Visualization of Wavefunctions of the Ionized Hydrogen Molecule

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1. Preliminary Information and Introduction

Goal

This document is designed to allow students to interactively explore the orbitals of the ionized hydrogen molecule. The first part reviews how the equations for the atomic orbitals are derived, how they can be plotted in Mathcad, and how linear combinations of solutions to the Schrodinger equation for the hydrogen atom can be used to approximate the orbitals of the ionized hydrogen molecule. This familiarizes the student with the procedures needed to solve the Schrodinger equation for the ionized hydrogen molecule and enables many of the similarities to be seen. In the second part, the exact Schrodinger equation for the ionized hydrogen molecule is solved numerically using the Shooting Method. The electronic charge densities and energies of the wavefunctions from the approximate and exact solutions are compared.

Prerequisites

This Mathcad document is designed to supplement an undergraduate physical chemistry course as an independent study project for advanced students. Students should have at least an introductory knowledge of quantum mechanics. While not necessary, it would be helpful if the students are familiar with the solution of Schrodinger's equation for the hydrogenic atom, and the equations that represent the hydrogenic orbitals and their corresponding energy levels. Moderate skills in Mathcad are required. This document requires Mathcad 2001 or higher.

Performance Objectives

After completing the work described in this Mathcad document the student should be able to:

1. Plot the spherical harmonics in three dimensions to describe the shape of atomic orbitals.
2. Use linear combinations of atomic orbitals (LCAO) to plot the approximate shapes of orbitals of the ionized hydrogen molecule and their probability distributions in spheroidal coordinates.
3. Use the Shooting Method to solve the two point boundary value problems that arise in solving the Schrodinger equation for the ionized hydrogen molecule.
4. Plot the spheroidal harmonics and probability distributions, which arise from the exact solution of the Schrodinger equation for the ionized hydrogen molecule.
5. Discuss differences in the electronic charge densities and in the shapes of the orbitals between the LCAO and exact solutions.
6. Explain why some energy states are bonding and some are anti-bonding.
7. Calculate the energies of the first eight states of the ionized hydrogen molecule as a function of internuclear distance.
Introduction

Visualization is a key factor in understanding solutions to differential equations, but most mathematical reference books focus on analytical methods with tables of solutions or computational methods with algorithms and source programs [1]. Society is becoming increasingly visual and new computational tools for visualization enable further exploration of the properties of the solutions to differential equations, such as the Schrodinger equation. For example, these computational tools have made it easy to show how orbitals arise from solutions to the Schrodinger equation for the hydrogenic atom. Visualization of the hydrogenic orbitals is critical since these solutions form the basis for understanding the structure of more complex atoms. Further, the linear combination of atomic orbitals (LCAO) method is often used to approximate molecular orbitals. This approach facilitates solution of the molecular Schrodinger equation as well as being conceptually easy to visualize. However, new computational tools enable direct comparison of the LCAO method with the exact solution for the ionized hydrogen molecule to better understand its capabilities and its limits.

Exact solutions for the molecular Schrodinger equation are only possible for the simplest molecule, the ionized hydrogen molecule, which consists of two protons and a single electron. Still, analytical solution is difficult and involves complicated power series expansions and recurrence relations [2,3]. However, the Schrodinger equation for the ionized hydrogen molecule can now be numerically solved using a personal computer and widely available software [4]. This capability makes it possible to show how molecular orbitals arise for this molecule and to explore their properties.
2. The Hydrogenic Atom

Before solving the ionized hydrogen molecule problem, let's first work through the familiar problem of the hydrogenic atom. Since they are analogous, reviewing the derivation and plotting of hydrogenic atom wavefunctions in Mathcad will prepare us for understanding the procedures used for finding and plotting the wavefunctions for the ionized hydrogen molecule. The hydrogenic atom wavefunctions will also be used as the basis functions in the LCAO method.

The Schrodinger equation for the hydrogenic atom used in the LCAO method is

$$\nabla^2 \psi + \frac{2m}{\hbar^2} \left( E + \frac{Zq^2}{4\varepsilon_0 r} \right) \psi = 0$$

(1)

where \( m \) is the mass of the electron, \( h \) is Planck's constant divided by \( 2\pi \), \( Z \) is the atomic number, \( q \) is the electronic charge, \( \varepsilon_0 \) is the permittivity of free space, and

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

(2)

in spherical coordinates.

Click here for a review of the spherical coordinate system

As shown in numerous textbooks, this equation can be separated by the trial solution

$$\Psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

(3)

The functions \( \Theta(\theta) \) and \( \Phi(\phi) \) are solutions to the separated angular equations and their products are the spherical harmonics. Solution of the \( \Phi \) equation gives rise to the quantum number \( m_l \) and solution of the \( \Theta \) equation involves the associated Legendre equation, which gives rise to a second quantum number \( l \). The integer \( l \) corresponds to the degree of the associated Legendre function while the integer \( m_l \) corresponds to its order. A third quantum number \( n \) arises from the solution of the separated radial equation \( R \), which involves the associated Laguerre equation. Its solutions are the associated Laguerre functions, and their properties require that \( 1 \leq n - 1 \).

The spherical harmonics give atomic orbitals their characteristic shapes. The effect of changing the quantum numbers on the \( \Theta \) and \( \Phi \) equations can be explored below in Section 2.1.
2.1. Spherical Harmonics

Select values for the quantum numbers \( l \) and \(|m|\). Note that \(|m|\) must be less than or equal to \( l \).

Angular momentum quantum number \( l := 1 \)

Magnetic quantum number \( m := 1 \)

The solution to the \( \Phi \) equation is given by

\[
\Phi(\phi) := e^{im\phi} \rightarrow \exp(i \cdot \phi)
\]

The normalization factor for this function is

\[
A := \frac{1}{\sqrt{2\pi}}
\]

Letting \( x = \cos \theta \), the solution to the \( \Theta \) equation (associated Legendre polynomial of the first kind) is given by

\[
\Theta(x) := \left(1 - x^2\right)^{\frac{m}{2}} \cdot \frac{d^{l+m}}{dx^{l+m}} \left[ \frac{1}{2^l l!} \cdot (x^2 - 1)^l \right] \rightarrow \left(1 - x^2\right)^{\frac{1}{2}}
\]

Note for the case in which \( l = 0, m = 0 \), MathCad cannot symbolically solve the above expression for the associated Legendre polynomial. The solution can be shown to be equal to 1. To plot the resulting spherical harmonic simply type \( \Theta(x) := 1 \) below.

