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Two Models Involving Excited States of Helium: Cavities in Liquid Helium, and Collisions of He(2^3s) with H_2

by

Albert Peet Hickman

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

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Abstract

Two Models Involving Excited States of Helium:
Cavities in Liquid Helium, and Collisions of He(2^3S) with H2

by Albert Peet Hickman

Two theoretical studies involving excited states of helium have been carried out. In Part I a model is developed in which excited helium atoms in liquid helium may exist in stable cavities of diameter 10 - 15 Å. A repulsive interaction between the excited atom and the remaining atoms in the ground state is responsible for cavity formation. The equilibrium shape of the cavity is determined by minimizing the total energy, which is the sum of the electronic perturbation due to the surrounding fluid, and the energy required to form the cavity. Each of these can be evaluated separately as a function of the cavity size. The energy required to form a cavity of radius R is approximated by the classical expressions for work done against the surface tension γ of liquid helium (4πR^2γ), and against the external pressure p on the liquid (4πR^3p). For a particular cavity size, the fluid may be considered a perturbing potential, and the response of the electronic wave function explicitly determined using variational theory. Previous models have used only first order perturbation theory.

The calculations indicate that the optical spectra of helium atoms in these cavities are only slightly perturbed, and agreement with observed spectra lends strong support to the cavity picture. We have obtained agreement with the observed emission transitions 2^3P+2^3S and 3^1S+2^1P, and also with the absorption 2^3S+2^3P, at saturated vapor pressure. Recently the change in these spectral lines as the external pressure is increased to 25 atm. has been measured. The model is in good agreement with the data for all lines in which the initial state is spherically symmetric.
The question of excitation transfer in the liquid is considered. A semiempirical determination of the long range $^{2}\text{E}_{g}$ and $^{2}\text{E}_{u}$ interaction potentials of He₂ is used to calculate cross sections for excitation transfer in $^{3}\text{He}(2^{3}\text{S}) - ^{3}\text{He}(1^{1}\text{S}_{0})$ collisions. The results indicate that such a mechanism would not inhibit the formation of stable cavities in the liquid.

Part II contains a close-coupling calculation of cross sections for elastic scattering, rotational excitation, and Penning ionization of H₂ by He($2^{3}\text{S}$). The real potential surface used was calculated by Cohen. The probability that the He($2^{3}\text{S}$) may ionize the H₂ is included by adding to the real potential energy an imaginary part defining the width. The extension of the close-coupling formalism to include a complex potential is developed, and the efficient solution of the coupled equations is discussed.

We find that at energies $E \leq 0.25$ eV, the cross sections for Penning ionization or rotational excitation are small (0 - 10 Å) relative to the elastic cross sections (160 - 190 Å²). A semiclassical picture of the collision process is developed, in which the width and the nonspherical parts of the potential are treated as perturbations. Even though the total cross sections are dominated by elastic collisions, rotational excitation and Penning ionization occur with high probability for certain trajectories. A modest semiempirical modification of the asymptotic form of Cohen's width is necessary to achieve agreement with existing data.
Acknowledgments

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Part I

The Nature of Excited Helium Atoms
in Liquid Helium: A Theoretical Model

A. Introduction

Previous theoretical\textsuperscript{1} and experimental studies\textsuperscript{2-7} have provided convincing evidence for the existence of microscopic cavities ("bubbles") surrounding certain atomic and molecular species in liquid helium. To summarize briefly: Dennis \textit{et al.}\textsuperscript{2} and Hill \textit{et al.}\textsuperscript{3} have reported spectroscopic data which they attribute to the presence of slightly perturbed excited states of He and He\textsubscript{2} in liquid helium. They interpret certain of these species as the energetic neutrals seen by Surko and Reif\textsuperscript{4}. Their data are not consistent with any model assuming an unperturbed distribution of helium atoms in the liquid, because such a distribution would greatly perturb and wave functions of the excited species, and hence result in energy shifts much larger than those observed. Also, the presence of vibrational and rotational fine structure in the observed molecular spectra gives further support to the idea that an excited atom or molecule can exist inside a small cavity, and be only slightly perturbed by the surrounding fluid. The present authors have shown\textsuperscript{1} that a local redistribution of helium atoms is energetically preferred, because of the strongly repulsive interaction between the electron in an excited orbital and the surrounding helium atoms. Thus, the cavity formation mechanism is the same as that involved in the theoretical description of "electron bubbles" in liquid helium\textsuperscript{8}. In the case of an excited atom,
however, the electron is strongly bound to the nucleus, and the resulting cavity is much smaller.

Only atomic helium excited states have been examined theoretically. In the initial investigation\(^1\), the states of \(2^3S\), \(2^1P\), and \(3^1S\) were represented by unperturbed wavefunctions, and the effect of the liquid environment determined by first order perturbation theory. The energies of the optical transitions between pairs of these states were taken to be shifted from the dilute gas values by amounts equal to the difference in the perturbed initial and final state energies. Reasonable agreement with experiment was obtained for the \(2^3S\leftrightarrow2^3P\) transitions, and rough agreement for the transitions \(3^1S\leftrightarrow2^1P\). Here we will present a more detailed theory of an excited atom in liquid helium. It will be shown that proper allowance for the change in the atomic wavefunction due to the liquid environment leads to improved energy shifts for the \(3^1S\leftrightarrow2^1P\) transitions.

B. Theoretical Model

Central to the model here presented is the idea that a single excited atom can exist in a microscopic cavity in liquid helium. The existence of cavities surrounding electrons in liquid helium is well established experimentally, and at least made plausible on theoretical grounds\(^8,9\). In this framework, we begin by listing our basic assumptions, and the contributions to the total energy which must be taken into account.

1) The distribution of normal helium atoms around the excited atom should be described in an average way by a density function which is zero at the center of the cavity (i.e., \(R = 0\)), and asymptotically (as \(R \to \infty\)) approaches the bulk fluid density. In our model\(^1\),
the liquid density is represented by a "trial" function of the form

\[ \rho(R; R_0, \alpha) = \begin{cases} O \quad & R \leq R_0. \\ \rho_0 \left\{ 1 - \left[ 1 + \alpha (R - R_0) \right] \right. & \left. e^{-\alpha (R - R_0)} \right\} \quad & R \geq R_0. \end{cases} \] (1)

The choice of notation emphasize that \( R_0 \) and \( \alpha \) are variational parameters to be determined by overall energy minimization. For brevity we shall generally write only \( \rho(R) \), it being understood that this represents an entire family of functions. It is useful to associate an effective cavity (or "bubble") radius \( R_b \) with each particular choice of the parameters \( R_0 \) and \( \alpha \) in \( \rho(R) \). The radius \( R_b \) is defined as the "center of mass" of the region of transition from zero density to the normal bulk density \( \rho_0 \). It is approximately given by \( R_b = R_0 + 2/\alpha \).

2) In determining the total energy of the excited atom in the liquid, the energy required to redistribute the fluid atoms and form the cavity (i.e., the cavity energy) must be included. We adopt the same model here as that used by Hiroike et al.\(^9\), \textit{viz.}, the classical expressions for the surface tension energy and pressure-volume work involved in creating a bubble of radius \( R_b \), plus a term representing the kinetic energy due to the density gradient at the edge of the cavity. Thus, we write

\[ E_{\text{cavity}} = 4 \pi R_b^2 \delta + \frac{4}{3} \pi R_b^3 \rho + \frac{1}{8 M} \int \left( \frac{\nabla \rho}{\rho} \right)^2 d^3R \] (2)
where \( \gamma \) is the surface tension of the liquid, and \( p \) is the external pressure on the liquid.

3) The excited atom is described by a single-atom wavefunction. In the most general case we shall allow this wavefunction to respond to changes in the radial distribution function.

4) We will assume that the interaction of the excited atom with each ground state atom is additive. This interaction is represented by a short-range repulsion (via an electron-helium pseudo-potential\(^9,11\)) between the excited electron and the ground state atoms, and the long-range dispersion force. This last interaction arises through an induced dipole-dipole potential \( V_d \), and is an approximate way of including long range correlation effects. It can be expressed as a function of the electrons' coordinates in the excited atom and the relative position \( R_j \) of the \( j \)th ground state atom, namely \( V_d(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}_j) \).

We therefore write the following approximate Hamiltonian for a system of \( N \) ground state helium atoms and one (distinguishable) excited atom:

(atomic units will be used throughout):

\[
H = \left[ -\frac{1}{2M} \sum_{j=1}^{N} \nabla_j^2 + \sum_{j<k} V(R_{jk}) \right] + \left[ -\frac{1}{2} \left( \nabla_{e_1}^2 + \nabla_{e_2}^2 \right) - \frac{2}{\mathbf{r}_1} - \frac{2}{\mathbf{r}_2} + \frac{1}{\mathbf{R}_j} \right]
+ \left[ \sum_{e=1}^{2} \sum_{j=1}^{N} V_{ps}(\mathbf{r}_e - \mathbf{R}_j) + \sum_{j=1}^{N} V_{d}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}_j) \right]
\]

(3)

The grouping of the terms in brackets follows by the natural identification of the three parts of the Hamiltonian. The first term is the Hamiltonian of \( N \) normal helium atoms (with coordinate operators \( \mathbf{R} \) and \( R_{jk} = - \frac{1}{2M} \sum_{j=1}^{N} \nabla_j^2 + \sum_{j<k} V(R_{jk}) \), the second term includes the excitation potential \( V_{ps} \), and the third term is the dipole-dipole interaction potential \( V_d \).
\[ |\vec{R}_j - \vec{R}_k|, \text{ and } M \text{ equal to the atomic mass in a.u.}. \] The second term is the two-electron Hamiltonian of the excited atom, whose nucleus is considered fixed at the origin. The final term, the interaction Hamiltonian, consists of the short-range repulsive pseudopotential \( V_{ps} \) between each electron and each fluid atom, and the dispersion energy \( V_d \) between the excited atom and each atom in the bulk liquid. Our calculations have shown\(^1\) that in the two atom case \( (N = 1) \), the sum of these last two terms adequately represents the adiabatic interaction potential for \( \text{He}(^2S) - \text{He}(^1S) \), for interatomic separations greater than about 8 \( a_0 \). Equation \( (3) \) should include a term for the interaction of the \( \text{He}^{++} \) nucleus with the atoms in the bulk liquid. For the cavity radii of interest, the short range contribution of such a term is not important. However, we will consider it to some extent later on. The long range contribution is included, phenomenologically, in the dispersion energy. The \( \text{He}^{++} \) nucleus is taken as fixed.

Following the procedure of Hiroike et al.,\(^9\), we adopt as a trial wavefunction the product of a single excited-atom wavefunction, and a liquid helium wavefunction, viz.,

\[
\Psi = \psi(\vec{r}_1, \ldots, \vec{r}_N) \psi(\vec{r}_n, \vec{r}_s) = \exp \left[ \frac{1}{2} \sum_{j \leq k} f(R_{jk}) + \sum_{j \neq i} g(R_{ij}) \right] \phi(\vec{r}_n, \vec{r}_s) \tag{4}
\]

where the radial coordinate \( \vec{R}_j \) is measured from the center of the cavity. We should then seek to minimize the expectation value of the total energy corresponding to this trial wavefunction,

\[
\langle E \rangle = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \tag{5}
\]
This would of course be exceedingly complicated. Thus, we have found it most convenient to follow the approximate treatment of Hiroike et al.⁹, where \( \langle E \rangle \) is expressed as a functional of \( \rho (R) \), the average single particle distribution function. Substitution of Equation (4) into (5) results in an expression for the approximate energy of the system

\[
\langle E \rangle = E_{\text{cavity}} + E_{\text{atom}}'
\]

where \( E_{\text{cavity}} \) is given approximately by Equation (2). The terms we designate by \( E'_{\text{atom}} \) involve the electronic wavefunction of the excited atom, and may be written

\[
E'_{\text{atom}} = \langle \psi | -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} + V_{ps} (\rho ; \bar{r}_1) + V_{ps} (\rho ; \bar{r}_2) + V_d (\rho ; \bar{r}_1, \bar{r}_2) | \psi \rangle
\]

In this derivation we have made use of the general result⁹

\[
\rho (\bar{R}) = \frac{\int |\psi (\bar{R}, \bar{R}_2, ..., \bar{R}_n) |^2 d^3 R_2 ... d^3 R_n}{\int |\psi (\bar{R}_1, \bar{R}_2, ..., \bar{R}_n) |^2 d^3 R_1 ... d^3 R_n}
\]

and have defined the functionals

\[
V_{ps} (\rho ; \bar{r}) = \int d^3 R \rho (R) V_{ps} (| \bar{r} - \bar{R} |)
\]

and

\[
V_d (\rho ; \bar{r}_1, \bar{r}_2) = \int d^3 R \rho (\bar{R}) V_d (\bar{r}_1, \bar{r}_2)
\]

The functional \( V_{ps} (\rho ; \bar{r}) \) is simply the total interaction potential energy of an electron at position \( \bar{r} \) with the rest of the liquid helium, distributed
according to \( \rho(R) \). We may interpret \( \langle \phi | V_a(\rho; \vec{r}_{12}) | \phi \rangle \) as the sum of the van der Waals interactions between the excited atom and the helium atoms in the liquid.

In the preceding formulation the interaction of the excited atom with the liquid has been approximated by a simple perturbing potential. For a particular \( \rho(R) \) we will assume that the excited atom is described by the Hamiltonian

\[
H_{atom}^{'} = -\frac{1}{2} \left( \frac{\nabla_1^2}{r_1^2} + \frac{\nabla_2^2}{r_2^2} \right) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} + V_{Ps} (\rho; \vec{r}_i) + V_{Ps} (\rho; \vec{r}_j) + V_d (\rho; \vec{r}_i, \vec{r}_j)
\]

(11)

For a given choice the density \( \rho \), the optimized trial function and atomic energy \( E_{atom}' \) are approximations to the eigenfunctions and eigenvalues of this perturbed Hamiltonian. Provided that the perturbations are small, these will be expected to differ only slightly from the wavefunctions and eigenenergies of the unperturbed atom. Thus, we have essentially decoupled the liquid energy from the excited-atom energy, since each can be evaluated separately as a functional of \( \rho(R) \). By suitable variation of \( \rho(R) \), we shall be able to find the equilibrium (minimum \( \langle E \rangle \)) configuration of liquid helium in the vicinity of the excited atom. The considerable simplification embodied in Equations (6) - (11) results, in part, from an adiabatic approximation equivalent to the Born-Oppenheimer approximation. It is assumed that the nuclei of all the atoms may be frozen while calculating the electronic energy. In addition, of course, the more severe approximation of replacing the liquid energy change by the cavity energy of equation (2) is also made.
C. Procedure

1. Absorption and Emission Transitions between the \(2^3\)S and \(2^3\)P States

In this section we discuss more fully the techniques used to find \(E_{\text{atom}}^{\dagger}\) and \(E_{\text{cavity}}\) for the case of \(2^3\)S and \(2^3\)P excited helium atoms immersed in the liquid. These calculations are discussed separately because the electronic problem, involving \(H_{\text{atom}}^{\dagger}\) (Equation (12)), has been found to be adequately treated by first order perturbation theory. Such is not the case for higher energy states.

The most interesting single feature of the experimental data in this case is the observation that the absorption and emission lines are shifted by different amounts as compared to the dilute gas values\(^{3,6}\). This is easily understood in terms of the model. We assume that the equilibrium cavity shape depends on the initial state, and that this average shape does not change in the short time required for an electronic transition to occur. Hence, the perturbation of the final state must be determined using the equilibrium \(\rho(R)\) found for the initial state. Since the initial cavity shape is not the same for \(2^3\)S and \(2^3\)P, the perturbations of the two states will differ in absorption and emission.

Because we are assuming that \(\phi(r_1, r_2)\) in an unperturbed function (e.g., that given by Morse, Young, and Haurwitz\(^{12}\) and previously discussed\(^1\)), certain simplifications in Equation (7) may be made resulting in

\[
E_{\text{atom}}^{\dagger} = E_{\text{atom}}^{\circ} + \langle \phi | V_p (\rho; \vec{r}_1) + V_p (\rho; \vec{r}_2) | \phi \rangle - \int \rho(\vec{R}) \frac{C}{R_0} d^3 R
\]

(12)

where the expectation value of \(H_{\text{atom}}^{\dagger}\) with respect to the unperturbed wavefunction has been replaced by \(E_{\text{atom}}^{\circ}\), the unperturbed energy. Also, the
integrated van der Waals attraction has been substituted for the averaged
dipole-dipole attractive potential. Since approximate values for C are
known, this saves considerable computation. Furthermore, preliminary cal-
culations shown that it is not necessary to use the full two-electron
spatial wavefunction

$$\psi(r_1, r_2) = \frac{1}{r_2} \left[ u_0(r_1) u(r_2) - u_0(r_2) u(r_1) \right]$$

(13)

which involves both a core 1s orbital $u_0$ and an excited orbital $u$. The
point is simply that for choices of $\rho$ (i.e., choices of $R_0$ and $a$) near
equilibrium, the overlap of the core orbital $u_0$ with the total pseudo-
potential interaction $V_{ps}(\rho; r_1)$ turns out to be negligible. Therefore,
we may write

$$E'_{atom} = E_{atom}^0 + \langle u(r) \mid V_{ps}(\rho; r) \mid u(r) \rangle - \int \rho(R) \frac{C}{R^6} d^3R$$

(14)

with negligible error. Since this implies that the excited electron
interacts separately with the liquid via the pseudopotential, we add a
term to represent the interaction of the He$^+$ core with the liquid.$^{13}$
This term is in fact small, but makes explicit the fact that we are con-
sidering the interaction of the excited helium atom with the liquid to
be composed of three distinct contributions:

1) The interaction of the excited electron with each He$(1s)$ atom
   via the pseudopotential $V_{ps}$

2) The interaction of the He$^+$ ion core with each He$(1s)$ atom,
   which we denote as $V_i(R)$

3) The van der Waals attraction resulting (in our approximation)
   from the polarization of each He$(1s)$ atom.
Thus, the perturbed excited state energy becomes

$$E'_{\text{atom}} = E^0_{\text{atom}} + \int |u(\vec{r})|^2 V_{ps}(\rho; \vec{r}) \, d^3r$$

$$+ \int \rho(\vec{R}) V\lambda(R) \, d^3R - \int \rho(R) \frac{c}{\vec{R}^6} \, d^3R \quad (15)$$

(Note that $\vec{r}$ locates the electron, and $\vec{R}$ a point in the bulk fluid.)

