16\alpha^2} \quad (2.18)$$

The values of parameters at which the bound function in equation (2.18) has a minimum and the corresponding ground state energy estimate are found numerically and tabulated in Table 2.3.

Atomic Number, Z	α_{\min}	c_{\min}	\tilde{E}_0 (in Hartrees)
1	0.8257	0.4934	-0.5088
2	1.8496	0.3658	-2.8911
3	2.8564	0.3354	-7.2682

Table 2.3: The value of parameters α_{\min} and c_{\min} with the energy minima \tilde{E}_0 for Z=1,2,3. (upto four decimal places)

2.3.4 Ansatz 4 : $\tilde{\psi}_4$

It was seen in the previous sections that the permanent and the repulsion term both have a significant contribution to the ground state energy estimate. In view of this, a better approximation of the wavefunction was provided in [10].

$$\tilde{\psi}_4(r_1, r_2) = (e^{-(\alpha r_1 + \beta r_2)} + e^{-(\alpha r_2 + \beta r_1)})(1 + cr_{12})$$

The energy integral is minimised (2.5) and the the ground state energy for the H⁻ ion is found to be, $\tilde{E}_0 = -0.52592$ Hartrees. This value is the closest to the actual ground state en-

ergy, amongst the trial functions studied in this work.

2.4 Results

The results obtained in this study for the approximate values of ground state energy for helium-like atoms for upto $Z=3$ have been summarised in Table 2.4 along with the relative error percentages.

Ansatz	Bound	H^- ion		He atom		Li^+ ion	
		\tilde{E}_0	Error %	\tilde{E}_0	Error %	\tilde{E}_0	Error %
$\tilde{\psi}_1$	Upper	-0.4727	10.06	-2.8477	1.93	-7.2227	0.78
$\tilde{\psi}_2$	Upper	-0.5133	2.32	-2.8756	0.97	-7.2487	0.42
$\tilde{\psi}_3$	Upper	-0.5088	3.18	-2.8911	0.43	-7.2681	0.16
$\tilde{\psi}_1$	Lower	-	-	-3.7389	-28.76	-8.6092	-18.26
$\tilde{\psi}_2$	Lower	-	-	-	-	-8.3823	-15.15
$\tilde{\psi}_1$	Variance	-	-	-3.7447	-28.96	-8.6138	-18.33
$\tilde{\psi}_2$	Variance	-0.7170	-36.43	-3.5830	-23.39	-8.4148	-15.59

Table 2.4: The ground state energy estimate \tilde{E}_0 (up to four decimal places) and relative error percentage (up to two decimal places) for $Z=1,2,3$.

The energy data is visualised using the bar graph in Figure 2.6.

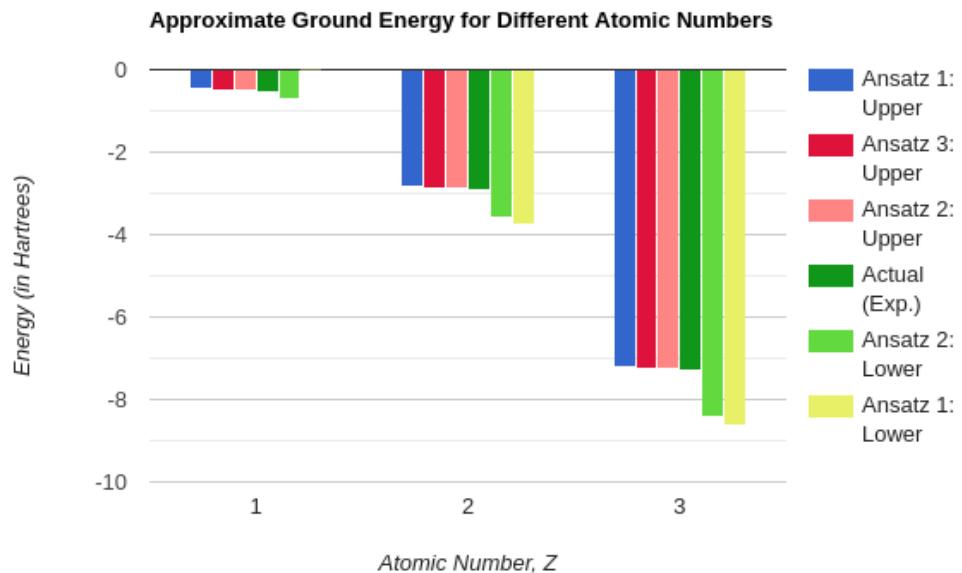


Figure 2.6: Bar Graph visualising the data in Table 2.4

Inferences

- The upper bound (2.5) (minimising the expectation value) gives better approximations of the ground state energy as compared to the lower bound (2.6) (maximising the difference of the expectation value and standard deviation). Minimising the variance gives the least accurate estimates.
- The ansätze with the permanent ($\tilde{\psi}_2$ and $\tilde{\psi}_4$) give a closer approximation of the ground state energy as compared to their counterparts without the permanent ($\tilde{\psi}_1$ and $\tilde{\psi}_3$).
- The ansätze $\tilde{\psi}_1$, $\tilde{\psi}_2$ and $\tilde{\psi}_3$ are not very good approximations to the ground state, so the corresponding lower bounds have significant errors, and they fail to give the approximate ground state energy for small Z.
- The relative error reduces with increasing Z. This implies that the method performs better for heavier atoms. It can also be noted that the repulsion term plays a smaller role for heavier atoms.

