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INTERACTION OF EXCITED AND GROUND-STATE HELIUM
ATOMS: POTENTIAL ENERGY CURVES AND INELASTIC
PROCESSSES

by

Walter J. Steets

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2. The Excited States of the He$_2$ Molecule</td>
<td>4</td>
</tr>
<tr>
<td>A. Calculation of the Potential Curves and Wavefunctions</td>
<td></td>
</tr>
<tr>
<td>a. Separation of center-of-mass and relative coordinates</td>
<td>4</td>
</tr>
<tr>
<td>b. The adiabatic coupled equations</td>
<td>9</td>
</tr>
<tr>
<td>c. Angular coupling</td>
<td>20</td>
</tr>
<tr>
<td>d. Radial coupling</td>
<td>23</td>
</tr>
<tr>
<td>e. The radial diabatic representation</td>
<td>30</td>
</tr>
<tr>
<td>f. Computation of adiabatic electronic wavefunctions</td>
<td>37</td>
</tr>
<tr>
<td>B. Qualitative Behavior of the Excited States of He$_2$</td>
<td>47</td>
</tr>
<tr>
<td>a. Rydberg states of the He$_2$ molecule</td>
<td>47</td>
</tr>
<tr>
<td>b. The behavior of the potential curves</td>
<td>52</td>
</tr>
<tr>
<td>C. Results and Discussion</td>
<td>61</td>
</tr>
<tr>
<td>a. The $^{3}\Pi_u$ states</td>
<td>63</td>
</tr>
<tr>
<td>b. The $^{3}\Sigma_u^+$ states</td>
<td>68</td>
</tr>
<tr>
<td>c. The $^{3}\Sigma_g^+$ states</td>
<td>83</td>
</tr>
<tr>
<td>3. B Core States</td>
<td>98</td>
</tr>
<tr>
<td>4. Cross Sections</td>
<td>111</td>
</tr>
<tr>
<td>A. The Landau-Zener Theory</td>
<td>111</td>
</tr>
<tr>
<td>B. Excitation Transfer</td>
<td>129</td>
</tr>
<tr>
<td>a. $^{3}S \rightarrow^{2}P$</td>
<td>131</td>
</tr>
<tr>
<td>b. $^{3}P \rightarrow^{3}S$</td>
<td>140</td>
</tr>
</tbody>
</table>
C. Associative Ionization

References  
Appendix I
Introduction

When excited and ground-state helium atoms collide at thermal energies, two inelastic processes are possible. These are nonresonant excitation transfer

\[ \text{He}^* + \text{He} \rightarrow \text{He}^* + \text{He} \]

and associative ionization

\[ \text{He}^* + \text{He} \rightarrow \text{He}_2^+ + e \]

These processes may be observed in gas discharges\textsuperscript{1,2} and afterglows. The rates of these reactions are important parameters for a system in the analysis of its potential as a laser\textsuperscript{3}.

These processes are described theoretically in terms of the coupling between molecular electronic states. The description begins with the time-independent Schroedinger equation in a space-fixed coordinate system. The center-of-mass and relative coordinates are separated. Adiabatic electronic molecular wavefunctions are constructed in a relative, body-fixed coordinate system. The heavy particle scattering problem is best described in a space-fixed system. The transformation between these two systems introduces angular coupling between adiabatic molecular states. Furthermore, radial coupling of electronic states arises from the finite mass of the nuclei. In some cases it is advantageous to remove this coupling by a transfor-
mation to a particular type of crossing or diabatic electronic state.

In the present work, several excited $^3\Sigma_u^+$, $^3\Pi_u$, and $^3\Sigma_g^+$ electronic states of $\text{He}_2$ have been calculated using the configuration interaction method. The behavior of the energies of single configuration wavefunctions may be described by a few simple rules. Then, in turn, important features of the full adiabatic potentials may be described in terms of these single configuration wavefunctions. Moreover, we have compared our states with the $^1\Sigma_u^+$ and $^1\Sigma_g^+$ states recently calculated by Guberman and Goddard\(^4\). The general behavior of these states should be very similar, yet significant differences exist. We have suggested reasons for these differences.

Rydberg states of $\text{He}_2$ are constructed on the bound $^2\Sigma_u^+$ state of $\text{He}_2^+$. Mulliken\(^5\) has suggested that states constructed on the repulsive $^2\Sigma_g^+$ state of $\text{He}_2^+$ could play an important role in associative ionization. A $^3\Sigma_g^+$ state with some of these properties is examined.

Cross sections for the nonresonant excitation transfer process $^3\Sigma - ^3\Pi$ and $^3\Pi - ^3\Sigma$ have been calculated using the Landau-Zener approximation. The cross sections are strongly dependent on the coupling matrix elements. Accurate values of these coupling elements are not available from our calculation of the states of $\text{He}_2$ so that only semi-quantitative predictions are possible.
3.

We have not calculated an associative ionization cross section. Using the molecular wavefunctions, we have suggested a more detailed mechanism than that contained in the usual two-state descriptions.
2. The Excited States of the He₂ Molecule

A. Calculation of the Electronic Wavefunction and Potential Energy Curves

There are three steps in the calculation of an atomic collision cross-section: i. construction of the Hamiltonian and separation of the nuclear and electronic motion; ii. choice of a representation for the electronic states and derivation of the nuclear motion equations in that representation; and iii. solution of the coupled nuclear equations to obtain the S-matrix and hence the cross-sections. This chapter contains a discussion of the approximations, procedures and solutions used in the first two steps, and a presentation of results for bound electronic states. In Chapter 3 autoionizing states are discussed. Chapter 4 contains a description of the procedures used to obtain cross-sections for inelastic excitation transfer between excited and ground state helium atoms.
a. Separation of Center-of-Mass and Relative Coordinates

Atomic collision processes at thermal energies are described well by the time-independent nonrelativistic Schroedinger equation. In space-fixed lab coordinates this equation is

\[
\left[ -\frac{i}{2} \sum_{i=1}^{n} \nabla_i^2 - \frac{i}{2 M_a} \nabla_a^2 - \frac{i}{2 M_b} \nabla_b^2 + V(\vec{r}_{oe}, \vec{R}_a, \vec{R}_b) \right] \psi_T(\vec{r}_{oe}, \vec{R}_a, \vec{R}_b) = E_T \psi_T(\vec{r}_{oe}, \vec{R}_a, \vec{R}_b)
\]

(2.1)

where \( n \) is the number of electrons, \( \nabla_i^2 \), \( \nabla_a^2 \), and \( \nabla_b^2 \) are the Laplacians for the \( i \)-th electron, nucleus \( a \) and nucleus \( b \) respectively in the lab coordinates, \( \vec{r}_{oe} \) represents all electronic coordinates, \( \vec{R}_a \) and \( \vec{R}_b \) are the nuclear coordinates, \( M_a \) and \( M_b \) are the nuclear masses, \( V(\vec{r}_{oe}, \vec{R}_a, \vec{R}_b) \) is the usual electrostatic potential, and \( \psi_T(\vec{r}_{oe}, \vec{R}_a, \vec{R}_b) \) is the total wavefunction. Atomic units are used throughout the thesis. Our discussion follows that of Geltman.

The first step is to transform from the space-fixed lab coordinates to space-fixed relative coordinates with the origin of the relative coordinates at the center of mass of the nuclei. The transformation is

\[
\vec{R} = \vec{R}_a - \vec{R}_b : \text{Relative coordinate}
\]

\[
(M_a + M_b) \vec{R}_N = M_a \vec{R}_a + M_b \vec{R}_b : \text{Center of mass of the nuclei}
\]
The transformation of the Laplacian operators from lab to relative coordinates is straightforward. The nuclear kinetic energy operators are

\[ -\frac{1}{2M_a} \nabla_a^2 - \frac{1}{2M_b} \nabla_b^2 = \frac{-1}{2(M_a + M_b)} \nabla_N^2 - \frac{1}{2\mu} \nabla_R^2 \]

where \( \mu = \frac{M_aM_b}{(M_a + M_b)} \) is the reduced mass of the nuclei and \( \nabla_N^2 \) and \( \nabla_R^2 \) are the Laplacians in center-of-mass of the nuclei and relative coordinates, respectively.

The potential \( V(\vec{r}_{oe}, \vec{R}_N, \vec{R}) \) still explicitly contains the center-of-mass of the nuclei coordinates \( \vec{R}_N \). To remove this coordinate, we must transform to the center of mass of the entire system. This requires that we choose an origin for the electron coordinates. Several reasonable choices are available. We shall define the electron coordinates relative to the center-of-mass of the nuclei. Another possibility is to divide the electrons into two groups, placing the origin of the coordinates of the first group on atom a and the origin of the second on atom b.

The transformation of the electron coordinates from lab to center-of-mass of the nuclei is

\[ \vec{r}_i = \vec{r}_{ei} - \vec{R}_N \quad : \quad \text{electron relative coordinates} \]

\[ M\vec{R}_{CM} = \sum_{i=1}^{n} \vec{r}_i + (M_a + M_b)\vec{R}_N \quad : \quad \text{center-of-mass coordinate} \]

where \( M = M_a + M_b + n \) is the total mass. The gradient operators for the electron and center-of-mass of the nuclei coordinates transform as
\[ \vec{\nabla}_i = \vec{\nabla} + \frac{i}{M} \vec{\nabla}_N \]
\[ \vec{\nabla}_N = \frac{(M_a + M_b)}{M} \vec{\nabla}_c - \sum_{i=1}^{n} \vec{\nabla}_i \]

The operators for the total kinetic energy transform as

\[ -\frac{1}{2} \sum_{i=1}^{n} \nabla_{i}^{2} - \frac{1}{2M_a} \nabla_{a}^{2} - \frac{1}{2M_b} \nabla_{b}^{2} = -\frac{1}{2} \sum_{i=1}^{n} \nabla_{i}^{2} - \frac{1}{2(M_a + M_b)} \nabla_{N}^{2} - \frac{1}{2\mu} \nabla_{R}^{2} \]
\[ = -\frac{1}{2M} \nabla_{cM}^{2} - \frac{1}{2} \sum_{i=1}^{n} \nabla_{i}^{2} - \frac{1}{2(M_a + M_b)} \sum_{i,j} \vec{\nabla}_{i} \cdot \vec{\nabla}_{j} - \frac{1}{2\mu} \nabla_{R}^{2}. \]

The potential energy term is expressed in relative coordinates as

\[ \nabla(\vec{r}_a, \vec{r}_b, \vec{r}_b) = \]
\[ = -\sum_{i=1}^{n} \frac{z_e}{|\vec{r}_i - \vec{r}_a|} - \sum_{i=1}^{n} \frac{z_b}{|\vec{r}_i - \vec{r}_b|} + \sum_{i \neq j} \frac{1}{|\vec{r}_i - \vec{r}_j|} + \frac{z_e z_b}{|\vec{r}_a - \vec{r}_b|} \]
\[ = -\sum_{i=1}^{n} \frac{z_e}{|\vec{r}_i - \frac{M_b}{(M_a + M_b)} \vec{R}|} - \sum_{i=1}^{n} \frac{z_b}{|\vec{r}_i - \frac{M_b}{(M_a + M_b)} \vec{R}|} + \sum_{i \neq j} \frac{1}{|\vec{r}_i - \vec{r}_j|} + \frac{z_e z_b}{|\vec{R}|} \]
\[ = \nabla(\vec{r}_e, \vec{R}) \]

Thus each term in the hamiltonian is expressed completely in terms of either the center of mass coordinate or the relative coordinates. The wavefunction may then be represented as the product

\[ \Psi_T(\vec{r}_e, \vec{R}, \vec{r}_{cM}) = e^{i \vec{r}_{cM} \cdot \vec{R}_{cm}} \Psi(\vec{r}_e, \vec{R}) \]
The relative energy is \( E = E_T - \frac{k^2}{2M} \). The center-of-mass motion may now be disregarded and only the relative motion considered in the following.

The relative hamiltonian contains the term

\[
\frac{1}{2(M_a + M_b)} \sum_{i,j} \vec{v}_i \cdot \vec{v}_j.
\]

This term is of order \( \frac{1}{(M_a + M_b)} \) with respect to the term \( \sum_{i=1}^{n} v_i^2 \) and will be neglected.
b. The Adiabatic Coupled Equations

The Schroedinger equation for the relative motion of the electrons and nuclei is

\[ \left( -\frac{i}{\hbar} \sum_{\ell=1}^{n} \nabla_{\ell}^{2} - \frac{1}{2} \frac{1}{\mu} \nabla_{R}^{2} + V(\vec{r}_{\ell}, \vec{R}) - E \right) \psi(\vec{r}_{\ell}, \vec{R}) = 0 \quad (2.2) \]

in a space-fixed coordinate frame. For the collision problems considered here, the speed of the electrons is about three orders of magnitude greater than nuclear speeds. This suggests that, for any \( R \), the electrons adjust to the position of the nuclei. Thus we seek solutions of Eq. (2.2) which neglect nuclear motion. These solutions may then be used to construct higher order solutions which include the effects of nuclear motion.

The Schroedinger equation for the zero-order electronic functions is obtained from Eq. (2.2) by neglecting the term \( \frac{1}{2\mu} \nabla_{R}^{2} \) and transforming the remaining terms to a coordinate frame which rotates with the internuclear axis. This rotation of axes does not change the form of the electronic Schroedinger equation. The angle variable will, however, refer to the rotating axes rather than the space-fixed axes. The Schroedinger equation obtained by this set of procedures is known as the Born-Oppenheimer approximation.

The zero-order electronic functions are found as solutions of
\[
\left( -\frac{i}{2} \sum_{i=1}^{n} \nabla_i^2 + V(\mathbf{r}_e, R) \right) \Phi_{\mathbf{r}} \left( \mathbf{r}_e, R \right) \\
= H_{e1} \left( \mathbf{r}_e, R \right) \Phi_{\mathbf{r}} \left( \mathbf{r}_e, R \right) \\
= E_{\mathbf{r}} \left( R \right) \Phi_{\mathbf{r}} \left( \mathbf{r}_e, R \right)
\] (2.3)

Since \( \{ \Xi_{\mathbf{r}} \} \), the set of solutions of Eq. (2.3), are eigenfunctions of \( H_{e1} \), they may also be eigenfunctions of the operators which commute with \( H_{e1} \). For the case we have been considering, the electronic spin is not strongly coupled to either the electronic or nuclear orbital angular momenta and the electronic orbital angular momenta is not strongly coupled to the nuclear angular momenta. In this case, the operators for the total electronic spin squared, \( \hat{S}^2 \), and for the projection of total electronic angular momentum along the internuclear axis, \( \hat{L}_z \), always commute with \( H_{e1} \). If the eigenvalues of \( \hat{L}_z \) are not zero, each level is doubly degenerate. The operator which reflects the electronic coordinates through a plane containing the internuclear axes also commutes with \( H_{e1} \). This reflection operator acting on the degenerate eigenfunctions of \( \hat{L}_z \) transforms them into each other. Thus two eigenfunctions of the reflection operator may be formed from the degenerate eigenfunctions of \( \hat{L}_z \). One of these is unchanged by reflection. The other changes sign. If the eigenvalue of \( \hat{L}_z \) is zero, no degeneracy exists. The eigenfunction of \( \hat{L}_z \) must then also be an eigenfunction of the reflection operator. Finally, for a homonuclear diatomic molecule,
the operator which inverts all electronic coordinates 
through the origin commutes with $H_{el}$.

The eigenvalues of these operators label the eigen-
functions of $H_{el}$. The eigenvalues of $\hat{S}^2$ are $S(S+1)$. The 
quantity $2S+1$, the spin multiplicity, is the label of the 
electronic states associated with the spin operator. The 
eigenvalues of $L_z$ are $\Lambda$ where $|\Lambda| = 0,1,2,...$. These states 
are referred to as $\Sigma$, $\pi$, $\Delta$, etc., respectively. If 
$|\Lambda| \neq 0$, eigenfunctions of $L_z$, rather than eigenfunctions 
of the reflection operator, are used in this thesis. For 
$\Sigma$ states, the eigenvalue of the reflection operator, $+1$ or 
$-1$, also labels the state. The eigenvalues of the inversion 
operator are $+1$ and $-1$. The labels gerade (g) or ungerade 
(u) correspond to these eigenvalues. The last three labels 
denote the symmetry of the state.

The potential curves of states of the same spin 
multiplicity and symmetry may be represented at each $R$ as 
roots of a secular determinant. This will be discussed in 
more detail in a later section. In general, these roots 
will be nondegenerate for all $R$. Hence the potential 
curves of the same symmetry and spin multiplicity do not 
cross in the adiabatic Born-Oppenheimer approximation. 
States of different spin multiplicity or symmetry do not 
mix in this approximation. Hence there is no prohibition 
against the potential curves of these states crossing.

In the following discussion, only bound electronic 
states are considered so that all $\hat{\phi}_R$ may be represented as
real functions. The procedures used to obtain these solutions are discussed in a later section.

The solutions of Eq. (2.3) form a complete, orthonormal set. The solutions of the complete Schroedinger equation (2.2) may be expanded in terms of these states.

\[ \psi(\vec{r}, \vec{R}) = \sum \Phi(\vec{r}) \Phi(\vec{R}) \]  

(2.4)

In the case of identical nuclei, this must be further symmetrized with respect to nuclear coordinates. The coupled equations for nuclear motion are formed by multiplying by a particular \( \Phi \) and integrating over all electronic coordinates and summing over all spin coordinates. Thus from

\[ \sum \int d^3 \Phi(\vec{r}) \Phi(\vec{R}) \left[ -\frac{1}{2\mu} \nabla^2 + H_{el} - E \right] \Phi(\vec{R}) \Phi(\vec{r}) \Phi(\vec{R}) = 0 \]

we obtain

\[ \left[ -\frac{1}{2\mu} \nabla^2 + E(\vec{R}) - E \right] \Phi(\vec{R}) \]

\[ = \frac{1}{\mu} \sum \Phi(\vec{r}) \cdot \int d^3 \Phi(\vec{r}) \Phi(\vec{R}) \nabla \Phi(\vec{R}) \Phi(\vec{r}) \]

\[ + \frac{1}{2\mu} \sum \Phi(\vec{r}) \int d^3 \Phi(\vec{r}) \Phi(\vec{R}) \nabla^2 \Phi(\vec{R}) \Phi(\vec{r}) \]

(2.5)

In the Born-Oppenheimer approximation, the right hand side of Eq. (2.5) is neglected. The Schroedinger equation for nuclear motion becomes
\[ \left[-\frac{1}{2\mu}\nabla^2_R + V_\Gamma(R) - \frac{K_\Gamma^2}{2\mu}\right] F_\Gamma^\circ(\vec{R}) = 0 \quad (2.6) \]

where \( V_\Gamma(R) = E_\Gamma(R) - E_\Gamma(\infty) \) defines the potential energy curve of the electronic state \( \Gamma \) and \( \frac{K_\Gamma^2}{2\mu} = E - E_\Gamma(\infty) \) is the incident relative kinetic energy. The solutions of Eq. (2.6) are zero-order approximations to the adiabatic coupled equations.

The evaluation of the coupling terms of Eq. (2.5) requires that \( \vec{v}_R \) and \( v_R^2 \) operate on \( \vec{\phi}_\Gamma \). These operations are taken with respect to fixed electronic coordinates. In the molecular electronic functions \( \vec{\phi}_\Gamma \), the electronic coordinates are defined with respect to the rotated body-fixed axes. The relation between the electronic coordinates in the two systems must be known in order that the nuclear angular derivatives may be taken with respect to stationary electronic coordinates in the space-fixed frame. To find these relations, we perform the rotation of the original coordinate system shown in Figure 1. The \( x' \) axis is rotated about the \( z' \) axis through an angle \( \nu \) so that the projection of \( \vec{R} \) onto the \( x'y' \) plane lies along the rotated \( x' \) axis. The electronic coordinates in this intermediate frame are related to the original coordinates by the transformation.
Figure 1. Relation between space-fixed and body-fixed coordinate systems.
\( \begin{bmatrix} x_i'' \\ y_i'' \\ z_i'' \end{bmatrix} = \begin{bmatrix} \cos \nu & -\sin \nu & 0 \\ \sin \nu & \cos \nu & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_i' \\ y_i' \\ z_i' \end{bmatrix} \)

Next the \( z' \) axis is rotated about the \( y \) axis through an angle \( \omega \) so that \( \vec{R} \) lies along the rotated \( z' \) axis. This defines the molecular body-fixed frame. The relation between the intermediate electronic coordinates and the body-fixed coordinates is given by

\( \begin{bmatrix} x_i \\ y_i \\ z_i \end{bmatrix} = \begin{bmatrix} \cos \omega & 0 & \sin \omega \\ 0 & 1 & 0 \\ -\sin \omega & 0 & \cos \omega \end{bmatrix} \begin{bmatrix} x_i'' \\ y_i'' \\ z_i'' \end{bmatrix} \)

Thus the relation between the electronic coordinates in the body-fixed frame and the space-fixed frame is given by

\( y_i = x_i' \sin \nu + y_i' \cos \nu \) \hspace{2cm} (2.7a)

\( x_i = -y_i' \cos \omega \sin \nu + x_i' \cos \omega \cos \nu + z_i' \sin \omega \) \hspace{2cm} (2.7b)

\( z_i = y_i' \sin \omega \sin \nu - x_i' \sin \omega \cos \nu + z_i' \cos \omega \) \hspace{2cm} (2.7c)

The angles \( \omega \) and \( \nu \) are the usual polar and azimuthal angles determining the position of the internuclear axis in the space-fixed frame. The operation of the derivation with respect to \( \omega \) and \( \nu \) on the electronic wavefunction for stationary space-fixed electronic coordinates may be
represented by using the chain rule and Eq. (2.7) as

$$\frac{\delta}{\delta \omega} = \left[ \sum_{i=1}^{n} \left( z_i \frac{\delta}{\delta x_i} - x_i \frac{\delta}{\delta z_i} \right) \right]$$

$$\frac{\delta}{\delta \nu} = \cos \omega \left[ \sum_{i=1}^{n} \left( x_i \frac{\delta}{\delta y_i} - y_i \frac{\delta}{\delta x_i} \right) \right] + \sin \omega \left[ \sum_{i=1}^{n} \left( y_i \frac{\delta}{\delta z_i} - z_i \frac{\delta}{\delta y_i} \right) \right]$$

The expression in square brackets may be identified with components of the total electronic orbital angular momentum in the body-fixed frame. These derivatives may be expressed as

$$\frac{\delta}{\delta \omega} = i L_y \quad (2.8a)$$

$$\frac{\delta}{\delta \nu} = i \cos \omega L_z + i \sin \omega L_y \quad (2.8b)$$

The gradient operator in spherical coordinates is

$$\vec{\nabla}_R = \hat{R} \frac{\delta}{\delta R} + \hat{\omega} \frac{1}{R} \frac{\delta}{\delta \omega} + \hat{\nu} \frac{1}{R \sin \omega} \frac{\delta}{\delta \nu}$$

where $\hat{R}$, $\hat{\omega}$, and $\hat{\nu}$ are the usual unit vectors in spherical coordinates. The action of the gradient operator on a molecular wavefunction can be represented with the use of Eq. (2.8) as

$$\vec{\nabla}_R \Phi_R (\vec{r}, R) = \hat{R} \frac{\delta}{\delta R} \Phi_R + i \hat{\omega} \frac{1}{R} L_y \Phi_R$$

$$+ i \hat{\nu} \frac{1}{R \sin \omega} \left( L_z \cos \omega + L_x \sin \omega \right) \Phi_R$$

The Laplacian in spherical coordinates is
\[
\frac{1}{R^2} \frac{1}{J_R} \left( R^2 \frac{1}{J_R} \right) + \frac{1}{R^2} \sin \omega \frac{1}{J_R} \left( \sin \omega \frac{1}{J_R} \right) + \frac{1}{R^2} \frac{\omega^2}{J_R^2}.
\]

The operation of the Laplacian on a molecular wavefunction may then be expressed as

\[
\nabla_R^2 \Phi_r = \frac{1}{R^2} \frac{1}{J_R} \left( R^2 \frac{1}{J_R} \Phi_r \right) - \frac{2}{R^2} \cot \omega \mathbf{L}_2 \cdot \mathbf{L}_x \Phi_r \\
- \frac{1}{R^2} \mathbf{L}_z^2 \Phi_r + \frac{1}{R^2} (1 - \cot^2 \omega) \mathbf{L}_z^2
\]

where we have used that

\[
\mathbf{L}^2 = \mathbf{L}_x^2 + \mathbf{L}_y^2 + \mathbf{L}_z^2
\]

and the commutation relation

\[
\left[ \mathbf{L}_z, \mathbf{L}_x \right] = i \mathbf{L}_y
\]

It will be useful to express \( \mathbf{L}_x \) and \( \mathbf{L}_y \) in terms of the electronic raising and lowering operators

\[
\mathbf{L}_x = \frac{i}{2} \left( \mathbf{L}_+ + \mathbf{L}_- \right) \\
\mathbf{L}_y = \frac{i}{2} \left( \mathbf{L}_- - \mathbf{L}_+ \right)
\]

The coupling terms of the right hand side of Eq. (2.5) are

\[
\frac{1}{2\mu} \left\{ 2 \langle \Phi_r | \frac{1}{J_R} \mathbf{L}_x | \Phi_r \rangle \left( \frac{1}{R} + \frac{1}{J_R} \right) + \langle \Phi_r | \frac{1}{J_R} \mathbf{L}_z | \Phi_r \rangle \frac{\omega}{J_R} \right\} \\
+ \frac{1}{R^2} \left[ \frac{2i \cos \omega}{\sin^2 \omega} \langle \Phi_r | \mathbf{L}_x | \Phi_r \rangle \frac{\omega}{J_R} + \frac{i}{\sin \omega} \langle \Phi_r | \mathbf{L}_z | \Phi_r \rangle \frac{\omega}{J_R} \\
+ \frac{i}{\sin \omega} \langle \Phi_r | \mathbf{L}_- | \Phi_r \rangle \frac{\omega}{J_R} + \langle \Phi_r | \mathbf{L}_+ | \Phi_r \rangle \frac{\omega}{J_R} - \langle \Phi_r | \mathbf{L}_+ | \Phi_r \rangle \frac{\omega}{J_R} \\
- \langle \Phi_r | \mathbf{L}_x^2 | \Phi_r \rangle + (1 - \cot^2 \omega) \langle \Phi_r | \mathbf{L}_x^2 | \Phi_r \rangle - \cot \omega \langle \Phi_r | \mathbf{L}_z | \Phi_r \rangle - \cot \omega \langle \Phi_r | \mathbf{L}_z | \Phi_r \rangle \right]\}
\]

(2.9)
where we have used the bra and ket notation to indicate integration over electronic coordinates.

