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Quantum Mechanical Theory of Reactive Collisions via Electronic Nonadiabatic Transitions. The Three-Dimensional $F(^2P_{3/2}, ^2P_{1/2}) + H_2$ System as a Test Case[†]

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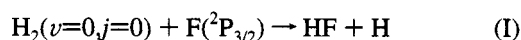
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In this work are presented transitions probabilities which follow from a formally accurate quantum mechanical study of reactive collisions taking place via electronic nonadiabatic transitions. The approach is based on the application of negative imaginary potentials (NIPs) which decouple all asymptotes. Reactive and electronic nonadiabatic $J = 0$ transition probabilities were calculated for the $F(^2P_{3/2}, ^2P_{1/2}) + H_2$ system. Two of the main findings are (a) electrrotational resonant transitions (transitions accompanied by the smallest rotational energy conversions) are not necessarily the dominant transitions and (b) weak electronic diabatic coupling terms suffice to significantly affect the reaction process taking place on the lower adiabatic (reactive) potential energy surface.

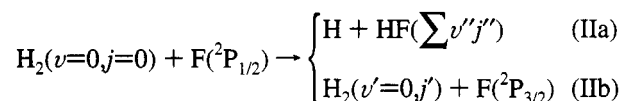
I. Introduction

To study electronic nonadiabatic effects which become apparent during atomic and molecular collisions, it is necessary to treat scattering processes on several potential energy surfaces (PESs).^{1,2} It is common knowledge that in order to be able to perform a sensible comparison between theory and experiment, one usually cannot ignore these effects. Nevertheless, quantum mechanical treatments of reactive (as well as nonreactive) processes are almost always done on a single PES and do not include any electronic effects,³ whereas treatments of such processes occurring on multisurfaces are seldom performed.^{1a,4,5} For the last two decades our group has been engaged in such studies, mainly for systems with fixed angular geometries. At the beginning, we considered collinear systems,^{1a} and later we treated them within the framework of the infinite order sudden approximation (IOSA).⁴ Recently we extended these studies and published a brief communication reporting on the first full three-dimensional calculation of reactive processes taking place via electronic nonadiabatic transitions.⁶ In the present publication we give the theory and describe, in greater detail, the calculated results.

Our ability to treat complicated three-dimensional tri- and tetra-atom systems is based on the application of negative imaginary potentials (NIPs) which decouple all arrangement channels (AC) and yield the wave function in the entire *finite* configuration space of the interacting particles.^{7–9} Once this wave function is calculated, one obtains the required S -matrix elements by projection over the asymptotic states. To test our approach we chose the $F + H_2$ system and considered the following processes:^{10,11}



and



Here process I is a regular adiabatic reactive process, but since the calculations are performed for two (coupled) surfaces, the diabatic coupling term may affect the results. Consequently, the results are expected to differ from those obtained with a single surface.⁸

The two processes IIa and IIb occur due to electronic nonadiabatic transitions; the first is a reactive process and the second an electronic inelastic process.

To perform the study we used, for the lower surface, the PES devised by Muckerman designated the M-5 potential.¹² The main reason for this choice is that about 10 years ago it was applied to study the same processes but for the *collinear* configuration,^{10,11} and we think that to compare the two types of results is instructive.

The paper is arranged in the following way: In the next section we present the theoretical background relevant to the multisurface scattering process; the potentials are described in the third section; in the fourth section we give information on the numerical aspects of the calculation; the results are presented and analyzed in the fifth section and the conclusions are given in the sixth section.

II. Theory

The theoretical section is divided into two parts: in the first we present the theory for the single-surface case, and in the second we extend it to the multisurface case.

II.1. Treatment of the Reactive Single-Surface Case.

II.1.1. Introductory Remarks. The aim of the numerical treatment is to obtain the $S(\Gamma_v \rightarrow \Gamma_\lambda) (= S(\Gamma_v \rightarrow \Gamma_\lambda))$ matrix element which describes an exchange process between two arrangement

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channels (AC) of interest, namely, λ and ν . The symbols stand for the transition from a given characteristic asymptotic set of quantum numbers, Γ_λ , in one AC to a given characteristic asymptotic set of quantum numbers, Γ_ν , in the other AC. In what follows we will distinguish between the two ACs; one is the AC where the full inelastic Schrodinger equation (SE), which contains also the NIPs, is solved, and the other is the AC where the unperturbed SE is solved. This solution is used to calculate the reactive S -matrix element, and under certain circumstances will become (as will be shown) part of the inhomogeneous term of the perturbed-like SE.

II.1.2. Methodology. The $S(\Gamma_\nu \leftarrow \Gamma_\lambda)$ matrix element is defined as

$$S(\Gamma_\nu \leftarrow \Gamma_\lambda) = \langle \Psi_{\Gamma_\nu} | V_\nu | \Psi_{\Gamma_\lambda} \rangle \quad (1)$$

where Ψ_{Γ_ν} is a solution of the ν unperturbed SE represented in terms of the unperturbed ν Hamiltonian H_ν :

$$(E - H_\nu) \Psi_{\Gamma_\nu} = 0 \quad (2)$$

V_ν is the ν -perturbation potential defined as

$$V_\nu = H - H_\nu \quad (3)$$

and Ψ_{Γ_λ} is the complete wave function associated with the asymptotic states defined in the λ AC. Ψ_{Γ_λ} is the solution of the full SE:

$$(E - H) \Psi_{\Gamma_\lambda} = 0 \quad (4)$$

Next we apply the perturbative-like approach and write Ψ_{Γ_λ} in the form

$$\Psi_{\Gamma_\lambda} = \chi_{\Gamma_\lambda} + \psi_{\Gamma_\lambda} \quad (5)$$

where ψ_{Γ_λ} is a solution of the λ unperturbed SE, represented in terms of the unperturbed λ Hamiltonian H_λ :

$$(E - H_\lambda) \psi_{\Gamma_\lambda} = 0 \quad (6)$$

Substituting eq 5 in eq 4 and recalling eq 6, it can be shown that χ_{Γ_λ} fulfills the following homogeneous SE:^{7b}

$$(E - H) \chi_{\Gamma_\lambda} = V_\lambda \psi_{\Gamma_\lambda} \quad (7)$$

where V_λ (like V_ν) is an interaction (perturbation) potential defined as

$$V_\lambda = H - H_\lambda \quad (8)$$

Our approach, as was mentioned in the Introduction, is based on deriving Ψ_{Γ_λ} in one AC as if the system under consideration is nonreactive. The fact that the system is after all reactive is incorporated in an *ad-hoc* fashion by adding to the physical Hamiltonian imaginary potentials defined along the open boundaries of the AC in which Ψ_{Γ_λ} is calculated. Thus if U_1 stands for the sum of these potentials, then the *ad-hoc* Hamiltonian H_1 to be applied in eq 7 is

$$H_1 = H + U \quad (9)$$

and consequently eq 7 becomes

$$(E - H_1) \chi_{\Gamma_\lambda} = V_\lambda \psi_{\Gamma_\lambda} \quad (7')$$

This completes the methodological section.

