**Theoretical Study of Intermolecular Energy Transfer Involving
Electronically Excited Molecules: $\text{He}(^1\text{S}) + \text{H}_2(\text{B } ^1\Sigma_u^+)$**

LBL--22466

DE87 006172

Ph. D. Thesis

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November 1986

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ABSTRACT

To further understanding of gas phase collision dynamics involving electronically-excited molecules, a fully quantum mechanical study of $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$ was undertaken. Iterative natural orbital configuration interaction (CI) calculations were performed to obtain the interaction potential between He and $\text{H}_2(\text{B } ^1\Sigma_u^+)$. The potential energy surface (PES) is highly anisotropic and has a van der Waals well of about 0.03 eV for C_{2v} approach. Avoided PES crossings occur with $\text{He} + \text{H}_2(\text{E,F } ^1\Sigma_g^+)$ and with $\text{He} + \text{H}_2(\text{X } ^1\Sigma_g^+)$ and cause a local maximum and a deep minimum in the $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$ PES, respectively. The crossing with $\text{He} + \text{H}_2(\text{X } ^1\Sigma_g^+)$ provides a mechanism for fluorescence quenching. The computed CI energies were combined with previous multi-reference double excitation CI calculations and fit with analytic functions for convenience in scattering calculations. Accurate dipole polarizabilities and quadrupole moment of $\text{H}_2(\text{B } ^1\Sigma_u^+)$ were computed for use in the

multipole expansion, which is the analytic form of the long-range PES.

Coupled-channel equations for rotational and rovibrational energy transfer were solved to obtain partial, integral, and differential cross sections at scattering energies up to 0.210 eV. Rotational energy transfer is efficient (e.g. $\sigma_{00 \rightarrow 02}$ is in the range 1-40 Å² for scattering energies above 0.03 eV). Feshbach resonances in $\sigma_{00 \rightarrow 02}$ are found at relative translational energies below 0.025 eV. Differential cross sections for rotational transitions with $\Delta j < 4$ are strongly forward peaked while those with $\Delta j > 4$ are almost flat. The vibrational differential cross sections have large contributions from backward scattering.

Ab initio CI nonadiabatic (NA) coupling matrix elements between the lowest two ¹A' states of HeH₂ were computed to facilitate the study of fluorescence quenching. The computed NA coupling is large and sharply peaked near the minimum on the excited-state PES. The avoided crossing of He + H₂(B ¹Σ_u⁺) and He + H₂(X ¹Σ_g⁺) occurs because the ground state PES is a repulsive covalent interaction while the excited state wave function is stabilized by an ionic configuration (i.e. HeH⁺ + H⁻). Diabatic electronic states were computed via a unitary transformation from the adiabatic states. The diabatic PESs were computed as functions of nuclear positions in order to locate the crossing seam. The accurate PES and NA coupling matrix elements computed in this study can be used in molecular dynamics calculations of rovibrational energy transfer and fluorescence quenching cross sections.

Dedication

To my father

Acknowledgements

I wish to express my gratitude to Professor William A. Lester, Jr. for his guidance and support during my years as a graduate student at the University of California. I am indebted to Dr. Michel Dupuis for sharing his expertise in all areas of quantum chemistry and for explaining the intricacies of the HONDO the computer code used to perform all electronic structure calculations described in this thesis. I would also like to thank Dr. Peter Reynolds for introducing me to the quantum Monte Carlo method for computing electronic energies and for all his help in applying it to excited states.

During my career at Berkeley, I have had rewarding interactions with the members of Professor Miller's and Schafer's research groups, and I thank these people. The members of Professor Lester's research group have all contributed in one way or another to this work. I would especially like to thank Rob Barnett for his help with Quantum Monte Carlo, and Chris Dateo and Brian Hammond for many invaluable discussions. These and all the other members of our group provided a great service by proofreading parts of this thesis. I also thank Millard Alexandar, Stavros Farantos, Earl Evleth, David Yarkony, Joe Gerratt, Bob Walker, William H. Miller, and S. H. Suck Salk for helpful discussions.

I thank Maudie Noyd for all of the work she has done. My deepest

thanks go to Monica Hendewerk who has helped make my life fun.

This research was supported by the Director, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

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CHAPTER 1

Introduction

Energy transfer induced by electronically adiabatic collisions between ground-state atoms and molecules (i.e. when nuclear motion occurs on a single electronic potential energy surface (PES)) is well studied both experimentally¹ and theoretically². However, collision processes that are electronically nonadiabatic (NA) (i.e. in which transitions take place between electronic states) are not as well understood even though they are important in a wide range of phenomena, including charge transfer, chemical reactions, and quenching of electronic excitation. Most theoretical treatments of molecular collisions utilize the Born-Oppenheimer approximation to separate electronic and nuclear motions as a first step. Therefore, the problem is solved in two parts: first the electronic PESs and NA couplings are computed; next the equations for nuclear motion under the influence of these potentials are solved to obtain differential and integral cross sections. Accurate PESs for electronically excited species are often difficult and time consuming to compute, thus not many exist. Recent ab initio excited-state PES calculations are reviewed by Hirst.³ Self-consistent-field (SCF) and configuration interaction (CI) NA couplings have been computed using finite-differences, by several groups⁴⁻⁷ over the last ten years. Very recently, ab initio gradient techniques have been adapted to compute NA couplings.⁸⁻¹⁰ Yarkony and co-workers have treated

systems of neutral and charge transfer species^{8,9} as well as excited-state atoms and ground-state-molecules.¹¹⁻¹³ Semiclassical and classical studies of the nuclear dynamics of NA processes, focusing on charge transfer and collisions of excited-atoms with ground-state molecules, are reviewed by Tully.¹⁴ The general quantum treatment of NA atom-diatom collisions along with an application to spin-orbit transitions in $F + H_2$ is well presented by Rebentrost and Lester¹⁷ and reviewed by Rebentrost.¹⁸ Quantum theory of NA processes in chemical reactions is developed and applied by Baer in a series of papers.¹⁹⁻²² The similar process of photodissociation has also been treated as a transition between diabatic electronic levels.²³

Collisions between electronically excited molecules and ground state atoms, however, have received little theoretical attention even though experimental interest has been renewed by the greater availability of tunable lasers to prepare target molecules. One example of such processes is collision induced fluorescence quenching. Experimental studies of fluorescence quenching in small molecules are summarized by Steinfeld.²⁴ The measured cross sections in many of these systems are accurately fit by a perturbation theory model^{24,25} in which long-range intermolecular forces provide the quenching mechanism. According to the model, quenching cross sections for a molecule are proportional to the polarizability of the collision partner.

One experimental study of fluorescence quenching, carried out by Moore and co-workers, focused on collisions between HD ($B^1\Sigma_u^+$) and rare gas

atoms.²⁶ Cross sections for rovibrational energy transfer and fluorescence quenching were measured for HD ($B\ ^1\Sigma_u^+$, $v=3$, $j=2$), excited using an argon lamp, in the presence of He, Ne and HD ($X\ ^1\Sigma_g^+$). Both rovibrational energy transfer and quenching cross sections were found to be large (i.e. $1-10\ \text{\AA}^2$) at room temperature. The quenching cross sections were not well represented by the perturbation theory model²⁵ suggesting that long-range interactions do not provide the only quenching mechanism. Schaefer, Wallach and Bender²⁷ carried out SCF plus CI calculations on closely related $\text{He} + \text{H}_2(B\ ^1\Sigma_u^+)$ in order to determine the cause of the quenching. They considered the C_{2v} approach of He with respect to H_2 and computed interaction energies for the 1A_1 ($\text{He} + \text{H}_2(X\ ^1\Sigma_g^+)$) and 1B_2 ($\text{He} + \text{H}_2(B\ ^1\Sigma_u^+)$) states as a function of R for $r=2.4\ \text{au.}$, the equilibrium separation of $\text{H}_2(B\ ^1\Sigma_u^+)$ (see Table 1.1 for the symmetries of the electronic states of $\text{He} + \text{H}_2$ and Fig. 1.1 for definition of the coordinates R , r , and θ). The calculations revealed a long-range attractive well in the 1B_2 state PES but no surface crossing to explain the efficient quenching. Römelt, Peyerimhoff and Buenker (RPB) computed interaction energies using the ab initio multi-reference double excitation configuration interaction (MRD-CI) technique for a number of states of HeH_2 along the C_{2v} and $C_{\infty v}$ approaches over a range of r .^{28,29} They located an avoided crossing between the second and third states of $^1\Sigma$ symmetry ($\text{He} + \text{H}_2(B\ ^1\Sigma_u^+)$ and $\text{He} + \text{H}_2(E,F\ ^1\Sigma_g^+)$) along the $C_{\infty v}$ approach.²⁹ This crossing causes transitions to $\text{HeH}_2(3\ ^1A')$, but there is not enough energy under the experimental conditions for dissociation to

$\text{He} + \text{H}_2(\text{E,F } ^1\Sigma_g^+)$. Therefore, this avoided crossing does not provide a mechanism for quenching because the system would continue to fluoresce, perhaps at a different wavelength than isolated $\text{H}_2(\text{B } ^1\Sigma_u^+)$.

The current work was undertaken to determine the mechanism of fluorescence quenching and to provide a quantum mechanical description of collisional energy transfer in $\text{H}_2(\text{B } ^1\Sigma_u^+)$ due to He impact using accurate *ab initio* PESs and NA couplings. Since the initiation of the present effort, Farantos, Theodorakopoulos and Nicolaides (FTN) extended the work of RPB by computing MRD-CI energies along the 45° approach.³⁰ Their calculations showed an avoided crossing between the first two states of $^1A'$ symmetry which correlate asymptotically with $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$ and $\text{He} + \text{H}_2(\text{X } ^1\Sigma_g^+)$, and are referred to as $\text{HeH}_2(2^1A')$ and $\text{HeH}_2(1^1A')$, respectively. This avoided crossing causes fluorescence of $\text{H}_2(\text{B } ^1\Sigma_u^+)$ to be quenched. Farantos and co-workers performed surface-hopping classical-trajectory calculations^{31,32} using their analytic representation of the PESs for the two $^1A'$ states of HeH_2 .³¹ Their computed energy-transfer and fluorescence quenching cross sections are in fair agreement with the experimental measurements. Farantos also computed the NA coupling term $\frac{\partial}{\partial R}$ and $\frac{\partial}{\partial r}$ as functions of R near the minimum of the $\text{HeH}_2(2^1A')$ PES.³²

In this work new multi-reference configuration interaction (MR-CI) calculations are combined with the MRD-CI results to obtain new analytic

representations of the $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$ PES. Special care is taken to provide an accurate long-range interaction as it governs rotational energy transfer. The coupled-channel (CC) equations for rovibrational energy transfer are solved using the energy-corrected-rigid-rotor³³ (ECRR) approximation, and the accurate vibrating-rotor (VR) description of the wave function and energy levels of H_2 . Differential and integral cross sections for rovibrational energy transfer in $\text{H}_2(\text{B } ^1\Sigma_u^+)$ due to He atom impact are computed for scattering energies below 0.210 eV. The NA process is addressed by computing ab initio MR-CI NA couplings, $\frac{\partial}{\partial R}$, $\frac{\partial}{\partial r}$, and $\frac{\partial}{\partial \theta}$, between the lowest two $^1\text{A}'$ states of HeH_2 as functions of R , r , and θ near the minimum of the $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$ PES. Transformation to a representation of the electronic wave functions, which is convenient for scattering calculations, is accomplished by utilizing a physical description of the avoided crossing.

Chapter 2 provides a brief resumé of the coupled-channel equations for rovibrational energy transfer along with those for rotational-vibrational-electronic energy transfer in adiabatic and diabatic electronic bases. The coupled-states³⁴ (CS) and infinite-order-sudden³⁵ (IOS) approximations are summarized as they apply to collisions of He with $\text{H}_2(\text{B } ^1\Sigma_u^+)$. Accurate ab initio CI PESs computed in this study are given in Chapter 3. Chapter 4 contains integral, and differential cross sections for rotational, and rovibrational energy transfer for $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$. The ab initio calculation of NA coupling between $\text{HeH}_2(1^1\text{A}')$ and $\text{HeH}_2(2^1\text{A}')$ and results are described in Chapter 5,

along with the transformation from adiabatic to diabatic electronic representation. The findings and conclusions of this study are summarized in Chapter 6.

Table 1.1: Irreducible representations of the electronic states of $\text{He} + \text{H}_2$ as a function of nuclear geometry.^a

Electronic State	Irreducible Representation		
	Angle of Approach, θ (Nuclear Point Group)		
	0 ($C_{\infty v}$)	$0 < \theta < 90$ (C_s)	90 (C_{2v})
$\text{He}(^1\text{S}) + \text{H}_2(\text{X } ^1\Sigma_g^+)$	$1 ^1\Sigma$	$1 ^1A'$	$1 ^1A_1$
$\text{He}(^1\text{S}) + \text{H}_2(\text{B } ^1\Sigma_u^+)$	$2 ^1\Sigma$	$2 ^1A'$	$1 ^1B_2$
$\text{He}(^1\text{S}) + \text{H}_2(\text{E,F } ^1\Sigma_g^+)$	$3 ^1\Sigma$	$3 ^1A'$	$2 ^1A_1$

^a Interaction energies at angles greater than 90° are generated by symmetry.

Figure 1.1: Internal coordinates for $\text{He} + \text{H}_2$ and space fixed (unprimed) and body fixed (primed) coordinate axes.

CHAPTER 2

Scattering Theory Formalism

2.1 Introduction

The goal of this work is to obtain accurate dynamical information (i.e. cross sections for rotational, vibrational and electronic energy transfer) by solving the time-independent Schrödinger equation for a collision of an S-state atom with a Σ -state diatomic molecule. In this section the time-independent treatment of electronically nonadiabatic collisions is given. It follows the developments of Tulley¹⁴ and Rebentrost¹⁸ and provides a framework for presenting the theoretical treatment of nuclear motion in this chapter and the treatment of electronic motion in Chapters 3 and 5. The notations of Tulley¹⁴ and of Yarkony and co-workers⁸ are combined with slight modification and used throughout this work.

The total Hamiltonian with center-of-mass (CM) motion removed is

$$H = T_{\mathbf{Q}} + H_{\text{el}}(\mathbf{Q}, \mathbf{q}) \quad (2.1)$$

where $T_{\mathbf{Q}}$ is the nuclear kinetic energy operator, H_{el} is the electronic Hamiltonian, $\mathbf{Q}$ is a vector of the remaining six nuclear coordinates and $\mathbf{q}$ is a vector of electronic coordinates. Both $\mathbf{Q}$ and $\mathbf{q}$ are referred to the CM of the nuclei (CMN). The nuclear kinetic energy operator, $T_{\mathbf{Q}}$ (in atomic units where

$$\hbar = m_e = e = 1)$$

is

$$T_Q = -\frac{1}{2\mu} \nabla_R^2 - \frac{1}{2m} \nabla_r^2 \quad (2.2)$$

where $\mathbf{R}$ is the vector from the CM of the diatom to the atom, $\mathbf{r}$ is the vector between the atoms of the diatom (see Fig. 1.1), μ and m are the reduced masses:

$$\mu = \frac{m_1(m_2 + m_3)}{m_1 + m_2 + m_3}, \quad m = \frac{m_2 m_3}{m_2 + m_3} \quad (2.3)$$

and m_1 , m_2 , and m_3 are the masses of the atom and the two atoms of the diatom respectively. The electronic Hamiltonian, neglecting mass polarization terms, which arise from the small difference between CM and CMN, and spin-orbit coupling, which should be small for this light-atom small-molecule system, is

$$\begin{aligned} H_{el} = & - \sum_i \frac{1}{2} \nabla_i^2 - \sum_{\alpha i} \frac{Z_\alpha}{|\mathbf{Q}_\alpha - \mathbf{q}_i|} - \\ & + \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta}{|\mathbf{Q}_\alpha - \mathbf{Q}_\beta|} + \sum_{i \neq j} \frac{1}{|\mathbf{q}_i - \mathbf{q}_j|} \end{aligned} \quad (2.4)$$

The disparity between the electron mass and the masses of the nuclei allows a separation of electronic and nuclear motions. This is accomplished by choosing a basis of electronic functions, Ψ_i , which depend parametrically on the nuclear coordinates, $\mathbf{Q}$. For any value of $\mathbf{Q}$ the Ψ_i s are assumed to be

orthonormal and complete in the subspace of electronic coordinates, $\mathbf{q}$. The total wave function, Ψ , is then expanded in terms of the electronic basis:

$$\Psi(\mathbf{q}, \mathbf{Q}) = \sum_{\mathbf{J}} \Psi_{\mathbf{J}}(\mathbf{q}; \mathbf{Q}) \Xi_{\mathbf{J}}(\mathbf{Q}) \quad (2.5)$$

Substituting Eq. (2.5) into the Schrödinger equation,

$$[H - E] \Psi = 0 \quad (2.6)$$

multiplying on the left by $\Psi_{\mathbf{I}}^*$, where the asterisk denotes complex conjugation, and integrating over electronic coordinates results in an infinite set of coupled equations for Ξ :

$$[T_{\mathbf{Q}} + T_{\mathbf{II}}^2 + V_{\mathbf{II}} - E] \Xi_{\mathbf{I}} = - \sum_{\mathbf{J} \neq \mathbf{I}} [T_{\mathbf{IJ}}^1 + T_{\mathbf{IJ}}^2 + V_{\mathbf{IJ}}] \Xi_{\mathbf{J}} \quad (2.7)$$

where

$$V_{\mathbf{IJ}} = \langle \Psi_{\mathbf{I}} | H_{\text{el}} | \Psi_{\mathbf{J}} \rangle_{\mathbf{q}} \quad (2.8)$$

$$T_{\mathbf{IJ}}^1 = - \frac{1}{2\mu} D_1(\mathbf{I}, \mathbf{J}, \mathbf{R}) \nabla_{\mathbf{R}} - \frac{1}{2m} D_1(\mathbf{I}, \mathbf{J}, \mathbf{r}) \nabla_{\mathbf{r}} \quad (2.9)$$

$$T_{\mathbf{IJ}}^2 = - \frac{1}{2\mu} D_2(\mathbf{I}, \mathbf{J}, \mathbf{R}) - \frac{1}{2m} D_2(\mathbf{I}, \mathbf{J}, \mathbf{r}) \quad (2.10)$$

$$D_1(\mathbf{I}, \mathbf{J}, \alpha) = \langle \Psi_{\mathbf{I}} | \nabla_{\alpha} \Psi_{\mathbf{J}} \rangle_{\mathbf{q}} \quad (2.11)$$

$$D_2(\mathbf{I}, \mathbf{J}, \alpha) = \langle \Psi_{\mathbf{I}} | \nabla_{\alpha}^2 \Psi_{\mathbf{J}} \rangle_{\mathbf{q}} \quad (2.12)$$

The notation $\langle \rangle_{\mathbf{q}}$ denotes integration over electronic coordinates. In Eq. (2.7) the diagonal elements, $V_{\mathbf{II}}$, are the PESs governing nuclear motion. The additional diagonal terms, $T_{\mathbf{II}}^2$, are diagonal corrections to the PESs. The off-diagonal terms, $T_{\mathbf{IJ}}^1$, $T_{\mathbf{IJ}}^2$, and $V_{\mathbf{IJ}}$ are NA interactions that promote transitions

between the electronic states. Notice that T_{ij}^1 in Eq. (2.7) tends to zero for low kinetic energy since it is proportional to the nuclear momentum.

In the sections that follow, an Arthurs and Dalgarno³⁶ (AD) type development of the CC equations will be summarized for collisions of He with $H_2(B\ ^1\Sigma_u^+)$ in two different energy regimes. At low energy virtually no coupling exists between the excited state, $He-H_2(B\ ^1\Sigma_u^+)$, and the ground state, $He-H_2(X\ ^1\Sigma_g^+)$. This is because a barrier (of about 0.15 eV) to reaching the crossing region exists on the excited-state PES.³¹ At these energies only rotational and vibrational energy transfer occur and nuclear motion takes place on a single electronic PES (V_{II} of Eq. (2.7)). The coupled equations for purely rotational and vibrational energy transfer are well documented in the literature^{37,38} and many methods³⁹⁻⁴⁸ exist to solve them. Section 2.2 provides a summary of these equations. When the scattering energy exceeds the barrier to fluorescence quenching and/or tunneling through the barrier plays an important role, electronic as well as rovibrational energy transfer takes place. Transitions take place between the PESs in addition to the transitions between rovibrational levels on the individual surfaces. The coupled equations involving electronic coupling^{14,18} are not as well studied as those for rovibrational energy transfer and they are given in Sec. 2.3.

The number of coupled equations grows rapidly with increasing scattering energy as a consequence of the $2j+1$ multiplicity associated with rotational states of the diatom. For $He + H_2(B\ ^1\Sigma_u^+)$ the number of CC equations is

greater than 100 for scattering energies greater than 0.165 eV. Decoupling approximations developed for rovibrationally inelastic scattering problems can be applied to reduce the computational effort. The application of the coupled-states (CS) and infinite order sudden (IOS) approximations to $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$ is discussed in Sec. 2.4.

2.2 Coupled-Channel Equations for Rovibrational Energy Transfer

The CC equations for rotational and vibrational energy transfer following the development of AD are summarized in this section. Without coupling between electronic states, the off-diagonal terms, T_{IJ}^1 , T_{IJ}^2 , and V_{IJ} are zero. Therefore, Eq. (2.7) reduces to

$$\left[T_Q + V - E \right] \Xi = 0 \quad (2.13)$$

where the subscripts denoting electronic state have been suppressed since there is no ambiguity. The diagonal corrections for nuclear motion, T_{II} s of Eq. (2.7), are usually very small⁴⁹ compared to V_{II} because of the mass difference between the electrons and the nuclei. These terms are neglected in Eq. (2.13). Therefore, the electronic and nuclear motions can be considered separately since ∇_α does not operate on Ψ_I . The kinetic energy operator of Eq. (2.13) with respect to a space-fixed (SF) coordinate system (the unprimed coordinate system of Fig. 1.1) is

$$\begin{aligned} T_Q = & -\frac{1}{2\mu} R^{-1} \left(\frac{\partial^2}{\partial R^2} \right) R + \frac{l^2}{2\mu R^2} \\ & -\frac{1}{2m} r^{-1} \left(\frac{\partial^2}{\partial r^2} \right) r + \frac{j^2}{2mr^2} \end{aligned} \quad (2.14)$$

where l is the orbital angular momentum of He relative to H_2 , and j is the rotational angular momentum of H_2 . For a 1S -state atom colliding with a $^1\Sigma$ -state diatomic there are no contributions to the angular momenta l and j from

electronic orbital or spin angular momentum, therefore these operators have a simple form whose eigenfunctions are the spherical harmonics, $Y_{jm_j}(\hat{r})$ and $Y_{lm_l}(\hat{R})$,

$$\left[\frac{j^2}{2mr^2} - \epsilon_j \right] Y_{jm_j}(\hat{r}) = 0 ; \quad \epsilon_j = \frac{j(j+1)}{2mr^2} \quad (2.15)$$

$$\left[\frac{l^2}{2\mu R^2} - \epsilon_l \right] Y_{lm_l}(\hat{R}) = 0 ; \quad \epsilon_l = \frac{l(l+1)}{2\mu R^2} \quad (2.16)$$

where $\hat{r} = \mathbf{r} / |\mathbf{r}|$ and $\hat{R} = \mathbf{R} / |\mathbf{R}|$.

Two forms of the Schrödinger equation for H_2 are considered in this study. The first is Eq. (2.15) with ϵ_j replaced by

$$\epsilon_j = hc[j(j+1)B_0 - j(j+1)^2D_0 + [j(j+1)]^3H_0] \quad (2.17)$$

where Eq. (2.17) is an energy-corrected-rigid-rotor (ECRR) expression⁵⁰ for the energy levels, and the second is the vibrating-rotor (VR) Schrödinger equation

$$\left[-\frac{1}{2m}r^{-1} \left(\frac{\partial^2}{\partial r^2} \right) r + \frac{j^2}{2mr^2} + V_{H_2(B)}(r) - \epsilon_i \right] \chi_i(r) Y_{jm_j}(\hat{r}) = 0 \quad (2.18)$$

where

$$i = vj$$

and v labels the vibrational level of H_2 . The ECRR expression for ϵ_j , Eq. (2.17), incorporates centrifugal distortion effects through inclusion of the second two terms on the right and provides a rotational manifold in closer accord with experiment (see Table 2.1). The spectroscopic constants, B_0, D_0

and H_0 , refer to the ground vibrational state of $H_2(B^1\Sigma_u^+)$ and are also given in Table 2.1. Equation (2.18) provides an exact treatment of H_2 when $V_{H_2(B)}$ is the accurate diatomic potential. (The potential of Kolos and Wolniewicz⁵¹ is used in this study.) Therefore ϵ_i and χ_i of Eq. (2.18) are exact eigenvalues and eigenfunctions of H_2 . The ϵ_i are given in Table 2.2.

Equation (2.13) is solved via an expansion method, i.e. the total wave function, Ξ , is expanded in a basis of eigenfunctions of total angular momentum, $Y_{jl}^{JM}(\hat{R}, \hat{r})$, vibrational functions, $\chi_i(r)$, and radial functions $u^J(R)$

$$\Xi_{vj}^{JM} = \sum_{v''j'l''} (Rr)^{-1} \chi_{v''j'l''}(r) Y_{jl}^{JM}(\hat{r}, \hat{R}) u_{v''j'l'' \leftarrow vj}^J(R) \quad (2.19)$$

The Y_{jl}^{JM} s contain all of the angular dependence of Ξ

$$Y_{jl}^{JM} = \sum_{m_j=-j}^j \sum_{m_l=-l}^l (jlm_j m_l | j l J M) Y_{jm_j}(\hat{r}) Y_{lm_l}(\hat{R}) \quad (2.20)$$

where the coefficients $(jlm_j m_l | j l J M)$ are Clebsch-Gordan coefficients.

Substituting (2.19) and (2.20) into (2.13), multiplying on the left by $r^{-1} \chi_{v'}^* Y_{j'l'}^{JM*}$, and integrating over r , $\hat{r}$, and $\hat{R}$ yields the usual set of coupled equations

$$\left[\frac{d^2}{dR^2} + k^2 - \frac{l'(l'+1)}{R^2} \right] u_{\kappa' \leftarrow \kappa}^J(R) = \sum_{\kappa''} \langle \kappa' | \tilde{V} | \kappa'' \rangle_{r, \hat{R}} u_{\kappa'' \leftarrow \kappa}^J(R) \quad (2.21)$$

where

$$\kappa = vj l \quad (2.22)$$

$$k_{\epsilon'}^2 = 2m(E - \epsilon_{\epsilon'}) \quad (2.23)$$

$$\tilde{V}(R, r, \theta) = V(R, r, \theta) - V_{H_2(B)}(r) \quad (2.24)$$

and

$$\langle \kappa' | \tilde{V} | \kappa'' \rangle = \iiint \chi_{\epsilon'} Y_{j' l'}^M \tilde{V} \chi_{\epsilon''} Y_{j'' l''}^M dr d\hat{r} d\hat{R} \quad (2.25)$$

Unprimed and primed quantum numbers denote values before and after the collision, respectively.