2.5 Frustration and Broken Symmetry

We attempt to understand the origin of the permanent structure in the ansatz $\tilde{\psi} = e^{-(\alpha r_1 + \beta r_2)} + e^{-(\alpha r_2 + \beta r_1)}$ and the conditions under which breaking the symmetry ($\alpha \neq \beta$) lowers energy. For this purpose, the coulombic repulsion term in the Hamiltonian (2.3) can be treated perturbatively by introducing a parameter λ .

$$\mathcal{H} = -\frac{1}{2}\nabla_{r_1}^2 - \frac{1}{2}\nabla_{r_2}^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{\lambda}{r_{12}} \quad (2.19)$$

- When $\lambda > 0$, the term indicates electron-electron repulsion with some strength. In this case, there are two attractive forces (between the nucleus and the two electrons) and one repulsive force (between the two electrons). This is a frustrated system.
 $\lambda = 1$ corresponds to the actual Hamiltonian of the system.
- When $\lambda < 0$, the term indicates that the electrons attract each other. In this case, there are three attractive forces, and there is no frustration.
- When $\lambda = 0$, there is no interaction between the electrons and the ground state wavefunction is given by equation (2.9).

The variational calculation is performed using the ansatz $\tilde{\psi} = e^{-(\alpha r_1 + \beta r_2)} + e^{-(\alpha r_2 + \beta r_1)}$ and the expectation value of the Hamiltonian in (2.19) is found to be,

$$\begin{aligned} \frac{\langle \psi | \mathcal{H} | \psi \rangle}{\langle \psi | \psi \rangle} &= (8(16\alpha\beta - 16Z(\alpha + \beta) + 5\alpha\lambda + 5\beta\lambda) + \frac{1}{\alpha^3\beta^3}(\alpha + \beta)^3(\alpha^5 + 3\alpha^4\beta + \beta^5 \\ &\quad - 2Z(\alpha + \beta)^4 + 2\alpha^3\beta(2\beta + \lambda) + \alpha\beta^3(3\beta + 2\lambda) + 2\alpha^2\beta^2(2\beta + 3\lambda))) \\ &\times \left(\frac{1}{16(\alpha + \beta)^6 \frac{1}{8\alpha^3\beta^3} + \frac{8}{(\alpha + \beta)^6}} \right) \end{aligned} \quad (2.20)$$

The expression in (2.20) is minimised to obtain the ground state energy \tilde{E}_0 at α_{min} and β_{min} , for $-2 \leq \lambda \leq 2$. To investigate the breaking of the symmetry, the locus of the point $(\alpha_{min}, \beta_{min})$ is plotted in the $\alpha - \beta$ plane as λ varies from -2 to 2 in Figure 2.7. The points go from green to red as λ varies from -2 to 2.

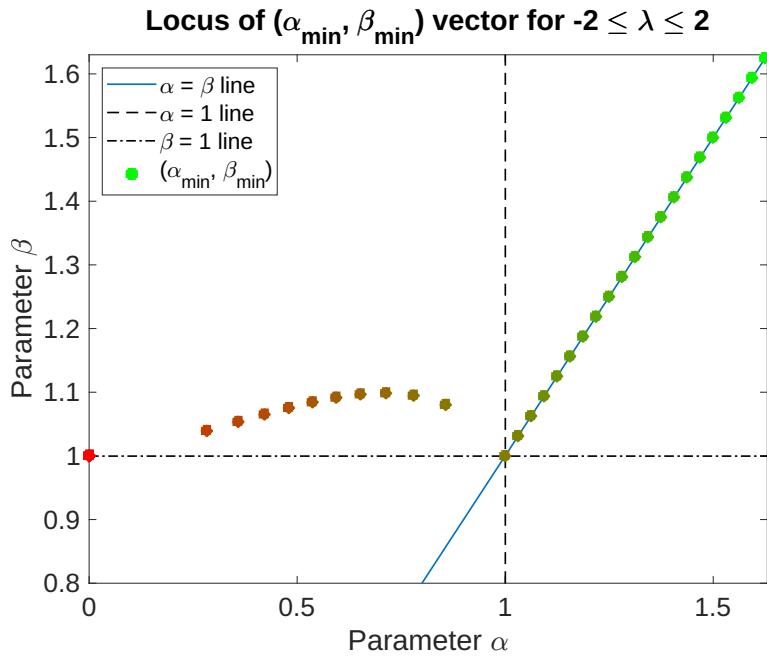


Figure 2.7: Locus of the point $(\alpha_{min}, \beta_{min})$ for $-2 \leq \lambda \leq 2$.

- For $-2 \leq \lambda \leq 0$, the points $(\alpha_{min}, \beta_{min})$ lie on the $\alpha = \beta$ line and the symmetry is preserved. For a non-frustrated system, the permanent does not appear in the wavefunction.
- For $0 < \lambda \leq 2$, the points $(\alpha_{min}, \beta_{min})$ do not lie on the $\alpha = \beta$ line. For this frustrated system, breaking the symmetry lowers the energy, and the wavefunction is a permanent. $\alpha \neq \beta$ denotes an **entangled quantum state**.

