Expansion Approach to Photodissociation Dynamics. I. Theory

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I. INTRODUCTION

Formal theories of photodissociation dynamics have shown that the amplitude of the partial linewidths can be rigorously separated into a product of a Franck-Condon overlap term and a scattering term. The Franck-Condon overlap term represents the photon impact transition from an initial vibronic state to intermediate (electronically excited) states. The scattering term describes the interaction between the receding fragments on the repulsive surface. The latter interaction is sometimes referred to as the final state interaction. Band and Freed have pointed out that the difference between the normal coordinates of the ground and excited states should be critical in the Franck-Condon overlap term.

In the actual representation of the formally factorized expression of the linewidth amplitude, zeroth order scattering wave functions are used. These functions are obtained as the solutions of uncoupled scattering Schrödinger equations. As a result, the coupling among the channels is not taken into account in the scattering wave functions themselves. Instead, the interchannel coupling is recovered by perturbation-theory-like methods, which is the case of off-the-energy-shell contributions if the exact solution is desired.

A natural approximation for dealing with the above problem is the "half-collision" approximation of Jortner et al. In this approach, only on-the-shell contributions of the expansion are extracted from the formally exact solution. The scattering term is described as \( I - i\alpha T \), where \( T \) is the on-the-shell transition matrix represented by the uncoupled wave functions. Using this compact, closed form, both the scattering term and the Franck-Condon terms can be estimated conveniently.

Beswick et al. and Atabek and Lefebvre have numerically tested the validity of the half-collision approximation. They found that this approximation is successful in producing the position of the maximum and width of the absorption cross sections. However, their results have also shown that detailed values such as the \( V-T \) energy transfer probabilities \( P_{ij} \) with \( j \geq 1 \) (which is related to estimates of the final state interaction) and the final vibrational state distributions predicted by the half-collision approximation are not always accurate.

In this paper, a factorized amplitude expression, which is similar to the half-collision expression mentioned above, will be rigorously derived. However, the scattering wave functions used to represent the \( T \)-matrix and the Franck-Condon overlaps are not zeroth order uncoupled wave functions, but rather the full scattering functions that embody interchannel coupling through their \( K \) (reactance)-matrix. The essential feature of the resulting expression is that it involves only on-the-energy-shell contributions that have been rigorously derived.

As noted above, accurate scattering wave functions (including interchannel coupling) are needed for the repulsive surface. Recently, a practical and stable variational approach to scattering theory has been developed. Since the wave functions obtained are described analytically, it should be easier to evaluate the Franck-Condon overlaps. In addition, computed partial linewidths will approach the exact values as the number of basis functions for the expansion technique increases. Thus, our approach is a kind of variational one for the partial linewidths.

II. DIRECT DISSOCIATION

A. Stationary state Schrödinger equation

For the sake of simplicity, we begin with a discussion of direct dissociation in which two potential surfaces are involved. We consider a molecule in a vibrational and rotational level \( \nu(Q) \) on the initial potential surface \( V_i(Q) \), described by the electronic wave function \( \Phi_i(q, Q) \). We suppose that the molecule dissociates by a transition that is induced by photon absorption (or more generally by the interaction \( X \)) onto the final surface \( V_f(Q) \) described by \( \Phi_f(q, Q) \). Here \( q \) and \( Q \) denote collectively the electronic and nuclear coordinates, respectively.

As usual, the total (unnormalized) wave function of the molecular system is

\[
\Psi(q, Q) = \Phi_i(q, Q) \chi_i(Q) + \Phi_f(q, Q) \chi_f(Q),
\]
where \(\chi_i(Q)\) can be written as a linear combination of the \(v_i(Q)\) :
\[
\chi_i = \sum_k C_k v_k(Q) .
\]
Equation (2.2) accounts for the redistribution of the population among the available levels (the \(v_i)\) following the deactivation of the excited molecule. Another nuclear wave function \(\chi_f\) represents the dissociating molecule. Only outgoing waves are considered in \(\chi_f\).