The potential energy, V , depends on the internal coordinates, R , r , and $\theta = \cos^{-1}(\hat{r} \cdot \hat{R})$ and is invariant with respect to rotation of the three-atom system, due to the isotropy of space. The potential is expanded in terms of Legendre polynomials of argument $\cos \theta$

$$\tilde{V} = \sum_{\lambda} v_{\lambda}(r, R) P_{\lambda}(\cos \theta) \quad (2.26)$$

When this expansion is substituted into Eq. (2.25) integration over $\hat{r}$ and $\hat{R}$ can be done analytically

$$\begin{aligned} \langle \kappa' | \tilde{V} | \kappa'' \rangle_{r, R} &= \sum_{\lambda} \iint Y_{j' l'}^M P_{\lambda} Y_{j'' l''}^M d\hat{r} d\hat{R} \int \chi_{\epsilon'} v_{\lambda} \chi_{\epsilon''} dr \\ &= \sum_{\lambda} \langle j' l' | P_{\lambda}(\cos \theta) | j'' l'' \rangle_{\hat{r}, \hat{R}} \langle \epsilon' | v_{\lambda} | \epsilon'' \rangle_r \\ &= \sum_{\lambda} f_{\lambda}(j' l' j'' l''; J) \langle \epsilon' | v_{\lambda} | \epsilon'' \rangle_r \end{aligned} \quad (2.27)$$

where the $f(j' l' j'' l''; J)$ are Percival-Seaton coefficients.⁵²

The integration over r is carried out before the CC equations are solved and grids of

$$v_{\lambda\ell'\ell''}(\mathbf{R}) = \langle \ell' | v_{\lambda} | \ell'' \rangle_{\mathbf{r}} \quad (2.28)$$

as a function of $\mathbf{R}$ are stored in data files. Matrix elements at arbitrary values of $\mathbf{R}$ are obtained by interpolation. The grid density and order of interpolation were adjusted to avoid the introduction of spurious inflection points between the computed values of $v_{\lambda\ell'\ell''}(\mathbf{R})$. Grid spacings of 0.2 au in the range $0 \text{ au} < R < 5.5 \text{ au}$ and 0.5 au for $R > 5.5 \text{ au}$ along with fourth order Lagrange interpolation⁵³ were found to be sufficient in these applications. The VIVAS algorithm^{47,48} employed to solve the CC equations requires first and second derivatives of the matrix elements (2.28) with respect to $\mathbf{R}$. Grids of the first and second derivatives were also stored and interpolated between to obtain their values at arbitrary $\mathbf{R}$. This was found to be more accurate than direct differentiation of the interpolation formula although it requires more computer storage space.

When the ECRR energy levels and RR wave function of H_2 are used, the coupling matrix elements simplify to

$$\langle j'l' | \tilde{V} | j''l'' \rangle_{\mathbf{r},\mathbf{R}} = \sum_{\lambda} v_{\lambda}(\mathbf{r}_i, \mathbf{R}) f_{\lambda}(j'l'j''l''; J) \quad (2.29)$$

where $\mathbf{r}_i$ is fixed. The two values of $\mathbf{r}_i$ used in this study are the equilibrium bond length for $\text{H}_2(\text{B}^1\Sigma_u^+)$ of 2.4 au (r_{eq}) and the more accurate vibrationally averaged bond length of 2.5 au (r_{va}). It is computationally advantageous to use the ECRR approximation rather than the exact description of H_2 because of the simpler form of the coupling matrix elements (i.e. Eq. (2.29) vs. Eq.

(2.27)); however, it is only an approximation and its accuracy must be checked. The Legendre expansion coefficients from Eq. (2.29) for use in scattering calculations are obtained for arbitrary R exactly as the $v_{\lambda l' l''}$ (see discussion following Eq. (2.28)).

The solution of the CC equations subject to the boundary conditions on the radial functions

$$u_{\kappa' \leftarrow \kappa}^J(0) = 0$$

and

$$\begin{aligned} u_{\kappa' \leftarrow \kappa}^J(R) \sim & k_{\nu'}^{-1/2} [\delta_{\nu\nu'} \delta_{jj'} \delta_{ll'} \exp[-i(k_l R - \frac{l\pi}{2})] \\ & - S_{\kappa' \leftarrow \kappa}^J \exp[i(k_{\nu'} R - \frac{l'\pi}{2})]] \end{aligned} \quad (2.30)$$

defines the scattering matrix, S^J .

The complete asymptotic solution, Ξ_{vij} , of Eq. (2.21) is a linear combination of the Ξ_{vij}^{JM} . Choosing the initial relative motion to be in the z direction

$$\begin{aligned} \Xi_{vij} \sim & \exp(ik_l z) \chi_l Y_{jm_l} \\ & + \sum_{\nu' j' m_j} f_{\nu' j' m_j \leftarrow \nu j m_j}(\hat{R}) R^{-1} \exp(ik_{\nu'} R) \chi_{l'} Y_{j' m_j} \end{aligned} \quad (2.31)$$

where f is the scattering amplitude. The outgoing parts of these two expansions are matched to obtain the scattering amplitudes

$$\begin{aligned}
f_{v'j'm_{v'}-vjm_j}(\hat{R}) &= i(k_i k_{i'})^{-1/2} \sum_{j=0l=|j-j|}^{\infty} \sum_{j'=|j-j|}^{j+j} \sum_{j''=|j-j'|}^{j+j'} \sum_{m_j=-l'}^{l'} \\
&\times i^{l-l'+1} (2l+1)^{1/2} (jlm_j 0 | jlm_j) \\
&\times (j'l'm_{j'}m_{j'} | j'l'JM) T_{\kappa' \leftarrow \kappa}^J Y_{l'm_j}(\hat{R})
\end{aligned} \quad (2.32)$$

where

$$T_{\kappa' \leftarrow \kappa}^J = \delta_{v'v} \delta_{jj'} \delta_{ll'} - S_{\kappa' \leftarrow \kappa}^J \quad (2.33)$$

Differential cross sections for the $i \rightarrow i'$ transition are then given by

$$\frac{d\sigma_{i \rightarrow i'}}{d\hat{R}} = (2j+1)^{-1} (k_{i'}/k_i) \sum_{m_j=-j}^j \sum_{m_{j'}=-j'}^{j'} |f_{v'j'm_{v'}-vjm_j}(\hat{R})|^2 \quad (2.34)$$

Blatt and Biedenharn⁵⁴ showed that Eq. (2.34) can be written as

$$\frac{d\sigma_{i \rightarrow i'}}{d\hat{R}} = (-1)^{j'-j} [4(2j+1)k_i^2]^{-1} \sum_{\gamma} A_{\gamma} P_{\gamma}(\cos\theta) \quad (2.35)$$

where

$$A_{\gamma} = \sum_{j_1} \sum_{j_2} \sum_{l_1} \sum_{l_2} \sum_{l'_1} \sum_{l'_2} Z(l_1 j_1 l_2 j_2; j \gamma) Z(l'_1 j'_1 l'_2 j'_2; j' \gamma) T_{v'j'_1 l'_1 \leftarrow v j l_1}^{J_1} T_{v j l_2 \leftarrow v' j'_2 l'_2}^{J_2} \quad (2.36)$$

and

$$\begin{aligned}
Z(abcd; ef) &= (-1)^{1/2(f-a+c)} [(2a+1)(2b+1)(2c+1)(2d+1)]^{1/2} \\
&\times (ac \ 00 | acf \ 0) W(abcd; ef)
\end{aligned} \quad (2.37)$$

Here W is a Racah coefficient.

The integral inelastic cross section is given by

$$\sigma_{i \rightarrow i'} = \sum_j \sigma_{i \rightarrow i'}^j \quad (2.38)$$

where

$$\sigma_{i \rightarrow i'}^j = \left[\frac{\pi(2j+1)}{k_i^2(2j+1)} \right] \sum_{\Pi'} |T_{\kappa' \leftarrow \kappa}^j|^2 \quad (2.39)$$

By microscopic reversibility

$$\sigma_{i \rightarrow i'} = k_i^2 k_{i'}^{-2} (2j' + 1)(2j + 1)^{-1} \sigma_{i' \rightarrow i} \quad (2.40)$$

Results of the scattering calculations are described in Chapter 4, and details are given in Appendix 1.

2.3 Coupled-Channel Equations for Electronic Energy Transfer

Equation (2.7) is the Schrödinger equation for collisions involving transfer of electronic energy. The $V_{\Pi\S}$ correspond to PESs as in Eq. (2.13) but coupling between electronic states is no longer small. Therefore the action of the nuclear kinetic energy operator on the electronic functions cannot be ignored. This means nuclear and electronic motions cannot be considered separately. Thus since all of the information on electronic wave functions is obtained in a coordinate system attached to the molecular plane, it is advantageous to transform the Hamiltonian into a body-fixed (BF) representation^{16,55} (the primed coordinates of Fig. 1.1). The BF frame, first utilized by Hirschfelder⁵⁶ and pursued by Curtiss and co-workers^{57,58}, is well known in atom-molecule collision theory and provides a basis for many angular momentum decoupling approximations^{34,59} (see Sec. 2.4). The transformation from SF to BF frames is readily accomplished using the Euler angle⁶⁰ (α , β , and γ) rotations. The BF coordinate system is defined to have its z axis along $\mathbf{R}$ and the three atoms in the y - z plane.⁶¹ In this frame $\mathbf{I}^2$ and $\mathbf{j}^2$ are given by

$$\mathbf{j}^2 = - \left[\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} - (\sin \theta)^{-2} (\mathbf{J}_z - \mathbf{L}_z)^2 \right] \quad (2.41)$$

$$\begin{aligned} \mathbf{I}^2 &= (\mathbf{J} - \mathbf{L} - \mathbf{j})^2 \\ &= (\mathbf{J} - \mathbf{L})^2 - 2(\mathbf{J}_z - \mathbf{L}_z)^2 + \mathbf{j}^2 \end{aligned} \quad (2.42)$$

$$+ 2\cot\theta(J_y - L_y)(J_z - L_z) - 2i(J_x - L_x)\frac{\partial}{\partial\theta} \quad (2.43)$$

where $\mathbf{L}$ is the total electronic angular momentum, and $\mathbf{J}$, the total angular momentum, is $\mathbf{j} + \mathbf{l} + \mathbf{L}$ (electron spin angular momentum has been neglected). Equations (2.14), (2.41), and (2.43) show that there are three types of coupling terms due to the nuclear kinetic energy operator: Born-Oppenheimer (BO)⁶² coupling which arises because of the parametric dependence of the electronic wave function on R, r , and θ ,

$$D_1(I, J, R) = \langle \Psi_I | \frac{\partial}{\partial R} \Psi_J \rangle_{\mathbf{q}} \quad (2.44)$$

$$D_1(I, J, r) = \langle \Psi_I | \frac{\partial}{\partial r} \Psi_J \rangle_{\mathbf{q}} \quad (2.45)$$

$$D_1(I, J, \theta) = \langle \Psi_I | \frac{\partial}{\partial \theta} \Psi_J \rangle_{\mathbf{q}} \quad (2.46)$$

angular or Coriolis coupling

$$L_1(I, J, i) = \langle \Psi_I | L_i | \Psi_J \rangle_{\mathbf{q}} \quad i = x, y, z \quad (2.47)$$

$$L_2(I, J, z) = \langle \Psi_I | L_z^2 | \Psi_J \rangle_{\mathbf{q}} \quad (2.48)$$

$$L_2(I, J, L) = \langle \Psi_I | L^2 | \Psi_J \rangle_{\mathbf{q}} \quad (2.49)$$

and mixed BO-Coriolis coupling,

$$L_2(I, J, x\theta) = \langle \Psi_I | L_x \frac{\partial}{\partial \theta} | \Psi_J \rangle_{\mathbf{q}} \quad (2.50)$$

The BO, $L_1(I, J, z)$, $L_2(I, J, z)$, and $L_2(I, J, L)$ terms couple states of the same symmetry for atom-diatom collisions (i.e. $A' \rightarrow A'$ or $A'' \rightarrow A''$ in C_s symmetry).¹⁸ The remaining terms may have non-zero elements between A' and A'' states.

As stated above, for collisions of S-state atoms with Σ -state diatomics the electronic angular momentum is zero and thus does not play a role so I^2 and j^2 simplify to:

$$j^2 = - \left[\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} - (\sin \theta)^{-2} J_z^2 \right] \quad (2.51)$$

$$\begin{aligned} I^2 &= (J - j) \\ &= J^2 - 2J_z^2 + j^2 + 2\cot\theta J_y J_z - 2i J_x \frac{\partial}{\partial \theta} \end{aligned} \quad (2.52)$$

This simplification eliminates the Coriolis and mixed BO-Coriolis NA coupling terms from the coupled equations. J and its components depend only on the Euler angles, which specify the orientation of the molecular plane with respect to the SF axes, and thus do not act on the electronic functions.

From Eq. (2.7) it is clear that the nature of the coupled equations will depend on the choice of electronic basis used to expand the total scattering wave function. So before deriving the CC equations for the radial wave functions two electronic basis sets, adiabatic and diabatic, will be described.

2.3.1 Adiabatic Electronic Basis

The adiabatic electronic functions, Ψ_l^{ad} , diagonalize the electronic Hamiltonian, H_{el} ,

$$H_{el} \Psi_l^{\text{ad}}(\mathbf{q}; \mathbf{Q}) = \epsilon_l^{\text{ad}}(\mathbf{Q}) \Psi_l^{\text{ad}}(\mathbf{q}; \mathbf{Q}) \quad (2.53)$$

(i.e. they are solutions of the electronic Schrödinger equation). Eigenvalues of

this equation, ϵ_i^{ad} , depend on the internal coordinates of the system but not on overall rotation or translation. The ϵ_i^{ad} are the adiabatic representations of V_{II} from Eq. (2.7). The electronic functions themselves, however, may depend on overall translation and rotation of the system^{7,55} because the atomic basis functions used in most standard quantum chemistry calculations translate with the molecular frame (this aspect of the calculation is discussed in more detail in Chapter 4).

These adiabatic electronic wave functions and PESs can be computed and many standard codes for this exist. Their use in scattering calculations, however, leads to complication because of their dependence on the nuclear coordinates. This can be seen by inserting the adiabatic basis into Eq. (2.5), so that Eq. (2.7) becomes

$$\left[T_Q + V_{\text{II}} - E \right] \Xi_i = - \sum_{j \neq i} \left[T_{ij} \right] \Xi_j \quad (2.54)$$

where the off-diagonal terms, V_{ij} , drop out because of the orthonormality of the electronic basis functions. Equation (2.54) can be converted into a set of CC equations for radial functions similar to Eq. (2.21). The resulting coupled equations contain velocity dependent couplings, which come from T_{ij} (see Eq. (2.9)). Therefore, existing methods that solve the CC equations for electronically adiabatic collisions cannot be used here. Therefore, it is advantageous to use an electronic representation that eliminates these terms. Such a representation is described in the next section.

2.3.2 Diabatic Electronic Basis

In practice the advantage of straightforward calculation of the adiabatic energy surfaces and wave functions is often outweighed by the fact that the NA couplings in the neighborhood of an avoided crossing (or an actual crossing) become large and the simplifying approximation of neglecting them breaks down. When the NA coupling is large, the problem is more naturally treated in a diabatic representation in which the electronic states are those that retain some simple molecular orbital structure or molecular property as they pass through the crossing region. The physical process implied by the diabatic representation is that the wave functions retain approximately the same character throughout the collision. The idea of abandoning the adiabatic representation in favor of a diabatic one was first suggested by Lichten⁵³ and later put on more quantitative footing for atom-atom collision systems by Smith.⁶⁴ Since then diabatic electronic bases have been used in a number of studies of NA processes in both atom-atom and atom-molecule collision systems.^{16,17,22,23}

In this work the diabatic basis set will be defined as the set which eliminates nonadiabatic coupling and whose members are orthonormal for fixed $\mathbf{Q}$ ¹⁸

$$\langle \Psi_i^d | \nabla_o \Psi_j^d \rangle_{\mathbf{q}} = 0 \quad (2.55)$$

$$\langle \Psi_i^d | \Psi_j^d \rangle_{\mathbf{q}} = \delta_{ij} \quad (2.56)$$

In terms of the diabatic electronic basis, the coupled equations for Ξ_i are

$$\left[T_Q + V_H^d + E \right] \Xi_i = - \sum_{j \neq i} V_{ij}^d \Xi_j \quad (2.57)$$

Notice that this set of electronic wave functions no longer diagonalize H_{el} ,

$$\langle \Psi_i^d | H_{el} | \Psi_j^d \rangle \neq 0 \quad (2.58)$$

however, standard methods can be used to solve the resulting CC equations.

The diabatic basis can be thought of as a generalization of the adiabatic basis and obtained from it by a R, r, θ -dependent unitary transformation:²⁰

$$\Psi_i^d = \sum_j \Psi_j^{ad} A_{ij}(R, r, \theta) \quad (2.59)$$

When only two electronic states are coupled (which is the case for $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$) the transformation is equivalent to a rotation by an angle $\omega(R, r, \theta)$:

$$(\Psi_1^d, \Psi_2^d) = (\Psi_1^{ad}, \Psi_2^{ad}) \begin{pmatrix} \cos\omega & \sin\omega \\ -\sin\omega & \cos\omega \end{pmatrix} \quad (2.60)$$

The diabatic BO coupling

$$D_1^d(1,2,\alpha) = \langle \Psi_1^d | \frac{\partial}{\partial \alpha} | \Psi_2^d \rangle \quad (2.61)$$

is obtained by substituting Eq. (2.60) into (2.61)

$$\begin{pmatrix} 0 & D_1^d(1,2,\alpha) \\ D_1^d(2,1,\alpha) & 0 \end{pmatrix} = \begin{pmatrix} \cos\omega & -\sin\omega \\ \sin\omega & \cos\omega \end{pmatrix} \begin{pmatrix} 0 & D_1^{ad}(1,2,\alpha) \\ D_1^{ad}(2,1,\alpha) & 0 \end{pmatrix} \\ \times \begin{pmatrix} \cos\omega & \sin\omega \\ -\sin\omega & \cos\omega \end{pmatrix} + \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \frac{\partial}{\partial \alpha} \omega \quad (2.62)$$

The condition

$$D_1^{\text{ad}}(1,2,\alpha) + \frac{\partial}{\partial \alpha} \omega = 0 \quad (2.63)$$

is necessary to satisfy Eq. (2.55) and determines the mixing parameter ω . The form of **A** shows that Eq. (2.56) is also satisfied. The basic formulas relating the adiabatic and diabatic representations are:

$$\epsilon_1^{\text{ad}} + \epsilon_2^{\text{ad}} = V_{11}^{\text{ad}} + V_{22}^{\text{ad}} = V_{11}^{\text{d}} + V_{22}^{\text{d}} \quad (2.64)$$

$$\epsilon_2^{\text{ad}} - \epsilon_1^{\text{ad}} = V_{11}^{\text{ad}} - V_{22}^{\text{ad}} = \left[(V_{11}^{\text{d}} - V_{22}^{\text{d}})^2 + 4(V_{12}^{\text{d}})^2 \right]^{1/2} \quad (2.65)$$

and

$$\tan 2\omega = \frac{2V_{12}^{\text{d}}}{(V_{11}^{\text{d}} - V_{22}^{\text{d}})} \quad (2.66)$$

where V_{11}^{d} , V_{22}^{d} , and V_{12}^{d} are the PESs and coupling in the diabatic representation.

Determination of the diabatic wave functions is thus accomplished by determining the rotation angle ω as a function of R , r , and θ . Baer has shown that ω can be determined by integrating the NA coupling terms²⁰

$$\begin{aligned} \omega(R, r, \theta) = \omega(R_0, r_0, \theta_0) &+ \int_{R_0}^R D_1^{\text{ad}}(1, 2, R)_{R', r, \theta} dR' \\ &+ \int_{r_0}^r D_1^{\text{ad}}(1, 2, r)_{R_0, r', \theta} dr' + \int_{\theta_0}^{\theta} D_1^{\text{ad}}(1, 2, \theta)_{R_0, r_0, \theta'} d\theta' \end{aligned} \quad (2.67)$$

It will be shown, in Chapter 5, however, that $\omega(R, r, \theta)$ can be associated with a physical property of HeH_2 and computed directly. It should be noted that the adiabatic and diabatic electronic bases will yield identical results if they

describe the same function space. In most applications numerical couplings are interpolated from a grid of computed values, as described in Sec. 2.2, which should have a simpler behavior near the crossing in the diabatic representation. This represents a further advantage of the diabatic electronic basis.

2.3.3 Coupled-Channel Equations for Electronic Energy Transfer in the Diabatic Representation

The discussion in this section closely parallels that of Sec. 2.2 extended to include electronically inelastic phenomena. The coupled equations for Ξ in terms of the diabatic electronic basis are given in Eq. (2.57). The elements of the electronic Hamiltonian matrix are independent of Euler angle rotations because electronic angular momentum plays no role in the collision. This allows the use of a SF frame to develop the CC equations. In the general case of atom-diatom scattering, electronic orbital and spin angular momentum are coupled to the nuclear angular momentum, and the use of BF coordinates allows a great simplification.^{18,55}

In the SF frame, Ξ is expanded using Eq. (2.19)

$$\Xi_{I\kappa}^{\mathbf{JM}} = \sum_{I'\kappa'} (Rr)^{-1} \chi_{I'\kappa'} Y_{I'\kappa'}^{\mathbf{JM}} u_{I'\kappa',-I\kappa}^{\mathbf{JM}} \quad (2.68)$$

where the index I is included to distinguish electronic states. The diagonal and off-diagonal elements of the electronic Hamiltonian are expanded in

Legendre polynomials:

$$\tilde{V}_{IJ} = \sum_{\lambda} v_{\lambda}^{IJ} P_{\lambda}(\cos\theta) \quad (2.69)$$

as suggested by Rebentrost and Lester.¹⁷ Substituting (2.68) and (2.69) into (2.57) yields

$$\begin{aligned} \left[\frac{d^2}{dR^2} + k_{I'I'}^2 - \frac{l'(l'+1)}{R^2} \right] u_{I'\kappa' \leftarrow I\kappa}^{JM} = \\ - \sum_{\kappa''} \langle \kappa' | \tilde{V}_{I'I'} | \kappa'' \rangle_{r,R} u_{I'\kappa' \leftarrow I\kappa}^{JM} \\ - \sum_{I'' \neq I', \kappa''} \langle \kappa' | \tilde{V}_{I'I''} | \kappa'' \rangle_{r,R} u_{I''\kappa'' \leftarrow I\kappa}^{JM} \end{aligned} \quad (2.70)$$

where

$$k_{I'I'}^2 = 2m(E - \epsilon_{I'I'}), \quad (2.71)$$

and

$$\langle \kappa' | \tilde{V}_{I'I''} | \kappa'' \rangle_{r,R} = \sum_{\lambda} f_{\lambda}(j'I'j''I''; J) \langle l' | v_{\lambda}^{I'I''} | l'' \rangle_r \quad (2.72)$$

The coupling in the first sum on the right of Eq. (2.70) causes transitions between the rovibrational levels of the I th electronic state analogous to the coupling in the pure rovibrational CC equations. The coupling in second sum promotes transitions to different electronic levels. The two terms can be combined into a single sum and the resulting coupled equations will have the same form as those for rovibrational energy transfer.

2.4 Decoupling Approximations

As stated above the major limiting factor in the application of the CC formalism is the $2j + 1$ degeneracy of each rotational level j . A number of approximations have been developed for the rovibrational energy transfer problem which reduce the number of CC equations by partially or totally decoupling j and l .⁵⁹ Equation (2.70) shows that the CC equations including electronic energy transfer for $\text{He-H}_2(\text{B } ^1\Sigma_u^+)$ have the same form as those for purely rovibrational energy transfer, Eq. (2.21). Therefore, application of these decoupling approximations is straightforward. In this Section the CS and IOS approximations are summarized.

The CS method was first developed by McGuire and co-workers³⁴ and separately reported by Pack.⁶⁵ It is probably the most accurate of the decoupling approximations and leads to a reduction from N CC equations to about $N^{1/2}$ CS equations.⁶⁶ Solution of the CC or CS equations requires a large amount of CPU time when the number of coupled equations > 100 -200; thus, the CS approximation will be most useful for treating rovibrational energy-transfer below about 1 eV total scattering energy.

The CS equations are obtained from the CC equations in the BF frame. The BF kinetic energy operator is given by Eqs. (2.14), (2.51), and (2.52) and as stated earlier electronic PESs, V in Eq. (2.13), are invariant with respect to the rotation defining the BF system relative to the SF system. The BF total

wave functions are obtained from the SF by

$$\Xi_i^{J\Omega} = \sum_{m_j=-j}^j D_{m_j\Omega}^j(\alpha, \beta, \gamma) \Xi_{vjm_j} \quad (2.73)$$

where $D_{m_j\Omega}^j$ are the matrix elements of the irreducible representation of the rotation operator⁶⁰ and Ω is the projection of j on the BF z-axis. The operator I^2 operates only on the angular part of Ξ , and its matrix elements have one contribution that is diagonal in Ω ,

$$\langle j\Omega | I^2 | j'\Omega \rangle = [J(J+1) + \delta_{jj'}j(j+1) - 2\Omega^2] \quad (2.74)$$

and one that is nondiagonal,

$$\langle j\Omega | I^2 | j'\Omega' \rangle = -\delta_{\Omega', \Omega \pm 1} [(J \pm \Omega + 1)(J \mp \Omega)]^{1/2} j^\mp \quad (2.75)$$

where $j^\pm$ are the raising and lowering operators for the rigid rotor.

The CS approximation is obtained by (1) neglecting the terms off-diagonal in Ω which amounts to ignoring Coriolis coupling and (2) approximating the diagonal terms by $\bar{l}(\bar{l}+1)$. The values of the $\bar{l}$ standardly used are $\bar{l} = J$ and $J-j$.³⁴ The best value of $\bar{l}$ for He+H₂ should be determined empirically by comparison with accurate CC results.

With the above approximations, the CS equations for rovibrational energy transfer take the form

$$\left[\frac{d^2}{dR^2} + k_{l'l'}^2 - \frac{\bar{l}'(\bar{l}'+1)}{R^2} \right] u_{l'\Omega'-\Omega}^M =$$

$$- \sum_{\iota' \Omega'} 2\mu \langle \iota' \Omega' | \tilde{V} | \iota'' \Omega'' \rangle_{r, R} u_{\iota' \Omega' - \iota \Omega}^{\lambda} \quad (2.76)$$

where

$$\langle \iota' \Omega' | \tilde{V} | \iota'' \Omega'' \rangle_{r, R} = \sum_{\lambda} g_{\lambda}(j' \Omega' j'' \Omega'') \langle \iota' | v_{\lambda} | \iota'' \rangle_r \quad (2.77)$$

and

$$g_{\lambda} = \delta_{\Omega' \Omega''} (-)^{\Omega'} \begin{pmatrix} j' & \lambda & j'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j' & \lambda & j'' \\ -\Omega' & 0 & \Omega'' \end{pmatrix} \times [(2j' + 1)(2j'' + 1)]^{1/2} \quad (2.78)$$

The essence of the approximation (2) is to neglect the effect of the rotating frame on the BF wavefunction thus standard expressions for differential and integral cross sections can be used.³⁴

The CS approximation is known to yield cross sections in good agreement with CC results for quite a few systems.² It has even been applied to NA collisions with excellent results.¹⁸ For $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$, however, under the conditions of the experiment the $v=3, j=2$ level of $\text{H}_2(\text{B } ^1\Sigma_u^+)$ is populated and $\approx 200 \text{ cm}^{-1}$ of translational energy is available, there are over 400 open channels in the CC expansion on the excited state surface alone. (A channel corresponds to one $|\nu_j|$ basis function in the expansion of the wave function. If the scattering energy is above ϵ_{ν_j} the channel is 'open' or energetically accessible otherwise it is closed) Even when the possibility of H_2 dissociation, which is energetically allowed, is neglected, as it is here, the CS equations will be too numerous to solve. A further level of decoupling is achieved in the IOS approximation developed and applied by Pack and co-workers^{35,65,67}. In its

original form its application was limited to systems for which $\tilde{V}$ could be represented by the simple expansion

$$\tilde{V} = v_0 + v_1 \sum_{\lambda} c_{\lambda} P_{\lambda}(\cos \theta) \quad (2.79)$$

Secrest⁵⁹ showed that this restriction is unnecessary and that potentials of the form (2.26) can be used. The IOS approximation is obtained by replacing l^2 by $\bar{l}(\bar{l} + 1)$ and j^2 by $\bar{j}(\bar{j} + 1)$. The total wave function is then expanded as

$$\Xi_{\bar{j}}^{\bar{l}} = \sum_{\nu} (Rr^{-1}) \chi_{\bar{j}}^{\bar{l}}(r) u_{\bar{j}}^{\bar{l}}{}_{-\nu}(R; \theta) \quad (2.80)$$

where $\chi_{\bar{j}}^{\bar{l}}$ is the solution of Eq. (2.19) with j^2 replaced by $\bar{j}(\bar{j} + 1)$ and $u^{\bar{l}}$ depends parametrically on θ . Substitution of (2.80) into (2.57) yields

$$\left[\frac{d^2}{dR^2} + (k_{\bar{j}}^{\bar{l}})^2 - \frac{\bar{l}(\bar{l} + 1)}{R^2} \right] u_{\bar{j}}^{\bar{l}}{}_{-l\nu}(R; \theta) = -2\mu \sum_{l''\nu''} \langle l'\nu' | \tilde{V}_{l'l''}(R, r; \theta) | l''\nu'' \rangle_r \times u_{\bar{j}}^{\bar{l}}{}_{-l''\nu''}(R; \theta) \quad (2.81)$$

For the $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$, $\text{He} + \text{H}_2(\text{X } ^1\Sigma_g^+)$ system twenty vibrational basis functions are required if two closed vibrational levels are included (six vibrational levels of $\text{H}_2(\text{B } ^1\Sigma_u^+)$ and all fourteen levels of $\text{H}_2(\text{X } ^1\Sigma_g^+)$). This gives twenty coupled equations which can be treated easily.