Chapter 3

Antiferromagnetic Spin Triangles

The antiferromagnetic spin triangle is a system where to minimise the energy, spins in each pair need to be aligned opposite to each other. Unit cells of larger systems like the Kagome lattice can be understood as being composed of spin triangles as shown in Figure 3.1.

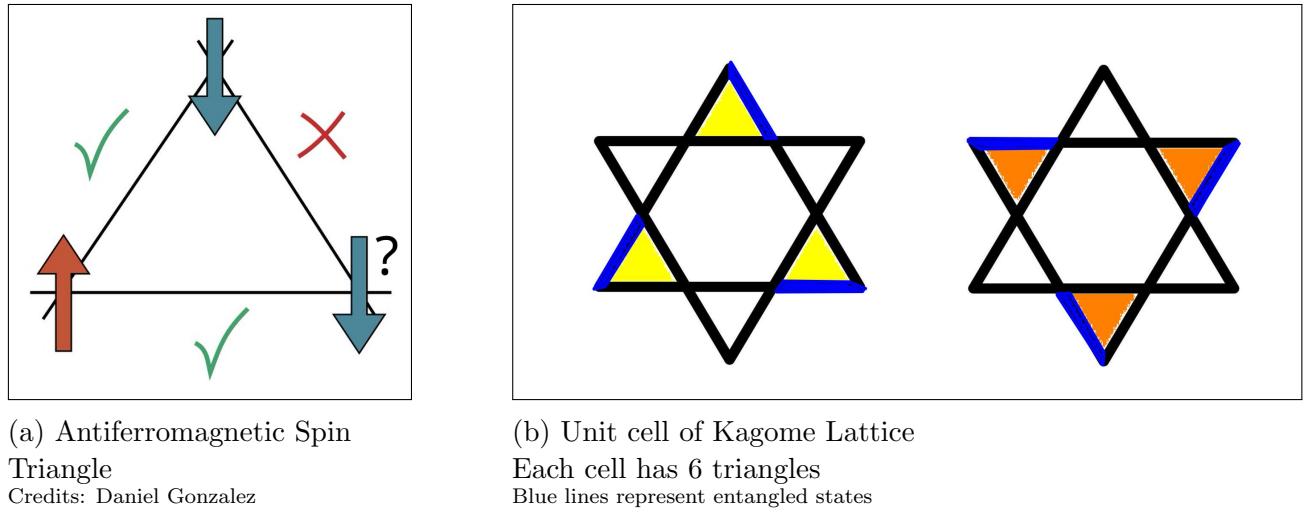


Figure 3.1: Frustrated Spin Systems

3.1 Formulation of the Problem

The Hamiltonian of the antiferromagnetic spin triangle is given by the Heisenberg model,

$$\mathcal{H} = \vec{\sigma}^1 \cdot \vec{\sigma}^2 + \vec{\sigma}^2 \cdot \vec{\sigma}^3 + \vec{\sigma}^3 \cdot \vec{\sigma}^1 \quad (3.1)$$

$$\mathcal{H} = \sum_{i=x,y,z} (\sigma_i^1 \sigma_i^2 + \sigma_i^2 \sigma_i^3 + \sigma_i^3 \sigma_i^1) \quad (3.2)$$

The matrix representation of this Hamiltonian is,

$$\mathcal{H} = \begin{bmatrix} 3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 & 2 & 0 & 0 & 0 \\ 0 & 2 & -1 & 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 2 & 2 & 0 \\ 0 & 2 & 2 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 & -1 & 2 & 0 \\ 0 & 0 & 0 & 2 & 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 3 \end{bmatrix}; \mathcal{H}_{block} = \begin{bmatrix} 3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 2 & 2 & 0 & 0 & 0 & 0 \\ 0 & 2 & -1 & 2 & 0 & 0 & 0 & 0 \\ 0 & 2 & 2 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 2 & 2 & 0 \\ 0 & 0 & 0 & 0 & 2 & -1 & 2 & 0 \\ 0 & 0 & 0 & 0 & 2 & 2 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 3 \end{bmatrix} \quad (3.3)$$

The rows and columns of this 8×8 matrix can be rearranged such that the matrix becomes block diagonal with two 1×1 blocks and two 3×3 blocks.

3.2 Solution using Diagonalisation

The exact solution for the energy eigenvalues and eigenstates for this system can be obtained by diagonalisation.