A useful relation involving the radial coupling elements may be found by noting that the electronic wave-function must be normalized for all $R$.

\[
\frac{1}{\sqrt{R}} \langle \Phi_r | \Phi_{r'} \rangle = 0
\]
\[
= \langle \frac{1}{\sqrt{R}} \Phi_r | \Phi_{r'} \rangle + \langle \Phi_r | \frac{1}{\sqrt{R}} | \Phi_{r'} \rangle
\]
\[
= \langle \Phi_{r'} | \frac{1}{\sqrt{R}} | \Phi_r \rangle + \langle \Phi_r | \frac{1}{\sqrt{R}} | \Phi_{r'} \rangle
\]

which implies that

\[
\langle \Phi_{r'} | \frac{1}{\sqrt{R}} | \Phi_r \rangle = -\langle \Phi_r | \frac{1}{\sqrt{R}} | \Phi_{r'} \rangle .
\]

(2.10a)

If $\Gamma = \Gamma'$, we have that

\[
\langle \Phi_r | \frac{1}{\sqrt{R}} | \Phi_r \rangle = 0
\]

(2.10b)

We first discuss the diagonal terms of Eq. (2.9). Equation (2.10b) allows us to eliminate one of the radial coupling terms. The matrix elements containing the raising and lowering operators vanish. Thus a first-order adiabatic Schroedinger equation can be written
\[
\left\{ -\frac{i}{\hbar} \nabla_R^2 + E_F^*(R) - E - \frac{1}{2\mu} \left[ \langle \Phi_r | \frac{\partial^2}{\partial R^2} | \Phi_r \rangle \right] \\
+ \frac{1}{R^3} \left( \frac{2i \cos \omega}{\sin^2 \omega} \langle \Phi_r | L_z | \Phi_r \rangle \right) \frac{1}{j - j_0} - \langle \Phi_r | L^2 | \Phi_r \rangle \\
+ (1 - \cot^2 \omega) \langle \Phi_r | L^2_z | \Phi_r \rangle \right] \right\} F_r(R) = 0
\]

Except at the lowest energies, the nuclear wavefunctions will be changing much more rapidly than the electronic wavefunction so the ratio
\[
\frac{\langle \Phi_r | \frac{\partial^2}{\partial R^2} | \Phi_r \rangle}{\langle F_r | \nabla_R^2 | F_r \rangle}
\]
will be small and we will neglect this term. If the molecule is in a sigma electronic state, \( \langle \Phi_r | L_z | \Phi_r \rangle = \langle \Phi_r | L^2_z | \Phi_r \rangle = 0 \).

The molecular wavefunction is not an eigenfunction of \( L^2 \), the total electronic angular momentum. However, the magnitude of the matrix element containing this operator should be approximately equal to the sum of the \( L^2 \) operator acting on the separated atoms. Thus, this term introduces a correction to the centrifugal barrier. Since \( \langle \Phi_r | L^2 | \Phi_r \rangle \) will, in general, not be greater than 3 or 4, this correction will only be important at very low energies where the scattering is determined by only a few partial waves.

When the molecule is not in a sigma state, the operators containing \( L_z \) do not vanish. This complicates the problem by removing the spherical symmetry. A partial wave expansion will produce a set of coupled equations. The coupling elements should be small compared to the centrifugal...
gal terms at all but the lowest energies. If this coupling is included, then the remaining coupling terms should probably also be considered.
c. Angular Coupling

Inelastic collisions are described in terms of the coupling between different molecular electronic states. The terms of Eq. (2.9) which couple different electronic states are

$$\frac{i}{2\mu} \left\{ -2 \langle \Phi_r | \frac{1}{3} \sigma \cdot \mathbf{R} | \Phi_{r'} \rangle \left( \frac{1}{R} + \frac{1}{3R^2} \right) + \langle \Phi_r | \frac{1}{3} \sigma \cdot \mathbf{R} | \Phi_{r'} \rangle \right\}
+ \frac{i}{R^2} \left[ \frac{i}{\sin \omega} \langle \Phi_r | L_+ | \Phi_{r'} \rangle \frac{1}{3} \omega + \frac{i}{\sin \omega} \langle \Phi_r | L_- | \Phi_{r'} \rangle \frac{1}{3} \omega + \langle \Phi_r | L_0 | \Phi_{r'} \rangle \frac{1}{3} \omega - \langle \Phi_r | L^2 | \Phi_{r'} \rangle \right]
- \cot \omega \langle \Phi_r | L_+ L_+ | \Phi_{r'} \rangle - \cot \omega \langle \Phi_r | L_0 L_- | \Phi_{r'} \rangle \right\}$$

We will consider first the angular coupling.

The terms

$$-\frac{i}{2\mu R^2} \left[ \langle \Phi_r | \sigma \cdot \mathbf{R} | \Phi_{r'} \rangle + \cot \omega \langle \Phi_r | L_z L_+ | \Phi_{r'} \rangle
+ \cot \omega \langle \Phi_r | L_z L_- | \Phi_{r'} \rangle \right]$$

are static coupling terms. These do not depend on the relative velocity between the two particles. The remaining angular coupling terms do depend on the velocity through the nuclear angular momentum operator and are called dynamic coupling terms.

For a given incident energy, Bates' describes two regions of strong angular coupling. The first is at large
R. The large nuclear angular momentum in this region can make the dynamic coupling terms large. Several electronic states of different $\Lambda$ may approach the same separated atomic states, so that the energy separation between molecular energy levels will be small. These large dynamic angular coupling terms may cause transitions between these levels. The physical picture for these distant collisions, however, is one of weak coupling. If in a collision the atoms do not closely approach each other, the electron charge clouds are not strongly coupled to the nuclear motion and tend not to rotate in space. The probability of an inelastic transition for these distant collisions should be small. The present formulation of the problem assumes this rotation does occur. Hence, in this case, the strong coupling represents a correction to a formulation which is not particularly appropriate for distant collisions. Such collisions will not be considered further.

Bates' second region of strong coupling is small R. Bates has calculated inelastic cross-sections for the scattering of protons and hydrogen atoms and uses that example to guide his analysis. The present work is concerned with the interaction of excited and ground state helium atoms. The angular coupling terms can be important at small R for this system but for different reasons. The excited states of He$_2$ will be described in more detail in later sections of this thesis. To understand the possibility of strong angular coupling among these states at
small $R$ we need only to know that these excited states are Rydberg states which are characterized by a nearly hydrogenic excited orbital surrounding small core orbitals. These Rydberg orbitals may be described by the hydrogenic quantum numbers $n \ell \lambda$ where the internuclear axis is the axis of quantization. The Born-Oppenheimer potential energy curves for states with the same $n$ and $\ell$ with $\ell > 1$ are nearly parallel in the vicinity of the equilibrium internuclear separation and are separated by energies of the order of $10^{-3}$ a.u. and, in some cases, cross each other. If we assume that the excited orbitals are pure hydrogenic states and that the contribution to the coupling from the core orbitals is negligible, it is easily shown that the non-vanishing coupling matrix elements of the form $$\frac{\langle \frac{\mathbf{L}}{2} | \mathbf{\hat{L}} \pm | \frac{\mathbf{L}}{2} \rangle}{2\mu R^2} \approx 10^{-4} \text{ a.u.}$$ The magnitude of the angular derivative terms acting on the nuclear wavefunction is roughly proportional to the nuclear angular momentum. Thus the coupling terms will be comparable to the separation of the Born-Oppenheimer energies for typically 1.5 a.u. Since the nuclear wavefunctions $F_\Gamma(R)$ for states of different $\lambda$ should be quite similar in this region, we expect coupling terms of this magnitude to rather strongly mix these states. For a given $n$ and $\ell$, there are $2\ell+1$ coupled equations so that a more detailed mathematical analysis is required for more quantitative predictions.
d. Radial Coupling

Much of this section and the following one is based on the work of F. T. Smith\textsuperscript{10}. The remaining coupling terms of Eq. (2.9)

\[ \frac{1}{2\mu} \left\{ 2 \langle \Phi_r | \frac{1}{2 \Delta R} | \Phi_{r'} \rangle \left( \frac{1}{R} + \frac{1}{\Delta R} \right) + \langle \Phi_r | \frac{1}{2 R^2} | \Phi_{r'} \rangle \right\} \]

are the radial coupling terms. These matrix elements are non-vanishing only between electronic states of the same spin multiplicity and symmetry. Thus the radial coupling terms couple only non-crossing states.

Usually the electronic wavefunction does not change much for small variations of R so that these terms are properly neglected. Occasionally, however, the electronic wavefunctions may change rapidly over a small range of R. In such a region, the separation between the Born-Oppenheimer potential curves may first decrease and then increase as R is increased. Such behavior is known as a pseudocrossing or avoided crossing of potential energy curves. The source of this behavior and its relation to the radial coupling matrix element is examined in a two-state model given below. This model will be useful in our discussions of avoided crossings in potential curves computed with multi-configuration atomic wavefunctions.

Let \( \Phi_1(\mathbf{r}_e, R) \) and \( \Phi_2(\mathbf{r}_e, R) \) be two normalized orthogonal basis functions. Diagonalization of the electronic Hamiltonian in this basis results in the approximate adiabatic functions
\[ \psi_a(\vec{r}, R) = -\sin \alpha(R) \psi_1(\vec{r}, R) + \cos \alpha(R) \psi_2(\vec{r}, R) \]  \hspace{1cm} (2.11a) \\

\[ \psi_b(\vec{r}, R) = \cos \alpha(R) \psi_1(\vec{r}, R) + \sin \alpha(R) \psi_2(\vec{r}, R) \]  \hspace{1cm} (2.11b) \\

where the condition has been imposed that \( \psi_a \) and \( \psi_b \) must be normalized and orthogonal. We also assume that \( \langle \psi_1 | \frac{\partial}{\partial R} | \psi_2 \rangle = 0 \).

The radial coupling matrix \( P \) is defined by

\[ P_{ij} = \langle u_i | \frac{1}{i R} | u_j \rangle \]  \hspace{1cm} (2.12) \\

where the \( \{u_i\} \) may be any set of approximate molecular wavefunctions. If the \( \{u_i\} \) are real and orthonormal, Eqs. (2.10) show that \( P \) is antisymmetric.

The result of the evaluation of \( P \) in the basis \( \psi_a, \psi_b \) of the two-state case is

\[ P^a = \frac{d \alpha(R)}{d R} \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \]  \hspace{1cm} (2.13) \\

The matrix elements of the operator \( \frac{\partial^2}{\partial R^2} \) in a complete, orthonormal basis can be expressed in terms of the elements of \( P \) in the same basis, viz.
\[
\langle \psi_a | \frac{\partial^2}{\partial R^2} | \psi_b \rangle = \langle \psi_a | \frac{1}{\partial R} \left( \sum_i \langle \psi_i | \frac{1}{\partial R} | \psi_b \rangle \right) \langle \psi_i | \frac{1}{\partial R} | \psi_b \rangle \rangle \\
= \sum_i \left[ \langle \psi_a | \frac{1}{\partial R} | \psi_i \rangle \langle \psi_i | \frac{1}{\partial R} | \psi_b \rangle + \langle \psi_a | \psi_i \rangle \frac{1}{\partial R} (\langle \psi_i | \frac{1}{\partial R} | \psi_b \rangle) \right] \\
= \left( \sum_i P_{ai} P_{ib} \right) + \frac{1}{\partial R} P_{ab}
\]  

(2.14)

The matrix $B$ is constructed from the elements $\langle u_i | \frac{\partial^2}{\partial R^2} | u_j \rangle$. If the set $\{u_i\}$ is complete and orthonormal, then, by Eq. (2.14),

\[
B = P \cdot P + \frac{1}{\partial R} P
\]

For the two-state case, the matrix $B$ is

\[
B^a = \begin{bmatrix}
-\left( \frac{d\alpha}{dR} \right)^2 & \frac{d^2\alpha}{dR^2} \\
-\frac{d^2\alpha}{dR^2} & -(\frac{d\alpha}{dR})^2
\end{bmatrix}
\]

The nuclear motion equations in the adiabatic representation are

\[
\left( -\frac{1}{2\mu} \nabla_R^2 + E_a(R) - E \right) F_a(\vec{R})
\]

\[
= \frac{1}{2\mu} \left\{ \left[ 2 \frac{d\alpha}{dR} \left( \frac{1}{\partial R} + \frac{1}{R} \right) + \frac{d^2\alpha}{dR^2} \right] F_a(\vec{R}) - \left( \frac{d\alpha}{dR} \right)^2 F_a(\vec{R}) \right\}
\]

(2.15a)

and
\begin{equation}
\left(-\frac{1}{2\mu}\nabla_R^2 + E_b(R) - E\right) F_b(R) = \frac{1}{2\mu} \left[ -2 \frac{d\alpha}{dR} \left( \frac{1}{R} + \frac{1}{R^2} \right) \right] F_a(R) - \frac{d^2\alpha}{dR^2} F_b(R) \right) 
\end{equation}

(2.15b)

Avoided crossings may be easily understood in terms of this two-state model. Let $H_{ij} = \langle \phi_j | H_{el} | \phi_i \rangle$ be the hamiltonian matrix elements in the original representation. The adiabatic potential curves are the eigenvalues of the matrix equation

$$H \psi = E \psi$$

The eigenvalues are

$$E_{a,b} = \frac{H_{22} + H_{11}}{2} \pm \frac{1}{2} \sqrt{(H_{22} - H_{11})^2 + 4 H_{12}^2}$$

The orthonormal eigenvectors $\psi_a$ and $\psi_b$ may be expressed, as in Eq. (2.11) where $\alpha(R)$ is given most simply as

$$\tan 2 \alpha(R) = \frac{2 H_{12}}{H_{22} - H_{11}}$$

(2.16)

Suppose $H_{22} > H_{11}$ for $R > R_x$, $H_{22} < H_{11}$ for $R < R_x$ and $\frac{H_{12}}{|H_{22} - H_{11}|} << 1$ for $|R - R_x| >> \Delta R$. For large $R$, $\alpha(R) \approx 0$, $\psi_a = \phi_2$, $\psi_b = \phi_1$, $E_a = H_{22}$, $E_b = H_{11}$ and $\frac{d\alpha}{dR} = 0$ so that there is no radial coupling in this limit. As $R$ approaches $R_x$, the electronic wavefunctions become a mixture of $\phi_1$ and
\[ \varphi_2, \text{ the adiabatic potential curves diverge from the potential curves } H_{11} \text{ and } H_{22} \text{ of the basis functions and the radial coupling elements increase. For } R = R_x, \alpha(R) = \pi/4 \text{ so that the electronic wavefunctions are equal mixtures of } \varphi_1 \text{ and } \varphi_2. \] 

The separation of the adiabatic potential curves at \( R_x \) is \( 2H_{12} \). As \( R \) becomes smaller, \( \alpha(R) \) approaches \( \pi/2 \), \( \psi_a = \varphi_1, \psi_b = \varphi_2, E_a = H_{11}, E_b = H_{22} \), and \( \frac{d\alpha(R)}{dR} = 0 \). Thus, the nuclear wavefunctions are again uncoupled in the small \( R \) limit.

The comments above suggest that the magnitude of the radial coupling depends upon how quickly the ratio \( H_{12}/(H_{22} - H_{11}) \) changes as \( R \) approaches \( R_x \). Following M. Oppenheimer\textsuperscript{11}, we may more clearly examine this dependence by expressing \( \frac{d\alpha(R)}{dR} \) in terms of the matrix elements \( H_{ij} \). Beginning with Eq. (2.16), we obtain

\[ \frac{d\alpha(R)}{dR} = \frac{(H_{22} - H_{11}) \frac{d}{dR} H_{12} - H_{12} \frac{d}{dR} (H_{22} - H_{11})}{(H_{22} - H_{11})^2 + 4 H_{12}^2} \]  

(2.17)

In particular, the value of the coupling matrix element at the crossing is

\[ \left. \frac{d\alpha(R)}{dR} \right|_{R_x} = \left. \frac{-\frac{d}{dR} (H_{22} - H_{11})}{4 H_{12}} \right|_{R_x} \]  

(2.18)

If, in the vicinity of the crossing point, \( H_{12} \) and \( (H_{22} - H_{11}) \) are only slowly varying functions, we may use the approximations
\[ H_{12}(R) = H_{12}(R_x) \]

and

\[ H_{22}(R) - H_{11}(R) = \frac{d}{d R} \left( H_{22}(R) - H_{11}(R) \right) \bigg|_{R_x} (R - R_x) \]

\[ = \Delta H (R - R_x) \]

to obtain an expression for the width of the coupling region.

With these approximations, we obtain

\[ \frac{d \alpha(R)}{d R} \approx - \frac{H_{12} \Delta H}{\Delta H^2 (R - R_x)^2 + 4 H_{12}^2} \]  \hspace{1cm} (2.19)

Thus \( \frac{d \alpha(R)}{d R} \) has a Lorentzian shape. The full width at half maximum is

\[ \Delta R = \left| \frac{4H_{12}}{\Delta H} \right| = \left| \frac{d \alpha(R_x)}{d R} \right|^{-1} \]  \hspace{1cm} (2.20)

The breakdown of the adiabatic Born-Oppenheimer approximation due to radial coupling may be characterized by the magnitude of \( H_{12} \) and the ratio \( \Delta H/4H_{12} \). Two limiting cases are of interest. In the first case, \( H_{12} \) is large and \( H_{11} \) and \( H_{22} \) are nearly parallel so that the ratio \( \Delta H/4H_{12} \) is small. Then by Eq. (2.18), the radial coupling matrix elements will tend to be small and the coupling region wide. The separation between the adiabatic potential curves is large since \( H_{12} \) is large. Thus the wavelengths of the nuclear wavefunctions are rather different in the coupling region. The adiabatic nuclear wavefunctions inter-
fere destructively over the rather wide coupling region so that the inelastic transition probabilities should be small.

In the second case, let $H_{12}$ be small and the ratio $\Delta H/4H_{12}$ be large. Then the coupling matrix element is large and localized to the region about $R_x$. Since the adiabatic potentials closely approach each other, the effective wave-lengths of the nuclear wavefunctions near $R_x$ are comparable. For some nuclear energies, these wavefunctions should interfere constructively in the vicinity of $R_x$ so that the adiabatic nuclear states are strongly coupled. The nuclear trajectories would seem better described by the crossing potentials $H_{11}(R)$ and $H_{22}(R)$ than the noncrossing ones, $E_a(R)$ and $E_b(R)$.

Although correct if all coupling terms are evaluated, the formulation of the collision problem in terms of adiabatic states does not appear to be physically well motivated in the case of strongly coupled adiabatic states. If approximations are made in the solution of the electronic and nuclear motion problems, a representation of the electronic states for which the nuclear motion equations are weakly coupled is desirable.
e. The Radial Diabatic Representation

The electronic functions used to derive the coupled nuclear motion equations were complete and orthonormal and diagonalized the electronic hamiltonian. These three requirements specified a unique representation of the electronic functions. A different set of coupled nuclear motion equations can be obtained from different electronic representations. O'Malley\textsuperscript{12} has developed a formalism which applies to collision problems in which a discrete electronic state develops into a resonance state at small $R$. The representation used is based on partitions of the full electronic Hilbert space. These ideas are interesting but O'Malley's formalism does not explicitly include radial and angular coupling. This should lead to some fundamental uncertainty in any calculations based on this formalism.

If a collision problem involves only discrete molecular states, the formalism developed by Smith should be considered. This approach makes use of the coupling elements to define a more appropriate electronic representation.

If there is no change of electronic state during a collision, the collision occurs adiabatically. The electronic states are usually defined in the Born-Oppenheimer approximation. Thus Born-Oppenheimer potential curves determine the trajectories of two colliding particles in the quasi-static or adiabatic limit. In the discussion of the coupling elements given above, we saw that the nuclear
motion equations may be strongly coupled over a small region of $R$ and that the potential determining the most probable nuclear motion may correspond to different adiabatic states for large and small $R$. A complete, orthonormal set of electronic functions which has this change of adiabatic states built into it or, more generally, which can be represented as a linear combination of adiabatic states, is properly called a diabatic representation. Smith's formalism provides a prescription for the construction of these diabatic states.

Any complete orthonormal representation may be related to any other by a unitary transformation given by a matrix $C(R)$. In particular for the two-state case discussed above, the transformation between the original representation $(\psi_1, \psi_2)$ and the adiabatic representation $(\psi_a, \psi_b)$ is just

$$C^a(\alpha(R)) = \begin{bmatrix} -\sin \alpha(R) & \cos \alpha(R) \\ \cos \alpha(R) & \sin \alpha(R) \end{bmatrix}$$

The Hamiltonian matrix in the original representation is diagonalized by this transformation. Different diabatic transformations are defined by the matrices which they diagonalize. Smith has suggested that a useful diabatic representation is one in which the matrix $P$, defined in Eq. (2.12) is diagonalized. As we now show, a transformation may always be found for which $P$ vanishes. Let $\{\psi^a_1\}$
be the set of electronic basis states for the diabatic representation and \( \{ u_i \} \) be the original basis.

\[
| \Phi_i^d \rangle = \sum_j \langle u_i | \Phi_i^d \rangle | u_j \rangle \\
= \sum_j c_{ij} | u_j \rangle
\]

Then an element of \( P \) in the diabatic basis is

\[
P_{ij}^d = \langle \Phi_i^d | \frac{1}{\sqrt{\mathcal{R}}} | \Phi_j^d \rangle \\
= \langle \Phi_i^d | \frac{1}{\sqrt{\mathcal{R}}} (\sum_k | u_k \rangle \langle u_k | \Phi_j^d \rangle) \\
= \sum_k \langle \Phi_i^d | \frac{1}{\sqrt{\mathcal{R}}} | u_k \rangle \langle u_k | \Phi_j^d \rangle + \sum_k \langle \Phi_i^d | u_k \rangle \frac{1}{\sqrt{\mathcal{R}}} (\langle u_k | \Phi_j^d \rangle) \\
= \sum_k \langle \Phi_i^d | u_k \rangle \frac{1}{\sqrt{\mathcal{R}}} \langle u_k | \Phi_j^d \rangle c_{jk} + \sum_k c_{jk} \langle \Phi_i^d | \frac{1}{\sqrt{\mathcal{R}}} (\frac{1}{\sqrt{\mathcal{R}}} c_{jk}) \\
= \sum_{k,l} \langle \Phi_i^d | u_l \rangle \langle u_l | \frac{1}{\sqrt{\mathcal{R}}} | u_k \rangle c_{jk} + \sum_k c_{jk} \frac{1}{\sqrt{\mathcal{R}}} c_{jk} \\
= \sum_{k,l} c_{lk}^\dagger P_{lk} c_{jk} + \sum_k c_{jk} \frac{1}{\sqrt{\mathcal{R}}} c_{jk} \\
= \sum_{k,j} c_{ij} P_{kj} c_{jk} + \sum_k c_{jk} \frac{1}{\sqrt{\mathcal{R}}} c_{jk}
\]

In matrix form, this is

\[
P^d = C P C^\dagger + C \frac{1}{\mathcal{R}} C^\dagger
\]
The matrix equation for the unitary transformation which determines the diabatic representation in which \( P \) vanishes is

\[
P \frac{C^+}{C^+} + \frac{1}{\delta R} C^+ = C^+ P^d = 0
\]  

(2.21)

The boundary condition usually is that \( C \) become identical to the transformation from the basis \( \{ u_i \} \) to the adiabatic representation as \( R \to \infty \).

The two-state case illustrates this. We start in the adiabatic representation using the orthonormal eigenfunctions \( \psi_a \) and \( \psi_b \) as the basis. The radial coupling matrix in this representation, \( P^a \), is given in Eq. (2.13).

The unitary transformation which satisfies Eq. (2.21) is

\[
C^+ (R) = \begin{bmatrix}
-\sin \alpha(R) & \cos \alpha(R) \\
\cos \alpha(R) & \sin \alpha(R)
\end{bmatrix}
\]

This is easily understood for the two-state case since the result of \( C^+ \) operating on the adiabatic states \( (\psi_a \psi_b) \) is the original basis \( (\psi_1 \psi_2) \). We assumed that the radial coupling elements between \( \psi_1 \) and \( \psi_2 \) vanished so that these are, in fact, diabatic states. The same procedure is followed in the general case. A solution to Eq. (2.21) is found and that solution used to generate the diabatic basis from the original basis.

The nuclear motion coupled equations are derived in the diabatic basis as in the adiabatic basis. The complete
wavefunction is expanded as in Eq. (2.4) using the complete
diabatic basis
\[ \Psi(r_e, R) = \sum_{\Gamma} \mathcal{G}_{\Gamma}(R) \Phi_{\Gamma}^d (r_e, R) \]

The nuclear-motion equations are obtained by multiplying
by a particular \( \mathcal{E}^d \Gamma(r_e, R) \) and integrating over all electron
coordinates. The equation
\[ \sum_{\Gamma} \int d^3 r_e \Phi_{\Gamma} (r_e, R) \left[ \frac{1}{2 \mu} \nabla^2 + H_d - E \right] \Phi_{\Gamma}^d (r_e, R) \mathcal{G}_{\Gamma}(R) = 0 \]
may be written
\[ \left[ \frac{1}{2 \mu} \nabla^2 + H_{\Gamma} (R) - E \right] \mathcal{G}_{\Gamma}(R) \]
\[ = \frac{1}{\mu} \sum_{\Gamma} \nabla_{R} \mathcal{G}_{\Gamma}(R) \cdot \int d^3 r_e \Phi_{\Gamma} (r_e, R) \nabla_{R} \Phi_{\Gamma}^d (r_e, R) \]
\[ + \frac{1}{2 \mu} \sum_{\Gamma} \mathcal{G}_{\Gamma}(R) \int d^3 r_e \Phi_{\Gamma} (r_e, R) \nabla^2_{R} \Phi_{\Gamma}^d (r_e, R) \]
\[ + \sum_{\Gamma} \mathcal{G}_{\Gamma}(R) \int d^3 r_e \Phi_{\Gamma} (r_e, R) H_d \Phi_{\Gamma}^d (r_e, R) \]
(2.22)
The angular coupling terms on the right hand side of this
equation have the same form as the angular coupling terms
derived using the adiabatic basis. Since we are interested
only in the radial and electronic coupling in this dis-
cussion, these angular terms will be neglected. The radial
coupling terms vanish since all involve \( F \) and this matrix
vanishes by construction of the diabatic states. The only
remaining coupling is that contained in the last sum of
Eq. (2.22). These are the electronic coupling terms. They couple only states of the same spin multiplicity and symmetry.

