Semiclassical Study of Collision-Induced Predissociation: Comparison of the Landau-Zener Model with the Method of Analytic Continuation

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Semiclassical calculations are carried out by two methods for the problem of collision-induced predissociation of electronically excited I_2. The first method is that of surface-hopping with the Landau–Zener model. The second method is similar to surface-hopping, except that analytic continuation of the adiabatic potential energy surfaces replaces the Landau–Zener model. Results of the calculations by the two methods compare favorably with each other and with experiment. The possible advantages of the second method are discussed.

Key words: Collision-induced predissociation – Landau–Zener model – Analytic continuation

1. Introduction

There is increasing theoretical interest in treating atom–diatom and ion–diatom collision processes which involve the coupling of two or more potential energy surfaces [1]. Although a fully quantum mechanical calculation is the most rigorous approach [2, 3], semiclassical calculations can often yield accurate results [4, 5]. The semiclassical approach is more appealing than the quantum approach in two ways: 1) it is generally

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easier to apply, and 2) it presents a simpler and clearer picture of the collision dynamics and hence lends more physical insight into the mechanism of switching surfaces. The main feature of the semiclassical approach is the assumption that nuclear degrees of freedom behave classically[1]. With a quantum description for the electronic degrees of freedom, the nuclei then follow classical trajectories on potential energy surfaces. While popular semiclassical theories all follow this procedure, they tend to differ with respect to the manner in which a trajectory makes a transition between surfaces.

In this paper we shall report on a comparative study of two such theories, one by Tully and Preston [6] and the other by Miller and George [7]. Tully and Preston define their theory to be a phenomenological extension of the standard (single surface) classical trajectory approach to a treatment of molecular collisions involving electronically non-adiabatic interactions. Within their approach a trajectory makes an electronic transition by "hopping" discontinuously from one surface to another. The theory of Miller and George, derived more rigorously, is somewhat more difficult to implement since it involves the integration of full complex-valued trajectories [8] on surfaces analytically continued to their complex intersection points, whereby trajectories switch surfaces smoothly at these points. Recently, a simplification to this theory has been introduced [4, 9], which no longer requires the integration of complex-valued trajectories, but rather real-valued trajectories which switch surfaces discontinuously as in the theory of Tully and Preston. However, the switching amplitude is still calculated by means of analytic continuation of surfaces to complex intersection points, in the spirit of Stueckelberg's approach [10]. On the other hand, this amplitude (or probability) is calculated by Tully and Preston using quantities defined on the real axis alone, such as by the Landau–Zener [11, 12].

The format of the paper is the following. In Sect. 2 we outline the surface-hopping method of Tully and Preston. In Sect. 3 we outline the approach of Miller and George, both in its original form and in its more recent simplified form. In Sect. 4 we compare calculations and results, for the approaches presented in Sects. 2 and 3, on a two-surface model for collision-induced predissociation of electronically excited I_2. Sect. 5 is the Conclusion.

2. Surface-Hopping Method and Landau–Zener Model

The surface-hopping model was introduced by Tully and Preston [6] as a means of using classical trajectories to describe molecular collision dynamics involving the coupling of two surfaces. We consider two electronically adiabatic surfaces of an atom–diatom system which exhibit an avoided crossing in some region of nuclear configuration space. Labelling these surfaces as 1 and 2, we then consider a collision process involving a transition from 1 to 2. We begin the integration of a classical trajectory on surface 1 and propagate up to the avoided crossing, where the trajectory splits into two branch trajectories. The "upper" branch proceeds on surface 2 while the "lower" branch proceeds on surface 1. The upper branch is created by a local electronic transition, wherein the

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[1] Sometimes it is more appropriate to treat only certain nuclear degrees of freedom classically, while the rest are handled quantum mechanically. See Ref. [4].

nuclear coordinates are continuous. However, there is a discontinuity in nuclear kinetic energy equal to the energy difference between the surfaces at the transition point. Since there are two or more nuclear degrees of freedom, there is no unique way to redistribute this energy difference among the various components of nuclear momentum on surface 2. However, Tully and Preston followed a reasonable (and perhaps best) procedure whereby this energy difference went entirely into the component of nuclear velocity which is perpendicular to the avoided crossing seam, which we call $v_\perp$.