Equation (15) may be evaluated as a functional of $\rho(R)$ once a form for $V_{ps}$ is specified. We have found the analytic form

$$V_{ps}(|\vec{R}-\vec{r}|) = V_{ps}(r') = -\frac{2}{r'} e^{-ar'} + b e^{-\frac{(r')^2}{2\sigma^2}} \quad (16)$$

to be a convenient representation of the electron - helium atom pseudo-potential calculated by Kestner et al.\textsuperscript{11}. We chose to use the pseudo-potential of Kestner et al. primarily because it had been used in the "electron bubble" problem, and therefore, some measure of its correctness had been determined\textsuperscript{9}. Typical values for the parameters were $a = 3.0 \, a_0^{-1}$, $b = 0.544 \, \text{a.u.}$, and $\sigma = 1.31 \, a_0$. In order to examine the sensitivity of the energies to the form of $V_{ps}(r')$, some calculations were performed with a truncated pseudopotential, where we set $V_{ps}(r') = 0$ for $r' \geq 3.5 \, a_0$. It is most convenient to express $V_{ps}$ as a sum, using the polar coordinates $R = (R, \vec{R}) = (R, \Theta, \Phi)$ and $r = (r, \vec{r}) = (r, \theta, \phi)$. If the angle between $\vec{R}$ and $\vec{r}$ is taken to be $\eta$, then the pseudopotential becomes

$$V_{ps}(r') = V_{ps}(\sqrt{R^2 + r^2 - 2Rr \cos \eta}) = \sum_{\lambda=0}^{\infty} V\lambda(R, r) P\lambda(\cos \eta)$$

$$= \sum_{\lambda=0}^{\infty} V\lambda(R, r) \frac{4\pi}{2\lambda+1} \sum_{\mu=\lambda}^{\lambda} Y\lambda\mu(\hat{R}) Y\lambda\mu(\hat{r}) \quad (17)$$
where the \( v_\lambda (R,z) \) are determined numerically. Now we can write

\[
V_{PS} (\rho; \hat{r}) = \int \rho (\hat{R}) \, v_{PS} (|\hat{R} - \hat{r}|) \, d^3 r
\]

\[
= \sum_{\lambda, \mu} \left[ \frac{4\pi}{2\lambda + 1} \int \rho (\hat{R}) \, v_{\lambda} (R, r) \, Y_{\lambda \mu}^* (\hat{R}) \, d^3 R \right] Y_{\lambda \mu} (\hat{r})
\]

(18)

Depending on the symmetry of \( \rho (\hat{R}) \), and the angular dependence of \( u (\hat{r}) \), all but a few of the terms in the above sum will vanish when integrated over the electronic coordinates in Equation (15). In fact, for our application it will turn out that only \( v_0 (R, r) \) and \( v_2 (R, r) \) are required, and they may be calculated analytically.

In absorption, the initial state is \( 2^3 S \), and the cavity shape is expected to be spherical. It then follows that \( \rho (\hat{R}) = \rho (R) \), and therefore

\[
V_{PS} (\rho; \hat{r}) = \left[ 4\pi \int \rho (R) \, v_0 (R, r) \, Y_{00} (\hat{R}) \, d^3 R \right] Y_{00} (\hat{r})
\]

\[
= \int_0^\infty \rho (R) \, v_0 (R, r) \, R^2 \, d R \quad \equiv \quad v_0 (\rho; r)
\]

(19)

The final integral is evaluated numerically for various choices of \( \rho (R) \).

Using Equations (1), (2), (15), and (19), and remembering that the choice of \( \rho (R) \) implicitly includes a value for the average cavity radius \( R_b \), we can write explicitly the total energy as a functional of \( \rho (R) \), viz.

\[
\langle E \rangle = E_{atom}^0 + \int |u_{2s} (\hat{r})|^2 \, v_0 (\rho; r) \, d^3 r + \int \rho (R) \, v_1 (R) \, d^3 R
\]

\[
- \int \frac{C}{R_b} \, d^3 R + \frac{4\pi R_b^2}{3} \, \bar{\lambda} + \frac{1}{8m} \int \frac{(\nabla \rho)^2}{\rho} \, 4\pi R^2 \, d R
\]

(20)

After finding the equilibrium density function \( \rho_S (R) \) which minimizes \( \langle E \rangle \) for the \( 2^3 S \) state, the perturbation of the final \( (2^3 P) \) energy is found
by substituting $u_{2p}(r)$ into Equation (20), keeping the same $\rho_s(r)$. Taking the difference between these perturbed energies, and subtracting off the free atom level separation, we obtain the shift of the absorption line relative to that of the dilute gas. The line shift determined in this manner is known to correspond to the shift in the mean of the line intensity as opposed to the shift in the peak of the intensity, within a static line-broadening theory\textsuperscript{14}. If the line shape turns out to be asymmetric, the shifts in mean and peak values can be very different. We will return to this point when discussing our results.

In the case of emission, the initial state is $2^3P$, and we must generalize the definition of the liquid density function to take account of the nonspherical nature of this state. This is done by introducing an "anisotropy parameter" $\beta$, and replacing $R_0$ in Equation (1) by $R_0[1 + \beta P_2(\cos\theta)]$, where $\theta$ is the polar angle of $\hat{R}$. The effect of this is to allow the cavity shape to pull in at the "equator" and thereby follow the contour of the "dumbbell-shaped" $2^3P_{m=0}$ wavefunction. Then from Equation (18) we obtain

$$V_{ps}(\rho; \hat{r}) = V_0(\rho; r) + V_2(\rho; r) P_2(\cos\theta) + \ldots$$

where $V_0(\rho; r)$ has been given in Equation (19) and where

$$V_2(\rho; r) = \int \rho(\hat{R}) V_2(R; r) P_2(\cos\theta) d^3R$$

The three dots indicate that additional terms are present, involving higher order Legendre polynomials. However, the higher-order terms all vanish when integrated over s or p excited orbital.

We can write an expression for the total energy similar to Equation (20), but it will include a term in $v_2(\rho; r)$. We also adopt the following
formulae (due to Rayleigh\textsuperscript{15}) for the energy of the cavity when \( \beta \neq 0 \):

If the "center of mass" of the cavity profile is given by

\[
R_b(\Theta) = R_b \left[ 1 + \beta_b P_2(\cos \Theta) \right]
\]  \hspace{1cm} (22)

then the pressure-volume energy is

\[
E_{PV} = \frac{4}{3} \pi R_b^3 \left[ 1 + \frac{3}{5} \beta_b^2 \right]
\]  \hspace{1cm} (23)

and the surface energy is

\[
E_{surf} = 4 \pi R_b^2 \left[ 1 + \frac{4}{5} \beta_b^2 \right]
\]  \hspace{1cm} (24)

Here we have assumed that the surface tension \( \gamma \) is the same everywhere on the non-spherical surface.

The calculations to find the equilibrium liquid density \( \rho(R) \) and the corresponding perturbed energies proceed exactly as before. The only difference is the presence of an extra variational parameter \( \beta \), and the added difficulty of the integrals.

2. The Emission Transitions \( 3^1,3s \rightarrow 2^1,3p \)

When the initial state of the system involves an electron excited to an \( n = 3 \) level, it is expected that the atomic wavefunction may differ appreciably from its unperturbed form due to the influence of the fluid. For this reason, the eigenfunctions and eigenenergies of the Hamiltonian given in Equation (11) corresponding to the \( 3^1,3s \) states were determined variationally\textsuperscript{37}. The following (spatial) basis functions were chosen:

\[
\psi_{n_l m}^{(\pm)} = \frac{1}{\sqrt{2}} \left( 1 \pm P_{12} \right) \left[ N_o e^{-\alpha r_1} y_{oo} (r_1) N_n r_2^{n-1} e^{-\beta r_2} y_{lm} (r_2) \right]
\]  \hspace{1cm} (25)
where $P_{12}$ is the operator which interchanges $\hat{r}_1$ and $\hat{r}_2$, and $N_o$ and $N_n$ are normalization constants. The +(-) sign corresponds to the singlet (triplet) states, and these two cases may be dealt with separately.

For each spin state we defined the matrices $H$ and $S$ whose elements are

$$H_{n'l'm',n'm} = \langle \phi_{n'l'm} | H | \phi_{n'm'} \rangle$$

and

$$S_{n'l'm',n'm} = \langle \phi_{n'l'm} | \phi_{n'm'} \rangle$$

The secular equation is then

$$\det | H - SE | = 0$$

Each root of which is an upper bound for the corresponding energy level of the perturbed atom. The roots depend implicitly on $\rho$, i.e., on the parameters $\alpha, R_o,$ and $\rho_o$ which define $\rho$. There are, of course, no matrix elements of $H_{atom}^l$ connecting basis sets of different spin, or different values of $l$ or $m$. We therefore confine our basis to functions of the form $\phi_{\eta\nu\sigma}$, since here we are interested only in $S$ states. It is not necessary to consider the perturbation of the final state for these transitions. Trial calculations showed that this was completely negligible since the $2^1,3^1$ states have a much smaller electron probability distribution and simply do not overlap with the liquid. The shift of each transition energy is therefore just equal to the perturbation of the energy of the upper $(3^1,3^3)$. state.

For each trial form of $\rho(R)$, the appropriate root of Equation (27) was minimized by varying the nonlinear parameters $Z_n$ (keeping fixed
A = 2.00 \ a_0^{-1}). This minimum value is just \( E_{\text{atom}}^{\prime} \) for the trial \( \rho(R) \), and is added to \( E_{\text{cavity}} \). The total energy is thus given as a functional of \( \rho(R) \) as in the previous section, and the calculations are carried out in the same manner.

D. Results and Discussion

1. \( 2^3S \leftrightarrow 2^3P \)

Before discussing in detail the results for these transitions, the qualitative behavior of the model will be analyzed. In the case of emission, the equilibrium cavity formed around the \( 2^3P_{m=0} \) state is anisotropic, being slightly pinched in at the "equator" where the "dumbbell-shaped" p electron probability density is a minimum. When the transition to the \( 2^3S \) state occurs, there results a considerable perturbation of the s electron where its spherical wavefunction overlaps the pinched-in portion of the cavity. The positive perturbation of the lower state is much greater than that of the upper state, and therefore the wavelength of the transition line is red-shifted. Conversely, when the initial state is \( 2^3S \), the initial equilibrium cavity is spherical, having a radius comparable to the average radius of the nonspherical \( 2^3P \) equilibrium cavity. In this case both states are only slightly perturbed, and the prediction of a small blue shift is in accord with experimental results. Both of these transitions are illustrated schematically in Figure 1.

With this qualitative picture in mind, consider the theoretical results listed in Table 1. Those at s.v.p. show agreement with experiment\(^3\) within \( \approx 30 \ \text{cm}^{-1} \) for a range of surface tensions \( \gamma \) and pseudopotentials \( v_{ps} \). (It should be noted that these small shifts are measured
Figure 1. Schematic illustration of absorption and emission between states $2^3P$ and $2^3S$ in liquid helium. The equilibrium shape of the cavity depends on the initial state of the system.
Table 1

Theoretical results for the energy shift in absorption and emission between the states $2^3S$ and $2^3P$ at saturated vapor pressure. For absorption, $\alpha = 1.0 \ a_0^{-1}$ and $\beta = 0.0$ in every case; $\alpha = 1.0 \ a_0^{-1}$ and $\beta = 0.3$ for every emission.

<table>
<thead>
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<td></td>
<td>$V_{ps(1)}$</td>
<td>$V_{ps(2)}$</td>
</tr>
<tr>
<td>$\gamma$ =</td>
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<td>+18 cm$^{-1}$</td>
</tr>
<tr>
<td>0.36 erg/cm$^2$</td>
<td>$R_o = 10.5 \ a_0$</td>
<td>$R_o = 10.0 \ a_0$</td>
</tr>
<tr>
<td>$\gamma$ =</td>
<td>+31 cm$^{-1}$</td>
<td>+18 cm$^{-1}$</td>
</tr>
<tr>
<td>0.52 erg/cm$^2$</td>
<td>$R_o = 10.0 \ a_0$</td>
<td>$R_o = 10.0 \ a_0$</td>
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<tr>
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<td>$V_{ps(2)}$</td>
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</tr>
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<td>-49 cm$^{-1}$</td>
</tr>
<tr>
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<td>$R_o = 9.5 \ a_0$</td>
</tr>
<tr>
<td>EXPERIMENT:</td>
<td>$\approx -68 \ cm^{-1}$</td>
<td></td>
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</tbody>
</table>
relative to the free-atom transition energy.) An appreciation of the overall nature of these results can be gained by considering their sensitivity to the major factors which determine them. We therefore examine their dependence on the wavefunctions, the van der Waals term, the cavity energy expression, and the electron-helium pseudopotential.

Unperturbed wavefunctions were found to be completely adequate to within the accuracy of the model for the $2^3S\leftrightarrow 2^3P$ transitions. The 2s and 2p electrons are fairly tightly bound, so that the excited orbital is not easily distorted. If the excited-electron probability distribution were "pulled-in" so that it would see less of the repulsive potential $v_{ps}(\rho;x)$, then the energy reduction would be largely cancelled by the increased Coulomb repulsion due to the inner 1s electron and the increased kinetic energy. This may be contrasted with the behavior of the $3^1,3^3S$ states, where, as expected, the outer-electron orbital is found to be much more easily distorted.

A cause of greater concern than the quality of the wavefunctions is the uncertainty in the van der Waals coefficients. For the $2^3S$ state, the value of 29.1 a.u. obtained by Victor et al.\textsuperscript{16} is based on an accurate calculation and is undoubtedly adequate. For the $2^3P$ state, however, no published calculations or experimental data exist. Our value\textsuperscript{1} of $50(1 + \frac{2}{5} P_2(\cos\theta))$ a.u. is probably reasonable. It was found that the choice of van der Waals constant had an especially noticeable effect on the degree to which the cavity distorted at the "equator," for there the electron probability density is low, and the electrostatic attraction is dominant. For purposes of comparison, the alternative value $C = 35(1 + \frac{2}{5} P_2(\cos\theta))$ a.u. was used, resulting in a slightly larger cavity, and hence smaller red shift on emission.
An appealing feature of the calculations is the degree of insensitivity of the calculated transition energy shifts to the exact definition of cavity energy. This insensitivity is fortunate because so little is known about calculating the energy of a perturbed fluid configuration. The "bubble model" of the cavity, where the energy is large determined by a surface tension and pressure volume energy term has been successfully used in describing the "electron bubble" in liquid helium. It is certainly a crude approximation, especially when the cavity diameter is only a few times larger than the average separation of the bulk fluid atoms. However, one can see by means of a rough calculation that the model is not entirely unreasonable. The binding energy per atom $w_b$ in liquid helium has been calculated to be $0.97 \times 10^{-15}$ erg. Hence, the energy content of a spherical volume of fluid (at normal density of radius $R$ is $\frac{4}{3} \pi R^3 \rho_0 w_b$, where $\rho_0 = 0.0218$ atoms/$\AA^3$). Approximately that amount of energy should be required to expel the atoms from within the sphere to create a cavity of the same radius. We therefore associate the energy $\frac{4}{3} \pi R^3 \rho_0 w_b$ with the surface area $4\pi R^2$, to estimate a surface tension $\gamma = \frac{1}{3} \rho_0 w_b$. The linear dependence of $\gamma$ on $R$ is merely a feature of this crude model; our point is that substituting $R = 5$ or 10 Å (the approximate radii of cavities surrounding $2^3S$ and $3^3S$ states, respectively) gives $\gamma = .3$ ergs/cm$^2$ and $\gamma = .6$ ergs/cm$^2$, respectively. These numbers compare well with the values of $\gamma$ actually used, which range from .18 to .50 ergs/cm$^2$. We suggest that the inaccuracy of this definition of cavity energy is largely masked by the relative insensitivity of our final results to the exact choice of $\gamma$.

Recent experimental results have made it possible to check the predicted transition energy shifts of the model as a function of pressure.
The only change necessary in the model is to change the pressure in $E_{PV}$ and to include the pressure-induced density change. The latter change was neglected for the $2^3S + 2^3P$ transition to permit comparison with the results of Steets. This change in density is 20% at $p = 25$ atm, but only causes the predicted mean shift to increase about 3%. Good agreement is obtained in the case of absorption, $2^3S + 2^3P$, as shown in Table 2, particularly with respect to the line widths. The line shifts at each pressure are given relative to the line position at saturated vapor pressure (S.V.P. = 0 atm); this quantity was more accurately determined experimentally than the exact line position. Because the observed lines are asymmetric, it should be remembered that the observed peak does not correspond to the mean calculated by the present theory. The experimental line shifts must be compared to the theoretical shift of the peaks. These peaks, and also the widths, were calculated by Steets using static line broadening theory. Steets assumed an equilibrium cavity shape as calculated by the present theory, and a constant bulk fluid density independent of pressure. The approximate numerical agreement between the computed mean and observed peak is coincidental.

Less satisfactory agreement was obtained for the case of emission, $2^3P + 2^3S$. The experimental line is blue shifted by 25 cm$^{-1}$ as the pressure increases from S.V.P. to 5 atm. The dependence is nearly linear. The model of a nonspherical bubble with constant surface tension predicts a much smaller shift in the opposite direction. The reason for this is that as the pressure is increased, the bubble distorts more easily at the "equator", because the electron charge density is concentrated at the "poles." The spherically symmetric $2^3S$ state which results from the emission of a
Table 2

Pressure Dependence of $2^3S\rightarrow2^3P$ Transition Energy Shift and Line Width.

The shift (of the peak of the line) is given relative to the position of the line in a dilute gas. For this line, the shift in energy units of cm$^{-1}$ (which is given) is numerically approximately equal to the shift in the wavelength in Å. The Wisconsin Data is a temperature average.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Wisconsin Data</th>
<th>Model Calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Shift</td>
<td>Width</td>
</tr>
<tr>
<td>s.v.p.</td>
<td>18 ±8</td>
<td>63</td>
</tr>
<tr>
<td>5 atm</td>
<td>21 ±8</td>
<td>70</td>
</tr>
<tr>
<td>10 atm</td>
<td>28 ±8</td>
<td>81</td>
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<tr>
<td>15 atm</td>
<td>33 ±8</td>
<td>92</td>
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<td>37 ±8</td>
<td>98</td>
</tr>
<tr>
<td>25 atm</td>
<td>43 ±8</td>
<td>109</td>
</tr>
</tbody>
</table>
photon is then perturbed more by the pinched-in bubble at higher pressures. Since this picture does not seem to be born out by experiment, it is clear that more theoretical research needs to be done. The assumption that the surface tension is constant over the surface of the nonspherical bubble may be too severe an approximation. More serious, perhaps, is the approximate form chosen for the \( 2^3P \) van der Waals potential. Alternatively, Steets\textsuperscript{18,19} has investigated spherically symmetric liquid distributions determined by non-monotonic functions \( \rho(R) \) which may yield better agreement with experiment.