For the two-state case discussed above, the diabatic nuclear motion equations are

$$\left[ -\frac{i}{2\mu} \nabla^2_R + H_{11}(R) - E \right] G_1(\vec{R}) = H_{12}(R) G_2(\vec{R}) \tag{2.23a}$$

$$\left[ -\frac{i}{2\mu} \nabla^2_R + H_{22}(R) - E \right] G_2(\vec{R}) = H_{21}(R) G_1(\vec{R}) \tag{2.23b}$$

One advantage of the diabatic coupled equations as compared to the adiabatic coupled equations is the absence of the radial derivative in the coupling terms. These two-state diabatic coupled equations will be the starting point for an approximate solution of the inelastic collision problem.

In the discussion following Eq. (2.20), we suggested that the adiabatic coupled equations are not always the best zero-order approximations for the inelastic transition problem. We implied that the formulation of the coupled equations in terms of diabatic states is superior when the adiabatic coupling is large for then the diabatic coupling might be small. The relative strength of the coupling may be approximately expressed by a simple ratio for the two state case.
The nuclear radial momentum operator is
\[ p_R = \left( \frac{d}{dR} + \frac{1}{R} \right) \frac{1}{13}. \]
We may approximate the factor \( \frac{1}{13} \left( \frac{d}{dR} + \frac{1}{R} \right) \) in the adiabatic coupled Eqs. (2.15) by the radial nuclear velocity \( v_R \). The magnitude of the factor \( \frac{d\alpha(R)}{dR} \) has been evaluated at the crossing in Eq. (2.18). Thus the ratio of the adiabatic to diabatic coupling at \( R_x \) is

\[
\lambda = \frac{d\alpha(R)}{dR} \frac{v_R}{H_{12}(R_x)}
\]

\[
= \frac{v_R(R_x) \left| \frac{d}{dR} \left( H_{22} - H_{11} \right) \right|}{4H_{12}^2}
\]

\[
= \frac{v_R(R_x)}{H_{12} \Delta R}
\]

(2.24)

where \( \Delta R \) is the width of the coupling region defined in Eq. (2.20). A small value of \( \lambda \) favors the adiabatic formulation, a large value the diabatic. Thus the adiabatic representation should be used when the separation of the adiabatic states is large, the crossing region wide and the relative heavy particle velocity small. In the opposite limit, the diabatic equations are appropriate. For a given incident energy, the nuclear radial velocity will decrease as the orbital angular momentum increases. It might be expected that as the angular momentum approaches the largest classically allowed angular momenta, the adiabatic limit is reached. This criterion will be used when we consider inelastic collisions in later sections.
f. Solutions of the Electronic Schroedinger Equation

Approximate eigenvalues and eigenfunctions of the adiabatic electronic Schroedinger equation (2.3) may be found by use of the Rayleigh-Ritz variational principle

\[ E_{r, \text{exact}} \leq \frac{\langle \Phi_r | H_e | \Phi_r \rangle}{\langle \Phi_r | \Phi_r \rangle} \]

where \( \Phi_r(\vec{r}_e, R) \) is a square integrable function containing a set of continuously variable parameters\textsuperscript{14}. When the trial function is of the form

\[ \Phi_r = \sum_i c_i \chi_i(\alpha; \vec{r}_e, R) \]

(2.25)

the use of the variational principle is called the configuration interaction (CI) method\textsuperscript{15}. Each \( \chi_j(\vec{r}_e, R) \) is a sum of \( N \) electron Slater determinants chosen to be eigenfunctions of the symmetry operators of the molecule and of spin and is known as a configuration. The \( c_j \) are the linear variational parameters and the \( \alpha_j \) are nonlinear variational parameters (orbital exponents) contained in the elementary basis functions which are used to construct the Slater determinants. The determination of the linear variational parameters yields the usual secular equation for the eigenvalues and eigenfunctions

\[ (\mathbf{H} - E \mathbf{S}) \mathbf{c} = \mathbf{0} \]

where \( \mathbf{H} \) is the electronic Hamiltonian matrix.
\[ H_{ij} = \langle \chi_i | H_{el} | \chi_j \rangle \]

and \( S \) is the overlap matrix

\[ S_{ij} = \langle \chi_i | \chi_j \rangle. \quad (2.26) \]

MacDonald\textsuperscript{16} has shown that the \( n^{\text{th}} \) root of the secular equation is a rigorous upper bound to the \( n^{\text{th}} \) true eigenvalue of the symmetry represented by the basis functions, where the roots and eigenvalues are labeled in order of increasing energy. This justifies our use of the CI method to calculate manifolds of excited states. When the eigenvalues and eigenvectors of only a single state are desired, the orbital exponents may be optimized by choosing a set which minimizes the root corresponding to the state of interest. This procedure will frequently cause the remaining roots to first decrease and then increase as the root of interest decreases with parameter variation. The elementary basis functions used in these calculations were the Slater-type orbitals (STO) centered on either nucleus A or B

\[ u_a^{nlm}(r_a) = \kappa_n r_a^{n-1} \exp(-\alpha r_a) Y_L^m(\theta_a, \phi_a) \]

where \( r_a, \theta_a, \) and \( \phi_a \) are the electronic coordinates with respect to nucleus \( a, \) \( N, L, \) and \( M \) are the quantum numbers characterizing the orbital, \( Y_L^M(\theta, \phi) \) is a normalized spherical harmonic, \( \alpha \) is the orbital exponent, and
\[ K_N = \left[ \frac{(2\alpha)^{2N+1}}{(2N)!} \right]^{1/2} \]

is chosen so that the orbitals are normalized.

The computations were performed using the University of Texas Molecular Physics Group's diatomic molecule program VARY as modified by Dr. Bobby Junker of the University of Georgia to run on IBM 360 and 370 series computers. The steps in the computation of molecular energies and functions \(^{15}\) and the details of VARY \(^{17,18}\) are available elsewhere and will be repeated here only as necessary to describe the calculations.

The use of VARY in the calculation of excited states of \(\text{He}_2\) reported here involved three steps: (i) the selection of the types of configurations to be used; (ii) the choice of specific orbitals, and (iii) the selection of orbital exponents for those orbitals. The construction of the configurations from the orbitals and of the terms in the wavefunction from the configurations is described in references 17 and 18.

Single configurations used in the calculation of molecular wavefunctions are constructed by either the molecular orbital (MO) or valence bond (VB) methods. The MO method frequently provides a better description of the molecule near the equilibrium separation while the VB method can more easily predict dissociation products \(^{19}\). If all possible configurations are constructed from a given
set of atomic orbitals (AO) by both methods and full CI calculations are performed, the methods are equivalent. Configurations may be constructed for use in VARY from either point of view. In this thesis the VB method was used to construct the configurations used to calculate the potential curves and a modified LCAO-MO method was used to investigate the contribution of different cores \( \text{He}_2^+ \) states to the wavefunction near the equilibrium separation.

The primary goal of the molecular calculations reported here is to produce a set of potential curves suitable for examining such features as avoided crossings. The significance of these features in a theoretical description of inelastic collisions has been discussed. Clearly all states of interest must be represented equally well. We have represented each separated atom state by a single covalent VB configuration with orbital exponents generally corresponding to those calculated for the separated atoms. These VB configurations have the form 

\[ |n_l A \bar{1}S_A A \bar{1}S_B B \bar{1}S_B \pm |n_l B \bar{1}S_B B \bar{1}S_B A \bar{1}S_A A \bar{1}S_A \].

Here \( n \) is a STO where \( N = n \), \( L = l \), and where the orbital exponent \( \alpha \) is determined from variational calculations on the separated atoms as described below. The value of \( \alpha \) is usually close to the hydrogenic value of \( 1/n \). The calculations of \( ^3\Sigma_u^+ \) and \( ^3\Pi_u \) states included ionic VB configurations. These configurations have the form 

\[ |1S_A \bar{1}S_B A \bar{1}S_B \pm |1S_B \bar{1}S_A B \bar{1}S_A |. \]

One ionic configuration was included for each covalent
configuration and was composed of the same orbitals (i.e. the same n, ℓ, and α) as the corresponding covalent configurations. We shall refer to covalent and ionic configurations constructed from the same orbitals as ionic-covalent pairs. The inclusion of ionic configurations improved some of the eigenenergies by several thousandths of an ev.

The configurations of the type chosen are constructed from a set of orbitals. As will be seen, the total molecular energy may be considered as a sum of terms representing qualitatively different contributions. Particular orbitals are chosen to give the best approximate energy to a particular term in this sum. The Molecular Physics Group at the University of Texas has performed a number of CI calculations on the lowest states of sigma and pi symmetry of $\text{He}_2$ (see references in 21). The most accurate of these to date are the calculation of the $\Pi^1_u$ and $\Pi^3_u$ states by Gupta and Matsen$^{21}$ using a 49-term wavefunction. They have further improved their potential curves by use of the semi-empirical method of adjustment given by Klein, Greenawalt, and Matsen$^{22}$. We have used a 14-term VB wavefunction including ionic-covalent pairs to compute the three lowest states of the $\Pi_u$ system. The lowest lying potential curve of this calculation is compared with the ab initio and adjusted curves of Gupta and Matsen in Table 1. For these intermediate internuclear separations, the present calculation provides a potential
<table>
<thead>
<tr>
<th>R</th>
<th>Present Calculation</th>
<th>Gupta &amp; Matsen ab initio</th>
<th>Ab initio-Present Calculation</th>
<th>Gupta &amp; Matsen Adjusted</th>
<th>Adjusted-Present Calculation</th>
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</thead>
<tbody>
<tr>
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<td>-.05853</td>
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</table>
curve which differs from the adjusted curve of Gupta and Matsen by approximately a constant amount. It should be noted that this state contains a large hump due to an avoided crossing between the 2p and 3d single configuration wavefunctions. The paper of Gupta and Matsen contains further examples which indicate that potentials calculated from wavefunctions using a rather small number of terms can be quantitatively correct to within a constant for intermediate internuclear separations.

The origin of the discrepancy between Gupta and Matsen's potential and that of the present calculation is understood by noting that the excited states of \( \text{He}_2 \) are Rydberg states. These are characterized by a single electron in an orbital of large radius surrounding a small core composed of the remaining three electrons in tightly bound orbitals. For most states there should be little penetration of the core by the excited orbital so that the energies of the excited electrons are determined primarily by the electrostatic potential of the core. The nature of these states is discussed in more detail in the following section. This brief discussion, however, motivates our choice of the basis set. The excited orbitals of the molecule are formed by mixing a number of different excited orbitals of the separated atoms. This flexibility allows these orbitals to be determined well. The core is formed from the same orbitals in each case. This essentially single configuration representation of the
core ignores, in particular, the core correlation energy which should be large. It does seem, however, to adequately represent the electrostatic charge distribution. Thus most of the discrepancy between the energies calculated by Gupta and Matsen and those of the present calculation is most likely to be due to our neglect of the core correlation energy. Table 2 contains a comparison of two calculations of the lowest $^2\Sigma_u^+$ state of He$_2^+$, the core for the bound states of He$_2$. The first is a single configuration VB calculation using the same orbitals as were used in our He$_2$ calculations. The second is the calculation of Reagan, Browne, and Matsen$^{22}$ who used a 26-term wavefunction. The difference between these two potentials is very nearly a constant, and approximately the same as that between the $^3\Pi_u$ potentials. This would seem to indicate that the source of the difference is the poor representation of the He$_2^+$ core in both our calculations. It is clear from Table 2 that this correlation energy varies rather slowly for intermediate internuclear separations and does not affect the shape of the calculated curves. Since these are Rydberg states, the positions of the minima in the potential energy and hence the equilibrium separation is determined largely by the core energies. Hence the equilibrium separation and the dissociation energies are probably not well represented in our calculations. This is also indicated by the rapid increase in the discrepancy between the two ion potential calculations for R less than
Table 2

$\text{He}_2^+ (2^2\Sigma_u^+)$: Comparison of Potentials Calculated from a Single Term and a 26-Term Wavefunction.

<table>
<thead>
<tr>
<th>$R$</th>
<th>Single Term</th>
<th>26-Term</th>
<th>Difference</th>
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</thead>
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<tr>
<td>10.0</td>
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</table>
2.5 a.u. Furthermore, several states of $\Sigma$ symmetry are
found in our calculations to possess small "nonobligatory"
humps at large R. The present comparison does not provide
assurance that these features are accurately computed
using the type of configurations we have described. As
will be discussed in the following sections, these small
humps are thought to be caused by the exchange interaction
of the excited orbital and the closed shell ground state
helium atom at large internuclear separations. The per-
turbation of the excited state is of the order of .003 a.u.
A wavefunction containing more terms for the ground state
helium atom should probably be used to more accurately
compute the energy of these humps. This was the method
followed by the U.T. Molecular Physics Group in their
investigation\textsuperscript{24} of the small hump which appears in the
lowest $^{3}\Sigma_{u}^{+}$ state.

Once the configurations and orbitals have been chosen,
the orbital exponents must be selected. There is no
general procedure for choosing the optional values of the
orbital exponents to be used in the STO\textsuperscript{15}. In VARY, one
may specify a root to be minimized, the orbital exponents
to be varied, and the sequence in which they are to be
optimized. For each set of orbital exponents in the
sequence, the program searches for a group of three ex-
ponents which bracket the minimum energy of the root
specified and then uses quadratic interpolation to find
values of the orbital exponents corresponding to the
minimum energy. There are several disadvantages to using the procedure in the present calculation. (a) It is very costly in computer time. (b) It must be used with restraint when accurate energies for several states are to be calculated from the same orbitals. The behavior of the roots of the secular equation as the orbital exponents are varied depends on the orbitals, the initial values of the exponents and the sequence in which the exponents are varied. In a number of cases, we have noticed that most of the roots will be lowered as the first adjustments of the orbital exponents are made. Continued minimization of one root, however, eventually causes the remaining roots to significantly increase. Thus, exponent optimization, if carried to completion, seems to produce a possibly good value only for the root minimized while the remaining roots are manifestly inaccurate. (c) The analysis of features such as avoided crossings in determining scattering information is simplified if only the mixing of static configurations need be considered.

For these reasons, most of the potential curves were calculated using the same orbital exponents for all internuclear separations. These orbital exponents were found by CI calculations on the lower excited states of the singlet and triplet S, P, D and F series of the separated atoms. The orbital exponents were optimized with respect to the root corresponding to the n = 3 level (n = 4 for the F series). A set of orbital exponents
which provided good approximations to several of the lower states in each series was chosen. These exponents, the energies calculated from them, and the spectroscopic energies\textsuperscript{25} of these states are given in Tables 3 and 4. The calculated energies of all $n = 2$ level states except the $3^1S$ are within .001 a.u. of the spectroscopic values. The spatial wavefunctions for the singlet system are symmetric under electron exchange and the overlap between the core and excited orbitals is greatest for $S$ states. Thus the correlation energy should be greatest for $1S$ states\textsuperscript{26} and a more elaborate variational wavefunction is required. Most of the molecular calculations, however, were performed on the triplet system so that more accurate singlet wavefunctions were not developed. The use of such atom-optimized basis sets has been discussed by Schaefer\textsuperscript{27}.\n
### Table 3

**Triplet Series**

<table>
<thead>
<tr>
<th>State</th>
<th>Orbital Exponent</th>
<th>Calculated Energy</th>
<th>Spectroscopic Energy</th>
<th>Difference</th>
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Table 4

Singlet Series

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B. Qualitative Behavior of the Excited States of He₂

a. Rydberg States of the Stable He₂ Molecule

The electronic eigenfunctions and eigenenergies of He₂ in the Born-Oppenheimer approximation are obtained as solutions to 2.3. For He₂, this equation is

\[-\frac{1}{2} \sum_{i=1}^{n} \nabla_i^2 - \sum_{i=1}^{n} \frac{2}{r_i} - \sum_{i=1}^{n} \frac{2}{r_{ij}} + \sum_{i<j} \frac{1}{r_{ij}} - E_n \psi_n = 0 \quad (2.27)\]

where \(n\) represents the quantum numbers of the eigenstate of energy \(E_n\).

The excited states of He₂ are known from optical spectroscopy to be Rydberg states²⁸. The energy of a Rydberg state is expressed as

\[E = E_C - \frac{1}{\left[2(n - \delta_{\lambda, \lambda})^2\right]} \quad \text{in a.u.}\]

Here \(E_C\) is the energy of the ionic core, \(n\) is a positive integer, and \(\delta_{\lambda, \lambda}\), the quantum defect, is a quantity which is approximately constant for a series of states with the same core and the same values of the total electronic angular momentum, \(l\), and the projection of \(l\) along the internuclear axis, \(\lambda\). The Rydberg orbital may be pictured as a large, diffuse orbital surrounding a small core. This suggests that zero-order Rydberg orbitals are simply hydrogen atom wavefunctions centered on the midpoint between the two nuclei. The quantum defect for a particular series
reflects the perturbation of these orbitals by the core. Following Matsen and Browne\textsuperscript{29} we may decompose the total electronic Hamiltonian to show the origin of the perturbing terms.

The He\textsubscript{2} Hamiltonian for Rydberg states may be written

\[ H = H^c + H^r + H' \]

The zero order terms are

\[ H^c = \frac{1}{\alpha} \sum_{i \neq K} \nabla^2 \psi_i - \sum_{i \neq K} \frac{2}{r_{ai}} - \sum_{i \neq K} \frac{2}{r_{bi}} + \frac{\mu}{r} + \sum_{i < j \neq K} \frac{1}{r_{ij}} \]

and

\[ H^r = -\frac{1}{2} \nabla^2 \psi_k - \frac{1}{r_{ck}} \]

where the index \( k \) refers to the electron in the Rydberg orbital, \( a \) and \( b \) refer to the atomic nuclei, and \( c \) refers to the midpoint between the two nuclei. The perturbation terms are

\[ H' = H^A + H^M \]

where

\[ H^A = \sum_{i \neq K} \frac{1}{r_{ik}} - \frac{3}{r_{ck}} \]

and

\[ H^M = -\frac{2}{r_{ak}} - \frac{2}{r_{bk}} + \frac{4}{r_{ck}} \]
The atomic perturbation, $H^A$, represents the deviation from a true Coulomb field due to the core electrons. The molecular perturbation, $H^M$, represents the non-spherically symmetric electrostatic terms of the nuclear field. $H^M$ vanishes as $R$ goes to 0. The perturbation terms become very small in the region of maximum charge density of a Rydberg orbital whose radius is much larger than the internuclear separation.

The inner part of the Rydberg orbital penetrates into the region in which the perturbation terms are large and the field deviates strongly from the $-1/r_{ck}$ hydrogenic potential. This displaces the position of the nodes of the hydrogenic orbitals. For atomic Rydberg orbitals, it is known that the amount of the shift is almost the same for all orbitals of a given $\ell$ \textsuperscript{30}. Mulliken has suggested that a series of molecular Rydberg orbitals (same $\ell$ and $\lambda$) should likewise have their nodes displaced by about the same amount \textsuperscript{31}.

The present calculations have been motivated by these considerations. The valence bond method has been used to construct the single configurations composing the basis. Several different configurations, each composed of a single excited orbital and identical representation of the core orbitals, were included for each molecular Rydberg state with a particular set of $\ell$ and $\lambda$ quantum numbers. In order that proper adiabatic correlations could be made between Rydberg states and separated atomic states, all
allowed Rydberg states were represented through the highest state of interest. The inclusion of an ionic configuration constructed from the same orbitals as the corresponding covalent configuration frequently lowered the energy eigenvalues by several thousandths of an atomic unit in the region of avoided crossing potential humps.

Consideration of the contributions to the total energy guides the selection of configurations. Several STO's of the same \( l \) and \( \lambda \) are required to represent the hydrogenic character of the Rydberg orbitals. The orbital exponents were chosen by means of variational calculations performed on the separated atomic states, optimized with respect to the \( n = 3 \) states and not varied with internuclear separation. Thus the \( n = 3 \) Rydberg states are better approximated than the remaining states. These orbitals are centered on either atomic nucleus, but, as is shown in the next section, should well approximate orbitals centered on the midpoint between the nuclei. The molecular perturbation energy of these states is calculated exactly by VARY. The atomic perturbation energy depends on the core orbitals. The \( s \) and \( p \sigma \) orbitals have inner loops which penetrate the core. The remaining orbitals do not. These penetrating orbitals are more sensitive to the exact form of the core orbitals than are the remaining orbitals. Table 5 contains effective quantum numbers \( n^* \) derived from our calculations (for \( R = 2.25 \)) and from spectroscopic data. As expected, the largest discrepancies between the calculated and
Table 5
Quantum Defects in Triplet System

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<th>Calculated $\delta$</th>
<th>Experimental $n^*$ (Ref. 32)</th>
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</table>
observed effective quantum numbers occur for s and pσ Rydberg orbitals.
b. The Behavior of the Potential Curves

The preceding discussion has shown that the energy of a Rydberg orbital may be represented as the sum of the energy of the core electrons, the smaller binding energy of the Rydberg electrons and the still smaller energies of the atomic and molecular perturbations. Hence the intermolecular potentials are determined largely by the behavior of the cores on which the Rydberg orbitals are constructed.

The two lowest energy states of \( \text{He}_2^+ \) are the \( ^2\Sigma_u^+ \), the "A core"; and the \( ^2\Sigma_g^+ \), the "B core". The \( ^2\Sigma_u^+ \) is stable with a dissociation energy of 2.47 \( \text{ev} \)^{33}. The \( ^2\Sigma_g^+ \) is unstable. These states may be represented by single configuration VB wavefunctions constructed from separated atomic and ionic single configuration wavefunctions. The rationalized dissociation energy

\[ \Delta E_{\text{calculated}}(\infty) - E_{\text{calculated}}(R_e) \]

is 2.12 \( \text{ev} \) for the \( ^2\Sigma_u^+ \) state.

The molecular wavefunctions used in the present calculation are of the form (2.25). In Appendix I we show that the single configuration VB wavefunctions of form described in section 2.A.c. have the property that

\[ |n_\alpha l_\alpha s_\alpha r_\alpha s_\beta r_\beta s_\beta r_\beta s_\alpha r_\beta l_\alpha s_\alpha r_\beta| \pm |n_\beta l_\beta s_\beta r_\beta s_\alpha r_\alpha s_\alpha r_\alpha| R \rightarrow R_e |n_\alpha l_\alpha s_\alpha r_\alpha s_\beta r_\beta s_\beta r_\beta s_\alpha r_\alpha| \pm |n_\beta l_\beta s_\beta r_\beta s_\beta r_\beta s_\beta r_\beta s_\alpha r_\beta| \]

where \( n_\alpha l_\alpha \) is a STO with the same values of \( n, \ell, \) and \( \alpha \) as \( n_\alpha l_\alpha \) and \( n_\beta l_\beta \) but which is centered on the midpoint of the
two nuclei. The derivation in Appendix I shows that the + wavefunction is a product of the Rydberg orbital and the B core state of $\text{He}_2^+$ and the - wavefunction is a product of the Rydberg orbital and the A core. Thus a single VB configuration may be physically interpreted at all internuclear separation. This is not so for single configuration LCAO-MO wavefunctions which frequently dissociate to a linear combination of ionic and neutral atomic species. These formal difficulties with LCAO-MO wavefunction require that major configuration mixing must occur in constructing states which dissociate properly\(^{31}\), which unnecessarily complicates a study of the behavior of the potentials. For this reason, we have used VB wavefunctions in the present calculation when the complete potential for states of a particular symmetry was desired.

Since the single configuration VB wavefunction may be represented as a product of Rydberg and core orbitals, the single configuration energy (SCE) expectation values are essentially a sum of the Rydberg orbital energy and core orbital energy. Since the variation of the core orbital energy is much greater than the variation of Rydberg orbital energy as the internuclear separation is changed, the SCE are dominated near the equilibrium separation by the core energies. Since the + wavefunctions have an A core factor and the - wavefunctions a B core factor, the + wavefunctions SCE are repulsive and the - wavefunction SCE are, in general, attractive. (Some - wavefunctions are
repulsive for some intermediate values of internuclear separation but these are best considered as exceptions to the rule.

The overall inversion symmetry of a single configuration VB wavefunction is determined both by the symmetry with respect to exchange of atomic nuclei (whether it is a \( + \) or \(-\) wavefunction) and by the parity of the orbitals. Orbitals of even electronic angular momentum are even under inversion, those with odd angular momentum are odd. This and the observations above give the following rules for the behavior of single configuration energies:

Gerade symmetry:

Even \( l \) configurations are repulsive
Odd \( l \) configurations are attractive

Ungerade symmetry:

Even \( l \) configurations are attractive
Odd \( l \) configurations are repulsive.

These rules are quite helpful in understanding the behavior of the \( \text{He}_2 \) potential curves.

The potential curves of the lowest \( ^1\Sigma_g^+ \) and \( ^3\Sigma_u^+ \) states of \( \text{H}_2 \) are the archetypes of potential energy curves. The \( ^1\Sigma_g^+ \) curve displays a single attractive well and the \( ^3\Sigma_u^+ \) is repulsive. Features of potential curves which deviate from these simple forms are thought of as irregularities. Three types of irregularities which could be present in the potential curves of \( \text{He}_2 \) are due to i. long-range interaction, ii. exchange interactions, and iii. avoided crossings.
By definition, long-range interactions do not involve electron charge cloud overlap. The most important interaction of this type for neutral atoms is usually the van der Waals interaction which varies as $R^{-6}$. Since the van der Waals interaction is second-order in the perturbation, it is clearly attractive for the case of two ground state helium atoms\(^{35}\). If one of the atoms is in an excited state, the sign of the interaction is usually not known without an explicit calculation. If the excited atom is in an \(n^1p\) state, the first-order perturbation term does not vanish and the dominant long-range interaction is the dipole-dipole resonance interaction which varies as $R^{-3}$. These interactions can cause small irregularities in potential curves at large internuclear separations. Such interactions are not studied in this work, which deals primarily with triplet states.

The second type of irregularities in potential curves arises from the exchange interaction and is only present in sigma states. Guberman and Goddard\(^4,36\) have performed calculations on the lowest $^1\Sigma_u^+$ and $^1\Sigma_g^+$ states of $\text{He}_2$ and have examined the terms which contribute to the potential energy at various internuclear separations. They found that both one-electron and two-electron exchange terms dominated the interaction at large $R$ if the orbitals on the separate centers overlapped. The one-electron terms (kinetic energy and nuclear attraction) were usually dominant. For the case of a single configuration wave-
function, not symmetrized with respect to inversion of the coordinate system, Goddard and Guberman found that single-center one-electron terms were attractive and two-center one-electron terms are repulsive. The two-center terms dominate at large $R$ and continue to dominate until the incoming ground state atom has penetrated the excited orbital. We should expect these exchange interactions to be largest at internuclear separations corresponding to the sum of the radii of the core and excited orbitals. We shall see that certain irregular features do appear in sigma states for such $R$.