Substituting \( \cos \theta \) for \( x \) gives \( \Theta \) as a function of \( \theta \)

\[
\Theta(\theta) := \Theta(\cos(\theta)) \rightarrow \left(1 - \cos(\theta)^2\right)^{\frac{1}{2}}
\]

The normalization factor for the \( \Theta \) function is

\[
B := \sqrt{\frac{2l + 1}{2} \cdot \frac{(1 - m)!}{(1 + m)!}}
\]
The spherical harmonic is given by the product of the $\Phi$ and $\Theta$ functions.

$$Y(\phi, \theta) := A \cdot B \Theta(\theta) \cdot \Phi(\phi) \rightarrow \frac{1}{8} \cdot \frac{1}{4} \cdot \frac{1}{2} \cdot \frac{1}{2} \cdot \frac{1}{2} \cdot \frac{1}{2} \cdot \frac{1}{2} \cdot \frac{1}{2} \cdot \frac{1}{2} \cdot \frac{1}{2} \cdot \frac{1}{2} \cdot \frac{1}{2} \cdot \frac{1}{2} \cdot \frac{1}{2} \cdot \frac{1}{2} \cdot \frac{1}{2} . \exp(i \cdot \phi)$$

The indices and equations needed to transform the spherical harmonics into Cartesian coordinates for plotting in Mathcad are contained in the hidden section below.

Click here for more background on transforming spherical coordinates into Cartesian coordinates.

Click on the graph to rotate the plot or change scales.

(Xs, Ys, Zs)
Problems

2.1 Show numerically using Mathcad that the $\Theta$ functions, $\Phi$ functions, and spherical harmonics are properly normalized.

2.2 For all states through $n = 3$ which spherical harmonics contain imaginary terms? Show how to convert them into purely real functions. Plot them through $n = 3$.

Open the collapsed section to see the answers.
Select values for the quantum numbers \( n \) and \( l \). Note that \( l \) must be less than or equal to \( n - 1 \).
The atomic number \( Z \) can also be varied, but the solutions are only valid for one-electron atoms.

Principal quantum number \( n := 3 \)

Angular momentum quantum number \( l := 2 \)

Atomic number \( Z := 1 \)

The solution to the R equation (Laguerre polynomial of the first kind) is given by

\[
R(\rho) := ((n + l)!)^2 \cdot \frac{-\rho}{2} \cdot \frac{1}{2} \cdot e^{-\frac{\rho}{2}} \cdot \sum_{k=0}^{n-l-1} \frac{(-1)^{k} \cdot \rho^{k}}{(2 \cdot 1 + 1 + k)! \cdot (n - 1 - k - 1)! \cdot k!} \rightarrow 120 \cdot \rho^2 \cdot \exp\left(-\frac{1}{2} \cdot \rho\right)
\]

where \( \rho \) is given by

\[
\rho(r) := \frac{2 \cdot Z \cdot r}{n}
\]

We'll express \( r \) in Bohr units (1 Bohr = 0.0529 nm) in this workbook.

The normalization factor for the R function is

\[
C := \sqrt{\frac{4 \cdot Z^3 \cdot (n - 1 - 1)! \cdot 1}{\frac{4}{n} \cdot ((n + l)!)^3 \cdot 34992000 \cdot 34992000^2}} \rightarrow \frac{1}{656100} \cdot 34992000^{\frac{1}{2}}
\]

The radial wavefunction is

\[
R_{ln}(r) := C \cdot R(\rho(r)) \rightarrow \frac{1}{656100} \cdot 34992000^{\frac{1}{2}} \cdot r^2 \cdot \exp\left(\frac{-1}{3} \cdot r\right)
\]
The radial wavefunction $R_{ln}(r)$, radial density function $R_{ln}^2(r)$, and radial distribution function $4\pi r^2 R_{nl}^2(r)$ are plotted below. Note that the scale may need to be modified depending on the selection of the quantum numbers.

The normalized hydrogenic wavefunctions are the products of the normalized real spherical harmonics and the normalized wavefunctions. These functions are summarized for the 1s, 2p, and 3d orbitals here.

Problems

2.3 Show numerically using Mathcad that the radial wavefunction is normalized.
2.4 Plot the normalized radial probability distributions through $n = 3$. What happens with increasing $n$ for constant $l$?

Open the collapsed section to see the answers.
3. The Ionized Hydrogen Molecule

In the sections below, wavefunctions for the ionized hydrogen molecule are first obtained by using the linear combination of atomic orbitals (LCAO) method and then by solving the exact Schrödinger equation using the numerical technique known as the Shooting Method. The solutions from the two different techniques are then compared. In both cases, the protons are assumed to be fixed at a distance $r_{AB}$ apart using the Born-Oppenheimer approximation \[5\] since they are much more massive than the electron.

3.1. LCAO Solution

In the LCAO view, the effects of each proton on the motion of the electron are considered separately. In other words, the electron is assumed to be completely governed by proton A when it is closer to proton A and to be completely controlled by proton B when it is closer to proton B. This results in an overlap region the area of which depends on the distance between the two protons. In a planar view, the position of the electron can be defined by its distance to the nearest proton, $r_A$ or $r_B$, and its angle, $\theta_A$ or $\theta_B$. This geometry, illustrated below, is best described in polar coordinates.

![Diagram of LCAO Solution](image)

Lines of constant $r$ are circles around the proton, while constant $\theta$ defines a line extending from the proton. Rotation about an axis creates spheres for constant $r$ and cones for constant $\theta$, which can be described in spherical coordinates, where $\phi$ is the angle of rotation.

[Click here for a review of the spherical coordinate system](#)
Linear combinations of the atomic hydrogen orbitals can be used to approximate the orbitals of the ionized hydrogen molecule. Both the sums and the differences of these atomic orbitals must be considered, which suggests the trial molecular orbitals

\[ \Psi_1 = c_1 \psi_A + c_2 \psi_B \]  
(4a)

and

\[ \Psi_2 = c_1 \psi_A - c_2 \psi_B \]  
(4b)

The coefficients can be determined from the variational principle.

To compare the molecular orbitals from the LCAO method to those of the exact method, the real hydrogenic orbitals must be converted from spherical to spheroidal coordinates. The necessary relationships between the spherical coordinates \( r, \theta, \) and \( \phi \) and the prolate spheroidal coordinates \( \xi, \eta, \phi \) are given below.

<table>
<thead>
<tr>
<th>Orbital centered on proton A</th>
<th>Orbital centered on proton B</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_A = \frac{r_{AB}}{2} (\xi + \eta) )</td>
<td>( r_B = \frac{r_{AB}}{2} (\xi - \eta) )</td>
</tr>
<tr>
<td>( \cos \theta_A = \frac{\xi \eta + 1}{\xi + \eta} )</td>
<td>( \cos \theta_B = \frac{\xi \eta - 1}{\xi - \eta} )</td>
</tr>
<tr>
<td>( \sin \theta_A = \frac{\sqrt{\xi^2 - 1} \sqrt{1 - \eta^2}}{\xi + \eta} )</td>
<td>( \sin \theta_B = \frac{\sqrt{\xi^2 - 1} \sqrt{1 - \eta^2}}{\xi - \eta} )</td>
</tr>
<tr>
<td>( \cos \phi_A = \cos \phi )</td>
<td>( \cos \phi_B = \cos \phi )</td>
</tr>
</tbody>
</table>

Click here for a review of the prolate spheroidal coordinate system.