II.1.3. Derivation of the Unperturbed Wave Functions ψ_α : $\alpha = \lambda, \nu$. To derive ψ_{Γ_α} ($\alpha = \lambda, \nu$), we have to consider eqs 2 and 6, namely,

$$(E - H_\alpha) \psi_{\Gamma_\alpha} = 0; \alpha = \lambda, \nu \quad (10)$$

where H_α is given in the form

$$H_\alpha = T_\alpha + W_\alpha; \alpha = \lambda, \nu \quad (11)$$

Here T_α is the kinetic energy and W_α is the unperturbed potential. In what follows we assume W_α to be an elastic potential of the form¹⁷

$$W_\alpha(R_\alpha r_\alpha \gamma_\alpha) = v_\alpha(r_\alpha) + w_\alpha(R_\alpha) \quad (12)$$

where $v_\alpha(r_\alpha)$ is the α -diatomic potential defined as^{7f}

$$v_\alpha(r_\alpha) = \lim_{R_\alpha \rightarrow \infty} U(R_\alpha r_\alpha \gamma_\alpha) \quad (13)$$

and $w_\alpha(R_\alpha)$ is the elastic distortion potential defined as^{7f}

$$w_\alpha(R_\alpha) = \frac{1}{2} \int_{-1}^{+1} d \cos \gamma_\alpha U(R_\alpha r_\alpha = r_{e\alpha} \gamma_\alpha) \quad (14)$$

Here $U(R_\alpha r_\alpha \gamma_\alpha)$ is the full potential, R_α and r_α are the α -translational and -vibrational coordinates (not mass scaled), γ_α is the Jacobi angle defined as

$$\gamma_\alpha = \cos^{-1}(\hat{R}_\alpha \cdot \hat{r}_\alpha) \quad (15)$$

and $r_{e\alpha}$ is the equilibrium distance of the diatomic molecule. Since the potential in eq 12 is separable in the three coordinates, the $\Psi_\alpha(\equiv \Psi_{\Gamma_\alpha})$ wave function will be written (within the j_z approximation) as

$$\Psi_\alpha(\Lambda_\alpha R_\alpha r_\alpha \gamma_\alpha | \Gamma_\alpha) = \frac{1}{R_\alpha r_\alpha} \sqrt{\frac{2J+1}{4\pi}} \phi_\alpha(r_\alpha | n_\alpha j_\alpha) \times D^J_{M\Omega_\alpha}(\Lambda_\alpha) y(\gamma_\alpha | j_\alpha \Omega_\alpha) \xi_\alpha(R_\alpha | \Gamma_\alpha) \quad (16)$$

where Λ_α stands for the three α -AC Euler angles, Γ_α represents four quantum numbers, namely,

$$\Gamma_\alpha \equiv (n_\alpha j_\alpha \Omega_\alpha J) \quad (17)$$

n_α and j_α are the α -vibrational and -internal angular momentum quantum numbers, $D^J_{M\Omega_\alpha}(\Lambda_\alpha)$ are the coefficients of the irreducible representation of the rotation group, $y(\gamma_\alpha | j_\alpha \Omega_\alpha)$ are the spherical harmonics, $\phi_\alpha(r_\alpha | n_\alpha j_\alpha)$ are the vibrational eigenfunctions of the α -diatomic molecule,

$$\left(-\frac{\hbar^2}{2\mu_\alpha} \frac{\partial^2}{\partial r_\alpha^2} + v_\alpha(r_\alpha) + \frac{\hbar^2}{2\mu_\alpha} \frac{j_\alpha(j_\alpha + 1)}{r_\alpha^2} - \epsilon(n_\alpha j_\alpha) \right) \times \phi_\alpha(r_\alpha | n_\alpha j_\alpha) = 0 \quad (18)$$

and $\xi_\alpha(R_\alpha | \Gamma_\alpha)$ are the solutions of the corresponding translational Hamiltonian

$$\left(-\frac{\hbar^2}{2M_\alpha} \frac{\partial^2}{\partial R_\alpha^2} + w_\alpha(R_\alpha) + \frac{\hbar^2}{2M_\alpha} \frac{J(J+1) + j_\alpha(j_\alpha + 1) - 2\Omega_\alpha^2}{R_\alpha^2} - (E - \epsilon(n_\alpha j_\alpha)) \right) \times \xi_\alpha(R_\alpha | \Gamma_\alpha) = 0 \quad (19)$$

In addition are encountered the eigenvalues of the diatomic molecule $\epsilon(n_\alpha j_\alpha)$ and the two reduced masses μ_α and M_α defined as

$$\mu_\alpha = \frac{m_B m_C}{m_B + m_C}; M_\alpha = \frac{m_A(m_B + m_C)}{m_A + m_B + m_C} \quad (20)$$

where m_A is the mass of the projectile and m_B and m_C are the masses of the two atoms of the α -diatomic molecule.

It is important to mention that within the j_z approximation the space-fixed z -component of J , namely, M , becomes a redundant quantum number.

II.1.4. Derivation of the Perturbed Function χ_{Γ_λ} . In what follows we consider eq 7'. Since $\chi_\lambda (= \chi_{\Gamma_\lambda})$ can be expressed either in terms of ν coordinates (and this implies that the derivation of χ_λ is done in the ν AC) or in term of λ coordinates, we will use the index α , which may stand either for λ or for ν .

The Hamiltonian H_I is presented as

$$H_I = T_\alpha + U_\alpha + U_{I\alpha} \quad (21)$$

Here U_α and $U_{I\alpha}$ are the full potential and the NIP expressed in terms of α coordinates and T_α is the α -kinetic energy operator written in the form

$$T_\alpha = -\frac{\hbar^2}{2\mu_\alpha} \frac{1}{r_\alpha} \frac{\partial^2}{\partial r_\alpha^2} r_\alpha - \frac{\hbar^2}{2M_\alpha} \frac{1}{R_\alpha} \frac{\partial^2}{\partial R_\alpha^2} R_\alpha + \frac{1}{2\mu_\alpha} \frac{\bar{j}_\alpha^2}{r_\alpha^2} + \frac{1}{2M_\alpha} \frac{\bar{l}_\alpha^2}{R_\alpha^2} \quad (22)$$

where \bar{j}_α and \bar{l}_α are the internal and orbital angular momentum operators. As for \bar{l}_α , it will be written as

$$\bar{l}_\alpha = \bar{J} - \bar{j}_\alpha \quad (23)$$

In what follows we employ the j_z (coupled states) approximation.¹³ The characteristic feature of this approximation is that the body z -component of J , namely, Ω_α (which is also equal to the corresponding z -component of j_α), is a good quantum number in the α -AC.

To continue the function, χ_λ , which will be designated as

$$\chi_{\Gamma_\lambda} = \chi(\Lambda_\alpha R_\alpha r_\alpha \gamma_\alpha | \Gamma_\lambda) \quad (24)$$

is expanded in terms of $D^J_{M\Omega_\alpha}(\Lambda_\alpha)$, the coefficients of the irreducible representation of the rotational group (Λ_α stands for the three Euler angles), namely,

$$\chi(\Lambda_\alpha R_\alpha r_\alpha \gamma_\alpha | \Gamma_\lambda) = \frac{1}{R_\alpha r_\alpha} \sqrt{\frac{2J+1}{8\pi^2}} \sum_{\Omega_\alpha} D^J_{M\Omega_\alpha}(\Lambda_\alpha) \xi(R_\alpha r_\alpha \gamma_\alpha | \Omega_\alpha' | \Gamma_\lambda) \quad (25)$$

Substituting eqs 25, 23, 22, and 21 into eq 8', multiplying it by $D^J_{M\Omega_\alpha}$, and integrating over Λ_α yields the following equation for $\xi(R_\alpha r_\alpha \gamma_\alpha | \Omega_\alpha | \Gamma_\lambda)$:

$$\left[E + \frac{\hbar^2}{2\mu_\alpha} \frac{\partial^2}{\partial r_\alpha^2} - \frac{\hbar^2}{2M_\alpha} \frac{\partial^2}{\partial R_\alpha^2} - \bar{j}^2 \left(\frac{1}{2\mu_\alpha r_\alpha^2} + \frac{1}{2M_\alpha R_\alpha^2} \right) - \frac{\hbar^2}{2M_\alpha R_\alpha^2} (J(J+1) - 2\Omega_\alpha^2) - U(R_\alpha r_\alpha \gamma_\alpha) - U_I(R_\alpha r_\alpha) \xi(R_\alpha r_\alpha \gamma_\alpha | \Omega_\alpha | \Gamma_\lambda) = \sqrt{2\pi} \frac{R_\alpha r_\alpha}{R_\lambda r_\lambda} \times d^J_{\Omega_\alpha \Omega_\lambda}(\Delta_{\alpha\lambda}) V_\lambda(R_\lambda r_\lambda \gamma_\lambda) \phi_\lambda(r_\lambda | n_\lambda j_\lambda) \gamma(r_\lambda | 0 | j_\lambda \Omega_\lambda) \xi_\alpha(R_\lambda | \Gamma_\lambda) \right] \quad (26)$$

To obtain eq 26, we used the following relations:

(a) Acting with $(\bar{J} - \bar{j})^2$ on $D^J_{M\Omega_\alpha}(\Lambda_\alpha)$ and activating the j_z approximation yields the result

$$(\bar{J} - \bar{j}_\alpha)^2 D^J_{M\Omega_\alpha} = [\hbar^2 (J(J+1) - 2\Omega_\alpha^2) + \bar{j}_\alpha^2] D^J_{M\Omega_\alpha} \quad (27)$$

(b) The $d^J_{\Omega_\alpha \Omega_\lambda}(\Delta_{\alpha\lambda})$ function on the r h s of eq 26 follows

from the fact that each $D^J_{M\Omega_\lambda}(\Lambda_\lambda)$ can be expanded in terms of the $D^J_{M\Omega_\alpha}(\Lambda_\alpha)$ basis set in the following way:

$$D^J_{M\Omega_\lambda}(\Lambda_\lambda) = \sum_{\Omega'_\alpha} D^J_{M\Omega'_\alpha}(\Lambda_\alpha) d^J_{\Omega'_\alpha \Omega_\lambda}(\Delta_{\alpha\lambda}) \quad (28)$$

where $d^J_{\Omega'_\alpha \Omega_\lambda}(\Delta_{\alpha\lambda})$ is defined as

$$d^J_{\Omega'_\alpha \Omega_\lambda}(\Delta_{\alpha\lambda}) = D^J_{\Omega'_\alpha \Omega_\lambda}(0, \Delta_{\alpha\lambda}, 0) \quad (29)$$

and $\Delta_{\alpha\lambda}$ is the angle between R_α and R_λ :

$$\Delta_{\alpha\lambda} = \cos^{-1}(\hat{R}_\alpha \cdot \hat{R}_\lambda) \quad (30)$$

In the case of $\alpha \equiv \lambda$ we have $\Delta_{\alpha\lambda} = 0$, and consequently

$$d^J_{\Omega'_\alpha \Omega_\lambda}(\Delta_{\alpha\lambda} = 0) = \delta_{\Omega'_\alpha \Omega_\lambda} \quad (31)$$

a known feature of the $d^J_{\Omega'_\alpha \Omega_\lambda}$ functions. It is important to mention that for the case $\alpha = \nu$ (and therefore $\alpha \neq \lambda$) the angle $\Delta_{\nu\alpha}$ is a function of $(R_\alpha r_\alpha \gamma_\alpha)$.

The next step is to treat $\xi(R_\alpha r_\alpha \gamma_\alpha | \Omega_\alpha | \Gamma_\lambda)$, and for this sake we added the NIPs so that the scattering problem is converted into a bound system problem. The $U_I(R_\alpha r_\alpha)$ is composed of two terms, namely,

$$U_I(R_\alpha r_\alpha) = -i(u_{I\nu}(r_\alpha) + u_{I\nu}(R_\alpha)) \quad (32)$$

where both are assumed to be Neuhauser–Baer linear-ramp potentials:¹⁴

$$u_{I\nu} = \begin{cases} u_{I\nu} \frac{x - x_1}{\Delta x_1}; & x_1 \leq x \leq x_1 + \Delta x_1 \\ 0; & \text{otherwise} \end{cases} \quad (33)$$

Here $u_{I\nu}$ and Δx_1 are expected to fulfill the two inequalities¹⁴

$$\frac{\hbar E_t^{1/2}}{\Delta x_1 \sqrt{8m}} \leq u_{I\nu} \leq \Delta x_1 \sqrt{8m E_t^{3/2}} / \hbar \quad (34)$$

where E_t and m are the translational energy and mass of the interacting particle with the NIP. The range $(x_1, x_1 + \Delta x_1)$ is located along a borderline of the respective AC.

The conversion of the scattering problem into a bound system problem enables the expansion of the ξ function in terms of square integrable L^2 functions.^{7,8,15} The ones we chose are localized functions along the translational coordinate R_α and basis sets related to the internal coordinates $(r_\alpha \gamma_\alpha)$.¹⁶ For this sake the translational axis is divided into N equidistant grid points (R_1, R_2, \dots, R_N) and to each grid point R_q is attached one Gaussian of the form

$$g(R|q) = \left(\frac{\alpha}{\sigma\sqrt{\pi}} \right)^2 \exp \left[-\frac{\alpha^2 (R - R_q)^2}{4\sigma^2} \right] \quad (35)$$

(here $\sigma (= R_q - R_{q-1})$ is the translational step size) and a complete set of functions $f(r_\alpha \gamma_\alpha | \Omega_\alpha | q)$ which are eigenfunctions of the equation

$$\left[-\frac{\hbar^2}{2\mu_\alpha} \frac{\partial^2}{\partial r_\alpha^2} + \bar{j}^2 \left(\frac{1}{2\mu_\alpha r_\alpha^2} + \frac{1}{2M_\alpha R_\alpha^2} \right) + U(R=R_q r_\alpha \gamma_\alpha) - \epsilon(t | \Omega_\alpha | q) \right] f(r_\alpha \gamma_\alpha | \Omega_\alpha | q) = 0 \quad (36)$$

Consequently, the ξ function is expanded in the following way:

$$\xi(R_\alpha r_\alpha \gamma_\alpha | \Omega_\alpha | \Gamma_\lambda) = \sum_{q't'} a^j(q't' | \Omega_\alpha | \Gamma_\lambda) g(R_\alpha | q') f(r_\alpha \gamma_\alpha | \Omega_\alpha | q't') \quad (37)$$

To solve the eigenvalue equation in eq 36, the $f(r_\alpha \gamma_\alpha | \Omega_\alpha | qt)$ is further expanded in terms of primitive basis sets, namely,

$$f(r_\alpha \gamma_\alpha | \Omega_\alpha | qt) = \sum_{n=1}^{\infty} \sum_{j \geq |\Omega_\alpha|} b(\Omega_\alpha | qt | jn) y(\gamma_\alpha 0 | j \Omega_\alpha) \eta(r_\alpha | n) \quad (38)$$

where $b(\Omega_\alpha | qt | jn)$ are expansion coefficients, $y(\gamma_\alpha 0 | j \Omega_\alpha)$ are the spherical harmonics, and $\eta(r_\alpha | nj)$ are normalized sine functions:¹⁷

$$\eta(r_\alpha | n) = \sqrt{2/s_r} \sin(\alpha_n r_\alpha) \quad (39)$$

Here

$$\alpha_n = \frac{n\pi}{s_r} \quad (40)$$

and s_r is the range of r_α , namely,

$$s_r = r_1 + \Delta r_1 \quad (41)$$

Substituting eq 37 into eq 26, multiplying it by $g(R_\alpha | q)$ $f(r_\alpha \gamma_\alpha | \Omega_\alpha | qt)$, and integrating over $(R_\alpha r_\alpha \gamma_\alpha)$ yields a system of algebraic equations:

$$(EQ - \mathbf{H}' + i\mathbf{B})\mathbf{a}' = \mathbf{Z}' \quad (42)$$

where \mathbf{a}' is a vector which contains the expansion coefficients given in eq 37 and \mathbf{H}' is a matrix which stands for

$$\mathbf{H}' = \mathbf{T}' + \mathbf{U} \quad (43)$$

Here the \mathbf{T}' matrix elements are

$$T^j(qt | \Omega_\alpha | q't') = \int dR_\alpha dr_\alpha d \cos \gamma_\alpha g(R_\alpha | q) f(r_\alpha \gamma_\alpha | \Omega_\alpha | qt) \times \left[\frac{\hbar^2}{2\mu_\alpha} \frac{\partial^2}{\partial r_\alpha^2} - \frac{\hbar^2}{2M_\alpha} \frac{\partial^2}{\partial R_\alpha^2} + \bar{j}^2 \left(\frac{1}{2\mu_\alpha r_\alpha^2} + \frac{1}{2M_\alpha R_\alpha^2} \right) + \frac{\hbar^2}{2M_\alpha} \frac{J(J+1) - 2\Omega_\alpha^2}{R_\alpha^2} \right] g(R_\alpha | q') f(r_\alpha \gamma_\alpha | \Omega_\alpha | q't') \quad (44)$$

and the \mathbf{U} -matrix elements are

$$U(qt | \Omega_\alpha | q't') = \int dR_\alpha dr_\alpha d \cos \gamma_\alpha g(R_\alpha | q) f(r_\alpha \gamma_\alpha | \Omega_\alpha | qt) U(R_\alpha r_\alpha \gamma_\alpha) \times g(R_\alpha | q') f(r_\alpha \gamma_\alpha | \Omega_\alpha | q't') \quad (45)$$