The solution of Eq. (2.81) subject to the boundary conditions

$$u_{l'l'-l_v}^{\bar{l}}(0;\theta) = 0$$

and

$$\begin{aligned} u_{l'l'-l_v}^{\bar{l}} \sim & k_{l'l'}^{\bar{l}} [\delta_{ll'} \delta_{vv'} \exp\{-i(k_{l'l'}^{\bar{l}} R - \frac{\bar{l} \pi}{2})\}] \\ & - S_{l'l'-l_v}^{\bar{l}} \exp[i(k_{l'l'}^{\bar{l}} R - \frac{l' \pi}{2})] \end{aligned} \quad (2.82)$$

define the IOS scattering matrix, $S_{l'l'-l_v}^{\bar{l}}$. The approximate scattering matrix for a $\kappa \rightarrow \kappa'$ transition is obtained by computing the matrix elements of the IOS scattering matrix and the eigenfunctions of total angular momentum

$$\tilde{S}_{l'\kappa' \rightarrow l\kappa}^J = |l+l'-2\bar{l} \rangle \langle j'l' | S_{l'l'-l_v}^{\bar{l}}(\theta) | j\rangle_{\hat{R}} \quad (2.83)$$

The θ -dependent S-matrix, Eq. (2.82), is computed at several values of θ , and the integral, Eq. (2.83), is then computed numerically.

Two reasonable choices for $\bar{l}$ are given by l , the initial orbital angular momentum, and l' the final orbital angular momentum. These choices of $\bar{l}$ allow a considerable simplification of $\tilde{S}$. In particular, Eq. (2.83) can be reduced to a one-dimensional integral over θ .⁶⁷ This reduces the computational effort required to obtain $\tilde{S}$ considerably. As in the CS calculations the best value of $\bar{l}$ for He+H₂ should be determined by comparison with more accurate calculations.

Calculations have not yet been performed with the CS and IOS approximations. The formulas have been included to demonstrate their applicability to the problem and show a next logical step in the study of higher energy collision processes in the $\text{He} + \text{H}_2$ system.

Table 2.1: Spectroscopic constants and energy levels for the energy corrected rigid rotator (ECRR).

Spectroscopic Constants ^a			
$B_0 = 19.4537$ $D_0 = 1.541 \times 10^{-2}$ $H_0 = 1.1 \times 10^{-5}$			
Energy Levels (eV)			
j	ϵ_j ^b	ϵ_{exact} ^c	$\Delta (\epsilon_{\text{exact}} - \epsilon_j)$
0	0.	0.	0.
1	0.00482	0.00485	0.00003
2	0.01442	0.01450	0.00008
3	0.02867	0.02885	0.00018
4	0.04748	0.04777	0.00029
5	0.07065	0.07108	0.00043
6	0.09803	0.09857	0.00054
7	0.12932	0.13000	0.00068
8	0.16427	0.16511	0.00084
9	0.20259	0.20364	0.00105
10	0.24402	0.24530	0.00128

^a Taken from Ref. 68.

^b ECRR energy levels from Eq. (2.17).

^c Computed using the potential from Ref. 51 including diagonal corrections.

Table 2.2: Rovibrational energy levels (v_j) of $H_2(B^1\Sigma_u^+)$.^a

Energy Levels (eV)				
j	v			
	0	1	2	3
0	0.0	0.163462	0.322388	0.476969
2	0.014496	0.177264	0.335592	0.489658
4	0.047770	0.208984	0.365980	0.513867
6	0.098571	0.257521	0.412536	0.563669
8	0.165119	0.321292	0.473828	0.622732
10	0.245311	0.398399	0.548120	0.694431
12	0.336936	0.486813	0.633532	0.776998
14	0.437846	0.584513	0.728160	0.868642
16	0.546093	0.689622	0.830210	0.967604

^a Potential for $H_2(B^1\Sigma_u^+)$, including diagonal corrections, taken from Ref. 51.

^b Energies are relative to $v_j=00$. Zero point energy is 0.084585 eV.

CHAPTER 3

Configuration Interaction PES for $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$

3.1 Introduction

A PES of 'chemical accuracy', i.e. one kcal/mole (0.04 eV) or better, is needed in order to compute accurate rovibrational energy-transfer cross sections. Even with the great success of ab initio quantum chemistry methods this accuracy requirement is responsible for the lack of PESs available for scattering calculations. To obtain a PES for $\text{HeH}_2(2 ^1A')$, CI calculations were carried out at a grid of points in R , r , and θ . The accuracy of these computed interaction energies is estimated to be better than one kcal/mole. The grid of values is combined with those of RBP and FTN to compute an analytic representation of the PES.

To facilitate the description of the calculations the surface is divided into two parts: a highly anisotropic short- to intermediate-range region; and a long-range region in which the interaction is weak. The dominating forces in these two regions have different physical origins and different methods are used to compute them. Dispersion forces dominate the long-range interaction for the neutral collision partners.⁶⁹ Therefore, the polarizability and quadrupole moment of $\text{H}_2(\text{B } ^1\Sigma_u^+)$ were computed for use in the multipole expansion of the

interaction energy and to assure that the basis set was adequate to describe the long-range interaction. In the short-range region electron correlation plays an important role particularly near avoided crossings so CI was used. The PES was then fit with analytic functions to facilitate scattering calculations. Two such representations were computed in this study: one is valid for rotational energy transfer in the rigid-rotor (RR) model and has r fixed at 2.4 au; the second is valid for rovibrational energy transfer and includes the full r dependence of the PES.

The following section describes the basis set and CI method used to compute the short-range $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$ grid of interaction energies. The polarizability and quadrupole moment calculations for $\text{H}_2(\text{B } ^1\Sigma_u^+)$ are described in Appendix 2. Section 3.3 contains results of the calculations including the analytic fits and discusses the features of the PES in relation to the scattering.

3.2 Basis Set and Method of Calculation

It is well known that rotational transitions are sensitive to long-range intermolecular forces. One goal of this study is to obtain accurate cross sections for purely rotational energy transfer in collisions of He with $\text{H}_2(\text{B } ^1\Sigma_u^+)$; thus, the long-range region of the PES must be described accurately. The multipole expansion of the long-range interaction is correct in the limit that the electron density of the two subsystems does not overlap. For this system the dominant contributions to the interaction energy are the dispersion terms with a leading R^{-6} and R^{-8} dependence⁶⁹

$$V_{lr} = - \frac{3U_{\text{He}}U_{\text{H}_2}\alpha_{\text{He}}}{2(U_{\text{He}}+U_{\text{H}_2})} \left[\alpha_{\text{H}_2}P_0(\cos\theta) + \frac{1}{3}(\alpha_{\parallel} - \alpha_{\perp})P_2(\cos\theta) \right] R^{-6} \\ - \frac{1}{3}\alpha_{\text{He}}\Theta^2P_4(\cos\theta)R^{-8} \quad (3.1)$$

where U_k is the ionization energy and α_k is the isotropic polarizability of species k , $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the parallel and perpendicular components of the H_2 polarizability, respectively; and Θ is the H_2 quadrupole moment. The He polarizability and ionization energies are taken from experiment; however, at present, no experimental $\text{H}_2(\text{B } ^1\Sigma_u^+)$ polarizability or quadrupole moment is available. For the purposes of this study both quantities were computed. The basis sets were chosen to be flexible enough to obtain accurate energies as well as multipole moments and polarizabilities of He (^1S) and $\text{H}_2(\text{B } ^1\Sigma_u^+)$. The

basis set for H was determined by studying the dependence of the $H_2(B\ ^1\Sigma_u^+)$ polarizability on basis set and correlation (see Appendix 2).

Large Gaussian basis sets were employed in all calculations. In the interest of reducing computational costs while preserving accuracy, the H atom basis is that of RPB. This basis provides a good description of the polarizability⁷⁰ and quadrupole moment⁷¹ as well as the energy²⁸ of $H_2(B\ ^1\Sigma_u^+)$. It includes a very diffuse s function and one set of diffuse p functions to describe the Rydberg character of $H_2(B\ ^1\Sigma_u^+)$. The near-Hartree-Fock-limit basis of Garrison, et al. was used for He.⁷² Basis sets for He and H are shown in Table 3.1.

Correlation effects must be included to compute an accurate polarizability of $H_2(B\ ^1\Sigma_u^+)$ (see Appendix 2). Therefore, the wave function chosen was a multi-configuration SCF (MCSCF) + CI function. The idea was to compute MCSCF MOs for $HeH_2(2\ ^1A')$ and use them to specify multi-reference single- and double-excitation CI (MRSD-CI) configuration spaces in PES calculations. A small complete-active-space SCF (CASSCF) wave function, including all configurations with two electrons in the lowest energy molecular orbital (MO) (the He 1s orbital asymptotically) and two electrons distributed among the next four a' MOs (the first two σ_g and σ_u MOs of H_2 at large R), was chosen to describe HeH_2 . In the region of the van der Waals interaction (large R) the CASSCF calculations converged easily. However, near the two avoided surface crossings, between $He + H_2(B\ ^1\Sigma_u^+)$ and $He + H_2(E,F\ ^1\Sigma_g^+)$ ²⁹ and between He

+ $H_2(B\ ^1\Sigma_u^+)$ and $He + H_2(X\ ^1\Sigma_g^+)$,³⁰ a standard application of MCSCF techniques does not converge. The problem that arises is known as 'root-flipping' and has been discussed by other authors.^{73,74} Root-flipping is a change in the energy ordering of the roots of the MCSCF Hamiltonian that occurs during the variational optimization (i.e. as the MOs are optimized to describe an excited state the energy of the ground-state increases until the ground state becomes the second root of the MCSCF Hamiltonian within the chosen configuration space). If optimization is taking place on the higher energy root when root-flipping occurs, the ground state, which is now the higher energy root, is optimized until the roots flip back. The process often continues indefinitely once it starts.

At this point, several CI methods, which are not plagued by this convergence problem, were tested. The most convenient approach was determined to be a variant of the iterative natural orbital (INO) method of Bender and Davidson.⁷⁵ INO and MRD-CI energies were found to agree to within about 1 m μ (0.03 eV) (see Table 3.2).⁷⁶

For our INO approach, calculation of a point on the PES is performed in three steps. First, the SCF orbitals of $He + H_2(C\ ^1\Pi_u)$ are computed.⁷⁷ These orbitals are used to define a set of reference configurations (RCs) as follows: (i) two electrons are chosen to occupy the $1a'$ orbital which is mainly He ($1s$) in character; (ii) the two remaining electrons are distributed in the $2a'$ and $3a'$ orbitals (the bonding and antibonding orbitals of H_2 asymptotically) in all

ways consistent with $^1A'$ symmetry. Second, an MRSD-CI calculation that includes all single and double excitations from the RCs is performed to obtain the natural orbitals (NOs) of $\text{HeH}_2(2^1A')$. A new, larger set of RCs is defined by placing two electrons in the $1a'$ NO and distributing the remaining two electrons in the $2a'$, $3a'$, $4a'$, and $5a'$ NOs in all ways consistent $^1A'$ symmetry. This is followed by a final SD-CI over the RCs constructed from the NO basis. The interaction energies calculated using the above procedure were combined with those of RBP and FTN to provide the PES used for cross section calculations.

3.3 Results and Discussion

The MRD-CI computations of RPB and FTN were carried out with the goal of providing insight on rovibrational energy transfer and electronic quenching. For this reason, attention in those studies was not directed to the long-range region that governs purely rotational energy transfer. In this study, calculations were carried out to determine accurately the molecular properties that dominate the interaction energy at large R , namely the dipole polarizability and quadrupole moment of $H_2(B\ ^1\Sigma_u^+)$ in order to assure a reliable description of this region. Additional ab initio energies were computed for large R ($13 \leq R \leq 16$ au) to determine the range of validity of the multipole expansion,⁶⁹ Eq. (3.1). The range of r values is determined from the turning points of the $H_2(B\ ^1\Sigma_u^+)$ potential ($V_{H_2(B)}$). The chosen grid spans the range $1.4\text{ au} < r < 7.5\text{ au}$, which are higher in energy than the turning points for $v = 9$ and over 1 eV above the experimental scattering energy. Table 3.3 contains a comparison of the INO calculated interaction energies with those from Eq. (3.1). The constants used in the multipole expansion are given in Table 3.4. Notice that α_{H_2} and Θ_{H_2} are computed as functions of the H_2 internuclear separation. Table 3.3 shows that the multipole expansion is in good agreement with the INO results when $R > 15$ au. This indicates that the multipole expansion is accurate beyond $R = 15$ au.

The interaction energy becomes very anisotropic for $R < 5$ au, espe-

cially for the larger values of r considered. *Ab initio* interaction energies were computed for two more angles of approach, 30° and 60° , for $R=1.0, 2.0, 3.0$, and 4.0 au and $r=1.8, 2.4, 4.0$, and 6.0 au to assure accurate determination of the anisotropy of the interaction. Additional calculations were carried out for $R \leq 1.0$ au to provide a better fit at higher energies and to increase the density of interaction energies owing to the limited number available from FMC and RPB. All of the computed INO energies are collected in Tables 3.5-3.9.

Analytic representations of the PES are used to facilitate scattering calculations. Three different analytic PESs were used in this study: (1) the analytic function of FMC, labeled V^{FMC} , which is described in Ref. 31 (2) a function, labeled V^{RR} , computed for this study with r fixed at 2.4 au, the equilibrium bond length of $\text{H}_2(\text{B}^1\Sigma_u^+)$, and (3) a second function, labeled V^{VR} , computed here that includes the full r dependence of the PES. The functions V^{RR} and V^{VR} are described below. They each fit the *ab initio* calculations with a root-mean-square deviation that is within chemical accuracy (0.04 eV); thus, no approximation is introduced by using them. In these fits, care was also taken not to introduce spurious inflection points, which can drastically affect scattering calculations. The strategy adopted in fitting V^{RR} and V^{VR} was to use different functional forms to describe different regions of the PES and to connect them smoothly.⁷⁸ This approach provides more flexibility than using a single function and makes it easier to attain high accuracy. Once the functions were obtained, many one-dimensional (i.e. fixed r and R , fixed r and θ , or

fixed R and θ) cuts through V^{RR} and V^{VR} were plotted to ensure that no spurious inflection points were generated.

For small R ($R \leq 5.5$ au) V^{RR} is a Sorbie-Murrell type function,⁷⁹ (V_{sr}^{RR}). This form was chosen because it is very flexible and the short-range part of V , from Eq. (2.13), is complex and varies rapidly. For $R \geq 15.0$ au the analytic multipole expansion, Eq. (3.1), is appropriate (V_{lr}). In the intermediate region V varies relatively slowly and a cubic spline function (V_{lr}) joins the short- and long-range functions together.

The short-range function is

$$V_{sr}^{RR}(R_1, R_2) = Q \exp(-\alpha(\rho_1 + \rho_2)) + b_1(\cos\theta)^{b_2} \exp(-b_3(R-b_4)^2) \quad (3.2)$$

where

$$\rho_i = R_i - R_i^0, \quad i=1,2; \quad R_1^0=R_2^0=1.4 \text{ au} \quad (3.3)$$

$$Q = a_0 + \sum_i a_i \rho_i + \sum_{i < j} a_{ij} \rho_i \rho_j + \dots + O(\rho_i^8) \quad i = 1,2 \quad (3.4)$$

and R_1 and R_2 are the two He-H bond lengths. The second term in Eq. (4.1) is a localized Gaussian that aids description of the local maximum associated with the $\text{He} + \text{H}_2(\text{E}, \text{F}^1\Sigma_g^+)$ avoided crossing. Nonlinear-least-squares techniques were used to optimize the a_i and b_i coefficients of Eqs. (3.2) and (3.4). All ab initio data below an interaction energy of 8.1 eV with $R \leq 5.5$ au was used in the optimization. The average deviation of the fit in the short-range region is 0.02 eV. The maximum deviation is 0.14 eV, but occurs for $V > 7$

eV, a region of the potential not likely to be sampled in the present cross section calculations. The accuracy of the fit is not known for energies above 8.1 eV which corresponds to R_1 or $R_2 < 0.95$ au. The parameters defining the short-range function are given in Table 3.10.

In the intermediate region, cubic splines were used to fill in the grids of ab initio values for $4.0 \text{ au} < R < 10.0 \text{ au}$ with $\theta = 0^\circ, 45^\circ$, and 90° . The coefficients of a three-term Legendre expansion were then computed using the formulas

$$V_{ir}^{RR}(R_i, \theta) = \sum_{\lambda} v_{\lambda}(R_i) P_{\lambda}(\cos \theta) \quad \lambda = 0, 2, 4 \quad (3.5)$$

$$V_{ai} = V(R_i, \theta=0^\circ) \quad (3.6)$$

$$V_{bi} = V(R_i, \theta=45^\circ) \quad (3.7)$$

$$V_{ci} = V(R_i, \theta=90^\circ) \quad (3.8)$$

$$v_0(R_i) = \frac{1}{15} [7V_{ai} - V_{bi} + 9V_{ci}] \quad (3.9)$$

$$v_2(R_i) = \frac{1}{21} [16V_{ai} - V_{bi} + 15V_{ci}] \quad (3.10)$$

$$v_4(R_i) = -\frac{4}{35} [2V_{ai} - V_{bi} + V_{ci}] \quad (3.11)$$

Cubic splines were also used to connect the grid of points computed using Eqs. (3.5)-(3.11) to the multipole expansion. The intermediate- and long-range functions, V_{ir}^{RR} and V_{lr} , reproduce the ab initio interaction energies exactly.

Figure 3.1 shows contour plots of the V^{RR} and V^{FMC} fits at $r=2.4$ au. The PES has several noteworthy features. An attractive interaction with a

minimum of about 0.03 eV is found near $R=4.0$ au, equilibrium H_2 bond length $r_{eq}=2.4$ au and $\theta=90^\circ$. An avoided crossing with the $He + H_2(E, F^1\Sigma_g^+)$ PES produces a barrier near $R=4.0$ au, and $\theta=0^\circ$. This arises when He penetrates the very diffuse σ_u orbital of $H_2(E, F^1\Sigma_g^+)$ and experiences a strong electrostatic attraction, while the $He + H_2(B^1\Sigma_u^+)$ interaction is repulsive. The avoided crossing and attractive well combine to make the PES highly anisotropic and thus are expected to influence translation-to-rotation-to-vibration energy exchange. The figure also shows that for $R < 1.0$ au, $\theta=90^\circ$ is not the lowest energy approach on V^{RR} (see Table 3.9). It will be shown in Chapter 5 that this feature is a manifestation of the avoided PES crossing between $HeH_2(1^1A')$ and $HeH_2(2^1A')$. The plot of the present fit shows these maxima and minima. The FMC fit has all of the above-mentioned features plus several more which are artifacts of the fitting procedure. For $\theta=90^\circ$ the FMC function has maxima near $R=6.0$ and 2.2 au and a saddle point near $R=1.8$ au, none of which are seen in the ab initio energies. The minimum of the FMC function is deeper by about a factor of five than the ab initio minimum.

The short-range parts of V^{RR} and V^{FMC} are readily expanded in Legendre polynomials (see Eq. 2.26) by using numerical quadrature to project the coefficient of each term⁸⁰

$$v_\lambda(R) = \frac{2\lambda + 1}{2} \int_0^\pi V^{FIT}(R, \theta) P_\lambda(\cos\theta) \sin\theta \, d\theta \quad (3.12)$$

where V^{FIT} is the analytic PES. By symmetry, only even terms contribute to the sum. The FMC function required 17 terms, while the present fit required 31. Most of the coefficients have appreciable magnitude only in the vicinity of $R=1.2$ au. This is due to the anisotropy introduced by the discontinuity in V as R_1 or R_2 goes to zero. The R dependence of v_λ , $\lambda=0,2,\dots,18$ is plotted for V^{RR} and V^{FMC} in Fig. 3.2. Both expansions are qualitatively similar and show unusually large anisotropies near $R=4.0$ au demonstrated by the local maxima in v_2-v_{10} for the present fit and in v_2 for the FMC fit. The long-range anisotropy is large in both expansions as $v_2 > v_0$ for $R \leq 8.0$ au. There are, however, several differences between the two expansions which may be expected to influence the energy transfer cross-sections. Most apparent is the less rapid variation of v_2 with R for the present fit. This feature and the differences in the maxima in the anisotropic terms v_4, v_6, v_8 , and v_{10} should affect the scattering results at higher energies (i.e. relative translational energy > 0.2 eV). The v_2 term in the present fit falls off more slowly with R than that of FMC and shows the different long-range anisotropies of V^{RR} and V^{FMC} , which should influence low-energy scattering results. The sensitivity of computed cross sections to these differences is explored in Chapter 4.

The analytic function V^{VR} is similar to V^{RR} but includes the dependence of V on r . The asymptotes of $\text{HeH}_2(2^1A')$, $\text{He} + \text{H}_2(B^1\Sigma_u^+)$ and $\text{He} + \text{HeH}(A^1\Sigma)$, are properly described by choosing V^{VR} to be a sum of two- and three-body interactions

$$V^{VR}(R, r, \theta) = V_{\text{HeH(A)}}(R_1) + V_{\text{HeH(A)}}(R_2) + V_{\text{H}_2\text{(B)}}(R_3) + \tilde{V}^{VR}(R, r, \theta) \quad (3.13)$$

where $R_3 \equiv r$ and $V_{\text{HeH(A)}}$ is chosen as the potential curve for $\text{HeH(A } ^1\Sigma)$ computed by Buenker and co-workers⁸¹ and fit by Farantos et al.³¹, and $\tilde{V}^{VR}$ becomes 0 as R_1 , R_2 , or R_3 go to ∞ . Notice that $\tilde{V}$ of Eq. (2.24) is

$$\tilde{V}(R, r, \theta) = \tilde{V}^{VR}(R, r, \theta) + V_{\text{HeH(A)}}(R_1) + V_{\text{HeH(A)}}(R_2) \quad (3.14)$$

$\tilde{V}^{VR}$ is represented by a function with the same form as V^{RR} .

The short-range function, $\tilde{V}_{sr}^{VR}$, is

$$\tilde{V}_{sr}^{VR} = Q \exp(-\alpha_1(\rho_1 + \rho_2) - \alpha_3(\rho_3)) + \tilde{B}^{VR} \quad (3.15)$$

where ρ_i is defined in Eq. (3.3), Q is given by (3.4) with $i = 1, 2, 3$, and $R_3^0 = r_{eq} = 2.4$ au, and $\tilde{B}^{VR}$ is

$$\tilde{B}_{VR} = G_1 + G_2 + A_1 + (G_3 + G_4)A_2 + (G_5 + G_6)C_1 + (G_7 + G_8)D_1 \quad (3.16)$$

where

$$G_i = b_{i1}(R - b_{i2})^{b_{i3}} \exp(b_{i4}(R - b_{i5})^2 + b_{i6}(r - b_{i7})^2) \quad (3.17)$$

$$A_1 = 1/2(\sin(4\theta - \pi/2) + 1)^2 \quad (3.18)$$

$$C_1 = \cos(\theta)^{20} \quad (3.19)$$

$$D_1 = 1/2 \exp(-4((\theta - \pi/6)(180/\pi))^2) \quad (3.20)$$

The second term in (3.15), $\tilde{B}^{VR}$, improves the fit in regions where the PES is complicated. The same nonlinear optimization was used to obtain the linear and nonlinear parameters which are given in Table 3.11. All ab initio data

below an interaction energy of 8.1 eV with $R \leq 5.5$ au were used in the fitting procedure. The average deviation of the fit is 0.033 eV and the largest deviations are of order 0.13 eV and occur above 5 eV.

In the intermediate region, exponential splines were used to fill in the grids of computed points for $5 \text{ au} < R < 15 \text{ au}$ with $r = 1.4, 1.8, 1.95, 2.2, 2.4, 2.6, 3.5, 4.0, 4.5, 5.0, 6.0,$ and 7.5 au . The coefficients of the Legendre expansions

$$V_{ir}^{VR}(R, r, \theta) = \sum_{\lambda} v_{\lambda}(R, r) P_{\lambda}(\cos \theta) \quad (3.21)$$

were generated by Gauss-Legendre integration (see Eq. (3.12)). The necessary grid points of V_{ir}^{VR} were generated using exponential spline interpolation. Integration was used rather than Eq. (3.5)-(3.11) because for $r > 3.5 \text{ au}$ a three-term expansion is not accurate. Figure 3.3 displays the R dependence of the first 7 expansion coefficients for $r = r_{va} = 2.5 \text{ au}$. These curves are significantly different than those for V^{RR} and V^{FMC} , and show that a small change in the bond length of H_2 leads to a change in the anisotropy of the PES.

A contour plot of V^{VR} at $r = 4.0 \text{ au}$ is depicted in Figure 3.4. An avoided crossing with the $He + H_2(X^1\Sigma_g^+)$ PES leads to a deep ($\approx 1.5 \text{ eV}$) well near $R=1.5 \text{ au}$, $r=4.0 \text{ au}$, and $\theta=45^\circ$. This crossing explains the experimentally observed fluorescence quenching.²⁶ There is also a barrier to the avoided crossing region of about 0.15 eV, centered near $R=1.3 \text{ au}$, $r=3.5 \text{ au}$, with

$\theta=60^\circ$. Overall the PES for electronically excited $\text{He-H}_2(\text{B } ^1\Sigma_u^+)$ is more complex than those typically encountered in scattering of ground state species.

To obtain a form of the PES useful for scattering calculations, $v_\lambda(R_i, r)$ must be integrated over the vibrational wave functions, χ_i , of $\text{H}_2(\text{B } ^1\Sigma_u^+)$ (see discussion preceeding Eq. (2.28)). The χ_i s were computed⁸² and stored as numerical grids. The integrals

$$v_{\lambda ii'} = \langle i | v_\lambda | i' \rangle \quad (3.22)$$

were computed using a modified Simpson's rule⁸³ with 500 grid points in the range 1.1 au to 7.0 au (the turning points of V_{H_2} for $v=3$ are about 1.7 au and 4.0 au). The grid of $v_\lambda(R_i, r)$ for $V_{\text{sr}}^{\text{VR}}$ were computed using 32 point Gauss-Legendre quadrature to solve Eq. (3.12) up to $\lambda = 16$ and 64 point formulas up to $\lambda = 38$. The grid points for $V_{\text{ir}}^{\text{VR}}$ were computed using exponential splines to interpolate between the computed values. The radial dependence of $\langle 00 | v_\lambda | 00 \rangle$ (see Eq. (2.28)) is shown in Fig. 3.5 for $0 < \lambda < 14$. These curves are quite similar to those in Fig. 3.4, but are in only fair agreement with those in Fig. 3.2. This implies that the ECRR approximation with $r = r_{v_2}$ will be more accurate than with $r = r_{\text{eq}}$ as expected.