We previously referred to the uncertainty in the electron-helium pseudopotential \( V_{ps} \), and argued that the asymptotic form of Equation (16) was probably too large. Transition energy shifts corresponding to the original \( V_{ps}(r') \) and to \( V_{ps}(r') \) cut off to zero for \( r' \geq 3.5 \ a_0 \), denoted as \( V_{ps}^{(1)} \) and \( V_{ps}^{(2)} \), respectively, are given in Table 1. These data show that making the pseudopotential less repulsive at long range generally causes the cavities to become smaller, and results in slightly better agreement with experiment. In the case of \( 2^3P+2^3S \) emission, there is a strong dependence of the energy shift on the exact shape of the cavity. In absorption, especially for smaller values of the surface tension, the sensitivity is not so pronounced. This is because in the latter case the perturbed energies of the upper and lower states tend to move up or down together as \( \gamma \) is varied, with little net change in the energy difference. This contrast in sensitivity is heightened by the fact that the absorption transition takes place in a spherical cavity, whereas the emission occurs in a nonspherical cavity. Thus, in the case of emission, the uncertainty as to how to compute the energy is compounded by the critical dependence on the exact amount of nonspherical distortion present.
Two other features of the model should be mentioned. First, the dependence on the $\text{He}^+\text{He}$ interaction $V_i$ does not seem to be critical. In the $2^3S$ cavity $V_i(R)$ is essentially zero for values of $R$ of the order of the cavity radius. In the $2^3P$ cavity, it is important to use the averaged form of $V_i = \frac{1}{2} \left[ V(2L_u^+) + V(2L_d^+) \right]$ so that it will be slightly repulsive at small $R$. This prevents the electrostriction effect from causing the cavity to collapse. A second point is that no form of screening has been included. The interaction of the excited atom with any other fluid atom has been assumed to be unaffected by the intervening fluid. This is not really a problem for $V_i$ and $V_{ps}$ since these potentials fall off very rapidly with distance. Only the van der Waals term has a significant long-range effect. The result of screening in this case may be estimated by assuming that the intervening fluid between two interacting atoms acts as a dielectric. Then the interaction energy $-C/R^6$ between the excited species and a ground state atom should be reduced by $\varepsilon^{-2}$ for $\text{He}(1^1S)$ atoms beyond the nearest neighbor shell. Since the dielectric constant for liquid helium is $1.055^{20}$, this effect is small, and will be neglected.

2. Emission $3^1S \to 2^1S + 2^1P$

An important feature of our results for the $n = 3$ states is the clear dependence of the electron wavefunction on the average cavity shape. We expect that as the cavity radius is decreased, the electron probability distribution should be pushed in. The variational calculations show this to be the case for both forms of $V_{ps}(r')$. Transition energy shifts are obtained for both forms of $V_{ps}(r')$. In our discussion of the $2^3S \to 2^3P$ transitions, we discussed the uncertainty in the pseudopotential.
Figure 2 shows why its exact form may not be so important for the $3^1,3^3_s + 2^1,3^p$ transitions. The truncated form of $V_{ps}$ is less repulsive at long range, and therefore the cavity surrounding the $3^1,3^3_s$ state is slightly smaller. However, the net perturbation of the state is about the same.

A greater sensitivity of the shifts to the value chosen for the surface tension was observed for this case. An increase in $\gamma$ results in a smaller cavity and a greater perturbation of the $3^1s$ or $3^3s$ excited state, and hence more of a blue shift in the wavelength of the $3^1,3^3_s+2^1,3^p$ transitions. It is illustrative to convert this $\gamma$ dependence to an "effective temperature" dependence, using the experimental $^21^1\gamma(T)$ given in Figure 3. In Figure 4, the average energy $\langle E \rangle$ and its components $E_{\text{cavity}}$ and $E_{\text{atom}}$ for the $3^3s$ state are plotted as a function of cavity radius $R_0$ for two effective temperatures, $T_{\text{eff}} = 2.0^oK$ and $T_{\text{eff}} = 3.5^oK$. At lower "effective temperatures," $T_{\text{eff}}$ the slope of the $E_{\text{cavity}}$ vs. $R_0$ curve is greater, and the minimum of $\langle E \rangle$ occurs at smaller $R_0$. In Figure 5 the transition energy shift is given as a function of "effective temperature." Choosing $T_{\text{eff}} = 3.5^oK (\gamma = 0.16 \text{ erg/cm}^2)$ results in significantly better agreement with experiment than the use of the actual temperature of 2.0$^oK (\gamma = 0.31 \text{ erg/cm}^2)$.

Our calculations include separate terms for the surface tension energy ($4\pi R_0^2 \gamma$) and for the volume kinetic energy ($\frac{1}{6M} \int \frac{(\mathbf{p})^2}{\rho} \, d^3r$). This latter term is certainly a surface effect, and varies almost exactly as $R_0^2$. Bowley$^{22}$ has suggested that it should already be included in the definition of the surface tension energy. If this is so, we estimate the best "effective temperature" to be $\approx 2.7^oK$, somewhat closer to the actual temperature of the liquid helium.
Figure 2. The net energy change of the $3^1S$ state is relatively insensitive to changes in $v_{ps}$. The solid lines show $\Delta E_{\text{atom}}$ (calculated variationally), $E_{\text{cavity}}$, and $E$ as a function of cavity radius for $v_{ps}(1)$. The minimum of $\langle E \rangle$ occurs at $R_0 = 25 \ a_0$, corresponding to a perturbation in $20 \ \text{cm}^{-1}$. If $\Delta E_{\text{atom}}$ is calculated (variationally) using $v_{ps}(2)$ (the truncated form), the minimum of $\langle E \rangle$ (dashed line) occurs at $R = 24.5 \ a_0$, corresponding to $\Delta E_{\text{atom}} = 24 \ \text{cm}^{-1}$. In both cases, $\gamma = 0.18 \ \text{ergs/cm}^2$ and $p = 0$. 

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Figure 3. Surface tension of liquid helium as a function of temperature.
Figure 4. A decrease in the surface tension $\gamma$ results in a smaller energy shift of the $3^3S$ state. Here $\Delta E_{\text{atom}}$ is calculated variationally using the truncated $V_{ps}$. For $\gamma = 0.31$ ergs/cm$^2$ ($T_{\text{eff}} = 2.0^\circ K$), the minimum of $\langle E \rangle$ occurs for $R_0 = 19.75$ a$_o$, corresponding to $\Delta E_{\text{atom}} = 32$ cm$^{-1}$ (solid lines). If $\gamma$ is decreased to 0.16 ergs/cm$^2$ ($T_{\text{eff}} = 3.5^\circ K$), the minimum of $\langle E' \rangle$ occurs for $R_0 = 20.5$ a$_o$. Since the cavity is larger, $\Delta E_{\text{atom}}$ is smaller, and is equal to 24 cm$^{-1}$. In both cases $p = 0$. 

- 27 -
Figure 5. Energy shifts of the $3^1S, 3^3S$ states in equilibrium cavities in liquid helium, shown as a function of the surface tension parameter $\gamma$ and the corresponding "effective temperature." The calculations were performed variationally, with $p = 0$, and the volume kinetic energy term is explicitly included.
Similar arguments concerning the dependence of the shift on pressure can be made. Comparison with the experimental data of Soley et al.\textsuperscript{17} strongly suggests that the pressure is correctly taken into account in our model. The shift of the emission line $3^3S+2^3P$ as a function of pressure (relative to its position at s.v.p.), as measured by Soley, is given in Table 3. Since the experimental lines are asymmetric, the position of the peak corresponds to the mean, which we calculate. The agreement with theory is considered quite good. We note that in this preliminary comparison, the increase in density (of 20\%) as the pressures from 0 to 25 atm was included by multiplying the variationally-determined $\Delta E_{\text{atom}}(R_B)$ by the density change factor. Also, these results were calculated using $V_{ps}^{(2)}$ and $\gamma = 0.16$ ergs/cm\(^2\) (which corresponds to an effective temperature of 3.5\(^{\circ}\)K).

The agreement for the $3^1S+2^1P$ transition is also quite good, although experimentally the lines could not be measured for $p \gtrsim 7$ atm. This is due to a quenching effect for the singlets, which is not well understood. At high pressures the transition $3^1S+1^1S$ may be greatly enhanced, whereas $3^3S+1^1S$ is still forbidden. Using the same model parameters and producers as in the triplet case, we obtain 75 cm\(^{-1}\) blue shift at 5 atm (relative to s.v.p.), compared to the experimental result of 68 cm\(^{-1}\). It should be noted that at 5 atm, both the theoretical and experimental shifts for the singlet transition is approximately twice those for the triplet transition. This appears to verify the prediction of the model that the $3^1S$ state exists in a somewhat larger cavity than does the $3^3S$. $E_{pv}$ is then larger for the singlet state, because of the dependence on $R_B^3$. Hence the singlet cavity is forced in more as the pressure increases, causing a greater shift.
Table 3

Pressure Dependence of $3^1S + 2^3P$ Transition Energy Shift.

Because the observed lines are symmetric, the observed peak corresponds to the calculated mean. The shifts are given relative to the position at saturated vapor pressure, and are in units of cm$^{-1}$.

<table>
<thead>
<tr>
<th>Pressure</th>
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<th>$3^1S+2^1P$</th>
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<tbody>
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In our variational calculations, the van der Waals constant has not been specified; for a given cavity shape it must be computed as for the variationally determined excited orbital. With no perturbation at all \( R_b \to \infty \), this estimate gives \( C = 190 \) a.u. for \( 3^3S \), and \( C = 287 \) a.u. for \( 3^1S \). This is not inconsistent with various rough estimates\(^{23} \), although the comparison is questionable because those formulas are derived for ground state atoms. Due to the influence of the liquid environment, the wavefunction is "pulled in" and \( C \) decreases. For the equilibrium cavity, \( C = 180 \) a.u. for \( 3^3S \), and \( 273 \) a.u. for \( 3^1S \).

We have emphasized the importance of calculating \( \phi(r_1, r_2) \) variationally to obtain the best possible solution for \( H^i_{\text{atom}} \). Calculations were also performed using first order perturbation theory as with the \( n = 2 \) transitions. The comparison is presented in Table 4; note that in every case the results are improved by using the variational method. Figure 6 shows that \( \Delta E_{\text{atom}} = E^i_{\text{atom}} - E^0_{\text{atom}} \) is always larger when the wavefunction is not permitted to deform. This seems to demonstrate quite clearly the importance of including the change of the wavefunction when computing the equilibrium state of \( 3^1, 3^3 \) excited atoms in the liquid.

A by-product of the variational calculation discussed here is an estimate of the energy of a single electron ejected into liquid helium (without cavity formation). We first note that as \( r \to \infty \), \( V_{\text{ps}}(\rho; r) \) approaches a constant value independent of \( \rho(R) \). This number is the repulsive energy of an electron completely surrounded by uniform density liquid helium. If \( V_{\text{ps}} \) is not cut off, this limit is 1.45 eV; for cutoff at 3.5 \( a_0 \), the limit is 1.33 eV. To this value we add the energy due to the polarization of the helium by the electron.
Table 4

Theoretical results for the emission transitions $^3S_1 + ^3P_2 \rightarrow ^3P_1$. In every case the variational parameter $\alpha$ is 0.67 $a_0^{-1}$, and saturated vapor pressure is assumed.

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<thead>
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<table>
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<tr>
<td>$V_{ps}(1)$</td>
<td>$V_{ps}(2)$</td>
</tr>
<tr>
<td>Variational Theory</td>
<td></td>
</tr>
<tr>
<td>15 cm$^{-1}$</td>
<td>13 cm$^{-1}$</td>
</tr>
<tr>
<td>$R_0 = 20.5$ $a_0$</td>
<td>$R_0 = 20.5$ $a_0$</td>
</tr>
<tr>
<td>Perturbation Theory</td>
<td></td>
</tr>
<tr>
<td>33 cm$^{-1}$</td>
<td>30 cm$^{-1}$</td>
</tr>
<tr>
<td>$R_0 = 21.0$ $a_0$</td>
<td>$R_0 = 21.0$ $a_0$</td>
</tr>
<tr>
<td>EXPERIMENT: 10 cm$^{-1}$</td>
<td></td>
</tr>
</tbody>
</table>
Figure 6. The energy shifts of the $3^1S, 3^3S$ states are always smaller when the variational method is used. This indicates that for a given cavity radius $R_0$, the electronic energy is reduced as the electron wavefunctions "pulls in" to avoid overlapping the bulk fluid.
\[ E_{\text{pol}} = -\frac{1}{2} \alpha \int_0^\infty R^2 \rho(R) R^{-4} dR \quad (\text{a.u.}) \quad (29) \]

Clearly, the integration cannot be carried out from 0 to \( \infty \). Roughly estimating that the closest helium atom is 2 \( a_0 \) from the electron gives \( E_{\text{pol}} = -0.38 \text{ eV} \). Hence an estimate for the energy of an electron in bulk liquid helium is roughly 1 eV. This number is very close to the experimental value of 1.05 eV\(^2\).

E. Additional Note: Metastability Exchange in \( ^3\text{He}(2^3S) \rightarrow ^3\text{He}(1^1S_0) \) Collisions

A basic assumption of the theoretical model developed in the preceding sections is that the excited helium atom remains localized in the liquid. The possibility that the excitation could be transferred from one atom to another has been ignored. As a by-product of the research described in this section, an estimate of the frequency of excitation transfer in liquid helium can be made. We shall see that the average time required for a metastability exchange to occur is longer than an atomic lifetime, and much longer than the probable time required for cavity formation.

1. Introduction

In 1968 Fitzsimmons, Lane, and Walters\(^{25} \) (FLW) obtained an approximate analytic expression for the asymptotic form of the potentials \( V_g \) and \( V_u \) for the helium molecular states \( ^3\Sigma_g^+ \) and \( ^1\Sigma_u^+ \). The particular long range forms for these potentials were chosen so that 1) the calculated \(^4\text{He} \) diffusion cross sections were in good agreement with their own diffusion scattering measurements, 2) the elastic scattering cross sections agreed
with the results of Rothe, Neynaber, and Trujillo\textsuperscript{26}, and 3) the $^3\text{He}(^2\text{S}) - ^3\text{He}(^1\text{S})$ metastability exchange cross sections $Q_{\text{TX}}$ were in fair agreement with the data of Colegrove, Schearer, and Walters\textsuperscript{27} (CSW). The CSW experiment consisted of a measurement of the rate constant $K$ for metastability exchange (i.e., the thermal average of $Q_{\text{TX}}$ times velocity) as a function of temperature from 4.2$^\circ$K to 500$^\circ$K, with particular emphasis on the higher temperatures. Recently, Rosner and Pipkin\textsuperscript{28} have obtained more accurate values for $\langle Q_{\text{TX}} \rangle$ in the low temperature range 15$^\circ$K to 115$^\circ$K. Furthermore, Dupont-Roc, Leduc, and Laloë\textsuperscript{29} (DLL) have found that a detailed analysis of the electronic coherence between all magnetic sublevels involved in $^3\text{He}$ metastability exchange implies that the results of CSW should be multiplied by a numerical factor of 9/4 before comparison with theoretical results. The purpose of the present work is to see what modification of the empirical $V_g$ and $V_u$ potentials is necessary to account for the new data.

2. Theoretical Approach

We shall summarize briefly the theoretical results used by FLW (following to some extent the discussion presented by Evans and Lane\textsuperscript{30}). If a $^3\text{He}(^2\text{S})$ and a $^3\text{He}(^1\text{S}_0)$ are brought together from infinity to a separation $R$, the electronic wavefunction $\psi(R; I_1)$ of the resulting homonuclear molecule must be either symmetric ($\psi = \psi_g$) or antisymmetric ($\psi = \psi_u$) under exchange of the nuclei, corresponding to the $^3\Sigma^+_g,u$ states. Asymptotically, these states are degenerate, and both must be included in a scattering calculation. We therefore write (the two state approximation)
\[
\psi(R_1, R_2) = F_g(R) \psi_g(\hat{R}, \hat{\xi}) + F_u(R) \psi_u(\hat{R}, \hat{\xi})
\]  

(30)

In the adiabatic approximation, the scattering wavefunctions \(F_g\) and \(F_u\) satisfy the following uncoupled equations (written in atomic units, with \(M\) the reduced mass):

\[
\left[ \nabla^2_R + k^2 - 2M V_{g,u}(R) \right] F_{g,u}(\hat{R}) = 0
\]

(31)

where \(k^2\), of course, is related to the initial kinetic energy \(E\) (in the center of mass frame) by

\[
k^2 = 2M E
\]

(32)

Phase shifts \(\eta^{(g)}_k\) and \(\eta^{(u)}_k\) may be calculated separately for the potentials \(V_g\) and \(V_u\), using standard techniques for solving Equation (31).

These are then used to form the scattering amplitudes

\[
f_{g,u}(\theta) = \frac{1}{2\lambda k} \sum_{\ell=0}^{\infty} (2\ell+1) \left[ e^{2i\lambda \eta^{(g,u)}_\ell} - 1 \right] P_\ell(\cos \theta)
\]

(33)

In principle, because, the \(^3\)He nuclei are identical, it is impossible to distinguish scattering at an angle \(\theta\) without metastability exchange, from scattering at angle \(\pi - \theta\) with metastability exchange. However, except at very low energy, these processes are distinguished in practice by associating metastability exchange with apparent back-scattering (\(\theta = \pi\)) of the excited atom. We can then write square of the full scattering amplitude (independent of nuclear symmetry) as

\[
|F(\theta)|^2 = \frac{1}{4} \left\{ |f_g(\theta) + f_u(\theta)|^2 + |f_g(\pi - \theta) - f_u(\pi - \theta)|^2 \right\}
\]

(34)
Furthermore, we may define a cross section for metastability exchange in this approximation, given by

\[ Q_{\tau \tau} = \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \ln^2 \left[ \eta_l^{(g)} - \eta_l^{(u)} \right] \]  \hspace{1cm} (35)

For diffusion of a He\(2^3S\) in a He\(1^1S_O\) gas, the appropriate cross section is then\(31\)

\[ Q_D = \frac{2\pi}{k^2} \sum_{l=0}^{\infty} (l+1) \ln^2 \left[ \eta_l^{(g)} - \eta_{l+1}^{(u)} \right] + \ln^2 \left[ \eta_l^{(g)} - \eta_l^{(u)} \right] \]  \hspace{1cm} (36)

In order to understand the process of metastability exchange, one must realize that the physical state corresponding to the excitation on one or the other of the identical nuclei is not an eigenstate of the Hamiltonian, but a linear combination of the eigenstates \(\psi_g\) and \(\psi_u\) (namely \(1/\sqrt{2} (\psi_g \pm \psi_u)\), the sign depending on which atom is excited). The time evolution of the coefficient of \(\psi_g(\psi_u)\) is determined by \(V_g(V_u)\), so that during the collision process their relative phase can change. This change of phase relationship of \(\psi_g\) and \(\psi_u\) is interpreted physically as an amplitude for the transfer of excitation.

We now briefly mention the techniques used by FLW to obtain analytic potentials. They used existing calculations of \(V_{g,u}(R)\) for \(R \leq 6\ a_0\), and matched these potentials to the following asymptotic forms:

\[ V_u = \alpha R^2 e^{-\beta R} - \frac{c}{R^6} \]  \hspace{1cm} (37)

\[ V_g = V_u + \gamma e^{-\Gamma R} \]

They found that the exact details of the matching at \(R = 6.0\ a_0\) were not critical, and that the exponential form of the difference potential \(V_d = V_g - V_u\) was an adequate approximation.
Due to a minor mistake\(^{32}\), the actual difference potential used by FLW actually had the somewhat more complicated form \(V_d = 1.53 e^{-1.43R} + 2.93 e^{-1.62R}\). In the present calculations we shall follow the same approach, and vary the parameters of Equations (8) and (9) in order to calculate diffusion and metastability exchange cross sections which agree with experiment.