The \mathbf{Q} -matrix elements are

$$Q(qt | \Omega_\alpha | q't') = \int dR_\alpha dr_\alpha d \cos \gamma_\alpha g(R_\alpha | q) f(r_\alpha \gamma_\alpha | \Omega_\alpha | qt) g(R_\alpha | q') \times f(r_\alpha \gamma_\alpha | \Omega_\alpha | q't') \quad (46)$$

the \mathbf{B} -matrix elements are

$$B(qt | \Omega_\alpha | q't') = \int dR_\alpha dr_\alpha d \cos \gamma_\alpha g(R_\alpha | q) f(r_\alpha \gamma_\alpha | \Omega_\alpha | qt) [u_{1R}(R_\alpha) + u_{1r}(r_\alpha)] g(R_\alpha | q') f(r_\alpha \gamma_\alpha | \Omega_\alpha | q't') \quad (47)$$

and the \mathbf{Z}' -matrix elements are

$$Z^j(qt | \Omega_\alpha | \Gamma_\lambda) = \sqrt{2\pi} \int dR_\alpha dr_\alpha d \cos \gamma_\alpha g(R_\alpha | q) f(r_\alpha \gamma_\alpha | \Omega_\alpha | qt) \frac{R_\alpha r_\alpha}{R_\lambda r_\lambda} \times d^j_{\Omega_\alpha \Omega_\lambda}(\Delta_{\alpha\lambda}) V_\lambda(R_\lambda r_\lambda \gamma_\lambda) \phi_\lambda(r_\lambda | n_\lambda j_\lambda) y(\gamma_\lambda 0 | j_\lambda \Omega_\lambda) \zeta_\lambda(R_\lambda | \Gamma_\lambda) \quad (48)$$

This concludes the derivation of the perturbed wave function $\chi(\Lambda_\alpha R_\alpha r_\alpha \gamma_\alpha | \Gamma_\lambda)$. In addition, we make the following comments:

(a) As can be seen, the adiabatic eigenvalues (introduced in eq 18) do not explicitly appear in the final expression of the algebraic equations. However, they are used to determine, at each grid point R_q , the number of functions to be included in the expansion of $\xi(R_\alpha r_\alpha \gamma_\alpha | \Omega_\alpha | \Gamma_\lambda)$ given in eq 37. One of the input parameters is E_{cut} , an energy value that controls these numbers. The value of each of these numbers is equal to the number of eigenvalues that smaller than E_{cut} at this particular grid point.

(b) The left-hand side (lhs) of eq 42 is energy independent except for the explicit term given there (namely, EQ), and so the calculations of the elements of \mathbf{Q} , \mathbf{H}' , and \mathbf{B} have to be done only once and then can be repeatedly used for each energy.

(c) The algebraic equation in eq 42 is complex, but as is seen, the imaginary term is easily calculated and appears in the equation in a simple form.

II.1.5. Derivation of Reactive State-to-State S-Matrix Elements and Cross Sections. To derive the reactive S-matrix elements, we substitute eq 5 into eq 1 and obtain

$$S(\Gamma_\nu \leftarrow \Gamma_\lambda) = S(\Gamma_\nu | \Gamma_\lambda) = S_B(\Gamma_\nu | \Gamma_\lambda) + S_C(\Gamma_\nu | \Gamma_\lambda) \quad (49)$$

where $S_B(\Gamma_\nu | \Gamma_\lambda)$ is the Born term given in the form

$$S_B(\Gamma_\nu | \Gamma_\lambda) = \langle \psi_{\Gamma_\nu} | V_\nu | \psi_{\Gamma_\lambda} \rangle \quad (50a)$$

and $S_C(\Gamma_\nu | \Gamma_\lambda)$ is the complementary part due to the interaction potential $V_\lambda(R_\lambda r_\lambda \gamma_\lambda)$:

$$S_C(\Gamma_\nu | \Gamma_\lambda) = \langle \psi_{\Gamma_\nu} | V_\nu | \chi_{\Gamma_\lambda} \rangle \quad (50b)$$

Substituting eq 16 for both $\alpha = \lambda$ and $\lambda = \nu$ into eq 50a and employing eq 28 yields for $S_B(\Gamma_\nu | \Gamma_\lambda)$ the result

$$S_B(\Gamma_\nu | \Gamma_\lambda) = 2\pi \int \frac{R_\nu r_\nu}{R_\lambda r_\lambda} dR_\nu dr_\nu d \cos \gamma_\nu \phi_\nu(r_\nu | n_\nu j_\nu) y(\gamma_\nu 0 | j_\nu \Omega_\nu) \zeta_\nu(R_\nu | \Gamma_\nu) \times V_\nu(R_\nu r_\nu \gamma_\nu) d^j_{\Omega_\nu \Omega_\lambda}(\Delta_{\nu\lambda}) \phi_\lambda(r_\lambda | n_\lambda j_\lambda) \times y(\gamma_\lambda 0 | j_\lambda \Omega_\lambda) \zeta_\lambda(R_\lambda | \Gamma_\lambda) \quad (51)$$

As for $S_C(\Gamma_\nu | \Gamma_\lambda)$, following eqs 25 and 37, we write it in the form

$$S_C(\Gamma_\nu | \Gamma_\lambda) = \sum_{qt} S_P(\Gamma_\nu | \Gamma_\alpha | qt) a(qt | \Omega_\alpha | \Gamma_\lambda) \quad (52)$$

where $S_P(\Gamma_\nu | \Gamma_\alpha | qt)$ is

$$S_P(\Gamma_\nu | \Gamma_\alpha | qt) = \sqrt{2\pi} \int dR_\nu dr_\nu d \cos \gamma_\nu \frac{R_\nu r_\nu}{R_\alpha r_\alpha} \phi_\nu(r_\nu | n_\nu j_\nu) y(\gamma_\nu 0 | j_\nu \Omega_\nu) \times \zeta_\nu(R_\nu | \Gamma_\nu) V_\nu(R_\nu r_\nu \gamma_\nu) d^j_{\Omega_\nu \Omega_\alpha}(\Delta_{\nu\alpha}) g(R_\alpha | q) f(r_\alpha \gamma_\alpha | \Omega_\alpha | qt) \quad (53)$$

Here (as before) α might be equal either to λ or to ν , and the final results should be independent of that choice. This is the situation when the numerical treatment is carried out without approximations. However, in the case of the j_z approximation

the final results depend on α and therefore the calculations are usually carried out twice, once for $\alpha = \lambda$ and once for $\alpha = \nu$.

Once the S -matrix elements are available, the various cross sections can be calculated. These are known to be given in the following forms.

(a) The state-to-state differential cross sections:

$$\frac{d\sigma}{d\theta}(n_{j\nu} \leftarrow n_{j\lambda} | \theta) = \frac{\pi}{k^2(n_{j\lambda})(2j_\lambda + 1)} \times \sum_{|\Omega_\nu| \leq j_\nu} \sum_{|\Omega_\lambda| \leq j_\lambda} \sum_{J \geq |\Omega|} (2J+1) S'(n_{j\nu}\Omega_\nu \leftarrow n_{j\lambda}\Omega_\lambda) d'_{\Omega_\lambda\Omega_\nu}(\theta)^2 \quad (54)$$

where θ is the center-of-mass scattering angle and Ω is defined as

$$|\Omega| = \max(|\Omega_\lambda|, |\Omega_\nu|) \quad (55)$$

(b) The state-to-state integral cross sections:

$$\sigma(n_{j\nu} \leftarrow n_{j\lambda}) = \frac{\pi}{k^2(n_{j\lambda})(2j_\lambda + 1)} \sum_J (2J+1) \sum_{|\Omega_\nu| \leq j_\nu} \sum_{|\Omega_\lambda| \leq j_\lambda} \times |S'(n_{j\nu}\Omega_\nu \leftarrow n_{j\lambda}\Omega_\lambda)|^2 \quad (56)$$

where τ_α is defined as

$$\tau_\alpha = \min(j_\alpha, J); \alpha = \lambda, \nu \quad (57)$$

Here $k(n_{j\lambda})$ is given in the form

$$k(n_{j\lambda}) = \sqrt{(2M_\lambda/\hbar^2)(E - \epsilon_{n_{j\lambda}})} \quad (58)$$

where ϵ_{n_j} is an eigenvalue of eq 18.