The 1s orbitals in spherical coordinates are given by

\[ \psi_{1sa} = \sqrt{\frac{1}{\pi}} e^{-r_A} \]  
(5a)

and

\[ \psi_{1sb} = \sqrt{\frac{1}{\pi}} e^{-r_B} \]  
(5b)

for orbitals centered on protons A and B, respectively. We'll assume the protons are two Bohr apart.

\[ r_{AB} := 2 \]
Thus, substituting the expressions for $r_A$ and $r_B$ given above transforms them into the following expressions in spheroidal coordinates

$$
\psi_{1sa}(\varepsilon, \eta) := \sqrt{\frac{1}{\pi}} \cdot e^{-\frac{r_{AB}(\varepsilon+\eta)}{2}}
$$

$$
\psi_{1sb}(\varepsilon, \eta) := \sqrt{\frac{1}{\pi}} \cdot e^{-\frac{r_{AB}(\varepsilon-\eta)}{2}}
$$

To determine the coefficients with the variational principle, we need to calculate the overlap integral, which in spheroidal coordinates is given by

$$
S := \int_{-1}^{1} \int_{0}^{2\pi} \int_{0}^{\infty} \psi_{1sa}(\varepsilon, \eta) \cdot \psi_{1sb}(\varepsilon, \eta) \cdot \frac{r_{AB}^3}{8} \cdot (\varepsilon^2 - \eta^2) \, d\phi \, d\eta \, d\varepsilon
$$

The coefficients can be calculated from the following expressions.

$$
c_b := \frac{1}{\sqrt{2 \cdot (S + 1)}} \\
c_b = 0.561
$$

$$
c_a := \frac{1}{\sqrt{2 \cdot (1 - S)}} \\
c_a = 1.1
$$

The LCAO $1\sigma_g$ orbital is

$$
\Psi_{1\sigma_g}(\varepsilon, \eta) := c_b \cdot \psi_{1sa}(\varepsilon, \eta) + c_b \cdot \psi_{1sb}(\varepsilon, \eta)
$$

and the LCAO $1\sigma_u$ orbital is

$$
\Psi_{1\sigma_u}(\varepsilon, \eta) := c_a \cdot \psi_{1sa}(\varepsilon, \eta) - c_a \cdot \psi_{1sb}(\varepsilon, \eta)
$$
Here is the plot of the LCAO approximation of the $1\sigma_g$ orbital and its probability distribution.

\[(X_{1\sigma_g}, Y_{1\sigma_g}, Z_{1\sigma_g})\]

\[(X_{s1\sigma_g}, Y_{s1\sigma_g}, Z_{s1\sigma_g}), (-X_{s1\sigma_g}, Y_{s1\sigma_g}, Z_{s1\sigma_g})\]
Here is the plot of the LCAO approximation of the $1\sigma_u$ orbital and its probability distribution.

\[
(X_1\sigma_u, Y_1\sigma_u, Z_1\sigma_u)
\]

\[
(X_{s1}\sigma_u, Y_{s1}\sigma_u, Z_{s1}\sigma_u), (-X_{s1}\sigma_u, Y_{s1}\sigma_u, Z_{s1}\sigma_u)
\]
Problems

3.1. Plot the overlap integral as a function of the internuclear distance $r$ for the $1\sigma_g$ orbital. Explain the values for $r = 0$ and for very large $r$.

3.2. Plot the linear combinations (sum and difference) of two $p_0$ orbitals separated by 2 Bohr. What molecular states do they approximate?

3.3. Plot the linear combinations (sum and difference) of two $p_1$ orbitals separated by 2 Bohr. What molecular states do they approximate?

Open the collapsed section to see the answers.
3.2 Exact Solution

The more accurate approach is to consider the effects of both protons on the motion of the electron simultaneously. In a planar view, the two protons fixed at a distance \( r_{AB} \) apart form the foci of an ellipse. The position of the electron can be defined by its distance to proton A, \( r_A \), and its distance to proton B, \( r_B \). This geometry, illustrated below, is best described in confocal elliptic coordinates, in which the major axis of the ellipse extends through the foci.

Rotation about the molecular axis creates ellipsoids for constant \( \xi \) and hyperboloids of revolution for constant \( \eta \) that can be described by prolate spheroidal coordinates. In this coordinate system the position of the electron can be redefined in terms of the coordinates \(\xi, \eta, \text{ and } \phi\).

Click here for a review of the prolate spheroidal coordinate system

The molecular Schrödinger equation for the ionized hydrogen molecule is

\[
\nabla^2 \psi + \frac{2m}{\hbar^2} \left[ E + \frac{q^2}{4\pi \varepsilon_0 r_A} + \frac{q^2}{4\pi \varepsilon_0 r_B} - \frac{q^2}{4\pi \varepsilon_0 r_{AB}} \right] \psi = 0
\]

where

\[
\nabla^2 = \frac{4}{r_{AB}^2 (\xi^2 - \eta^2)^2} \left\{ \frac{\partial}{\partial \xi} \left[ (\xi^2 - 1) \frac{\partial}{\partial \xi} \right] + \frac{\partial}{\partial \eta} \left[ (1 - \eta^2) \frac{\partial}{\partial \eta} \right] + \frac{\xi^2 - \eta^2}{(\xi^2 - 1)(1 - \eta^2)} \frac{\partial^2}{\partial \phi^2} \right\}
\]

in oblate spheroidal coordinates. Note that although we will use prolate spheroidal coordinates for plotting purposes, the solutions to the Schrödinger equation for the ionized hydrogen molecule are oblate spheroidal wavefunctions.
The internuclear repulsion energy \( q^2/4 \pi \varepsilon_0 r_{AB} \) is unchanged in the final expression and can be omitted here and added later. Similarly to the case of the hydrogenic atom, separated equations can be obtained using the trial solution:

\[
\Psi(\xi, \eta, \varphi) = \Xi(\xi) \mathcal{H}(\eta) \Phi(\varphi)
\]

Substitution of this trial solution into the proceeding Schrodinger equation separates it into the following equations:

\[
- \frac{1}{\Phi} \frac{d^2 \Phi}{d \varphi^2} = m^2
\]

\[
\frac{d}{d \eta} \left[ (1-\eta^2) \frac{d \mathcal{H}}{d \eta} \right] + \left( \mu - \frac{m^2}{1-\eta^2} - \lambda^2 \eta^2 \right) \mathcal{H} = 0
\]

\[
\frac{d}{d \xi} \left[ (\xi^2 - 1) \frac{d \Xi}{d \xi} \right] + \left( \lambda^2 \xi^2 - \frac{m^2}{\xi^2 - 1} + \frac{2r_{AB} \xi}{a_0} - \mu \right) \Xi = 0
\]

where

\[
\lambda^2 = \frac{m r_{AB}^2}{2 \hbar^2} \left( E - \frac{q^2}{4 \pi \varepsilon_0 r_{AB}} \right)
\]

and \( a_0 \) is the Bohr radius.

