5-2008

Molecular Hydrogen: A theoretical investigation into the one electron densities of the first three 1Σ+g states

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Molecular Hydrogen: A theoretical investigation into the one electron densities of the first three $^1\Sigma^+_g$ states

A thesis submitted in partial fulfillment of the requirement for the degree of Bachelor of Science in Chemistry from the College of William and Mary,

by

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Accepted for:

(Honors, High Honors, Highest Honors)

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May 2007
B.1.1 Evaluation of G .................................................. 26
B.1.2 Evaluation of F .................................................. 27

C Contour Values ...................................................... 28

List of Tables

1 R values for the minima and transition maxima ...................... 7
2 (2,1,0,0|2) Basis Set ............................................. 9
3 Basis set and corresponding energies (hartrees) ...................... 15

List of Figures

1 Elliptical Cylindrical Coordinate Diagram .......................... 6
2 Energy vs Internuclear distance (R) for the first three $^{1}\Sigma_{g}^{+}$ states of H$_{2}$. (The ground state has been shifted up by 0.26 a.u. in (a).) ............ 15
3 Ground state one electron densities at given R values. Density values can be found in Appendix C. ........................................ 29
4 EF state one electron densities at given R values. Density values can be found in Appendix C. ........................................ 30
5 GK state one electron densities at given R values. Density values can be found in Appendix C. ........................................ 31
6 GK state selected one electron density plots ............................ 32
7 X coordinate vs R for new critical points in the GK state. The saddle at X=0 is the saddle between the nuclei. ................................. 33
8 Z coordinate vs R for new critical points and the three expected (two maxima and a saddle) in the GK state ................................. 34
9 Axial density plots where $\psi$ is the density and q is a generalized coordinate. .................................................. 35
Abstract

One electron densities are a convenient way to study the behavior of a single electron in a multi-electron compound. The critical points within those densities can be investigated in order to deduce information about bonding and the character of a given electronic state. The system under investigation here is molecular hydrogen (H$_2$). The one electron densities and subsequent critical points will be studied for the first three $^1\Sigma_g^+$ electronic states. The results of those calculations will be presented and discussed. These results should give insight into how the orbital character of each electronic state might change over a given range of internuclear distances.
1 Introduction

Molecular hydrogen has been the subject of theoretical studies by many research groups since the advent of quantum mechanics in the early twentieth century. While this is one of the simplest molecules, only containing two protons and two electrons, there are many complexities that arise. One such complexity is the double minimum total energy curve of some excited states. Heitler and London conducted one of the earliest studies on \( \text{H}_2 \).\(^1\) Their work, along with others,\(^2\) are considered the beginning of valence bond theory. Valence bond theory is defined by the localized sharing of an electron pair between two atoms. This early theory was the basis for the more modern molecular orbital (MO) approach to bonding, one big difference in the theories being that MO theory does not require the localization of electrons.

Experimental work on molecular hydrogen has been conducted for much longer than the theoretical. In 1766, Henry Cavendish conducted experiments with acids and metals. One product of these reactions was hydrogen gas and Cavendish is therefore generally given credit for its discovery.\(^3\) More recently, however, experiments have probed the ground state extensively yielding a very extensive rovibrational spectrum, as well as dissociation energy values and other important molecular parameters obtained from different spectroscopic techniques. Gilligan et al report the transition EF→X to be 99,164.782(3) cm\(^{-1}\) (0.4520744 hartrees).\(^4\) The value of this transition according to our calculations from the ground state minimum of \( R = 1.4 \) a.u. to the EF state at the same R value is 0.481807 hartrees, which is roughly 0.03 hartrees off of the experimental value. The calculations in this study also do not take into account for the zero-point vibrations which could reduce the energy further. The equilibrium bond dissociation energy is another piece of data on which experiment and theory coincide quite well. This energy is found by subtracting the energy of the equilibrium bond length in a given electronic state and the energy of the dissociation limit of the same excited state. For the ground state, the equilibrium bond length is 1.4 a.u. and the dissociation energy limit is -1.0 hartrees. Levine cites\(^5\) the equilibrium dissociation energy, \( D_e \), of the ground state to be 4.75 eV (0.175 hartrees), and the calculations
presented here found this energy to be 4.71 eV (0.173 hartrees), a difference of only 0.04 eV (0.002 hartrees). This corroboration lends validation to the data being calculated in this study. Clearly these two examples are just a few among many showing just how well experiment and theory coincide regarding this system.

The goal of this project is to study the behavior of one electron densities in the ground state and first two excited $1\Sigma_g^+$ states called the EF and GK states respectively. The approach of James and Coolidge$^6$ will be used to determine the basis sets, wavefunctions, and energies. After calculation of the densities, the critical points will then be studied. Three critical points should be easily identified in the system: a maximum at each nucleus and a saddle between the nuclei. If new critical points should arise, this will give some insight into how bonding might change between the nuclei as the internuclear distance increases in a given electronic state and comparisons between different electronic states.

In the following sections the calculation methods will be discussed. This will cover the coordinate change, resultant Schrödinger Equation, and how the basis set was selected. The methods section will also discuss evaluation of the one electron densities and the critical points within those densities. After all of the methods have been explained, the results will be presented. Discussion of those results will then follow. Cartesian coordinates are cumbersome for many body problems and so first the coordinate transformation will be explained.

## 2 Calculation Methods

### 2.1 Coordinates

In this study the Born-Oppenheimer approximation$^7$ will be employed. The B-O approximation states that the nuclei are heavy in comparison to the electrons. Therefore the motion of the nuclei with respect to the electrons is slow. The approximation is then to consider the nuclei fixed in place while the electrons are allowed to roam. This is considered an adiabatic approach to solutions of this system. Standard Cartesian coordinates are very
inconvenient for many body problems and so a change into elliptical cylindrical coordinates will help to simplify the problem at hand.

\[ r_a = \sqrt{(x-x_a)^2 + (y-y_a)^2 + (z+z_a)^2} = \sqrt{x^2 + y^2 + (z + R/2)^2} \]

\[ r_b = \sqrt{(x-x_b)^2 + (y-y_b)^2 + (z-z_b)^2} = \sqrt{x^2 + y^2 + (z - R/2)^2} \]

\[ \lambda = \frac{r_a + r_b}{R}; \quad \eta = \frac{r_a - r_b}{R}; \quad \phi = \tan^{-1}(y/x) \]

![Figure 1: Elliptical Cylindrical Coordinate Diagram](image)