The final type of irregularity we consider arises from the interaction between single configuration wavefunctions. There are two possible cases. The first case concerns the interaction of attractive and repulsive single configuration energy curves. A characteristic of this first type is the appearance of a hump in the adiabatic potential curve of the lower state at intermediate internuclear separations. The second case concerns the interaction of two nearly parallel single configuration energy curves. Instances of this type of interaction are more important at large and small values of $R$ rather than at intermediate values.

The first type of interaction between single configuration wavefunctions is usually referred to as an avoided crossing. It is understood in terms of the behavior of single configuration energies previously described. Because
nodeless STO's are used in this calculation and because the orbital exponents are determined by multi-configuration variational calculations on the separated atomic states, several single configuration wavefunctions with the same \( l \) will, in general, significantly contribute to the electronic wavefunction at large \( R \). The potential corresponding to that wavefunction will be either attractive or repulsive at intermediate \( R \) depending on the overall inversion symmetry of the wavefunction and on \( l \) as previously described. The rapidly increasing energy of the \( B \) core and rapidly decreasing energy of the \( A \) core ion states compared to the spacing of excited atomic states will force the single configuration energies to approach each other and eventually cross. Since these single configuration wavefunctions are of the same symmetry, they will interact in the CI calculation and a hump will be formed in the lower CI potential curve. The behavior of the upper curve depends on its interactions with the states lying above it but in some cases a hump will occur at an \( R \) slightly less than the \( R \) corresponding to the lower hump.

The description and effects of the interaction of parallel single configuration energies differs depending on whether the interaction occurs at large or at small \( R \) values. We first describe the large \( R \) case.

As the principal quantum number of the excited states of the helium atom increases, the separation between adjacent angular momentum states generally decreases. States of
sigma symmetry may be formed from all excited states. As $R$ decreases the energy levels of sigma states are perturbed by the exchange interaction as was described above. It appears that the exchange interaction may cause mixing of adjacent states when the energy separation between the adjacent states is small. Moreover, since the exchange interaction perturbs the energies over distances at several Bohr radii, the mixing of the wavefunctions occurs over a fairly wide range of $R$. This interaction, however, is not necessarily described as an avoided crossing. The exchange interaction apparently diminishes as the maximum density of the excited orbital of the wavefunction involved passes the position of the ground state helium atom. This may happen before the region in which the core interaction is important is reached. Hence there can be an interval in which the wavefunctions do not mix and the initial relative positions of the energy levels is restored. No net crossing of configurations has occurred. The same result is obtained if the core interaction causes the configuration from which the lower state was initially constructed to become attractive. The configurations initially forming the upper state are then generally repulsive. Again no net crossing will occur. The effects of the interaction are seen by comparing the perturbations produced by the exchange interaction on two adjacent potential curves. It sometimes happens that the magnitudes of the perturbations are considerably different. If the interaction described here is
responsible for this difference, the structure projections of the two states will indicate it.

As has been described, when the internuclear separation becomes small compared to the size of the excited orbital, the molecular states of He₂ become Rydberg states. As the principal quantum number increases, the potential curves of adjacent states closely approach each other. The mixing of configurations of different ℓ among these wavefunctions is very small in the vicinity of the equilibrium internuclear separation. Occasionally, however, it happens that the wavefunctions for two adjacent states appear essentially just reversed at some intermediate R. The configurations which were dominant in one wavefunction are now dominant in the other and vice versa. We may think of this as a crossing of single configuration wavefunctions of different ℓ. Because the interaction between configurations of different ℓ is very weak in this region, the change in the adiabatic wavefunction is very abrupt. Several instances of the sort of crossing are found among the states discussed in this thesis.

These irregularities in the potential curves play an important role in theoretical descriptions of collisions between excited and normal helium atoms. The behavior of the wavefunctions in the region of the irregularity has been described above. One indication of the width of the region in which two states interact is the abruptness with which the structure projections for the two states change.
The structure projections for the states studied indicate that the width of the interaction interval decreases rapidly with $R$. In terms of the discussion of section 2.A.e., this suggests that the collision problem should be discussed in terms of coupled adiabatic states at large $R$ and coupled diabatic states at small $R$. Avoided crossings at intermediate $R$ seem to form a transition region in which each instance must be considered separately. Several collisions are considered in Chapter 4.
C. Results and Discussion

This section contains a discussion of several of the lower states of the $^3\Pi_u$, $^3\Sigma_u^+$, and $^3\Sigma_g^+$ systems of He$_2$. A description of the wavefunction is given for each symmetry. For each state, the potential curve, the significant features of the potential, comparison with other work, explanation of the features and possible effects due to these features are included in the discussion. The notation of Guberman and Goddard$^4$ will be used for the complete designation of a particular state. For example the lowest bound state of He$_2$ is the $^3\Sigma_u^+$ (2sσ, 2s). Here $^3\Sigma_u^+$ is the usual notation of the spin multiplicity and symmetry of this state, 2sσ is the united atomic orbital (UAO) description of the Rydberg state of the molecule, 2s is the excited orbital of the separated atoms to which this state adiabatically dissociates, and a is the alphabetic designation of this state used by Herzberg$^{37}$. While alphabetic designations have been assigned to most of the states we will discuss, this symbol does not convey much information and will be used here only for the lowest states for which the alphabetic designations have been extensively employed in the literature. When there is no chance of confusion, only the orbital notation will be employed. Thus the $^3\Sigma_u^+$ (2sσ, 2s) state may be denoted as (2sσ, 2s).

The configurations used in the wavefunction have been discussed in section 2.A.c. The configuration notation is that of Gupta and Matsen$^{21}$ in which the orbitals within
parentheses are spin paired and the orbitals in square brackets are used to construct fully symmetrized configurations of the types described in section 2.A.c.

It is desirable to have a quantitative measure of the contribution of a particular configuration to the wavefunction. Since the configurations used are not orthogonal, the squares of the expansion coefficients are not a true indication of this contribution. The structure projections\textsuperscript{38}

\[ p_i = c_i \sum_m S_{im} c_m \]

are such indicators. The \( c_i \) are the expansion coefficients of Eq. (2.25) and the \( S_{im} \) are the elements of the overlap matrix of Eq. (2.26). Since the wavefunctions are normalized, the sum of the structure projections for a particular state is unity.
a. The $^3\Pi_u$ States

The potential curves of the three lowest states of $^3\Pi_u$ symmetry are shown in Figure 2, the wavefunction is described in Table 6, and the numerical values of the potential are tabulated in Table 7. The choice of basis configurations is determined by the behavior of the single configuration energies discussed in sections 2.B.a and 2.B.b. In particular since our interest is in states dissociating to the $n = 3$ level, we include the configurations containing the $2p$, $3p$, and $3d$ orbitals. Since these states pass adiabatically to the three lowest Rydberg orbitals, the $3d\pi$, $4d\pi$, and $5d\pi$, we include configurations containing these orbitals. The presence of three configurations containing $d\pi$ orbitals with rather different orbital exponents provides a better representation of the $d\pi$ Rydberg states than would a single $d\pi$ configuration alone and compensates for the absence of exponent variation in our calculation. The rather good agreement between the calculated and observed effective quantum numbers for these states shown in Table 5 would seem to indicate that there would be little gained by exponent variation. The configurations containing the $4p$ and $5p$ orbitals are not necessary but do contribute noticeably to the $(4d\pi, 3p)$ and $(5d\pi, 3d)$ states probably indicating some distortion of Rydberg orbitals due to the two-centered core. Finally the presence of an ionic configuration for each covalent configuration is
Table 6
Wavefunctions for the $^3\pi_u$ States

$$\psi_{14} = C_1[1S'_a2p_{+a}(1S_b1S_b)] + C_2[1S'_a2p_{+b}(1S_b1S_b)]$$
$$+ C_3[1S'_a3p_{+a}(1S_b1S_b)] + C_4[1S'_a3p_{+b}(1S_b1S_b)]$$
$$+ C_5[1S'_a3d_{+a}(1S_b1S_b)] + C_6[1S'_a3d_{+b}(1S_b1S_b)]$$
$$+ C_7[1S_a4p_{+a}(1S_b1S_b)] + C_8[1S_a4p_{+b}(1S_b1S_b)]$$
$$+ C_9[1S_a4d_{+a}(1S_b1S_b)] + C_{10}[1S_a4d_{+b}(1S_b1S_b)]$$
$$+ C_{11}[1S_a5p_{+a}(1S_b1S_b)] + C_{12}[1S_a5p_{+b}(1S_b1S_b)]$$
$$+ C_{13}[1S_a5d_{+a}(1S_b1S_b)] + C_{14}[1S_a5d_{+b}(1S_b1S_b)]$$

Orbital Exponents

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Table 7

\(^3\pi_u\)

*ab initio* Potential Energy (a.u.)

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<th>R (a₀)</th>
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Adjusted Potential Energy (a.u.)

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not necessary but does improve the energies by allowing a better representation of the A core and will be used in discussing of suggestions of Mulliken\textsuperscript{5} concerning B core states.

i. $f^3\pi_u(3d^\pi,2p)$

This state possesses a large hump at $R = 3.182\ a_0$. The magnitude of this hump calculated from ion-core adjusted potential curves is .01837 a.u. with respect to the calculated separated atomic energies and .02169 a.u. with respect to the spectroscopic separated atomic energies. This agrees well with the calculations of Gupta and Matsen\textsuperscript{21} for this state. They found the hump at $R = 3.1826\ a_0$ with a height of .02114 a.u. and .02225 a.u. with respect to calculated and spectroscopic separated atomic energies respectively. The generally good agreement between our ion-core adjusted potential and the potential of Gupta and Matsen has been discussed in section 2.A.c. The spectroscopically derived potential curves of Ginter and Battino\textsuperscript{28} are consistent with this barrier but the height of the barrier and its location are not known experimentally. Finally these values agree with the lower estimate of Mulliken\textsuperscript{5} for the magnitude of this hump.

Since the excited $p^\pi$ orbital is orthogonal by symmetry to the orbitals of the ground state atom, we should expect no irregularities in the potential curves due to the exchange interaction. The large hump at $R = 3.182\ a_0$ is due to an avoided crossing and may be taken as the
Figure 2. The adiabatic potential curves of the three lowest $^3\Pi_u$ states.
prototype of avoided crossings in the $\text{He}_2$ system. Some single configuration energies are shown in Figure 3. Here $n\ell\pi$ and $+n\ell\pi$ refer to covalent and ionic single configuration wavefunctions respectively. The behavior of these single configuration energies is understood in terms of the discussion presented in section 2.B.b. In particular, the $2p\pi$ and $+2p\pi$ energies are repulsive at small $R$. The $3d\pi$ and $+3d\pi$ are attractive. The near degeneracy of ionic and covalent energies for small $R$ for configurations composed of the same orbitals is expected since both the ionic and covalent configurations tend toward a limit in which the excited orbital is centered on the midpoint between the two nuclei. The hump at $R = 3.182$ results from an avoided crossing of the $2p\pi$ single configuration with several $d\pi$ single configurations. For large $R$, the adiabatic energy closely follows the $2p\pi$ single configuration energy. At about $R = 3.75$, this configuration begins to mix with the $d\pi$ configurations and the rise in the adiabatic potential begins to taper off. The $d\pi$ configuration energies dominate on the small $R$ side of the hump. A mixture of $d\pi$ configurations is required to adequately represent the $3d\pi$ Rydberg orbital.

ii. $^3\Pi_u (4d\pi,3p)$

There are no large irregularities in the potential curve of the $\left(4d\pi,3p\right)$ states. Again this is understood in terms of the single configuration energies. The $\pi$
Figure 3. Single configuration energies for several $^3\Pi_u$ configurations.
character of the excited orbital guarantees that the exchange interaction will be absent. The proximity of the $3^3P$ and $3^3D$ atomic states and the lack of the exchange interaction does not allow a large hump to form in this state as the $p\pi$ and $d\pi$ configurations begin to mix, although a further investigation of the potential between 5.0 and 6.0 $a_0$ might reveal a small hump due to this effect. The only remaining source of an irregularity is the interaction of the $d\pi$ configurations with the $2p\pi$ configurations around 3.0 $a_0$. There is a small bulge on the potential curve in this region which is probably due to this effect. Only spectra from the lowest vibrational level of this state has been obtained\textsuperscript{32}, so there is no spectroscopic information available concerning the region of the potential around the bulge. The agreement between calculated and measured effective quantum numbers is very good (see Table 5).

iii. $3^3\Pi_u (5d\pi,3d)$

The hump in the potential of this state is located at 4.0 $a_0$ with a magnitude of 0.0056 a.u. (using the ion-core adjusted potential) with respect to the calculated separated atomic energies. The wavefunction for this state exchanges character with the $(4d\pi,3p)$ state in the vicinity of 5.5 $a_0$. The $p\pi$ single configuration energies cause the potential curve to rise until it interacts with the higher $d\pi$ configurations. As in the $(3d\pi,2p)$ case, this causes a hump to be formed near 4.0 $a_0$. For smaller $R$, the $(5d\pi,3d)$
state is attractive due to the $d\pi$ configurations forming the $5d\pi$ Rydberg orbital. The spectroscopic effective quantum number is available for this state and agrees well with the calculated one (see Table 5).
b. The $^3\Sigma_u^+$ States

The five lowest states of the $^3\Sigma_u^+$ symmetry have been investigated. The potential energy curves for these states are shown in Figure 4, tables of the potential energy and ion-core adjusted potential energy are contained in Tables 8 and 9, and the wavefunction is given in Table 10. We are interested in the states of this symmetry which correlate with the three $n = 3$ states of helium at large $R$. Since we must also include the states which correlate with the two $n = 2$ states, we must choose a basis which can describe the five lowest molecular Rydberg states of this symmetry. The requirements are met by a basis which includes all excited Rydberg orbitals of the separated atoms through the 4d. Again we have ionic-covalent pairs constructed from these orbitals to achieve a slight improvement of the calculated energies and to test a suggestion of Mulliken's$^5$ concerning B core states.

i. $^3\Sigma_u^+(2s\sigma,2s)$

The potential curves for this state and for the corresponding singlet state display a small hump around 4.5 $a_0$. Guberman and Goddard have discussed the origin of the hump in terms of the exchange interaction (see section 2.B.b.) for the $^1\Sigma_u^+(2s\sigma,2s)$ state. The hump in the triplet state should have the same source. The U.T. Molecular Physics Group has investigated the magnitude of the hump in a series of calculations$^{24}$. Their latest calculation
Figure 4. The adiabatic potential curves of the five lowest $3\Sigma_u^+$ states.
Table 8

$^3\Sigma_u^+$

\textit{ab initio} Potential Energy (a.u.)

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<th>$R(a_0)$</th>
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Table 9

\[ ^3\Sigma^+ \]

\[ u \]

Adjusted Potential Energy (a.u.)

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<th>State</th>
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\[ \psi_{16} = c_1[1S'_a2S_a(1S_b1S_b)] + c_2[1S'_a2S_b(1S_b1S_b)] \\
+ c_3[1S'_a2p_{oa}(1S_b1S_b)] + c_4[1S'_a2p_{ob}(1S_b1S_b)] \\
+ c_5[1S'_a3S_a(1S_b1S_b)] + c_6[1S'_a3S_b(1S_b1S_b)] \\
+ c_7[1S'_a3p_{oa}(1S_b1S_b)] + c_8[1S'_a3p_{ob}(1S_b1S_b)] \\
+ c_9[1S'_a3d_{oa}(1S_b1S_b)] + c_{10}[1S'_a3d_{ob}(1S_b1S_b)] \\
+ c_{11}[1S'_a4S_a(1S_b1S_b)] + c_{12}[1S'_a4S_b(1S_b1S_b)] \\
+ c_{13}[1S'_a4p_{oa}(1S_b1S_b)] + c_{14}[1S'_a4p_{ob}(1S_b1S_b)] \\
+ c_{15}[1S'_a4d_{oa}(1S_b1S_b)] + c_{16}[1S'_a4d_{ob}(1S_b1S_b)] \]

**Orbital Exponents**

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<th>Exponent</th>
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showed a hump of .00588 a.u. with respect to the separated atomic energy located at 4.6 \, a_0. We find almost no rise in the potential relative to the separated atomic energy. The wavefunctions we used have orbital exponents chosen to give accurate \( n = 3 \) level atomic energies. As shown in Table 3, the error in the \( 2^3S \) separated atom energy is almost equal to the size of the Texas Group's calculation of the hump. Comparing our ion-adjusted value at \( R = 5.00 \, a_0 \) with the spectroscopic separated atom energy gives a hump of .00633 a.u., which agrees reasonably well with the Texas calculation.

The procedure of adjusting the ab initio energies by the ion-core energies for this state is more questionable than for most of the remaining states. The structure projections for this state show that the \( 2s\sigma \) state has a larger \( p\sigma \) component than higher \( s\sigma \) states. This indicates a larger interaction with the core so that a more accurate treatment of the core than the simple ion core adjustment we have used is indicated. The larger discrepancy between calculated and spectroscopic effective quantum numbers for this symmetry compared with that for the \( 3\Pi_u \) symmetry also indicates need for a better core representation.

ii. \( d^3\Sigma_u^+(3s\sigma,2p) \)

The most significant feature of this state is the large hump. The hump is located at 3.68 \, a_0 and has a magnitude of .0249 a.u. calculated from the ion-core
adjusted potentials. The source of the hump is almost the same as that for the hump in the $^3\Pi_u (3d\pi, 2p)$ state. The repulsive $2p\sigma$ single configuration wavefunction interacts with the attractive $s\sigma$ and $d\sigma$ single configuration wavefunctions causing an avoided crossing hump. The $2p\sigma$ single configuration wavefunction is more repulsive than the $2p\pi$ single configuration wavefunction due to the exchange interaction. The $d\sigma$ configuration is less attractive for the same reason. Thus the hump is higher and located at a larger internuclear separation than the corresponding hump in the ($3d\pi, 2p$) state. Goddard and Guberman report a hump of .02311 a.u. at $R = 3.77$ $a_0$ in the analogous singlet state.

A second interesting feature of this state is suggested by the proximity of this state and the ($3d\sigma, 3s$) state. Figure 5 shows structure projections as a function of internuclear separation summed over all configurations of the same $l$. From $R = 7.00$ to $R = 2.75$ $a_0$, the $d\sigma$ configurations are increasing and the $p\sigma$ configurations generally decreasing due to the avoided crossing described above. Between $R = 2.50$ and 2.75 $a_0$, the wavefunction abruptly changes and the $s\sigma$ configurations are dominant. This is an example of an avoided crossing of the second type described in section 2.B.b. The structure projections for this state and the ($3d\sigma, 3s$) taken together illustrate the sequence of configuration mixing described here. The
Figure 5. Cumulative structure projections for the $3\Sigma^+_u$ (3s, 2p) state.

Figure 6. Cumulative structure projections for the $3\Sigma^+_u$ (3d, s, 3s) state.
smallest separation of these states is .0004876 a.u. at 
\( R = 2.72 \, a_0 \). Guberman and Goddard seem to have found that 
the analogous singlet state shows this same sort of behavior. 

\( \text{iii. } ^3\Sigma_u^+(3d\sigma,3s) \)

There are two significant features in the potential 
curve of this state. The first is a small hump of .0009 
a.u. near \( R = 10.0 \, a_0 \). The location of this hump and the 
absence of crossing states indicate that the hump arises 
from the exchange interaction. The experience of the 
Texas Group with the \((2s\sigma,2s)\) state has been that the mag-
nitude of the hump is rather sensitive to the quality of 
the wavefunction. The size of the hump given here is 
probably an upper bound to the true hump size. Guberman 
and Goddard report finding a small maximum of .00015 a.u. 
near \( R = 11.5 \, a_0 \) in the analogous singlet state.

The avoided crossing of this state with the \((3s\sigma,2p)\) 
state is described in the discussion of the \((3s\sigma,2p)\) state. 
The structure projections for the \((3d\sigma,3s)\) state are shown 
in Figure 6. The structure projections clearly indicate 
the abrupt change in the wavefunction which occurs near 
\( R = 2.75 \, a_0 \). Very little mixing of this state with \( p\sigma \) 
configurations occurs. It is this lack of mixing which 
causes the \( d\sigma \) configurations to dominate in the adiabatic 
state, the \((3s\sigma,2p)\), lying below the \((3d\sigma,3s)\) and thus 
which requires the avoided crossing mentioned above in 
order that the Rydberg states be properly formed.
The spectroscopic energy separation\textsuperscript{32} between the $v = 0$, $J = 0$ levels of these two states is .005276 a.u. The calculated energy separation at $R = 2.25$ a.u. The spectroscopic and calculated effective quantum numbers for the $(3d\sigma,3s)$ state are in very good agreement as is shown in Table 5. The agreement between these quantities for the $(3s\sigma,2p)$ state is not as good. The structure projections shown in Figures 5 and 6 indicate that the $(3d\sigma,3s)$ state is composed largely of $d\sigma$ configurations near the equilibrium separation (approximately $R = 2.25$ a$_o$ in the calculation) and that the $(3s\sigma,2p)$ is almost a pure $S$ state. The much smaller penetration by $d\sigma$ configurations of the core as compared to the penetration by $s\sigma$ configurations of the core accounts for the better energy of the $3d\sigma$ state. Finally Ginter\textsuperscript{28} shows the $(3s\sigma,2p)$ and $(3d\sigma,3s)$ states crossing at about 2.71 a$_o$ in good agreement with our interpolated crossing point of 2.72 a$_o$.

iv. $^3\Sigma_u^+(4s\sigma,3p)$

In this case the potential curve possesses several small humps. Near 10. a$_o$ the ion-core adjusted potential rises to a maximum of .00054 a.u. A minimum of .00014 a.u. occurs near 7. a$_o$. The curve rises again near 5. a$_o$ to a maximum of .00051 a.u. The fourth energy level of the singlet system corresponds to the $^1\Sigma_u^+(4d\sigma,3d)$ state. For this and other reasons, it is clear that the singlet analog of the $^3\Sigma_u^+(4s\sigma,3p)$ state is, for intermediate internuclear
separations, the $^1\Sigma_u^+(4d\sigma,3d)$. Guberman and Goddard have found that this singlet state possesses small humps and a minimum similar to those just described for the triplet state.

The outer hump occurs at about the internuclear separation at which the overlap of the $3p$ orbital on one atom with the closed-shell $1s$ orbital on the other atom is greatest. Thus this hump would seem to be caused by the exchange interaction. As $R$ decreases, the greatest density of the $p$ orbital moves beyond the ground state helium atom so that a minimum in the potential curve becomes possible. The cumulative structure projections indicate that the mixture of $d$-type configurations into the wavefunction as a function of $R$ correlates with the magnitude of the outer hump. The $d$-type cumulative structure projection reaches a peak of about .25 near $10. a_o$. By $7. a_o$, it has fallen to .08. This is an instance of mixing in the electronic wavefunction at large $R$ of the type described in section 2.B.b.

For somewhat smaller $R$, the single configuration energies of the $p\sigma$ orbitals become repulsive as they tend to become dominated by the repulsive $B$ core interaction and the potential again rises. The attractive $d\sigma$ configurations begin to mix strongly with the $p\sigma$ configurations so that the potential curve begins to become attractive and a second hump is formed. Finally as $R$
approaches its equilibrium value, the d and s configurations interact. A second avoided crossing occurs which is very similar to the avoided crossing between the d and s configurations in the case of the (3sσ,2p) state. The structure projections for this state would be quite similar to those shown in Figure 5 for the (3sσ,2p) state.

\[ v. \quad ^3\Sigma_u^+(4dσ,3d) \]

The potential curve for this state is dominated by a rather large, broad hump at large R. The ion-core adjusted curve has a peak of about 0.0064 a.u. near 7. a₀. The hump is about an order of magnitude greater than the humps for similar values of R in the lower states. As in those cases, the exchange interaction is probably responsible for this hump. The greater density of the 3dσ charge cloud along the internuclear axis probably explains the larger size of the hump for this state. The analogous singlet state studied by Guberman and Goddard is the \[ ^1\Sigma_u^+(4sσ,3p) \]. They do not report a position or magnitude for a peak in the potential curve of this state but their figures indicate that the behavior of this state for large R is similar to the behavior we have found for the (4dσ,3d) state as should be expected.

As R becomes smaller, the dσ configurations mix with the pσ configurations from the (4sσ,3p) state causing the potential curve of the (4dσ,3d) state to be somewhat flatter in the region between 4. and 5. a₀ than would otherwise be
expected. The \(4s\sigma\) configuration mixes with this wavefunction for \(R\) less than 4. \(a_\circ\) and the potential curve becomes attractive. There is the avoided crossing between the \(s\sigma\) and \(d\sigma\) configurations. The interpolated minimum separation between the potential curves is 0.00050 a.u. at 2.628 \(a_\circ\). Dieke\(^{39}\) has examined the spectroscopic data from the higher rotational levels of the \(v = 0\) levels of \((4s\sigma, 3p)\) and \((4d\sigma, 3d)\) states. He found that the nearly degenerate \(J = 17\) rotational levels are perturbed due to the interaction of the two states. Finally for the smallest values of \(R\), the \(s\sigma\) and \(p\sigma\) structure projections are negligible compared to the \(d\sigma\) structure projections.

Table 5 indicates that the agreement between computed and experimental effective quantum numbers is fairly good although not as good as in the \((3d\sigma, 3s)\) case. This reflects a general tendency in these calculations for the energies of higher states to be slightly less accurate than those of lower states of the same type. This could probably be corrected by the addition of configurations containing orbitals of the same \(l\) and \(\lambda\) but larger \(n\). In this case, the addition of configurations containing \(5d\sigma\) orbitals should improve the energy. The agreement between computed and experimental effective quantum numbers for this state is better than for the \((4s\sigma, 3p)\) state for the reasons given in the discussion of the \((3d\sigma, 3s)\) state. The computed energy difference between this state and the \((4s\sigma, 3p)\) state
is 0.00159 a.u. for \( R = 2.25 \). The spectroscopic energy separation is 0.00201 a.u.

The potential curve for the fifth energy level of the singlet system is reported by Guberman and Goddard. It is similar to the potential curve of the fifth energy level in the triplet system, our \((4d\sigma, 3d)\) state, for \( R \) greater than 4. \( a_0 \). For smaller \( R \), Guberman and Goddard's potential curve is repulsive and crosses the potential curve of the \( \text{He}_2^+ \) \( \Lambda \) core state. For still smaller \( R \), their curve peaks near 2.5 \( a_0 \), passes through a minimum at 2. \( a_0 \), and then rises monotonically. Guberman and Goddard suggest that the basis set used in their calculations is not adequate for a reasonable description of this state. It is important to realize potentials obtained from rigorous variational solutions of the Born-Oppenheimer equation cannot behave as does Guberman and Goddard's. In particular, the Born-Oppenheimer potential curve for this state does not cross the \( \text{He}_2^+ \) \( \Lambda \) core potential curve. An electronic state which lies above the \( \text{He}_2^+ \) \( \Lambda \) core potential is degenerate with the continuum of free electron states. The methods used for computing bound electronic states frequently produce energies which lie in this continuum. One must, however, be careful in attaching significance to those energies. Chapter 3 contains a discussion of such states. Moreover, a state which crosses the \( \Lambda \) core potential curve would play a crucial role in a theoretical description of
associative ionization and its inverse, dissociative recombination. Gubernar and Goddard's (4sσ,3p) state is not a Born-Oppenheimer state which crosses the He₂⁺ potential and lies in the continuum. Using this state as an example, we show below that there are no Born-Oppenheimer states with these properties. Chapter 3 contains a discussion of such crossing curves and the possible role which the repulsive single configuration wavefunctions might have in constructing these curves.