In order to conserve total probability at the transition point, the upper branch trajectory is weighted by a probability factor p while the lower branch proceeds with a probability $1 - p$. The factor p can be calculated in various ways, although in most applications it has been determined by the Landau–Zener model (as used in the calculation discussed in Sect. 4) and is given as

$$p = \exp\left(-2\pi A^2/\hbar B v_\perp\right) \tag{1}$$

where A and B are parameters which we shall assign in Sect. 4. A given branch can split into other branches as it encounters the avoided crossing seam, so that an overall weight factor for a trajectory with a specific "branching pattern" will be a product of factors, e.g., $p_1 p_2(1 - p_3)$ . . ., where the subscript labels the particular transition point. The overall weight factors are then incorporated into a Monte Carlo averaging procedure for the initial boundary conditions of the trajectories.

3. Method of Analytic Continuation

Continuing with the atom-diatom (A + BC) collision involving an electronic transition between adiabatic surfaces 1 and 2 with an avoided crossing, we shall summarize the results of the Miller–George theory in its original form [7, 13–16]. For simplicity in the rest of this paragraph we restrict ourselves to collinear collisions, although the discussion for three-dimensional collisions is straightforward. The quantity of interest is the S-matrix element S_{fi}, which is a transition amplitude connecting initial state i (initial vibrational state of BC on surface 1) to final state f (final vibrational state of either BC, AB or AC on surface 2, depending on the particular process under consideration). This element is expressed as (for a given collision energy)

$$S_{fi} = \Sigma P^{1/2}[2\pi\hbar(\partial n_2/\partial q_1)_{n_1}]^{-1/2} \exp\left(i\,\mathrm{Re}\,\Phi/\hbar\right). \tag{2}$$

The initial boundary conditions depend on the quantities n_1 and q_1, where n_1 is the integer value of an action variable n and corresponds to the initial vibrational state, and q_1 is the initial value (between 0 and 2π) of the angle q conjugate to n. The final boundary conditions are similarly specified in terms of n_2 and q_2. Re Φ is the real part of the complex classical action Φ, which is calculated along the trajectory propagating from n_1, q_1 to n_2, q_2 and is expressed as

$$\Phi = -\int_{-\infty}^{\infty} dt[R(t)\dot{p}_R(t) + q(t)\dot{n}(t)], \tag{3}$$

where R is the distance from the center of mass of BC to A and $\dot{p}_R$ is the time derivative of the momentum conjugate to R. P is the probability factor of the sample form

$P = p_1 p_2 (1 - p_3) \ldots$, where p_i is the local switching probability in analogy to that of Tully and Preston. The summation is taken over all trajectories (including all branching patterns [8, 13], which propagate from n_1 to n_2, where each trajectory corresponds to a different value of q_1 (and likewise a different value of q_2).

The integral of Eq. (3) is carried out in the complex time plane, where the variables in the integrand follow a complex-valued classical trajectory. The trajectory propagates on surface 1 analytically continued off the real axis to actual intersection points with surface 2 (also analytically continued). A transition then occurs smoothly at an intersection point so that nuclear momenta as well as nuclear coordinates are continuous through the transition point. In practice the trajectory need not pass through the intersection point itself, but must simply go "over" the point. The reason for this is that each surface corresponds to a particular branch of a square root function, so that an intersection point is equivalent to a branch point and going "over" the point is tantamount to crossing a branch cut [17–19].