In all instances R is the internuclear distance and r is the distance between any other two bodies. The \( \lambda \) coordinate forms a hyperbole that is perpendicular to the \( \eta \) coordinate. Figure 1 shows the coordinate scheme. The nuclei will be chosen to lie on the x-axis with varying z-coordinates depending on the internuclear distance. \( r_a \) extends from the origin to the nuclei above the x-axis while \( r_b \) extends from the origin to the nuclei below the x-axis. Using this coordinate scheme will greatly reduce the burden of Cartesian coordinates involved in integration as well as terms in the Schrödinger Equation.
2.2 Schrödinger Equation

The corresponding time-independent Schrödinger equation and Hamiltonian (in atomic units) for this system are:

\[ \hat{H}\Psi = E\Psi \]

\[ \hat{H} = \hat{T} + \hat{U} \]

\[ \hat{T} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) ; \hat{U} = \frac{1}{R} + \frac{1}{r_{1,2}} - \frac{1}{r_{1,a}} - \frac{1}{r_{1,b}} - \frac{1}{r_{2,a}} - \frac{1}{r_{2,b}} \]

Solutions to the Schrödinger equation give an energy which can be plotted against the internuclear distance to generate a total energy curve. Energy is a time-independent quantity in this system and this is why the time-independent Schrödinger equation is used. Table 1 shows the R values for the minima of each state as well as the transition maximum. X is the ground state.

<table>
<thead>
<tr>
<th>State</th>
<th>Minima (a.u.)</th>
<th>Trans. Maximum (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>1.4</td>
<td>N/A</td>
</tr>
<tr>
<td>EF</td>
<td>1.9 &amp; 4.4</td>
<td>3.1</td>
</tr>
<tr>
<td>GK</td>
<td>2.2 &amp; 3.3</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Table 1: R values for the minima and transition maxima

The ground state has a relatively uninteresting energy curve with its minimum at 1.4 a.u. Both the EF and GK states are known to have a double minimum total energy curve. According to Wolniewicz and Dressler, the EF state has its first minimum located at R=1.9 a.u.(E) and the second located at R=4.4 a.u.(F) and the GK state has its first minimum at R=2.2 a.u.(G) and the second minimum at R=3.3 a.u.(K). There is a third extremum in both the EF and GK state which will be called the transition maximum or height. This extremum is a local maximum that exists between the minima of a double minimum energy curve. The transition maximum is a result of curve crossing in electronic states and is the place where the electronic state shifts from one minimum to the other.
The transition from the E to the F minimum is located at \( R=3.1 \text{ a.u.} \) and the transition from G to K at \( R=2.7 \text{ a.u.} \). In order to generate a double minimum for both of these states an adequate basis set must be chosen.

### 2.3 Basis Set Selection

The selection of the basis set used in this study is the same as that of Bishop and Cheung. In all cases, unless specified explicitly, these derivations come from internal documents. A primitive wavefunction is defined by James and Coolidge as:

\[
\phi = \phi(N_1, N_2, L_1, L_2; \beta) = |N_1, N_2, L_1, L_2, S\rangle = \frac{1}{2\pi} \lambda_1^{N_1} \eta_1^{L_1} \lambda_2^{N_2} \eta_2^{L_2} \rho^S \exp(-\beta(\lambda_1 + \lambda_2)), \quad \rho = \frac{2}{R} r_{12}
\]

where \( R \) is again defined as the internuclear distance, \( r_{12} \) is the distance between electrons, \( N_i \) are the exponents of the \( \lambda_i \) coordinate, \( L_i \) are the exponents of the \( \eta_i \) coordinate, \( S \) is the power of the \( \rho \) term, and \( \beta \) is a constant exponential factor. All exponents are non-negative, and the same exponent factor has been chosen for both electrons. This wavefunction is *gerade* for \( L_1 + L_2 \) even and *ungerade* for odd. *Gerade* wavefunctions are such that an inversion through a point midway between both nuclei gives the same sign as before the inversion. *Ungerade* refers to wavefunctions that change sign under this same inversion. *Singlet*, *gerade* states are the only states considered in this study. Singlet states have all electrons paired and therefore have a net spin of zero yielding a spin multiplicity of one according to \( 2s+1 \), where \( s \) is the total spin. Values of \( S \) (the exponent of \( \rho \)) greater than zero introduce what is now called correlation into the wavefunction. In order to preserve proper symmetry a combination of the primitive wavefunctions is taken to produce the fundamental function:

\[
\chi_n(r_1, r_2) = \phi \pm \mathcal{P}_{12} \phi = \left[ \lambda_1^{N_1} \eta_1^{L_1} \lambda_2^{N_2} \eta_2^{L_2} \pm \lambda_1^{N_2} \eta_1^{L_2} \lambda_2^{N_1} \eta_2^{L_1} \right] \rho^S \exp(-\beta(\lambda_1 + \lambda_2))
\]

Here \( \mathcal{P} \) represents the permutation operator. This can be rewritten in a simpler form using bra-ket notation:

\[
\chi_n(r_1, r_2) = |N_1, N_2, L_1, L_2, S\rangle \pm |N_2, N_1, L_2, L_1, S\rangle
\]
where the wavefunction is represented by the exponents of the coordinates and $\rho$. From these fundamental wavefunctions, spatial wavefunctions can be constructed as a sum over coefficients for varying values of the internuclear distance:

$$\Psi(\vec{r}_1, \vec{r}_2; R) = \sum_{n=1}^{N} c_n(R) \chi_n(\vec{r}_1, \vec{r}_2)$$  \hspace{1cm} (3)

These expansion coefficients ($c_n$) are determined using the eigenvalue process, and while it is possible to vary $\beta$ for varying internuclear distances, we have kept the same exponent ($\beta = 0.95$) for all values of $R$.

In order to simplify the selection notation of our basis sets, we will follow the same approach as Bishop and Cheung$^{12}$ mentioned earlier. We will specify the primitive wavefunctions to be included in our basis set by $(a_0, a_1, a_2, a_3|b)$. The integers $a_i$ are the maximum values of $N_1 + L_1$ in the basis for terms with $\rho^i$, which is also the maximum value of $N_2 + L_2$. The integer $b$ specifies the maximum value for the sum of $N$’s and $L$’s permitted in the basis. The basis set includes all functions whose exponents have smaller values than the maximum allowed sums. Take for example the basis set $(2,1,0,0|2)$ which contains 10 total basis functions. Table 2 shows the basis set exponents for Equation 2. Larger basis sets are constructed in the same manner.