The stationary state Schrödinger equation which represents the decay of an initial state \(\Phi_i v_i^*\) may be written:
\[
(E - H - \frac{1}{2}i\Gamma_i)v_i^*(\Phi_i v_i^* | \psi) = 0 ,
\]
where the total Hamiltonian \((H = H_0 + X)\) includes the molecular Hamiltonian \(H_0\) and the interaction \(X\) which induces the dissociation and \(\Gamma_i\) is the total linewidth for the decaying state. In order to arrive at the final equation for the outgoing flux for each channel, \(\langle \Phi_i | v_i)\) and \(\langle \phi_f | \phi_f)\) are applied to Eq. (2.3) to yield
\[
(E - H_i - \frac{1}{2}i\Gamma_i)v_i^*(\Phi_i v_i^* | \chi_i) = X_{fi} | \chi_f) .
\]
and
\[
(E - H_f) | \chi_f) = X_{fi} | \chi_i) .
\]
The operators in the above equations are defined as
\[
H_i = -\frac{1}{2} \sum_{k} \frac{1}{\mu_i} \frac{\partial^2}{\partial Q_k^2} + V_i(Q) ,
\]
and
\[
X_{fi} = \int \Phi_i^*(Q) \Phi_j(Q) dm_dQ\text{d}Q .
\]
\(H_f\) and \(X_{fi}\) are defined similarly. In Eq. (2.5), \(\mu_i\) is the reduced mass associated with the \(i\)th coordinate and \(V_f\) represents the potential surfaces of the initial and final states. So, \(H_f\) is the Hamiltonian that describes a multichannel (inelastic) scattering process on the repulsive surface \(V_f\).

Caplan and Child\(^{12}\) applied the Green's function method to Eq. (2.4). In representing the Green's operator, they (and also Mukamel and Jortner\(^{5}\)) used some uncoupled scattering wave functions. As a result their formalism necessitates the introduction of off-the-energy-shell terms\(^{6,12,13}\) to estimate the final state interaction. As an alternative, the relationship between the outgoing solution \(\chi_f\) of the inhomogeneous Schrödinger equation [Eq. (2.4b)] and the eigensolutions of its homogeneous counterpart will be investigated here.

B. Formal solution of \(\chi_f\)

Since Eqs. (2.4a) and (2.4b) are coupled, \(\chi_i\) and \(\chi_f\) must be obtained simultaneously. Formally, however, one can only solve Eq. (2.4b) assuming \(\chi_i\) is known. Since our primary interest is in the dissociating state, the following discussion will concentrate on the solution of \(\chi_f\).

For simplicity, it will be assumed that \(X_{fi}\), \(X_{fi}\), and \(\chi_i\) are real functions.\(^{14}\) Then it follows that if \(\chi_f = \chi_f^* + i\phi_f\),
\[
(E - H_f) | \chi_f^*) = 0 .
\]

Further, assuming \(\langle \chi_i | \chi_i) = 1\), we have
\[
\Gamma_{fi} = -2i \text{Im} \langle \chi_i | X_{fi} | \chi_f^*\rangle .
\]
According to Eq. (2.7a), the imaginary part of \(\chi_f\) is one of the real eigenfunctions of the full-collision problem. On the other hand, the real part of \(\chi_f\) is the solution of the inhomogeneous Schrödinger equation, which must satisfy the standing wave boundary condition. Furthermore, Eq. (2.7a) represents the optical theorem for the scattering theory,\(^6\) which can be derived as a consequence of the conservation of probability. The dependence of \(\Gamma_{fi}\) on \(\chi_f^*\) can be seen by rewriting Eq. (2.7a), with the help of Eq. (2.7b), as (assuming \(X\) to be Hermitian)
\[
\Gamma_{fi} = -2 \langle \chi_f^* | (E - H_f) | \chi_f\rangle .
\]
In Eq. (2.9) there is no explicit dependence on \(\chi_i\).