The ground state energy eigenvalue is found to be $E_- = -3$ and there are four linearly independent states that have the same eigenvalue. The energy eigenstates are

$$|\psi_{-,1}\rangle = (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)(|\uparrow\rangle), \quad |\psi_{-,2}\rangle = (|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle)(|\downarrow\rangle) \\ |\psi_{-,3}\rangle = (|\downarrow\rangle)(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle), \quad |\psi_{-,4}\rangle = (|\uparrow\rangle)(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \quad (3.4)$$

The excited state energy eigenvalue is found to be $E_+ = +3$ and there are four orthogonal states that have the same eigenvalue. The energy eigenstates are

$$|\psi_{+,1}\rangle = |\uparrow\uparrow\uparrow\rangle, \quad |\psi_{+,2}\rangle = \frac{1}{\sqrt{3}}(|\downarrow\downarrow\uparrow\rangle + |\downarrow\uparrow\downarrow\rangle + |\uparrow\downarrow\downarrow\rangle) \\ |\psi_{+,3}\rangle = |\downarrow\downarrow\downarrow\rangle, \quad |\psi_{+,4}\rangle = \frac{1}{\sqrt{3}}(|\uparrow\uparrow\downarrow\rangle + |\uparrow\downarrow\uparrow\rangle + |\downarrow\uparrow\uparrow\rangle) \quad (3.5)$$

Inference Frustration in the system leads to degeneracy in the ground state. The ground state wavefunctions exhibit entanglement - two of the spins form a Bell pair. The Kagome lattice ground state is also composed of spins in Bell pairs. The unit cell has a ground state energy eigenvalue $E_0 = -18$, with six Bell pairs in doubly degenerate ground states. In general, for spins in a ring with only nearest-neighbour antiferromagnetic coupling, there is frustration if there are odd number of spins. In more complex frustrated systems, the ground state can be a spin-liquid or a spin-glass with massive degeneracy.

Chapter 4

Hydrogen Molecular Ion

The hydrogen molecular ion system is the simplest of all molecules and consists of two nuclei (protons) and an electron. Its study is important because older studies using the semi-classical quantum theory failed to produce results that agreed with experiments [25], but the quantum theory using the Schrödinger equation formulation succeeded [8].

4.1 Formulation of the Problem

The Hamiltonian for the system is given by,

$$\mathcal{H}\psi = \left(\frac{P_1^2}{2M} + \frac{P_2^2}{2M} + \frac{p^2}{2m} - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{r_{12}} \right) \psi = E'\psi \quad (4.1)$$

where m is the mass of the electron, M is the mass of the proton, \vec{r}_1 and \vec{r}_2 are the distance vectors between the electron and the nuclei, r_{12} is the distance between the two nuclei, and P_1^2 , P_2^2 and p^2 are the momenta of the two protons and the electron.

Empirical data of molecular spectroscopy shows that energy scales of molecules are well-separated. The treatment of electronic, vibrational and rotational excitations can hence be performed separately in a step-by-step manner. This is known as the Born-Oppenheimer approximation [12]. The nuclei are very heavy in comparison with the electron, so we can set their kinetic energies to zero. This means the distance between the nuclei is fixed to $r_{12} = R$. The Hamiltonian (in a.u.) simplifies to

$$\mathcal{H}\psi = \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_1} - \frac{1}{r_2} \right) \psi = E\psi \quad (4.2)$$

where $E = E' - \frac{1}{R}$.

4.2 Separation of Variables

The equation (4.2) is separable in prolate spheroidal coordinates [3]. With the z-axis as the inter-nuclear axis, the coordinates are defined as,

$$\begin{aligned}\xi &= \frac{r_1 + r_2}{R}, \quad 1 \leq \xi < \infty \\ \eta &= \frac{r_1 - r_2}{R}, \quad -1 \leq \eta \leq 1 \\ \phi &= \text{azimuth angle}, \quad 0 \leq \phi < 2\pi\end{aligned}$$

The Laplacian in these coordinates is given by

$$\nabla^2 = \frac{4}{R^2(\xi^2 - \eta^2)} \left(\frac{\partial}{\partial \xi} \left((\xi^2 - 1) \frac{\partial}{\partial \xi} \right) + \frac{\partial}{\partial \eta} \left((1 - \eta^2) \frac{\partial}{\partial \eta} \right) + \left(\frac{1}{\xi^2 - 1} + \frac{1}{1 - \eta^2} \right) \frac{\partial^2}{\partial \phi^2} \right) \quad (4.3)$$

The wavefunction has the product form $\psi(\xi, \eta, \phi) = X(\xi)Y(\eta)\Phi(\phi)$. Substituting this, along with the Laplacian in (4.3), in (4.2) gives the following linear second order ordinary differential equations.

$$\frac{d^2\Phi}{d\phi^2} + m^2\Phi = 0 \quad (4.4)$$

$$\frac{\partial}{\partial \eta} \left((1 - \eta^2) \frac{\partial Y}{\partial \eta} \right) + \left(p^2\eta^2 - \frac{m^2}{1 - \eta^2} - A \right) Y = 0 \quad (4.5)$$

$$\frac{\partial}{\partial \xi} \left((\xi^2 - 1) \frac{\partial X}{\partial \xi} \right) + \left(-p^2\xi^2 + 2R\xi - \frac{m^2}{\xi^2 - 1} + A \right) X = 0 \quad (4.6)$$

where $p^2 = -\frac{ER^2}{2}$ and A are the separation parameters that link the equations.