<table>
<thead>
<tr>
<th>Basis #</th>
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<th>$N_2$</th>
<th>$L_1$</th>
<th>$L_2$</th>
<th>$S$</th>
<th>$N_1$</th>
<th>$N_2$</th>
<th>$L_1$</th>
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<td>1</td>
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</tbody>
</table>

Table 2: $(2,1,0,0|2)$ Basis Set
The basis set chosen for this study was \((8,0,4,0|8)\) consisting of 201 total basis functions. Several smaller basis sets were first investigated but these basis sets did not produce a double minimum in the GK state. The failure to produce a double minimum curve is related to the small powers of \(\lambda\) in those basis sets. This basis, \((8,0,4,0|8)\), gives excellent agreement by eyesight with the literature values for the minima of each state.\(^{10}\) This basis set has a small amount of correlation \((a_2 \neq 0)\). More correlation is possible with \(a_1 \neq 0\); however, it creates a large computational problem that will be addressed after explanation of the one electron density calculation. The lack of correlation should not affect the qualitative data presented in this study, but rather cause small changes in the energy value and location of the transition heights in the EF and GK states. After the basis set was selected and the eigenvectors found, the one electron densities can then be found.

2.4 One Electron Densities

The one electron density represents the probability of finding an electron at a given distance from the nuclei. The definition of the one electron density for molecular hydrogen is:\(^5\)

\[
\rho(\vec{r}_1) = 2 \int \Psi^*(\vec{r}_1, \vec{r}_2; R)\Psi(\vec{r}_1, \vec{r}_2; R)d\tau_2
\]  

(4)

The wavefunctions used are real so the complex symbol can be dropped. Substituting in the definitions for the fundamental and then primitive wavefunctions (eq 1 & 2) gives:

\[
\rho_1(\vec{r}_1) = 2 \sum_{t,u} c_t c_u \left[ p_{t,u} \pm p_{t,\bar{u}} + p_{\bar{t},u} + p_{\bar{t},\bar{u}} \right]; \quad p_{t,u} = \int \phi_t(\vec{r}_1, \vec{r}_2; R) \phi_u(\vec{r}_1, \vec{r}_2; R) d\tau_2
\]  

(5)

remembering that the volume element for the second electron is \(d\tau_2 = \left( \frac{R}{2} \right)^3 (\lambda_2^2 - \eta_2^2) d\lambda_2 d\eta_2 d\varphi_2\).

Each primitive component can be factored to give

\[
p_{n,m}(\vec{r}_1) = (R/2)^3 \left( \frac{1}{2\pi} \right)^2 \lambda_1^{N_1+n+N_1m}\eta_1^{L_1+n+L_1m} e^{-2\beta\lambda_1} \lambda_2^{N_2+n+N_2m}\eta_2^{L_2+n+L_2m} \rho^{S_n+S_m} e^{-2\beta\lambda_2} (\lambda_2^2 - \eta_2^2) d\lambda_2 d\eta_2 d\varphi_2
\]  

(6)

\[
= (R/2)^3 [D(n_1, \ell_1; n_2 + 2, \ell_2, s) - D(n_1, \ell_1; n_2, \ell_2 + 2, s)]
\]  

(7)
with
\[ D(n_1, \ell_1; n_2, \ell_2, s) = \frac{1}{4\pi^2} \lambda_1^{n_1} \eta_1^{\ell_1} e^{-2\beta \lambda_1} \int \lambda_2^{n_2} \eta_2^{\ell_2} \rho^s e^{-2\beta \lambda_2} d\lambda_2 d\eta_2 d\varphi_2 \] (8)

These integrals would be relatively simple to solve, but the $\rho^s$ term must be handled using a recursion formula and this causes the integrals to become very complicated. The recursion, however, can be handled by expansion of $\rho^2$ into cases for $s$ even and odd:

\[ \rho^2 = P - 2M \cos(\Delta \varphi), \quad P = \lambda_1^2 + \lambda_2^2 + \eta_1^2 + \eta_2^2 - 2 - 2\lambda_1 \lambda_2 \eta_1 \eta_2; \] (9)

\[ M = \sqrt{(\lambda_1^2 - 1)(\lambda_2^2 - 1)(1 - \eta_1^2)(1 - \eta_2^2)}; \quad \Delta \varphi = \varphi_2 - \varphi_1 \] (10)

The recursion can be implemented in the form of a new integral involving a multiplication of $D$ by $M^q$ and $\cos^q(\Delta \varphi)$.

\[ Z(n_1, \ell_1, n_2, \ell_2, s, q) = \frac{1}{4\pi^2} \lambda_1^{n_1} \eta_1^{\ell_1} e^{-2\beta \lambda_1} \int \lambda_2^{n_2} \eta_2^{\ell_2} e^{-2\beta \lambda_2} \rho^s M^q \cos^q(\Delta \varphi) d\lambda_2 d\eta_2 d\varphi_2 \] (11)

Substitution involving equation 9 produces

\[ Z(n_1, \ell_1, n_2, \ell_2, s, q) = Z(n_1 + 2, \ell_1, n_2, \ell_2, s - 2, q) + Z(n_1, \ell_1 + 2, n_2, \ell_2, s - 2, q) + Z(n_1, \ell_1, n_2 + 2, \ell_2, s - 2, q) + Z(n_1, \ell_1, n_2, \ell_2 + 2, s - 2, q) - 2Z(n_1 + 1, \ell_1 + 1, n_2 + 1, \ell_2 + 1, s - 2, q) - 2Z(n_1, \ell_1, n_2, \ell_2, s - 2, q + 1) \] (12)

After substitution, the only values needed for recursion in $\rho^s$ are $s=0$ and $s=-1$. Despite the initial expressions involving $q \equiv 0$, more general definitions of $Z$ require higher values of $q$. Odd value recursion extends to -1 in order to make use of the following relation

\[ \frac{1}{\rho} = \sum_{\tau=0}^{\infty} \sum_{\nu=0}^{\tau} D_{\tau,\nu} Q_{\tau,\nu}(\lambda_{>}, \lambda_{<}) P_{\tau,\nu}(\eta_{1}) P_{\tau,\nu}(\eta_{2}) \cos(\nu \Delta \varphi) \] (13)

where $D$ is an expansion coefficient and the symbolism $\lambda_{>\langle<}$ means the larger (smaller) of $\lambda_1$ and $\lambda_2$. $P$ and $Q$ refer to associated Legendre polynomials of the first and second kind, respectively. Several other integrals are necessary in the evaluation of the one electron densities. These are given in Appendix A.

