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ELASTIC AND INELASTIC SCATTERING BETWEEN $2^3S$
METASTABLE AND GROUND STATE HELIUM ATOMS
AND BETWEEN HELIUM IONS AND $2^3,1^1S$ METASTABLES

by

Stephen A. Evans

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Problem I: Helium Metastable-atom Collisions
Introduction to Problem I

The nature of the $^3\zeta^+_{g,u}$ molecular potentials associated with the scattering of the $2^3S$ metastable from a ground state helium atom has been of considerable interest to both theorists$^1-8$ and experimentalists.$^9-12$ The interest lies in the unusual repulsive barriers in both curves at intermediate internuclear distances. In addition, the metastable behavior of the $2^3S$ atomic state makes this system suitable for collisional studies in various types of experiments.

The repulsive behavior in the $^3\zeta^+_{u}$ was first shown theoretically by Buckingham and Dalgarno.$^1$ They also demonstrated that the excitation transfer cross section should decrease rapidly at low temperatures due to the repulsive barrier in the $^3\zeta^+_{u}$ potential.$^2$

Colegrove, Scheerer, and Walters$^9$ measured at low temperatures (4.2° K to 500° K) the excitation transfer cross section for the same system using optical pumping techniques. Their cross sections decreased rapidly with temperature in agreement with Buckingham and Dalgarno.$^2$ However, the experimental results were larger in magnitude.

More sophisticated calculations of the $^3\zeta^+_{g,u}$ interaction potentials have been done by the Molecular Physics Group$^4$ at the University of Texas. Their results show repulsive barriers in both potential curves. The barrier in the $^3\zeta^+_{g}$ curve is the result of an avoid crossing with the next highest
$^{3}\Sigma^+_g$ curve.

A detailed investigation of the quantitative nature of the repulsive interaction for large internuclear separations was carried out by Fitzsimmons, Lane, and Walters. On the basis of their experimental diffusion data, they adjusted the long range repulsive interaction potentials until the calculated and experimentally determined diffusions cross sections agreed. Using these potentials, they calculated total and excitation transfer cross sections. Their results were in good agreement with previous experimental measurements.

Recently, a two state theory and the WKB approximation were employed by Evans and Lane to calculate the total and excitation transfer cross section for the metastable-atom system. The range of energy covered was much larger than in previous theoretical calculations (.003 eV to 500 eV). In their treatment of the problem, they used the Born-Oppenheimer adiabatic approximation. In this assumption the electronic potentials are required to go smoothly over to the united atom states of Be that give rise to the lowest $^{3}\Sigma^+_g$ molecular states. Crossing with states whose molecular angular momentum quantum numbers and symmetry are the same is prohibited by the non-crossing rule. Oscillatory behavior in the energy dependence obtained in both the total and excitation transfer cross sections was shown to be a characteristic of the multi-configuration
adiabatic potentials used in the calculation. They demonstrated this by making a detailed investigation of the phase shifts at a number of energies and by relating changes in the magnitude and oscillatory behavior of the cross sections to arbitrary changes in the $^3\Sigma_g^+$ potentials. Thus, disagreement with the experimental measurements of Hollstein et al.\textsuperscript{12} suggested two possibilities: (1) more accurate adiabatic potentials are necessary, (2) non-adiabatic effects are important. Both suggestions are implied by the strong dependence of the cross sections on the potentials that describe the collision process.

The primary goal of this dissertation is to investigate possible non-adiabatic behavior in helium metastable-atom collisions. In doing this, the "perturbed stationary state"\textsuperscript{14-17} method was used. The total wave function was then chosen to be a superposition of the wave functions representing the two lowest "diabatic" $^3\Sigma_g^+$ states of di-atom system. Diabatic molecular states are obtained from single configuration calculations and can therefore cross other states of the same angular momentum and symmetry.

In this formulation of the problem, two types of coupling can give rise to inelastic transitions between the $^3\Sigma_g^+$ ($1s2s^3S$) and the $^3\Sigma_g^+$ ($1s2p_0^3P$) molecular states: normal potential coupling arising from matrix elements of the electronic hamiltonian and gradient or non-adiabatic coupling which can be large in the region of an avoided crossing.
The latter type of coupling can give rise to non-adiabatic behavior.

If the diabatic wave functions are symmetrized products of atomic orbitals, then the gradient coupling terms will be identically zero since pure atomic orbitals are independent of internuclear separation. In this case, one would be doing the collision problem in a diabatic representation. The total wave function, thus, must be chosen as a superposition of these electronic functions.

In the other extreme the total wave function could be chosen as a superposition of adiabatic molecular wave functions. In this adiabatic representation the potential coupling matrix would be diagonal and the gradient coupling terms will be significant near any avoided crossings.

Solving the collision problem in either representation should give the same result as long as all important coupling is included. In other words, a unitary transformation between the two systems is possible.

There would be much simplification in the problem if one could neglect the coupling in one representation or the other. If this is done in the diabatic representation, then scattering would be described entirely by single configuration potential curves. Lichten\textsuperscript{18-20} has suggested that in many physical problems diabatic curves give a good description of the scattering process. Application of this method to the He-He\textsuperscript{+} problem by Marchi and Smith\textsuperscript{21} has been very
successful. They have found both the magnitude and some aspects of the structure of the total differential cross section to be in agreement with the experimental measurements of Lorents and Aberth. 22

In calculating the excitation transfer cross section for He-He* collisions, Evans and Lane 6 have assumed the gradient interaction terms in the adiabatic representation to be negligible and, thereby allowing the scattering to be described entirely by adiabatic potential curves. As suggested above, this may or may not be a good approximation.

The questions one would like to answer about the helium metastable-atom system are the following: (1) Can the system be described entirely by adiabatic or diabatic interaction potentials? (2) If not, would it be easier to solve the coupled equations describing the system in one representation or the other? (3) As suggested by Smith 23 and Levine et al. 24, would it be easier to do the problem in an intermediate representation?

A particularly interesting aspect of this problem is the crossing that occurs between the diabatic \( ^3\Sigma^+_g \) \((1s2s^3S)\) and \( ^3\Sigma^+_g \) \((1s2p^3P)\) potential curves. A great deal of information can be obtained by a detail study of the nature of the di-atom system in the region of the crossing. In doing this we have made use of the Stueckelberg 25, Landau 26-Zener 27 approximation for the inelastic cross section. This semiclassical approximation is frequently used in curve crossing.
problems\textsuperscript{28-34} because of its simplicity and its classical interpretation. We will use it in this problem in an attempt to interpret and describe our results in terms of classical ideas.

In Part I, the theory of atom-atom collisions is discussed in general and then specialized to the helium metastable-atom system. Also, the method of obtaining the potential curves and the method used in solving the collision equations are discussed in some detail. In the last section of Part I, the Landau-Zener approximation as derived by Zener is discussed in terms of its applicability and limitations.

In Part II, results that verify the abibabatic assumption of Evans and Lane\textsuperscript{6} are presented. In addition, a simple model is discussed and used to interpret the behavior of the elastic and inelastic cross sections. Finally L-Z, close coupling results are compared at a number of different energies and strengths of the potential coupling matrix element.
Part I: Theory and Procedure
I. The Theory of Atom-Atom Collisions

Consider the general problem where atom A and atom B, with nuclear charges $Z_A$ and $Z_B$ and with mass $M_A$ and $M_B$, collide.\textsuperscript{14, 17} The Hamiltonian representing the relative motion of the system is given by

$$H = -\frac{\hbar^2}{2M} \frac{\nabla^2}{\hat{R}} + \frac{Z_A Z_B e^2}{\hat{R}} - \sum_{i \neq j} \frac{Z_i Z_j e^2}{\hat{r}_{ij}} + \frac{1}{2} \sum_{i} \frac{e^2}{\hat{r}_{iA}} - \frac{Z_A e^2}{\hat{r}_{iA}} - \frac{Z_B e^2}{\hat{r}_{iB}}, \quad (1)$$

where $\hat{R}$ is the relative separation of the two nuclei and $\hat{r}_{ij}$ is the relative separation of the electrons. $\hat{r}_i$ locates an electron $i$ with respect to the center of mass of the two nuclei. $M$ is the reduced mass $M_A M_B / (M_A + M_B)$ and $\mu$ is the reduced mass of an electron and the nuclei, $m_e (M_A + M_B) / (m_e + M_A + M_B) = m_e$. ($m_e$ is the electron mass.) Here we have made the assumption that the CM of an atom is the same as the nucleus.

The first two terms in (1) may be called the nuclear Hamiltonian $H_N$ since they represent only nuclear motion. The remaining terms form the electronic Hamiltonian $H_e$. Schroedinger's equation may then be written as

$$(H_N + H_e - E)\psi(\hat{R}, \hat{r}_i) = 0, \quad (2)$$

where $\psi$ is the total wave function and $E$ is the total energy for the di-atom system. $\psi$ may be expanded in a complete set of functions given by
\[ \psi(\vec{R}, \vec{r}_i) = \sum \gamma F_\gamma(\vec{R}) \psi_\gamma(\vec{R}, \vec{r}_i) , \]  

(3)

where \( \psi_\gamma \) may be any set of orthonormal basis functions depending on relative nuclear coordinates as well as electron coordinates.

\( F_\gamma \) will be a function only of the relative nuclear separation \( \vec{R} \). The use of molecular wave functions is commonly referred to as the perturbed stationary state method.\(^{14-17}\)

Substituting the total wave function \( \psi(\vec{R}, \vec{r}_i) \) into Eq. (2) yields

\[ (H_N + H_e - E) \sum \gamma F_\gamma(\vec{R}) \psi_\gamma(\vec{R}, \vec{r}_i) = 0. \]  

(4)

Multiplying by \( \psi_\nu^*(\vec{R}, \vec{r}_i) \) and integrating over all electron coordinates gives

\[ (H_N - E) F_\nu(\vec{R}) = \sum \gamma [(- H_{\nu\gamma} + \vec{A}_{\nu\gamma} \cdot \vec{v} + \vec{B}_{\nu\gamma} F_\gamma(\vec{R}))] , \]  

(5)

where

\[ H_{\nu\gamma} = \int \psi_\nu^*(\vec{R}, \vec{r}_i) H_e \psi_\gamma(\vec{R}, \vec{r}_i) d\vec{r}_i , \]  

(6)

\[ \vec{A}_{\nu\gamma} = \frac{\alpha^2}{M} \int \psi_\nu^*(\vec{R}, \vec{r}_i) \vec{v} \psi_\gamma(\vec{R}, \vec{r}_i) d\vec{r}_i , \]  

(7)

\[ \vec{B}_{\nu\gamma} = \frac{\alpha^2}{2M} \int \psi_\nu^*(\vec{R}, \vec{r}_i) \vec{v} \psi_\gamma(\vec{R}, \vec{r}_i) d\vec{r}_i . \]  

(8)

The gradient interaction terms \( \vec{A}_{\nu\gamma}(\vec{R}) \) and \( \vec{B}_{\nu\gamma}(\vec{R}) \) contain both angular and radial coupling terms. If the \( \psi_\nu \) were just linear combinations of symmetrized products of
unperturbed atomic wave functions then \( \tilde{A}_{\nu \gamma}(\vec{R}) \) and \( B_{\nu \gamma}(\vec{R}) \) would be identically zero, since there would be no \( R \) dependence. However, in the calculation of the \( \psi_\nu \), non-linear parameters which appear in the exponential functions of the orbitals were considered as variational parameters; thus, allowing an \( R \) dependence in \( \psi_\nu \), and a finite value for the gradient interaction terms. Because of the \( R \) dependence, \( \tilde{A}_{\nu \gamma}(\vec{R}) \) and \( B_{\nu \gamma}(\vec{R}) \) could be significant, but only in \( R \)-regions where the potential curves change rapidly. Therefore, they are frequently important in curve crossing situations where rapid changes in the \( \psi_\nu \) can occur. These terms are, however, neglected in solving the scattering equations above, since, as will be argued later, the terms are suspected to be small. Reasons for doing this are discussed in the results and in Appendix A.

A. Metastable-atom Problem

Considerable truncation of eq. (5) is possible if a "close coupling" approximation is used. In the case of the collision between He(1s\(^2\) 1S) and He(1s2s\(^3\)P), the \( ^3\Sigma_u^+ \) molecular state is not strongly coupled to any other state since it experiences no avoided crossing. But the adiabatic \( ^3\Sigma_g^+ \) does experience such an avoided crossing with the next highest \( ^3\Sigma_g^+ \) state.\(^3\) It follows then, that in studying inelastic transitions from the He(1s2s\(^3\)S) to higher states, the most important terms in \( \psi \) will be the two lowest \( ^3\Sigma_g^+ \) molecular
wave functions.

Instead of using strictly adiabatic wave functions, single configuration, valence bond functions were chosen. The functions are "diabatic" in nature, in that they are associated with crossing potential energy curves. These wave functions and the potentials will be discussed in more detail below.

The truncated wave function will then appear as

$$\psi(\hat{\mathbf{r}}, \hat{\mathbf{r}}') = F_{1g}(\hat{\mathbf{R}}) \psi_1(\hat{\mathbf{r}}, \hat{\mathbf{r}}', 3_\Sigma_g) + F_{2g}(\hat{\mathbf{R}}) \psi_2(\hat{\mathbf{r}}, \hat{\mathbf{r}}', 3_\Sigma_g)$$

(9)

where

$$\psi_1(3_\Sigma_g)_{R \rightarrow \infty} \phi(A) \chi(B^*) + \chi(A^*) \phi(B) \rightarrow \text{He}(ls^2) + \text{He}(ls2s^2S) ,$$

(10)

$$\psi_2(3_\Sigma_g)_{R \rightarrow \infty} \phi(A) \theta(B^*) + \theta(A^*) \phi(B) \rightarrow \text{He}(ls^2) + \text{He}(ls2p^3P).$$

where $\phi$, $\chi$, and $\theta$ represent atomic wave functions and $+$ points to the corresponding separated atom configuration. Assuming a spherical potential and using the method of partial waves, we expand $F_{vg}(\hat{\mathbf{R}})$ as

$$F_{vg}(\hat{\mathbf{R}}) = R^{-\frac{1}{2}} \sum_l \frac{\ell \ell^*}{\ell} y_{\ell}(\hat{\mathbf{R}}) P_{\ell}(\hat{\mathbf{k}} \cdot \hat{\mathbf{R}}).$$

(11)

Schroedinger's equation now reduces to a set of coupled equations given in atomic units as

$$\left[ \frac{d^2}{dR^2} + k_1^2 - \frac{\ell (\ell + 1)}{R^2} - U_{11}(R) \right] y_{1\ell}(R) = U_{12}(R) y_{2\ell}(R) ,$$

(12)
\[
\left[ \frac{d^2}{dR^2} + k_2^2 - \frac{\ell(\ell+1)}{R^2} - U_{22}^d(R) \right] y_{2\ell}^\ell(R) = U_{21}^d(R) y_{2\ell}^\ell(R),
\]

where

\[
U_{\nu\gamma}^d(R) = \frac{2M_{\nu\gamma}}{m_e} U_{\nu\gamma}^d(R) = \frac{2M}{m_e} (H_{\nu\gamma}(R) - E_{\nu}(\infty) + \frac{4}{R}),
\]

\[
k_1^2 = \frac{2M}{m_e} (E - E_1(\infty)),
\]

\[
k_\nu^2 = k_1^2 + \frac{2M}{m_e} (E_1(\infty) - E_{\nu}(\infty))
\]

and where \( \nu \) labels the molecular state. The \( U_{11,22}^d(R) \) are the so-called "adiabatic" potentials of the two lowest \( ^3\Sigma_g^+ \) states and \( U_{12}^d(R) \) is the direct coupling matrix element. The terms in Schrödinger's equation which were neglected will be referred to as non-adiabatic or gradient interaction terms.