Note that unlike the hydrogenic atom, in which the energy eigenvalues only appear in the radial equation \( R \), for the ionized hydrogen molecule, they appear in both the \( \mathcal{H} \) and \( \Xi \) equations. The energy eigenvalues depend on \( r_{AB} \). When \( r_{AB} = 0 \), the protons have coalesced into an atom with nuclear charge \( Z = 2 \). When \( r_{AB} \) goes to infinity, the protons have separated and we have a hydrogen atom and a bare proton. To find the equilibrium internuclear distance, we need to calculate the electronic energy as a function of \( r_{AB} \).
As in the case of the hydrogenic atom, the $\Phi$ equation has the solution

$$\Phi(\varphi) = Ae^{im\varphi}$$ (13)

where $m_l$ is an integer. The $H$ and $\Xi$ equations are more difficult to solve. Several approximate, but increasingly refined solutions were derived in the late 1920's and early 1930's [6]. One of the most accurate solutions was derived by E.A. Hylleraas [7] using second order perturbation theory. However, modern computational techniques have greatly increased the ease of obtaining numerical solutions. One technique for solving the $H$ and $\Xi$ equations that is well suited for numerical computation is the Shooting Method [2]. Decoupling of the equations can be done using the same procedure as that of Hylleraas. The $H$ equation is solved first to determine the relationship between the eigenvalues $\mu$ and $\lambda$. The expression for $\mu(\lambda)$ can then be substituted into the $\Xi$ equation, which is solved to determine the relationship between $E$ and $r_{AB}$. This procedure must be repeated for different energy states. This method is used to solve the separated and decoupled equations in Section 3.2.1.

The functions $H(\eta)$ and $\Phi(\phi)$ are solutions to the separated angular equations and their products are the spheroidal harmonics, which have properties similar to the spherical harmonics. They can also be defined by the quantum numbers $m_l$ and $l$, which correspond to the order and degree of the spheroidal angular functions. As for the spherical harmonics, $m_l$ is an eigenvalue of the $\Phi$ equation and takes on the values 0, 1, 2, … States with equal positive and negative values of $m_l$ have the same energy. Note that $l(l+1)$ is not an angular eigenvalue of the $H$ equation. The eigenvalue of the $H$ equation is not an integer. A third integer $n$ arises from the radial equation $\Xi$. This integer represents the order of the root of the radial equation. Unlike the Laguerre functions, $l$ is not restricted by $n$.

The spheroidal harmonics give the ionized hydrogen molecular orbitals their characteristic shapes. The effect of changing the quantum numbers on the $H$ and $\Phi$ equations can be explored below in Section 3.2.2.

Conventional nomenclature for molecular energy states is similar to that of the s, p, d, f, … notation used to describe atomic energy states. States with $m_l = 0$ are referred to as $\sigma$ states, those with $m_l = +/-1$ as $\pi$ states, and those with $m_l = +/-2$ as $\delta$ states [8]. Additionally, as with the atomic wavefunctions, some angular wavefunctions are zero. The phase (or sign) changes that occur as the total angular wavefunction $H(\eta)\Phi(\phi)$ passes through an angular node determine the symmetry of the state. The wavefunction $\Phi(\phi)$ is even if $m_l$ is even and odd if $m_l$ is odd. Even (gerade) wavefunctions do not change sign and are symmetric. They are denoted by the subscript $g$. Odd (ungerade) wavefunctions do change sign and are antisymmetric. They are denoted by the subscript $u$.

Different nomenclature is sometimes used to describe molecular energy states determined from the LCAO approach [9]. The Greek letter designations and subscripts remain the same, but they are preceded by the designation for the energy state of the ionized helium atom that results from union of the protons at $r_{AB} = 0$. This nomenclature is often referred to as the united atom designation, while the conventional nomenclature is referred to as the separated atom designation.

The two nomenclatures are correlated here. A neutral hydrogen atom results if the two protons are separated by $r_{AB} = 8$ and its energy level is included in Table II in comparison to the ionized helium atom.
The linear combinations of atomic orbitals that approximate the molecular orbital states are also given. Combinations of s orbitals, which are symmetric about the z-axis, produce \( \sigma \) molecular orbitals. Since \( m_l = 0 \) is even for s orbitals, they have positive phase for all \( \theta \) and \( \phi \), their sum is symmetric (gerade) and their difference is antisymmetric (ungerade).

The p orbitals are more complicated since they have both positive and negative phases. The sums of two \( p_x \) orbitals and two \( p_y \) orbitals constructively interfere, while their differences destructively interfere. However, since \( m_l = 1 \), they produce \( \pi \) orbitals, which are not symmetric about the z-axis. Since \( m_l \) is odd, their sum represents the ungerade state and their difference represents the gerade state. Combinations of two \( p_z \) orbitals are symmetric about the z-axis since \( m_l = 0 \) so they produce \( \sigma \) molecular orbitals. However, their sums destructively interfere, while their differences constructively interfere. Thus, their sum represents the ungerade state and their difference represents the gerade state.
3.2.1. The Shooting Method

We can use the Shooting Method [21] to solve the H equation to determine the relationship between $\lambda^2$ (defined as the variable $\lambda^2$ in the workbook) and $\mu$. The shooting method involves selecting values for $\lambda^2$ and $m$ and guessing a value for $\mu$ that gives the required value at a specified boundary point. If the H function has an even number of roots between 1 and -1, the function will be symmetric, otherwise it will be anti-symmetric. Both cases must be considered.

3.2.1.1. Symmetric Case

First let's work through the symmetric case. We'll start with the following values of $\lambda^2$ and $m$.

$$\lambda^2 := -24$$

$$m := 0$$

One $\mu$ value that solves the H equation is -2.191. Another is -15.318. The different $\mu$ values correspond to different energy states. If we were doing this for the first time, we would have to make iterative guesses. Care is needed to correlate the $\mu$ eigenvalues with the molecular states for which we wish to solve. Tables of the $\mu$ eigenvalues for the spheroidal harmonics such as those given by Abramowitz and Stegun [3] can be referenced for guidance. For demonstration of the solution with Mathcad, we'll use -2.191 for the value of $\mu$, which corresponds to the $3\sigma_g$ state.

$$\mu := -2.191$$

We'll consider 100 points between -1 and 0 and use symmetry to determine the function from 0 to 1, thus

$$\text{step} := 0.01$$

$$n := \frac{1 - \text{step}}{\text{step}}$$

The solution to the H equation can be found numerically using Mathcad's built-in "rkfixed" routine, but we need some boundary conditions. The $\text{H}(\eta)$ equation can be defined in terms of a new function $f(\eta)$, which is well behaved over the whole range of $\eta$ and is a solution of the following equation [4].

$$(1-\eta^2) f'' - 2(m+1)\eta f' - \left[m(m+1) - \mu + \lambda^2 \eta^2\right] f = 0$$

(14)

The limiting form of this equation when $\eta = +/-1$ gives us $f'(-1)$, which is the slope of the function at -1.

$$\text{slope} := \frac{m \cdot (m + 1) + \lambda^2 - \mu}{2 \cdot (m + 1)}$$
The boundary values $y_0$ and $y_1$ can then be defined by:

$$y := \begin{pmatrix} 1 + \text{step} \cdot \text{slope} \\ \text{slope} \end{pmatrix}$$