Table 3.1: Atomic orbital basis sets employed in the PES calculations for $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$.

He atom ^a			H atom ^b		
	Exponent	Contraction		Exponent	Contraction
s	4840.88855	0.000059	s	68.16	0.0255
s	723.10892	0.000463	s	10.2465	0.01938
s	164.29971	0.002422	s	2.34648	0.09280
s	46.63626	0.009995	s	0.67332	1.0
s	15.27779	0.034249	s	0.22466	1.0
s	5.52690	0.096302	s	0.082217	1.0
s	2.13288	1.0	s	0.025	1.0
s	0.84967	1.0	p	0.7	1.0
s	0.34364	1.0	p	0.2	1.0
s	0.13871	1.0	p	0.035	1.0
p	1.0	1.0			
p	0.2	1.0			

^a From Ref. 72

^b From Ref. 28

Table 3.2: Comparison of INO and MRDCI interaction energies for He + H₂(B ¹Σ_u⁺).^a

R (au)	r (au)	θ (°)	V _{INO} ^b	V _{MRDCI} ^c	ΔV ^d
20.0	1.4	0	50.864	50.855	0.009
2.0	2.4	0	271.445	270.495	0.950
3.0	3.4	0	22.906	22.272	0.634
4.0	2.4	0	23.634	23.548	0.086
6.0	2.4	0	5.607	5.875	-0.268
3.0	3.5	0	39.238	37.974	1.264
4.0	3.5	0	32.051	33.053	-1.002
20.0	3.5	0	12.524	12.589	-0.065
1.5	2.4	45	98.390	98.771	-0.381
6.0	2.4	45	1.971	2.209	-0.238
1.5	4.0	45	-54.541	-55.792	1.251
20.0	4.0	45	22.163	22.288	-0.125
4.0	2.4	90	-1.267	-1.280	0.013
6.0	2.4	90	-0.351	-0.340	-0.011
20.0	3.5	90	12.525	12.761	-0.236

^a Interaction energies computed relative to total electronic energy at r=2.4 au, θ=0°, 45°, and 90°. The INO and MRDCI energies at these geometries are: θ=0° ε_{INO}^{ad}=-3.650218 au, ε_{MRDCI}^{ad}=-3.650825 au; θ=45° ε_{INO}^{ad}=-3.650218 au, ε_{MRDCI}^{ad}=-3.649893 au; θ=90° ε_{INO}^{ad}=-3.650218 au, ε_{MRDCI}^{ad}=-3.650796 au.

^b Interaction energies are in millihartrees. See text for description of the INO method.

^c The MRDCI energies for θ=0° and 90° are from Ref. 28. The energies for θ=45° are from Ref. 30.

^d ΔV=V_{INO}-V_{MRDCI}

Table 3.3: Comparison of computed INO and multipole-expansion interaction energies for $\text{He} + \text{H}_2(\text{B}^1\Sigma_u^+)$ with $r=2.4$ au.^a

R(au)	Interaction Energies (cm^{-1})			
	θ			
	0°		90°	
	V_{INO}	V_{lr}	V_{INO}	V_{lr}
13.0	-0.88	-2.409	-0.73	-1.09
14.0	-1.1	-1.541	-0.44	-0.70
15.0	-0.88	-1.02	-0.26	-0.46
16.0	-0.61	-0.69	-0.15	-0.31

^a See text for description of the INO calculations. The multipole expansion is given by Eq. (3.1).

Table 3.4: Parameters of the long-range interaction energy, V_{lr} , for both the rigid-rotor and vibrating-rotor potential functions.^a

Molecular Properties Defining V_{lr}			
$U_{He} \text{ (eV)} = 24.58^b$ $U_{H_2} \text{ (eV)} = 4.237^c$ $\alpha_{He} \text{ (au)} = 1.3845^d$			
$r \text{ (au)}$	$\alpha_{ } \text{ (au)}^e$	$\alpha_{\perp} \text{ (au)}^e$	$\Theta \text{ (au)}^e$
1.10	1986.	112.	-16.26
1.40	1177.	100.	-10.04
1.80	553.	77.	-7.96
1.95	442.	70.	-7.37
2.20	320.	59.	-6.39
2.40	259.	51.	-5.83
2.43	257.	50.	-5.52
2.60	222.	44.	-4.92
3.00	213.	35.	-3.66
3.50	351.	29.	-2.29
4.00	410.	28.	-1.13
4.50	360.	30.	-0.05
5.00	220.	35.	1.00
6.00	100.	51.	3.14
40.00	64.5	64.5	11.86

- ^a Equation (3.1) is the expression for V_{lr} . Polarizabilities, Quadrupole moments and U_{H_2} refer to $H_2(B^1\Sigma_u^+)$.
- ^b Ref. 84.
- ^c Ionization potential is from ground vibrational state of $H_2(B^1\Sigma_u^+)$ to the ground vibrational state of H_2^+ (Ref. 85).
- ^d Ref. 86.
- ^e Full CI with the RPB basis set.

Table 3.5: Computed INO interaction energies for $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$ with $\theta=0^\circ$,^a

R (au)	Interaction Energy (mh)					
	r (au)					
	1.4	2.2	2.4	3.5	4.0	4.5
0.5			519.4			
1.5						270.
2.0			271.445			
2.5		26.031				
3.0			22.906	39.238	104.943	
3.5			24.149			
4.0			23.634	32.051	19.772	
5.0					29.634	
6.0			5.607		26.856	
20.0	50.864		0.0		12.524	

R (au)	Interaction Energy (mh)				
	r (au)				
	5.0	5.5	6.0	6.5	7.5
1.0	-31.	-15.	6.	31.	
1.25		-30.			
1.5		-21.	-23.4	-4.	48.6
2.0			56.6		
2.5					-15.6
4.0	14.224		108.188		
4.5			15.629		331.957
5.0			25.864		43.300
6.0			55.191		56.761
8.0			63.697		86.948
10.0			63.597		88.629
20.0			63.612		88.589

^a See text for description of the INO method.

Table 3.6: Computed INO interaction energies for $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$ with $\theta=30^\circ$.^a

R (au)	Interaction Energy (mh)			
	r (au)			
	1.8	2.4	4.0	6.0
0.5		419.8		
1.0	1204.	723.322	-5.978	25.693
2.0	14.562	76.643	58.621	-20.610
3.0	30.433	14.562	-13.071	-8.713
4.0	18.845	13.832	15.5	66.825
5.0			29.006	55.672

^a See text for description of the INO method.

Table 3.7: Computed INO interaction energies for $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$ with $\theta=45^\circ$.^a

Interaction Energy (mh)					
R (au)	r (au)				
	2.2	2.4	2.6	3.5	4.0
0.5		275.4			
0.85		298.1			
1.0		258.0	185.		
1.5	135.04				
5.0				15.845	24.719

Interaction Energy (mh)				
R (au)	r (au)			
	4.5	5.0	6.0	7.5
1.0				72.2
2.0				66.806
3.0				64.146
5.0	33.047	41.159	58.278	
6.0				86.282
8.0				89.224
20.0				88.589

^a See text for description of the INO method.

Table 3.8: Computed INO interaction energies for $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$ with $\theta=60^\circ$.^a

R (au)	Interaction Energy (mh)			
	r (au)			
	1.8	2.4	4.0	6.0
0.5	215.2			
0.6	173.4			
1.0	291.929	109.603	-6.737	56.746
2.0	33.425	7.865	-23.537	46.635
3.0	9.826	3.377	11.510	57.544
4.0			22.661	67.785

^a See text for description of the INO method.

Table 3.9: Computed INO interaction energies for $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$ with $\theta=90^\circ$.^a

Interaction Energy (mh)					
R (au)	r (au)				
	1.4	2.2	2.4	2.6	3.5
0.0			250.7		65.395
0.5			213.9		61.540
1.0	365.039	155.351	124.685	100.652	52.109
1.5			57.839		37.600
2.0					28.847
3.5	46.262	-0.874		0.315	
4.0					13.910

Interaction Energy (mh)					
R (au)	r (au)				
	4.0	4.5	5.0	6.0	7.5
0.0	52.295	53.001	59.855	78.787	
0.5	50.946			78.769	
1.0	46.850				
1.5				77.478	101.145
3.5				69.420	94.385
6.0				64.225	89.587
8.0				63.640	88.723
10.0				63.591	88.592
20.0				63.612	88.589

^a See text for description of the INO method.

E.2 Performance

E.2.1 Current

The new coatings provided marginally higher beam current than the original sources. However, the major gain was in longevity. The first of the two recoated sources we used lasted for nine months of regular use, and the second lasted for over a year. The source presently in use is a test formulation made by A.A. Warwick during his research on source fabrication for the MBE-4 accelerator experiment [51].

E.2.2 Source Emittance

The lower bound $\epsilon_{\min}$ on the normalized source emittance ($4\epsilon_{\text{RMS}}$) is given by the source radius, R_s , and the mean thermal energy $\frac{kT}{2}$ in each transverse plane as

$$\epsilon_{\min} = 2R_s \sqrt{\frac{kT}{mc^2}} = 0.23 \times 10^{-7} \pi \text{ meter radian.} \quad (E.1)$$

This is about a factor of 5 below the measured beam emittance, and indicates that there is a significant perturbation to the transverse velocity spread of the particles even before they exit the gun. Additional perturbations to the emittance of the beam, due to passage through grids at the exit of the gun, are calculated and compared with measurements in Appendix C.

E.2.3 Beam Purity

When our in-house sources were first installed, the Cs^+ beam was very pure. As the sources aged, they all began to yield a small proportion of light ions along with the bulk Cs^+ beam. The appearance of the light ions is accompanied by a decrease in the cesium component of the beam. When the light-ion fraction grew to about 5%, the source was no longer deemed

Table 3.11: Parameters of the vibrating-rotor short-range potential function, $\tilde{V}_{\text{sr}}^{\text{VR}}$, for $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$.^a

Parameters of $\tilde{V}_{\text{sr}}^{\text{VR}}$								
a_1	=	0.231116	$a_{1111113}$	=	0.645839	b_{21}	=	-1.63
a_3	=	1.530452	$a_{1111122}$	=	-0.694310	b_{22}	=	0
a_{11}	=	-2.792323	$a_{1111123}$	=	-0.017259	b_{23}	=	2
a_{12}	=	1.994314	$a_{1111133}$	=	-1.722151	b_{24}	=	-4.0
a_{13}	=	1.208391	$a_{1111222}$	=	0.467144	b_{25}	=	0
a_{33}	=	-0.662361	$a_{1111223}$	=	-0.528807	b_{26}	=	-0.5
a_{111}	=	-6.652986	$a_{1111233}$	=	-1.406190	b_{27}	=	6.0
a_{112}	=	4.518002	$a_{1111333}$	=	1.972106	b_{31}	=	-0.26
a_{113}	=	0.352857	$a_{1112223}$	=	0.592492	b_{32}	=	0
a_{123}	=	-2.397266	$a_{1112233}$	=	1.668503	b_{33}	=	0
a_{133}	=	1.354423	$a_{1112333}$	=	1.900602	b_{34}	=	-4.0
a_{333}	=	-0.662361	$a_{1113333}$	=	-0.763900	b_{35}	=	1.5
a_{1111}	=	11.690751	$a_{1122333}$	=	-0.855451	b_{36}	=	-1.0
a_{1112}	=	-15.711474	$a_{1123333}$	=	-0.250403	b_{37}	=	3.5
a_{1113}	=	-6.349879	$a_{1133333}$	=	-0.102876	b_{41}	=	0.99
a_{1122}	=	22.181812	$a_{1233333}$	=	0.599049	b_{42}	=	-1.5
a_{1123}	=	-6.584024	$a_{1333333}$	=	0.070486	b_{43}	=	2
a_{1133}	=	-0.462705	$a_{3333333}$	=	-0.104939	b_{44}	=	-10.0
a_{1233}	=	-6.584024	$a_{11111111}$	=	0.079080	b_{45}	=	1.5
a_{1333}	=	2.062351	$a_{11111112}$	=	-0.318292	b_{46}	=	-1.0
a_{3333}	=	0.100832	$a_{11111113}$	=	-0.250855	b_{47}	=	3.5
a_{11111}	=	-4.820791	$a_{11111122}$	=	0.874916	b_{51}	=	0.81
a_{11112}	=	-0.716029	$a_{11111123}$	=	0.584863	b_{52}	=	0
a_{11113}	=	1.288355	$a_{11111133}$	=	0.459826	b_{53}	=	0
a_{11122}	=	-0.591254	$a_{11111222}$	=	-1.408877	b_{54}	=	-4.0
a_{11123}	=	-4.670286	$a_{11111223}$	=	-0.736558	b_{55}	=	3.0
a_{11133}	=	-6.896874	$a_{11111233}$	=	-0.490640	b_{56}	=	-4.0
a_{11223}	=	11.362107	$a_{11111333}$	=	-0.555581	b_{57}	=	1.8
a_{11233}	=	5.661053	$a_{11112222}$	=	1.596933	b_{61}	=	-2.0
a_{11333}	=	0.050891	$a_{11112223}$	=	0.382777	b_{62}	=	3.0
a_{12333}	=	-4.137043	$a_{11112233}$	=	1.668503	b_{63}	=	2
a_{13333}	=	4.911766	$a_{11112333}$	=	0.258526	b_{64}	=	-3.0
a_{33333}	=	-0.552432	$a_{11113333}$	=	0.352352	b_{65}	=	3.0

Parameters of $\tilde{V}_{sr}^{VR}$ (cont.)								
a_{111111}	=	0.953611	$a_{11122233}$	=	-1.164936	b_{66}	=	-4.0
a_{111112}	=	3.855403	$a_{11122333}$	=	-0.124054	b_{67}	=	1.8
a_{111113}	=	0.490508	$a_{11123333}$	=	-0.311316	b_{71}	=	0.17
a_{111122}	=	-6.470331	$a_{11133333}$	=	-0.139552	b_{72}	=	0
a_{111123}	=	-3.966622	$a_{11223333}$	=	0.198006	b_{73}	=	0
a_{111133}	=	3.318820	$a_{11333333}$	=	-0.147726	b_{74}	=	-4.0
a_{111222}	=	0.467144	$a_{11333333}$	=	-0.270324	b_{75}	=	3.5
a_{111223}	=	1.546058	$a_{12333333}$	=	0.420217	b_{76}	=	-4.0
a_{111233}	=	3.102444	$a_{13333333}$	=	0.202493	b_{77}	=	2.4
a_{111333}	=	4.794422	$a_{33333333}$	=	0.133304	b_{81}	=	-0.34
a_{112233}	=	-5.747489	a_0	=	6.135083	b_{82}	=	3.5
a_{112333}	=	-1.810081	b_{11}	=	0.13	b_{83}	=	2
a_{113333}	=	1.434424	b_{12}	=	0	b_{84}	=	-10.0
a_{123333}	=	-2.359118	b_{13}	=	-10.0	b_{85}	=	3.5
a_{133333}	=	1.150129	b_{14}	=	0	b_{86}	=	-4.0
a_{333333}	=	-0.446758	b_{15}	=	0	b_{87}	=	1.8
$a_{1111111}$	=	-0.335307	b_{16}	=	-0.5	α_1	=	1.1
$a_{1111112}$	=	0.159021	b_{17}	=	5.0	α_3	=	0.5

^a $\tilde{V}_{sr}^{VR}$ parameters refer to Eq. (3.15). $a_2=a_1$, etc. by symmetry. Energy units are eV. Length units are bohr.

Figure 3.1: Contour plots of the analytic potential functions for $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$, V^{RR} (labeled 'present') and V^{FMC} . Dots mark the positions of hydrogen atoms. The contour interval is 0.1 eV and the lowest energy contours are: (1) the contours that extend to the border of the plot, $V=0.0$ eV, for V^{RR} ; (2) the dashed contours, $V=-0.1$ eV, for V^{FMC} . Mild attraction along $\theta=90^\circ$ for V^{RR} is not observed on the scale of the plot.

Figure 3.2: Radial dependence of the first ten Legendre coefficients of V^{RR} (labeled 'present') and V^{FMC} .

Figure 3.3: Radial dependence of the first seven Legendre coefficients of V^{VR} with $r=r_{va}=4.0$ au.

Figure 3.4: Contour diagram of the analytic potential function for $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$, $\tilde{V}^{\text{VR}}$ with $r=4.0$ au. Dots mark the positions of the hydrogen atoms. The contour interval is 0.5 eV and the lowest energy contours are the four smallest dashed ovals, $\tilde{V}=-2.0$ eV.

Figure 3.5: Radial dependence of the first seven Legendre coefficients of V^{VR} integrated over the lowest rovibrational wave function of $H_2(B^1\Sigma_u^+)$, χ_{00} .

CHAPTER 4

Energy Transfer Cross Sections

4.1 Introduction

The CC equations for rovibrational scattering of a diatomic molecule by an atom (Eq. 2.21) are solved with the interaction potentials, V^{RR} and V^{VR} described in Chapter 3 as well the FMC potential, V^{FMC} . Partial, differential and integral cross sections are computed for rovibrational transitions at scattering energies less than or equal to 0.210 eV.

Cross sections, labeled σ^{FMC} , σ^{ECRR} , and σ^{VARR} , for rotational energy transfer were computed on the three analytic PESs⁸⁷ $V^{FMC}(r=r_{eq})$, $V^{RR}(r=r_{eq})$, and $V^{VR}(r=r_{va})$ (V^{VARR}) using ECRR energy levels and rigid-rotor wave functions for $H_2(B\ ^1\Sigma_u^+)$. All computed rotational cross sections are compared to those for $He + H_2(X\ ^1\Sigma_g^+)$.⁸⁸ There is fair agreement between σ^{ECRR} , σ^{VARR} , and σ^{FMC} ; however, significant differences are found for some transitions.

An accurate VR description of H_2 along with the full V^{VR} PES is used to compute rotational and rovibrational cross sections, labeled σ^{VR} , up to a scattering energy of 0.210 eV. There is only fair agreement between σ^{VARR} and σ^{VR} near threshold for rotational transitions. Zero-point vibrational

motion is found to be important in collisions of He with $\text{H}_2(\text{B } ^1\Sigma_u^+)$ even when only rotational excitation occurs. Sharp peaks are found in $\sigma_{00 \rightarrow 02}$ at low scattering energies, $0.017 < E < 0.023$ eV. These apparent Feshbach resonances have cross sections that are dominated by a single partial wave contribution and differential cross sections (DCSS) that are nearly symmetric about a CM scattering angle of 90° . The DCSSs, or angular distributions, are also presented for rotational and rovibrational transitions at higher scattering energies (< 0.210 eV).

In section 4.2, σ^{FMC} , σ^{ECRR} , and σ^{VARR} are presented and compared. Integral and differential cross sections determined with the VR PES are given in section 4.3.

4.2 Cross Sections for Rotational Energy Transfer

The CC equations (2.21) were solved using the VIVAS^{47,48} and Gordon³⁹ algorithms. The accuracy of selected partial cross sections, σ^J , was checked using DeVogelaere's method.^{40,41} Integral cross sections were converged to two significant figures by the inclusion of both open and closed rotational levels in the expansion basis (see Eq. 2.19). At all energies, partial waves computed using the FMC potential were converged with all open and two closed rotational levels included in the expansion basis; however, some partial waves computed using the present surfaces required the inclusion of three closed rotational levels (see Appendix 1 for more details of the calculations).

Rotational integral cross sections were computed for energies in the range 0.015-0.150 eV. Partial cross sections (PCSs) for rotationally inelastic transitions are displayed in Figs. 4.1-4.4 for V^{RR} and V^{FMC} at several different relative translational energies. These figures show that the PCSs computed on the two surfaces are roughly the same order of magnitude. Figure 4.1 shows the appearance of maxima in σ_{00-02}^J for both potentials at 0.03 eV. The peaks are less pronounced and more numerous for V^{RR} . They increase in magnitude and shift to larger J , but otherwise change very little with increasing energy. The σ_{00-02}^J extend to larger J for V^{RR} , due to the larger long-range anisotropy mentioned in Sec. 3.3. For σ_{02-04}^J (Fig. 4.3) the present values are about a

factor of 2 smaller than those computed using V^{FMC} . The shapes of the PCS curves are, however, quite similar. The FMC and ECRR results for $\sigma_{00 \rightarrow 04}^J$ (Fig. 4.4) show qualitative differences in shape. The ECRR PCSs have one pronounced maximum at each of the three energies shown; however, the FMC $\sigma_{00 \rightarrow 04}^J$ plots are more like those for $\sigma_{00 \rightarrow 02}^J$ in that they have multiple maxima as a function of J .

The peaks in $\sigma_{00 \rightarrow 02}^J$ are unusual. Low energy collisions in ground state atom-diatom systems generally have only one or in some cases two broad maxima in $\sigma_{v_i \rightarrow v_j'}^J$ as a function of J .⁸⁹ Such structure can indicate resonances; however, the peaks in $\sigma_{00 \rightarrow 02}^J$ remain nearly constant as a function of energy as mentioned above (see Figs. 4.1 and 4.2). This appears to rule out resonances, which are expected to be energy dependent. The peaks are not caused by competition between different inelastic channels because they appear below the $v_j' = 04$ threshold (0.047 eV). Furthermore, the main features of $\sigma_{00 \rightarrow 02}^J$ are well reproduced by a four-channel ($j_l = 00, 2-2, 20, 22$) calculation which samples only the v_0, v_2 and v_4 terms of the Legendre expansion of the potential. It appears that the structure in $\sigma_{00 \rightarrow 02}^J$ is mainly due to the PES anisotropy.

To test this notion, the v_0, v_2 and v_4 coefficients of V^{RR} were varied and four-channel computations carried out. The modifications were made as follows; (1) the outer maxima in v_2 and v_4 near $R=4.0$ au were eliminated, v_0 remained unchanged; (2) the small outer maximum in v_0 near $R=4.0$ au was eliminated, v_2 and v_4 remained unchanged; (3) v_2 was replaced by v_2/R .

Modification (1) tests the sensitivity of $\sigma_{00 \rightarrow 02}^J$ to variations in v_2 and v_4 with R . Specifically it provides an indication of how the maxima in v_2 and v_4 affect the low energy partial cross sections for the $00 \rightarrow 02$ transition. Modification (2) tests the sensitivity of $\sigma_{00 \rightarrow 02}^J$ to variations in v_0 with R at intermediate R . Modification (3) tests the sensitivity of $\sigma_{00 \rightarrow 02}^J$ to variations in v_2 for large R , and probes the long-range effects. The effects of (1) and (2) on $\sigma_{00 \rightarrow 02}^J$ were minor; however, (3) eliminated all peaks in $\sigma_{00 \rightarrow 02}^J$ and reduced the cross section by about an order of magnitude. Hence the structure in $\sigma_{00 \rightarrow 02}^J$ is not a direct result of the maxima in v_0 , v_2 and v_4 . Modification (3) causes v_0 to dominate the PES in the classically accessible region, $R > 3.5$ au, characteristic of most ground-state systems studied to date. Thus, the maxima in $\sigma_{00 \rightarrow 02}^J$ appear to be caused by the dominance of v_2 for $0.6 \text{ au} \leq R \leq 12.0 \text{ au}$.

The peaks in $\sigma_{00 \rightarrow 02}^J$ can be understood more clearly in terms of the features of the PES (see Fig 3.1 and discussion in text). For this purpose it is convenient to use an approximate correspondence between the classical impact parameter and J .⁹⁰ Classically the orbital angular momentum, l , is

$$l = \mu v b \quad (4.1)$$

where v is the relative velocity of He and $\text{H}_2(\text{B}^1\Sigma^+)$ and b is the impact parameter. The quantum mechanical total angular momentum is

$$\mathbf{J} = \mathbf{j} + \mathbf{l} = \mathbf{j}' + \mathbf{l}' \quad (4.2)$$

and if the initial and final rotational angular momenta $\mathbf{j}$ and $\mathbf{j}'$ are zero,

$$J = l = l' \quad (4.3)$$

Otherwise this relation holds only in an average sense. The semiclassical approximation of l is⁹¹

$$l_{cl} \approx l + 1/2 \quad (4.4)$$

Thus from Eq. (4.1), (4.3), and (4.4), the impact parameter is approximately given by

$$b \approx \frac{(J + 1/2)}{\hbar k_{vj}} = \frac{(J + 1/2)}{k_{vj}} \quad (4.5)$$

where

$$\hbar k_{vj} = \mu v_{vj} \quad (4.6)$$

This relationship transforms the partial cross section from a function of J to an approximate function of b . The impact parameters corresponding to the values of J at which σ^J is a maximum are given in Table 4.1 for V^{FMC} and V^{RR} .

The maxima in $(\sigma^J)^{ECRR}$ (this notation means σ^J for V^{RR} within the ECRR approximation) occur near the same values of b at different energies. The outer maximum, near $b=7.5$ au, is a long-range effect that is not seen in $(\sigma^J)^{FMC}$. This is because V^{RR} has the proper analytic representation of the dispersion interaction. The maximum near $b=4.7$ au is caused by the potential well near $R=4.0$ au. The cross sections for rotational energy transfer are known to increase as the depth of such a well increases.⁹² The third maximum,

near $b=3.3$ au, is probably caused by collisions which sample the region of the PES around the saddle point along the C_{ov} approach that occurs near $R=3.0$ au. The maximum at the smallest value of J corresponds to an impact parameter of about $b=1.7$ au and is probably caused by tunneling of the scattering wave function into the highly anisotropic regions of the potential. As a result this peak is very small compared to the others (see Figs. 4.1 and 4.2). The maxima in σ^{FMC} do not occur at the same impact parameter for different energies with the regularity of those for σ^{RR} . There do, however, appear to be peaks near $b=5.0$ au, 3.0 au and 1.0 au which are probably caused by the same features of the PES that cause the inner three maxima in σ^{ECRR} . Again the long-range behavior of the PES is not properly accounted for in V^{FMC} so the outer maxima in σ^{ECRR} is not seen.

Figure 4.5 displays ECRR integral cross sections computed using V^{FMC} , V^{RR} and V^{VARR} along with the $\text{He} + \text{H}_2(\text{X } ^1\Sigma_g^+)$ results of Eastes and Secrest⁸⁸ as a function of relative translational energy. The cross sections for $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$ are also given in Table 4.2. Differences in cross sections reflect the differences in PESs because the ECRR approximation is used in all three calculations. The results for the three PESs are in reasonable agreement above the thresholds for the transitions for which Δj equals 2 or 4. The σ^{FMC} near thresholds are larger than σ^{ECRR} which are larger than σ^{VARR} . This is due to the relative well depths and anisotropies of the three PESs. The potential V^{FMC} has the deepest well near $R=4.0$ au of the three at about 0.15eV .

The anisotropy is also high in this region as the v_2 term of the Legendre expansion is larger than those for V^{RR} and V^{VARR} . These features cause a correspondingly large cross section. The V^{RR} surface has the next deepest well at about 0.03eV and smaller anisotropy; thus it has a smaller σ_{00-02} cross section. The V^{VARR} surface has a well of about 0.02eV but a higher anisotropy than the V^{RR} surface because of its longer $H_2(B^1\Sigma_u^+)$ bond length, 2.5 au vs. 2.4 au. The higher anisotropy increases σ and the more shallow well decreases it compared to σ^{ECRR} . The combination of these competing effects, as indicated by the calculation, reduces the cross section near threshold. These cross sections show that the approximate inclusion of vibrational motion in the description of $H_2(B^1\Sigma_u^+)$ via V^{VARR} is important for describing rotational transitions near their thresholds.