11
The one electron density calculations were carried out over a grid of points eighty by eighty in size. This grid was then taken and plotted\textsuperscript{15} producing graphs like those in Figures 3 and 4. Computational costs are basis set dependent. The more correlation included in the basis set, the more the computational cost increases. The range of data also increases computational costs. Data presented here was carried out over a range 3.5 times the value of R. On average, the actual time involved in the calculation of a single one electron density was about forty minutes. This limited the number of calculations that could be carried out and as a result an interval of 0.1 a.u. was chosen between each R value. This same grid of points was then later used to find the critical points. The calculation of the critical points will be discussed after assessing how the integrals were solved.

2.4.1 Integral Evaluation

The first case when $s=0$ and $q=0$ can be easily solved and then used to generalize the $Z$ functions.

$$Z(n_1, \ell_1; n_2, \ell_2, 0, 0) = e^{-2\beta \lambda_1} \int_1^\infty \lambda_2^{n_2} e^{-2\beta \lambda_2} d\lambda_2 \int_{-1}^{+1} \eta_2^{\ell_2} d\eta_2 = e^{-2\beta \lambda_1} \lambda_1^{n_1} \eta_1^{\ell_1} A_{n_2} C_{0,0}(\ell_2)$$

(14)

where definitions for the A and C integrals can be found in Appendix A.

$$Z(n_1, \ell_1, n_2, \ell_2, s = 0, q) = e^{-2\beta \lambda_1} \int e^{-2\beta \lambda_2} \lambda_2^{n_2} \eta_2^{\ell_2} M_q \cos^q(\Delta \varphi) d\lambda_2 d\eta_2 d\varphi_2$$

$$= 2^{-q} \left( \frac{q}{q/2} \right) \delta_{q, even} e^{-2\beta \lambda_1} \lambda_1^{n_1} \eta_1^{\ell_1} \int e^{-2\beta \lambda_2} \lambda_2^{n_2} \eta_2^{\ell_2} M_q d\lambda_2 d\eta_2$$

$$= 2^{-q} \left( \frac{q}{q/2} \right) \delta_{q, even} e^{-2\beta \lambda_1} \lambda_1^{n_1} \eta_1^{\ell_1} M_1^{q} \int e^{-2\beta \lambda_2} \lambda_2^{n_2} \eta_2^{\ell_2} M_q^{q/2} d\lambda_2 d\eta_2$$

(15)

where the expression will vanish if $q$ is odd and $s=0$. $\binom{n}{k}$ refers to binomial coefficients.
2.4.2 \( s=0 \)

Looking closely at the integral in eq. (8) reveals that it can be factored into basic forms when \( s=0 \), and the form for the \( \rho \) version substitutes in the factor \( [A(n_2 + 2)C_{0,0}(\ell_2) - A(n_2)C_{0,0}(\ell_2 + 2)] \). The \( C_{0,0} \) integral will vanish, however, if \( \ell_2 \) is odd. This integral (the \( \rho \) version) also factors and it only needs to be evaluated once, because all of the dependence on the coordinates of electron one \( (\lambda_1, \eta_1) \) is contained in the prefactor.

2.4.3 \( s=-1 \)

For cases when \( s \) is odd, the recursion relies on \( s=-1 \), as mentioned earlier. If \( a_1 \neq 0 \), then these integrals must be evaluated. Since this case is not handled in this study, the derivation can be found in Appendix B. The proper integrals were very difficult to program, hence limiting computation of \( s=-1 \). The current code in use was relying on numerical integration and not analytic solutions. The numerical code was based around Gauss quadratures. The time involved in evaluating these integrals numerically is astronomical in comparison to their analytic counterparts, between two and three weeks. Computational cost was the main reason why correlation was ignored in this study. While most computational costs can be determined by a standard scaling factor, these calculations did not scale in an obvious manner. The calculation is slow far from the nuclei, decreases dramatically, almost to a stop, as the calculation draws close to the origin, and then the speed increases as it goes away from the nuclei. Further work is being carried out by Dr. Knudson in order to develop analytical solutions and subsequently program them in order to handle basis sets with \( a_1 \neq 0 \).

2.5 Critical Point Calculation

Critical points are points in a function where

\[
\nabla f(x_1, x_2, \ldots x_n) = 0
\]
and when one of the following three conditions is satisfied.

\[ \nabla^2 f(x_1, x_2, \ldots, x_n) = 0 \]
\[ \nabla^2 f(x_1, x_2, \ldots, x_n) > 0 \]
\[ \nabla^2 f(x_1, x_2, \ldots, x_n) < 0 \]

When the second condition is met, the point is called a minimum, and when the third is met, the point is a maximum. Saddle points are the third type of critical point and these occur whenever a critical point is neither a maximum or minimum. Typically, a bond can be characterized by at least a saddle point between the nuclei and maxima at the nuclei.\textsuperscript{16} Appearance of new critical points, or a shift in the behavior of a dynamical function may be due to a topological bifurcation point. At this point the behavior of a function changes dramatically. If these points are found in the one electron densities, then perhaps a more accurate assessment of the types of orbitals can be determined as the place where one orbital behavior shifts to another.

3 Results

3.1 Energies

As mentioned above, solutions of the Schrödinger equation produce an energy which can be plotted against the internuclear distance in order to obtain a total energy curve. Figure 2 (a) contains the total energy curves for the ground state and first two excited $^1\Sigma_g^+$ states, the EF and GK states, respectively. From the graph it is clear that the minimum for the ground state lies at $R=1.4$ a.u., which is in excellent agreement with the literature.\textsuperscript{11} Figure 2 (b) contains the energy curves for only the EF and GK state. There is also excellent agreement with the minima for both the EF and GK states, but there is some discrepancy with the transition maximum in the EF state. The EF state, according to Ugalde \textit{et al},\textsuperscript{11} has its transition from the E to F minimum located at $R=3.1$ a.u. Calculations performed in the course of this study have the transition maximum located at $R = 3.4$. a.u. The GK state has its transition maximum located at $R=2.7$ a.u. which is the same for the calculations.
presented here and in the literature.\textsuperscript{11}

Figure 2: Energy vs Internuclear distance (R) for the first three $^1\Sigma_g^+$ states of H$_2$. (The ground state has been shifted up by 0.26 a.u. in (a).)

Table 3: Basis set and corresponding energies (hartrees).