3. Results and Discussion

The present work is primarily concerned with temperatures in the range \(15^\circ - 115^\circ\) K. At these temperatures thermal collisions are determined almost entirely by the intermediate-range repulsive barriers of \(V_g\) and \(V_u\), and the exact details such as barrier height are not too important. Nevertheless, the short range values of the potentials we use are consistent with the calculations of Matsen and Scott\(^ {33}\), Greenawalt\(^ {34}\), and with the more recent calculations of Gupta\(^ {35}\). Similarly, the exact long range van der Waals attraction is not crucial to our results because the lowest energies of interest are several times the depth of the van der Waals attractive well. We do use the accurate value of the van der Waals constant \(C = 29.1\) a.u. as calculated by Victor et al.\(^ {16}\).

A range of difference potentials of the form \(V_d = \gamma e^{-\tau R}\) was found to yield calculated values of \(\langle Q_{\text{TR}} \rangle\) in satisfactory agreement with experiment. Table 5 gives these analytic forms of \(V_g\) and \(V_u\) in terms of the parameters in Equations (8) and (9). The previous estimate of \(V_d\), and the \(V_d's\) corresponding to the present potentials, are plotted in Figure 7. Figure 8 contains a graph of \(Q_{\text{TR}}\) as a function of \(k^2\) (where the energy in eV is given by \(E = 0.0037 k^2\)). The increase in \(Q_{\text{TR}}\) for very low energies is a reflection of the attractive van der Waals part of the potential.
Table 5

Parameters for the Analytic Expressions for $V_g$ and $V_u$.

The new form of $V_g$ and $V_u$ which gave the best agreement with experiment is indicated, although all three forms listed gave satisfactory agreement.

<table>
<thead>
<tr>
<th></th>
<th>Old $V_d$</th>
<th>New $V_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(FLW) (1) (best)</td>
<td>(2)</td>
</tr>
<tr>
<td>$\alpha$ (a.u.)</td>
<td>0.820</td>
<td>0.299</td>
</tr>
<tr>
<td>$\beta$ ($a_o^{-1}$)</td>
<td>1.6</td>
<td>1.4</td>
</tr>
<tr>
<td>$C$ (a.u.)</td>
<td>0.0</td>
<td>29.1</td>
</tr>
<tr>
<td>$\gamma$ (a.u.)</td>
<td>1.54*</td>
<td>999.0</td>
</tr>
<tr>
<td>$\tau$ ($a_o^{-1}$)</td>
<td>1.43*</td>
<td>2.23</td>
</tr>
</tbody>
</table>

*correction to this noted in text.
Figure 7. Several difference potentials $V_d = \gamma e^{-\tau R}$ lying in the hashed region of the figure were found to give satisfactory scattering cross sections. The solid line is the approximate $V_d$ used by FLW, which does not yield excitation transfer cross sections in agreement with recent experiments.
Figure 8. Excitation transfer cross section as a function of $k^2$. (The center of mass frame energy in electron volts is $E = .0037 \, k^2$, where $k^2$ is in $a_o^{-2}$.) This calculation was performed with $V_g$ and $V_u$ defined by the parameters which gave the best fit to the experimental rate constants, namely, $\alpha = 0.299$ a.u., $\beta = 1.4 \, a_o^{-1}$, $C = 29.1$ a.u., $\gamma = 999.0$ a.u., and $\tau = 2.23 \, a_o^{-1}$. 

- 41 -
This increase would affect the rate constant only for $T \leq 1^\circ{}K$, and the effect would certainly be too small to measure. Experimentally, as previously noted, only the thermal average $\langle q_{\text{Tr}}v \rangle$ is determined. Figure 9 therefore shows the rate constant $K$ as a function of temperature for various forms of $Q_d$, and also the experimental data of Rosner and Pipkin. It can be seen that at $R = 6 a_o$, $V_d$ is larger than previously thought, but falls off much more rapidly with increasing $R$.

FLW found that to a good approximation, the diffusion cross sections $Q_d$ depends only on $\bar{V}$, the average of $V_g$ and $V_u$, whereas $Q_{\text{Tr}}$ is very sensitive to the difference $V_d$. We found this still to be the case, even though $V_d(R)$ is now much larger for $R = 6 - 7 a_o$. As expected, the modifications which were necessary in the parameters of the expressions (8) and (9) for $V_u$ and $V_g$ did not significantly alter $\bar{V}$ from the previous estimate of FLW. Consequently, the new, empirical long range potentials yield 1) diffusion cross sections in agreement with the earlier data of FLW, 2) elastic scattering results in agreement with Rothe, Neynaber, and Trujillo$^{26}$, and 3) values of $Q_{\text{Tr}}$ (and hence $\langle q_{\text{Tr}}v \rangle$) in agreement with the data of Rosner and Pipkin.

We have also found that the high temperature data of CSW (multiplied by 9/4), and the results of DLL, are consistent with rate constants for metastability exchange calculated using our modified $V_g$ and $V_u$. At $T = 300^\circ{}K$ to $500^\circ{}K$, the barrier height of $V_u$ is important in determining cross sections; therefore, our theoretical results are somewhat sensitive to the exact form of this barrier. The calculation of Gupta$^{35}$ has given a barrier height of 0.14 eV; there is some indication$^{36}$ it may be as low as 0.08 eV. Using the form of $V_u$ and $V_g$ which gives the best exchange
Figure 9. The rate constant for excitation transfer in $^3$He($^2$S) - $^3$He($^1$S₀) collisions. The experimental data is that of Rosner and Pipkin. The upper solid curve gives the best agreement and corresponds to $V_d(1)$ in Table 5. The lower solid curve was calculated using $V_d(2)$ in Table 5, and the estimate of $V_d$ of FLW yielded the dashed curve.
cross sections at low temperature (#1 in Table 5, which corresponds to a barrier height of 0.14 eV), and estimating the uncertainty due to the shape of the barrier, we estimated the rate constants for metastability exchange at \( T = 300^\circ \) and \( 500^\circ \)K. These estimates agree, within error limits, with experimental data as shown in Table 6.

4. Relation to Cavity Formation

We can use the excitation transfer cross sections calculated above to determine whether excitation transfer in liquid helium is consistent with the cavity model. We first note that at \( T = 2^\circ \)K, thermal velocities are on the order of \( 10^4 \) cm/sec. Since an average cavity diameter is \( \approx 10 \) Å, a time typical for cavity formation around an excited state would be \( 10^{-11} \) sec. Once inside the cavity, this atom continually undergoes collisions with \( \text{He}(1^1S_0) \) atoms which could lead to excitation transfer. For such a collision in a dilute gas, the energy is exactly the same regardless of which atom is excited, and the cross section for excitation transfer is about \( 0.01 \) Å\(^2\) (see Figure 8 for \( k = 0.25 \) a\(_\text{0}^{-1}\)). The calculation depends critically on the exact resonance nature of the collision\(^31\). In the liquid, of course, transfer of excitation from the atom at the center of the cavity to one near the edge results in a configuration of much higher electronic energy. We may therefore regard \( 0.01 \) Å as a serious overestimate. Assuming that the flux of \( \text{He}(1^1S_0) \) is \( \rho_0 \nu \), where \( \rho_0 = 2 \times 10^{22} \) atoms/cm\(^3\) and \( \nu = 10^4 \) cm/sec, we see that the average time \( T \) required before an excitation transfer takes place is

\[
T \geq \left( \frac{Q_{TR} \rho_0 \nu}{1} \right)^{-1} \approx 10^{-8} \text{ sec.} \quad (38)
\]
Table 6

Theoretical and Experimental Rate Constants for Metastability Exchange at $T = 300^\circ$ and $500^\circ$.

The theoretical estimate is approximate because of uncertainty in the exact barrier height of the ungerade potential. The units are $10^{-12}$ cm$^2$/sec.

<table>
<thead>
<tr>
<th>Theoretical Estimate</th>
<th>CSW</th>
<th>DLL</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T = 300^\circ$K</td>
<td>155 ± 7</td>
<td>152 ±12</td>
</tr>
<tr>
<td>$T = 500^\circ$K</td>
<td>225 ±35</td>
<td>254 ±28</td>
</tr>
</tbody>
</table>
This is roughly the time required for an optical transition, and very long compared to the time necessary for cavity formation. Since we overestimated $Q_{Tr}$, we conclude that $T$ is significantly longer than an atomic lifetime. The process of excitation transfer might therefore be a possible broadening mechanism, but it certainly does not occur rapidly enough to inhibit the formation of a stable cavity.
Part II

He(2^3S) - H_2 Collisions: Elastic Scattering, Rotational Excitation, and Penning Ionization

A. Introduction

In a low energy collision involving a metastable atom and another atom or molecule, a number of interesting processes may occur. These include elastic scattering, and, if the target is a molecule, rotational and perhaps vibrational excitation. More dramatic possibilities may be investigated when the electronic excitation energy of the metastable atom exceeds the ionization potential of the target. Of particular interest are the following reactions involving metastable helium:

\[ \text{He}^* + \text{H} \rightarrow \text{He} + \text{H}^+ + e^- \]  \hspace{1cm} (1)
\[ \rightarrow \text{HeH}^+ + e^- \hspace{1cm} (PI) \]

\[ \text{He}^* + \text{H}_2 (j) \rightarrow \text{He}^* + \text{H}_2 (j') \]
\[ \rightarrow \text{He} + \text{H}_2^+ + e^- \hspace{1cm} (PI) \]
\[ \rightarrow \text{HeH}_2^+ + e^- \hspace{1cm} (AI) \]
\[ \rightarrow \text{He} + \text{H} + \text{H}^+ + e^- \]

These processes illustrate elastic scattering, rotational excitation (from state j to j'), Penning ionization (PI), and associative ionization (AI). Several experiments\textsuperscript{1-8} have measured ionization cross sections for He(2^1S) + H, He(2^3S) + H, and He(2^3S) + H_2. This part of the thesis will deal with calculations on the latter system. We shall use the term Penning ionization to refer to all ionization channels.
From the theoretical point of view, this type of reaction is very interesting, but rather difficult to treat\textsuperscript{9-18}. No longer valid is the standard technique of constructing real, adiabatic potential curves, and then solving the scattering equations using the Born-Oppenheimer approximation. The problem arises because of the nature of the solutions to the electronic Hamiltonian (at a fixed nuclear geometry). For $E$ close to some resonance energy $E_r > 0$, the exact wavefunctions are characterized by a large amplitude for the electrons to be "bound" in a He* - H (or H$_2$) configuration, but asymptotically these solutions become oscillatory Coulomb functions. At time $t = 0$ a wave packet must be formed to represent the "bound" state, such that the asymptotic oscillations of the eigensolutions destructively interfere. As the system (still with fixed nuclei) evolves in time, the initial phase relationship between the eigensolutions is lost, and the amplitude of the asymptotic form of the wave packet increases. This corresponds to a net outward flux of ionized electrons.

The ordinary variational method\textsuperscript{19} is not intended for the determination of wavefunctions for energies greater than zero. A continuum of states lies between zero energy and $E_r$, and it is impossible to orthogonalize an arbitrary finite set of trial functions to all of these states.

An effective, although not completely rigorous formalism has been developed to calculate adiabatic potential curves in this situation\textsuperscript{10}. The "stabilization method" involves using particular care in choosing a trial basis set which corresponds to one's intuitive notion of which configurations should contribute most to the "bound" part of the wavefunction. Only orbitals which decay asymptotically are permitted. It is
found that wavefunctions may be constructed which seem to correspond well
to the exact solution at short range, but which asymptotically decay.
For a particular nuclear geometry, the range of energies near \( E_r \) for which
"bound" solutions exist is called \( \Gamma \). It can be shown that\(^{18}\)
\[
\Gamma = 2\pi \rho \left| \langle \psi_s | H_{el} - E_r | \chi \rangle \right|^2
\]  
(2)

where \( \rho \) is the density of continuum states, \( \psi_s \) is the stabilized, asymptotically decaying wavefunction, and \( \chi \) is a continuum function describing the ejected electron and the molecular ion.

Equation (2) is similar in form to the standard result from perturbation theory for the transition rate from a discrete state to a continuum\(^{20}\). This analogy becomes apparent in the rigorous derivation using Feshbach projection operators\(^{21}\). To suggest this analogy, and to provide an alternative to the wave packet interpretation of PI discussed previously, it is instructive to consider the matrix elements of \( H_{el} \) with respect to a particular basis set. We construct this set by beginning with \( \psi_s \) and then adding a complete set of continuum functions, \( \{ \chi^\perp_k \} \), corresponding to the molecular ion \( \text{HeH}_2^+ \), plus an ejected electron of wavevector \( \mathbf{k} \). To form an orthogonal basis we must redefine each \( \chi^\perp_k \):
\[
\chi^\perp_k = \chi^\perp_k - \langle \psi_s | \chi^\perp_k \rangle \psi_s
\]  
(3)

This insures that \( \chi^\perp_k \) is orthogonal to \( \psi_s \). Since \( \psi_s \) is not an exact eigenfunction, we expect transitions to other "states" \( \chi^\perp_k \) to depend on the matrix element
\[
\langle \psi_s | H_{el} | \chi^\perp_k \rangle = \langle \psi_s | H_{el} \left[ | \chi^\perp_k \rangle - \langle \psi_s | \chi^\perp_k \rangle | \psi_s \rangle \right]
\]  
(4)
\[ = \langle \psi_s | H_{el} | X_K^r \rangle - \langle \psi_s | H_{el} | \psi_s \rangle \langle \psi_s | X_K^r \rangle \]
\[ = \langle \psi_s | H_{el} - E_r | X_K^r \rangle \]

The transition rate is determined by squaring this quantity and integrating over the continuum states $X_K^r$ with energy close to $E_r$. This accounts for the density of states factor in Equation (2).

A satisfactory theoretical treatment of the scattering processes in Equations (1) is achieved within the Born-Oppenheimer approximation by using the potential function $V$ determined by the stabilization method, but adding an imaginary "width" $-i\Gamma/2$\textsuperscript{22}. This is analogous to the optical potential\textsuperscript{23} used in nuclear physics to account for absorption. Roughly speaking, the modulus of the wavefunction is proportional to

\[ \left| e^{\exp \left[ -i (V - i \Gamma/2) t / \hbar \right]} \right|^2 = e^{\exp \left[ -\Gamma t / \hbar \right]} \]

This decay corresponds to the gradual loss of metastable atoms in the ionization process.

Cohen and Lane have considered\textsuperscript{12} the real and imaginary parts of the $2^2\Pi^+$ interaction of He($2^3S - H$, He($2^1S) - H$, and He($2^3S - H_2$). They used these complex potentials to compute elastic and ionization cross sections. The ratio of the calculated cross section for PI of H by the singlet and triplet metastable atom is in good agreement with the experimental\textsuperscript{3} ratio, and the process seems well understood. However, their calculations of the PI cross section for He($2^3S$) on $H_2$ are an order of magnitude smaller than experiment\textsuperscript{3} for $E = 0.05$ eV. Certain limitations of this latter calculation warrant further study. Rather than rigorously including the full
(non-spherical) potential, Cohen\textsuperscript{24} used simpler potentials corresponding to fixed orientations of the H\textsubscript{2} ("end-on" and "broadside" collisions). This provided approximate upper and lower bounds for the PI cross section. Such an approach is not so crude as to cause a factor of ten disagreement with experiment if the potentials were exact. It is more likely that the smallness of the width, coupled with the strongly repulsive real potential surface, makes the PI cross sections extremely sensitive to the asymptotic form of $\Gamma$. This problem was not present in the He$^*$ - H calculations, because in this case the real potential surface is attractive. The PI cross sections even at low energies are determined predominantly by the region where $\Gamma$ is more accurately known.

The present work was undertaken as an extension of the scattering calculations of Cohen and Lane. Elastic, rotational excitation, and PI cross sections for He(2\textsuperscript{3}S) - H\textsubscript{2} collisions have been obtained in the close-coupling approximation. The adaptation of Cohen's potential surface for this calculation is discussed in Section B. The formalism will be explained in Section C, and Section D will deal with the numerical techniques involved. The inclusion of the rotationally inelastic channels in the proper manner has led to a much better qualitative understanding of the collision process. As expected, a discrepancy still remains between the calculated and experimental PI cross sections. We have found, however, that a semi-empirical modification of $\Gamma$ in the region where Cohen's calculation is least accurate leads to satisfactory agreement with experiment. A semiclassical analysis of the theoretical cross sections suggests a very intuitive physical picture of the collision process. These results will all be discussed in Section D.
At the present time there is a great need for more experimental research in this area of resonance phenomena. Measurements of elastic cross sections, and for PI cross sections over a greater range of energy, would provide a much more stringent test of our models.

B. The Potential Surface

The potential curves (surfaces) used in the present work were calculated by Cohen. A detailed report of their calculation may be found elsewhere. In this section only more general comments pertaining to their application and interpretation will be made.

Figure 1 shows the geometry of the He* - H₂ molecular system. R is the internuclear separation of the H₂, the distance between the He* and the center of the H₂ molecule at a is X, and θ is the angle of orientation of the H₂. Three-center molecular potentials are difficult to evaluate; to facilitate the calculation, Cohen used a single-center expansion of the H₂ orbitals (about the point a). He calculated the potential V (real part) at θ = 0°, 22.5°, 45°, 67.5°, and 90° for several values of X between 2 a₀ and 18 a₀. In every case R is fixed at 1.4 a₀, the equilibrium internuclear separation of the isolated molecule. A posteriori, this seems a reasonable simplification to make. At the energies of interest (≤ 0.25 eV), vibrational excitation is not an open channel (when PI does not occur). Furthermore, the potential is strongly repulsive. The classical turning points occur at fairly large values of X, so that the equilibrium value of R would not be expected to change much during an adiabatic collision.