The theoretical advantage which this theory offers over the approach of Tully and Preston is that the problem of a discontinuity in a trajectory at a transition point is eliminated. However, this is a numerical disadvantage of this theory in that it requires the integration of full complex-valued classical trajectories. While we have demonstrated the feasibility of such a task (for both collinear and three-dimensional $H^+ + D_2 \rightarrow HD^+ + D$ involving two surfaces) [8], it is certainly more difficult than the integration of real-valued trajectories. To circumvent this difficulty we have introduced a modification to the original theory whereby we combine the integration of real-valued trajectories with the local analytic continuation of surfaces [5]. In so doing we weaken the original theory since our real-valued trajectories now experience discontinuities at transition points (i.e., the real parts of the branch points). However, we shall retain the feature of analytic continuation since the local switching probabilities will require the analytic continuation of surfaces and not the quantum coupling.

In describing our modification we should point out that it is applicable to the general multi-surface problem. The interaction among three (or more) surfaces can be broken down into a sum of local interactions between two surfaces[2] [15, 17]. Although we have not derived a general proof of this, our intuition and experience have convinced us that within the adiabatic representation there is usually a particular direction in nuclear coordinate space along which localized interactions occur between pairs of surfaces. This is not necessarily true in a diabatic representation, which is a fundamental reason for our choice of the adiabatic representation in the semiclassical theory.

In a given region where two adiabatic surfaces (which we call W_1 and W_2) interact, our modification begins by representing the potential interaction as the effective surface $W(X)$,

$$W(X) = W_1(X)h[f(X)] + W_2(X)h[-f(X)], \tag{4}$$

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[2] In the event that such pairwise interactions overlap, we must introduce appropriate uniformization procedures as discussed in Ref. [13].

where $f(X)$ is some function of nuclear coordinates X which is positive (negative) for points on the "W_1" ("W_2") side of the "surface" defined by $f(X) = 0$ and $h[f]$ is the usual Heaviside step function, i.e., $h[f] = 1$ for $f > 0$ and $h[f] = 0$ for $f < 0$. The "surface" defined by $f(X) = 0$ is traced out by the *real* parts of the intersection points (branch points) connecting W_1 and W_2. We emphasize here that the nuclear coordinates X are real in our discussion (provided we have already analytically continued the surfaces locally to branch points to find the real "surface" defined by $f(X) = 0$).

Having defined a local effective surface $W(X)$, we then integrate a real-valued classical trajectory on W_1 up to where $f(X) = 0$, at which point is switches surfaces to W_2. The prescription for switching surfaces is as follows. By mapping out the real parts of the branch points, we find the direction along which they are localized. This is approximately perpendicular to the seam of the avoided crossing. (For situations where there is no avoided crossing, there is no seam. However, we can still map out the real parts of branch points, so that this procedure does not require an avoided crossing [5].) If this direction is along the coordinate $X^{(1)}$, then $f(X) = 0$ is equivalent to

$$X^{(1)} = \operatorname{Re} X_*^{(1)}[X^{(2)}, X^{(3)}, \ldots, X^{(N)}] \tag{5}$$

where N is the number of nuclear degrees of freedom ($N = 2$ for collinear A + BC collisions). Depending on the coordinate system under consideration, $X^{(1)}$ might be some linear combination of coordinates rather than a particular single coordinate. $X_*^{(1)}[X^{(2)}, X^{(3)}, \ldots, X^{(N)}]$ is the locus of complex intersection points along the complex $X^{(1)}$-axis as a function of all the remaining nuclear degrees of freedom.

When a trajectory reaches the "surface" defined by Eq. (5), we freeze the variables $X^{(2)}, X^{(3)}, \ldots, X^{(N)}$ and their conjugate momenta. We then perform a one-dimensional phase integral of the Stueckelberg-like form [10]

$$\alpha = \int_{\operatorname{Re} X_*^{(1)}}^{X_*^{(1)}} dX^{(1)} k_1 + \int_{X_*^{(1)}}^{\operatorname{Re} X_*^{(1)}} dX^{(1)} k_2 \tag{6}$$

where k_i is the momentum conjugate to $X^{(1)}$. For example, if $X^{(1)}$ is the radial translational coordinate, then k_i is given as