4.3 The Azimuthal Equation

Equation (4.4) or the azimuth equation is solvable directly and has physical solutions (single-valued) for discrete m .

$$\Phi(\phi) = e^{(\pm im\phi)}, \quad m = 0, 1, 2, \dots \quad (4.7)$$

The integer m corresponds to angular momentum along the inter-nuclear axis. Our aim is to obtain the ground state (experimentally found to be the ${}^2\Sigma_g^+$ state) of the dihydrogen cation and for this state $m = 0$.

4.4 The Angular Equation

Equation (4.5) is the angular equation and we need to obtain the relation between A and p^2 to solve this equation. There are many studies that use various methods to obtain this relation and we shall

discuss Hylleraas's method in the following section.

4.4.1 Series solution using Associated Legendre polynomials

The angular equation can be written as

$$(1 - \eta^2) \frac{d^2Y}{d\eta^2} - 2\eta \frac{dY}{d\eta} + (p^2\eta^2 - A)Y = 0 \quad (4.8)$$

The solution is attempted using a series of associated Legendre polynomials as suggested by Hylleraas [21].

$$Y(\eta) = \sum_{l=0}^{\infty} a_l P_l^0(\eta) \quad (4.9)$$

Substituting (4.9) in (4.8) and using the equation satisfied by associated Legendre functions, we obtain the equation,

$$\sum_{l=0}^{\infty} a_l (p^2\eta^2 - A - l(l+1)) P_l^0(\eta) = 0 \quad (4.10)$$

Associated Legendre functions have the recurrence relation,

$$(2l+1)\eta P_l^m(\eta) = (l+m)P_{l-1}^m(\eta) + (l-m+1)P_{l+1}^m(\eta) \quad (4.11)$$

We use 4.11 to get an expression for $\eta^2 P_l^0$ in terms of $P_{l-2}^0(\eta), P_l^0(\eta)$ and $P_{l+2}^0(\eta)$ and substitute it in 4.10 to get the following recurrence relation between the coefficient a_l .

$$a_{l+2} \frac{p^2(l+2)(l+1)}{(2l+3)(2l+5)} + a_l \left(\frac{p^2l^2}{(2l+1)(2l-1)} + \frac{p^2(l+1)(l-1)}{(2l+1)(2l+3)} - A - l(l+1) \right) + a_{l-2} \frac{p^2(l-1)l}{(2l-3)(2l-1)} = 0 \\ a_{l-2}\alpha(l) + a_l\beta(l) + a_{l+2}\gamma(l) = 0 \quad (4.12)$$

The coefficients form a tridiagonal matrix.

$$M = \begin{bmatrix} \frac{p^2}{3} - A & \frac{2p^2}{15} & 0 & 0 & \dots \\ \frac{2p^2}{3} & \frac{11p^2}{21} - A - 6 & \frac{4p^2}{21} & 0 & \dots \\ 0 & \frac{12p^2}{35} & \frac{39p^2}{77} - A - 20 & \frac{30p^2}{143} & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix}$$

This tridiagonal matrix can be decomposed into a lower triangular and upper triangular matrix.

$$M = LU = \begin{bmatrix} 1 & 0 & 0 & \dots \\ l_0 & 1 & 0 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} d_0 & u_0 & \dots & \dots \\ 0 & d_1 & u_1 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} = \begin{bmatrix} d_0 & u_0 & \dots & \dots \\ l_0 d_0 & d_1 + l_0 u_0 & u_1 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}$$

For a non-trivial solution the determinant of the matrix of coefficients must be zero.

$$|M| = |L||U| = |U| = \prod_0^{\infty} d_n = 0$$

The diagonal elements are obtained as $d_n = \beta(2n) - \frac{\alpha(2n)\gamma(2n-2)}{d_{n-1}}$ with $d_0 = \beta(0) = \frac{p^2}{3} - A$

Approximate solutions for the relation between p^2 and A are obtained by setting $d_N = 0$ for some N and solving the $(N+1)^{th}$ degree equation for A in terms of p^2 . For $N=1$, we get A by solving the quadratic equation,

$$A^2 + A \left(-\frac{p^2}{3} + 6 \right) + \left(\frac{3p^4}{35} - 2p^2 \right) = 0$$

For the ground state, the series representation of A as a function of p^2 is given by,

$$A(p^2) = \frac{p^2}{3} + \frac{2p^4}{135} + \frac{4p^6}{8505} + O(p^8)$$

Now we can solve the radial equation since A has been found as a function of p^2 . The radial equation gives a relation between R and p^2 , which is needed to determine the energy as a function of the inter-nuclear distance.

4.4.2 Power Series Solution: Frobenius Method

The most accurate results for the separation parameters, inter-nuclear separation and energy eigenvalues have been obtained in [2]. The values of p and A depend on the value of R . For $R = 2$ a.u., which is very close to the actual inter-nuclear separation, they are

$$p = 1.48501462, \quad A = 0.811729585. \quad (4.13)$$

The angular equation has regular singular points as $\eta = \pm 1$, hence according to Fuch's theorem we can obtain atleast one solution by the Frobenius series method about an ordinary point like $\eta = 0$.