From these boundary values we can numerically solve the second order differential equation for $f$

$$f(x, y) := \begin{bmatrix} y_1 \\ 2x \cdot (m + 1) \cdot y_1 + \left[ m \cdot (m + 1) - \mu + \lambda 2 \cdot x^2 \right] \cdot y_0 \cdot \frac{1}{1 - x^2} \end{bmatrix}$$

$$y := \text{rkfixed}(y, -1 + \text{step}, 0, n, f)$$

Now we can convert this vector solution into a function via linear interpretation and use symmetry to obtain the solution for $0 < \eta < 1$

$$Y(n) := \begin{cases} \text{linterp}(y^{(0)}, y^{(1)}, n) & \text{if } n \leq 0 \\ \text{linterp}(y^{(0)}, y^{(1)}, -n) & \text{if } n > 0 \end{cases}$$

This numerical solution can then be used to calculate the solution to the H equation.

$$H(\eta) := \left( 1 - \eta^2 \right)^{\frac{m}{2}} \cdot Y(\eta)$$
The solution to the $H$ equation is plotted below.

![Graph showing $H(\eta)$ against $\eta$]

To confirm that $\mu$ is a solution, calculate $H'(\eta \to 0)$.

\[
\eta_0 := -0.001
\]
\[
H(\eta_0) = -0.458
\]
\[
\frac{d}{d\eta_0}H(\eta_0) = -6.157 \times 10^{-5}
\]

If $H'(\eta \to 0) = 0$ then $\mu$ is a solution. If not, then guess another value for $\mu$. (Note: this process would seem to be amenable to an automated routine; however, the rkfixed command cannot handle vectors and cannot be used within a program. If anyone knows a way around this in Mathcad please let the author know.)

An example showing the solution converging to $\mu = -0.35$ for $\lambda^2 = -1$ is shown below. This $\mu$ value corresponds to the $1\sigma_g$ state.
Tables of the relationships between $\lambda^2$ and $\mu$ can be put together for different states. These values are summarized for the $1\sigma_g$ state in the following table:

<table>
<thead>
<tr>
<th>$\lambda^2$</th>
<th>$\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>-1</td>
<td>-0.35</td>
</tr>
<tr>
<td>-1.5</td>
<td>-0.537</td>
</tr>
<tr>
<td>-2</td>
<td>-0.733</td>
</tr>
<tr>
<td>-2.5</td>
<td>-0.936</td>
</tr>
<tr>
<td>-3</td>
<td>-1.149</td>
</tr>
<tr>
<td>-4</td>
<td>-1.6</td>
</tr>
<tr>
<td>-6</td>
<td>-2.607</td>
</tr>
<tr>
<td>-8</td>
<td>-3.743</td>
</tr>
<tr>
<td>-12</td>
<td>-6.318</td>
</tr>
<tr>
<td>-18</td>
<td>-10.661</td>
</tr>
<tr>
<td>-24</td>
<td>-15.318</td>
</tr>
<tr>
<td>-36</td>
<td>-25.116</td>
</tr>
</tbody>
</table>
We can use Mathcad to find a polynomial expression to describe the relationship between $\lambda^2$ and $\mu$. We'll use the built-in "regress" function to find the coefficients for a fourth order polynomial.

$$z := \text{regress}\left(\text{data}\left(\begin{array}{l}0\end{array}\right), \text{data}\left(\begin{array}{l}1\end{array}\right), 4\right)$$

$$z = \begin{bmatrix} 3 \\ 3 \\ 4 \\ -0.014 \\ 0.311 \\ -0.023 \\ -5.184 \times 10^{-4} \\ -4.629 \times 10^{-6} \end{bmatrix}$$

Thus, a fourth order polynomial relationship between $\mu$ and $\lambda^2$ is given by

$$\mu(\lambda^2) := z_0 + z_4 \cdot \lambda^2 + z_5 \cdot \lambda^2^2 + z_6 \cdot \lambda^2^3 + z_7 \cdot \lambda^2^4$$

Let's plot this polynomial in comparison to that determined by Hylleraas [7],

$$\mu(\Lambda^2) := \frac{1}{3} \cdot \Lambda^2 + \frac{2}{135} \cdot \Lambda^2^2 + \frac{4}{8505} \cdot \Lambda^2^3 - 0.000013 \cdot \Lambda^2^4 - 0.0000028 \cdot \Lambda^2^5$$

and to that determined by Grivet [4],

$$L(c^2) := 0.3127477 \cdot c^2 - 0.0231669 \cdot c^2^2 - 0.0005110 \cdot c^2^3 - 0.0000045 \cdot c^2^4$$
3.2.1.2. Anti-Symmetric Case

The anti-symmetric case can be solved very similarly. The differences are that the slope at $f'(-1)$ is negative and so is the boundary value $y_0$. Values for $\mu$ are guessed until $H(\eta \to 0) = 0$. An example showing the solution converging to $\mu = 1.393$ for $\lambda^2 = -1$ is shown below.
As with the symmetric case, tables of the relationships between $\lambda^2$ and $\mu$ can be put together for different states. These values are summarized for the $1\sigma_u$ state in the following table:

<table>
<thead>
<tr>
<th>$\lambda^2$</th>
<th>$\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>-1</td>
<td>1.393</td>
</tr>
<tr>
<td>-1.5</td>
<td>1.085</td>
</tr>
<tr>
<td>-2</td>
<td>0.774</td>
</tr>
<tr>
<td>-2.5</td>
<td>0.459</td>
</tr>
<tr>
<td>-3</td>
<td>0.14</td>
</tr>
<tr>
<td>-4</td>
<td>-0.505</td>
</tr>
<tr>
<td>-6</td>
<td>-1.831</td>
</tr>
<tr>
<td>-8</td>
<td>-3.2</td>
</tr>
<tr>
<td>-12</td>
<td>-6.051</td>
</tr>
<tr>
<td>-18</td>
<td>-10.572</td>
</tr>
<tr>
<td>-24</td>
<td>-15.284</td>
</tr>
<tr>
<td>-36</td>
<td>-25.11</td>
</tr>
</tbody>
</table>

We can then find a fourth order polynomial to describe the relationship between $\lambda^2$ and $\mu$ as we did before.

\[
z := \text{regress}\left(\text{data}\langle 0 \rangle, \text{data}\langle 1 \rangle, 4\right)
\]

\[
z = \begin{pmatrix} 3 \\ 3 \\ 4 \\ 1.999 \\ 0.598 \\ -7.249 \times 10^{-3} \\ -1.078 \times 10^{-4} \\ -7.144 \times 10^{-7} \end{pmatrix}
\]

Thus, a fourth order polynomial relationship between $\mu$ and $\lambda^2$ is given by

\[
\mu(\lambda^2) := 1.9988 + 0.5984 \cdot \lambda^2 - 7.2486 \cdot 10^{-3} \cdot \lambda^2^2 - 1.0778 \cdot 10^{-4} \cdot \lambda^2^2^2 - 7.144 \cdot 10^{-7} \cdot \lambda^2^2^3
\]
Let's plot this polynomial in comparison to that determined by Grivet [4].

\[ L(c_2) := 2 + 0.6043499 \cdot c_2 - 0.0061888 \cdot c_2^2 + 0.0000589 \cdot c_2^3 \]

Problems

3.4. How do the Mathcad polynomials compare to those from the literature?

3.5. Construct tables of \( \lambda^2 \) and \( \mu \) values for the \( 1\pi_u, 1\pi_g, 3\sigma_g, \) and \( 3\sigma_u \) states. Find polynomial expressions to describe the relationships between them.