For the calculation of rotational excitation cross sections, it is convenient to expand the potential V(X,θ) as
Figure 1. Geometry of the He* - H₂ or HeH₂⁺ molecular system. Electronic orbitals are centered at a and b.
\[ V(X, \Theta) = \sum_{n=0}^{\infty} v_n(X) P_n(\cos \Theta) \]  \hfill (5)

Because of the symmetry of the \( H_2 \), only even values of \( n \) contribute.
Naturally, it was hoped that the series would converge quickly. If \( V \)
is known as a continuous function of \( \Theta \) for a particular \( X \), then all the
\( v_n \) are determined exactly by the formal relation
\[ v_n(X) = \frac{2n+1}{2} \int_0^\pi V(X, \Theta) P_n(\cos \Theta) \sin \Theta \, d\Theta \]  \hfill (6)

Because of the complexity of the structure calculations, Cohen did not
determine \( V \) at a sufficient number of values of \( \Theta \) for many of these inte-
grals to be evaluated accurately. At some values of \( X \) he determined \( V \)
only for \( \Theta = 0^\circ, 45^\circ, \) and \( 90^\circ \). For these \( X \) the assumption was made that
the first three terms were dominant in the series (5). The \( v_0(X) \), \( v_2(X) \),
and \( v_4(X) \) are the solutions to the three simultaneous equations
\[ v_0(X) P_0(\cos \Theta) + v_2(X) P_2(\cos \Theta) + v_4(X) P_4(\cos \Theta) \]  \hfill (7)
\[ = V(X, \Theta_\alpha) \]  \hfill \( \Theta_\alpha = 0^\circ, 45^\circ, 90^\circ \)

The results strongly suggest that this procedure gives an accurate expan-
sion of the potential. From Figure 2, it is seen that \( v_0 \) is indeed the
dominant term, and that \( v_4 \) is generally smaller than \( v_2 \). A further test
of this expansion was possible. At some values of \( X \), Cohen also computed
\( V \) at the intermediate angles \( \Theta = 22.5^\circ \) and \( 67.5^\circ \). At these \( X \), the \( v_n \)
were found by the above procedure and used to evaluate
\[ \sum_{n=0,2,4} v_n(X) P_n(\cos \Theta_\alpha) \]  \hfill (8)
\[ \Theta_\alpha = 22.5^\circ, 67.5^\circ \]
Figure 2. The real part of the potential surface $V = \sum_{n=0,2,4} V_n(X) P_n(\cos \theta)$ for He($2^3S$) - H$_2$. The functions $v_0$, $v_2$, and $v_4$ were determined from Cohen's calculation of $V(X, \theta)$ as discussed in the text.
Three-significant-figure agreement was obtained between this expression and Cohen's computed \( V \) at \( X = 7.0 \ a_0 \).

Special care was taken to insure the proper long range form of the potential. Cohen obtained the shallow well characteristic of a potential repulsive at short range but weakly attractive asymptotically. For \( X \geq 18 \ a_0 \) (the largest value used by Cohen), the potential was constrained to approach \( -C_\parallel /X^6 \) for \( \theta = 0^\circ \) and \( -C_\perp /X^6 \) for \( \theta = 90^\circ \), where Dalgarino and Victor\(^25\) have given \( C_\parallel = 135.9 \) a.u. and \( C_\perp = 96.5 \) a.u. (± 2%). Since \( v_4(X) = 0 \) for \( X \geq 18 \ a_0 \), \( C_\parallel \) and \( C_\perp \) are sufficient to determine the long range form of \( v_0 \) and \( v_2 \).

Numerical values of \( v_0, v_2, \) and \( v_4 \) are tabulated in Table 1, and the curves are plotted in Figure 2. An interesting feature of \( v_0 \) is the "hump" occurring for \( X = 4 - 5 \ a_0 \). Cohen has discussed its interpretation in his thesis. It appears to be an effect of the same sort used to derive the pseudopotential describing the \( e^- - He(1^1S_0) \) repulsion, which was discussed in Part I in connection with the cavity model. The loosely-bound outer electron of \( He(2^3S) \) must be orthogonalized to any adjacent closed-shell systems \([He(1^3S_0) \) or \( H_2(1^1S) \)], and this results in an effective short range repulsive interaction which may be added to the interaction potential of the \( He^+ \) core. This mechanism accounted for the existence and stability of cavities in liquid helium; here it will have an interesting effect on the scattering cross sections.

So far little attention has been given to the width \( \Gamma \). Cohen has improved his original rough calculation by including his full variational wavefunction\(^26\). His latest \( \Gamma \) is only a factor of two to three larger than the original estimate at large values of \( X \). It was found that \( \Gamma \) is very
Figure 3. The solid curves show the widths $\Gamma$ for ionization in the He($2^3S$) - H system due to Miller and Schaeffer, and in the He($2^3S$) - H$_2$ system calculated by Cohen. The dashed line shows the modification of Cohen's $\Gamma$ which yielded a much improved value of the Penning ionization cross section at 0.04 eV.
insensitive to \( \theta \); hence the present calculations were simplified by assuming \( \Gamma = \Gamma(X) \) only. Figure 3 is a semilog plot of the width for He(2\(^3\)S) – H\(_2\) calculated by Cohen, and the modification eventually necessary to improve agreement with experiment. Miller and Schaeffer's\(^{10}\) calculation of the width for He(2\(^3\)S) – H is included for comparison.

The nearly linear behavior of \( \ln \Gamma \) as a function of \( X \) is not surprising since \( \Gamma \) depends on the overlap of exponentially decaying orbitals a distance \( X \) apart. What is surprising is that for \( X \geq 6 \) a\(_0\), the decay is so much more rapid for the He* – H\(_2\) width than for the He – H width. The calculations of PI cross sections for \( E \leq 0.10 \) eV are sensitive to \( \Gamma \) in this region. In view of the large discrepancy between theory and experiment for \( E = 0.05 \) eV, it is sensible to view the rapid decay of the width with some skepticism.

We shall present a naive argument which suggests that at long range, the width for ionization of H should decay at about the same rate as the width for ionization of H\(_2\). In the case of H, the major contribution to the width comes from an integral of the type

\[
\int \left[ \frac{1}{r_{12}} + \frac{1}{r_{13}} \right] |s'(1)\phi(2)|s'(3)\, d^3r_1\, d^3r_2\, d^3r_3
\]

(The primes on the final helium 1s orbitals indicate a change of orbital exponent, and \( \phi_H \) is a continuum Coulomb function centered on H.) The major part of this integral comes from the perturbing Coulomb interaction of the electrons:

\[
\int |s(1)\phi(2)|s(3)\, d^3r_1\, d^3r_2\, d^3r_3
\]
Table 1.

Numerical Form of the He(2^3S) - H₂ Potential.

Values not calculated by Cohen were obtained by cubic spline interpolation.

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<th>x (a₀)</th>
<th>v₀ (a.u.)</th>
<th>v₂ (a.u.)</th>
<th>v₄ (a.u.)</th>
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<tr>
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<td>0.10880</td>
<td>0.08768</td>
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<td>0.00129</td>
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</tr>
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<tr>
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<td>9.3 x 10⁻⁶</td>
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<td>1.5 x 10⁻⁷</td>
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<tr>
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<td>-2.6 x 10⁻⁷</td>
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<tr>
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<td>-1.2 x 10⁻⁷</td>
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<td>-8.1 x 10⁻⁸</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>30.0</td>
<td>-1.5 x 10⁻⁷</td>
<td>-3.6 x 10⁻⁸</td>
<td>0.0</td>
</tr>
</tbody>
</table>
\( \phi_H(2) \) is centered on \( H \), but has a peak which overlaps strongly the \( 2s_{\text{He}} \) orbital. All the other orbitals except \( 1s_{\text{H}}(1) \) are centered on \( \text{He} \). The integral therefore depends critically on the overlap of the \( 1s_{\text{H}}(1) \) orbital with the \( \text{He}(2^3S) \) core.

In the case of \( H_2 \), a similar argument suggests that the most important part of the width should come from the following integral:

\[
\sum |s_{H_2}(1) s_{\text{He}}(2) s_{\text{He}}(3) s_{H_2}(4) \left[ \frac{1}{r_1} + \frac{1}{r_2} \right] s_{\text{He}}'(1) \phi_{H_2}(2) s_{\text{He}}'(3) d^3r_1 d^3r_2 d^3r_3 d^3r_4
\]

\( \propto \sum |s_{H_2}(1) s_{\text{He}}(2) s_{\text{He}}(3) \left[ \frac{1}{r_1} + \frac{1}{r_3} \right] s_{\text{He}}'(1) \phi_{H_2}(2) s_{\text{He}}'(3) d^3r_1 d^3r_3\)

Here, too, the integral will depend critically in the overlap of the \( 1s_{H_2}(1) \) orbital with the \( \text{He}(2^3S) \) core. This orbital may be naively estimated by recalling the one-parameter variational calculation of Rosen:

\( 1s_{H_2}(1) 1s_{H_2}^{2}(4) \propto \exp[-\alpha(r_1+r_4)] \), where \( \alpha \approx 1.2 \) for the equilibrium internuclear separation of \( H_2 \). However, this approximation is most accurate when \( r_1 \) and \( r_4 \) are small. If electron 1 is close to the \( \text{He}(2^3S) \) core, it "sees" a parent charge of +1, because the other electron (4) almost completely shields the second photon. Hence it does not seem unreasonable to suggest that the significant overlap in integral (11) comes for a range of \( r_1 \) such that the orbital exponent of \( 1s_{H_2}(1) \) should be \( \approx 1 \).

This, of course, would make the \( H_2 \) width at long range much closer to the \( H \) width and much larger than that calculated by Cohen.

"A more cogent form of the above argument is to observe that \( \Gamma \) depends on the overlap at long range of orbitals determined by the variational method. It is known that the asymptotic form of a wavefunction may often be drastically altered without seriously affecting the total energy. It appears that the ionization width at long range may depend critically on the part of the \( H_2 \) wavefunction least well determined by
the variational method. If this is the case, the eventual modification of the width for $X \geq 6 a_0$ would seem to be justifiable.

C. Scattering Theory

1. Close Coupling Formalism: The Formation and Solution of Schroedinger's Equation in Matrix Form

This section will present the formalism of Arthurs and Dalgarno\textsuperscript{28} for the scattering of a particle by a rigid rotator. For heuristic reasons, the matrix form of the scattering equations will be explicitly developed, and the physical interpretation of the well-known scattering boundary conditions will be discussed. Subsequent sections will deal with the numerical solution of the matrix scattering equations, and the determination of the $S$ matrix from the asymptotic form of this solution.

a. Derivation of the Coupled Equations

The Hamiltonian of a rigid rotator ($H_2$) interacting with a structureless point particle ($He^*$) is (in the center of mass frame and using atomic units $\hbar = e = m_e = 1$)

$$H = H_R - \frac{1}{2m} \nabla_X^2 + V(\hat{X}, \hat{R})$$ \hspace{1cm} (13)

where $m$ is the reduced mass of the He* - H\textsubscript{2} system in a.u., and $H_R$ is the Hamiltonian of a rigid rotator with moment of inertia $I$. The spectrum of $H_R$ is defined by

$$H_R Y_{j m_j}(\hat{R}) = \frac{j(j+1)}{2I} Y_{j m_j}(\hat{R})$$ \hspace{1cm} (14)
for $j = 0, 1, 2, \ldots$, and $m_j = -j, -j+1, \ldots, +j$. Recalling the discussion of the form of $V$ in Section B, we find it convenient to write

$$H = H_0 + H_1$$  \hspace{1cm} (15)

where

$$H_0 = H_R - \frac{1}{2m} \nabla^2_{\chi} + \left[ v_0 (\chi) - \kappa \Gamma (\chi) / 2 \right]$$  \hspace{1cm} (16)

and

$$H_1 = \sum_{n=2,4} v_n (\chi) P_n (\cos \Theta)$$  \hspace{1cm} (17)

This separates $H$ into two parts. The first is relatively easy to handle; the second may be considered a perturbation. For simplicity we shall assume $\Gamma = 0$. This will not affect the present development, and the general case of $\Gamma \neq 0$ will be discussed later.

Consider the equation

$$\left( H_0 - E \right) \Psi^0 = 0$$  \hspace{1cm} (18)

It is necessary to choose a set of quantum numbers to label the eigen-solutions to this equation. Since the potential term of $H_0$ is radial (depends only on $\chi$), the particle exerts no torque on the rotator, and hence orbital and rotational angular momentum are separately conserved. A naive choice of a complete set of quantum numbers would thus be $(j, m_j, \ell, m_\ell)$, where $j(\ell)$ is the rotational (orbital) angular momentum quantum number, and $m_j (m_\ell)$ its projection along some space-fixed $z$ axis. It is more cunning, however, to take advantage of the conservation of total angular momentum, and use the set $(j, \ell, J, M)$. $J$ is the total angular momentum quantum number, and $M$ its projection. Basis sets for these two
sets of quantum numbers are related, of course, by a unitary matrix whose elements are the appropriate Clebsch-Gordan coefficients.\(^{29}\)

For \(\Psi^0_{j_2j_1JM}\) to be a solution to (18), it must have the form

\[
\Psi^0_{j_2j_1JM} = \frac{1}{X} \ U^0_{j_2j_1JM} (X) \ Y_{j_2j_1JM} (\hat{r}, \hat{R})
\]

where

\[
Y_{j_2j_1JM} (\hat{r}, \hat{R}) = \sum_{m_j = -j}^{j} \ \sum_{m_z = -l}^{l} \ (j_{\ell} m_j, m_z | j_{2} l_{1}JM) \ Y_{m_j} (\hat{r}) Y_{m_z} (\hat{R})
\]

For any total (translational and rotational) energy \(E = k^2/2m > 0\) (\(h = 1\)), we can generate the exact solution \(\Psi^0_{j_2j_1JM}\) to (18) by solving a radial equation for \(U^0_{j_2j_1JM}\). This is done by substituting (15), (19), and (20) into (18) to obtain

\[
\left[ \hat{H}_R - \frac{1}{2m} \ \frac{d^2}{dX^2} + \frac{l^2}{2mX^2} + V_0 (X) - \frac{k^2}{2m} \right] \ \frac{1}{X} \ U^0_{j_2j_1JM} (X) \ Y_{j_2j_1JM} (\hat{r}, \hat{R}) = 0
\]

and then separating the radial equation:

\[
\left[ \ \frac{d^2}{dX^2} + k_j^2 \ - \ \frac{\ell(j+1)}{X^2} - 2mV_0 (X) \right] \ U^0_{j_2j_1JM} (X) = 0
\]

where

\[
k_j^2 = k^2 - 2m \ \frac{j(j+1)}{2I}
\]

In light of this development, what must be done to solve the complete equation

\[
(H_o + H_i - E) \ \Psi = 0 \ \ ?
\]

We have shown that \(H_o\) is diagonal in the basis \(\Psi^0_{j_2j_1JM}\). We shall solve (24) by choosing a basis set \(\Psi_{j_2j_1JM}\) such that \(H\) is diagonal in \(J\) and \(M\). However,
because of $H_1$, $H$ may have matrix elements between states $\psi_{j\ell JM}$ and $\psi_{j'\ell' JM}$.

Physically this means that the $\psi_{j\ell JM}$ are still approximate eigenstates, but the internal torques in the system may cause transitions between them.

Let us try to find a solution to (24) of the form

$$\Psi_{JM} = \sum_{n=1}^{N} \frac{1}{X} U_{jn} l_n JM (X) \psi_{j_n l_n JM} (X, \hat{R})$$

(25)

Since four quantum numbers are necessary to specify a unique eigenstate, we expect that more than one solution $\Psi_{JM}$ will exist. If we substitute (25) into (24), multiply by $Y_{j'i'\ell'JM}$ for $i=1,2,\ldots,N$ and integrate over $\hat{X}$ and $\hat{R}$ we obtain $N$ coupled equations which may be written in matrix form as follows:

$$\begin{bmatrix}
\frac{d^2}{dX^2} + k^2 - \nu_0 (X) - \frac{\nu_n (X)}{X^2} \\
\ldots \\
\frac{d^2}{dX^2} + k^2 - \nu_0 (X) - \frac{\nu_n (X)}{X^2}
\end{bmatrix}
\begin{bmatrix}
c_{1n} \\
\vdots \\
c_{Nn}
\end{bmatrix} +
\begin{bmatrix}
U_{j1JM} (X) \\
\vdots \\
U_{jNJM} (X)
\end{bmatrix} = 0$$

(26)

The coupling matrix $C$ is, in general, nondiagonal. The $(i,m)$ element is given by

$$C_{im} = \nu_2 (X) f_{im}^{(2)} (J, M) + \nu_4 (X) f_{im}^{(4)} (J, M)$$

(27)

where

$$f_{im}^{(n)} (J, M) = \int y_{j_n l_n JM} (X, \hat{R}) P_n (\cos \Theta) y_{j m l_m JM} (X, \hat{R}) dX d\hat{R}$$

(28)

This quantity may be expressed\(^{30}\) in terms of Clebsch-Gordan coefficients and Racah coefficients $(W)$:

...
\[ f_{(n)}^{(m)} (J, M) = (-1)^{J} (2J + 1)^{J} \left[ (2J + 1)(2l + 1)(2m + 1)(2p + 1) \right]^{\frac{1}{2}} \] 
\[ \times (l \ l_m n_0 l \ l_m n_0)(j \ j_m n_0 j \ j_m n_0) W (j \ j \ l \ l \ m \ j \ m \ j \ n) \] 

There are 2N linearly independent solutions to Equation (26), N of which are regular at the origin \((U(0) = 0)\). These may be explicitly exhibited in the special case \(v_2 = v_4 = 0\), when the coupling matrix \(C\) vanishes and Equation (26) separates into N equations of the type (22).

Denoting the \(p^{th}\) regular solution by a superscript, we have

\[
\begin{bmatrix}
U^{(p)}_{j_1 l_1 j_{1M}} \\
\vdots \\
U^{(p)}_{j_n l_n j_{JM}}
\end{bmatrix}
= 
\begin{bmatrix}
o \\
\vdots \\
o \\
U_{j_p l_p j_{JM}}
\end{bmatrix}
\]

The general form of the \(p^{th}\) regular solution to (26) should now be clear. It will correspond to the system beginning the the approximate eigenstate \(\Psi_{jp l p JM}\). The off diagonal coupling terms \(v_2 f_{(2)}^{(2)} (J, M) + v_4 f_{(4)}^{(4)} (J, M)\) will lead to non-zero values of \(U^{(p)}_{j_p l_p j_{JM}} = U^{(p)}_{j_p l_p j_{JM}}\) which are related to the amplitude for a transition to the approximate eigenstate \(\Psi_{j_p l_p JM}\).