We use the values in (4.13) and attempt a power series of the form,

$$Y(\eta) = \sum_{j=0}^{\infty} a_j \eta^{s+j} \quad (4.14)$$

Substituting (4.14) in (4.8), we obtain the following recurrence relation.

$$a_{j+2}(s+j+2)(s+j+1) - a_j((s+j)(s+j+1) + 2A) + a_{j-2}p^2 = 0$$

The series converges for $|\eta| \leq 1$.

The indicial equation is $a_0 s(s-1) = 0$.

The ground state of H_2^+ is symmetric in r_1 and r_2 , so we choose the solution even in η .

The series solution is plotted in Figure. 4.1 by taking a sum of 1000 terms (j=1000).

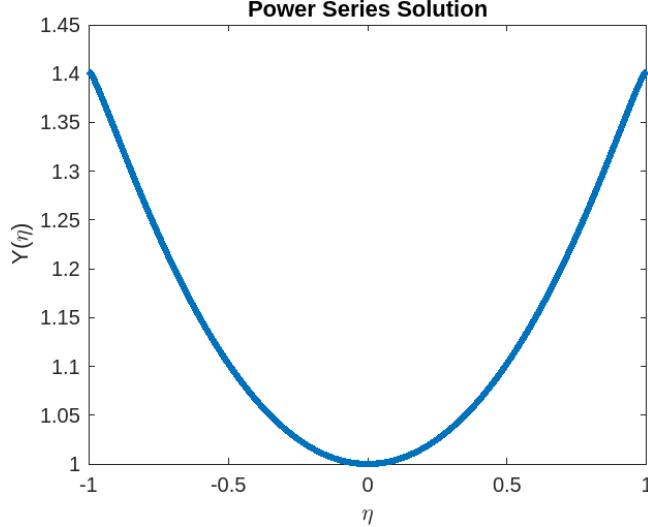


Figure 4.1: Power series solution for $Y(\eta)$ with 1000 terms.

4.4.3 Solution in terms of Confluent Heun Functions

With the substitution $x = 1 - \eta^2$ in the equation (4.8), the following differential equation for the function $y(x) = Y(\eta)$ is obtained.

$$x(x-1)y'' + \left(\frac{3}{2}x - 1\right)y' + \frac{1}{4}(p^2x + A - p^2)y = 0 \quad (4.15)$$

This is a non-symmetrical confluent Heun equation and has solutions (one regular at $x=1$ and other at $x=0$) of the form [18],

$$\begin{aligned} y_0(x) &= \text{HeunC}\left(0, -\frac{1}{2}, 0, -\frac{p^2}{4}, \frac{A+1}{4}, 1-x\right) \\ y_1(x) &= \text{HeunC}\left(0, 0, -\frac{1}{2}, \frac{p^2}{4}, \frac{A-p^2+1}{4}, x\right) \end{aligned}$$

Transforming back to the variable η ,

$$Y_0(\eta) = \text{HeunC}\left(0, -\frac{1}{2}, 0, -\frac{p^2}{4}, \frac{A+1}{4}, \eta^2\right) \quad (4.16)$$

$$Y_1(\eta) = \text{HeunC}\left(0, 0, -\frac{1}{2}, \frac{p^2}{4}, \frac{A-p^2+1}{4}, 1-\eta^2\right) \quad (4.17)$$

For the right values of A and p^2 , the solutions become linearly dependent. The Wronskian can be used to find the right values of A and p^2 , because it is zero for linearly dependent solutions [7].

The solution is plotted using values from 4.13 in Figure. 4.2.

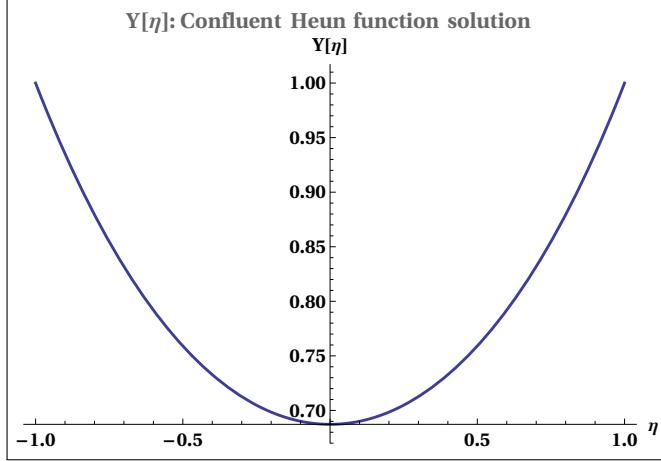


Figure 4.2: $Y(\eta)$ in terms of confluent Heun function

Figure 4.1 and 4.2 differ only by a proportionality constant.

4.5 The Radial Equation

Equation (4.6) is the radial equation and we need to obtain the relation between R and p^2 to solve this eigenvalue equation. We discuss Jaffe's method in the following section.