Asymptotically, the \( y_{\nu\ell}^\ell(R) \) may be represented by a sum of incoming and outgoing spherical waves,

\[
y_{\nu\ell}^\ell(R) \mid_{R=\infty} = \delta_{\nu\ell} e^{-i(k_1 R - i\pi/2)} - (k_1/k_\nu)^{\frac{3}{2}} S_{\nu\ell} e^{-i(k_\nu R - i\pi/2)},
\]

when the incident particle is in state \((1)\). The outgoing wave is modified by a phase factor \( S_{\nu\ell} \). For incidence in state \((2)\), the phase is given by \( S_{\nu2} \). It can easily be shown\(^{16}\) that the cross sections are given by

\[
Q_{\nu\gamma} = \frac{\Sigma Q_{\nu\gamma}^\ell}{2} = \frac{\pi}{k_\gamma^2} (2\ell + 1) |T_{\nu\gamma}|^2,
\]

where

\[
T = 1 - S,
\]
and $\hat{S}$ is the symmetric scattering matrix.

In practice it is easier to deal with real solutions of the coupled equations. The asymptotic boundary condition (16a) then becomes

$$Y_{\nu\nu'}(R)_{R+\infty} \sim \sin(k_{\nu}R-\ell \pi/2)\delta_{\nu\nu'} -(k_{\nu}/k_{\nu'})^2 R_{\nu\nu'} \cos(k_{\nu}R-\ell \pi/2) , \quad (16b)$$

where $\nu'$ labels the initial state, $\hat{S} = (1+i\ell)(1-i\ell)^{-1}$, and where $\hat{R}$ is real and symmetric. Properties of $\hat{S}$ and $\hat{R}$ are discussed in Mott and Massey.\textsuperscript{14}

B. Interpretation of Inelastic Cross Sections

For proper interpretation of the transition cross section, one imposes some initial boundary conditions and then examines the asymptotic form of the wave function. At large internuclear separations the nuclear wave functions are given by

$$F_{1u}(\hat{R})_{R+\infty} = \alpha \{ e^{ik_1 \cdot \hat{R}} - 1 \} e^{ik_1 R} f_{1u}(\theta) , \quad (18a)$$

$$F_{1g}(\hat{R})_{R+\infty} = \beta \{ e^{ik_1 \cdot \hat{R}} - 1 \} e^{ik_1 R} f_{1g}(\theta) ,$$

$$F_{2g}(\hat{R})_{R+\infty} = \alpha \{ e^{-ik_2 R} - 1 \} e^{ik_2 \cdot \hat{R}} f_{2g}(\theta) ,$$

where $f_{\nu g,u}$ represent the scattering amplitudes, and $\alpha, \beta$ are constants, chosen to satisfy the asymptotic boundary conditions. The asymptotic electronic functions, $\psi_1(3\Sigma_g^+)$
and $\psi_2(3^+_g)$ are given in Eq. (10). $\psi_1(3^+_u)$ is given by

$$\psi_1(3^+_u) = \phi(A) \chi(B^*) - \chi(A^*) \phi(B).$$

$F_{2u}(\vec{R})$ is neglected in (18a) because no transitions are expected to occur between the two lowest $3^+_u$ electronic states.

Since this problem deals with identical He$^4$ nuclei, the total wave function must be symmetric under interchange of nuclear coordinates. Symmetrizing the wave function and choosing $\alpha$ and $\beta$ such that the metastable is incident along the $z$ axis in a positive direction, one can show, using the formalism of Massey and Smith$^{15}$, that

$$\psi_s(R) = R^{-1} e^{i|kR|} \{ \phi(A) \chi(B^*) \{ f_g(\theta) + f_g(\pi-\theta) - f_u(\theta) - f_u(\pi-\theta) \}$$
$$+ \chi(A^*) \phi(B) \{ f_g(\theta) + f_g(\pi-\theta) - f_u(\theta) + f_u(\pi-\theta) \}$$
$$+ \phi(A) \delta(B^*) \{ f_{2g}(\theta) + f_{2g}(\pi-\theta) \}$$
$$+ \delta(A^*) \phi(B) \{ f_{2g}(\theta) + f_{2g}(\pi-\theta) \} \}, \quad (18b)$$

where $\psi_s$ represents the scattered wave, and where $\phi(A) \chi(B^*)$ identifies the elastically scattered flux and $\chi(A^*) \phi(B)$ identifies the transfer of excitation from B to A. The coefficient of $\phi(A) \delta(B^*)$ represents the scattering amplitude for an inelastic transition from the He(1s2s$^1S$) to He(1s2p$^1P$). The label B corresponds to the final excited atom. The coefficient of $\delta(A^*) \phi(B)$ represents the scattering amplitude for an inelastic transition from the $^3S$ to the $^3P$, where A
now corresponds to the final excited atom. These four processes will be referred to, respectively, as direct elastic scattering (DE), excitation transfer (ET), inelastic scattering (I) and inelastic excitation transfer (IET). The scattering amplitudes associated with the last two processes are given by (18b) as

\[ f_I(\theta) = f_{\text{IET}}(\theta) = [f_{2g}(\theta) + f_{2g}(\pi-\theta)] \]

It follows then that the total inelastic cross section is given by

\[ Q_{21} = \frac{1}{2} Q_I + \frac{1}{2} Q_{\text{IET}} \]

The initial flux will split equally between the \( ^3\tau_{1g}^+ \) and \( ^3\tau_{1u}^+ \) states, thereby reducing the amount of flux that can be excited to the upper state by half. In our close coupling calculation, it was assumed that all the flux went in on the \( ^3\tau_{1g}^+ \) curve. One must then divide our results by two in order to get the correct magnitude of the inelastic cross section.

C. Differential Scattering Cross Section

Often it is important to look at the differential cross section for comparison to experimental results or for further interpretation of theoretical calculations. In terms of the T matrix in Eq. (17), one can write

\[ \frac{\text{d}Q}{\text{d}\Omega} = \frac{1}{4k^2 v^2} |\tau(2\lambda+1)(T)_{\nu\nu}'P_{\frac{1}{2}}(\cos \theta)|^2, \]
where \( \theta \) is the angle between the incident and the scattered flux.

In a single channel problem, the phase shift \( \eta_\ell \) associated with scattering in a particular state is real. The cross section is given by\textsuperscript{14}

\[
Q^2 = \frac{4\pi}{k^2} (2\ell+1) \sin^2 \eta_\ell .
\]

Classically there is a direct correspondence between each partial wave phase shift \( \eta_\ell \) and the scattering angle \( \theta \). It is given by\textsuperscript{14}

\[
2|\frac{\partial \eta_\ell}{\partial \ell}| = \theta .
\]

Also, there is a classical correspondence between the impact parameter \( b \) and \( \ell \), which is given by\textsuperscript{14}

\[
(m v_0 b)^2 \rightarrow \hbar^2 \ell (\ell+1) ,
\]

where \( v_0 \) is the initial velocity. Thus, one can associate the scattering behavior at particular impact parameters with particular angles of scattering. It has been shown by Evans and Lane\textsuperscript{6} that at moderate energies, the \( \eta_\ell \) closely reflect the behavior of the potential curves. So, for potentials that have a change in slope, there may be more than one \( \ell \) associated with a particular \( \theta \).

For the multi-state problem where phase shifts are complex the correlation is not as obvious, but it seems reasonable that some correspondence can be made, particularly for the elastic cross sections.
II. Method of Obtaining Potential Energy Curves

Matrix elements of the type given in the Eq. (6) must be calculated before the scattering equations can be solved. In the paragraphs that follow and in Appendix B, the procedure for choosing the wave functions and calculating the resulting matrix elements of the electronic hamiltonian will be discussed in detail.

For inelastic collisions between He(1s$^2$ 1S) and He(1s2s$^3$S), the molecular states which are included in \( \psi \) of Eq. (9) are the two lowest \( ^3\Sigma_g^+ \). Proper choices for \( \psi_{1,2} \) must be eigenfunctions of the operators \( (S_a + S_b)^2 \) and \( S_{az} + S_{bz} \) where \( a \) and \( b \) label the separated atoms and the following equalities hold:

\[
(S_a + S_b)^2 \psi_{1,2} = 2\hbar^2 \psi_{1,2}, \quad (21)
\]

\[
(S_{az} + S_{bz}) \psi_{1,2} = \pm \hbar \psi_{1,2} \text{ or } 0.
\]

For large internuclear separations, \( \psi_{1,2} \) must separate into eigenfunctions of \( S^2_{a,b}, S_{az,bz} \) where

\[
S^2_a \psi_{1,2} = S_{az} \psi_{1,2} = 0, \quad (22)
\]

\[
S^2_b \psi_{1,2} = 2\hbar^2 \psi_{1,2},
\]

\[
S_{bz} \psi_{1,2} = \pm \hbar \psi_{1,2} \text{ or } 0.
\]

Following the method given by Slater$^{35}$ for constructing properly symmetrized wave functions, \( \psi_{1,2} \) are formed obeying
conditions (21) and (22). In determinantal form they are written as

$$\psi_1 = |l_s a \bar{l}_s a \bar{2} s_b \bar{l}_s b| + |l_s a \bar{l}_s a \bar{2} s_b l_s b| + a \rightarrow b,$$

$$\psi_2 = |l_s a \bar{l}_s a \bar{2} p_b \bar{l}_s b| + |l_s a \bar{l}_s a \bar{2} p_b l_s b| + a \rightarrow b,$$

(23)

where \(l_s a\), \(2p_b\), etc. are chosen to be Slater orbitals (analytic form of the orbitals is given in Appendix B). In performing the variational calculation discussed below it is not necessary for the component wave functions to be orthonormal; however, they must still obey conditions (21) and (22).

The wave functions chosen then are a non-orthonormal (except as \(R \rightarrow \infty\)) set \(\chi_1, 2\). Linear combinations of the form

$$\chi = c_1 \chi_1 + c_2 \chi_2$$

(24)

are constructed to give a better representation of the molecular states, one in which configuration interaction is included.

Applying the well known variational principal, an upper bound on the lowest energy eigenvalue is obtained in (25).

$$\bar{E} = \frac{\int \chi \dagger \mathcal{H} \chi d\bar{r}}{\int \chi \dagger \chi d\bar{r}}.$$  

(25)

The next step is to minimize \(\bar{E}\) at each \(R\) with respect to \(c_1\) and \(c_2\). The resulting secular equation is given by

$$\sum_{j=1}^{2} C_j (h_{ij} - A_{ij} E) = 0, \quad i = 1, 2$$

(26)
where $h_{ij} = \int \chi_i^* \mathcal{H} \chi_j \, d\hat{r}$ and $\Lambda_{ij} = \int \chi_i^* \chi_j \, d\hat{r}$. The non-linear parameters in the Slater orbitals are then varied to minimize $E_1$ and $E_2$ which are the two roots obtained by solving (26).

The matrix elements $h_{ij}$ and $\Lambda_{ij}$ were obtained from J. C. Browne by private communication. He calculated them using the procedure above in connection with a study of some excited states of the helium molecule.\textsuperscript{6}

The matrix elements in raw form were calculated from non-orthonormal wave functions. In Section I the internal electronic functions were assumed to be orthonormal. So a simple procedure, discussed in Appendix B, was used to orthonormalize these functions and calculate the matrix elements of the electronic Hamiltonian $H_{ij}$.

The diagonal elements $\frac{2}{m_e} (H_{ii})$ are the electronic parts of the diabatic potentials mentioned in the last section. These diabatic potentials are shown in Fig. (4). The separated atom energy of the lowest electronic state has been subtracted off. The direct coupling matrix element is plotted in Fig. (5). Analytic fits of the potential energy matrix elements are given in Appendix B.
III. Method of Calculation

The problem of calculating cross sections for atom-atom collisions is reduced in Section I to the solution of coupled equations of the form

$$\frac{d^2}{dR^2} - \frac{k(i+1)}{R^2} + k^2 - U_{v'v'}(R)u_{v'v'}^\ell = \sum_{\gamma \neq v} \sum_{\gamma' \neq v'} U_{v'v'}^{\ell \gamma \gamma'} u_{\gamma \gamma'}^\ell,$$  \hspace{1cm} (27)

where the new index $v'$ labels the initial state.

For a general $N$ channel problem involving the solution of $N$ second order coupled equations, there are $2N$ possible solutions of the form

$$\tilde{u}_v^\ell = \begin{pmatrix} u_{1v}^\ell \\ u_{2v}^\ell \\ \vdots \\ u_{2Nv}^\ell \end{pmatrix}.$$  \hspace{1cm} (28)

Imposing the boundary condition that $\tilde{u}_v^\ell \to 0$ as $R \to 0$, reduces the number of linearly independent solutions to $N$. Lane and Geltman\textsuperscript{36} have explained in detail how one solves such equations in order to get the desired cross sections. For the sake of completeness, a brief discussion of this procedure will be repeated. The numerical difficulties encountered in applying this method to potential-barrier problems will also be discussed.
Equation (27) may be rewritten in a more compact form as

\[ \frac{d^2}{dR^2} u^j_{\nu \nu} = G^j_{\nu \nu} u^j_{\nu \nu}, \]  

(29)

where

\[ G^j_{\nu \nu} = U^j_{\nu \nu} - \kappa^2_{\nu} \delta^j_{\nu \nu} - 2(\ell+1) \delta^j_{\nu \nu} / R^2. \]

In matrix form, Equation (29) may be written as

\[ \begin{bmatrix} 1 & \frac{d}{dR^2} \\ \frac{d}{dR^2} & -G \end{bmatrix} \begin{bmatrix} u^j \end{bmatrix} = \begin{bmatrix} 0 \end{bmatrix}. \]  

(30)

Differential equations which contain no first derivative can be solved numerically using the Numerov method, which is based on the theory of finite differences.\(^\text{37}\) The algorithm is given by

\[ u(i+1) = \left\{ \left[ 1 - \frac{h^2}{12} G^j(i+1) \right]^{-1} \right\} \left\{ [2 + \frac{5}{6} h^2 G^j(i)] u(i) - [1 - \frac{h^2}{12} G^j(i-1)] u(i-1) \right\}, \]  

(31)

where \( h \) is the step size in the integration process and \( i \) labels the solution at a point. Given the solution at points \( i \) and \( i-1 \), eq. (31) predicts the solution at \( i+1 \).