In order to connect Eq. (2.7a) with Eq. (2.7b), the boundary condition for \(\chi_f\) must be considered. The asymptotic wave of \(\chi_f\) should be composed of the outgoing waves coming from all channels, through which \(\chi_f^*\) and \(\chi_f\) are related. Prior to the explicit description of the boundary condition, it is useful to introduce some auxiliary functions to define the full-collision eigenfunctions. For simplicity, the dissociation is assumed to take place only along a coordinate \(Q_m\), and the remaining coordinates (collectively denoted \(Q\)) are described by vibrational and rotational states \(\xi_n(Q)\). Further, \(N_e\) is defined as the number of open channels for a given energy \(E\). Then, using the following long-range functions and associated conditions (atomic units \(\hbar = e = m_e = 1\) are used throughout),
\[
S_m = \sum_{Q \rightarrow \infty} \left(\frac{\mu_d}{k_n}\right)^{1/2} \sin(k_nQ_m)\xi_n(Q) ,
\]
\[
S_m = 0 \text{ at } Q \rightarrow \infty ,
\]
and
\[
C_m = \sum_{Q \rightarrow \infty} \left(\frac{\mu_d}{k_n}\right)^{1/2} \cos(k_nQ_m)\xi_n(Q) ,
\]
\[
C_m = 0 \text{ at } Q \rightarrow \infty ,
\]

\(\xi_n(Q)\) together with short-range (square integrable or \(L^2\)) functions \(\{g_n(Q)\} \{(h = 1, 2, \ldots)\), each of the \(N_e\) independent eigenfunctions (denoted by \(\lambda_n\)) of the homogeneous Schrödinger equation is expanded as
\[
\lambda_m = S_m + \sum_n C_n K_{nm} + \sum_n g_n D_{nm}
\]
\(H_m = 0 \text{ for } (m = 1, 2, \ldots, N_e) .
\]

In Eqs. (2.10) and (2.11), \(k_m\) is the wave number of the relative motion of the receding molecules. The real symmetric matrix \(K\), the reactance matrix or \(K\)-matrix,\(^6\) and the real coefficients \(D_{nm}\) in Eq. (2.12) may be determined by the variational method.\(^{6,14}\)

According to Eq. (2.7a), \(\chi_f^*\) can be written as a superposition of the \(\lambda_m\),
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\[ \chi_f = \sum_m A_m \chi_m. \]

Thus, \( \chi_f \) has the asymptotic form

\[ \chi_f \quad \text{as} \quad Q \to \infty \approx \sum_m \left( A_m S_m + B_m C_m \right) \]

with

\[ B_m = \sum_n K_{mn} A_n. \]

In order for \( \chi_f \) to satisfy the outgoing-wave boundary condition, \( \chi_f \) must have the asymptotic form

\[ \chi_f \quad \text{as} \quad Q \to \infty \approx \sum_m (A_m S_m + A_m C_m) \]

\[ = \sum_m A_m \left( C_m - \sum_n S_n K_{nm} \right). \]

Thus, we have

\[ \chi_f \quad \text{as} \quad Q \to \infty \approx \sum_m \left( A_m + iB_m \right) \left( C_m + iS_m \right) \approx \sum_m \left( A_m^2 + B_m^2 \right)^{1/2} \times \left( \frac{k_m}{k_m^2} \right)^{1/2} \exp \left( i \left( k_m Q + \delta_m \right) \right) \xi_n(Q), \]

where

\[ \delta_m = \tan^{-1} \frac{B_m}{A_m}. \]

Since every \( S_m \) and \( C_m \) is normalized in order to have unit flux, the square of the coefficient \( (A_m^2 + B_m^2)^{1/2} \) in Eq. (2.19) represents the outgoing flux of the \( m \)th channel. That is

\[ \Gamma_m^f = \sum_m \Gamma_m^f, \]

\[ \Gamma_m^f = A_m^2 + B_m^2. \]

Therefore, all that is needed to obtain \( \Gamma_m^f \) is an expression for the \( A_m \).

C. Expression for \( \Gamma_m^f \)

One way to calculate \( A_m \) is to solve directly an algebraic equation corresponding to Eq. (2.7b) in which \( \chi_f \) is expanded in a set of known \( \delta_m \) and \( (C_m - \sum_n S_n K_{nm}) \) \( m = 1, 2, \ldots, Nc \) [see Eq. (2.18)] as short- and long-range functions, respectively. Two drawbacks to this method are that an explicit expression for \( \lambda_m \) cannot be obtained. An alternative approach is as follows. Multiply Eq. (2.7b) on the left by \( \lambda_m \) and integrate. This gives

\[ \left( \lambda_m \right) \left( E - H_f \right) \chi_f = \left( \lambda_m \right) \chi_f. \]