4.5.1 Series solution

The radial equation can be written as

$$(\xi^2 - 1) \frac{d^2 X}{d\xi^2} + 2\xi \frac{dX}{d\xi} + (2R\xi - p^2\xi^2 + A)X = 0 \quad (4.18)$$

Let the function $X(\xi)$ have the form [22],

$$X(\xi) = e^{-p\xi} (\xi + 1)^{\frac{R}{p}-1} f(x), \quad x = \frac{\xi - 1}{\xi + 1} \quad (4.19)$$

Substituting equation (4.19) in the radial equation leads to a differential equation for $f(x)$.

$$x(1-x)^2 f'' + ((1-2\sigma)x^2 + 2(\sigma-2p-1)x + 1)f' + (\sigma^2 x + \sigma(1+2p) + A - p^2)f = 0 \quad (4.20)$$

where $\sigma = \frac{R}{p} - 1$

Equation (4.20) can be solved using a power series about the origin.

$$f(x) = \sum_{n=0}^{\infty} a_n x^n \quad (4.21)$$

Substituting (4.21) in (4.20) gives the following three-term recurrence relation.

$$a_{n+1}(n+1)^2 + a_n(2n(\sigma - 2p - n) + \sigma(1 + 2p) + A - p^2) + a_{n-1}(n-1-\sigma)^2 = 0 \quad (4.22)$$

The series solution converges for $0 \leq x \leq 1$. For a convergent solution, the three-term recurrence relation can be expressed as an infinite continued fraction. It can be used to relate the values of p , A and R , and hence determine the dependence of E on R .

4.5.2 Solution in terms of Confluent Heun Functions

The radial equation has two regular singularities at the $\xi = \pm 1$. The solutions for the radial equation in terms for the confluent Heun functions are,

$$\begin{aligned} X_1(\xi) &= e^{-p(\xi-1)} \text{HeunC}\left(4p, 0, 0, -4R, 2R - p^2 + A, \frac{1-\xi}{2}\right) \\ X_{-1}(\xi) &= e^{p(\xi+1)} \text{HeunC}\left(4p, 0, 0, -4R, -2R - p^2 + A, \frac{1+\xi}{2}\right) \end{aligned} \quad (4.23)$$

The point $\xi = -1$ is not physical and corresponds to a negative distance. The physical solution for the radial equation is plotted in Figure. 4.3.

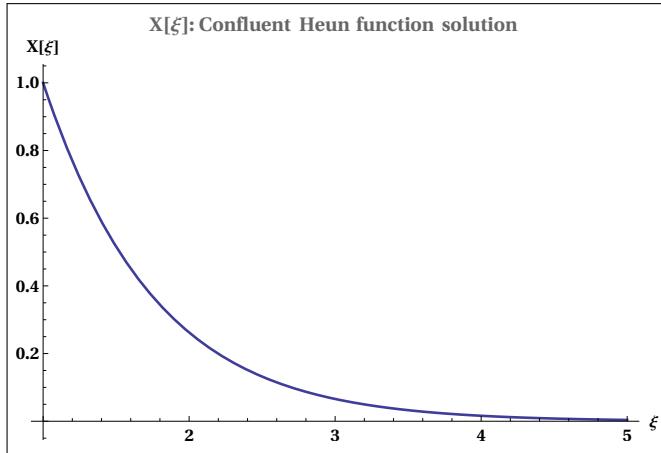


Figure 4.3: $X(\xi)$ in terms of confluent Heun function

4.6 The Ground State

The ground state wavefunction of the hydrogen molecular ion is given by the product of the solutions to the radial and angular equations.

$$\begin{aligned}\psi(\xi, \eta) &= e^{-p(\xi-1)} \text{HeunC} \left(4p, 0, 0, -4R, 2R - p^2 + A, \frac{1-\xi}{2} \right) \\ &\quad \times \text{HeunC} \left(0, 0, -\frac{1}{2}, \frac{p^2}{4}, \frac{A-p^2+1}{4}, 1-\eta^2 \right)\end{aligned}\quad (4.24)$$

The coordinates are changed from prolate spheroidal to cylindrical to visualise the wavefunction.

$$\rho = \frac{R}{2} \sqrt{(\xi^2 - 1)(1 - \eta^2)}, \quad 0 \leq \rho \leq \infty$$

$$z = \frac{R}{2} \xi \eta, \quad -\infty \leq z \leq \infty$$

Let the transformed functions be $X(\rho, z)$ and $Y(\rho, z)$.

The functions $X(\rho, z)$, $Y(\rho, z)$ and $\psi(\rho, z)$ are plotted in the Figure 4.4, with the choice $R=2$.