II.2. Treatment of the Multisurface Case. To study electronic transitions taking place during molecular collisions, it is necessary to consider several PESs. In general, one can perform such a study within either the adiabatic or the diabatic framework.¹⁻³ In the present case the study is performed within the diabatic framework characterized by a potential matrix \mathbf{U} of dimension N , where N is the number of electronic states included in the numerical treatment. The total nuclear wave function $\Psi_\lambda^{(i)}$ is defined as a column vector where the component $\Psi_{\lambda j}^{(i)}$ refers to an electronic state which becomes asymptotically the j th electronic state, λ stands for the initial (reagents) AC, and i designates the initial electronic state which correlates asymptotically with the i th electronic state. The Schrodinger equation (SE) to be solved is given in the form^{1a}

$$(E\mathbf{I} - \mathbf{H}_\lambda) \Psi_\lambda^{(i)} = 0 \quad (59)$$

where E is the total energy, \mathbf{I} is the unit matrix (of dimension N), and \mathbf{H}_λ is the Hamiltonian given in the form

$$\mathbf{H}_\lambda = T_\lambda \mathbf{I} + \mathbf{U} \quad (60)$$

Here T_λ is the kinetic energy expressed in terms of the λ -AC coordinates and \mathbf{U} is the diabatic potential matrix (as described in section II.1). To solve eq 59, the perturbative approach is employed, and consequently it becomes

$$(E\mathbf{I} - \mathbf{H}_\lambda) \chi_\lambda^{(i)} \rightarrow \mathbf{V}_\lambda \psi_\lambda^{(i)} \quad (61)$$

where $\psi_\lambda^{(i)}$ is the unperturbed part of the total wave function with the components

$$\psi_{\lambda i'}^{(i)} = \delta_{i'i} \psi_{\lambda i} \quad (62)$$

$\chi_\lambda^{(i)}$ is the perturbed part of the total wave function, and

consequently is given in the form

$$\chi_\lambda^{(i)} = \Psi_\lambda^{(i)} - \psi_\lambda^{(i)} \quad (63)$$

and \mathbf{V}_λ , the perturbation matrix, is defined as

$$\mathbf{V}_\lambda = \mathbf{U} - \mathbf{W}_\lambda \quad (64)$$

Here \mathbf{W}_λ , the unperturbed matrix, is a diagonal matrix, namely,

$$W_{\lambda i'i} = \delta_{i'i} W_{\lambda i} \quad (65)$$

where $W_{\lambda i}$ is an elastic potential related to the i th electronic state in the λ -AC. The single nonzero component of $\psi_\lambda^{(i)}$, namely, $\psi_{\lambda i}$, is obtained from the equation

$$(E - H_{0\lambda}^{(i)}) \psi_{\lambda i} = 0 \quad (66)$$

where

$$H_{0\lambda}^{(i)} = T_\lambda + W_{\lambda i} \quad (67)$$

Equation 61 describes a nonreactive (no exchange) process. To make it relevant for a reactive system, a (diagonal) negative imaginary potential matrix \mathbf{U}_1 is added to the Hamiltonian to ensure the decoupling of the reactive ACs.^{7a} Thus H_λ , introduced in eq 60, will be replaced by $\mathbf{H}_{\lambda 1}$, defined as

$$\mathbf{H}_{\lambda 1} = T_\lambda \mathbf{I} + \mathbf{U} + \mathbf{U}_1 \quad (60')$$

A NIP is also used to eliminate the asymptotic region of the reagents permitting the application of L^2 basis sets to solve for $\chi_\lambda^{(i)}$.^{7b-h,15} Thus, as in the previous single-surface treatment, the λ -AC translational coordinate is divided into M sectors, and one translational localized basis function (Gaussian) and a whole set of adiabatic electrovibrational functions are attached to each sector.¹⁶ Consequently, if $\chi_{\lambda i'}^{(i)}$, designated as

$$\chi_{\lambda i'}^{(i)} = \chi^{(i)}(\Lambda_\lambda R_\lambda r_\lambda \gamma_\lambda | i' T_\lambda) \quad (68)$$

is expanded in terms of the previously mentioned $D_{M\Omega_\lambda}^J(\Lambda_\lambda)$ functions, namely,

$$\chi^{(i)}(\Lambda_\lambda R_\lambda r_\lambda \gamma_\lambda | i' T_\lambda) = \frac{1}{R_\lambda r_\lambda} \sqrt{\frac{2J+1}{8\pi^2}} \sum_{\Omega_\lambda} D_{M\Omega_\lambda}^J(\Lambda_\lambda) \xi^{(i)}(R_\lambda r_\lambda \gamma_\lambda | \Omega_\lambda | i' T_\lambda) \quad (69)$$

then $\xi^{(i)}(R_\lambda r_\lambda \gamma_\lambda | \Omega_\lambda | i' T_\lambda)$ will be presented in the form

$$\xi^{(i)}(R_\lambda r_\lambda \gamma_\lambda | \Omega_\lambda | i' T_\lambda) = \sum_{q' t'} a^{(i)}(q' t' | \Omega_\lambda | i' T_\lambda) g(R_\lambda | q') f(r_\lambda \gamma_\lambda | \Omega_\lambda | q' t' i') \quad (70)$$

Here the $a^{(i)}(q' t' | \Omega_\lambda | i' T_\lambda)$ are the expansion coefficients which will be solved once eqs 69 and 70 are submitted into eq 61, the $g(R_\lambda | q)$ are as before, the localized translational basis functions defined with respect to the q th grid point (see eq 35), and the $f(r_\lambda \gamma_\lambda | \Omega_\lambda | q' t' i')$ are the components of the f column vector which solves the following eigenvalue problem:

$$[T_\lambda \mathbf{I} + \mathbf{U}(R_\lambda = R_{\lambda q} r_\lambda \gamma_\lambda) - \epsilon(q | \Omega_\lambda | t)] f(r_\lambda \gamma_\lambda | \Omega_\lambda | q t) = 0 \quad (71)$$

Here $\epsilon(q | \Omega_\lambda | t)$ is a matrix which contains the corresponding eigenvalues. Once the eigenfunctions $f(r_\lambda \gamma_\lambda | \Omega_\lambda | q' t' i')$ are solved, they are substituted together with Gaussians into eq 70, which is then substituted in eq 61, and which, following the usual series of multiplications and integrations, becomes a set of algebraic equations for the a coefficients in eq 70. Once these are solved, we are in a position to employ the expressions for the S -matrix

elements as derived in Appendix A, namely,

$$S(\alpha i' \leftarrow \lambda i) = \exp(i\phi_{\alpha i'}) \{ \delta_{i' \alpha \lambda} + (m/\hbar^2) [\langle \psi_{\alpha i'} | V_{\alpha i'} | \Psi_{\lambda i'}^{(i)} \rangle + \sum_{k \neq i'} \langle \psi_{\alpha i'} | U_{i'k} | \Psi_{\lambda k}^{(i)} \rangle] \} \quad (72)$$

where now we distinguish between the λ (reagents)-AC and the α (which may or may not be equal to λ)-AC. Here, to shorten the notation, i and i' designate, in addition to electronic states, also vibrotational states. The phase $\phi_{\alpha i'}$ is the elastic phase shift calculated for the i' electronic state in the α -AC.