$$k_i = \{2\mu[E - W_i - \epsilon]\}^{1/2} \tag{7}$$

where μ is the reduced mass of A and BC, E is the total energy and ϵ is the internal nuclear energy of BC at the "surface" defined by Eq. (5). For the branch of the trajectory which continues on surface 2 we attach the local amplitude $p^{1/2}$, where

$$p = \exp(-2\operatorname{Im}\alpha), \tag{8}$$

and for the branch which continues on surface 1 we attach the amplitude $(1 - p)^{1/2}$. The phase integral of Eq. (6) is calculated along a one-dimensional trajectory in the imaginary $X^{(1)}$-direction on surface 1 up to the branch point and then back to the real axis on surface 2. This one-dimensional trajectory in the complex plane is the solution of just two coupled equations and hence is decoupled from the real-valued trajectory which is the solution of $2N$ coupled equations. However, all coordinates and momenta are continuous along both trajectories taken together, where the coordi-

nates return to their same values at the end of the one-dimensional trajectory as they were at the beginning, and the momentum conjugate to $X^{(1)}$ absorbs the change in electronic energy while the other momenta remain unchanged. The real-valued trajectory alone experiences a discontinuity along the branch which continues on surface 2. It is important to realize that the numerical integrator for the $2N$ coupled Hamilton's equations of motion involves only real variables: the one-dimensional phase integral in the complex plane is simply added as a separate "subroutine". When a given branch of the trajectory encounters again the surface defined by Eq. (5), we repeat the switching procedure.

With this modified theory we can calculate S-matrix elements through Eq. (2) by using real-valued trajectories. The imaginary part of the total action Φ is accumulated in an additive fashion from each local contribution, i.e., $\text{Im}\,\Phi = \Sigma\,\text{Im}\,\alpha$ where the sum is over all points on the surface defined by Eq. (5) at which a trajectory makes a transition between surfaces. Since we are no longer integrating full complex-valued trajectories, we could alternatively carry out a Monte Carlo calculation in the same fashion as Tully and Preston [6]. Although this does not yield rigorous state-selected transition amplitudes as through Eq. (2), it does avoid the need for finding "root" trajectories which propagate from an initial to a final state [7, 8]. In the next section we shall compare results on a model for collision-induced predissociation from Monte Carlo calculations using our modified semiclassical theory and the Landau–Zener model as suggested by Tully and Preston.

4. Calculations and Results

Calculations were based on a model for collision induced predissociation of electronically excited I_2 for collinear collisions, which was previously studied by Garetz, Rubinson and Steinfeld [20] using the surface-hopping method and Landau–Zener model. The collision system involves I_2 in the excited electronic state $B\,^3\Pi_{0_u^+}$ in the presence of rare-gas atoms. The observed quenching process [21] is assumed to occur due to the interaction of this excited state with other states and in particular with the 0_g^+ repulsive state which correlates to two ground-state iodine atoms, $I(^2P_{3/2}) + I(^2P_{3/2})$. This process is

$$I_2(B\,^3\Pi_{0_u^+}, v) + \text{rare-gas} \rightarrow 2I(^2P_{3/2}) + \text{rare-gas} \tag{8}$$
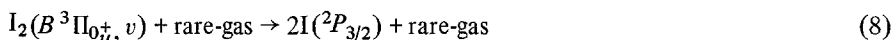
which can be viewed in terms of transitions between two adiabatic surfaces to be discussed shortly. While this process involves an overall electronic transition, the process

$$I_2(B\,^3\Pi_{0_u^+}, v) + \text{rare-gas} \rightarrow I_2(B\,^3\Pi_{0_u^+}, v') + \text{rare-gas} \tag{9}$$
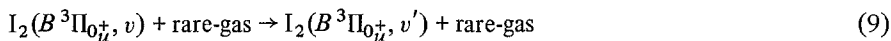
does not involve an overall electronic transition, although it can also be viewed in terms of local transitions between two adiabatic surfaces. The potential energy curves corresponding $B\,^3\Pi_{0_u^+}, 0_g^+$ states are given by $V_1(r)$, $V_2(r)$, respectively [20, 22],