The solution of equations of this type is called the close coupling approximation\(^{31}\). The method is approximate because the series (25) is truncated at a finite value of \(N\). However, for a particular \(J\), we are normally interested in solutions corresponding to an initial value \(j = 0, 1, \) or 2, and hence initial \(k\) in the range \(J-2\) to \(J+2\). If \(H_1\) is small it is natural to believe that the inclusion of states with \(j'\) very different from \(j\) is not necessary. Furthermore, the \(f_{(n)}^{(n)}\) vanish unless \(j\)
changes by an even number. For concreteness, we list the channels included in the scattering equations for a particular $J > 2$:

\[
\begin{align*}
  j_1 &= 0 & l &= J \\
  j_2 &= 2 & l_2 &= J+2 \\
  j_3 &= 2 & l_3 &= J \\
  j_4 &= 2 & l_4 &= J-2
\end{align*}
\] (31)

In order to establish rigorously the above interpretation of the $U_{j, l}^{J, \lambda, \mu}$, it is necessary to discuss the appropriate scattering boundary conditions. To motivate this procedure in the $N$ channel problem, it is instructive to start with the one channel case $N = 1$. Instead of the usual phase shift analysis, we shall establish the more easily generalized $S$ matrix approach.

b. Single Channel Boundary Conditions

A physical solution is desired which asymptotically corresponds to an incoming plane wave and an outgoing, spherical scattered wave which is modulated as a function of angle

\[
\psi = e^{ik\cdot X} + \frac{1}{X} \Psi(S) e^{ikX}
\] (32)

Mathematically we separate and solve the scattering equations by assuming a solution

\[
\psi \propto \sum_{l=0}^{\infty} (2l+1) \frac{1}{X} U_l(X) P_l(\cos \Theta)
\] (33)

The conditions thereby imposed on $U_l(X)$ are seen by expanding (33) using

\[
e^{ik\cdot X} = \sum_{l=0}^{\infty} (2l+1) i^l j_l(kX) P_l(\cos \Theta)
\] (34)
\[ \psi(\Theta) = \frac{1}{2\pi k} \sum_{k=0}^{\infty} \left( 2L+1 \right) \left( S_{\ell} - 1 \right) \mathcal{P}_{L} \left( \cos \Theta \right) \] 

Hence
\[ \psi = \sum_{k=0}^{\infty} \left( 2L+1 \right) i^{L} \left[ j_{\ell}(kX) + \frac{1}{2\pi k} i^{-L} \frac{\Gamma}{X} e^{ikX} (S_{\ell} - 1) \right] \mathcal{P}_{L} \] 

Since \( i^{-L} = e^{-i\pi/2} \) and
\[ j_{\ell}(kX) \sim \frac{1}{kX} \sin (kX - L\pi/2) \] 

\[ = \frac{1}{2\pi kX} \left[ e^{-i(kX - L\pi/2)} - e^{-i(kX - L\pi/2)} \right] \] 

we can express
\[ \psi \sim \frac{-1}{2\pi k} \sum_{k=0}^{\infty} \left( 2L+1 \right) i^{L} \frac{1}{X} \left[ e^{-i(kX - L\pi/2)} - e^{-i(kX - L\pi/2)} \right] \mathcal{P}_{L} \] 

This gives the required asymptotic form of \( U_{\ell} \):
\[ U_{\ell}(X) \sim e^{-i(kX - L\pi/2)} - S_{\ell} e^{-i(kX - L\pi/2)} \] 

\( c. \) N Channel Boundary Conditions

What should be the physical form of the solution to the N channel problem for large values of \( X \)? If the initial state of the rotator is \((j_{p},m_{j_{p}})\), there must be an incoming plane wave incident on the molecule in this state, plus N different outgoing spherical waves corresponding to the motion after a transition to \((j_{i},m_{j_{i}})\) has taken place:\n
\[ \psi_{j_{p}m_{j_{p}}} \sim e^{i\hat{\mathbf{k}}_{i} \cdot \hat{\mathbf{X}}} Y_{j_{p}m_{j_{p}}} (\hat{\mathbf{R}}) \] 

\[ + \sum_{n=1}^{N} \left( \frac{k_{s}}{k_{i_{n}}} \right)^{2} \frac{1}{k_{j_{p}}} \sum_{j_{i}m_{j_{i}}} f^{j_{i}}(\hat{\mathbf{R}}) e^{i\hat{k}_{s} \cdot \hat{\mathbf{X}}} Y_{j_{i}m_{j_{i}}} (\hat{\mathbf{R}}) \]
(The summation includes the elastic scattering case: \(n = p\)). It can be shown that this may be expressed

\[
\Psi_{j_p, j_p} \sim \frac{\lambda \pi \lambda^2}{k_{j_p}} \sum_{j = 0}^{\infty} \sum_{M = -J}^{J} \sum_{J' = |J - j_p|}^{J + j_p} (j_p, l m_j o, j_p, l, J, M) \times \lambda^{l + (2l + 1)} \sum_{n = 1}^{N} \frac{i}{\chi} U_{j_p, l, n, J, M}(X) \mathcal{Y}_{j_p, l, n, J, M}(\hat{X}, \hat{R})
\]

(40)

for the particular choice of the asymptotic form of \(U_{j_p, l, J, M}\) given by

\[
U_{j_p, l, J, M} \sim \delta_{j_p} \left( -i (k_{j_p} X - \ell_p \pi/2) \right) \left( \frac{k_{j_p}^2}{k_{j_x}^2} \right)^{\ell_p} \sum_{i_p = -\ell_p}^{\ell_p} \sum_{j_x = -\ell_x}^{\ell_x} e^{i (k_{j_x} X - \ell_x \pi/2)}
\]

(41)

The derivation is lengthy, and results in a complicated form for the scattering amplitudes:

\[
f_j \sum_{j_p m_{j_p}} \rightarrow j_i m_{j_i} = \sum_{j = 0}^{\infty} \sum_{M = -J}^{J} \sum_{J' = |J - j_p|}^{J + j_p} \sum_{\ell = -\ell'}^{\ell'} \left( \lambda^{l - \ell'} \pi \lambda^2 (2\ell + 1)^{\ell} \right) \chi (j_p, l m_j o, j_p, l, J, M)(X) e^{i (k_{j_x} X - \ell_x \pi/2)}
\]

(42)

Expanding as in the one channel case, and using the above expression for \(f\), the final result is

\[
\Psi_{j_p, j_p} \sim \frac{\lambda \pi \lambda^2}{k_{j_p}} \sum_{j = 0}^{\infty} \sum_{M = -J}^{J} \sum_{J' = |J - j_p|}^{J + j_p} \left( j_p, l m_j o, j_p, l, J, M \right) \times \lambda^{l + (2l + 1)^{\ell/2}} \sum_{n = 1}^{N} \left[ \delta_{j_p, l} \delta_{j_p, n} e^{-i (k_{j_p} X - \ell_p \pi/2)} - \left( \frac{k_{j_p}^2}{k_{j_p}^2} \right)^{\ell_p} \sum_{\ell = -\ell_p}^{\ell_p} e^{i (k_{j_x} X - \ell_x \pi/2)} \right] \mathcal{Y}_{j_p, l, n, J, M}
\]

(43)

The expression in brackets is independent of \(M\). It defines the desired asymptotic form of the solutions \(U_{-j_p, l, J, M}(X)\) for a given \(J\). The Numerov algorithm may be used to generate \(N\) linearly independent regular solutions \(\psi^{(p)}(p = 1, 2, \ldots, N)\) to Equation (26), but there is no guarantee
they will have the form (43). The next section will describe the procedure for taking linear combinations of the computed solutions \( Y^{(p)} \) to form

the desired solutions \( U^{(p)}_{j l} \), and hence evaluate the S matrix.

2. Determination of the S Matrix and Cross Sections

a. The S Matrix

For this section we will suppose that \( N \) linearly independent regular solutions to Equation (26) have been generated. We desire to take appropriate linear combinations of them to form solutions which behave for large \( X \) as

\[
U^{(p)}_{j l} \overset{\propto}{\sim} \sum_{i} e^{-i(k_{j} X - l_{i} \pi/2)} \left( \frac{k_{j}}{k_{i}} \right)^{l_{i}} \sum_{\ell} e^{i(k_{j} X - \ell_{i} \pi/2)}
\]

For a given \( J, M \) these functions may be represented as elements of a square matrix of indices \( i \) and \( p \). The \( \ell^{\text{th}} \) column represents the \( \ell^{\text{th}} \) vector solution to Equation (26); the components of this solution are labelled by the index \( i \).

For brevity of notation, let us drop all indices except \( i \) and \( p \).

We write the exponentials of Equation (44) in terms of the spherical Bessel functions and Handel functions\(^{33}\) as follows:

\[
h_{p}^{\pm} = n_{p} (k_{j} X) \pm \imath f_{p} (k_{j} X)
\]

\[
\overset{\propto}{\sim} \frac{1}{k_{j} X} \left[ \cos (k_{j} X - l_{p} \pi/2) \pm \imath \sin (k_{j} X - l_{p} \pi/2) \right]
\]

Hence

\[
e^{\pm i(k_{j} X - l_{p} \pi/2)} = k_{j} X h_{p}^{\pm}
\]
and we can rewrite (44) as

\[ U_{\lambda p} \xrightarrow{x \to \infty} \delta_{\lambda p} \, k_{j_p} \times h_p^- - \left( \frac{k_{j_p}}{k_{j_1}} \right)^{\frac{1}{2}} \, S_{\lambda p} \, k_{j_1} \times h_1^+ \]  \hspace{1cm} (47)

This equation becomes more transparent in matrix form. Thus we may write

\[ U \xrightarrow{x \to \infty} \begin{bmatrix} k_{j_1} \times h_1^- & 0 & \cdots & 0 \\ 0 & k_{j_N} \times h_N^- \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & k_{j_N} \times h_N^- \end{bmatrix} \begin{bmatrix} k_{j_1} \times h_1^+ & 0 & \cdots & 0 \\ 0 & k_{j_N} \times h_N^+ \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & k_{j_N} \times h_N^+ \end{bmatrix}^{-\frac{1}{2}} \begin{bmatrix} S_{11} & \cdots & S_{1N} \\ \vdots & \ddots & \vdots \\ S_{N1} & \cdots & S_{NN} \end{bmatrix} \begin{bmatrix} k_{j_1} \times h_1^- & 0 & \cdots & 0 \\ 0 & k_{j_N} \times h_N^- \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & k_{j_N} \times h_N^- \end{bmatrix}^{\frac{1}{2}} \]  \hspace{1cm} (48)

In terms of these matrices, we write

\[ U \xrightarrow{x \to \infty} H^- - H^+ K^{-\frac{1}{2}} S K^{\frac{1}{2}} \]  \hspace{1cm} (49)

where

\[ H_{\lambda p}^\pm = \delta_{\lambda p} \, k_{j_p} \times h_p^\pm \]  \hspace{1cm} (50)

and

\[ k_{\lambda p} = \delta_{\lambda p} \, k_{j_p} \]  \hspace{1cm} (51)

Now let the columns of the matrix \( \bar{Y} \) be the computed solutions to Equation (26). In general, \( \bar{Y} \) will not have the asymptotic form of \( \bar{U} \) in Equation (49). We can, however, write in general

\[ \bar{Y} \xrightarrow{x \to \infty} H^+ A + H^- B \]  \hspace{1cm} (52)
This expresses each column of $\mathbf{Y}$ as a linear combination of the $N$ linearly independent columns of $\mathbf{H}^-$ and the $N$ linearly independent columns of $\mathbf{H}^+$. We may always solve uniquely for $\mathbf{A}$ and $\mathbf{B}$ since the $2N$ columns of $\mathbf{H}^+$ and $\mathbf{H}^-$ are linearly independent and span all solutions.

The matrices $\mathbf{A}$ and $\mathbf{B}$ are easily found if $\mathbf{Y}$ is known at two points (labelled 1 and 2). In particular, for two large separations $X_1$ and $X_2$ we have

$$
\begin{align*}
\mathbf{H}_1^- \mathbf{A} + \mathbf{H}_1^+ \mathbf{B} &= \mathbf{Y}_1 \\
\mathbf{H}_2^- \mathbf{A} + \mathbf{H}_2^+ \mathbf{B} &= \mathbf{Y}_2
\end{align*}
$$

Multiplying (53) by $\mathbf{H}_2^+$ (on the left) and (54) by $\mathbf{H}_1^+$ (on the left), and observing that $\mathbf{H}_1^+$ and $\mathbf{H}_2^+$ commute, we solve for $\mathbf{A}$. A similar procedure gives $\mathbf{B}$. The result is

$$
\begin{align*}
\mathbf{A} &= \mathbf{D}^{-1} \left( \mathbf{H}_2^+ \mathbf{Y}_1 - \mathbf{H}_1^+ \mathbf{Y}_2 \right) \\
\mathbf{B} &= -\mathbf{D}^{-1} \left( \mathbf{H}_2^- \mathbf{Y}_1 - \mathbf{H}_1^- \mathbf{Y}_2 \right)
\end{align*}
$$

where

$$
\mathbf{D} = \mathbf{H}_2^+ \mathbf{H}_1^- - \mathbf{H}_1^+ \mathbf{H}_2^-
$$

We now observe that from Equation (52)

$$
\mathbf{S} = -\mathbf{K}^{Y_2} \mathbf{B} \mathbf{A}^{-1} \mathbf{K}^{-Y_2}
$$

Comparing this with Equation (49) for $\mathbf{U}$ we obtain the desired result:

$$
\mathbf{Y} \mathbf{A}^{-1} \xrightarrow{x \to \infty} \mathbf{H}^- + \mathbf{H}^+ \mathbf{B} \mathbf{A}^{-1}
$$
It should be noted in conclusion that the above derivation is not the normal procedure for obtaining $S$. If the solutions $Y$ are real, it is easier to specify boundary conditions in terms of a real $R$ matrix, from which the $S$ matrix is obtained. This technique has been treated elsewhere\textsuperscript{30,35}. In the present calculation, the evaluation of the $R$ matrix is not in general appropriate, because the solutions $Y$ are complex when the width $\Gamma$ is included. Therefore, whenever $\Gamma \neq 0$, Equation (58) was used for the $S$ matrix.

b. Formulas for Cross Sections

This section is concluded by presenting formulas for various total cross sections (i.e., integrated over angle) in terms of the $S$ matrix.

If $\Gamma = 0$, the standard result\textsuperscript{28} is

$$
\sigma_{j \rightarrow j'} = \frac{\pi}{(2j+1)} k_j^2 \sum_{J=0}^{\infty} \sum_{J'} (2J+1) | T_{J \rightarrow J'} |^2
$$

(59)

where the transition matrix $T$ is defined\textsuperscript{28} by

$$
T^J = I - S^J
$$

(60)

Equation (59) represents an average over initial states of the rotator ($m_j$) and a sum over final states ($m_{j'}$). The result remains valid even when $\Gamma \neq 0$.

The PI cross section is derived by using the asymptotic form of the scattering wavefunction to calculate the net inward flux of particles into the scattering region. The case of interest is when the initial state of the rotator is $j = 0$, $m_j = 0$. Then Equation (43) becomes

$$
\psi_{00} \sim \sum_{k=0}^{\infty} \frac{\alpha k^h}{k_s} \sum_{J=0}^{\infty} \frac{i^J (2J+1)}{V^J} \sum_{n=1}^{\infty} \left[ \frac{\delta_{0J} \delta_{0n}}{k_{nJ}} \right] e^{-\gamma (k_s X - \mu n)} \left[ \frac{k_{nJ}}{k_{nJ}} \right] \sum_{J' \rightarrow J} \sum_{n' \rightarrow n} e^{i (k_{nJ} X - \mu n' \pi^{1/2})} y_{J',n'} y_{J,n}
$$

(61)
It is necessary to evaluate the radial flux

\[ \frac{\hbar}{2im} \left[ \psi_{oo}^* \frac{\partial \psi_{oo}}{\partial X} - \psi_{oo} \frac{\partial \psi_{oo}^*}{\partial X} \right] \]  \hspace{1cm} (62)

and then to integrate this over \( \hat{\mathbf{k}} \) and \( \hat{\mathbf{r}} \). This integration allows us to utilize the orthogonality of the angular functions,

\[ \int d\hat{\mathbf{k}} \int d\hat{\mathbf{r}} \, Y_{j'}^o \delta_{J'O} \, Y_{10} \, \delta_{JM} = \delta_{jJ} \delta_{ee'} \delta_{\alpha\alpha'} \delta_{MM'}, \]  \hspace{1cm} (63)

and evaluate the flux associated with each partial wave and each channel separately. Thus, the radial part of the \( J \)th term of Equation (61) may be written

\[ \frac{\hbar}{m} \frac{(2J + 1)^{1/2}}{k_0 \mu} \left\{ \left[ e^{-i(k_0 \mu - J \pi/2)} - \sum_{oJ \to oJ} e^{i(k_0 \mu - J \pi/2)} \right] \right. 
\[ + \sum_{n \neq l} \left[ \frac{(-k_0 l_n)^2}{k_0 n_n} \sum_{oJ \to j_n l_n} e^{-i(k_n \mu - l_n \pi/2)} \right] \} \]  \hspace{1cm} (64)

where the restriction \( n \neq l \) in the summation is because the \( n = l \) term \((j_1 = 0, k_1 = J)\) has been explicitly written. Each bracketed expression may be used to calculate the radial flux in the corresponding channel.

The result is the net number of particles with angular momentum \( J \) leaving the scattering region:

\[ \frac{\hbar}{m} \frac{\pi (2J + 1)}{k_0^2} \left[ 1 - \left| \sum_{oJ \to oJ} \right|^2 - \sum_{n \neq l} \left| \sum_{oJ \to j_n l_n} \right|^2 \right] \]  \hspace{1cm} (65)

The term in brackets is the \((1,1)\) element of \( 1 - (S^J)^* S^J \); it is clear that the amount of flux "lost" into the PI channels is determined by the lack of unitarity of the \( S \) matrix. To derive the cross section for PI of \( H_2 \) (in the \( j = 0 \) state), we note that since Equations (39), (43), and (61) are normalized to one incoming particle per unit volume, the incident
flux is just \( \frac{4k_0}{m} \). Forming the ratio of the number of particles which undergo PI [minus one times (65), summed over J] to the incident flux, we obtain

\[
\frac{\sigma_{\text{r}}}{\sigma_{\text{ri}}} = \frac{\pi}{k_0^2} \sum_{j=0}^{\infty} (2j+1) \left[ 1 - \left( S^j \right)^* \left( S^j \right) \right]_{\nu,1} 
\]

(66)

D. Numerical Techniques

Because of the complexity of the coupled differential equations to be solved, a great deal of time was spent optimizing the computer programs used for the calculations. Fast and accurate algorithms were necessary to avoid loss of numerical accuracy and excessive programming time. This section will discuss the implementation of the Numerov algorithm and other methods used to solve Equations (26), (55), and (58), as well as the accuracy and reliability of the results achieved.

1. Case Where Potential is Real

Equation (26) may be compactly written in the form

\[
\frac{d^2}{dX^2} Y = G(X) Y 
\]

(67)

For the present we assume all quantities are real. \( Y \), of course, is an \( N \times N \) matrix, each column containing one of \( N \) linearly independent solutions regular at the origin. If \( Y \) is known initially at two values of \( X \), say \( X_{n-1} \) and \( X_n = X_{n-1} + h \), then we may generate the solution at \( X_{n+1} = X_n + h \) using the well-known Numerov algorithm:

\[
Y_{n+1} = \left[ 1 - \frac{h^2}{12} G_n \right]^{-1} \left[ \left( 2 + \frac{5h^2}{6} G_n \right) Y_n - \left( 1 - \frac{h^2}{12} G_{n-1} \right) Y_{n-1} \right] 
\]

(68)
The iteration may be started by assuming \( Y_0 = Y(X=0) = 0 \) and \( Y_1 = Y(X=h) = a \). If \( a \) is nonsingular, the solutions generated will be linearly independent. It is normal to choose \( a = 1 \). The normalization is not important, since \( Y \) may be scaled by any constant.