<table>
<thead>
<tr>
<th>a0</th>
<th>a1</th>
<th>a2</th>
<th>a3</th>
<th>b</th>
<th>R</th>
<th>X</th>
<th>EF</th>
<th>GK</th>
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<tr>
<td>8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>8</td>
<td>1.4</td>
<td>-1.161345</td>
<td>-0.689984</td>
<td>-0.602136</td>
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<tr>
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<td>4</td>
<td>0</td>
<td>8</td>
<td>1.4</td>
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<td>-0.691337</td>
<td>-0.602642</td>
</tr>
<tr>
<td>8</td>
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<td>0</td>
<td>0</td>
<td>8</td>
<td>1.4</td>
<td>-1.174355</td>
<td>-0.691117</td>
<td>-0.602326</td>
</tr>
<tr>
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<td>0</td>
<td>8</td>
<td>1.4</td>
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<td>-0.602421</td>
</tr>
<tr>
<td>8</td>
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<td>-0.691396</td>
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</tr>
<tr>
<td>8</td>
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<td>2</td>
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<td>8</td>
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<tr>
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<td>1.4</td>
<td>-1.173144</td>
<td>-0.691337</td>
<td>-0.602642</td>
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</tbody>
</table>

Table 3 shows the accuracy of the energy values for a given basis set for the ground, EF, and GK states with the exponential factor $\beta = 0.95$. Recall that the integers $a_i$ are the maximum values of $N_1 + L_1$ in the basis for terms with $\rho^i$, which is also the maxi-
mum value of $N_2 + L_2$, and that the integer b specifies the maximum value for the sum of N’s and L’s permitted in the basis. The columns labeled X, EF, and GK refer to their respective electronic states with X as the ground state. The R value chosen was that of the minimum of the ground state, 1.4 a.u. The difference between the lowest calculated energy (8,4,2,0|8) and the basis set chosen for this study (8,0,4,0|8) is -0.00133 hartrees. The value reported by Bishop and Cheung using (6,4,5,3|7), which contains 247 total basis functions, is -1.17447565 hartrees. The difference between that value and the one given by (8,0,4,0|8) is also -0.00133 hartrees. This difference is quite small. The differences for the excited states are also small. This indicates that the proper choice of a basis set with little correlation and large powers of $\lambda$ can still be good enough to produce accurate energies.

3.2 One Electron Density Results

All the one electron density contour plots presented here share the same density line values. These values can be found in Appendix C. The ground state electronic configuration is 1s$^2$. At the united atom limit the ground state becomes a Helium atom and at the dissociation limit two hydrogen atoms with their respective electrons in 1s orbitals. The minimum for the ground state is located at R=1.4 a.u. Figure 3 shows the ground state one electron densities at increasing values of R. Three critical points in the ground state are two maxima, one at each nuclei, and a saddle between them. No new critical points were found for this state for any value of R treated. The EF state is the first excited $^1\Sigma_g^+$ state of molecular hydrogen. The EF state’s one electron densities are presented next.

The EF state is known to have an electron configuration of 1s2s at the united atom limit and moves toward a ground state atom and an atom in the 2s excited state as the molecule dissociates. During the transition from the E minimum to the F minimum, however, the electrons undergo a transition from an excited Rydberg state to an ionic state where both electrons are found in the same 1s orbital for the same hydrogen atom. This behavior is somewhat reflected in the densities. Recall that the E minimum is located at R=1.9 and the transition occurs at R=3.4. Looking at Figure 4, some odd behavior is clearly occurring.
at $R=2.8$ and $R$ values close to it. This odd character, however, disappears upon reaching the F minimum at $R=4.4$.

To help understand the odd behavior, the critical points for the EF state were evaluated over a range of $R$ from 0.9 to 8 a.u. No new critical points of interest were found. As $R$ increases the maxima should move out on the nuclei and the saddle should remain in exactly the same place. The two maxima at the nuclei and the saddle between them were consistently found and their behavior was entirely as predicted. Assessing the critical points did not lead to any conclusions for the odd character in the densities of Figure 4. The GK state, however, turned out not to be so predictable.

The GK state also has a known electron configuration at the untied atom and dissociation limits. The G minimum ($R=2.2$) is a $3d\sigma_g$ type orbital that also has $1s\sigma_g$ character.\textsuperscript{11} The $\sigma$ in these configurations refers to orbitals which are symmetric about their internuclear axis.\textsuperscript{14} Wolniewicz and Dressler also report a $3d\sigma_g$ type orbital in the inner potential well.\textsuperscript{10} The K minimum ($R=3.3$) is reported to be an ionic $(1s)^2$ orbital with contributions from the Rydberg $1s2p$ configuration.\textsuperscript{11} Looking at Figure 5, the 3d character is clearly visible in the one electron densities. Looking at Figure 6, the Rydberg $1s2p$ character is also evident in the densities at higher values of $R (>3.0)$. New critical points also appear to be developing as $R$ moves from the transition point (2.7 a.u.) to the second minimum at 3.3 a.u. These new critical points do in fact show up in computation of the critical points.

### 3.3 Critical Point Results

Determination of the critical points was a somewhat complicated task. The calculations used in finding the energies, wavefunctions, and eigenvectors subsequently used in the one electron density calculation are variational in nature. This means that at farther and farther distances from the nuclei, the wavefunction becomes less and less reliable. Small oscillations in the wavefunction are entirely possible and this caused the critical point calculation to find a multitude of extrema. The calculation mainly found minima type critical points at
coordinates in the system far from the nuclei as well as a few seemingly random saddle type points. These extrema are most likely due to the small oscillations and were thrown out of consideration.

### 3.3.1 Critical Points Along Z=0

Examining the graphs in Figure 5 starting with R=3.0 a.u., it is clear that at least two new critical points should be appearing on the same axis as the saddle point (Z=0). Other new critical points were also found in the calculation that lie along the same axis as the nuclei (X=0), but these will be addressed later. The points along the Z-axis actually appeared in the calculation as two different extrema close together. They were found to be either a saddle and a minimum, or a maximum and a minimum. Figure 7 shows the new critical points plotted as their X-coordinate versus the R value where they were found. This is a qualitative representation as the type of critical point actually shifts depending on the R value. For the range of R from 1.6 to 1.9, the points are a maximum and a saddle. In the region from 1.9 to 3.1 no critical points were found. From R=3.1 to 3.7, the extrema are a saddle and a minimum, and from 3.8 on, they are a maximum and a saddle. The references to 1 and 2 are solely to distinguish on which side of the nuclei the critical points are found, with 1 being in the negative X region and 2 being in the positive. The appearance and disappearance of these critical points can be gleaned by looking at the one electron density plots.