Open the collapsed section to see the answers.
3.2.2. Spheroidal Harmonics

Select values for the degree \( l \) up to 3 and for the order \( m \). Note that \( |m| \) must be less than or equal to \( l \). Only the \( m = 0 \) case is plotted when \( l = 3 \) is this workbook.

\[
\begin{align*}
\text{Degree} & : l := 2 \\
\text{Order} & : m := 0
\end{align*}
\]

Since \( r_{AB} \), \( E \), \( \lambda^2 \), and \( \mu \) are all interdependent, we need to make some assumptions and use some of the relationships between these variables before plotting the spheroidal harmonics. For starters, we'll assume that the two protons are separated by two Bohr, thus

\[
r_{AB} := 2.0
\]

Further, we'll assume that the energy is

\[
E := -2.196
\]

which we'll show later is approximately the minimum energy for the \( l = 0 \), \( m = 0 \) case (\( 1\sigma_g \) state).

Since the \( q^2/r_{ab} \) term in equation 7 that arises from the repulsive charge between the nuclei can be ignored for now and added back later, \( \lambda^2 \) can be shown to be equal to

\[
\lambda^2 := \frac{r_{AB}^2 \cdot E}{4}
\]

where \( r_{AB} \) is in Bohr and \( E \) is in Rydbergs (1 Rydberg = 13.6 eV).

Finally, we need the values of \( \mu \) for \( \lambda^2 = 2.196 \) for each set of \( l \) and \( m \) values. They can be determined from the Shooting Method as described above. We'll summarize the results in the following matrix where the row corresponds to \( l \) and the column corresponds to \( m \).

\[
\begin{pmatrix}
-0.793 & 0 & 0 \\
0.6509 & 1.55 & 0 \\
4.9037 & 5.033 & 5.65 \\
10.8926 & 0 & 0
\end{pmatrix}
\]
The solution to the \( \Phi \) equation is the same as that for the hydrogenic atom and is given by

\[
\Phi(\phi) := e^{i\cdot m \cdot \phi} \rightarrow 1
\]

To find the solution to the \( H \) equation we define boundary conditions and use Mathcad's built-in "rkfixed" routine as described in **Section 3.2.1**.

\[
slope := (-1)^{1-m} \cdot \frac{m \cdot (m + 1) + \lambda \cdot 2 - \mu_1 \cdot m}{2 \cdot (m + 1)}
\]

\[
y := \begin{pmatrix} (-1)^{1-m} + \text{step} \cdot \text{slope} \\ \text{slope} \end{pmatrix}
\]

\[
f(x,y) := \begin{pmatrix} y_1 \\ 2x \cdot (m + 1) \cdot y_1 + \left[ m \cdot (m + 1) - \mu_1 \cdot m + \lambda \cdot 2 \cdot x^2 \right] \cdot y_0 \end{pmatrix} \cdot \frac{1}{1 - x^2}
\]

\[
y := \text{rkfixed}(y,-1 + \text{step},0,n,f)
\]

\[
Y(n) := \begin{cases} \text{linterp}(y^{\langle 0 \rangle},y^{\langle 1 \rangle},n) & \text{if } n \leq 0 \\ \text{linterp}[y^{\langle 0 \rangle},(-1)^{1-m} \cdot y^{\langle 1 \rangle},-n] & \text{if } n > 0 \end{cases}
\]

\[
H(\eta) := \left( 1 - \eta^2 \right)^{\frac{m}{2}} \cdot Y(\eta)
\]

The spheroidal harmonic is given by the product of the \( H \) and \( \Phi \) functions. (Note for now we will only concern ourselves with the shape of the spheroidal harmonic and not its normalization. Later we'll normalize the probability distribution for the ionized hydrogen molecule.)

\[
Z_{\text{Im}}(\eta,\phi) := H(\eta) \cdot \Phi(\phi)
\]
Plot the spheroidal harmonic. Click on the graph to rotate the plot or change scales.

Problems

3.6. Show how to convert the spheroidal harmonics into purely real functions. Plot them through $l = 2$ as well as the case of $l = 3, m = 0$.

3.7. How do the spheroidal harmonics compare to the LCAO orbitals? How could the accuracy of the LCAO orbitals be improved?

Open the collapsed section to see the answers.
The solution to the R equation can be found using the following procedure, which is the same as for the H equation. Let’s first look at the case of $r_{AB} = 2.0$ Bohr, $E = -2.202924$ Rydbergs and plot the radial wavefunction for the bonding ground state ($1\sigma_g$).

Thus,

$$r_{AB} := 2.0$$

$$E := -2.202924$$

For the ground state

$$1 := 0 \quad m := 0$$

Using the relationships between $E$, $\lambda^2$, and $\mu$ discussed in Section 3.2.1 and Section 3.2.2.

$$\lambda^2 := \frac{r_{AB} \cdot E}{4}$$

$$\mu := -0.807134$$

As with the H equation, the solution to the R equation can be found numerically using Mathcad's built-in "rkfixed" routine, but again we need some boundary conditions. The $R(\xi)$ equation can be defined in terms of a new function $g(\xi)$, which is well behaved over the whole range of $\xi$ and is a solution of the following equation [4].

$$(\xi^2 - 1)g'' + 2(m + 1)\xi g' + \left[2r_{AB}\xi + \lambda^2 \xi^2 + m(m + 1) - \mu\right]g = 0$$

(15)

The limiting form of this equation when $\xi = +/-1$ gives us $g(-1)$, which is the slope of the function at -1.

$$\text{slope} := \frac{-\left(2 \cdot r_{AB} + \lambda^2 + m \cdot (m + 1) - \mu\right)}{2 \cdot (m + 1)}$$

The boundary values $z_0$ and $z_1$ can then be defined by:

$$z := \left(\frac{1 + \text{step} \cdot \text{slope}}{\text{slope}}\right)$$

From these boundary values we can numerically solve the second order differential equation for $g$. 