With the help of a fundamental identity, \( \langle S_m | (E - H_f) | C_n \rangle = \langle C_n | (E - H_f) | S_m \rangle - \frac{i}{2} \delta_{mn}, \)

and the symmetry of the \( K \) matrix, the left-hand side of Eq. (2.23) becomes

\[ \langle \lambda_m | (E - H_f) \chi_f \rangle = -\frac{i}{2} \left( A_m + \sum_n K_{mn} B_n \right) + \langle \chi_f | (E - H_f) | \lambda_m \rangle. \]

Since the last term in Eq. (2.25) is zero due to Eq. (2.13), Eq. (2.23) becomes

\[ -\frac{i}{2} \left( A_m + \sum_n K_{mn} B_n \right) = \langle \lambda_m | X_{f1} | \chi_f \rangle. \]

Note that Eq. (2.25) is correct for \( \chi_f \) in general since the short-range part of \( \chi_f \) will be incorporated in the second term on the right-hand side of Eq. (2.25). In matrix notation we have

\[ A + KB = -2W, \]

where \( A, B, \) and \( W \) are column vectors whose \( m \)th elements are \( A_m, B_m, \) and \( \langle \lambda_m | X_{f1} | \chi_f \rangle, \) respectively. Further, inserting Eq. (2.16) into Eq. (2.27), we have the final results

\[ A = -2(I + K)^{-1}W, \]

and

\[ B = -2K(I + K^2)^{-1}W, \]

where \( I \) denotes the \( N_c \) by \( N_c \) unit matrix. Thus \( A \) and \( B \) have been expressed in terms of \( K, \lambda_m, \) and \( X_{f1}. \) If one wishes to invoke a Franck-Condon-like approximation, the integral \( \langle \lambda_m | X_{f1} | \chi_f \rangle \) may be replaced by \( \chi_f^* \left( \langle \lambda_m | \chi_f \rangle \right), \) where \( \chi_f^* \) is some average value of \( X_{f1}. \)

The results of Eq. (2.28) may be rewritten by use of the on-the-shell scattering matrix \( S. \) Insertion of \( \mathbf{K} = -i(S - I)(S + I)^{-1} \) into Eq. (2.28a) and (2.28b) gives for the amplitude vector of \( \chi_f \) [Eq. (2.19)]:

\[ A + iB = -(I + S)W, \]

Equation (2.28) or, equivalently, Eq. (2.30) is the fundamental result of this paper. These equations are exact within the two potential formalism, Eq. (2.1).

It is of interest at this point to consider the mathematical similarity between Eq. (2.30) and the half-collision approximation of Jortner et al. Introducing the \( F \)-matrix,

\[ F = \frac{1}{2} (I + S) = I - iST, \]

Equation (2.30) may be rewritten as

\[ A + iB = -2FW. \]

Now, on the right-hand side of Eq. (2.32) replace the \( \lambda_m \) (which include interchannel coupling) by zeroth order uncoupled scattering functions to represent both \( F \) and \( W. \) The latter are usually the eigenfunctions of some "elastic" Hamiltonian. See, for example, Eqs. (17) and (51) of Ref. 2b. Then Eq. (2.32) coincides exactly with the half-collision approximation. That approximation was derived by retaining only on-the-energy-shell contributions from the exact expression of the infinite series in the perturbation expansion. In this sense, the "half-collision" result may be regarded as an approximation of Eq. (2.30). Note that in practice there can be various versions of the half-collision approximation, corresponding to the different choices of zeroth order Hamiltonian that may be used. Since the half-collision approximation amounts to a truncation of the infinite series, the resultant partial linewidths cannot be exact, unless the off-the-shell contributions are accidentally zero or (equivalently) unless the interchannel coupling is zero.
In practical applications of Eq. (2.30), one must replace the exact functions \( \lambda_n \) by some approximate wave functions. These functions must be designed to include interchannel coupling as correctly as possible.\(^{1,10}\) Then, \( \Gamma_{\text{fs}} \) computed through Eq. (2.30) approaches the exact value as the accuracy of the trial functions increases. Viewed in this way, such an approximation within the scheme proposed here may be referred to as an "extended half-collision approximation."