$$V_1(r) = D_e\{1 - \exp\,[-\beta(r - r_e)]\}^2 \tag{10}$$

$$V_2(r) = 6.5761 \times 10^{-6}/r^9 - 0.34361 \quad \text{(eV)} \tag{11}$$

where r is the I–I intermolecular separation (in a.u.), $D_e = 0.5444$ eV, $r_e = 5.7284$ a.u. and $\beta = 0.969878$ a.u.$^{-1}$ (1 a.u. $= 0.59172 \times 10^{-8}$ cm). These two diabatic potentials cross at $r = 6.2752$ a.u. The rare-gas collision partner, however, destroys the inversion symmetry, resulting in two electronic states of the same symmetry which then interact. The presence of the rare-gas atom is taken into account through the coupling term

$$V_{12}(R) = CR^{-6}, \tag{12}$$

where R is the distance from the center of mass of I_2 to the rare-gas atom and C is a constant given in terms of quantities such as the ionization potentials of excited I_2 and the rare-gas atom, etc., as presented in Ref. [20]. We shall return to this constant shortly.

The two adiabatic surfaces W_1 and W_2, obtained as solutions of a 2 x 2 secular determinant, are expressed as

$$W_1(r, R) = \tfrac{1}{2}[V_1(r) + V_2(r)] - \tfrac{1}{2}\{[V_1(r) - V_2(r)]^2 + 4V_{12}^2(R)\}^{1/2} \tag{13}$$

$$W_2(r, R) = \tfrac{1}{2}[V_1(r) + V_2(r)] + \tfrac{1}{2}\{[V_1(r) - V_2(r)]^2 + 4V_{12}^2(R)\}^{1/2} \tag{14}$$

Each surface corresponds to a branch of the square root function $\{\ \}^{1/2}$, and the intersection points (branch points) correspond to the roots of the equation

$$(V_1 - V_2)^2 + 4V_{12}^2 = 0. \tag{15}$$

A map of these roots reveals that the real parts of the branch points tend to be most localized along the r-axis, so that the "surface", or more appropriately the "line", corresponding to Eq. (5) is

$$r = \mathrm{Re}\, r_*(R). \tag{16}$$

In Table 1 we list the values of $\mathrm{Re}\, r_*$ and $\mathrm{Im}\, r_*$ for values of R ranging from 20.0 a.u. to 6.0 a.u., where we see that $\mathrm{Re}\, r_*$ is localized around 6.2 a.u. It begins to deviate from 6.2 a.u. for values of R less than 8.0 a.u.; but for these values of R, the branch point moves far enough in the imaginary direction (e.g., $0.7691i$ for $R = 7.0$ a.u.), in which case $\mathrm{Im}\,A$ in Eq. (8) is large so that transitions at these branch points are insignificant. We should point out that the values of $\mathrm{Re}\, r_*$ and $\mathrm{Im}\, r_*$ are weakly dependent on the imaginary part of R; i.e., Table 1 shows values for $\mathrm{Im}\,R = 0$, but similar values are found for, say $\mathrm{Im}\,R = 0.1i, 0.2_i$, etc.

Integrating trajectories on the surfaces given by Eqs. (13) and (14) and switching at the line of Eq. (16) via analytic continuation in the manner discussed in Sect. 4, we have carried out Monte Carlo calculations for the collision systems I_2 + He, I_2 + Ar and I_2 + Xe. Following the procedure of Ref. [20], we expressed C in Eq. (12) as

$$C = -\tfrac{3}{2}FI_PI_Q(I_P + I_Q)^{-1}\alpha_Q\alpha_P^0 \tag{17}$$

where I_P and I_Q are the ionization potentials of excited I_2 and the rare-gas atom, respectively, α_Q is the ground-state polarizability of the quencher and α_P^0 is the ground-state polarizability of I_2. With C written in the above manner, F is a unitless quantity which is equal to the product of the Franck–Condon factor and the excited state polarizability of I_2 divided by α_P^0. Since neither the Franck–Condon factor nor the