3.2.3 Radial Wavefunctions

The solution to the R equation can be found using the following procedure, which is the same as for the H equation. Let's first look at the case of $r_{AB} = 2.0$ Bohr, $E = -2.202924$ Rydbergs and plot the radial wavefunction for the bonding ground state ($1\sigma_g$).
\[ g(x, z) := \begin{bmatrix} z_1 \\ -2 \cdot (m + 1) \cdot x \cdot z_1 - \left[ 2 \cdot r_{AB} \cdot x + \lambda \cdot x^2 + m \cdot (m + 1) - \mu \right] \cdot z_0 \cdot \frac{1}{x^2 - 1} \end{bmatrix} \]

\[ z := \text{rkfixed}(z, 1 + \text{step}, 12, n, g) \]

Now we can convert this vector solution into a function via linear interpretation and use symmetry to obtain the solution for \( \xi < -1 \)

\[ Z(n) := \begin{cases} \text{linterp}(z^{(0)}, z^{(1)}, n) & \text{if } n \geq 1 \\ \text{linterp}(z^{(0)}, z^{(1)}, -n) & \text{if } n \leq -1 \end{cases} \]

This numerical solution can then be used to calculate the solution to the \( H \) equation.

\[ R(\xi) := \left( \frac{m}{\xi^2 - 1} \right)^{\frac{1}{2}} \cdot Z(\xi) \]

The solution to the \( R \) equation is plotted below.
Problems

3.8. For $E = -2.202924$ and $\mu = -0.807134$, the R equation goes to 0 for $\xi = -10$ and $\xi = 10$.
Plot the solution to the R equation for the following values of $E$: -2.0, -2.15, -2.19, -2.21, -2.25, and -2.4 Rydbergs. What happens to R at $\xi = 10$ for these cases?

Open the collapsed section to see the answers.
3.2.4 Electronic Charge Densities

From the products of the spheroidal harmonics and the radial wavefunctions we can plot electronic charge densities for different states. But, before plotting them, let’s first look at the case of \( r_{AB} = 2.0 \) Bohr, \( E = -2.202924 \) Rydbergs and plot the wavefunction along the molecular axis for the bonding ground state \((1\sigma_g)\). We already have the radial wavefunction from the preceding section. Now we need to find the angular wavefunctions.

Thus,

\[
r_{AB} := 2.0
\]

\[
E := -2.202924
\]

For the ground state

\[
l := 0 \quad m := 0
\]

Using the relationships between \( E, \lambda^2 \), and \( \mu \) discussed in Section 3.2.1 and Section 3.2.2.

\[
\lambda^2 := \frac{r_{AB}^2 \cdot E}{4} \quad \mu := -0.807134
\]

The solution to the \( \Phi \) equation is

\[
\Phi(\phi) := e^{{i m \phi}} \rightarrow 1
\]

where the normalization coefficient is

\[
A := \frac{1}{\sqrt{2\pi}}
\]

The solution to the \( H \) equation can be solved using the following procedure described in Section 3.2.1.1.

\[
slope := \frac{m \cdot (m + 1) + \lambda^2 - \mu}{2 \cdot (m + 1)} \quad y := \left( 1 + \text{step} \cdot \text{slope} \right) \cdot \left( \frac{1}{\text{slope}} \right)
\]

\[
f(x, y) := \left[ y_1 \right]
\]

\[
\begin{aligned}
&\left[ 2x \cdot (m + 1) \cdot y_1 + \left[ m \cdot (m + 1) - \mu + \lambda^2 \cdot x^2 \right] \cdot y_0 \right] \cdot \frac{1}{1 - x^2}
\end{aligned}
\]
\[ y := \text{rkfixed}(y, -1 + \text{step}, 0, n, f) \]

\[
Y(n) := \begin{cases} 
\text{interp}(y^{(0)}, y^{(1)}, n) & \text{if } n \leq 0 \\
\text{interp}(y^{(0)}, y^{(1)}, -n) & \text{if } n > 0 
\end{cases}
\]

\[
H(\eta) := \left(1 - \eta^2\right)^{\frac{m}{2}} \cdot Y(\eta)
\]

Now we can find the normalization coefficient to the product of the solutions to the R and H equations

\[
B := \frac{1}{\int_{-1}^{1} \int_{-1}^{10} \left( |R(\xi) \cdot H(\eta)| \right)^2 \cdot \frac{r_{AB}^3}{8} \cdot \left(\xi^2 - \eta^2\right) d\xi d\eta}
\]

\[
B = 1.145
\]

The solution to the H equation is plotted below
Now let's plot both the H and R equations along the z axis (the molecular axis) to get the wavefunction $\psi$ for the bonding ground state ($1\sigma_g$).

Electronic charge densities $|\psi|^2$ can be constructed from the complete wavefunctions, which are products of the $\Phi(\phi)$, $H(\eta)$, and $\Xi(\xi)$ functions for the exact solution. Let's plot the electronic charge density for the bonding ground state ($1\sigma_g$) for a plane through the molecular axis.

$(X_s, Y_s, Z_s), (-X_s, Y_s, Z_s)$
Problems

3.9. Explain why the electronic charge density of the $1\sigma_g$ state results in the formation of a stable molecule. Graphically compare the wavefunction along the molecular axis for the exact solution with that for the LCAO method.

Open the collapsed section to see the answers.
Now let's plot the electronic charge density for the first anti-bonding ground state ($1\sigma_u$) for a plane through the molecular axis for $r_{AB} = 2.0$ Bohr and $E = -1.334950$ Rydbergs. Thus,

$$r_{AB} := 2.0$$

$$E := -1.334950$$

For the first excited state

$$l := 0 \quad m := 0$$

Using the relationships between $E$, $\lambda^2$, and $\mu$ discussed in Section 3.2.1 and Section 3.2.2.

$$\lambda^2 := \frac{r_{AB}^2 \cdot E}{4} \quad \mu := 1.1873$$

Again, the solution to the $\Phi$ equation is

$$\Phi(\phi) := e^{im\phi} \rightarrow 1$$

where the normalization coefficient is

$$A := \frac{1}{\sqrt{2\pi}}$$

The solution to the $H$ equation can be solved using the following procedure described in Section 3.2.1.2.

$$\text{slope} := \frac{-m \cdot (m + 1) + \lambda^2 - \mu}{2 \cdot (m + 1)}$$

$$y := \left( -1 + \text{step} \cdot \text{slope} \right) / \text{slope}$$

$$f(x, y) := \left[ \frac{y_1}{2x \cdot (m + 1) \cdot y_1 + \left[ m \cdot (m + 1) - \mu + \lambda^2 \cdot x^2 \right] \cdot y_0} \cdot \frac{1}{1 - x^2} \right]$$

$$y := \text{rkfixed}(y, -1 + \text{step}, 0, n, f)$$
Y(n) := linterp\left(y^{(0)}, y^{(1)}, n\right) \text{ if } n < 0
\begin{align*}
\text{linterp}\left[y^{(0)}, (-y)^{(1)}, -n\right] & \text{ if } n > 0
\end{align*}

H(\eta) := \left(1 - \eta^2\right)^{\frac{m}{2}} \cdot Y(\eta)

The solution to the H equation is plotted below.