Figure 6(a) is the one electron density plot for the GK state at R=1.6. The new critical points found would lie in the region to the left and right of the saddle between the nuclei. While the density contours chosen do not show them explicitly, the critical point calculation places them in the open region of the density. New critical points appear to be developing above and below both nuclei, but again this will be discussed later. Figure 6(c) is the one electron density for the GK state at R=1.8. The critical points are less evident from looking at the graph, but still found in the critical point calculation. These points then disappear after R=1.9 and do not reappear until R=3.1, which is after the transition from G to K (R=2.7) but before the K minimum at R=3.3. At this point only the saddle is present until
R=3.3 (the K minimum) when the saddle point splits again into two different extrema: a saddle and a minimum. These two extrema persist until R=3.8 where they suddenly jump from moving closer to the nuclei to a distance roughly equal to 2R from the nuclei. Their type also changes from a saddle and a minimum to a maximum and a saddle. These critical points then follow the trend of the maxima at the nuclei and move out linearly as R increases from 3.8 to 8 a.u. Figure 6(d) clearly shows that the critical points should be located to the left and right of the saddle in the pocket created by the shown density lines. The rates at which these two extrema move away from the nuclei are different, as seen by the difference in slope of the lines. R=3.3 and R=3.8 are possible candidates for bifurcation points mentioned earlier, but these will be examined in the discussion section. These new critical points are not the only ones that were found. More new critical points were found along the internuclear axis with X=0.

3.3.2 Critical Points with X=0

It is clear from looking at Figure 6(a) that there should be new critical points located in line with the nuclei. The density contour that is closed in the figure and not surrounding the nuclei is clear evidence of these critical points. The calculation did, in fact, find new critical points with an X-coordinate equal to zero. Figure 8 shows the new critical points as a plot of their Z-coordinate versus R. These critical points have no change in behavior and always appear as saddles. Their first appearance is at R=1.2 and they seem to be following the same linear trend as the nuclei until R=2.3, which is the same R value as the G minimum, where they disappear. Two new maxima also appear at R=2.0 and disappear by R=2.3. The saddle then reappears at R=3.8, which is shortly after the K minimum (R=3.3). This new critical point then follows the same trend as the nuclei maxima, moving outward linearly as R increases, but at a faster rate than the nuclei themselves. With all these critical points in mind, their meaning will now be discussed.
4 Discussion

Several new critical points, all of different types, appear in the GK state at varying values of R. Their appearance, disappearance, and subsequent reappearance, seem to suggest that there are some unique features of this particular electronic state. The possibility for the existence of bifurcation points is indicated by the somewhat erratic appearance and disappearance of these critical points. There are, however, some issues with the data presented here.

Most of the density values where the critical points are being found are far from the nuclei. Since the approach for calculating the densities is based on a basis set, the accuracy of the density in the regions of interest outside the nuclei is somewhat dubious. The variational nature of the calculation, as mentioned previously, can cause oscillations in the wave function. The critical points being found by the calculation could be in the region of the oscillations. If that is the case, then these points are of no consequence to the study because they are the result of the inaccuracies in the densities. Another possible problem stems from the lack of correlation. In general, the correlation should not cause a severe change in the nature of the density, but counterintuitive effects of electron correlation are well known in computational chemistry. Further work must be conducted in order to verify the validity of these points and to interpret their meaning.

5 Further Work

Addressing the issue with the basis set is very straightforward. A larger basis set would mean more accurate calculations in the energy and subsequently better densities. A larger basis would involve both higher values of $a_i$ and $b_i$, but a compromise between size and efficiency would have to be established at some point. Access to more powerful computers would surely be necessary in order to do an extensive basis set. Along the same line as the basis set error is the variational nature of the calculation and its oscillations far from the nuclei. This problem, unfortunately, is difficult to eliminate entirely. A possible method for inspecting the oscillations would be to use a 3D plot and ensure that the range of data it
represents extends far from the nucleus. Then the oscillations could be clearly visible and make for an easier determination in the validity of the critical points.

Another computational issue is correlation. As was presented previously, the one electron density calculations with \( a_1 \neq 0 \) proved very difficult to program analytic solutions. The solutions to the integrals are found in Appendix B. Since the numerical calculations take an unreasonable amount of time with a large basis set, the analytic solutions are an absolute must for further work. Once these more fully correlated basis sets can be handled, then the same calculations presented here should be checked. While it is suspected that correlation should not cause a dramatic change in the behavior of the densities, it will surely affect the actual density values and also where the extrema (both critical points and the energy curve maxima/minima) are located.

While contour plots have been a good way to represent the “bigger picture” of the densities, axial plots would be another approach that could be used to investigate the validity and type of the new critical points. Axial plots are generated by taking data with the same \( x \) or \( z \) coordinate as a fixed value and varying the other coordinate. An example of this can be seen in Figure 9. Here the nuclei can be seen clearly in the leftmost graph as the two peaks. The saddle in this direction is a minimum, and is also evident. This graph would represent the axial plot with the \( x \)-coordinate equal to zero and the \( z \)-coordinate taken over the range of interest. Using this plot, the new critical points which appeared on this axis (Section 3.3.2) are represented in a clear manner without having to look at the surrounding points. The second plot to the right in Figure 9 is an example of a plot with the \( z \)-coordinate equal to zero and the \( x \)-coordinate varying over the range of interest. In this direction the saddle is a maximum and can be seen as the maximum in the plot. The new critical points which appear along this axis (Section 3.3.1) can be studied and their type confirmed. If, in fact, a new saddle point is developing along this axis, then a combination of axial plots down the proper coordinates would confirm which direction they are maxima and which direction they are minima. The scale and range of each of these plots would have to be adjusted in order to see the critical points since they are appearing far from the nuclei. Axial plots are not the
only new data that must be generated in the process of confirming these new critical points.

More calculations need to be run at intermittent values of R between the ones chosen in this study. Using a smaller step size between R values, 0.05 or 0.01 a.u. for example, would help locate the values of R where the critical points appear and disappear. These smaller values would also allow for a better interpretation of how the densities are changing as R is changing. All of these checks must be performed before any final conclusions can be drawn with the data presented here.