One would normally proceed by setting \( u^2_l = 0 \) at \( R = 0 \) and \( u^l_1 = q \) at \( R = h \). In order to satisfy the condition of linear independence, \( q \) must be non-singular. Due to the highly repulsive potentials associated with problems of this kind, the solutions rapidly become linearly dependent.
This difficulty can be avoided, if the potential is assumed to be infinite at some distance $R_s$ from the origin. This is a good approximation as long as $u_{vv}^l(R_v^l) \ll u_{vv}^l(R_o^l)$ where $R_o^l$ is just the well known classical turning point satisfying the condition that $G_{vv}^l(R_o^l) = 0$. Bernstein has gotten reasonable results by letting $R_s$ be the distance for which the potential is approximately 100 times the incident relative kinetic energy. In our problem, each solution $u_{vv}^l(R)$ was started at $R_v^l = (R_o^l - 0.6)$. This procedure worked well for $R_o > 2a_o$.

Because of the arbitrariness in choosing the starting solutions, the $u^l$ are not the same as the $\gamma^l$ in Section I. The procedure then is to combine the $N$ linearly independent solutions of eq. (30) with arbitrary coefficients such that the asymptotic boundary conditions given in (16b) are satisfied. For large internuclear distances $u$ may be written (the supercript $\lambda$ has been dropped for clarity)

$$u = B_1A + B_2B,$$

where

$$
(B_1)_{vv}^l = \delta_{vv}^l(k_v R_j^l)j_j^l(k_v R),
$$

$$
(B_2)_{vv}^l = \delta_{vv}^l(k_v R)\eta_j^l(k_v R).
$$

The functions of $j_j^l$ and $\eta_j^l$ are spherical Bessel functions of the first and second kind, respectively, and $A$ and $B$ are constant matrices.
At two boundary matching points $R_a$ and $R_b$ the asymptotic solutions $u_a$ and $u_b$ are given by

$$u_a = B_{1a} A + B_{2a} B,$$

$$u_b = B_{1b} A + B_{2b} B.$$  \hspace{1cm} (34a)

Equations (34a) and (34b) can then be solved to get $A$ and $B$.

Substituting in the asymptotic forms $B_1$ and $B_2$, $u$ may be written as

$$(u)_{\nu\nu} = [\delta_{\nu\gamma} \sin(k_{\nu} R - \xi \pi/2) (A)_{\gamma\nu} + \delta_{\nu\gamma} \cos(k_{\nu} R - \xi \pi/2) (B)_{\gamma\nu}]$$  \hspace{1cm} (35)

By comparing (35) with (16b), one can see that the asymptotic boundary conditions are met if $u$ is multiplied by $A^{-1}$ such that

$$u A^{-1} = B_1 + B_2 (B A^{-1})$$  \hspace{1cm} (36)

$$(u A^{-1})_{\nu\nu} = (B_1)_{\nu\nu} + \sum_{\gamma} (B_2)_{\nu\gamma} (B A^{-1})_{\gamma\nu},$$

$$= \delta_{\nu\nu} \sin(k_{\nu} R - \xi \pi/2) + \sum_{\gamma} \delta_{\nu\gamma} \cos(k_{\nu} R - \xi \pi/2) (B A^{-1})_{\gamma\nu},$$

$$= \delta_{\nu\nu} \sin(k_{\nu} R - \xi \pi/2) + \cos(k_{\nu} R - \xi \pi/2) (B A^{-1})_{\nu\nu}.  \hspace{1cm} (37)$$

Comparing with (16b) one obtains for the $R$ matrix

$$R = K_{\xi} (B A^{-1}) K_{-\xi},$$  \hspace{1cm} (38)

where

$$(K)_{\nu\nu} = \delta_{\nu\nu} k_{\nu}.$$
The computer program used to perform the above calculation is discussed in Appendix C. Also mentioned are typical step sizes, number of partial waves necessary for complete cross sections and various methods of data storage.
IV. A Semi-Classical Method for Obtaining Transition Cross Sections

The expression for the transition cross section given in Section I is exact when obtained by the method described in Section III (within the adiabatic, close coupling assumption). It is beneficial though, to discuss the same cross section in terms of a classical or semi-classical method. In the discussion that follows, several methods will be described, emphasizing their limitations and applicability to the type of scattering problem discussed in Section I.

The well known Landau-Zener method (L-Z) has been used for qualitative understanding of many scattering problems. The crossing of single configuration molecular energy curves (described by the same molecular quantum numbers), is a common phenomenon, occurring in many di-atom systems. When the potential curves are obtained with configuration interaction included, they repel as required by the non-crossing rule. The crossing curves are commonly called diabatic, while the non-crossing ones are referred to as adiabatic. The asymptotic behavior of both is given in the diagram below. When the interaction (the coupling matrix element of Section I) causing the repulsion between smooth curves is small, they approach each other in some small region $\Delta R_c$. In this case there will be in the process of a collision a high probability of following the broken curve instead of the smooth adiabatic
The wave function used in Zener's time dependent perturbation formulation is

$$\psi(\vec{r}, t) = \sum_{s=1}^{2} a_s(t) \psi_s(\vec{r}) \exp[-i E_s t / \hbar]$$  \hspace{1cm} (39)

where $\psi_s$, $E_s$ are the wave function and energy values satisfying the Hamiltonian of the unperturbed atom, and $a_s(t)$ is the probability amplitude for being in a diabatic state $s$ at time $t$. In solving Schroedinger's time dependent equation, Zener makes two important assumptions: (1) $\psi(\vec{r}, t)$ is only slightly perturbed during the time of the collision, (2) practically all transitions occur in a small region around the crossing point. Zener's derivation of the probability $a_s(\infty)^2$ is well documented in the literature and therefore will not be repeated here. \cite{14, 27} The expression obtained for $|a_s(\infty)|^2$ is given in atomic units as

$$|a_s(\infty)|^2 = 1 - \exp[-2\gamma_s] \hspace{1cm} (40)$$
where

\[ \gamma_\ell = \pi \left| \frac{v_{21}^2}{(v_{11}^* - v_{22}^*) v_\ell} \right|_{R=R_C} , \]

and

\[ v_\ell(R_C) = \frac{m e}{M} \left[ k_1^2 - \frac{2MV_{11}(R_C)}{m s} - (\ell+\frac{1}{2})^2/R_C^2 \right]^{1/2} . \]

In this formulation of the problem, only non-adiabatic transitions are allowed. This means that as the particles follow their collision path, only transitions from the initial to the final state are possible.

It is obvious from the diagram above that if \( P_\ell^k \) is the probability of a transition between state (1) and state (2) in the adiabatic basis, then \( P_\ell^k = 1 - |a_s(\infty)|^2 = e^{-2\gamma_\ell} \).

When one includes all possible paths for transitions to occur, the total probability is given by

\[ 2P_\ell^k (1 - P_\ell^k) \quad (41) \]

and the cross section is

\[ Q_LZ = \sum_\ell Q_LZ^\ell = \frac{\pi}{k_1^2} (2\ell+1) 2P_\ell^k (1-P_\ell^k) . \quad (42) \]

Almost the same result was obtained by Stueckelburg in a semi-classical time independent derivation. He first reduced the coupled equations in Eq. (12) to one fourth-order equation in \( y_0 \) by means of elimination. He then expanded the coefficients in powers of \( \hbar \) and, corresponding to the
WKB process, replaced \( y_0 \) by \( y_0 = \exp(\frac{1}{R}(S_0 + hS_1 + h^2S_2 \ldots)) \). The resulting cross section differs from (42) only by the multiplicative factor \( \sin^2 \tau_\xi \). Thus we obtain

\[
Q_s = \frac{2\pi}{\kappa^2_1} (2\ell + 1) 2\ell^2 (1 - \ell^2) \sin^2 \tau_\xi,
\]

where

\[
\tau_\xi = \int_R^C g_1 \, dr - \int_R^C g_2 \, dr,
\]

\[
g_{1,2} = \frac{1}{2}(f_{1} + f_{2}) \pm \frac{1}{2}(f_{1} - f_{2})^2 + 4u_{21}^2 \frac{1}{\kappa^2_1},
\]

\[
f_{1,2} = \kappa^2_{1,2} - u_{11,22} - \frac{(\ell + \kappa)^2}{R^2}.
\]

If \( \tau_\xi \) is a rapidly varying function of \( \xi \), then \( \sin^2 \tau_\xi \) can be replaced by \( 1/2 \). Zener's result (42) is then just an average over partial waves of (43).

An important tool in the analysis of the inelastic cross sections is an understanding of the oscillatory structure predicted by Eq. (43). If the particle flux starts out in state (1), there are four possible paths or trajectories it can follow from the diabatic point view. These are shown in Diagram (2). Two of the paths are elastic and two are inelastic. Particle flux traversing path III will be out of phase with the unscattered flux by a phase \( \Delta \), modulo \( 2\pi \), where \( 0 \leq \Delta \leq 2\pi \). Since \( \Delta \) is a function of the impact parameter and since classically one can associate each impact parameter with a partial wave, the final partial wave cross section for inelastic scattering in path III will
Diagram (2)

oscillate with \( \hat{z} \). A similar statement can be made about scattering in path IV.

In addition to these normal scattering oscillations, interference can occur in the cross section. Originally the incoming flux is coherent. In the process of the collision the flux can take either path III or IV. The outgoing flux can then interfere coherently \( \hat{\mathbf{R}} \geq R_C \).

The effect described above is not easily seen in (43), because \( \tau_\lambda \) is a rather complicated function. Smith and Olson \(^{28}\) have re-expressed the transition cross section in a reduced form

\[
\rho_{21}(\theta) = \theta \sin \theta Q_{21}(\theta),
\]

where \( \theta \) is the scattering angle in the center mass system.
They show that $\rho_{21}(\theta)$ is proportional to the flux associated with each path plus an interference term. This term is proportional to the cosine of the difference between functions associated with trajectory III and trajectory IV. One can then think of the oscillatory structure as an effect due to the interference between scattering from two different impact parameters and that due to just normal scattering from paths III and IV.

Bates et al.\textsuperscript{29} have critized the L-Z method on the basis that it has the wrong velocity dependence at very high energies and does not allow for transitions away from the crossing. Heinrichs\textsuperscript{30} points out that within a range of velocities the L-Z method is good and that corrections can be made to account for transitions in a wider region around the crossing point. He derives a precise criterion for the validity of his corrected L-Z formula based on the width of the transition region. In the literature there are many critiques\textsuperscript{29, 33} and corrections\textsuperscript{30-32} to the L-Z method.

In this paper the Landau-Zener approximation is used to explain qualitatively the behavior of the close coupling cross sections. The coupling matrix element and the energy are varied to find a region in which the L-Z method is quantitatively correct. The failure of the L-Z method for low energy and for strong coupling cases will be demonstrated.
Part II: Results and Conclusions
I. Presentation of the Results and Verification of an Adiabatic Assumption

The work being presented in this section was done to answer questions arising out of earlier calculations of the total elastic and excitation transfer cross sections for scattering of $2^3S$ metastables from ground state helium atoms. The best available adiabatic potential curves$^4, 11$ for the $3\Sigma^+_g,u$ states were used in the previous calculations. They are shown in Fig. (1). The hump in the $3\Sigma_g^-$ curve is due to an avoided crossing with the next highest $3\Sigma_g^-$ state.

The total elastic cross sections are shown in Fig. (2). They exhibit an oscillatory behavior in the energy dependence that has been shown by Evans and Lane$^6$ to be characteristic of the potential energy curves. The excitation transfer cross section (Fig. 3) also exhibits an oscillatory behavior at energies exceeding the barrier heights of the potentials. It goes to zero as $E \rightarrow 0$ due to the presence of the barriers.

Similar calculations using a hypothetical diabatic curve (Fig. 3) for the $3\Sigma_g^-$ state were carried out.$^6$ The average magnitude of the excitation transfer cross section remained almost the same, but the character of the oscillatory behavior was significantly changed. These results, coupled with the experimental measurements of Sheridan et al.$^{12}$, shown also in Fig. (3), implied that the collision
FIGURE 1: Adiabatic $^3_{L_g}$ and $^3_{L_u}$ interaction potentials$^4,11$ between ground state and $2^3S$ metastable helium atoms. The dotted line represents a hypothetical diabatic $^3_{R_g}$ potential curve.
FIGURE 2: Total cross sections $Q_g$ and $Q_u$ calculated in the adiabatic approximation.
FIGURE 3: Comparison of excitation transfer cross sections in the adiabatic and diabatic approximations. The measurements\textsuperscript{12} are given in the closed circles. The dashed curve shows the effect of increasing the long-range difference between the gerade and ungerade potentials. This curve is in good agreement with low-energy measurements\textsuperscript{9} and is discussed in detail by Evans and Lane\textsuperscript{6}. 
may not occur adiabatically. In the remainder of this section, the results of the method used to test the adiabatic assumption will be presented.

A two state close coupling calculation was carried out for collisions between He(1s2s^3S) and He(1s^2 1S). Transitions to He(1s2p^3P) are made possible by the inclusion of the next highest ^3R_g state in the total wave function. The diabatic potentials corresponding to diagonal matrix elements in the close coupling calculation are shown in Fig. (4). The coupling matrix element is displayed in Fig. (5). One should note here that the diabatic potentials cross at R \approx 3.2 (a_0) and that the value of the coupling matrix element at this point is .056 a.u. Since each angular momentum \ell can be associated with a classical turning point, the partial wave contributions to the cross section can be associated with particular internuclear separations. Especially interesting is that region around the crossing point.

The inelastic cross section at 10 eV, resulting from the direct coupling between the 1s2s^3S and 1s2p^3P states, shows (Fig. 6) that the maximum partial wave contribution occurs in the region of the crossing, indicated by an arrow at \ell = 146. However, the total inelastic cross section is quite small.