The solution to the R equation can be solved using the procedure described in Section 3.2.3.

\[
slope := \frac{-\mu + m \cdot (m + 1) + 2 \cdot r_{AB} + \lambda \cdot 2}{2 \cdot (m + 1)}
\]

\[
z := \left(1 + \text{step} \cdot \text{slope}\right)
\]

\[
g(x, z) := \begin{bmatrix} z_1 \\
-2 \cdot (m + 1) \cdot x \cdot z_1 - \left[2 \cdot r_{AB} \cdot x + \frac{m \cdot (m + 1) - \mu + \lambda \cdot 2 \cdot x^2}{2} \cdot z_0\right] \cdot \frac{1}{x^2 - 1}\end{bmatrix}
\]

\[
z := \text{rkfixed}(z, 1 + \text{step}, 12, n, g)
\]

Z(n) := linterp\left(z^{(0)}, z^{(1)}, n\right) \text{ if } n \geq 1
\begin{align*}
\text{linterp}\left(z^{(0)}, z^{(1)}, -n\right) & \text{ if } n \leq -1
\end{align*}
The normalization coefficient is

\[
B := \frac{1}{\int_{-1}^{1} \int_{1}^{10} (|R(\xi)\cdot H(\eta)|)^2 \cdot \frac{r_{AB}^3}{8} \cdot (\xi^2 - \eta^2) \, d\xi \, d\eta}
\]

\[B = 1.136\]

The solution to the R equation is plotted below
Now let's plot both the H and R equations along the z axis (the molecular axis) to get the wavefunction $\psi$ for the first anti-bonding state ($1\sigma_u$).

Let's plot the electronic charge density for the first anti-bonding state ($1\sigma_u$) for a plane through the molecular axis.

$$(X_s, Y_s, Z_s), (-X_s, Y_s, Z_s)$$
Problems

3.10. Explain why the electronic charge density of the $1\sigma_u$ state does not result in the formation of a stable molecule. Graphically compare the wavefunction along the molecular axis for the exact solution with that for the LCAO method.

3.11. Plot the electronic charge densities from the LCAO method for the $3\sigma_g$, $3\sigma_u$, $1\pi_g$, and $1\pi_u$ states. What can be inferred about the bonding of these states from the electronic charge densities?

Open the collapsed section to see the answers.
4. Electronic and Molecular Energies

The exact solution can be used to calculate accurate values of the electronic and molecular energies as a function of the internuclear distance. The electronic energy $E$ is calculated by solving the $H(\eta)$ equation to determine the relationship between its eigenvalue and the eigenvalue for the $\Xi(\xi)$ equation. This expression is then substituted into the $\Xi(\xi)$ equation, which is solved to determine the relationship between $E$ and $r_{AB}$. This procedure must be repeated for different energy states. An example is given below for the $1\sigma_g$ state.

To determine the relationship between $E$ and $r_{AB}$ we can again use the Shooting Method with the $\Xi(\xi)$ equation like we did for the $H(\eta)$ equation in Section 3.2.1. We select a value for $r_{AB}$ and guess a value for $E$.

$$r_{AB} := 2.0 \quad m := 0 \quad E := -2.202924$$

$$\text{step} := 0.01 \quad n := \frac{1 - \text{step}}{\text{step}}$$

$$\lambda^2 := \frac{r_{AB}^2}{4} \cdot \frac{E}{4}$$

We'll use the fourth order polynomial relationship between $\mu$ and $\lambda^2$ determined in Section 3.2.1 for the $1\sigma_g$ and $2\sigma_g$ states: $l = 0, m = 0$

$$\mu := -0.0139 + 0.311 \cdot \lambda^2 - 0.0234 \cdot \lambda^2^2 - 5.1838 \cdot 10^{-4} \cdot \lambda^2^3 - 4.6286 \cdot 10^{-6} \cdot \lambda^2^4$$

The solution to the $R$ equation can be solved using the procedure described in Section 3.2.3.

$$\text{slope1} := \left[-\mu + m \cdot (m + 1) + 2 \cdot r_{AB} + \lambda^2 \right] \left[2 \cdot (m + 1) \right]$$

$$z1 := \left(1 + \text{step} \cdot \text{slope1}\right) \left[1 \bigg/ \lambda^2 \right]$$

$$g1(x,z1) := \left[\left[-2 \cdot (m + 1) \cdot x \cdot z1 - \left[2 \cdot r_{AB} \cdot x + m \cdot (m + 1) - \mu + \lambda^2 \cdot x^2 \right] \cdot z1_0 \right] \bigg/ \lambda^2 \right]$$

$$z1 := \text{rkfixed}(z1, 1 + \text{step}, 12, n, g1)$$
\[ Z1(n) := \begin{cases} \text{linterp}(z1^{\langle 0 \rangle}, z1^{\langle 1 \rangle}, n) & \text{if } n \geq 1 \\ \text{linterp}(z1^{\langle 0 \rangle}, z1^{\langle 1 \rangle}, -n) & \text{if } n \leq -1 \end{cases} \]

\[ R(\xi) := \left(\frac{m}{2}\right)^2 Z1(\xi) \]

\[ \xi := -10, -9.9, \ldots, 10 \]

The solution to the \( R \) equation is plotted below:

![Graph of R(\xi) vs \( \xi \)]

\( E \) is a solution if \( R(\xi = 10) \) goes to 0. If not, then guess another value for \( E \).

\[ R(10) = 4.981 \times 10^{-4} \]

Tables of the relationships between \( E \) and \( r_{AB} \) can be put together for different states. Below is a summary of \( E \) and \( r_{AB} \) values for the \( 1\sigma_g \) state: \( l = 0, m = 0 \).
The inter-nuclear repulsion energy is given by

\[ E_{m1s} := \frac{2}{r_{ab}} \]

The electronic energy \( E_e \) and the inter-nuclear repulsion energy \( E_m \) as functions of internuclear distance are plotted below.
The total molecular energy is given by

$$E_{1\sigma g} := E_{e 1s} + E_{m 1s}$$

which is plotted below.
Problems

4.1. What internuclear distance minimizes the total molecular energy? What happens if the nuclei come closer together? What happens if the nuclei move further away? What value does the total molecular energy approach as \( r_{AB} \) gets very large? How does the minimum energy for the ionized hydrogen molecule compare with that of a neutral hydrogen atom? What does this say about the stability of the ionized hydrogen molecule?

4.2. Plot the relationships between electronic energy and the total molecular energy as functions of internuclear distance for the \( 1\sigma_u, 2\sigma_g, 2\sigma_u, 1\pi_u, 1\pi_g, 3\sigma_g, \) and \( 3\sigma_u \) states. What can be inferred from these plots about the bonding nature of these states?

Open the collapsed section to see the answers.
5. Conclusions

By using Mathcad, the wavefunctions of the ionized hydrogen molecule can be graphically shown for both the exact solution and the LCAO method. The properties of the spheroidal harmonics arising from the exact solution have similar properties to the spherical harmonics used in the LCAO method. A comparison of the resulting orbital shapes shows the limitations of the LCAO method and helps to clarify molecular orbital nomenclature as well as the importance of orbital symmetry in understanding chemical bonding. An improved understanding of these concepts for the simple case of the ionized hydrogen molecule provides a good foundation for understanding chemical bonding of more complex molecules.

6. References