There is one significant difference between the n = 3 level atomic states of the singlet and triplet systems. The 3^3P state lies below the 3^3D state whereas the 3^1P state lies above the 3^1D state. This is reflected in the designation of the molecular states which are formed from these atomic states. Noting this distinction, we assert that the fourth and fifth singlet energy levels of \( \Sigma_u^+ \) symmetry correspond to the (4sσ,3d) and (4dσ,3p) states, respectively, and that these should behave qualitatively for intermediate and small R as the triplet (4sσ,3p) and (4dσ,3d) states, respectively. Both spectroscopic evidence and theoretical considerations lead to this conclusion.

Spectroscopic information for the triplet 4sσ and 4dσ molecular states has already been presented. Both of these states have been observed. The reported effective quantum numbers and the separation between these levels are in semi-quantitative agreement with the results of our
calculation. The observation of rotational perturbations by Dieke confirms that the potential curves of these two states do slowly approach each other in the vicinity of the equilibrium R value.

Much less spectroscopic information is available for the singlet system than the triplet. Spectral features have been identified as originating from the 4s\(^2\) level. The quantum defect for this state is consistent with those reported for the singlet 3s\(^2\) and 2s\(^2\) states which supports this identification. This also implies that the singlet 4s\(^2\) state occupies the same position relative to the lower singlet states as the triplet 4s\(^2\) state does relative to the remaining triplet states. In particular, the singlet 4s\(^2\) state does not lie above the He\(_2^+\) A core potential curve where Guberman and Goddard have placed it. No spectral information seems to be available for the singlet 4d\(^2\) state. However, using the average of the quantum defects reported for the singlet 3d\(^2\) and 5d\(^2\) states, the approximate energy of the 4d\(^2\) state is found to be approximately .0023 a.u. higher than the 4s\(^2\) state. Thus, the relative positions of the two singlet states are nearly the same as that of the two triplet states. The spectroscopic evidence clearly supports our assertion.

There are theoretical reasons for believing that the results of Guberman and Goddard may be in error for the \(n = 4\) Rydberg states. Their potential curves were computed
by the generalized valence bond (GVB) method. This is an analytic self-consistent field method using valence bond wavefunctions. In the GVB method, a set of one-electron eigenvalue equations for each orbital is solved self-consistently. Excited orbitals are found as the solutions of the one-electron equations corresponding to the higher orbital eigenvalues. The basis set used by Goddard and Guberman consisted of 6 s-type, 2 p-type, and 1 d-type contracted gaussians on each nucleus. Four of their s-type orbitals were chosen to represent the core orbitals. The remaining orbitals represent the excited orbitals.

In section 2.B.a., we described the hydrogenic character of the Rydberg orbitals of $\text{He}_2$. This suggested one criterion for the selection of a basis set for our VB CI calculation. The basis set should include all configurations necessary to approximately represent the hydrogenic orbitals corresponding to the largest Rydberg states. Thus in order to calculate all Rydberg states of the $^3\Sigma_u^+$ system through the 4dσ and 4sσ, we included configurations containing ndσ and ns STO's where $n = 2,3, \text{ and } 4$ with appropriate orbital exponents.

The difficulty with Guberman and Goddard's calculation is evident. Their basis was adequate to represent the 2s, 3s, and 3dσ Rydberg states. However, it contained no orbitals which could represent the 4s and 4dσ states. Thus they obtained completely erroneous results for the 4s state.
Their basis set was apparently able to better represent the 4dσ state. However, the absence of the 4s state below the 4dσ resulted in an erroneous correlation of the 4dσ state with the 3^1D atomic state. Guberman and Goddard do state that their basis set is not adequate to represent the 4s state but they do not indicate that this state is as much in error as it is.

Guberman and Goddard have the potential curves of wavefunctions constructed from the orbitals of the atoms (at R = ∞). They refer to these wavefunctions as frozen orbital (FO) wavefunctions. The interaction of FO wavefunctions is used to explain features such as avoided crossings. The inadequacy of the basis set used by Guberman and Goddard for the 4s and 4dσ states is easily seen by examining their FO potential curves. For the 1Σ_u^+ system, there are three attractive and two repulsive FO curves. The attractive curves approximate the potential curves of the 2s, 3s, and 3dσ states near the equilibrium separation. The repulsive curves lie above the He_2^+ A core potential and are steeply rising near the equilibrium separation. If the adiabatic states are to be understood in terms of the FO wavefunctions, it is easy to see that the lowest three states could be well represented and the two higher states, the 4s and 4dσ, not so well represented with the basis functions used by Guberman and Goddard.

We have shown that Guberman and Goddard's 1Σ_u^+(4sσ,3p) state does not cross the potential curve of the He_2^+ A core...
and rise into the continuum. We now show that there can be no potential curves obtained from rigorous variational solutions of the Born-Oppenheimer equation which have this property. There are a countably infinite number of excited states of the helium atom. For each system of molecular states of a particular symmetry, there are a countably infinite number of bound molecular Rydberg states. The non-crossing rule prevents the intersection of the potential curves of molecular states of the same spin multiplicity and symmetry. Thus for each molecular symmetry, there is a one-to-one mapping between the subset of bound molecular states and the countably infinite subset of excited atomic states to which these molecular states dissociate. Every adiabatic Born-Oppenheimer state which arises from the interaction of an excited and a ground state helium atom must correlate with a bound molecular state. Mulliken\textsuperscript{40} seems to have reached this same conclusion.

This result is true only for molecular states in the Born-Oppenheimer approximation. For highly excited molecular states lying close to the continuum, the neglected coupling terms can strongly mix the Born-Oppenheimer states. An adiabatic description is probably not as appropriate for describing processes involving these highly excited states. For lower excited states, the diabatic coupling between adiabatic states may be large. Processes, such as collisions, involving these states may be better described by the diabatic states discussed in section 2.A.e.
These results further confirm that Guberman and Goddard's $^{1\Sigma_u^+}(4s\sigma,3p)$ state cannot be a Born-Oppenheimer state. This state might be thought of as an approximate diabatic state. We believe, however, that such an identification should be based on a detailed consideration of the coupling between this state and the states it must cross. Guberman and Goddard have provided no such discussion.
c. The $^3\Sigma_g^+$ States

The eight lowest states of $^3\Sigma_g^+$ symmetry have been calculated. The states which correlate with $n = 2$ and $n = 3$ atomic states are of greatest interest and are discussed in detail in this section. The potential energy curves for all eight states are shown in Figure 7. Tables 11 and 12 contain tabulations of the ab initio and ion-core adjusted potentials.

The $^3\Sigma^+$ atomic state correlates with the 5p$\sigma$ molecular Rydberg state. In order to accurately represent all molecular states which correlate with $n = 3$ atomic states, the basis set should include covalent VB configurations containing two s-type, four p-type, one d-type and one f-type STO's. Since we are not varying orbital exponents, it is desirable to include configurations containing several different orbitals of a particular type. Configurations containing another d-type and another f-type orbital should be added to the basis. Thus a minimum of ten configurations are required. Including an ionic configuration for each covalent configuration doubles the size of the basis. The cost of calculating potential curves with a twenty-term basis is high. Moreover, preliminary calculations of states of this symmetry indicated that several adiabatic states might interact in a way favorable to associative ionization. It is desirable to further investigate this possibility by calculating several of the molecular states lying above the
Table 11

$3\Sigma^+$

$\Sigma_g$

ab initio Potential Energy (a.u.)

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\[ \Sigma^+ \quad g \]

\textbf{ab initio Potential Energy (a.u.)}

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Table 12
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Table 12 (cont'd)

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3_\Sigma^+_{g}
\]

Adjusted Potential Energy (a.u.)

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<td>( \infty )</td>
<td>4.957000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 13
17 Term Wavefunction for \( ^3\Sigma^+_g \) States

\[
\psi_{17} = C_1[1s_a^2s_a(1s_b^2s_b)] + C_2[1s_a^2p_{oa}(1s_b^2s_b)] \\
+ C_3[1s_a^3s_a(1s_b^1s_b)] + C_4[1s_a^3p_{oa}(1s_b^1s_b)] \\
+ C_5[1s_a^3d_{oa}(1s_b^1s_b)] + C_6[1s_a^4s_a(1s_b^2s_b)] \\
+ C_7[1s_a^4p_{oa}(1s_b^2s_b)] + C_8[1s_a^4d_{oa}(1s_b^2s_b)] \\
+ C_9[1s_a^4f_{oa}(1s_b^2s_b)] + C_{10}[1s_a^5s_a(1s_b^2s_b)] \\
+ C_{11}[1s_a^5p_{oa}(1s_b^2s_b)] + C_{12}[1s_a^5d_{oa}(1s_b^2s_b)] \\
+ C_{13}[1s_a^5f_{oa}(1s_b^2s_b)] + C_{14}[1s_a^5g_{oa}(1s_b^2s_b)] \\
+ C_{15}[1s_a^6p_{oa}(1s_b^2s_b)] + C_{16}[1s_a^6f_{oa}(1s_b^2s_b)] \\
+ C_{17}[1s_a^6h_{oa}(1s_b^2s_b)]
\]

Orbital Exponents

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>1.687</td>
</tr>
<tr>
<td>1s'</td>
<td>2.000</td>
</tr>
<tr>
<td>2s</td>
<td>0.500</td>
</tr>
<tr>
<td>2p_o</td>
<td>0.550676</td>
</tr>
<tr>
<td>3s</td>
<td>0.320241</td>
</tr>
<tr>
<td>3p_o</td>
<td>0.335467</td>
</tr>
<tr>
<td>3d_o</td>
<td>0.334027</td>
</tr>
<tr>
<td>4s</td>
<td>0.265964</td>
</tr>
<tr>
<td>4p_o</td>
<td>0.358822</td>
</tr>
<tr>
<td>4d_o</td>
<td>0.275</td>
</tr>
</tbody>
</table>
Figure 7. Adiabatic potential curves for the eight lowest $^3\Sigma_g^+$ states.
5p\sigma. This requires additional configurations. For these reasons it was decided to forego the slight improvement of the energies obtained by including ionic configurations and instead to use the seventeen configuration basis described in Table 13.

The features of these potential curves are described in terms of the energies of the single configuration wavefunction. Since these are all states of gerade symmetry, the p, f, and h single configuration energies become attractive for small R, as is discussed in section 2.B.b. The remaining configurations are purely repulsive. Since these are sigma states, we can expect additional features due to the exchange interaction.

i. $c^3\Sigma_q^+(3p\sigma,2s)$

The significant structure projections for the wavefunction of this state are shown in Table 14 for several values of R. The 2s configuration is dominant at large R. As R decreases, the energy of the configuration rises and crosses the energy curves of p-type configurations. These configurations strongly interact and a hump is formed. The hump in the ion-core adjusted potential has a peak of .0107 a.u. located at 3.54 a_0. The exchange interaction causes this hump to be rather wide. The energy of the 2p configuration also begins to rise near 6. a_0 due to the exchange interaction. After R has decreased by several Bohr radii, the energy of the 2p configuration begins to decrease.
Table 14

Significant Structure Projections

$^3\Sigma_g^+ (3p\sigma, 2s)$ State

<table>
<thead>
<tr>
<th>Configuration</th>
<th>2.00</th>
<th>3.00</th>
<th>4.00</th>
<th>5.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>2s</td>
<td>0.09021</td>
<td>0.48150</td>
<td>0.94404</td>
<td>1.09341</td>
</tr>
<tr>
<td>2p</td>
<td>0.19149</td>
<td>0.26327</td>
<td>0.17495</td>
<td>0.06555</td>
</tr>
<tr>
<td>3s</td>
<td>-0.01875</td>
<td>-0.12280</td>
<td>-0.20836</td>
<td>-0.22771</td>
</tr>
<tr>
<td>3p</td>
<td>1.63726</td>
<td>0.73620</td>
<td>0.07441</td>
<td>0.02609</td>
</tr>
<tr>
<td>3d</td>
<td>0.02840</td>
<td>0.02288</td>
<td>0.00973</td>
<td>0.00704</td>
</tr>
<tr>
<td>4s</td>
<td>-0.00195</td>
<td>0.01798</td>
<td>0.04641</td>
<td>0.05469</td>
</tr>
<tr>
<td>4p</td>
<td>-0.93695</td>
<td>-0.39613</td>
<td>-0.03628</td>
<td>-0.01474</td>
</tr>
</tbody>
</table>

$^3\Sigma_g^+ (4p\sigma, 2p)$ State

<table>
<thead>
<tr>
<th>Configuration</th>
<th>2.00</th>
<th>3.00</th>
<th>4.00</th>
<th>5.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>2s</td>
<td>0.01155</td>
<td>0.13422</td>
<td>0.13505</td>
<td>0.06872</td>
</tr>
<tr>
<td>2p</td>
<td>0.00977</td>
<td>-0.00577</td>
<td>0.22817</td>
<td>0.83320</td>
</tr>
<tr>
<td>3s</td>
<td>0.03364</td>
<td>-0.00657</td>
<td>0.01945</td>
<td>-0.01738</td>
</tr>
<tr>
<td>3p</td>
<td>-1.11393</td>
<td>-0.55673</td>
<td>0.49976</td>
<td>-0.17362</td>
</tr>
<tr>
<td>3d</td>
<td>0.00647</td>
<td>0.00146</td>
<td>0.09607</td>
<td>0.13582</td>
</tr>
<tr>
<td>4p</td>
<td>1.99013</td>
<td>1.4041</td>
<td>0.05905</td>
<td>0.19502</td>
</tr>
<tr>
<td>4d</td>
<td>0.00876</td>
<td>0.02156</td>
<td>-0.01809</td>
<td>-0.04714</td>
</tr>
<tr>
<td>5p</td>
<td>0.09052</td>
<td>0.02968</td>
<td>-0.02289</td>
<td>-0.00842</td>
</tr>
<tr>
<td>6p</td>
<td>-0.01939</td>
<td>-0.00715</td>
<td>0.00349</td>
<td>0.00105</td>
</tr>
</tbody>
</table>
Thus the crossing of these single configuration energies at larger R is prevented by the exchange interaction and a rather wide hump appears. Moreover, in the vicinity of this crossing, the maximum density of the larger p-type orbitals has passed beyond the position of the ground state atom. The attractive A core ionic interactions causes the energies of these larger configurations to decrease. Thus the avoided crossing is due to the interaction of the 2s orbital with several p-type orbitals. These larger p-type orbitals continue to mix strongly in the electronic wavefunction at the equilibrium separation.

Browne has calculated the potential curves of the two lowest states of this symmetry. He used a two-term wavefunction consisting of the first two configurations of the wavefunction used in the present calculation. The potential curves were calculated using orbital exponents optimized for each state for each internuclear separation. For the (3pσ,2s) state, the hump has a peak of .0294 a.u. at 3.75 a₀. It seems somewhat surprising that the peak in Browne's curve is almost three times larger than the peak obtained in the present calculation. Even if Browne's peak is compared to the peak in our ab initio potential, Browne's peak is still larger by more than a factor of two. The explanation for these differences is apparently that the 3pσ molecular state is a Rydberg state. The orbital exponents used in Browne's calculation are contained in
the thesis of Cohen. The orbital exponent of the 2p orbital decreases from .5 to .34 between the peak and the equilibrium position of the potential curve, indicating the 3p character of the 3pσ Rydberg orbital. However, the quantum defect for this state is large indicating that core penetration is important. The structure projections of Table 14 show that, in the present calculation, there are significant contributions to the wavefunction from the inner core region, as indicated by 2s and 2p projections, and from the outer hydrogenic region, as indicated by the 3p and 4p projections, for small R. The magnitude of humps due to avoided crossings depends on the interaction of different types of configurations. Apparently the strength of this interaction is fairly sensitive to the quality of the wavefunctions. The single p orbital in Browne's calculation could not both expand to represent the 3p character of the Rydberg molecular state and also adequately represent the inner region where it overlapped the 2s orbital. The multi-configuration wavefunction of the present calculation is better able to do this and, hence to obtain a lower hump.

The available spectroscopic data for the \( ^3\Sigma^+ \) system is not nearly as extensive as that for the systems previously discussed. Of the states we have calculated, effective quantum numbers are available only for the 3pσ state. Table 5 contains calculated and observed effective quantum numbers and the calculated quantum defects. The geometry of the pσ
states forces their Rydberg orbitals to penetrate the core more than the Rydberg orbitals of any other states. This is clearly reflected in the magnitude of the quantum defects. Nevertheless, there is still fairly good agreement between the observed and calculated effective quantum numbers for the $3p\sigma$ state.

The comparison between the observed and calculated hump is more complicated. Ginter and Battino have reported that the nonexistence of this hump is extremely unlikely. They have not, however, observed direct evidence of the hump. The largest $R$ for which they have been able to reconstruct the potential is about 3.0 $a_o$. The potential at this point lies about .012 a.u. above the separated atom limit. Their estimate of the curve beyond this point places the peak near 3.4 $a_o$ with a magnitude of about .018 a.u. The differences between these results and the results obtained from our ion-core adjust potential are probably due to two factors. First, the magnitude of the calculated hump is taken with respect to the calculated separated atom energy. For this case, the separated atom energy lies .00224 a.u. above the spectroscopic energy. Thus, assuming that there is no problem with the ion-core adjustment procedure, the upper bound for the hump is .0129 a.u. Second, the hump in the calculated curve becomes very flat near the peak. The extrapolated potential of Ginter and Battino is more sharply peaked. Ginter and Battino have based the
construction of their potential to \( R = 3.0 \, \text{a}_0 \) on band spectra from the first five vibrational levels of this state. Ginter\(^{43}\) remarks that considerable effort was made to extend the vibrational data with no success. This could, of course, indicate that the potential is not as sharply peaked as assumed by the extrapolation of Ginter and Battino but, instead, becomes rather flat as shown in our calculations. It is also possible that the larger interaction of the core and excited orbital described above makes the simple ion-core adjustment procedure used here less reliable for this state than it is for less penetrating states.

Guberman and Goddard have calculated potential curves and wavefunctions for the five lowest states of the \( ^3\Sigma^+_g \) system. Their potential curve for the lowest singlet state is very similar to our potential for the lowest triplet state. However, they regard the excited orbital near the equilibrium separation as a diffuse 2p orbital and label this state \((2p\sigma, 2s)\). Likewise, their labels for the excited orbitals are \(3p\sigma, 4p\sigma, \) and \(5p\sigma\). In our work the normal UAO designations are used. The UAO \(2p\sigma\) singlet is the unstable state formed by two-ground state helium atoms. The UAO \(2p\sigma\) triplet is forbidden by the Pauli principle. Thus for both the singlet and triplet systems, \( n = 3 \) for the lowest bound np\(\sigma\) state.

We have used the UAO designations for two reasons. First this is the notation used by Herzberg\(^{37}\) and Rosen\(^{32}\)
in their tabulations of the properties of the Rydberg states of He$_2$ and by Ginter$^{28,43,44}$ in his spectroscopic studies of these states. The change of labels suggested by Guberman and Goddard would seem to needlessly confuse things. Second the theoretical motivation for changing the notation is not sufficiently convincing. In section 2.B.a. we have described qualitatively the relation between quantum defects and shifts of the hydrogenic wavefunction which approximates the Rydberg orbital. The very large quantum defects of the npσ states in UAO notation indicate an inward shift of the approximate hydrogenic orbital. The behavior of the orbital exponent in Browne's calculation and the large projections of the 3p and 4p configurations in the present calculation show that the lowest npσ state is in size intermediate between hydrogenic 2p and 3p orbitals. Thus, whether one wishes to regard this orbital as a diffuse 2p or contracted 3p seems to be largely arbitrary.

ii. $3\Sigma^+_g$(4pσ,2p)

A very large hump dominates the potential curve of this state. The peak in the ion-core adjusted potential has a magnitude of .0394 a.u. near 3.76 a$_0$. The hump is due to both the exchange interaction and an avoided crossing. The dominant structure projections for several values of R are given in Table 14. For large R the wavefunction is dominated by the 2p configuration. The 2p single configuration energy is repulsive for intermediate values of
R due to the exchange interaction. Thus the adiabatic potential curve begins to rise at about 7. \( a_o \) due to this effect. As \( R \) decreases to about 4. \( a_o \), the repulsive 2s configuration mixes into the wavefunction and contributes to the formation of the hump. The larger p-type configurations are attractive in this region. These configurations begin to contribute to the wavefunction in the vicinity of 4. \( a_o \) causing the adiabatic potential curve to peak. The wavefunction at smaller \( R \) is dominated by the 3p and 4p configurations. The Rydberg orbital near the equilibrium separation is perhaps best described as a contracted 4p hydrogenic orbital.

The analogous state in the calculations of Guberman and Goddard is the \( ^1\Sigma_g^+ (3p\sigma, 2p) \). They find that the potential curve has a peak of .03769 a.u. at 3.52 \( a_o \). The qualitative behavior of the singlet wavefunction is very similar to that described here for the triplet.

iii. \( ^3\Sigma_q^+ (4f\sigma, 3s) \)

The potential curve for this state contains two small humps. The first peaks in the vicinity of 10. \( a_o \) and has a magnitude of .00058 a.u. Its location and the absence of possible crossing configurations indicates that this is due to the exchange interaction. The potential decreases very slightly and then rises again. The peak of this second hump has a magnitude of .00216 a.u. at 4.688 \( a_o \).

The structure projections of single configurations are not
as significant for this state as they were for the two previous states. A better indicator of important changes in the wavefunction are the cumulative structure projections which are obtained by algebraically summing over the structure projections for a particular type of configuration. These cumulative structure projections are shown in Figure 8 for this state. These show that the wavefunction consists almost entirely of s-type configurations for large R. In the vicinity of the second hump, p-type configurations are abruptly mixed in. Since the core interaction first becomes important at about this internuclear separation and since the \( (5p\sigma,3p) \) state lies just above the state we are discussing, repulsive s-type and attractive p-type configurations should cross in the vicinity of this internuclear separation. Thus the adiabatic \( (4f\sigma,3s) \) wavefunction rapidly becomes a mixture of these two types of configurations as indicated by the cumulative structure projections. The second hump in the potential curve is due to this avoided crossing.

As R becomes smaller, the wavefunction mixes in more p-type configurations. Near \( 3. a_0 \), the potential curve again closely approaches the potential of the \( (5p\sigma,3p) \) state. An avoided crossing of the second kind, described in section 2.B.b., occurs here. Since two attractive states are involved, there is no hump in the potential curve. The avoided crossing, however, is clearly indicated in the
Figure 8. Cumulative structure projections for the $^3\Sigma_g^+(4f\sigma, 3s)$ state.

Figure 9. Cumulative structure projections for the $^3\Sigma_g^+(5p\sigma, 3p)$ state.
cumulative structure projections by the very abrupt change in the character of the wavefunction near 3. \( a_0 \). For \( R \) close to the equilibrium separation, the wavefunction is dominated by \( f \)-type configurations as is expected since this represents the \( 4f\sigma \) Rydberg state.

Guberman and Goddard have calculated the wavefunction and potential curve for the \( ^1\Sigma_g^+ (4f\sigma, 3s) \) state. They find a small hump of .00015 a.u. near 11.51 \( a_0 \) and a second small hump of .00109 a.u. at 5.14 \( a_0 \). The explanation of these humps and the general behavior of their wavefunction is very similar to that of the triplet state described above for \( R \) greater than 3.5 \( a_0 \). For \( R \) less than this, their potential curve rises again to a peak near 3.0 \( a_0 \) and then decreases to the bonding minimum. A description of the calculation and the basis set used by Guberman and Goddard has been included in our discussion of the \( ^3\Pi_u^- (4d\sigma, 3d) \) state. They explain their hump at 3.0 \( a_0 \) in terms of a strong interaction with the 2s FO state which is very repulsive in this region. The wavefunction near the equilibrium separation seems to be described as a mixture of \( 4f\sigma \) and \( 4p\sigma \) states with possible contributions from the \( 5f\sigma \) and \( 5p\sigma \) states. It will be recalled from our discussion of the \( ^3\Sigma_g^+ (3p\sigma, 2s) \) state that Guberman and Goddard's \( 4p\sigma \) and \( 5p\sigma \) states correspond to \( 5p\sigma \) and \( 6p\sigma \) UAO states, respectively. They do mention that their basis set does not provide a good description of these states.
It appears to us that the behavior of the potential curves obtained by Guberman and Goddard at small $R$ is probably incorrect. The evidence for this is based on rather rough estimates of the position of this state from spectroscopic data and on theoretical considerations.

The only state of the singlet np$\sigma$ series which is known spectroscopically is the 3p$\sigma$. The quantum defect for this state is $7149^{32}$. Using this quantum defect, the approximate energies of the 4p$\sigma$ and 5p$\sigma$ states are easily calculated. The energy separations between these states may be compared with the separations obtained by Guberman and Goddard. We find that the separation between Guberman and Goddard's 2p$\sigma$ and 3p$\sigma$ states agrees with the approximate spectroscopic separation between the UAO 3p$\sigma$ and 4p$\sigma$ to about .001 a.u. which seems quite reasonable considering the approximations. However, the separation between Guberman and Goddard's 2p$\sigma$ and 4p$\sigma$ and between their 3p$\sigma$ and 4p$\sigma$ differs from the separations between the corresponding spectroscopic levels by about .016 a.u. This seems much too large indicating that their 4p$\sigma$ state is too high by about .016 a.u. Since in both their calculation and our calculation, the 4f$\sigma$ state lies just below the p$\sigma$ state, we conclude that Guberman and Goddard's 4f$\sigma$ state also is too high by about this amount.

Theoretical considerations also tend to indicate that there is a problem with Guberman and Goddard's calculation
of this state. The basis they used included no f-type orbitals and only two p-type orbitals. For these states, our basis set included three f-type and five p-type orbitals. We have mentioned that Guberman and Goddard attribute the rise of their potential curve for the 4fσ state to a small maximum near 3.0 a₀ to the interaction of the repulsive 2s F0 state. In our calculation, we find that the dominant contributions to the wavefunction for this state between 3.5 and 3.0 a₀ are from the largest p-type configurations. We remind the reader that p-type configurations are attractive for this symmetry. At 3.0 a₀, the avoided crossing mentioned above occurs. Our wavefunction is represented almost entirely by f-type configurations in this region. We believe the singlet wavefunction should behave in a similar fashion. Thus it seems very clear that both the hump at 3.0 a₀ and the anomalously high energy of the 4fσ state found in Guberman and Goddard's calculation are not correct, but merely reflect the limited basis set used.