R	Re r_*	Im r_*
20.0	6.2752	0.0018
19.0	6.2752	0.0024
18.0	6.2752	0.0033
17.0	6.2752	0.0047
16.0	6.2752	0.0068
15.0	6.2751	0.0100
14.0	6.2751	0.0151
13.0	6.2749	0.0235
12.0	6.2745	0.0380
11.0	6.2731	0.0639
10.0	6.2687	0.1129
9.0	6.2527	0.2103
8.0	6.1884	0.4086
7.0	5.9402	0.7691
6.0	5.2487	1.1161

Table 1. The complex line of intersection, $r_*(R)$, between the two adiabatic surfaces for the I_2 + Ar system

excited state polarizability is known experimentally, F was treated as a single parameter to be fitted to experimental data. We performed a few initial test runs with I_2 ($v = 25$) + Ar to determine the best value of this parameter, which was found to be 6.5. We then carried out calculations for I_2 ($v = 43$) + He, Ar, Xe where the initial vibrational momentum was "quantized" at $v = 43$. The vibrational phase was chosen randomly, and the collision energy was chosen in a Monte Carlo fashion to fit a Boltzmann distribution corresponding to the experimental temperature. The resulting quenching probabilities are shown in Table 2 along with the experimental results. Quenching probabilities are also shown from Ref. [20], where the surface-hopping model was used with the Landau–Zener model via Eq. (1); $A = V_{12}$ and $B = |dV_1/dr - dV_2/dr|$, where A and B were both evaluated at the avoided crossing. We should point out that the value of F was different for the calculations carried out with the Landau–Zener method, namely 1.0 (since the ground-state polarizability of I_2 is 13.7 Å^3, this corresponds to a value of 13.7 Å^3 for the product of the Franck–Condon factor and the excited state polarizability, which was incorrectly reported to be 137 Å^3 in Ref. [20]). In other words, the determination of this parameter was taken to be part of the method. This provides a more global, physical comparison between the method of analytic continuation and the Landau–Zener method than if the same parameter were used in both sets of calculations. However, it would be interesting in the future to see a comparison between the two methods for a given collision system using the same potential matrix.

5. Conclusion

From the reasonable agreement among the three sets of results in Table 2, it appears that the method of analytic continuation provides an accurate as well as interesting means for calculating electronic transition probabilities in atom–diatom systems. Since the amount of labor involved in implementing this method is comparable to that for

Table 2. Quenching probability

System	Semiclassical Decoupling Calculation (Present Work)	Surface-Hopping Calculation (Ref. [20])	Experimental	Number of Trajectories (Present Work)
I_2 ($v = 43$) + He	0.032	0.026	0.027	100
I_2 ($v = 43$) + Ar	0.20	0.16	0.15	100
I_2 ($v = 43$) + Xe	0.30	0.27	0.45	50

the surface-hopping method with the Landau–Zener model, we should iterate the possible advantages of the method of analytic continuation. First of all, it does not require any knowledge of the coupling between surfaces, but simply their analytic continuation up to a complex intersection. For the model presented in the previous section, this is probably not an advantage, since we know the electronic Hamiltonian matrix. However, there might be situations where we have available only the two adiabatic surfaces themselves, say, from *ab initio* calculations, and do not have the matrix or non-adiabatic coupling. Secondly, the switching conditions from the method of analytic continuation depend on the real parts of the intersection points, and hence situations in which there are no avoided crossings are treated in precisely the same fashion as for avoided crossings. An example of this is in the $F + H_2 \rightarrow FH + H$ reaction [1, 23, 24], where the surfaces exhibit an exponential splitting. Although there is no avoided crossing, there is still a complex "surface" of intersection whose real part is localized along the $F + H_2$ translational coordinate.

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