The close coupling elastic cross sections for 10 eV are presented in Fig. (7). These results contain all significant coupling and are therefore expected to be the best,
FIGURE 4: The dashed curves are the diabatic $^3\Sigma^+_q(1s2s^3S)$ and $^3\Sigma^+_q(1s2p^3P)$ interaction potentials associated with helium metastable-atom collisions. The solid curves are the corresponding adiabatic potentials obtained by a unitary transformation between representations.
FIGURE 5: The solid curve is the coupling matrix element between the $^3_{1^+}2(1s2s^2S)$ and the $^3_{1^+}2(1s2p^3P)$ molecular states of helium. The other curves represent arbitrary reductions in the coupling matrix element.
FIGURE 6: Inelastic partial wave cross section for $^3\Sigma_g^+(1s2s^2S \rightarrow 1s2p^2^3P)$ transitions in helium metastable-atom collisions for $E=10$ eV. The arrow locates the partial wave $I$ associated with crossing point of the diabatic potential curves. The maximum $Q_{11}^2$ occurs near the crossing.
TRANSITION CROSS SECTION (1→2)
CLOSE COUPLING
E=10 eV (CM)
FIGURE 7: Comparison of elastic close coupling and adiabatic partial wave cross sections. The partial wave associated with the crossing of the potential curves ($\ell=146$) is indicated by the arrow.
ELASTIC CROSS SECTIONS
CLOSE COUPLING - 10 eV(CM)

ADIABATIC
\[ ^3\Sigma_g^+(1S^21S2P_0) - \Theta \]
\[ ^3\Sigma_g^+(1S^21S2S) - \Delta \]

\[ Q^k (a_0^2) \]

\[ \lambda \]

\[ 0 \quad 100 \quad 150 \quad 200 \quad 250 \quad 300 \quad 350 \quad 400 \quad 450 \]
within the accuracy of the potential curves. The obvious procedure now is to calculate purely diabatic and adiabatic cross sections at the same energy and then compare to see which most closely resemble the close coupling results.

The diabatic cross sections were obtained by setting the coupling matrix element to zero and proceeding as above. Elastic scattering of a particle incident in state (1) is now described entirely by $V^{d}_{11}$ and similarly for $V^{d}_{22}$. From Fig. (8), it is easy to see that the purely diabatic cross sections are in total disagreement with the close coupling results in Fig. (7).

In calculating the adiabatic cross sections at 10 eV, one must first transform to the adiabatic representation which diagonalizes the potential energy matrix. The potential energy curves obtained from this transformation do not cross, but instead experience an avoided crossing at $R \sim 3.2 \ (a_0)$. These curves are shown as solid lines in Fig. (4).

The cross sections are now calculated with the adiabatic curves, neglecting several non-adiabatic coupling terms generated by the transformation in the hamiltonian, all of which are expected to be small here. This type of coupling is known as momentum coupling and will be discussed in more detail in the next section. A comparison (Fig. 7) of the close coupling and the adiabatic result are given in the region of the crossing.
FIGURE 8: Elastic diabatic (no coupling) cross sections. The arrow points to the partial wave associated with the crossing of the potential curves.
ELASTIC CROSS SECTIONS
DIABATIC POTENTIALS (no coupling)
E=10 eV (CM)

$Q^2 (a_0^2)$

$^3 \Sigma_g^+(1S^21S2S)$

$^3 \Sigma_g^+(1S^21S2P_0)$
FIGURE 9: A qualitative example of the partial wave phase shifts and cross sections associated with attractive and repulsive potentials.
The concurrence of these results could have been predicted from an analysis of the behavior of the close coupling elastic partial wave cross sections. The argument will be outlined here for the benefit of the reader who wishes to apply the method to other systems.

The phase shift $\eta^\ell$ for elastic potential scattering can be obtained in the classical region $(E>(\ell+1)/R^2+U(R))$ by using the well known WKB approximation:

$$\eta^\ell = \int_{R_0}^{\infty} \left(k^2-U(R)-(\ell+\frac{1}{2})^2/R^2\right)^{1/2} dR - \int_{R'_0}^{\infty} \left(k^2-(\ell+\frac{1}{2})^2/R^2\right)^{1/2} dR, \quad (47)$$

where $R_0$ and $R'_0$ are just the zeros for their respective integrands. Evans and Lane\textsuperscript{6} have shown that the behavior of $\eta^\ell$ strongly reflects the behavior of $U(R)$ at reasonably low energies ($0<E<10$ eV). Qualitative examples of this similarity are seen in Fig. (9), a-b, d-e. Remembering that the single channel (no coupling) total elastic cross section is given by

$$Q^\ell = \frac{4\pi}{k^2}(2\ell+1)\sin^2\eta^\ell, \quad (48)$$

the behavior of the $Q^\ell$ in c and f of Fig. (9) follows directly: rapidly changing $\eta^\ell$ in c causes high frequency oscillations in $Q^\ell$ while the slowly changing behavior of $\eta^\ell$ in b results in low frequency oscillations in $Q^\ell$. Destructive or constructive interference effects will be superimposed on c if the minimum in $\eta^\ell$ in b occurs respectively at a value of $\eta\pi$ or $\eta\pi/2$.\textsuperscript{6} This simple picture then allows one
FIGURE 9: A qualitative example of the partial wave phase shifts and cross sections associated with attractive and repulsive potentials.
to assign characteristic behaviors to both repulsive and attractive potentials.

The application to this problem is obvious. The behavior of the close coupling $Q^{\ell}$ associated asymptotically with He($1s2s^3S$) resembles closely the behavior one would expect for scattering described by $V_{11}^\Lambda$ and similarly the $Q^{\ell}$ associated with He($1s2p^3P$) resembles scattering described by $V_{22}^\Lambda$.

The adiabatic cross sections were found to agree with the close coupling up to 200 eV (Fig. 10 and 11). The total elastic adiabatic cross sections are plotted in Fig. (12) for 10 eV ≤ $E ≤$ 100 eV. The average magnitude is in good agreement with the more accurate calculations in Fig. (2). The oscillations differ in phase and in magnitude. This is expected due to the sensitivity of the $3\Sigma_g^+(1s2s)$ to changes in depth of the potential well and the height of the potential barrier. The $3\Sigma_g^-$ curve shown in Fig. (2) was calculated from a five term wave function and is thus slightly lower than the one used in this problem.

One concludes then that the scattering of $2^3S$ metastables from ground state helium atoms occurs adiabatically up to 200 eV. This covers a large range of our previous calculations of the excitation transfer cross section. Better agreement with experimental results must depend on a more precise knowledge of the behavior of the wells and barriers in the adiabatic $3\Sigma_g,u(1s2s^3S)$. 
FIGURE 10: Comparison of elastic, close coupling and adiabatic partial wave cross sections in the region of the crossing for E=10 and 20 eV.
FIGURE 11: Comparison of elastic, close coupling and adiabatic partial wave cross sections in the region of the crossing for $E=50$, $100$, and $200$ eV.
FIGURE 12: Total elastic, close coupling cross section representing scattering in the $^3\Sigma_g^+(1s2s^3S)$ and $^3\Sigma_g^+(1s2p^3P)$ molecular states of He$_2$. 
II. Simple Model and Its Application to Real Problems

Quantitative results for a system in which diabatic curve crossing occurs were presented in the last section. Because of the occurrence of a well defined curve crossing within a simple two state framework, this system offers a wonderful opportunity to study and clarify some of the most basic concepts in atomic collision theory.

Assume that in some very low energy collision the adiabatic potential curves $U_{11}^a$ and $U_{22}^a$ describe respectively

![Diagram (3)]

the behavior of the orbital electrons when the atoms are initially in state (1) and state (2), respectively. One can think of this process simply as a particle following an "energy path" or potential curve. As the energy increases, it becomes more difficult for the orbital electrons to re-adjust to the sudden changes in direction of the path, within the time $T_o$ of the collision. At some intermediate energy there will be an equal probability of taking either path
(solid or dotted curves). If the energy is boosted up enough, it will become almost impossible for the electrons to readjust in time, thus forcing the particle to follow only the dotted or diabatic curves.

Instead of varying the energy, we can examine this by varying the separation between the curves at the avoided crossing. Since the separation between the curves at the crossing is twice the potential coupling matrix element $U_{21}^d$, one simply varies $U_{21}^d$ (that $2\Delta E = U_{21}^d = 1/2(U_{11}^d + U_{22}^d)$ can be shown easily by solving the secular equation for a two term system at the crossing). Initially let $U_{21}^d$ be very large. $U_{11}^a$ and $U_{22}^a$ will be widely separated and suffer no abrupt changes in path at the crossing. Scattering then must be described by the adiabatic paths. Since almost no readjustments of the electronic orbitals is required, the system will remain adiabatic even for moderate increases in the energy. If $U_{21}^d$ is reduced the curves will approach each other and it will become increasingly easier for particles to shoot across on the dotted curves. At sufficiently small $U_{21}^d$ only dotted curves will be followed.

It follows then that for a given $U_{21}^d$ one can always find an $E$ at which there is a maximum transition probability and similarly, for a given $E$, one can always find a $U_{21}^d$ at which there is a maximum transition probability. Also if $U_{21}^d$ is very large, the adiabatic assumption may hold over a wider range of $E$. 
Before going on to a qualitative discussion of the two state system in terms of the simple model, it would be useful to look at the non-adiabatic terms generated in a transformation from a diabatic basis set to an adiabatic basis. Starting from eq. (12)

$$
\left[ \frac{d^2}{dR^2} + \xi^2\frac{\ell(\ell+1)}{R^2} - U \right] \tilde{y}(R) = 0 \tag{49}
$$

where

$$(\xi)_{ij} = \delta_{ij} \kappa_i^2 \quad \text{and} \quad (U)_{ij} = U_{ij},$$

the $\tilde{y}(R)$ are transformed by

$$\tilde{y}'(R) = C\tilde{y}(R),$$

where $C$ is a transformation such that

$$CUC^{-1} = U',$$

and

$$(U')_{ij} = \delta_{ij}U'_{ij}.$$

Substituting into (49) we get

$$
\left[ \frac{d^2}{dR^2} + \xi^2\frac{\ell(\ell+1)}{R^2} - CUC^{-1} \right] C^{-1}\tilde{y}'(R) = 0 ,
$$

$$
\left[ \frac{d^2}{dR^2}C^{-1}\tilde{y}'(R) + \xi^2\frac{\ell(\ell+1)}{R^2} - U' \right] y'(R) = 0 .
$$

Expansion of the first term in (50) gives

$$
C\frac{d^2}{dR^2}C^{-1}\tilde{y}'(R) = \frac{d^2}{dR^2} \tilde{y}'(R) + 2\frac{dC}{dR} \frac{d\tilde{y}'(R)}{dR} + C^{-1}\frac{d^2C}{dR^2} \tilde{y}'(R) .
$$

$$
\tag{51}
$$
The last two terms on the right side of (51) give rise to coupling. These are precisely the terms, in a slightly different form, that are obtained by Smith\textsuperscript{23} and Levine \textit{et al.}\textsuperscript{24} A transformation given by both these authors which diagonalizes $U$ is

$$
\zeta(R) = \begin{pmatrix}
\cos \alpha & \sin \alpha \\
-\sin \alpha & \cos \alpha
\end{pmatrix}
$$

(52)

where

$$
tan 2\alpha(R) = \frac{2V_{21}(R)}{V_{22}(R) - V_{11}(R)} .
$$

and $U_{ij} = \frac{2MV_{ij}}{m_e}$ is a diabatic potential. The largest coupling term generated by this transformation as derived by Smith is

$$
P^a_R(R)p_R = \begin{pmatrix}
0 & -1 \\
1 & 0
\end{pmatrix} a'(R)v(R) ,
$$

(53)

where $P^a_R(R)$ is the adiabatic momentum and $p_R$ is the relative nuclear velocity. $a'(R)$ at a curve crossing is

$$
a'(R_c) = \frac{1}{2}[V'_{11}(R_c) - V'_{22}(R_c)]/2V_{21}(R_c) .
$$

One can see immediately the relationship of (53) to our simple model. $P^a_Rp_R$ is proportional to $\sqrt{E}$ and inversely proportional to $U_{21}$. In the adiabatic representation it is evident that transitions occurring at higher $E$ and associated with lower $U_{21}$ are caused mainly by the momentum coupling term above. In the general Eq. (5), both momentum and potential
coupling occur. However, in the diabatic representation (curve crossing allowed) the former is assumed small and neglected for reasons given in Appendix A.

Having looked at the curve crossing problem both from a physical and mathematical view, we will use these ideas to explain the unusual behavior observed in both elastic and inelastic partial wave cross sections obtained by varying both $E$ and $\nu_{21}$.

One should remember in discussions about "scattering off potential curves," that for $l > 0$, the distance of closest approach is determined by an effective potential

$$U^{\text{eff}}(R) = \frac{l(l+1)}{R^2} + U(R)$$

For a given $l$, increasing the energy allows the particle associated with that $l$ to approach closer to the nucleus. Thus, the number of partial waves at which significant scattering occurs would increase with $E$. The turning point $R_{0}^{\text{max}}$ associated with the largest partial wave contribution in the elastic scattering process must become smaller with an increase in $E$. To show this, consider a particle whose closest approach to a scattering center is $R_1$. Increasing the energy will allow the particle to approach to the same $R_1$ with less deviation. Thus, for the same amount of scattering to occur at higher energy, the particle must approach closer. These important points about the scattering process are readily verified for a real system in Table (1), Appendix C.
III. Close Coupling Elastic and Inelastic Cross Sections: A Closer Look

The effect of the coupling matrix element $V_{21}$ on the adiabatic potentials was discussed in the last section. To give the reader an idea how strong $V_{21}$ really is, the maximum $Q_{21}^l$ has been plotted versus the strength of coupling in Fig. (13). The maximum $Q_{21}^l$ was calculated using both the distorted wave and the close coupling approximations. One can conclude from this graph that the full $V_{21}$ (i.e. FRAC=1.0) is far too strong for distorted wave or any other weak coupling approximation to work. Note, at this point, the maximum in $Q_{21}^l$. In terms of our model, this corresponds to a coupling strength where crossing and non-crossing are equally probable.

To test the sensitivity of the cross sections to slight changes in the coupling matrix element, we calculated close coupling cross sections with $V_{21}$ reduced by 10%. The results are shown in Fig. (14). An overlay comparison with the full coupling results in Fig. (7) would show a definite change. The frequency of oscillation of $Q_{22}^l$ has decreased by a shifting toward smaller $l$'s and the frequency of $Q_{11}^l$ has increased by an opposite shift. The overall magnitude and character of $Q_{21}^l$ in Fig. (15) changed little with the reduction in coupling. However, a closer inspection reveals a reduction in the number and magnitude of "lobes" occuring outside the
FIGURE 13: Maximum partial wave cross section, $Q_{21}^2$, calculated using both close coupling and distorted wave approximations, is given as a function of the strength of $V_{21}(R)$. 
Maximum Partial Wave Cross Section vs Coupling Matrix Ratio

$E = 10\,\text{eV (CM)}$

$\text{MAX } Q_x' (i-2) \text{ WHERE } V_{21} = (\text{FRAC}) \cdot V_{21}$

△ Distorted Wave
○ Close Coupling

MAX $Q_x' (\alpha_0^2)$ vs FRAC
FIGURE 14: Elastic, close coupling partial wave cross section with the coupling matrix element $V_{21}(R)$ reduced by 10%.
FIGURE 15: Inelastic, close coupling partial wave cross section with the coupling matrix element $V_{21}(R)$ reduced by 10%.
associated with the crossing point. This can be interpreted as a movement away from non-classical behavior, since classically, no transitions can occur outside the crossing point. Experimentally, one should observe a smaller differential cross section at small angles for this case of reduced coupling.