At higher scattering energies the trend is reversed and the ordering of the rotationally inelastic cross sections becomes $\sigma^{VARR} > \sigma^{ECRR} > \sigma^{FMC}$ (see e.g. σ_{00-02} in Fig 4.5). More of the PES is sampled by the scattering wave function at higher energies. In particular the highly anisotropic, small R, region becomes more important. The V^{VR} is more anisotropic at small R than V^{RR} which is more anisotropic than V^{FMC} , and this anisotropy rather than the well region will dominate the dynamics. At translational energies > 0.05 eV the agreement between σ^{ECRR} and σ^{VARR} improves, and as shown in the next section, both are in reasonable agreement with σ^{VR} .

All three PESs give cross sections roughly two orders of magnitude

larger than those for scattering of $H_2(X\ ^1\Sigma_g^+)$. This is consistent with the relative magnitudes of the Legendre coefficients and the relative moments of inertia of the two states of H_2 . In summary the scattering of $H_2(B\ ^1\Sigma_u^+)$ by He at low relative translational energies is characterized by large rotational cross sections caused by the high anisotropy of the interaction energy.

4.3 Accurate Cross Sections for Rovibrational Energy Transfer

In this section, integral and differential cross sections, σ^{VR} and $\partial\sigma^{\text{VR}}/\partial\hat{R}$, for rotational and rovibrational energy transfer, between 0.015eV and 0.210eV, are presented using the vibrating rotor energy levels and wave functions for $\text{H}_2(\text{B } ^1\Sigma_u^+)$. Below and even slightly above the threshold for vibrational excitation the ECRR approximation provides an accurate description of $\text{H}_2(\text{X } ^1\Sigma_g^+)$ in collisions with Li^+ .³³ The σ^{VR} are compared with σ^{VARR} at energies below and above this threshold (0.165 eV for $\text{H}_2(\text{B } ^1\Sigma_u^+)$) to further assess the accuracy of the ECRR approximation.

In Figure 4.6, integral cross sections σ^{VR} and σ^{VARR} are shown. The σ^{VARR} (at energies not reported in Table 4.2) and σ^{VR} are also given in Tables 4.3 and 4.4. Again the less accurate results, σ^{VARR} , are too large near the threshold for excitation and slightly too small at higher energies; although the agreement at higher energies is quite good for most transitions. The σ^{VARR} were computed at 0.180 and 0.210 eV, which are above the threshold for vibrational excitation, to ascertain the validity of the ECRR approximation at higher energies for this system. There is no indication (see Table 4.3) that the approximation breaks down to a greater extent because vibrationally inelastic transitions are energetically open.

As the scattering energy increases it will be easier to overcome the barrier to reaching the avoided crossing and fluorescence quenching will become

important (see discussion in Chapter 1). The PES near the avoided crossing has a drastically different shape than the long-range region (see Figs. 3.1 and 3.4) which is important at very low scattering energies. Therefore, this should be reflected in large changes in σ^{VR} as the scattering wave function begins to sample the avoided crossing region. The cross sections listed in Tables 4.3 and 4.4 do not show drastic changes near $E=0.150$ eV, the classical barrier to the avoided crossing minimum on V^{VR} . This is due to the effect of zero point vibrational motion. The asymptotic zero point energy is about 0.09 eV whereas near the avoided crossing it is 0.42 eV.⁹³ Therefore, the true barrier to quenching is likely to be between 0.15 and 0.48 eV above the asymptotic zero point energy, and the scattering calculations performed here should be accurate even though fluorescence quenching has been neglected.

At very low scattering energies 0.015-0.045 eV a dense grid of cross section calculations were performed. The results between 0.015 and 0.030 eV are given in Figure 4.7 and all are given in Table 4.5. The integral cross section for transitions from $v_j=00$ to $v'_j'=02$, $\sigma_{00 \rightarrow 02}$, has maxima at relative translational energies 0.0171, 0.019, and 0.021. At each of these energies $\sigma_{00 \rightarrow 02}$ is dominated by a different single partial wave contribution (0.0171 eV - $J=3$, 0.019 eV - $J=4$, and 0.021 eV - $J=5$). These two features have been attributed to resonances in other atom-diatom collision systems.^{33,94-96} The peaks disappear when the $v_j=04$ basis function is removed from the expansion (see Eq. 2.19), and suggests a Feshbach type resonance.⁹⁷ A Feshbach resonance is

one in which relative translational energy is temporarily converted to internal energy and a collision complex is formed. When the transition to an open rotational state is made the complex dissociates.

One model that has found some success in predicting resonance energies of a model problem^{98,99} is the adiabatic model of Muckerman and co-workers¹⁰¹⁻¹⁰³. In the model the 'fast' rotational motion is integrated over and the 'slow' translational motion is governed by the adiabatic potentials in much the same way the electronic and nuclear motions are treated in Eq. (2.6). Resonance energies within the adiabatic model are found to be nearly equal to the energy levels of the resulting one-dimensional equations neglecting off-diagonal coupling terms.

Adiabatic potential curves including diagonal corrections were computed for $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$. However, no attractive wells were found in the adiabatic potentials that correlate to closed rotational levels in the asymptotic region. Because the initial rotational energy of the diatom is zero for these transitions, a sudden-type approximation may be more accurate. To gain insight into this possibility, effective potentials ($V_{\text{eff}} = \tilde{V} + \frac{l(l+1)}{2\mu R}$) were computed along the minimum energy approach of $\theta=90^\circ$ for $r=2.4$ au. The V_{eff} show the van der Waals well modified by the centrifugal barrier potential, and they should be capable of supporting bound levels in the energy range needed for a Feshbach resonance with the $v_j=0_4$ level.

The angular distributions for $E=0.015, 0.016, 0.0171, 0.018, 0.019,$

0.020, 0.021, and 0.022 eV are shown in Figures 4.8-4.15. The differential cross sections (DCSs) at the resonance energies display two striking features: (1) they are symmetric with respect to a CM scattering angle (θ_{CM}) of 90° ; and (2) the number of peaks increases as a function of energy (0.017 eV - 2 peaks, 0.019 eV - 3 peaks, and 0.021 eV - 4 peaks). Similar symmetry and peaks are observed in the DCSs for a $H_2 + N_2$ model calculation by von Seggern and Toennies;⁹⁴ however, the features are more striking here. The angular distributions off-resonance are dominated by mainly forward scattering. The formula for DCSs is analyzed to gain insight into the origin of these two features of the computed angular distributions.

The DCS is given by Eq. (2.36). The angular distribution is defined by the A_γ s, and the analysis begins with them. There are several relationships which simplify the expression for A_γ and the Z coefficients at the resonance energies:

(1) The sums over J_1 and J_2 can be contracted to 1 term ($J_1=J_2=J_R$) because the T-matrix elements are large only for one value of J, J_R , at each resonance energy.

(2) All of the orbital angular momenta are restricted by triangular inequalities $|J-j| \leq 1 \leq J+j$. Therefore, in light of (1), $l_1(l_2)=J_R$ and $J_R-2 \leq l_1'(l_2') \leq J_R+2$.

(3) Parity is conserved during collisions so asymptotic channels with $j+l=\text{even}$ are decoupled from those with $j+l=\text{odd}$. The basis set is made up of even and odd parity levels ($|j|=2(J_R-1), 2(J_R+1)$) and ($|j|=0, J_R, 2(J_R-2), 2(J_R+2)$) (which ones are even and which ones are odd will depend on J_R). Contributions to σ_{00-02} come only from

the second set, and because of (1) only one parity state contributes to the $\sigma_{00 \rightarrow 02}$ at a resonance energy (see (1) and (2)).

(4) The expressions for Z require $l_1' + l_2' + \gamma$ to be even for Z to be nonzero. Thus since l_1' and l_2' are both even or both odd (see (3)), γ must be even.

5) The Racah coefficients in Z also require j and γ to satisfy the triangular inequalities:

$$0 \leq j' \leq 2J_R \quad 0 \leq \gamma \leq 2J_R \quad \text{for } l_1' = l_2' = J_R$$

$$2 \leq j' \leq 2J_R - 2 \quad 0 \leq \gamma \leq 2J_R - 4 \quad \text{for } l_1' = l_2' = J_R - 2$$

$$0 \leq j' \leq 2J_R - 2 \quad 2 \leq \gamma \leq 2J_R - 2 \quad \text{for } l_1' \text{ or } l_2' = J_R - 2 \text{ the other} = J_R$$

Note: $l_1'(l_2') = J_R + 2$ has not been considered here since that T-matrix element is small at the resonance energies.

The angular distribution is symmetric with respect to $\theta_{CM} = 90^\circ$ because only even order Legendre polynomials contribute to the differential cross section (see (4) above). Anytime contributions to the cross section come from only one parity state the DCS will possess this symmetry. This has been pointed out by several authors¹⁰⁴⁻¹⁰⁶ and shown explicitly for resonances in electron-molecule scattering.¹⁰⁶

At 0.0171 eV A_γ is approximately given by

$$\begin{aligned} A_\gamma(0.0171 \text{ eV}) \approx & Z(3333;0\gamma) Z(1313;2\gamma) T_{003-021}^3 * T_{003-021}^3 \\ & + Z(3333;0\gamma) Z(1333;2\gamma) T_{003-021}^3 * T_{003-023}^3 \\ & + Z(3333;0\gamma) Z(3113;2\gamma) T_{003-023}^3 * T_{003-021}^3 \\ & + Z(3333;0\gamma) Z(3333;2\gamma) T_{003-023}^3 * T_{003-023}^3 \end{aligned} \quad (4.7)$$

Computed values of the A_γ s for this resonance with A_0 normalized to one, are given in Table 4.6. Row one contains the result of solving the CC equations.

Assuming l is conserved (i.e. that only the first term of Eq. (4.7) is large) gives the second row with the same normalization described above. If $l_1' = l_2' = J_R - 2$ (i.e. only the fourth term of Eq. (4.7) is large) row three is obtained. Rows two and three are not in good agreement with the computed $A_{\gamma s}$, row one. This implies that the interference terms, the second and third of Eq. (4.7), must be important and the $A_{\gamma s}$ computed only using them are given in row four. To show that the DCS arises mainly from the two T-matrix elements discussed, row five contains the $A_{\gamma s}$ computed using only $T_{003-023}^3$ and $T_{003-021}^3$. The agreement between rows one and five is quite good.

Symmetry of the DCSs is easily demonstrated; however, the number of peaks depends on the sign and magnitude of the interference terms described above and are inherently dynamical quantities.

The only effort to locate the resonance positions more precisely was made at 0.0171 eV because they are so narrow. Unfortunately, experimental verification of the resonances via molecular beam scattering is probably impossible because the energy resolution of such experiments is far too broad.

Integral cross sections for all excitation transitions were computed and are displayed in Figure 4.6, and are given in Tables 4.3-4.5. Vibrational cross sections and rotational cross sections with large multiquantum jumps, $\Delta j > 4$, are not as well converged as the others at the highest two energies (see Appendix 1).

The partial cross sections are not shown because they are very similar

to those for V^{RR} shown in Figures 4.1-4.4. Inclusion of vibrational motion does not wash out the structure in these PCSs. For a given initial state the energy-gap law, which states that the larger the energy difference between levels, the smaller the transition probability or cross section, holds for all rotational transitions. The cross section for rotational transitions from a given initial state decrease with increasing Δj . The cross sections also increase with increasing scattering energy, with the exception of the resonances (the 00→02 cross sections at high energies are constant to the accuracy of the calculations).

The vibrationally inelastic cross sections are more interesting. For a fixed final state the energy-gap law does not hold. The initial state with the largest cross section for a transition to $v'j' = 10$ is 04 not 08 which is nearly degenerate with 10. Similarly for final state $v'j' = 12$ the initial state with the largest cross section is 06. Therefore, at these scattering energies, much but not all of the rotational energy is transferred into vibration and translation during vibrational excitation. This result is consistent with the findings of Moore et al. that on vibrational de-excitation about 40% of the energy was transferred into rotation.²⁶

Differential cross sections for various transitions are given in Figures 4.16-4.19. Figure 4.16 shows the differential cross sections for the 00→02 transition at the scattering energies 0.090, 0.150, and 0.210 eV. The cross section is dominated by forward scattering at all of these energies. The 10→12 DCS

is shown at 0.180, 0.195, and 0.210 eV. in Figure 4.17. Again the cross section is peaked in the forward direction, although, the effect is less pronounced than for $\sigma_{00 \rightarrow 02}$ at these energies. The multiquantum transitions from $v_j=00$ are displayed in Figure 4.18 at 0.180 eV. The $00 \rightarrow 04$ transition is again forward peaked. The $00 \rightarrow 06$ and $00 \rightarrow 08$ angular distributions are more nearly constant as functions of θ_{CM} . The magnitudes of these two cross sections are orders of magnitude lower than those for $00 \rightarrow 02$ and $00 \rightarrow 04$. Differential cross sections for a few vibrational transitions are shown in Figure 4.19 at 0.180 eV. The angular distributions are very nearly symmetric as the resonance DCSs were. This is caused by large partial wave contributions for even values of J so conservation of parity requires only even order Legendre polynomials to contribute to A_γ , Eq. (2.36).

In general the low energy angular distributions for rotational energy transfer in $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$ are dominated by forward scattering while the vibrationally inelastic distributions have a large component in the backward direction. The vibrational angular distributions may be difficult to measure because of the very large rotational DCSs. Nonetheless, it would be very interesting to attempt to measure the vibrational DCSs, and see this symmetry.

Table 4.1: Impact parameters at which σ_{00-02} is a maximum for V_{RR} and V_{FMC} .^a

Peak	Impact Parameters (au)				
	Relative Translational Energy (eV)				
	0.030	0.045	0.060	0.075	0.090
1	2.4(5) ^b	1.2(3)	1.4(4)	1.8(6)	1.9(7)
	0.7(1)		1.1(3)	2.0(7)	2.6(10)
2	4.1(9)	3.3(9)	3.4(11)	3.4(13)	
	3.7(8)	2.6(7)	3.2(10)	3.7(13)	3.9(15)
3	5.0(11)	5.5(15)	4.7(15)	4.8(17)	4.6(18)
		4.8(13)	5.0(16)	5.3(19)	4.6(18)
4	7.5(17)	7.6(21)	7.5(24)	7.2(26)	7.3(29)

^a The value above is for V_{RR} and the one below is for V_{FMC} .

^b The value of total angular momentum (J) at the maximum is given in parentheses.

Table 4.2: Rotational integral cross sections for V^{RR} , V^{FMC} , and V^{VARR} in the energy range 0.015-0.150 eV.^a

Total Scattering Energy (eV) ^b	$\sigma_{v_j \rightarrow v'_j} (\text{\AA}^2)$					
	$\sigma_{00 \rightarrow 02}$	$\sigma_{00 \rightarrow 04}$	$\sigma_{02 \rightarrow 04}$	$\sigma_{00 \rightarrow 06}$	$\sigma_{02 \rightarrow 06}$	$\sigma_{04 \rightarrow 06}$
0.015	2.8(-1) ^c					
	1.3(-1)					
	8.8(-3)					
0.030	3.5					
	7.0					
	3.1					
0.045	1.0(1)					
	1.2(1)					
	1.0(1)					
0.060	1.8(1)	2.0(-2)	7.1(-1)			
	1.5(1)	1.2(-1)	4.2(-1)			
	1.8(1)	2.1(-2)	8.7(-1)			
0.075	2.4(1)	1.8(-1)	5.3(-1)			
	1.9(1)	7.1(-1)	1.7			
	2.5(1)	1.6(-1)	5.3(-1)			
0.090	2.9(1)	5.0(-1)	1.5			
	2.1(1)	1.6	3.3			
	2.9(1)	4.6(-1)	1.4			
0.105	3.2(1)	1.1	2.9	5.5(-5)	1.2(-4)	2.2(-3)
	2.1(1)	2.5	5.1	1.3(-3)	2.4(-3)	1.7(-2)
	3.1(1)	9.8(-1)	2.7	4.3(-5)	8.5(-5)	1.1(-3)

Total Scattering Energy (eV) ^b	$\sigma_{v_j \rightarrow v'_j} (\text{\AA}^2) \text{ (cont.)}$					
	$\sigma_{00 \rightarrow 02}$	$\sigma_{00 \rightarrow 04}$	$\sigma_{02 \rightarrow 04}$	$\sigma_{00 \rightarrow 06}$	$\sigma_{02 \rightarrow 06}$	$\sigma_{04 \rightarrow 06}$
0.120	3.4(1)	1.8	4.6	2.3(-3)	3.7(-3)	4.3(-2)
	2.3(1)	3.7	6.5	2.2(-2)	3.8(-2)	1.9(-1)
	3.3(1)	1.6	4.3	9.8(-4)	2.0(-3)	2.3(-2)
0.135	3.5(1)	2.6	6.4	1.8(-2)	2.9(-2)	3.1(-1)
	2.3(1)	4.6	7.8	9.3(-2)	1.5(-1)	6.2(-1)
	3.6(1)	2.5	6.1	1.0(-2)	1.7(-2)	1.4(-1)
0.150	3.7(1)	3.6	8.2	5.7(-2)	9.4(-2)	5.7(-1)
	2.4(1)	5.6	9.2	2.3(-1)	3.5(-1)	1.2
	3.9(1)	3.6	8.0	4.1(-2)	6.8(-2)	4.2(-1)

- ^a See text for a discussion of V^{RR} and V^{VR} . The upper entry in each row corresponds to V^{RR} , the middle entry to V^{FMC} , and the lower entry to V^{VARR} .
- ^b Total scattering energy includes the initial rotational energy for transitions such as $02 \rightarrow 04$.
- ^c Notation is $2.8(-1) \equiv 2.8 \times 10^{-1}$.

Table 4.3: Rotational integral cross sections for V^{VR} in the energy range 0.015-0.150 eV.^a

Total Scattering Energy (eV) ^b	$\sigma_{vj \rightarrow v'j'} (\text{\AA}^2)$					
	$\sigma_{00 \rightarrow 02}$	$\sigma_{00 \rightarrow 04}$	$\sigma_{02 \rightarrow 04}$	$\sigma_{00 \rightarrow 06}$	$\sigma_{02 \rightarrow 06}$	$\sigma_{04 \rightarrow 06}$
0.015	1.3(-3) ^c					
0.030	1.1					
0.045	5.4					
0.060	1.4(1)	4.1(-3)	7.1(-2)			
0.075	2.2(1)	8.3(-2)	4.0(-1)			
0.090	2.8(1)	3.0(-1)	1.1			
0.105	3.2(1)	6.4(-1)	2.2	3.0(-5)	6.4(-5)	2.5(-4)
0.120	3.5(1)	1.2	3.5	1.5(-3)	3.5(-2)	2.3(-2)
0.135	3.8(1)	1.7	4.9	1.6(-2)	3.0(-2)	1.8(-1)
0.150	4.1(1)	2.5	6.7	5.4(-2)	1.0(-1)	5.3(-1)

^a See text for a description of V^{VR} and V^{VR} .

^b Total scattering energy includes the initial rotational energy for transitions such as 02 $\rightarrow$ 04.

^c Notation is 1.3(-3) $\equiv 1.3 \times 10^{-3}$.

Table 4.4: Rovibrational integral cross sections for V^{VR} and rotational cross sections for V^{VARR} in the energy range 0.165-0.210 eV.^a

$v_j \rightarrow v'_j$	$\sigma_{v_j \rightarrow v'_j} (\text{\AA}^2)$			
	Total Scattering Energy (eV) ^b			
	0.165	0.180	0.195	0.210
00→02	4.3(1) ^c	4.1(1) 4.0(1)	4.1(1)	4.1(1) 3.8(1)
00→04	3.5	4.3 6.0	4.0	6.1 8.1
00→06	1.3(-1)	2.9(-1) 2.1(-1)	4.3(-1)	6.1(-1) 5.2(-1)
00→10	1.7(-6)	7.2(-3)	2.0(-2)	4.3(-2)
00→08		5.2(-5) 1.4(-5)	9.9(-4)	6.4(-3) 1.7(-3)
00→12		3.7(-6)	1.0(-3)	7.5(-3)
00→14				1.7(-7)
02→04	8.2	9.4 1.2(1)	1.1(1)	1.2(1) 1.5(1)
02→06	2.3(-1)	5.8(-1) 3.4(-1)	8.4(-1)	1.2 8.5(-1)
02→10	3.6(-7)	1.2(-2)	3.3(-2)	5.7(-2)
02→08		2.9(-4) 3.0(-5)	2.0(-3)	1.1(-2) 2.3(-3)
02→12		1.4(-5)	7.6(-3)	2.2(-2)

$\sigma_{vj \rightarrow v'j'} (\text{\AA}^2) \text{ (cont.)}$				
<u>Total Scattering Energy (eV)^b</u>				
$vj \rightarrow v'j'$	0.165	0.180	0.195	0.210
02→14				6.1(-7)
04→06	1.1	2.3 1.5	3.2	3.9 2.9
04→10	1.2(-7)	2.3(-2)	4.7(-2)	6.8(-2)
04→08		9.5(-4) 9.4(-5)	1.3(-2)	3.5(-2) 5.8(-3)
04→12		1.9(-5)	2.7(-2)	5.9(-2)
04→14				5.2(-6)
06→10	8.3(-8)	9.4(-3)	2.5(-2)	4.3(-2)
06→08		5.3(-3) 1.4(-3)	6.0(-2)	1.6(-1) 3.8(-2)
06→12		1.9(-4)	1.0(-1)	1.8(-1)
06→14				8.4(-6)
10→12		1.2(-2)	1.5	7.7
10→14				2.6(-5)

$\sigma_{vj \rightarrow v'j'} (\text{\AA}^2) \text{ (cont.)}$				
<u>Total Scattering Energy (eV)^b</u>				
$vj \rightarrow v'j'$	0.165	0.180	0.195	0.210
08 $\rightarrow$ 10		9.4(-4)	6.1(-3)	1.3(-2)
08 $\rightarrow$ 12		4.4(-3)	1.9(-2)	9.3(-2)
08 $\rightarrow$ 14				2.4(-3)
12 $\rightarrow$ 14				1.7(-4)

- ^a See text for descriptions of V^{VR} and V^{VARR} . The upper entry in each column corresponds to V^{VR} , and the lower entry to V^{VARR} .
- ^b Total scattering energy includes the initial rotational energy for transitions such as 02 $\rightarrow$ 04.
- ^c Notation is $4.3(1) \equiv 4.3 \times 10^1$

Table 4.5: Rotational integral cross sections for the 00→02 transition in the energy range 0.015-0.045 eV for the V^{VR} analytic potential function.^a

Relative Translational Energy (eV)	$\sigma_{00 \rightarrow 02} (\text{\AA}^2)$	Relative Translational Energy (eV)	$\sigma_{00 \rightarrow 02} (\text{\AA}^2)$
0.015	1.3(-3)	0.030	1.1
0.016	3.7(-3)	0.031	1.3
0.017	1.3(-2)	0.032	1.5
0.018	6.3(-3)	0.033	1.7
0.019	2.1(-1)	0.034	2.0
0.020	2.0(-2)	0.035	2.2
0.021	2.1(-1)	0.036	2.5
0.022	7.2(-2)	0.037	2.8
0.023	1.3(-1)	0.038	3.1
0.024	2.8(-1)	0.039	3.4
0.025	2.7(-1)	0.040	3.6
0.026	4.3(-1)	0.041	3.9
0.027	5.9(-1)	0.042	4.2
0.028	6.6(-1)	0.043	4.5
0.029	8.5(-1)	0.044	4.8
		0.045	5.4

^a See text for a description of V^{VR} .

Table 4.6: Legendre expansion coefficients of the differential cross section for the $00 \rightarrow 02$ transition at the resonance energy of 0.0171 eV. The rows of the table contain the values computed using: (1) the CC results; (2) T-matrix elements with $J=3$ and $l=l'$; (3) T-matrix elements with $J=3$ and $l'=l-2$; (4) T-matrix elements with $J=3$ and $l_1' \neq l_2'$; (5) only the T-matrix elements with $J=3$. The first column of each row is normalized.

A_0	A_2	A_4	A_6
1.	0.151	-1.41	0.549
1.	0.421	-0.817	1.26
1.	0.800	0.0	0.0
0.0	0.525	1.30	0.0
1.	0.254	-1.24	0.453

Figure 4.1: Partial integral cross sections for the $00 \rightarrow 02$ rotational transition in $\text{H}_2(\text{B } ^1\Sigma_u^+)$ for V^{RR} (labeled 'present') and V^{FMC} .

Figure 4.2: Partial integral cross sections for the $00 \rightarrow 02$ rotational transition in $\text{H}_2(\text{B } ^1\Sigma_u^+)$ for V^{RR} (labeled 'present') and V^{FMC} .

Figure 4.3: Partial integral cross sections for the 02→04 rotational transition in $\text{H}_2(\text{B } ^1\Sigma_u^+)$ for V^{RR} (labeled 'present') and V^{FMC} .

Figure 4.4: Partial integral cross sections for the $00 \rightarrow 04$ rotational transition in $\text{H}_2(\text{B}^1\Sigma_u^+)$ for V^{RR} (labeled 'present') and V^{FMC} .

Figure 4.5: Integral cross sections for rotational energy transfer $\sigma_{j \rightarrow j'}$ ($v=v'=0$) with V^{RR} (—), V^{VARR} (— · —), and V^{FMC} (---). Results of Eastes and Secrest, for $\text{He} + \text{H}_2(\text{X } ^1\Sigma_g^+)$, are also given (···).

Figure 4.6: Integral cross sections for rotational energy transfer $\sigma_{j \rightarrow j'}$ ($v=v'=0$) with V^{VARR} (---) and V^{VARR} (—). Results of Eastes and Secrest, for $\text{He} + \text{H}_2(X^1\Sigma_g^+)$, are also given ($\cdots$).

Figure 4.7: Integral cross section for the rotational transition $00 \rightarrow 02$ between 0.015 and 0.045 eV.

Figure 4.8: Differential cross section for the $00 \rightarrow 02$ transition at 0.015 eV.

Figure 4.9: Differential cross section for the $00 \rightarrow 02$ transition at 0.016 eV.

Figure 4.10: Differential cross section for the $00 \rightarrow 02$ transition at 0.0171 eV.

Figure 4.11: Differential cross section for the 00→02 transition at 0.018 eV.

Figure 4.12: Differential cross section for the $00 \rightarrow 02$ transition at 0.019 eV.

Figure 4.13: Differential cross section for the $00 \rightarrow 02$ transition at 0.020 eV.

Figure 4.14: Differential cross section for the 00 $\rightarrow$ 02 transition at 0.021 eV.

Figure 4.15: Differential cross section for the $00 \rightarrow 02$ transition at 0.022 eV.

Figure 4.16: Differential cross sections for the $00 \rightarrow 02$ transition at 0.090, 0.150, and 0.210 eV.

Figure 4.17: Differential cross sections for the $10 \rightarrow 12$ transition at 0.180, 0.195, and 0.210 eV.

Figure 4.18: Differential cross sections for multiquantum rotational transitions at 0.180 eV.

Figure 4.19: Differential cross sections for rovibrational excitation to $v'j'=10$ at 0.180 eV.

CHAPTER 5

Configuration Interaction Nonadiabatic Coupling

5.1 Introduction

As discussed in Chapter 2, the nuclear kinetic energy operator causes three types of NA coupling.¹⁸ The relative motion of the nuclei couples states of the same symmetry due to the parametric dependence of the electronic wave functions on the internal coordinates (BO-coupling). The electronic orbital angular momentum operator couples states of the same symmetry as well as those of different symmetries (Coriolis coupling). Mixed couplings also arise from coupling of the rotation of the diatom with the electronic angular momentum. The Coriolis and mixed terms are zero for collisions of ^1S atoms with $^1\Sigma$ diatomic molecules because $\mathbf{L}$ and $\mathbf{s}$ are both zero. Therefore, only the BO coupling between $\text{HeH}_2(1\ ^1\text{A}')$ and $\text{HeH}_2(2\ ^1\text{A}')$ is computed in this chapter.