III. The Potential Energy Surface

In the present treatment two PESs and a diabatic coupling term are included. Consequently, the potential matrix \hat{U} is a 2×2 matrix with the following elements:

$$\hat{U} = \begin{pmatrix} U_1 & u_{12} \\ u_{12} & U_2 \end{pmatrix} \quad (73)$$

In what follows, \hat{U} will be written as a sum of two matrices:

$$\hat{U} = U_a + U_{so} \quad (74)$$

where U_a is of the form

$$U_a = \begin{pmatrix} u_{a1} & 0 \\ 0 & u_{a2} \end{pmatrix} \quad (75a)$$

and U_{so} is of the form¹⁰

$$U_{so} = \frac{\lambda}{3} \begin{pmatrix} 1 & -\sqrt{2} \\ -\sqrt{2} & 2 \end{pmatrix} \quad (75b)$$

Here u_{ai} ($i = 1, 2$) are essentially two adiabatic surfaces: the lower one—a reactive PES—is taken to be a London–Eyring–Polanyi–Sato (LEPS) potential parametrized by Muckerman and is designated as the M-5 potential,¹² and the upper one—a nonreactive PES—is a modified version of the valence-bond potential worked out by Blais and Truhlar.¹⁸ The coupling potential matrix U_{so} yields the spin–orbit coupling which has its origin in the atomic fluorine. The parameter λ appearing in eq 75b is equal to the spin–orbit splitting of the fluorine, namely, $\lambda = 0.0501$ eV.

In the actual calculations we employed the PES matrix U , defined as

$$U = A \hat{U} A^* \quad (76)$$

such that for $R \rightarrow \infty$ the matrix U becomes

$$\lim_{R \rightarrow \infty} U = \begin{pmatrix} \nu & 0 \\ 0 & \nu + \lambda \end{pmatrix} \quad (77)$$

where ν is the diatomic potential of H_2 . Consequently, the orthogonal transformation matrix A is the one which diagonalizes the matrix

$$\hat{U}(R \rightarrow \infty) = \begin{pmatrix} \nu + \frac{1}{3}\lambda & -\frac{\sqrt{2}}{3}\lambda \\ -\frac{\sqrt{2}}{3}\lambda & \nu + \frac{2}{3}\lambda \end{pmatrix} \quad (78)$$

(the eigenvalues are $(\nu - (1/3)\lambda)$ and $(\nu + (2/3)\lambda)$). As for U , it is similar to \hat{U} with the following elements (see eq 73):

$$\begin{aligned} U_{11} &= S^2 U_1 + C^2 U_2 + 2SC u_{12} \\ U_{22} &= S^2 U_2 + C^2 U_1 - 2SC u_{12} \end{aligned} \quad (79)$$

$$U_{12} = U_{21} = SC(U_2 - U_1) + u_{12}(S^2 - C^2)$$

TABLE 1: Electronic Nonadiabatic Transition Probabilities for $F(^2P_{3/2}) + H_2(\nu=0, j) \rightarrow F(^2P_{1/2}) + H_2(\nu'=0, j')$ As Calculated for $E_{tot} = 0.48$ eV

j'	j				
	0	1	2	3	4
0	1.66(-2) ^a	0.00	1.78(-3)	0.00	3.08(-4)
1	0.00	1.07(-2)	0.00	9.73(-4)	0.00
2	1.73(-3)	0.00	1.09(-2)	0.00	1.79(-3)
3	0.00	3.66(-4)	0.00	1.49(-2)	0.00
4	1.81(-6)	0.00	2.92(-6)	0.00	4.71(-5)

^a Numbers in parentheses refer to powers of 10. The value 1.66(-2) means 1.66%.

TABLE 2: Electronic Nonadiabatic Transition Probabilities for $F(^2P_{1/2}) + H_2(\nu' = 0, j') \rightarrow F(^2P_{3/2}) + H_2(\nu = 0, j)$ As Calculated for $E_{tot} = 0.48$ eV

j	j'				
	0	1	2	3	4
0	1.67(-2) ^a	0.00	1.73(-3)	0.00	1.79(-6)
1	0.00	1.07(-2)	0.00	3.70(-4)	0.00
2	1.79(-3)	0.00	1.09(-2)	0.00	2.91(-6)
3	0.00	9.84(-4)	0.00	1.49(-2)	0.00
4	3.09(-4)	0.00	1.80(-3)	0.00	4.71(-5)

^a Numbers in parentheses refer to powers of 10. The value 1.67(-2) means 1.67%.

where S and C (both are functions of λ and ν only) are the elements of A :

$$A = \begin{pmatrix} S & -C \\ C & S \end{pmatrix} \quad (80)$$

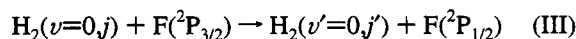
and fulfill the relation $S^2 + C^2 = 1$.

IV. Numerical Details

To carry out the calculations, the translational axis in the range 0.6–3.8 Å is divided into 46 grid points. Attached to each grid point are a Gaussian (see eq 35) and a set of electrovibrational basis functions (see eq 36). To present these basis functions, 24 sine functions defined along the range of r_λ , namely, 0.4–3.0 Å, and 26 Legendre polynomials with respect to γ_λ were used for both PESs. The number of basis functions employed in the expansion in eq 12 is controlled by a single energy value, E_{cut} , such that the expansion includes all basis eigenfunctions of eq 14 with eigenvalues lower than E_{cut} . In the present case E_{cut} was assumed to be 0.9 eV, and consequently the total number of basis functions included in the calculations (for the two surfaces) was ~2900.

To form absorbing boundary conditions, we used the Neuhauser–Baer linear ramp NIP (see eq 33). For the present study three such potentials were used: two to decouple the translational asymptotic regions of the two electronic states, namely, $F(^2P_{1/2}) + H_2$ and $F(^2P_{3/2}) + H_2$, and one along the vibrational coordinate of the lower surface to decouple the reactive $HF + H$ ACs. No vibrational NIP was assumed along the vibrational coordinate of the upper surface, as this surface is nonreactive. The calculations were done assuming $u_{oR} = 0.8$ eV, $u_{or} = 0.2$ eV, $\Delta R_1 = 0.5$ Å, and $\Delta r_1 = 1.0$ Å. This set of values was determined following an extensive parametric study.

In addition to testing the convergence of the results with respect to variations of the parameters, we performed calculations that enable checking the hermicity of the S matrix (or the symmetry of the probability matrix). In Table 1 the state-to-state transition probabilities are presented for the process



as calculated for $J = 0$ and $E_{tot} = 0.48$ eV. In Table 2 the

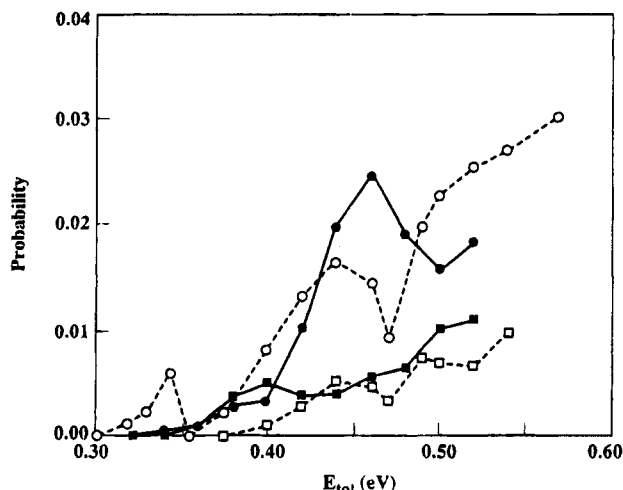
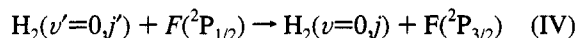


Figure 1. Electronic nonadiabatic $J = 0$ transition probabilities as a function of total energy: (O, ●) $F(^2P_{1/2}) + H_2(j=0, v=0) \rightarrow F(^2P_{3/2}) + H_2$ (inelastic process); (□, ■) $F(^2P_{1/2}) + H_2(j=0, v=0) \rightarrow HF + H$ (exchange process); (—) results due to full 3-D ($J = 0$) calculation; (---) results from a collinear treatment (ref 11).

results for the reverse reactions are presented, namely,



It is important to emphasize that these two calculations are, to a certain extent, independent and therefore serve as a check for the reliability of the numerical treatment.

V. Results and Discussion

In what follows are presented three-dimensional reactive and nonreactive transition probabilities as calculated for $J = 0$ along the energy range $0.31 \leq E_{\text{tot}} \leq 0.52$ eV. The emphasis will be on processes accompanied by electronic nonadiabatic transitions.