The result of further reduction in the coupling is shown in Fig. (16). Also plotted are cross sections calculated in the adiabatic representation with no coupling. Comparison of the two shows the effect of neglecting the momentum coupling when $V_{21}$ is reduced by 90%. The switching of behavior in the close coupling cross sections can be easily seen: $Q^2(1s2s^3S)$ is beginning to behave more like a cross section calculated from a repulsive potential and $Q^2(1s2p^3P)$ is taking on the opposite behavior. For this particular strength of coupling the probability of a transition occurring is maximized (Fig. 13), resulting in an intermediate behavior in the elastic partial wave cross sections. One can conclude that if $V_{21}$ were reduced enough, scattering would be described entirely by the diabatic potentials in Fig. (4). In accordance with earlier discussions, increasing the energy must have the same effect.

In a further study of collision properties for crossing curves, both the energy and the coupling were varied over a wide range of values. Interesting structure was observed in the elastic $Q^2(1s2s^3S)$ at higher energies and at
FIGURE 16: Comparison of elastic, close coupling and adiabatic partial wave cross section in the region of the crossing with the coupling matrix element reduced by 90%.
ELASTIC CROSS SECTIONS - 10 eV (CM)
COUPLING MATRIX ELEMENTS REDUCED
\[ V_{21}^\prime = (0.1) \cdot V_{21} \]

\[ Q^1(a^2) \]

ADIABATIC
CLOSE COUPLING
\[ ^3\Sigma_g^+ (1S^2 1S 2P_o) \]

\[ Q^1(a^2) \]

ADIABATIC
CLOSE COUPLING
\[ ^3\Sigma_g^+ (1S^2 1S 2S) \]
smaller values of the coupling matrix element. A comparison is given between the close coupling and the adiabatic results in Fig. (17). Mathematically, the disagreement between the close coupling and the adiabatic results is due to the neglect of the momentum coupling terms discussed in the last section (also in Appendix A). There are two effects to be observed in the close coupling cross sections: a shift toward diabatic behavior and an interference or structure.

These effects are due to both coherent and incoherent mixing of phase shifts $\delta^\pm$. In the limits (1) and (2), which are discussed below, $\delta^\pm$ can be associated respectively with adiabatic and diabatic potential curves.

To show this, we recast $Q_{11}$ and $Q_{21}$ of eq. (17) in a form given by Mott and Massey\(^\text{14}\) as

$$Q_{11}^\ell = \frac{4\pi (2\ell+1)}{k_1^2(k_1+k_2\chi_\ell^2)} \left\{ k_1 \sin^2 \delta_{\ell}^+ + k_2 \chi_\ell^2 \sin^2 \delta_{\ell}^- \right\} - Q_{21}^\ell, \quad (54a)$$

$$Q_{21}^\ell = \frac{4\pi (2\ell+1)}{k_1(k_1+k_2\chi_\ell^2)^2} k_2 \chi_\ell^2 \sin^2 (\delta_{\ell}^+ - \delta_{\ell}^-), \quad (54b)$$

where $\delta_{\ell}^\pm$ are real eigen-phase shifts (phase shifts) associated with the scattering process. $\chi_\ell$ is now a mixing parameter which is given by Mott and Massey\(^\text{14}\) as

$$\chi_\ell = \frac{k_2}{k_1} \tan \epsilon \quad , \quad (55)$$

where $\tan 2\epsilon = R_{21}/(R_{22}-R_{11})$ and where $R_{ij}$ is an element of the matrix $R$ discussed in Section III of Part I. Expressions
FIGURE 17: Comparison of elastic, close coupling and adiabatic partial wave cross sections for a variation in both energy and strength of coupling. Structure in the close coupling cross section is thought to be the result of coherent mixing of the outgoing flux from two different elastic scattering paths.
similar to (54a) and (54b) can be written for \( Q_{22}^g \) and \( Q_{12}^g \).

The tangents of the phase shifts \( \delta^\pm \) form a diagonal matrix written as

\[
\tan \eta = \begin{pmatrix}
\tan \delta^+ & 0 \\
0 & \tan \delta^-
\end{pmatrix}
\]

\( \tan \eta \) is found by diagonalizing \( R \) with a unitary transformation given by

\[
\eta = URU^+
\]

where

\[
U = \begin{pmatrix}
\cos \epsilon & \sin \epsilon \\
-\sin \epsilon & \cos \epsilon
\end{pmatrix}
\]

One can easily show then that the phase shifts \( \delta^\pm \) are defined as

\[
\tan \delta^\pm = \frac{1}{2}(R_{11} + R_{22}) \pm \frac{1}{2}[(R_{11} - R_{22})^2 + 4R_{21}^2]^{1/2}
\]

(56)

Now in discussing the adiabatic and diabatic representation as limiting descriptions of the scattering process, we will first summarize the asymptotic conditions discussed in Section II of Part II:

limit (1): \( E \to \infty \) or \( V_{21} \to \text{small} \) \( \Rightarrow Q_{21} \to 0 \) \hspace{1cm} (57)

limit (2): \( E \to 0 \) or \( V_{21} \to \text{large} \) \( \Rightarrow Q_{21} \to 0 \) \hspace{1cm} (58)

where \( Q_{21} \to 0 \) implies that \( R_{21} \to 0 \). (See Section I, Part I)

Also we remind the reader that \( Q_{21} \) can have a significant value at the intermediate \( E \) or \( V_{21} \).
Imposing condition (58) reduces \( \tan \delta^\pm \) to

\[
\tan \delta^+ = R_{11},
\]
\[
\tan \delta^- = R_{22}.
\]

Also, \( \chi_\ell \), which is strongly dependent on \( R_{21} \) (Eq. 55), goes to zero. The scattering cross section in Eq. (54a) is then uniquely defined by \( \delta_\ell^+ \) which can now be associated with an adiabatic potential curve. An example of this is given in Fig. (7) where adiabatic (no coupling) and close coupling cross sections are in good agreement.

By increasing \( E \) or decreasing \( V_{21} \), the terms in Eq. (54a) depending on \( \chi_\ell \) will become important. The effects on \( Q_{11} \) are seen in Fig. (17). The increase in \( Q_{21} \) with energy is demonstrated by Figs. (18-20), (24). It should be made clear at this point that we are talking now about moderate changes in \( E \) and \( V_{21} \). The behavior of the partial wave cross sections can still be associated with adiabatic potential curves.

However, at some intermediate energy or strength of coupling all the terms in (54a) will contribute significantly. In this case, a unique description of scattering in one state or the other is impossible since \( Q_{11,22}^\ell \) will consist of a mixture of terms depending on both \( \delta_\ell^+ \) and \( \delta_\ell^- \). In addition, \( \delta^\pm \) (eq. 56) must now be defined by a complicated expression involving all the elements of \( R \).

Looking now at limit (2) we see that \( \delta^\pm \) can again be
FIGURE 18: Inelastic partial wave cross section representing $^3\Sigma^+(1s2s^3S\rightarrow 1s2p^3P)$ transitions in the helium metastable-atom collisions for $E=20$ eV. The maximum $Q_{21}^1$ occurs near the partial $\hat{q}$ (noted by $+$) associated with the crossing of the potential curves.
$3 \Sigma_g^+ (\sigma^2 s^2 \sigma - \sigma^2 s^2 \pi)$

20 eV

$^0 \Sigma_g^+ (\sigma^2 s^2 \sigma - \sigma^2 s^2 \pi)$

$(^0 \Sigma_g^+)^{12}D$
FIGURE 19: Inelastic partial wave cross section representing $^3\Sigma_g^+(1s2s^3S\rightarrow 1s2p_0^3P)$ transitions in the helium metastable-atom collisions for $E=50$ eV. The maximum $Q_{21}^i$ occurs away from the $i$ associated with the crossing (+).
$50 \text{ eV}$

$\Sigma^+_g (1s2s2^3S \rightarrow 1s2p^3P)$

$\lambda$ vs. $(^2D)_{^{12}O}$
FIGURE 20: Inelastic partial wave cross section representing $^3\Sigma^+(1s2s^3S + 1s2p^3P)$ transitions in the helium metastable-atom collisions for $E=100$ eV. The maximum $Q_{21}^5$ occurs near the $\phi$ associated with the crossing ($\dagger$).
described by

\[ \tan \delta^+ = R_{11}, \]
\[ \tan \delta^- = R_{22}. \]

Also, \( \chi_k \), which is a strong function of \( R_{21} \) goes to zero.

The elastic scattering cross sections \( Q_{11,22} \) are again uniquely defined, respectively, by \( \delta^+ \) and \( \delta^- \). \( \delta^\pm \) are now associated with purely diabatic potentials. An example of diabatic cross sections is shown in Fig. (8). In this case, \( E = 10 \) eV and \( V_{21} = 0 \).

Using Eq. (54a) and (54b) and the ideas developed above, we can now explain the structure that appears in the \( Q_{11}^k \) cross sections at higher energies and for reduced coupling. For \( E = 100 \) eV in Fig. (17a), the overall behavior is almost adiabatic since the adiabatic and the close coupling cross sections are in fair agreement. Therefore, one can still relate \( \delta^+ \) with scattering on \( V_{11}^{a1} \) and \( \delta^- \) with scattering on \( V_{22}^{A2} \). From our discussion in Section I of Part II and by examining Fig. (4) and (9), we can deduce that \( \delta^- \) will be large at small \( k \) (i.e., \( k \) less than the \( k \) associated with the crossing of the potential curves) and decrease rapidly as \( k \) increases. \( \delta^+ \) will be small compared to \( \delta^- \) at small \( k \) and will vary slowly as \( k \) increases. Looking now at \( Q_{21}^k \) in Eq. (54b), we see that \( \delta^- \) will dominate \( \sin^2(\delta^+ - \delta^-) \) at small \( k \) and, thus, the rapid decrease in \( \delta^- \) will result in high frequency oscillations in \( Q_{21}^k \) in the small \( k \) region. This behavior in \( Q_{21}^k \) is seen in Fig. (20) and it also occurs
at lower energies (Figs. 18, 19). The rapid variation of \( \delta^- \) is felt in \( Q_{11}^\ell \) since \( \chi^\ell \) and \( Q_{21}^{\ell} \) are now large enough to have an effect on \( Q_{11}^\ell \). At 100 eV, the last two terms on the right side of the equal sign in Eq. (54a) are slightly out of phase at small \( \ell \) since the first is proportional to \( \sin^2 \delta^- \) and the second is proportional to \( \sin^2(\delta^+-\delta^-) \). In addition, these terms are about 1/10 the size of the first term. The effect is most clearly seen in Fig. (17a) as an irregular structure superimposed on the slower oscillations for \( 300 \leq \ell \leq 400 \). At large \( \ell \), \( \delta^- \) ceases to dominate \( \delta^+ \) because of the similar behavior of the adiabatic potentials (Fig. 4) associated with each phase shift for \( R > R_c \). Thus, the effect of the interference terms is no longer observed. Also for \( R > R_o \), \( Q_{21}^{\ell} \) decreases rapidly (Figs. 18-20). Similar arguments would hold in explaining Figs. 17b, c and d.

The elastic cross sections \( Q_{22}^\ell \) for \( E = 10, 20, 50 \) and 100 eV contain no apparent structure. This can be explained by examining the expressions for \( Q_{22}^\ell \) and \( Q_{12}^\ell \):

\[
Q_{22}^\ell = \frac{4\pi(2\ell+1)}{k_2^2(k_2+k_1x_2^\ell)^2} \{k_2\sin^2 \delta^- + k_1x_2^\ell \sin \delta^+ \} - Q_{12}^\ell , \quad (39a)
\]

\[
Q_{12}^\ell = \frac{4\pi(2\ell+1)x_1^\ell \sin^2(\delta^- - \delta^+)}{k_2^2(k_2+k_1x_2^\ell)^2} \quad (57b)
\]

where \( x_\ell \) and \( \delta^\pm_\ell \) are defined as before. Since at 100 eV, \( \delta^+ \) is slowly varying and \( x_\ell \) is small, the effect of the term proportional to \( x_\ell^2 \sin^2 \delta^+ \) would be extremely hard to see in
$Q_{22}^l$. $Q_{12}^l$ is only slightly out of phase with $Q_{22}^l$ at small $l$. As $l$ increases, their phase difference will increase as $\delta_+^l$ and $\delta_-^l$ become more alike. Thus, at some intermediate value of $l$, comparison of the purely adiabatic (no coupling) $Q_{22}^l$ and the close coupling $Q_{22}^l$ would reveal a slight phase difference between the two partial cross sections. This phase difference should be most apparent at the maxima. At larger $l$, $Q_{12}^l$ will decrease and the difference will disappear. This effect, although small, is observed in $Q_{22}^l$ for $E = 50$ eV and $E = 100$ eV.
IV. Landau-Zener Approximation: A Tool For Understanding

Cross sections for transitions between $\text{He}(ls2s^3S)$ and $\text{He}(ls2p^3P)$ have been calculated using the Landau-Zener approximation. The energy and the strength of the coupling matrix element $V_{21}$ were varied in order to obtain both quantitative and qualitative comparison with close coupling. To simplify the calculations, $\tau_{\ell}$ in eq. (43) was arbitrarily set to $\pi/2$. Consequently, the results shown in Fig. (21) and (22) as dotted lines, represent only the envelope, tracing out the maxima of the oscillations. This procedure is valid only if the random phase approximation is good. In that approximation, one replaces $\sin^2\tau_{\ell}$ by $1/2$. The arrows point to the partial wave associated with the crossing point of the potential curves. A contour plot in Fig. (23) gives the maximum $Q_{21}^\ell$ (normalized to 9) as a function of energy and strength of coupling.