The calculated quantum defect for the 4fσ state is shown in Table 5. There seems to be no spectroscopic data available on any Rydberg states with ℓ greater than 2. However, we should expect the 4fσ Rydberg orbital to penetrate very little into the core region. The small calculated quantum defect is consistent with this expectation. That the quantum defect is negative is puzzling. It is
possible that this indicates that the calculated energy lies too high. However, the small size of the quantum defect implies that, if this is the case, the error is small.

\[ \text{iv. } 3\Sigma^+ (5p\sigma, 3p) \]

There is a small hump at large \( R \) with a peak of about \( 0.00057 \) a.u. near \( 10. a_o \). The position of this peak indicates that it arises from the exchange interaction. The cumulative structure projections for this state are shown in Figure 9. The mixture of the adjacent d-type configurations as a function of \( R \) seems to correlate with the magnitude of the hump. For larger values of \( R \), the mixture of d-type configurations diminishes. Since the wavefunction regains its p character, this should not be considered an avoided crossing. This point was discussed in section 2.B.B. The behavior of this state in this region is very similar to that of the \( 3\Sigma_u^+ (4s\sigma, 3p) \) state as should be expected since the core interaction plays no role at large \( R \).

As \( R \) decreases, the attractive p-type configurations cause the potential curve to fall to a minimum of \( 0.00044 \) a.u. near \( 4.68 \) a_o. The cumulative structure projections indicate that this feature is due to an avoided crossing with the lower \( (4f\sigma, 3s) \) state. A second maxima of \( 0.00164 \) a.u. occurs near \( 3.92 \) a_o due to an interaction with the attractive f-type configurations. Finally there is the abrupt transition at \( 3. \) a_o as the wavefunction assumes the \( 5p\sigma \) character.
The corresponding state calculated by Guberman and Goddard is their \((4p\sigma,3p)\). Their potential curve generally resembles ours. However, as was discussed in connection with the \((4f\sigma,3s)\) state above, the energy they obtained for this state near the equilibrium separation is probably somewhat too high.

\[ v. \quad ^3\Sigma_u^+(5f\sigma,3d) \]

The behavior of this state at large \(R\) is essentially the same as that of the \(^3\Sigma_u^+(4d\sigma,3d)\) since the core interaction is negligible in this region. As \(R\) decreases, a large hump with a peak of \(0.0102\) a.u. at \(4.66\ a_o\) develops.

In the calculation of Guberman and Goddard, the singlet equivalent of this state is shown crossing the \(\text{He}_2^+\) A core potential curve. The theoretical arguments against this state having this behavior are the same as those discussed in connection with the \(^3\Sigma_u^+(4d\sigma,3d)\) state.

We will not describe all the avoided crossings which occur in this state. However, we are interested in the interactions of this state with the diabatic B core state described in Chapter 3. This diabatic state is formed from configurations containing the smaller s and p orbitals. The cumulative structure projections between \(3.00\) and \(4.25\ a_o\) are shown in Figure 10. The s component of the wavefunction consists of configurations containing the smaller s orbitals. We take this as an indication of the passage of the diabatic state through this region.
Figure 10. Cumulative structure projections for the $^{3}\Sigma_{g}^{+}$, $(5\Sigma_{g},3d)$, $(6\Pi_{g},4s)$, $(6\Sigma_{g},4p)$, and $(6\Delta_{g},4d)$ states.
vi. The $^3\Sigma_q^+(6p\sigma,4s)$, $(6f\sigma,4p)$ and $(6h\sigma,4d)$ States

We shall not discuss the many avoided crossings which occur involving these states. As with the previous state, we are interested in the possible interactions of these states with the diabatic B core state described in Chapter 3.

The cumulative structure projections for these states are shown in Figure 10. Again the s component consists predominantly of the configurations containing the smaller s orbitals. The diabatic state is dominated by contributions from the small (3s,3p) orbitals, as described in Chapter 3. The structure projections indicate that the contributions from configurations containing these orbitals peak near 3.25 $a_0$. The correlation between s and p cumulative structure projections near 3.25 $a_0$ reflects this. The p-type contribution is large when the s-type is large near 3.25 $a_0$ for two reasons. First, part of the p-type contribution arises from the diabatic state itself. Second, because it consists predominantly of s and p-type configurations, the diabatic state interacts more strongly with wavefunctions containing large contributions from the larger p-type configurations than it does with wavefunctions consisting of f or h-type configurations. Thus, the structure projections indicate that the lowest diabatic state crosses these states near 3.25 $a_0$. 
3. B Core States

All electronic states described in the previous sections are based on variational solutions of Eq. (2.3), the Born-Oppenheimer approximation. However, the results of certain experiments seem to indicate that nuclear trajectories are not always determined by the potentials corresponding to these states. Excitation transfer is said to occur when the collision of a ground state atom and an excited atom results in a ground state atom and an atom in a different excited state. Excitation transfer collisions involving the $n = 3$ excited states of helium atoms have been observed\(^1\),\(^4\),\(^5\). We feel that these collisions may be ascribed to the coupling between different Born-Oppenheimer electronic states as discussed in the first sections of this chapter. In a second type of collision between ground state and excited state helium atoms, the observed products are a helium molecular ion and a free electron. This kind of inelastic collision, known as associative ionization or the Hornbeck-Molnar process, has also been observed for $n = 3$ excited states of helium\(^2\). Additional theoretical assumptions must be made before this type of collision can be adequately described by Born-Oppenheimer states. In particular, the use of the variational method to obtain the relevant Born-Oppenheimer electronic states in this case is questionable, and must be justified.
In our discussion of the $^{3}_{\Sigma^{+}}(4d\sigma, 3d)$ state, we showed that no potential curve obtained from the rigorous variational solutions of the Born-Oppenheimer equation could cross the potential curve of the A state of He$_2^+$. In some cases, however, it is possible to attach significance to energies lying in the continuum above the He$_2^+$ curve. In other cases, these energies are artifacts of the basis set to which no clear meaning may be attached.

It has long been known that there exist quasi-discrete electronic states which are degenerate with the continuum. In spectroscopy, these are known as autoionizing states, and in scattering theory they appear as resonances. There is probably no reason why these states should not, in general, be described as well by the Born-Oppenheimer approximation as normal bound states. The problems lie in the construction of the solution.

In section 2.B.b. we described the two lowest states of the He$_2^+$ ion. Wavefunctions for the Rydberg series He$_2^+$ are constructed by building orbitals on the lowest of the ion states, the $^{2}_{\Sigma^+}$. In this context this state is known as the "A core". The molecular orbital configuration of this state is $(1\sigma_g)^2(1\sigma_u)$. The higher state, the "B-core"; is $^{2}_{\Sigma^+}$ with molecular orbital configuration $(1\sigma_g)(1\sigma_u)^2$. At $R = 2.00$ a$_0$, the potential curve of this state lies 0.3837 a.u. above the potential curve for the A core state. Mulliken has suggested that this B state could
provide the core for a series of Rydberg states. In the vicinity of the equilibrium internuclear separation of the A core, these B core Rydberg states would lie entirely in the continuum.

If we try to construct wavefunctions for these states as solutions of the Born-Oppenheimer equation by the variational principle, we encounter the difficulty discussed above. By rigorously minimizing each successive root of the secular equation formed from a good approximation to a complete set of basis states, a sequence of A core Rydberg states is obtained, since there is an infinity of such states and the A-core energies are the lowest of the symmetry. However, it seems clear that if we can describe these B core states in the Born-Oppenheimer approximation, we should be able to calculate them. O'Malley\textsuperscript{12} has developed a formalism which shows how this can be done.

The difficulty with the use of the usual variational method is in the choice of a complete basis set. O'Malley's formalism requires the use of restricted basis set. Thus, if we use a basis set which is orthogonal to all A core states, the energies and wavefunctions found in a variational calculation are rigorously B core states. The A core states may be formally eliminated from the basis set by a projection operator technique. In practice, A core states may be eliminated in an approximate variational calculation by simply excluding A core states from the
set of basis functions, and by insuring that A core states are not formed by any parameter variation performed. Such bases may be easily formed and used in CI calculations reported here. These calculations are described below.

The discussion of B core Rydberg states is perhaps most naturally expressed in terms of wavefunctions constructed from molecular orbitals. It is well known that such single configuration wavefunctions do not, in general, dissociate properly. At least two such configurations must be combined to properly describe dissociation correctly. One such linear combination represents the separated neutral atoms. The other correlates asymptotically with a positive and a negative ion. Mulliken\textsuperscript{5} seems to indicate that such ionic states will have the effect on the adiabatic potential curve of introducing additional minima at intermediate internuclear separations.

The configurations used to calculate the potential curves described in Chapter 2 were constructed by the VB method. For the $^3\Pi_u$ and $^3\Sigma_u^+$ system, ionic and covalent configurations were formed from the same orbitals. This was done to better represent the wavefunctions near the equilibrium separation. These ionic configurations are present in the bases of these states at larger R. The energy curves of several ionic single configurations are shown in Figure 3. In his paper\textsuperscript{5}, Mulliken provides a sketch of estimated potential curves for $\text{He}_2$. He has
included curves which are B core Rydberg states at small R and dissociate to ions. These curves are qualitatively similar to our ionic configuration curves. We note that the covalent and ionic configurations tend to become degenerate at small R. This behavior has been explained in section 2.B.b. We have seen no unexplained humps or wells in the potential curves at larger R where these configurations become non-degenerate. The inclusion of these ionic configurations does cause a small quantitative improvement in the energy of the states especially in the vicinity of features such as avoided crossings. Thus we conclude that the qualitative features of the potential curves are adequately described in terms of the covalent VB description and that the additional minima suggested by Mulliken apparently do not exist.

We have stressed that no adiabatic Born-Oppenheimer states may cross into the continuum. Nevertheless certain of the special states which are described by single-configuration wavefunctions as discussed above, several of the frozen orbitals and GVB states of Guberman and Goddard's calculation, and the qualitative B core states of Mulliken, all cross the potential curve of the $^{2}\Sigma_u^+$ A core state and extend upwards into the continuum. Guberman and Goddard have explained this behavior in their calculations as a tendency for certain FO wavefunctions to develop B cores as R becomes small. This same explanation applies to some of
our single configuration wavefunctions as shown in section 2.B.b. These results suggest that B core states could act as diabatic states which pass through the bound states and into the continuum. We have investigated this possibility in some detail for the \( ^3\Sigma^+ \) states.

The wavefunctions and potential curves of the highest \( ^3\Sigma^+ \) states have been discussed in the last chapter. The evidence presented there indicated that these states were crossed near \( 3.25 \, \text{a}_o \) by a diabatic state composed of small s and p orbitals. A prescription for the formation of these states was given in section 2.A.e. The use of this method requires that the radial coupling matrix elements be computed. The operator \( \partial \partial R \), which appears in the radial coupling matrix elements, may be expressed in terms of operators involving the electronic coordinates by the use of commutation relations\(^{10,47}\). Browne\(^{15}\) and Junker\(^ {48}\), however, suggested that if these operators are used with approximate molecular wavefunctions, the results are probably unreliable. Melius\(^ {49}\) has recently suggested the expression

\[
\langle \Phi_j(R) \frac{\partial}{\partial R} \Phi_i(R) \rangle \equiv \langle \Phi_j(R) \Phi_i(R+\delta) \rangle / \delta
\]

where \( \delta \) is of the order of \( 10^{-3} \, \text{a}_o \) can be used. We have not, however, evaluated these matrix elements for the wavefunction used here and consequently have not explicitly constructed a diabatic representation. The indications of
a crossing by a diabatic state discussed above, together
with the results presented below concerning the existence
of continuum states, strongly indicates that such states
exist.

We have calculated wavefunctions and potential curves
for $\Sigma^+ \frac{3}{g}$ states using six, thirteen, and seventeen term
wavefunctions. The six and thirteen term wavefunctions
are described in Tables 15 and 16. The seventeen term
wavefunction has been previously described in Table 13.

Using the results of section 2.B.b., we should expect
three configurations of the six configuration calculation
to evolve into A core wavefunctions at small R. Likewise
six of the thirteen configuration and nine of the seventeen
configuration calculations should evolve into A core wave-
functions. Let $n$ be the number of configurations which
develop attractive A cores for a particular basis set.

When the calculation is performed, we find that the single
configuration energies behave as expected. The potential
curves relevant to the current discussion are displayed in
Figure 11. The lowest state of this symmetry, the $(3p\sigma,2s)$
is calculated with all three bases. We show the potential
curve of this state merely to provide some indication of
the relative improvement of the energy obtained by in-
creasing the number of configurations. The improvement is
of the order of $10^{-3}$ a.u. The highest bound potential
curve and the state it corresponds to are also shown. In
Table 15
6 Term Wavefunction for $^3\Sigma_g^+$ States

$$\psi_6 = C_1[1s'_a 2s_a (1s_b 1s_b)] + C_2[1s'_a 2p_{oa} (1s_b 1s_b)]$$
$$+ C_3[1s'_a 3s_a (1s_b 1s_b)] + C_4[1s'_a 3p_{oa} (1s_b 1s_b)]$$
$$+ C_5[1s'_a 4s_a (1s_b 1s_b)] + C_6[1s'_a 4p_{oa} (1s_b 1s_b)]$$

Orbital Exponents

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<th>Exponent</th>
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<td>4p_o</td>
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Table 16
13 Term Wavefunction for $^3\Sigma_g^+$ States

$$\psi_{13} = C_1[1s'_a2s_a(1s_b1s_b)] + C_2[1s'_a2p_{oa}(1s_b1s_b)]$$
$$+ C_3[1s'_a3s_a(1s_b1s_b)] + C_4[1s'_a3p_{oa}(1s_b1s_b)]$$
$$+ C_5[1s'_a3d_{oa}(1s_b1s_b)] + C_6[1s'_a4s_a(1s_b1s_b)]$$
$$+ C_7[1s'_a4p_{oa}(1s_b1s_b)] + C_8[1s'_a4d_{oa}(1s_b1s_b)]$$
$$+ C_9[1s'_a5s_a(1s_b1s_b)] + C_{10}[1s'_a5p_{oa}(1s_b1s_b)]$$
$$+ C_{11}[1s'_a5d_{oa}(1s_b1s_b)] + C_{12}[1s'_a5f_{oa}(1s_b1s_b)]$$
$$+ C_{13}[1s'_a5f_{oa}(1s_b1s_b)]$$

Orbital Exponents

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<thead>
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<th>Exponent</th>
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Figure 11. Potential curves corresponding to the highest and lowest bound states and the two lowest continuum $^3\Sigma_g^+$ states obtained from six, thirteen, and seventeen configuration calculations. For comparison the lowest continuum potential curves obtained from six configuration wavefunctions constructed from exclusively A and B cores are shown.
each case there are $n-1$ bound states. As a reference, the $\text{He}_2^+ \ 2^{\Sigma_u^+}$ single configuration potential curve has also been included.

It is the behavior of the $n^{th}$ potential curve which is of most interest. For each calculation, the $n^{th}$ potential develops as a normal bound state potential from large R to about 3.125 $a_o$. At that point it becomes repulsive and rises into the continuum, crossing the $\text{He}_2^+$ curve at about 2.88 $a_o$. It is important to note that the difference between the potential curves obtained from the three calculations is rather small especially in the immediate vicinity of the crossing point. This seems to indicate two things. First, the wavefunction representing this feature does not strongly interact with the configurations containing the larger orbitals. Clearly, if it were to interact strongly with these configurations, we should expect its position to be very different in these three calculations. Second, the wavefunction of this feature should be adequately represented in terms of the configurations used in the six configuration calculation.

The characteristics of this feature are, of course, fully consistent with its interpretation as a $2s\sigma$ B core state. To further investigate this possibility, we constructed the B core wavefunction shown in Table 17. This wavefunction was obtained from the primitive wavefunction formed by the product of an LCAO-MO containing
Table 17

B Core Wavefunction

\[ \Psi_B = C_1 \left\{ [ls_B^1 2s_A (ls_B^1 ls_A)] + [ls_A^2 (ls_B^1 ls_B)] \right\} \\
+ C_2 \left\{ [ls_B^1 2p_{oa} (ls_A^1 ls_A)] + [ls_A^2 p_{oa} (ls_B^1 ls_B)] \right\} \\
+ C_3 \left\{ [ls_B^1 3s_A (ls_A^1 ls_A)] + [ls_A^2 3s_A (ls_B^1 ls_B)] \right\} \\
+ C_4 \left\{ [ls_B^1 3p_{oa} (ls_A^1 ls_A)] + [ls_A^2 3p_{oa} (ls_B^1 ls_B)] \right\} \\
+ C_5 \left\{ [ls_B^1 4s_A (ls_A^1 ls_A)] + [ls_A^2 4s_A (ls_B^1 ls_B)] \right\} \\
+ C_6 \left\{ [ls_B^1 4p_{oa} (ls_A^1 ls_A)] + [ls_A^2 4p_{oa} (ls_B^1 ls_B)] \right\} \]

A Core Wavefunction

\[ \Psi_A = C_1 \left\{ [ls_B^1 2s_A (ls_A^1 ls_A)] - [ls_A^2 2s_A (ls_B^1 ls_B)] \right\} \\
+ C_2 \left\{ [ls_B^1 2p_{oa} (ls_A^1 ls_A)] - [ls_A^2 2p_{oa} (ls_B^1 ls_B)] \right\} \\
+ C_3 \left\{ [ls_B^1 3s_A (ls_A^1 ls_A)] - [ls_A^2 3s_A (ls_B^1 ls_B)] \right\} \\
+ C_4 \left\{ [ls_B^1 3p_{oa} (ls_A^1 ls_A)] - [ls_A^2 3p_{oa} (ls_B^1 ls_B)] \right\} \\
+ C_5 \left\{ [ls_B^1 4s_A (ls_A^1 ls_A)] - [ls_A^2 4s_A (ls_B^1 ls_B)] \right\} \\
+ C_6 \left\{ [ls_B^1 4p_{oa} (ls_A^1 ls_A)] + [ls_A^2 4p_{oa} (ls_B^1 ls_B)] \right\} \]

The orbital exponents are given in Table 15.
the excited orbital and a single-configuration VB representation of the $^3\Sigma_g^+$ B state. Thus, this wavefunction differs from a complete LCAO-MO representation by the absence of multiply ionized terms. Rather, the configurations used in this wavefunction are simply linear combinations of covalent and ionic configurations chosen to represent only B core states. We feel that results obtained with this B core wavefunction offer a better comparison with results of our earlier calculations than would a full LCAO-MO wavefunction. We have constructed A core wavefunctions by the same procedure and performed calculations in which both types of configurations were contained in the basis. We find that the B core configurations are nearly orthogonal to the A core configurations. The overlap matrix elements between configurations built on different cores are several orders of magnitude less than overlaps between configuration built on the same core.

In Figure 11, the curve labeled "B core" indicates the lowest potential obtained from the calculation using only B core configurations. The position of this curve with respect to the VB potential curves described above suggest that the VB wavefunctions in the vicinity of the He$_2^+$ curve do represent the 2s\sigma B core wavefunction in this region and that a diabatic state which crosses into the continuum near this point probably does exist. However, the situation clearly becomes more complicated as R
decreases. The B core state rises somewhat faster than the lowest continuum VB potentials. Near 2. \( a_0 \), the B core state potential approaches the next higher VB continuum potentials. We have constructed an A core wavefunction by the same procedure used to construct the B core wavefunction. This wavefunction is shown in Table 17. There is one potential curve which lies in the region we have been discussing. This is the potential labeled "A core" in Figure 11.

To understand the behavior of these potentials, we need to examine the wavefunctions. The cumulative structure projections indicate that the B core wavefunction is dominated by s-type configurations. The VB wavefunctions for the lowest continuum state are approximately equal mixtures of the smaller s-type and p-type configurations in the crossing region. As \( R \) decreases, the p-type contributions grow. Near 2. \( a_0 \), the cumulative structure projections for p-type configurations are greater than .80 in each of the three VB calculations. The VB wavefunctions for the second continuum states are also roughly equal mixtures of s-type and p-type configurations in the vicinity of the crossing point. As \( R \) decreases, these wavefunctions become dominated by contributions from s-type configurations. Near 2. \( a_0 \), the cumulative structure projections for s-type configurations are greater than .90. The cumulative structure projections for the A core wavefunction indicate that
the p-type configurations become more important as \( R \) becomes smaller but that neither s-type nor p-type configurations dominate the wavefunction below 2. and 3. \( a_o \).

The exact nature of the A core state is not clear. There should be no reason to expect a quasi-discrete (i.e. "resonance") A core state in the continuum. Thus, we believe that it represents a crude approximation to the inner part of the A core continuum wavefunction at least in the vicinity of the equilibrium internuclear separation. Further calculations have shown that the energy of this state may be varied by including larger p\( \sigma \) configurations in the basis set. To the extent that these p\( \sigma \) configurations approximate the continuum wavefunction, this would indicate a strong coupling between this A state and the continuum.

The nature of the states which cross the ion core potential is somewhat clearer in the vicinity of the crossing. The 2s atomic orbital is small and should not be classified as a Rydberg orbital near the crossing. Thus the excited orbital of the diabatic state which crosses the continuum should probably be described in MO terms as an sp hybrid. This explains the relatively large mixture of the smaller p-type configurations into the wavefunction of this state. As \( R \) decreases, this state apparently begins to interact strongly with the continuum A core state. This interaction has two possibly important effects. First it
implies that the autoionization probability should be large from this state. Second, this state is not as repulsive as it would be as a pure B core state. Thus in a collision, the classical turning point occurs at smaller $R$ so that the autoionization would be enhanced.

We feel that the energy and position of the crossing of this diabatic state and the ion potential obtained in our calculations represent upper bounds for these quantities. The ion-core adjustment procedure lowers both the diabatic state and the ion potential curves by several thousands of an atomic energy unit at the crossing point. Thus the crossing point would occur at an energy which is almost degenerate with the $3^3\text{P}$ and $3^3\text{D}$ separated atomic levels. Also the exchange interaction is important for the small orbitals involved in this state at these internuclear separations. A better representation of the core would probably decrease the magnitude of this interaction and lower the energy of the diabatic state.

Finally, the potential obtained by Guberman and Goddard for the corresponding singlet state, the $1\Sigma_g^+(5p\sigma,3p)$, crosses the A core potential near 3.0 $a_0$. It rises into the continuum until about 2.0 $a_0$ where a small shoulder occurs. Since a B core state should increase monotonically as $R$ decreases, this feature is probably explained in terms of an interaction with some A core state. It occurs at an energy of $-4.875$ a.u. which is rather close to the energy of our continuum A core state in this region.
Thus it seems possible that the potential obtained by Guberman and Goddard may be explained in much the same way as the lowest continuum state in our calculation.
4. Inelastic Collisions

A goal of this work is to describe several collision processes involving \( n = 3 \) excited states of helium in terms of the potential curves discussed in the previous chapters. The first section of this chapter reviews the theory of inelastic transitions in the Landau-Zener approximation. In the second section, the results of calculations using this approximation are presented and compared with experimental results. The last section, a mechanism for associative ionization is discussed in terms of the B core diabatic state described in Chapter 3.

A. The Landau-Zener Model of Inelastic Transitions

The inelastic collisions discussed in this chapter are described in terms of the interaction of two electronic states. The radial diabatic states of the two-state model developed in Chapter 2 are used as the electronic basis states. The reader will recall that these were two normalized, orthogonal molecular wavefunctions, \( \varphi_1(\vec{r}_e, R) \) and \( \varphi_2(\vec{r}_e, R) \), chosen such that the radial coupling matrix \( P = 0 \). The nuclear motion will be treated classically through the introduction of a trajectory \( \vec{R} = \vec{R}(t) \). The coupled equations determining the transition probability are obtained from the time-dependent Schrödinger equation and are solved using the Landau-Zener approximation. The derivation below closely follows that of Zener\(^{50}\), as described by Geltman\(^{51}\).
We suppose that as $t \to -\infty$, the system is known to be in electronic state 1. The two-state time-dependent wave-function is

$$
\Psi_i (\vec{r}_e, t) = c_{1i} (t) \Psi_1 (\vec{r}_e, t) \exp \left(-i \int_t^0 dt \ H_{ii} \right) \\
+ c_{12} (t) \Psi_2 (\vec{r}_e, t) \exp \left(-i \int_t^0 dt \ H_{22} \right).
$$

(4.1)

The classical nuclear trajectory $R = R(t)$ determines the time dependence of $H_{ii}(R)$.

Putting $\Psi_1 (\vec{r}_e, t)$ into the time-dependent Schroedinger equation

$$
i \frac{1}{\hbar} \Psi (\vec{r}_e, t) = H_{el} \Psi (\vec{r}_e, t),
$$

(4.2)

multiplying through this equation, first by $\varphi_1$ and then by $\varphi_2$, noting that $\frac{\partial}{\partial t} \varphi_i (t) = V_R (t) \frac{\partial}{\partial R} \varphi_i (R)$ where $V_R$ is the nuclear velocity, integrating over the electronic coordinates and using the three properties given above of this electronic basis set, we obtain the coupled equations

$$
c'_{1i} = -i c_{12} H_{12} \exp \left[-i \int_t^0 dt \ (H_{22} - H_{ii}) \right]
$$

(4.3a)

$$
c'_{12} = -i c_{11} H_{12} \exp \left[-i \int_t^0 dt \ (H_{11} - H_{22}) \right]
$$

(4.3b)
We recall that the diabatic potential curves, $H_{11}$ and $H_{22}$, cross. The Landau-Zener approximation includes the assumption that the transition probability between electronic states is dominated by the elements of the diabatic Hamiltonian in the vicinity of the crossing point, $R_x$. The specific approximations of the Landau-Zener model are

$$H_{22}(t) - H_{11}(t) \simeq \frac{1}{\hbar} \left( H_{22}(R(t)) - H_{11}(R(t)) \right) (t - t_x)$$

$$= \mathcal{V}_h(R_x) \left. \frac{d}{dR} \left( H_{22}(R) - H_{11}(R) \right) \right|_{R_x} (t - t_x)$$

$$= \alpha (t - t_x) \quad (4.4)$$

and

$$H_{12}(t) \simeq H_{12}(R_x) = \beta \quad (4.5)$$

where $R(t_x) = R_x$.