The BO couplings $\frac{\partial}{\partial R}$, $\frac{\partial}{\partial r}$, and $\frac{\partial}{\partial \theta}$ were computed between $\text{HeH}_2(1\ ^1\text{A}')$ and $\text{HeH}_2(2\ ^1\text{A}')$ using large MRSD-CI wave functions. The computed matrix elements contain a spurious contribution that does not disappear asymptotically. An analytic representation of the spurious contribution was

computed and subtracted from the computed BO coupling to yield accurate NA matrix elements. The adiabatic to diabatic transformation matrix, $\mathbf{A}$ (see Eq. (2.59) and (2.60)) was determined by associating ω with a physical property of the system. For the $\text{HeH}_2(1^1\text{A}')\text{-HeH}_2(2^1\text{A}')$ avoided PES crossing ω is found to be the angle that diagonalizes the component of the adiabatic dipole moment matrix along the H_2 axis. The angle ω was computed at a set of R , r , and θ to determine the position of the avoided crossing seam.

Section 5.2 presents the method used to compute BO-NA coupling matrix elements. The calculation of Coriolis and mixed terms, although not performed in this study, is straightforward, and it is discussed in Appendix 3. Spurious contributions are eliminated in Section 5.3. Section 5.4 contains the dipole moments and transition dipoles between the first two A' states of HeH_2 along with the transformation from the adiabatic to diabatic representations.

5.2 Method of Calculation of BO-NA Coupling and Results

BO coupling calculations are discussed by several authors;⁴⁻¹⁰ however, these calculations are still far from commonplace. In light of the limited number of these studies this section contains a description of the method of BO coupling computation. Results for HeH_2 are given.

In most BO-NA matrix element studies partial derivatives with respect to internal coordinates, R , r , and θ are computed using finite differences.^{4,6,7} Derivatives computed in internal coordinates can be dependent on the origin used to compute them because the atomic basis functions employed in most ab initio calculations translate with the atomic centers. This makes transformation to other coordinates systems very difficult. This problem was overcome by Yarkony and co-workers who used analytic gradient methods to compute analytic NA matrix elements.⁸⁻¹³ The analytic derivatives are computed with respect to atom-centered Cartesian coordinates and later transformed to a coordinate system convenient for scattering calculations.¹¹ Atom-centered Cartesian derivatives are independent of the origin used to compute them; therefore, they are preferred. Analytic methods also have the advantage that all derivatives can be computed in a single calculation rather than the $3N + 1$ (where N is the number of atoms) required to obtain finite difference derivatives. Finite difference formulas are, however, straightforward to implement, and they are general. In this study finite-difference derivatives, with respect to

atom-centered Cartesian coordinates, are computed and then transformed into the BF CMN set of internal coordinates.

The general form of the matrix element to be evaluated is given by

$$D_1^{ad}(I,J,a) = \langle \Psi_I^{ad} | \frac{\partial \Psi_J^{ad}}{\partial Q_a} \rangle_q \quad (5.1)$$

where Q_a are atom-centered Cartesian coordinates. The D_1^{ad} and D_2^{ad} described in Chapter 2 (see Eq. (2.7)-(2.12)) can be related by inserting the complete set, Ψ_K , into D_2^{ad} to obtain:

$$\begin{aligned} D_2^{ad}(I,J,a) &= \sum_K \left[(\langle \Psi_I | \nabla_a \Psi_K \rangle_q + \delta_{IK} \nabla_a) \langle \Psi_K | \nabla_a \Psi_J \rangle_q \right] \\ &= \sum_K \left[D_1^{ad}(I,K,a) D_1^{ad}(K,J,a) \right] + \nabla_a D_1^{ad}(I,J,a) \end{aligned} \quad (5.2)$$

When only two states are strongly coupled the set Ψ_K can be truncated to those two states. This is done in the present study so only D_1^{ad} is computed explicitly.

The electronic wave functions in Eq. (5.2) are the adiabatic functions of Eq. (2.53). Explicitly the wave function is a linear combination of configuration state functions CSFs, ψ_k s,

$$\Psi_I^{ad}(\mathbf{q}; \mathbf{Q}) = \sum_k C_{Ik}(\mathbf{Q}) \psi_k(\mathbf{q}; \mathbf{Q}) \quad (5.3)$$

Each ψ_k is a linear combination of Slater determinants of MOs

$$\psi_k(\mathbf{q}; \mathbf{Q}) = P \prod_{i=1}^n \phi_{k_i}(\mathbf{q}_i; \mathbf{Q}) \quad (5.4)$$

where ϕ_i is an MO. Here, P is a geometry independent space, spin, and particle-exchange projector, and each ϕ_i is a linear combination of AOs, η_r :

$$\phi_j(\mathbf{q}; \mathbf{Q}) = \sum_r c_{jr}(\mathbf{Q}) \eta_r(\mathbf{q}; \mathbf{Q}) \quad (5.5)$$

The atomic basis functions, η_r , are atom-centered Gaussians. The c_{jr} are MO expansion coefficients, and the ϕ_j are orthonormal.

Using the above definitions the derivative of the electronic wave function with respect to Q_a is

$$\frac{\partial \Psi_1^{\text{ad}}}{\partial Q_a} = \sum_k [C_{1k} \frac{\partial \psi_k}{\partial Q_a} + \frac{\partial C_{1k}}{\partial Q_a} \psi_k] \quad (5.6)$$

so the matrix element of interest is

$$D_1^{\text{ad}}(I, J, a) = \sum_{kk'} C_{1k} \frac{\partial C_{Jk'}}{\partial Q_a} \langle \psi_k | \psi_{k'} \rangle + C_{1k} C_{Jk'} \langle \psi_k | \frac{\partial \psi_{k'}}{\partial Q_a} \rangle \quad (5.7)$$

$$= D_1^{\text{CI}}(I, J, a) + D_1^{\text{CSF}}(I, J, a) \quad (5.8)$$

The CSFs are sums of products of one-electron orbitals so the derivative operator, D_1^{CSF} , is equivalent to a sum of one-electron operators

$$\frac{\partial}{\partial Q_a} = \sum_{i=1}^n d_a(i) \quad (5.9)$$

where

$$d_a(i)\phi_k(q_i) = \frac{\partial \phi_k(q_i)}{\partial Q_a} \quad (5.10)$$

Therefore,

$$D_1^{CSF}(I, J, a) = \sum_{ij} \gamma_{ij}^{IJ} \langle \phi_i | \frac{\partial \phi_j}{\partial Q_a} \rangle \quad (5.11)$$

Here γ_{ij}^{IJ} is the one-particle transition density matrix between states ψ_i and ψ_j ,

$$\gamma_{ij}^{IJ} = \sum_{kk'} C_{Ik} C_{Jk'} \langle \psi_k | a_i^\dagger a_j | \psi_{k'} \rangle \quad (5.12)$$

where $a_i^\dagger$ and a_j are creation and annihilation operators. Notice that γ^{IJ} is not symmetric so the full (square) matrix must be computed.

The matrix elements involving MO derivatives are expanded in terms of AOs via Eq. (5.5),

$$\langle \phi_i | \frac{\partial \phi_j}{\partial Q_a} \rangle = \sum_{rs} [c_{ir} \langle \eta_r | \eta_s \rangle \frac{\partial c_{js}}{\partial Q_a} + c_{ir} \langle \eta_r | \frac{\partial \eta_s}{\partial Q_a} \rangle c_{js}] \quad (5.13)$$

Substitution of (5.13) into (5.2) gives the final expression for D_1^{ad}

$$\begin{aligned} D_1^{ad}(I, J, a) = & \sum_{kk'} C_{Ik} \frac{\partial C_{Jk'}}{\partial Q_a} + \sum_{ij} [\gamma_{ij}^{IJ} \\ & \times \sum_{rs} [c_{ir} \langle \eta_r | \eta_s \rangle \frac{\partial c_{js}}{\partial Q_a} + c_{ir} \langle \eta_r | \frac{\partial \eta_s}{\partial Q_a} \rangle c_{js}]] \end{aligned} \quad (5.14)$$

If the electronic wavefunctions for two electronic states of interest are expanded in a common set of CSFs, the expression for D_1^{CI} , see Eq. (5.7) and (5.8), simplifies to:

$$D_1^{CI} = \sum_k C_{1k} \frac{\partial C_{jk}}{\partial Q_a} \quad (5.15)$$

In this case the computation of D_1^{ad} requires a set of MOs capable of describing the two states of $\text{He} + \text{H}_2$ accurately. It also requires the CI coefficients, C , and their derivatives for Ψ_1^{ad} and Ψ_j^{ad} , the derivatives of the MO coefficients, the AO overlap matrix, S , the derivative overlap matrix, and the full square one-particle transition density matrix, γ^{IJ} .

In this work MOs are obtained from a state-averaged MCSCF (SA-MCSCF) calculation.⁷³ The SA-MCSCF calculation optimizes the variational parameters of Ψ^{ad} to minimize a weighted sum of the energies for the two states rather than the energy of one or the other. The SA-MCSCF wave function contains the configurations of the CASSCF function described in Sec. 3.2. The two states of HeH_2 were weighted equally ($w_1=0.5, w_2=0.5$); thus MRSD-CI wave functions constructed from these MOs should provide an unbiased description of the two states of HeH_2 . The coupling elements D_1^{ad} are computed with an MRSD-CI wave function constructed from the SA-MCSCF MOs. The CI function contains all single- and double-replacements of electrons, from configurations with two electrons in the $1a'$ MO and two electrons distributed among the $2a'$ and $3a'$ orbitals into all virtual orbitals, consistent with $^1A'$ symmetry. This results in 4100 CSFs in C_s symmetry and provides energies in good agreement with the INO results described in Chapter 3. Coupling elements computed using these wave functions were compared

with those of several more extensive CASSCF functions to assure their accuracy. All derivatives were computed using central-difference formulas,¹⁰⁷

$$C_{lk} \frac{\partial C_{lk}}{\partial Q_a} \bigg|_Q = \frac{C_{lk}(Q)[C_{Jk}(Q-\Delta Q) - C_{Jk}(Q+\Delta Q)]}{2\Delta Q} \quad (5.16)$$

A conservative estimate of the accuracy of the computed derivatives for these wave functions is ten percent (see Appendix 4).

Derivatives with respect to the atomic Cartesian coordinates x_{He} , y_{He} , x_{H_1} , y_{H_1} , x_{H_2} , and y_{H_2} are computed by the above method and transformed into a set of CMN internal coordinates. Derivatives with respect to out-of-plane motions z_{H_1} , z_{H_2} , and z_{He} are zero by symmetry and are not computed. The internal coordinates are X_{CM} , Y_{CM} , ϕ , R , r , and θ , where X_{CM} and Y_{CM} are the x' and y' coordinates of the CMN (see Fig. 1.1), ϕ defines the orientation of the HeH_2 triangle in the x' - y' plane, and R , r , and θ have the meanings given in Chapter 2. The transformation to internal coordinates is accomplished via an intermediate polar coordinate system¹¹ with origin at the CMN in which (R, ξ) and (r, ς) are the vectors $\mathbf{R}$ and $\mathbf{r}$ (see Figure 5.1) where $\phi = \xi - \varsigma$ and $\theta = \xi + \varsigma$. The transformation is straightforward but tedious. The final results are

$$\frac{\partial}{\partial X_{\text{CM}}} = \frac{\partial}{\partial x_{\text{He}}} + \frac{\partial}{\partial x_{\text{H}_1}} + \frac{\partial}{\partial x_{\text{H}_2}} \quad (5.17)$$

$$\frac{\partial}{\partial Y_{\text{CM}}} = \frac{\partial}{\partial y_{\text{He}}} + \frac{\partial}{\partial y_{\text{H}_1}} + \frac{\partial}{\partial y_{\text{H}_2}} \quad (5.18)$$

$$\begin{aligned} \frac{\partial}{\partial R} = & \left[\cos\theta \left[\frac{M_{H_2}}{M} \frac{\partial}{\partial x_{He}} - \frac{M_{He}}{M} \left(\frac{\partial}{\partial x_{H_1}} + \frac{\partial}{\partial x_{H_2}} \right) \right] \right. \\ & \left. + \sin\theta \left[\frac{M_{H_2}}{M} \frac{\partial}{\partial y_{He}} - \frac{M_{He}}{M} \left(\frac{\partial}{\partial y_{H_1}} + \frac{\partial}{\partial y_{H_2}} \right) \right] \right] \end{aligned} \quad (5.19)$$

$$\begin{aligned} \frac{\partial}{\partial \xi} = & - \left[R \sin\theta \left[\frac{M_{H_2}}{M} \frac{\partial}{\partial x_{He}} - \frac{M_{He}}{M} \left(\frac{\partial}{\partial x_{H_1}} + \frac{\partial}{\partial x_{H_2}} \right) \right] \right. \\ & \left. + R \cos\theta \left[\frac{M_{H_2}}{M} \frac{\partial}{\partial y_{He}} - \frac{M_{He}}{M} \left(\frac{\partial}{\partial y_{H_1}} + \frac{\partial}{\partial y_{H_2}} \right) \right] \right] \end{aligned} \quad (5.20)$$

$$\frac{\partial}{\partial r} = \frac{1}{2} \left[\frac{\partial}{\partial x_{H_1}} - \frac{\partial}{\partial x_{H_2}} \right] \quad (5.21)$$

$$\frac{\partial}{\partial \zeta} = \frac{r}{2} \left[\frac{\partial}{\partial y_{H_1}} - \frac{\partial}{\partial y_{H_2}} \right] \quad (5.22)$$

The partial derivatives $\frac{\partial}{\partial \phi}$ and $\frac{\partial}{\partial \theta}$ are given in terms of the angular derivatives in the polar coordinate system by

$$\frac{\partial}{\partial \theta} = \frac{1}{2} \left(\frac{\partial}{\partial \xi} - \frac{\partial}{\partial \zeta} \right) \quad (5.23)$$

$$\frac{\partial}{\partial \phi} = \frac{1}{2} \left(\frac{\partial}{\partial \xi} + \frac{\partial}{\partial \zeta} \right) \quad (5.24)$$

The elements of $\mathbf{D}_I^{\text{ad}}$ in the vicinity of the minimum of the excited $^1A'$ PES of HeH_2 are shown in Tables 5.1-5.6.

The derivatives $\frac{\partial}{\partial X_{\text{CM}}}$, $\frac{\partial}{\partial Y_{\text{CM}}}$, and $\frac{\partial}{\partial \phi}$ are non-zero because the AO basis functions are attached to the nuclei and translate with them. From Eq.

(5.14) the coupling due to translation of the CMN and overall rotation of the system is

$$D_1^{\text{ad}}(I, J, a) = \sum_{ij} \gamma_{ij}^{IJ} \sum_{rs} c_{ir} \langle \eta_r | \frac{\partial \eta_s}{\partial Q_a} \rangle c_{js} \quad (5.25)$$

The other terms from Eq. (5.14) drop out because the variational parameters, C and c , do not change with CMN motion or overall rotation. Equation (5.25) shows how the origin dependence of D_1^{ad} arises. The partial derivative of a gaussian basis function with respect to the position of its center is not necessarily zero (i.e. for an s function the derivative is zero, for a p function it is not) This leads to a spurious coupling which contributes to $\frac{\partial}{\partial R}$, $\frac{\partial}{\partial r}$, and $\frac{\partial}{\partial \theta}$. Delos and Thorson¹⁰⁸ point out that the origin dependence must be removed before an accurate transformation to the diabatic representation can be made since the NA coupling to be eliminated by the transformation are those due to the change of the variational parameters with relative geometry of the three nuclei.

5.3 Elimination of Spurious Coupling

Couplings that do not disappear at large interfragment separations (see Eq. (5.23)) are discussed by a number of authors^{18,108-110} often with reference to electron translation factors.^{108,110} These couplings cause the computed derivatives to depend on the origin used to compute them. For atom-atom collisions the origin dependence is proportional to the electronic transition dipole matrix element $\langle \Psi_i^{ad} | \sum_i z_i | \Psi_j^{ad} \rangle$ where z_i is the projection of the position of the i th electron along the internuclear axis.¹⁰⁹ Therefore spurious couplings exist in HeH_2 , at least asymptotically because the X- and B-states of H_2 have a non-zero transition dipole moment. The origin dependence can be eliminated in many systems by choosing an origin coincident with the CMN of the fragment responsible for the coupling.^{7,109} As long as the CMN of this fragment remains stationary the spurious coupling is zero. For HeH_2 , however, the fragment is H_2 , and the CMN of the system is not very close to the CMN of H_2 ; thus, this is not a physically reasonable solution.

Rebentrost¹⁸ concludes that the spurious coupling is of the order of the mass polarization terms neglected in the electronic Hamiltonian and can thus be neglected. He points out, however, that distinguishing between the genuine and spurious coupling is difficult when the collision partners are close together. For HeH_2 the spurious terms can be distinguished from the genuine coupling and then subtracted from the computed values to obtain the genuine coupling.

The coupling term $\frac{\partial}{\partial\phi}$, given in Table 3, is non-zero for all R , r , and θ ; however, ϕ is a function of Euler angles only which Ψ_1^{ad} depends on through the terms like Eq. (5.25). The simple function

$$\left(\frac{\partial}{\partial\phi} \right)_{\text{spur}} = \frac{\sin\theta}{2}(aR + br + c) \quad (5.26)$$

with $a = 0.31$, $b = -0.24$, and $c = 1.25$, fits $\frac{\partial}{\partial\phi}$ to within 10% for all R , r , and θ where it has been computed. As $R \rightarrow \infty$, $\frac{\partial}{\partial x_{H_1}}$ and $\frac{\partial}{\partial x_{H_2}}$ are the only non-zero atom-centered Cartesian derivatives because the transition dipole for the X-B transition lies along the H_2 axis. Therefore the asymptotic spurious coupling in $\frac{\partial}{\partial\phi}$ comes entirely from $\frac{\partial}{\partial\xi}$ (see Eq. (5.22) and (5.24)). Because (5.26) fits $\frac{\partial}{\partial\phi}$ for all R , r , and θ , including the asymptotic region, and $\frac{\partial}{\partial\zeta}$ has no spurious contribution as $R \rightarrow \infty$, it is assumed that there is no spurious contribution to $\frac{\partial}{\partial\zeta}$ for all R , r , and θ , i.e.

$$\frac{\partial}{\partial\theta} = \frac{\partial}{\partial\zeta} ; \quad \frac{\partial}{\partial\phi} = 0 \quad (5.27)$$

Thus the spurious part of $\frac{\partial}{\partial\theta}$ is removed.

As $R \rightarrow \infty$, the spurious component of $\frac{\partial}{\partial R}$ that is related to the spurious part of $\frac{\partial}{\partial\phi}$ (see Eq. (5.19) and Eq. (5.24))

$$\left(\frac{\partial}{\partial R} \right)_{\text{spur}} = - \frac{2 \cot \theta}{R} \left(\frac{\partial}{\partial \phi} \right)_{\text{spur}} \approx \frac{\cos \theta}{R} (aR + br + c) \quad (5.28)$$

Assuming that this result holds for all R , r , and θ the genuine part of $\frac{\partial}{\partial R}$ is the computed value minus Eq. (5.26)

$$\left(\frac{\partial}{\partial R} \right)_{\text{gen}} = \left(\frac{\partial}{\partial R} \right)_{\text{comp}} + \frac{2 \cot \theta}{R} \left(\frac{\partial}{\partial \phi} \right)_{\text{spur}} \quad (5.29)$$

The $\frac{\partial}{\partial r}$ term has no spurious contribution as $R \rightarrow \infty$. Therefore, consistent with the other assumptions, the spurious coupling in this term is assumed to be zero everywhere. Tables 5.7-5.9 give the BO coupling matrix elements without the spurious contributions.

The genuine coupling elements are complicated functions of R , r , and θ , however, some general features can be discerned. The magnitude of the coupling tends to be largest near $R=1.5$ au, $r=4.0$ au, and $\theta=45^\circ$ and decreases away from this geometry. The ordering of the magnitudes of the three BO terms is found to be $|D_1^{\text{ad}}(1^1A', 2^1A', \theta)| > |D_1^{\text{ad}}(1^1A', 2^1A', R)| > |D_1^{\text{ad}}(1^1A', 2^1A', r)|$ (see Tables 5.7-5.9). This suggests that rotational motion may be the most efficient means of causing electronic transitions with relative translational motion next and vibrational motion after that. The nuclear velocity multiplies the D_1^{ad} s in the CC equations (see Eq. 2.7) and must be taken into account in a qualitative analysis of their effect on fluorescence quenching. Therefore, the rovibrational population of $\text{H}_2(\text{B } ^1\Sigma_u^+)$ should

have a strong effect on electronic energy transfer. Under the experimental conditions, $v=3$, $j=2$ of $H_2(B^1\Sigma_u^+)$ is populated and collisions occur at room temperature. Therefore, most of the available collision energy is present in vibration, i.e. the wave vectors for the three types of motion are ordered $k_{vib} > k_{trans} > k_{rot}$. This implies that vibrational motion should be more efficient than rotation or translation in promoting electronic transitions for these collisions. This is seen in the classical trajectory calculations of Farantos.³² The classical quenching cross section increases rapidly with increasing vibrational level. A less pronounced increase with increasing translational energy is also seen. Rotational excitation enhances the cross section slightly for low j , but as j increases the electronic energy transfer probability decreases rapidly. This result appears to contradict the analysis of the ab initio NA coupling calculations, however, final determination will come with accurate dynamics calculations such as those outlined in Chapter 2.

The computed coupling matrix elements change rapidly with nuclear geometry. This behavior was seen by Farantos,³² however, the present NA couplings change sign in a much different fashion than those of the previous study. As discussed earlier the sign of the matrix element at any point is arbitrary; but, once the relative phases of Ψ_1^{ad} and Ψ_2^{ad} are chosen the sign of the coupling is fixed. This phase relation must be used consistently at all geometries. To ensure that the same phase relation was used, the CI coefficients and MOs for important configurations were monitored. When the

signs of these parameters indicated that only one of the adiabatic wave functions had changed sign, the signs of the NA coupling elements were changed. The simple function used to represent the spurious coupling in $\frac{\partial}{\partial\phi}$ yields results consistent with observation of the wave function phases.

5.4 Adiabatic to Diabatic Transformation Matrix

The CC equations are put into a more convenient form by using the diabatic basis described in Sec. 2.4. A rotation angle, $\omega(R,r,\theta)$, defines the transformation matrix, **A**, for a two state problem. Once computed, the NA coupling can be integrated to obtain ω (see Eq. (2.67)). Numerical integration of Eq. (2.67) is difficult, however, for two reasons: first the NA coupling is time consuming to compute and a dense grid of values is required for numerical integration; and second small inaccuracies in the computed points may not cancel when they are summed resulting in a poor value for the integral. Therefore, it is desirable to compute ω directly for a given nuclear geometry. This has been done in the past for $F + H_2$ and LiF by associating ω with a physical property which can be evaluated via ab initio methods.^{16,5} The character of the wave function and value of the physical property change abruptly during the collision for the adiabatic wave functions. In the diabatic representation both change smoothly near the adiabatic avoided PES crossing. It should be pointed out that matrix elements of the diabatic electronic Hamiltonian have been computed directly, bypassing the need to know ω , for diatomics-in-molecules (DIM) wave functions¹¹¹ and for certain ab initio wave functions by restricting the configuration spaces to include only one of the diabatic states.²³

In order to determine the physical property of the system that

corresponds to ω consider the nature of the two adiabatic electronic functions near the avoided crossing. At $r=4.0$ au the wave function for isolated $H_2(B\ ^1\Sigma_u^+)$ has a large ionic contribution.¹¹² The ground state $H_2(X\ ^1\Sigma_g^+)$ wave function at $r=4.0$ au is predominantly made up of the $1s\sigma_g^2$ and $1s\sigma_u^2$ covalent configurations. As He approaches $H_2(X\ ^1\Sigma_g^+)$ there is a closed-shell closed-shell interaction that has a very weak van der Waals well and is steeply repulsive when the electron clouds begin to overlap. When He approaches $H_2(B\ ^1\Sigma_u^+)$ at angles other than 90° the ionic configurations describing H_2 completely dominates the wave function. The two ' H_2 electrons' effectively localize on the H atom furthest from He. The He atom experiences an attractive interaction with the bare proton and the incipient HeH^+ is stabilized by the H^- ion. In the region near $R=1.5$ au, $r=4.0$ au, and $\theta=45^\circ$ these ionic and covalent surfaces would cross, however, the adiabatic wave functions change character and interact with one another; thus, their PESs avoid one another. This qualitative picture of the PES crossing will be used to describe the ab initio calculations, and the diabatic states will be referred to as ionic and covalent states. The idea of an ionic interaction in HeH_2 was used by FTN to locate the minimum of the $HeH_2(2\ ^1A')$ PES which they termed the maximum ionicity excited state (MIES). The MIES appears to be a common phenomenon in collisions of $H_2(B\ ^1\Sigma_u^+)$, and it has been observed in calculations on the collision partners Ne, Ar, and $H_2(X\ ^1\Sigma_g^+)$.¹¹³⁻¹¹⁵ In each case the ionic and covalent states should provide a useful qualitative description of multisurface scattering

phenomena.

The dipole moment functions for the ionic and covalent diabatic states of HeH_2 , μ_i^d and μ_c^d will be very different. Therefore, the adiabatic dipole moment functions, μ_1^{ad} and μ_2^{ad} , are expected to show rapid variation as the system moves through the crossing region. The ionic state will have a large dipole moment along the H_2 axis pointing toward the H atom furthest from He, μ_i^d . The covalent diabatic state should have a small component of the dipole moment along H_2 , μ_c^d .

The adiabatic dipole moments, μ_1^{ad} and μ_2^{ad} , and transition dipole, μ_{12}^{ad} are computed using the MRSD-CI wave functions described in Sec. 5.2. The values are displayed in Tables 5.10-5.12. The dipole moments of the adiabatic wave functions change rapidly between 30° and 45° (Table 5.10) indicating the avoided crossing. A similar change is observed as a function of r in Table 5.11 between 3.5 and 4.0 au. The dipole moments as a function of R in Table 5.12 do not really show this behavior although they do change significantly near $R=4.0$ au. The computed μ_{12}^{ad} is also large near the avoided crossing. These results are consistent with the qualitative description of the PES crossing and observations that rotational and vibrational motion will be important in promoting electronic transitions while it appears that, at least along the cut of the PES with $r=4.0$ au and $\theta=45^\circ$ (see Table 5.12), relative translational motion plays a minor role.

Meyer⁵ showed that for LiF, the rotation angle, ω , can be associated

with the angle, ω_μ , that diagonalizes μ^{ad} . From the preceding evidence ω was chosen to be the angle that diagonalizes the component of μ^{ad} (ω_μ) along the H_2 axis. To test the accuracy of this association for HeH_2 , finite-difference derivatives of ω_μ were computed at $R=1.5$ au, $r=4.0$ au and $\theta=45^\circ$ and compared with D_1^{ad} in Table 5.13. The agreement is acceptable considering that the spurious coupling was eliminated using an empirically determined fit and that finite-differences, not analytic, derivatives are computed.