In examining Fig. (21) to (23), we should look again at the L-Z expression for the probability of a transition

$$P_T^\ell = \sum_{\ell} P_T^\ell = \sum_{\ell} 2P_T^\ell (1 - P_T^\ell) ,$$

where

$$P_T^\ell = \exp(-2\gamma_{\ell}) ,$$

$$\gamma_{\ell} = \pi V_{21}^2 / (|V_{11}' - V_{22}'| V_{\ell}^\ell)_R C$$
\[ v_1(R_c) = \frac{m_e}{M} k_1^2 - 2Mv_{11}(R_c) - (\ell + \delta)^2/R_c^2 \frac{1}{2}. \]

For a given set of diabatic crossing potentials, one can see that \( P_2 \) depends entirely on the value of \( v_2/V_{21}^2 \) and that the maximum \( P_T^2 \) occurs when \( P_2 = .5 \). The asymptotic limits for \( P_T^2 \) are given by

\[
\text{constant } v_2 \begin{cases} 
V_{21}(R_c) = 0 \rightarrow P_2 = 1 \rightarrow P_T^2 = 0 \\
V_{21}(R_c) \text{ very large} \rightarrow P_2 = 0 \rightarrow P_T^2 = 0
\end{cases}
\]

\[
\text{constant } V_{21}(R_c) \begin{cases} 
v_2(R_c) = 0 \rightarrow P_2 = 0 \rightarrow P_T^2 = 0 \\
v_2(R_c) \text{ very large} \rightarrow P_2 = 1 \rightarrow P_T^2 = 0
\end{cases}
\]

Qualitatively the total cross section will show the same behavior (Fig. 23). It is assumed that the maximum \( Q^2(E,V_{21}') \) is approximately proportional to \( Q^T(E,V_{21}') \) where \( V_{21}' = (\text{FRAC})(V_{21}) \). The L-Z approximation predicts then that the transition cross section will go through a maximum if one varies the energy or the coupling over a large enough range. In other words, it predicts changes from adiabatic to diabatic and vice versa. This is demonstrated graphically for a variation of \( V_{21}' \) in Fig. (21) and a variation of \( E \) in Fig. (22). The reasonable agreement between L-Z and close coupling results shown in Fig. (21) and (22) indicate that the contour plot is fairly accurate in the range covered. It is evident from a plot of the total inelastic cross section (Fig. 24) with the full coupling on, that its maximum is beyond the
FIGURE 21: Comparison of close coupling and L-Z inelastic partial wave cross sections for variations in the strength of the coupling matrix element. The arrows point to the partial wave \( \ell \) associated with the crossing of the potential curves.
FIGURE 22: Comparison of close coupling and L-2 inelastic partial wave cross sections for variations in the initial kinetic energy. The arrows point to the partial wave $\delta$ associated with the crossing of the potential curves.
FIGURE 23: Landau-Zener contour plot. The maxima $Q^j_{21}$ are given as a function of energy and the strength of the coupling matrix element where $V_{21}(R) = (\text{FRAC}) V_{21}(R)$. All $Q^j_{21}$ are normalized to nine. For the sake of clarity, only odd values of $Q^j_{21}$ are plotted. The even values of $Q^j_{21}$ correspond to the white un-numbered areas.
FIGURE 24: Total inelastic, close coupling cross section representing transitions between the $^3\Sigma_g^+(1s2s^3S)$ and the $^3\Pi_g(1s2p^3P)$ molecular states of He$_2$. 
$^{3}\Sigma_{g} (1S2S_{2}^{3}S - 1S2P_{0}^{3}P)$

$E(\text{ev})(\text{CM})$

$(10^{-16}\text{cm}^{2})^{12}O$
limits of our calculations. This is in agreement with our previous conclusion that the He-He* system is still mostly adiabatic up to 200 eV.

Another effect predicted by the L-Z formalism is the movement of the maximum $Q^{21}_{21}$ toward partial waves associated with smaller $R$ with an increase in $V^{21}_{21}$ or a decrease in $E$. In proving this, consider the maximum $Q^{2}(E, V^{21}_{21})$, with which one can associate a particular $v_{\ell}$. $V^{21}_{21}$ is the strength of coupling that will give $P_{T}$ its maximum value of .5. Now, if the $V^{21}_{21}$ is increased to $V^{21}_{21}'$, the velocity $v_{\ell}$ will no longer maximize $P_{T}$ since the ratio $V^{21}_{21}/v_{\ell}$ has increased. The condition

$$V^{21}_{21}(R_{C})/v_{\ell}(R_{C}) = V^{21'}_{21}(R_{C})/v'_{\ell}(R_{C})$$

requires $\ell' < \ell$ since $v_{\ell}$'s associated with smaller partial waves at a given energy penetrate further into the scattering center and thus have a greater velocity at the crossing $R_{C}$. A similar argument can be made for a reduction in the energy. The relative movement of the maximum $Q^{21}_{21}$ inward can be observed in both Fig. (21) and Fig. (22). One can even see the effect in Fig. (19) and (20), where the full coupling is on. However, the L-Z method is quantitatively in disagreement as demonstrated by the comparison at 50 and 100 eV.

If all coupling terms are maintained after a unitary transformation between representations, the adiabatic and
diabatic representations will produce equivalent results in a close coupling calculation. Thus, one can think of our exact close coupling calculation in terms of scattering on adiabatic potentials with electronic transitions being caused by the momentum coupling discussed above. Comparison between $P_{\text{LZ}}^\lambda$ and $\alpha'(R_C)v(R_C)$ of Eq. (53) shows them both to have a similar functional dependence at the crossing

$$\alpha'(R_C)v(R_C) \sim [V_{11}' - V_{22}']v_\lambda(R_C)/V_{21},$$

$$P_{\text{LZ}}^\lambda \sim |[V_{11}' - V_{22}']|v_\lambda(R_C)/V_{21}^2.$$  

One can see that qualitatively these terms will vary in much the same way at the crossing. Now if the momentum coupling terms were almost delta functions centered about the crossing for all values of $E$ and $V_{21}$, then the L-Z method might always be good since that is the principle approximation made in the derivation. However, a plot of $\alpha'(R)$ for various strengths of the coupling matrix element in Fig. (25) shows both an asymmetry and a spreading effect.

The spreading of terms like $\alpha'(R)$ cause contributions to the cross section from transitions away from the crossing. The L-Z approximation neglects all contributions resulting from the spread of the momentum coupling terms into the region $R > R_C$. In Fig. (21c) and (22d) the close coupling $Q_1^\lambda$'s rise above the L-Z results due to a spreading of $\alpha'(R)$ type coupling into the region $R < R_C$. Even though
FIGURE 25: The gradient interaction term $\alpha'(R)$ for various strengths of the coupling matrix element $V_{21}'(R)$. 
the L-Z method does not account for the spreading of the momentum coupling, it would still predict where the maximum \( Q_{21}^2 \) occurred if \( a' \) type coupling were symmetrical about the crossing point. But this is not the case as is shown in Fig. (25). The movement of the maximum in \( a' \) to larger \( R \) for strong potential coupling predicts a movement of the maximum from \( Q_2^2 \) to \( Q_2'^2 \) where \( Q' \) is associated with a larger turning point than \( Q \). This can be seen qualitatively by comparing Fig. (6), (21) and (6), (18), (19) or quantitatively, by checking Table (1), Appendix C.
Problem II: Helium Ion-metastable (atom) Collisions
Introduction to Problem II

The helium metastable-atom collisions discussed in Problem I were best described by scattering on adiabatic potential curves. The experience gained in this work suggested that a study of a less adiabatic system would further clarify the role of the diabatic and adiabatic potentials in determining the collision process. For this purpose, we chose the helium ion-metastable (atom) collision system.

Interest in He$^+$-He collisions has been considerable among both experimentalists$^{22, 39-42}$ and theorists.$^{18, 21, 43-48}$ The non-adiabatic nature of the lowest $^2\Sigma_g^+$ was first shown by Lichten.$^{18}$ He obtained a parameter $\langle E_a \rangle$ by integrating the difference between the electronic energies of the $^2\Sigma_g^+$ and $^2\Sigma_u^+$ molecular states associated with He(ls$^2$)-He(ls) charge exchange collisions. $\langle E_a \rangle$ is a measurable quantity$^{49}$ of atomic dimensions that is associated with the frequency of charge exchange. The $^2\Sigma_u^+, \Sigma_g^+$ potentials were obtained by applying Koopmans$^{50}$ rule to Phillipson's$^{43}$ single configuration (diabatic) potentials for He atom-atom collisions. The value Lichten found for $\langle E_a \rangle$ was in agreement with the experimentally determined value obtained by Ziemba and Russek.$^{39}$

Marchi and Smith$^{21}$ calculated elastic differential cross sections for low energy He$^+$-He collisions. By using
the adiabatic \( ^2\Sigma^+_u \) curve of Reagon et al.\(^{44}\) and the diabatic \( ^2\Sigma^+_g \) of Lichten\(^{17}\)-Phillipson\(^{43}\), they were able to reproduce the magnitude and many aspects of the structure in the differential cross sections observed by Lorents and Aberth.\(^{22}\)

In a later study, Smith et al.\(^{45}\) were able to identify perturbations in the elastic differential cross section with a particular crossing of the diabatic \( ^2\Sigma^+_g \) with a higher state of the same symmetry at \( R \approx 1.73 \) a\(_o\).

J. C. Browne\(^{46}\) calculated a number of the potential curves for the excited states of He\(_2^+\), including the lowest \( ^2\Sigma^+_g \). He suggested that an extreme flatness in the second lowest \( ^2\Sigma^+_g \) curve between \( R = 1.5 \) and \( 3.0 \) a\(_o\) was caused by an avoided crossing between the two lowest adiabatic \( ^2\Sigma^+_g \) states. In the diabatic representation, a crossing would probably occur at \( R = 1.5 \), in agreement with the prediction of Smith et al.\(^{44}\).

More accurate \( ^2\Sigma^+_g \) and \( ^2\Sigma^+_u \) potential curves describing He(1s\(^2\))-He(1s) collisions have been calculated by Gupta and Matsen.\(^{47}\) A 26 term valence bond wave function was used to calculate the curves for \( R \geq 0.378 \) a\(_o\). They confirmed the existence of the aberration in the \( ^2\Sigma^+_g \) curve near \( R = 1.5 \) a\(_o\) which Browne interpreted as an avoided crossing.

Emission cross sections have been measured by Dworetzky et al.\(^{40}\) for transitions from the \( n = 3 \) level, which occur when He is bombarded by He\(^+\). In most cases, the cross sections reached a large fraction of their maximum value
within a few eV of their threshold energy. Dworetsky interpreted these results as a failure of the "adiabatic criterion." This principle says that, in a collision, a transition between electronic states is most probable when

$$v_{\text{max}} = \Delta E_a / \hbar,$$

where $\Delta E$ is the separation between the states at $R = \infty$ and $a$ is an effective range parameter of atomic dimensions.

In a later work, Rosenthal\textsuperscript{48} attributed the strong oscillatory energy dependence of the $3^3S - 2^3P$ and the $3^1S - 2^1P$ emission cross sections, measured by Dworetsky \textit{et al}.\textsuperscript{40}, to avoided crossings in the adiabatic potential curves at large $R$.

Dworetsky, Novick and Tolk\textsuperscript{41} performed an experiment to check Rosenthal's result. They first studied the potential curves of the excited states of $\text{He}^+_2$. Finding that no outer crossing exists for the excited 2P states, they measured the $2^1P - 2^1S$ emission cross section for $\text{He}^+ - \text{He}$ collisions. No oscillatory energy dependence was found.

Recently, MacVicar-Whelan and Borst\textsuperscript{42} measured cross sections for metastable production in low energy $\text{He}^+ - \text{He}$ collisions. They observed that the metastable production increased from threshold at approximately 22 eV to a maximum at 27 eV and decreased to a minimum at 32 eV. An increase in the metastable cross section after 32 eV was attributed to excitation of higher states. The states
contributed to the observed target current by cascading to the metastable states. Most of the inelastic flux observed must be from $1^1S-2^1P$ transitions since these states have the same spin.

In the present work, we have made use of the close coupling approximation to calculate all the elastic and inelastic cross sections associated with collisions in the three lowest $2^2L_g^+$ states of $\text{He}_2^+$. In doing so, we have tried to answer some of the questions arising from the experimental and theoretical investigations discussed above.

In Part I, the elastic and inelastic cross sections are discussed separately and then compared to the results obtained in Problem I. Heavy reliance is made on interpretive methods developed in Part II of Problem I.
Part I: Theory and Procedure
I. Theory

The differential equations that describe helium ion-metastable (atom) collisions are precisely those discussed in Section I of Problem I. The criteria for choosing the wave function will be the same. The second lowest, single configuration $^2\Sigma^+_g$ potential crosses the third lowest $^2\Sigma^+_g$ at $R = 3.75 \ a_0$ and approaches closely the lowest $^2\Sigma^+_g$ at $R = 1.5 \ a_0$. No crossings or near crossings occur between the three lowest $^2\Sigma^+_u$ potential curves. The total wave function may then be approximated by

$$
\psi(\vec{R}, \vec{r}_i) = F_{1g}(\vec{R}) \psi_1(\vec{R}, \vec{r}_i; ^2\Sigma^+_g) + F_{2g}(\vec{R}) \psi_2(\vec{R}, \vec{r}_i; ^2\Sigma^+_g) + F_{3g}(\vec{R}) \psi_3(\vec{R}, \vec{r}_i; ^2\Sigma^+_g),
$$

where

$$
\psi_1(^2\Sigma^+_g) \underset{R \to \infty}{\to} \phi(A) \chi(B^+) + \chi(A^+) \phi(B) + \text{He}(1s) + \text{He}(1s^2),
$$

$$
\psi_2(^2\Sigma^+_g) \underset{R \to \infty}{\to} \theta(A^*) \chi(B^+) + \chi(A^+) \theta(B^*) + \text{He}(1s) + \text{He}(1s2s^3S),
$$

$$
\psi_3(^2\Sigma^+_g) \underset{R \to \infty}{\to} \delta(A^*) \chi(B^+) + \chi(A^+) \delta(B^*) + \text{He}(1s) + \text{He}(1s2s^1S),
$$

where $\theta$, $\phi$ and $\chi$ represent atomic wave functions, $A$ and $B$ label atom $A$ and $B$ and $\rightarrow$ points to the corresponding separated atom configuration. $F_\nu$ may be expanded as

$$
F_\nu(\vec{R}) = R^{-1}\Sigma^\nu_{\frac{\ell}{2}} \mathcal{P}_{\ell}(\vec{k}_1 \cdot \vec{R})
$$
Schroedinger's equation, in this case, reduces to three second order coupled differential equations. They are given in atomic units as

\[
\begin{align*}
\left[ \frac{d}{dr^2} + k_1^2 \frac{r(r+1)}{r^2} U_{11}(r) \right] y_1^\ell(r) &= U_{12}^d(r) y_2^\ell(r) + U_{13}^d(r) y_3^\ell(r), \\
\left[ \frac{d}{dr^2} + k_2^2 \frac{r(r+1)}{r^2} U_{22}(r) \right] y_2^\ell(r) &= U_{21}^d(r) y_1^\ell(r) + U_{23}^d(r) y_3^\ell(r), \\
\left[ \frac{d}{dr^2} + k_3^2 \frac{r(r+1)}{r^2} U_{33}(r) \right] y_3^\ell(r) &= U_{31}^d(r) y_1^\ell(r) + U_{32}^d(r) y_2^\ell(r),
\end{align*}
\]

where

\[ U_{\nu\gamma}^d(r) = \frac{2M}{m_e} V_{\nu\gamma}^d(r) = \frac{2M}{m_e} (H_{\nu\gamma} - E_{\nu}(\infty) + \frac{4}{r}) \],

\[ k_1^2 = \frac{2M}{m_e} (E - E_{1}(\infty)) \],

\[ k_\nu^2 = k_1^2 + \frac{2M}{m_e} (E_{1}(\infty) - E_{\nu}(\infty)) \],

and where \( \nu \) labels the molecular state. \( U_{11}^d, 22, 33(r) \) are the diabatic potentials of the three lowest \( 3\Sigma^+ \) states and \( U_{21}^d, 32, 21(r) \) are the direct coupling matrix elements. The non-adiabatic terms have again been neglected. The final expression for the cross section is given in Eq. (17). The transition cross sections can be interpreted in precisely the same way as those for the metastable-atom problem. The only difference will be the replacement of the excitation transfer processes by charge exchange processes.
II. Potential Energy Curves and Procedure

Matrix elements of the electronic hamiltonian must be calculated before the coupled equations in (63) can be solved. The procedure is the same as discussed above.