In Figures 1 and 2 the reactive and the inelastic transition probabilities are presented for processes IIa and IIb as a function of the total energy, where the energy is measured from the bottom of the collinear dominating surfaces (the M-5 PES is such a surface).

Presented in Figure 2 are the transition probabilities for reactions IIa and IIb for several $j \geq 0$ cases as a function of E_{tot} . The following can be said:

(a) The threshold energies for both the reactive and the inelastic transition probabilities are strongly dependent on the initial rotational state j . Moreover, not only does the threshold energy increase with j but it shifts approximately as $Bj(j+1)$, where B is the rotational constant of H_2 (~ 0.0076 eV). This may not be surprising since the energy stored in the rotations is not expected to be significant in overcoming translational potential barriers.

(b) It is noticed that the partitioning between the reactive and the nonreactive probabilities is about equal (note the different scales of Figure 2a,b). This is reminiscent of what happens in the single-surface case, where the reactive and the nonreactive probabilities are about equal.

(c) It is noticed that for each j , once the energy becomes larger than the corresponding threshold energy, both the (electronic nonadiabatic) reactive and nonreactive probability functions increase as a function of energy. However, at higher energies the reactive probability function continues to increase, whereas the nonreactive decreases. Thus, it is expected that at higher energies the reactive process will become dominant.

Electrorotational state-to-state transition probabilities for the nonreactive process given in eq IIb are presented in Figure 3 for the energy $E_{\text{tot}} = 0.50$ eV. Similar results were obtained

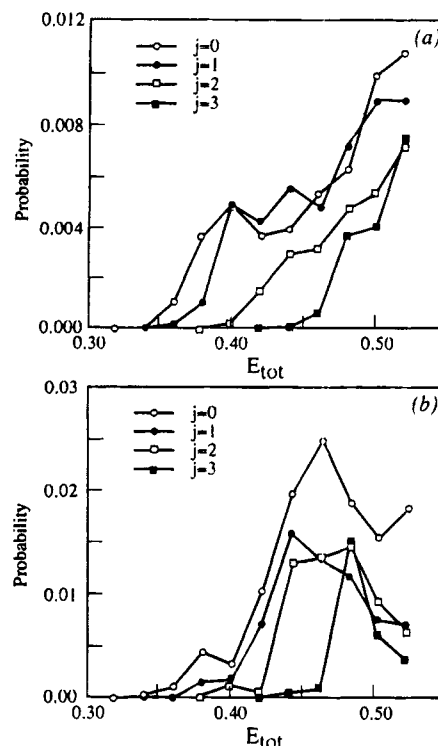


Figure 2. Electronic nonadiabatic transition probability as a function of total energy: (a) results for the reactive process $F(^2P_{1/2}) + H_2(v=0, j|J=0) \rightarrow HF(\Sigma(v'j')) + H$; (b) results for the inelastic process $F(^2P_{1/2}) + H_2(v=0, j|J=0) \rightarrow F(^2P_{3/2}) + H_2(v'=0, j'|J=0)$.

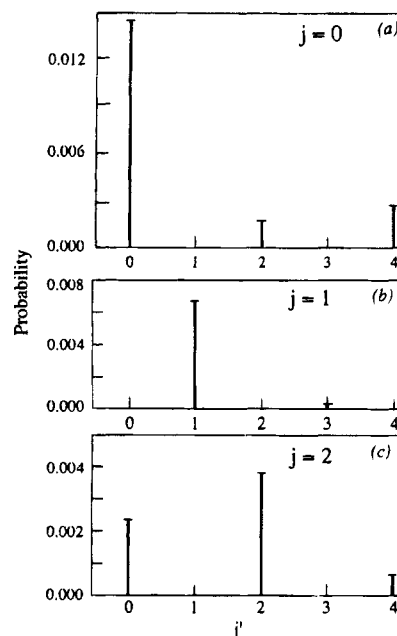


Figure 3. Stick diagram for the rotational state-to-state transition probabilities as calculated at $E_{\text{tot}} = 0.48$ eV. $F(^2P_{1/2}) + H_2(v=0, j|J=0) \rightarrow F(^2P_{3/2}) + H_2(v'=0, j'|J=0)$. Note that even \rightarrow odd transitions are not allowed.

for other energies. The results are, to a certain extent, surprising. Our accumulated experience on electronic nonadiabatic transitions tells us that resonant transitions, namely, the transitions between states (belonging to different electronic states) with the smallest energy gap, are those with the highest probability. In the case of $j = 0$, the transition ($j = 0 \rightarrow j' = 2$) is the one with the smallest energy gap (see Figure 4), but as can be seen from Figure 3, the largest probability is obtained for the ($j = 0 \rightarrow j' = 0$) transition. In all other cases the situation is not so clear mainly because the (odd \rightarrow even) and (even \rightarrow odd)

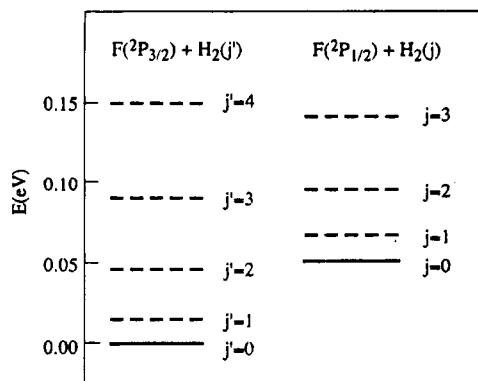


Figure 4. Asymptotic rotational states for the two electronic spin states of the F atom (the difference $E(1/2) - E(3/2)$ is 0.0501 eV).

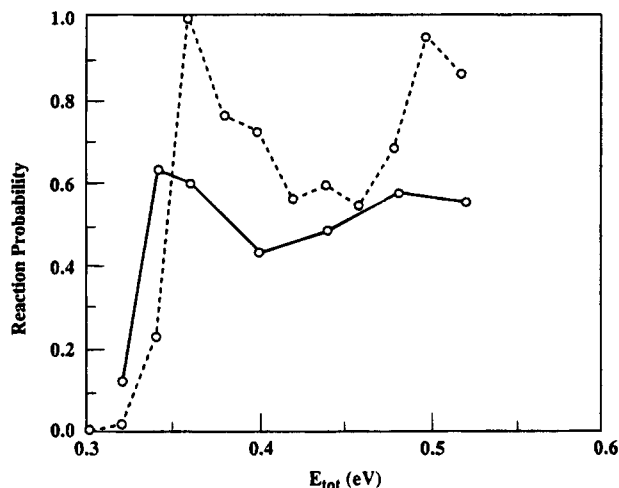
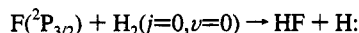


Figure 5. Reactive $J = 0$ transition probabilities for the process



(---) a two-surface calculation; (—) a single-surface calculation (ref 8).

transitions are not allowed. At least part of the explanation for this behavior lies in the PES employed in the calculation. In the matrix \mathbf{U} of eq 23, the term responsible for the nonadiabatic transitions is the off-diagonal term, and if that term is not dependent (or only weakly dependent) on γ_λ ($=\cos^{-1}(\hat{\mathbf{R}}_\lambda \cdot \hat{\mathbf{r}}_\lambda)$), then electronic transitions, accompanied by rotational transitions, are not likely to occur. As can be seen from the third equation of eq 23, the off-diagonal term is made up of two expressions: one ($=u_{12}(S^2 - C^2)$) is not dependent on γ_λ because S , C , and u_{12} , by definition, are not dependent on γ_λ , and the second term ($=SC(U_2 - U_1)$) is only weakly dependent on γ_λ . This follows from the fact that, for intermediate R_λ values, the two surfaces U_2 and U_1 become similar and consequently, as R_λ increases, the difference ($U_2 - U_1$) rapidly approaches a constant not dependent on γ_λ . Since the dependence on γ_λ is weak, collisions in which rotational transitions occur are not likely, and therefore the effect of the energy gap becomes secondary. It is important to mention that in other studies of the (the nonreactive) $\text{F}(^2\text{P}_{1/2}, ^2\text{P}_{3/2}) + \text{H}_2$ system^{5b,c} in which a strong anisotropic diabatic coupling term was employed, not only were large electronic nonadiabatic probabilities (>30%) obtained but pronounced resonant transitions were also found to exist.