In the asymptotic regions where R goes to 0 or ∞ , μ_1^{ad} and μ_2^{ad} become 0 but μ_{12}^{ad} remains non-zero. Therefore, ω_μ approaches 45° in both limits. This behavior is unphysical because it requires the off-diagonal elements of the electronic Hamiltonian to become infinite in these limits (see Eq. (2.66)), which is certainly not correct for large R . Inadequacy of the ionic/covalent description of the system away from the crossing region probably causes this behavior (i.e. for large R neither adiabatic state has a dipole moment so neither corresponds to the ionic diabatic state). One solution to this problem was suggested by Meyer.⁵ As the system moves away from the crossing region, the energy difference between the two states increases. Therefore, the probability of an electronic transition decreases rapidly, and the transition dipole can be multiplied by a function of the form

$$\exp(-a(V_{11}^{\text{ad}} - V_{22}^{\text{ad}})) \quad (5.30)$$

without modifying the physics of the process. The accuracy of this

modification should be verified for HeH_2 .

Discussion of the NA coupling has thus far centered around geometries near the minimum of the $\text{HeH}_2(2^1\text{A}')$ PES, however, the diabatic PESs which are three-dimensional cross along a two-dimensional seam.¹⁴ The dipole moment matrix was computed on a grid of R , r , and θ to determine the location of this seam. Tables 5.14-5.16 give the rotation angle, ω_μ , on this grid. When $\omega_\mu=0^\circ$ (i.e. in the asymptotic region) the diabatic states are degenerate with the adiabatic ones. Near the crossing seam, ω_μ changes rapidly from 0° to 90° . The values of the coordinates where $\omega_\mu=45^\circ$ define the crossing seam. When $\omega_\mu=90^\circ$ (i.e. as R and r become 0) the diabatic and adiabatic states again become degenerate. These calculations show that the crossing seam exists not only at $\theta=45^\circ$ but at angles from 0° to 75° and probably even larger. Consistent with the qualitative description of the PES crossing there is no seam at $\theta=90^\circ$ because along this approach there is no force that 'pushes' the H_2 electrons onto one H atom. Therefore, the ionic contribution to the wave function is not as dominant as it is at other angles.

Figures 5.1-5.3 display the cuts through the adiabatic and diabatic PESs along with the off diagonal elements of the electronic Hamiltonian in the diabatic representation constructed using ω_μ . Points on the crossing seam are the points where the diabatic curves cross one another. Figure 5.1 shows that the crossing seam runs roughly parallel to R in the vicinity of the excited-state PES minimum. This also indicates that relative translational motion will not

be effective in causing fluorescence quenching unless it is efficiently converted into rotational or vibrational motion.

At very small angles, $\theta \approx 0$, the crossing occurs between 5.0 au and 5.5 au for $R=1.5$ au. This means the He atom is actually between the two hydrogens. As the angle increases the crossing seam occurs at smaller r for fixed R . When $R=1.5$ and $\theta=75^\circ$, the crossing occurs between $r=2.5$ au and 2.0 au. This is confirmed in the interaction energies and analytic PESs (see Sec. 3.3) which show a decrease in the interaction energy as θ decreases from 90° . The minimum energy approach on the $\text{HeH}_2(2^1A')$ for $r=2.4$ au and small R is close to 75° . This part of the seam is well above the experimental scattering energy; therefore, it should not be an important factor in causing fluorescence quenching. It appears that the energy difference between the adiabatic PESs along the seam increases away from the minimum of the excited state HeH_2 PES. Therefore, it is unclear if any regions of the crossing seam other than those in the neighborhood of the excited-state PES minimum will strongly affect the electronic energy transfer probability.

Table 5.1: CI nonadiabatic coupling matrix element $D_1^{\text{ad}}(1^1A', 2^1A', X_{\text{CM}})$.^a

		$D_1^{\text{ad}}(1^1A', 2^1A', X_{\text{CM}})$				
		R (au)				
θ	r (au)	0.50	1.00	1.50	2.00	2.50
15 °	4.0			0.34		
30 °	4.0			-0.03		
45 °	3.0			0.05		
	3.5		-0.14	-0.01	0.11	
	4.0	-0.26	-0.16	-0.04	0.06	0.15
	4.5		-0.16	-0.07	0.03	
	5.0			-0.08		
60 °	4.0			-0.04		
75 °	4.0			-0.02		

^a These values include the spurious terms discussed in the text.

Table 5.2: CI nonadiabatic coupling matrix element $D_1^{ad}(1^1A', 2^1A', Y_{CM})$.^a

		$D_1^{ad}(1^1A', 2^1A', Y_{CM})$				
		$R \text{ (au)}$				
θ	$r \text{ (au)}$	0.50	1.00	1.50	2.00	2.50
15 °	4.0			-0.04		
30 °	4.0			-0.01		
45 °	3.0			0.04		
	3.5		0.01	0.00	-0.01	
	4.0	0.01	0.03	0.02	0.02	-0.02
	4.5		0.04	0.04	0.03	
	5.0			0.04		
60 °	4.0			0.05		
75 °	4.0			0.05		

^a These values include the spurious terms discussed in the text.

Table 5.3: CI nonadiabatic coupling matrix element $D_I^{\text{ad}}(1^1A', 2^1A', \phi)$.^a

		$D_I^{\text{ad}}(1^1A', 2^1A', \phi)$				
		<u>R (au)</u>				
θ	r (au)	0.50	1.00	1.50	2.00	2.50
15 °	4.0			0.08		
30 °	4.0			0.25		
45 °	3.0			0.42		
	3.5		0.27	0.33	0.41	
	4.0	0.14	0.23	0.29	0.35	0.34
	4.5		0.19	0.25	0.29	
	5.0			0.21		
60 °	4.0			0.31		
75 °	4.0			0.34		

^a These values include the spurious terms discussed in the text.

Table 5.4: CI nonadiabatic coupling matrix element $D_1^{\text{ad}}(1^1A', 2^1A', R)$.^a

		$D_1^{\text{ad}}(1^1A', 2^1A', R)$				
		$R \text{ (au)}$				
θ	$r \text{ (au)}$	0.50	1.00	1.50	2.00	2.50
15°	4.0	0.39				
30°	4.0	0.78				
45°	3.0	1.29				
	3.5	0.90 2.71 0.42				
	4.0	0.17	0.10	-2.05	-0.33	-0.09
	4.5	-0.14 -0.66 -0.55				
	5.0	-0.31				
60°	4.0	-0.71				
75°	4.0	-0.42				

^a These values include the spurious terms discussed in the text.

Table 5.5: CI nonadiabatic coupling matrix element $D_I^{\text{ad}}(1^1A', 2^1A', r)$.^a

		$D_I^{\text{ad}}(1^1A', 2^1A', r)$				
		$R \text{ (au)}$				
θ	$r \text{ (au)}$	0.50	1.00	1.50	2.00	2.50
15 °	4.0			-0.14		
30 °	4.0			-0.18		
45 °	3.0			-0.18		
	3.5		-0.77	-0.66	0.60	
	4.0	-0.22	-0.62	-0.78	0.78	0.35
	4.5		-0.30	-0.12	0.34	
	5.0			-0.05		
60 °	4.0			0.11		
75 °	4.0			0.08		

^a These values include the spurious terms discussed in the text.

Table 5.6: CI nonadiabatic coupling matrix element $D_I^{ad}(1^1A', 2^1A', \theta)$.^a

		$D_I^{ad}(1^1A', 2^1A', \theta)$				
		R (au)				
θ	r (au)	0.50	1.00	1.50	2.00	2.50
15°	4.0			-0.30		
30°	4.0			-0.12		
45°	3.0			1.18		
	3.5		-2.02	0.80	2.89	
	4.0	-0.33	-1.58	-4.93	2.22	1.01
	4.5		-0.75	-1.10	0.25	
	5.0			-0.53		
60°	4.0			-0.37		
75°	4.0			-0.17		

^a These values include the spurious terms discussed in the text.

Table 5.7: Nonadiabatic coupling matrix element $D_I^{\text{ad}}(1\ ^1A', 2\ ^1A', R)$.^a

		$D_I^{\text{ad}}(1\ ^1A', 2\ ^1A', R)$				
		<u>R (au)</u>				
θ	r (au)	0.50	1.00	1.50	2.00	2.50
15 °	4.0			0.78		
30 °	4.0			1.36		
45 °	3.0			1.85		
	3.5		1.43	3.16	0.84	
	4.0	0.72	0.56	-1.66	0.02	0.18
	4.5		0.25	-0.32	-0.27	
	5.0			-0.03		
60 °	4.0			-0.47		
75 °	4.0			-0.30		

^a These values do not include the spurious terms discussed in the text.

Table 5.8: Nonadiabatic coupling matrix element $D_I^{\text{ad}}(1\ ^1A', 2\ ^1A', r)$.^a

		$D_I^{\text{ad}}(1\ ^1A', 2\ ^1A', r)$				
		R (au)				
θ	r (au)	0.50	1.00	1.50	2.00	2.50
15°	4.0			-0.14		
30°	4.0			-0.18		
45°	3.0			-0.18		
	3.5		-0.77	-0.66	0.60	
	4.0	-0.22	-0.62	-0.78	0.78	0.35
	4.5		-0.30	-0.12	0.34	
	5.0			-0.05		
60°	4.0			0.11		
75°	4.0			0.08		

^a These values do not include the spurious terms discussed in the text.

Table 5.9: Nonadiabatic coupling matrix element $D_1^{\text{ad}}(1^1A', 2^1A', \theta)$.^a

		$D_1^{\text{ad}}(1^1A', 2^1A', \theta)$				
		R (au)				
θ	r (au)	0.50	1.00	1.50	2.00	2.50
15 °	4.0			-0.38		
30 °	4.0			-0.37		
45 °	3.0			0.76		
	3.5		-2.29	0.46	2.43	
	4.0	-0.47	-1.79	-5.23	1.87	0.67
	4.5		-0.95	-1.35	0.04	
	5.0			-0.75		
60 °	4.0			-0.69		
75 °	4.0			-0.51		

^a These values do not include the spurious terms discussed in the text.

Table 5.10: Component of the dipole moment matrix for $\text{HeH}_2(1^1\text{A}')$ and $\text{HeH}_2(2^1\text{A}')$ along the H_2 axis along with the rotation angle, ω_μ for $R=1.5$ au and $r=4.0$ au.^a

θ	μ_1 (debye)	μ_2 (debye)	μ_{12} (debye)	ω_μ
15°	7.534	-5.174	-1.059	85.3°
30°	5.224	0.656	-5.104	82.6°
45°	-0.159	6.494	-3.279	22.3°
60°	-0.732	7.946	-0.600	3.9°
75°	-0.308	8.134	-0.253	1.2°

^a See text for description of the calculation of μ and ω_μ .

Table 5.11: Component of the dipole moment matrix for $\text{HeH}_2(1^1\text{A}')$ and $\text{HeH}_2(2^1\text{A}')$ along the H_2 axis along with the rotation angle, ω_μ for $R=1.5$ au and $\theta=45^\circ$.^a

r (au)	μ_1 (debye)	μ_2 (debye)	μ_{12} (debye)	ω_μ
3.0	5.781	-1.027	-2.102	74.2°
3.5	7.116	-1.533	-0.488	86.8°
4.0	-0.159	6.494	-3.279	22.3°
4.5	-0.884	8.282	-2.022	11.9°
5.0	-0.864	9.646	-1.500	8.0°

^a See text for description of the calculation of μ and ω_μ .

Table 5.12: Component of the dipole moment matrix for $\text{HeH}_2(1^1\text{A}')$ and $\text{HeH}_2(2^1\text{A}')$ along the H_2 axis along with the rotation angle, ω_μ for $\theta=45^\circ$ and $r=4.0 \text{ au}$.^a

R (au)	μ_1 (debye)	μ_2 (debye)	μ_{12} (debye)	ω_μ
0.5	0.713	4.184	-4.046	33.4 °
1.0	1.499	4.046	-4.461	30.1 °
1.5	-0.159	6.494	-3.279	22.3 °
2.0	-0.768	8.968	-0.936	20.2 °
2.5	0.581	7.216	-2.987	21.0 °

^a See text for description of the calculation of μ and ω_μ .

Table 5.13: Genuine Born-Oppenheimer coupling matrix elements and derivatives of ω_μ evaluated at $R=1.5$ au, $r=4.0$ au, and $\theta=45^\circ$.^a

α	$D_1^{\text{ad}}(1^1A', 2^1A', \alpha)$	$-\frac{\partial \omega_\mu}{\partial \alpha}$
R	-1.66	-1.99
r	-0.78	-0.84
θ	-5.23	-4.84

^a See text for description of the calculations. Lengths are in au. Angles are in rad.

Table 5.14: Adiabatic to diabatic rotation angle, ω_μ , for $R=1.0$ au.^a

r (au)	Rotation Angle ω_μ		
	θ		
	30 °	45 °	60 °
3.5	74.93 °	61.72 °	26.36 °
4.0	54.20 °	30.14 °	21.56 °
4.5	31.42 °	21.41 °	14.93 °

^a See text for description of calculation of ω_μ .

Table 5.15: Adiabatic to diabatic rotation angle, ω_μ , for $R=1.5$ au.^a

r (au)	Rotation Angle ω_μ					
	θ					
	0°	15°	30°	45°	60°	75°
1.5					69.89°	54.02°
2.0					56.07°	45.17°
2.5					47.26°	27.32°
3.0				74.15°	24.58°	9.89°
3.5			87.65°	86.78°	0.79°	0.62°
4.0		85.27°	82.59°	22.30°	3.93°	1.17°
4.5		87.66°	32.59°	11.90°	4.53°	
5.0	78.94°	64.42°	20.81°	7.96°		
5.5	38.48°	26.29°				
6.0	16.36°					

^a See text for description of calculation of ω_μ .

Table 5.16: Adiabatic to diabatic rotation angle, ω_μ , for $R=2.0$ au.^a

r (au)	Rotation Angle ω_μ		
	θ		
	30 °	45 °	60 °
3.5	74.79 °	38.71 °	19.26 °
4.0	78.19 °	20.20 °	9.67 °
4.5	82.69 °	5.44 °	4.78 °

^a See text for description of calculation of ω_μ .

Figure 5.1: Coordinate systems. The unprimed coordinates are those of the CI calculations and the primed coordinates are the polar system used to transform the cartesian derivatives to internal derivatives.

Figure 5.2: Adiabatic (V_I^{ad}) and diabatic (V_I^{d}) potential energy curves and diabatic coupling elements (V_{12}^{d}) of the electronic Hamiltonian for $R=1.5$ au and $r=4.0$ au as functions of θ . The energy scale on the right is for V_{12}^{d} .

Figure 5.3: Adiabatic (V_l^{ad}) and diabatic (V_l^{d}) potential energy curves and diabatic coupling elements (V_{12}^{d}) of the electronic Hamiltonian for $R=1.5$ au and $\theta=45^\circ$ as functions of r . The energy scale on the right is for V_{12}^{d} .

Figure 5.4: Adiabatic (V_i^{ad}) and diabatic (V_i^d) potential energy curves and diabatic coupling elements (V_{12}^d) of the electronic Hamiltonian for $\theta=45^\circ$ and $r=4.0$ au as functions of R . The energy scale on the right is for V_{12}^d .

CHAPTER 6

Summary, Conclusions, and Recommendations

6.1 Summary

In order to further the understanding of gas phase collision dynamics, a fully quantum study of the atom-diatom collision system $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$ was undertaken. This system is of interest for two main reasons: (1) it is a small system that has initial electronic excitation in the diatom that can be treated nearly exactly theoretically; (2) large cross sections for rovibrational energy transfer and fluorescence quenching have been measured.

A grid, in R , r , and θ , of accurate CI interaction energies was computed. This grid was combined with the published calculations of RBP and FTN and fit with two analytic functions: (1) V^{RR} that describes the region needed to study rotational energy transfer in the rigid-rotor approximation; (2) V^{VR} that describes the region needed to study rovibrational energy transfer. The polarizability and quadrupole moment of $\text{H}_2(\text{B } ^1\Sigma_u^+)$ were computed and used in the multipole expansion of the long-range interaction energy. Therefore, the dispersion interaction that dominates the long-range interaction is properly accounted for in both potentials.

The CC equations for rotational and rovibrational energy transfer were solved using standard integration techniques. Rotational partial and integral cross sections were computed within the ECRR approximation on three analytic PESs and compared to assess the validity of the ECRR approximation. The PESs were the two computed in this study and that computed by FTN. Integral, and differential cross sections at energies less than or equal to 0.210 eV were also computed using an accurate vibrating-rotor description of $\text{H}_2(\text{B } ^1\Sigma_u^+)$.

The fluorescence quenching process was studied by computing ab initio CI nonadiabatic coupling between $\text{HeH}_2(1 ^1\text{A}')$ and $\text{HeH}_2(2 ^1\text{A}')$ which are responsible for the quenching. The BO coupling matrix elements were computed with respect to atom-centered Cartesian coordinates using central difference formulas. Spurious contributions, which do not disappear at large R , exist in the ab initio computed BO NA coupling elements. These terms were removed by fitting an analytic representation to the computed points and then subtracting this function from the computed values. The angle, ω , that defines the transformation from adiabatic to diabatic electronic representations was found to correspond to a physical angle of the system (i.e. the angle that diagonalizes the component of the dipole moment matrix along the H_2 bond). The dipole moment matrix was computed on a grid in R , r , and θ to locate the two-dimensional avoided crossing seam.

6.2 Conclusions

The PES for He interacting with $\text{H}_2(\text{B } ^1\Sigma_u^+)$ is much more complex than those for most ground-state molecules with rare gas atoms. Much of the complexity of the PES can be attributed to the Rydberg character of $\text{H}_2(\text{B } ^1\Sigma_u^+)$. The B-state of H_2 has a long bond length (2.4 au); and its electron distribution is much more elongated than that of $\text{H}_2(\text{X } ^1\Sigma_g^+)$. This leads to an interaction that depends strongly on θ , the angle of approach of He relative to the H_2 bond. The features of interest on the PES include an attractive well along the C_{2v} approach, about 0.03 eV deep. Along the C_{cov} approach there is an avoided crossing with $\text{He} + \text{H}_2(\text{E,F } ^1\Sigma_g^+)$, that causes a local maximum in the PES.²⁹ A second avoided crossing, this one with $\text{He} + \text{H}_2(\text{X } ^1\Sigma_g^+)$, provides the fluorescence quenching mechanism and causes an attractive well of about 1.5 eV near $R=1.5$ au, $r=4.0$ au, and $\theta=45^\circ$.³⁰ All of these features influence the dynamics of $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$ collisions.

The computed integral cross sections for rotational energy transfer in $\text{He} + \text{H}_2(\text{B } ^1\Sigma_u^+)$ are large compared to those for ground-state $\text{He} + \text{H}_2(\text{X } ^1\Sigma_g^+)$. This is consistent with the more anisotropic interaction energy. The ECRR approximation does not work as well for translational energies and transitions near threshold as it does for translational energies above 0.05 eV. Collisions that have low relative translational energy (< 0.03 eV) as well as collisions resulting in multiquantum excitation are very sensitive to the

description of the PES. At translational energies above 0.05 eV the ECRR approximation is in reasonable agreement with the VR cross sections.

Narrow resonances (with widths < 0.001 eV) occur in σ_{00-02} at 0.0171, 0.019, 0.021, and 0.023 eV using the VR PES, energy levels, and wave functions of $H_2(B\ ^1\Sigma_v^+)$. These resonances are characterized by partial cross sections that are dominated by a single partial wave contribution, and by DCSs that are nearly symmetric with respect to $\theta_{CM}=90^\circ$. Differential cross sections for rotational energy transfer are strongly forward peaked for $\Delta j < 4$ and almost flat for $\Delta j > 4$. The vibrational DCSs have a large contribution from backward scattering; however, they are very small compared to those for rotational energy transfer.

The computed BO coupling (minus the spurious terms) are large for angular and relative translational motion and smaller for vibrational motion. These terms are multiplied by the velocity of that motion in the CC equations; thus, this suggests that rotational and vibrational motion will be effective in promoting fluorescence quenching under the experimental conditions.

The avoided crossing with $He + H_2(X\ ^1\Sigma_g^+)$ occurs along a seam in R , r , and θ space, not just at a point. The crossing seam exists at larger r as θ increases for fixed R . The energy separation of the PESs appears to increase along the seam as the system moves away from the minimum of the excited-state PES. Therefore, even though the crossing occurs along a seam, the region in the neighborhood of the minimum on the excited-state surface will be

the most efficient at promoting fluorescence quenching.

6.3 Recommendations

The calculations performed in this study provide a great deal of insight into the dynamics of collisions of He with $H_2(B\ ^1\Sigma_u^+)$. Many questions, however, remain unanswered. Some of the more important calculations remaining to be done are listed below.

(1) A Hellmann-Feynmann type relation for the NA coupling

$$\langle \Psi_I | \frac{\partial}{\partial \alpha} | \Psi_J \rangle \approx (E_J - E_I)^{-1} \langle \Psi_J | \frac{\partial H_{el}}{\partial \alpha} | \Psi_I \rangle \quad (8.1)$$

has been used in several studies of NA coupling processes.^{109,116} This expression is simpler to compute than (Eq. 5.14); however, there has not been any verification of its accuracy by comparison with the NA coupling computed via Eq. (5.14). Such a comparison could easily be undertaken for HeH_2 .

(2) The spurious coupling in HeH_2 (see section 5.2) was eliminated in an ad hoc manner in this work. Better understanding of these terms is needed. A rigorous justification of the functional representation used to eliminate the spurious coupling might provide a good beginning for this understanding.

(3) The accuracy of approximate methods for treating the collision dynamics (e.g. CS and IOS) should be tested. These could be used to extend the energy range for accurate cross sections. (and observe the onset of fluorescence quenching by large changes in rovibrational cross sections as a function of energy).

(4) The IOS approximation should be tested and used to compute cross sections for rotational, vibrational and electronic energy transfer at the experimental scattering energy. This would not only provide a better understanding of the dynamics of these collisions at higher energies but also serve as a benchmark for testing more approximate, easier to use methods for treating multisurface scattering.

APPENDIX 1

Details of Cross Section Calculations

Two versions of the program MOLSCAT were used to solve the CC equations, an older version¹¹⁷ distributed by the National Resource for Computation in Chemistry (NRCC) and a newer version¹¹⁸ modified to take advantage of vector processing available on the CRAY supercomputers. One or more of the VIVAS,^{47,48} Gordon,³⁹ and DeVogeleare^{40,41} algorithms were employed to solve the CC equations at each scattering energy. Sample input files are shown on pages 166-167. Subroutines that generate the potential coupling elements by the interpolation scheme described following Eq. (2.28) were written. The data files of grids of the coupling matrix elements, described in Chapter 2, were stored on disk.

Table A1.1 lists the basis sets used in different calculations at the various scattering energies. At least two closed rotational levels within each vibrational level were included in all calculations. Cross sections are covered to two significant figures at all except the highest two energies for vibrational and multiquantum rotational energy transfer. At 0.195 eV and 0.210 eV there are convergence problems which seem to be related to the initialization of the

wave function in the classically inaccessible region. An infinite potential is placed at a small value of R ($r_{\min}$ of the sample inputs) to start the integration. The value of $r_{\min}$ is determined empirically as the largest value of R that does not affect the cross section. The calculations at 0.180 eV, 0.195 eV, and 0.210 eV use $r_{\min}=1.5$ au. Decreasing $r_{\min}$ causes the partial cross sections for vibrational and multiquantum ($\Delta j > 4$) rotational transitions to vary; however, for values of $r_{\min} < 1.5$ au the cross sections do not converge. This is probably due to the shape and magnitude of the PES at very small R . The interaction energy at $R=0.0$ au, with the He atom at the H_2 midpoint, is only 7.5 eV at $r=2.4$ au. The calculations at 0.195 eV and 0.210 eV indicate that it may be necessary to start the integration in a more rigorous fashion use the proper at $R=0.0$ au as is done in electron-molecule scattering calculations.¹¹⁹ Nevertheless, the computed cross sections at 0.195 eV and 0.210 eV should be within an order of magnitude of the correct values.

Differential cross sections were computed using the code DCS2 developed by Truhlar and co-workers¹²⁰. A subroutine was written to convert the S-matrices output by MOLSCAT to T-matrices for input to DCS2. All computed partial waves were used in the DCS calculations. The program DCS2 was also converted to compute partial integral cross sections and a sample output is shown on pages 168-171 (the beginning of the output is the input file).