One must first construct a wave function that satisfies the following conditions:

\[(S_a + S_b)^2 \psi_{1,2,3} = \frac{3\hbar^2}{4} \psi_{1,2,3}, \quad (64)\]

\[(S_{az} + S_{bz}) \psi_{1,2,3} = \frac{1}{2} \hbar \psi_{1,2,3} \]

where \(a\) and \(b\) label ion and the atom respectively and \(\psi_v = \psi_v(\vec{R}, \vec{r}_i)\). Asymptotically \(\psi_{1,2,3}\) must satisfy

\[S_a^2 \psi_{1,2,3} = \frac{3\hbar^2}{4} \psi_{1,2,3}, \]

\[S_{az} \psi_{1,2,3} = \frac{1}{2} \hbar \psi_{1,2,3}, \]

\[S_b^2 \psi_{1,3} = S_{bz} \psi_{1,3} = 0, \quad (65)\]

\[S_b^2 \psi_2 = 2\hbar^2 \psi_2, \]

\[S_{bz} \psi_2 = \pm \hbar \psi_2 \text{ or } 0. \]

The properly symmeterized wave functions are then written as

\[\psi_1 = |1s_b \overline{1s_b} l_s a| - |1s_b 1s_b 1s_a| + a + b, \]

\[\psi_2 = |1s_b \overline{2s_b} l_s a| + |1s_b 2s_b 1s_a| - 2 |1s_b 2s_b l_s a| + a + b, \]

\[\psi_3 = |1s_b \overline{2s_b} l_s a| - |1s_b 2s_b 1s_a| + a + b. \]
These wave functions and the matrix elements of the electronic hamiltonian were calculated using a program supplied by J. C. Browne. Both linear and non-linear parameters were varied. The resulting diagonal potential matrix element (diabatic curves) plus nuclear repulsion are plotted in Fig. (26). The coupling matrix elements are shown in Fig. (27).

The adiabatic potential curves are also shown in Fig. (26). Comparison of these with a five term calculation carried out by Browne\textsuperscript{46} shows good agreement, particularly in the $V^a_{22,33}(R)$ potential curves.

In order to solve the scattering equations, good diabatic potentials that go to the proper asymptotic limits are necessary. The failure of $V^d_{11,33}(R)$ to separate properly can be seen in Fig. (26). Apparently the valence bond, single configuration, singlet wave functions $\psi_{1,3}$ do not become eigenfunctions of $S_b$ as $R \to \infty$. One concludes then that the valence bond functions are not a good representation of the system in the diabatic basis when the same spin and angular momentum are involved. However, linear combinations of these functions do give good adiabatic wave functions.

The problem mentioned above increased the complexity of the procedure immensely. It was necessary to solve the coupled equations in the diabatic representation and then transform to the adiabatic basis. The transformation was
FIGURE 26: The dashed curves are the diabatic $^{2}L_{1}^{+}(1s^{2}1S)$, $^{2}L_{2}^{+}(1s2s3S)$, and $^{2}L_{3}^{+}(1s2s3P)$ interaction potentials associated with He$^{+}$-He collisions. The solid curves are the corresponding adiabatic potentials obtained by a unitary transformation between representations. The asymptotic behavior of $V_{31}^{2}(R)$ and $V_{33}^{3}(R)$ reflects the failure of the singlet diabatic wave functions to separate properly at large $R$. A crossing occurs between the diabatic $^{2}L_{g}^{+}(1s2s^{3}S)$ and $^{2}L_{g}^{+}(1s2s^{1}S)$ interaction potentials at $R=3.75$ a$_{0}$. 
FIGURE 27: The coupling matrix elements associated with the three lowest \( 2\Sigma^+ \) states of \( \text{He}_2^+ \). The failure of \( V_{31}(R) \) to \( \to \) zero at large \( R \) reflects the behavior of the singlet wave functions which fail to separate properly at large \( R \).
made at $R = 9.5 \ a_0$ and all coupling terms generated by the transformation were neglected. In following this procedure, we assumed that the momentum coupling was small enough at $R = 9.5 \ a_0$ as to have little effect on solutions started at $R \approx 9.5 \ a_0$. The transformation can not be carried out at larger internuclear separations due to the size of $V_{31}$. Large coupling terms cause instabilities in the Numerov solutions and thus errors in the cross sections.

To summarize, the following steps were followed in calculating the cross sections:

1. The wave function was chosen according to conditions (64) and (65);
2. A variational calculation was performed to obtain the matrix elements of the electronic hamiltonian;
3. The solutions to the coupled equations were started according to the criteria discussed in Problem I;
4. The solutions were developed numerically in the diabatic basis to $R = 9.5 \ a_0$;
5. A transformation to the adiabatic basis was performed such that
   \[ \mathbf{y}' = \mathbf{C} \mathbf{y} \mathbf{C}^{-1}, \]
   and
   \[ \mathbf{\dot{y}}' = \mathbf{C}^{-1} \mathbf{\dot{y}}. \]
Momentum coupling was neglected;
6. The solutions were developed in the adiabatic basis out to large $R$;
Boundary matching was performed at large $R$ in order to determine the scattering matrix $\hat{S}$. The cross sections were then obtained from $\hat{S}$ according to eq. (17).
Part II: Results and Conclusions
I. Elastic Cross Sections

Elastic close coupling partial wave cross sections for scattering in the $^2_e^- (1s^2 1S)$, $^2_e^+ (1s2s^3 S)$, and $^2_e^+ (1s2s^1 S)$ molecular states are given respectively in Fig. (28a, b, c) for $E = 75$ eV. The range of partial waves obtained is limited at small $R$ ($R<2.5$ a$_0$) by the size of the $V_{32}(R)$ coupling matrix element and at large $R$ ($R>9.5$ a$_0$) by the size of $V_{31}(R)$. Solutions started in the region of large coupling tend to become singular due to numerical round off error. This problem is discussed in more detail by Cohen.$^7$

Purely adiabatic cross sections (no coupling) are also plotted in Fig. (28). This comparison is particularly interesting because a whole range of effects is observed. In the following discussion, the procedure will be, first to study the potential matrix elements and then try to predict properties of the elastic $Q^e$.

$Q_{11}^e$ should exhibit a slow oscillatory behavior with possible distortion since $V_{11}(R)$ is attractive and has a change in sign of its slope. Because scattering in this channel is most strongly affected by $V_{31}(R)$, agreement with the purely adiabatic cross sections will depend on its strength. Looking now at Fig. (28a), one can see that indeed the oscillations are slow and distorted and that the greatest disagreement between the close coupling and the adiabatic results occurs in a region of partial waves which
FIGURE 28: Comparison of elastic, close coupling and adiabatic partial wave cross sections for $E=75$ eV. The partial wave associated with the crossing of the potential curves ($\ell=450$) is indicated by the arrow.
can be associated with the turning points between \( R = 3.5 \, a_o \) and \( 7 \, a_o \). This is just the region in which \( V_{31}(R) \) is smallest. This result follows if one remembers that whenever potential coupling becomes small, momentum coupling can become large (see Eq. 53). The momentum coupling was neglected entirely in calculating the adiabatic cross sections.

The potential that describes scattering in the \( ^2 \ell^+_g \) (1s2s\(^3\)S) channel is repulsive for \( R < 7 \, a_o \) and attractive for \( R > 7 \, a_o \). Thus, \( Q^\ell_{22} \) should reflect the characteristics associated with both types of potentials. In addition, elastic scattering processes should be most strongly affected by the \( V_{32}(R) \) and \( V_{21}(R) \) matrix elements. A study of the actual cross sections in Fig. (28b) shows the oscillations to be regular with an intermediate frequency for \( \ell < 675 \) (\( R \geq 6.6 \, a_o \)). For \( \ell > 675 \, a_o \) distortion appears. Also, the agreement between the close coupling and the purely adiabatic cross sections disappears slowly with increasing \( \ell \), due to the decrease in the magnitude of \( V_{32}(R) \) and \( V_{21}(R) \) with \( R \). Similar predictions could be made about the \( Q^\ell_{33} \) based on a knowledge of \( V_{33}(R) \), \( V_{31}(R) \), and \( V_{32}(R) \).

Several conclusions can be drawn from the discussion above. First of all, the comparison of the close coupling and the adiabatic results indicate that the system is not adiabatic, particularly for the higher partial waves. The behavior of the close coupling \( Q^\ell \) shows that a totally
diabatic (no coupling) representation is not a good description of the system either. Secondly, the importance of the momentum coupling over a wide range of $\ell$'s in all three elastic cross sections would make the Landau-Zener approximation totally inadequate for the calculation of transition cross sections. Finally, the failure of the close coupling and the adiabatic results to converge at large $R$ requires that the transformation point be moved to larger $R$ if $Q^\ell$ associated with $\ell \leq 1150$ is desired.
II. Inelastic Cross Sections

The cross section for transitions between the $^2\!\!_g(1s2s^1S)$ and $^2\!\!_g(1s2s^3S)$ molecular states of the ion-metastable system has been calculated. $Q_{23}^\ell$ is plotted in Fig. (29). $Q_{31}^\ell$ and $Q_{21}^\ell$ were also found but are only qualitative due to their sensitivity to the transformation point. Both are very small since no crossings are involved and since the molecular states are widely separated.

III. Comparison to He-He* System

A number of the conclusions about the results in Problem I were obtained by relating potential characteristics to partial wave cross sections. The study of the He-He* system was initiated because the potential matrix elements that describe both elastic and inelastic scattering are characteristically different from those in the He-He* problem. In Section I and II of the results, we have used the guidelines for predicting cross section properties that were formulated in Problem I. This was done to show the validity of these guidelines over a wide range of problems. In the paragraphs that follow, specific comparisons between the two systems will be made.

It has been shown in the metastable-atom problem that
FIGURE 29: Inelastic partial wave cross section for $^2\Pi^+_g(1s2s^1S-1s2s^3S)$ transitions in helium ion-metastable collisions for $E=75$ eV. $\ell\approx450$ is the partial wave associated with the crossing of the potential curves.
scattering in both the \(3^+_g(1s2s^3S)\) and the \(3^+_g(1s2p^3P)\) channels can be described adiabatically. In the ion-metastable collision, the adiabatic representation was found to be inadequate, particularly at larger \(L\) for the \(2^+_g(1s2s^3S)\) and the \(2^+_g(1s2s^1S)\) molecular states. This difference can be explained if one compares the crossing curves of each system.

Diagram 4

The separation and slope of the curves in (b) allow transitions to occur over a large region of \(R\). In (a) these same properties cause most transitions to occur in the region of the crossing where the size of \(V_{21}(R)\) (Fig. 5) allows one to neglect momentum coupling in an adiabatic transformation. This approximation is not valid for \(R \approx 3.7 a_0\) in case (b), due to a decrease in the magnitude of \(|V_{21}(R)| + |V_{32}(R)|\) (Fig. 27).

A study of Fig. (18) - (20), (29) demonstrates a
significant difference in the behavior of the inelastic cross sections associated with the two systems. In the same way that the $Q_{21}^\ell$ of the metastable-atom system reflected the irregularity of the potentials, the oscillations of $Q_{23}^\ell$ in Fig. (20) reflect the smooth regular behavior of the $^2I_g^+(1s2s^1s_3^1S)$ potentials in Fig. (26). One would expect structure in $Q_{23}^\ell$ inside the crossing. Since the two potentials have a similar repulsive behavior, both inelastic scattering paths will be important. Thus, the preliminary results of Fig. (29) support this deduction but further investigation will be necessary before a firm conclusion can be made.