We eliminate $C_{11}$ by expressing Eqs. (4.3) as a second order ordinary differential equation. Using the Landau-Zener approximations (4.4) and (4.5), we obtain

$$\ddot{c}_{12} - i \alpha (t - t_x) \dot{c}_{12} + \beta^2 c_{12} = 0 \quad (4.6)$$

The changes of variable

$$z = \alpha' \frac{1}{2} e^{i \pi/4} (t - t_x) \quad (4.7)$$
and

\[ b_{12} = c_{12} \exp \left( -\frac{z^2}{4} \right) \quad (4.8) \]

lead to the differential equation

\[ \frac{d^2}{dz^2} b_{12} + \left[ \frac{1}{4} - i \frac{\beta^2}{\alpha} - \frac{1}{4} z^2 \right] b_{12} = 0 \quad (4.9) \]

Let \( \nu = -i \frac{\beta^2}{\alpha} \). Then Eq. (4.9) is in the standard form of Weber's equation. Four forms of the solutions are the parabolic cylinder functions, \( D_{\nu}(z) \), \( D_{\nu}(-z) \), \( D_{-\nu-1}(iz) \), and \( D_{-\nu-1}(-iz) \) where at most only two of these solutions are linearly independent. The asymptotic form of \( D_{\nu}(x) \) depends on the value of \( \arg x \). As \( |x| \to \infty \), for \( |\arg x| < \frac{3}{4} \pi \),

\[ D_{\eta}(x) \to \exp \left( -\frac{x^2}{4} \right) x^{\eta} \left\{ 1 - \frac{\eta(\eta-1)}{2 x^2} + \cdots \right\} \quad (4.10) \]

and for \( \frac{5}{4} \pi > \arg x > \frac{1}{4} \pi \),

\[ D_{\eta}(x) \to \exp \left( -\frac{x^2}{4} \right) x^{\eta} \left\{ 1 - \frac{\eta(\eta-1)}{2 x^2} + \cdots \right\} - \frac{(2\pi)^{\nu}}{\Gamma(-\eta)} e^{\eta \pi i} \exp \left( x^2/4 \right) x^{-\eta-1} \left\{ 1 + \frac{(\eta+1)(\eta+2)}{2 x^2} + \cdots \right\} \quad (4.11) \]

while for \( -\frac{1}{4} \pi > \arg x > -\frac{5}{4} \pi \), the asymptotic forms are the same with \( e^{\eta \pi i} \) replaced by \( e^{-\eta \pi i} \). This specifies the complete asymptotic behavior of \( D_{\nu}(z) \) for \( -\pi \leq \arg x \leq \pi \).
The asymptotic boundary condition is that $C_{12} \to 0$ as $(t-t_x) \to -\infty$. A solution which satisfies this condition is

$$b_{12} = A \ D_{-\nu-1} \left(i\frac{z}{2}\right) \quad (4.12)$$

since, as $(t-t_x) \to -\infty$, $z \to -\infty e^{i\pi/4} = \infty e^{-3i\pi/4}$, the asymptotic form (4.10) gives

$$b_{12} \to A \ \exp \left(i \frac{z}{2}/4\right) \ i^{-(\nu+i)} \ z^{-(\nu+i)} \quad (4.13)$$

and

$$c_{12} \to (\text{const}) \ \lim_{|z| \to \infty} \left[ i \frac{z}{2} \ |z|^{-\nu-1} \right] = 0$$

The magnitude of $A$ is determined by the asymptotic condition that $|C_{12}| \to 1$ as $t \to -\infty$. From Eq. (4.3b)

$$|C_{12}| = \left| \frac{i}{\beta} \dot{C}_{12} \right| = \left| \frac{\alpha}{\beta} \frac{d}{d\frac{z}{2}} \ C_{12} \right| = \left| \frac{\alpha}{\beta} \left( \frac{d}{d\frac{z}{2}} + \frac{\frac{z}{2}}{\beta} b_{12} \right) \exp \left(i \frac{z}{2}/4\right) \right|$$

From Eq. (4.13)

$$\frac{d}{d\frac{z}{2}} b_{12} = A \ \exp \left(i \frac{z}{2}/4\right) \ i^{-(\nu+i)} \ z^{-(\nu+i)} \left( \frac{\frac{z}{2}}{\beta} - \frac{z}{2} \right)$$

Then

$$|C_{12}| \to \left| \frac{\alpha}{\beta} \ A \ \exp \left(i \frac{z}{2}/4\right) e^{-i \pi (\nu+i)/2} \ z^{-\nu} \right|$$
where we have used the identity $i^{-(\nu+1)} = e^{-i\pi(\nu+1)/2}$.

Taking the limit as $z \to \infty e^{-3i\pi/4}$, we obtain

$$|c_{11}| \to \left| \frac{\alpha^{1/2}}{\beta} A e^{i\nu \pi/4} \right| = 1.$$  

Using $\nu = -i \beta^2/\alpha$, we obtain

$$|A| = \left| \beta/\alpha^{1/2} \right| \exp \left[ -i \frac{\beta^2}{2\alpha} \right].$$  

(4.14)

We now go to the post-collision limit, $(t-t_x) \to \infty$, where $z \to \infty e^{i\nu \pi/4}$. In the asymptotic expansion, Eq. (4.11), we let $x = |z| e^{i3\pi/4}$ and $\eta = -\nu-1$. Only the second term in this expansion contributes to $|b_{12}|$ as $|z| \to \infty$. Thus we have

$$|b_{12}| \to \left( \frac{2\pi}{\Gamma(\nu+1)} \right)^{1/2} \left| A \right| \left| e^{-i \pi \nu/4} \right| \left| \Gamma(\nu+1) \right|^{-1/2} \left| \Gamma(-i \beta^2/\alpha) \right|^{-1/2} \left| \Gamma(i \beta^2/\alpha) \right|.$$  

Note that

$$\Gamma(\nu+1) = \Gamma(1-i \beta^2/\alpha)$$

$$= -i \beta^2/\alpha \Gamma(-i \beta^2/\alpha)$$

Then

$$\left| \Gamma(\nu+1) \right|^2 = \beta^4/\alpha^2 \left| \Gamma(-i \beta^2/\alpha) \Gamma(i \beta^2/\alpha) \right|$$

but
\[ \Gamma(z) \Gamma(-z) = \frac{-\pi}{(z \sin \pi z)} \]

so that
\[
\left| \Gamma'(n+1) \right|^2 = \frac{2\pi \beta^2}{\alpha \left[ \exp(\pi \beta^2/\alpha) - \exp(-\pi \beta^2/\alpha) \right]} \]

Thus
\[
| \beta_{12} |^2 \to 1 - \exp\left(-2\pi \beta^2/|\alpha|\right) \quad (4.15)
\]

This is the probability that a transition has occurred for one passage through the crossing point. The same result is obtained for \(|\beta_{12}|^2\) since the result depends on \(|\alpha|\), not \(\alpha\).

Let
\[
p = \exp\left[-2\pi (\beta^2/|\alpha|)\right] \quad (4.16)
\]

be the probability that the system does not make a transition while going through the crossing point. Suppose the system is initially in state 1. After going through the crossing point once there is the probability \(p\) that it is still in 1 and the probability \(1-p\) that it has made a transition to 2. In this model the system must dissociate by passing again through the crossing point. The total probability of ending up in state 2 having begun in state 1 is
\[ P_{12} = p(1-p) + (1-p)p \]
\[ = 2p(1-p) \]  
(4.17)

which is the Landau-Zener formula. The first term is the product of the probability that the system remains in 1 after the first crossing and the probability that it makes the transition to 2 in the second crossing. The second term is the product that the system is in 2 after the first crossing and the probability that it stays in 2 after the second crossing.

The processes discussed here involve helium atoms in some \( n^3L \) excited state colliding with ground state, \( 1^1S \), helium atoms. Since \( S \) atomic states are either the initial or final states and since we ignore angular coupling, the inelastic collisions can involve only \( \Sigma \) molecular states. The partial cross sections, in this case, are given by\(^{52}\)

\[ \sigma_i = \frac{\pi (2L_i+1)}{(2L_i+1)} \left| S_{i2} \right|^2 \]  
(4.18)

where \( L_i \) is the electronic orbital angular momentum of the incident atom, \( K_i^2 = 2mE \) where \( E \) is the incident energy in the relative system, and \( S_{12} \) is the element of the scattering matrix between states 1 and 2. In forming the total inelastic cross section for collisions involving He\(^4\) atoms, we must insure that the total wavefunction is symmetric under exchange of the nuclei. For the collisions
discussed here, the behavior of the $\Sigma_u$ and $\Sigma_g$ potentials is such that the inelastic collisions at thermal energies can occur for collisions involving only one symmetry. Thus the total cross sections are

$$\sigma_{u,g} = \sum_{l \text{ odd, even}} \sigma_l \quad (4.19)$$

The element $S_{12}$ of the scattering matrix is the probability amplitude for finding the system at $t = +\infty$ in the state $\psi_2$ if it was known to have been in state $\psi_1$ at $t = -\infty$. Thus $|S_{12}|^2$ with $p_{12}$ of the Landau-Zener formula, Eq. (4.16), the expression for the partial cross sections becomes

$$\sigma_l = \frac{2\pi (2l+1) p (1-p)}{(2L+1) \kappa_l^2} \quad (4.20)$$

Using Eqs. (4.4) and (4.5), $p$ is

$$p = \exp \left( -2\pi H_{zz}^2 \right) \left| \frac{d}{dR} (H_{zz} - H_{ll}) \right| \quad (4.21)$$

where

$$v_x^2 = \frac{2}{\mu} \left[ E - \frac{l(l+1)}{2\mu R^2} - H_{ll}(R) \right] \quad (4.22)$$

is the radial velocity squared of the $l$th partial wave and all quantities are evaluated at the crossing point $R_x$. 
The applicability of the Landau-Zener result to a particular collision depends on the validity of its two assumptions. First we must be able to describe the nuclear motion classically and second, the transition region must be narrow in order that the approximations of the Hamiltonian matrix elements, Eqs. (4.4) and (4.5), are justified.

The assumption of classical nuclear motion may be examined and, if necessary, modified by the semiclassical method discussed by Smith. In the semiclassical description, the nuclei move along classical trajectories. A complex probability amplitude is associated with this motion. When motion along several trajectories is possible, these probability amplitudes must be added and then squared to obtain cross sections for particular processes. The interference among these scattering amplitudes can result in oscillation in the cross sections.

The scattering matrix, $S$, is unitary and symmetric. For the two-state case, these conditions allow $S$ to be expressed in terms of these real parameters. These are chosen as two phases, $\eta_1(E,\theta)$ and $\eta_2(E,\theta)$, and an amplitude $A(E,\theta)$. The elements of $S$ are

$$S_{11} = (1 - A^2)^{1/2} \exp \left( 2i \eta_1 \right)$$  \hspace{1cm} (4.23a)

$$S_{22} = (1 - A^2)^{1/2} \exp \left( 2i \eta_2 \right)$$  \hspace{1cm} (4.23b)

$$S_{21} = S_{12} = A \exp \left[ i \left( \delta_1 + \delta_2 + \pi/2 \right) \right]$$  \hspace{1cm} (4.23c)
However, in deriving Eq. (4.20), we identified the $|S_{12}|^2$ with $P_{12}$, the Landau-Zener transition probability. In the semiclassical method $P_{12}$ should approximate the average of $|S_{12}|^2$ over a range of partial waves. Thus

$$A_{av}^3 = 2P(1-P).$$  (4.24)

Using the semiclassical method, the S-matrix elements should be made up of terms corresponding to the classical trajectories available for each elastic and inelastic collision. Figure 12 contains a sketch of typical diabatic potential curves for states 1 and 2. Turning points $R_1$ and $R_2$ are also shown. The diagrams describe the classical trajectories. In those diagrams, $S_i$ is the initial or final state and $R_j$ is a classical turning point. Horizontal lines indicate a nuclear trajectory along the potential curve connecting $S_i$ and $R_i$ in which no transition occurs. Diagonal lines denote a trajectory in which one transition occurs. Elements of the S-matrix are constructed by including a factor of $p^\frac{1}{2}$ for each horizontal line, a factor of $(1-p)^\frac{1}{2}$ for each diagonal line, and a phase factor for each diagram and summing over all diagrams. Thus the elements of the S-matrix are

$$S_{i2} = \left[ P(1-P) \right]^\frac{1}{2} (e^{2i\delta_i} + e^{2i\delta_f})$$  (4.25a)

$$S_{ii} = P e^{2i\delta_i} + (1-P) e^{2i\delta_f}$$  (4.25b)
Figure 12. Description of the trajectories used in the semiclassical formation of the elements of the scattering matrix. $E$ is the total energy, $V$ the potential energy, and $R$ the internuclear separation. $R_1$ and $R_2$ are the classical turning points for energy $E$ and $S_1$ and $S_2$ are any initial and final states. In the diagrams, horizontal lines indicate a nuclear trajectory in which no transition occurs. Diagonal lines indicate a trajectory in which one transition occurs.
TRAJECTORIES FOR $S_{12}$

I

II

III

IV

TRAJECTORIES FOR $S_{11}$

V

VI

TRAJECTORIES FOR $S_{22}$
\[ S_{22} = p e^{2i\delta_{22}} + (1-p) e^{2i\delta_{22}} \] (4.25c)

Semiclassically the phases \( \delta_J \) may be replaced by the first two terms of an expansion as in the WKB method\(^5\)

\[ 2 \delta_J = 2 \Delta_J (E, \ell) + \gamma_J \] (4.26)

where

\[
\Delta_J (E, \ell) = \lim_{R \to \infty} \int_{R_J}^R \left\{ 2\mu \left[ E - V_J (R) - \frac{(\ell + \gamma_J)^2}{2\mu R^2} \right] \right\}^{\frac{1}{2}} dR

- 2 \left( 2\mu E \right)^{\frac{1}{2}} R + \ell \pi
\] (4.27)

and \( \gamma_J \) is the remainder. Equations (4.23) can be used to determine several relations among the phases \( \delta_J \). In particular, we obtain

\[ |S_{ii}|^2 = |S_{22}|^2 = 1 - |S_{12}|^2 = 1 - A^2. \] (4.28)

Equations (4.25) give

\[ |S_{ii}|^2 = 1 - 2p(1-p) \left[ 1 - \cos \left[ \frac{2}{\mu} (\delta_{ii} - \delta_{22}) \right] \right] \] (4.29a)

\[ |S_{22}|^2 = 1 - 2p(1-p) \left[ 1 - \cos \left[ \frac{2}{\mu} (\delta_{22} - \delta_{12}) \right] \right] \] (4.29b)

\[ |S_{12}|^2 = 2p(1-p) \left[ 1 + \cos \left[ \frac{2}{\mu} (\delta_{12} - \delta_{22}) \right] \right]. \] (4.29c)
First note that

\[
\Delta_{\text{III}} - \Delta_{\text{I}} = \left\{ \int_{R_1}^{R_2} \left\{ 2\mu \left[ E - V_\gamma (R) - \frac{(l + \nu_2)^2}{2\mu R^2} \right] \right\} \frac{dR}{ \sqrt{R}} \right\} = \Delta_d
\]

Likewise

\[
\Delta_{\text{IV}} - \Delta_{\text{I}} = \Delta_d.
\]

Thus

\[
2 ( \delta_{\text{III}} - \delta_{\text{IV}} ) = 2 \Delta_d + \gamma_{\text{III}} - \gamma_{\text{IV}} = 2 \Delta_d + 2 \gamma_d,
\]

\[
2 ( \delta_{\text{IV}} - \delta_{\text{I}} ) = 2 ( \delta_{\text{III}} - \delta_{\text{IV}} ) = 2 \Delta_d + 2 \gamma_d,
\]

and

\[
2 ( \delta_{\text{I}} - \delta_{\text{II}} ) = 2 ( \delta_{\text{III}} - \delta_{\text{IV}} ) + \pi = 2 \Delta_d + 2 \gamma_d - \pi.
\]

These relations do not determine \( \gamma_d \). However, in the limit of small coupling \( (p - 1) \) and larger energies, the WKB distorted wave approximation gives \( \gamma_d = \pi/4 \). Using this value of \( \gamma_d \) and a few trigonometric identities, we obtain

\[
|S_{21}|^2 = A^2 = 4p(1-p)\sin^2[\Delta_d + \pi/4]
\]

(4.31)
which is the usual Landau-Zener-Stueckelberg result$^{50,57}$. It is clear that Zener's result, Eq. (4.17), represents an average over a range of partial waves as asserted in Eqs. (4.24).

Thus, we have followed Zener in obtaining a transition probability based on purely classical nuclear motion. This result was improved by using the semiclassical method which takes into account the quantal phase interference along classical trajectories. However, there comes a partial wave, $l_c$, in every collision when the classical velocity vanishes at the crossing point, $R_x$. Classically, there is no contribution to the transition probability from $l > l_c$. Of course, the classical description of nuclear motion has failed by this point since, through quantum mechanical tunnelling, partial waves greater than $l_c$ can contribute to the transition probability. This clearly will have an effect on the results obtained above. Equation (4.21) requires $p$ to vanish as $l \to l_c$ so that the Landau-Zener formula (4.16) cannot be valid in this region. Moreover, the additional phase term $\gamma_d$ was found in an approximation which is only good at higher energies so that it becomes suspect.

Both these effects may be treated for $l$ close to $l_c$ by methods developed by Nikitin$^{58}$. When the specific cases we are treating are discussed in the next section, however, we will see that the tunnelling effect is not important for these collisions. The choice of a proper value for $\gamma_d$, however, is not so clear.
The dependence of $\gamma_d$ on $l$ and on $H_{12}$ is not yet completely understood. Studies by Delos and Thorson\textsuperscript{59} seem to indicate that $\gamma$ tends toward zero as the energy and coupling are decreased. Olsen and Smith\textsuperscript{60} have calculated inelastic cross sections for the excitation of Ne by He\textsuperscript{+} using the close-coupled and distorted wave methods. Nikitin and Reznikov\textsuperscript{61} have repeated Smith and Olson's calculation using the Landau-Zener-Stueckelberg formula, Eq. (4.31). They found that all three methods yielded the same partial cross sections from $l = 0$ through the partial wave corresponding to the last peak in the partial cross sections. Since this is a case of higher energy and weak coupling, their results indicate that $\gamma = \pi/4$ is the proper choice for $\gamma_d$ under the conditions given above.

Miller\textsuperscript{62} has developed an extended semiclassical method in which the usual semiclassical phase factor appears as the asymptotic limit of an Airy function. He has suggested\textsuperscript{63} that this result be used in the Landau-Zener-Stueckelberg formula. For the case of diabatic potentials, Miller's expression for the transition probability is

$$\left| S_{_{12}} \right|^2 = 4\pi p (1 - p) \Xi^{1/2} A_i^2 (- \Xi)$$  \hspace{1cm} (4.32)

where

$$\Xi = \left( 3 \Delta_d / 2 \right)^{3/3}$$
We refer to Eq. (4.32) as the Landau-Zener-Stueckelberg-Miller formula (LZSM).

We have used the LZSM formula to obtain inelastic cross sections and have compared these with the results of close-coupling calculations. In our program, interpolated potential points are obtained by use of a natural cubic spline. The Airy functions are evaluated by Gordon's method.

Cohen and Cohen, Evans, and Lane have performed quantum-mechanical close-coupling calculations for \(2^3S \rightarrow 2^3P\) excitations in collisions between \(2^3S\) metastable and ground-state helium atoms. They have studied the changes in the behavior of the elastic and excitation cross sections as a scale factor \(f\) in the coupling matrix element \(f H_{12}\) is varied from 0.1 to 1.0. For a collision energy of 10.0 ev and \(f \leq 0.1\), they find that the diabatic coupling is weak. Thus, the LZSM approximation should be good in this case. The inelastic partial cross sections obtained from these close-coupling (c.c.) calculations and from the LZSM formula are shown in Figure 13. The separations between successive maxima and minima are almost the same in the two calculations. The differences in the magnitudes of the peaks increases with \(l\) and is due to the tunnelling effect described above. This causes the total inelastic LZSM cross section to be about seven per cent smaller than the c.c. result. Thus, on the basis of the comparisons presented
Figure 13. Comparison between LZSM results and the results of Cohen's close coupling calculations for $2^3S \rightarrow 2^3P$ inelastic partial wave cross sections at 10. eV. for the diabatic coupling reduced by a factor of 0.1.
TRANSITION CROSS SECTION
REDUCED INTERACTION: 0.1 $H_{12}$

$\sigma_{21}^{\text{C.C.}} = 4.4 \ a_0^2$

$L_{ZSM} = 4.1 \ a_0^2$

$\sigma_{21}$

$\lambda$

$\sigma_{21}^\prime (a_0^2)$
here, we expect the LZSM formula to be an accurate approximation in the weak diabatic coupling case whenever the tunnelling region can be neglected.

The second criterion for the validity of the Landau-Zener result was that the approximations of the Hamiltonian matrix elements, Eqs. (4.4) and (4.5), be justified. We should expect these approximations to become better as the width of the coupling region becomes smaller. An approximation for this width is the $\Delta R$ of Eq. (2.20). In the calculation of Cohen et al. for $f = 0.1$, this width amounted to $\Delta R = .19 a_o$.

The LZSM formula was derived for the weak diabatic case. This formula breaks down as the coupling between states increases and the adiabatic limit is approached. Figure 14 shows the partial cross sections obtained from the LZSM formula and the close-coupling calculations of Cohen et al. for $f = 0.3$. The positions of the peaks of the LZSM partial cross sections are shifted since the diabatic potentials no longer describe the zero-order nuclear trajectories. Cohen et al. have calculated partial elastic cross sections using the WKB distorted wave formula for both diabatic and adiabatic potentials for $f = 0.1$ and $0.3$ and have compared these with the results of their close coupling calculations. They find that the cross sections for $f = 0.3$ are mainly adiabatic and for $f = 0.1$ are mainly diabatic. The differences between their diabatic and close-
Figure 14. Comparison between LZSM results and the results of Cohen's close coupling calculation for $2^3S \rightarrow 2^3P$ inelastic partial wave cross sections at 10. eV. for the diabatic coupling reduced by a factor of 0.3.
TRANSITION CROSS SECTION
REDUCED INTERACTION: 0.3 \( H_{12} \)

\[
\sigma_{21} = 3.0 \, a_0^2
\]

\[
\sigma_{LZSM} = 2.7 \, a_0^2
\]

C.C. --

LZSM

\( \sigma_{21} (a_0^2) \) vs \( \ell \)
coupling calculations for \( f = 0.3 \) for \( l > l^*_x \) are similar to the differences shown in Figure 13 for similar reasons.

The magnitude of \( \lambda \) of Eq. (2.24) may indicate whether a diabatic or an adiabatic coupling case exists. For the two cases, \( f = 0.1 \) and 0.3, Cohen gives for \( \lambda \) the values 10. and 1., respectively, for \( l = 0 \). We will use these as a guide in the applications of the Landau-Zener formula described below. It is important to note, however, that in our previous comparisons the magnitude of the total Landau-Zener cross sections agreed fairly well with the close coupling results.
B. Excitation Transfer

Two inelastic processes are possible in collisions between \( n = 3 \) excited and ground-state helium atoms at thermal energies. These are nonresonant excitation transfer (N.E.T.)

\[
\text{He}^* + \text{He} \rightarrow \text{He}^*' + \text{He} \quad (4.33)
\]

and associative ionization (A.I.)

\[
\text{He}^{**} + \text{He} \rightarrow \text{He}_2^+ + \text{e} \quad (4.34)
\]

Here \( \text{He}^* \) represent any \( n = 3 \) excited state of helium. \( \text{He}^{**} \) is any other energetically allowed excited state. As we shall see, both theoretical considerations and experimental results tend to favor transitions to adjacent states of the same spin. \( \text{He}^{**} \) represents an \( n = 3 \) excited state other than the \( 3^1S \) and \( 3^3S \) states. N.E.T. is discussed in this section and A.I. in the following section.

We have reviewed in the first sections of Chapter 2 and the first section of this chapter some of the theory of inelastic processes. We have seen that the appearance of an avoided crossing in the adiabatic potential curves and wavefunctions signals the possibility of a N.E.T. reaction. Clearly the simplest case is the one in which only two states (one crossing) need be considered. We have
discussed the validity of approximate formulas for inelastic cross sections in the two-state case. Among the states for which we have calculated wavefunctions and potential curves, it appears that there are only two possible cases of N.E.T. which should be described well in the two-state approximation. Results of calculations of the cross sections for these states are discussed below.
a. $^3S \rightarrow ^2P$

There seems to be little experimental data on this collision. In 1965 Bennett, Kindlman, and Mercer (BKM) measured total inelastic cross sections for a number of excited states of helium. In their experiment, excited states are produced by pulsing an electron gun. The transient decay of the light intensity of one optical transition line is measured as a function of gas pressure. If there is only one collisional destruction mechanism and if it is irreversible, the decay of the density of the upper state obeys

$$n = n_0 e^{-Rt}$$

where

$$R = A + n_0 \nu \sigma$$

Here $A$ is the total radiative decay rate of the level, $n$ is the density of ground-state atoms, $\nu$ is the mean velocity and $\sigma$ is the velocity-averaged total destructive cross section. Thus measurements of the light intensity decay at several pressures give the velocity averaged cross sections.

BKM report that the decay of the $^3S$ state was describable by a single exponential decay. They felt that
this indicated that the single, irreversible collisional deactivation process responsible was A.I.

Wellenstein and Robertson\textsuperscript{1} (WR) have reported an upper bound on this cross section. Their experiment involved the use of the positive column of a glow discharge as the reaction chamber in which to measure the rate constants for N.E.T. between the $n = 3$ states of helium. Each state was selectively modulated by absorption of radiation. By monitoring the in-phase component of radiation from adjacent $n = 3$ states over a range of discharge currents and pressures, the rate constants of N.E.T. were determined. They report no measurable cross sections for the excitation transfer reactions $3^3S \rightarrow 3^3P$ and $3^3S \rightarrow 3^3D$. By monitoring the $\text{He}_2^+$ ion concentration, they determined\textsuperscript{2} an upper bound for A.I. from $\text{He}(3^3S)$ as $0.01 \text{ Å}^2$. Their upper bound\textsuperscript{67} on the total collisional deactivation cross section, however, was $8.0 \text{ Å}^2$.