References


A Additional Integrals

This appendix contains the additional integrals required in the evaluation of the one electron densities presented in section 2.4.

\[ C_{\tau,\nu}(\ell) = \int_{-1}^{1} y^{\ell} (1 - y^2)^{\nu/2} P_{\tau,\nu}(y) \, dy = \int_{-1}^{1} y^{\ell} P_{\tau,\nu}(y) \, dy; \quad (16) \]

\[ C_{\tau,\nu}(\ell; q) = \int_{-1}^{1} (1 - y^2)^{q/2} y^{\ell} P_{\tau,\nu}(y) \, dy = \int_{-1}^{1} (1 - y^2)^{q/2} y^{\ell} \bar{P}_{\tau,\nu}(y) \, dy, \quad \bar{q} = (q - \nu)/2 \quad (17) \]

\[ A_n = \int_{1}^{\infty} x^n e^{-\gamma x} \, dx \quad (18) \]

\[ I_q = \int_{0}^{2\pi} \cos(q - \varphi_1) \, d\varphi_2 = 2^{-q} \left( \frac{q}{q/2} \right) \delta_{q, \text{even}} \quad (19) \]

\[ I_{\nu,q} = \frac{1}{2\pi} \int_{0}^{2\pi} \cos(\nu \Delta \varphi) \cos^q(\Delta \varphi) \, d\varphi = \frac{1}{2^{q+1}} \sum_{k=0}^{q} \left( \frac{q}{k} \right) \left( \delta(n + q, 2k) + \delta(n + 2k, q) \right) \quad (20) \]

\[ \cos(nx) \cos^q(x) = \frac{1}{2^{q+1}} \left[ (e^{inx} + e^{-inx})(e^{ix} + e^{-ix})^q \right] = \frac{1}{2^{q+1}} \sum_{k=0}^{q} \left( \frac{q}{k} \right) \left( e^{inx} + e^{-inx} \right)^{q-2k} \]

\[ = \frac{1}{2^{q+1}} \sum_{k=0}^{q} \left( \frac{q}{k} \right) \left[ e^{i(n+2k-q)x} + e^{-i(n+2k-q)x} \right] \]

if the exponential factor happens to be 0, integration gives \(2\pi\), while the integral vanishes otherwise. Since \(n, q,\) and \(k\) are all non-negative,

\[ I_{n,q} = \frac{1}{2\pi} \int_{0}^{2\pi} \cos(nx) \cos^q(x) \, dx = \frac{1}{2^{q+1}} \sum_{k=0}^{q} \left( \frac{q}{k} \right) \left( \delta(n + q, 2k) + \delta(n + 2k, q) \right) \]

When \(q \equiv 0,

\[ \frac{1}{2\pi} \int_{0}^{2\pi} \cos(nx) \, dx = \frac{1}{2} \left[ \delta(n, 0) + \delta(n, 0) \right] = \delta(n, 0) \]

When \(q \equiv 1,

\[ I_{n,1} = \frac{1}{4} \sum_{k=0}^{1} \left( \frac{1}{k} \right) \left( \delta(n + 1, 2k) + \delta(n + 2k, 1) \right) = \frac{1}{4} \left[ \left( \frac{1}{0} \right) \delta(n, 1) + \left( \frac{1}{1} \right) \delta(n, 1) \right] = (1/2)\delta(n, 1) \]

When \(q \equiv 2,

\[ I_{n,2} = \frac{1}{3} \sum_{k=0}^{2} \left( \frac{2}{k} \right) \left[ \delta(n + 2, 2k) + \delta(n + 2k, 2) \right] = \frac{1}{4} \left[ 2\delta(n, 0) + \delta(n, 2) \right] \]

We can program in these specific cases and a test to see if higher \(q\) values are required.
B One Electron Densities with $s=-1$

This appendix comes directly from internal documents. Evaluation of the integral with odd values of $\rho$ can be discussed most efficiently in terms of the $Z$ integral. We consider first the case with $q=0$:

$$Z(n_1, \ell_1, n_2, \ell_2, -1, 0) = \frac{1}{4\pi^2} \lambda_1^{n_1} \eta_1^{\ell_1} e^{-2\beta \lambda_1} \sum_{\nu=0}^{\infty} D_{\tau,0} P_{\nu,0}(\eta_1) \int \frac{\lambda_2^{n_2} \eta_2^{\ell_2}}{2} Q_{\tau,\nu}(\lambda >) P_{\nu,\nu}(\lambda <) P_{\tau,\nu}(\eta_2) \cos(\nu \Delta \varphi) e^{-2\beta \lambda_2} d\lambda_2 d\eta_2 d\varphi_2$$

The integral over the angle $\varphi_2$ vanishes except for the case $\nu \equiv 0$,

$$\int_0^{2\pi} \cos(n \Delta \varphi) d\varphi_2 = 2\pi \delta_{n,0}$$

and the integral in the variable $\eta_2$ factors to the form in eq. (16), so this becomes

$$Z(\ldots, -1, q = 0) = \left( \frac{1}{2\pi} \right) \lambda_1^{n_1} \eta_1^{\ell_1} e^{-2\beta \lambda_1} \sum_{\tau=0}^{\ell_2} D_{\tau,0} P_{\tau,0}(\eta_1) C_{\tau,0}(\ell_2) w_{\tau,0}(n_2; \lambda_1)$$

where

$$w_{\tau,\nu}(n; \lambda_1) = (\lambda_1^2 - 1)^{\nu/2} \int_1^{\infty} x^n e^{-\gamma x} (x^2 - 1)^{\nu/2} Q_{\tau,\nu}(>) P_{\nu,\nu}(<) dx$$

(21)

Notice that $\tau$ must be of the same parity as $\ell_2$, else the $C$ integral vanishes. It would seem that we need to find an expression for $Z(\rho = -1, q)$, and then recursion can handle all cases with odd $s$.

$$Z(\ldots, -1, q) = \left( \frac{1}{2\pi} \right) \lambda_1^{n_1} \eta_1^{\ell_1} e^{-2\beta \lambda_1} \sum_{\tau=0}^{\min(q, \ell_2)} D_{\tau,0} P_{\tau,0}(\eta_1) \mathcal{I}_{\nu,q} \int \frac{\lambda_2^{n_2} \eta_2^{\ell_2}}{2} Q_{\tau,\nu}(\lambda >) P_{\nu,\nu}(\lambda <) P_{\tau,\nu}(\eta_2) e^{-2\beta \lambda_2} M^q d\lambda_2 d\eta_2$$

where $D$ is an expansion coefficient and the symbolism $\lambda_{>}(<)$ means the larger (smaller) of $\lambda_1$ and $\lambda_2$. $P$ and $Q$ refer to associated Legendre polynomials of the first and second kind, respectively. The integration over the angle has already been carried out; there are parity restrictions, in that $\nu$ and $q$ must be of the same parity, or the angular integral $\mathcal{I}$ vanishes.