A Landau-Zener contour plot similar to the one in Fig. (23) is given in Fig. (30). In the calculation of the maximum $Q_{21}^\ell(E, V_{21}')$ for the plot in Fig. (30), the only significant difference from the metastable-atom problem is the value of $|V_{22}' - V_{11}'|$. Thus, Fig. (30) and Fig. (24) show how the variation of the transition cross section with energy and strength of coupling reflects the behavior of the potential curves at the crossing.
FIGURE 30: Landau-Zener contour plot. The maxima $Q_{23}^k$ are given as a function of energy and the strength of the coupling matrix element where $V_{23}(R) = (\text{FRAC})(V_{23}(R))$. All $Q_{23}^k$ are normalized to nine. For the sake of clarity, only odd values of $Q_{23}^k$ are plotted. The even values of $Q_{23}^k$ correspond to the white un-numbered areas.
Appendix A

The non-adiabatic terms in $\mathbf{q}$. (5) can be important under certain conditions. Written in matrix form $\mathbf{q}$. (5) appears as

$$(H_{\text{nu}} - E\mathbf{I}) \hat{\mathbf{p}}(\mathbf{R}) = (-\mathbf{U} + \mathbf{A} \cdot \mathbf{v} + \mathbf{B}) \hat{\mathbf{p}}(\mathbf{R})$$

Smith has expressed this equation in a particularly simple form

$$(\mathbf{T} + \mathbf{U} - \mathbf{E}) \hat{\mathbf{p}}(\mathbf{R}) = 0,$$  \hspace{1cm} (66)

where

$$\mathbf{T} = \frac{\mathbf{1}}{\mathbf{2}} \mathbf{H}_{\text{nu}} + (2M)^{-\mathbf{1}} \mathbf{p} \cdot \mathbf{p} + \mathbf{p}_{\text{nu}} \cdot \mathbf{p} + M^{-\mathbf{1}} \mathbf{p} \cdot \mathbf{p}_{\text{nu}},$$

and

$$\mathbf{A} = M^{-\mathbf{1}} \mathbf{p}, \mathbf{B} = \mathbf{p} \cdot \mathbf{p} + \mathbf{p}_{\text{nu}} \cdot \mathbf{p}.$$  

Since the electronic wave functions were calculated in a molecular representation, it is necessary to transform from a system where $\mathbf{v}$ is taken with $\mathbf{r}_i$ fixed in an XYZ system to a system where $\mathbf{v}$ is taken with $\mathbf{r}_i$ fixed in a system rotating with $\mathbf{R}$. The spherical polar components of the necessary gradient and divergent terms in the molecular representation as derived by Smith are given as
\[
\begin{align*}
\mathbf{p}_{\text{grad}}_R &= \frac{\hbar}{i} \frac{\partial}{\partial R} \\
\mathbf{p}_{\text{grad}}_\theta &= \frac{\hbar}{iR} \frac{\partial}{\partial \theta} = \frac{L_Y}{R} \\
\mathbf{p}_{\text{grad}}_\phi &= \frac{\hbar}{iR \sin \theta} \frac{\partial}{\partial \phi} = \frac{L_x + \cot \theta L_z}{R} \\
\mathbf{p}_{\text{div}}_R &= \frac{\hbar}{i} \left[ \frac{2}{R} + \frac{3}{\partial R} \right] \\
\mathbf{p}_{\text{div}}_\theta &= \frac{\hbar}{i} \left[ \cot \theta + \frac{3}{\partial \theta} \right] \\
\mathbf{p}_{\text{div}}_\phi &= \frac{\hbar}{iR \sin \theta} \frac{\partial}{\partial \phi}
\end{align*}
\]

Substitution of these into eq. (66) gives

\[
\tau = \hbar n u + (2M)^{-1} S_R + (2MR^2)^{-1} S_\Omega,
\]

\[
S_R = p_{2x}^2(R) + \frac{\hbar}{i} \left[ \frac{2}{R} p_{R}^x(R) + \frac{3p_{R}^y(R)}{\partial R} + 2p_{R}^x(R) \frac{\partial}{\partial R} \right],
\]

\[
S_\Omega = \frac{L_x^2(R)}{R^2} + \frac{L_y^2(R)}{R^2} + \frac{L_z^2(R)}{R^2} \cot \theta - \frac{2\hbar}{i} \frac{\cos \theta}{\sin^2 \theta} \frac{L_z(R)}{\partial \phi} - \frac{\partial}{\partial \phi}
\]

\[
X = \cot \theta [L_x(R)L_z(R) + L_z(R)L_x(R) - i\hbar L_y(R)]
\]

\[
- \frac{2\hbar L_x(R)}{i \sin \theta} \frac{\partial}{\partial \phi} + \frac{2\hbar L_y(R)}{i} \frac{\partial}{\partial \theta},
\]

where \( S_R \) represents all radial coupling and \( S_\Omega \) represents all angular coupling. \( S_R \) and \( S_\Omega \) are the terms neglected in this calculation.

The \( S_R \) terms can only be important if the electronic wave functions vary rapidly with \( R \). For low energies the velocity is slow enough to allow time for the rearrangement of the orbital electrons. The only parameters allowed to
vary as a function of $R$ in the calculation of the electronic wave functions are the non-linear $\alpha$'s in the Slater orbitals. For the He-He* problem, they vary slowly as a function of internuclear separation. In the He-He* problem, the non-linear $\alpha$'s vary slowly for $2.25 \ a_0 \leq R \leq 10.0 \ a_0$. This covers the region of internuclear separations important in the calculations reported.

$S_n$ consist of diagonal terms which contribute nothing to the coupling and terms which can be combined to form step up and step down operators giving rise to coupling between $\Lambda$ and $\Lambda \pm 1$. ($\Lambda$ represents the projection of the orbital angular momentum along the internuclear axis.) A thorough examination of the importance of this coupling could be the topic of another Ph.D. thesis. Smith considers a special case in which he ignores the out-of-plane momentum term $\frac{3}{2} \phi$ (sets $\phi = 0$). Since the diagonal terms do not contribute, it is necessary to consider only

$$X_S = \cot \theta (L_x(R)L_z(R) + L_z(R)L_x(R) - i\hbar L_y(R)),$$

$$X_d = 2L_y(R)J_y,$$

where $i\hbar \partial / \partial \phi$ is identified with the nuclear angular momentum $J_y = mv_\phi b$ ($b =$ impact parameter). Smith dismisses the static terms $X_S$ as being of no special interest since they behave much like potential coupling. He goes on to say that $X_d$ may be the dominant coupling term for higher velocities.
Mulliken\textsuperscript{10} and Watson\textsuperscript{51} indicate that there is, in fact, a $^3\pi_g$ that crosses the lower $^3\Sigma_g$ at small $R$ for collisions of the helium metastable with the ground state. This crossing then allows angular coupling if the initial kinetic energy is large enough. Since all calculations are done at relatively low energy, angular coupling is neglected. More discussion of this type of coupling is given by Hirschfelder et al.\textsuperscript{52, 53}
Appendix B

I. Orthonormalization Procedure

The problem is to find a transformation matrix $\mathbf{M}$ such that

$$\hat{\psi} = \mathbf{M} \hat{\chi},$$

(67)

and

$$\int \psi_i^* \psi_j d\mathbf{r}^+ = \delta_{ij}.$$

(68)

For a two term wave function

$$\psi_1 = a_1 \chi_1,$$

$$\psi_2 = a_2 (\chi_1 - a \chi_2),$$

where one of the elements of $\mathbf{M}$ has been arbitrarily set to zero. Imposing condition (68) we are left with three equations and three unknowns.

Solving for the three unknowns results in

$$a_1 = \frac{1}{\Lambda_{11}},$$

$$a = \Lambda_{11}/\Lambda_{12},$$

$$a_2 = \frac{1}{\left[ \frac{\Lambda_{11} \Lambda_{22}}{\Lambda_{12}} - \Lambda_{11} \right]^{1/2}},$$

where

$$\Lambda_{ij} = \int \chi_i \chi_j d\mathbf{r}^+.$$

The potential coupling matrix becomes
\[ H_{11} = a_1^2 h_{11}, \]
\[ H_{12} = a_1 a_2 (h_{11} - h_{12}), \]
\[ H_{22} = a_2^2 (h_{11} + 2h_{22} - 2h_{12}), \]

where
\[ h_{ij} = \int \overline{\chi_i} H\chi_j d\vec{r}. \]

For a three state problem, the procedure is exactly analogous.

II. Analytic Form of a Slater Orbital

For the benefit of the reader, the form of the Slater-type orbitals is given below. The description is a direct quote from Scott et al. 8

"The two nuclei for the di-atom system are labeled A and B. Localized cartesian coordinates are set up on each nucleus so that the \( z \) direction lies along the internuclear axis. The coordinate frames are parallel, with the positive \( z \) axis pointing in the same direction on each nucleus. Slater-type orbitals are then defined on each nucleus in spherical polar coordinates referred to the cartesian frames:

\[ t_a (j) = K^{N_t -1}_{t\alpha_j} \exp(-\alpha t \overline{r}_{\alpha_j}) \overline{Y}_t(\theta_{\alpha_j}, \phi_j), \]
\[ t_b (j) = K^{N_t -1}_{t\beta_j} \exp(-\alpha t \overline{r}_{\beta_j}) \overline{Y}_t(\theta_{\beta_j}, \phi_j), \]
where \( j \) indexes the set of coordinates of electron \( j \); \( a \) or \( b \) indicates the origin of the \( j \) coordinate set is on nucleus A or B; \( r_{aj} \) and \( r_{bj} \) are distances of electron \( j \) from nucleus A and B respectively; \( N_t \), \( L_t \) and \( M_t \) are the principal, azimuthal, and magnetic quantum numbers for orbital \( t \); \( a_t \) is the orbital exponent for orbital \( t \) (this is the non-linear parameter varied by Browne\(^3\)); \( K_t^T \) is the normalization constant for the radial coordinate of orbital \( t \), it is defined as

\[
K_t^T = \left[ \frac{(2a_t)^{2N_t+1}}{(2N_t)!} \right]^\frac{1}{2}
\]

\( Y_{L_t}^{M_t}(\theta_{ai}, \phi_i) \) and \( Y_{L_t}^{M_t}(\theta_{bi}, \phi_j) \) are normalized spherical harmonics. The convention used regarding signs of these functions is that those with negative, odd \( M_t \) are negative."\(^8\)

III. Analytic Form of the Potentials (He*-He)

\( V_{11} \) (atomic units)

\[
V_{11} = 5.0 \cdot \exp(-1.012209 \cdot R) / R \quad 0 < R \leq 2.5
\]

\[
V_{11} = 2.2 \cdot \exp(-1.050848 \cdot R) \quad 2.5 < R \leq 3.5
\]

\[
V_{11} = .328 \cdot \exp(-.53961 \cdot R) \quad 3.5 < R \leq 6.0
\]

\[
V_{11} = 4.0 \cdot \exp(-.957434 \cdot R) \quad 6.0 < R
\]

\( V_{22} \) (atomic units)

\[
V_{22} = 4.0 \cdot \exp(-1.858449 \cdot R) / R \quad 0 < R \leq 1.5
\]
\[ V_{22} = 0.04 + 0.04259 \exp(-2.0 \cdot (R - 2.2) \cdot 1.73) \\
- 2.0 \cdot \exp[-(R - 2.2) \cdot 1.73]) \]
\[ 1.5 < R \leq 2.5 \]
\[ V_{22} = 0.0466956 \cdot R - 0.112359 \]
\[ 2.5 < R \leq 3.5 \]
\[ V_{22} = 0.0516 \cdot \exp(-(R - 3.65)^2 / 2.202612) \]
\[ 3.5 < R \leq 4.5 \]
\[ V_{22} = 0.9 \cdot \exp(-0.708198 \cdot R) \]
\[ 4.5 < R \leq 6.0 \]
\[ V_{22} = 4.0 \cdot \exp(-0.957434 \cdot R) \]
\[ 6.6 < R \]

\[ V_{12} \] (atomic units)
\[ V_{12} = 0.466 \cdot \exp(-0.6544104 \cdot R) \]
\[ 0 < R \leq 3.0 \]
\[ V_{12} = 0.465 \cdot \exp(-0.65383 \cdot R) \]
\[ 3.0 < R \leq 5.5 \]
\[ V_{12} = 23.0 \cdot \exp(-1.362979 \cdot R) \]
\[ 5.5 < R \]
Appendix C

I. Program

The calculations presented in this thesis were carried out on the Burroughs 5500 at Rice and the CDC 6600 at the University of Texas at Austin. The limitations discussed below are those of the 6600. The program used is a modified version of one used by Lane and Geltmann in an electron-molecule scattering problem. All subroutines pertaining to angular coupling were deleted and the rest of the program was modified to suit the boundary conditions arising in atom-atom collisions.

The program may be separated into three parts: part (1) reads the data, calculates the potentials (or reads them off tape), finds suitable starting points for the solutions according to the boundary condition and the non-singular requirement; part (2) uses the Numerov algorithm to develop the solutions out to boundary matching points; part (3) matches boundary conditions, calculates and prints out R, S, T, and the cross sections.

II. Reference Data

A. Step size criteria - the solutions to coupled equations oscillate at large R with a wave length
approximately equal to $2\pi/K$. For any finite difference method the step size must be small enough such that the solutions are well defined over one oscillation. The criteria used in this calculation are the following:

(1) coupled channels - 15 steps per $\lambda$
(2) single channel - 20 steps per $\lambda$

B. Reference tables - the following tables contain information used in data analysis and for the reader who desires to make a similar calculation.

### Elastic $\text{He}(1s^2) + \text{He}(1s2s)$

<table>
<thead>
<tr>
<th>$\ell_{\text{end}}$</th>
<th>$R_0$</th>
<th>$\ell_{\text{max}}$</th>
<th>$R_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 eV</td>
<td>490</td>
<td>9.50</td>
<td>350</td>
</tr>
<tr>
<td>20 eV</td>
<td>725</td>
<td>9.93</td>
<td>465</td>
</tr>
<tr>
<td>50 eV</td>
<td>1050</td>
<td>9.07</td>
<td>670</td>
</tr>
<tr>
<td>100 eV</td>
<td>1400</td>
<td>8.57</td>
<td>840</td>
</tr>
</tbody>
</table>

### Inelastic $\text{He}(1s2s^3S \rightarrow 1s2p_o^3)$

<table>
<thead>
<tr>
<th>$\ell_{\text{end}}$</th>
<th>$R_0$</th>
<th>$\ell_{\text{max}}$</th>
<th>$R_0$</th>
<th>$\ell_{\text{cross}}$</th>
<th>$R_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 eV</td>
<td>264</td>
<td>5.15</td>
<td>142</td>
<td>3.18</td>
<td>146</td>
</tr>
<tr>
<td>20 eV</td>
<td>385</td>
<td>5.35</td>
<td>202</td>
<td>2.78</td>
<td>220</td>
</tr>
<tr>
<td>50 eV</td>
<td>630</td>
<td>5.48</td>
<td>276</td>
<td>1.93</td>
<td>360</td>
</tr>
<tr>
<td>100 eV</td>
<td>1150</td>
<td>5.05</td>
<td>460</td>
<td>2.84</td>
<td>510</td>
</tr>
</tbody>
</table>
Table 1: $\lambda_{\text{end}}$ is the largest $\lambda$ contribution to the cross section, $\lambda_{\text{max}}$ is $\lambda$ at the largest $Q_{21}^2$, $\lambda_{\text{cross}}$ is $\lambda$ for which the classical turning point corresponds to the crossing point of the curves, $R_0$ is the classical turning point associated with $\lambda$.

III. Data Storage

The step size required in solving the coupled equations by the Numerov method is determined by the criteria set above. At 100 eV this requires knowledge of the potential at 6400 points if the integration is carried out to $R = 16$. The potential can be inputted in three ways: (1) calculated at every point, (2) calculated and stored in core in an array, (3) stored on tape and read at each point. The second method is by far the fastest if sufficient core is available. If the arrays are too big to be stored efficiently in core, one must resort to a fast input-output scheme using tape or disk. Method (1) is too slow under any circumstance.
Acknowledgments

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Bibliography


11. For $R>6.0$ the experimentally determined $^{3}I_{0}^{+}$ potentials of W. A. Fitzsimmons, N. F. Lane, and G. K. Walters, Phys. Rev. 174, 193 (1968) were used.


50. T. A. Koopmans, Physica 1, 104 (1933).

51. M. Watson at the University of Texas (private communication).