Finally we would like to refer to reaction I. Figure 5 shows reactive transition probabilities calculated in two ways: one employing only a single surface⁸ and the other including two coupled surfaces. In general the two probability curves are similar: the thresholds for the reaction are close, and at higher

energies the shape of the curves is similar. Nevertheless, the two treatments yield results different enough so that if they persist for higher J values, they will be noticeable in scattering experiments, particularly in those experiments where detailed magnitudes, such as differential cross sections, are measured. The fact that the weak spin-orbit coupling has a significant effect on $J = 0$ reaction probabilities should seriously be taken into account, in particular when quantum mechanical results are compared with spectroscopic measurements. Recently, such comparisons were carried out¹⁹ regarding photodetaching an electron from FH_2^- , where the quantum mechanical calculations were based on a single PES. Encouraging agreements were obtained. The question that always will be asked is whether including electronic nonadiabatic interactions such as the spin-orbit coupling will affect the calculated outcomes and therefore spoil a nice agreement. The present study indicates that this possibility cannot be ignored.

VI. Conclusions

In this study we applied the NIP approach to treat reactive (exchange) processes which take place via electronic nonadiabatic transitions. For this purpose we extended the theory, originally devised for a single-surface case, to a multisurface system. In essence, particular nontrivial parts were added for the calculations of the relevant S -matrix elements.

The approach was applied to the two-surface $\text{F} + \text{H}_2$ system, and calculations were done for the $J = 0$ case. The main findings are as follows:

(a) Due to the weak spin-orbit coupling the electronic nonadiabatic transition probabilities are small: not more than a few percent.

(b) As for the partitioning between the inelastic and the reactive probabilities, the following can be said: (1) around the threshold region the two types of probabilities are similar, but (2) as the energy increases, the reactive process starts to dominate at the expense of the inelastic transitions. Consequently, the probabilities for these processes decrease.

(c) Due to the weak anisotropy of the electronic diabatic coupling term, resonant transitions are of negligible importance.

(d) Although weak, the spin-orbit coupling has a non-negligible effect on the reaction (exchange) process taking place on the lower surface.

The results derived so far cannot be directly compared with scattering experiments. We intend to apply our approach to a system with a more relevant potential matrix and calculate integral and differential cross sections that can be compared with experiment.

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Appendix A

Derivation of the Electronic Nonadiabatic S-Matrix Element. To carry out this derivation, we consider a single-coordinate system which extends from 0 to $+\infty$. The relevant

set of Schrodinger equations is

$$(T + U_{jj} - E)\chi_j^{(i)} + \sum_{j \neq k} U_{jk}\chi_j^{(i)} = -[V_i\delta_{ij} + U_{ij}(1 - \delta_{ij})]\psi_i \quad (1A)$$

Here i stands for the initial electronic state and j and k designate other electronic states; ψ_i is the unperturbed wave function which solves the equation

$$(T + W_i - E)\psi_i = 0 \quad (2A)$$

where W_i is an unperturbed potential which fulfills the condition

$$\lim_{R \rightarrow \infty} W_i = w_i = \text{const} \quad (3A)$$

U_{jj} is a diabatic electronic state which correlates with the j th electronic asymptotic state, U_{jk} is a diabatic (potential) coupling term, V_i is the perturbed i th potential defined as

$$V_i = U_{ii} - W_i \quad (4A)$$

and δ_{ij} is the Kronecker delta function.

The function $\chi_j^{(i)}$ is the perturbed part of the j th component of the total wave function $\Psi^{(i)}$ defined as

$$\Psi_j^{(i)} = \begin{cases} \psi_i + \chi_i^{(i)}, & j=i \\ \chi_j^{(i)}, & j \neq i \end{cases} \quad (5A)$$

The asymptotic representation of $\Psi_j^{(i)}(R)$ is given in the form

$$\lim_{R \rightarrow \infty} \Psi_j^{(i)} = \sqrt{1/k_j} [\delta_{ij} \exp(-ik_j R) + S_{ij} \exp(ik_j R)] \quad (6A)$$

where k_j is

$$k_j = \sqrt{2m(E - w_j)/\hbar^2} \quad (7A)$$

and the aim is to obtain S_{ij} once eq 1A is solved for $\chi_j^{(i)}$. The usual procedure is to analyze the asymptotic region, namely, match the $\Psi_j^{(i)}$ function with a given asymptotic representation (see eq 6A) and extract the S_{ij} elements. However when the asymptotic representation of $\Psi_j^{(i)}$ (or $\chi_j^{(i)}$) is not known, as for instance when absorbing boundary conditions are applied, an algebraic procedure must be developed to calculate S_{ij} . For this purpose we consider two equations, namely, eq 1A and an equation similar to eq 2A, but for the j th case. Thus

$$(T + U_{jj} - E)\chi_j^{(i)} + \sum_{k \neq j} U_{jk}\chi_k^{(i)} = -U_{ij}\psi_i \quad (8A)$$

and

$$(T + W_j - E)\Psi_j = 0 \quad (9A)$$

where the asymptotic form of ψ_j is assumed to be

$$\lim_{R \rightarrow \infty} \psi_j = 2i/\sqrt{k_j} \sin(k_j R + (\varphi_j/2)) \exp(i(\varphi_j/2)) \quad (10A)$$

Here φ_j is the elastic phase shift.

Taking the complex conjugate of eq 9A, multiplying it by $\chi_j^{(i)}(R)$, and subtracting from it eq 8A multiplied by $\psi_j^*(R)$, one obtains

$$\chi_j^{(i)} T \psi_j^* - \psi_j^* T \chi_j^{(i)} = [\Psi_j^* V_j \chi_j^{(i)} + \psi_j^* \sum_{k \neq j} U_{jk} \chi_k^{(i)} + \Psi_j^* U_{ij} \psi_i] \quad (11A)$$

where V_j is defined similarly to V_i (see eq 4A). Recalling that

T is of the form

$$T = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} \quad (12A)$$

eq 12A is substituted into eq 11A, and the resulting equation is integrated from 0 to infinity. Continuing in the ordinary way, it can be shown that S_{ij} becomes

$$S_{ij} = \frac{m}{\hbar^2} i \exp(i\varphi_j) [\langle \psi_j | V_j | \chi_j^{(i)} \rangle + \langle \Psi_j | U_{ij} | \psi_i \rangle + \sum_{k \neq j} \langle \psi_j | U_{jk} | \chi_k^{(i)} \rangle] \quad (13A)$$

where we recall that $j \neq i$.

In the same way one obtains the expression for the elastic case, namely,

$$S_{ii} = \exp(i\varphi_i) \left\{ 1 + \frac{m}{i\hbar^2} [\langle \psi_i | V_i | (\chi_i^{(i)} + \psi_i) \rangle + \sum_{k \neq i} \langle \psi_i | U_{ik} | \chi_k^{(i)} \rangle] \right\} \quad (13A')$$

Equations 13A and 13A' can be written in terms of one expression in the form

$$S_{ij} = \exp(i\varphi_j) \left\{ \delta_{ij} + \frac{m}{i\hbar^2} [\langle \psi_j | V_j | \Psi_j^{(i)} \rangle + \sum_{k \neq j} \langle \psi_j | U_{jk} | \Psi_k^{(i)} \rangle] \right\} \quad (14A)$$

for every i and j . In case of two states, this expression, for $i = 1$ and $j = 2$, becomes

$$S_{12} = -\frac{m}{\hbar^2} i \exp(i\varphi_2) [\langle \psi_2 | V_2 | \Psi_2^{(1)} \rangle + \langle \psi_2 | U_{21} | \Psi_1^{(1)} \rangle] \quad (15A)$$

and for $i = j = 1$ it becomes

$$S_{11} = \exp(i\varphi_1) \left\{ 1 - \frac{m}{\hbar^2} i [\langle \psi_1 | V_1 | \Psi_1^{(1)} \rangle + \langle \psi_2 | U_{12} | \Psi_2^{(1)} \rangle] \right\} \quad (16A)$$

where $\psi_j^{(1)}$ ($j = 1, 2$) are defined in eq 5A.

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