Sample MOLSCAT Input File:

VIVAS Integration

```

$input
label = 'he-h2(b singlet) potential -- vivas production run #13',
ured = 1.3405,
intflg = 4,
lastin = 1,
mxsig = 8,
prntlv = 10,
ithrow = 0,
isigpr = 1,
jtotl = 37,
jtotu = 69,
jstep = 2,
dtol = 1.0d0,
ctol = 5.0d-4,
ncac = 4,
dnrg = -1.5d-2,
nnrg = 3,
energy = 0.210,
eunits = 5,
ntemp = 0,
ngauss = 6,
isaveu = 12,
isigu = 10,
iscru = 30,
nlprbr = 0,
lprbru = 11,
line = 0,
ifegen = 0,
ltype = 0,
ksave = 0,
mset = 0,
irmset = 0,
rmin = 1.5d0,
rmax = 3.0d1,
steps = 6.0d0,
rvivas = 4.0,
tolhi = 2.0d-4,
ialpha = 0,
ialfp = .true.,
idiag = .true.,
isym = .true.,
stabil = 5.0d0,
stest = 5.0d-4,
$end
$basia
itype = 7,
nlevel = 11,
jlevel = 0,0, 2,0, 4,0, 6,0,
0,1, 8,0, 2,1, 4,1, 10,0,
6,1, 12,0,
ellevel = 1.0d-10, 1.1602d-2, 3.8529d-2, 7.9502d-2
1.31840d+3, 1.33178d+3, 1.42972d+3, 1.68556d+3, 1.97855d+3,
2.07703d+3, 2.71755d+3,
eunits = 1,
$end
$spotl
n = 11,
nvj = 0,0, 0,2, 0,4, 0,6,
1,0, 0,8, 1,2, 1,4, 0,10,
1,0, 0,12,
lamax = 13,
nb = 1,2,3,4,
10,5,11,12,6,
13,7,
$end

```

Sample MOLSCAT Input File:

de Vogelaere Integration

```

$input
label = 'he-h2(b singlet) potential -- DeVogelaere prd run #7',
ured = 1.3405,
intflg = 2,
lastin = 1,
mxsig = 2,
prntlv = 10,
ithrow = 0,
isigpr = 1,
jtotl = 0,
jtou = 0,
jstep = 5,
dtol = 1.0d0,
otol = 1.0d-4,
ncac = 4,
dnrg = -1.0d-3,
nnrg = 1,
energy = 0.024,
eunits = 5,
ntemp = 0,
ngauss = 0,
isaveu = 12,
isigu = 10,
is cru = 30,
nlprbr = 0,
lprbru = 11,
line = 0,
ifegen = 0,
itype = 0,
ksave = 0,
msat = 0,
irmset = 0,
rmin = 2.0d0,
rmax = 3.0d1,
steps = 10.0d0,
rvivas = 4.0,
tolhi = 3.0d-4,
ialpha = 0,
ialfp = .true.,
idialg = .true.,
iasym = .true.,
stabil = 5.0d0,
stest = 5.0d-4,
$end
$basis
itype = 7,
nlevel = 5,
jlevel = 0,0, 2,0, 4,0, 6,0,
0,0,
eleval = 1.6d-10, 1.1602d+2, 3.8529d+2, 7.9502d+2
1.33170d+3,
eunits = 1,
$end
$potl
n = 5,
nvj = 0,0, 0,2, 0,4, 0,6,
0,0,
lamax = 9,
nb = 1,2,3,4,
5,
$end

```



```

0      0.1457059e-03
1      0.3456311e-03
2      0.2565292e-03
3      0.2845494e-04
4      0.1042767e-03
5      0.3031071e-03
6      0.2473453e-03
7      0.9070023e-04
8      0.5941347e-05
9      0.5670499e-08
10     0.0427670e-07
11     0.1501060e-07
12     0.1247913e-08
13     0.5174722e-10
14     0.1055574e-10
15     0.2454091e-10
16     0.2311041e-11
17     0.2398843e-11
18     0.5176107e-11
19     0.1507203e-11
20     0.4173065e-13
21     0.9294794e-12
--
21     0.1005608e-02

```

transition probability and opacity as a function of l

@relative orbital angular momentum transition probability from $u=1, s=0$
to $u=1, s=2$

l	even parity	odd parity
0	4.401925e-04	0.
1	0.	3.520042e-04
2	1.571110e-04	0.
3	0.	0.940297e-06
4	3.540020e-05	0.
5	0.	1.000522e-04
6	5.020431e-05	0.
7	0.	1.974300e-05
8	1.070233e-00	0.
9	0.	0.000050e-10
10	1.220026e-09	0.
11	0.	2.11951e-09
12	1.620574e-10	0.
13	0.	6.000010e-12
14	1.050397e-12	0.
15	0.	2.424000e-12
16	2.144540e-13	0.
17	0.	2.000024e-13
18	4.203100e-13	0.
19	0.	1.230023e-13
20	3.110026e-15	0.
21	0.	0.619323e-14

transition probability from $u=1, s=0$
to all other states

l	even parity	odd parity
0	4.401925e-04	0.
1	0.	3.520042e-04
2	1.571110e-04	0.
3	0.	0.940297e-06
4	3.540020e-05	0.
5	0.	1.000522e-04
6	5.020431e-05	0.
7	0.	1.974300e-05
8	1.070233e-00	0.
9	0.	0.000050e-10
10	1.220026e-09	0.
11	0.	2.11951e-09
12	1.620574e-10	0.
13	0.	6.000010e-12
14	1.050397e-12	0.
15	0.	2.424000e-12
16	2.144540e-13	0.
17	0.	2.000024e-13
18	4.203100e-13	0.
19	0.	1.230023e-13
20	3.110026e-15	0.
21	0.	0.619323e-14

@ l trans. prob. from $u=1, s=0$ to $u=1, s=2$ trans. prob. from $u=1, s=0$ partial integral cross section summed thru l

	even + odd	even + odd	even + odd	even	odd
0	4.461925e-04	4.461925e-04	5.203289e-04	5.203289e-04	0.
1	3.520842e-04	3.520842e-04	1.754000e-03	6.283289e-04	1.234271e-03
2	1.571110e-04	1.571110e-04	2.670603e-03	1.436412e-03	1.234271e-03
3	0.948207e-05	0.948207e-05	2.743728e-03	4.436412e-03	1.387317e-03
4	3.548829e-05	3.548829e-05	3.116188e-03	1.888791e-03	1.387317e-03
5	1.060522e-04	1.060522e-04	4.484209e-03	1.888791e-03	2.675418e-03
6	5.826431e-05	5.826431e-05	5.367495e-03	2.692078e-03	2.675418e-03
7	1.974306e-05	1.974306e-05	6.712847e-03	2.692078e-03	3.020789e-03
8	1.070233e-05	1.070233e-05	5.734864e-03	2.713294e-03	3.020789e-03
9	0.909058e-05	0.909058e-05	6.734784e-03	2.713294e-03	3.020789e-03
10	1.228925e-05	1.228925e-05	5.734385e-03	2.713595e-03	3.020789e-03
11	2.119551e-05	2.119551e-05	5.734442e-03	2.713595e-03	3.020789e-03
12	1.528574e-05	1.528574e-05	5.734446e-03	2.713595e-03	3.020789e-03
13	5.069019e-05	5.069019e-05	5.734446e-03	2.713595e-03	3.020789e-03
14	1.959397e-05	1.959397e-05	5.734446e-03	2.713595e-03	3.020789e-03
15	2.424889e-05	2.424889e-05	5.734446e-03	2.713595e-03	3.020789e-03
16	2.144549e-05	2.144549e-05	5.734446e-03	2.713595e-03	3.020789e-03
17	2.098824e-05	2.098824e-05	5.734446e-03	2.713595e-03	3.020789e-03
18	4.203168e-05	4.203168e-05	5.734446e-03	2.713595e-03	3.020789e-03
19	1.238623e-05	1.238623e-05	5.734446e-03	2.713595e-03	3.020789e-03
20	3.118925e-05	3.118925e-05	5.734446e-03	2.713595e-03	3.020789e-03
21	0.619323e-04	0.619323e-04	5.734446e-03	2.713595e-03	3.020789e-03

the bi coefficients of the legendre polynomials in the dcs formula of biatt and biadenharn (in a02)

0	1.229351e-03	1	1.227657e-04	2	9.787318e-04	3	-2.191768e-04	4	-4.115188e-04	5	-2.975197e-04	6	-2.233184e-04
7	4.115742e-04	8	-7.066925e-05	9	1.448823e-04	10	2.081254e-04	11	1.201186e-04	12	-5.212095e-05	13	-2.281222e-05
14	-2.280121e-06	15	5.565788e-06	16	5.738974e-05	17	9.830786e-07	18	-1.068085e-06	19	-1.208400e-07	20	3.971014e-07
21	3.071993e-08	22	-2.882687e-07	23	8.088237e-08	24	5.840729e-08	25	-1.074806e-07	26	1.117107e-07	27	8.878159e-08
28	-4.588275e-08	29	-1.656848e-08	30	-6.612375e-11	31	9.838181e-10	32	1.181273e-10	33	7.402156e-11	34	1.086781e-11
35	-2.740811e-11	36	5.719728e-11	37	-2.948897e-11	38	-5.163840e-12	39	1.079208e-11	40	-0.283565e-12	41	-0.848146e-13
42	3.689333e-12												

integrated integral cross section = 5.734446e-03 a02
= 1.665888e-03 ang2

4.0*pi*b0 = 5.734446e-03 a02
= 1.885888e-03 ang2

momentum transfer cross section (arthurs-dalgarno def.) = 5.643582e-03 a02
= 1.562356e-03 ang2

differential cross section (ang2/er)

0	2.1388e-04	1	2.1337e-04	2	2.1289e-04	3	2.1098e-04	4	2.0716e-04	5	2.0364e-04	6	1.9956e-04	7	1.9501e-04
8	1.9014e-04	9	1.8507e-04	10	1.7995e-04	11	1.7492e-04	12	1.7011e-04	13	1.6567e-04	14	1.6171e-04	15	1.5833e-04
16	1.5504e-04	17	1.5369e-04	18	1.5266e-04	19	1.5225e-04	20	1.5278e-04	21	1.5435e-04	22	1.5632e-04	23	1.5922e-04
24	1.6288e-04	25	1.6895e-04	26	1.7165e-04	27	1.7058e-04	28	1.8187e-04	29	1.8717e-04	30	1.9191e-04	31	1.9711e-04
32	2.0275e-04	33	2.0729e-04	34	2.1127e-04	35	2.1477e-04	36	2.1769e-04	37	2.1972e-04	38	2.2106e-04	39	2.2161e-04
40	2.2136e-04	41	2.2011e-04	42	2.1848e-04	43	2.1593e-04	44	2.1270e-04	45	2.0887e-04	46	2.0451e-04	47	1.9972e-04
48	1.9459e-04	49	1.8919e-04	50	1.8364e-04	51	1.7803e-04	52	1.7242e-04	53	1.6680e-04	54	1.6162e-04	55	1.5633e-04
56	1.5137e-04	57	1.4688e-04	58	1.4221e-04	59	1.3891e-04	60	1.3404e-04	61	1.2928e-04	62	1.2605e-04	63	1.2329e-04

64 1.1000e-04	65 1.1652e-04	66 1.1310e-04	67 1.0981e-04	68 1.0637e-04	69 1.0283e-04	70 9.9283e-05	71 9.5474e-05
72 9.1681e-05	73 8.7786e-05	74 8.3892e-05	75 8.0017e-05	76 7.6214e-05	77 7.2643e-05	78 6.9063e-05	79 6.5837e-05
80 6.2921e-05	81 6.0375e-05	82 5.8247e-05	83 5.6516e-05	84 5.5304e-05	85 5.4722e-05	86 5.4607e-05	87 5.4926e-05
88 5.5793e-05	89 5.7112e-05	90 5.8878e-05	91 6.1027e-05	92 6.3612e-05	93 6.6270e-05	94 6.9236e-05	95 7.2342e-05
96 7.5621e-05	97 7.9785e-05	98 8.1970e-05	99 8.4834e-05	100 8.7683e-05	101 9.0758e-05	102 9.2697e-05	103 9.4649e-05
104 9.6369e-05	105 9.7751e-05	106 9.8705e-05	107 9.9594e-05	108 9.9861e-05	109 9.9944e-05	110 9.9833e-05	111 9.9455e-05
112 9.8908e-05	113 9.8244e-05	114 9.7520e-05	115 9.6795e-05	116 9.6127e-05	117 9.5575e-05	118 9.5104e-05	119 9.4833e-05
120 9.5140e-05	121 9.5574e-05	122 9.6340e-05	123 9.7500e-05	124 9.9053e-05	125 1.0102e-04	126 1.0341e-04	127 1.0623e-04
128 1.0940e-04	129 1.1309e-04	130 1.1710e-04	131 1.2140e-04	132 1.2613e-04	133 1.3108e-04	134 1.3627e-04	135 1.4163e-04
136 1.4713e-04	137 1.5270e-04	138 1.5839e-04	139 1.6387e-04	140 1.6936e-04	141 1.7471e-04	142 1.7997e-04	143 1.8479e-04
144 1.8943e-04	145 1.9374e-04	146 1.9780e-04	147 2.0122e-04	148 2.0433e-04	149 2.0698e-04	150 2.0910e-04	151 2.1085e-04
152 2.1205e-04	153 2.1275e-04	154 2.1297e-04	155 2.1271e-04	156 2.1190e-04	157 2.1083e-04	158 2.0928e-04	159 2.0735e-04
160 2.0509e-04	161 2.0252e-04	162 1.9971e-04	163 1.9669e-04	164 1.9352e-04	165 1.9023e-04	166 1.8689e-04	167 1.8352e-04
168 1.8019e-04	169 1.7694e-04	170 1.7391e-04	171 1.7085e-04	172 1.6809e-04	173 1.6567e-04	174 1.6331e-04	175 1.6138e-04
176 1.5972e-04	177 1.5843e-04	178 1.5766e-04	179 1.5693e-04	180 1.5674e-04			

total elapsed time(seconds) in cross = 1.485488e+00

Output from DCS2 (cont.)

Table A1.1: Basis sets of rotational and rovibrational functions, $|v j\rangle$, used in Coupled-channel cross section calculations.

Total Scattering Energy (eV)	Coupled-Channel Basis Sets			
	Potential Energy Function			
	V_{FMC}^a	V_{RR}	V_{VARR}	V_{VR}
0.015-0.045	00, 02, 04, 06	00, 02, 04, 06, 08	00, 02, 04, 06, 08	00, 02, 04, 06
0.060-0.090	+ 08 ^b	+ 010	+ 010	+ 08
0.105-0.150	+ 010	+ 012	+ 012	+ 010, 10
0.165-0.210				+ 12, 14

^a See Chapter 3 for a description of these PESs.

^b Notation + 010 means all basis functions at lower energies plus $vj=010$ were included.

APPENDIX 2

Basis Set and Correlation Dependence of the Polarizability of $H_2(B\ ^1\Sigma_u^+)$

In order to determine an accurate basis set for hydrogen capable of describing the multipole properties of $H_2(B\ ^1\Sigma_u^+)$ the basis set and correlation dependence of $\alpha_{H_2}(B)$ were studied. An accurate quadrupole moment was also computed.

All basis sets were constructed as augmentations of the set given in Table A2.1 denoted (7s,5p)/[5s,5p]. The exponents and contraction coefficients of the first five s functions are taken from Huzinaga.¹²¹ The two additional s exponents were optimized to minimize the energy of $H_2(B\ ^1\Sigma_u^+)$ at $R=2.43$ au. The following procedure was used to generate the set of p functions: (1) Three p exponents (1.313, 0.282, and 0.090) were energy optimized in the presence of the [5s] set. (2) The p function with the largest exponent, 1.313, was replaced by two p functions with exponents $3x$ and 3^2x larger than the middle p exponent (0.282) and are the entries 2.538 and 0.846 of Table A2.1. (3) Finally, a diffuse p function with exponent 0.030 was added.

Table A2.2 lists the full CI energies for $H_2(X\ ^1\Sigma_g^+)$ and $H_2(B\ ^1\Sigma_u^+)$, calculated with this basis set. At $R=2.43$ au the $H_2(B\ ^1\Sigma_u^+)$ energy is only

0.001401 au above the very accurate KW result. We note that the present basis set also provides a good description of $H_2(X^1\Sigma_g^+)$. Our basis set differs from that of RPB in the choice of the most diffuse s exponent which is energy optimized in this study, and in the inclusion of a set of p functions. The most diffuse s and p functions were chosen to provide additional flexibility for description of the perpendicular ($\alpha_\perp$) and parallel ($\alpha_\parallel$) polarizabilities.

The polarizability results discussed in this section were obtained with a single configuration HF wavefunction using the finite-field method of Cohen and Roothaan.¹²³ The basis set described in the previous section was augmented with additional diffuse functions to assess their influence on the calculated polarizability. The results are given in Table A2.3.

In the absence of an electric field, the HF wave function of $H_2(B^1\Sigma_u^+)$ may be written

$$\Psi_{\text{HF}} = 2^{-1/2} (|1\sigma_g 1\bar{\sigma}_u| - |1\bar{\sigma}_g 1\sigma_u|). \quad (3.1)$$

To obtain $\alpha_\parallel$, the field must be directed along the molecular axis. The electron density becomes polarized along the field direction, and the molecular orbitals lose gerade and ungerade symmetry. Therefore the $B^1\Sigma_u^+$ state becomes the second state of $^1\Sigma^+$ symmetry following the ground state. In this case the wavefunction is a linear combination of the three configurations

$$|1\sigma 1\bar{\sigma}|, \quad 2^{-1/2} (|1\sigma 2\bar{\sigma}| - |1\bar{\sigma} 2\sigma|), \quad |2\sigma 2\bar{\sigma}|. \quad (3.2)$$

The SCF equations are then solved for the second root of the 3x3 Hamiltonian

matrix. We note that this complication does not arise for $\alpha_{\perp}$ since the $X^1\Sigma_g^+$ and $B^1\Sigma_u^+$ states retain different symmetries (1A_1 and 1B_2) when a field is applied perpendicularly to the bond. The same considerations are encountered in the correlated wave function calculations of the polarizability described later.

The data of Table A2.3 show that both components of the polarizability are very large. This is not surprising in light of the very diffuse character of the σ_u orbital, and of the Rydberg character of $H_2(B^1\Sigma_u^+)$. The addition of diffuse functions to the [5s,5p] basis set of Table A2.1, has only a minor effect on $\alpha_{\perp}$. Variations in $\alpha_{\parallel}$ are most important. An even-tempered s function increases $\alpha_{\parallel}$ by 4% and an even-tempered diffuse p function increases it by 2%. The effects of adding the s and p functions are nearly independent; the combined increase is 6%. The diffuse s and p exponents were three times smaller than the smallest exponents in the [5s,5p] basis set. A d function with exponent 0.282 (same as the middle p exponent) added to the [5s,5p] basis set resulted in negligible change of the polarizability. A d exponent of 0.116 increased $\alpha_{\parallel}$ by 2%. From the [5s,5p] basis set including both the diffuse s and p functions. We estimate the HF limit of the dipole polarizability components (in au) to be

$$\alpha_{\perp} = 71 \pm 2\%, \quad \alpha_{\parallel} = 354 \pm 8\%.$$

We note that RP3's basis set has fewer diffuse functions than the present basis set resulting in slightly smaller polarizability components.

To study the influence of electron correlation on the calculated polarizabilities, we carried out MCHF and CI calculations of $\alpha_{\perp}$ and $\alpha_{\parallel}$. The computational effort was reduced by using RPB's basis set, which is nearly equivalent to the large basis used to compute the results in Table A2.3 to study the correlation effects on the components of α . The full CI values of these components were also computed.

Using a full CI wave function $\alpha_{\perp}=50$, $\alpha_{\parallel}=257$, ($\alpha_{\perp}=51$, $\alpha_{\parallel}=259$)¹²⁴ were obtained, which are 23% and 24% smaller than the corresponding HF values. Werner and Meyer¹²⁵ (WM) qualitatively related correlation effects on the polarizability to correlation effects on the electron distribution. More specifically, they determined that the inclusion of correlation contributions that increase the polarizability also increase the size of the electron distribution. The expectation values of $\langle r^2 \rangle_{\perp}$ and $\langle r^2 \rangle_{\parallel}$ calculated using correlated wavefunctions are given in Table A2.4. The electron distribution from the CI wave function is found to be smaller than the HF electron distribution resulting in smaller polarizabilities.

In order to analyze the various correlation effects on the polarizability, a series of MCHF wave functions were constructed as follows. A set of active σ and π orbitals was selected and all configurations obtained by distributing two electrons among these orbitals in all possible ways consistent with $^1\Sigma_g^+$ or $^1\Sigma_u^+$ symmetry were included. The first wave function included the HF orbitals $1\sigma_g$ and $1\sigma_u$. The second wave function, denoted MC($1\sigma_g, 1\sigma_u, 2\sigma_g, 2\sigma_u$),

included an additional set of σ orbitals - a compact σ_u orbital to correlate the $1\sigma_g$, and a diffuse σ_g orbital to correlate the $1\sigma_u$. The third wave function, MC($1\sigma_g, 1\sigma_u, 1\pi_u, 1\pi_g$), included an additional set of π rather than σ orbitals to describe angular correlation. Finally, the fourth wave function MC($1\sigma_g, 1\sigma_u, 2\sigma_g, 2\sigma_u, 1\pi_u, 1\pi_g$), included both sets of additional σ and π orbitals.

The dipole polarizabilities and mean values of r^2 calculated with these wave functions are given in Table A2.4. The results indicate that electron correlation is responsible for the decrease in both components of the polarizability and $\langle r^2 \rangle$. Angular correlation in MC($1\sigma_g, 1\sigma_u, 1\pi_u, 1\pi_g$) is more important than left-right correlation in MC($1\sigma_g, 1\sigma_u, 2\sigma_g, 2\sigma_u$). Both types of correlation lead to a reduction of the nuclear screening, and thus to a contraction of the electron density. These correlation contributions are nearly independent and additive, as exemplified by the result for MC($1\sigma_g, 1\sigma_u, 2\sigma_g, 2\sigma_u, 1\pi_u, 1\pi_g$). Polarizabilities obtained with this wave function are nearly identical to full-CI polarizabilities. The results of Table A2.4 confirm the proportionality between $\langle r^2 \rangle$ and polarizability, as suggested by WM.¹²⁵ We note also that correlation effects are not nearly as significant for ground-state H_2 .¹²⁶

The quadrupole moment was calculated using the [5s,5p] basis set of Table A2.1. The calculation was done using standard analytic methods.¹²⁷ The full CI result is -5.63 au. Again this value is quite large, roughly an order of magnitude larger than the ground state value.

Table A2.1: Hydrogen atom basis set.

(7s)/[5s]			(5p)/[5p]		
	Exponent	Contraction		Exponent	Contraction
s	68.16	0.00255	p	2.538	1.0
s	10.25	0.01938	p	0.846	1.0
s	2.346	0.09280	p	0.282	1.0
s	0.6733	1.0	p	0.090	1.0
s	0.2247	1.0	p	0.030	1.0
s	0.0822	1.0			
s	0.0276	1.0			

Table A2.2: Calculated energies (au) for $H_2(X \ ^1\Sigma_g^+)$ and $H_2(B \ ^1\Sigma_u^+)$.

	Exact ^a	RPB ^b	This work ^c
$H_2(X \ ^1\Sigma_g^+)$ $R=1.40 \text{ au}$	-1.174475	-1.170009	-1.171841
$H_2(B \ ^1\Sigma_u^+)$ $R=2.43 \text{ au}$	-0.756661	-0.754780	-0.755280

^a From Ref. 51 and 122.

^b Full CI with RPB basis set from Ref. 28.

^c Full CI with $[5s,5p]$ basis set.

Table A2.3: Basis set dependence of Hartree-Fock polarizability components (au) of $\text{H}_2(\text{B}^1\Sigma_u^+)$.

Basis Set	$\alpha_{\parallel}$	$\alpha_{\perp}$
[5s,5p]	69	335
[5s,5p] + s (0.0093)	69	348
[5s,5p] + p (0.010)	70	341
[5s,5p] + s (0.0093) + p (0.010)	71	354
[5s,5p] + d (0.282)	69	334
[5s,5p] + d (0.116)	69	341
RPB ^a	67	338

^a Basis set taken from Ref. 28.

Table A2.4: MCSCF and CI polarizability and $\langle r^2 \rangle$ components (au) of $H_2(B^1\Sigma_u^+)$.^a

Wave Function	$\alpha_{\perp}$	$\alpha_{\parallel}$	$\langle r^2 \rangle_{\perp}$	$\langle r^2 \rangle_{\parallel}$
MC($1\sigma_g 1\sigma_u$) or HF ^b	67	338	2.33	7.21
MC($1\sigma_g 1\sigma_u 2\sigma_g 2\sigma_u$)	60	319	2.23	6.86
MC($1\sigma_g 1\sigma_u 1\pi_u 1\pi_g$)	55	274	2.18	6.67
MC($1\sigma_g 1\sigma_u 2\sigma_g 2\sigma_u 1\pi_u 1\pi_g$)	50	264	2.10	6.38
Full CI	50	257	2.08	6.32

^a All computations performed with RPB basis set of Ref. 28.

^b See text for description of notation.

APPENDIX 3

Checks on the Accuracy of Computed NA Coupling Elements

There are not many NA coupling calculations in existence and even fewer can be easily reproduced in order to test the accuracy of a new computer program. This appendix contains the checks of the modified version of HONDO¹²⁹ used to compute the NA coupling elements described in Chapter 5.

Several tests for accuracy can be derived by differentiating the orthogonality relationships. First the orthogonality constraint between two electronic wave functions

$$\langle \Psi_i^{ad} | \Psi_j^{ad} \rangle_q = 0 \quad (\text{A3.1})$$

can be differentiated to yield:

$$\frac{\partial}{\partial Q_a} \langle \Psi_i^{ad} | \Psi_j^{ad} \rangle_q = \langle \frac{\partial \Psi_i^{ad}}{\partial Q_a} | \Psi_j^{ad} \rangle_q + \langle \Psi_i^{ad} | \frac{\partial \Psi_j^{ad}}{\partial Q_a} \rangle_q \quad (\text{A3.2})$$

so

$$\langle \frac{\partial \Psi_i^{ad}}{\partial Q_a} | \Psi_j^{ad} \rangle_q = - \langle \Psi_i^{ad} | \frac{\partial \Psi_j^{ad}}{\partial Q_a} \rangle_q \quad (\text{A3.3})$$

or

$$D_1(I, J, a) = -D_1(J, I, a) \quad (A3.4)$$

Next, the sum of the product of the CI coefficients is zero if the same set of MOs is used for both states

$$\sum_k C_{Ik} C_{Jk} = 0 \quad (A3.5)$$

and by the same steps,

$$\sum_k C_{Ik} \frac{\partial C_{Jk}}{\partial Q_a} = - \sum_k \frac{\partial C_{Ik}}{\partial Q_a} C_{Jk} \quad (A3.6)$$

or

$$D_1^{CI}(I, J, a) = -D_1^{CI}(J, I, a) \quad (A3.7)$$

This means that

$$D_1^{CSF}(I, J, a) = -D_1^{CSF}(J, I, a) \quad (A3.8)$$

Thus the derivative matrix is anti-symmetric as are the CI and CSF pieces that make it up. The anti-symmetry of the BO coupling matrices is used as the first test of the program. In applications the conditions A3.4 and A3.7, and thus A3.8, are satisfied to 0.1-0.01%.

Another test of the program can be made by performing orbital rotations that leave the wave function and energy unchanged. If the SA-MCSCF orbitals and CI state vectors are used to compute D_1 , and rotations are made among the valence orbitals, the CI and CSF components of D_1 will vary but the total should be unchanged. The modified version of HONDO¹²⁹ is set up

to use either the SA-MCSCF or SA-NO orbitals. Calculations done using the SA-MCSCF and SA-NO orbitals agree to about 1%.

Tests were performed by reproducing the calculations of Lengsfeld et al. on Mg-H_2 .⁸ Accuracy of about 90-95% was obtained for matrix elements for geometries with Mg 3.5 and 4.0 au from the H_2 bond midpoint.

Note that since the wave functions are arbitrary to within a phase the orbitals and CI coefficients must be checked to make sure the phases don't change with the geometry. Within a given run the program checks and corrects the phases, however, calculations at different geometries must be checked by the user to ensure accurate NA matrix elements. If the wave functions do change phase the sign of the matrix elements must be changed.

APPENDIX 4

Calculation of Coriolis Couplings and Transition Dipoles

Even though the Coriolis coupling can be neglected for the He-H₂ electronic states under study their calculation is straight forward and does not seem to be reported in the literature in much detail^{16,18} so it is given in this section. Transition dipole computation¹²⁸ is similar and is described as well. Computation of the Coriolis coupling requires matrix elements of the operators L_x, L_y, L_z in the atomic orbital basis. These are all one-electron operators and standard methods can be used to compute them. The Coriolis coupling is given by

$$\langle \Psi_I^{ad} | \sum_k L_{\alpha_k} | \Psi_J^{ad} \rangle_q = \sum_{ij} \gamma_{ij}^{IJ} \langle \phi_i | L_{\alpha} | \phi_j \rangle_q \quad \alpha=x,y,z \quad (A4.1)$$

where the index alpha denotes the component of L, and the index k runs over electrons. Similarly the expression for the transition dipole moment is

$$\langle \Psi_I^{ad} | \sum_k \alpha_k | \Psi_J^{ad} \rangle_q = \sum_{ij} \gamma_{ij}^{IJ} \langle \phi_i | \alpha | \phi_j \rangle_q \quad \alpha=x,y,z \quad (A4.2)$$

where alpha is one component of the position of the electron. This calculation requires the reduced one-particle transition density matrix between states I

and J and the atomic integrals of the electronic angular momentum operators. The density matrix is computed for the radial couplings and the integrals over atomic basis functions are easily computed using standard integration routines for gaussian orbitals.

To obtain the remaining Coriolis couplings analytically requires the reduced two-particle transition density matrix since these are two-electron operators. An approximate formula containing only matrix elements of one-electron operators can be derived by inserting complete sets of states as follows:

$$\begin{aligned} \langle \Psi_i^{ad} | \sum_k L_{z_k} \cdot \sum_l L_{z_l} | \Psi_j^{ad} \rangle_q = \\ \sum_K \langle \Psi_i^{ad} | \sum_k L_{z_k} | \Psi_K^{ad} \rangle_q \langle \Psi_K^{ad} | \sum_l L_{z_l} | \Psi_j^{ad} \rangle_q \end{aligned} \quad (A4.3)$$

Expression (A4.3) is exact; however, the sum over K is infinite so it is not useful. If Coriolis coupling is strong between a small subset of the adiabatic wave functions

$$\begin{aligned} \langle \Psi_i^{ad} | \sum_k L_{z_k} | \Psi_M^{ad} \rangle_q \gg \\ \langle \Psi_i^{ad} | \sum_k L_{z_k} | \Psi_N^{ad} \rangle_q \quad N > M, I \leq M \end{aligned} \quad (A4.4)$$

the sum can be truncated without a great loss of accuracy. This expression may not find much use in the calculation of $L_2(I, J, zz)$ or $L_2(I, J, LL)$ since they can be computed analytically using the two-particle transition density matrix which can be computed for the SA-MCSCF wave function. However, the

mixed BO-Coriolis coupling term, $L_2(I, J, \mathbf{x}\theta)$, is much more difficult to compute analytically, and a formula similar to Eq. (A4.4) can be derived for it as well.

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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