In applying Eq. (2.30), one also needs \( \chi_i \). The simplest first approximation for \( \chi_i \) is\(^{5,12}\)

\[
\chi_i = \chi_i^0 .
\]  

(2.33)

This approximation implies that we neglect the photon-emission deactivation of the excited molecule at the outset [see Eq. (2.21)]. The Franck–Condon overlap then becomes \( \langle \lambda_n | \chi_i^0 \rangle \) in place of \( \langle \lambda_n | \chi_i \rangle \). A higher approximation for \( \chi_i \) can be obtained by the insertion of \( \chi_i \) and \( \Gamma_{\text{fs}} \), which have already been calculated under the assumption of Eq. (2.33), into Eq. (2.4a). Thus we have an iterative method to solve the coupled equations (2.4a) and (2.4b).

Before closing this subsection it is important to show that \( \Gamma_{\text{fs}} \) of Eq. (2.8) is identical with \( \Gamma_{\text{fs}} \) of Eq. (2.21), since their mathematical forms seem quite different. To see this, it is more convenient to start from Eq. (2.9) than Eq. (2.8). Application of the identity Eq. (2.24) to Eq. (2.9) yields

\[
\Gamma_{\text{fs}} = -2 \langle \chi_f^* | (E - H_f) | \chi_f \rangle
\]

\[
= \sum_n \left( A_{n}^* + B_{n}^* \right) - \langle \chi_f^* | (E - H_f) | \chi_f^0 \rangle
\]

\[
= \sum_n \left( A_{n}^* + B_{n}^* \right) \quad \text{[by Eq. (2.13)]} .
\]

(2.34)

This completes the proof. Equations (2.34) and (2.21) show that \( \Gamma_{\text{fs}}^\text{exact} \) can be obtained without an explicit functional form for \( \chi_f^* \).

**D. Golden-rule type expression for \( \Gamma_{\text{fs}} \)**

It may be worthwhile to reformulate \( \Gamma_{\text{fs}} \) in order to have a form of the golden-rule type, since many discussions\(^{14,11,15}\) have been put forth based on golden-rule calculations or its analog, even in the case of polyatomic dissociation. Combining Eqs. (2.22) and (2.28), we have for the total flux

\[
\Gamma_{\text{fs}} = 4W^* (1 + K^2)^{-1} W .
\]  

(2.35)

The factor \( 1 + K^2 \) comes from the definition of \( \lambda_n \) [Eq. (2.12)]. The \((m, n)\) element of the matrix \((1 + K^2)\) can be regarded as the flux that originates from the interference between \( \lambda_m \) and \( \lambda_n \). Therefore, the factor \((1 + K^2)^{-1}\) may be thought of as a constant of flux normalization. Recalling that eigenchannel functions\(^{4}\) are defined in order to diagonalize the \( K \) matrix, the orthogonal matrix \( U \), which diagonalizes \( K \),

\[
U K U^* = \text{diag}(\kappa_1, \kappa_2, \ldots, \kappa_N)
\]  

(2.36)

defines the corresponding eigenchannel functions \( \Phi_j \)

\[
\Phi_j = [2(1 + \kappa_j^2)]^{-1/2} \sum_m U_{jm} \lambda_m \quad (j = 1, \ldots, N). 
\]  

(2.37)

Using these functions, \( \Gamma_{\text{fs}} \) in Eq. (2.35) reduces to the simpler form (golden-rule-type expression)

\[
\Gamma_{\text{fs}} = \sum_j \langle \Phi_j | X_{fi} | \psi_{fi} \rangle^2 .
\]  

(2.38)

Although \( \Gamma_{\text{fs}} \) is the direct sum over the contributions from each channel, we should note that the eigenchannels do not have a one-to-one correspondence with the physical channels. Thus we are not interested in each term \( \langle \Phi_j | X_{fi} | \psi_{fi} \rangle^2 \).