The interpretation of BKM of their inelastic cross section for $3^3S$ in terms of A.I. seems clearly refuted by the data of WR. The theoretical discussion in the following section supports WR. The absence of a measurable cross section for N.E.T. from $3^3S$ to another $n = 3$ level is easily understood in terms of the separations of the $n = 3$ energy levels (Table 3). The $3^3P$ state lies $0.010 \text{ a.u.}$ ($0.272$ ev.) above the $3^3S$ but $kT$ at $300^\circ K$ is only about $0.001 \text{ a.u.}$ ($0.027$ ev.). Thus, if the inelastic BKM cross
section is due to N.E.T., it must result in an n = 2 excited state of helium. Only \( \Sigma \) molecular states are produced by the interaction between a \( 3^3S \) and ground-state helium atom. No mechanism for N.E.T. appears possible among the \( 3^3\Sigma_g^+ \) states since there are no avoided crossings between the \( (4f\sigma,3s) \) state and lower states. An apparently favorable crossing does exist between the \( (3d\sigma,3s) \) and \( (3s\sigma,2p) \) states of the \( 3^3\Sigma_u \) system. Thus we suggest that the inelastic cross section measured by BKM corresponds to the process \( 3^3S \rightarrow 2^3P \).

The experimental evidence seems consistent with this interpretation. BKM reported that their data indicated that an irreversible mechanism was responsible for this cross section. The large separation between the \( 2^3P \) and \( 3^3S \) energy levels insure irreversibility of the proposed reaction.

We have calculated inelastic cross sections for this reaction using the two-state approximation. Using quadratic interpolation, the minimum energy separation between the adiabatic potential curves for the \( (3s\sigma,2p) \) and \( (3d\sigma,3s) \) states is \( 4.88 \times 10^{-4} \) a.u. (.013279 ev.) at \( R = 2.708 \) a.\( _0 \). Diabatic (crossing) potential curves, \( H_{11} \) and \( H_{22} \), were constructed by interpolating between the \textit{ab initio} adiabatic potential curves. A cubic spline constructed from all calculated adiabatic potential points except the point at \( R = 2.75 \) a.\( _0 \) was used in the interpolation. These diabatic
potentials crossed at \( R = 2.718 \ a_0 \). This value is consistent with the point of minimum separation given above and with the apparent crossing point of these potentials given by Ginter and discussed in section 2.C.b.ii. The discussion in section 2.A.d. indicates that the two-state diabatic matrix element equals half the separation of the adiabatic potential curves at the crossing point so that
\[
H_{12} \equiv 2.44 \times 10^{-4} \ \text{a.u.} \ (6.64 \times 10^{-3} \ \text{ev.})
\]
The value of
\[
\Delta H = \left| \frac{d}{dR} (H_{22} - H_{11}) \right|_{R_x}
\]
.0096 a.u./\( a_0 \). The ratio of adiabatic to diabatic coupling, given by Eq. (2.24) is, for zero incident energy and \( \ell = 0, \lambda = 226 \). This indicates that this is a case of weak diabatic coupling. The width of the coupling region given by Eq. (2.20) is \( \Delta R = .10 \ a_0 \). This is consistent with the very abrupt change in the cumulative structure projections for these states in the vicinity of 2.75 \( a_0 \) which was described in the discussion of these states. Thus, the indications are that Landau-Zener formula, Eq. (4.20), should be a good approximation when used to calculate total inelastic cross sections.

In the description of the \((3d\sigma, 3s)\) state, we noted the presence of a small barrier with a peak near 10. \( a_0 \) of about 9.\( \times 10^{-4} \) a.u. (.0244 ev.) relative to the separated atom energies. In addition to preventing the \( 3^3S \rightarrow 2^3P \) reaction for relative energies much below the peak value, the hump also causes the truncation of the partial wave
expansion due to the rapid rise of the usual centrifugal barrier over the hump region. Of course, a quantum mechanical barrier penetration is possible. We have taken this into account approximately by multiplying each partial cross section, $\sigma_\ell$, by the WKB transmission coefficient $T_\ell$, where

$$T_\ell = \exp \left\{ -2 \int_{R_{\text{in}}}^{R_{\text{out}}} \left[ 2\mu \left( H_{s\ell} (R) + \frac{(\ell + \frac{1}{2})^2}{2\mu R^2} - E \right) \right]^{1/2} dR \right\}. $$

and $R_{\text{in}}$ and $R_{\text{out}}$ are the inner and outer classical turning points of the centrifugal barrier. These turning points were found by searching the natural cubic spline constructed from the ab initio potential points. An iterated Simpson's rule method was used to compute the integral.

Let $\ell_0$ be the largest classically allowed partial wave for a given incident energy. We found that only the first one or two partial waves greater than $\ell_0$ contributed to the cross sections. This is due to the width of the barrier rather than its height.

We have calculated inelastic cross sections for the $3^3S \rightarrow 2^3P$ process using the Landau-Zener formula. The coupling matrix element is taken to be $f H_{12}$ where the scaling parameter $f$ is included to examine sensitivity to the coupling and to make possible a semi-empirical determination if desirable. The dependence of the cross section on the coupling elements was examined by performing calcu-
lations for \( f = 0.5, 1.0, \) and 2.0. In one set of calculations the potential barrier was completely neglected, presumably giving us an upper limit for the cross section. When the barrier was included, the separated atom energy was taken as the value of the potential at \( R = 15.0 \) \( a_0 \). This reduces the barrier height to \( 4 \times 10^{-4} \) a.u. (0.0109 ev.). We feel that the \textit{ab initio} calculation probably overestimates the size of these barriers. A better representation of the ground-state helium atom wavefunction should be used to accurately compute these barriers. Moreover, the size of the inelastic cross section with the original barrier would be negligible at thermal energy. The calculated cross sections are shown in Figure 15.

There are several features of these cross sections which are not dependent upon the exact values of parameters. The cross sections calculated without the barrier rise monotonically as the energy is reduced. This is easily understood in terms of the relative smallness of the energy changes shown here compared to the energy at the crossing point. Thus, for the same partial wave, the velocity of the particles at the crossing point is about the same for any energy in this range and so the exponential factor \( p \) in Eq. (4.20) is about the same. The energy dependence of the cross sections is determined by the factor \( 1/K^2 \) where \( K \) is the wavevector of the incident particle.
Figure 15. Total $^{3}\Sigma_{u}^{-}(3^{3}S \rightarrow 2^{3}P)$ inelastic cross sections using the Landau-Zener approximation. The interaction matrix element is $f_{H_{12}}$. The barrier in the potential curve has a peak of .0109 eV. at $R = 10. a_{o}$. 
TRANSITION CROSS SECTIONS
$3\Sigma_u^+ (3^3S \rightarrow 2^3P)$

CROSS SECTION ($\text{Å}^2$)

ENERGY ($\times 10^{-3}$ a.u.)

WITH BARRIER

WITHOUT BARRIER
When the barrier is included in the calculation, the cross sections are reduced by about an order of magnitude and their behavior for small energies is just the opposite of what it was before. The simple Landau-Zener partial cross section, for the transition described here, is a monotonically increasing function of $\lambda$. Typically about twenty-five partial waves contribute to the total cross section. Thus, when the barrier is introduced, those partial waves which contributed most to the cross section are eliminated. As the incident energy is reduced to the barrier height, only a few small partial cross sections contribute and the total cross section is rapidly reduced.

Another significant feature is that the curves representing the cross sections for different values of $f$ are nearly parallel. This reflects the fact that we have a case of very weak diabatic coupling as is indicated by the large value of $\lambda$ given above. In this case, the exponential factor $p$ is given approximately by

$$p \approx 1 - \pi/2\lambda$$

so that the inelastic cross sections are proportional to $H_{12}^2$. Thus, in the semi-log graph of Figure 15, curves corresponding to different values of $f$ are parallel.

The strong dependence of the cross section on the coupling element and the hump height makes it difficult to
suggest a best theoretical estimate for the cross section. The peak of the barrier is probably overestimated in these calculations. As the barrier decreases, the cross sections will rise and the point at which it begins to sharply fall off will move to lower energies.

The difficulty in obtaining accurate values of the coupling matrix element and the hump height is, of course, the small magnitude of those numbers compared to the total electronic energy. We feel that a wavefunction which includes a more accurate representation of the core orbitals must be used in a calculation before the magnitudes of these quantities may be known with more certainty.

These results, however, do indicate that experimental studies of the inelastic cross section as a function of temperature could be quite useful in determining the height of the barrier at large R. The temperature dependence of the total inelastic cross section for the $3^1P$ state has recently been studied by Hunter and Leinhardt\textsuperscript{45}. They found that the cross section increased at very low temperatures ($\sim 22^\circ$K). They refer to further experimental work by Driscoll and Smith in which this same behavior is found. The theoretical description of inelastic processes originating from the $3^1P$ level is more complex and subject to more uncertainty than the collision dealt with in this section. We feel that the theoretical simplicity of collisional processes originating from the $3^3S$ or $3^1S$ states
would make an experimental study of the temperature dependence of these states particularly interesting.
b. \( 3^3P \rightarrow 3^3S \)

In the experiment described above, Wellenstein and Robertson have also measured the \( 3^3P \rightarrow 3^3S \) velocity averaged N.E.T. cross section. They report a value of \( 2.9 \pm 0.3 \, \text{Å}^2 \) for this cross section at 400\(^\circ\)K.

There does not seem to be a mechanism for this reaction among the ungerade molecular states. In the \( ^3\Sigma_g^+ \) system, however, there is an avoided crossing between the \( (4f\sigma,3s) \) and \( (5p\sigma,3p) \) states near 4.75 \( a_0 \). We have used this feature to describe the \( 3^3P \rightarrow 3^3S \) process. There is another crossing of these states near 3.0 \( a_0 \). However, the large hump in the \( (5p\sigma,3p) \) potential near 3.75 \( a_0 \) should prevent transitions occurring at this crossing from leading to excitation transfer for all but the lowest partial waves. These states should be strongly diabatic so that the contribution of these small partial waves to the total cross section is small and can probably be neglected.

We have used the same procedure as in the previous case to obtain the interaction matrix element and the diabatic potentials. The interaction matrix element, \( H_{12} \), is \( 1.87 \times 10^{-3} \, \text{a.u.} \) (.0509 ev.) and the magnitude of the force difference at the crossing point, \( \Delta R \), is .0215 a.u./\( a_0 \). Using these parameters, the ratio of adiabatic to diabatic coupling, \( \lambda \), for \( \ell = 0 \) and zero incident energy is 3. The width of the crossing region, \( \Delta R \), is .35 \( a_0 \). Clearly the weak diabatic coupling approximation will not be as good in
this case as in the previous case. Nevertheless if there are enough partial cross sections, then the weak diabatic total cross sections should be approximately correct. Moreover, the width of the coupling region is greater in this case than in the previous case. This is consistent with the behavior of the cumulative structure projections for these states. These do not change as rapidly in the crossing region for this case as they did in the previous case.

We have computed total inelastic cross sections for this case using both the LZ and the LZSM formulas. Using the LZ formula, cross sections were computed with the coupling element $f H_{12}$ where $f = 0.5, 1.0, 1.5$, and $2.0$. Only the original coupling matrix element, $H_{12}$, was used in the LZSM calculation. These cross sections are shown in Figure 16. Usually about sixteen or seventeen partial waves contributed to the total cross section. There is a barrier with a peak of about $6 \times 10^{-3}$ a.u. (.0163 ev.) located at $10. a_0$ in the upper state potential curve. The effect of this barrier was not included in the calculations. It was felt that the small number of partial waves which would contribute if the barrier were included and the absence of a clear case of weak diabatic coupling would make results of such calculations quantitatively unreliable. Qualitatively, the effect of the barrier in the total cross section should be similar to the barrier effects in the previous case, and thus could lower the cross sections significantly.
Figure 16. Comparison between total 
$^{3}_{\Sigma}^{+}(3^{3}P \rightarrow 3^{3}S)$ inelastic cross 
sections calculated in the LZ and 
LZSM approximation. The inter-
action matrix element is $f_{H_{12}}$. 
The transition cross sections display several interesting features. First, the LZSM cross section shows oscillations due to phase interference along different trajectories. The LZ cross sections agree with the LZSM cross sections to within about twenty per cent.

Second, the effect of scaling the interaction matrix element is very different in this case than it was in the previous case. The maximum cross sections are found for \( f = 1.0 \). This may be understood in terms of the ratios of adiabatic to diabatic coupling. For \( f = 0.5, 1.0, 1.5, \) and 2.0, the values of this ratio are \( \lambda = 12., 3., 1.33, \) and .75 respectively. The states may be considered diabatic for \( \lambda \) less than 3.0. Thus, as the coupling increases, so does the cross section. For values of \( \lambda \) greater than 3.0, the states become more adiabatic. As the coupling increases, the adiabatic coupling and, hence, the cross section decrease. This behavior is consistent with the results of Cohen et al.
C. Associative Ionization

The second collisional process we have considered is associative ionization, Eq. (4.34). The most recent and detailed experimental investigation of this reaction is that of Wellenstein and Robertson\textsuperscript{2} which was described in the previous section. Their paper contains a review of previous experimental work. They report A.I. cross sections of 1.6 ± 0.1 and 4.5 ± 0.5 Å\textsuperscript{2} for the 3\textsuperscript{3}P and 3\textsuperscript{3}D states respectively. They could only place an upper bound of .01 Å\textsuperscript{2} on the A.I. cross section from the 3\textsuperscript{3}S state and suggested that this low value probably indicates this cross section should be zero.

Two models of A.I. have been proposed using the two-state approximation. In both models, one of these states must correspond to the A.I. reaction products. In this final state, the electronic wavefunction represents a free electron in the field of an He\textsubscript{2}\textsuperscript{+} ion. The rotational and vibrational states of the He\textsubscript{2}\textsuperscript{+} ion are represented by the nuclear part of the wavefunction. These two models are distinguished by the form of the initial state and the nature of the interaction between the states.

Berry and Nielsen have developed the vibronic coupling model\textsuperscript{69} and applied it to associative ionization in H\textsubscript{2}\textsuperscript{70}. The incident state in this model is composed of a bound adiabatic electronic state and a continuum nuclear wavefunction. The radial coupling between adiabatic states
(vibronic coupling) is discussed in section 2.A.d. That
discussion assumed bounded electronic wavefunctions but
this is not essential. The strength of this coupling
depends on the similarity of the de Broglie wavelengths
for a wide range of separations. The higher bound elec-
tronic states of H\textsubscript{2} form a Rydberg series similar to that
of He\textsubscript{2}. Berry and Nielsen have found cases in which the
integral over the coupling matrix element between the inci-
dent and final nuclear wavefunctions is accumulated over
much of the range of the potential well due to the similitu-
dy of the de Broglie wavelengths. They find that the rate
constants are largest when, for a particular nuclear angular
momentum, the incident energies are as close to the bound
vibrational-rotational state energies as possible, i.e. the
rate constants peak for resonance energies. The rate
constants are also strongly dependent upon the electronic
states involved. However, they report that their calculated
rates for A.I. in H\textsubscript{2} are about two orders of magnitude less
than the experimental values report for helium. Since the
electronic molecular states of H\textsubscript{2} and He\textsubscript{2} are similar, we
should expect that A.I. cross sections calculated with this
model would be of the same magnitude. Hence we should con-
sider a different mechanism for A.I. in helium.

The second A.I. model involves electronic coupling.
The repulsive potential curve of the incident electronic
state crosses the He\textsubscript{2}\textsuperscript{+} ion potential and becomes degenerate
with the continuum of electronic states. The coupling occurs in this region through the interaction between the bound and continuum electronic states. As we have discussed in section 2.C.b., no adiabatic Born-Oppenheimer states of He₂ may behave in this fashion. The B-core states of Mulliken, several of the frozen orbital states of Guberman and Goddard, and several of the single configuration states of our C.I. calculation, do have these properties as has been described in Chapter 3. The use of any of these in an A.I. collision problem at thermal energies, however, presents certain difficulties.

A rigorous practical prescription for the construction of these states is lacking. In Chapter 3, however, we examined several different representations of the repulsive $^3\Sigma_g^+$ continuum states and found a stabilized potential in the vicinity of the crossing point. Guberman and Goddard have reported a $^1\Sigma_g^+$ state with similar behavior. Our $^3\Sigma_g^+$ continuum potential, the He₂⁺ ion potential, and the potentials corresponding to the three adiabatic states which dissociate to n = 3 excited atomic states are shown in Figure 17. All potentials have been modified by the ion-core adjustment procedure. The continuum potential shown here represents an average of the three VB potentials shown in Figure 11. The exact location of the point at which this potential crosses the ion potential is uncertain by about $\pm 10^{-3}$ a.u. However, this point seems to lie at
least $2 \times 10^{-3}$ a.u. above the $3^3D$ atomic state. Thus, even if this state is responsible for A.I., some quantum mechanical tunneling would have to occur for the transition to take place. The vibrational energy levels of the $\text{He}_2^+$ potential are indicated in Figure 17. The continuum electronic state crosses the ion potential in the vicinity of the $v = 4$ vibrational state. Such a near resonance would enhance the tunneling probability. Of course, the existence of this resonance and the location of the crossing point depend on the adjustment procedure used. A more accurate calculation would probably lower both the ion curve and the crossing curve with respect to the separated atomic energies by at least several thousandths of an a.u. Aside from these difficulties, the accurate computation of the coupling between the quasi-discrete continuum electronic state and the free electron continuum state degenerate with it is a formidable problem.

The behavior of the continuation of the continuum state into the region of discrete states presents additional difficulties. Our hope in taking up this study had been that the existence of the repulsive state would be clearly indicated by a series of closely avoided crossings between adiabatic potential curves. Such structure is not evident in the curves shown in Figure 7. The barriers at large $R$ present additional problems. Thus, an accurate description of A.I. will probably be rather complicated. However, we can speculate on some points.
Figure 17. The dashed line indicates a possible diabatic potential representing a mechanism for associative ionization.
The WR results given above indicate that collisions between ground state and both $3^3P$ and $3^3D$ excited-state helium atoms can result in A.I. at thermal energies. The $^3\Sigma_g^+$ potential curves for these states are shown in Figure 17. It is clear that (5fσ,3d) state cannot be involved in the mechanism for intermediate R since its potential curve has a large barrier in these regions. The coupling between the (5pσ,3p) and (5fσ,3d) states at large R is described in section 2.C.c. This coupling could allow for transfer from the (5fσ,3d) state to the (5pσ,3p) at large R. As R becomes smaller, the trajectory for A.I. could be determined by the (5pσ,3p) adiabatic potential through the crossing at 4.75 $a_0$ to near the peak of the barrier at 4.0 $a_0$. This barrier is due to an avoided crossing. The rapid change of the wavefunction in this region could strongly couple the (5fσ,3d) and (5pσ,3p) states. The location of the repulsive potential in the region below the ion potential is determined approximately by the behavior of the structure projections discussed in section 2.C.c. Electronic mixing of these states is indicated in this region. Moreover, these higher adiabatic molecular states are closed channels at thermal energies. Thus, the coupling between these states could be strong when the incident energy is degenerate with a bound vibrational level of one of these higher states. The combination of strong electronic and nuclear coupling might be represented as a diabatic potential similar to that shown in Figure 17.
There are a number of other states which can be formed from the \(^3\)D and \(^3\)P states. The behavior of these states either has been described in Chapter 2 of this thesis or may be inferred from the rules for the behavior of the major configurations from which these states would be constructed. The requirements for a possible A.I. mechanism are that a repulsive single configuration potential cross the adiabatic states to induce electronic coupling and that the separation between the potentials be small in order that the nuclear wavefunctions overlap constructively.

There are two \(\Delta\) states which may be formed from the \(^3\)D atomic state. The \(^3\Delta_u\) \((3d\delta, 3d)\) should be purely attractive and not interact strongly with any other molecular states of the \(^3\Delta_u\) symmetry. It may interact with \(^3\) \(u\) states through angular coupling terms near the equilibrium separation. This interaction results in excitation transfer to the \(^2\)P state but not in A.I. The \(^3\Delta_g\) \((4f\delta, 3d)\) is initially repulsive at intermediate \(R\) due to the unfavorable core and probably does not couple strongly with any other molecular state.

Four \(\Pi\) states arise from the \(^3\)P and \(^3\)D atomic states. The \(^3\Pi_g\) \((3p\pi, 3p)\) state is purely attractive. This potential should cross the \(^3\Sigma_g^+\) \((4p\sigma, 2p)\) potential. There may be a small angular coupling to this state which could result in excitation transfer, but no contribution to A.I. seems likely. The \(^3\Pi_g\) \((4p\pi, 3d)\) should have a hump
at intermediate internuclear separations which prevents its interacting with other states. The $^3\Sigma_u^-$ states are shown in Figure 2. A mechanism for excitation transfer from $^3\Sigma$ to $^3\Pi$ clearly exists. However, the separation of the (4dπ, 3p) state from adjacent states and the hump in the (5dπ, 3d) state probably precludes any direct contribution to A.I.

Finally there are the Σ states. The $^3\Sigma_u^+$ states are shown in Figure 4. It seems clear that no mechanism exists for A.I. from the (3dσ, 3s) state. The large barrier in the (4dσ, 3d) state at large R and the smaller barriers in the (4sσ, 3p) state at intermediate R made it somewhat unlikely that these states are involved in the A.I. mechanism. Nevertheless, if smaller barriers were found in a calculation using a larger basis set, then the mechanism indicated for the $^3\Sigma_g^+$ states should be considered.
References


48. B. Junker, University of Georgia, private communication.
49. Carl Melius, Sandia Laboratories, private communication.
51. S. Geltman, op. cit., p. 213.


Appendix I

Factoring of Valence Bond Wavefunctions for Small Internuclear Separations.

We wish to show that

\[ |n l_A' 1s_A^1 1s_B^1 \mp n l_B' 1s_A^1 1s_B^1| \xrightarrow{R \rightarrow R_e} |n l_c' 1s_A^1 1s_B^1 \mp n l_c' 1s_A^1 1s_B^1| \]

A STO with \( N = n, L = l \), and centered on nucleus \( A \) may be written

\[ n l_A = \frac{1}{2} n l_+ + \frac{1}{2} n l_- \]

where

\[ n l_\pm = (n l_A \pm n l_B) \]

The product of the core orbitals may be written

\[ 1s_A' 1s_B 1s_A^1 = \frac{1}{2} \Sigma_g + \frac{1}{2} \Sigma_u \]

where

\[ \Sigma_{g,u} = (1s_A' 1s_B 1s_A^1 \pm 1s_B' 1s_A 1s_A^1) \]

Likewise

\[ n l_B = \frac{1}{2} n l_+ - \frac{1}{2} n l_- \]

\[ 1s_B' 1s_A 1s_A^1 = \frac{1}{2} \Sigma_g - \frac{1}{2} \Sigma_u \]

\[ 1s_B' 1s_A^1 1s_A = \frac{1}{2} \Sigma_g + \frac{1}{2} \Sigma_u \]
and
\[ l s'_{A} \bar{s}_{B} l s_{B} = \frac{1}{2} \bar{\Sigma}_{g} - \frac{1}{2} \bar{\Sigma}_{u} \]

where
\[ \bar{\Sigma}_{g,u} = (l s'_{A} \bar{s}_{B} l s_{B} \pm l s_{B} \bar{s}_{A} l s_{A}) \).

We are considering specifically a single configuration valence bond wavefunction for states of \(^3\Sigma\) symmetry. Except for anti-symmetrization with respect to electron exchange, the complete single configuration wavefunction may be written
\[
\left[ n l_{A} l s'_{A} l s_{B} \bar{s}_{B} - n l_{A} l s'_{A} \bar{s}_{B} l s_{B} \right] \pm \left[ n l_{B} l s'_{A} l s_{A} \bar{s}_{B} - n l_{B} l s'_{A} \bar{s}_{B} l s_{A} \right]
\]
\[ = \left[ (n l_{+} + n l_{-}) (\Sigma_{g} + \Sigma_{u}) - (n l_{+} + n l_{-}) (\bar{\Sigma}_{g} + \bar{\Sigma}_{u}) \right] \]
\[ \pm \left[ (n l_{+} - n l_{-}) (\Sigma_{g} - \Sigma_{u}) - (n l_{+} - n l_{-}) (\bar{\Sigma}_{g} - \bar{\Sigma}_{u}) \right] \]
\[
= \begin{cases} 
  n l_{+} \Sigma_{g} + n l_{-} \Sigma_{u} - n l_{+} \bar{\Sigma}_{g} - n l_{-} \bar{\Sigma}_{u} & \text{for + wavefunction} \\
  n l_{+} \Sigma_{u} + n l_{-} \Sigma_{g} - n l_{+} \bar{\Sigma}_{u} - n l_{-} \bar{\Sigma}_{g} & \text{for - wavefunction} 
\end{cases}
\]

where we have ignored overall factors of 2.

As the internuclear separation decreases, \( n l_{-} \to 0 \) and \( n l_{+} \to n l_{c} \) an orbital centered on the midpoint between the two atoms. Hence the + wavefunction becomes
\[ n l_{c} \Sigma_{g} - n l_{c} \bar{\Sigma}_{g} \] and the - wavefunction is \( n l_{c} \Sigma_{u} - n l_{c} \bar{\Sigma}_{u} \).
Expansion of the $+$ wavefunction gives

$$n \ell_c \Sigma_g - n \ell_c \overline{\Sigma}_g$$

$$= n \ell_c 1s_A' 1s_B \overline{1s}_B + n \ell_c 1s_B' 1s_A \overline{1s}_A - n \ell_c 1s_A' \overline{1s}_B 1s_B - n \ell_c 1s_B' \overline{1s}_A 1s_A$$

$$= n \ell_c \left[ 1s_A' 1s_B \overline{1s}_B + 1s_B' 1s_A \overline{1s}_A - 1s_A' \overline{1s}_B 1s_B - 1s_B' \overline{1s}_A 1s_A \right].$$

Likewise expansion of the $-$ wavefunction gives

$$n \ell_c \Sigma_u - n \ell_c \overline{\Sigma}_u$$

$$= n \ell_c 1s_A' 1s_B \overline{1s}_B - n \ell_c 1s_B' 1s_A \overline{1s}_A - n \ell_c 1s_A' \overline{1s}_B 1s_B + n \ell_c 1s_B' \overline{1s}_A 1s_A$$

$$= n \ell_c \left[ 1s_A' 1s_B \overline{1s}_B - 1s_B' 1s_A \overline{1s}_A - 1s_A' \overline{1s}_B 1s_B + 1s_B' \overline{1s}_A 1s_A \right].$$

The spin-orbitals in square brackets of the $+$ wavefunction represent the $^2\Sigma_g^+$ ion state and of the $-$ wavefunction, the $^2\Sigma_u^+$ ion state. Thus, the $+$ wavefunction factors as a Rydberg orbital and a B core and the $-$ wavefunction as a Rydberg orbital and an A core. The complete antisymmetrized wavefunction for the $+$ wavefunction is $|n\ell_c' 1s_A' 1s_B \overline{1s}_B| + |n\ell_c' 1s_B' 1s_A \overline{1s}_A|$ and for the $-$ wavefunction is $|n\ell_c' 1s_A' 1s_B \overline{1s}_B| - |n\ell_c' 1s_B' 1s_A \overline{1s}_A|$, which is what we wished to show.