When the potential is highly repulsive for small \( X \), the elements of \( Y \) will be extremely small for \( X \approx 0 \). This is due to the exponential decay of the wavefunction in the nonclassical region. Numerical accuracy may be improved by setting \( Y_0 = Y(X_0) = 0 \) for \( X_0 > 0 \). It is found that for Cohen's \( \text{He}(2^3S) - H_2 \) potential, \( X_0 = 2.0 \ a_0 \) was a suitable choice for \( E = 0.10 \) eV. For \( E = 0.05 \) eV, \( X_0 = 3.0 \ a_0 \) was used when \( J \leq 15 \), and \( X_0 = 4.0 \ a_0 \) when \( J = 20 \). (The classical turning point moves outward for higher angular momenta.) These values of \( X_0 \) were determined by examining the results obtained for trial calculations using various starting points. Whenever \( X_0 \) could be increased by \( 0.2 \ a_0 \) without changing the final \( X \) matrix elements (in the first eight significant figures), the larger \( X_0 \) was assumed a reliable starting point.

The most efficient way to implement Equation (68) is not by inverting the matrix \( \mathbf{I} - (\hbar^2/12) \mathbf{G}_{n+1} \). In general, to evaluate the matrix product \( \mathbf{A}^{-1} \mathbf{B} \), it is not necessary to find \( \mathbf{A}^{-1} \) explicitly and then perform the multiplication. Fewer arithmetic operations are required if one solves the equation \( \mathbf{AY} = \mathbf{B} \) directly. Therefore, \( Y_{n+1} \) is best found by solving

\[
\left[ I - \frac{\hbar^2}{12} \mathbf{G}_{n+1} \right] Y_{n+1} = \left[ (2 + \frac{5\hbar^2}{6} \mathbf{G}_n) Y_n - (1 - \frac{\hbar^2}{12} \mathbf{G}_{n-1}) Y_{n-1} \right]
\]

(69)

The particular form of the matrix \( \mathbf{I} - (\hbar^2/12) \mathbf{G}_{n+1} \) may be exploited. This matrix is symmetric since \( \mathbf{G} \) is itself symmetric, and it is approximately equal to \( \mathbf{I} \) since \( \hbar^2/12 \) is very small. Specialized algorithms...
may be used to solve $AX = B$ when $A$ is symmetric and positive definite. (A matrix is positive definite if and only if its eigenvalues are all positive; \( 1 - (h^2/12)G = 1 \) was assumed to satisfy this condition.) We did not rigorously prove that this matrix was positive definite for all \( X \), but we did perform comparison calculations using the specialized algorithm, and the conventional algorithm for all arbitrary matrix \( A \). Results identical to eight significant figures were obtained, and the entire program ran about 15\% faster when the specialized algorithm was included.

2. Case Where Potential is Complex

At this point it is appropriate to consider the extension of the above technique when a (spherically symmetric) imaginary part is added to the potential. If \( v_\circ(X) \) is replaced by \( v_\circ(X) - i\Gamma(X)/2 \), the change in Equation (67) is

\[
\frac{d^2}{dx^2} (Y + iZ) = \left[ \mathcal{G}(X) + i\mathcal{J}(X) \right] (Y + iZ) \quad (70)
\]

Where \( \mathcal{G}(X) = -m \Gamma(X) \), and the imaginary part of the solution is explicitly denoted by \( Z \). In principle, the entire procedure remains unchanged. One still begins the solution at two points with 0 and some \( g \). It is only necessary to carry out all operations with complex arithmetic.

From a practical point of view, however, it is preferable to perform only real arithmetic operations on the computer. Therefore the real and imaginary parts of Equation (70) are separated into two simultaneous equations:

\[
\frac{d^2}{dx^2} Y = \mathcal{G}(X) Y - \mathcal{J}(X) Z \quad (71)
\]

\[
\frac{d^2}{dx^2} Z = \mathcal{J}(X) Y + \mathcal{G}(X) Z
\]
This is conveniently rewritten
\[
\begin{bmatrix}
\frac{d^2}{dx^2} & 0 \\
0 & \frac{d^2}{dx^2}
\end{bmatrix}
\begin{bmatrix}
Y \\
Z
\end{bmatrix}
= \begin{bmatrix}
G & -g \\
g & G
\end{bmatrix}
\begin{bmatrix}
Y \\
Z
\end{bmatrix}
\] (72)

In this form the similarity to Equation (67) is evident, and any particular solution may be formally developed according to the 2N dimensional Numerov algorithm. There are, however, only N regular solutions: the matrix \(Y \Gamma \) has only N columns. The solution must be started with
\[
\begin{bmatrix}
Y_0 \\
Z_0
\end{bmatrix} = \begin{bmatrix}
0 \\
0
\end{bmatrix}, \quad \begin{bmatrix}
Y_1 \\
Z_1
\end{bmatrix} = \begin{bmatrix}
\alpha \\
\beta
\end{bmatrix}
\] (73)

where the appropriate restriction to guarantee linear independence is the nonsingularity of the N x N (complex) matrix \(a + i\beta\). The development of the solution is explicitly given by solving at each integration point
\[
\begin{bmatrix}
1 - \frac{h^2}{12} G_{n+1} & \frac{h^2}{12} g_{n+1} & 1 \\
-\frac{h^2}{12} g_{n+1} & 1 - \frac{h^2}{12} G_{n+1}
\end{bmatrix}
\begin{bmatrix}
Y_{n+1} \\
Z_{n+1}
\end{bmatrix}
= \begin{bmatrix}
Y_n \\
Z_n
\end{bmatrix}
\] (74)

\[
\begin{bmatrix}
\frac{5h^2}{6} g_n & -\frac{5h^2}{6} g_n & 1 \\
\frac{5h^2}{6} g_n & 2 + \frac{5h^2}{6} G_n
\end{bmatrix}
\begin{bmatrix}
Y_n \\
Z_n
\end{bmatrix}
- \begin{bmatrix}
1 - \frac{h^2}{12} G_{n-1} & \frac{h^2}{12} g_{n-1} & 1 \\
-\frac{h^2}{12} g_{n-1} & 1 - \frac{h^2}{12} G_{n-1}
\end{bmatrix}
\begin{bmatrix}
Y_{n-1} \\
Z_{n-1}
\end{bmatrix}
\]

The \(Y_{n+1}, Z_{n+1}\) may be found by solving Equation (74) using techniques for an arbitrary 2N x 2N matrix equation. This is not the most efficient approach, however. We rewrite Equation (74) schematically as
\[
\begin{bmatrix}
A & -a & 1 \\
a & A & 1
\end{bmatrix}
\begin{bmatrix}
Y \\
Z
\end{bmatrix}
= \begin{bmatrix}
B \\
C
\end{bmatrix}
\] (75)
By taking advantage of the block structure of the left hand matrix, and using the fact that $a_1$ is small and diagonal (since $\Gamma(x)$ is small and independent of $\theta$), a solution $\begin{bmatrix} Y \\ Z \end{bmatrix}$ may be found solely in terms of operations involving $N \times N$ symmetric, positive definite matrices. It is easily verified that

$$\begin{bmatrix} Y \\ Z \end{bmatrix} = \begin{bmatrix} \mathcal{A}^{-1} \left[ \mathcal{L}^2 + (\mathcal{A}^{-1})^2 \right]^{-1} \mathcal{B} + \mathcal{A}^{-1} \left[ \mathcal{L}^2 + (\mathcal{A}^{-1})^2 \right]^{-1} \mathcal{C} \\ \mathcal{A}^{-1} \left[ \mathcal{L}^2 + (\mathcal{A}^{-1})^2 \right]^{-1} \mathcal{C} - \mathcal{A}^{-1} \left[ \mathcal{L}^2 + (\mathcal{A}^{-1})^2 \right]^{-1} \mathcal{B} \end{bmatrix} \tag{76}$$

Although this may at first appear to be a cumbersome expression, it may be evaluated much more quickly on a computer than the solution to an arbitrary $2N \times 2N$ matrix equation.

3. Numerical Determination of S Matrix

This completes the discussion of the techniques used to find the radial solutions to Equation (26). The procedure for substituting into Equations (55) and (58) to obtain the $S$ matrix will now be briefly considered. As in Section C.2, the procedure for finding $S$ using the $R$ matrix is standard and need not be discussed.

Since the matrix $D$ (Equation (56)) is diagonal and in fact real, evaluation of $D^{-1}$ presents no problem. From Equation (58) it is clear that $S^T$ (S transpose) is the solution to an equation of the form

$$\begin{bmatrix} A + \mathcal{Q} \end{bmatrix}^T \left[ \operatorname{Re}(S^T) + i \operatorname{Im}(S^T) \right] = \begin{bmatrix} B + \mathcal{C} \end{bmatrix}^T \tag{77}$$

Separating the real and imaginary parts as before, we see that $S^T$ may be found by solving the equation

$$\begin{bmatrix} A^T & -\mathcal{Q}^T \\ \mathcal{Q}^T & A^T \end{bmatrix} \begin{bmatrix} \operatorname{Re}(S^T) \\ \operatorname{Im}(S^T) \end{bmatrix} = \begin{bmatrix} B^T \\ \mathcal{C}^T \end{bmatrix} \tag{78}$$
This was done in a straightforward manner by treating Equation (78) as 2N simultaneous equations. The technique of iterative refinement of the solution was invoked to insure accuracy\textsuperscript{37}.

4. Tests of Numerical Procedure

We conclude this section by mentioning some of the tests used to insure the reliability of the computer program, and to assess the accuracy obtained.

1) The routines which calculate spherical Bessel functions were checked extensively against tables\textsuperscript{38} and found accurate to 10 significant digits.

2) The entire program\textsuperscript{36} (OPen CHANnel) was used to calculate cross sections for 0 \to 2 rotational excitation of H\textsubscript{2} by He(1\textsuperscript{1}S\textsubscript{0}), using the interaction potential of Roberts\textsuperscript{39}. Total excitation cross sections for several energies were published by Allison and Dalgarno\textsuperscript{40} and independently checked by Lane\textsuperscript{41}. Complete agreement was obtained with selected partial cross sections calculated by Lane.

3) The program as revised to handle a complex potential (OPen CHANnel compleX) was checked against the independent calculation of Cohen\textsuperscript{24} of PI cross sections for the He(2\textsuperscript{3}S) \to H\textsubscript{2} process using the \theta = 0^\circ and 90^\circ potentials. The exact values of the width used by Cohen were not known, but an estimate was made using a simple analytic fit to his tabulated points. Agreement within 5\% was obtained at selected energies.
4) OPCHANX was compared with OPCHAN in calculations with \( \Gamma \) set to zero. Eight significant figure agreement was obtained. Then the starting conditions were changed in OPCHANX: \( \sqrt{2} \) was set equal to \( \sqrt{1 + 1} \) (instead of \( \sqrt{1} \)). There was no change in the final results to six significant figures.

The above checks give assurance that OPCHAN and OPCHANX calculate exactly what they are supposed to, without programming error. We must now assess errors caused by the inexactness of the Numerov algorithm (truncation error), and by round off error (the computer stores only a finite number of digits, and rounds off after each operation). Double precision calculations (≈ 15 decimal digits on the IBM 370/155) were used to minimize such round off errors, and inner products (in the matrix operations) were accumulated in extended precision (≈ 30 digits). Because of these precautions, it is felt that round off error is not a significant source of error.

The most convenient test of the accuracy of the algorithm and the reliability of the results is to monitor the symmetry and convergence of the S matrix (or R matrix, if \( \Gamma = 0 \)). Symmetry is guaranteed theoretically; the lack of it is due to numerical error. Boundary matching was always performed at several asymptotic values of the solution; the agreement of the S matrix as calculated at different points determines the convergence. In the present calculations convergence was slow, requiring integration out of 40 or 50 \( a_0 \) because of the long range character of the van der Waals interaction. Average results for \( N = 4 \) and the full complex potential were S matrices (at any one boundary match)
symmetric to 5 or 6 places, but overall convergence no better than 4 or 5 significant figures.

E. Results and Discussion

In this section we shall discuss the various intermediate results and actual cross sections which have been calculated, and attempt to explain what has been learned about the collision process. Initially, it was found instructive not to attack the problem in all its generality. Instead, calculations were first performed using only the spherically symmetric part of the real potential. Then the non-spherical terms were added, and finally the width. Certain features of the results persisted through all of these refinements; other efforts were explicitly seen to arise from one or the other of the correction terms. It was found that the behavior of the He* - H₂ system, as determined by exact quantum mechanical calculations, could be well understood from a semiclassical point of view. It was also possible from the viewpoint to understand how the interaction potential would have to be modified in order to obtained better agreement with experimental data.

We first present the results obtained by assuming Γ = 0. Figures 4a, 4b, and 5, and Table 2 contain the partial and total cross sections for elastic scattering and rotational excitation of H₂ by He(2³S) for several energies between 0.03 eV and 0.25 eV. The elastic cross sections decrease slightly at higher energies, and are very insensitive to whether or not the inelastic channels are included. The rotational excitation cross section is always very small but increases rapidly as the energy is increased.
Figure 4a. Partial elastic cross sections for He(2S) - H₂ at various center of mass energies, calculated using only V = v₀(X). On this scale, no difference could be seen if the full nonspherical real potential were used.
Figure 4b. Partial elastic cross sections for $\text{He}(2^3\text{S}) - \text{H}_2$ at various center of mass energies, calculated using only $V = v_0(X)$ (solid lines), and the full nonspherical real potential (shown in dotted lines where different).
Figure 5. Partial inelastic cross sections for rotational excitation of H$_2$ (from $j = 0$ to $j = 2$) by He($2^3S$), using only the real part of Cohen's potential surface.
Table 2

Total Cross Sections $\sigma_{0+0}$ and $\sigma_{0+2}$ for He($^3S$) - H$_2$

at various energies (in the center of mass frame) using the real part of
the potential calculated by Cohen, with and without the nonspherical
part. In the former case, not every partial cross section was calcu-
lated. All cross sections are given in units of $\AA^2$.

<table>
<thead>
<tr>
<th>$E$(eV)</th>
<th>$\sigma_{0+0}$ ($\AA^2$)</th>
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<td>157</td>
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*calculated by James Cohen.
It should be noted that calculations were not performed for every partial wave at every energy. In elastic scattering, it is known\(^{42}\) that if \((-1)\) times the absolute phase shift (not reduced mod \(2\pi\)) is plotted vs. partial wave angular momentum, a smooth curve results that is qualitatively similar to the radial potential function. Intermediate phase shifts are easily interpolated from this curve. Such a graph is shown in Figure 6. Even in a multi-channel problem, it was found that for the \(J\)th partial wave, the \((l, l)\) element of the \(S\) matrix could be equated to \(e^{2i\varphi_{J}}\) for an appropriate "phase shift" \(\varphi_{J}\) which was a smooth function of \(J\). Normally, performing the exact calculation for every fourth value of \(J\) was sufficient to insure that there was no ambiguity about how many multiples of \(2\pi\) to add. The inelastic partial cross sections exhibited a smooth dependence on \(J\), and could be interpolated directly. In certain instances, calculations at higher energies were carried out for every other partial wave. Total elastic and rotational excitation cross sections can be accurately obtained with this procedure, and at great savings of computer time. Differential cross sections, however, were not rigorously calculated. To do that would probably require every \(S\) matrix element.

1. Interpretation of Results, \(\Gamma = 0\)

How can we interpret the results of the quantum mechanical scattering calculations? The elastic partial cross sections (Figures 4a and 4b) do not exhibit any unexpected features. However, the inelastic partial cross sections \(C^{J}_{0\rightarrow 2}\) show unusual structure as a function of \(J\). We shall try to explain this behavior in terms of a simple, physical picture of the collision process. This picture itself is not intended to be rigorous; it is
Figure 6. Minus the phase shift $\eta_J$ (including appropriate multiples of $2\pi$) plotted vs. $J$ gives a curve qualitatively similar to the potential. These $\eta_J$ were calculated using $V = v_0(X)$. 

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presented only to give qualitative insight into the behavior of a complicated system. In this framework we list three assumptions of the picture:

1) For the energies of interest, the spherically symmetric part of the potential determines a "classical trajectory" for the colliding atoms, even if the target becomes rotationally excited. This is suggested by the almost negligible size of the excitation cross sections, and by the accuracy of the elastic cross sections in the single channel approximation. We shall later see that the classical trajectory is relatively independent of energy, and hence might not be expected to change significantly when translational energy is converted into rotational excitation.

2) The probability of a rotational transition (from $j = 0$ to $j = 2$) for a given impact parameter (partial wave) depends on the amount of $v_2$ "seen" on the classical trajectory determined by $v_0$. Roughly speaking, the more the molecules "see" the perturbing potential $v_2$ (which carries the torque), the greater is the probability of a transition, although this is sometimes violated for small $J$.

3) The effect of the hump in $v_0$ may be understood by considering two smooth, repulsive potentials of different slope which cross. $v_0$ is then viewed as a composite of these curves. In certain limits the cross sections are similar to those obtained from one or the other of the smooth curves.
The idea of a "classical trajectory" in a quantum problem is well-defined if the de Broglie wavelength $\lambda$ is small compared to the distance over which the potential changes by a significant fraction. For our energies, $\lambda \approx 1$ or $2 \, a_0$, so it seems safe to talk about a well-defined trajectory. Given this trajectory, it is clear that there exists a relation between the impact parameter $b$ (or partial wave $J$) and the angle of scattering $\theta$, as illustrated in Figure 7. In general, we will speak interchangeably of impact parameter ($b$) and partial wave ($J$); the approximate relation between these quantities is\(^{42}\)

$$b \approx \frac{J + \frac{1}{2}}{k}$$  \hspace{1cm} (79)

The classical deflection function $\theta(J)$ for a potential $v_o(x)$ is given in terms of the WKB phase shifts by\(^{31,42}\)

$$\theta(J) = 2 \frac{d \eta_J}{dJ}$$  \hspace{1cm} (80)

We shall use this result even though our phase shifts were calculated quantum mechanically. It is assumed, of course, that $\eta_J$ is a sufficiently smooth function of $J$ to be interpolated (as discussed previously) and then differentiated. In Figure 6, this is seen to be the case. The results of this procedure (using $\eta_J$ determined using only $v_o(x)$) are presented in Figure 8. As expected, $\theta(J)$ mimics $v_o(x)$. At energies $E \leq 0.15$ eV, the hump is inside the classical turning point for all partial waves, so the abrupt change of slope of the potential has little effect. (It only affects the exponential decay of the wavefunction in the non-classical region.) The
Figure 7. Schematic relation between impact parameter and angle of scattering for a smooth repulsive potential. The classical deflection function $\theta(b)$ looks qualitatively similar to $V(r)$. 

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Figure 8. The classical deflection function $\theta(J)$ [or $\theta(b)$] can be calculated as described in the text, assuming $\eta'_j$ to be the smooth function of $J$ shown in Figure 6. At sufficiently high energy, $\theta(J)$ reflects the shoulder of Cohen's $v_0(x)$.
same is true at higher energies if J is large enough so that the classical turning point for the effective potential (including the $J(J+1)/x^2$ centrifugal barrier) occurs at sufficiently large $X$. Only at small J and high energy can the approaching He* and H$_2$ probe the hump in $v_o$. This effect causes the ripple in $\theta(J)$ for $E = 0.25$ eV.