However, if the \( K \) matrix is assumed to be diagonal from the beginning, then the \( U \) in Eq. (2.37) should be the unit matrix and \( \Phi_j \) corresponds to a particular physical channel \( \lambda_j \). Further Caplan and Child\(^{12}\) assumed

\[
\lambda_m (Q) = L_j (Q) \psi_m (Q) .
\]  

(2.39)

with

\[
\psi_m (Q) \sim 2 (1 + \kappa_m^2)^{-1/2} \mu_m / h \mu_m \exp \left( -\mu_m^2 Q^2 / 4 \right) .
\]  

(2.40)

This assumption they used an explicit Green's function to obtain the golden-rule expression for polyatomic dissociations,\(^{12}\)

\[
\Gamma_{\text{fs}}^\text{exact} = \langle \Phi_j (Q) \psi_m (Q) | X_{fi} | \psi_{fi} \rangle^2 .
\]  

(2.41)

Band and Freed\(^{2}\) have used this equation extensively with a correct treatment of normal coordinates and with the Airy-function approximation for \( \psi_m \). In their general theory,\(^{3}\) the final state interaction, which is completely neglected in Eq. (2.41), is taken into account semiclassically. As for other formal theories, off-the-shell contributions are necessary for exact computations.\(^{15,14}\)

**III. PREDISSOCIATION**

In this section, the theory of direct dissociation, in which only two potential surfaces are involved, is extended to the three potential problem, which is encountered in predissociation or other sequential decay models.\(^{16,17}\) To avoid unnecessary terminological confusion, the discussion will be restricted to simple predissociation. After the general theory is developed, a special case for which no direct interaction between initial and final states is observed will be considered.

**A. General**

In analogy with the case of direct dissociation, Eq. (2.1), the wave function for predissociation is written as

\[
\psi(q, Q) = \Phi_i (q, Q) \chi_i (Q)
\]

\[
+ \Phi_s (q, Q) \chi_s (Q) + \Phi_f (q, Q) \chi_f (Q) ,
\]  

(3.1)

where \( \Phi_i (q, Q) \) denotes an excited state via which the ground state \((i)\) molecule undergoes a transition to the final state \((f)\). The interactions are defined by \( X^{\text{sr}} \) and \( X^{\text{sf}} \), where the former causes nonradiative coupling between states \( s \) and \( f \), while the latter is the radiative dipole interaction inducing the transition between \( i \) and \( f \), or between \( i \) and \( s \).

The Schrödinger equation is also similarly defined by

\[
(E - H - \frac{1}{2} \Gamma_{\text{fs}} | \Phi_i \chi_i + \Phi_s \chi_s + \Phi_f \chi_f ) = 0 ,
\]  

(3.2)

\[
\frac{\partial \psi}{\partial t} = \text{H} \psi (E + \Gamma_{\text{fs}}^\text{exact} | \Phi_i \chi_i + \Phi_s \chi_s + \Phi_f \chi_f ) = 0 ,
\]  

(3.2)
where \( H = H_0 + X^{ab} + X^{sr} \). Equation (3.2) can be divided into two parts on the basis of the same assumption made for the direct dissociation. Furthermore, if we let \( |\lambda_s^f\rangle = |v_s^f\rangle \) and \( |\lambda_f^s\rangle = 0 \) as the zeroth order approximation, we have

\[
(E - H) \Phi_s^{(s)} + \Phi_f^{(s)} = \frac{1}{2} \Gamma_{sA} \Phi_s^{(s)},
\]

\[
(E - H) \Phi_s^{(f)} + \Phi_f^{(f)} = -\frac{1}{2} (E - H) \Phi_f^{(f)}. \tag{3.3a}
\]

From Eq. (3.3a), \( \Gamma_{sA} \) is found to be

\[
\Gamma_{sA} = -2(\Phi_s^{(s)} | X^{ab}_s \rangle \langle X^{ab}_s | \Phi_f^{(f)} \rangle + \langle \Phi_s^{(s)} | X^{ab}_s \rangle | \Phi_f^{(f)} \rangle), \tag{3.4}
\]

though \( \chi_s^f \) and \( \chi_f^s \) are as yet unknown.