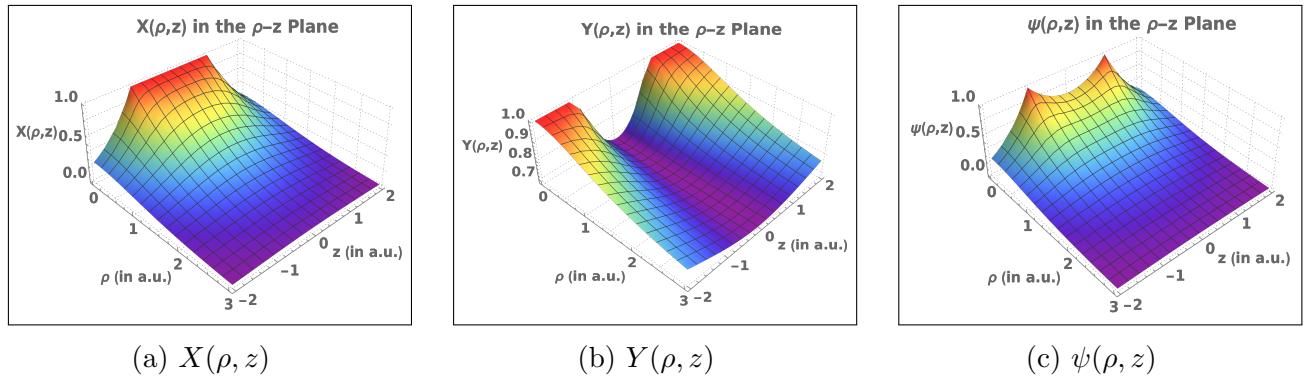


Figure 4.4: $X(\rho, z)$, $Y(\rho, z)$ and $\psi(\rho, z)$ in the $\rho - z$ plane

The probability density of the electron, shown in the figure below, is given by

$$P(\rho, z) = |\psi(\rho, z)|^2 \rho.$$

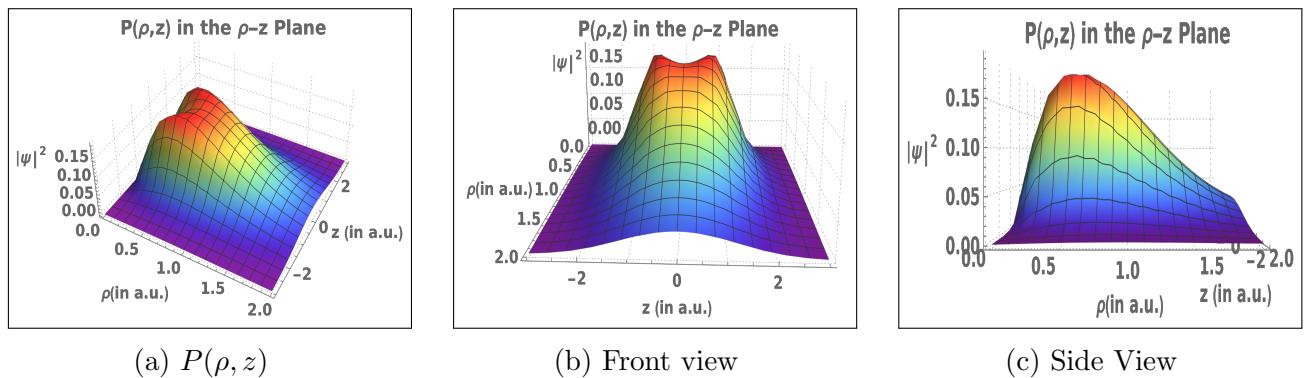


Figure 4.5: Probability density of the electron

It can be seen in Fig. 4.5 that there are two peaks, indicating a high probability of finding the electron in those areas. The location of the peaks is found numerically to be,

$$\rho_1 = 0.546097, \quad z_1 = 0.71125$$

and

$$\rho_2 = 0.546097, \quad z_2 = -0.71125$$

The ground state energy is obtained by minimising $E' = E + \frac{1}{R}$. In more detailed calculations, that gives the ground state values [2].

$$R = 1.997193319969992, \quad E' = -0.6026346191065398$$

Inference In the ground state, the electron is more likely to be found near one of the nuclei, rather than in the middle. The nuclei are located at $z = \pm 1$ and $\rho = 0$, whereas the peaks occur at $|z|$ less than unity and ρ greater than zero. This is the structure of the chemical bond between the two protons. The double-peak wavefunction indicates tunnelling of the electron between the nuclei.

Chapter 5

Conclusion

The analysis of quantum correlations in various frustrated systems was conducted in this project. The ground state of the helium atom was found to be entangled. It was seen that frustration in the system led to the state having a permanent structure. Developing algorithms to generate the permanent form more efficiently is a significant open problem that can be worked on with the understanding of such systems.

The preparation of ground states of many complex systems involves entangled states, as seen in the antiferromagnetic Kagome lattice model. The analysis of the antiferromagnetic spin triangle also showed that frustration led to degeneracy in the ground state. Geometrically frustrated systems like this lack long-range magnetic order. The spins pair up, and such valence bond solids break certain spatial symmetries. Distinguishing between different types of quantum paramagnets remains an open and computationally challenging question. Interesting physics is exhibited by such materials, and they have exotic properties. At very low temperatures, highly entangled spins condense and form a liquid called quantum spin liquid. Some of these materials possess topological order and are of significance because they have the potential to aid the creation of topologically protected states for quantum information processing and computation.

The analysis of the hydrogen molecular ion revealed the structure of the chemical bond by unveiling the phenomenon of tunnelling. Tunnelling of the electron between the nuclei to form a bond is an essential concept because it can be extended to understand other types of bonds. The hydrogen bond can be understood analogously as the tunnelling of a proton between two heavier atoms. Understanding hydrogen bonds is essential in studying many practically important systems in quantum chemistry and biology. Hydrogen bonds are present extensively in biological systems. The most important system with a network of hydrogen bonds is water. Water has many unique properties and anomalies unexplained by classical modelling. Quantum mechanical modelling of the system using the understanding developed in the studies performed in this project may aid the analysis of such complex systems.

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