A further semiclassical result is that\textsuperscript{31,42}

$$\frac{d\sigma}{d\theta} = \frac{J + \frac{1}{2}}{\frac{l}{\sin \theta}} \left| \frac{d\theta}{dJ} \right|^{-1} \quad (P1)$$

Realizing that the second derivative of an interpolated curve will not be very accurate, we nevertheless evaluate this expression to obtain differential elastic cross sections. The assumption is made that $\theta(J)$ is single-valued, or equivalently that $v_o(X)$ is monotonic. This ignores the tiny attractive part of $v_o(X)$ due to long range van der Waals forces. The values of $dc/d\theta$ plotted in Figure 9 are given in arbitrary units to emphasize these sources of uncertainty. The expected trends are nevertheless very clear. The cross section for large angle scattering is very small because that only occurs for small impact parameters. Furthermore, the effect of the hump is (weakly) seen at sufficiently high energy.

The previous discussion indicates that the effect of the hump in $v_o$ does not strongly affect the elastic cross sections. The inelastic cross sections, however, are much more sensitive to this anomaly. Figure 10 illustrates schematically how $\sigma_o^{J+2}$ would appear for the smooth potentials $v_o^{(a)}$ and $v_o^{(b)}$. For each of these potentials, as the energy is increased, the $\sigma_o^{J+2}$ curve generally becomes larger, and reaches a maximum at a larger value of J. This is clear because for a given J, the colliding particles will get closer to each other as their energy increases. When the energy
Figure 9. The semiclassical approximation to the differential elastic cross section. $d\sigma/d\theta$ is calculated from $\theta(J)$ (Figure 8) as described in the text.
Figure 10. $\nu_0$ may be regarded as a composite of two smooth curves, $\nu_0^{(a)}$ and $\nu_0^{(b)}$. This provides an interpretation of the unusual structure of the rotational excitation partial cross sections as discussed in the text. The energies are ordered $E_1 < E_2 < E_3$. 

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is higher, the trajectory is more influenced by \( v_2 \) and \( v_4 \); and hence there is a greater probability for inelastic excitation. The difference between the cross sections corresponding to \( v_0^{(a)} \) and \( v_0^{(b)} \) is also easily understood. At low energies, and at large values of \( J \) (large impact parameters) at high energies, the classical turning point for \( v_0^{(a)} \) occurs at a smaller value of \( X \) than for \( v_0^{(b)} \). Colliding particles whose trajectory is determined by \( v_0^{(b)} \) are much less influenced by \( v_2 \) and \( v_4 \) (which are assumed not to change). Hence the maximum of \( \sigma_{0+2}^J \) corresponding to \( v_0^{(b)} \) occurs at a smaller \( J \), and the cross sections are generally smaller. With this in mind, the final graph in Figure 10 shows how the exact partial inelastic cross sections may be nicely correlated with the range of the potential probed for a particular energy and angular momentum. At low energies, the scattering is determined by the part of \( v_0 \) which resembles \( v_0^{(a)} \). If the energy is sufficiently high, \( \sigma_{0+2}^J \) exhibits a composite structure, because colliding particles with sufficiently small impact parameters can probe the part of \( v_0 \) which is approximated by \( v_0^{(b)} \). The picture would be that approaching particles with high energy and low \( J \) see an unexpectedly large amount of \( v_2 \) after passing over the hump.

The question arises of whether the unusual behavior of \( \sigma_{0+2}^J \) could be observed experimentally as a differential cross section. Since calculations for every value of \( J \) were not performed, the quantum mechanical \( d\sigma_{0+2}/d\theta \) was not evaluated. However, in the spirit of our intuitive picture, it is possible to guess the approximate results. We need only recall assumption (1) of our picture, that the classical trajectory does not change much even if an inelastic transition takes place. If the \( H_2 \) and \( He^* \) initially have angular momentum quantum number \( J \), and if the \( H_2 \)
is excited from $j = 0$ to $j = 2$, then the total inelastic cross section for scattering to all angles is $\sigma_{0+2}$. But we are assuming that most of the scattered particles go to the solid angle near $\theta(J)$. We therefore identify $\sigma_{0+2}^J$ as the differential inelastic scattering cross section $d\sigma_{0+2}/d\theta$, for $\theta = \theta(J)$. The results of these are shown in Figure 11.

Although the approximation is obviously quite crude, two important features should be noticed. First, at higher energies, the cross section reaches a maximum for smaller scattering angles. This corresponds to more transitions occurring in collisions with larger impact parameters. The particles have enough energy for a closer approach, so the transition probability is high, and the geometrical weighting factor $2J+1$ is larger. Secondly, there is an increase in the inelastic cross section for large angle scattering at high energy. This is, of course, the same hump of $\sigma_{0+2}^J$ for small $J$. The particles on a trajectory with small impact parameter tend to be back-scattered, but are also the most strongly affected by the non-spherical part of the potential.

2. Cross Sections for the Spherically Symmetric Complex Potential

At this point the most interesting physical effect, Penning ionization, still has not been examined. Fortunately, the intuitive ideas which have been developed to relate the form of the real scattering potential to the final cross sections will still be useful when the potential becomes complex. The exact results again indicate that to a good approximation, the classical trajectory is determined by $v_0$, and that the probability of PI is determined by the amount of $\Gamma(X)$ seen on this trajectory. However, in the case of ionization, there is a saturation effect. For
Figure 11. Estimate of differential inelastic cross section (simultaneous excitation of $\text{H}_2$ from $j = 0$ to $j = 2$, and scattering of the $\text{He}(2^3\text{S})$ to an angle $\theta$).
some trajectories, corresponding to a very small classical turning point, there is almost 100% probability of ionization. This is very interesting, since the total cross section for the ionization process is quite small.

Calculations were first performed for a complex potential with only a spherically symmetric real part \( u_0 \) (not necessarily \( v_0 \)). The greater the range of \( u_0 \), which was repulsive except for a tiny van der Waals attractive part, the further out were the classical turning points, and the smaller the cross sections for PI. As Cohen\(^{24}\) predicted, taking \( u_0 \) equal to the \( \theta = 90^\circ \) and \( 0^\circ \) curves results in upper and lower bounds for the exact cross sections. Figure 12 shows \( v_0, v(0^\circ), \) and \( v(90^\circ) \).

Figures 13a and 13b show the partial PI cross sections for \( u_0 = v(0^\circ) \) and \( v(90^\circ) \). Comparison with Figures 19a and 19b shows that the \( \sigma_{0 \rightarrow \text{PI}} \) for \( v_0 \) lie between those for \( v(0^\circ) \) and \( v(90^\circ) \) at each energy, as expected. This is also true for the total PI cross sections, as shown in Figure 14. \( \sigma_{0 \rightarrow \text{PI}} \) exhibits a sharply increasing behavior as a function of energy, then becomes relatively constant.

The graph of \( S^*S \) in Figure 15 illustrates the saturation effect mentioned earlier. The case shown is for \( u_0 = v_0 \); similar results were obtained for the other choices of \( u_0 \), and also for the full nonspherical potential. [In the latter case, \( (S^*S)^J \) would be plotted.] The higher the energy, or the smaller the impact parameter, the closer the \( \text{He}^* \) and \( \text{H}_2 \) approach, and the greater the probability of PI. This probability is proportional to the deviation of the S matrix (for a particular \( J \)) from unitarity, \( 1 - (S^J)^*S^J \); the partial cross section includes a factor \((2J+1)\). According to Cohen's calculation, the width is large for \( X \approx 3 \) or \( 4 \, a_0 \), but then falls off very rapidly. If the \( \text{He}^* \) and \( \text{H}_2 \) approach closely
Figure 12. $v^{(0^\circ)}(X)$ and $v^{(90^\circ)}(X)$ correspond to $V(X,\theta)$ for fixed orientations $\theta$ of $H_2$. $V_0(X)$ is shown for comparison.
Figure 13a. Partial Penning ionization cross sections calculated with $v^{(0^\circ)}$ and $v^{(90^\circ)}$ at the following energies:

1. 0.03 eV.
2. 0.05 eV.
3. 0.10 eV.
Figure 13b. Partial Penning ionization cross sections calculated with $v^{(0^\circ)}$ and $v^{(90^\circ)}$ at the following energies:

1. 0.15 eV.
2. 0.20 eV.
3. 0.25 eV.
Figure 14. Total Penning ionization cross sections as a function of energy, for three different potentials depending only on $X$. As expected from the form of these potentials in Figure 12, cross sections calculated with $v^{(90^\circ)}$ and $v^{(0^\circ)}$ provide approximate upper and lower bounds to the cross section calculated from $v_0$. Further results are shown in Figure 20.
Figure 15. The deviation of the S matrix from unitarity (i.e., the deviation of $(s^J)^*s^J$ from unity) corresponds to a loss of flux into the ionization channel. The curves here were calculated at various energies using $v = v_o(x)$. 
enough to be influenced by the width in the region where the width is large, then ionization occurs with high probability.

The only other observation to make concerning these results is that the behavior of $S^*S$ illustrates the lack of back-coupling with a complex potential. Once ionized, the $H_2$ cannot recapture the ejected electron. Mathematically, the close coupling equations do not represent a flow of probability in and out of the PI channel. Once flux is lost, it is destroyed forever. This is in contrast to the four channel close coupling equations representing only a real potential. A possible explanation for the non-monotonic form of the transition probabilities in Figure 16 is this flux of probability in and out of the inelastic channels. Even though the coupling to the inelastic channels is weak, the transition probability is not strictly proportional to the amount of $v_2$ "seen" on the classical trajectory.

3. Multi-Channel Case - Ionization and Rotational Excitation

We now consider the cross sections as calculated in the most general case: the non-spherical real potential plus the width. The total cross sections obtained for various channels are listed in Table 3. Let us now examine in turn the results for elastic scattering, rotational excitation, and PI.

As before, the elastic cross section $\sigma_{0+0}^J$ is not sensitive to the addition of inelastic channels. Figures 4a, 4b, 17a, and 17b show $\sigma_{0+0}^J$ for several different approximations to the full potential. At lower energies, $\sigma_{0+0}^J$ is accurately calculated by assuming $V = V_0$. At higher energies, the oscillations of $\sigma_{0+0}^J$ are slightly displaced for small values of $J$ when $v_2$
Figure 16. The probability of rotational excitation of H$_2$ by He(2$^3$S) as a function of partial wave number (impact parameter). This is obtained by summing the squares of the absolute values of the appropriate T matrix elements. The energies are

1) 0.10 eV.
2) 0.15 eV.
3) 0.20 eV.
4) 0.25 eV.
Table 3

Total Cross Sections $\sigma_{0\to 0}$, $\sigma_{0\to 2}$, and $\sigma_{0\to \text{PI}}$ for He($2^3S$) – H$_2$

at various energies (in the center of mass frame) using the full complex potential calculated by Cohen, with and without the nonspherical real part. Not every partial cross section was calculated. All cross sections are given in units of $\AA^2$.

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<th>$\sigma_{0\to 0}$</th>
<th>$\sigma_{0\to \text{PI}}$</th>
<th>$\sigma_{0\to 0}$</th>
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*calculated by James Cohen.
Figure 17a. Partial elastic cross sections for He(2\textsuperscript{3}s) - H\textsubscript{2} at various center of mass energies, calculated using $V = v_o - i\Gamma/2$ of Cohen. No change visible on this scale would result if the nonspherical terms $v_2$ and $v_4$ were included. In fact, these curves are indistinguishable from those in Figure 4a calculated using $V = v_o$.
Figure 17b. Partial elastic cross sections using $V = V_o - i\Gamma/2$ (solid lines), and with the full complex potential of Cohen (shown in dotted lines where different). The damping at low $J$ results from the non-unitarity of the $S$ matrix.
and $v_4$ are included, and they are damped when $\Gamma$ is put in. This is easily explained by recalling Equation (59), which yields

$$
\sigma^J_{0\rightarrow 0} = \frac{\pi}{k^2} (2J+1) \left| 1 - S^J_{0\rightarrow 0} \right|^2
$$

Whenever $|S^J_{0\rightarrow 0}| = 1$, the oscillations of $\sigma^J_{0\rightarrow 0}$ are bounded by the envelop $\sigma^J_{0\rightarrow 0} = (4\pi/k^2)(2J+1)$. However, as $|S^J_{0\rightarrow 0}| \rightarrow 0$, $\sigma^J_{0\rightarrow 0} \rightarrow (\pi/k^2)(2J+1)$. The sum over $J$ is not significantly changed by these perturbations. Physically, the only collisions which lead to something other than elastic scattering are those involving a small impact parameter and hence a close approach. Although the probability for a non-elastic process may then be large, the cross section is small because of the geometrical weighting factor $(2J+1)$.

Figure 18 shows $\sigma^J_{0\rightarrow 2}$ for several energies. For large $J$, they are essentially the same as those obtained with $\Gamma = 0$. This is expected when the distance of closest approach is larger than 4 or 5 $a_0$; in that case $\Gamma$ is negligible over the physical trajectory. However, at small $J$, the "hump" obtained previously disappears. It seems that in collisions involving a very close approach, nearly all the flux is drained off by $\Gamma$, leaving little for rotational excitation without PI. Because of this, $d\sigma^J_{0\rightarrow 2}/d\theta$ will not show the increase for $\theta = \pi$ discussed previously.

As the $\sigma^J_{0\rightarrow 2}$ decrease, the $\sigma^J_{0\rightarrow \text{PI}}$ increase. Figures 19a and 19b show the (interpolated) partial cross sections for PI calculated with the full potential of Cohen. At low energies, it is clear that the rotational excitation channels may be neglected. At higher energies, however, an increase in $\sigma^J_{0\rightarrow \text{PI}}$ is noted when compared to the calculations with $v_2$ and $v_4$ neglected. This is a necessary result in physical grounds. The classical trajectory determined by $v_0$ is averaged over all possible orientations.
Figure 18. Partial inelastic cross sections using the full complex He* - H₂ potential surface of Cohen. Comparison with Figure 5 shows the effect of Γ at small partial waves.
Figure 19a. Partial cross sections for the ionization of $H_2$ (initially in the $j = 0$ state), calculated with $V = v_o - i\Gamma/2$ (side A) and with the full complex potential of Cohen (Side B). The curves correspond to energies:

(1) 0.03 eV.
(2) 0.05 eV.
(3) 0.10 eV.
Figure 19b. Partial cross sections for the ionization of H₂ (initially in the j = 0 state), calculated with $V = v_0 - i\pi/2$ (side A) and with the full complex potential of Cohen (side B). The curves correspond to energies:

(1) 0.15 eV.
(2) 0.20 eV.
(3) 0.25 eV.
of the $H_2$. If the He* approaches from the $\theta = 90^\circ$ direction ("broadside"), it will clearly penetrate further than if the collision occurs in the $\theta = 0^\circ$ direction. Past discussion indicates that the exponential growth of the width for decreasing $X$ causes the ionization cross section to be much larger for a $90^\circ$ collision than for $0^\circ$. The effect of rigorously including the entire potential must be to give $\theta = 90^\circ$ collisions their proper weight. In fact, Figure 14 suggests that for a quick approximation, $\nu = \nu^{(90^\circ)} - i\Gamma/2$ is a better choice than $\nu = \nu_0 - i\Gamma/2$.

4. Comparison with Experiment

The preceding discussion has dwelt at length on the qualitative aspects of the He* - $H_2$ collision process, and on the quantitative theoretical results. Now the question of agreement with experiment must be faced. The lack of data on elastic and rotational excitation cross sections make a full test of the theory impossible. As shown in Figure 20, the experimental cross section for PI at approximately 0.04 eV is significantly larger than predicted by the preceding calculations. Does this imply serious weaknesses in the theoretical approach, or would a reasonable empirical adjustment at some point lead to satisfactory agreement with the data?

Our qualitative picture suggests that a modification of Cohen's width at long range should be sufficient to raise the calculated PI cross section at low energies. At $E \approx 0.05$ eV the He* and $H_2$ can approach no closer than $\approx 7 \ a_0$ (see Figure 2). Hence the PI cross section is determined by the width in a region where the width seems to fall off unusually fast, and may be inaccurate as discussed in Section B. A dramatic increase in $\sigma_{0-\pi}$ at 0.05 Ev, from 0.12 to 2.3 $\AA^2$, was obtained using the modified
Figure 20. Total Penning ionization cross sections for the $\text{He}(2^3\text{s}) - \text{H}_2$ system. The experimental data is that of Howard, Riola, Rundel, and Stebbings. Curve (1) is calculated with the full complex potential of Cohen. Curve (2) is calculated with the full real potential of Cohen, but with $\Gamma$ modified as shown in Figure 3. Curve (3) is calculated with Cohen's width, and a spherically symmetric real potential which does not exhibit a "hump" or shoulder.
width shown in Figure 3. This change is caused partly by the modest increase in \( \Gamma(X) \) for \( X = 6 - 7 \ a_0 \). Equally important, however, is the relatively greater increase in \( \Gamma(X) \) for larger values of \( X \). This leads to significant partial cross sections for many larger values of \( J \), and hence a much larger total cross section for \( \Pi \). Cross sections at several energies are plotted in Figure 20. It is important to realize that a relatively small change in \( \Gamma(X) \) is sufficient to produce much improved agreement with experiment. We stress that \( \Gamma(X) \) is only altered for \( X \geq 6 \ a_0 \); in this range it is never greater than \( 10^{-4} \) a.u. anyway. The asymptotic form of the new \( \Gamma'(X) \) is somewhat similar to that for Miller and Schaeffer's He(2\(^3\)s) - H width; this is consistent with the argument in Section B.

For completeness we note that, alternatively, a modification of Cohen's real potential might be expected to produce the same effect. For example, the hump of \( v_0 \) could be eliminated, and \( v_0 \) forced to fall off rapidly like \( v_0^{(a)} \) in Figure 9. A calculation was performed using

\[
 v_0'(X) = 0.19864 \ e^{-0.8361X} \tag{83}
\]

The cross sections obtained by assuming \( V = v_0'(X) - i\Gamma(X)/2 \) are plotted in Figure 19. Although they are similar to those obtained by modifying only \( \Gamma \), it is felt that the change required in \( v_0 \) was too drastic, and without physical basis.

5. Summary

We have attempted to give insight into complicated quantum mechanical phenomena by stressing an intuitive, semiclassical point of view. For the He(2\(^3\)s) - \( \text{H}_2 \) collision, this is a satisfying approach, because the quantum
mechanical effects are noticeable but not dominant. Furthermore, the unusual resonance (autoionizing) nature of the system is itself extremely interesting. Our study of the collision process indicates that elastic scattering is the most likely process, but that for certain trajectories rotational excitation or Penning ionization may occur. We hope that further experimental results will soon be available in order to provide a full test of our overall model, and of the validity of our semiempirical modification of the width.
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41. Neal F. Lane, Rice University, private communication.