The outgoing flux on the surface \( V_f \) may be calculated by the following procedure. Carrying out the same manipulation used to obtain Eq. (2.4), one finds from Eq. (3.3a),

\[
\begin{pmatrix}
E - H_s & -X^{sr}_s \\
-X^{sr}_s & E - H_f
\end{pmatrix}
\begin{pmatrix}
|\lambda_s^f\rangle \\
|\lambda_f^s\rangle
\end{pmatrix} = 0. \tag{3.5}
\]

Similarly, from Eq. (3.3b),

\[
\begin{pmatrix}
E - H_s & -X^{sr}_s \\
-X^{sr}_s & E - H_f
\end{pmatrix}
\begin{pmatrix}
|\lambda_s^f\rangle \\
|\lambda_f^s\rangle
\end{pmatrix} = \begin{pmatrix}
X^{ab}_s & |v_s^f\rangle \\
|v_f^s\rangle & X^{ab}_s
\end{pmatrix} \begin{pmatrix}
|\lambda_s^f\rangle \\
|\lambda_f^s\rangle
\end{pmatrix}. \tag{3.6}
\]

These two simultaneous equations should be solved under the outgoing-wave boundary condition. If \( N_c \) channels are open, \( N_c \) independent solutions may be found for the homogeneous equation

\[
\begin{pmatrix}
E - H_s & -X^{sr}_s \\
-X^{sr}_s & E - H_f
\end{pmatrix}
\begin{pmatrix}
|\lambda_s^f\rangle \\
|\lambda_f^s\rangle
\end{pmatrix} = 0 \quad (m = 1, 2, \ldots, N_c). \tag{3.7}
\]

\(|\lambda_m^s\rangle\) is defined as before [see Eq. (2.12)], while \(|Y_m^s\rangle\) may be described by the linear combination of the vibrational and rotational functions \( |v_b\rangle (b = 1, 2, \ldots) \) on the potential surface \( V_s \). The column vector of Eq. (3.5) can then be expressed exclusively in terms of the solutions of Eq. (3.7),

\[
\begin{pmatrix}
|\lambda_s^f\rangle \\
|\lambda_f^s\rangle
\end{pmatrix} = \begin{pmatrix}
A_m \\
B_m
\end{pmatrix} |\lambda_m^s\rangle. \tag{3.8}
\]

Defining \( B_m = \Sigma A_m A_n \), we have [following the arguments used to obtain Eq. (2.22)]

\[
\Gamma_{sA} = A_m^2 + B_m^2, \tag{3.9}
\]

where the \( A_m \) are obtained by solving Eq. (3.6) in the manner outlined in Sec. IIIC. The result is

\[
A = -2(I + K^s)^{-1} \begin{pmatrix} W_s^s & W_s^f \end{pmatrix}, \tag{3.10a}
\]

\[
B = -2K(I + K^s)^{-1} \begin{pmatrix} W_s^s & W_s^f \end{pmatrix}, \tag{3.10b}
\]

or

\[
A + iB = -(I + S) \begin{pmatrix} W_s^s & W_s^f \end{pmatrix}, \tag{3.10c}
\]

where \( W_s^s = \langle \lambda_m^s | X^{ab}_s | v_s^f \rangle \) and \( W_s^f = \langle \lambda_m^s | X^{ab}_s | v_f^s \rangle \).

Naturally, the \( K \) matrix is determined on the combined surfaces of \( V_s \) and \( V_f \), which are connected by the interaction \( X^{sr} \). On the other hand, in the photon absorption step, only the interaction \( X^{ab} \) appears and the contribution from the \( s \) and \( f \) states is additive.

**B. Case of \( X^{ab}_{sf} = X^{ab}_{fs} = 0 \)**

Equations (3.10) are the general expressions for predissociation. However, in a typical calculation, some assumptions\(^{15,17}\) are made that reduce the three potential problem to a two potential one. First, \( X^{ab}_{sf} = 0 \) is assumed, so that the oscillator strength is not carried from \( i \) to \( f \). Second, the spacing among the energy levels on the \( s \) surface is assumed to be so wide that these levels remain almost unchanged and isolated even when the interaction \( X^{sr} \) is taken into account (the assumption of isolated resonances). It has been well established\(^{26,14,15}\) that in this case the theories for direct dissociation and predissociation are transferable to one another. With the above assumptions, the molecule may be prepared\(^{10}\) on a certain decaying state \( v_s^f \) by photon absorption. Then we have