The integral over $\eta_2 = y$ factors:

$$\int_{-1}^{+1} y^{\ell_2} (1 - y^2)^q P_{\tau,\nu}(y) dy$$

25
which introduces restrictions on $\nu$ and on the maximum value of $\tau$ which may occur. A single integral, over $\lambda_2$, remains

$$Z(\ldots, -1, q) = \frac{1}{2\pi} \lambda_1^{n_1} \eta_1^1 e^{-2\beta_1} \sum_{\tau=0}^{L_2+q \text{min}(q, \tau)} \sum_{\nu=0}^{\tau} D_{\tau, \nu} \mathcal{I}_{\nu, q} M_1^q P_{\tau, \nu}(\eta_1) C_{\tau, \nu}(L2, q) w_{\tau, \nu}(n_2; j, \lambda_1)$$

where $(x \to \lambda_2)$

$$w_{\tau, \nu}(n; j; \lambda_1) = (\lambda_1^2 - 1)^{\nu/2} \int_1^{\lambda_1} x^n e^{-\gamma x} (x^2 - 1)^{\nu/2} Q_{\tau, \nu}(>) P_{\tau, \nu}(<) \, dx$$

$$= (\lambda_1^2 - 1)^{\nu/2} \left[ Q_{\tau, \nu}(\lambda_1) \int_1^{\lambda_1} x^n e^{-\gamma x} (x^2 - 1)^{\nu/2} P_{\tau, \nu}(x) \, dx + P_{\tau, \nu}(\lambda_1) \int_{\lambda_1}^{\infty} x^n e^{-\gamma x} (x^2 - 1)^{\nu/2} Q_{\tau, \nu}(>) \, dx \right]$$

$$= q_{\tau, \nu}(\lambda_1) \int_1^{\lambda_1} x^n e^{-\gamma x} (x^2 - 1)^{\nu/2} p_{\tau, \nu}(x) \, dx + p_{\tau, \nu}(\lambda_1) \int_{\lambda_1}^{\infty} x^n e^{-\gamma x} (x^2 - 1)^{\nu/2} q_{\tau, \nu}(x) \, dx$$

where $p_{L,M}(x) = (x^2 - 1)^{M/2} P_{L,M}(x)$ and $q_{L,M}(x) = (x^2 - 1)^{M/2} Q_{L,M}(x)$. There are parity constraints as well; $\tau$ must be of the same parity as $L_2$, for example, and the parity constraints from the phi integral remain.

**B.1 Evaluation of $w$**

The two integrals must be treated separately. So we write

$$w_{L,M}(n, \lambda_1; \gamma) = q_{L,M}(\lambda_1) G_{L,M}(n, \lambda_1; \gamma) + p_{L,M}(\lambda_1) F_{L,M}(n, \lambda_1; \gamma)$$

$$G_{L,M}(n, \lambda_1; \gamma) = \int_1^{\lambda_1} x^n e^{-\gamma x} (x^2 - 1)^{M/2} P_{L,M}(x) \, dx = \int_1^{\lambda_1} x^n e^{-\gamma x} p_{L,M}(x) \, dx$$

$$F_{L,M}(n, \lambda_1; \gamma) = \int_{\lambda_1}^{\infty} x^n e^{-\gamma x} (x^2 - 1)^{M/2} Q_{L,M}(x) \, dx = \int_{\lambda_1}^{\infty} x^n e^{-\gamma x} q_{L,M}(x) \, dx$$

Evaluation of the two integrals found in $w$ proceeds by looking at the easiest cases.

**B.1.1 Evaluation of $G$**

Thus, take $L=M=0$, and consider

$$G_{0,0}(n, \lambda_1) = \int_1^{\lambda_1} x^n e^{-\gamma x} \, dx = A_n(\gamma) - \lambda_1^{n+1} A_n(\gamma \lambda_1); \quad G_{1,0}(n, \lambda_1) = \int_1^{\lambda_1} x^n e^{-\gamma x} \, dx = G_{0,0}(n+1)$$
A recursion relation in $L$ then permits extension to higher values of $L$:

$$P_{L,0}(x) = \frac{1}{L} \left[ (2L - 1)xP_{L-1,0}(x) - (L - 1)P_{L-1,0} \right]$$  \hspace{1cm} (25)$$

$$G_{L,0}(n, \lambda_1) = \frac{1}{L} \left[ (2L - 1)G_{L-1,0}(n + 1, \lambda_1) - (L - 1)G_{L-1,0}(n, \lambda_1) \right]$$

Another recursion relation applies to incrementing the other index:

$$p_{L,M+1}(x) = (L - M)xp_{L,m}(x) - (L + M)p_{L-1,M}(x)$$

Notice that this applies to the $p$ function, not to the associated Legendre function $P$ itself. It makes generation of $G$ values simple:

$$G_{L,M+1}(n, \lambda_1) = (L - M)G_{L,m}(n + 1, \lambda_1) - (L + M)G_{L-1,M}(n, \lambda_1)$$  \hspace{1cm} (26)$$

so, for example, $G_{1,1}(0) = G_{1,0}(1) - G_{0,0}(0)$. The same recursion formulae apply to the $F$ function.

**B.1.2 Evaluation of $F$**

This is a more difficult integral, but fortunately has already been done in the determination of the Hamiltonian (and overlap) matrix elements.
C Contour Values

All one electron density plots were generated using a single set of contour values. These values are:

<table>
<thead>
<tr>
<th>Contour Values</th>
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<tbody>
<tr>
<td>0.00005</td>
</tr>
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<td>0.000075</td>
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</tr>
<tr>
<td>0.00045</td>
</tr>
<tr>
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</tr>
<tr>
<td>0.005</td>
</tr>
<tr>
<td>0.0070</td>
</tr>
</tbody>
</table>
Figure 3: Ground state one electron densities at given R values. Density values can be found in Appendix C.
Figure 4: EF state one electron densities at given R values. Density values can be found in Appendix C.
Figure 5: GK state one electron densities at given R values. Density values can be found in Appendix C.
Figure 6: GK state selected one electron density plots.
Figure 7: X coordinate vs R for new critical points in the GK state. The saddle at X=0 is the saddle between the nuclei.
Figure 8: Z coordinate vs R for new critical points and the three expected (two maxima and a saddle) in the GK state
Figure 9: Axial density plots where $\psi$ is the density and $q$ is a generalized coordinate.