\[
(E - H_f) |\lambda_s^f\rangle = \alpha_s X^{ab}_s |v_s^f\rangle, \tag{3.11}
\]

where \( \alpha_s \) is a constant such that \( |\alpha| \) represents the population of \( v_s^f \). Since Eq. (3.11) has the same structures as Eq. (2.4b), one can apply exactly the same procedure developed for direct dissociation, except for the determination of \( \alpha_s \). However, when only a relative distribution of energy is of interest, e.g., \( \Gamma_{sb} / \Gamma_{fs} \), \( \alpha_s \) does not affect the results.

**IV. CONCLUDING REMARKS**

It has been assumed, for simplicity, that \( X_{sf}^b \) and \( X_{fs}^b \) are real. However, they are not necessarily real (for example, if \( X_{sf} \) includes rotationally excited functions). In such cases, the outline of the calculation is as follows. Let us suppose \( \chi_i = e_i + il_i \), then we have

\[
(E - H_f) |\chi_i^f\rangle = X_{hf} |\chi_i^f\rangle \tag{4.1a}
\]

and

\[
(E - H_f) |\chi_i^s\rangle = X_{hf} |\chi_i^s\rangle \tag{4.1b}
\]

with the boundary condition, Eqs. (2.15) and (2.17).

Now, however, Eq. (2.16) does not hold. After operating with \( |\lambda_m^f\rangle \), one has a set of simultaneous equations for \( A \) and \( B \):

\[
\begin{pmatrix} K & -I \\ I & K \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} = -2 \begin{pmatrix} W_s^s \\ W_s^f \end{pmatrix}, \tag{4.2}
\]

where \( W_s^s = \langle \lambda_m^s | X_{hf} | v_s^f \rangle \) and \( W_s^f = \langle \lambda_m^s | X_{hf} | v_f^s \rangle \). It is a simple task to solve Eq. (4.2). The results are

\[
A = -2(I + K^s)^{-1} (K W_s^s + W_s^f), \tag{4.3a}
\]

and

\[
B = -2(I + K^s)^{-1} (-W_s^s + K W_s^f), \tag{4.3b}
\]

or

\[
A + iB = -(I + S)(W_s^s + i W_s^f). \tag{4.4}
\]

This is the general form of Eq. (2.30).

Thus we have obtained an expression for \( \Gamma_{sf} \) that allows us to apply a variational (or expansion) approach.
The equation involves only on-the-shell contributions, because the exact scattering wave functions on the repulsive surface are used in the formalism and due to the principle of energy conservation.

The relationship between the present approach and the half-collision approximation has been discussed. From the viewpoint of formal theory, numerical results given by our formalism should be the same as those of the other time-independent approaches, if the complete computation including the estimate of the final state interaction is performed. However, it is important to stress again that our expression [Eq. (2.30)] is closed in the sense that only on-the-shell components are involved.

With the formalism discussed here, one can make use of highly accurate scattering functions for which various methods are already available. Among these methods, the expansional (algebraic) variational technique appears to be promising, since the expansional wave functions will be convenient for the Frohlich-Cond bound operator and since the resultant $K$ matrix is stable. If the basis set for the scattering functions is large enough, one may approach the exact value of $\Gamma_{fi}^0$ through Eqs. (2.30) or (4.4). However, the present derivation of the expression for $\Gamma_{fi}^0$, which is quite different from the other methods, suggests the existence of a correction formula for $\Gamma_{fi}^0$ that yields an accurate result even when a relatively poor basis set is used. This additional merit of the theory is presented in the following paper, together with some numerical examples.

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4 For example, (a) M. Shapiro, Isr. J. Chem. 11, 691 (1973); (b) U. Halvov and M. Shapiro, Chem. Phys. 21, 105 (1977).


10 As pointed out by Band and Freed (Ref. 3), the coordinate system of states $i$ and $f$ may be different. Although we recognize this, no symbolic distinction is introduced.


13 This is not an essential assumption. See the discussion in Sec. IV.


17 The general theory of Mukamel and Jortner (Ref. 2) includes the time-dependent approach.

18 K. Takatsuka and M. S. Gordon (to be published).